



รายงานวิจัยฉบับสมบูรณ์

โครงการ “การสังเคราะห์ โครงสร้างผลึก สมบัติสเปกโทรสโกปี
และสมบัติทางแม่เหล็ก ของสารเชิงซ้อนมอนอนิวเคลียร์
และพอลินิวเคลียร์คอปเปอร์(II)”

โดย รศ.ดร. สุกิตรา ย้งมี และคณะ

กรกฎาคม 2552

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คณะผู้วิจัย

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|------------------------------|-------------------------------------|
| 1. รศ.ดร. สุจิตรา ย้งมี | มหาวิทยาลัยขอนแก่น |
| 2. ผศ.ดร. เซวง ภาควัตถุ | มหาวิทยาลัยสงขลานครินทร์ |
| 3. รศ.ดร. ณรงค์ศักดิ์ ชัยชิต | มหาวิทยาลัยธรรมศาสตร์ |
| 4. Prof. Jan Reedijk | Leiden University, The Netherlands. |

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สัญญาเลขที่ BRG4980007

โครงการ “การสังเคราะห์ โครงสร้างผลึก สมบัติสเปกโทรสโกปี และสมบัติทางแม่เหล็ก ของสารเชิงซ้อน
มอนอนิวเคลียร์และพอลินิวเคลียร์คอปเปอร์(II)”
รายงานวิจัยฉบับสมบูรณ์

บทคัดย่อ

งานวิจัยนี้เป็นการศึกษาหาสภาวะการเตรียม สมบัติทางสเปกโทรสโกปี (IR, solid state VIS, EPR) โครงสร้างผลึกและสมบัติทางแม่เหล็กของสารเชิงซ้อนพอลินิวเคลียร์คอปเปอร์(II) ที่มีซูโดเฮไลต์ คาร์บอเนต และคาร์บอกซิเลตเป็นลิแกนด์สะพาน เชื่อมระหว่างไอออนคอปเปอร์(II) และมีได-2-พริดีลามีน (dpyam) 2,2'-ไบพริดีน (bpy) และ 1,10-ฟีแนนโทรลีน (phen) เป็นคีเลตลิแกนด์ รวมทั้งศึกษาความสัมพันธ์ระหว่างโครงสร้างกับสมบัติทางแม่เหล็ก โดยเปรียบเทียบกับสารอื่นในระบบที่ใกล้เคียงกัน นอกจากนี้ยังได้ศึกษาวิถีทางของการเปลี่ยนแปลงโครงสร้างในอนุกรมของสารเชิงซ้อนมอนอนิวเคลียร์คอปเปอร์ (II) แบบ 5-coordinate ที่มีเฮไลต์และซูโดเฮไลต์เป็นลิแกนด์สะพานร่วม

ผลิตภัณฑ์ที่สังเคราะห์ได้สำหรับระบบที่มีหมู่ซูโดเฮไลต์เป็นลิแกนด์สะพาน ได้แก่ สารเชิงซ้อนไดนิวเคลียร์ $[\text{Cu}_2(\text{dpyam})_2(\mu\text{-NCO-N,N'}(\text{NCO-N})_2)]$ (I), เตตระนิวเคลียร์ $[\text{Cu}_4(\text{dpyam})_4(\mu_{1,3}\text{-NCS})_6(\text{O}_2\text{CH})_2(\text{H}_2\text{O})_2]$ (II), ไตรนิวเคลียร์ $[\text{Cu}_3(\text{dpyam})_2(\mu_{1,3}\text{-N}_3)_2(\mu\text{-CH}_3\text{COO-}\kappa\text{-O}^1)(\mu\text{-CH}_3\text{COO-}\kappa\text{-O}^1,\text{O}^2)]\cdot 2\text{H}_2\text{O}$ (III), ไดนิวเคลียร์ $[\text{Cu}_2(\text{dpyam})_2(\mu_{1,1}\text{-N}_3)_2(\text{O}_2\text{CH})_2]$ (IV), $[\text{Cu}_2(\text{dpyam})_2(\mu_{1,1}\text{-N}_3)_2(\text{O}_2\text{CCH}_3)_2]$ (V) and $[\text{Cu}_2(\text{dpyam})_2(\mu_{1,1}\text{-N}_3)_2(\text{O}_2\text{CCH}_2\text{CH}_3)_2]$ (VI) จากการศึกษาสมบัติทางแม่เหล็ก พบว่าสาร I, IV, V และ VI มีอันตรกิริยาระหว่างไอออนคอปเปอร์(II) แบบเฟอร์โรแมกเนติก และมีค่า singlet-triplet splitting (J) เท่ากับ 6.03, 63.3, 63.8 และ 5.1 cm^{-1} ตามลำดับ ส่วนสาร II และ III มีอันตรกิริยาแบบแอนติเฟอร์โรแมกเนติกแบบอ่อนที่มีค่า J น้อยมาก นอกจากนี้ยังได้ศึกษาวิถีทางของการเปลี่ยนแปลงโครงสร้างในอนุกรมของสารเชิงซ้อนมอนอนิวเคลียร์คอปเปอร์ (II) แบบ 5-coordinate ด้วย

กรณีสารเชิงซ้อนที่มีหมู่คาร์บอเนตเป็นลิแกนด์สะพานนั้น ผลิตภัณฑ์ที่สังเคราะห์ได้ ได้แก่ สารเชิงซ้อนไดนิวเคลียร์ $[\text{Cu}_3(\text{chelate})_6(\mu_3\text{-CO}_3)](\text{CF}_3\text{SO}_3)_4(\text{H}_2\text{O})_{0.5}$ เมื่อ chelate = bpy (I) และ phen (II), เฮกซะนิวเคลียร์ $[\text{Cu}_6(\text{bpy})_{10}(\mu\text{-OH})_2(\mu\text{-CO}_3)_2]Y$ เมื่อ $Y = (\text{CF}_3\text{SO}_3)_6(\text{DMF})_2(\text{H}_2\text{O})_4$ (III) และ $(\text{BF}_4)_6(\text{H}_2\text{O})_{0.5}$ (IV), ออกตะนิวเคลียร์ $[\text{Cu}_8(\text{phen})_{12}(\mu_3\text{-OH})_2(\mu\text{-OH})_2(\mu_3\text{-CO}_3)_2](\text{CF}_3\text{SO}_3)_8(\text{DMF})_2(\text{H}_2\text{O})_{0.5}$ (V) และพอลินิวเคลียร์ $\{[\text{Cu}_3(\text{bpy})_3(\mu\text{-OH})_2(\mu\text{-CO}_3)_2](\text{H}_2\text{O})_{6.5}\}_n$ (VI) จากการศึกษาสมบัติทางแม่เหล็กเบื้องต้นในช่วงอุณหภูมิ 5 ถึง 350 เคลวิน พบว่าสาร I-VI มีอันตรกิริยาระหว่างไอออนคอปเปอร์(II) เป็นเฟอร์โรแมกเนติกแบบอ่อน

ผลิตภัณฑ์ที่สังเคราะห์ได้สำหรับระบบที่มีหมู่คาร์บอกซิเลตเป็นลิแกนด์สะพานและมีโครงสร้างแบบ paddle-wheel ได้แก่ $[\text{Cu}_4(\text{dpyam})_2(\text{OCOC}_2\text{H}_5)_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)_6(\text{H}_2\text{O})_2][\text{Cu}_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)_4(\text{H}_2\text{O})_2](\text{DMF})_2$ (I), $[\text{Cu}_6(\text{phen})_2(\text{H}_2\text{O})_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)_{12}]_n[\text{Cu}_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)_4(\text{H}_2\text{O})_2]_{2n}(\text{H}_2\text{O})_{0.5n}$ (II), $\{[\text{Cu}_4(\text{phen})_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)](\text{H}_2\text{O})\}_n$ (III), $[\text{Cu}_2(\mu\text{-O}_2\text{CC}_6\text{H}_4\text{OH})_4(\text{C}_7\text{H}_7\text{NO})_2](\text{H}_2\text{O})_6$ (IV) และ $[\text{Cu}_2(\mu\text{-O}_2\text{CCH}_3)_4(\text{C}_7\text{H}_7\text{NO})_2]$ (V) จากการศึกษาสมบัติทางแม่เหล็ก พบว่าสาร III-V มีอันตรกิริยาระหว่างไอออนคอปเปอร์(II)

แบบแอนติเฟอร์โรแมกเนติก และมีค่า singlet-triplet energy splitting (J) เท่ากับ -299.5, -278.5 และ -287 cm^{-1} ตามลำดับ

สัญญาเลขที่ BRG4980007

โครงการ “การสังเคราะห์ โครงสร้างผลึก สมบัติสเปกโทรสโกปี และสมบัติทางแม่เหล็ก ของสารเชิงซ้อน
มอนอนิวเคลียร์และพอลินิวเคลียร์คอปเปอร์(II)”
รายงานวิจัยฉบับสมบูรณ์

Abstract

This research sets out to examine the preparation, spectroscopic properties (IR, solid state VIS, EPR), X-ray crystal structures and magnetism of the pseudohalide, carbonato- and carboxylato-bridged polynuclear copper(II) complexes containing the di-2-pyridylamine (dpyam), 2,2'-bipyridyl (bpy) and 1,10-phenanthroline (phen) as chelating ligand. The magneto-structural correlation and superexchange pathway for the polynuclear complexes are investigated and discussed in comparison with other relevant complexes. The structural pathway in a series of 5-coordinate mononuclear copper(II) complexes containing halide and pseudohalide ligands is also studied.

The synthesis and characterization of the polynuclear copper(II) complexes containing the pseudohalide anion (NCO^- , NCS^- and N_3^-) and mixed pseudohalide/carboxylate as a bridging ligand and the di-2-pyridylamine as a chelate didentate terminal ligand: $[\text{Cu}_2(\text{dpyam})_2(\mu\text{-NCO-}N,N')(\text{NCO-}N)_2]$ (**I**), $[\text{Cu}_4(\text{dpyam})_4(\mu_{1,3}\text{-NCS})_6(\text{O}_2\text{CH})_2(\text{H}_2\text{O})_2]$ (**II**), $[\text{Cu}_3(\text{dpyam})_2(\mu_{1,3}\text{-N}_3)_2(\mu\text{-CH}_3\text{COO-}\kappa\text{-O}^1)(\mu\text{-CH}_3\text{COO-}\kappa\text{-O}^1, \text{O}^2)_2 \cdot 2\text{H}_2\text{O}]$ (**III**), $[\text{Cu}_2(\text{dpyam})_2(\mu_{1,1}\text{-N}_3)_2(\text{O}_2\text{CH})_2]$ (**IV**), $[\text{Cu}_2(\text{dpyam})_2(\mu_{1,1}\text{-N}_3)_2(\text{O}_2\text{CCH}_3)_2]$ (**V**) and $[\text{Cu}_2(\text{dpyam})_2(\mu_{1,1}\text{-N}_3)_2(\text{O}_2\text{CCH}_2\text{CH}_3)_2]$ (**VI**) are described. The magnetic properties of compounds **I**, **IV**, **V** and **VI** show a medium to weak ferromagnetic exchange interactions between the Cu(II) ions dominated by the bridging cyanato or azido ligands, with a singlet-triplet splitting (J) of 6.03, 63.3, 63.8 and 5.1 cm^{-1} , for compounds **I**, **IV**, **V** and **VI**, respectively. While compounds **II** and **III** reveal a weak antiferromagnetic interaction with a small J value. Additionally, the structural pathway in a series of 5-coordinate mononuclear copper(II) complexes containing halide and pseudohalide ligands have been analysed and discussed.

In case of the carbonato-bridged copper(II) compounds, the polynuclear copper(II) complexes $[\text{Cu}_3(\text{bpy})_6(\mu_3\text{-CO}_3)](\text{CF}_3\text{SO}_3)_4(\text{H}_2\text{O})_{0.5}$ (**I**), $[\text{Cu}_3(\text{phen})_6(\mu_3\text{-CO}_3)](\text{CF}_3\text{SO}_3)_4(\text{H}_2\text{O})_{0.5}$ (**II**), $[\text{Cu}_6(\text{bpy})_{10}(\mu\text{-OH})_2(\mu\text{-CO}_3)_2](\text{CF}_3\text{SO}_3)_6(\text{DMF})_2(\text{H}_2\text{O})_4$ (**III**), $[\text{Cu}_6(\text{bpy})_{10}(\mu\text{-OH})_2(\mu\text{-CO}_3)_2](\text{BF}_4)_6(\text{H}_2\text{O})_{0.5}$ (**IV**), $[\text{Cu}_8(\text{phen})_{12}(\mu_3\text{-OH})_2(\mu\text{-OH})_2(\mu_3\text{-CO}_3)_2](\text{CF}_3\text{SO}_3)_8(\text{DMF})_2(\text{H}_2\text{O})_{0.5}$ (**V**) and $\{[\text{Cu}_3(\text{bpy})_3(\mu\text{-OH})_2(\mu\text{-CO}_3)_2](\text{H}_2\text{O})_{6.5}\}_n$ (**VI**) have been synthesized and characterized crystallographically and spectroscopically. The magnetic properties as preliminary results of complexes **I-VI** have been studied in a range from 5 to 350 K, showing a weak ferromagnetic exchange interactions between copper(II) ions. The magnetic behavior and properties of the magnetic orbitals are discussed.

In case of the polynuclear carboxylato-bridged copper(II) *paddle-wheel* complexes, the synthesis, spectroscopic characterization and X-ray structure of a hexanuclear $[\text{Cu}_4(\text{dpyam})_2(\text{OCOC}_2\text{H}_5)_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)_6(\text{H}_2\text{O})_2][\text{Cu}_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)_4(\text{H}_2\text{O})_2](\text{DMF})_2$ (**I**), two polymeric chain complexes $[\text{Cu}_6(\text{phen})_2(\text{H}_2\text{O})_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)_{12}]_n[\text{Cu}_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)_4(\text{H}_2\text{O})_2]_{2n}(\text{H}_2\text{O})_{0.5n}$ (**II**) and $\{[\text{Cu}_4(\text{phen})_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)_8](\text{H}_2\text{O})\}_n$ (**III**) and two dinuclear complexes $[\text{Cu}_2(\mu\text{-O}_2\text{CC}_6\text{H}_4\text{OH})_4(\text{C}_7\text{H}_7\text{NO})_2](\text{H}_2\text{O})_6$ (**IV**) and $[\text{Cu}_2(\mu\text{-O}_2\text{CCH}_3)_4(\text{C}_7\text{H}_7\text{NO})_2]$ (**V**) are reported. The magnetic properties of complexes **III-V** are investigated and reveal a very strong antiferromagnetic coupling with $J = -299.5$, -278.5 and -287 cm^{-1} , respectively.

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นิวเคลียร์และพอลินิวเคลียร์คอปเปอร์ (II)”
รายงานสรุปความก้าวหน้าของโครงการประจำปี

Executive Summary

The more insight in the structural aspects of polynuclear transition metal compounds that influence their magnetic properties has been the primary objective of this research. Because of the varieties of geometries and coordination numbers displayed by the copper(II) ion and in order to extend a search to polynuclear copper(II) complexes with different coordination modes of bridging ligands, the polynuclear copper(II) complexes with the three different bridging ligands, namely pseudohalide, carbonate and carboxylate are prepared in order to relate the structural parameters to their magnetic properties, besides the coordination chemistry of these kinds of complexes. The aim of the research is threefold, **First** to synthesize new polynuclear copper(II) complexes containing the pseudohalide, carbonate and carboxylate as bridging ligands with variety of coordination and bridging modes resulting different environments around the copper(II) ion. The structural modification for each series is based on the preparative conditions and type of anion and solvent molecule. Measuring the temperature variable magnetic susceptibilities of these new compounds brings up the **second** aim of the research; to investigate structural factors that influence the type and magnitude of magnetic interaction between copper(II) ions and the superexchange pathway investigated and discussed in comparison with other relevant complexes. **Thirdly**, to study the structural pathway in a series of 5-coordinate mononuclear copper(II) complexes containing halide and pseudohalide.

This research is divided into three parts. **Part I** describes the synthesis, characterization (elemental analysis, IR, EPR, and X-ray analysis) and magneto-structural correlation of the polynuclear pseudohalide-bridged copper(II) complexes and the structural pathway of 5-coordinate mononuclear copper(II) complexes containing halide and pseudohalide. The synthesis, characterization and magneto-structural correlation of the polynuclear carbonate-bridged and carboxylate-bridged copper(II) complexes are described in **Part II** and **Part III** of the research, respectively.

Part I addresses the synthesis, characterization and magneto-structural correlation of a series of polynuclear pseudohalide-bridged copper(II) complexes with the di-2-pyridylamine as the terminal ligand. The spectroscopic and magnetic characterization, the X-ray crystal structure and the magneto-structural correlation in this complex system are investigated and discussed in comparison with other relevant complexes. The polynuclear pseudohalide-bridged copper(II) complexes $[\text{Cu}_2(\text{dpyam})_2(\mu\text{-NCO-}N,N')(\text{NCO-}N)_2]$ (**I**), $[\text{Cu}_4(\text{dpyam})_4(\mu_{1,3}\text{-NCS})_6(\text{O}_2\text{CH})_2(\text{H}_2\text{O})_2]$ (**II**), $[\text{Cu}_3(\text{dpyam})_2(\mu_{1,3}\text{-N}_3)_2(\mu\text{-CH}_3\text{COO-}\kappa\text{-O}^1)_2]$

(μ -CH₃COO- κ -O¹,O²)₂].2H₂O (**III**), [Cu₂(dpyam)₂($\mu_{1,1}$ -N₃)₂(O₂CH)₂] (**IV**), [Cu₂(dpyam)₂($\mu_{1,1}$ -N₃)₂(O₂CCH₃)₂] (**V**) and [Cu₂(dpyam)₂($\mu_{1,1}$ -N₃)₂(O₂CCH₂CH₃)₂] (**VI**) were prepared directly from the mole ratio in different conditions. Good quality single crystals for X-ray analyses of complexes **I-VI** were obtained. All product were analysed by elemental microanalyses and characterized spectroscopically (IR, EPR, solid state VIS). The room temperature magnetic moment and the temperature variable magnetic susceptibilities (5-280 K) of all products are investigated and discussed together with the magneto-structural correlation and superexchange pathways.

Complexes **I**, **IV-VI** contain five-coordinate copper centers bridged by pseudohalide groups from the axial position of one chromophore to the equatorial position of the other one. Each copper chromophore in **I**, **IV-VI** exhibits the square-pyramidal geometry, whereas **II** and **III** display an square-pyramidal geometry together with octahedral geometry. The magnetic susceptibility measurements have revealed a ferromagnetic interaction between the copper(II) atoms for complexes **I** and **IV-VI**, with a singlet-triplet energy gap (J) of +6.03 and +63.3, +63.8, +5.1 cm⁻¹, respectively. Complexes **II** and **III** have a very weak antiferromagnetic interaction between Cu ions. The magneto-structural correlation and superexchange pathways of these complexes are also described.

For the study of structural pathway in a series of the 5-coordinate mononuclear copper(II) complexes containing halide and pseudohalide, the results are divided in to two series of this complex system: a series of [Cu(dpyam)₂(NCO)][Y] complexes and a series of [Cu(chelate)₂X]⁺ cation, where chelate = 2,2'-bipyridine (bipy), 1,10-phenanthroline (phen) and di-2-pyridylamine (dpyam), X = a pseudohalide ligand (NCO, NCS, N₃ and C₂N₃).

The crystal structures of eight new [Cu(dpyam)₂(NCO)][Y] complexes which Y = Br⁻ (**1**), CF₃SO₃ (**2**) BF₄⁻·dpyam (**3**), Cl⁻·4H₂O (**4**), NO₃⁻ (**5**), PF₆⁻ (**6**), ClO₄⁻ (**7**) and BPh₄⁻(**8**), respectively have been determined by X-ray crystallography. Five of the complexes, **1-5** (τ = 0.09–0.30) have a CuN₄N' chromophore with a trigonal bipyramidal distorted square based pyramidal (TBDSBP) stereochemistry, **6** and **7** (τ = 0.53–0.54) involve an intermediate five-coordinate stereochemistry, while **8** (s = 0.76) involves a square base pyramidal distorted trigonal bipyramidal (SBPDTB) stereochemistry. The structures of **1-8** are compared by scatterplot analysis with [Cu(dpyam)(NCO)][SO₄]_{0.5}·dpyam·0.5H₂O (**9**), the only complex of known crystal structure within this series reported to date. Scatterplots of the cations distortion isomers of the [Cu(dpyam)₂(NCO)][Y] series of complexes suggests that all nine complexes lie on a common structural pathway, involving a mixture of symmetric, ν_{sym} , C₂ and asymmetric, ν_{asym} , non-C₂ modes of vibration of the CuN₄N' chromophore. The resulting linear and parallel structural pathways are consistent with the direct observation of the effect of vibronic coupling on the stereochemistries of the complexes, which can range from SBPDTB to TBDSBP which correlate with electronic spectral data. The EPR spectra (K-band and V-band) of complexes **1-7** are in rhombic type, while complex **8** is axial with $g_{\parallel}$ = 2.185 and $g_{\perp}$ = 2.005, consistent with a d_{z2} ground state for the approximately trigonal bipyramidal stereochemistry of

the CuN₄N' chromophore. These are in agreement with electronic reflectance spectra of the complexes and correspond to their stereochemistries

For the second series, the crystal structures of four distortion isomers of the [Cu(chelate)₂X]⁺ cation, where chelate = 2,2'-bipyridine (bipy), 1,10-phenanthroline (phen) and di-2-pyridylamine (dpyam), X = a pseudohalide ligand (NCO, NCS, N₃ and C₂N₃), have been compared by scatterplot analysis with 25 [Cu(chelate)₂X]Y complexes of known crystal structure. The four new complexes [Cu(phen)₂NCO]Br (**1**), [Cu(phen)₂N₃]BPh₄·H₂O (**2**), [Cu(dpyam)₂(N₃)]NO₃·H₂O (**3**) and [Cu(dpyam)₂(N₃)]ClO₄ (**4**) involve a near regular square-based pyramidal stereochemistry (RSBP). The structures of complexes (**1**) and (**2**) are of the rare cases found for the phen analogue. Scatterplots of the 29 cation distortion isomers of the [Cu(chelate)₂X]Y series of complexes suggest that most of the 29 complexes lie on a common structural pathway, involving a mixture of the symmetric, C₂, and the asymmetric, non-C₂, in-plane modes of vibration of the CuN₄N' chromophore. Some datapoints are found to lie on extended routes. The resulting structural pathways are consistent with the direct observation of the effect of the modes of vibration on the stereochemistries of the complexes. A comparison of the trends in the 29 datasets suggests a size effect of the phen, bipy and dpyam ligands.

Part II of this research describes the synthesis, characterization (elemental analysis, IR, EPR, and X-ray analysis) and magnetic properties of six carbonato-bridged polynuclear copper(II) complexes containing the 2,2'-bipyridyl (bpy) and 1,10-phenanthroline (phen). The magnetostructural correlation and superexchange pathway for the polynuclear complexes are investigated and discussed in comparison with other relevant complexes. The polynuclear copper(II) complexes, [Cu₃(chelate)₆(μ₃-CO₃)](CF₃SO₃)₄(H₂O)_{0.5} where chelate = bpy (**I**) and phen (**II**), [Cu₆(bpy)₁₀(μ-OH)₂(μ-CO₃)₂]Y where Y = (CF₃SO₃)₆(DMF)₂(H₂O)₄ (**III**) and (BF₄)₆(H₂O)_{0.5} (**IV**), [Cu₈(phen)₁₂(μ₃-OH)₂(μ-OH)₂(μ₃-CO₃)₂](CF₃SO₃)₈(DMF)₂(H₂O)_{0.5} (**V**) and {[Cu₃(bpy)₃(μ-OH)₂(μ-CO₃)₂](H₂O)_{6.5}]_n (**VI**) were obtained from the mole ratio method. The crystal structures of **I-VI** are determined crystallographically and their IR, reflectance and EPR spectra characterized.

Complexes **I** and **II** are the trinuclear complexes in which three Cu atoms are linked through oxygen atoms of the carbonato bridge in a μ₃-η¹:η¹:η¹-CO₃ coordinated fashion. Complexes **III** and **IV** consist of the di-μ-hydroxido-bis(bpy)dicopper(II) groups coordinated with *trans*-axially at each copper atom by [μ-carbonato-bis(bpy)copper(II)] moieties, forming a hexanuclear copper(II) complex with a μ₃-η²:η¹-CO₃ mode. Complex **V** consists of two symmetry related di-μ-hydroxido-bis(phen)dicopper(II) groups which held together by long oblique Cu-O(H) bonds, creating Cu₂(OH)₂ core of tetranuclear hydroxido-bridged copper(II) unit, further coordinated with *trans*-axially at copper(II) ions of di-μ-hydroxidodicopper(II) group by [μ₃-carbonato-bis(phen)copper(II)] moieties, forming an octanuclear copper(II) complex. A polymeric chain complex **VI** consists of two independent di-μ-hydroxido-bis(bpy)copper(II) dimeric units, [Cu(1)/Cu(1)A] and [Cu(3)/Cu(3)B] units which are connected to the central Cu(2) moiety by two different

coordination modes of the carbonato bridges, $\mu\text{-}\eta^1\text{:}\eta^1$ (*anti-anti*) and $\mu\text{-}\eta^2\text{:}\eta^1\text{-CO}_3$ modes. The magnetic properties as preliminary results of complexes **I–VI** have been studied in a range from 5 to 350 K, showing a weak ferromagnetic exchange interactions between copper(II) ions. The magnetic behavior and properties of the magnetic orbitals are discussed in comparison with other relevant complexes.

Part III describes the synthesis, characterization and magneto-structural correlation of five polynuclear carboxylato-bridged copper(II) *paddle-wheel* complexes $[\text{Cu}_4(\text{dpyam})_2(\text{OCOC}_2\text{H}_5)_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)_6(\text{H}_2\text{O})_2][\text{Cu}_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)_4(\text{H}_2\text{O})_2](\text{DMF})_2$ (**I**), $[\text{Cu}_6(\text{phen})_2(\text{H}_2\text{O})_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)_{12}]_n[\text{Cu}_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)_4(\text{H}_2\text{O})_2]_{2n}(\text{H}_2\text{O})_{0.5n}$ (**II**), $\{[\text{Cu}_4(\text{phen})_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)_8](\text{H}_2\text{O})\}_n$ (**III**), $[\text{Cu}_2(\mu\text{-O}_2\text{CC}_6\text{H}_4\text{OH})_4(\text{C}_7\text{H}_7\text{NO})_2](\text{H}_2\text{O})_6$ (**IV**) and $[\text{Cu}_2(\mu\text{-O}_2\text{CCH}_3)_4(\text{C}_7\text{H}_7\text{NO})_2]$ (**V**).

The crystal structure of the hexanuclear $[\text{Cu}_4(\text{dpyam})_2(\text{OCOC}_2\text{H}_5)_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)_6(\text{H}_2\text{O})_2][\text{Cu}_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)_4(\text{H}_2\text{O})_2](\text{DMF})_2$ (**I**) consists of centrosymmetric tetranuclear $[\text{Cu}_4(\text{dpyam})_2(\text{OCOC}_2\text{H}_5)_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)_6(\text{H}_2\text{O})_2]$ units, independent dinuclear $[\text{Cu}_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)_4(\text{H}_2\text{O})_2]$ units and DMF molecules. In the tetranuclear unit, the “outer” Cu ions involve an intermediate five-coordinate geometry while the “inner” Cu ions have a square pyramidal geometry. The two Cu(II) ions in the inner unit are bridged by four *syn,syn*- $\eta^1\text{:}\eta^1\text{:}\mu$ propionates, showing the *paddle-wheel* cage type. The “outer” and “inner” are linked by propionato bridges showing an *anti-syn*- $\eta^1\text{:}\eta^1\text{:}\mu$ coordination mode. The one-dimensional structure of complex $[\text{Cu}_6(\text{phen})_2(\text{H}_2\text{O})_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)_{12}]_n[\text{Cu}_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)_4(\text{H}_2\text{O})_2]_{2n}(\text{H}_2\text{O})_{0.5n}$ (**II**), consists of zig-zag chains of mononuclear $\text{Cu}(\mu\text{-O}_2\text{CC}_2\text{H}_5)_2(\text{H}_2\text{O})(\text{phen})$ repeating units running along the b-axis, which are connected along the unit cell diagonal via $\text{Cu}_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)_4$ *paddle-wheel* dinuclear units. Within mononuclear and dinuclear units, the Cu(II) ions exhibit a square pyramidal geometry. In addition, the outer sphere of compounds **I** and **II** contains the independent $\text{Cu}_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)_4(\text{H}_2\text{O})_2$ *paddle-wheel* molecule in which Cu(II) ions exhibit a square pyramidal geometry with water molecules occupying the axial positions. Compound $\{[\text{Cu}_4(\text{phen})_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)_8](\text{H}_2\text{O})\}_n$ (**III**) exhibits one-dimensional structure generated by an alternating classical dinuclear *paddle-wheel* unit and an unusual dinuclear $\text{Cu}_2(\mu\text{-OCOC}_2\text{H}_5)_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)_2(\text{phen})_2$ unit, which are connected to each other via *syn,anti*-triatomic propionato bridge in an axial-equatorial configuration. The adjacent chains are connected to generate a 2D structure through the face-to-face $\pi\text{-}\pi$ interaction between phen rings.

Compounds $[\text{Cu}_2(\mu\text{-O}_2\text{CC}_6\text{H}_4\text{OH})_4(\text{C}_7\text{H}_7\text{NO})_2](\text{H}_2\text{O})_6$ (**IV**) and $[\text{Cu}_2(\mu\text{-O}_2\text{CCH}_3)_4(\text{C}_7\text{H}_7\text{NO})_2]$ (**V**) are the dinuclear molecules, in which two Cu(II) ions are bridged by four *syn,syn*- $\eta^1\text{:}\eta^1\text{:}\mu$ carboxylates with nitrogen atom of 4-acetylpyridine ligand at the apical positions, showing a *paddle-wheel* cage type with a square-pyramidal geometry. The electronic properties of all *paddle-wheel* complexes correspond with the determined structures. The IR spectra of these complexes exhibit the $\nu_{\text{as}}(\text{COO})$ and $\nu_{\text{s}}(\text{COO})$ bands. The EPR spectra of all complexes and the magnetic susceptibilities of three complexes, **III–V** reveal a very strong antiferromagnetic interaction between copper(II) centers with $J = -299.5$, -278.5 and -287 cm^{-1} , respectively. This behavior is usually found for the interaction between copper(II) centers of the *paddle-*

wheel unit which bridged by the *syn-syn* triatomic carboxylato bridges in an equatorial-equatorial configuration.

According to the structural data of complex **III**, the antiferromagnetic interaction is participated by the superexchange through the *syn-syn* propionato bridges in an equatorial-equatorial configuration and monoatomic propionato bridges in an axial-equatorial configuration, whereas the weak ferromagnetic interaction may be propagated by the poorly efficient *anti-syn* propionato bridges in an axial-equatorial configuration. The net superexchange coupling constant found between the copper atoms corresponds to the combined interaction due to all three bridges.

The results of this research would be used as basis for suggestion for further research in the field of magnetochemistry research and would benefit as a basic knowledge for structural modification in order to design the potential magnetic materials. Parts of this research have been published for publication as attached in the back of the research report.

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LIST OF ABBREVIATIONS

dpyam	Di-2-pyridylamine or 2,2'-bipyridylamine
bipy	2,2'-bipyridyl or di-2-pyridyl
phen	1,10-phenanthroline
DMF	Dimethylformamide
DMSO	Dimethylsulfoxide
μ_B	Bohr magneton
μ_{eff}	Magnetic moment
EPR	Electron paramagnetic resonance
mT	miliTesla
kK	KiloKeyser (1000 cm^{-1})
χ	Magnetic susceptibility
J	singlet-triplet energy gap
h	Plank's constant ($6.63 \times 10^{-34}\text{ Js}$)
β	Bohr magneton
N	Avogadro's number ($6.022 \times 10^{23}\text{ mol}^{-1}$)
k	Boltzmann constant ($1.381 \times 10^{-23}\text{ VCK}^{-1}$)
H	the magnetic field strength
g	Lande' multiplet splitting factor (2.0023)
EPR	Electron paramagnetic resonance
SP	Square pyramid
TBP	Trigonal bipyramid
eq	equatorial
ax	axial

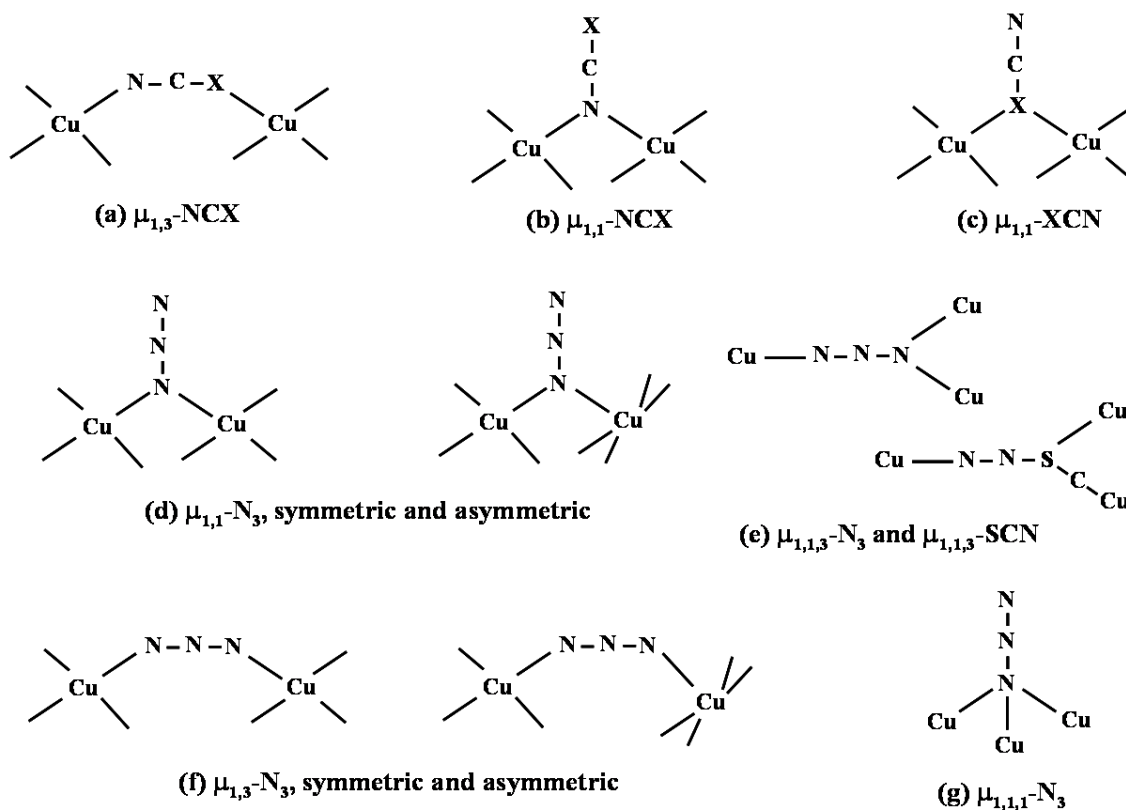
Part I

Synthesis, Crystal Structure, Spectroscopic and Magnetic Properties
of Pseudohalide and mixed Pseudohalide/Carboxylate-bridged
Polynuclear Copper(II) Complexes containing
the Di-2-pyridylamine

Synthesis, Crystal Structure, Spectroscopic and Magnetic Properties of Pseudohalide and mixed Pseudohalide/Carboxylate-bridged Polynuclear Copper(II) Complexes containing the Di-2-pyridylamine

1.1 Introduction

The design and synthesis of polynuclear coordination compounds, aiming at understanding the structural and chemical factors that control the exchange coupling between magnetic orbitals, are of continuing interest in biology, chemistry and physics. Focused on the development of supramolecular chemistry¹⁻² and molecular magnetism³, bridging ligands play an important role in the magnetic exchange pathways between paramagnetic centres. The pseudohalides (N_3^- , NCS^- , NCO^-) have been well



Scheme 1

documented for their numerous bonding abilities leading to various species⁴. Among them, the azide anion has received the major attention owing to its versatility as a ligand and the wide variety of magnetic behaviours. The magnetic characters of the azido-bridged compounds are readily predicted in view of its binding pattern: the most common bridging modes of azide are the end-on ($\mu_{1,1}$ -N₃, EO) and the end-to-end ($\mu_{1,3}$ -N₃, EE) fashions⁵⁻⁶, which generally lead to ferromagnetic and antiferromagnetic interactions, respectively (see *Scheme 1*). However, the end-on bridging does result in antiferromagnetism; the critical angle for accidental orthogonality is 108.5°, when the bridging angle exceeds a critical value⁷. This correlation is valid only for basal–basal coordination, sometimes also applied to basal–apical coordination mode, which may lead to confusion. In the basal–apical type of compounds, usually the coupling is very small as the magnetic orbital describing the single electron is mainly of a $d_{x^2-y^2}$ type lying in the basal plane of the metal center and has only a small contribution on the axis perpendicular to the basal plane⁸.

The literature available for magneto-structural studies on copper(II) complexes containing bridging thiocyanate or cyanate groups (NCS⁻ or NCO⁻) is still limited, as this ligand is less versatile and less efficient as a transmitter of magnetic interactions than azide⁹. The different modes exhibited by the thiocyanate group towards Cu²⁺ ion are: the end-to-end and end-on fashions. In thiocyanate-bridged polynuclear copper(II) compounds the end-to-end coordination mode is usually found in dinuclear¹⁰⁻¹², 1-dimensional^{9,13}, 2-dimensional¹⁴ or 3-dimensional compounds¹⁵. Only one dinuclear¹⁶ and one 1-dimensional¹⁷ polynuclear thiocyanate-bridged copper(II) complexes are known to present the end-on coordination mode.

In this study, six novel polynuclear pseudohalide-bridged copper(II) complexes: a cyanato-bridged dinuclear compound [Cu₂(dpyam)₂($\mu_{1,1}$ -NCO)₂(NCO)₂] (**I**), a thiocyanato-bridged tetranuclear compound [Cu₄(dpyam)₄($\mu_{1,3}$ -NCS)₆(O₂CH)₂(H₂O)₂] (**II**), an azido-bridged trinuclear compound [Cu₃(dpyam)₂($\mu_{1,1}$ -N₃)₂(μ -CH₃COO- κ -O¹)₂(μ -CH₃COO- κ -O¹, O²)₂]:2H₂O (**III**) and four azido-bridged dinuclear compounds [Cu₂(dpyam)₂($\mu_{1,1}$ -N₃)₂(X)₂] where X = CHO₂⁻ (**IV**), CH₃CO₂⁻ (**V**) and CH₃CH₂CO₂⁻ (**VI**) are reported.

1.2 Aims and Scopes

The objective of the first part of this research is to examine and develop the preparation work of the polynuclear copper(II) complexes containing the pseudohalide anion (NCO⁻, NCS⁻ and N₃⁻) and mixed pseudohalide/carboxylate as a bridging ligand and the di-2-pyridylamine as a chelate didentate terminal ligand. The spectroscopic properties (IR, solid state VIS, EPR (room temperature and liquid nitrogen temperature)) are characterized and the X-ray crystal structure determined. The room temperature magnetic moment and the temperature variable susceptibilities are measured and the magneto-structural correlation together with the superexchange pathways are investigated and discussed in comparison with other relevant complexes.

1.3 Experimental

1.3.1 Reagents and physical measurements

All reagents are commercial grade materials and were used without further purification. Elemental analyses (C, H, N) were determined on a Perkin–Elmer PE 2400 CHNS/O Analyzer. IR spectra were recorded with a Perkin–Elmer Spectrum One FT-IR spectrophotometer as KBr pellets in the 4000 – 450 cm^{-1} spectral range. Solid-state (diffuse reflectance) electronic spectra were recorded as polycrystalline samples on a Perkin-Elmer Lambda2S spectrophotometer over the range 8000–18000 cm^{-1} . X-band powder EPR spectra were obtained on a Jeol RE2x electron spin resonance spectrometer using DPPH ($g = 2.0036$) as a standard. Magnetic susceptibility measurements (5–280 K) were carried out using a Quantum Design MPMS-5 5T SQUID magnetometer (measurements carried out at 1000 Gauss). Data were corrected for magnetization of the sample holder and for diamagnetic contributions, which were estimated from the Pascal constants.

1.3.2 Syntheses

1.3.2.1 $[\text{Cu}_2(\text{dpyam})_2(\mu\text{-NCO-}N,N')(\text{NCO-}N)_2]$ (I)

The compound **I** was prepared by adding a hot solution of dpyam (0.171 g, 1.0 mmol) in 15 ml of dimethylformamide, to a warm solution of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.085 g, 0.5 mmol) in 10 ml of water and 0.081 g of KNCO (1 mmol) in 5 ml of water was added. Dark green crystals of **I** formed overnight (Yield 60%). Anal. Calc. for $\text{C}_{12}\text{H}_9\text{CuN}_5\text{O}_2$: C, 45.22; H, 2.84; N, 21.97. Found: C, 45.17; H, 2.67; N, 22.04%.

1.3.2.2 $[\text{Cu}_4(\text{dpyam})_4(\mu_{1,3}\text{-NCS})_6(\text{O}_2\text{CH})_2(\text{H}_2\text{O})_2]$ (II)

Compound **II** was prepared by adding a warm solution of dpyam (0.17 g, 1.0 mmol) in 20 ml of methanol, to a warm solution of copper formate, $\text{Cu}(\text{O}_2\text{CH})_2$ (0.31 g, 2.0 mmol) in 10 ml of water. Then a solution of KSCN (0.05 g, 0.5 mmol) and NaOH (0.02 g, 0.5 mmol) in 10 ml of water was slowly added. Dark green crystals were formed overnight. Yield: 80%. Anal. Calc. for $\text{C}_{48}\text{H}_{42}\text{Cu}_4\text{N}_{18}\text{O}_6\text{S}_6$ (%): C, 40.78; H, 2.99; N, 17.83. Found: C, 40.88; H, 2.75; N, 17.76.

1.3.2.3 $[\text{Cu}_3(\text{dpyam})_2(\mu_{1,3}\text{-N}_3)_2(\mu\text{-CH}_3\text{COO-}\kappa\text{-O}^1)_2(\mu\text{-CH}_3\text{COO-}\kappa\text{-O}^1, \text{O}^2)] \cdot 2\text{H}_2\text{O}$ (III)

Compound **III** was prepared by adding di-2-pyridylamine (0.17 g, 1 mmol) to a solution of copper (II) acetate hydrate (0.36 g, 2 mmol) in a methanol : DMF mixture (20:5 ml), then an aqueous solution (2 ml) of NaN_3 (0.65 g, 1 mmol) was added dropwise. Addition of 5 ml DMF to the resulting solution and standing at room temperature for one week produced green crystals. Yield ca. 60%. Anal. Calc. for $\text{C}_{28}\text{H}_{34}\text{Cu}_3\text{N}_{12}\text{O}_{10}$: C, 37.8; H, 3.9; N, 18.9. Found: C, 38.0; H, 3.9; N, 19.0%.

1.3.2.4 [Cu₂(dpyam)₂(μ_{1,1}-N₃)₂(O₂CH)₂] (IV)

Compound **IV** was prepared by adding dpyam (0.17 g, 1 mmol), dissolved in methanol/DMF (20/5 ml) and a solid of Cu(O₂CH)₂ · nH₂O (0.31 g, 2 mmol) were mixed together, followed by addition of an aqueous solution of NaN₃ (0.065 g, 1 mmol, in 2 ml) with continuous stirring. The green solution was slowly evaporated at room temperature until brownish crystals of **IV** separated. Yield ca. 80%. Anal. Calc. for C₂₂H₂₀Cu₂N₁₂O₄: C, 41.06; H, 3.13; N, 26.12. Found: C, 40.90; H, 2.96; N, 26.32%.

1.3.2.5 [Cu₂(dpyam)₂(μ_{1,1}-N₃)₂(O₂CCH₃)₂] (V)

Compound **V** synthesized from Cu(O₂CCH₃)₂ · nH₂O (0.364 g, 2 mmol) and NaN₃ (0.650 g, 1 mmol) in a similar procedure as **IV**. The green solution was slowly evaporated at room temperature until brownish-green crystals of **V** separated. Yield ca. 70%. Anal. Calc. for C₂₄H₂₄Cu₂N₁₂O₄: C, 42.92; H, 3.60; N, 25.02. Found: C, 42.60; H, 3.36; N, 25.32%.

1.3.2.6 [Cu₂(dpyam)₂(μ_{1,1}-N₃)₂(O₂CCH₂CH₃)₂] (VI)

Compound **VI** synthesized from Cu(OH)₂ (0.195 g, 2 mmol), NaO₂CCH₂CH₃ (0.192 g, 2 mmol) and NaN₃ (0.650 g, 1 mmol) in a similar procedure as **IV**. The resulting green solution was allowed to stand at room temperature. Green crystals appeared. Yield ca. 70%. Anal. Calc. for C₂₆H₂₈Cu₂N₁₂O₄: C, 44.63; H, 4.03; N, 24.02. Found: C, 44.89; H, 3.90; N, 24.00%.

1.3.3 Crystallography

The X-ray single-crystal data for the six compounds were collected at 293 K for compounds **I-III** and **VI** and at 273 K for **IV** and **V**, respectively, on a 1 K Bruker SMART CCD area detector diffractometer using graphite monochromated Mo Kα radiation (λ = 0.71073 Å) at a detector distance of 4.5 cm and swing angle of -30°. A hemisphere of the reciprocal space was covered by combination of three sets of exposures; each set had a different φ angle (0, 88, 180°) and each exposure of 40s covered 0.3° in ω. Data reduction and cell refinements were performed using the program SAINT¹⁸. An empirical absorption correction by using the SADABS program¹⁹ was applied, which resulted in transmission coefficients ranging from 0.606 to 1.000 for **I**, 0.845 to 1.0000 for **II**, 0.311 to 1.000 for **III** and 0.741 to 1.0000 for **IV**, 0.608 to 1.000 for **V** and 0.818 to 1.0000 for **VI**. The structures were solved by direct methods and refined by full matrix least-squares method on (Fobs)² with anisotropic thermal parameters for all non-hydrogen atoms using the SHELXTL-PC V 6.12 software package²⁰. All hydrogen atoms were located in a difference Fourier map and refined isotropically, except H atoms of acetate (compound **V**) and propionate anions (compound **VI**) which were fixed geometrically with the HFIX utility. The molecular graphics were created by using SHELXTL-PC²⁰ package.

1.4 Results and Discussion

1.4.1 Description of the crystal structures

1.4.1.1 Description of $[\text{Cu}_2(\text{dpyam})_2(\mu_{1,1}\text{-NCO})_2(\text{NCO})_2]$ (I)

A view of dinuclear complex is depicted in Fig. 1 together with the used numbering scheme. The structure consists of dinuclear $[\text{Cu}_2(\text{dpyam})_2(\mu_{1,1}\text{-NCO})_2(\text{NCO})_2]$ units. The copper atoms are doubly bridged by N atoms of cyanate anions in an end-on fashion with an intradinuclear $\text{Cu}\cdots\text{Cu}$ separation of 3.516(3) Å. Each copper(II) ion has a distorted square pyramidal geometry with a $\text{CuN}_4\text{N}'$ chromophore and a τ value of 0.19 ($\tau = 0$ for a square pyramidal geometry, and $\tau = 1$ for a trigonal bipyramidal geometry)²¹.

The basal plane consist of four short bonds from two pyridyl nitrogen atoms of the dpyam ligand [$\text{Cu}(1)\text{--N}(1)$, 2.016(3) and $\text{Cu}(1)\text{--N}(2)$, 2.007(3) Å], a nitrogen atom of the NCO terminal ligand [$\text{Cu}(1)\text{--N}(5)$, 1.956(3) Å] and a nitrogen atom from one of the NCO bridging ligand [$\text{Cu}(1)\text{--N}(4)$, 1.963(3) Å]. The apical position is occupied by N(4)A atom of the other NCO bridged ligand at 2.631(4) Å. The Cu metal atom lies 0.097(3) Å above the basal plane toward the axial site. When a very long Cu–O contact of 3.227(1) Å is considered, the packing the packing of the dinuclear entities shows a two-dimensional lattice, through both oxygen atoms of the NCO terminal ligands of the nearby dinuclear units. The lattice is stabilized by relatively strong hydrogen bonds between the amide nitrogen and an oxygen atom of a neighbouring NCO anion ($\text{N}(3)\text{--O}(2)$ 2.932(4) Å), generating a 1 D lattice (Fig. 2). In the literature Cu(II) dinuclear $\mu_{1,1}\text{-NCO}$ -bridged compounds have a $\text{Cu--N}_{\text{NCO}}\text{--Cu}$ angle, which lies between 92.3 and 96.3 Å. In the title compound this angle is 98.85 Å, which is, to the best of our knowledge, the largest Cu--NNCO--Cu angle for this type of dinuclear compounds observed so far. The dpyam ligands are essentially planar, with a dihedral angle of 27.98°. The average plane to plane distance of the dpyam pyridine rings of two dinuclear entities is 3.834(1) Å, which indicates a weak $\pi\text{--}\pi$ interactions through dpyam ligands in the neighbouring dinuclear entities.

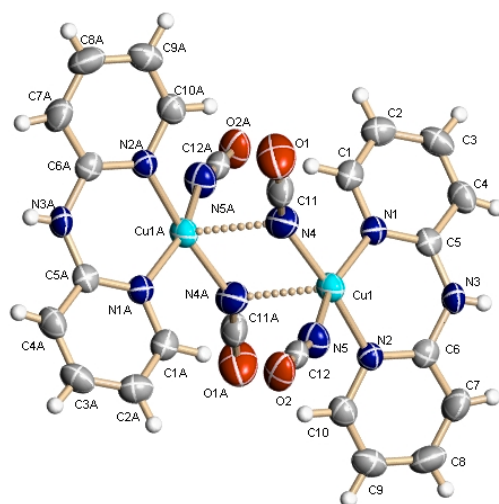


Figure 1. Thermal ellipsoid (50% probability) plot of $[\text{Cu}_2(\text{dpyam})_2(\mu_{1,1}\text{-NCO})_2(\text{NCO})_2]$ (**I**). Atoms with an "A" are generated by a mirror plane.

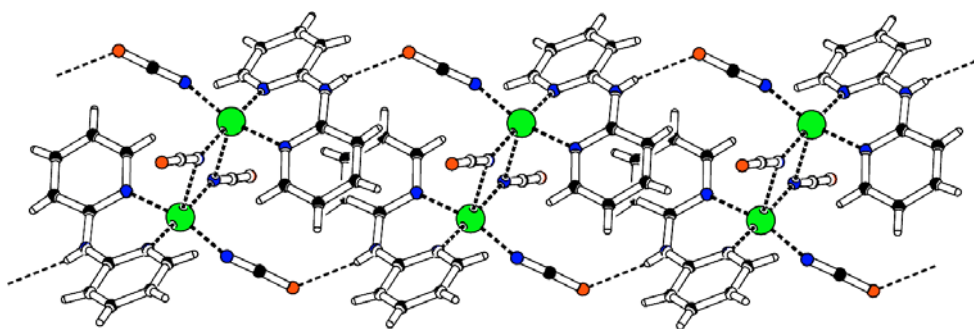


Figure 2. H-bond system providing an one-dimensional array of **I**.

1.4.1.2 Description of $[\text{Cu}_4(\text{dpyam})_4(\mu_{1,3}\text{-NCS})_6(\text{O}_2\text{CH})_2(\text{H}_2\text{O})_2]$ (**II**)

Each Cu(II) ion is doubly bridged by NCS^- anions. To the best of our knowledge, this compound is the first tetranuclear copper(II) units linked by thiocyanato groups only. A perspective view of the molecular structure is depicted in Fig. 3 together with the used numbering scheme. The tetranuclear structure has an inversion centre at the Cu2–S3 line. The basal plane of the outer Cu(II) ions (Cu1, Cu1A) consists of 2 nitrogen atoms of the dpyam ligand with Cu–N distances of 1.980(2) and 2.008(2) Å, one nitrogen atom of a bridging thiocyanate anion (Cu–N distance 1.961(3) Å) and an oxygen atom of a formate molecule (Cu–O distance 1.977(1) Å). The axial positions are occupied by an oxygen atom of a water molecule (Cu–O distance 2.518(1) Å) and by a sulfur atom of a bridging thiocyanate atom at a semi-coordination distance of 3.048(1) Å. The geometry around these outer Cu ions can best be described as axial elongated octahedral.

The “inner” Cu atoms (Cu2, Cu2A) have also the same type of geometry. However, the basal plane is now formed by 2 nitrogen atoms of the dpyam ligand with Cu–N distances of 1.995(2) and 2.018(3) Å and two nitrogen atom of two bridging thiocyanate anions (Cu–N distances 1.946(3), 1.976(3) Å). The axial positions are occupied by two sulfur atoms of two bridging thiocyanate anions (Cu–S distances are semi-coordinated at 2.875(1) and 3.126(1) Å). Each Cu ion is bridged by two $\mu_{1,3}$ -NCS anions (in an equatorial-axial bridging mode) forming in this way a zigzag tetranuclear unit. The thiocyanato groups are quasi-linear [178.3(3)°, 179.3(3)° and 178.3(3)° for N(7)–C(21)–S(1), N(8)–C(22)–S(2) and N(9)–C(23)–S(3), respectively]. The dihedral angles between the aromatic rings of a dpyam ligand are 27.8(3)° for the outer Cu(II) ion and 29.6(3)° for the inner Cu(II) ion. The N–Cu–N bite angles of the inner and outer dpyam ligands are 88.3(3)°. The intrachain metal–metal separations are 5.375(1) Å for Cu(2)–Cu(2)A and 5.556(1) Å for Cu(1)–Cu(2) which are shorter than the singly (5.93(4) Å¹¹) and doubly (5.72, 5.575 Å)¹⁴) thiocyanato-bridged copper(II) complexes. The lattice is stabilized by relatively strong hydrogen bonds between the amide nitrogen and an oxygen atom of a neighbouring formate anion, (N(3)–H(5)···O(2), 2.979(4) Å and N(6)–H(15)···O(2), 2.868(1) Å) and weak hydrogen bonds between the water hydrogen atom and a sulfur atom and formate oxygen atoms (O(1W)–H(1W)···S(1), 3.457(3) Å, O(1W)–H(2W)···O(1), 3.277(4) Å and O(1W)–H(2W)···O(2), 3.205(4) Å), leading to 3-dimensional infinite network (Fig. 4).

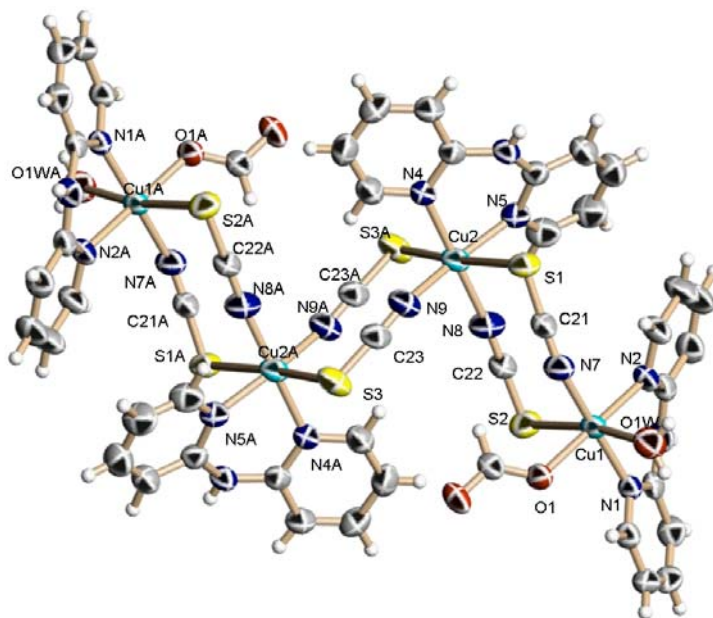


Figure 3. Thermal ellipsoid (50% probability) plot of [Cu₄(dpyam)₄($\mu_{1,3}$ -NCS)₆(O₂CH)₂(H₂O)₂] (**II**). The tetranuclear structure has an inversion centre at the Cu2–S3 line.

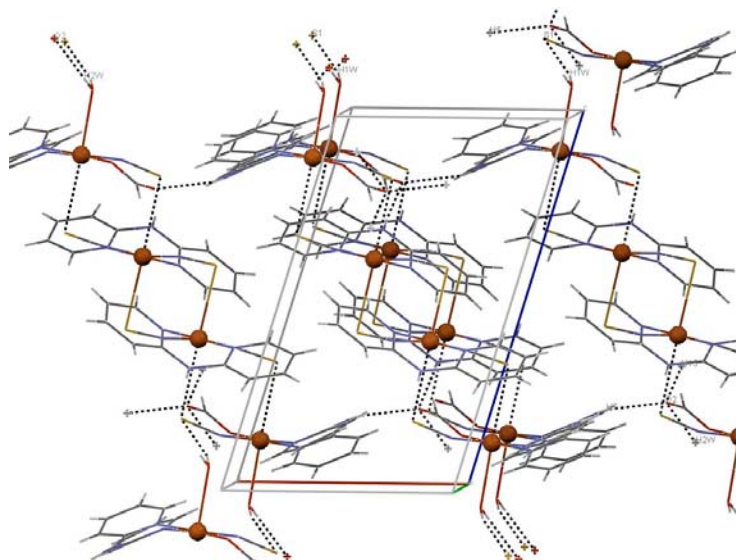


Figure 4. View along the c-axis of the 3-dimensional structure of **II**.

1.4.1.3. $[\text{Cu}_3(\text{dpyam})_2(\mu_{1,3}\text{-N}_3)_2(\mu\text{-CH}_3\text{COO-}\kappa\text{-O}^1)_2(\mu\text{-CH}_3\text{COO-}\kappa\text{-O}^1, \text{O}^2)_2]$ (**III**)

Each Cu(II) ion is bridged by a bis-chelating acetate, a monochelating acetate and azide anions. A perspective view of the molecular structure is depicted in Fig. 5 together with the used numbering scheme. The central Cu(II) ion lies on an inversion centre, while the basal plane consists of two nitrogen atoms from two bridging azide anions with Cu–N distances of 2.033(3) Å and two oxygen atoms of two bridging acetate ligands (Cu–O distances 1.973(3) Å). Two oxygen atoms of two monoatomic-bridging acetate ligands (Cu–O distances 2.495(3) Å) occupy the axial positions. The geometry around this central Cu(II) ion can best be described as axially elongated octahedral. The coordination geometry around each terminal Cu(II) atom (Cu2, Cu2A) is distorted square pyramidal with a $\text{CuN}_2\text{O}_2\text{N}'$ chromophore, $\tau = 0.16$. The four shorter bonds of the basal plane involve two nitrogen atoms of the dpyam ligand with Cu–N distances of 1.997(3) and 2.004(3) Å, two oxygen atoms from two bridging acetate anions (Cu–O distances 1.975(3) and 1.979(3) Å). A nitrogen atom of a bridging azide anion (Cu–N distance 2.295(3) Å) occupies the axial position. One of the carboxylato oxygen atoms (O4) is at a semicoordinating distance of 2.843(5) Å, thereby generating a kind of distorted octahedral geometry. The dihedral angle between the CuN_2 and CuO_2 planes is 15.7°, indicating a slight tetrahedral twist of the square base. The central Cu(II) atom is connected to each terminal Cu(II) atom by two acetate ligands and one azide anion. One of the acetate ligand is in the bidentate $\kappa\text{-O}^1, \text{O}^2$ bridging mode and the other is in a monoatomic-bridging mode. This feature is similar to those of the dinuclear triply bridged Cu(II) compounds $[\text{Cu}_2(\mu\text{-O}_2\text{CH})_2(\mu\text{-OH})(\text{dpyam})_2](\text{PF}_6)$, $\tau = 0.71$ and $[\text{Cu}_2(\mu\text{-O}_2\text{CCH}_2\text{CH}_3)_2(\mu\text{-OH})(\text{dpyam})_2](\text{ClO}_4)$, $\tau = 0.43$ and 0.22^{22} . The triatomic carboxylato bridge in both compounds connects two Cu(II) centers in axial–axial and axial–equatorial configurations for the

formate and propionate compounds, respectively. However, the present compound differs in structure in that the dihedral angle between the central and terminal bases of 25.5° leads to the partial face-to-face basal planes and a syn-syn/equatorial-equatorial configuration of the triatomic acetato bridge. The bridging angle of the monoatomic acetato bridge, Cu(2)–O(3)–Cu(1), is 89.2(1)°, while that of the azide bridge, Cu–N_{azide}–Cu, is 93.6(1)°. The Cu(1)–Cu(2) separation of 3.161(4) Å in the dinuclear unit is slightly larger than that found in the compound [Cu₃(μ_{1,1}-N₃)₄(N₃)₂(Meinic)₂(DMF)₂] with a distance of 3.088(1) Å (Meinic = methylisonicotinate)⁸, but much shorter than that found in the linear trinuclear azido-bridged complexes [Cu₃(2-aminopyrimidine)₂(μ_{1,1}-N₃)₄(μ_{1,3}-N₃)₂(dmf)₂]¹² and [Cu₃(4-amino-1,2,4-triazole)₄(N₃)₆]¹³ with Cu–Cu distances of 3.901(1) Å and 3.450(1) Å, respectively. The azide groups are quasi-linear (N(7)–N(8)–N(9) 178.2(5)°). The lattice is stabilized by relatively strong hydrogen bonds between the water oxygen atom and an oxygen atom of a neighbouring acetato anion, O(5)⋯O(4), with a distance of 2.767(3) Å; between the amine nitrogen atom and the oxygen atom of water, N(2)⋯O(5), with a distance of 2.883(6) Å and a weak hydrogen bond between the water hydrogen atom and a nitrogen from the azide anion, O(5)⋯N(9), with a distance of 3.106(3) Å, providing in this way a 2D polymeric system.

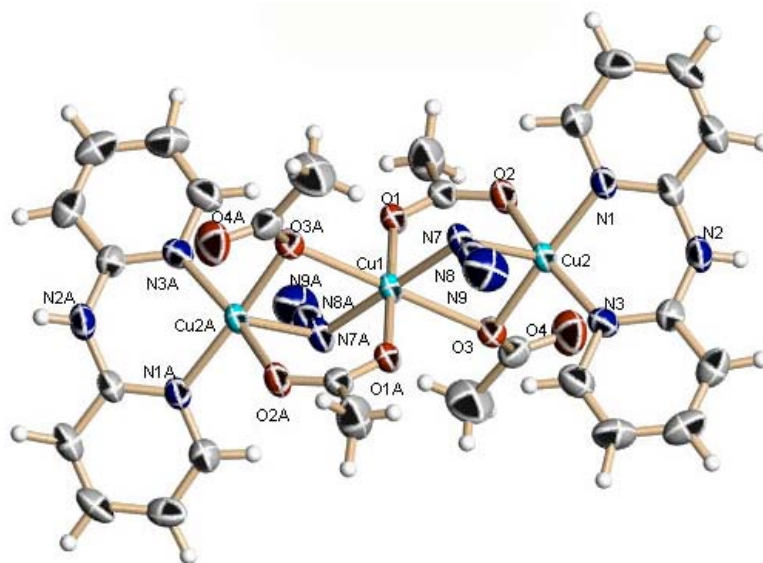


Figure 5. Thermal ellipsoid (50% probability) plot of [Cu₃(dpyam)₂(μ_{1,1}-N₃)₂((μ-CH₃COO-κ-*O'*)₂(μ-CH₃COO-κ-*O'*,*O'*²)₂].2H₂O (**III**).

1.4.1.3 Description of [Cu₂(dpyam)₂(μ_{1,1}-N₃)₂(O₂CH)₂] (**IV**)

The structure of compound **IV** consists of neutral dinuclear entities. Each of them results from the pairing of two mononuclear units related via an inversion centre. A view of the dinuclear species is given in Fig. 6. Each copper(II) ion has a markedly distorted square pyramidal geometry with a high τ value of 0.38. The structure consists of the CuN₄O chromophore, with two nitrogen atoms of the two bridging azide

ligands (Cu–N distances 1.991(1), 2.143(1) Å), a nitrogen of the dpyam ligand (Cu–N distance 1.988(1) Å) and an oxygen atom of the formate ligand (Cu–O distance 2.014(1) Å) forming the basal plane. The axial site of each copper(II) atom is occupied by another nitrogen atom of the dpyam ligand (Cu–N distance 2.129(1) Å) which is slightly shorter than the equatorial bond, Cu(1)–N(4), indicating an unusual square-pyramidal geometry found in compound **IV**. The copper(II) atoms of the compound are linked through a double azido bridges in an end-on bridging mode from the equatorial position of one copper chromophore to the equatorial position of the other one. The tetrahedral twist of the square base defined by a dihedral angle between the CuN₂ and CuNO planes is at a quite high value of 34.0° and consequently, the copper atom is displaced 0.36 Å from its individual plane. The Cu···Cu separation is 3.195 Å, while the Cu–Nazido–Cu bridging angle is 101.1(1)°, which is an usual angle of azide bridges in most metal compounds²⁵⁻²⁶. The dpyam ligand is slightly folded, as the value of the dihedral angle between the planar pyridine rings is 4.9°. An oxygen atom of the formate ligand is at a distance of 2.945(1) Å from the copper (II) atom, which is slightly too long to be considered as a semi-coordination bond. The crystal lattice is stabilized by hydrogen bonding between the amine N and an oxygen atom of neighboring formate group with a N···O contact of 2.829(7) Å leading to the formation of the 2D network.

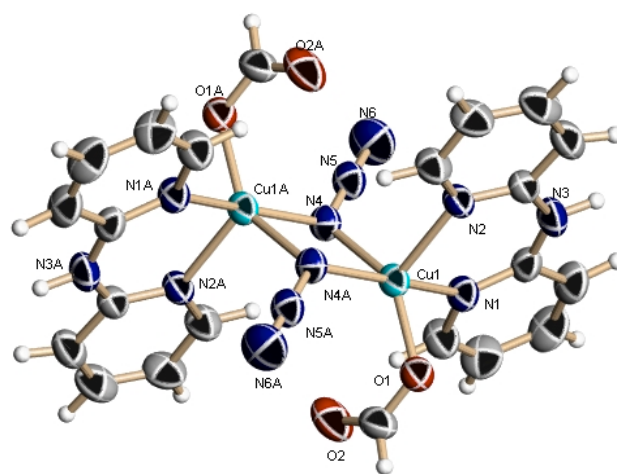


Figure 6. ORTEP 50% probability plot of [Cu₂(dpyam)₂(μ_{1,1}-N₃)₂(O₂CH)₂] (**IV**).

1.4.1.4 Description of [Cu₂(dpyam)₂(μ_{1,1}-N₃)₂(O₂CCH₃)₂] (**V**)

The structure of **V** (Fig. 7) consists of a dinuclear unit [Cu₂(dpyam)₂(μ_{1,1}-N₃)₂(O₂CCH₃)₂] in which the copper(II) atoms are bridged by two azido ions in an end-on fashion. Each of them results from the pairing of two mononuclear units related via an inversion centre. The five-coordinate CuN₄O chromophore around the copper(II) ion consists of two nitrogen atoms of two bridging azide ligands (Cu–N distances 1.997(2), 2.143(2) Å), two nitrogen atoms of a dpyam ligand (Cu–N distances 1.987(2), 2.120(2) Å) and an

oxygen atom of an acetato ligand (Cu–O distance 1.967(2) Å). The largest basal angles are 172.1(1)° and 143.3(1)°, the distortion parameter τ in this case is 0.48, so the geometry can be described as an extremely distorted square pyramidal geometry with the axial site Cu(1)–N(2), both copper(II) ions of the compound are linked through a double azido bridges in an end-on bridging mode from the equatorial position of one copper chromophore to the equatorial position of the other one. The tetrahedral twist of the square base defined by a dihedral angle between the CuN₂ and CuNO planes is at a high value of 36.0° and consequently, the copper atom is displaced 0.36 Å from its individual plane. The Cu...Cu separation is 3.200(1) Å, while the Cu–N_{azido}–Cu bridging angle is 101.2(8)°. An oxygen atom of the acetato ligand is at a distance of 2.997(2) Å from the copper(II) atom, which is also too long to be considered as a semi-coordination bond. The crystal lattice is stabilized by hydrogen bonding between the amine N and an oxygen atom of neighboring formate group with a N...O contact of 2.864(9) Å leading to the formation of the 2D network.

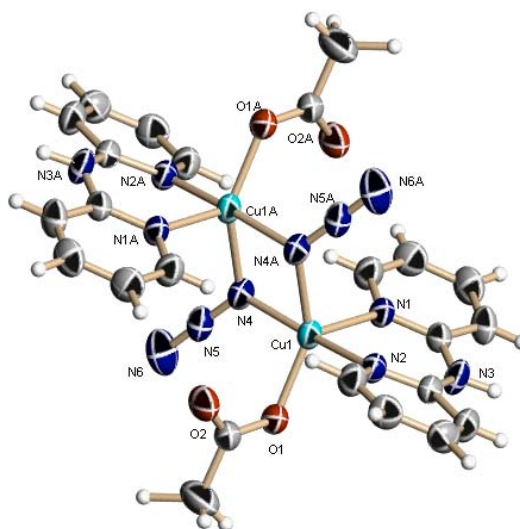


Figure 7. ORTEP 50% probability plot of [Cu₂(dpyam)₂(μ_{1,1}-N₃)₂(O₂CCH₃)₂] (V)

1.4.1.5 Description of [Cu₂(dpyam)₂(μ_{1,1}-N₃)₂(O₂CCH₂CH₃)₂] (VI)

Compound **VI** is made up of one-half [Cu₂(dpyam)₂(μ_{1,1}-N₃)₂(O₂CCH₂CH₃)₂]⁺ moiety, the other half being symmetry related via a centre of symmetry. This unit is depicted in Fig. 8. Each copper(II) ion is five coordinated in the form of distorted square pyramidal geometry ($\tau = 0.30$) of the CuN₄O chromophore (see Fig. 9). The square base comprises two nitrogen atoms of the dpyam ligand (Cu–N distances 2.011(1), 1.999(1) Å), an oxygen atom of the propionate ligand (Cu–O distance 1.960(1) Å) and a nitrogen atom of the azido ligand (Cu–N distance 2.006(1) Å), with a tetrahedral twist between the CuN₂ and CuNO planes of 21.0°. The coordination of the apical position is formed by a nitrogen atom from another azido anion (Cu–N distance 2.348(1) Å). Both copper(II) atoms of the compound are linked

through a double azido bridge in an end-on bridging mode from the equatorial position of one copper chromophore to the axial position of the other one. Both square bases are parallel in a partial face-to-face manner. The copper atom is displaced 0.16 Å from the square plane. The Cu...Cu separation is 3.247 Å, while the Cu–N_{azido}–Cu bridging angle is 96.2(1)°. The dpyam ligand is non-planar, a dihedral angle of 17.3° occurs between the individual pyridine rings and the dpyam bite angle is 89.2(1)°. An oxygen atom of the propionato ligand is at a distance of 2.848(1) Å from the copper(II) atom, which is too long to be considered as a semi-coordination bond. The hydrogen bonding involving the amine N and an oxygen atom of acetato group with a N...O contact of 2.796(7) Å, leads to the formation of the 2D network.

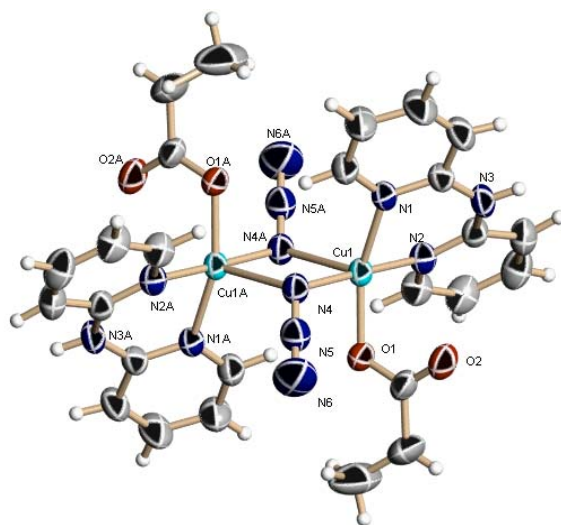


Figure 8. ORTEP 50% probability plot of $[\text{Cu}_2(\text{dpyam})_2(\mu_{1,1}\text{-N}_3)_2(\text{O}_2\text{CCH}_2\text{CH}_3)_2]$ (VI)

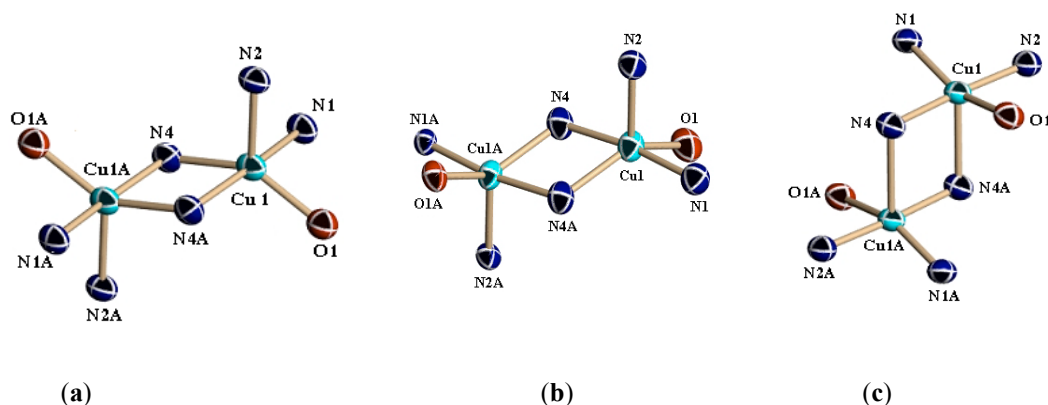


Figure 9. The chromophore of (a) $[\text{Cu}_2(\text{dpyam})_2(\mu_{1,1}\text{-N}_3)_2(\text{O}_2\text{CH})_2]$ (IV), (b) $[\text{Cu}_2(\text{dpyam})_2(\mu_{1,1}\text{-N}_3)_2(\text{O}_2\text{CCH}_3)_2]$ (V) and (c) $[\text{Cu}_2(\text{dpyam})_2(\mu_{1,1}\text{-N}_3)_2(\text{O}_2\text{CCH}_2\text{CH}_3)_2]$ (VI)

1.4.2 IR spectra

The infrared spectrum of **I** displays the characteristic bands of the isocyanate bridging¹³ ligand, ν_{asym} (NCO) at 2214 and 2180 cm^{-1} corresponding to those of other isocyanate-bridged copper(II) complexes and two types of isocyanato group with in dimer. Absorption bands at *ca.* 3000 cm^{-1} was observed, indicative of the presence of N-H stretching vibrations in this complex. The highest energy pyridine ring vibration at 1630 cm^{-1} owing to the dpyam complexes.

The IR spectrum of complex **II** displays a strong single band splitting into two peaks at 2125 and 2098 cm^{-1} , this characteristic is expected for two independent end-to-end bridging thiocyanate groups. Absorption bands at *ca.* 3000 cm^{-1} was observed, indicative of the presence of N-H stretching vibrations in this complex. The coordinated water molecules are consistent with the occurrence of broad absorption centered at 3440 cm^{-1} (symmetric and asymmetric OH stretchings)²⁷. Absorption of formate group in **II** appear at 1566s and 1370, corresponds to $\nu_{\text{as}}(\text{COO}^-)$ and $\nu_{\text{s}}(\text{COO}^-)$, respectively, The highest energy pyridine ring vibration at 1643 cm^{-1} owing to the dpyam complexes. All these IR results are well consistent with the crystal structures.

Complexes **III-VI** display a strong single band of azide bridged ligand, $\nu_{\text{asym}}(\text{N}_3)$ at 2064 cm^{-1} for **III**, 2062 cm^{-1} for **IV**, 2060 cm^{-1} for **V** and 2047 cm^{-1} for **VI** corresponding to those of other azido-bridged copper(II) complexes. Absorption bands at *ca.* 3000 cm^{-1} was observed, indicative of the presence of N-H stretching vibrations in this complex. The highest energy pyridine ring in **III-VI** vibration at $\sim$ 1630 cm^{-1} owing to the dpyam complexes. Absorption of formate group in **IV** (1581s and 1340 cm^{-1}), acetato groups in **III** (1580s and 1395 cm^{-1}) and **V** (1567s and 1402 cm^{-1}) and propionato group in **VI** (1555s and 1426 cm^{-1}), corresponds to $\nu_{\text{as}}(\text{COO}^-)$ and $\nu_{\text{s}}(\text{COO}^-)$.

1.4.3 Electronic Reflectance spectra

The electronic diffuse reflectance spectrum of **I** consists of an unsymmetrical, broad band centered at *ca.* 15 400 cm^{-1} comparable to that of **II**, 15 480 cm^{-1} (Fig. 10). The single broad peak of compound **I** is consistent with the square pyramidal stereochemistry and assigned to be the $d_{xy}, d_{xz}, d_{yz} d_{z^2} \rightarrow d_{x^2-y^2}$ transition. The single broad peak of compound **II** is consistent with an elongated octahedral stereochemistry and assigned to be the $d_{xy}, d_{xz}, d_{yz} d_{z^2} \rightarrow d_{x^2-y^2}$ transition. The diffuse reflectance spectrum of **III** displays an asymmetric broad band at 16 300 cm^{-1} and a lower energy shoulder at 11 840 cm^{-1} (Fig. 11c), while the typical main peak around 15 000 cm^{-1} , which is typical for a square pyramidal geometry, is not well resolved. This feature is consistent with distorted square pyramidal and elongated octahedral geometries within the complex. The $d_{xz}, d_{yz} \rightarrow d_{x^2-y^2}$ and $d_{xy}, d_{z^2} \rightarrow d_{x^2-y^2}$ transitions are assigned for a broad band and a lower energy shoulder, respectively. The electronic diffuse reflectance spectrum of **VI** shows an asymmetric broad band at 14890 cm^{-1} and low-energy shoulder at 11 580 cm^{-1} (Fig. 11f). This feature is consistent with the distorted square pyramidal geometry and the $d_{z^2}, dxz, dyz \rightarrow d_{x^2-y^2}$ and $d_{xy} \rightarrow$

$d_{x^2-y^2}$ transitions, respectively. In case of compounds **IV** and **V** (Fig. 11d and 11e), the spectrum shows two bands with nearly equal intensity at 12 980 and 9660 cm^{-1} (for compound **IV**) and 12 580 and 9690 cm^{-1} (for compound **V**). The unusual apparent at low frequencies in **IV** and **V** arises due to large tetrahedral twist of the square base and a shorter axial bond distance as compared to those of **VI**. However, both bands of **IV** and **V** are assigned to be the $d_{xy}, d_{yz}, d_{xz} \rightarrow d_{x^2-y^2}$ and $d_{z^2} \rightarrow d_{x^2-y^2}$ transitions²

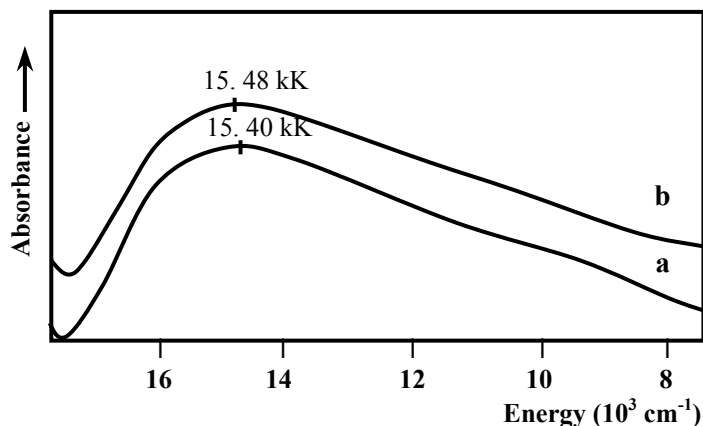


Figure 10. The electronic reflectance spectra of

- (a) $[\text{Cu}_2(\text{dpyam})_2(\mu_{1,1}\text{-NCO})_2(\text{NCO})_2]$ (**I**) and
- (b) $[\text{Cu}_4(\text{dpyam})_4(\mu_{1,3}\text{-NCS})_6(\text{O}_2\text{CH})_2(\text{H}_2\text{O})_2]$ (**II**)

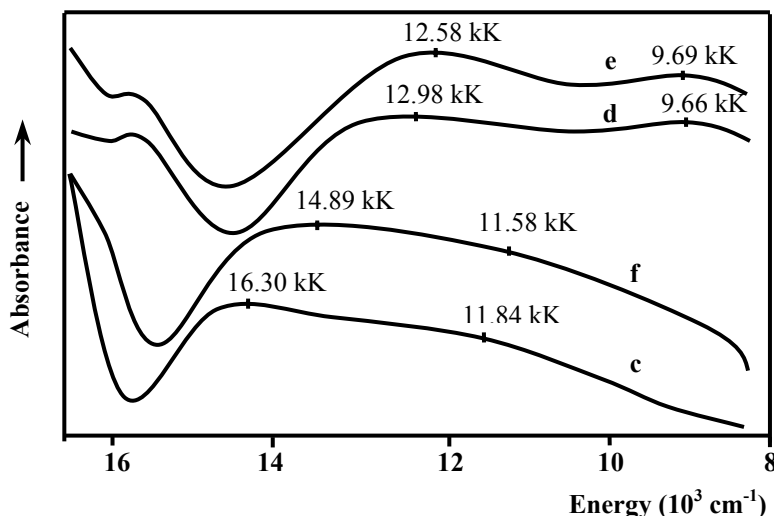


Figure 11. The electronic reflectance spectra of

- (c) $[\text{Cu}_3(\text{dpyam})_2(\mu_{1,3}\text{-N}_3)_2(\mu\text{-CH}_3\text{COO-}\kappa\text{-O}^1)(\mu\text{-CH}_3\text{COO-}\kappa\text{-O}^1, \text{O}^2)_2] \cdot 2\text{H}_2\text{O}$ (**III**)
- (d) $[\text{Cu}_2(\text{dpyam})_2(\mu_{1,1}\text{-N}_3)_2(\text{O}_2\text{CH})_2]$ (**IV**)
- (e) $[\text{Cu}_2(\text{dpyam})_2(\mu_{1,1}\text{-N}_3)_2(\text{O}_2\text{CCH}_3)_2]$ (**V**) and
- (f) $[\text{Cu}_2(\text{dpyam})_2(\mu_{1,1}\text{-N}_3)_2(\text{O}_2\text{CCH}_2\text{CH}_3)_2]$ (**VI**)

1.4.3 EPR spectra

The X-band powder EPR spectra of complex **I** at room temperature and 77 K show in Fig. 12. At both temperatures a normal $S = 1/2$ signal was observed with $g_{\perp} = 2.08$ and $g_{\parallel}$ of 2.29, which is in agreement with the observed geometry²⁸. Besides these signals, corresponding to the $\Delta M_s = \pm 1$ allowed transitions, around 160 mT a weak (so called half-field (Fig. 12c)) signal was observed, corresponding to the $\Delta M_s = \pm 2$ forbidden transition, which indicates a magnetic coupling between the two Cu(II) ions.

The same type of spectrum was also observed for some other NCO-bridged Cu(II) dinuclear compounds, although only in one case also the half-field signal was observed¹¹. When EPR of **I** is measured as a frozen solution (DMF) at 77 K a resolved $d_{x^2-y^2}$ spectrum is obtained with a $g_{\perp}$ value of 2.05, a $g_{\parallel}$ of 2.29, with a $A_{\parallel}$ value of 16.2 mT (no half-field signal was observed any more). Also nine superhyperfine (Fig. 12d) lines with an $A_{N\perp}$ of 1.55 mT was observed, which indicates four nitrogen donors. This observation indicates that the dinuclear compound dissociate in this solution.

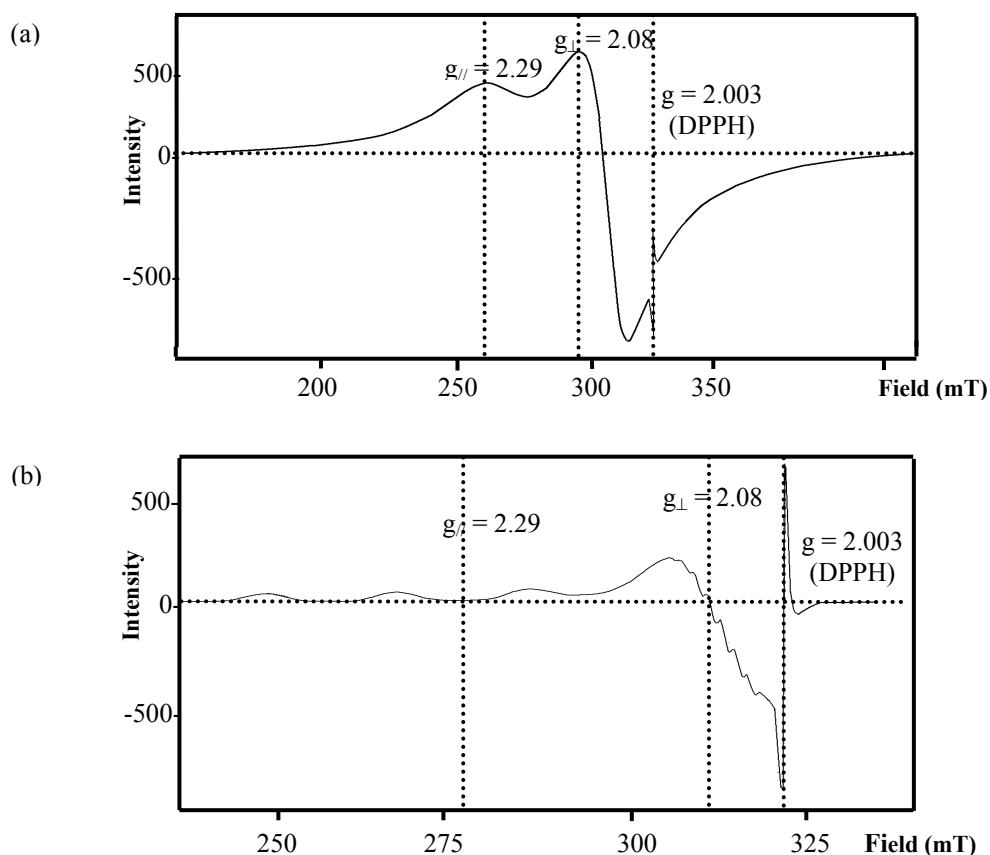


Figure 12. The EPR spectra of $[\text{Cu}_2(\text{dpyam})_2(\mu_1\text{-NCO})_2(\text{NCO})_2]$ (**I**) at

- | | |
|-----------------------|-------------------------------|
| (a) room temperature | (b) low-temperature (77 K) |
| (c) half-field signal | (d) nine superhyperfine lines |

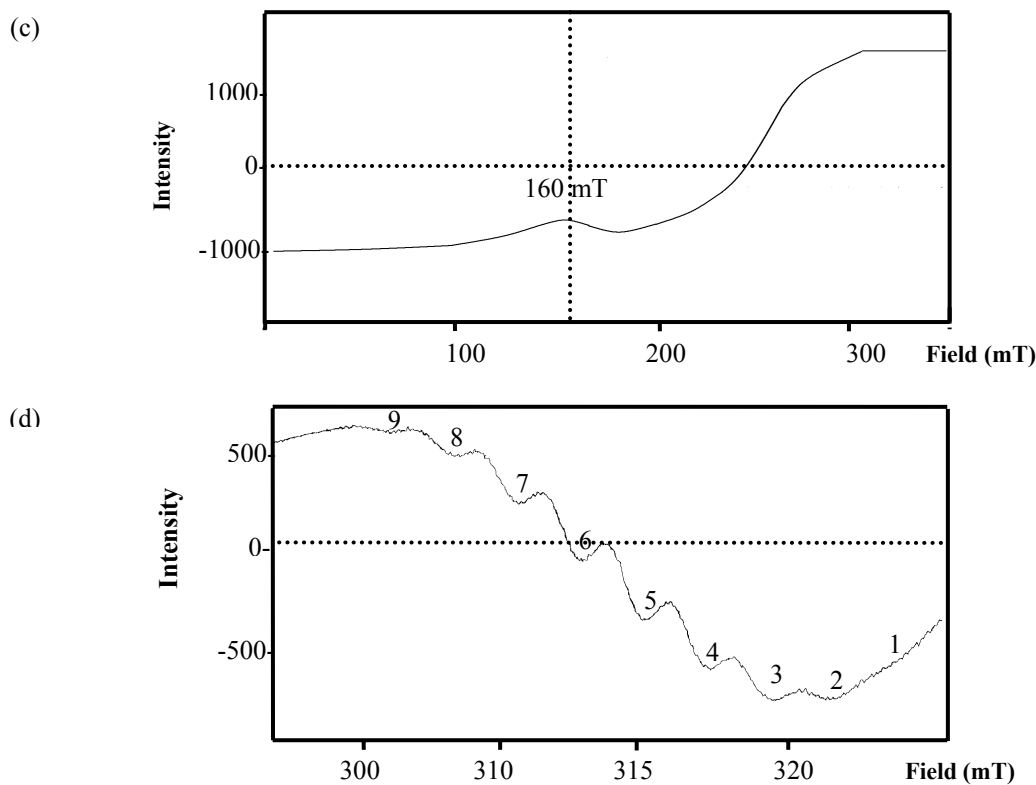


Figure 12. The EPR spectra of $[\text{Cu}_2(\text{dpyam})_2(\mu_{1,1}\text{-NCO})_2(\text{NCO})_2]$ (**I**) at (cont.)

(a) room temperature

(b) low-temperature (77 K)

(c) half-field signal

(d) nine superhyperfine lines

The EPR spectrum of the powdered complex **II** reveals at room temperature and at 77 K (Fig. 13) an axial signal with $g_{\perp} = 2.06$ and an unresolved $g_{\parallel} = 2.27$. The signals are consistent with the $d_{x^2-y^2}$ ground state and the distorted octahedral geometry. No triplet signal has been observed.

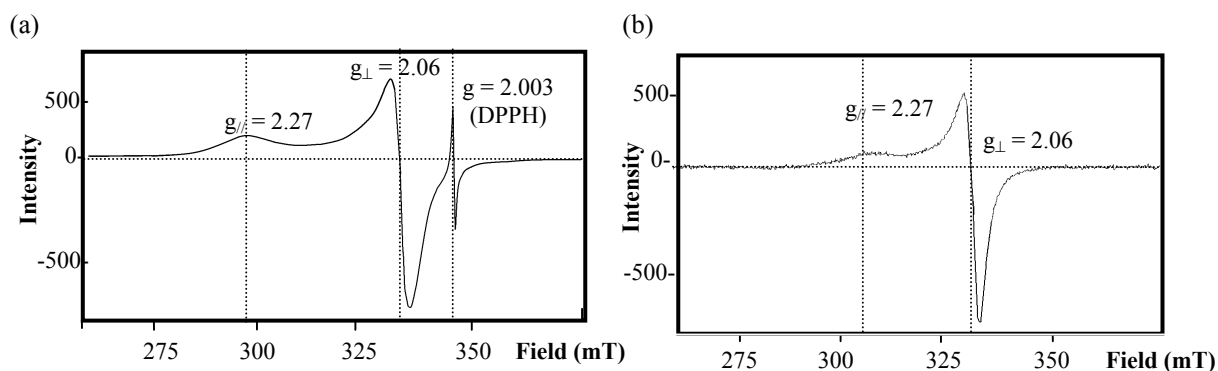


Figure 13. The EPR spectra of $[\text{Cu}_4(\text{dpyam})_4(\mu_{1,3}\text{-NCS})_6(\text{O}_2\text{CH})_2(\text{H}_2\text{O})_2]$ (**II**) at

(a) room temperature

(b) low-temperature (77 K)

The X-band powder EPR spectrum of **III** shows at RT and at 77K an axial signal with a $g_{\perp}$ of 2.09 and unresolved $g_{\parallel}$ of 2.27. No half-field signal or other signals typical for trinuclear Cu(II) compounds could be obtained at RT or 77K. Similar EPR features/signals are also found in other trinuclear compounds²⁹.

The EPR spectra of compounds **IV** and **V** were recorded as a polycrystalline powder at RT and 77 K from 0-800 mT at X-band frequency ($h\nu = 0.325 \text{ cm}^{-1}$).

The observed EPR spectrum of compound **IV** and **V** reveals typical triplet spectra with a zero-field splitting parameter $D < h\nu$. The spectra are almost identical for both compounds and hardly no change is observed at RT and 77 K. Two representative EPR spectra are given as Fig. 14a (compound **IV** at RT) and Fig. 14 (compound **VI** at RT). Others are given as supplementary material. Compound **IV** shows very broad absorptions (at RT) at 110, 250 and 460 mT (110, 275 and 490 mT for compound **V**), which are too broad for assignment and/or simulation. A rough estimate for the zero-field splitting is 0.4 cm^{-1} . The sharp weak absorptions at around 320 mT are from monomeric impurity.

The EPR spectrum of compound **VI** was recorded at RT and 77 K from 220-420 mT, and both show an axial $S = \frac{1}{2}$ spectrum with a $g_{\perp}$ of 2.09 and unresolved $g_{\parallel}$ of 2.26. These values are in agreement with a $d_{x^2-y^2}$ ground state.

At RT a very weak half-field signal is observed at 160 mT, typical for dinuclear species. However, at 77 K this signal is not observed. The observed EPR spectra are in agreement with the magnetic behaviour of the three compounds (vide infra).

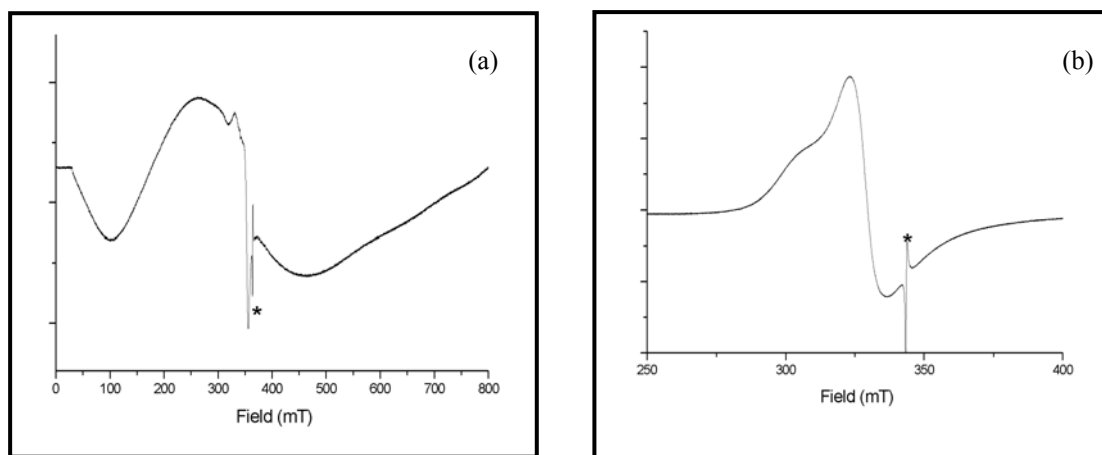


Figure 14. EPR spectrum of compounds **IV** and **VI** at RT (The starred peak is the internal reference, DPPH).

1.4.5 Magnetic properties and superexchange mechanism

The magnetic susceptibility of a powdered sample of compound **I** was measured from 5 to 300 K. The magnetic properties is depicted in Fig. 15 in the form of μ_{eff} versus T for two Cu(II) ions. At 300 K the μ_{eff} starts at a value of about $2.64 \mu_{\text{B}}$ (this values is close to what is expected for two spin = $\frac{1}{2}$ uncoupled centres). Upon cooling the effective moment stays almost constant and at about 50 K is started to increase to reach the value of $2.81 \mu_{\text{B}}$ at 5 K. This behaviour is typical for a weak ferromagnetic interaction.

The theoretical expression for the magnetic susceptibility for two interacting $S = 1/2$ centres, which is based on the general Hamiltonian³⁰ is: $H_{\text{ex}} = -JS_1S_2$, in which the exchange parameter J , is negative for antiferromagnetic and positive for ferromagnetic interaction. The magnetic data were fitted to the equation given in the literature for dinuclear copper compounds³⁰:

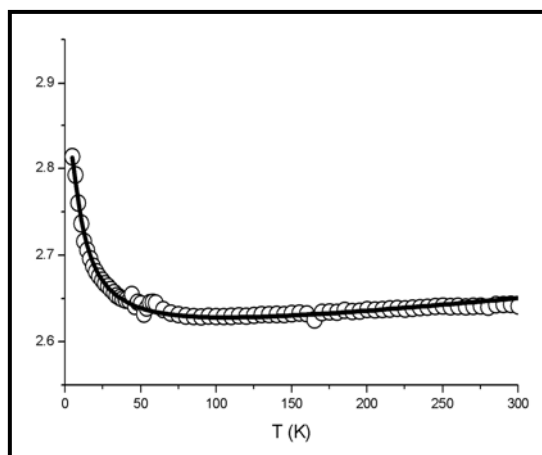
$$\chi_{\text{m}} = (2Ng^2\beta^2)[kT - (2zJ' / (3 + \exp(-J/kT)))]^{-1} [3 + \exp(-J/kT)]^{-1} (1-p) + \chi_{\text{p}} + \text{TIP}$$

in which N , g , β , k and T have their usual meanings. The parameter p denotes the fraction of paramagnetic impurity in the sample and zJ' the interaction between neighbouring dinuclear identities. A temperature independent paramagnetism (TIP) was also considered and fixed at 60×10^{-6} per copper ion. The fit was accomplished by minimisation of $R = \sum (\chi_{\text{m}} \cdot T_{\text{calc}} - \chi_{\text{m}} \cdot T_{\text{obs}})^2 / (\chi_{\text{m}} \cdot T_{\text{obs}})^2$ by least-squares procedure. The best fit was obtained for $J = 6.03 \text{ cm}^{-1}$, $g = 2.11$, $zJ' = -1.24 \text{ cm}^{-1}$, $p = 0.06$, with a final R of 6.9×10^{-7} Fig. 15).

Only a few Cu(II) dinuclear $\mu_{1,1}$ -NCO bridged compounds are known in the literature of which the X-ray structure as well as the magnetic susceptibility is reported. For two compounds, $[\text{Cu}(2,3\text{-bis}(\text{2-pyridyl})\text{pyrazine})(\mu_{1,1}\text{-NCO})_2]_n$ and $[\text{Cu}_2(\mu_{1,1}\text{-NCO})_2(4\text{-methyldiethylenetriamine})_2](\text{ClO}_4)_2$, a weak antiferromagnetic interaction is observed with $J = -1.0 \text{ cm}^{-1}$ and $J = -4.6 \text{ cm}^{-1}$, respectively³¹⁻³². However the geometry is not quite the same as the title compound, as the first compound has a distorted octahedral Cu(II) geometry and the second compound has two different dinuclear units in the unit cell. In the only other compound, which has almost the same geometry, $[\text{Cu}_2(\mu_{1,1}\text{-NCO})_2(\text{NCO})_2(1,10\text{-phenanthroline})_2]$ ³³, also a ferromagnetic interaction is observed between the Cu(II) ions with $J = 13.75 \text{ cm}^{-1}$. Due to this limited number of compounds, no conclusions can be drawn from these results.

Figure 15. Plots of μ_{eff} vs. T of $[\text{Cu}_2(\text{dpyam})_2(\mu_{1,1}\text{-NCO})_2(\text{NCO})_2]$ (**I**)

Compound **I** has the magnetic $d_{x^2-y^2}$ orbital with lobe directed toward the bridging N atom of the isocyanate group, which is positioned in the apical site of each square pyramidal copper(II) chromophore. This feature should cause the



ferromagnetic superexchange pathway that can occur through this bridging ligand in an end-on coordination mode, as there is the orthogonality between the copper magnetic orbital and the nitrogen orbital of the isocyanate bridge (Fig. 16).

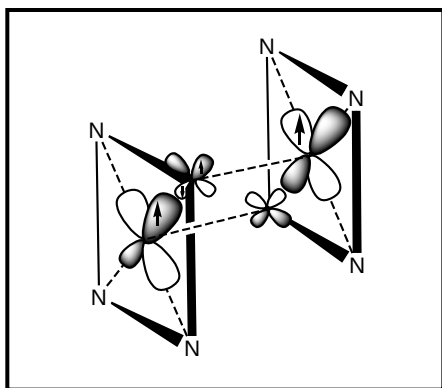


Figure 16. Model predicting the magnetic interactions in isocyanate bridge for $[\text{Cu}_2(\text{dpyam})_2(\mu_{1,1}\text{-NCO})_2(\text{NCO})_2]$ (**I**)

The magnetic susceptibility of a powdered sample of complex **II** was measured from 5 to 200 K. The magnetic properties are given in Fig. 17 in the form of a $\chi_m T$ vs. T plot (for 4 Cu ions). At 200 K the $\chi_m T$ value is circa $1.35 \text{ cm}^3 \text{ mol}^{-1}$. This value is somewhat lower than the theoretical value for 4 uncoupled spin $\frac{1}{2}$ centres ($1.5 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ with $g = 2$). Upon lowering the temperature this value stays almost constant until at about 20 K the value decreases till about $1.28 \text{ cm}^3 \text{ mol}^{-1}$ at 5 K, all of which is indicative for a weak antiferromagnetic interaction.

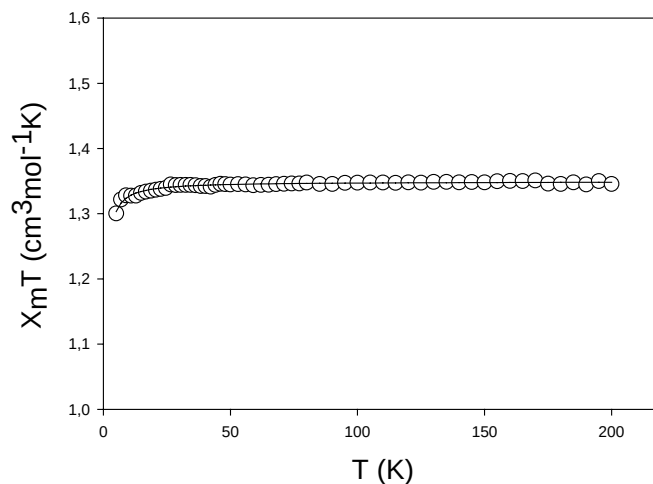


Figure 17. Plots of μ_{eff} vs. T of $[\text{Cu}_4(\text{dpyam})_4(\mu_{1,3}\text{-NCS})_6(\text{O}_2\text{CH})_2(\text{H}_2\text{O})_2]$ (**II**)

Despite that this tetranuclear compound is topologically different from a linear tetranuclear copper compound, the Hamiltonian which can be used is identical³⁴:

$$H = -2 \cdot J_1 (\mathbf{S}_1 \mathbf{S}_2) - 2 \cdot J_2 (\mathbf{S}_1 \mathbf{S}_3 + \mathbf{S}_2 \mathbf{S}_4) - 2 \cdot J_3 (\mathbf{S}_2 \mathbf{S}_3 + \mathbf{S}_1 \mathbf{S}_4) - 2 \cdot J_4 (\mathbf{S}_3 \mathbf{S}_4)$$

The interpretation of the Hamiltonian can be done with the use of Fig. 18. The first term corresponds to the interaction between the two “central” coppers of the tetranuclear unit Cu₂-Cu_{2A}. The second term of the Hamiltonian corresponds to the interaction of each of the central copper atoms with its nearest neighbour external copper centre, Cu₂-Cu_{1A} and Cu₁-Cu_{2A}. The third term represents the interaction between next-nearest neighbour interactions, Cu₁-Cu₂ and Cu_{1A}-Cu_{2A}. The fourth term is the interaction between the two external coppers, Cu₁-Cu_{1A}.

The energy levels and the spin quantum numbers are as follows:

$$S_1 = 2 \quad E_1 = -J_1 - J_2/2 - J_3 - J_4/2$$

$$S_2 = 1 \quad E_2 = -J_1 - J_2/2 + J_3 - J_4/2$$

$$S_3 = 1 \quad E_3 = (J_2 + J_4)/2 + [(J_2 - J_4)^2 + (J_3 - J_1)^2]^{1/2}$$

$$S_4 = 1 \quad E_4 = (J_2 + J_4)/2 - [(J_2 - J_4)^2 + (J_3 - J_1)^2]^{1/2}$$

$$S_5 = 0 \quad E_5 = J_1 + J_3 + (J_2 + J_4)/2 + [4(J_1^2 + J_3^2) + J_2^2 + J_4^2 - 2J_1(J_2 + 2J_3 + J_4) - 2J_2(J_3 - J_4) - 2J_3J_4]^{1/2}$$

$$S_6 = 0 \quad E_6 = J_1 + J_3 + (J_2 + J_4)/2 - [4(J_1^2 + J_3^2) + J_2^2 + J_4^2 - 2J_1(J_2 + 2J_3 + J_4) - 2J_2(J_3 - J_4) - 2J_3J_4]^{1/2}$$

An expression for the magnetic susceptibility per tetranuclear unit is described by:

$$\chi_M = (N_A g^2 \beta^2 / k_B T) [10 \exp(-E_1 / K_B T) + 2 \exp(-E_2 / K_B T) + 2 \exp(-E_3 / K_B T) + 2 \exp(-E_4 / K_B T)] / [5 \exp(-E_1 / K_B T) + 3 \exp(-E_2 / K_B T) + 3 \exp(-E_3 / K_B T) + 3 \exp(-E_4 / K_B T) + \exp(-E_5 / K_B T) + \exp(-E_6 / K_B T)] + \text{TIP}$$

An identical g value for each copper has been considered and the TIP per copper atom was fixed to 60×10^{-4} cgs units³⁰. As the distance between the external copper atoms is large (Cu₁...Cu_{1A}, 13.097 Å), the interaction parameter J₄ was fixed to J₄ = 0. The best set of parameters were obtained as 2J₁ = 0.05 cm⁻¹, 2J₂ = -0.37 cm⁻¹, 2J₃ = -0.09 cm⁻¹ and g = 1.9 (given as a straight line in Fig. 17). The values obtained are reasonable by chemical intuition and can be explained in light of their structural parameters. All interaction parameters are small, as distances between the copper ions are large and no clear interaction pathway is observed. The parameter J₁ is positive, pointing at a weak ferromagnetic interaction between the two central copper ions. These two central copper ions are in a square pyramidal geometry (SP), with a d_{x2-y2} magnetic orbital (that which includes the unpaired electron). The two possible pathways for the magnetic interaction must occur via the thiocyanate anions. In both cases this involves a magnetic orbital of one copper (d_{x2-y2}) and a non-magnetic orbital (d_{z2}) of the other copper, thus explaining the weak interaction observed. It is only the almost perfect SP geometry of the two copper centres that leads to an effective delocalisation of the unpaired electrons allowing the interaction. The fact that the d_{z2} and d_{x2-y2} orbitals

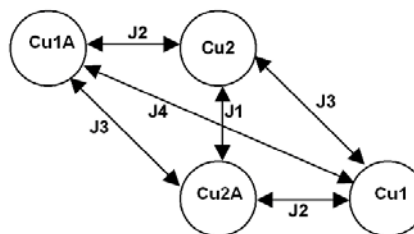


Figure 18. Scheme of the magnetic interactions in a zig-zag tetranuclear unit of compound **II**

(angles) are completely perpendicular to each other, probably makes the interaction ferromagnetic. This phenomenon has also been observed in the literature³⁴.

The interaction between the central copper centres with their corresponding external copper atoms (nearest neighbour), J_2 , is weak and antiferromagnetic. The overall magnetic behaviour seems to be dominated by this weak antiferromagnetic interaction, resulting in a singlet ground state. Also in this case the interaction must occur via the thiocyanate groups, giving an antiferromagnetism interaction. The interaction between next-nearest neighbours, J_3 , is weak antiferromagnetic. The distances between the copper ions are large ($\text{Cu}_{1A} \cdots \text{Cu}_{2A}$, 8.327 Å) and its interaction is almost 0 and negligible. In order to confirm these fitting parameters, a modified Bleany Bowers fit with intermolecular interactions was performed, giving a good fit with the same type (both sign and order of magnitude) of interaction parameters.

As in previously reported cases with thiocyanate bridging ligands, the compound shows weak interactions³⁴ (Table 1). The $N_{eq}\text{-}S_{ax}$ bridging mode of the thiocyanate implies that the magnetic path is through two orbitals which are perpendicular to each other (E_g and T_{2g}), normally leading to ferromagnetic interactions, as is the case for the two central coppers (J_1). The "overall" magnetic behaviour is dominated by a weak antiferromagnetic interaction between the central dimer and its outer copper neighbours that apparently masks the very weak "intra-dimer" ferromagnetic interaction. This result is in concordance with other compounds showing the $N_{eq}\text{-}S_{ax}$ bridging mode of the thiocyanate³⁴.

The thiocyanate in complex **II**, bridges link equatorial-axial coordination sites of elongated octahedral neighboring copper(II) centres and delocalisation of unpaired electron density along the axial coordination site should be very poor and the magnetic orbitals are almost orthogonal; consequently, the antiferromagnetic interaction should be very weak, which is in agreement with the observed coupling constants $2J_1 = 0.05 \text{ cm}^{-1}$, $2J_2 = -0.37 \text{ cm}^{-1}$ and $2J_3 = -0.09 \text{ cm}^{-1}$.

Thiocyanate with the *end-to-end* mode of coordination has been found able to transmit weak ferro- or antiferromagnetic interactions (Table 1.1) depending on the geometry and the bridging mode in the Cu–NCS–Cu entity: the equatorial-axial disposition (EA) of the thiocyanate bridging leads to very weak or zero overlap between the involved magnetic orbitals and consequently weak magnetic interaction (ferro- or antiferromagnetic) is observed. However, the equatorial-equatorial (EE) disposition enables significant overlap of the orbitals of the bridging entities with the magnetic orbitals of the metal atoms and so strong antiferromagnetic interaction takes place. Theoretically, the EA disposition leads to the accidental orthogonality of the MO arising from the metallic orbitals, minimising the antiferromagnetic component of the global J constant.

The magnetic susceptibility of **III** was measured from 5 to 300 K. The magnetic behaviour of the title compound is depicted in Fig. 19 in the form of $\chi_M T$ vs T and $\chi_M T$ vs T for three Cu(II) ions. At 300 K the $\chi_M T$ product has a value of 1.16 cm³mol⁻¹K which is very close to the theoretical value of three non-interacting copper (II) $S = 1/2$ spins (1.125 cm³mol⁻¹K). The $\chi_M T$ value stays almost constant till about 85 K and then decreases gradually to a value of 0.42 cm³mol⁻¹K at 5 K. This behaviour agrees with a very weak antiferromagnetic interaction between the Cu(II) ions, remaining a $S = 1/2$ ground state at 5 K. Detailed study of this low-T state was not possible due to instrumental limitations below 5 K.

The theoretical expression for the magnetic susceptibility for three interacting $S = 1/2$ centres is based on the Hamiltonian³⁰: $\hat{H} = J(\hat{S}_1\hat{S}_2 + \hat{S}_2\hat{S}_3) + J'\hat{S}_1\hat{S}_3$, in which the exchange parameter J , is negative for antiferromagnetic and positive for ferromagnetic interaction. J' is the interaction between terminal Cu(II) atoms and can be neglected ($J' = 0$) as the magnetic interaction between neighbouring Cu (II) atoms is the dominant pathway. The magnetic data were fitted to the equation given in the literature for a linear trinuclear copper(II) compound:

$$\chi_M = \frac{Ng^2\beta^2}{4KT} \cdot \frac{1 + e(J/KT) + 10e(3J/2KT)}{1 + e(J/KT) + 2e(3J/2KT)} + \text{TIP},$$

in which N , g , β , k and T have their usual

meanings³⁰. Also a TIP, with a fixed value of 60x10⁻⁶ cm³mol⁻¹ per each Cu(II) has been considered. The fit was accomplished by minimisation of $R = (\chi_m \cdot T_{\text{calc}} - \chi_m \cdot T_{\text{obs}})^2 / (\chi_m \cdot T_{\text{obs}})^2$ by a least-squares procedure. The best fit, depicted in Fig. 19 as a solid line, was obtained for $J = -10.2$ cm⁻¹, $g = 2.05$, with a final R of $8 \cdot 10^{-5}$. The values obtained are reasonable and can be explained in light of their structural parameters. This weak interaction is also comparable with the compound Cu₃(diethylenetriamine)₂(N₃)₆ with a reported J value of -2.1 cm⁻¹⁸.

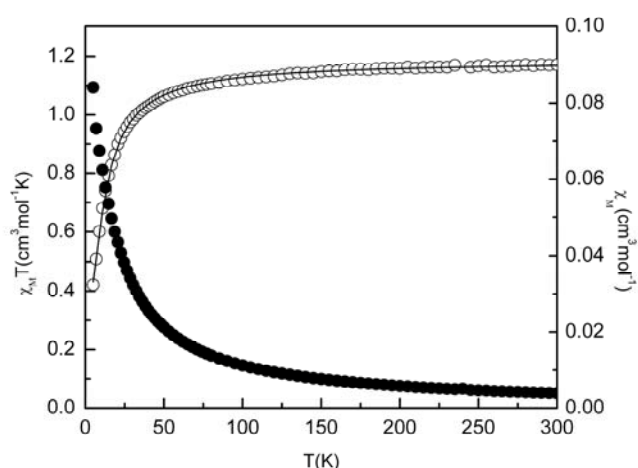


Figure 19. A plot of the temperature dependence of $\chi_M T$ vs T (○) and χ_M vs T (●) for the title compound. The solid line represents the calculated curve for the parameters $J = -10.2$ cm⁻¹, $g = 2.05$.

The possible pathways for the magnetic interaction must occur via the azide anion or the oxygen O3 from the monoatomic acetate molecule. Due to the fact that all copper ions, despite a small difference in geometry have a $d_{x^2-y^2}$ ground state, these orbitals are orthogonal to each other when Cu1-O3 and Cu2-N7 are taken as the apical positions with distances of 2.495(3) and 2.295(3) Å, respectively, explaining the weak interaction observed.

The magnetic susceptibility of compounds **IV-VI** has been measured from 5-300 K. The magnetic properties of the compounds are depicted in Figs. 20, 21 and 22, for compounds **IV**, **V** and **VI**, respectively, in the form of μ_{eff} versus T plots for one copper(II) ion. Compounds **IV** and **V** show a very similar magnetic behaviour. At 300 K the μ_{eff} is 1.89 μ_B per copper ion for compound **IV** (1.84 μ_B , for **V**), which is somewhat above the spin-only value for a single uncoupled spin $S = 1/2$ copper(II) centre. Upon cooling it raises gradually to reach 2.02 and 2.04 μ_B , at around 25 K, for compounds **IV** and **V**, respectively. This behaviour is typical for medium to strong ferromagnetically coupled copper(II) dinuclear compound. Below that temperature, μ_{eff} then diminishes till a value around 1.92 μ_B for compound **IV** (2.00 μ_B for **V**) at 5 K, which may originate from intermolecular antiferromagnetic interactions, or from the paramagnetic impurities present in the samples (vide infra).

The magnetic properties of compound **VI** differ from that of compounds **IV** and **V**. At 300 K the μ_{eff} is 1.74 μ_B per copper ion for compound **VI**, which is about the spin-only value calculated for an uncoupled spin $S = 1/2$ copper(II) centre. Upon cooling, this value stays almost constant till about 50 K, where it increases gradually to reach 1.86 μ_B , at 5 K (see Fig. 21). This magnetic behaviour is typical for very weak ferromagnetically coupled copper(II) ions in a dinuclear compound.

The theoretical expression for the magnetic susceptibility for two interacting $S = 1/2$ centers, based on the general Hamiltonian³⁰ is: $H_{ex} = -JS_1S_2$, in which the exchange parameter J , is negative for antiferromagnetic and positive for ferromagnetic interaction. The magnetic data were fitted to the equation given in the literature for dinuclear copper compounds³⁰:

$\chi_m = (2Ng^2\beta^2)[kT(2zJ' / (3 + \exp(-J/kT)))]^{-1} [3 + \exp(-J/kT)]^{-1} (1-p) + \chi_p p + \text{TIP}$, in which N , g , β , k and T have their usual meanings.

The parameter p denotes the fraction of paramagnetic impurity in the sample and zJ' refers to the interaction between neighbouring dinuclear identities. A temperature independent paramagnetism (TIP) was also considered and fixed at 60×10^{-6} per copper ion. The fit was accomplished by minimisation of $R = \sum(\chi_m \cdot T_{calc} - \chi_m \cdot T_{obs})^2 / (\chi_m \cdot T_{obs})^2$ by least-squares procedure. The best fit was obtained for compound **IV** with the following values: $J = 63.3 \text{ cm}^{-1}$, $g = 2.06$, $zJ' = -3.3 \text{ cm}^{-1}$, $p = 0.04$, with a final R of 2.0×10^{-4} (see solid line in Fig. 20). For compound **V** these values are $J = 63.8 \text{ cm}^{-1}$, $g = 2.05$, $zJ' = -0.8 \text{ cm}^{-1}$, $p = 0.01$, with a final R of 9.0×10^{-5} (see solid line in Fig. 21). For compound **VI** these values are $J = 5.1 \text{ cm}^{-1}$, $g = 2.02$, $zJ' = -2.2 \text{ cm}^{-1}$, $p = 0.06$, with a final R of 1.5×10^{-3} (see solid line in Fig. 22). These values are in agreement with the structural results.

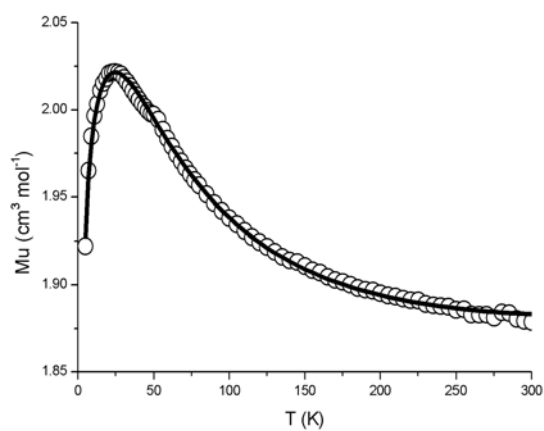


Figure 20. A plot of the temperature dependence of μ_{eff} vs. T per Cu(II) ion for compound **IV**. The solid line represents the calculated curve (see text).

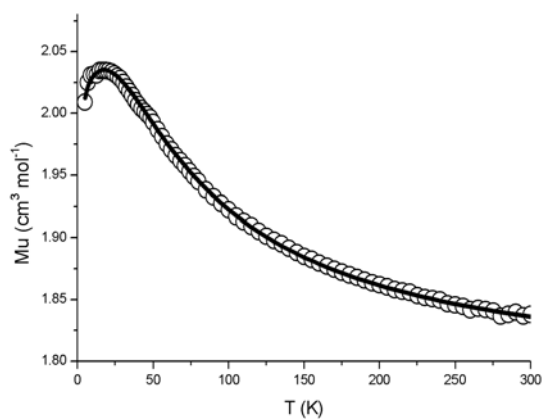


Figure 21. A plot of the temperature dependence of μ_{eff} vs. T per Cu(II) ion for compound **V**. The solid line represents the calculated curve (see text).

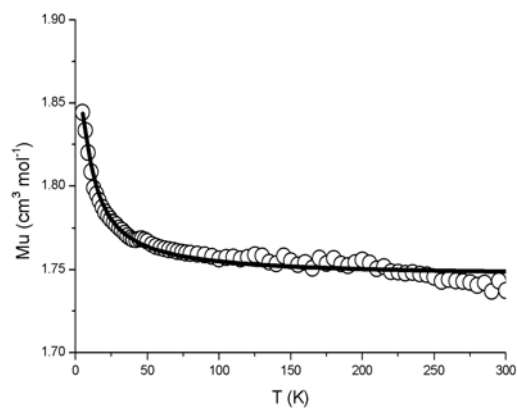


Figure 22. A plot of the temperature dependence of μ_{eff} vs. T per Cu(II) ion for compound **VI**. The solid line represents the calculated curve (see text).

1.5 Conclusions

The first part of this research sets out to examine and develop the preparative work of a series of polynuclear copper(II) complexes containing the pseudohalide anion (NCO^- , NCS^- and N_3^-) and mixed pseudohalide/carboxylate as a bridging ligand and the di-2-pyridylamine as a chelate didentate terminal ligand. The spectroscopic and magnetic characterization, the X-ray crystal structure and the magneto-structural correlation of the complex system are investigated and discussed in comparison with other relevant complexes.

The complexes $[\text{Cu}_2(\text{dpyam})_2(\mu\text{-NCO-}N,N')(\text{NCO-}N)_2]$ (**I**), $[\text{Cu}_4(\text{dpyam})_4(\mu_{1,3}\text{-NCS})_6(\text{O}_2\text{CH})_2(\text{H}_2\text{O})_2]$ (**II**), $[\text{Cu}_3(\text{dpyam})_2(\mu_{1,3}\text{-N}_3)_2(\mu\text{-CH}_3\text{COO-}\kappa\text{-O}^1)(\mu\text{-CH}_3\text{COO-}\kappa\text{-O}^1, \text{O}^2)] \cdot 2\text{H}_2\text{O}$ (**III**), $[\text{Cu}_2(\text{dpyam})_2(\mu_{1,1}\text{-N}_3)_2(\text{O}_2\text{CH})_2]$ (**IV**), $[\text{Cu}_2(\text{dpyam})_2(\mu_{1,1}\text{-N}_3)_2(\text{O}_2\text{CCH}_3)_2]$ (**V**) and $[\text{Cu}_2(\text{dpyam})_2(\mu_{1,1}\text{-N}_3)_2(\text{O}_2\text{CCH}_2\text{CH}_3)_2]$ (**VI**) were prepared successfully from the mole ratio method and characterized by elemental analyses. The crystal structures of **I-VI** were determined crystallographically and their spectroscopic properties (IR, EPR (r.t. and 77 K), solid state VIS) investigated. The temperature variable magnetic susceptibilities (5-280 K) of compounds **I-VI** were measured. The exchange interaction between two Cu(II) centres and the superexchange pathways are investigated and discussed.

Complexes **I**, **IV**, **V** and **VI** consist of a dinuclear unit in which both Cu(II) ions are connected through two end-on cyanato or azido bridges providing a distorted square pyramidal geometry with CuN_5 and CuN_4O chromophore. The structure of a new unique tetranuclear complex **II** involves six thiocyanate ligands bridging four copper atoms in an end-to-end fashion with an equatorial-axial configuration. The geometry around these copper atoms can best be described as elongated octahedral. Complex **III** is a unique azido-acetato bridged trinuclear triply bridged Cu(II) compound. In the centrosymmetric compound, the central Cu atom is linked to two terminal Cu atoms by a double acetato bridge and an azido bridge, thereby providing a linear trinuclear unit. The coordination geometry around each of the terminal Cu(II) ions is distorted square pyramidal, while the geometry of the central Cu(II) ion is elongated octahedral.

The magnetic properties of compounds **I**, **IV**, **V** and **VI** show a medium to weak ferromagnetic exchange interactions between the Cu(II) ions dominated by the bridging cyanato or azido ligands, with a singlet-triplet splitting (J) of 6.03, 63.3, 63.8 and 5.1 cm^{-1} , for compounds **I**, **IV**, **V** and **VI** respectively.

For the complex **II**, the thiocyanate bridges link equatorial-axial coordination sites of elongated octahedral neighboring copper(II) centres and delocalisation of unpaired electron density along the axial coordination site should be very poor and the magnetic orbitals are almost orthogonal; consequently, the antiferromagnetic interaction should be very weak, which is in agreement with the observed coupling constants $2J_1 = 0.05 \text{ cm}^{-1}$, $2J_2 = -0.37 \text{ cm}^{-1}$ and $2J_3 = -0.09 \text{ cm}^{-1}$.

The magnetic susceptibilities of complex **III** reveal a weak antiferromagnetic interaction between copper(II) centers with a J value of -10.2 cm^{-1} . This behavior is found for the trinuclear complexes in which the end-on azido ligand links two copper(II) centers in an axial-equatorial configuration. According to the

structural data, the antiferromagnetic interaction corresponds to the superexchange through the syn-syn acetato bridge, whereas the very weak ferromagnetic interaction may be propagated by the poorly efficient azido and monoatomic acetato bridges which link at the long distance (apical disposition). The net superexchange coupling constant found between the copper atoms corresponds to the combined interactions due to all three bridges. The influence of these factors may decrease the antiferromagnetic interaction in the syn-syn acetato bridged copper(II) family which is mainly caused by the countercomplementary interaction. Also the partial face-to-face bases of each copper chromophore can assume that this distortion in complex **III** decreases the overlap between the magnetic orbitals which is in agreement with the weak antiferromagnetic behavior observed from experimental data.

The results of all products obtained in this complex system have been published³⁹⁻⁴³.

The results of the study on structural pathway in a series of 5-coordinate mononuclear copper(II) complexes containing halide and pseudohalide are not given in detail here but are addressed as in the publication papers⁴⁴⁻⁴⁵ (in appendix).

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Table 1.1 Structural and magnetic data of thiocyanato-bridged polynuclear copper(II) complexes

Complex ^a	Type	Bridging mode	Cu...Cu (Å)	Chromophore	Tetragonality	Geometry ^b	Bridging configuration ^c	J ^d (cm ⁻¹)	Reference
[Cu ₄ (dpyam) ₄ (μ _{1,3} -NCS) ₄ (NCS) ₂ (O ₂ CH) ₂ (H ₂ O) ₂] (II)	tetrameric	end-to-end	5.375 5.556	CuN ₃ OSO' CuN ₄ S ₂	0.712 0.661	Oct	EA	2J ₁ = 0.05 2J ₂ = -0.37 2J ₃ =-0.09	This work
[Cu(dpp)(NCS) ₂] ₂ (6)	dimeric	end-to-end	5.432	CuN ₄ S		SP	EA	-	32
[Cu(H ₂ O)(dpp)(NCS) ₂] ₂ ·2H ₂ O (7)	dimeric	end-to-end	5.371	CuN ₄ O'S	0.727	Oct	EA	-1.01	32
[Cu(dpta)(NCS)(ClO ₄) ₂] (8)	dimeric	end-to-end	-	CuN ₄ OS	0.704	Oct	EA	-	39
[Cu ₂ (μ-SCN) ₂ (Et ₃ dien) ₂](ClO ₄) ₂ (9)	dimeric	end-to-end	5.718	CuN ₄ O'S	0.732	Oct	EA	+7.7	11
[Cu ₂ (μ-SCN) ₂ (ept) ₂](ClO ₄) ₂ (10)	dimeric	end-to-end	5.462	CuN ₄ O'S	0.707	Oct	EA	+1.3	11
[Cu ₂ (μ-SCN) ₂ (Me ₅ dien) ₂](ClO ₄) ₂ (11)	dimeric	end-to-end	5.575	CuN ₄ S		SP	EA	+1.6	11
[{Cu(NCS) ₂ (dpk·CH ₃ OH)} ₂] (12)	dimeric	end-to-end	5.389	CuN ₄ O'S	0.772	Oct	EA	-0.9	12

^a Abbreviation used: dpta = di(3-aminopropyl)amine, Et₃dien = 1,4,7-triethyldiethylenetriamine, ept = N-(2-aminoethyl)-1,3-propanediamine, dpk = di-2-pyridyl-ketone, dpp = 2,3-bis(pyridyl)pyrazine, Me₅dien = 1,1,4,7,7-pentamethyldiethylenetriamine, bpy = 2,2'-bipyridyl, bpm = bipyrimidine, Hmtpo = 4H,7H-5-methyl-7-oxo[1,2,4]triazolo[1,5-a]pyrimidine, im2-py = 2-(2'-pyridyl)-4,4,5,5-tetramethylimidazoline-1-oxyl, L³ = 2-methylamino-5-pyridin-2-yl-1,3,4-Oxadiazole, L⁴ = tridentate Schiff base (L = C₁₄H₉N₂O), im = imidazole. ^bOct: octahedral, SP: square pyramidal. ^cEE: equatorial-equatorial, EA: equatorial-axial. ^dH = -JS₁S₂ from magnetic susceptibility measurements, neg: negligible interaction.

Table 1.1 Structural and magnetic data of thiocyanato-bridged polynuclear copper(II) complexes (Cont.)

Complex ^a	Type	Bridging mode	Cu ^{II} –Cu (Å)	Chromophore	Tetragonality	Geometry ^b	Bridging configuration ^c	J ^d (cm ⁻¹)	Reference
[Cu(bpy)(μ-NCS) ₂] _n (13)	1D	end-to-end	6.113	CuN ₄ S ₂	0.618	Oct	EA	-0.1	9
[{Cu(NCS) ₂ (dpk-CH ₃ OH)} _n] (14)	1D	end-to-end	5.994	CuN ₄ O'S	0.721	Oct	EA	-0.3	12
[Cu(bpm)(NCS) ₂] _n (15)	1D	end-to-end	5.328	CuN ₄ S ₂	0.622	Oct	EA	-0.6	35
[Cu(NCS)(μ-NCS)(Hmtpo)(H ₂ O)] ₂ (16)	1D	end-to-end	5.499	CuN ₃ OS ₂	0.765	Oct	EE	-74.0	36
[Cu(im2-py)(NCS) ₂] _n (17)	1D	end-to-end	5.929	CuN ₄ S ₂	0.664	Oct	EA	-0.83	37
[AsPh ₄][Cu(SCN) ₃] (18)	1D	end-to-end	5.549 5.559	CuN ₃ S ₂		SP	EE/EA	-90.0	14
[{Cu(L ³)(NCS) ₂ } _n] (19)	1D	end-to-end	5.599	CuN ₄ S		SP	EA	neg	38
[Cu(L ⁴)(μ-NCS)] _n (20)	1D	end-to-end	6.268	CuN ₃ OS		SP	EA	-0.57	13
[Cu(bpy)(NCS) ₂] _n (21)	2D	end-to-end	5.930	CuN ₄ S ₂ CuN ₄ S	0.538	Oct /SP	EA	-1.0	14
[Cu(im) ₂ (NCS) ₂] (22)	3D	end-to-end	5.722	CuN ₄ S ₂	0.639	Oct	EA	-	15

^a Abbreviation used: dpta = di(3-aminopropyl)amine), Et₃dien = 1,4,7-triethyldiethylenetriamine,), ept = N-(2-aminoethyl)-1,3-propanediamine, dpk = di-2-pyridyl-ketone, dpp = 2,3-bis(pyridyl)pyrazine, Me₅dien = 1,1,4,7,7-pentamethyldiethylenetriamine, bpy = 2,2'-bipyridyl, bpm = bipyrimidine, Hmtpo = 4H,7H-5-methyl-7-oxo[1,2,4]triazolo[1,5-a]pyrimidine, im2-py = 2-(2'-pyridyl)-4,4,5,5-tetramethylimidazoline-1-oxyl), L³ = 2-methylamino-5-pyridin-2-yl-1,3,4-Oxadiazole, L⁴ = tridentate Schiff base(L = C₁₄H₉N₂O), im = imidazole. ^bOct: octahedral, SP: square pyramidal. ^cEE: equatorial-equatorial, EA: equatorial-axial. ^dH = -JS₁S₂ from magnetic susceptibility measurements, neg: negligible interaction.

Part II

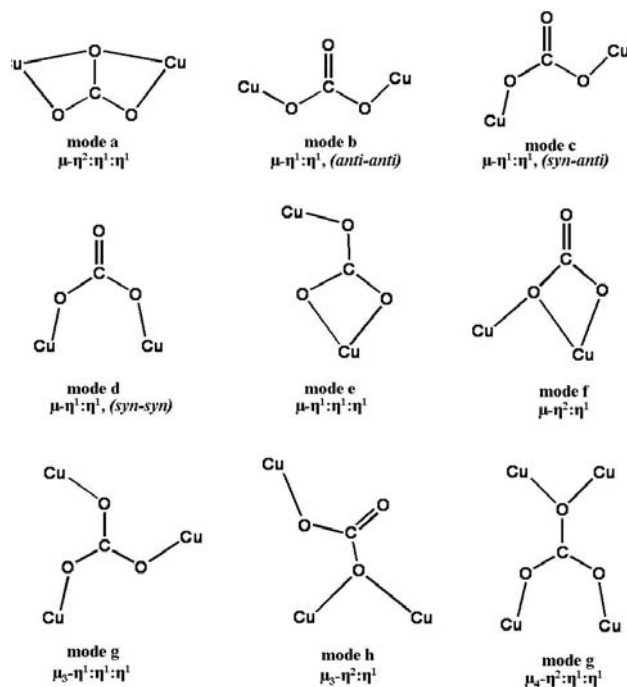
Synthesis, Crystal Structure, Spectroscopic and Magnetic Properties
of Polynuclear Carbonato-bridged Copper(II) Complexes
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Synthesis, Crystal Structure, Spectroscopic and Magnetic Properties of Polynuclear Carbonato-bridged Copper(II) Complexes containing the 2,2'-Bipyridyl and 1,10-Phenanthroline

2.1 Introduction

The coordination chemistry of the carbonate anion has received considerable attention for many years, especially in polynuclear carbonato-bridged copper(II) compounds. The carbonate anion is an extremely versatile bridging ligand, each oxygen atom of this anion may act as a monodentate, bridging bifunctional or trifunctional ligand, able to generate compounds with different nuclearity including dinuclear¹, trinuclear², tetranuclear³, hexanuclear species⁴ and even one- or two-dimensional⁵ systems. The coordination modes described to date for the carbonate ion when it acts as a bridge in polynuclear copper (II) compounds with nuclearities between two to four are summarized in Scheme 1. In function of the coordination mode of the carbonate ligand, the magnetic behavior of complexes varies greatly: from

strongly coupled to moderate or weak antiferromagnetic compounds and even ferromagnetic ones. Our recent interest has focused on the synthesis of polynuclear Cu (II) complexes containing the carbonate and alternating carbonato/hydroxido bridges with a view of studying their ability to propagate magnetic exchange interactions as the carbonate anion is capable of varied coordination modes including various bridging dispositions. Several polynuclear carbonato-bridged copper(II) compounds resulted from fixation of CO₂ from air^{4,6,7} and from direct preparation from the carbonate salt.



Scheme 1. Representation of the coordination modes of carbonate bridging ligand of di-, tri- and tetranuclear copper(II) complexes.

The polynuclear carbonato-bridged copper(II) complexes, [Cu₃(bpy)₆(μ₃-CO₃)](CF₃SO₃)₄(H₂O)_{0.5} (**I**), [Cu₃(phen)₆(μ₃-CO₃)](CF₃SO₃)₄(H₂O)_{0.5} (**II**), [Cu₆(bpy)₁₀

$(\mu\text{-OH})_2(\mu\text{-CO}_3)_2](\text{CF}_3\text{SO}_3)_6(\text{DMF})_2(\text{H}_2\text{O})_4$ (**III**), $[\text{Cu}_6(\text{bpy})_{10}(\mu\text{-OH})_2(\mu\text{-CO}_3)_2](\text{BF}_4)_6(\text{H}_2\text{O})_{0.5}$ (**IV**), $[\text{Cu}_8(\text{phen})_{12}(\mu_3\text{-OH})_2(\mu\text{-OH})_2(\mu_3\text{-CO}_3)_2](\text{CF}_3\text{SO}_3)_8(\text{DMF})_2(\text{H}_2\text{O})_{0.5}$ (**V**) and $\{[\text{Cu}_3(\text{bpy})_3(\mu\text{-OH})_2(\mu\text{-CO}_3)_2](\text{H}_2\text{O})_{6.5}\}_n$ (**VI**) were prepared successfully from the mole ratio method and characterized by elemental analyses. The crystal structures of **I-VI** were determined crystallographically and their spectroscopic properties (IR and Reflectance spectra) investigated. The magnetic properties of compounds **I-VI** were measured in a range from 5-350 K. The exchange interaction between two Cu(II) centres and the superexchange pathways are investigated and discussed.

2.2 Aims and Scopes

The objective of the second part is to study the preparation of the carbonato-bridged polynuclear copper(II) complexes containing the 2,2'-bipyridyl (bpy) and 1,10-phenanthroline (phen). The spectroscopic properties (IR, solid state VIS, EPR (room temperature and liquid nitrogen temperature)) are characterized and the X-ray crystal structure determined. The room temperature magnetic moment and the temperature variable susceptibilities (5-350 K) are measured and the magneto-structural correlation together with the superexchange pathways are investigated and discussed in comparison with other relevant complexes.

2.3 Experimental

2.3.1 Reagents and physical measurements

All reagents are commercial grade materials and were used without further purification. Elemental analyses (C, H, N) were determined on a Perkin-Elmer PE 2400 CHNS/O Analyzer. IR spectra were recorded with a Perkin-Elmer Spectrum One FT-IR spectrophotometer as KBr pellets in the 4000–450 cm^{-1} spectral range. Solid-state (diffuse reflectance) electronic spectra were recorded as polycrystalline samples on a Perkin-Elmer Lambda2S spectrophotometer over the range 8000–18000 cm^{-1} . X-band powder EPR spectra were obtained on a Jeol RE2x electron spin resonance spectrometer using DPPH ($g = 2.0036$) as a standard. Magnetic susceptibility measurements were carried out using a Quantum Design MPMS-5 5T SQUID magnetometer (measurements carried out at 1000 Gauss). Data were corrected for magnetization of the sample holder and for diamagnetic contributions, which were estimated from the Pascal constants.

2.3.2 Syntheses

2.3.2.1 $[\text{Cu}_3(\text{bpy})_6(\mu_3\text{-CO}_3)](\text{CF}_3\text{SO}_3)_4(\text{H}_2\text{O})_{0.5}$ (I)

Compound **I** was prepared by adding a warm solution (10 ml) of bpy (0.312 g, 2.0 mmol) in dimethylformamide (DMF), to a warm aqueous solution (10 ml) of $\text{Cu}(\text{CF}_3\text{SO}_3)_2$ (0.362 g, 1.0 mmol) and then a warm aqueous solution (5 ml) of Na_2CO_3 (0.052 g, 0.5 mmol) was added. On slow evaporation in air, blue crystals of **I** formed after two weeks. Yield ca. 55 %. $\text{C}_{65}\text{H}_{49}\text{Cu}_3\text{N}_{12}\text{O}_{16}$; *Anal. Calc.* (%): C, 43.1; H, 2.7; N, 9.3 %. Found: C, 43.2; H, 2.6; N, 9.3 %.

2.3.2.2 $[\text{Cu}_3(\text{phen})_6(\mu_3\text{-CO}_3)](\text{CF}_3\text{SO}_3)_4(\text{H}_2\text{O})_{0.5}$ (II)

A warm aqueous solution (10 ml) of $\text{Cu}(\text{CF}_3\text{SO}_3)_2$ (0.362 g, 1.0 mmol) was added by a warm solution (7 ml) of phen (0.396 g, 2.0 mmol) in 5:2 ratio of methanol:DMF, followed by a warm aqueous solution (5 ml) of Na_2CO_3 (0.035 g, 0.3 mmol). After two weeks, green crystals of **II** were formed. The crystals were filtered off and dried in air. Yield ca. 60 %. $\text{C}_{77}\text{H}_{49}\text{Cu}_3\text{N}_{12}\text{O}_{16}$; *Anal. Calc.* (%): C, 47.8; H, 2.4; N, 8.7 %. Found: C, 47.6; H, 2.5; N, 8.7 %.

2.3.2.3 $[\text{Cu}_6(\text{bpy})_{10}(\mu\text{-OH})_2(\mu\text{-CO}_3)_2](\text{CF}_3\text{SO}_3)_6(\text{DMF})_2(\text{H}_2\text{O})_4$ (III)

Compound **III** was prepared by adding a warm solution (10 ml) of bpy (0.312 g, 2.0 mmol) in DMF into an aqueous solution (10 ml) of $\text{Cu}(\text{CF}_3\text{SO}_3)_2$ (0.362 g, 1.0 mmol). After that an aqueous solution (10 ml) of Na_2CO_3 (0.052 g, 0.5 mmol) was added. On slow evaporate in air, for several days the suitable greenish-blue crystals for X-ray analysis were obtained. Yield ca. 66 %. Compound **III** was also prepared by the same method and starting materials with the mole ratio of 1: 2: 0.3 in mixed H_2O -MeOH (15: 5 mL). Up on standing for a week, greenish-blue crystals of **III** were deposited. Yield ca. 60 %. $\text{C}_{114}\text{H}_{96}\text{Cu}_6\text{N}_{22}\text{O}_{32}\text{F}_{18}\text{S}_6$; *Anal. Calc.* (%): C 43.1; H 3.1; N 9.4 % Found: C 43.0; H 3.1; N 9.3 %.

2.3.2.4 $[\text{Cu}_6(\text{bpy})_{10}(\mu\text{-OH})_2(\mu\text{-CO}_3)_2](\text{BF}_4)_6(\text{H}_2\text{O})_{0.5}$ (IV)

A warm solution (10 ml) of bpy (0.312 g, 2.0 mmol) in DMF was transferred into an aqueous solution (10 ml) of $\text{Cu}(\text{BF}_4)_2 \cdot n\text{H}_2\text{O}$ (0.255 g, 1.0 mmol). After that an aqueous solution (10 ml) of Na_2CO_3 (0.052 g, 0.5 mmol) was added. On slow evaporation in air, for several days the suitable blue-green crystals of **IV** were obtained. Yield ca. 66 %. $\text{C}_{102}\text{H}_{82}\text{Cu}_6\text{N}_{20}\text{O}_9$; *Anal. Calc.* (%): C, 46.9; H, 3.2; N, 10.7 %, Found: C, 46.7; H, 3.1; N, 10.6 %.

2.3.2.5 $[\text{Cu}_8(\text{phen})_{12}(\mu_3\text{-OH})_2(\mu\text{-OH})_2(\mu_3\text{-CO}_3)_2](\text{CF}_3\text{SO}_3)_8(\text{DMF})_2(\text{H}_2\text{O})_{0.5}$ (V)

A warm solution (5 ml) of phen (0.199 g, 1.0 mmol) in 3:2 ratio of ethanol: dimethylformamide (DMF) was added to a warm aqueous solution (5 ml) of $\text{Cu}(\text{CF}_3\text{SO}_3)_2$ (0.182 g, 0.5 mmol) and then a warm aqueous solution (5 ml) of Na_2CO_3 (0.026 g, 0.25 mmol) was added. On slow evaporation in air, only green crystals of **V** formed after a week. Yield ca. 80 %. $\text{C}_{160}\text{H}_{114}\text{Cu}_8\text{N}_{26}\text{O}_{38}\text{F}_{24}\text{S}_8$; *Anal. Calc.* (%): C, 45.4; H, 2.7; N, 8.6 %. Found: C, 45.6; H, 2.8; N, 8.6 %. To study the pH effect, the pH of solution was adjusted ranging from 8.5 to 12.0 with NaOH solution, resulted the green crystals of **V** were also obtained.

2.3.2.6 Preparation of $\{[\text{Cu}_3(\text{bpy})_3(\mu\text{-OH})_2(\mu\text{-CO}_3)_2](\text{H}_2\text{O})_{6.5}\}_n$ (VI)

Compound **VI** was prepared by adding a warm solution (10 ml) of bpy (0.312 g, 2.0 mmol) in DMF, to a warm aqueous solution (10 ml) of $\text{Cu}(\text{CF}_3\text{SO}_3)_2$ (0.362 g, 1.0 mmol) and then 0.052 g of Na_2CO_3 (0.5 mmol) was added. Green crystals of **VI** formed after two weeks. Yield ca. 50 %. $\text{C}_{32}\text{H}_{38}\text{Cu}_3\text{N}_6\text{O}_{14}$ asymmetric unit: *Anal. Calc.* (%): C 41.7; H 4.2; N 9.1 %. Found: C 41.5; H 4.0; N 9.1 %.

2.3.3 Crystallography

X-ray single-crystal data were collected at 273 K for compounds **I-VI**, respectively on a 4 K Bruker SMART APEX CCD area-detector diffractometer (rotating anode, graphite-monochromated Mo K_α radiation, $\lambda = 0.71073 \text{ \AA}$) using SMART program. Raw data frame integration was performed with SAINT, which also applied correction for Lorentz and Polarization effects. An empirical absorption correction by using the SADABS program was applied, which resulted in transmission coefficients ranging from 1.000 to 0.606, 1.000 to 0.841, 1.000 to 0.747, 1.000 to 0.840, 1.000 to 0.789 and 1.000 to 0.537 for **I-VI**, respectively. The structures were solved by direct methods and refined by full-matrix least-squares method on $(F_{\text{obs}})^2$ with anisotropic thermal parameters for all non-hydrogen atoms using the SHELXTL-PC V 6.12 software package. All hydrogen atoms in **I** were geometrically fixed and allowed to ride on the attached C atoms. All oxygen and fluoride atoms of trifluoromethanesulfonate groups in **I** are disordered with site occupancies of 0.50 including one carbon atom of a triflate molecule. All hydrogen atoms in **II** were geometrically fixed and allowed to ride on attached atoms. The carbonate group in **II** found to be disordered with oxygen atoms given occupancies of 0.5. Two water oxygen atoms of **II** are refined with site occupancies of 0.25. All oxygen and fluoride atoms of three trifluoromethanesulfonate groups in **II** are found to be disordered with site occupancies of 0.50. The fourth triflate group found also to be disordered and attempts have been made in range possibilities to locate disordered atoms but were unsuccessful.

Compound **III**, all hydrogen atoms were introduced in calculated positions and refined with fixed geometry with respect to their carrier atoms except H(51) of the hydroxido bridge. Two triflate groups, one DMF molecule and one water molecule are disordered with site occupancies of 0.5. The third triflate group was also disordered and attempts have been made in range possibilities to locate disordered atoms but unsuccessful. Finally, we decide to refine as the ordered molecule with quite high but reliable temperature factors. The bond distances of DMF and some distances of the triflate molecules were restrained with the DFIX 1.47(1), 1.35(1) and 1.23(1) commands for N-C(methyl), N-C(C=O) and C=O bonds, respectively in DMF and the DFIX 1.57(1), 0.5(1), 1.86(1) and 1.32(1) commands for the S(2)-O(10)A, F(2)-F(2)A, C(54)-S(3) and C-F bond lengths, respectively in the triflate molecules. All non-H atoms were refined anisotropically except one C, four F and four O atoms of the triflate molecules and one C atom of DMF. The remaining four oxygen atoms of water molecules were refined with site occupancies of 0.25. The quite high R value of compound **III** is attributed to these disordered molecules with some restrained distances

and isotropic refinement of some non-H atoms which is usually found. All hydrogen atoms in **IV** were located by a difference Fourier map and refined isotropically, except H(42), H(44), H(47), H(48) and H(49). These hydrogen atoms were geometrically fixed and allowed to ride on attached atoms and an oxygen atom of the lattice water molecule is refined with site occupancy of 0.5. All non-hydrogen atoms were refined anisotropically and all tetrafluoroborate groups are disordered with site occupancies of 0.5.

All hydrogen atoms of phen ligands and DMF molecule in **V** were geometrically fixed and allowed to ride on attached atoms except H(4) and H(5) of the hydroxide bridge. The first three triflate molecules are modeled as disordered forms with site occupancies of 0.5 with reasonable bond lengths and bond angles and a few DFIX treatments of bond distances (C-F 1.340(1) Å). Additionally, isotropic refinement of some atoms was introduced. The fourth triflate and a DMF molecule were also disordered and attempts have been made in many possibilities to locate disordered atoms, but unsuccessful. Finally, we decide to refine as the ordered molecules with restrained bond distances (C-S 1.800(1), C-F 1.340(1), S-O 1.400(1) Å for a triflate molecule and N-C_{methyl} 1.470(1), N-C_{carbonyl} 1.350(1), C=O 1.230(1) Å for a DMF molecule). Additionally, the isotropic refinement of some atoms was introduced, leading to the quite high temperature factor of some atoms and an unreasonable N-C-O angle (77.80°) of a DMF molecule. Hydrogen atoms of a DMF could not be fixed and located. A water oxygen atom was located with an isotropic refinement and site occupancy of 0.25 without located hydrogen atoms.

In compound **VI**, all hydrogen atoms were geometrically fixed and allowed to ride on attached atoms except those of water molecules, H(31), H(32), H(33), H(34) and H(35). These hydrogen atoms were located by difference synthesis and refined isotropically on three oxygen water atoms, while the other hydrogen atoms of the remaining three water molecules could not be located. Three water oxygen atoms in the latter case were modeled as disordered and two of those were refined with site occupancies of 0.5 and another one with site occupancies of 0.7 and 0.3 for both conformers.

2.4 Results and Discussion

2.4.1 Description of the crystal structures

2.4.1.1 Description of [Cu₃(bpy)₆(μ₃-CO₃)](CF₃SO₃)₄(H₂O)_{0.5} (**I**) and [Cu₃(phen)₆(μ₃-CO₃)](CF₃SO₃)₄(H₂O)_{0.5} (**II**)

The structure of compound **I** consists of trinuclear [Cu₃(bpy)₆(μ₃-CO₃)]⁴⁺ units which is shown in Fig. 1. The asymmetric unit also contains four non-coordinating trifluoromethansulfonate anions and half a molecule of lattice water. The three copper(II) atoms are connected to each other through the oxygen atoms from the bridging carbonato group with μ₃-η¹:η¹:η¹-CO₃ coordination mode, giving a triangular array of copper(II) atoms. Each copper(II) ion has a five-coordinate environment, four nitrogen atoms from

bpy ligands and one oxygen atom from a carbonate bridging ligand. The five-coordinate coordination of Cu(1) is a distorted square pyramid with a τ value of 0.39, the structure index is defined as $\tau = (\beta - \alpha)/60$, where β and α are the largest coordination angles, τ describes the relative amount of trigonality, $\tau = 0$ for a square pyramid and $\tau = 1$ for a trigonal bipyramid. The basal plane comprises of three nitrogen atoms of the bpy ligand and an oxygen atom of the bridging carbonate ligand with distances ranging 1.952(3)-2.018(3) Å. The fifth apical coordination site is occupied by a nitrogen atom of the bpy ligand with a Cu(1)-N(2) distance of 2.196(4) Å, providing a distorted square pyramidal CuN₃O(N) chromophore. The Cu(1) atom lies 0.22 Å, above the basal plane toward N(2). The coordination geometry of Cu(2) ($\tau = 0.04$) is distorted square pyramidal environment with a basal plane formed by three nitrogen atoms of the two bpy groups and the oxygen atom of the bridging carbonate group with distances ranging 1.997(3)-2.023(3) Å. The apical position is formed at the copper by the fourth nitrogen atom of the bpy with a distance of 2.171(3) Å. The Cu(2) atom lies 0.03 Å, above the basal plane toward N(8). The environment geometry around Cu(3) ($\tau = 0.56$) is intermediate five-coordinate but slightly distorted towards a trigonal bipyramid via a Berry-Twist process [16]. The three longer bonds in the trigonal planar plane are two nitrogen atoms of the bpy ligand (Cu-N(10) 2.129(3) and Cu-N(11) 2.066(3) Å) and one oxygen of carbonate ligand (Cu-O(3) 2.006(3) Å). The two shorter bonds in the axial positions involve two nitrogen atoms of the different two bpy ligands (Cu-N(9) 1.988(3) and Cu-N(12) 1.970(3) Å). This is typical for the trigonal-bipyramidal geometry. The distances between the copper(II) atoms are approximately Cu(1)-Cu(2) 5.192, Cu(1)-Cu(3) 4.680 and Cu(2)-Cu(3) 4.566 Å, respectively. The influence of intra- and intermolecular bpy-bpy π - π -stacking (contact distance 3.777 Å) and the CH- π interactions (contact distance ranging 2.802-2.898 Å) has been considered to play a role in this molecular structure, forming the one-dimensional chains along a c-axis. The structure of compound **II** is similar to that of compound **I**, the chromophore and also the intra- and intermolecular interactions are all similar to that of compound **I**. The carbonate bridging ligand

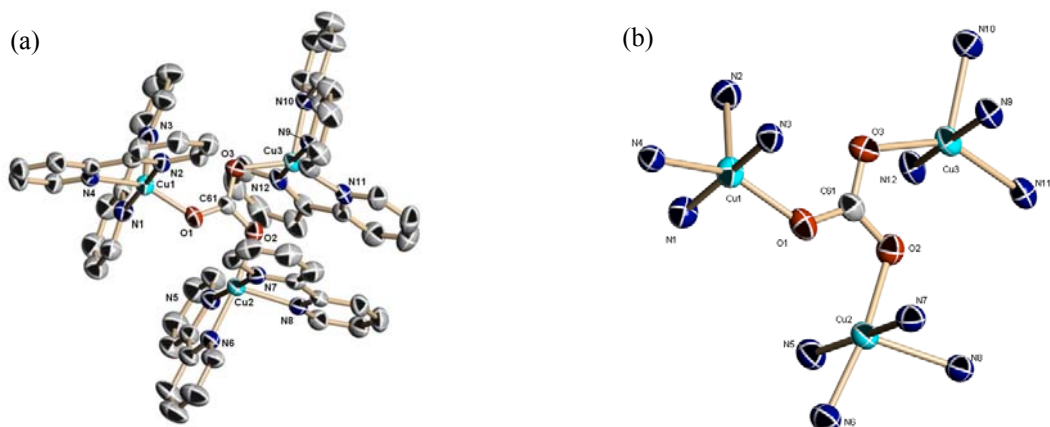


Figure 1. (a) Molecular structure of **I** and **II**.

(b) Thermal ellipsoids are shown at 50 % level of the copper(II) chromophores.

disordered with occupancies of oxygen atoms of 0.5. The geometries of all three copper(II) centers are described as being intermediate five-coordinate with τ values of 0.58, 0.56 and 0.54 for Cu(1), Cu(2) and Cu(3), respectively.

2.4.1.2 Description of $[\text{Cu}_6(\text{bpy})_{10}(\mu\text{-OH})_2(\mu\text{-CO}_3)_2](\text{CF}_3\text{SO}_3)_6(\text{DMF})_2(\text{H}_2\text{O})_4$ (III)

The crystal structure of compound **III** consists of the [di- μ -hydroxido-bis(2,2'-bipyridine)copper (II)] moieties, coordinated *trans*-axially at each copper atom by μ -carbonato-bis(2,2'-bipyridine)copper (II) moieties (Fig. 2). The compound **III** also contains six trifluoromethanesulfonate counteranions, two *N,N*-dimethylformamide (abbreviation as DMF) molecules and nine lattice water. The Cu(3)-Cu(3)A separation of 2.844(2) Å and Cu(3)-O(4)-Cu(3)A bridging angle of 94.3(3)° fall within the range found for similarly coordinated di- μ -hydroxidocopper(II) dimers. The environment of central copper atoms are nearly regular square-pyramidal geometry, being coordinated by two nitrogen donors from the bpy ligand and two oxygen atoms from the bridging hydroxido group, forming the CuN_2O_2 chromophores with distances ranging 1.934(7)-1.997(8) Å, an apical position is occupied by O(1) from the bridging carbonate species at a distance of 2.341(6) Å. The corresponding τ value for the square-pyramidally disposed Cu(3) atom is 0.10. The Cu(3) atom lies 0.07, above the basal plane toward O(1). The carbonate oxygen O(1) bridging atom also coordinates with Cu(1), forming an asymmetric monoatomic bridge between Cu(3) and Cu(1); Cu(3)-O(1) 2.341(6) Å, Cu(1)-O(1) 2.037(6) Å, with a Cu(3)-O(1)-Cu(1) bridging angle of 132.6 (3)°. The coordination geometry around Cu(1) is best described as being square-pyramidal with distortion toward trigonal bipyramidal ($\tau = 0.42$). The basal plane consists of three nitrogen atoms of bpy ligands and an O(1) atom of carbonate bridging ligand with distances ranging from 1.990(8) to 2.089(9) Å. The apical position is occupied by N(2) atom of bpy ligand with a bond length of 2.183(10) Å. The Cu(1) atom lies 0.28, above the basal plane toward N(2). Moreover, this carbonate group so also linked to Cu(2) through O(2) at a distance of 1.958(6) Å, forming a triatomic bridge between Cu(1) and Cu(2) (*anti,anti*) and likewise between Cu(2) and Cu(3) (*syn,anti*). The environment geometry of Cu(2) can be described with a distorted pyramidal geometry ($\tau = 0.40$). The basal plane contains three nitrogen atoms of bpy ligands and an oxygen atom of carbonate ligand with distances ranging 1.958(6)-2.075(8) Å. The fifth position is occupied by N(8) atom of bpy ligand with 2.199(9) Å. The Cu(2) atom lies 0.23, above the basal plane toward N(8). The tetrahedral twists of the square bases defined by dihedral angles between two trigonal planes are 30.87, 28.19 and 7.5°, for Cu(1), Cu(2) and Cu(3), respectively. The carbonate moieties coordinate to three copper(II) atoms with $\mu_3\text{-}\eta^2\text{:}\eta^1\text{-CO}_3$ coordinated fashion [Cu(1)-Cu(2) 5.091, Cu(2)-Cu(3) 5.321 and Cu(1)-Cu(3) 4.011 Å]. The centrosymmetric nature of the complex results in the above array being repeated at Cu(1)A, Cu(2)A and Cu(3)A center atoms. The influence of intra- and intermolecular bpy-bpy π -stacking interactions has been considered to play a role in this molecular structure. Inspection of the bipyridine rings show that they are essentially parallel to each other,

corresponding to the incorporation of the N(1)-N(2), N(9)-N(10) and N(8)A rings (3.671-3.983 Å) within the molecules. The intermolecular π - π interactions with the face-to-face distance being 3.619 Å form a 1-D chain is stacked along the *b*-axis.

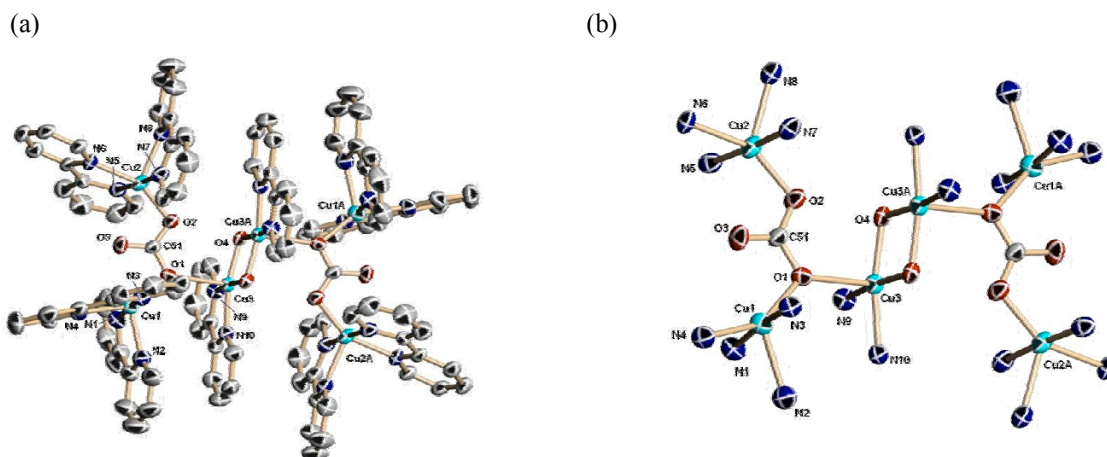


Figure 2. (a) Molecular structure of **III**.
(b) showing the copper(II) chromophores.

2.4.1.3 Description of $[\text{Cu}_6(\text{bpy})_{10}(\mu\text{-OH})_2(\mu\text{-CO}_3)_2](\text{BF}_4)_6(\text{H}_2\text{O})_{0.5}$ (**IV**)

The crystal structure of compound **IV** consists of the $[\text{di-}\mu\text{-hydroxido-bis(2,2'-bipyridine)copper(II)}]$ moieties, coordinated *trans*-axially at each copper atom by μ -carbonato-bis(2,2'-bipyridine)copper(II) moieties (Fig. 3). Compound **IV** also contains six tetrafluoroborate counter anions and half a molecule of lattice water. The Cu(3)-Cu(3)A separation of 2.844(1) Å and Cu(3)-O(4)-Cu(3)A bridging angle of 95.0 (1)° fall within the range found for similarly coordinated di- μ -hydroxidocopper(II) dinuclear species. The environment of central copper atoms are nearly regular square-pyramidal geometry ($\tau = 0.03$), being coordinated by two nitrogen donors from the bpy ligand and two oxygen atoms from the bridging hydroxido group, forming the CuN_2O_2 chromophore with distances ranging 1.925(3)-1.998(5) Å, an apical position is occupied by O(1) from the bridging carbonato species at a distance of 2.345(3) Å. The Cu(3) atom lies 0.05 Å, above the basal plane toward O(1). The carbonato oxygen O(1) bridging atom also coordinates with Cu(1), forming an asymmetric monoatomic bridge between Cu(3) and Cu(1); Cu(3)-O(1) 2.345(3) Å, Cu(1)-O(1) 1.990(3) Å, with a Cu(3)-O(1)-Cu(1) bridging angle of 130.5(1)°. The coordination geometry around Cu(1) is best described as being square-pyramidal with distortion towards trigonal bipyramidal ($\tau = 0.42$). The basal plane consists of three nitrogen atoms of bpy ligands and an O(1) atom of carbonate bridging ligand with distances ranging from 1.981(4) to 2.077(4) Å. The apical position is occupied by N(2) atom of bpy ligand with a bond length of 2.205(4) Å. The Cu(1) atom lies 0.33 Å, above the basal plane toward N(2). Moreover, this carbonate group also linked to Cu(2) through O(2), forms a

triatomic bridge between Cu(2) and Cu(3) (*anti,anti*) and likewise between Cu(1) and Cu(2) (*syn,anti*). The environment geometry of Cu(2) can be described with a distorted pyramidal geometry ($\tau = 0.22$). The basal plane contains three nitrogen atoms of bpy ligands and an oxygen atom of carbonate ligand with distances ranging 1.938(3)-2.039(3) Å. The fifth position is occupied by N(5) atom of bpy ligand with a distance of 2.203(4) Å. The Cu(2) atom lies 0.17 Å, above the basal plane toward N(5). The tetrahedral twists of the square bases defined by dihedral angles between two trigonal planes are 35.92, 19.91 and 13.6°, for Cu(1), Cu(2) and Cu(3), respectively. The carbonate moieties coordinate to three copper(II) atoms with $\mu_3-\eta^2:\eta^1-\text{CO}_3$ coordinated fashion [Cu(1)-Cu(2) 4.401, Cu(2)-Cu(3) 5.979 and Cu(1)-Cu(3) 3.939 Å]. The centrosymmetric nature of the complex results in the above array being repeated at Cu(1)A, Cu(2)A and Cu(3)A center atoms. The influence of intra- and intermolecular bpy-bpy π -stacking interactions has been considered to play a role in this molecular structure. The intermolecular π - π interactions with the face-to-face distance being 3.612 Å form a 1-D chain which stacked along the *a*-axis. Furthermore, the packing structure has the CH- π interactions with the adjacent chain (contact distance 3.890 Å) to form two-dimensional layers within the crystallographic *ac*-plane.

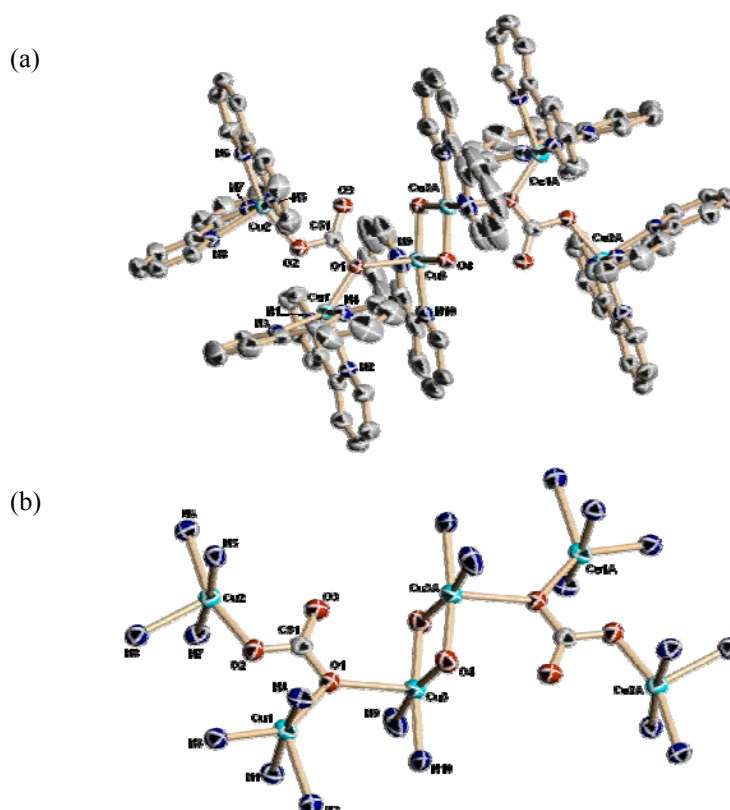


Figure 3. (a) Molecular structure of **IV**.

(b) Thermal ellipsoids are shown at 30 % level represented of the copper(II) chromophores.

2.4.1.4 Description of $[\text{Cu}_8(\text{phen})_{12}(\mu_3\text{-OH})_2(\mu\text{-OH})_2(\mu_3\text{-CO}_3)_2](\text{CF}_3\text{SO}_3)_8\cdot(\text{DMF})_2(\text{H}_2\text{O})_{0.5}$ (V)

The overall molecular structure of **V** consists of eight trifluoromethanesulfonate counteranions, two *N,N*-dimethylformamide (DMF) molecules and a half of lattice water molecule. A centrosymmetric $[\text{Cu}_8(\text{phen})_{12}(\mu_3\text{-OH})_2(\mu\text{-OH})_2(\mu_3\text{-CO}_3)_2]^{8+}$ unit (Fig. 4) contains two [di- μ -hydroxido-bis(1,10-phenanthroline)dicopper(II)] moieties, phen-Cu-(OH)₂-Cu-phen moieties which are held together by long Cu-O(H) bonds, creating Cu₂(OH)₂ core of tetranuclear hydroxido-bridged copper(II) unit. These dihydroxido-bridged copper(II) units are further coordinated *trans*-axially at Cu(3) and Cu(3)A to two [μ -carbonato-tetrakis(1,10-phenanthroline) dicopper(II)] moieties. Within the dinuclear dihydroxido-bridged copper(II) unit, the Cu(3)-Cu(4) separation of 2.853(1) Å, the Cu(3)-O(4)-Cu(4) and Cu(3)-O(5)-Cu(4) bridging angles of 95.8(2) and 93.5(1)° fall within the range found for similarly coordinated di- μ -hydroxido copper(II) dinuclear compounds. The environment of two crystallographically independent copper atoms is in a nearly regular square-pyramidal geometry, $\tau = 0.19$ and 0.05 with an apical distances of Cu(3)-O(3) 2.156(4) Å and Cu(4)-O(5)A 2.4926 (41) Å. Consequently, the phen-Cu-(OH)₂-Cu-phen moieties held together by long Cu-O(H) bonds at 2.4926 (41) Å, the two copper centers and two oxygen atoms of bridging hydroxido ligands are placed on the vertexes of a rectangle, creating a Cu₂(OH)₂ core of tetranuclear hydroxido-bridged copper(II) unit. The Cu(3) and Cu(4) atoms lie 0.13 and 0.06, above the basal planes toward O(3) and O(5)A, respectively.

The Cu(3) and Cu(3)A centers of di- μ -hydroxido copper(II) moieties are further linked to two symmetry-related [μ -carbonato-tetrakis(1,10-phenanthroline)dicopper-(II)] units *via* the $\mu_3\text{-}\eta^1\text{:}\eta^1\text{:}\eta^1\text{-CO}_3$ coordination mode of carbonate bridging ligand, giving a triangular array of copper atoms. The Cu(1) and Cu(2) of this unit are in an intermediate five-coordinate geometry with a τ values of 0.59 and 0.33, respectively. However, the coordination geometry around Cu(1) is slightly distorted towards a trigonal bipyramid *via* a Berry-Twist process with the trigonal planar distances of Cu-N(1) 2.175(5), Cu-N(4) 2.129 (5) and Cu-N(3) 2.000(5) Å and the axial distances of Cu-O(1) 1.949(4) and Cu-N(2) 1.996(5) Å. This is typical for the trigonal-bipyramidal geometry. While the environment geometry around Cu(2) is slightly distorted towards a square pyramid ($\tau = 0.33$) with the apical distance of Cu-N(7) 2.246(6) Å. The crystal structure was stabilized by the intermolecular hydrogen-bonding interactions between the oxygen atom of the hydroxido bridges and the oxygen atom of triflate molecules [O(4)⋯O (7) = 3.040 Å, H(4)⋯O(7) = 2.464 Å, and O(4)-H(4)⋯O(7) = 164.36° and O(5)⋯O(9)A = 3.146 Å, H(5)⋯O(9)A = 2.527 Å, and O(5)-H(5)⋯O(9)A = 170.32°. These interactions displace the hydrogen atoms of the hydroxido groups out of the Cu-O-Cu plane by $\gamma = 55.4$ and 47.0° , respectively. The influence of intramolecular phen-phen π -stacking interactions has been considered to play a role in this molecular structure. The adjacent molecules are interlocked through π - π interactions involving the phen ligand and also play a role in the apparent molecular structure of the present complex, thus favor its formation. These intermolecular π - π interactions with separation of *ca.* 3.714 Å, form a 2D sheet within the crystallographic *bc*-plane.

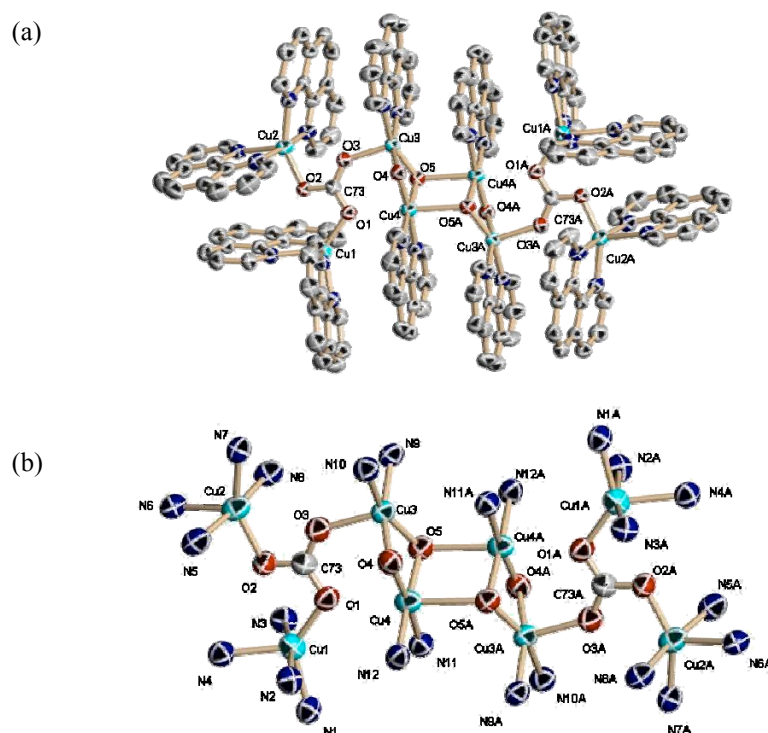


Figure 4. (a) Molecular structure of **V**.
(b) Thermal ellipsoids are shown at the 50 % level of the copper(II) chromophores.

2.4.1.5 Description of $\{[\text{Cu}_3(\text{bpy})_3(\mu\text{-OH})_2(\mu\text{-CO}_3)_2](\text{H}_2\text{O})_{6.5}\}_n$ (**VI**)

The crystal structure of compound **VI** involves a polymeric chain of the asymmetric repeating units, $[\text{Cu}_3(\text{bpy})_3(\mu\text{-OH})_2(\mu\text{-CO}_3)_2]_n$. This compound consists of two independent di- μ -hydroxido-bis(2,2'-bipyridine)copper(II) dinuclear moieties, $[\text{Cu}(1)/\text{Cu}(1)\text{A}]$ and $[\text{Cu}(3)/\text{Cu}(3)\text{B}]$, each connected to the central $\text{Cu}(2)$ unit via two carbonate bridges with different bridging modes, resulting to the pentanuclear unit (Fig. 5). These pentanuclear units are repeated to form one-dimensional chain along the b axis. The central $\text{Cu}(2)$ atom is coordinated by two nitrogen atoms from a bpy ligand and two oxygen atoms from two different carbonate bridges with the $\mu\text{-}\eta^1\text{:}\eta^1\text{-}$ and $\mu\text{-}\eta^2\text{:}\eta^1\text{-CO}_3$ coordination modes, forming a square base with distances ranging 1.938(7)-2.018(7) Å. The axial position is then occupied by another oxygen atom of the latter carbonate bridge with Cu-O distance of 2.419(6) Å, giving a distorted square-pyramidal geometry with a τ value of 0.22. Consequently, the latter carbonate bridge is bidentately coordinated to Cu (2) centre and monodentately coordinated to Cu(3) atom. A dihedral angle between the CuN_2 and CuO_2 planes is 20.2(4)° and the Cu(2) atom lies 0.21 Å above the basal plane toward the apical site. The di- μ -hydroxido-bis(2,2'-bipyridine)copper(II) moiety, $[\text{Cu}(1)/\text{Cu}(1)\text{A}]$ is a dinuclear unit, copper(II) ions are solely bridged with two hydroxido ligands. Each copper(II) ion is five-coordinate with N_2O_3 donor set. The

square base consists of two nitrogen atoms from bpy ligand and two oxygen atoms from each bridging hydroxido group, with bond distances varying from 1.939(5) to 2.035(7) Å. The apical position is then occupied by O(2) from the $\mu\text{-}\eta^1\text{:}\eta^1$ carbonate bridging ligand with a distance of 2.175(6) Å. The τ value of 0.16 corresponds to a distorted square pyramidal geometry. The Cu–Cu separation within the dinuclear unit is 2.913(2) Å and the bridging Cu(1)–O(1)–Cu(1)A angle is 96.8(2)°. These features are very close to those observed in the corresponding di- μ -hydroxido bridged copper(II) dimers. The di- μ -hydroxido-bis(2,2'-bipyridine)copper(II) moiety, [Cu(3)/Cu(3)B] is structurally similar to that of the [Cu(1)/Cu(1)A] moiety (τ = 0.16), bond distances of the square base vary from 1.920(7) to 2.025(8) Å. The apical position is occupied by O(6) of the $\mu\text{-}\eta^2\text{:}\eta^1$ carbonate bridging ligand with a distance of 2.199(6) Å. The Cu–Cu separation within the dinuclear unit is 2.875(2) Å and the bridging Cu(3)–O(8)–Cu(3)B angle is 96.8(3)°. The dihedral angles between trigonal planes of the square bases are 19.8, 20.2 and 15.6°, for Cu(1), Cu(2) and Cu(3), respectively. Moreover, there are the intramolecular interactions, π - π stacking between the neighboring pyridine groups of Cu(2) and Cu(3) chromophores (ring to ring distance 3.691 Å). The adjacent Cu chains interdigitate through π - π interaction, which involve each bpy ligand (3.309 Å as closest contacts) and leads to formation of 2D sheets. The lattice is further stabilized by relatively hydrogen bonds between the water molecules and the carbonate and hydroxido oxygen atoms of the adjacent layers, leading to 3-dimensional infinite framework.

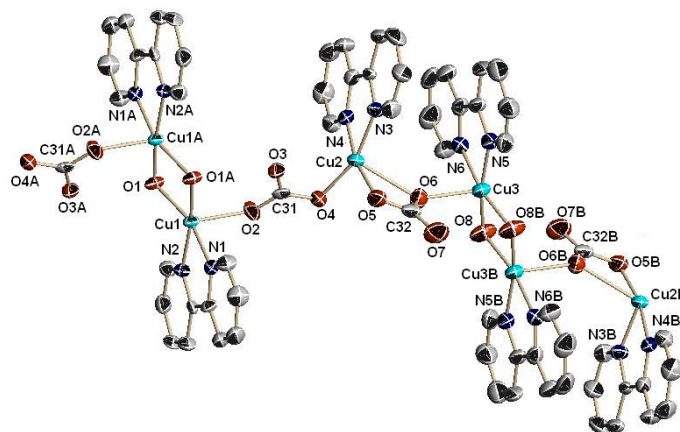


Figure 5. Crystal structure of **VI**. Hydrogen atoms and water molecules are omitted for clarity.

2.4.2 IR spectra

The infrared spectra of complexes **I–VI**, display a broad band of $\nu(\text{O-H})$ centered at 3340–3587 cm^{-1} , which are consistent with the presence of water molecules and bis- μ -hydroxido species. The IR spectra of **I** and **II** also show bands characteristic of the carbonate bridge with a $\mu_3\text{-}\eta^1\text{:}\eta^1\text{:}\eta^1$ CO_3 mode which appeared as the out-of-plane vibration^{8, 9} at 836 cm^{-1} for **I** and the in-plane vibration at 755 cm^{-1} for **II**, as these

spectral ranges are completely absent in the mononuclear compounds $[\text{Cu}(\text{bpy})_3](\text{CF}_3\text{SO}_3)_2$ and $[\text{Cu}(\text{phen})_3](\text{CF}_3\text{SO}_3)_2$. Two bands at 1500 and 837 cm^{-1} for **III** and 1381 and 842 cm^{-1} for **IV** are assigned to the $\nu_{\text{as}}(\text{CO}_3)$ and the out of plane vibration of bridging $\mu_3\text{-}\eta^2\text{:}\eta^1\text{-CO}_3$ group¹⁰. In case of compound **V**, the characteristic peaks of the carbonate anions are observed as the asymmetric C-O stretching vibration at 1357 cm^{-1} and a weak band at 774 cm^{-1} may be assigned to the in-plane deformation. The symmetric C-O stretching vibration¹¹ of the bridging carbonate expected at $\sim 1050 \text{ cm}^{-1}$ is dominated^{8-9, 11} by the phen ligands. The bands at 1583 and 1348 cm^{-1} , correspond to anti- and symmetric carbonate stretching vibrations, respectively and a weak band at 934 cm^{-1} may be assigned to the out-of-plane deformation^{8-9, 11} for compound **VI**.

The IR spectra display the characteristic intense bands of the stretching of the ionic CF_3SO_3^- ¹² at 1276 $\nu_{\text{as}}(\text{S-O})$, 1158 $\nu_{\text{as}}(\text{C-F})$ and 1031 $\nu_{\text{s}}(\text{S-O}) \text{ cm}^{-1}$ for **I**, 1277 $\nu_{\text{as}}(\text{S-O})$, 1153 $\nu_{\text{as}}(\text{C-F})$ and 1029 $\nu_{\text{s}}(\text{S-O}) \text{ cm}^{-1}$ for **II**, 1272s $\nu_{\text{as}}(\text{S-O})$, 1148m $\nu_{\text{as}}(\text{C-F})$, 1033s $\nu_{\text{s}}(\text{S-O}) \text{ cm}^{-1}$ for **III** and 1272s $\nu_{\text{as}}(\text{S-O})$, 1153m $\nu_{\text{as}}(\text{C-F})$ and 1033s $\nu_{\text{s}}(\text{S-O}) \text{ cm}^{-1}$ for **V**. In case of **IV**, the spectrum also shows the broad and intense bands of the stretching vibrations at 1076s $\nu_{\text{as}}(\text{B-F})$ of the ionic BF_4^- ¹³.

2.4.3 Electronic Reflectance spectra

The electronic spectrum of **I**, which has a range of mixed stereochemistries, shows two well-resolved bands with nearly equal intensity at approximately 14 200 and 10 200 cm^{-1} , $\Delta E = 4\,000 \text{ cm}^{-1}$. Complex **II** which involves an intermediate five-coordinated geometry ($\tau = 0.58, 0.54, 0.56$) displays a similar spectral feature with lower energy peaks at 13 100 and 9 900 cm^{-1} , $\Delta E = 3\,200 \text{ cm}^{-1}$. The lower energy peaks and lower ΔE value as compared to those of the distorted square pyramidal complexes are typical and consistent with the intermediate five-coordinate geometry of complex **II**. The one electron ground-state configuration is assigned to the $d_{x^2-y^2} > d_{z^2} > d_{xy} > d_{xz} \approx d_{yz}$. The transitions may be assigned as the $d_{xy}, d_{yz}, d_{zx} \rightarrow d_{x^2-y^2}$ transition for high energy band and $d_{z^2} \rightarrow d_{x^2-y^2}$ transition for the lower energy band.

The electronic diffuse reflectance spectra of polynuclear alternating hydroxido/carbonato bridged copper(II) complexes show two broad, not well-resolved bands at approximately 14 000 and 10 220 cm^{-1} , $\Delta E = 3\,780 \text{ cm}^{-1}$ for **III**, 14 880 and 10 840 cm^{-1} , $\Delta E = 4\,040 \text{ cm}^{-1}$ for **IV** and 14 080 and 10 140 cm^{-1} , $\Delta E = 3\,980 \text{ cm}^{-1}$ for **VI**. This spectral character of the compounds is consistent with the distorted square-pyramidal geometry, $\tau = 0.42, 0.40$ and 0.10 for **III**, $0.42, 0.22$ and 0.03 for **IV** and $0.16, 0.22$ and 0.00 for **VI**. The spectral bands of these complexes are assigned to be the $d_{xy}, d_{yz}, d_{zx} \rightarrow d_{x^2-y^2}$ and $d_{z^2} \rightarrow d_{x^2-y^2}$ transitions. The electronic diffuse reflectance spectrum of compound **V** ($\tau = 0.59, 0.33, 0.19, 0.05$) consists of a single broad band, seem to be slightly separated into two broad bands but unresolved from approximately 14 970 to 10 240 cm^{-1} . This apparent spectral character arises due to the mixed geometries

of the complex from square pyramid to distorted trigonal bipyramid, thus this single broad band contains the $d_{xy}, d_{yz}, d_{zx} \rightarrow d_{x^2-y^2}$ and $d_{z^2} \rightarrow d_{x^2-y^2}$ transitions for the distorted square pyramidal chromophores superimposed⁴⁴ to the $d_{x^2-y^2} \rightarrow d_{z^2}$ and $d_{yz}, d_{zx} \rightarrow d_{z^2}$ transitions of a distorted trigonal bipyramidal chromophore.

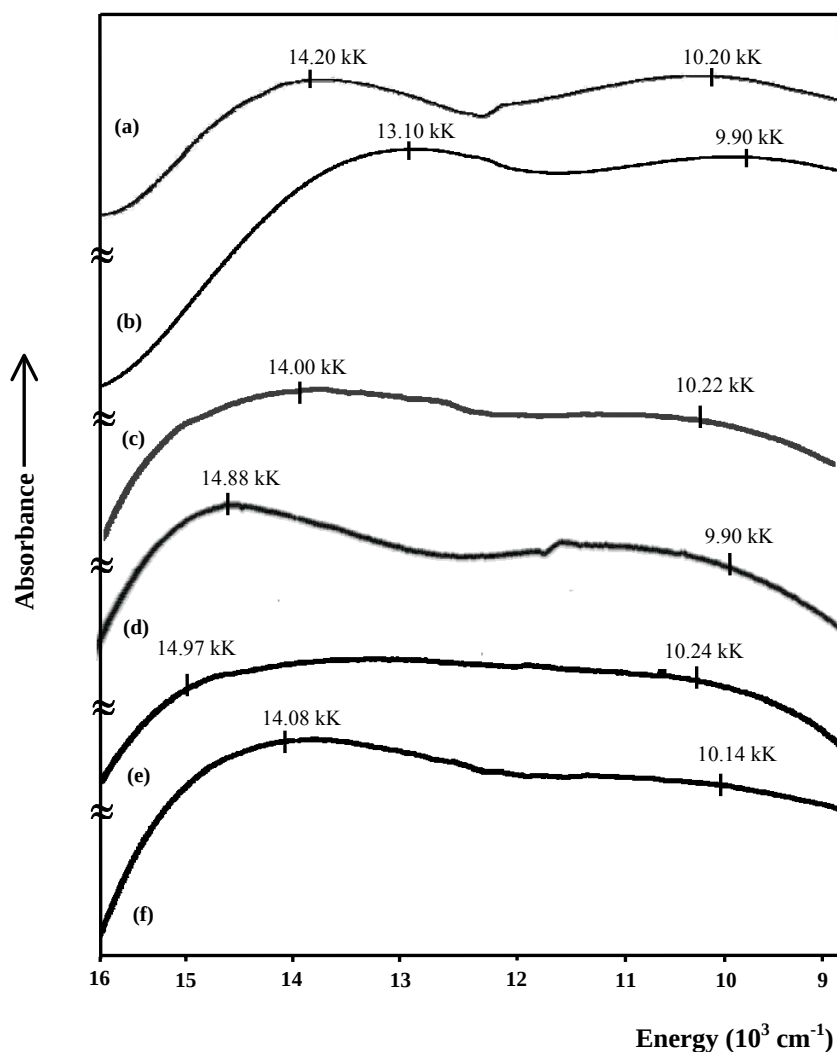


Figure 6. The electronic diffuse reflectance spectra of

- (a) $[\text{Cu}_3(\text{bpy})_6(\mu_3\text{-CO}_3)](\text{CF}_3\text{SO}_3)_4(\text{H}_2\text{O})_{0.5}$ (**I**)
- (b) $[\text{Cu}_3(\text{phen})_6(\mu_3\text{-CO}_3)](\text{CF}_3\text{SO}_3)_4(\text{H}_2\text{O})_{0.5}$ (**II**)
- (c) $[\text{Cu}_6(\text{bpy})_{10}(\mu\text{-OH})_2(\mu\text{-CO}_3)_2](\text{CF}_3\text{SO}_3)_6(\text{DMF})_2(\text{H}_2\text{O})_4$ (**III**)
- (d) $[\text{Cu}_6(\text{bpy})_{10}(\mu\text{-OH})_2(\mu\text{-CO}_3)_2](\text{BF}_4)_6(\text{H}_2\text{O})_{0.5}$ (**IV**)
- (e) $[\text{Cu}_8(\text{phen})_{12}(\mu_3\text{-OH})_2(\mu\text{-OH})_2(\mu_3\text{-CO}_3)_2](\text{CF}_3\text{SO}_3)_8(\text{DMF})_2(\text{H}_2\text{O})_{0.5}$ (**V**)
- (f) $\{[\text{Cu}_3(\text{bpy})_3(\mu\text{-OH})_2(\mu\text{-CO}_3)_2](\text{H}_2\text{O})_{6.5}\}_n$ (**VI**)

2.4.4 EPR spectra

The EPR spectra were recorded as a polycrystalline powder from 0-600 mT at X-band frequency ($h\nu = 0.325 \text{ cm}^{-1}$) at room temperature for complex **I** and at RT and 77 K for complex **II** (Figs. 7 and 8). Complex **II** showed almost similar spectra at RT and 77 K. A very broad signal $g = 2.13$ for **I** and $g = 2.13$ and 2.34 for **II** can be values attributed to the mononuclear impurity. The signals at $g = 1.80$ for **I** and 1.81 for **II** are assigned to $S = 1$ triplet signals. Other triplet signals seem to be obscured by the broad signal at around $g = 2.13$. In complex **II**, also a half-field signal of $\Delta M_s = \pm 2$ is observed at around $g = 4.33$ (164 mT), which supports the existence of a weak coupling between the copper ions.

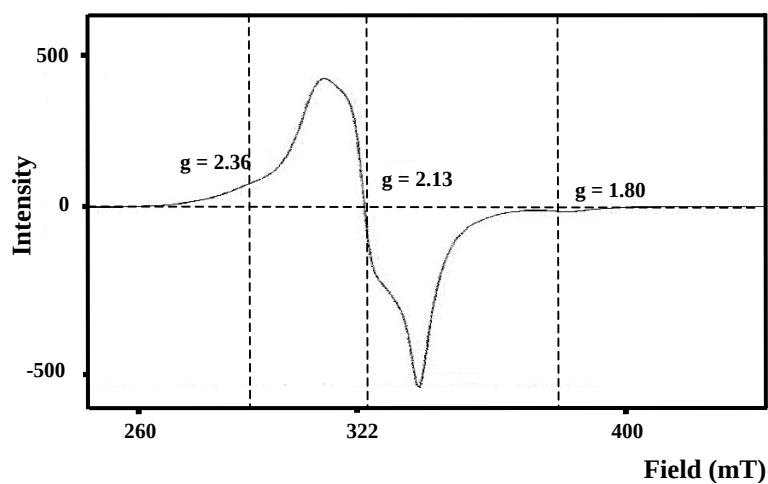


Figure 7. The X-band powder EPR spectrum at room temperature of $[\text{Cu}_3(\text{bpy})_6(\mu_3\text{-CO}_3)](\text{CF}_3\text{SO}_3)(\text{H}_2\text{O})_{0.5}$ (**I**)

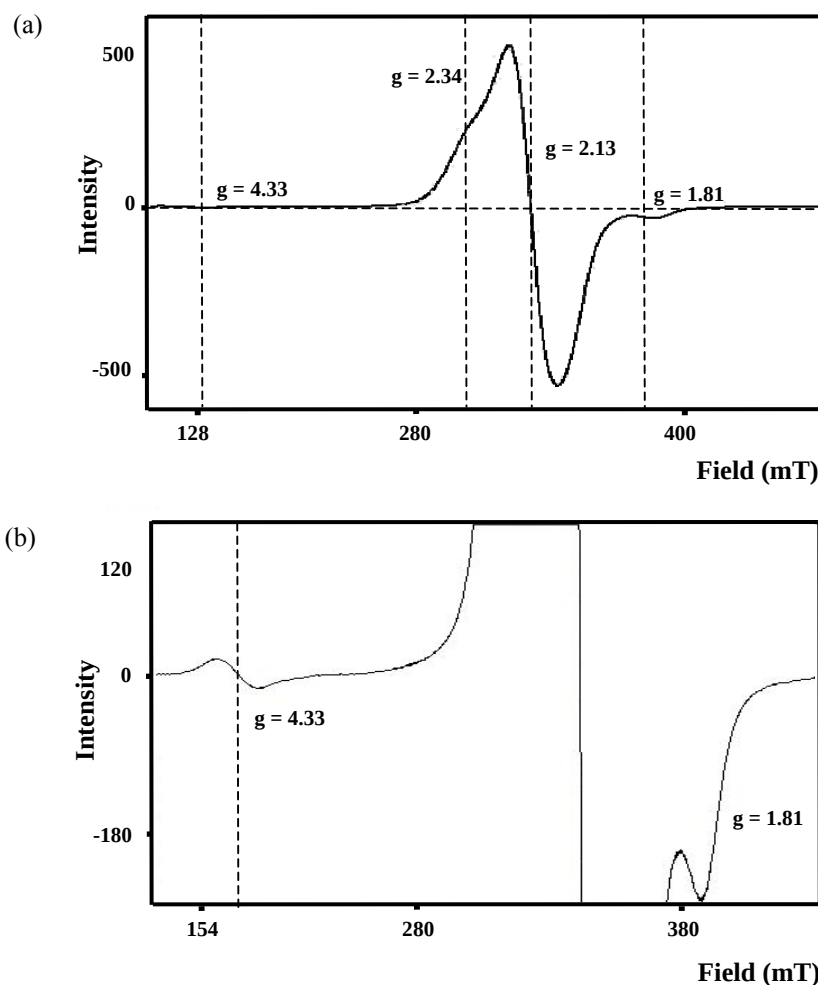


Figure 8 The X-band powder EPR spectra of $[\text{Cu}_3(\text{phen})_6(\mu_3\text{-CO}_3)](\text{CF}_3\text{SO}_3)_4(\text{H}_2\text{O})_{0.5}$ (II)

(a) At room temperature and 77 K (similar spectra)

(b) (b) The expanded region for clarity

The polycrystalline EPR spectra of compounds **III** are very similar both at RT and at 77 K (Fig. 9). EPR signals of **III** at $g = 2.46$, 2.11 and 1.77, which are values attributed to the a monomeric impurity and also a half-field signal is observed at $g = 4.44$ (155 mT), which supports the existence of a weak coupling between copper ions. The EPR spectrum of **IV** shows a very complicated spectrum with a large number of bands attributed to the $S = 1$ triplet signals with the sharp band at 320 mT as the mononuclear impurity (Fig. 10). At 77 K these signals become much stronger which is in agreement with the weak ferromagnetic nature. Due to the complicated nature of the signals no attempts were undertaken to analyze the spectra in detail.

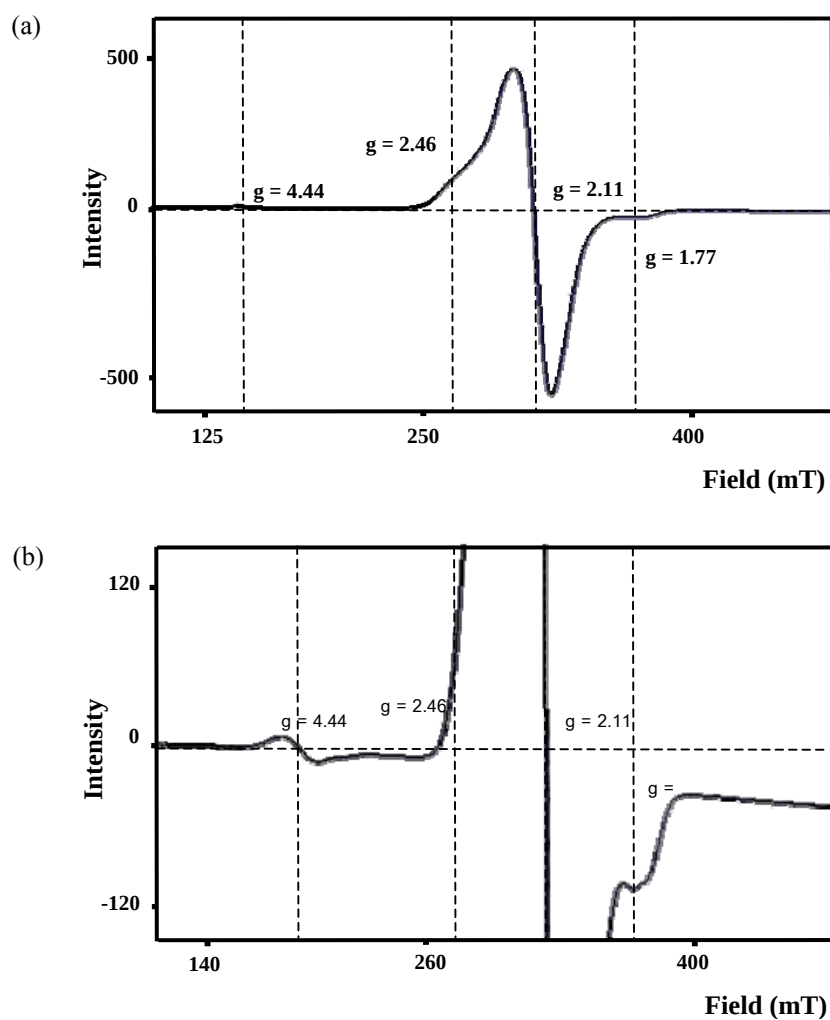


Figure 9. The EPR spectrum of $[\text{Cu}_6(\text{bpy})_{10}(\mu\text{-OH})_2(\mu\text{-CO}_3)_2](\text{CF}_3\text{SO}_3)_6(\text{DMF})_2(\text{H}_2\text{O})_4$ (III)

(a) The X-band powder EPR spectrum at room temperature and 77 K

(b) The expanded low-field region for clarity

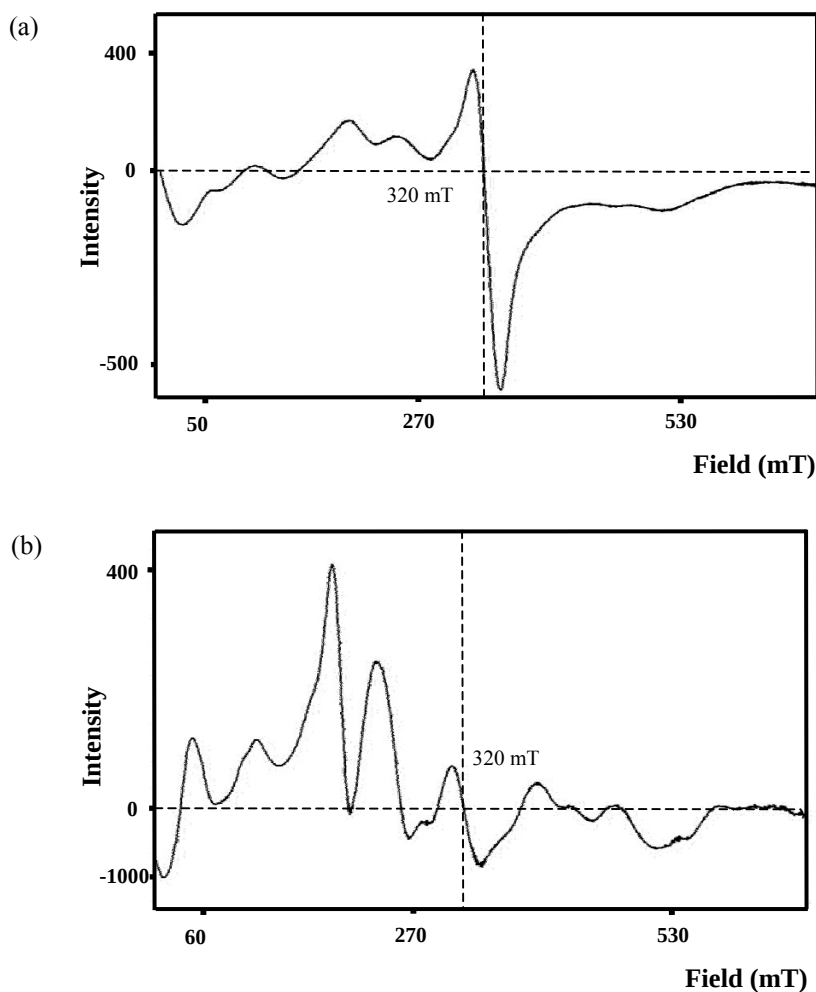


Figure 10. The X-band powder EPR spectrum of $[\text{Cu}_6(\text{bpy})_{10}(\mu\text{-OH})_2(\mu\text{-CO}_3)_2](\text{BF}_4)_6(\text{H}_2\text{O})_{0.5}$ (**IV**) at
 (a) room temperature
 (b) 77 K

The EPR spectra at RT and at 77 K of **V** were found to be similar (Fig. 11) and the spectrum consists of a very broad and strong signal centered around 320 mT, assigned to a monomeric impurity. Furthermore, a weak signal was observed at about 368 mT, which can be assigned to $S = 1$ triplet signal, other triplet signals seem to be obscured by the broad signal at 320 mT. The signal at around 160 mT can be assigned to the forbidden half-field signal ($\Delta M_s = \pm 2$). The polycrystalline EPR spectra of compound **VI** are very similar both at RT and at 77 K. The spectrum of **VI** shows a signal of a monomeric impurity at ~ 330 mT and a half-field signal at ~ 160 mT, indicative for a weak coupling between the copper ions (Fig. 12).

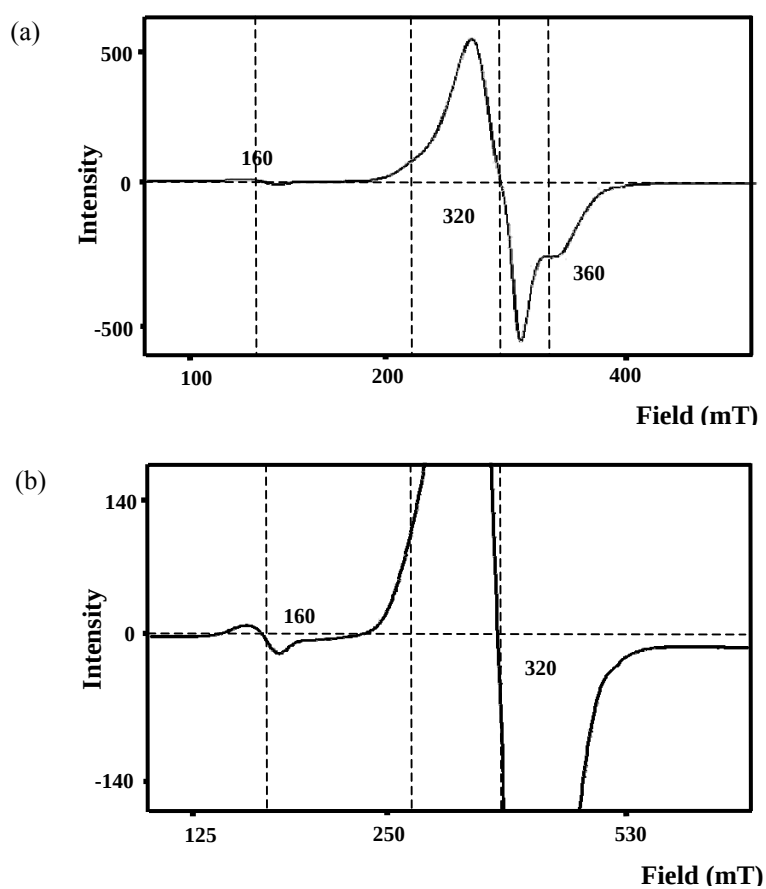


Figure 11. The EPR spectrum of $[\text{Cu}_8(\text{phen})_{12}(\mu_3\text{-OH})_2(\mu\text{-OH})_2(\mu_3\text{-CO}_3)_2](\text{CF}_3\text{SO}_3)_8(\text{DMF})_2(\text{H}_2\text{O})_{0.5}$ (**V**)
 (a) The X-band powder EPR spectrum at room temperature and 77 K
 (b) The expanded low-field region for clarity

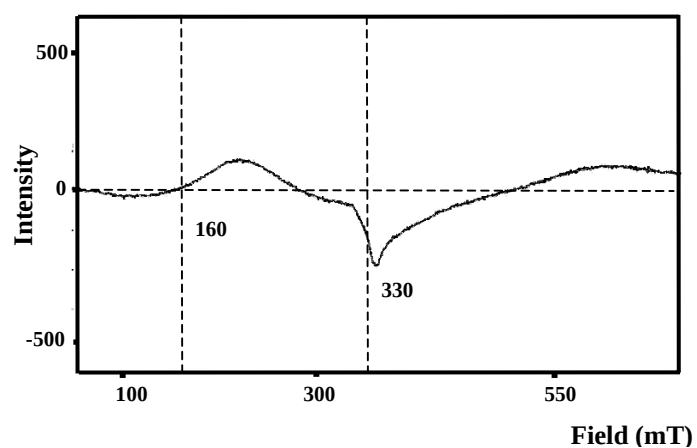


Figure 12. The X-band powder EPR spectrum at room temperature and at 77 K of $\{[\text{Cu}_3(\text{bpy})_3(\mu\text{-OH})_2(\mu\text{-CO}_3)_2](\text{H}_2\text{O})_{6.5}\}_n$ (**VI**)

2.4.5 Magnetic properties and superexchange mechanism

2.4.5.1 The trinuclear carbonato-bridged $[\text{Cu}_3(\text{chelate})_6(\mu_3\text{-CO}_3)](\text{CF}_3\text{SO}_3)_4(\text{H}_2\text{O})_{0.5}$ where chelate = bpy (I) and phen (II)

The magnetic susceptibilities of powdered samples were measured from 5 to 350 K for complexes I and II. The magnetic properties which are given in the form of $\chi_M T$ versus T for one Cu(II) ion are depicted in Figs. 13 and 14. The magnetic susceptibilities of complex II are in good acceptance. At 350 K the $\chi_M T$ product of II has a value of $0.37 \text{ cm}^3 \text{ K mol}^{-1}$, which is very close to the spin-only value for one non-interacting Cu(II) ion of $0.38 \text{ cm}^3 \text{ K mol}^{-1}$ at RT. With lowering the temperature from 350 K the $\chi_M T$ product increases gradually to a value of $0.83 \text{ cm}^3 \text{ K mol}^{-1}$ at 5 K. This magnetic behavior is typical for weakly ferromagnetically coupled copper(II) ions, which is comparable to those of the previously reported triangular trinuclear carbonato-bridged copper(II) complexes (Table 2.1). For the two closely related complexes with similar τ values, $[\text{Cu}_3(\text{dmbpy})_6(\mu_3\text{-CO}_3)](\text{BF}_4)_4(\text{C}_2\text{H}_5\text{OH})(\text{H}_2\text{O})$ (2) ($\tau = 0.43, 0.26, 0.71$),⁸ $[\text{Cu}_3(\text{bpy})_6(\mu_3\text{-CO}_3)](\text{BF}_4)_4(\text{H}_2\text{O})(\text{C}_2\text{H}_6\text{O})$ (3) ($\tau = 0.21, 0.10, 0.66$),⁹ a weak ferromagnetic interaction is observed with $2J = +29.3$ and $+10.6 \text{ cm}^{-1}$, respectively. Additionally, it is noted that the other related complexes in Table 2.1 which solely involves the distorted square pyramidal geometry, also exhibit the weak ferromagnetic behavior. However, only a complex $[\text{Cu}_3(\text{TPA})_3(\mu_3\text{-CO}_3)](\text{ClO}_4)_4$ (10) from the literature displays a very weak antiferromagnetic coupling with $2J = -1.19 \text{ cm}^{-1}$. This indicates that the distortion of five coordinate copper(II) chromophore within a complex has no significant effect on the magnetic interaction, but the topology and disposition of all three Cu(II) chromophores as triangular arrangement via the $\mu_3\text{-}\eta^1\text{:}\eta^1\text{:}\eta^1\text{-CO}_3$ bridging mode may play a key role in allowing some degree of the orbital orthogonality, resulting then a weak ferromagnetic interaction.

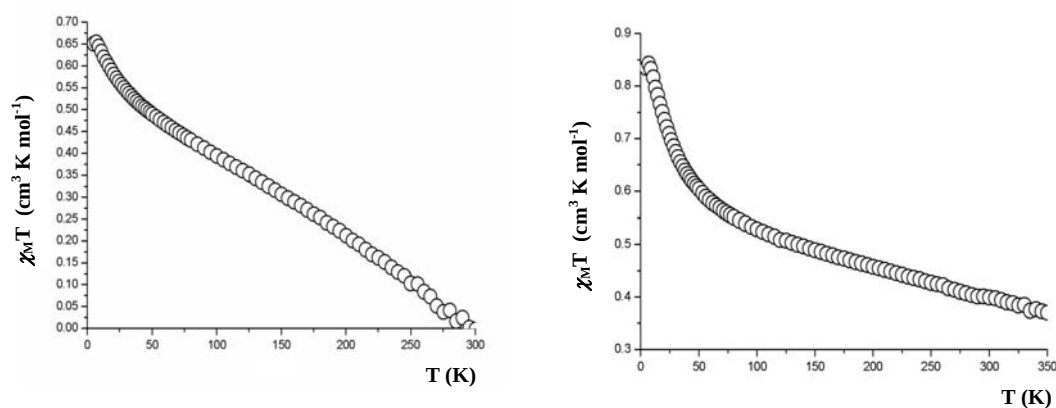


Figure 13. A plot of $\chi_M T$ versus T per Cu(II) ion for
(a) $[\text{Cu}_3(\text{bpy})_6(\mu_3\text{-CO}_3)](\text{CF}_3\text{SO}_3)_4(\text{H}_2\text{O})_{0.5}$ (I) and
(b) $[\text{Cu}_3(\text{phen})_6(\mu_3\text{-CO}_3)](\text{CF}_3\text{SO}_3)_4(\text{H}_2\text{O})_{0.5}$ (II)

2.4.5.2. Superexchange mechanism

Intramolecular interactions of trinuclear copper(II) complexes through a carbonate bridging ligand

The present trinuclear carbonate-bridged complexes **I** and **II** show a weak ferromagnetic coupling. The result is in agreement with literature for this type of complexes and confirms the ability of the carbonate group to couple ferromagnetically Cu(II) ions as given in Table 2.1., Fig. 14 shows the copper (II) chromophores and the model predicting the magnetic interactions with shape and disposition of Cu $d_{x^2-y^2}$ orbitals and O p orbitals in the $[\text{Cu}_3(\text{bpy})_6(\mu_3\text{-CO}_3)]^{4+}$ unit ($\tau = 0.39, 0.04, 0.56$ for **I** and $0.58, 0.54, 0.56$ for **II**) in which each oxygen atom of the carbonate group is bonded to different copper atoms, giving a triangular array of copper atoms. The magnetic orbital which contains the unpaired electron in each copper (II) ion, is considered to be mainly $d_{x^2-y^2}$ for the distorted square pyramidal chromophores and the admixture of $d_{x^2-y^2}$ and d_{z^2} for the intermediate five-coordinate chromophores. The carbonate bridge is positioned in the equatorial planes of three Cu(II) chromophores. The partial coupling of unpaired electrons between copper(II) ions can occur through p orbital of oxygen atoms in this bridging ligand with some degree of orbital orthogonality between the Cu $d_{x^2-y^2}$ orbitals and the O p orbitals, resulting the overall, ferromagnetic interaction in nature.

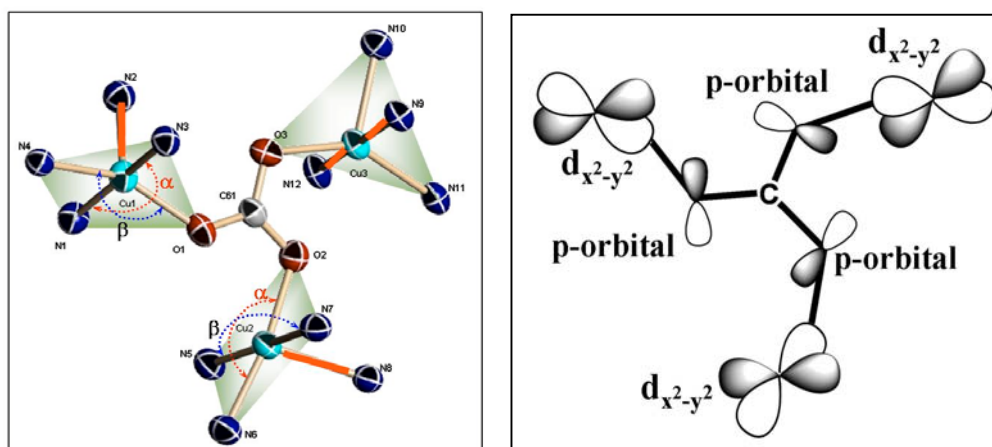


Figure 14. The model predicting the magnetic interactions through the carbonate bridge for triangular trinuclear carbonate-bridged copper(II) complex

For comparative purposes, the most related complexes with a triangular array of three copper(II) ions linked via the $\mu_3\text{-}\eta^1\text{:}\eta^1\text{:}\eta^1\text{-CO}_3$ bridging mode, also show a weak ferromagnetic interaction in nature (Table 2.1) notwithstanding the differences in geometric distortion. This ferromagnetic behavior may be attributed from the accidental orthogonality between the Cu $d_{x^2-y^2}$ magnetic orbitals and O p orbitals through the carbonate ligand with the *syn-anti*, eq-eq bridging mode. Besides, a weak ferromagnetic

coupling is also observed in complexes with the same bridging mode, the one-dimensional $[\text{Cu}(\text{CO}_3)(4\text{-apy})_2](\text{H}_2\text{O})^{14}$ (4-apy = 4-aminopyridine) ($2J = +11.0 \text{ cm}^{-1}$) and a dinuclear $[\text{Cu}_2(\text{ascidH}_2)(\text{CO}_3)(\text{H}_2\text{O})_2](\text{H}_2\text{O})_2^{15}$ (ascidH₂ = ascidiacyclamide) ($2J = +1.6 \text{ cm}^{-1}$).

2.4.5.3 The hexa-, octa- and polynuclear carbonato-bridged copper(II) complexes III-VI

The magnetic susceptibilities of complexes **III-V** have been measured from 5-300 K, while those of **VI** have been measured from 5-250 K. The magnetic properties are depicted as preliminary results in Figs. 15 and 16 for complexes **III**, **IV**, **V** and **VI**, respectively, in the form μ_{eff} versus T and $\chi_{\text{M}}T$ versus T plot for one copper(II) ion.

At 300 K for **III**, the μ_{eff} product is 1.75 BM per Cu ion, which is about the spin-only value calculated for an uncoupled spin $S = 1/2$ Cu(II) centre. Upon cooling, the value slightly increases to a value of 2.35 BM at ~ 5 K then tend to decrease. A similar behaviour is also observed for complex **IV**, at 350 K the $\chi_{\text{M}}T$ product has a value of $0.48 \text{ cm}^3 \text{ K mol}^{-1}$, which is a little above the spin-only value for a non-interacting Cu(II) ion ($0.38 \text{ cm}^3 \text{ K mol}^{-1}$ at RT). From 350 K the $\chi_{\text{M}}T$ product increases gradually to a value of $0.90 \text{ cm}^3 \text{ K mol}^{-1}$ at 5 K. The magnetic susceptibility of a powdered sample **V**, at 300 K the $\chi_{\text{M}}T$ product has a value of $0.36 \text{ cm}^3 \text{ K mol}^{-1}$, which is close to the spin-only value for one non-interacting Cu(II) ion ($0.38 \text{ cm}^3 \text{ K mol}^{-1}$ at RT). From 300 K the $\chi_{\text{M}}T$ product increases gradually to a value of $0.56 \text{ cm}^3 \text{ K mol}^{-1}$ at 5 K. The magnetic susceptibility data (5-250 K) of complex **VI**, at 250 K the μ_{eff} is lower than 1.75 BM per Cu ion, which is about the spin-only value calculated for an uncoupled spin $S = 1/2$ Cu(II) centre. Upon cooling, the value slightly increases to a value of 0.87 BM at ~ 7 K, then tend to decrease. These features of magnetic properties for all complexes reveal the weak ferromagnetic interaction.

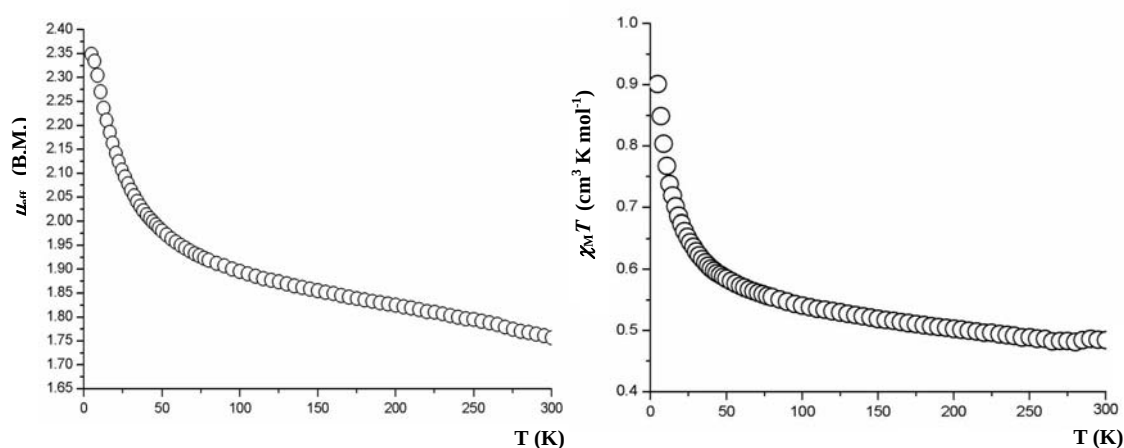


Figure 15. A plot of μ_{eff} versus T per Cu(II) ion for (a) $[\text{Cu}_6(\text{bpy})_{10}(\mu\text{-OH})_2(\mu\text{-CO}_3)_2](\text{CF}_3\text{SO}_3)_6(\text{DMF})_2(\text{H}_2\text{O})_4$ (**III**) and (b) $[\text{Cu}_6(\text{bpy})_{10}(\mu\text{-OH})_2(\mu\text{-CO}_3)_2](\text{BF}_4)_6(\text{H}_2\text{O})_{0.5}$ (**IV**)

In summary, the weak ferromagnetic behaviours of four alternating carbonato/hydroxido copper (II) complexes have been concurrently agree with the experimental data. However, due to the preliminary nature and the complicated structure, fitting against magnetic parameters was not possible.

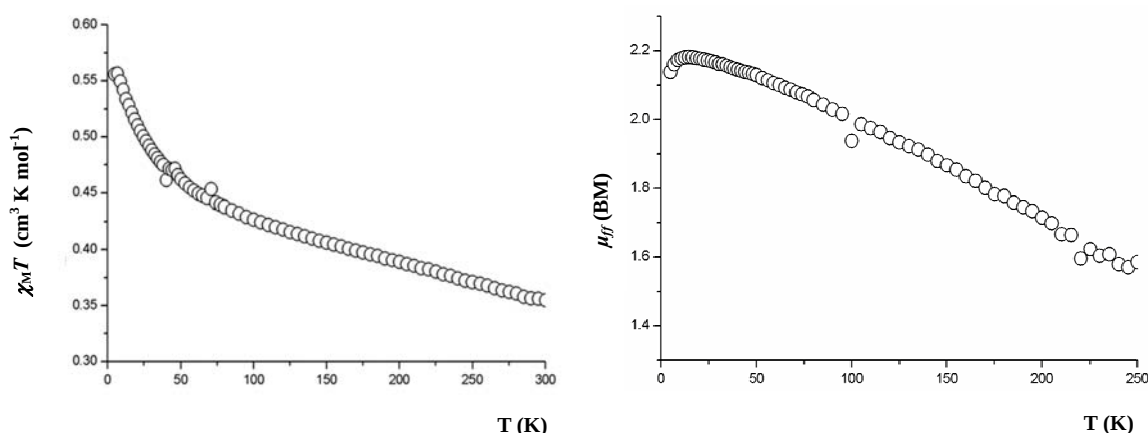


Figure 16. (a) A plot of $\chi_M T$ versus T per Cu(II) ion for $[\text{Cu}_8(\text{phen})_{12}(\mu_3\text{-OH})_2(\mu\text{-OH})_2(\mu_3\text{-CO}_3)_2](\text{CF}_3\text{SO}_3)_8(\text{DMF})_2(\text{H}_2\text{O})_{0.5}$ (**V**) and (b) A plot of μ_{eff} versus T per Cu(II) ion for $[\text{Cu}_3(\text{bpy})_3(\mu\text{-OH})_2(\mu\text{-CO}_3)_2](\text{H}_2\text{O})_{6.5}$ (**VI**)

2.4.5.4 Superexchange mechanism

Intramolecular interactions through a carbonato and hydroxydo bridging ligand

From the magnetic results, complexes **III-VI** show the weak ferromagnetic behavior. This behavior of a $\chi_M T$ versus T or μ_{eff} versus T plot is typical for weakly ferromagnetically coupled copper(II) ions, corresponding with those of the previously reported polynuclear alternating carbonato/hydroxido-bridged Cu(II) complexes as given in Table 2.2. In the structural periodicity for **III-VI**, two exchange pathways are distinguished: one involving the carbonato bridges and the other one concerning the hydroxido bridges. The representations of predicted superexchange mechanism of the hexanuclear, octanuclear and polynuclear alternating carbonato/hydroxydo-bridged copper(II) complexes are given in Figs. 17, 18 and 19, respectively.

The superexchange mechanism in **III** and **IV** through oxygen p-orbitals of the $\mu_3\text{-}\eta^2\text{:}\eta^1$ carbonato bridges are shown in Fig. 17, respectively. From a magnetic point of view the magnetic orbitals would be defined as mainly $d_{x^2-y^2}$, based on the τ values of 0.42, 0.40, 0.10 of **III** and 0.42, 0.22, 0.03 of **IV** for Cu (1), Cu(2) and Cu(3), respectively. From Fig. 17, the three possible superexchange pathways are considered as following; (i) the interaction between two terminal copper(II) atoms which bridged by the *anti-anti* and *syn-anti* triatomic bridged carbonato groups in an eq-eq configuration for **III** and **IV**, respectively, (ii) the interaction between a terminal copper(II) ion and a copper(II) center of the hydroxido-bridged copper(II)

unit which bridged by the *syn-anti* and *anti-anti* triatomic-bridged carbonato groups in an ax-eq configuration for **III** and **IV**, respectively and (iii) the interaction between an another terminal copper(II) ion and a copper(II) center of the hydroxido-bridged copper(II) unit which bridged by the monoatomic-bridged carbonato group in an ax-eq configuration for both complexes.

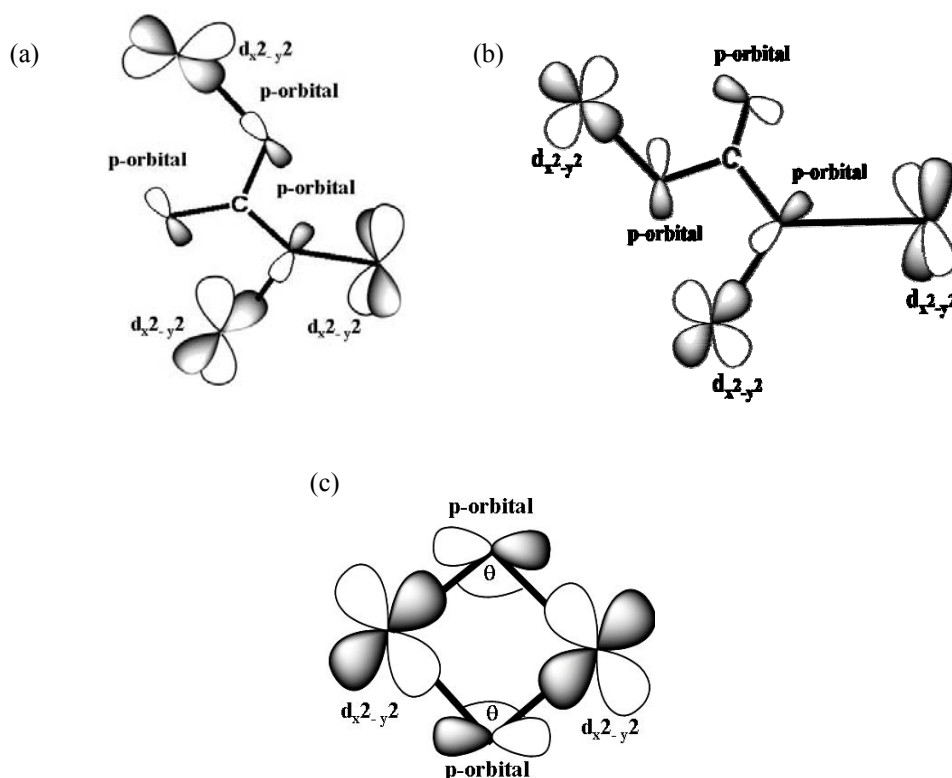


Figure 17. The superexchange mechanism in **III** and **IV** through oxygen p -orbitals of carbonato (a) for **III** and (b) for **IV**) and hydroxido (c) bridges

The *anti-anti* carbonato bridge with an eq-eq configuration in **III** is comparable to that in the dinuclear complexes $[\text{Cu}_2(\text{bpy})_4(\mu\text{-CO}_3)](\text{PF}_6)(\text{DMF})_2$ ($2J = -140.4 \text{ cm}^{-1}$),¹⁰ $[\text{Cu}_2(\text{dpyam})_4(\mu\text{-CO}_3)](\text{BF}_4)_2(\text{H}_2\text{O})_4$ ($2J = -88.2 \text{ cm}^{-1}$)¹³ and $[\text{Cu}_2(\text{dpyam})_4(\mu\text{-CO}_3)](\text{ClO}_4)_2(\text{H}_2\text{O})$ ($2J = -90.4 \text{ cm}^{-1}$)¹³. These complexes perform the moderately strong antiferromagnetic behavior whereas the weak ferromagnetic coupling is observed with complexes involving the *syn-anti* carbonato bridge and an eq-eq configuration, a polynuclear $\{[\text{Cu}(\text{CO}_3)(4\text{-apy})_2](\text{H}_2\text{O})\}_n$ (4-apy = 4-aminopyridine) ($2J = +11.0 \text{ cm}^{-1}$),¹⁴ a dinuclear $[\text{Cu}_2(\text{ascidH}_2)(\text{CO}_3)(\text{H}_2\text{O})_2](\text{H}_2\text{O})_2$ (ascidH₂ = ascidiacyclamide) ($2J = +1.6 \text{ cm}^{-1}$)¹⁵ and a hexanuclear $[\text{Cu}_6(\text{bpy})_{10}(\mu\text{-OH})_2(\mu\text{-CO}_3)_2](\text{ClO}_4)_6(\text{H}_2\text{O})_4$ (**1**) ($2J_{\text{syn-anti}} = +5.5 \text{ cm}^{-1}$)¹⁰ complexes. In cases of the *syn-anti* and *anti-anti* triatomic carbonato bridge with the ax-eq configuration in **III** and **IV** including the monoatomic carbonato bridge with an ax-eq

arrangement, the weak ferromagnetic interactions are normally observed, as found in the hexanuclear complex **1** ($2J = +5.5, +5.5$ and $+6.5 \text{ cm}^{-1}$). Consequently, it is suggested that the carbonato-bridged copper(II) unit in **III** may contribute a dominant antiferromagnetic interaction while all three pathways of this carbonato unit in complex **IV** contribute the weak ferromagnetic interaction. This distinct may result in the overall, weaker ferromagnetic interaction for complex **III** than that of complex **IV**.

As indicated earlier, studies of di- μ -hydroxido-bridged Cu(II) dimers have been pivotal in the development of structure-magnetism correlations. Experimentally, Hodgson and Hatfield²⁶ found that for dimers with planar or near-planar $[\text{Cu}_2(\mu\text{-OH})_2]^{2+}$ cores, the exchange constant (J) varies linearly with the Cu-O-Cu angle (θ), $2J = -74.53\theta + 7270 \text{ cm}^{-1}$. Thus the interaction is predicted to be antiferromagnetic ($S = 0$ ground state) for $\theta > 97.5^\circ$ and ferromagnetic ($S = 1$ ground state) for $\theta < 97.5^\circ$. The superexchange mechanism of the di- μ -hydroxido bridges in **III** and **IV** are shown Figure 16(c). For complexes **III** and **IV**, the Cu_2O_2 network is exactly planar (dihedral angle between CuO_2 and CuO_2 planes, 180.0°) and the bridging hydroxido O(4) atom is positioned in the eq planes of both Cu(3) and Cu(3)A chromophores with the Cu-O(H)-Cu angles of 94.3 and 95.0° for **III** and **IV**, respectively. Thus the coupling can occur through this bridging ligand which results in the ferromagnetic interaction with the predicted $2J$ values of $+241.8$ and $+189.6 \text{ cm}^{-1}$ for **III** and **IV**, respectively. In addition, the magnitude of the antiferromagnetic character would be slightly decreased, supported by a degree of deviation from planarity; the dihedral angles between CuN_2 and CuO_2 planes of 14.6 and 13.6° for complexes **III** and **IV**, respectively, providing the more ferromagnetic interaction. The magnetic interaction of complex **IV** may be in a similar trend to that of the closely related complex $[\text{Cu}_6(\text{bpy})_{10}(\mu\text{-OH})_2(\mu\text{-CO}_3)_2](\text{ClO}_4)_6(\text{H}_2\text{O})_4$ (**1**)¹⁰ ($\tau = 0.41, 0.23, 0.05$ and $\theta = 95.1$, $2J_{\text{predicted}} = +190.0 \text{ cm}^{-1}$) both of which having a similar structure with the same carbonato bridging mode and an identical Cu-OH-Cu bridging angle. The magnetic interaction of the hexanuclear complex **1** was well analyzed previously to be weak ferromagnetic in nature with the dominant ferromagnetic interaction from di- μ -hydroxido copper(II) species ($2J = +48.0 \text{ cm}^{-1}$) rather than the carbonato pathways ($2J = +5.5, +7.5$ and $+5.5 \text{ cm}^{-1}$). In case of complex **III**, the calculated $2J$ value ($+241.8 \text{ cm}^{-1}$) suggests the more ferromagnetic interaction than that of complexes **IV** and **1** ($2J_{\text{calculated}} = +190.0 \text{ cm}^{-1}$) and the carbonato bridge dispositions in a different arrangement, *anti-anti*, eq-eq configuration for **III** and *syn-anti*, eq-eq configuration for **IV**. Complexes with these bridging modes are normally found to contribute the moderately strong antiferromagnetic interaction and the weak ferromagnetic interaction,¹⁴⁻¹⁵ respectively. Consequently, the overall weak ferromagnetic interaction would be expected for both complexes.

The superexchange mechanism of the octanuclear copper(II) complex **V** is predicted as shown in Fig. 18. In complex **V**, the copper(II) atoms involve a distorted square pyramidal geometry and an intermediate geometry which is slightly distorted toward a trigonal bipyramidal geometry ($\tau = 0.59, 0.33, 0.19, 0.05$). The magnetic orbitals which contain the unpaired electron in each copper(II) ion, are considered to be mainly $d_{x^2-y^2}$. Two terminal copper(II) ions are linked by $\mu_3\text{-}\eta^1\text{:}\eta^1\text{:}\eta^1$ carbonato bridging

ligand which occupies an equatorial position. The resulting unit is connected to an apical position of the copper(II) ion of the di- μ -hydroxido species via this carbonato bridge (see Fig. 18(a)). The extremely weak magnetic interaction is expected through two carbonato pathways, *syn-anti*, eq-eq [Cu(1)(μ -CO₃)Cu(2)] and *syn-anti*, ax-eq [Cu(1)(μ -CO₃)Cu(3) and Cu(2)(μ -CO₃)Cu(3)] with small values of the spin densities in the O(3) and O(3)A axially coordinated atoms.

The dominant coupling between copper atoms of compound **V** is predicted with the ferromagnetic interaction mainly couplings through di- μ -hydroxido pathway (Fig. 18(b)). Similar trend is evident from the suggesting di- μ -hydroxido pathway of the hexanuclear complexes. The values of the bridging angles of **V** are 95.8 and 93.5° corresponding to the ferromagnetic interactions with the predicted $2J$ value of +137.5 and +256.7 cm⁻¹, respectively. Furthermore, a distortion between CuO₂ and CuO₂ planes (dihedral angle of 154.6°) from planarity of two independent di- μ -hydroxido copper(II) units may play the influence in the decrease of the antiferromagnetic contribution, then providing the overall, moderately strong ferromagnetic interaction when considering the cooperative antiferromagnetic interaction contributed from the carbonato-bridged copper(II) units.

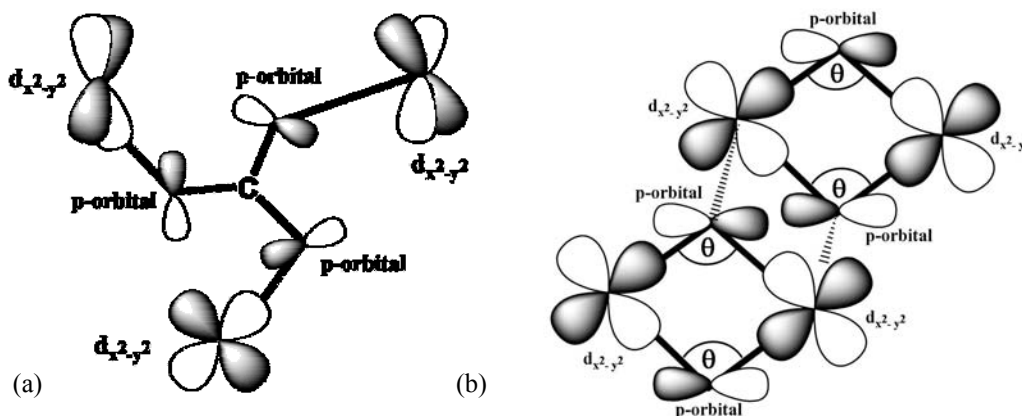


Figure 18. The superexchange mechanism in **V** through oxygen p-orbitals of carbonato (a) and hydroxido (b) bridges

For complex **VI**, the copper(II) ions involve a distorted square pyramidal geometry ($\tau = 0.16, 0.22, 0.00$). The magnetic $d_{x^2-y^2}$ orbital is located on the basal plane of the square pyramidal copper(II) chromophore. Complex **VI** is a polymeric chain structure containing the di- μ -hydroxido bridge with the planar Cu₂O₂ network (dihedral angle between CuO₂ and CuO₂, 180.0°) and two different types of carbonato bridging modes, μ - η^1 : η^1 (*anti-anti*, ax-eq) and μ - η^2 : η^1 (*syn-anti*, ax-eq). The dispositions of both carbonato bridges are in a similar arrangement to some pathways of complexes **III** and **IV** which show the

interactions between a terminal copper(II) ion and a copper(II) center of the hydroxido group, bridged by the *syn-anti* and *anti-anti* triatomic-bridged carbonato group in an ax-eq configuration for **III** and **IV**, respectively. Consequently, the expected interactions would be in a range from a weak antiferromagnetic to weak ferromagnetic coupling. The superexchange mechanism of two different types of carbonato bridges are shown Fig. 19(a) and (b), respectively. The dominant coupling between copper atoms of compound **VI** is predicted to occur through the di- μ -hydroxido pathway (Fig. 19(c)). The bridging Cu-O(H)-Cu angles of 96.8° suggest the moderate ferromagnetic coupling with the predicted $2J$ values of $+55.5 \text{ cm}^{-1}$ which may masks the magnetic interaction contributed from the carbonato-bridged copper(II) unit. Thus the net magnetic coupling in complex **VI** is a dominant ferromagnetic interaction which is comparable to that of the closely related complex $\{[\text{Cu}_3(\text{bpy})_3(\mu\text{-OH})_2(\mu\text{-CO}_3)_2](\text{H}_2\text{O})_{11}\}_n$ (**2**)²⁷ with $2J_{\text{experiment}}$ of $+154.0$ and $+135.0 \text{ cm}^{-1}$.

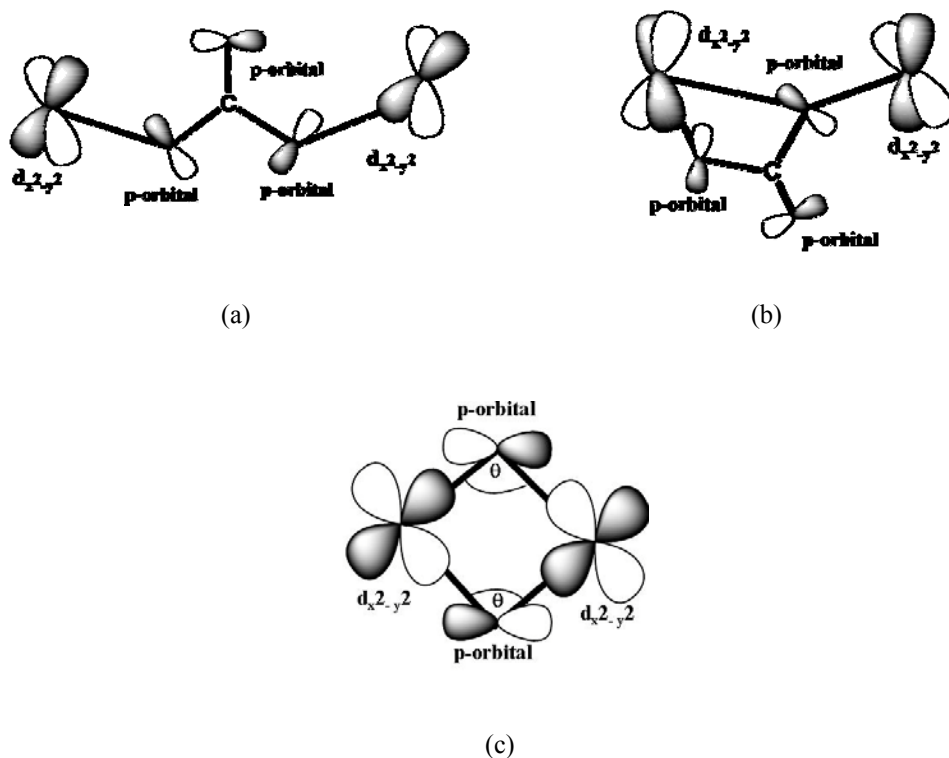


Figure 19. The superexchange mechanism in **VI** through oxygen p-orbitals of carbonato (a, b) and hydroxido (c) bridges

2.5 Conclusions

The second part of this research sets out to examine and develop the preparative work of a series of the carbonato-bridged polynuclear copper(II) complexes containing the 2,2'-bipyridyl (bpy) and 1,10-phenanthroline (phen). The spectroscopic and magnetic characterization, the X-ray crystal structure and the magneto-structural correlation of the complex system are investigated and discussed in comparison with other relevant complexes.

The copper(II) products $[\text{Cu}_3(\text{bpy})_6(\mu_3\text{-CO}_3)](\text{CF}_3\text{SO}_3)_4(\text{H}_2\text{O})_{0.5}$ (**I**), $[\text{Cu}_3(\text{phen})_6(\mu_3\text{-CO}_3)](\text{CF}_3\text{SO}_3)_4(\text{H}_2\text{O})_{0.5}$ (**II**), $[\text{Cu}_6(\text{bpy})_{10}(\mu\text{-OH})_2(\mu\text{-CO}_3)_2](\text{CF}_3\text{SO}_3)_6(\text{DMF})_2(\text{H}_2\text{O})_4$ (**III**), $[\text{Cu}_6(\text{bpy})_{10}(\mu\text{-OH})_2(\mu\text{-CO}_3)_2](\text{BF}_4)_6(\text{H}_2\text{O})_{0.5}$ (**IV**), $[\text{Cu}_8(\text{phen})_{12}(\mu_3\text{-OH})_2(\mu\text{-OH})_2(\mu_3\text{-CO}_3)_2](\text{CF}_3\text{SO}_3)_8(\text{DMF})_2(\text{H}_2\text{O})_{0.5}$ (**V**) and $\{[\text{Cu}_3(\text{bpy})_3(\mu\text{-OH})_2(\mu\text{-CO}_3)_2](\text{H}_2\text{O})_{6.5}\}_n$ (**VI**) were prepared successfully from the mole ratio method and characterized by elemental analyses. The crystal structures of **I-VI** were determined crystallographically and their spectroscopic properties (IR, EPR (r.t. and 77 K), solid state VIS) investigated. The temperature variable magnetic susceptibilities (5-280 K) of compounds were measured. The exchange interaction between two Cu(II) centres and the superexchange pathways are investigated and discussed.

In the structure of products $[\text{Cu}_3(\text{bpy})_6(\mu_3\text{-CO}_3)](\text{CF}_3\text{SO}_3)_4(\text{H}_2\text{O})_{0.5}$ (**I**) and $[\text{Cu}_3(\text{phen})_6(\mu_3\text{-CO}_3)](\text{CF}_3\text{SO}_3)_4(\text{H}_2\text{O})_{0.5}$ (**II**), the carbonate ligand acts as a bridge linking between three copper(II) centers within a unit in a $\mu_3\text{-}\eta^1\text{:}\eta^1\text{:}\eta^1\text{-CO}_3$ coordination mode with an eq-eq configuration. The coordination environments around copper ions of complex **I** are ranging from the square pyramidal to intermediate five-coordinate environment with the τ values of 0.39, 0.04 and 0.56. While, complex **II** exhibits the intermediate five-coordinate geometry with the τ values of 0.58, 0.54 and 0.56. This magnetic behavior is comparable to those of the previously reported triangular trinuclear carbonato-bridged copper(II) complexes, indicating that the distortion of five coordinate copper(II) chromophores within complexes has no significant effect on the magnetic interaction. However, the topology and disposition of all three Cu(II) chromophores as a triangular arrangement via the $\mu_3\text{-}\eta^1\text{:}\eta^1\text{:}\eta^1\text{-CO}_3$ bridging mode may play a key role in allowing some degree of orbital orthogonality, resulting a weak ferromagnetic interaction.

The structures, electronic properties and magnetism of the alternating carbonato/hydroxido copper (II) complexes: two hexanuclear complexes $[\text{Cu}_6(\text{bpy})_{10}(\mu\text{-OH})_2(\mu\text{-CO}_3)_2]\text{Y}$ where $\text{Y} = (\text{CF}_3\text{SO}_3)_6(\text{DMF})_2(\text{H}_2\text{O})_4$ (**III**) and $(\text{BF}_4)_6(\text{H}_2\text{O})_{0.5}$ (**IV**), the octanuclear complex $[\text{Cu}_8(\text{phen})_{12}(\mu_3\text{-OH})_2(\mu\text{-OH})_2(\mu_3\text{-CO}_3)_2](\text{CF}_3\text{SO}_3)_8(\text{DMF})_2(\text{H}_2\text{O})_{0.5}$ (**V**) and the polynuclear copper(II) complex $\{[\text{Cu}_3(\text{bpy})_3(\mu\text{-OH})_2(\mu\text{-CO}_3)_2](\text{H}_2\text{O})_{6.5}\}_n$ (**VI**) have been studied. These polynuclear copper(II) complexes consist of the carbonate ligand which acts as various bridges linking between the Cu(II) centers within units in a $\mu_3\text{-}\eta^2\text{:}\eta^1\text{-CO}_3$ mode for **III** and **IV**, $\mu_3\text{-}\eta^1\text{:}\eta^1\text{:}\eta^1\text{-CO}_3$ mode for **V** and $\mu\text{-}\eta^2\text{:}\eta^1$ and $\mu\text{-}\eta^1\text{:}\eta^1$ (*anti-anti*) modes for **VI**, and the di- μ -hydroxidodicopper(II) species. Copper atoms in complexes **III-VI** have the geometries ranging from an

intermediate five-coordinate environment to a square pyramidal geometry. The EPR spectra and magnetic susceptibilities of these complexes reveal the overall weak ferromagnetic behavior in nature.

In the structural periodicity for **III-VI**, two exchange pathways are distinguished: one involving the carbonato bridges and the other one concerning the hydroxido bridges. All complexes are considered to involve mainly the Cu $d_{x^2-y^2}$ magnetic orbitals with lobe directed toward the bridging oxygen atom of carbonate groups with different coordination mode. The different topologies and dispositions of the copper (II) chromophores and the large Cu...Cu distances suggest a weak antiferromagnetic to ferromagnetic interaction for the carbonato-bridged unit. For the di- μ -hydroxido bridges, the magnetic orbitals, $d_{x^2-y^2}$ of copper centers located in their respective basal planes. From Hodgson and Hatfield magneto-structural correlation²⁶ for the planar di- μ -hydroxido-bridged copper(II) species, an antiferromagnetic character is found for complexes with θ larger than 97.5° , while ferromagnetism appears for smaller values of θ . Therefore, the strong ferromagnetic couplings are expected through the di- μ -hydroxido pathway because of the small values of bridging angles (θ), 94.3° for **III**, 95.0° for **IV**, 93.5 and 95.8° for **V** and 98.6° for **VI**, corresponding to the ferromagnetic interaction with the singlet-triplet energy gap ($2J$ value) of $+241.8 \text{ cm}^{-1}$ for **III**, $+189.6 \text{ cm}^{-1}$ for **IV**, $+256.7$ and $+137.5 \text{ cm}^{-1}$ for **V**, and $+55.5 \text{ cm}^{-1}$ for **VI**. However, a slight reduction of the antiferromagnetic contribution may be observed when the planar di- μ -hydroxido copper(II) unit becomes deviated, suggesting the more ferromagnetic coupling through the hydroxido pathways. Consequently, the overall, weak to moderate ferromagnetic is expected for the present complexes, based on the theoretical analysis.

Parts of the results of this complexes system have been published²⁸⁻³¹.

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Table 2.1 Selected magneto-structural data for triangular trinuclear carbonato-bridged copper(II) complexes

Compound *	Chromophore	Geometry **	τ Cu1,Cu2, Cu3	Cu...Cu (Å)	EPR (solid, RT)	2J (cm ⁻¹)	Ref.
{[Cu(4-apy) ₂] ₃ (μ ₃ -CO ₃) ₂ (ClO ₄) ₂ (CH ₃ OH) _{0.5}] _n (1)	CuN ₂ O ₂	Sq Planar	0.00, 0.00, 0.00	4.578	-	+6.4	17
[Cu ₃ (dmbpy) ₆ (μ ₃ -CO ₃)](BF ₄) ₄ (C ₂ H ₅ OH)·(H ₂ O) (2)	CuN ₃ O(N)	SP - TBP	0.43, 0.26, 0.71	4.767	g _⊥ = 2.13 (br) g = 2.49 (vw)	+29.3	8
[Cu ₃ (bpy) ₆ (μ ₃ -CO ₃)](BF ₄) ₄ (H ₂ O) ₂ (C ₂ H ₆ O) (3)	CuN ₃ O(N)	SP - TBP	0.21, 0.10, 0.66	4.787	g _⊥ = 2.13 (br) g = 2.42 (vw)	+10.6	9
[Cu ₃ (bpy) ₆ (μ ₃ -CO ₃)](CF ₃ SO ₃) ₄ (H ₂ O) _{0.5} (I)	CuN ₃ O(N)	SP - Interm	0.39, 0.04, 0.56	4.813	2.36, 2.21, 2.13, 2.03	weak F	This work
[Cu ₃ (phen) ₆ (μ ₃ -CO ₃)](CF ₃ SO ₃) ₄ (H ₂ O) _{0.5} (II)	CuN ₃ O(N)	Interm	0.58, 0.54, 0.56	4.723	2.34, 2.13	weak F	This work
[Cu ₃ (pip) ₃ (H ₂ O) ₃ (μ ₃ -CO ₃)](NO ₃) ₄ (4)	CuN ₃ O(O _w)	SP	-	4.630	2.12	+9.64	18
[Cu ₃ (pip) ₃ (H ₂ O) ₃ (μ ₃ -CO ₃)](ClO ₄) ₄ (5)	CuN ₃ O(O _w)	SP	-	-	2.14	+8.94	18
[Cu ₃ (Medpt) ₃ (μ ₃ -CO ₃)](ClO ₄) ₃ (ClO ₄) (6)	CuN ₃ O(O _{ClO4})	SP	0.16, 0.13, 0.12	-	2.11	+12.6	16
[Cu ₃ (L) ₃ (μ ₃ -CO ₃)](ClO ₄) ₄ (7)	CuN ₃ O(O)	SP	0.19, 0.19, 0.19	4.654	2.10 (br)	+8.2	19
[Cu ₃ (L ₂) ₃ (μ ₃ -CO ₃)](ClO ₄) ₄ (H ₂ O) ₂ (8)	CuN ₃ O(N)	SP	-	-	-	+17.2	20
[Cu ₃ (Et ₃ dien) ₃ (μ ₃ -CO ₃)](ClO ₄) ₃ (ClO ₄) (9)	-	-	-	-	-	+6.7	21
[Cu ₃ (TPA) ₃ (μ ₃ -CO ₃)](ClO ₄) ₄ (10)	CuN ₃ O(N)	SP	-	-	-	-1.19	22
[Cu ₃ (dpt) ₃ (μ ₃ -CO ₃)](ClO ₄) ₂ (OH ₂)](ClO ₄) ₂ (H ₂ O) (11)	CuN ₃ O(O)	SP	0.04, 0.13, 0.13	-	2.11	+13.89	23
[{(L ³) ₃ Cu(OCIO ₃) ₃ }(μ ₃ -OCO ₂)](ClO ₄) (12)	CuN ₃ O(O _{ClO4})	SP	0.11, 0.11, 0.11,	4.654	-	-	24
[{(mpepma)Cu(OCIO ₃) ₃ }(μ ₃ -OCO ₂)](ClO ₄) (13)	CuN ₃ O(O _{ClO4})	SP	0.01, 0.01, 0.01	4.695	2.11	+18.0	25

Abbreviations: * 4-apy = 4-aminopyridine; dmbpy = 4,4'-dimethyl-2,2'-bipyridine; bpy = 2,2'-bipyridine; 1,10-phenanthroline; pip = 2-[2-(2-pyridyl)ethyliminomethyl]pyridine; Medpt = bis(3-aminopropyl)methylamine; L = macrocycle [15]aneN₃O₂; L₂ = 1,4,7,10-tetraazabicyclo[5.5.3]pentadecane; Et₃dien = N,N',N''-triethylbis(2-aminoethane)amine; bis(3-aminopropyl)methylamine; TPA = tris(pyridylmethyl)amine; dpt = bis(3-aminopropyl)amine; L³ = N-methyl-N,N-bis(2-pyridylmethyl)amine; mpepma = methyl[2-(2-pyridyl)ethyl](2-pyridylmethyl)amine. ** Sq Planar = square planar, SP = distorted square pyramidal geometry, Interm = Intermediate geometry between square pyramid and trigonal bipyramid, TPB = distorted trigonal bipyramidal geometry, F = ferromagnetic, - = not available.

Table 2.2 Selected magneto-structural data for carbonato/hydroxido-bridged polynuclear copper(II) complexes

Compound ^a	Geometry /Cu ^b	τ Cu1, Cu2, Cu3, Cu4	Bridging configuration ^c	Bridging mode of CO ₃ ²⁻	Cu-O(H)- Cu / °	Cu...Cu (Å) (OH unit)	2J (cm ⁻¹)	Ref.
Hexanuclear carbonato/hydroxido-bridged copper(II) complexes								
[Cu ₆ (bpy) ₁₀ (μ-CO ₃) ₂ (μ-OH) ₂](CF ₃ SO ₃) ₆ (DMF) ₂ (H ₂ O) ₄ (III)	SP	0.42, 0.40, 0.10	eq-eq (μ-CO ₃) ax-eq (μ-CO ₃) ax-eq (μ-CO ₃) eq-eq (μ-OH)	μ ₃ -η ² :η ¹	94.3	2.844	-	This work
[Cu ₆ (bpy) ₁₀ (μ-CO ₃) ₂ (μ-OH) ₂](BF ₄) ₆ (H ₂ O) _{0.5} (IV)	SP	0.42, 0.22, 0.03	eq-eq (μ-CO ₃) ax-eq (μ-CO ₃) ax-eq (μ-CO ₃) eq-eq (μ-OH)	μ ₃ -η ² :η ¹	95.0	2.844	-	This work
[Cu ₆ (bpy) ₁₀ (μ-CO ₃) ₂ (μ-OH) ₂](ClO ₄) ₆ (H ₂ O) ₄ (1)	SP	0.41, 0.23, 0.05	eq-eq (μ-CO ₃) ax-eq (μ-CO ₃) ax-eq (μ-CO ₃) eq-eq (μ-OH)	μ ₃ -η ² :η ¹	95.1	2.845	+5.5 (μ-CO ₃) +6.5 (μ-CO ₃) +5.5 (μ-CO ₃) +48.0 (μ-OH)	10
Octanuclear carbonato/hydroxido-bridged copper(II) complex								
[Cu ₈ (phen) ₁₂ (μ ₃ -OH) ₂ (μ-OH) ₂ (μ-CO ₃) ₂](CF ₃ SO ₃) ₈ (DMF) ₂ (H ₂ O) _{0.5} (V)	SP-TBP	0.59, 0.33, 0.19, 0.05	eq-eq (μ-CO ₃) eq-eq (μ-CO ₃) ax-eq (μ-CO ₃) eq-eq (μ-OH) eq-eq (μ-OH)	μ ₃ -η ¹ :η ¹ :η ¹	93.5, 95.8	2.853	-	This work
Polymeric carbonato/hydroxido-bridged copper(II) complexes								
{[Cu ₃ (bpy) ₂ (μ-OH) ₂ (μ-CO ₃) ₂](H ₂ O) _{6.5} } _n (VI)	SP	0.16, 0.22, 0.00	eq-eq (μ-OH) eq-eq (μ-OH)	μ-η ¹ :η ¹ , μ-η ² :η ¹	96.8, 96.8	2.913, 2.875	-	This work
{[Cu ₃ (bpy) ₂ (μ-OH) ₂ (μ-CO ₃) ₂](H ₂ O) ₁₁ } _n (2)	SP	0.16, 0.22, 0.00	eq-eq (μ-OH) eq-eq (μ-OH)	μ-η ¹ :η ¹ , μ-η ² :η ¹	94.6, 96.5	2.871, 2.923	+154 (μ-OH) +135 (μ-OH)	27

Abbreviations: ^a dpt = bis(3-aminopropyl)amine, Medpt = Bis(3-aminopropyl)methylamine, TPPNOL = *N,N,N'*-tris-(2-pyridylmethyl)-1,3-diaminopropan-2-ol, L¹ = 6-aryl substituted tris(2-pyridylmethyl)amine, H₃L² = (2-(2-hydroxyphenyl)-1,3-bis[4-(2-hydroxyphenyl)-3-azabut-3-enyl]-1,3-imidazolidine), bpy = 2,2'-bipyridine; phen = 1,10-phenanthroline. ^b SP = distorted square pyramidal geometry, TBP = distorted trigonal pyramidal geometry, - = not available

Part III

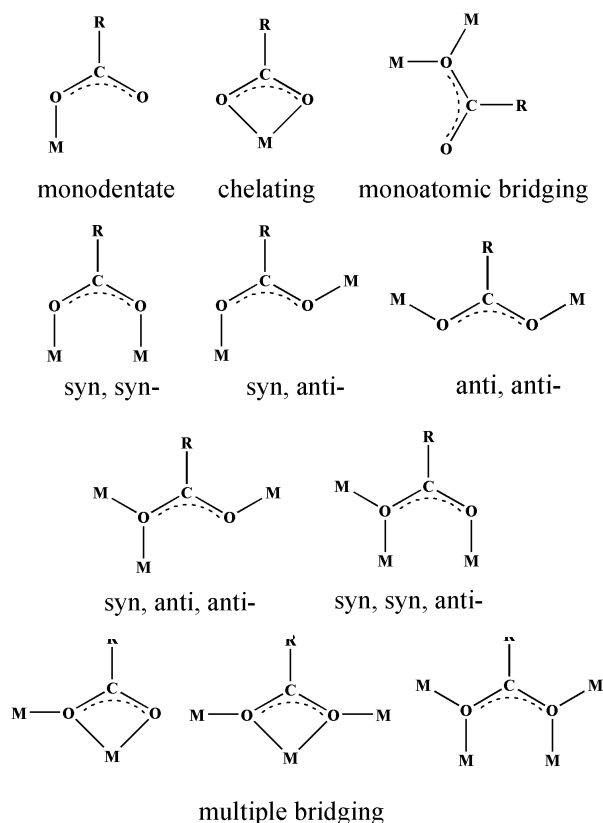
Synthesis, Crystal Structure, Spectroscopic and Magnetic
Properties of Polynuclear Carboxylato-bridged
Copper(II) *Paddle-wheel* Complexes

Synthesis, Crystal Structure, Spectroscopic and Magnetic Properties of Polynuclear Carboxylato-bridged Copper(II) *Paddle-wheel* Complexes

3.1 Introduction

The chemistry of copper carboxylates has been extensively investigated since many years due to their relevance for certain copper containing enzymes¹⁻⁷ and their interesting magnetostructural correlations which focus on the effects of the structural and chemical factors to control the exchange coupling interactions between paramagnetic centers through mono- and multiatomic bridges⁷⁻¹¹. Furthermore, the diverse coordination modes of carboxylato anions largely contribute to the formation of various structural types for copper carboxylates, such as mononuclear, dinuclear and polynuclear structural units^{1,11-13}. The carboxylate chemistry is interesting due to two reasons: Firstly they play a vital role as ligands in biochemical systems involving mono-, di- or polymetallic active sites; secondly polynuclear carboxylates are very good investigators for exchange coupling interactions between adjacent metal ions. Carboxylato anions can bind toward metal cations in various ways: monodentate, chelate, monoatomic bridges, bridging didentate (μ - η^1 ; η^1), bridging tridentate (μ_3 - η^1 ; η^2), as well as less common multiple bridges¹³⁻¹⁶, as shown in **Scheme 1**.

Chelate ligands di-2-pyridylamine (dpym), 2,2'-bipyridine (bpy) and 1,10-phenanthroline (phen) are the instances of alpha-diimine chelating didentates which play a key role in these studies because their rigidity and planarity efficiently provide π - π stacking interactions among their aromatic moieties either intra- or intermolecular stacks. This feature potentially

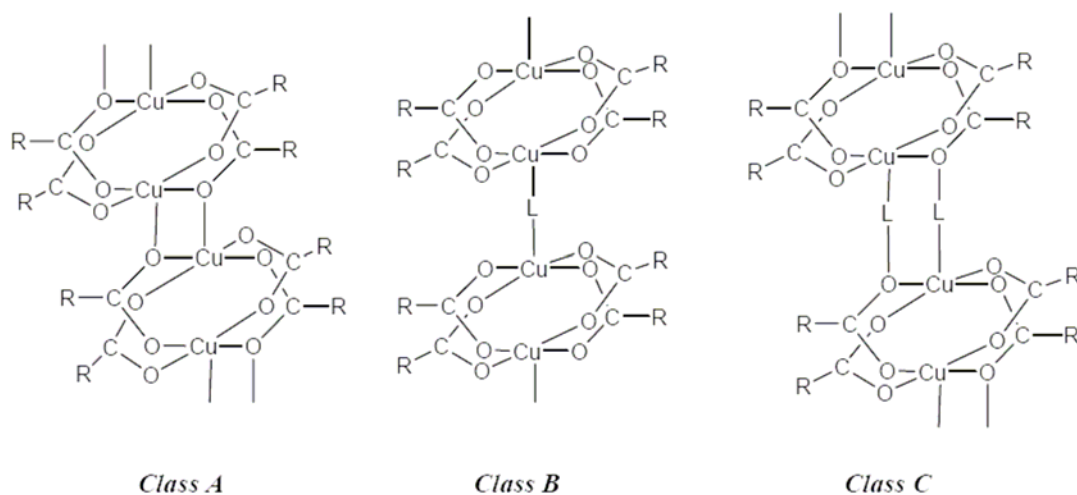


Scheme 1

contributes the stability of polynuclear structures as well as the formation of extended supramolecular structures with bridging anionic ligands^{10, 17-20}.

A large number of *paddle-wheel* type dimeric copper(II) carboxylate adducts, $[\text{Cu}_2(\text{RCO}_2)_4\text{L}_2]$, where L is an apical ligand with an oxygen or a nitrogen atom, have been reported in an effect to clarify the factors influencing the magnitude of the intramolecular magnetic exchange interaction which occurs between two Cu(II) ions of a *paddle-wheel* moiety²¹⁻²⁴. The polynuclear copper(II) carboxylates were found to exhibit three classes of local *paddle-wheel* structure: (A) stepped polymeric structure with the second lone pair is donated to a metal ion of another *paddle-wheel* unit²²; (B) stepped without additional ligands with polymeric structures can also be obtained by means of ligands which are able to bridge between dinuclear units²³; (C) the bridging ligand coordinates axially to a Cu ion and at the same time interacts with a carboxylate oxygen atom of another *paddle-wheel* unit²⁴. An example of each class is presented in **Scheme 2**.

This part report five new polynuclear copper(II) compounds, a hexanuclear $[\text{Cu}_4(\text{dpyam})_2(\text{OCOC}_2\text{H}_5)_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)_6(\text{H}_2\text{O})_2][\text{Cu}_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)_4(\text{H}_2\text{O})_2](\text{DMF})_2$ (**I**), two polymeric chain compounds $[\text{Cu}_6(\text{phen})_2(\text{H}_2\text{O})_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)_{12}]_n[\text{Cu}_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)_4(\text{H}_2\text{O})_2]_{2n}(\text{H}_2\text{O})_{0.5n}$ (**II**) and $\{[\text{Cu}_4(\text{phen})_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)_8](\text{H}_2\text{O})\}_n$ (**III**) and two dinuclear $[\text{Cu}_2(\mu\text{-O}_2\text{CC}_6\text{H}_4\text{OH})_4(\text{C}_7\text{H}_7\text{NO})_2](\text{H}_2\text{O})_6$ (**IV**) and $[\text{Cu}_2(\mu\text{-O}_2\text{CCH}_3)_4(\text{C}_7\text{H}_7\text{NO})_2]$ (**V**). The magnetic susceptibility measurement in a rang 2-350 K of the three later compounds are investigated are discussed in comparison with other related compounds.



Scheme 2

3.2 Aims and Scopes

The objective of the first part of this research is to examine and develop the preparation work of the Polynuclear Carboxylato-bridged Copper(II) *Paddle-wheel* Complexes. The spectroscopic properties (IR,

solid state VIS, EPR (room temperature and liquid nitrogen temperature)) are characterized and the X-ray crystal structure determined. The room temperature magnetic moment and the temperature variable susceptibilities are measured and the magneto-structural correlation together with the superexchange pathways are investigated and discussed in comparison with other relevant complexes.

3.3 Experimental

3.3.1 Reagents and physical measurements

All reagents are commercial grade materials and were used without further purification. Elemental analyses (C, H, N) were determined on a Perkin–Elmer PE 2400 CHNS/O Analyzer. IR spectra were recorded with a Perkin–Elmer Spectrum One FT-IR spectrophotometer as KBr pellets in the 4000–450 cm^{-1} spectral range. Solid-state (diffuse reflectance) electronic spectra were recorded as polycrystalline samples on a Perkin-Elmer Lambda2S spectrophotometer over the range 8000–18000 cm^{-1} . X-band powder EPR spectra were obtained on a Jeol RE2x electron spin resonance spectrometer using DPPH ($g = 2.0036$) as a standard.

3.3.2 Syntheses

3.3.2.1 $[\text{Cu}_4(\text{dpyam})_2(\text{OCOC}_2\text{H}_5)_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)_6(\text{H}_2\text{O})_2][\text{Cu}_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)_4(\text{H}_2\text{O})_2](\text{DMF})_2$ (I)

Compound **I** was obtained as a mixing solution of dpyam (0.171 g, 1.0 mmol) in DMF:EtOH (20:10 ml) was added to a warm aqueous solution (10 ml) of $\text{Cu}(\text{CO}_3) \cdot \text{Cu}(\text{OH})_2 \cdot n\text{H}_2\text{O}$ (0.332 g, 1.5 mmol). Then an aqueous solution (10 ml) of $\text{NaO}_2\text{CCH}_2\text{CH}_3$ (0.144 g, 1.5 mmol) was added to the mixture yielding a blue solution and the blue precipitate formed in a few minutes. Its color became light blue by slow addition of the concentrate propionic acid (5 ml) yielding a clear, light blue solution. After a month, greenish-blue polygon-shape crystals of compound **I** were obtained which were filtered off, washed with the mother liquid and air-dried. Yield *ca.* 65%. $\text{C}_{62}\text{H}_{102}\text{Cu}_6\text{N}_8\text{O}_{30}$; *Anal.* Calc. (%): C, 40.90; H, 5.65; N, 6.15 %. Found: C, 40.50; H, 5.61; N, 6.04 %.

3.3.1.2 $[\text{Cu}_6(\text{phen})_2(\text{H}_2\text{O})_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)_{12}]_n[\text{Cu}_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)_4(\text{H}_2\text{O})_2]_{2n}(\text{H}_2\text{O})_{0.5n}$ (II)

A mixing solution of 1,10-phenantroline (phen) (0.198 g, 1.0 mmol) in ACN:EtOH (20:10 ml) was added to a warm aqueous solution (10 ml) of $\text{Cu}(\text{CO}_3) \cdot \text{Cu}(\text{OH})_2 \cdot n\text{H}_2\text{O}$ (0.332 g, 1.5 mmol). Then an aqueous solution (10 ml) of $\text{NaO}_2\text{CCH}_2\text{CH}_3$ (0.144 g, 1.5 mmol) was added to the mixture yielding a blue solution and the blue precipitate formed in a few minutes. The resulting solution became clear and light blue in color by slow addition of the concentrate propionic acid (7 ml). After a month, blue polygon-shaped crystals of **II** were obtained which were filtered off, washed with the mother liquid and air-dried. Yield *ca.*

50%. $C_{168}H_{254}Cu_{20}N_3O_{93}$; *Anal.* Calc. (%): C, 39.22; H, 4.98; N, 2.17 %. Found: C, 39.05; H, 4.41; N, 2.01 %.

3.3.2.3 $\{[Cu_4(phen)_2(\mu-O_2CC_2H_5)_8](H_2O)_n\}_n$ (III)

An aqueous solution (10 ml) of $Cu(CO_3) \cdot Cu(OH)_2$ (0.221 g, 1 mmol) was stirred and a blue precipitate formed within a few minutes. The resulting solution became clear and light blue in color by slow addition of the concentrate propionic acid (2 ml) and stirred for 1 h. A solution of phen (0.197 g, 1.0 mmol) in ACN:EtOH (20:10 ml) was added to the mixture, followed by addition of an aqueous solution of $NaO_2CCH_2CH_3$ (0.095 g, 1 mmol) with continuous stirring. After a month, blue polygon-shaped crystals of **III** were obtained which were filtered off, washed with the mother liquid and air-dried. Yield, *ca.* 70%. $C_{48}H_{54}Cu_4N_4O_{17}$; *Anal.* Calc. (%): C, 47.40; H, 4.70; N, 4.60 %. Found: C, 47.30; H, 4.70; N, 4.60 %.

3.3.2.4 $[Cu_2(\mu-O_2CC_6H_4OH)_4(C_7H_7NO)_2](H_2O)_6$ (IV)

A warm solution of 3-Hydroxybenzoic acid (0.139 g, 1.0 mmol) in MeOH (20 ml) was added to a hot aqueous solution (10 ml) of $Cu(BF_4)_2$ (0.237 g, 1 mmol). An aqueous solution (10 ml) of 4-Acetylpyridine (0.121 g, 1 mmol) was then added. The light blue solution was slowly evaporated at room temperature. After several days, green rod crystals of **IV** were formed. The crystals were filtered off, washed with mother liquid and air-dried. Yield, *ca.* 80%. $C_{42}H_{41}Cu_2N_2O_{20}$; *Anal.* Calc. (%): C, 49.20; H, 4.50; N, 2.70 %. Found: C, 51.00; H, 4.20; N, 2.80 %.

3.3.2.5 $[Cu_2(\mu-O_2CCH_3)_4(C_7H_7NO)_2]$ (V)

The ligand 4-Acetylpyridine (0.121 g, 1 mmol), dissolved in ACN (10 ml) and a warm solution of $Cu(CH_3COO)_2$ (0.182 g, 1 mmol) were mixed together. The blue solution was slowly evaporated at room temperature until dark blue plate-shape crystals of **V** separated. Yield *ca.* 70%. $C_{22}H_{26}Cu_2N_2O_{10}$; *Anal.* Calc. (%): C, 43.60; H, 4.30; N, 4.60 %. Found: C, 43.40; H, 4.10; N, 4.60 %.

3.3.3 Crystallography

X-ray single-crystal data were collected at 273 K for compounds **I**, **IV** and **V** and at 293 K for compounds **II** and **III**, respectively on a 4 K Bruker SMART APEX CCD area-detector diffractometer (rotating anode, graphite-monochromated Mo- K_α radiation, $\lambda = 0.71073$ Å) using SMART program. Raw data frame integration was performed with SAINT, which also applied correction for Lorentz and Polarization effects. An empirical absorption correction by using the SADABS program was applied, which resulted in transmission coefficients ranging from 1.000 to 0.848, 1.000 to 0.674, 1.000 to 0.624, 1.000 to 0.845 and 1.000 to 0.695 for **I-V**, respectively. The structures were solved by direct methods and refined by full-matrix least-squares method on $(F_{obs})^2$ with anisotropic thermal parameters for all non-hydrogen atoms using the SHELXTL-PC V 6.12 software package.

For the structure determination of compound **I**, one of propionate groups showed disorder; the occupancies of the disordered positions were initially refined and later fixed at 0.50. The DMF group is

disordered with site occupancies of 0.50. All hydrogen atoms of the dpyam and propionate ligands in **I** were fixed and allowed to ride on the attached atoms, hydrogen atoms of coordinated water molecules were located geometrically and refined isotropically. For the structure determination of complex **II**, eighteen of propionate groups showed disorder; the occupancies of the disordered positions were initially refined and later fixed at 0.50 for both conformers. All hydrogen atoms of the phen ligand in **II** were fixed and allowed to ride on the attached atoms, while hydrogen atoms of coordinated water molecules were located geometrically and refined isotropically. The H atoms of the propionate groups in **III**, were fixed geometrically with the HFIX utility and the hydrogen atoms of one water molecule in **III** were unable to locate and also could not be located at fixed positions. The terminal C atom in three propionate groups of **III** showed disorder; the occupancies of the disordered positions were initially refined and later fixed at 0.5. All hydrogen atoms of complexes **IV** and **V** were located in a difference Fourier map and refined isotropically, except the H atoms of the four water molecules in **IV**, which were unable to locate and also could not be located at fixed positions.

The maximum and minimum peaks in the final difference Fourier synthesis are 0.57 and -0.44 e.Å⁻³ for **I**, 0.48 and -0.37 e.Å⁻³ for **II**, 0.53 and -0.65 e.Å⁻³ for **III**, 0.36 and -0.23 e.Å⁻³ for **IV** and 0.30 and -0.24 e.Å⁻³ for **V**. The molecular graphics for compounds **I-VI** were produced by using SHELXT-PC package. Packing figures were produced with Platon program.

3.4 Results and Discussion

3.4.1 Description of the structure

3.4.1.1 Description of hexanuclear compound [Cu₄(dpyam)₂(OCOC₂H₅)₂(μ-O₂CC₂H₅)₆(H₂O)₂][Cu₂(μ-O₂CC₂H₅)₄(H₂O)₂](DMF)₂ (**I**)

The crystal structure of **I** consists of centrosymmetric tetranuclear [Cu₄(dpyam)₂(OCOC₂H₅)₂(μ-O₂CC₂H₅)₆(H₂O)₂] units (Fig. 1a), dinuclear [Cu₂(μ-O₂CC₂H₅)₄(H₂O)₂] units and noncoordinating DMF molecules. The “outer” Cu ions (Cu(1), Cu(1)A), with a CuN₂O₂O’ chromophore, have an intermediate geometry (Fig. 1b). The Cu(II) atom is five-coordinated with a basal plane consisting of two N atoms (Cu–N 1.983(3) and 2.033(3) Å) of dpyam and two O atoms (Cu–O 1.942(2) and 1.963(2) Å) of two different propionate ligands. The coordinated water molecule O(1) occupies the apical position at a distance of 2.259(2) Å. The CuN₂O₂ chromophore is non-planar with tetrahedral twist of 31.2(1)°. The copper line above this plane, 0.252(1) Å is toward O(1). The copper chromophore can be described as having an intermediate geometry. The distortion of intermediate geometry can be best described by the structural parameter τ ($\tau = 0$ for square pyramid and $\tau = 1$ for trigonal bipyramid), within this case is 0.483.

The “inner” Cu ions (Cu(2), Cu(2)A) involve a five-coordinate $\text{CuO}_4\text{O}'$ chromophore (Fig. 1c), four oxygens of four different carboxylate groups coordinate to Cu(2) in equatorial positions, at mean distance of 1.967(3) Å. Another propionate O atom coordinate at the apical position, at 2.100(2) Å, completing the square pyramidal coordination geometry with τ value of 0.003. Four propionate anions bridge two copper ions in a syn,syn- $\eta^1:\eta^1:\mu$ showing the *paddle-wheel* unit with $\text{Cu}\cdots\text{Cu}$ distance of 2.632(1) Å. The basal plane is non-planar with a slight tetrahedral twist of 16.5(1)° at Cu(2). The Cu metal atom lies 0.202(1) Å above the basal plane toward the axial site. The “outer” and “inner” units are linked by propionate bridges showing syn,anti- $\eta^1:\eta^1:\mu$ coordination mode from an axial position of one chromophore to an equatorial position of the other one. An uncoordinate molecule of $[\text{Cu}_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)_4(\text{H}_2\text{O})_2]$ similar to the “inner”, involves a centrosymmetric dinuclear *paddle-wheel* unit in which four propionato groups are bridging the two Cu atoms, in a syn,syn- $\eta^1:\eta^1:\mu$ disposition. An O atom of water molecule occupies the axial position of each Cu atom at a distance of 2.156(2) Å, completing the square

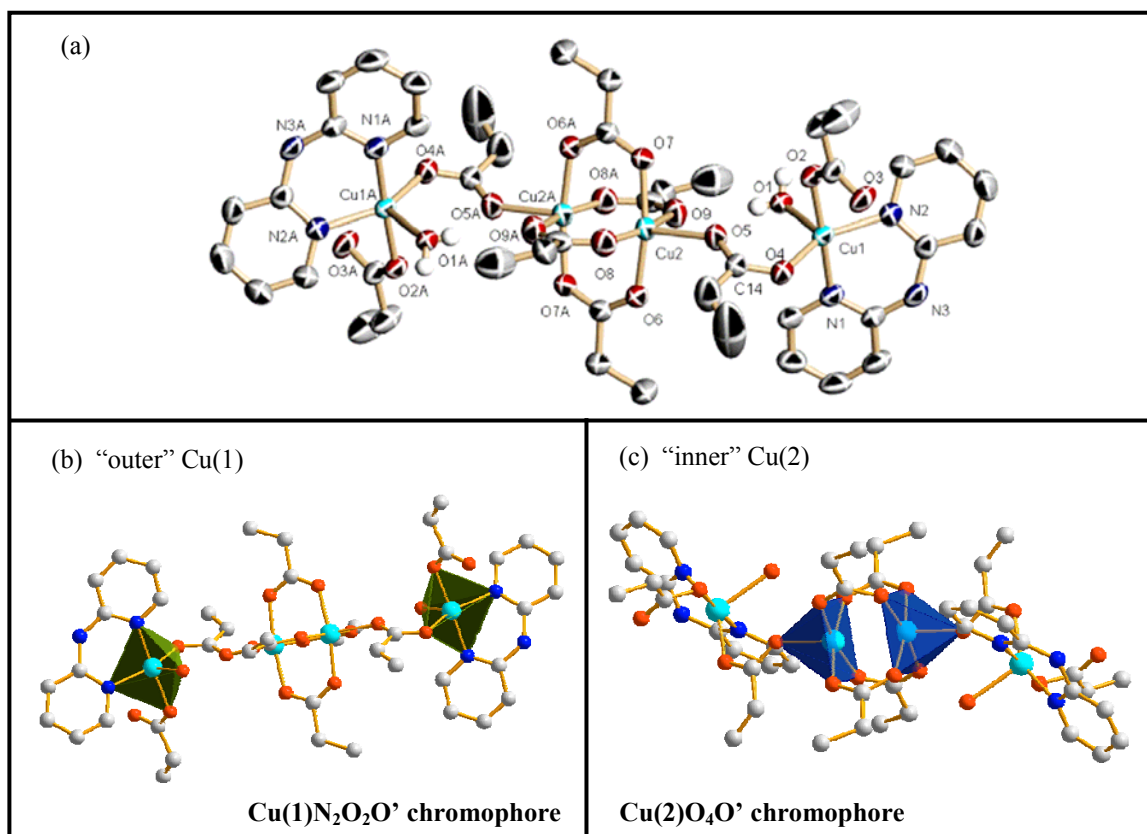


Figure 1. (a) A plot of the tetranuclear $[\text{Cu}_4(\text{dpyam})_2(\text{OCOC}_2\text{H}_5)_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)_6(\text{H}_2\text{O})_2]$ unit of $[\text{Cu}_4(\text{dpyam})_2(\text{OCOC}_2\text{H}_5)_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)_6(\text{H}_2\text{O})_2][\text{Cu}_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)_4(\text{H}_2\text{O})_2]\cdot(\text{DMF})_2$ (**I**). Hydrogen atoms in dpyam and propionate ligands are omitted for clarity. (b) The intermediate five coordinate $\text{Cu}(1)\text{N}_2\text{O}_2\text{O}'$ chromophore of “outer” Cu. (c) The square pyramidal $\text{Cu}(2)\text{O}_4\text{O}'$ chromophore of “inner” Cu.

pyramidal coordination geometry with τ value of 0.001. The Cu(3)···Cu(3)A distance is 2.647(1) Å. The basal plane is non-planar with a slight tetrahedral twist of 17.2(1)° at Cu(3). The Cu metal atoms lies 0.210(1) Å above the basal plane toward the axial site. The structural parameters of compound **I** are in the normal ranges found for the *paddle-wheel* copper(II) dimers statistically analyzed.

3.4.1.2 Description of polynuclear compound $[\text{Cu}_6(\text{phen})_2(\text{H}_2\text{O})_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)_{12}]_n[\text{Cu}_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)_4(\text{H}_2\text{O})_2]_{2n}(\text{H}_2\text{O})_{0.5n}$ (**II**)

The asymmetric unit of a polynuclear compound **II** consists of a hexanuclear $[\text{Cu}_6(\text{phen})_2(\text{H}_2\text{O})_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)_{12}]$, a dinuclear $[\text{Cu}_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)_4(\text{H}_2\text{O})_2]$, two halves of two independent dinuclear $[\text{Cu}_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)_4(\text{H}_2\text{O})_2]$, and a half of water molecule. Compound **II** involves one-dimensional structure arised from the hexanuclear units and consists of zig-zag chains of mononuclear $\text{Cu}(\mu\text{-O}_2\text{CC}_2\text{H}_5)_2(\text{H}_2\text{O})(\text{phen})$ repeating units running along the b-axis, which are connected along the unit cell diagonal via $\text{Cu}_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)_4$ *paddle-wheel* dinuclear units. This structure is depicted in Fig. 2 together with the numbering scheme. Both mononuclear and dinuclear units are linked by the syn-anti, triatomic propionato bridge in an axial-equatorial configuration. There are four outer distinct Cu···Cu separations along the b-axis which alternate according to the sequence ABCD, where (using the viewpoint of Fig. 3) A = Cu(1)···Cu(2) = 5.074(1) Å; B = Cu(3)···Cu(4) = 4.287(1) Å; C = Cu(4)···Cu(5) = 5.077(1)Å; D = Cu(6)···Cu(1)' = 4.293(1) Å. The inner distinct Cu(2)···Cu(3) = 2.621(1) Å; Cu(5)···Cu(6) = 2.621(1) Å.

The *paddle-wheel* dinuclear $\text{Cu}_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)_4$ units in the chain contain four bridging propionates in the *syn,syn*- $\eta^1:\eta^1:\mu$ coordination mode, as found in the previously reported compound $[\text{Cu}_2(\text{O}_2\text{CC}_2\text{H}_5)_4(\text{H}_2\text{O})_2]$ and complex **I**. The square pyramidal coordinations at Cu(2), Cu(3), Cu(5) and Cu(6) are completed by oxygen atoms of another propionate bridging, with the τ values of 0.045, 0.053, 0.046 and

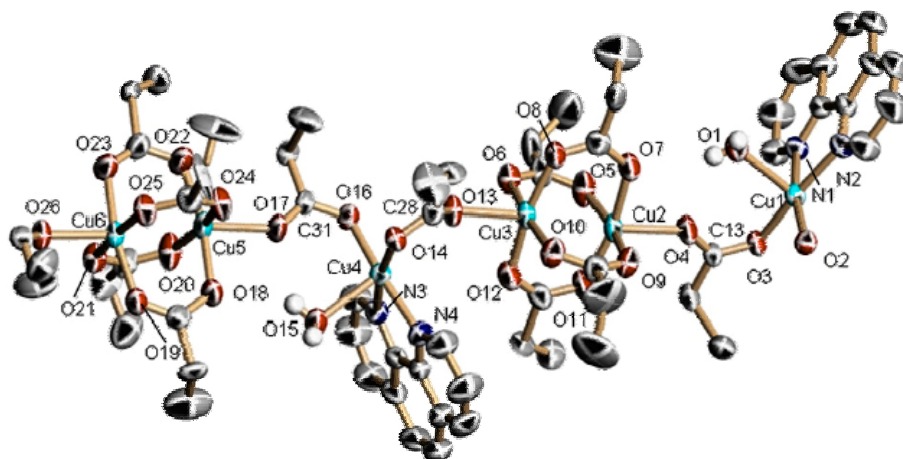


Figure.2 Plot of hexanuclear $[\text{Cu}_6(\text{phen})_2(\text{H}_2\text{O})_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)_{12}]$ unit of **II**. Hydrogen atoms in phen, propionato ligands and H_2O are omitted for clarity.

0.048, respectively. The Cu(2)⋯Cu(3) and Cu(5)⋯Cu(6) separations are slightly longer than the 2.611(2) Å separation in [Cu₂(O₂CC₂H₅)₄(H₂O)₂] and almost identical to that in **I**.

The mononuclear Cu(μ-O₂CC₂H₅)₂(H₂O)(phen) units (Cu(1), Cu(4)), with a CuN₂O₂O' chromophore, have a square pyramidal geometry with the small τ values of 0.017 and 0.015 for Cu(1) and Cu(4), respectively, in contrast to those of compound **I** (τ = 0.483). The basal plane of a square pyramidal chromophore consists of two N atoms of phen and two O atoms of two different propionate bridges. The coordinated water molecules (O(1), O(15)) occupy the apical positions at distances. The Cu(1) and Cu(4) atoms line above the basal planes, 0.135 and 0.136 Å toward O(1) and O(15), respectively.

Three discrete independent [Cu₂(μ-O₂CC₂H₅)₄(H₂O)₂] units also involve the dinuclear *paddle-wheel* unit with comparable structural data to those of another *paddle-wheel* units of compounds **I** and **II**. The square pyramidal coordinations are completed by oxygen atoms of water molecules at the axial position, with the τ values of 0.077, 0.076, 0.001 and 0.061 for Cu(7), Cu(8), Cu(9) and Cu(10), respectively. The Cu⋯Cu distances are 2.636(1) Å for Cu(7)⋯Cu(8), 2.632(1) Å for Cu(9)⋯Cu(9)A and 2.627(1) Å for Cu(10)⋯Cu(10)A. The structural parameters of compound **II** are in the normal ranges found for the *paddle-wheel* copper(II) dimers statistically analyzed.

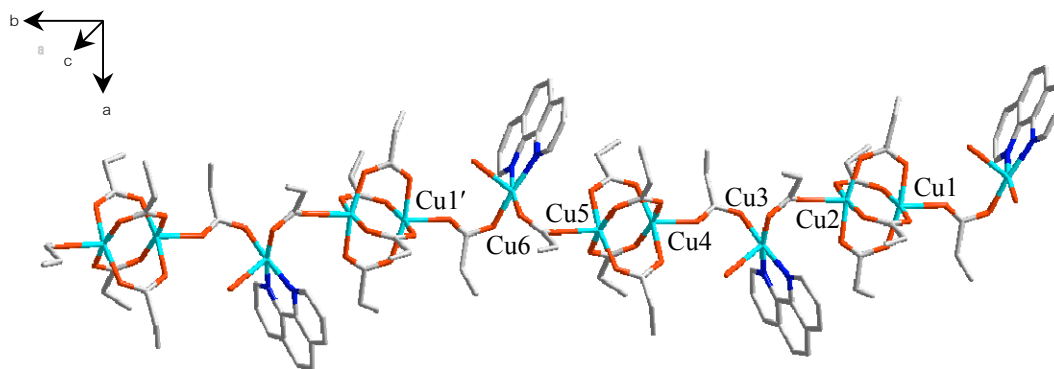


Figure 3. View of the 1-D polymeric chain in compound **VI** along the crystallographic b-axis

3.4.1.3 Description of polynuclear compound {[Cu₄(phen)₂(μ-O₂CC₂H₅)₈](H₂O)}_n (**III**)

The structure of compound **III** involves a one-dimensional overall structure constructed from tetranuclear units and consists of chains of dinuclear Cu₂(μ-OCOC₂H₅)₂(μ-O₂CC₂H₅)₂(phen)₂ repeating units which are connected to each other along the unit cell diagonal by *paddle-wheel* dinuclear Cu₂(μ-O₂CC₂H₅)₄ units (Fig. 4). The two district dinuclear units are linked by the syn,anti triatomic propionato bridge in an axial-equatorial configuration. The *paddle-wheel* dinuclear Cu₂(μ-O₂CC₂H₅)₄ unit in the chain contains four bridging propionates in the syn,syn-η¹:η¹:μ coordination mode, as known for the previously reported compound [Cu₂(μ-O₂CC₂H₅)₄(H₂O)₂]. The geometry around the Cu(2) and Cu(2)A atoms is square

pyramidal with a τ value of 0.005 arising from five oxygen atoms of five different propionate groups. The corresponding Cu–O distances in the basal plane are in the range 1.952(3)–1.962(3)(2) Å. An O atom of a bridging propionate molecule occupies the axial position at a distance of 2.120(2) Å. The basal planes have a slight tetrahedral twist of 16.72(1)°. The Cu atoms are displaced from the basal planes at distances of 0.003 Å. The Cu(2)–Cu(2)A distance is 2.623(1) Å and is slightly longer than the Cu···Cu distance in the previously reported compound $[\text{Cu}_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)_4(\text{H}_2\text{O})_2]$ (2.611(2) Å).

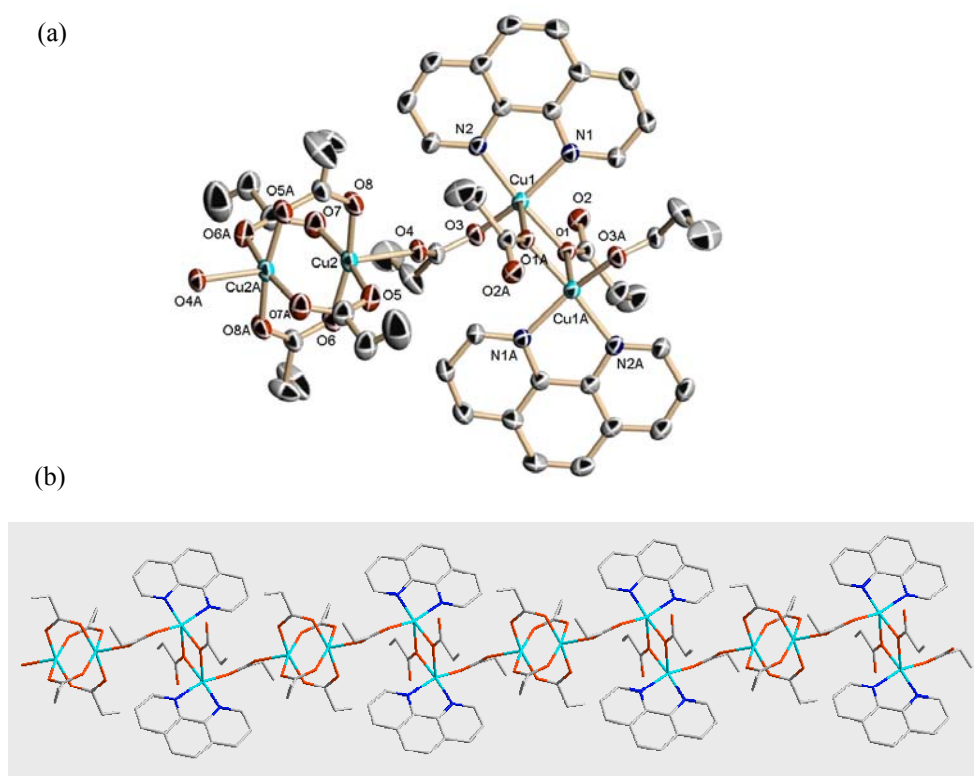


Figure 4. (a) Thermal ellipsoid (30% probability) plot of the tetranuclear $[\text{Cu}_4(\text{phen})_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)_8]$ unit of $\{[\text{Cu}_4(\text{phen})_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)_8] \cdot (\text{H}_2\text{O})\}_n$ (**III**). Hydrogen atoms and water molecules are omitted for clarity. (b) View of the 1D polymeric chain.

The dinuclear $[\text{Cu}_2(\mu\text{-OCOC}_2\text{H}_5)_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)_2(\text{phen})_2]$ unit has a $\text{CuN}_2\text{O}_2\text{O}'$ chromophore and the geometry around the Cu(II) ions (Cu(1) and Cu(1)A) is distorted square pyramidal with a τ value of 0.290. The basal plane of $\text{CuN}_2\text{O}_2\text{O}'$ chromophore consists of two N atoms from the phen ligand and two O atoms from two different propionate bridging groups and is non-planar with a slight tetrahedral twist of 24.05(1)°. An O atom of a propionate bridging ligand occupies the axial position with a distance of 2.354(2) Å. The Cu atoms are situated above the basal planes, 0.215 Å toward the axial sites. Both Cu(1) and Cu(1)A are linked by doubly bridged monoatomic propionate groups in an axial-equatorial configuration with

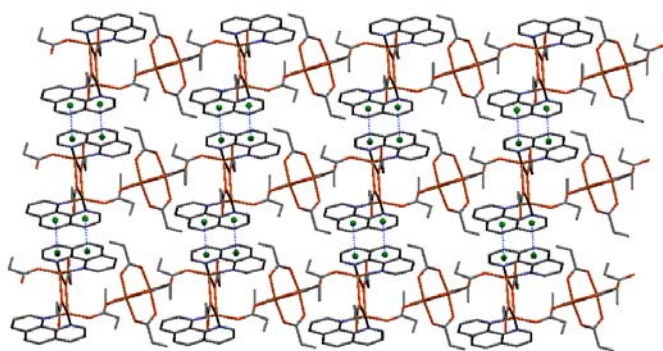


Figure 5. 2D structure of $\{[\text{Cu}_4(\text{phen})_2(\mu\text{-O}_2\text{C C}_2\text{H}_5)_8](\text{H}_2\text{O})\}_n$ (**III**) connected by face-to-face π - π interaction between pyridine rings of phen ligand.

a $\text{Cu}\cdots\text{Cu}$ distance of 3.408(1) Å. The angle of Cu-O-Cu in this case is 103.98 (1)°. The interplanar distances between the phen rings of two adjacent chains are 3.488-3.494 Å, suggesting π -stacking interactions. The π - π interactions between parallel phen rings of different chains. The 2D layer resulting from stacks in the crystal is presented in Fig. 5.

3.4.1.4 Description of dinuclear compounds $[\text{Cu}_2(\mu\text{-O}_2\text{CC}_6\text{H}_4\text{OH})_4(\text{C}_7\text{H}_7\text{NO})_2]\cdot 6\text{H}_2\text{O}$ (**IV**) and $[\text{Cu}_2(\mu\text{-O}_2\text{CCH}_3)_4(\text{C}_7\text{H}_7\text{NO})_2]$ (**V**)

The structures of compounds **IV** and **V** are quite similar as shown in Fig. 6. The structures consist of centrosymmetric dinuclear *paddle-wheel* unit. Both Cu(II) ions are linked by four carboxylato groups of the 3-hydroxybenzoate ligand for **IV** and acetate ligand for **V** in a $\text{syn}, \text{syn-}\eta^1:\eta^1:\mu$ disposition. The pyridyl nitrogen atom of 4-acetylpyridine is axially coordinated giving a CuO_4N chromophore, completing the square pyramidal coordination geometry with a τ value of 0.002 for both compounds. The $\text{Cu}\cdots\text{Cu}$ distance is 2.654(1) (**IV**) and 2.631(4) (**V**) Å. The CuO_4N chromophore is non-planar with a slight tetrahedral twist of 17.2(1)° (**IV**) and 18.15(1)° (**V**). The copper atoms are displaced by 0.001 Å from the basal planes toward the apical positions.

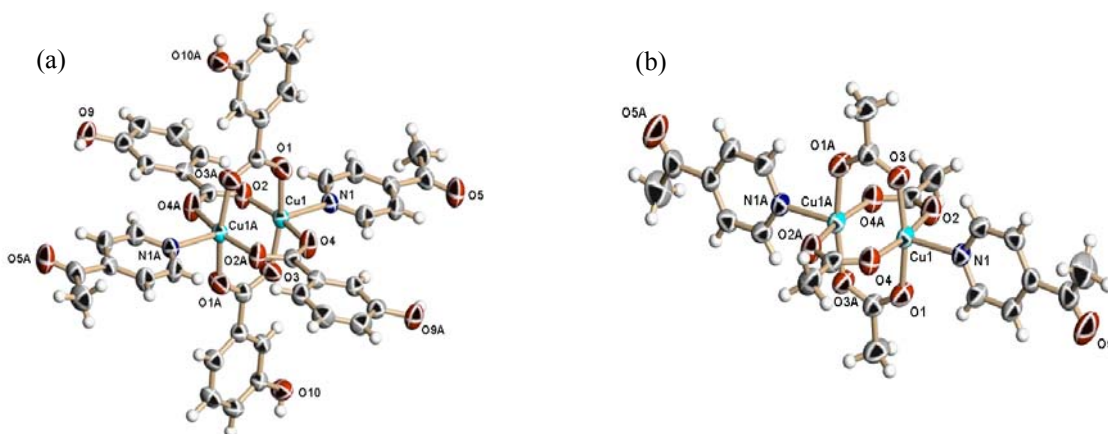


Figure 6. Thermal ellipsoid (50% probability) plots of (a) $[\text{Cu}_2(\mu\text{-O}_2\text{CC}_6\text{H}_4\text{OH})_4(\text{C}_7\text{H}_7\text{NO})_2](\text{H}_2\text{O})_6$ (**IV**) H_2O molecules are omitted for clarity and (b) $[\text{Cu}_2(\mu\text{-O}_2\text{CCH}_3)_4(\text{C}_7\text{H}_7\text{NO})_2]$ (**V**).

3.4.2 IR spectra

The IR spectra of complexes **I-V** exhibit the antisymmetric and symmetric carboxylate stretching vibrations at 1588 (**I**), 1591 (**II**), 1588 (**III**), 1578 (**IV**), 1625 (**V**) and 1483 (**I**), 1467 (**II**), 1465 (**III**), 1416 (**IV**), 1433 cm^{-1} (**V**), respectively. They are shown in Figures 4.15-4.17. These bands are assigned to the stretching modes of the triatomic carboxylate bridges. The strong bands at 1558 and 1421 cm^{-1} for **I**, 1566 and 1424 cm^{-1} for **II**, 1567 and 1426 cm^{-1} for **III** are assigned to the antisymmetric and symmetric carboxylate stretching modes of the monoatomic carboxylate group. The highest energy pyridine ring vibration varies in a range of 1617-1698 cm^{-1} for all complexes. In addition, the broad bands in a range 3650-3427 cm^{-1} are assigned to the $\nu(\text{O-H})$ of water molecule in compounds **I-IV**.

3.4.3 Electronic reflectance spectra

The electronic reflectance spectra of all complexes are shown in Fig. 7. The spectra of complex **I** consists of a single broad peak centered at 13 860 cm^{-1} , resulting from the overlap of two nearly equal energy peaks, a higher energy peak of the square pyramidal chromophore and a lower energy peak of an intermediate stereochemistry. The one-electron ground state configuration is $d_{x^2-y^2} > d_{z^2} > d_{xy} > d_{xz} \approx d_{yz}$. The $d_{xy}, d_{xz}, d_{yz}, d_{z^2} \rightarrow d_{x^2-y^2}$ transitions are assigned as for both distorted geometries. The electronic diffuse reflectance spectra of complexes **II, III, IV** and **V** exhibit a broad band centered at 13 800 for **II**, 13 510 cm^{-1} for **III**, 13460 cm^{-1} for **IV** and 14 170 cm^{-1} for **V**. These features are consistent with the square pyramidal based geometry and all $d_{xy}, d_{yz}, d_{xz}, d_{z^2} \rightarrow d_{x^2-y^2}$ transitions are assigned to this broad band.

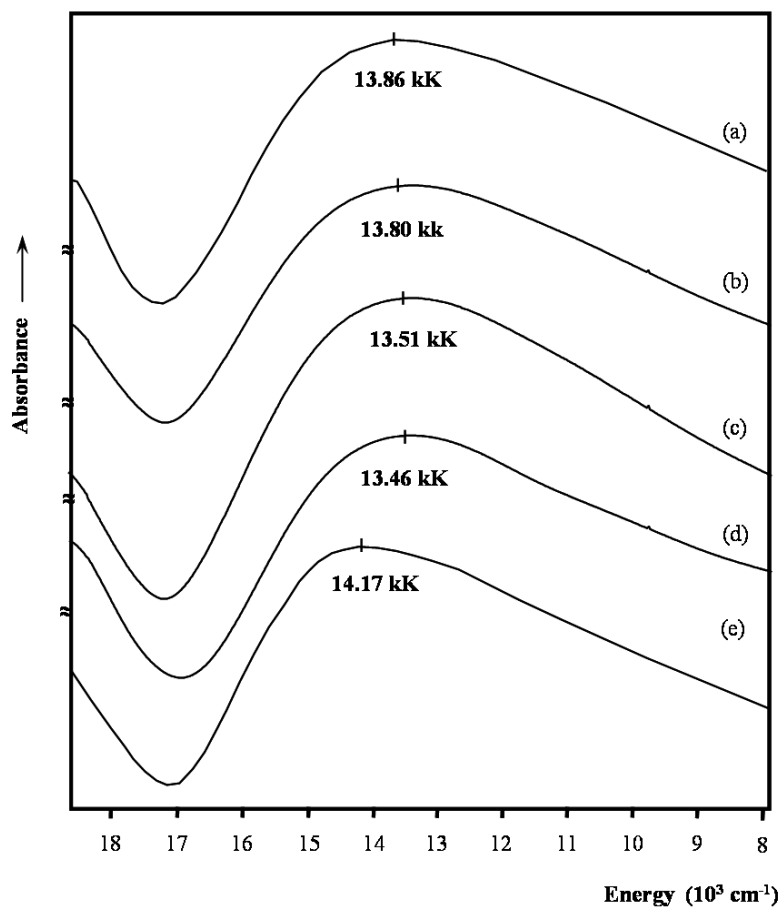


Figure 7 The electronic diffuse reflectance spectra of

- (a) $[\text{Cu}_4(\text{dpyam})_2(\text{OCOC}_2\text{H}_5)_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)_6(\text{H}_2\text{O})_2][\text{Cu}_2(\mu\text{-O}_2\text{C-C}_2\text{H}_5)_4(\text{H}_2\text{O})_2](\text{DMF})_2$ (**I**)
- (b) $[\text{Cu}_6(\text{phen})_2(\text{H}_2\text{O})_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)_{12}]_n[\text{Cu}_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)_4(\text{H}_2\text{O})_2]_{2n}(\text{H}_2\text{O})_{0.5n}$ (**II**)
- (c) $\{[\text{Cu}_4(\text{phen})_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)_8](\text{H}_2\text{O})\}_n$ (**III**)
- (d) $[\text{Cu}_2(\mu\text{-O}_2\text{CC}_6\text{H}_4\text{OH})_4(\text{C}_7\text{H}_7\text{NO})_2](\text{H}_2\text{O})_6$ (**IV**)
- (e) $[\text{Cu}_2(\mu\text{-O}_2\text{CCH}_3)_4(\text{C}_7\text{H}_7\text{NO})_2]$ (**V**)

3.4.4 EPR spectra

The EPR spectrum of the compound **I** was recorded as a polycrystalline powder at RT and 77 K from 0 to 800 mT at X-band frequency ($h\nu = 0.325 \text{ cm}^{-1}$). The EPR spectrum of compound **I** is shown in Fig. 8. It is isotropic at room temperature. It shows a broad asymmetric absorption with a centre at approx. $g = 2.09$, giving no information regarding the electronic ground state. No half-field signal was observed at room temperature. At liquid nitrogen temperature (77 K) this value is just slightly increased ($g = 2.11$).

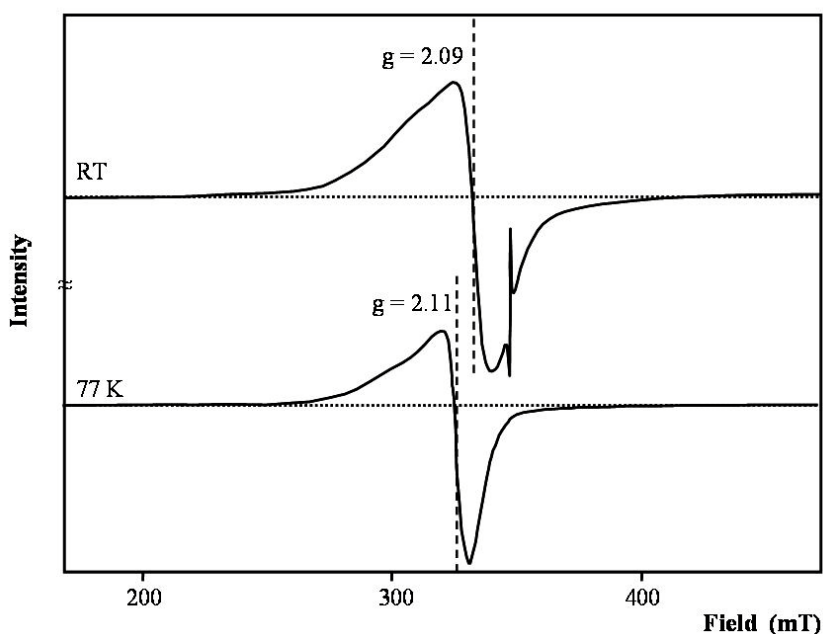


Figure 8. EPR spectra of $[\text{Cu}_4(\text{dpyam})_2(\text{OCOC}_2\text{H}_5)_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)_6(\text{H}_2\text{O})_2][\text{Cu}_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)_4(\text{H}_2\text{O})_2] \cdot (\text{DMF})_2$ (**I**) at room temperature and 77 K.

The EPR spectra of the complex **II** were recorded at RT and 77 K and compound **III** were recorded at RT and 70 K. The EPR spectra of both compounds are quite similar. These are rather complicated and consist at RT of a very broad and strong signal centered around 318 mT for compound **II** (see Fig. 9a) and 290 mT for compound **III** (see Fig. 10a) and a shoulder at 249 mT for both compounds. Furthermore weak signals are observed at about 76, 515 and 625 mT for compound **II** and 25, 369, 469 and 532 mT for compound **III**, which can be assigned to $S = 1$ triplet signals⁹⁰⁻⁹⁴. The signal at 144 mT(**II**) and 159 mT(**III**) can be assigned to the forbidden half-field signal ($\Delta Ms = \pm 2$). At low temperature the signal decreases in intensity (see Figs. 9b and 10b), due to the depopulation of the triplet state and in this case at 341 mT(**II**), 325 mT(**III**) the $S = 1/2$ resonance from a monomeric impurity, which usually is present in dinuclear Cu(II) compounds, becomes visible. At RT this band is hidden under the strong resonance at 318 mT(**II**), 290 mT(**III**). For compound **III**, the g values calculated from the EPR spectrum (considering the fact that the lines are broad and not resolved) are estimated as $g_{xy} = 2.06$ and $g_z = 2.25$, values considered normal for a Cu(II) signal.

The EPR spectra of the complexes **IV** and **V** were recorded at RT, 70 and 120 K for complex **IV** and at RT and 70 K for compound **V**. As complexes **IV** and **V** are almost isostructural, also the EPR spectra of both complexes are very similar as expected. The EPR spectrum of complex **IV** is shown in Fig. 11 at RT, 120 and 70 K. The spectrum at RT (Fig. 11a) shows three bands at 23, 470 and 600 mT (the last band is only partly visible due to the limitations of the EPR magnetic field). These bands are typical for a triplet state of a copper(II) acetate hydrate type. The small feature at around 320 mT is from a monomeric impurity, which is in most cases always present in dinuclear bulk material. At 70 K the triplet signal becomes very weak (Fig. 11c), and therefore the monomeric impurity at 320 mT appears as relatively very strong. The same type of signals was observed for compound **V** (Fig. 12). Similar spectra with the same type of bands are observed for the clearly related complexes $[\text{Cu}_2(\text{OOCCH}_3)_4(\text{urea})_2]$ and $\{[\text{Cu}_2(\beta\text{-alanine})_4(\text{H}_2\text{O})_2](\text{NO}_3)_4(\text{H}_2\text{O})_4\}$. For these complexes the zero-field splitting parameter D was calculated as being 0.34 cm^{-1} , so we can estimate that the value of D is also around 0.34 cm^{-1} for compounds **IV** and **V**.

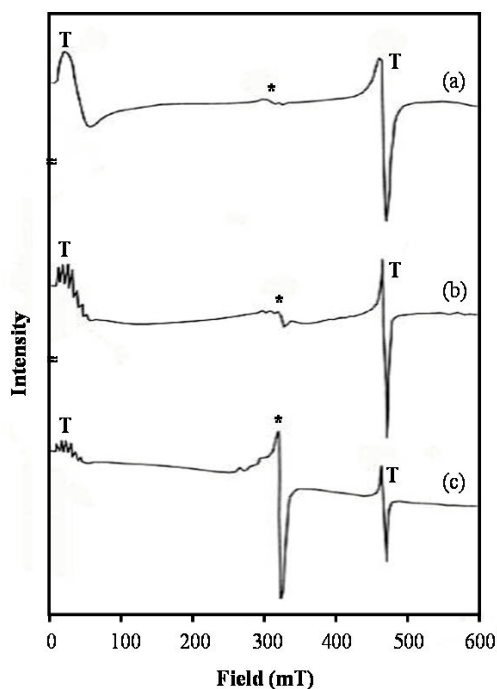


Figure 11. X-band powder EPR spectrum of complex **IV** at (a) RT, (b) 120 K and (c) 70 K. (* = signal of the mononuclear signal; T = triplet signal).

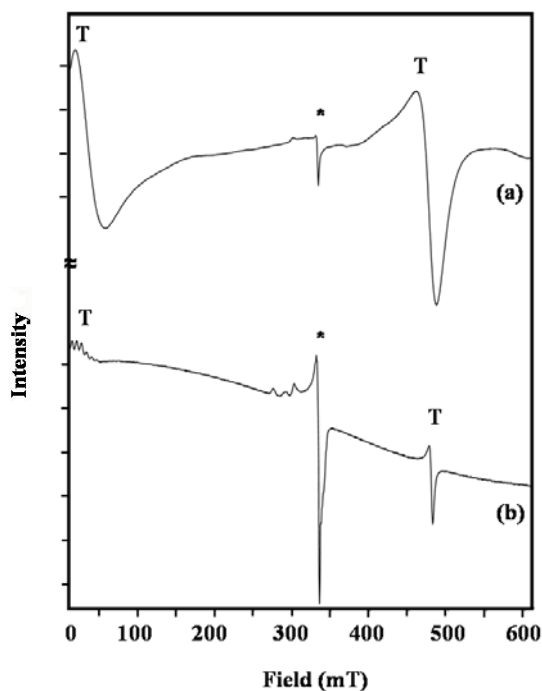


Figure 12. The EPR spectra of $[\text{Cu}_6(\text{phen})_2(\text{H}_2\text{O})_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)_{12}]_n[\text{Cu}_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)_4(\text{H}_2\text{O})_2]_{2n}(\text{H}_2\text{O})_{0.5n}$ (**V**) at room temperature and 77K (* = signal of the mononuclear signal; T = triplet signal)

3.4.5 Magnetic properties and superexchange mechanism

The magnetic susceptibilities of a powdered sample of complex **III** were measured from 2 to 320 K under a constant magnetic field of 0.1 T. The magnetic behavior is depicted in Fig. 13 in the form of $\chi_M T$ versus T for four Cu(II) ions. At 320 K the $\chi_M T$ product has a value of $1.60 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$, which is just a little higher than the value expected for four uncorrelated Cu(II) ions ($1.40 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ for $g = 2$) showing at best a very weak interaction between the metallic centers at 320 K. Upon cooling the $\chi_M T$ product gradually decreased as the temperature was lowered and reached a value of $1.05 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ at 75 K, stays constant till about 20 K, where it decreases till it reached a value of $0.98 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ at 2 K. This magnetic behaviour agrees with an overall strong antiferromagnetic interaction, at least for part of the Cu(II) ions.

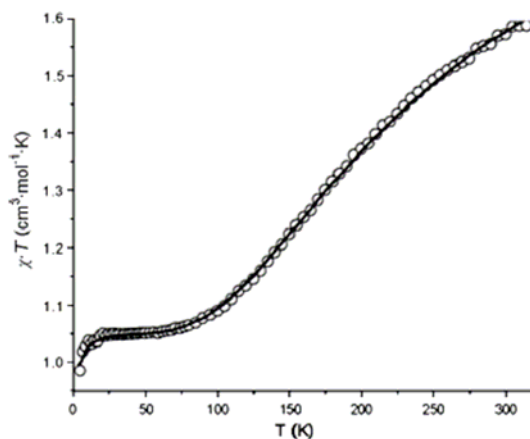


Figure 13. Temperature dependence of $\chi_M T$ for compound **III** in the range 2-320 K.

To explain the magnetic interaction of compound **III** the general Heisenberg Hamiltonian⁸ $H_{\text{ex}} = -JS_1S_2$, in which the exchange parameter J , is negative for antiferromagnetic and positive for ferromagnetic interaction.

To simplify the expression for the susceptibility it was decided to use a combination of a two-term contribution, i.e. $\chi = \chi_{\text{Cu}(1)} + \chi_{\text{Cu}(2)}$, in which $\chi_{\text{Cu}(1)} = 2Ng_1^2\beta^2[kT(3+\exp(-J_1/kT))]^{-1}$ and $\chi_{\text{Cu}(2)} = 2Ng_2^2\beta^2[kT(3+\exp(-J_2/kT))]^{-1}$. In these expressions J_1 and J_2 correspond to the singlet-triplet energy gap for the two dinuclear subunits in compound **III** (J_1 for the Cu(1)-Cu(1)A unit; J_2 for the Cu(2)-Cu(2)A unit), and N , g , β , k and T have their usual meanings⁸. The interaction between Cu(1)-Cu(2) is disregarded for the fitting procedure as it involves the syn,anti coordination mode with an axial-equatorial configuration and quite long Cu(1)···Cu(2) distance, thus a very weak interaction would be expected. The best-fit parameters, depicted in Fig. 13 as a solid line, were: $g_1 = 2.35$, $g_2 = 2.22$, $J_1 = -0.75 \text{ cm}^{-1}$, $J_2 = -299.5 \text{ cm}^{-1}$, with $R = 5 \times 10^{-5}$, the agreement factor defined as $\sum_i (\chi_{\text{calcd}} - \chi_{\text{obs}})^2 / \sum_i (\chi_{\text{obs}})^2$. In a first approximation the g values obtained by EPR have been used to properly fit the magnetic behavior, however, a poor result was

achieved likely due to the fact that the formula of the magnetic susceptibility is of course based on a number of approximations.

The three possible superexchange pathways are considered as following (Fig. 14); (i) the interaction between copper(II) centers of *paddle-wheel* unit bridged by the syn,syn triatomic carboxylato bridges in an equatorial-equatorial configuration, (ii) the interaction between copper(II) ion of *paddle-wheel* unit and copper(II) ion of a dinuclear $[\text{Cu}_2(\mu\text{-OCOC}_2\text{H}_5)_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)_2(\text{phen})_2]$ unit bridged by the syn,anti triatomic carboxylato bridges in an axial-equatorial configuration (iii) the interaction between copper(II) ions in a dinuclear $[\text{Cu}_2(\mu\text{-OCOC}_2\text{H}_5)_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)_2(\text{phen})_2]$ unit doubly bridged by the monoatomic carboxylato bridges in an axial-equatorial configuration.

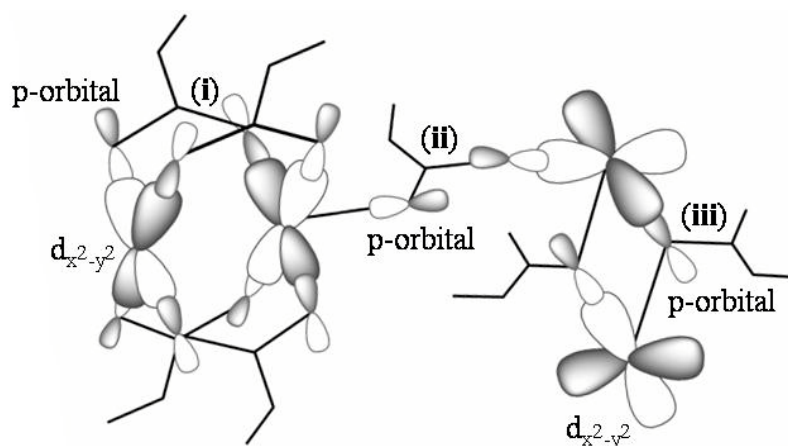


Figure 14. The superexchange mechanism in $\{[\text{Cu}_4(\text{phen})_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)_8](\text{H}_2\text{O})\}_n$ (**III**) through triatomic Cu-O-C-O-Cu (**i** and **ii**) and monoatomic Cu-O-Cu (**iii**) pathways.

The first pathway (**i**) involves in an syn,syn triatomic carboxylato bridges in an equatorial-equatorial configuration of compound **III**. The $d_{x^2-y^2}$ magnetic orbitals of copper(II) centers are directed toward the oxygen atom of four carboxylato bridges, resulting in good overlap and the great value of antiferromagnetic contribution.

The second pathway (**ii**) involves in an syn,anti triatomic carboxylato bridges with an axial-equatorial configuration. As far as it is known this linkage will always gives a weak ferromagnetic interaction if the copper(II) environments are not highly distorted. In the light of structural features, it is evident that the $d_{x^2-y^2}$ copper(II) orbitals are mismatched for interaction to take place between them through the carboxylate group, since the exchange pathway involves an equatorial position on one copper (x^2-y^2 direction) and an axial position on the other copper atom (z^2 direction). It was found that the single acetate-bridged polymeric compounds, $\{[\text{Cu}(\text{dpa})(\text{CH}_3\text{COO})](\text{ClO}_4) \cdot 0.5\text{THF}\}_n$ and $\{[\text{Cu}(\text{diethylenetri-amine})(\mu\text{-O}_2\text{C}_2\text{H}_3)]_n(\text{ClO}_4)_n\}$, revealed a very weak ferromagnetic interaction with J values of 0.21 and 0.52,

respectively²⁵. Deviations from the idealized symmetry might allow some mixture with the d_{z^2} orbital, but in any case the overlap would be weak. This would lead to a negligible antiferromagnetic contribution so that the ferromagnetic one becomes predominant.

The last pathway (iii) involves a monoatomic carboxylato-bridge with an axial-equatorial configuration. According to previously reports, the related dinuclear complexes containing the monoatom carboxylato-bridged Cu_2O_2 core exhibit ferromagnetic or antiferromagnetic character²⁶⁻²⁸, and the structural feature that shows a crucial role in the determination the exchange coupling constant J is the Cu-O-Cu angle (θ), an antiferromagnetic character is found for complexes with θ angle ranging between 95.3 - 101.9° , while ferromagnetism appears for values larger than 101.9° , as reported in $[\text{Cu}(\text{tda})(\text{phen})]_2 \cdot \text{H}_2\text{tda}$ ²⁹. However, a number of monoatomic carboxylato-bridged compounds exhibiting antiferromagnetic interaction even at θ larger than 101.9° were reported: $[\text{Cu}_2(\text{HCO}_2)_4(3\text{-pyOH})_4]$ ²⁸ ($\theta = 102.5(2)^\circ$, $J = -1.05 \text{ cm}^{-1}$) and $[\{\text{Cu}(\text{C}_7\text{H}_8\text{N}_4\text{S})\text{HCOO}\}_2]$ ($\theta = 105.4(9)^\circ$, $J = -3.30 \text{ cm}^{-1}$)³⁰. A similar feature has been found in compound **III** ($\theta = 103.99(9)^\circ$, $J = -0.75 \text{ cm}^{-1}$) which exhibited antiferromagnetic interaction. This arises as they have concomitant factors which involved in the values of the exchange coupling constants for these compounds. For this reason, a very weak antiferromagnetism found in **III** and a weak ferromagnetism observed in the related $[\text{Cu}_2(\text{HCO}_2)_4(3\text{-pyOH})_4]$ ²⁸ may be resulted from the differences in Cu-L distances, as well as combined with their monoatomic Cu-O-Cu bridges (**III**: $1.960(2)$, $2.354(2) \text{ \AA}$ and $103.99(9)^\circ$; 3-pyOH: $1.986(1)$, $2.415(1) \text{ \AA}$ and $102.5(2)^\circ$). Shorter distances in **III** raise the magnetic orbital overlap, and thus the ferromagnetic contribution to the extent that antiferromagnetism predominates.

Thus, it can be concluded that this (μ_2 -oxo) type of monoatomic bridging by carboxylate ligands produces complexes with magnetic parameters in the vicinity of the crossover value necessary to switch from weak antiferromagnetic to weak ferromagnetic coupling⁹.

Consequently, compound **III** should exhibit the overall strong antiferromagnetic interaction which is dominantly contributed from the syn,syn carboxylato-bridged *paddle-wheel* species rather than the anti,syn and monoatomic carboxylato bridges.

The magnetic susceptibilities of powdered samples of compounds **VI** and **V** were measured from 5 to 350 K. As the two compounds are structurally similar, also the magnetic properties are similar. The magnetic properties of the compounds are depicted in Fig. 15 in the form of $\chi_M T$ versus T for two Cu(II) ions. At 350 K the $\chi_M T$ product of **VI** has a value of $0.575 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ ($0.554 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ for **V**), which is below the spin-only value for two non-interacting Cu(II) ions ($0.75 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ at RT). From 350 K the $\chi_M T$ product decreases gradually to a value of $0.014 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ for compound **IV** at 50 K ($0.006 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ for **V**) and stays constant till 5 K. This magnetic behaviour agrees with a strong antiferromagnetic interaction.

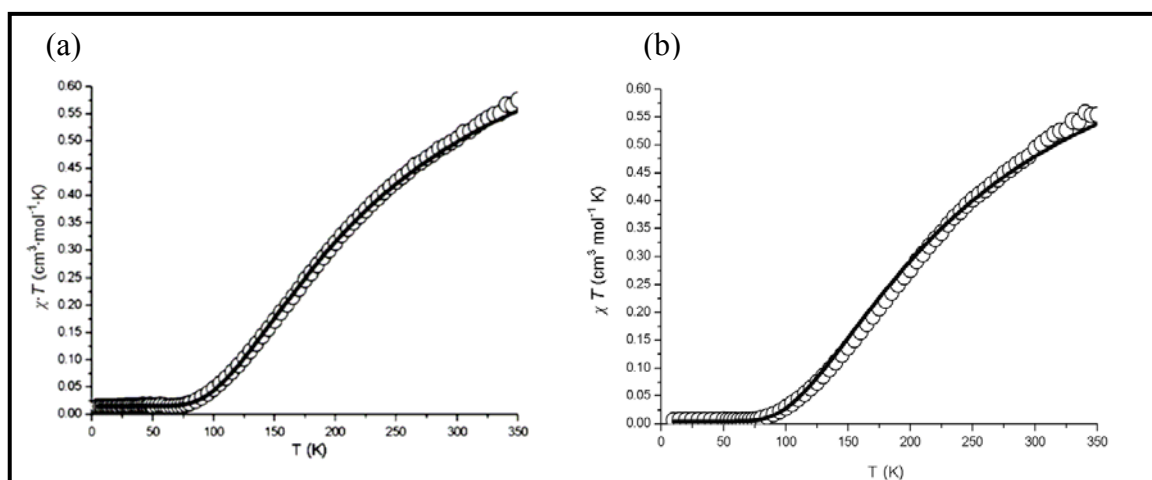


Figure 14. Temperature dependence of $\chi_M T$ for (a) $[\text{Cu}_2(\mu\text{-O}_2\text{CC}_6\text{H}_4\text{OH})_4(\text{C}_7\text{H}_7\text{NO})_2](\text{H}_2\text{O})_6$ (**IV**) and (b) $[\text{Cu}_2(\mu\text{-O}_2\text{CCH}_3)_4(\text{C}_7\text{H}_7\text{NO})_2]$ (**V**).

The theoretical expression for the magnetic susceptibility for two interacting $S = 1/2$ centres, which is based on the general Hamiltonian⁸ is: $H_{\text{ex}} = -JS_1S_2$, in which the exchange parameter J , is negative for antiferromagnetic and positive for ferromagnetic interaction. The magnetic data were fitted to the equation given in the literature⁸ for dinuclear copper compounds: $\chi_M = (2Ng^2\beta^2)[kT - (2zJ'/(3 + \exp(-J/kT)))]^{-1}[3 + \exp(-J/kT)]^{-1}(1-p) + \chi_p p$, where N , g , β , k and T have their usual meanings⁸. The parameter p denotes the fraction of paramagnetic impurity in the sample and zJ' the interaction between neighbouring dinuclear entities. The fit was accomplished by minimisation of $R = (\chi_M T_{\text{calc}} - \chi_M T_{\text{obs}})^2 / (\chi_M T_{\text{obs}})^2$ by a least-squares procedure. The best fit for compound **IV**, depicted in Fig. 14a as a solid line, was obtained for $J = -278.5 \text{ cm}^{-1}$, $g = 2.15$, $zJ' = -26.3 \text{ cm}^{-1}$, $p = 0.02$, with a final R of $1.5 \cdot 10^{-2}$. The best fit for compound **V** was obtained for $J = -287.0 \text{ cm}^{-1}$, $g = 2.15$, $zJ' = -24.7 \text{ cm}^{-1}$, $p = 0.01$, with a final R of 1.5×10^{-2} Fig. 14b. The R values appear a bit high, but can be ascribed to the fact that susceptibility measurements above 300 K are less accurate due to a reduced accuracy in temperature, in fact when only the temperature range of 5-280 K is considered the R -value is much better, *i.e.* 3×10^{-3} .

Compounds **IV** and **V** exhibit strong antiferromagnetic behaviour these dinuclear compounds bridged by a carboxylato in the syn,syn conformation should also show strong antiferromagnetic interaction. The magnetic orbitals of the two copper(II) centers may be conceived from crystallographic results. The square pyramidal geometry of two copper(II) centers in compounds **IV** ($\tau = 0.002$) and **V** ($\tau = 0.002$) indicate magnetic orbital mainly to be $d_{x^2-y^2}$. Fig. 15 shows the schematic structural drawing and the model predicting the magnetic interactions with shape and disposition of $d_{x^2-y^2}$ orbital in a Cu-O-C-O-Cu core for the square pyramidal geometry. The equatorial planes of both compounds are parallel. The

partial coupling of unpaired electron between copper(II) ions can occur through p orbitals of oxygen atoms in carboxylato bridges, resulting in an antiferromagnetic interaction.

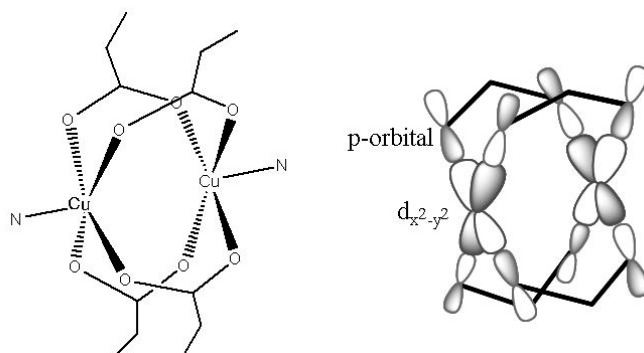


Figure 15. The model predicting the magnetic interaction through carboxylato bridges for equatorial-equatorial mode in *paddle-wheel* unit of $[\text{Cu}_2(\mu\text{-O}_2\text{CC}_6\text{H}_4\text{OH})_4(\text{C}_7\text{H}_7\text{NO})_2](\text{H}_2\text{O})_6$ (**IV**) and $[\text{Cu}_2(\mu\text{-O}_2\text{CCH}_3)_4(\text{C}_7\text{H}_7\text{NO})_2]$ (**V**).

3.4.6 Structure magnetism relationship

Recently, Rodríguez-Forte et al³¹ have reported a density functional study of the exchange coupling in carboxylato-bridged dinuclear copper(II) compounds. They compared the J values for several substituents in $[\text{Cu}_2(\mu\text{-RCOO})_4\text{L}_2]$ *paddle-wheel* units and concluded that the electron-withdrawing groups reduce the strength of the exchange coupling. Another factor is the Cu–O bridging bond in copper(II) carboxylate dinuclear units, which is considered to be quite important in the superexchange mechanism; it is the basis for the superexchange pathway of the Cu–O–C(R)–O–Cu fragments. When R is strongly σ -bonded to the carboxylato carbon, the strong coordination of the Cu–O bonds in the CuO_4 basal plane will become stronger, in order to maintain the electron neutrality over the whole molecule. Thus, the J value increases when the Cu–O bond length decreases. In addition the coupling constant is weakly dependent on the Cu...Cu distance. If the Cu...Cu distance increases, the overlap of the δ -bonding between the two Cu atoms decreases and the J value would be slightly lower.

The structure of compound **III** is compared with the most related carboxylato-bridged compound $[\text{Cu}_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)_4(\text{H}_2\text{O})_2]$ (**7**) ($J = -311 \text{ cm}^{-1}$)³² in Table 3.1. When water molecules in axial positions of compound **7** are replaced by propionate bridges (compound **III**), the average Cu–O distance is 1.959 Å and the Cu...Cu distance is 2.623 Å, both of which are longer than those of the corresponding compound **7** (1.948 and 2.575 Å, respectively). Thus, the strong Cu–O bonds in the CuO_4 basal plane of **III** will become weaker than those of compound **7**; this may result in a decreased J value. In addition, a longer Cu...Cu distance would lead to a smaller $-J$ value (in this case -299 cm^{-1}). Nevertheless, it should be mentioned that

the approximation used to obtain the Hamiltonian to calculate the J value is somewhat simplified, which can explain that the g values are somewhat higher than expected for Cu(1) and Cu(2). Indeed, it was observed that below 50 K the magnetism of compound **III** can be depicted as a unidimensional assembly of antiferromagnetically coupled $S = 1/2$ spins. Confirmation of this magnetic chain behaviour is seen from the linear $\ln \chi_M T$ versus T^{-1} curve in this temperature range³³. In addition, the value of the dinuclear coupling via Cu(1)–Cu(1)A for compound **VII** is expected to be small, as predicted by the theoretical calculation. The Cu(1)–O(1)–Cu(1)A pathway involve the d_{z^2} orbital for Cu(1) and $d_{x^2-y^2}$ orbital for Cu(1) A, because of the copper symmetry, the unpaired electron around copper(II) are described mainly by a magnetic orbital built from the $d_{x^2-y^2}$, confirming the theoretical result.

Complexes with the $\text{Cu}_2(\mu\text{-O}_2\text{CCH}_3)_4$ basic unit all have relatively high negative magnetic exchange coupling constants. For $[\text{Cu}_2(\mu\text{-O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2]$ (**2**)³¹ with a coupling constant J of -299 cm^{-1} , water molecules in axial positions are replaced by NH_3 for compound (**3**)³¹, or MeNHpy for compound (**4**)³⁴ the coupling constant is slightly less negative of -284 and -285 cm^{-1} , respectively (see Table 3.1). It is indicating that the change of the axial ligand induces small variations in the coupling constant. Consequently, compound **V** with the axial 4-acetylpyridine ligands, the slightly decreased $-J$ value ($J = -287 \text{ cm}^{-1}$) is observed. When the acetate groups in compound **V** are replaced by 3-hydroxybenzoate groups in compound **IV**, which is a stronger electron-withdrawing group, the slightly decreased $-J$ value is expected ($J = -278.5$ and -287.0 cm^{-1} for complexes **IV** and **V**, respectively). However, several factors such as deviation of the metal ion from the basal plane and Cu-O distances should be considered as the combined effect to participate in the change of the exchange coupling constant.

3.5 Conclusions

The first part of this research sets out to examine and develop the preparative work of a series of polynuclear carboxylato-bridged copper(II) *paddle-wheel* complexes. The polynuclear carboxylato-bridged copper(II) *paddle-wheel* complexes, a hexanuclear $[\text{Cu}_4(\text{dpyam})_2(\text{OCOC}_2\text{H}_5)_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)_6(\text{H}_2\text{O})_2][\text{Cu}_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)_4(\text{H}_2\text{O})_2](\text{DMF})_2$ (**I**), two polymeric chain $[\text{Cu}_6(\text{phen})_2(\text{H}_2\text{O})_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)_{12}]_n[\text{Cu}_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)_4(\text{H}_2\text{O})_2]_{2n}(\text{H}_2\text{O})_{0.5n}$ (**II**) and $\{[\text{Cu}_4(\text{phen})_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)_8](\text{H}_2\text{O})\}_n$ (**III**) and two dinuclear $[\text{Cu}_2(\mu\text{-O}_2\text{CC}_6\text{H}_4\text{OH})_4(\text{C}_7\text{H}_7\text{NO})_2](\text{H}_2\text{O})_6$ (**IV**) and $[\text{Cu}_2(\mu\text{-O}_2\text{CCH}_3)_4(\text{C}_7\text{H}_7\text{NO})_2]$ (**V**) were prepare directly from their components by the molar ratio method. The crystal structures of all complexes were determined by X-ray crystallography. The crystal structure of the hexanuclear $[\text{Cu}_4(\text{dpyam})_2(\text{OCOC}_2\text{H}_5)_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)_6(\text{H}_2\text{O})_2][\text{Cu}_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)_4(\text{H}_2\text{O})_2](\text{DMF})_2$ (**I**) consists of centro-symmetric tetranuclear $[\text{Cu}_4(\text{dpyam})_2(\text{OCOC}_2\text{H}_5)_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)_6(\text{H}_2\text{O})_2]$ units, an independent dinuclear $[\text{Cu}_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)_4(\text{H}_2\text{O})_2]$ and DMF molecules. In the tetranuclear unit, the “outer” Cu ions involve an intermediate five-coordinate geometry while the “inner” Cu ions have a square pyramidal geometry. The two Cu(II) ions in the inner unit are bridged by four *syn,syn*- $\eta^1:\eta^1:\mu$ propionates, showing the *paddle-wheel* cage type. The “outer” and

“inner” linked by propionato bridges showing an *syn,anti*- $\eta^1:\eta^1:\mu$ coordination mode. The one-dimensional structure of complex $[\text{Cu}_6(\text{phen})_2(\text{H}_2\text{O})_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)_{12}]_n[\text{Cu}_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)_4(\text{H}_2\text{O})_2]_{2n}(\text{H}_2\text{O})_{0.5n}$ (**II**), consists of zig-zag chains of mononuclear $\text{Cu}(\mu\text{-O}_2\text{CC}_2\text{H}_5)_2(\text{H}_2\text{O})(\text{phen})$ repeating units running along the b-axis, which are connected along the unit cell diagonal via $\text{Cu}_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)_4$ *paddle-wheel* dinuclear units. Within mononuclear and dinuclear units, the Cu(II) ions exhibit a square pyramidal geometry. In addition, the outer sphere of compounds **I** and **II** consists of the independent $\text{Cu}_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)_4(\text{H}_2\text{O})_2$ *paddle-wheel* molecule in which Cu(II) ions involve a square pyramidal geometry.

For compounds **III-V**, all three compounds consist of dinuclear units, in which two Cu(II) ions are bridged by four *syn,syn*- $\eta^1:\eta^1:\mu$ carboxylates, showing a *paddle-wheel* cage type with a square-pyramidal geometry, arranged in different ways. The structure of compound **III** consists of an one-dimensional structure generated by an alternating classical dinuclear *paddle-wheel* unit and an unusual dinuclear $\text{Cu}_2(\mu\text{-OCOC}_2\text{H}_5)_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)_2(\text{phen})_2$ unit, which are connected to each other via a *syn,anti*-triatomic propionato bridge in an axial-equatorial configuration. The adjacent chains are connected to generate a 2D structure through the face-to-face π - π interaction between phen rings. Structures of compounds **IV** and **V** both consist of a symmetric dinuclear Cu(II) carboxylate *paddle-wheel* core and pyridyl nitrogen atom of 4-acetylpyridine ligand at the apical positions, and just differ in the substituents of the equatorial ligands. The electronic properties of all complexes correspond with the determined structures. The EPR spectra of all compounds and magnetic susceptibilities of complexes **III-V** reveal a very strong antiferromagnetic interaction between copper(II) centers with $J = -299.5$, -278 and -287 cm^{-1} , respectively. This behavior is usually found for the interaction between copper(II) centers of the *paddle-wheel* unit which bridged by the *syn-syn* triatomic carbonato bridges in an equatorial-equatorial configuration.

The magnetic properties of compounds **IV-V** have been measured and correlated with the molecular structures. It is found that in the two classical *paddle-wheel* compounds **IV** and **V** the Cu(II) ions are strongly antiferromagnetically coupled with $J = -278.5$ and -287.0 cm^{-1} , respectively. In compound **III** the magnetic susceptibilities could be fitted with two different, independent Cu(II) units, one strongly coupled and one weakly coupled; the *paddle-wheel* dinuclear unit has the strongest antiferromagnetic coupling with a J value of -299.5 cm^{-1} , whereas the Cu(II) ions in the propionate bridged dinuclear unit display a very weak antiferromagnetic coupling with a J value of -0.75 cm^{-1} , due to the orthogonality of the magnetic orbitals. Also the exchange within the chain is therefore very weak. The magneto-structural correlations for complexes **III-V** have been discussed on the basis of the structural parameters and magnetic data for the complexes.

The results of all products obtained in this complex series have been published³⁸⁻⁴¹.

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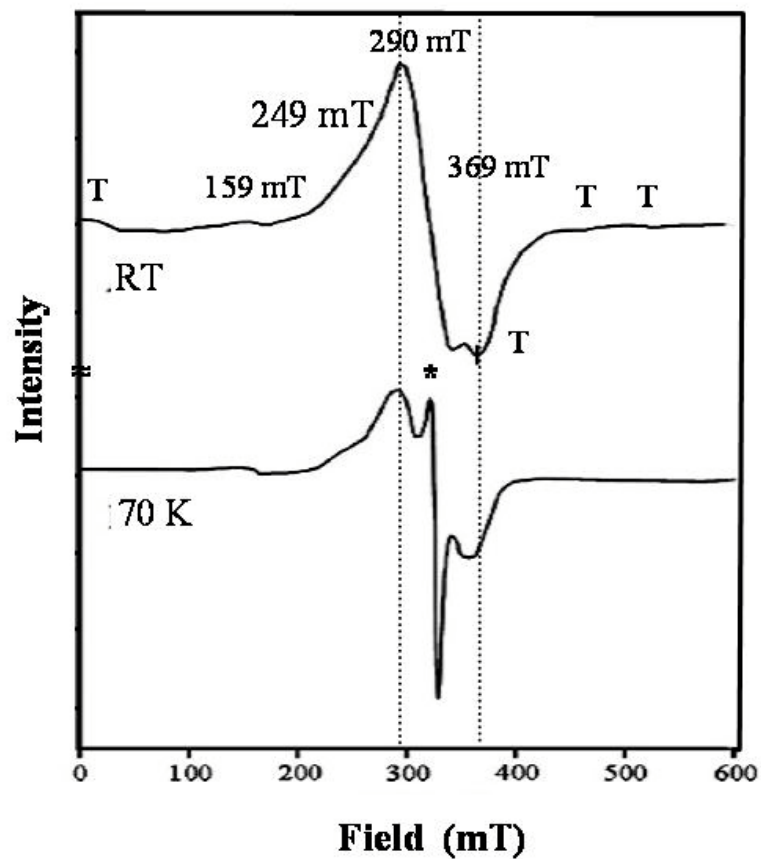


Figure 9. The EPR spectra of $[\text{Cu}_6(\text{phen})_2(\text{H}_2\text{O})_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)_{12}]_n$ $[\text{Cu}_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)_4(\text{H}_2\text{O})_2]_{2n}(\text{H}_2\text{O})_{0.5n}$ (**II**) at room temperature and 77 K (* = signal of the mononuclear signal; T = triplet signal)

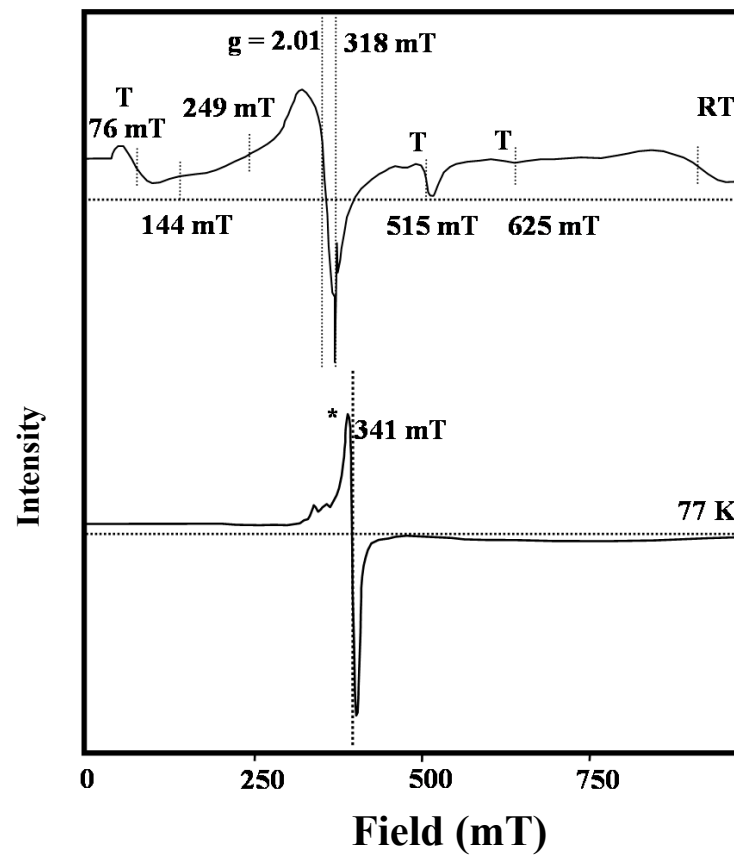


Figure 10. X-band powder EPR spectrum of complex **III** at room temperature and 70 K (* = signal of the mononuclear signal; T = triplet signal)

Table 3.1 Structural data and magnetic properties for some relevant *paddle-wheel* copper(II) complexes

Complex ^a	Structure type	Chromophore	τ ^b	Cu...Cu (Å)	J (cm ⁻¹)	Ref.
[Cu ₄ (dpyam) ₂ (OCOC ₂ H ₅) ₂ (μ-O ₂ CC ₂ H ₅) ₆ (H ₂ O) ₂] [Cu ₂ (μ-O ₂ C-C ₂ H ₅) ₄ (H ₂ O) ₂](DMF) ₂ (I)	tetramer	CuO ₄ O'	0.003	2.632	-	This work
[Cu ₆ (phen) ₂ (H ₂ O) ₂ (μ-O ₂ CC ₂ H ₅) ₁₂] _n [Cu ₂ (μ-O ₂ CC ₂ H ₅) ₄ (H ₂ O) ₂] _{2n} (H ₂ O) _{0.5n} (II)	polymer	CuO ₄ O'	0.045-0.53	2.623	-	This work
{[Cu ₄ (phen) ₂ (μ-O ₂ CC ₂ H ₅) ₈](H ₂ O)} _n (III)	polymer	CuO ₅	0.005	2.623	-299.5	This work
[Cu ₂ (μ-O ₂ CC ₆ H ₄ OH) ₄ (C ₇ H ₇ NO) ₂](H ₂ O) ₆ (IV)	dinuclear	CuO ₄ N	0.002	2.654	-278.5	This work
[Cu ₂ (μ-O ₂ CCH ₃) ₄ (C ₇ H ₇ NO) ₂] (V)	dinuclear	CuO ₄ N	0.002	2.631	-287	This work
[Cu ₂ (μ-O ₂ CH) ₄ (DMF) ₂] (1)	dinuclear	CuO ₄ O'	0	2.651	-470	35
[Cu ₂ (μ-O ₂ CCH ₃) ₄ (H ₂ O) ₂] (2)	dinuclear	CuO ₄ O'	-	2.620	-299	31
[Cu ₂ (μ-O ₂ CCH ₃) ₄ (NH ₃) ₂] (3)	dinuclear	CuO ₄ N	-	2.620	-284	31
[Cu ₂ (μ-O ₂ CCH ₃) ₄ (MeNHpy) ₂] (4)	dinuclear	CuO ₄ N	0.004	2.272	-285	34
[Cu ₂ (μ-O ₂ CCH ₃) ₄ (NITpPy) ₂] (5)	dinuclear	CuO ₄ N	-	2.622	-172	36
[Cu ₂ (μ-O ₂ CC(CH ₃) ₃) ₄ (NITpPy) ₂](C ₆ H ₆) (6)	dinuclear	CuO ₄ N	-	2.614	-192	36
[Cu ₂ (μ-O ₂ CC ₂ H ₅) ₄ (H ₂ O) ₂] (7)	dinuclear	CuO ₄ O'	-	2.575	-311	32
[Cu ₂ (μ-DMB) ₄ (H ₂ O) ₂] (8)	dinuclear	CuO ₄ O'	-	2.619	-325	37
[Cu ₂ (μ-DMB) ₂ (μ-O ₂ CCH ₃) ₂ (H ₂ O) ₂] (9)	dinuclear	CuO ₄ O'	-	2.597	-250	37

^a Abbreviation: MeNHpy = 2-methylaminopyridine, NITpPy = 4,4,5,5-tetramethyl-2-(4-pyridyl)-2-imidazoline-N¹-oxyl N³-oxide and DMB = 2,6-dimethoxybenzoate, ^b τ : calculated from structural data, -: not available.

OUTPUT OF THE RESEARCH

M.Sc. Students

1. Mr. Jaturong Phatchimkun: (2002- 2005) “Copper(II) Complexes with Pseudohalides and Di-2-pyridylamine ligands: Synthesis, Crystal Structure, Spectroscopic and Magnetic Properties” Master of Science Thesis in Chemistry, Graduate School, Khon Kaen University.
2. Miss Thidarat Chotkhun: (2004-2007) “Synthesis, Crystal Structure, Spectroscopic and Magnetic Properties of Pseudohalide-Bridged Polynuclear Copper(II) Complexes containing the Di-2-pyridylamine and Carboxylate as co-ligands” Master of Science Thesis in Chemistry, Graduate School, Khon Kaen University.
3. Mr. Nathawat Wannarit: (2004-2008) “Synthesis, Crystal Structure, Spectroscopic and Magnetic Properties of Polynuclear Carbonato-bridged Copper(II) Complexes Containing the 2,2'- Bipyridyl and 1,10-Phenanthroline” Master of Science Thesis in Chemistry, Graduate School, Khon Kaen University.
4. Miss Achareeya Cheansirisomboon: (2005-2008) “Synthesis, Crystal structure, Spectroscopic and Magnetic properties of Polynuclear Carboxylato-bridged Copper(II) complexes” Master of Science Thesis in Chemistry, Graduate School, Khon Kaen University.

PUBLICATION PAPERS

1. S. Youngme, J. Phatchimkun, U. Suksangpanya, C. Pakawatchai, G.A. van Albada, J. Reedijk “Synthesis, spectroscopic characterization, X-ray crystal structure and magnetic properties of dinuclear copper(II) complex with dual end-to-end and end-on cyanate bridges: $[\text{Cu}_2(\mu\text{-NCO-N,N'})_2(\text{NCO-N})_2(\text{dpyam})_2]$ ”, *Inorg. Chem. Commun.*, 2005, **8**, 882-885.
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PRESENTATIONS

1. S. Youngme, N. Chaichit, C. Pakawatchai, A.L. Spek, J. Reedijk “Planar and Roof-shaped Hydroxo-bridged Dinuclear Copper(II) Complexes: Structures, Magnetic Properties and Phase Transitions” *Invited as a keynote lecture at the 4th PERCH Annual Scientific Congress*, Chonburi, Thailand. 8-11 May 2005.
2. J. Phatchimkun, U. Suksangpanya, C. Pakawatchai, N. Chaichit, S. Youngme “Plasticity effect in a series of [Cu(dpyam)₂(NCO)]Y, Y = Br⁻, CF₃SO₃⁻, Cl⁻·4H₂O, BF₄⁻·dpyam, NO₃⁻, PF₆⁻, ClO₄⁻ and BPh₄⁻:

- Crystal structures structural pathway and electronic properties” **Oral presented at the 31th Congress on Science and Technology of Thailand**, Khon Kaen, Thailand. 18-20 October 2006.
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 4. T. Chotkhun, S. Leelasubcharoen, N. Chaichit, C. Pakawatchai, S. Youngme “The Cu(II)-di-2-pyridylamine-azide system: Synthesis, crystal structure and magnetic properties of $[\text{Cu}_2(\text{dpyam})_2(\text{N}_3)_2(\text{OXO})_2]$ ($\text{OXO} = \text{O}_2\text{CH}^-$, O_2CCH_3^- , $\text{O}_2\text{CC}_2\text{H}_5^-$)” **Oral presented at the 32th Congress on Science and Technology of Thailand**, Khon Kaen, Thailand. 10-12 October 2006.
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 10. T. Chotkhun, S. Leelasubcharoen, N. Chaichit, C. Pakawatchai, S. Youngme “Azido-bridged Polynuclear Copper(II) Complexes with Di-2-pyridylamine and Carboxylate as Co-ligands: Magneto-structural Studies” **Poster presented at the 5th PERCH-CIC Congress**, Chonburi, Thailand. 6-9 May 2007. **Best PERCH-CIC Fellow Poster Award.**
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- Crystal Structure and Magnetic Properties” **Poster** presented at the 5th PERCH-CIC Congress, Chonburi, Thailand. 6-9 May 2007. **Best PERCH-CIC Fellow Poster Award.**
12. S. Youngme, N. Chaichit, C. Pakawatchai, J. Reedijk “Dinuclear Triply-bridged Copper(II) Complexes: Structure and Magnetism Relationships” **Invited as a keynote lecture** at the 1st Asian Conference on Coordination Chemistry (ACCC), Okazaki, Japan. 29 July-2 August 2007.
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 15. N. Wannarit, T. Remsungnen, N. Chaichit, C. Pakawatchai, J. Reedijk, S. Youngme “The Polynuclear Carbonato-Bridged Copper(II) System: Synthesis, Crystal Structure, Spectroscopic and Magnetic Properties” **Oral** presented at the 10th Symposium on Graduate Research KKU, Khon Kaen, Thailand, 18 January 2008.
 16. A. Cheansirisomboon, S. Youngme, C. Danvirutai, N. Chaichit, C. Pakawatchai, “Synthesis, X-ray Structure and Spectroscopic Characterization of five new Polynuclear Paddle wheel Copper(II) Complexes containing carboxylate as a bridging ligand” **Oral** presented at the 10th Symposium on Graduate Research KKU, Khon Kaen, Thailand, 18 January 2008. **Best KKU Fellow Oral Award.**
 17. S. Youngme, C. Pakawatchai, N. Chaichit, G.A. van Albada, J. Reedijk “Synthesis, Crystal structures, Spectroscopic and Magnetic Properties of polynuclear Carbonato-bridged Copper(II) complexes” **Poster** presented at the International Symposium on Molecular Materials Chemistry, Solid State Physics, Theory, Nanotechnology From Molecule to Molecular Device (MOLMAT), Toulouse, France, 8-11 July 2008.
 18. A. Cheansirisomboon, N. Chaichit, C. Pakawatchai, J. Reedijk and S. Youngme “Polynuclear Paddle-wheel Copper(II) Complexes: Synthesis, Crystal Structure, Spectroscopic and Magnetic Properties” **Oral** presented at the 6th PERCH-CIC Congress, Chonburi, Thailand. 6-9 May 2009. **Best PERCH-CIC Fellow Oral Award.**

APPENDICES

PUBLICATION PAPERS OF PART I



Synthesis, spectroscopic characterization, X-ray crystal structure and magnetic properties of dinuclear copper(II) complex with dual end-to-end and end-on cyanate bridges: [Cu₂(μ-NCO-*N,N'*)₂(NCO-*N*)₂(dpyam)₂]

Sujittra Youngme^{a,*}, Jaturong Phatchimkun^a, Unchulee Suksangpanya^a,
Chaveng Pakawatchai^b, Gerard A. van Albada^c, Jan Reedijk^c

^a Department of Chemistry, Faculty of Science, Khon Kaen University, Khon Kaen 40002, Thailand

^b Department of Chemistry, Faculty of Science, Prince of Songkla University, Hatyai, Songkla 90112, Thailand

^c Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden University, PO Box 9502, 2300 RA Leiden, The Netherlands

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Abstract

A new dinuclear copper(II) complex [Cu₂(μ_{1,1}-NCO)₂(NCO)₂(dpyam)₂] (dpyam = di-2-pyridylamine) has been synthesized and characterized by X-ray diffraction. Two N-bonded cyanato ligands bridge two copper ions in an end-on fashion and two others act as the N-bonded terminal ligands. The copper ion has a distorted square-pyramidal environment.

The magnetic susceptibility, measured from 5 to 300 K, has revealed a weak ferromagnetic interaction between the Cu(II) atoms with a singlet–triplet energy gap (J) of 6.03 cm^{−1}. The EPR spectrum, measured as a powdered solid at RT and 77 K, shows an *S* = 1/2 signal with *g*_⊥ = 2.08 and an unresolved *g*_{||} of 2.29.

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Keywords: Copper(II); Pseudohalides; EPR; Magnetism; Di-2-pyridylamine; Cyanate

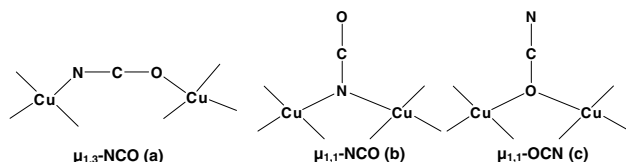
The pseudohalide (NCO[−], N₃[−], NCS[−], etc.) ligands can coordinate to transition metal atoms in different ways, for example as a terminal, or as a bridging ligand between metal atoms. For two metal ions the most common modes are: end-to-end (a) or an end-on fashions (b, c) (Scheme 1). In cyanate-bridged polynuclear copper(II) compounds the end-on coordination mode is usually found. Indeed, thirteen out of fifteen reported cyanate-bridged dinuclear copper(II) compounds show end-on coordination [1–13], and only two have an end-to-end coordination [13,14]. Four structural exam-

ples of two-dimensional end-to-end cyanate-bridged copper(II) compounds [15–18] and four one-dimensional (one end-on [19] and three end-to-end [20–22]) cyanate-bridged compounds have been reported.

It is well known that phen and bipy type ligands have given a great stimulant to almost every branch of transition metal coordination chemistry. Among them, the somewhat flexible molecule, di-2-pyridylamine (dpyam), has attracted considerable interest in the relationship of the spectroscopic, magnetic and structural geometries of its bivalent metal complexes, especially for Cu(II) [23–26]. However, the number of dinuclear Cu(II) compounds with a μ_{1,1}-NCO bridge which are investigated by X-ray crystallography as well as magnetically are very limited [11–13].

* Corresponding author. Tel.: +66 043 202 22241; fax: +66 043 202 373.

E-mail address: sujittra@kku.ac.th (S. Youngme).



Scheme 1.

In this study, we report the synthesis and characterization of the novel dinuclear copper(II) complex $[\text{Cu}_2(\mu_{1,1}\text{-NCO})_2(\text{NCO})_2(\text{dpyam})_2]$ containing both dpyam and $\mu_{1,1}\text{-NCO}$ bridges.¹ Also the magnetic susceptibility is studied. This is a rare example of a dinuclear end-on and end-to-end cyanate-bridged copper(II) compound.

A view of dinuclear complex is depicted in Fig. 1 together with the used numbering scheme. The structure consists of dinuclear $[\text{Cu}_2(\mu_{1,1}\text{-NCO})_2(\text{NCO})_2(\text{dpyam})_2]$ units. The copper atoms are doubly bridged by N atoms of cyanate anions in an end-on fashion with an intradinuclear $\text{Cu}\cdots\text{Cu}$ separation of 3.516(3) Å. Each copper(II) ion has a distorted square pyramidal geometry with a $\text{CuN}_4\text{N}'$ chromophore and a τ value of 0.19 ($\tau = 0$ for a square pyramidal geometry, and $\tau = 1$ for a trigonal bipyramidal geometry) [27].

The basal plane consist of four short bonds from two pyridyl nitrogen atoms of the dpyam ligand [$\text{Cu}(1)\text{--N}(1)$, 2.016(3) and $\text{Cu}(1)\text{--N}(2)$, 2.007(3) Å], a nitrogen atom of the NCO terminal ligand [$\text{Cu}(1)\text{--N}(5)$, 1.956(3) Å] and a nitrogen atom from one of the NCO bridging ligand [$\text{Cu}(1)\text{--N}(4)$, 1.963(3) Å]. The apical position is occupied by N(4)A atom of the other NCO bridged ligand at 2.631(4) Å. The Cu metal atom lies 0.097(3) Å above the basal plane toward the axial site. When a very long Cu–O contact of 3.227(1) Å is considered, the packing the packing of the dinuclear entities shows a two-dimensional lattice, through both oxygen atoms of the NCO terminal ligands of the nearby dinuclear units. The lattice is stabilized by relatively strong hydrogen bonds between the amide nitrogen and an oxygen atom of a neighbouring NCO anion ($\text{N}(3)\text{--O}(2)$ 2.932(4) Å), generating a 1 D lattice (Fig. 2).

In the literature Cu(II) dinuclear $\mu_{1,1}\text{-NCO}$ -bridged compounds have a $\text{Cu--N}_{\text{NCO}}\text{--Cu}$ angle, which lies between 92.3 and 96.3 Å [8–13]. In the title compound this angle is 98.85 Å, which is, to the best of our knowledge, the largest $\text{Cu--N}_{\text{NCO}}\text{--Cu}$ angle for this type of dinuclear

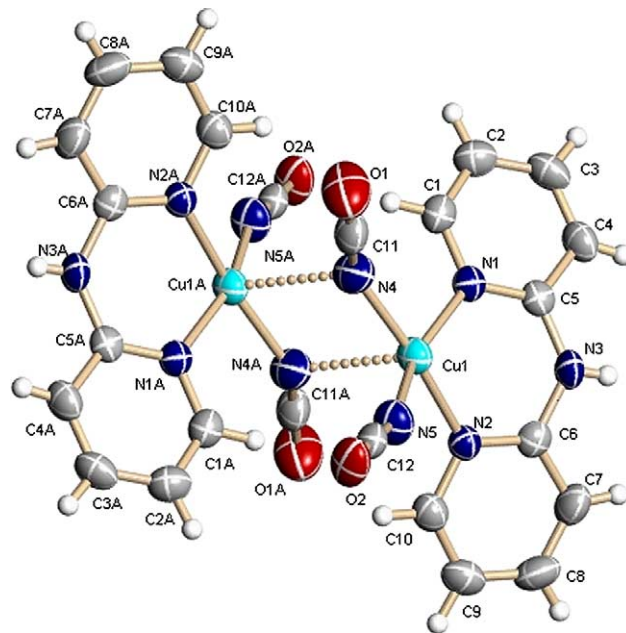


Fig. 1. Thermal ellipsoid (50% probability) plot of $[\text{Cu}_2(\mu_{1,1}\text{-NCO})_2(\text{NCO})_2(\text{dpyam})_2]$. Atoms with an “A” are generated by a mirror plane. Selected bond lengths (Å) and angles (°): $\text{Cu}(1)\text{--N}(1)$ 2.016(3), $\text{Cu}(1)\text{--N}(2)$ 2.097(2), $\text{Cu}(1)\text{--N}(4)$ 1.963(3), $\text{Cu}(1)\text{--N}(5)$ 1.956(3), $\text{Cu}(1)\text{--N}(4)\text{A}$ 2.631(4), $\text{N}(4)\text{--Cu}(1)\text{A}$ 2.631(4), $\text{N}(4)\text{--C}(11)$ 1.171(5), $\text{N}(5)\text{--C}(12)$ 1.153(4), $\text{N}(1)\text{--C}(1)$ 1.357(4), $\text{N}(1)\text{--C}(5)$ 1.340(4), $\text{N}(2)\text{--C}(10)$ 1.357(4), $\text{N}(2)\text{--C}(6)$ 1.337(4), $\text{C}(12)\text{--O}(2)$ 1.211(4), $\text{C}(11)\text{--O}(1)$ 1.189(5) and $\text{N}(5)\text{--Cu}(1)\text{--N}(4)$ 91.44(1), $\text{N}(5)\text{--Cu}(1)\text{--N}(2)$ 89.95(1), $\text{N}(4)\text{--Cu}(1)\text{--N}(2)$ 172.46(1), $\text{N}(5)\text{--Cu}(1)\text{--N}(1)$ 160.96(1), $\text{N}(4)\text{--Cu}(1)\text{--N}(1)$ 92.71(1), $\text{N}(2)\text{--Cu}(1)\text{--N}(1)$ 88.37(1), $\text{N}(4)\text{--C}(11)\text{--O}(1)$ 176.80(1), $\text{N}(5)\text{--C}(12)\text{--O}(2)$ 178.00(1), $\text{N}(5)\text{--Cu}(1)\text{--N}(4)\text{A}$ 91.44(1), $\text{N}(5)\text{--Cu}(1)\text{--N}(4)\text{A}$ 103.31(2), $\text{N}(1)\text{--Cu}(1)\text{--N}(4)\text{A}$ 95.69(3), $\text{N}(2)\text{--Cu}(1)\text{--N}(4)\text{A}$ 91.32(2), $\text{Cu}(1)\text{--N}(4)\text{--Cu}(1)\text{A}$ 98.85(1). Symmetry codes $A = (1 - x, -y + 1, -z)$.

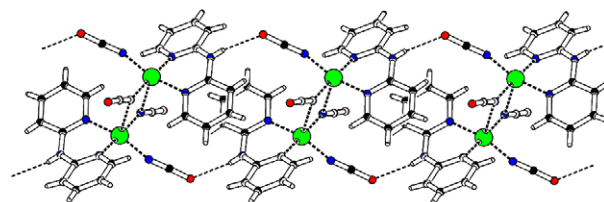


Fig. 2. H-bond system providing an one-dimensional array.

compounds observed so far. The dpyam ligands are essentially planar, with a dihedral angle of 27.98°. The average plane to plane distance of the dpyam pyridine rings of two dinuclear entities is 3.834(1) Å, which indicates a weak $\pi\text{--}\pi$ interactions through dpyam ligands in the neighbouring dinuclear entities.

The electronic reflectance spectrum shows a broad band at 15,400 cm^{-1} , in agreement with a distorted square pyramidal geometry [28].

The EPR of the powdered solid was measured at room temperature and at 77 K. At both temperatures a normal $S = 1/2$ signal was observed with $g_{\perp} = 2.08$

¹ All reagents were commercial grade materials and were used without further purification. The title compound was prepared by adding a hot solution of dpyam (0.171 g, 1.0 mmol) in 15 ml of dimethylformamide, to a warm solution of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.085 g, 0.5 mmol) in 10 ml of water and 0.081 g of KNCO (1 mmol) in 5 ml of water was added. Dark green crystals of **1** formed overnight (Yield 60%). Anal. Calc. for $\text{C}_{12}\text{H}_9\text{CuN}_5\text{O}_2$: C, 45.22; H, 2.84; N, 21.97. Found: C, 45.17; H, 2.67; N, 22.04%. IR (KBr, disc) $\nu(\text{NCO})$ 2214, 2180 cm^{-1} .

and, due to *inter* dinuclear couplings, an unresolved $g_{\parallel}$ of 2.29, which is in agreement with the observed geometry [28].

Besides these signals, corresponding to the $\Delta M_s = \pm 1$ allowed transitions, around 160 mT a weak (so called half-field) signal was observed corresponding to the $\Delta M_s = \pm 2$ forbidden transition, which indicates a magnetic coupling between the two Cu(II) ions. The same type of spectrum was also observed for some other NCO-bridged Cu(II) dinuclear compounds [11,22], although only in one case also the half-field signal was observed [7]. When EPR is measured as a frozen solution (DMF) at 77 K a resolved $d_{x^2-y^2}$ spectrum is obtained with a $g_{\perp}$ value of 2.05, a $g_{\parallel}$ of 2.29, with a $A_{\parallel}$ value of 16.2 mT (no half-field signal was observed any more). Also 9 superhyperfine lines with an $A_{N\perp}$ of 1.55 mT was observed, which indicates four nitrogen donors. This observation indicates that the dinuclear compound dissociate in this solution.

The magnetic susceptibility of a powdered sample of the title compound was measured from 5 to 300 K. The magnetic properties is depicted in Fig. 3 in the form of μ_{eff} versus T for two Cu(II) ions. At 300 K the μ_{eff} starts at a value of about $2.64 \mu_B$ (this values is close to what is expected for two spin = 1/2 uncoupled centres). Upon cooling the effective moment stays almost constant and at about 50 K is started to increase to reach the value of $2.81 \mu_B$ at 5 K. This behaviour is typical for a weak ferromagnetic interaction.

The theoretical expression for the magnetic susceptibility for two interacting $S = 1/2$ centres, which is based on the general Hamiltonian [29] is: $H_{\text{ex}} = -JS_1S_2$, in which the exchange parameter J , is negative for antiferromagnetic and positive for ferromagnetic interaction. The magnetic data were fitted to the equation given in the literature for dinuclear copper compounds [29,

p. 131]: $\chi_m = (2Ng^2\beta^2)[kT - (2zJ'/(3 + \exp(-J/kT)))^{-1} [3 + \exp(-J/kT)]^{-1} (1 - p) + \chi_p p + \text{TIP}]$, in which N , g , β , k and T have their usual meanings. The parameter p denotes the fraction of paramagnetic impurity in the sample and zJ' the interaction between neighbouring dinuclear identities. A temperature independent paramagnetism (TIP) was also considered and fixed at 60×10^{-6} per copper ion. The fit was accomplished by minimisation of $R = (\chi_m \cdot T_{\text{calc}} - \chi_m \cdot T_{\text{obs}})^2 / (\chi_m \cdot T_{\text{obs}})^2$ by least-squares procedure. The best fit was obtained for $J = 6.03 \text{ cm}^{-1}$, $g = 2.11$, $zJ' = -1.24 \text{ cm}^{-1}$, $p = 0.06$, with a final R of 6.9×10^{-4} (see Fig. 3).

Only a few Cu(II) dinuclear $\mu_{1,1}$ -NCO bridged compounds are known in the literature of which the X-ray structure as well as the magnetic susceptibility is reported. For two compounds, $[\text{Cu}(2,3\text{-bis}(2\text{-pyridyl})\text{pyrazine})(\mu_{1,1}\text{-NCO})_2]_n$ and $[\text{Cu}_2(\mu_{1,1}\text{-NCO})_2(4\text{-methyl-diethylenetriamine})_2](\text{ClO}_4)_2$, a weak antiferromagnetic interaction is observed with $J = -1.0$ and $J = -4.6 \text{ cm}^{-1}$, respectively [12,13]. However the geometry is not quite the same as the title compound, as the first compound has a distorted octahedral Cu(II) geometry and the second compound has two different dinuclear units in the unit cell. In the only other compound, which has almost the same geometry, $[\text{Cu}_2(\mu_{1,1}\text{-NCO})_2(\text{NCO})_2(1, 10\text{-phenanthroline})_2]$, also a ferromagnetic interaction is observed between the Cu(II) ions with $J = 13.75 \text{ cm}^{-1}$ [11]. Due to this limited number of compounds, no conclusions can be drawn from these results.

Supplementary material

Crystal data for **1**: $\text{C}_{12}\text{H}_9\text{CuN}_5\text{O}_2$, Monoclinic, $P2_1/c$ (No. 14), $a = 8.2481(10)$, $b = 9.3022(12)$, $c = 16.077(2) \text{ \AA}$, $\beta = 91.103(3)^\circ$, $V = 1233.3(3) \text{ \AA}^3$, $T = 293(2) \text{ K}$, $Z = 4$, $D_c = 1.717 \text{ g cm}^{-3}$, $\mu = 1.780 \text{ mm}^{-1}$, $F(000) = 644$, $\lambda(\text{Mo K}\alpha) = 0.71073 \text{ \AA}$. A total of 7642 reflections were measured in the setting angles $6.0^\circ < h < 28.28^\circ$ by x scan method, of which 2710 were independent reflections. The crystal structure was solved by direct method, and refined by full-matrix least squares on F^2 . Empirical absorption corrections were applied, which resulted in transmission coefficients ranging from 0.606 to 1.000 for **1**. The structure was solved by direct methods and refined by full-matrix least-squares method on $(F_{\text{obs}})^2$ with anisotropic thermal parameters for all nonhydrogen atoms using the SHELXTL-PC V 6.1 software package, and converging to $R_1 = 0.046$ and $wR_2 = 0.094$ [$I > 2\sigma(I)$]. CCDC-266691 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Center (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223 336033; e-mail: deposit@ccdc.cam.ac.uk].

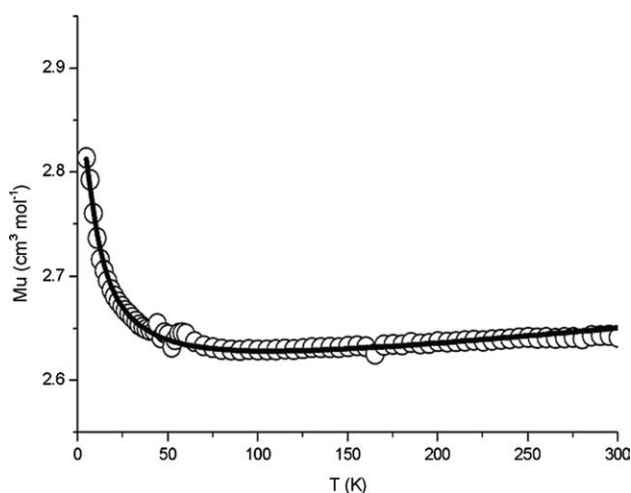


Fig. 3. A plot of the temperature dependence of μ_{eff} versus T for the title compound. The solid line represents the calculated curve for $g = 2.11$ and $J = 6.03 \text{ cm}^{-1}$ (see text).

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A new unique tetranuclear Cu(II) compound with double bridging thiocyanate anions: Synthesis, X-ray structure and magnetism of $[\text{Cu}_4(\mu_{1,3}\text{-NCS})_6(\text{dpyam})_4(\text{O}_2\text{CH})_2(\text{H}_2\text{O})_2]$ (dpyam = di-2-pyridylamine)

Sujittra Youngme^{a,*}, Jaturong Phatchimkun^a, Unchulee Suksangpanya^a,
Chaveng Pakawatchai^b, Gerard A. van Albada^c, Manuel Quesada^c, Jan Reedijk^c

^a Department of Chemistry, Faculty of Science, Khon Kaen University, Khon Kaen 40002, Thailand

^b Department of Chemistry, Faculty of Science, Prince of Songkla University, Hatyai, Songkla 90112 Thailand

^c Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden University, P.O. Box 9502, 2300 RA Leiden, The Netherlands

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Abstract

A new unique tetranuclear copper(II) complex doubly-bridged by thiocyanate anions $[\text{Cu}_4(\mu_{1,3}\text{-NCS})_6(\text{dpyam})_4(\text{O}_2\text{CH})_2(\text{H}_2\text{O})_2]$ (dpyam = di-2-pyridylamine) has been synthesized and characterized by X-ray diffraction methods and magnetic measurements.

The “outer” Cu ions, with a $\text{CuN}_3\text{O}(\text{S}, \text{O})$ chromophore, have an axially elongated octahedral geometry. The basal plane of these outer Cu(II) ions consist of 2 nitrogen atoms of the dpyam ligand with Cu–N distances of 1.980(2) and 2.008(2) Å, one nitrogen atom of a bridging thiocyanate anion (Cu–N distance 1.961(3) Å) and an oxygen atom of a formate molecule (Cu–O distance 1.977(1) Å). The axial positions are occupied by an oxygen atom of a water molecule (Cu–O distance 2.518(1) Å) and by a sulfur atom of a bridging thiocyanate anion at a semi-coordination distance of 3.048(1) Å.

The “inner” Cu atoms, with a $\text{CuN}_4(\text{S}_2)$ chromophore do also have an axially elongated octahedral geometry. The basal plane is formed by 2 nitrogen atoms of the dpyam ligand with Cu–N distances of 1.995(2) and 2.018(3) Å and two nitrogen atoms of two bridging thiocyanate anions (Cu–N distances 1.946(3), 1.976(3) Å). The axial positions are occupied by two sulfur atoms of two bridging thiocyanate anions (Cu–S semi-coordinating distances are 2.875(1) and 3.126(1) Å). Each Cu ion is bridged by two $\mu_{1,3}\text{-NCS}$ anions (in an equatorial-axial bridging mode) forming in this way a zigzag tetranuclear unit.

The magnetic susceptibility data of the compound have been investigated between 5 and 200 K. The compound shows a very weak antiferromagnetic interaction between the Cu ions, in agreement with the non-overlapping magnetic orbitals of each Cu ion.

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Keywords: Copper(II); Crystal structure; EPR; Magnetism; Di-2-pyridylamine; Thiocyanate-bridging ligands

In the last few years, building new molecular species and addressing their architectures in order to control their physical properties, has been a topic for many research groups, dealing, for example, with supramolecular chemistry [1]

and molecular magnetism [2]. Bridging ligands play an important role in the magnetic exchange pathways between paramagnetic centres: pseudo-halides (N_3^- , NCS^- , NCO^-) have been well documented for their numerous bonding abilities leading to various species [3]. End-on ($\mu_{1,1}\text{-N}_3/\text{NCS}/\text{NCO}$) [4] and end-to-end ($\mu_{1,3}\text{-N}_3/\text{NCS}/\text{NCO}$) [5] bridged complexes are known to mediate ferromagnetic [6] and antiferromagnetic [7] exchange interactions, respec-

* Corresponding author. Fax: +66 043 202 373.

E-mail addresses: sujittra@kku.ac.th, sujittra@mail.kku.ac.th (S. Youngme).

tively. The literature available for magneto-structural studies on copper(II) complexes containing bridging thiocyanate groups is still limited, as this ligand is less versatile and less efficient as a transmitter of magnetic interactions than azide [8]. The different modes exhibited by the thiocyanate group towards Cu^{2+} ion are: end-to-end (a) or an end-on fashions (b,c) (see Scheme 1). In thiocyanate-bridged polynuclear copper(II) compounds the end-to-end coordination mode is usually found in dinuclear [9], 1-dimensional [8–10], 2-dimensional [11] or 3-dimensional compounds [12]. Only one dinuclear [13] and one 1-dimensional [14] polynuclear thiocyanate-bridged copper(II) complexes are known to present the end-on coordination mode.

In this study, we present the tetranuclear thiocyanate bridged Cu(II) compound $[\text{Cu}_4(\mu_{1,3}\text{-NCS})_6(\text{dpyam})_4(\text{O}_2\text{CH})_2(\text{H}_2\text{O})_2]$ (dpyam = di-2-pyridylamine) in which each Cu(II) ion is doubly bridged by NCS-anions. To the best of our knowledge, this compound is the first tetranuclear copper(II) units linked by thiocyanato groups only.

A perspective view of the molecular structure is depicted in Fig. 1 together with the used numbering scheme.

The tetranuclear structure has an inversion centre at the $\text{Cu}2\text{--S}3$ line. The basal plane of the outer Cu(II) ions ($\text{Cu}1$, $\text{Cu}1\text{A}$) consists of 2 nitrogen atoms of the dpyam ligand with Cu--N distances of 1.980(2) and 2.008(2) Å, one nitrogen atom of a bridging thiocyanate anion (Cu--N distance 1.961(3) Å) and an oxygen atom of a formate molecule (Cu--O distance 1.977(1) Å). The axial positions are occupied by an oxygen atom of a water molecule (Cu--O distance 2.518(1) Å) and by a sulfur atom of a bridging thiocyanate atom at a semi-coordination distance of 3.048(1) Å. The geometry around these outer Cu ions can best be described as axial elongated octahedral.

The “inner” Cu atoms ($\text{Cu}2$, $\text{Cu}2\text{A}$) have also the same type of geometry. However, the basal plane is now formed by 2 nitrogen atoms of the dpyam ligand with Cu--N distances of 1.995(2) and 2.018(3) Å and two nitrogen atoms of two bridging thiocyanate anions (Cu--N distances 1.946(3), 1.976(3) Å). The axial positions are occupied by two sulfur atoms of two bridging thiocyanate anions (Cu--S distances are semi-coordinated at 2.875(1) and 3.126(1) Å). Each Cu ion is bridged by two $\mu_{1,3}$ -NCS anions (in an equatorial-axial bridging mode) forming in this way a zigzag tetranuclear unit.

The thiocyanato groups are quasi-linear [178.3(3)°, 179.3(3)° and 178.3(3)° for $\text{N}(7)\text{--C}(21)\text{--S}(1)$, $\text{N}(8)\text{--C}(22)\text{--S}(2)$ and $\text{N}(9)\text{--C}(23)\text{--S}(3)$, respectively]. The dihedral

angles between the aromatic rings of a dpyam ligand are 27.8(3)° for the outer Cu(II) ion and 29.6(3)° for the inner Cu(II) ion. The N--Cu--N bite angles of the inner and outer dpyam ligands are 88.3(3)°.

The intrachain metal–metal separations are 5.375(1) Å for $\text{Cu}(2)\text{--Cu}(2)\text{A}$ and 5.556(1) Å for $\text{Cu}(1)\text{--Cu}(2)$ which are shorter than the singly (5.93(4) Å [11]) and doubly (5.72, 5.575 Å [9b]) thiocyanato-bridged copper(II) complexes. The lattice is stabilized by relatively strong hydrogen bonds between the amide nitrogen and an oxygen atom of a neighbouring formate anion, ($\text{N}(3)\text{--H}(5)\cdots\text{O}(2)$, 2.979(4) Å and $\text{N}(6)\text{--H}(15)\cdots\text{O}(2)$, 2.868(1) Å) and weak hydrogen bonds between the water hydrogen atom and a sulfur atom and formate oxygen atoms ($\text{O}(1\text{W})\text{--H}(1\text{W})\cdots\text{S}(1)$, 3.457(3) Å, $\text{O}(1\text{W})\text{--H}(2\text{W})\cdots\text{O}(1)$, 3.277(4) Å and $\text{O}(1\text{W})\text{--H}(2\text{W})\cdots\text{O}(2)$, 3.205(4) Å), leading to 3-dimensional infinite network (Fig. 2).

The electronic reflectance spectrum of the title compound reveals a broad band at $15,480\text{ cm}^{-1}$, corresponding to a favorable square pyramidal stereochemistry and assignment of the band as the d_{xy} , d_{yz} , d_{xz} , $d_{z^2} \rightarrow d_{x^2-y^2}$ transition.

The EPR spectrum of the powdered compound reveals at room temperature and at 77 K an axial signal with $g_{\perp} = 2.06$ and an unresolved $g_{\parallel} = 2.27$. The signals are consistent with the $d_{x^2-y^2}$ ground state and the distorted octahedral geometry. No triplet signal has been observed.

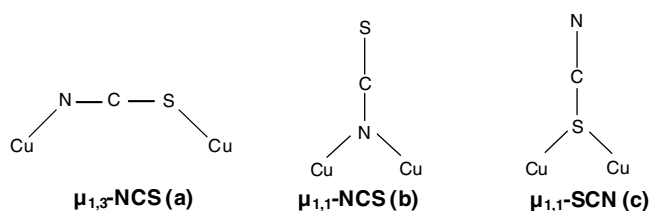
The magnetic susceptibility of a powdered sample was measured from 5 to 200 K. The magnetic properties are given in Fig. 3 in the form of a $\chi_m T$ vs. T plot (for 4 Cu ions). At 200 K the $\chi_m \cdot T$ value is ca. $1.35\text{ cm}^3\text{ mol}^{-1}$. This value is somewhat lower than the theoretical value for 4 uncoupled spin 1/2 centres ($1.5\text{ cm}^3\text{ mol}^{-1}\text{ K}$ with $g = 2$). Upon lowering the temperature this value stays almost constant until at about 20 K the value decreases till about $1.28\text{ cm}^3\text{ mol}^{-1}$ at 5 K, all of which is indicative for a weak antiferromagnetic interaction.

Despite that this tetranuclear compound is topologically different from a linear tetranuclear copper compound, the Hamiltonian which can be used is identical [15]:

$$H = -2J_1(S_1S_2) - 2J_2(S_1S_3 + S_2S_4) - 2J_3(S_2S_3 + S_1S_4) - 2J_4(S_3S_4)$$

The interpretation of the Hamiltonian can be done with the use of Scheme 2. The first term corresponds to the interaction between the two “central” coppers of the tetranuclear unit $\text{Cu}_2\text{--Cu}_{2\text{A}}$. The second term of the Hamiltonian corresponds to the interaction of each of the central copper atoms with its nearest neighbour external copper centre, $\text{Cu}_1\text{--Cu}_{2\text{A}}$ and $\text{Cu}_2\text{--Cu}_{1\text{A}}$. The third term represents the interaction between next-nearest neighbour interactions, $\text{Cu}_1\text{--Cu}_2$ and $\text{Cu}_{1\text{A}}\text{--Cu}_{2\text{A}}$. The fourth term is the interaction between the two external coppers, $\text{Cu}_1\text{--Cu}_{1\text{A}}$.

The energy levels and the spin quantum numbers are as follows:



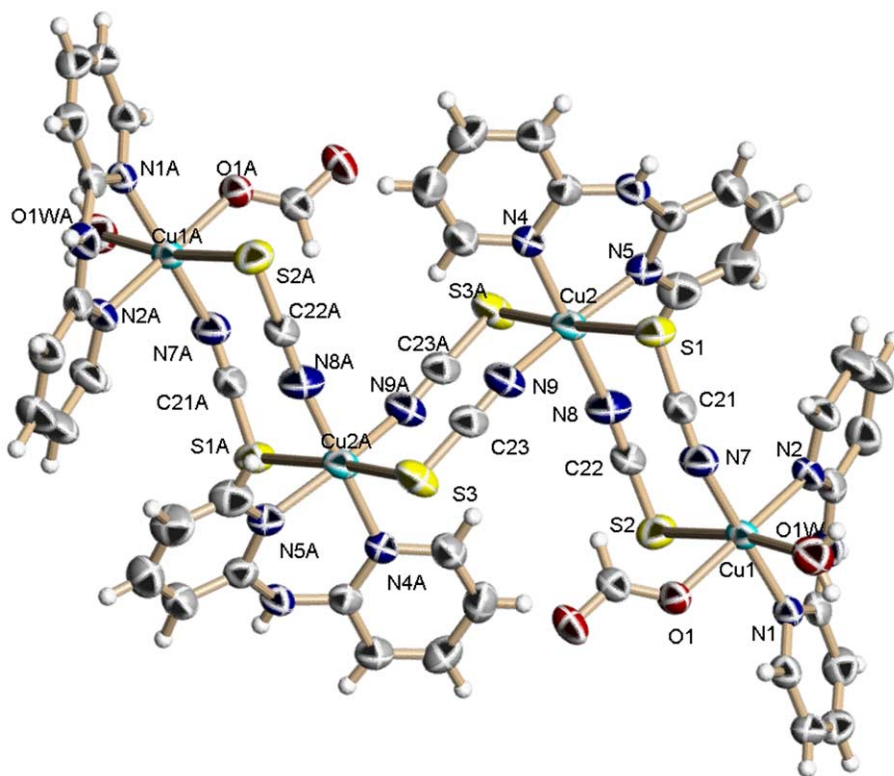


Fig. 1. Thermal ellipsoid (50% probability) plot of $[\text{Cu}_4(\mu_{1,3}\text{-NCS})_6(\text{dpyam})_4(\text{O}_2\text{CH})_2(\text{H}_2\text{O})_2]$. The tetranuclear structure has an inversion centre at the Cu2–S3 line. Selected bond lengths (Å) and angles ($^\circ$): Cu(1)–N(1) 1.980(2), Cu(1)–N(2) 2.008(2), Cu(1)–N(7) 1.961(3), Cu(1)–O(1) 1.977(1), Cu(1)–O(1W) 2.518(1), Cu(2)–N(5) 2.018(3), Cu(2)–N(4) 1.995(2), Cu(2)–N(9) 1.976(3), Cu(2)–N(8) 1.946(3), N(7)–C(21) 1.156(4), S(1)–C(21) 1.627(3), N(8)–C(22) 1.147(4), S(2)–C(22) 1.628(3), N(9)–C(23) 1.142(4), S(3)–C(23) 1.634(3), C(24)–O(2) 1.243(3), C(24)–O(1) 1.249(4), Cu(2)–S(3)A 2.875(1), Cu(1)–S(2) 3.048(1), Cu(2)–S(1) 3.126(1) and N(1)–Cu(1)–N(2) 88.3(1), N(7)–Cu(1)–O(1) 90.9(1), N(1)–Cu(1)–N(7) 177.0(1), N(2)–Cu(1)–O(1) 173.6(1), S(2)–Cu(1)–O(1W) 171.6(1), Cu(1)–N(7)–C(21) 160.5(3), Cu(1)–O(1)–C(24) 124.3(1), N(7)–C(21)–S(1) 178.3(3), N(4)–Cu(2)–N(5) 88.3(1), O(1)–C(24)–O(2) 124.3(1), N(4)–Cu(2)–N(8) 179.8(1), N(5)–Cu(2)–N(9) 170.0(1), S(1)–Cu(2)–S(3)A 176.3(1), Cu(2)–N(8)–C(22) 172.9(3), N(8)–C(22)–S(2) 179.3(3), Cu(2)–N(9)–C(23) 164.3(3), N(9)–C(23)–S(3) 178.3(3). $A = 1 - x, 1 - y, 1 - z$.

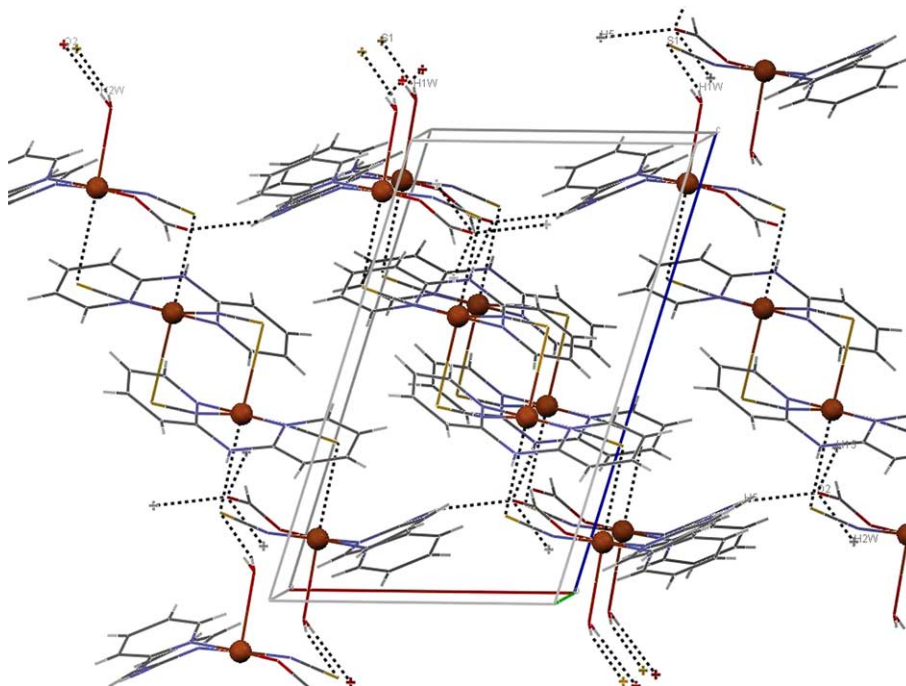


Fig. 2. View along the c -axis of the 3-dimensional structure of the title complex.

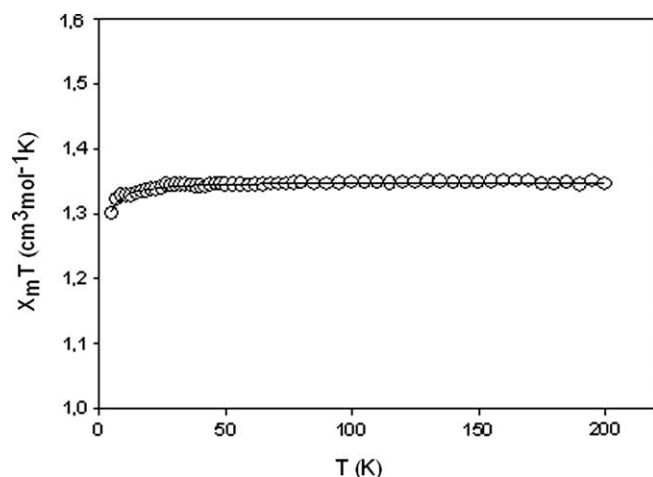
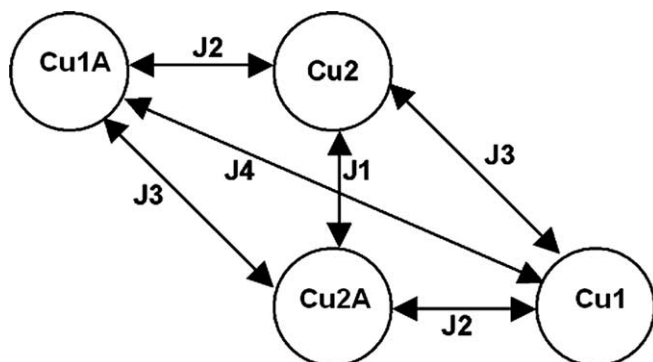


Fig. 3. χT vs. T plot for the title compound and its calculated curve (solid line), for the parameters given in the text.



Scheme 2. Scheme of the magnetic interactions in a zigzag tetranuclear unit.

$$\begin{aligned}
 S_1 = 2 \quad E_1 &= -J_1 - J_2/2 - J_3 - J_4/2 \\
 S_2 = 1 \quad E_2 &= -J_1 - J_2/2 + J_3 - J_4/2 \\
 S_3 = 1 \quad E_3 &= (J_2 + J_4)/2 + [(J_2 - J_4)^2 + (J_3 - J_1)^2]^{1/2} \\
 S_4 = 1 \quad E_4 &= (J_2 + J_4)/2 - [(J_2 - J_4)^2 + (J_3 - J_1)^2]^{1/2} \\
 S_5 = 0 \quad E_5 &= J_1 + J_3 + (J_2 + J_4)/2 + [4(J_1^2 + J_3^2) + J_2^2 \\
 &\quad + J_4^2 - 2J_1(J_2 + 2J_3 + J_4) - 2J_2(J_3 - J_4) \\
 &\quad - 2J_3J_4]^{1/2} \\
 S_6 = 0 \quad E_6 &= J_1 + J_3 + (J_2 + J_4)/2 - [4(J_1^2 + J_3^2) + J_2^2 \\
 &\quad + J_4^2 - 2J_1(J_2 + 2J_3 + J_4) - 2J_2(J_3 - J_4) \\
 &\quad - 2J_3J_4]^{1/2}
 \end{aligned}$$

An expression for the magnetic susceptibility per tetranuclear unit is described by

$$\begin{aligned}
 X_M = & (N_A g^2 \beta^2 / k_B T) [10 \exp(-E_1/K_B T) + 2 \\
 & \times \exp(-E_2/K_B T) + 2 \exp(-E_3/K_B T) + 2 \\
 & \times \exp(-E_4/K_B T)] / [5 \exp(-E_1/K_B T) + 3 \\
 & \times \exp(-E_2/K_B T) + 3 \exp(-E_3/K_B T) + 3 \\
 & \times \exp(-E_4/K_B T) + \exp(-E_5/K_B T) \\
 & + \exp(-E_6/K_B T)] + \text{TIP}
 \end{aligned} \quad (1)$$

An identical g value for each copper has been considered and the TIP per copper atom was fixed to 60×10^{-4} cgs units [2b]. As the distance between the external copper atoms is large ($\text{Cu}_1 \cdots \text{Cu}_{1A}$, 13.097 Å), the interaction parameter J_4 was fixed to $J_4 = 0$. The best set of parameters were obtained as $2J_1 = 0.05 \text{ cm}^{-1}$, $2J_2 = -0.37 \text{ cm}^{-1}$, $2J_3 = -0.09 \text{ cm}^{-1}$ and $g = 1.9$ (given as a straight line in Fig. 3). The values obtained are reasonable by chemical intuition and can be explained in light of their structural parameters. All interaction parameters are small, as distances between the copper ions are large and no clear interaction pathway is observed. The parameter J_1 is positive, pointing at a weak ferromagnetic interaction between the two central copper ions. These two central copper ions are in a square pyramidal geometry (SP), with a $d_{x^2-y^2}$ magnetic orbital (that which includes the unpaired electron). The two possible pathways for the magnetic interaction must occur via the thiocyanate anions. In both cases this involves a magnetic orbital of one copper ($d_{x^2-y^2}$) and a non-magnetic orbital (d_{z^2}) of the other copper, thus explaining the weak interaction observed. It is only the almost perfect SP geometry of the two copper centres that leads to an effective delocalisation of the unpaired electrons allowing the interaction. The fact that the d_{z^2} and $d_{x^2-y^2}$ orbitals (angles) are completely perpendicular to each other, probably makes the interaction ferromagnetic. This phenomenon has also been observed in the literature [15c].

The interaction between the central copper centres with their corresponding external copper atoms (nearest neighbour), J_2 , is weak and antiferromagnetic. The overall magnetic behaviour seems to be dominated by this weak antiferromagnetic interaction, resulting in a singlet ground state. Also in this case the interaction must occur via the thiocyanate groups, giving an antiferromagnetism interaction. The interaction between next-nearest neighbours, J_3 , is weak antiferromagnetic. The distances between the copper ions are large ($\text{Cu}_1 \cdots \text{Cu}_2$, 8.327 Å) and its interaction is almost 0 and negligible. In order to confirm these fitting parameters, a modified Bleaney Bowers fit with intermolecular interactions was performed, giving a good fit with the same type (both sign and order of magnitude) of interaction parameters.

As in previously reported cases with thiocyanate bridging ligands, the compound shows weak interactions ([8,9b,9c,10a,15c] and the data in Table 1). The $N_{\text{eq}}\text{--}S_{\text{ax}}$ bridging mode of the thiocyanate implies that the magnetic path is through two orbitals which are perpendicular to each other (E_g and T_{2g}), normally leading to ferromagnetic interactions, as is the case for the two central coppers (J_1). The “overall” magnetic behaviour is dominated by a weak antiferromagnetic interaction between the central dimer and its outer copper neighbours that apparently masks the very weak “intra-dimer” ferromagnetic interaction. This result is in concordance with other compounds showing the $N_{\text{eq}}\text{--}S_{\text{ax}}$ bridging mode of the thiocyanate [8,9b,9c,10a,15c].

Table 1
Structural and magnetic data of relevant polynuclear copper(II) end-to-end thiocyanate complexes

Complex ^a	Type	Chromophore	Geometry ^b	Tetragonality	Mode	Cu··Cu (Å)	<i>J</i> (cm ^{−1})	References
[Cu ₄ (NCS) ₆ (dpyam) ₄ (O ₂ CH) ₂ (H ₂ O) ₂]	Tetranuclear	CuN ₃ O'O'	Oct	0.712	End-to-end	5.375	2 <i>J</i> ₁ = 0.05	This work
		CuN ₄ S' ₂		0.661		5.556	2 <i>J</i> ₂ = −0.37 2 <i>J</i> ₃ = −0.09	
[Cu ₂ (NCS) ₂ (Et ₃ dien) ₂](ClO ₄) ₂	Dinuclear	CuN ₄ O'S'	Oct	0.732	End-to-end	5.718	+7.7	[9b]
[Cu ₂ (NCS) ₂ (ept) ₂](ClO ₄) ₂	Dinuclear	CuN ₄ O'S'	Oct	0.707	End-to-end	5.462	+1.3	[9b]
[{Cu(NCS) ₂ (dpk·CH ₃ OH)} ₂]	Dinuclear	CuN ₄ O'S'	Oct	0.744	End-to-end	5.389	−0.9	[9c]
[Cu(H ₂ O)(dpp)(NCS) ₂] ₂ ·2H ₂ O	Dinuclear	CuN ₄ O'S'	Oct	0.727	End-to-end	5.371	−1.01	[9d]
[Cu ₂ (NCS) ₂ (Me ₅ dien) ₂](ClO ₄) ₂	Dinuclear	CuN ₄ S'	SP		End-to-end	5.575	+1.6	[9b]
[Cu(bpy)(NCS) ₂] _n	1D	CuN ₄ S' ₂	Oct	0.618	End-to-end	6.113	−0.1	[8]
[{Cu(NCS) ₂ (dpk·CH ₃ OH)} _n]	1D	CuN ₄ O'S'	Oct	0.746	End-to-end	5.994	−0.3	[9c]
[Cu(bpm)(NCS) ₂] _n	1D	CuN ₄ S' ₂	Oct	0.622	End-to-end	5.328	−0.6	[10a]
[Cu(NCS) ₂ (pyz)] _n	1D	CuN ₄ S' ₂	Oct	0.665	End-to-end	5.690	<i>J</i> / <i>k</i> _B = −8.0(1) K	[10d]
[Cu(L4)(NCS)] _n	1D	CuN ₃ OS'	SP		End-to-end	6.268	−0.57	[10g]
[Cu(bpy)(NCS) ₂] _n	2D	CuN ₄ S' ₂	Oct	0.538	End-to-end	6.103	−1.0	[11]
		CuN ₄ S'	SP			5.940 5.909		

^a Abbreviation used: Et₃dien = 1,4,7-triethyldiethylenetriamine, ept = *N*-(2-aminoethyl)-1,3-propanediamine, dpk = di-2-pyridyl-ketone, bpy = 2,2'-bipyridyl, bpm = 2,2'-bipyrimidine, pyz = pyrazine, L4 = tridentate Schiff base (L = C₁₄H₉N₂O), im = imidazole.

^b Oct: octahedral, SP: square pyramidal.

The crystal structure determination of the reported thiocyanate bridged system reveals a tetranuclear copper(II) complex, with a unique doubly NCS-only bridges.

A consequence of this distinct feature is that the magnetic system is rather complicated and the “overall” magnetic interaction is very weak antiferromagnetic.

In Table 1 a number of relevant related end-to-end thiocyanate doubly-bridged compounds are presented. As can be seen from that table, due to the fact that the Cu··Cu distances are large, the magnetic interaction must occur in all cases via the thiocyanate bridges and is either very weakly ferromagnetic or very weakly antiferromagnetic, respectively.

Supplementary material

Crystal data

C₄₈H₄₂Cu₄N₁₈O₆S₆ (*M*_w = 1413.62), Triclinic, $\bar{P}1$, *a* = 9.2585(7) Å, *b* = 10.9382(8) Å, *c* = 14.9177(12) Å, α = 95.300(1)°, β = 104.882(1)°, γ = 104.196(1)°, *V* = 1395.9(2) Å³, *T* = 293(2) K, *Z* = 1, *D*_c = 1.682 Mg/m³, μ = 1.794 mm^{−1}, *F*(000) = 716, *k*(Mo Kα) = 0.71073 Å, 16,392 reflections measured (3.07 < *h* < 28.28°), 6564 unique (*R*_{int} = 0.0201), *R*₁ = 0.0413, *wR*₂ = 0.0997. Reflection data were collected on a 1K Bruker SMART CCD area-detector diffractometer. Data reduction and cell refinements were performed using the program SAINT [16]. An empirical absorption correction by using the SADABS [17] program was applied, which resulted in transmission coefficients ranging from 0.845 to 1.000. The structure was solved by direct methods and refined by full-matrix least-squares method on (*F*_{obs})² with anisotropic thermal parameters for all non-hydrogen atoms using the SHELXTL-PC V 6.12 [18] software package. All hydrogen atoms were located and refined isotropically. The molecular graphics were created by using SHELXTL-PC [18]. CCDC

No. 288257. See <http://www.ccdc.cam.ac.uk> for crystallographic data in CIF format.

Synthesis

The title compound was prepared by adding a warm solution of dpyam (0.17 g, 1.0 mmol) in 20 ml of methanol, to a warm solution of copper formate, Cu(O₂CH)₂ (0.31 g, 2.0 mmol) in 10 ml of water. Then a solution of KSCN (0.05 g, 0.5 mmol) and NaOH (0.02 g, 0.5 mmol) in 10 ml of water was slowly added. Dark green crystals were formed overnight. Yield: 80%. *Anal.* Calc. for C₄₈H₄₂Cu₄N₁₈O₆S₆ (%): C, 40.78; H, 2.99; N, 17.83. Found: C, 40.88; H, 2.75; N, 17.76. IR (KBr, disc) *v*_{as}(NCS) 2125, 2098 cm^{−1}, *v*_{as}(COO) 1566 cm^{−1}, *v*_s(COO) 1370 cm^{−1}.

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An unique trinuclear triply bridged Cu(II) compound containing double acetato and single azido bridges: Synthesis, X-ray structure and magnetism of $[\text{Cu}_3(\text{dpyam})_2(\mu_{1,1}\text{-N}_3)_2(\mu\text{-CH}_3\text{COO-}\kappa\text{-O}^1)_2(\mu\text{-CH}_3\text{COO-}\kappa\text{-O}^1, \text{O}^2)_2] \cdot 2(\text{H}_2\text{O})$ (dpyam = di-2-pyridylamine)

Sujittra Youngme^{a,*}, Thidarat Chotkhun^a, Somying Leelasubcharoen^a,
Narongsak Chaichit^b, Gerard A. van Albada^c, Marta Viciano-Chumillas^c, Jan Reedijk^c

^a Department of Chemistry, Faculty of Science, Khon Kaen University, Khon Kaen 40002, Thailand

^b Department of Physics, Faculty of Science and Technology, Thammasat University Rangsit, Pathumthani 12121, Thailand

^c Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden University, P.O. Box 9502, 200 RA Leiden, The Netherlands

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Abstract

The synthesis, characterization, crystal structure and magnetic properties of the unique azido-acetato bridged trinuclear triply bridged Cu(II) compound, $[\text{Cu}_3(\text{dpyam})_2(\mu_{1,1}\text{-N}_3)_2(\mu\text{-CH}_3\text{COO-}\kappa\text{-O}^1)_2(\mu\text{-CH}_3\text{COO-}\kappa\text{-O}^1, \text{O}^2)_2] \cdot 2(\text{H}_2\text{O})$, is reported. In the centrosymmetric compound, the central Cu atom is linked to two terminal Cu atoms by a double acetato bridge and an azido bridge, thereby providing a linear trinuclear unit. The coordination geometry around each of the terminal Cu(II) ions is distorted square pyramidal, while the geometry of the central Cu(II) ion is elongated octahedral. The magnetic susceptibility measurements, measured from 5 to 300 K revealed a weak antiferromagnetic interaction between the Cu(II) ions with a J value of -10.2 cm^{-1} . In the EPR no signals for the low-lying doublet are resolved at 77 K.

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Keywords: Copper(II); Crystal structure; EPR; Magnetism; Di-2-pyridylamine; Azide bridges

The design and synthesis of polynuclear coordination compounds, aiming at understanding the structural and chemical factors that control the exchange coupling between magnetic orbital, are of continuing interest in biology, chemistry and physics. Focused on the development of supramolecular chemistry [1] and molecular magnetism [2], bridging ligands play an important role in the magnetic exchange pathways between paramagnetic centres. The pseudo-halides (N_3^- , NCS^- , NCO^-) have been well documented for their numerous bonding abilities leading to various species [3]. End-on ($\mu_{1,1}\text{-N}_3/\text{NCS}/\text{NCO}$) [4] and

end-to-end ($\mu_{1,3}\text{-N}_3/\text{NCS}/\text{NCO}$) [5] bridged compounds are known to mediate ferromagnetic [6] and antiferromagnetic [7] exchange interactions, respectively. In fact, the end-on bridging will result in antiferromagnetism when the bridging angle exceeds a critical value (108.5°) [8]. The amount of reports concerning magneto-structural studies of azido bridged compounds with first-row transition ion is quite impressive [9]. However, only a very few X-ray structures of Cu(II) complexes containing mixed azide and carboxylate bridges have been reported in the literature [9c,10]. In this study, we present the synthesis [11], X-ray structure [12] and the magnetic measurements of a unique linear trinuclear Cu(II) complex, $[\text{Cu}_3(\text{dpyam})_2(\mu_{1,1}\text{-N}_3)_2(\mu\text{-CH}_3\text{COO-}\kappa\text{-O}^1)_2(\mu\text{-CH}_3\text{COO-}\kappa\text{-O}^1, \text{O}^2)_2] \cdot 2(\text{H}_2\text{O})$ (dpyam = di-2-pyridylamine), in which each Cu(II)

* Corresponding author. Fax: +66 043 202 373.

E-mail address: sujittra@kku.ac.th (S. Youngme).

ion is bridged by a bis-chelating acetate, a monochelating acetate and azide anions. A perspective view of the molecular structure is depicted in Fig. 1 together with the used numbering scheme. The central Cu(II) ion lies on an inversion centre, while the basal plane consists of two nitrogen atoms from two bridging azide anions with Cu–N distances of 2.033(3) Å and two oxygen atoms of two bridging acetate ligands (Cu–O distances 1.973(3) Å). Two oxygen atoms of two monoatomic-bridging acetate ligands (Cu–O distances 2.495(3) Å) occupy the axial positions. The geometry around this central Cu(II) ion can best be described as axially elongated octahedral.

The coordination geometry around each terminal Cu(II) atom (Cu2, Cu2A) is distorted square pyramidal with a $\text{CuN}_2\text{O}_2\text{N}'$ chromophore, $\tau = 0.16$ (The structural parameter τ describes the relative amount of trigonality; $\tau = 0$ for square pyramid and $\tau = 1$ for trigonal bipyramidal) [13]. The four shorter bonds of the basal plane involve two nitrogen atoms of the dpyam ligand with Cu–N distances of 1.997(3) and 2.004(3) Å, two oxygen atoms from two bridging acetate anions (Cu–O distances 1.975(3) and 1.979(3) Å). A nitrogen atom of a bridging azide anion (Cu–N distance 2.295(3) Å) occupies the axial position. One of the carboxylato oxygen atoms (O4) is at a semi-coordinating distance of 2.843(5) Å, thereby generating a kind of distorted octahedral geometry. The dihedral angle

between the CuN_2 and CuO_2 planes is 15.7° , indicating a slight tetrahedral twist of the square base. The central Cu(II) atom is connected to each terminal Cu(II) atom by two acetate ligands and one azide anion. One of the acetate ligand is in the bidentate $\kappa\text{-O}^1, \text{O}^2$ bridging mode and the other is in a monoatomic-bridging mode. This feature is similar to those of the dinuclear triply bridged Cu(II) compounds $[\text{Cu}_2(\mu\text{-O}_2\text{CH})_2(\mu\text{-OH})(\text{dpyam})_2](\text{PF}_6)$, $\tau = 0.71$ and $[\text{Cu}_2(\mu\text{-O}_2\text{CCH}_2\text{CH}_3)_2(\mu\text{-OH})(\text{dpyam})_2](\text{ClO}_4)$, $\tau = 0.43$ and 0.22 [14]. The triatomic carboxylato bridge in both compounds connects two Cu(II) centers in axial–axial and axial–equatorial configurations for the formate and propionate compounds, respectively. However, the present compound differs in structure in that the dihedral angle between the central and terminal bases of 25.5° leads to the partial face-to-face basal planes and a syn–syn/equatorial–equatorial configuration of the triatomic acetato bridge. The bridging angle of the monoatomic acetato bridge, $\text{Cu}(2)\text{--O}(3)\text{--Cu}(1)$, is $89.2(1)^\circ$, while that of the azide bridge, $\text{Cu}\text{--N}_{\text{azide}}\text{--Cu}$, is $93.6(1)^\circ$. The $\text{Cu}(1)\text{--Cu}(2)$ separation of 3.161(4) Å in the dinuclear unit is slightly larger than that found in the compound $[\text{Cu}_3(\mu_{1,1}\text{-N}_3)_4(\text{N}_3)_2(\text{Meinic})_2(\text{DMF})_2]$ with a distance of 3.088(1) Å (Meinic = methylisonicotinate) [15], but much shorter than that found in the linear trinuclear azido-bridged complexes $[\text{Cu}_3(2\text{-aminopyrimidine})_2(\mu_{1,1}\text{-N}_3)_4(\mu_{1,3}\text{-N}_3)_2(\text{dmf})_2]$ [16]

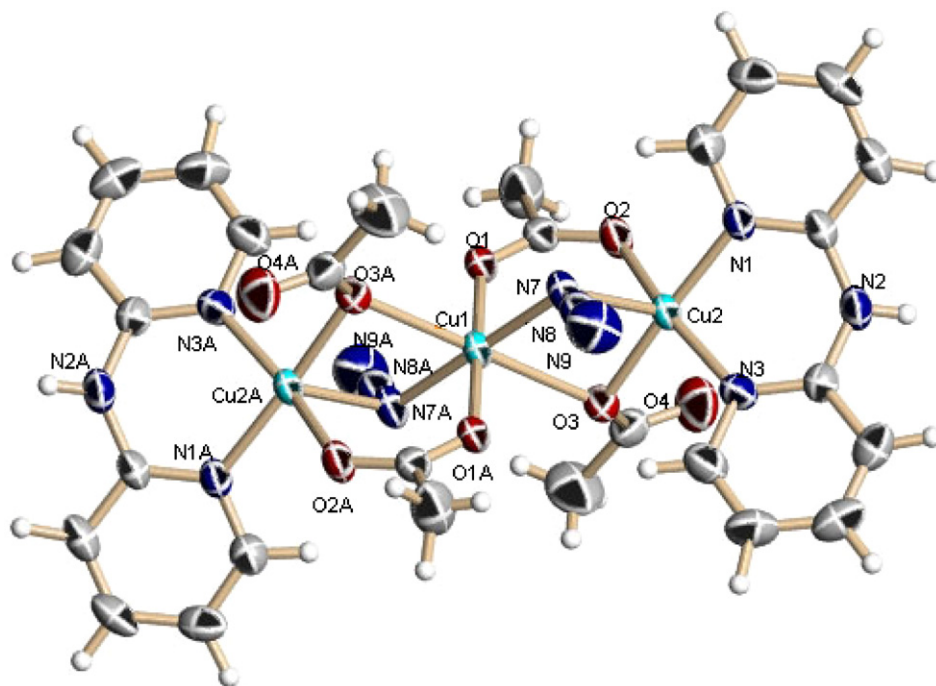


Fig. 1. Thermal ellipsoid (50% probability) plot of $[\text{Cu}_3(\text{dpyam})_2(\mu_{1,1}\text{-N}_3)_2((\mu\text{-CH}_3\text{COO-}\kappa\text{-O}^1, \text{O}^2)_2)] \cdot 2\text{H}_2\text{O}$. Selected bond lengths (Å) and angles ($^\circ$): Cu(1)–O(1) 1.973(3), Cu(1)–N(7) 2.033(3), Cu(1)–O(3) 2.495(3), Cu(1)–Cu(2) 3.1607(4), Cu(2)–O(3) 1.975(3), Cu(2)–O(2) 1.979(3), Cu(2)–N(3) 1.997(3), Cu(2)–N(1) 2.004(3), Cu(2)–N(7) 2.295(3), O(1A)–Cu(1)–N(7A) $93.1(1)^\circ$, O(1)–Cu(1)–N(7A) $86.9(1)^\circ$, O(1A)–Cu(1)–O(3) $96.4(1)^\circ$, O(1)–Cu(1)–O(3) $83.5(1)^\circ$, N(7A)–Cu(1)–O(3) $97.9(1)^\circ$, N(7)–Cu(1)–O(3) $82.1(1)^\circ$, O(3)–Cu(2)–O(2) $89.0(1)^\circ$, O(3)–Cu(2)–N(3) $90.8(1)^\circ$, O(2)–Cu(2)–N(3) $165.0(1)^\circ$, O(3)–Cu(2)–N(1) $174.8(1)^\circ$, O(2)–Cu(2)–N(1) $89.9(1)^\circ$, N(3)–Cu(2)–N(1) $89.0(1)^\circ$, O(3)–Cu(2)–N(7) $88.7(1)^\circ$, O(2)–Cu(2)–N(7) $93.6(1)^\circ$, N(3)–Cu(2)–N(7) $101.3(1)^\circ$, N(1)–Cu(2)–N(7) $96.4(1)^\circ$, O(3)–Cu(2)–Cu(1) $52.1(1)^\circ$, Cu(2)–O(3)–Cu(1) $89.2(1)^\circ$, Cu(1)–N(7)–Cu(2) $93.6(1)^\circ$, N(9)–N(8)–N(7) $178.2(5)^\circ$. A = $-x + 2, -y + 2, -z + 1$.

and $[\text{Cu}_3(4\text{-amino-1,2,4-triazole})_4(\text{N}_3)_6]$ [17] with Cu–Cu distances of 3.901(1) Å and 3.450(1) Å, respectively. The azide groups are quasi-linear (N(7)–N(8)–N(9) 178.2(5)°).

The lattice is stabilized by relatively strong hydrogen bonds between the water oxygen atom and an oxygen atom of a neighbouring acetato anion, O(5)··O(4), with a distance of 2.767(3) Å; between the amine nitrogen atom and the oxygen atom of water, N(2)··O(5), with a distance of 2.883(6) Å and a weak hydrogen bond between the water hydrogen atom and a nitrogen from the azide anion, O(5)··N(9), with a distance of 3.106(3) Å, providing in this way a 2D polymeric system.

The diffuse reflectance spectrum [18] displays an asymmetric broad band at $16,300\text{ cm}^{-1}$ and a lower energy shoulder at $11,840\text{ cm}^{-1}$, while the typical main peak around $15,000\text{ cm}^{-1}$, which is typical for a square pyramidal geometry, is not well resolved. This feature is consistent with distorted square pyramidal and elongated octahedral geometries within the complex. The d_{xz} , $d_{yz} \rightarrow d_{x^2-y^2}$ and d_{xy} , $d_{z^2} \rightarrow d_{x^2-y^2}$ transitions are assigned for a broad band and a lower energy shoulder, respectively [19].

The X-band powder EPR spectrum [18] shows at RT and at 77 K an axial signal with a $g_{\perp}$ of 2.09 and unresolved $g_{\parallel}$ of 2.27. No half-field signal or other signals typical for trinuclear Cu(II) complexes could be obtained at RT or 77 K. Similar EPR features/signals are also found in other trinuclear complexes [24–27].

The magnetic susceptibility of a powdered sample was measured from 5 to 300 K. The magnetic behaviour of the title complex is depicted in Fig. 2 in the form of χ_M vs T and $\chi_M T$ vs T for three Cu(II) ions. At 300 K the $\chi_M T$ product has a value of $1.16\text{ cm}^3\text{ mol}^{-1}\text{ K}$ which is very close to the theoretical value of three non-interacting copper (II) $S = 1/2$ spins ($1.125\text{ cm}^3\text{ mol}^{-1}\text{ K}$). The $\chi_M T$ value stays almost constant till about 85 K and then decreases gradually to a value of $0.42\text{ cm}^3\text{ mol}^{-1}\text{ K}$ at 5 K. This

behaviour agrees with a very weak antiferromagnetic interaction between the Cu(II) ions, remaining a $S = 1/2$ ground state at 5 K. Detailed study of this low- T state was not possible due to instrumental limitations below 5 K.

The theoretical expression for the magnetic susceptibility for three interacting $S = 1/2$ centres is based on the Hamiltonian [2b]: $\hat{H} = J(\hat{S}_1\hat{S}_2 + \hat{S}_2\hat{S}_3) + J'\hat{S}_1\hat{S}_3$, in which the exchange parameter J is negative for antiferromagnetic and positive for ferromagnetic interaction. J' is the interaction between terminal Cu(II) atoms and can be neglected ($J' = 0$) as the magnetic interaction between the neighbouring Cu(II) atoms is the dominant pathway. The magnetic data were fitted to the equation given in the literature [2b] for a linear trinuclear copper(II) complex:

$$\chi_M = \frac{Ng^2\beta^2}{4KT} \cdot \frac{1+e(J/KT)+10e(3J/2KT)}{1+e(J/KT)+2e(3J/2KT)} + \text{TIP},$$

in which N , g , β , k and T have their usual meanings [2]. Also a TIP with a fixed value of $60 \times 10^{-6}\text{ cm}^3\text{ mol}^{-1}$ per each Cu(II) has been considered. The fit was accomplished by minimisation of $R = (\chi_M \cdot T_{\text{calc}} - \chi_M \cdot T_{\text{obs}})^2 / (\chi_M \cdot T_{\text{obs}})^2$ by a least-squares procedure. The best fit, depicted in Fig. 2 as a solid line, was obtained for $J = -10.2\text{ cm}^{-1}$, $g = 2.05$, with a final R of 8×10^{-5} . The values obtained are reasonable and can be explained in light of their structural parameters. This weak interaction is also comparable with the complex $\text{Cu}_3(\text{diethylenetriamine})_2(\text{N}_3)_6$ with a reported J value of -2.1 cm^{-1} in which the end-on azido ligands link two Cu(II) centers in an axial–equatorial configuration [20].

It was found that the singly acetato-bridged polymeric compounds, $\{[\text{Cu}(\text{dpa})(\mu\text{-O}_2\text{C}_2\text{H}_3)](\text{ClO}_4) \cdot 0.5\text{THF}\}_n$, $\tau = 0.06$ and $\{[\text{Cu}(\text{diethylenetriamine})(\mu\text{-O}_2\text{C}_2\text{H}_3)]_n(\text{ClO}_4)_n\}$, revealed a weak ferromagnetic interaction with J values of 0.21 and 0.52 cm^{-1} , respectively [28]. The magnetic interaction in both compounds occurs via the Cu–O–C–O–Cu pathway with syn–anti bridging mode and axial–equatorial configuration of the acetato bridge. In contrast, the syn–syn carboxylate and end-on azido bridges, with equatorial–equatorial configuration and the Cu–N_{azide}–Cu angle larger than 108.5° , cause antiferromagnetic coupling [9b]. However, to the best of our knowledge, the magnetic properties of polynuclear Cu(II) compounds containing a single carboxylato bridge with the syn–syn mode are unknown.

In the present compound, the azide and monoatomic acetato bridges connect two Cu(II) centres in an axial–equatorial configuration and their contribution to the superexchange interaction is quite poor. However, the single triatomic bridge with a syn–syn mode links two equatorial sites and an antiferromagnetic interaction is expected. The weak antiferromagnetic interaction observed is lower than that expected for a single triatomic bridge with syn–syn coordination mode as compared to that the classic paddle-wheel dinuclear Cu(II) compounds containing four triatomic carboxylato bridges, $[\text{Cu}_2(\text{CH}_3\text{COO})_4(\text{H}_2\text{O})_2]$ with $J = -142\text{ cm}^{-1}$ [29]. This may due to the partial face-to-face bases of the present compound.

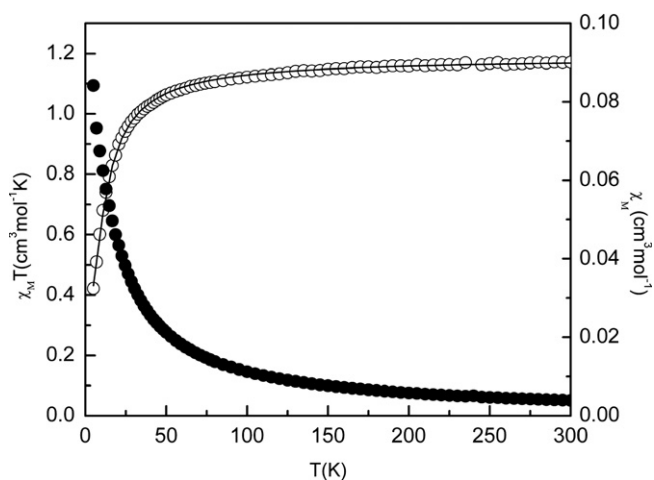


Fig. 2. A plot of the temperature dependence of $\chi_M T$ vs T (○) and χ_M vs T (●) for the title compound. The solid line represents the calculated curve for the parameters $J = -10.2\text{ cm}^{-1}$, $g = 2.05$ (see text).

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Three new dinuclear bis- μ -azido-bridged Cu(II) compounds with di-2-pyridylamine as a ligand: Syntheses, X-ray structure and magnetic measurements

Sujittra Youngme^{a,*}, Thidarat Chotkhun^a, Somying Leelasubcharoen^a,
Narongsak Chaichit^b, Chaveng Pakawatchai^c, Gerard A. van Albada^d, Jan Reedijk^d

^a Department of Chemistry, Faculty of Science, Khon Kaen University, Khon Kaen 40002, Thailand

^b Department of Physics, Faculty of Science and Technology, Thammasat University Rangsit, Pathumthani 12121, Thailand

^c Department of Chemistry, Faculty of Science, Prince of Songkla University, Hatyai, Songkla 90112, Thailand

^d Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden University, P.O. Box 9502, 2300 RA Leiden, The Netherlands

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Abstract

Three new dinuclear copper(II) compounds: $[\text{Cu}_2(\text{dpyam})_2(\mu_{1,1}\text{-N}_3)_2(\text{O}_2\text{CH})_2]$ (**1**), $[\text{Cu}_2(\text{dpyam})_2(\mu_{1,1}\text{-N}_3)_2(\text{O}_2\text{CCH}_3)_2]$ (**2**) and $[\text{Cu}_2(\text{dpyam})_2(\mu_{1,1}\text{-N}_3)_2(\text{O}_2\text{CCH}_2\text{CH}_3)_2]$ (**3**) have been synthesized and characterized crystallographically and spectroscopically. Compounds **1**, **2** and **3** consist of a dinuclear unit in which both Cu(II) ions are connected through two end-on azido bridges providing a distorted square pyramidal geometry with a CuN_4O chromophore. The $\text{Cu}\cdots\text{Cu}$ separations are 3.195, 3.200 and 3.247 Å for compounds **1**, **2** and **3**, respectively. The magnetic properties have been measured in the range from 5 to 300 K and correlated with the molecular structures. All three compounds show a medium to weak ferromagnetic exchange interactions between the Cu(II) ions dominated by the bridging azido ligands, with a singlet-triplet splitting (J) of 63.3, 63.8 and 5.1 cm^{-1} , for compounds **1**, **2** and **3**, respectively. A large zero-field splitting of about 0.4 cm^{-1} is observed in the EPR for compounds **1** and **2**.

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Keywords: Copper(II); Crystal structure; Azido-bridged; EPR; Magnetism

1. Introduction

Recently, the synthesis of pseudohalide bridged compounds, N_3^- , NCS^- , NCO^- , continue being the great interest subject, and intensive investigations have taken place as a result of their diverse structures and applications in magnetic materials [1]. The use of a variety of different bridging ligand has afforded an interesting array of molecular systems with a new architecture. Therefore, it is essential to choose appropriate bridges to rationally design magnetic systems with desirable property [2]. Among them, the azide anion has received the major attention owing to

its versatility as a ligand and the wide variety of magnetic behaviours [1–20]. The magnetic characters of the azido-bridged compounds are readily predicted in view of its binding pattern: the most common bridging modes of azide are the end-on ($\mu_{1,1}\text{-N}_3$, EO) [2–4,9,10] and the end-to-end ($\mu_{1,3}\text{-N}_3$, EE) fashions [2,4–8], which generally lead to ferromagnetic and antiferromagnetic interactions, respectively. However, the end-on bridging does result in antiferromagnetism; the critical angle for accidental orthogonality is $\approx 108.5^\circ$, when the bridging angle exceeds a critical value [11–14]. This correlation is valid only for basal–basal coordination, sometimes also applied to basal–apical coordination mode, which may lead to confusion [1d]. In the basal–apical type of compounds, usually the coupling is very small as the magnetic orbital describing the single electron is mainly of a $d_{x^2-y^2}$ type lying in the basal plane of the

* Corresponding author. Fax: +66 43 202 373.

E-mail address: sujittra@kku.ac.th (S. Youngme).

metal center and has only a small contribution on the axis perpendicular to the basal plane [15]. The magnetic behaviour for three compounds having doubly bridged azido ligands, in the basal–basal mode for compounds **1** and **2** and in the basal–apical mode for compound **3**, predicts a medium (compounds **1** and **2**) to a weak (compound **3**) ferromagnetic coupling [1]. Based on structural considerations, the end-on bridge is responsible for a ferromagnetic route.

In this study, the synthesis, X-ray crystal structures, spectroscopic and magnetic properties of three dinuclear copper(II) compounds, $[\text{Cu}_2(\text{dpyam})_2(\mu_{1,1}\text{-N}_3)_2(\text{O}_2\text{CH})_2]$ (**1**), $[\text{Cu}_2(\text{dpyam})_2(\mu_{1,1}\text{-N}_3)_2(\text{O}_2\text{CCH}_3)_2]$ (**2**) and $[\text{Cu}_2(\text{dpyam})_2(\mu_{1,1}\text{-N}_3)_2(\text{O}_2\text{CCH}_2\text{CH}_3)_2]$ (**3**) (dpyam = di-2-pyridylamine), all containing bridging azide anions, are reported.

2. Experimental

2.1. Materials and measurements

The di-2-dipyridylamine was purchased as commercial chemicals from Aldrich. All reagents are commercial grade materials and were used without further purification. Elemental analyses (C, H, N) were determined on a Perkin–Elmer PE 2400 CHNS/O Analyzer.

IR spectra were recorded on a Perkin–Elmer Spectrum One FT-IR spectrophotometer as KBr disc in the 4000–450 cm^{-1} spectral range. Solid-state (diffuse reflectance) electronic spectra were measured as polycrystalline samples on a Perkin–Elmer Lambda2S spectrophotometer. The X-band powder EPR spectra were obtained on polycrystalline samples at room temperature and 77 K with a JEOL RE2X electron spin resonance spectrometer. Magnetic susceptibility measurements (5–300 K) were carried out using a Quantum design MPMS-5S SQUID magnetometer (measurements carried out at 0.1 mT). Data were corrected for magnetization of the sample holder and for diamagnetic contributions, which were estimated from the Pascal constants.

Caution: Azido complexes of transition metal ions containing organic ligands are potentially explosive. Only a small amount of material should be prepared and handled with care.

2.2. Syntheses

2.2.1. $[\text{Cu}_2(\text{dpyam})_2(\mu_{1,1}\text{-N}_3)_2(\text{O}_2\text{CH})_2]$ (**1**)

The ligand dpyam (0.17 g, 1 mmol), dissolved in methanol/DMF (20/5 ml) and a solid of $\text{Cu}(\text{O}_2\text{CH})_2 \cdot n\text{H}_2\text{O}$ (0.31 g, 2 mmol) were mixed together, followed by addition of an aqueous solution of NaN_3 (0.065 g, 1 mmol, in 2 ml) with continuous stirring. The green solution was slowly evaporated at room temperature until brownish crystals of **1** separated. Yield ca. 80%. *Anal.* Calc. for $\text{C}_{22}\text{H}_{20}\text{Cu}_2\text{N}_{12}\text{O}_4$: C, 41.06; H, 3.13; N, 26.12. Found: C, 40.90; H, 2.96; N, 26.32%.

2.2.2. $[\text{Cu}_2(\text{dpyam})_2(\mu_{1,1}\text{-N}_3)_2(\text{O}_2\text{CCH}_3)_2]$ (**2**)

Compound **2** synthesized from $\text{Cu}(\text{O}_2\text{CCH}_3)_2 \cdot n\text{H}_2\text{O}$ (0.364 g, 2 mmol) and NaN_3 (0.650 g, 1 mmol) in a similar procedure as **1**. The green solution was slowly evaporated at room temperature until brownish-green crystals of **2** separated. Yield ca. 70%. *Anal.* Calc. for $\text{C}_{24}\text{H}_{24}\text{Cu}_2\text{N}_{12}\text{O}_4$: C, 42.92; H, 3.60; N, 25.02. Found: C, 42.60; H, 3.36; N, 25.32%.

2.2.3. $[\text{Cu}_2(\text{dpyam})_2(\mu_{1,1}\text{-N}_3)_2(\text{O}_2\text{CCH}_2\text{CH}_3)_2]$ (**3**)

Compound **3** synthesized from $\text{Cu}(\text{OH})_2$ (0.195 g, 2 mmol), $\text{NaO}_2\text{CCH}_2\text{CH}_3$ (0.192 g, 2 mmol) and NaN_3 (0.650 g, 1 mmol) in a similar procedure as **1**. The resulting green solution was allowed to stand at room temperature. Green crystals appeared. Yield ca. 70%. *Anal.* Calc. for $\text{C}_{26}\text{H}_{28}\text{Cu}_2\text{N}_{12}\text{O}_4$: C, 44.63; H, 4.03; N, 24.02. Found: C, 44.89; H, 3.90; N, 24.00%.

2.3. Crystallography

The X-ray single-crystal data for the three compounds were collected at 273 K for compounds **1**, **2** and at 293 K for **3**, respectively, on a 1 K Bruker SMART CCD area-detector diffractometer using graphite monochromated $\text{Mo K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at a detector distance of 4.5 cm and swing angle of -30° . A hemisphere of the reciprocal space was covered by combination of three sets of exposures; each set had a different ϕ angle (0° , 88° , 180°) and each exposure of 40 s covered 0.3° in ω . Data reduction and cell refinements were performed using the program SAINT [21]. An empirical absorption correction by using the SADABS [22] program was applied, which resulted in transmission coefficients ranging from 0.741 to 1.000 for compound **1**, 0.608 to 1.000 for compound **2** and 0.818 to 1.000 for compound **3**. The structures were solved by direct methods and refined by full matrix least-squares method on $(F_{\text{obs}})^2$ with anisotropic thermal parameters for all non-hydrogen atoms using the SHELXTL-PC V 6.12 software package [23]. All hydrogen atoms were located in a difference Fourier map and refined isotropically, except H atoms of acetate (compound **2**) and propionate anions (compound **3**) which were fixed geometrically with the HFIX utility. The molecular graphics were created by using SHELXTL-PC [23] package. The crystal and refinement details for three compounds are listed in Table 1.

3. Results and discussion

3.1. Crystal structure of $[\text{Cu}_2(\text{dpyam})_2(\mu_{1,1}\text{-N}_3)_2(\text{O}_2\text{CH})_2]$ (**1**)

The structure of compound **1** consists of neutral dinuclear entities. Each of them results from the pairing of two mononuclear units related via an inversion centre. A view of the dinuclear species is given in Fig. 1. Relevant bond distances and angles are reported in Table 2. Each copper(II) ion has a markedly distorted square pyramidal

Table 1
Crystal and refinement data for compounds **1**, **2** and **3**

Compound	1	2	3
Molecular formula	C ₂₂ H ₂₀ Cu ₂ N ₁₂ O ₄	C ₂₄ H ₂₄ Cu ₂ N ₁₂ O ₄	C ₂₆ H ₂₈ Cu ₂ N ₁₂ O ₄
Molecular weight	643.58	671.63	699.68
<i>T</i> (K)	273(2)	273(2)	293(2)
Crystal system	monoclinic	orthorhombic	monoclinic
Space group	<i>P</i> 2(1)/ <i>n</i>	<i>Pbca</i>	<i>P</i> 2(1)/ <i>c</i>
<i>a</i> (Å)	7.6120(1)	11.6453(4)	7.3022(4)
<i>b</i> (Å)	16.4007(1)	14.2258(5)	9.7478(6)
<i>c</i> (Å)	10.5104(1)	16.4774(6)	20.915(1)
β (°)	103.674(1)	90.00	90.874(1)
<i>V</i> (Å ³)	1274.95(2)	2729.7(2)	1488.5(2)
<i>Z</i>	2	4	2
<i>D_c</i> (g cm ^{−3})	1.676	1.634	1.561
μ (mm ^{−1})	1.724	1.614	1.484
<i>F</i> (000)	652	1368	716
Crystal size (mm)	0.22 × 0.27 × 0.40	0.35 × 0.50 × 0.70	0.32 × 0.23 × 0.14
Number of reflection collected	9275	18801	12733
Number of unique reflections [<i>R</i> _{int}]	3637 [0.0220]	4013 [0.0593]	3583 [0.0197]
Data/restraints/parameter	3637/0/221	4013/0/227	3580/0/255
Goodness-of-fit	1.108	1.072	1.073
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.033, <i>wR</i> ₂ = 0.076	<i>R</i> ₁ = 0.036, <i>wR</i> ₂ = 0.098	<i>R</i> ₁ = 0.028, <i>wR</i> ₂ = 0.079
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.043, <i>wR</i> ₂ = 0.080	<i>R</i> ₁ = 0.051, <i>wR</i> ₂ = 0.106	<i>R</i> ₁ = 0.031, <i>wR</i> ₂ = 0.082
Largest difference in peak and hole (e Å ^{−3})	0.42 and −0.41	0.66 and −0.88	0.32 and −0.38

$$R = \sum ||F_o| - |F_c|| / \sum |F_o|, R_w = [\sum w\{|F_o| - |F_c|\}^2 / \sum w|F_o|^2]^{1/2}.$$

geometry with a high τ value of 0.38. The structure index is defined as $\tau = (\beta - \alpha)/60$, where β and α are the largest coordination angles, $\tau = 0$ for square pyramidal (SP) and $\tau = 1$ for trigonal bipyramidal (TBP) geometry [24,25], of the CuN₄O chromophore, with two nitrogen atoms of the two bridging azide ligands (Cu–N distances 1.991(1), 2.143(1) Å), a nitrogen of the dpyam ligand (Cu–N distance 1.988(1) Å) and an oxygen atom of the formate ligand (Cu–O distance 2.014(1) Å) forming the basal plane.

The axial site of each copper(II) atom is occupied by another nitrogen atom of the dpyam ligand (Cu–N distance 2.129(1) Å) which is slightly shorter than the equatorial bond, Cu(1)–N(4), indicating an unusual square pyramidal geometry found in compound **1**. The copper(II) atoms of the compound are linked through a double azido bridges in an end-on bridging mode from the equatorial position of one copper chromophore to the equatorial position of the other one. The tetrahedral twist of the square base

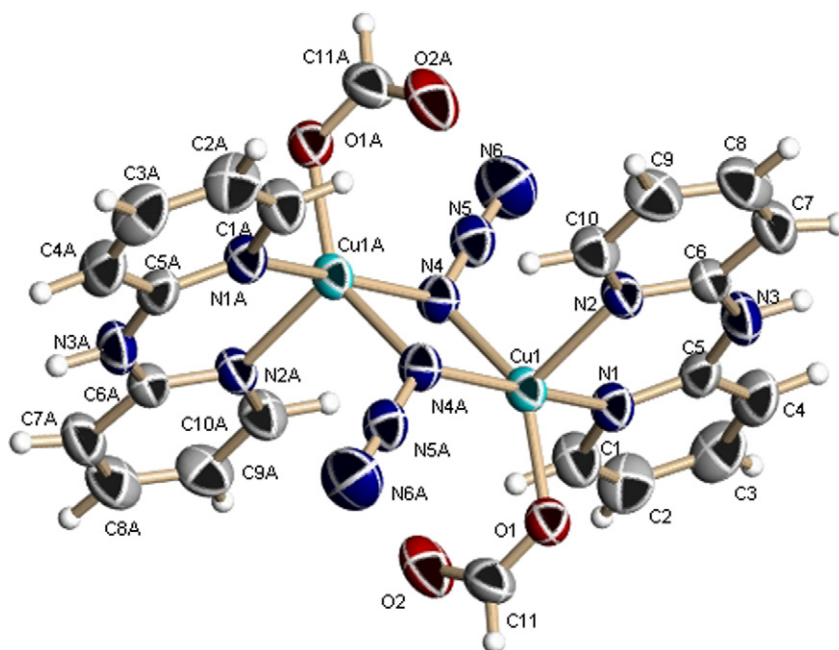


Fig. 1. ORTEP 50% probability plot of [Cu₂(dpyam)₂(μ_{1,1'}-N₃)₂(O₂CH)₂] (**1**).

Table 2
Selected bond lengths (Å) and angles (°) of $[\text{Cu}_2(\text{dpyam})_2(\mu_{1,1}-\text{N}_3)_2(\text{O}_2\text{CH})_2]$ (**1**)

Cu(1)–N(1)	1.988(2)	Cu(1)–O(1)	2.014(2)
Cu(1)–N(2)	2.129(2)	Cu(1)–N(4)A	1.991(2)
Cu(1)–N(4)	2.143(2)	Cu(1)–Cu(1)A	3.193(3)
Cu(1)–O(2)	2.945(1)	N(5)–N(6)	1.139(3)
N(4)–N(5)	1.209(2)		
N(1)–Cu(1)–N(4)A	168.9(1)	N(1)–Cu(1)–N(4)	91.1(1)
N(4)A–Cu(1)–O(1)	93.5(1)	N(1)A–Cu(1)–N(4)	78.9(1)
N(4)A–Cu(1)–N(2)	96.6(1)	N(2)–Cu(1)–N(4)	102.9(1)
N(1)–Cu(1)–O(1)	92.1(1)	N(1)–Cu(1)–N(2)	90.3(1)
O(1)–Cu(1)–N(4)	146.1(1)	Cu(1)–N(4)–Cu(1)A	101.1(1)
O(1)–Cu(1)–N(2)	110.8(1)	O(2)–Cu(1)–N(2)	159.4(1)
N(6)–N(5)–N(4)	178.7(2)		
Hydrogen bonds	D–H	H···A	D···A
N(3)–H(5)···O(2) [1/2 – x, 1/2 + y, 1/2 – z]	0.91	1.92	2.829(7)

defined by a dihedral angle between the CuN_2 and CuNO planes is at a quite high value of 34.0° and consequently, the copper atom is displaced $0.36 \text{ \AA}$ from its individual plane. The $\text{Cu}\cdots\text{Cu}$ separation is $3.195 \text{ \AA}$, while the $\text{Cu}-\text{N}_{\text{azido}}-\text{Cu}$ bridging angle is $101.1(1)^\circ$, which is an usual angle of azide bridges in most metal compounds [26–28]. The dpyam ligand is slightly folded, as the value of the dihedral angle between the planar pyridine rings is 4.9° . An oxygen atom of the formate ligand is at a distance of $2.945(1) \text{ \AA}$ from the copper(II) atom, which is slightly too long to be considered as a semi-coordination bond.

The crystal lattice is stabilized by hydrogen bonding between the amine N and an oxygen atom of neighboring formate group with a $\text{N}\cdots\text{O}$ contact of $2.829(7) \text{ \AA}$ leading to the formation of the 2D network. Details of the hydrogen bonding are listed in Table 2.

3.2. Crystal structure $[\text{Cu}_2(\text{dpyam})_2(\mu_{1,1}-\text{N}_3)_2(\text{O}_2\text{CCH}_3)_2]$ (**2**)

The structure of **2** (Fig. 2) consists of a dinuclear unit $[\text{Cu}_2(\text{dpyam})_2(\mu_{1,1}-\text{N}_3)_2(\text{O}_2\text{CCH}_3)_2]$ in which the copper(II)

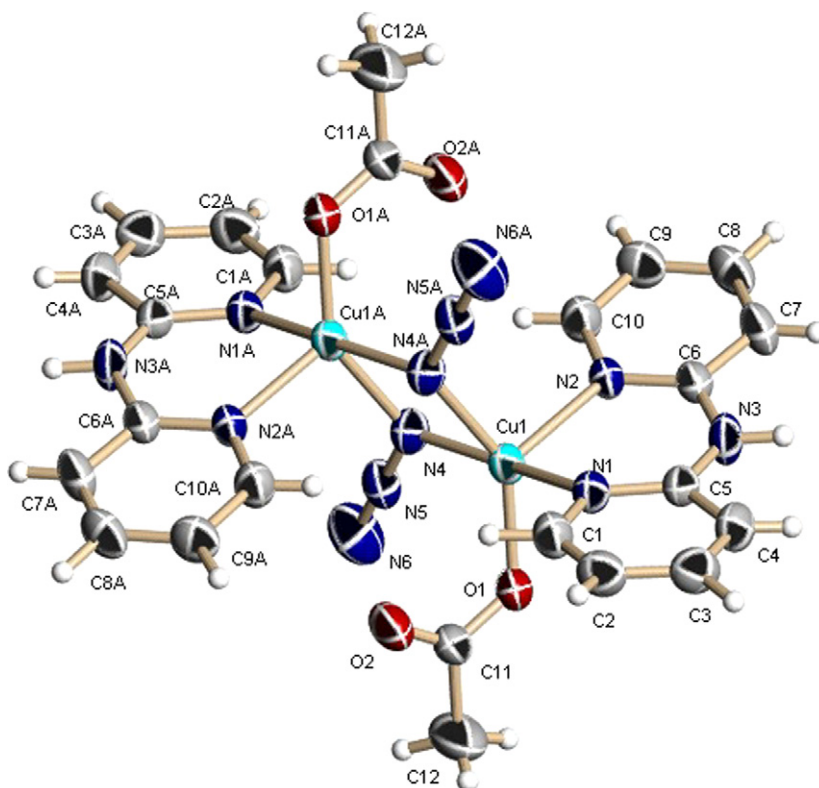


Fig. 2. ORTEP 50% probability plot of $[\text{Cu}_2(\text{dpyam})_2(\mu_{1,1}-\text{N}_3)_2(\text{O}_2\text{CCH}_3)_2]$ (**2**).

Table 3
Selected bond lengths (Å) and angles (°) of $[\text{Cu}_2(\text{dpyam})_2(\mu_{1,1}\text{-N}_3)_2(\text{O}_2\text{CCH}_3)_2]$ (**2**)

Cu(1)–N(1)	1.987(2)	Cu(1)–O(1)	1.967(2)	
Cu(1)–N(2)	2.120(2)	Cu(1)–N(4)A	2.143(2)	
Cu(1)–N(4)	1.997(2)	Cu(1)–Cu(1)A	3.200(1)	
Cu(1)–O(2)	2.997(2)	N(5)–N(6)	1.141(3)	
N(4)–N(5)	1.206(2)			
N(1)–Cu(1)–N(4)A	94.1(1)	N(1)–Cu(1)–N(4)	172.2(1)	
N(4)A–Cu(1)–O(1)	143.3(1)	N(4)–Cu(1)–N(4)A	78.8(1)	
N(4)A–Cu(1)–N(2)	103.3(1)	N(2)–Cu(1)–N(4)	95.7(1)	
N(1)–Cu(1)–O(1)	90.8(1)	N(1)–Cu(1)–N(2)	89.2(1)	
O(1)–Cu(1)–N(4)	93.0(1)	Cu(1)–N(4)–Cu(1)A	101.2(1)	
O(1)–Cu(1)–N(2)	113.2(1)	N(5)–N(4)–Cu(1)A	125.7(1)	
N(6)–N(5)–N(4)	179.0(2)	N(5)–N(4)–Cu(1)	122.4(2)	
Hydrogen bonds	D–H	H···A	D···A	D–H···A
N(3)–H(5)···O(2) [1/2 – x, 1/2 + y, 1/2 – z]	0.86	2.01	2.864(8)	173

atoms are bridged by two azido ions in an end-on fashion. Each of them results from the pairing of two mononuclear units related via an inversion centre. Relevant bond distances and angles are reported in Table 3.

The five-coordinate CuN_4O chromophore around the copper(II) ion consists of two nitrogen atoms of two bridging azide ligands (Cu–N distances 1.997(2), 2.143(2) Å), two nitrogen atoms of a dpyam ligand (Cu–N distances 1.987(2), 2.120(2) Å) and an oxygen atom of an acetato ligand (Cu–O distance 1.967(2) Å). The largest basal angles are $172.1(1)^\circ$ and $143.3(1)^\circ$, the distortion parameter τ in this case is 0.48, so the geometry can be described as an extremely distorted square pyramidal geometry with the axial site Cu(1)–N(2), both copper(II) ions of the compound are linked through a double azido bridges in an end-on bridging mode from the equatorial position of one copper chromophore to the equatorial position of the other one. The tetrahedral twist of the square base defined by a dihedral angle between the CuN_2 and CuNO planes is at a high value of 36.0° and consequently, the copper atom is displaced 0.36 Å from its individual plane. The Cu···Cu separation is 3.200(1) Å, while the Cu–N_{azido}–Cu bridging angle is $101.2(1)^\circ$. An oxygen atom of the acetato ligand is at a distance of 2.997(2) Å from the copper(II) atom, which is also too long to be considered as a semi-coordination bond. The crystal lattice is stabilized by hydrogen bonding between the amine N and an oxygen atom of neighboring formato group with a N···O contact of 2.864(9) Å leading to the formation of the 2D network. Details of the hydrogen bonding are listed in Table 3.

3.3. Crystal structure of $[\text{Cu}_2(\text{dpyam})_2(\mu_{1,1}\text{-N}_3)_2(\text{O}_2\text{CCH}_2\text{CH}_3)_2]$ (**3**)

Compound **3** is made up of one-half $[\text{Cu}(\text{dpyam})-(\mu_{1,1}\text{-N}_3)(\text{O}_2\text{CCH}_2\text{CH}_3)]^+$ moiety, which the other half being symmetry related via a centre of symmetry. This unit depicted in Fig. 3. Selected bond distances and angles are reported in Table 4. Each copper(II) ion is five coordinated in the form of distorted square pyramidal geometry

($\tau = 0.30$) of the CuN_4O chromophore (see Fig. 4c). The square base comprises two nitrogen atoms of the dpyam ligand (Cu–N distances 2.011(1), 1.999(1) Å), an oxygen atom of the propionato ligand (Cu–O distance 1.960(1) Å) and a nitrogen atom of the azido ligand (Cu–N distance 2.006(1) Å), with a tetrahedral twist between the CuN_2 and CuNO planes of 21.0° . The coordination of the apical position is formed by a nitrogen atom from another azido anion (Cu–N distance 2.348(1) Å). Both copper(II) atoms of the compound are linked through a double azido bridge in an end-on bridging mode from the equatorial position of one copper chromophore to the axial position of the other one. Both square bases are parallel in a partial face-to-face manner. The copper atom is displaced 0.16 Å from the square plane. The Cu···Cu separation is 3.247 Å, while the Cu–N_{azido}–Cu bridging angle is $96.2(1)^\circ$. The dpyam ligand is non-planar, a dihedral angle of 17.3° occurs between the individual pyridine rings and the dpyam bite angle is $89.2(1)^\circ$. An oxygen atom of the propionato ligand is at a distance of 2.848(1) Å from the copper(II) atom, which is too long to be considered as a semi-coordination bond. The hydrogen bonding involving the amine N and an oxygen atom of acetato group with a N···O contact of 2.796(7) Å, leads to the formation of the 2D network. Details of the hydrogen bonding are listed in Table 4.

3.4. Spectral characterization

3.4.1. Electronic and IR spectra

The IR spectra show an intense absorption peak at 2062, 2060 and 2047 cm^{-1} for compounds **1**, **2** and **3**, respectively, which can be assigned to the $\nu_{\text{as}}(\text{N}_3)$ stretching vibration of the azide ligand in the end-on coordination mode. The strong bands at $1581, 1340\text{ cm}^{-1}$ for **1**, 1567 and 1402 cm^{-1} for **2** and $1555, 1426\text{ cm}^{-1}$ for **3** are assigned to the $\nu_{\text{as}}(\text{COO}^-)$ and $\nu_{\text{s}}(\text{COO}^-)$ modes of the carboxylate group within a dinuclear species.

The electronic diffuse reflectance spectrum of **3** shows an asymmetric broad band at $14\,890\text{ cm}^{-1}$ and low-energy

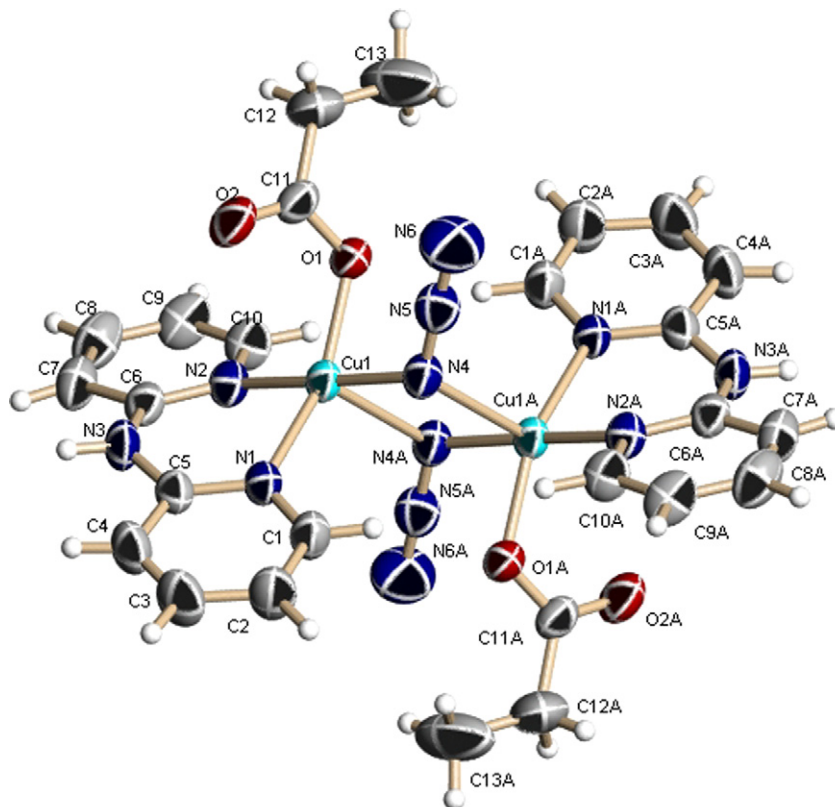
Fig. 3. ORTEP 50% probability plot of $[\text{Cu}_2(\text{dpyam})_2(\mu_{1,1}\text{-N}_3)_2(\text{O}_2\text{CCH}_2\text{CH}_3)_2]$ (**3**).

Table 4

Selected bond lengths (Å) and angles (°) of $[\text{Cu}_2(\text{dpyam})_2(\mu_{1,1}\text{-N}_3)_2(\text{O}_2\text{CCH}_2\text{CH}_3)_2]$ (**3**)

Cu(1)–N(1)	2.011(1)	Cu(1)–O(1)	1.960(1)
Cu(1)–N(2)	1.999(1)	Cu(1)–N(4)A	2.348(1)
Cu(1)–N(4)	2.006(1)	Cu(1)–Cu(1)A	3.247(2)
Cu(1)–O(2)	2.848(1)	N(5)–N(6)	1.144(2)
N(4)–N(5)	1.201(2)		
N(1)–Cu(1)–N(4)A	106.6(1)	N(1)–Cu(1)–N(4)	93.5(1)
N(4)A–Cu(1)–O(1)	94.4(1)	N(2)–Cu(1)–N(4)	177.1(1)
N(4)A–Cu(1)–N(2)	94.2(1)	N(1)–Cu(1)–N(2)	89.2(1)
N(1)–Cu(1)–O(1)	159.0(1)	Cu(1)–N(4)–Cu(1)A	96.2(1)
O(1)–Cu(1)–N(4)	88.8(1)	O(1)–Cu(1)–N(2)	89.2(1)
N(5)–N(4)–Cu(1)	119.7(1)	N(5)–N(4)A–Cu(1)	120.0(1)
O(2)–Cu(1)–N(4)A	144.7(1)	N(6)–N(5)–N(4)	177.9(2)
Hydrogen bonds			
	D–H	H···A	D···A
N(3)–H(5)···O(2) [1/2 – x, 1/2 + y, 1/2 – z]	0.86	1.93	2.796(7)
			177

shoulder at $11\,580\text{ cm}^{-1}$. This feature is consistent with the distorted square pyramidal geometry and the d_{z^2} , d_{xz} , $d_{yz} \rightarrow d_{x^2-y^2}$ and $d_{xy} \rightarrow d_{x^2-y^2}$ transitions, respectively. In case of compounds **1** and **2**, the spectrum shows two bands with nearly equal intensity at $12\,980$ and 9660 cm^{-1} (for compound **1**) and $12\,580$ and 9690 cm^{-1} (for compound **2**). The unusual apparent at low frequencies in **1** and **2** arises due to large tetrahedral twist of the square base and a shorter axial bond distance as compared to those of **3**. However, both bands of **1** and **2** are assigned

to be the $d_{xy}, d_{yz}, d_{xz} \rightarrow d_{x^2-y^2}$ and $d_{z^2} \rightarrow d_{x^2-y^2}$ transitions [29].

3.4.2. EPR and magnetic properties

The EPR spectra of compounds **1** and **2** were recorded as a polycrystalline powder at RT and 77 K from 0 to 800 mT at X-band frequency ($h\nu = 0.325\text{ cm}^{-1}$).

The observed EPR spectrum of compound **1** and **2** reveals typical triplet spectra with a zero-field splitting parameter $D < h\nu$. The spectra are almost identical for both

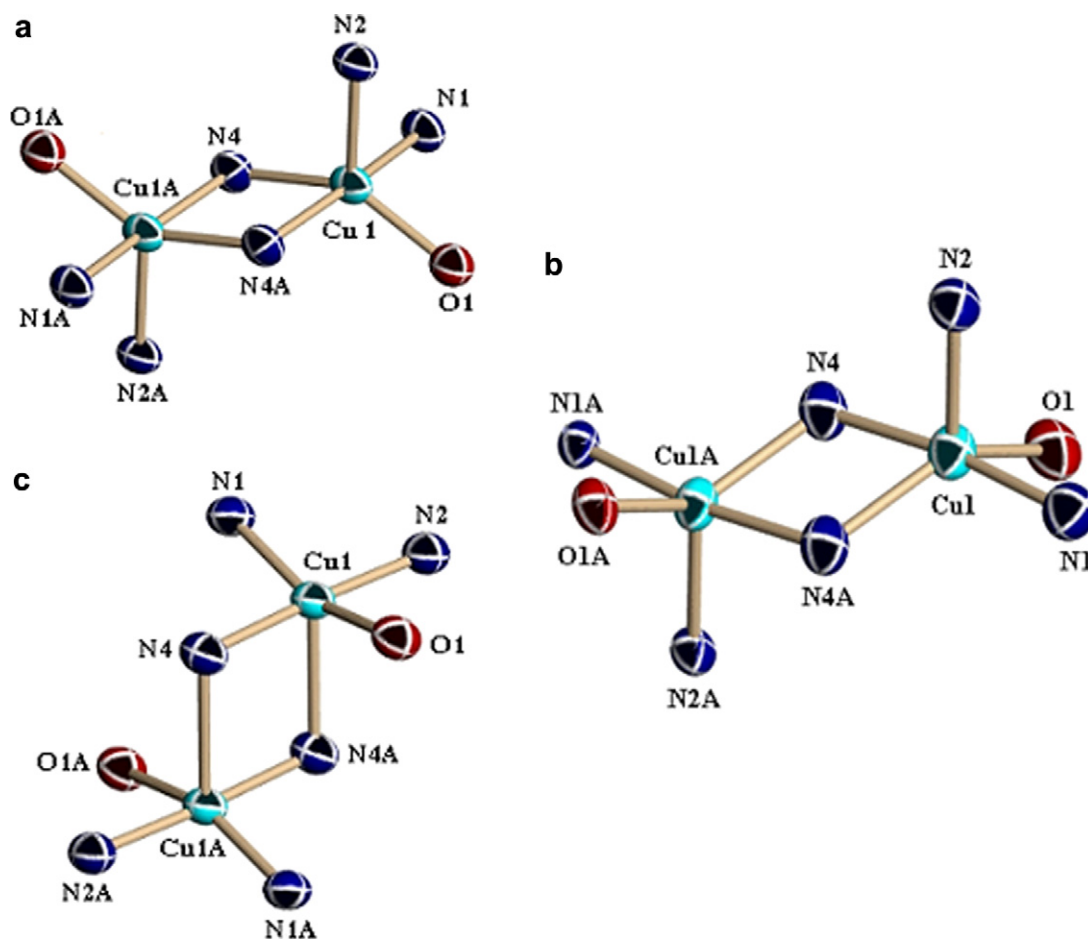


Fig. 4. The chromophore of (a) $[\text{Cu}_2(\text{dpyam})_2(\mu_{1,1'}\text{-N}_3)_2(\text{O}_2\text{CH})_2]$ (**1**), (b) $[\text{Cu}_2(\text{dpyam})_2(\mu_{1,1'}\text{-N}_3)_2(\text{O}_2\text{CCH}_3)_2]$ (**2**) and (c) $[\text{Cu}_2(\text{dpyam})_2(\mu_{1,1'}\text{-N}_3)_2(\text{O}_2\text{CCH}_2\text{CH}_3)_2]$ (**3**).

compounds and hardly no change is observed at RT and 77 K. Two representative EPR spectra are given as Fig. 5 (compound **1** at RT) and Fig. 6 (compound **3** at RT). Others are given as [supplementary material](#). Compound **1** shows very broad absorptions (at RT) at 110, 250 and 460 mT (110, 275 and 490 mT for compound **2**), which are too broad for assignment and/or simulation. A rough estimate for the zero-field splitting is 0.4 cm^{-1} . The sharp weak absorptions at around 320 mT are from monomeric impurity.

The EPR spectrum of compound **3** was recorded at RT and 77 K from 220 to 420 mT, and both show an axial $S = 1/2$ spectrum with a $g_{\perp}$ of 2.09 and unresolved $g_{\parallel}$ of 2.26. These values are in agreement with a $d_{x^2-y^2}$ ground state [29].

At RT a very weak half-field signal is observed at 160 mT, typical for dinuclear species. However, at 77 K this signal is not observed. The observed EPR spectra are in agreement with the magnetic behaviour of the three compounds (vide infra).

The magnetic susceptibility of all three compounds has been measured from 5 to 300 K. The magnetic properties of the compounds are depicted in Figs. 7–9, for compounds **1–3**, respectively, in the form of μ_{eff} versus T plots for one

copper(II) ion. Compounds **1** and **2** show a very similar magnetic behaviour. At 300 K the μ_{eff} is $1.89\ \mu_{\text{B}}$ per copper ion for compound **1** ($1.84\ \mu_{\text{B}}$, for **2**), which is somewhat

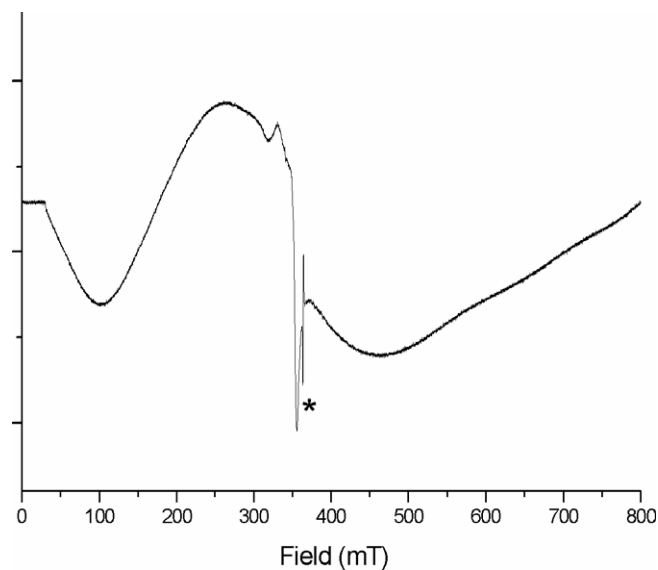


Fig. 5. EPR spectrum of compound **1** at RT (the starred peak is the internal reference, DPPH).

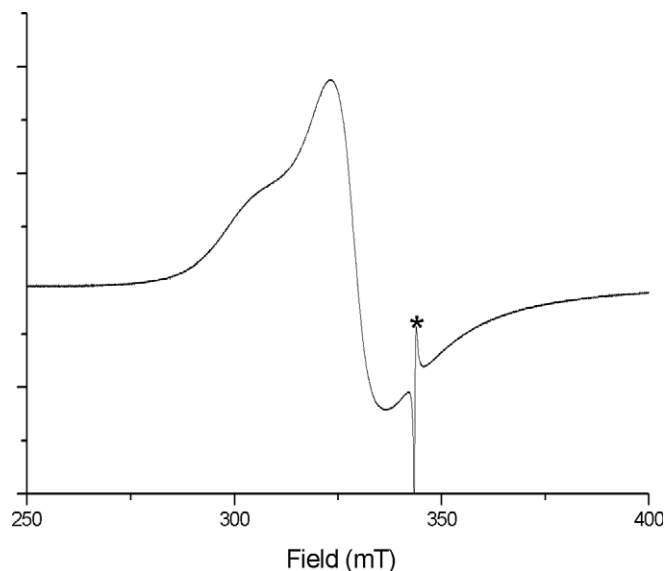


Fig. 6. EPR spectrum of compound **3** at RT (the starred peak is the internal reference, DPPH).

above the spin-only value for a single uncoupled spin $S = 1/2$ copper(II) centre. Upon cooling it raises gradually to reach 2.02 and 2.04 μ_B , at around 25 K, for compounds **1** and **2**, respectively. This behaviour is typical for medium to strong ferromagnetically coupled copper(II) dinuclear compound. Below that temperature, μ_{eff} then diminishes till a value around 1.92 μ_B for compound **1** (2.00 μ_B for **2**) at 5 K, which may originate from intermolecular antiferromagnetic interactions, or from the paramagnetic impurities present in the samples (vide infra).

The magnetic properties of compound **3** differ from that of compounds **1** and **2**. At 300 K the μ_{eff} is 1.74 μ_B per copper ion for compound **3**, which is about the spin-only value calculated for an uncoupled spin $S = 1/2$ copper(II) centre. Upon cooling, this value stays almost constant till about 50 K, where it increases gradually to reach 1.86 μ_B , at

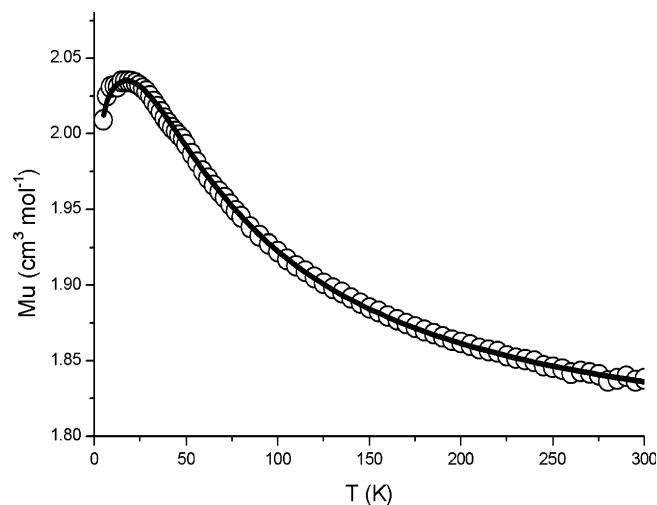


Fig. 8. A plot of the temperature dependence of μ_{eff} vs. T per Cu(II) ion for compound **2**. The solid line represents the calculated curve (see text).

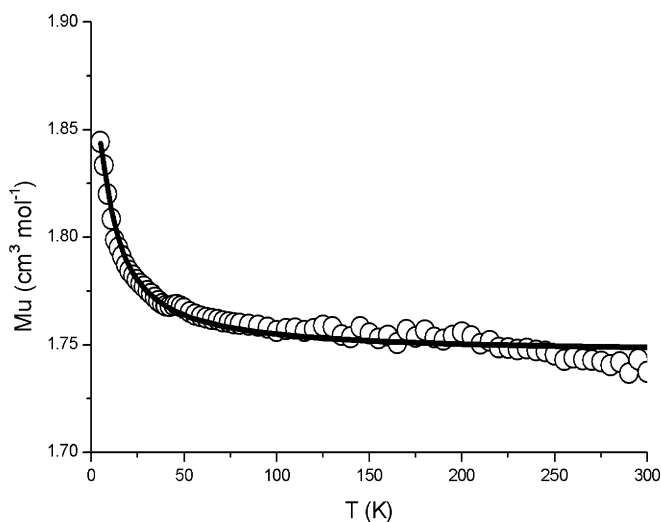


Fig. 9. A plot of the temperature dependence of μ_{eff} vs. T per Cu(II) ion for compound **3**. The solid line represents the calculated curve (see text).

5 K (see Fig. 8). This magnetic behaviour is typical for very weak ferromagnetically coupled copper(II) ions in a dinuclear compound.

The theoretical expression for the magnetic susceptibility for two interacting $S = 1/2$ centers, based on the general Hamiltonian [30] is: $H_{\text{ex}} = -JS_1S_2$, in which the exchange parameter J , is negative for antiferromagnetic and positive for ferromagnetic interaction. The magnetic data were fitted to the equation given in the literature for dinuclear copper compounds ([30], p. 132):

$$\chi_m = (2Ng^2\beta^2)[kT - (2zJ'/(3 + \exp(-J/kT)))]^{-1} \times [3 + \exp(-J/kT)]^{-1}(1 - p) + \chi_p p + \text{TIP},$$

in which N , g , β , k and T have their usual meanings.

The parameter p denotes the fraction of paramagnetic impurity in the sample and zJ' refers to the interaction between neighbouring dinuclear identities. A temperature

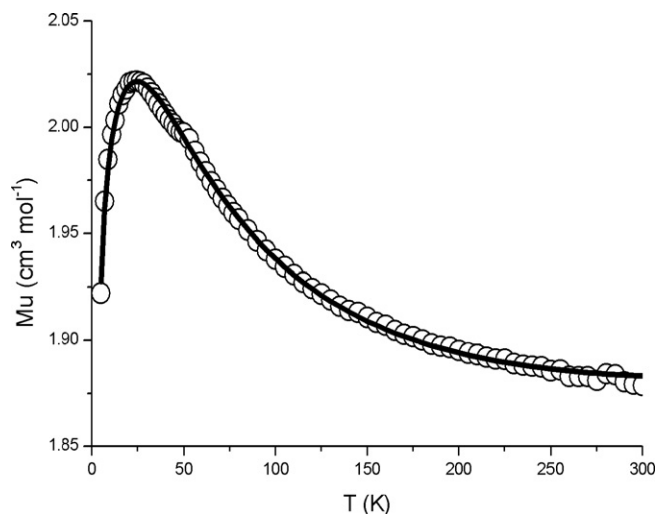


Fig. 7. A plot of the temperature dependence of μ_{eff} vs. T per Cu(II) ion for compound **1**. The solid line represents the calculated curve (see text).

Table 5

Selected magneto-structural data for double end-on azido-bridged dinuclear Cu(II) compounds

Compound ^a	Chromophore mode ^b	Configuration	Geometry ^c	τ	Cu–N _a (Å) ^d	Cu–N _b (Å) ^e	θ (°) ^f	Cu–Cu (Å)	J (cm ^{−1})	Reference
[Cu ₂ (dpyam) ₂ (μ _{1,1} -N ₃) ₂ (O ₂ CH) ₂] (1)	CuN ₃ ON'	eq–eq	Spy.	0.38	1.991, 2.143		101.1	3.19	+63.3	this work
[Cu ₂ (dpyam) ₂ (μ _{1,1} -N ₃) ₂ (O ₂ CCH ₃) ₂] (2)	CuN ₄ O	eq–eq	Spy.	0.48	1.997, 2.142		101.2	3.20	+63.8	this work
[Cu ₂ (N ₃) ₂ (4-Etpy) ₄ (NO ₃) ₂] (13)	CuN ₂ OO'	eq–eq	Oct.		1.996, 2.004		98.2	3.02	+230.1	[15]
[Cu ₂ (N ₃) ₂ (3-ampy) ₄ (NO ₃) ₂] · C ₂ H ₅ OH (14)	CuN ₂ O ₂	eq–eq	Oct.		2.000, 2.006		97.5	3.01	+223.2	[15]
[Cu ₂ (dpyam) ₂ (μ _{1,1} -N ₃) ₂ (O ₂ CCH ₂ CH ₃) ₂] (3)	CuN ₃ ON'	ax–eq	Spy.	0.30	2.003	2.348	96.2	3.25	+5.1	this work
[Cu(terpy)(N ₃)(H ₂ O)] ₂ (PF ₆) ₂ (4)	CuN ₄ ON'	ax–eq	Oct.		1.927	2.851	95.7	3.60	−2.9	[9]
[Cu(bipy)(N ₃) ₂] _n (5)	CuN ₄ N'	ax–eq	Spy.	0.06	1.961	2.684	96.8	3.51	−2.7	[34]
[Cu(dpp)(N ₃) ₂] _n (6)	CuN ₄ N'	ax–eq	Spy.	0.12	1.953	2.744	96.9	3.57	−2.3	[31]
[Cu(aepi)(N ₃) ₂] ₂ (7)	CuN ₄ N'	ax–eq	Spy.	0.15	2.016	2.381	98.8	3.35	−3.1	[2]
[Cu ₂ L ₂ (N ₃) ₂] (8)	CuN ₃ ON'	ax–eq	Spy.	0.18	2.019	2.551	86.9	3.17	+24	[32]
[{Cu(terpy)(N ₃) ₂ }(PF ₆) ₂] (9)	CuN ₄ N'	ax–eq	Spy.		1.954	2.469	96.3	3.31	−0.5	[9]
[Cu(L ¹)(N ₃) ₂] (10)	CuN ₃ ON'	ax–eq	Spy.	0.02	2.039	2.440	90.5	3.19	−1.8	[33]
[Cu(L ²)(N ₃) ₂] (11)	CuN ₃ ON'	ax–eq	Spy.	0.17	2.020	2.546	86.8	3.16	−3.1	[33]
[Cu(L ³)(N ₃) ₂] (12)	CuN ₃ ON'	ax–eq	Spy.	0.26	2.060	2.475	93.6	3.32	+2.9	[33]

^a Abbreviations: L = 7-amino-4-methyl-5-aza-3-hepten-2-onato (1-); L¹ = *N*-(3-aminopropyl)salicylaldimine; L² = 7-amino-4-methyl-5-azahept-3-en-2-one; L³ = 8-amino-4-methyl-5-azaoct-3-en-2-one; me₂tn = 2,2-dimethylpropane-1,3-diamine; bipy = 2,2'-bipyridine; terpy = 2,2':6'2''-terpyridine; dien = diethylenetriamine; aepi = 1-(2-aminoethyl)piperidin; dpp = 2,3-bis(2-pyridyl)pyrazine; 4-Etpy = 4-ethylpyridine; 3-ampy = 3-aminopyridine; dpa = di-2-pyridylamine.

^b eq = equatorial, ax = axial.

^c Spy. = square pyramidal, TBP = trigonal bipyramidal, Oct. = octahedral.

^d The basal Cu–N_(azido) bond length.

^e The apical Cu–N_(azido) bond length.

^f The angle at Cu–N_(azido)–M.

independent paramagnetism (TIP) was also considered and fixed at 60×10^{-6} per copper ion. The fit was accomplished by minimisation of $R = \sum (\chi_m \cdot T_{\text{calc}} - \chi_m \cdot T_{\text{obs}})^2 / (\chi_m \cdot T_{\text{obs}})^2$ by least-squares procedure. The best fit was obtained for compound **1** with the following values: $J = 63.3 \text{ cm}^{-1}$, $g = 2.06$, $zJ' = -3.3 \text{ cm}^{-1}$, $p = 0.04$, with a final R of 2.0×10^{-4} (see solid line in Fig. 7). For compound **2** these values are $J = 63.8 \text{ cm}^{-1}$, $g = 2.05$, $zJ' = -0.8 \text{ cm}^{-1}$, $p = 0.01$, with a final R of 9.0×10^{-5} (see solid line in Fig. 8). For compound **3** these values are $J = 5.1 \text{ cm}^{-1}$, $g = 2.02$, $zJ' = -2.2 \text{ cm}^{-1}$, $p = 0.06$, with a final R of 1.5×10^{-3} (see solid line in Fig. 9). These values are in agreement with the structural results (see Section 4).

3.4.3. Comparison of structures and magnetic properties

The compounds together with a number of related dinuclear copper(II)-azido compounds are listed in Table 5 in which two copper(II) atoms are bridged through two bridging azide anions with the basal–basal coordination; $[\text{Cu}_2(\text{N}_3)_2(4\text{-Etpy})_4(\text{NO}_3)_2]$ (**13**) and $[\text{Cu}_2(\text{N}_3)_2(3\text{-mpy})_4(\text{NO}_3)_2] \cdot \text{C}_2\text{H}_5\text{OH}$ (**14**) [15], and basal–apical mode; $[\text{Cu}(\text{terpy})(\text{N}_3)(\text{H}_2\text{O})_2(\text{PF}_6)_2]$ (**4**) and $[\{\text{Cu}(\text{terpy})(\text{N}_3)\}_2](\text{PF}_6)_2$ (**9**) [9], $[\text{Cu}(\text{bipy})(\text{N}_3)_2]_n$ (**5**) ($s = 0.06$) [34], $[\text{Cu}(\text{dpp})(\text{N}_3)_2]_n$ (**6**) ($s = 0.12$) [31], $[\text{Cu}(\text{aepi})(\text{N}_3)_2]_2$ (**7**) ($s = 0.15$) [2], $[\text{L}_2(\text{N}_3)_2\text{Cu}_2]$ (**8**) ($s = 0.18$) [33], $[\text{Cu}(\text{L}^1)(\text{N}_3)_2]$ (**10**) ($s = 0.02$), $[\text{Cu}(\text{L}^2)(\text{N}_3)_2]$ (**11**) ($s = 0.17$) and $[\text{Cu}(\text{L}^3)(\text{N}_3)_2]$ (**12**) ($s = 0.26$) [33]. For compounds with the basal–basal coordination, **13** and **14** are strong ferromagnetic with the high J values of 230.1 and 223.2 cm^{-1} , corresponding to the small θ angles of 98.2° and 97.5° , respectively ($<108.5^\circ$) [11–14]. The present compounds **1** and **2** which involve the larger θ angles, 101.1° and 101.2° , respectively ($<108.5^\circ$) reasonably provide a weaker ferromagnetic coupling. In addition, the marked distortion in Cu(II) geometry of both compounds may also be responsible for the lower J values of **1** and **2**, lower than expected, leading to a medium strong ferromagnetic interaction. In the case of basal–apical bridging fashion as in other remaining compounds in Table 5 including the present compound **3**, θ is not the determining factor of magnetic nature [15]. Their magnetic properties are weak ferromagnetic, compounds **3**, **8** and **12**, or weak antiferromagnetic interaction, compounds **4–7** and **9–11**. In these compounds the bridges connect an equatorial site with a high spin density to an apical site which has a weak spin density explaining the weak interaction observed.

4. Conclusion

In this paper we have presented the synthesis and magnetic study of three new azido-bridged copper(II) compounds with dpyam. The coordination geometry around each copper(II) ion is distorted square pyramidal for all three compounds. The azide ions in the compounds bridge two copper centers through one nitrogen atom (end-on bridging mode). Both azido bridges in compounds **1** and **2** involve the basal–basal coordination while each bridging

N atom in compound **3** occupies an equatorial position on Cu1 and an axial position on Cu1A. The strong magnetic interaction requires good σ orientation of magnetic orbitals and superexchange properties of bridging ligand. In the basal–basal type of compounds **1** and **2**, the magnetic orbital is $d_{x^2-y^2}$ for copper center directed toward the bridging azido ligand corresponding to a medium strong ferromagnetic interaction, but a reduction of the ferromagnetic contribution will be observed when the geometry becomes distorted. The overlap of the orbitals thus becomes weaker and also such interaction becomes weaker. For compound **3**, the coupling is very small as the magnetic orbital of a $d_{x^2-y^2}$ type lying in the basal plane of the copper center and has only a small contribution on the axis perpendicular to the basal plane. All three compounds display a dominant ferromagnetic behaviour, but the magnitude of the exchange interaction is much smaller in the case of **3**.

Acknowledgements

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Appendix A. Supplementary material

CCDC 616469, 616470 and 616471 contain the supplementary crystallographic data for **1**, **2** and **3**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2006.09.073.

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Copper(II) azide complexes of $[\text{Cu}(\text{acac})(\text{N}_3)(\text{dpyam})]$ and $[\text{Cu}(\mu\text{-N}_3\text{-}\kappa^{\text{N}1})(\text{C}_2\text{N}_3\text{-}\kappa^{\text{N}1})(\text{dpyam})]_2$: Synthesis, crystal structure and magnetism

Sujittra Youngme ^{a,*}, Thidarat Chotkhun ^a, Narongsak Chaichit ^b,
Gerard A. van Albada ^c, Jan Reedijk ^c

^a Department of Chemistry, Faculty of Science, Khon Kaen University, Khon Kaen 40002, Thailand

^b Department of Physics, Faculty of Science and Technology, Thammasat University Rangsit, Pathumthani 12121, Thailand

^c Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden University, P.O. Box 9502, 200 RA Leiden, The Netherlands

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Abstract

Two new compounds, $[\text{Cu}(\text{acac})(\text{N}_3)(\text{dpyam})]$ (**1**), (acac = acetylacetonate; dpyam = di-2-pyridylamine) and $[\text{Cu}(\mu\text{-N}_3\text{-}\kappa^{\text{N}1})(\text{C}_2\text{N}_3\text{-}\kappa^{\text{N}1})(\text{dpyam})]_2$ (**2**), have been synthesized and characterized by single-crystal X-ray diffraction and magnetic analyses. Compound **1** is a mononuclear compound in which each of two independent Cu(II) ions is penta-coordinated with a distorted square pyramidal geometry with distortion parameters $\tau = 0.21$ and 0.16 . In contrast, compound **2** is an azido-bridged dinuclear compound with monodentate dicyanamide anions and the Cu(II) ions display a distorted trigonal bipyramidal geometry with $\tau = 0.73$ and end-on azido bridges providing an equatorial–axial position between the metal ions. The EPR spectra of powdered samples for **1** and **2** have also been investigated. Magnetic susceptibility measurements of compound **2** reveal a very weak ferromagnetic interaction between the Cu(II) ions with a J value of $+5.8 \text{ cm}^{-1}$.

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The azido group N_3^- is one of the most interesting in inorganic coordination compounds found so far. This topic attracted much attention according to two main reasons. At first, the azide anion can behave as a didentate bridging ligand (end-on, $\mu_{1,1}\text{-N}_3$ “EO” [1–6], or end-to-end, $\mu_{1,3}\text{-N}_3$, “EE”, bridging modes [7–10]), and as a tridentate bridging ligand ($\mu_{1,1,1}\text{-N}_3$ [11] or $\mu_{1,1,3}\text{-N}_3$ [11–14]). Both types of didentate coordinations can mediate ferromagnetic and anti-ferromagnetic interactions between the metallic ions. The exchange between Cu(II) ions is known to be strongly dependent upon the coordination geometries of the copper ions and the disposition of the azido bridges. With copper(II) compounds containing $\mu(\text{N}_1)$ -azido bridges, the sign

and magnitude of the magnetic interactions were correlated with the value of the Cu–N–Cu bridging angle, the ferromagnetic coupling being usually associated with angles $< 108^\circ$ [2,15–17]. Studies that are more recent show that this type of correlation is valid only for the basal–basal exchange pathway between square pyramidal Cu(II) ions [18,19]. The second reason deals with the structural diversity of the anionic ligand, its great versatility as a ligand, which affords a great variety of structural types spanning from discrete molecules to three-dimensional compounds.

It is noteworthy that most of the double “EO” azido-bridged dicopper(II) compounds reported so far have shown square pyramidal Cu(II) coordination geometries, and that EO azido-bridged Cu(II) compounds with the trigonal bipyramidal geometry are still unusual. To the best of our knowledge, only the magnetic properties in

* Corresponding author. Fax: +66 043 202 373.

E-mail address: sujittra@kku.ac.th (S. Youngme).

$[\text{Cu}_2(\text{DMP})_2(\text{N}_3)_4]$, with a $\tau = 0.64$, has been measured and this compound exhibits an antiferromagnetic interaction with a J value of -27.6 cm^{-1} [20]. Although much effort has recently been focused on the studies of Cu(II) compounds with the azido anionic ligand, including bidentate chelate such as 2,2'-bipyridine [21,22] and 1,10-phenanthroline [13], very few azido compounds with dpyam as the co-ligand have been reported [23,24]. In order to study further how the nature of the co-ligand affected the structures and properties of azide compounds, we report herein the syntheses [25], crystal structures [26], electronic and magnetic properties of two new compounds, the mononuclear compound $[\text{Cu}(\text{acac})(\text{N}_3)(\text{dpyam})]$ (**1**) and the dinuclear compound $[\text{Cu}(\mu\text{-N}_3\text{-}\kappa^{\text{N}1})(\text{C}_2\text{N}_3\text{-}\kappa^{\text{N}1})(\text{dpyam})]_2$ (**2**) (in which acac = acetylacetonate; dpyam = di-2-pyridylamine). Compound **2** which is a rare case observed with a distorted trigonal bipyramidal geometry for azido-bridged Cu(II) dimers.

The asymmetric unit of compound **1** (Fig. 1) is made up of two crystallographically independent $[\text{Cu}(\text{acac})(\text{N}_3)(\text{dpyam})]$ neutral molecules (A and B). The Cu(II) ions of both molecules are five-coordinated with a $\text{CuN}_2\text{O}_2\text{N}'$ chromophore. The coordination around each Cu(II) ion consists of two dpyam nitrogen atoms (Cu–N distances 1.993(2), 2.010(2) Å for A and 2.004(2), 2.005(2) Å for B) and two acac oxygen atoms (Cu–O distances 1.931(2), 1.950(2) Å for A and 1.939(2), 1.952(2) Å for B). The apical position is occupied by one terminal N atom from an azide group (Cu–N distances 2.222(2) Å for A and 2.237(2) Å for B). Both of the copper atoms exhibit a slightly distorted square pyramidal environment, with τ values (the structural

parameter τ describes the relative amount of trigonality; $\tau = 0$ for square pyramid and $\tau = 1$ for trigonal bipyramidal [27]) of 0.21 and 0.16 for Cu1 and Cu2, respectively. The dihedral angles in each unit between the planes N–Cu–N of dpyam and O–Cu–O of acac are $20.9(1)^\circ$ and $21.0(1)^\circ$ for Cu1 and Cu2, respectively. The dpyam ligands are not essentially planar, with dihedral angles between two pyridine rings of $30.9(1)^\circ$ for Cu1 and $33.9(1)^\circ$ for Cu2. The copper atoms are displaced by 0.229(1) Å for Cu1 and 0.194(1) Å for Cu2 from the mean basal plane towards the apical positions. The intermolecular hydrogen-bonding interactions between the amide nitrogen and nitrogen atom of a neighbouring azido ligand [N–N = 2.885, 2.909 and 2.960 Å, H–N = 2.20, 2.21 and 2.25 Å and N–H–N = 137 , 139 and 140°] provide a one-dimensional lattice (Fig. 2).

Compound **2** is made up of one-half $[\text{Cu}(\mu\text{-N}_3\text{-}\kappa^{\text{N}1})(\text{C}_2\text{N}_3\text{-}\kappa^{\text{N}1})(\text{dpyam})]$ moiety, which the other half being symmetry related via a centre of symmetry. This unit is depicted in Fig. 3. Each Cu(II) ion is five coordinated with a distorted trigonal bipyramidal geometry ($\tau = 0.73$) and a $\text{CuN}_2\text{N}'_3$ chromophore. A nitrogen atom of the monoatomic bridged azido ligand (Cu1–N7ⁱ, 2.191(3) Å), a nitrogen atom of the dicyanamido ligand (Cu1–N10, 2.009(3) Å) and a nitrogen atom of the dpyam ligand (Cu1–N2, 2.046(3) Å) comprise the trigonal plane. The axial sites of each Cu(II) atom are occupied by another nitrogen atom of the dpyam ligand (Cu1–N1, 1.990(3) Å) and a nitrogen atom of bridged azido ligand (Cu1–N7, 1.999(1) Å) which are typically shorter than those in trigonal plane. The Cu–Cu separation is 3.258(3) Å, while the Cu–N_{azido}–Cu bridging angle is $102.0(1)^\circ$, which falls in

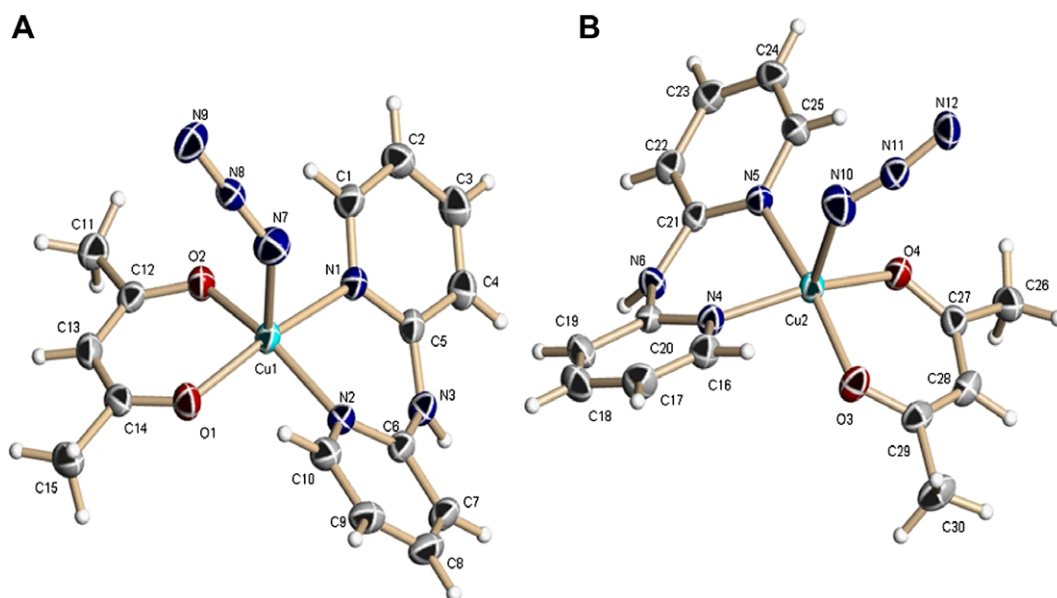


Fig. 1. The molecular structure of **1** with 50% probability displacement ellipsoids. Selected bond lengths (Å) and angles ($^\circ$): Cu2–O3 1.9388(15), Cu1–O1 1.9306(16), Cu2–O4 1.9519(16), Cu1–O2 1.9498(16), Cu2–N4 2.0037(17), Cu1–N1 1.9927(18), Cu2–N5 2.0048(16), Cu1–N2 2.0096(17), Cu2–N10 2.237(2), Cu1–N7 2.222(2), O3–Cu2–O4 $92.66(7)$, O1–Cu1–O2 $92.71(7)$, O3–Cu2–N4 $89.35(7)$, O1–Cu1–N1 $172.75(7)$, O4–Cu2–N4 $160.99(7)$, O2–Cu1–N1 $88.04(7)$, O3–Cu2–N5 $170.26(7)$, O1–Cu1–N2 $88.94(7)$, O4–Cu2–N5 $87.75(7)$, O2–Cu1–N2 $160.13(7)$, N4–Cu2–N5 $87.15(7)$, N1–Cu1–N2 $87.92(7)$, O3–Cu2–N10 $92.89(9)$, O1–Cu1–N7 $94.69(8)$, O4–Cu2–N10 $103.79(8)$, O2–Cu1–N7 $102.68(8)$, N4–Cu2–N10 $94.98(8)$, N1–Cu1–N7 $92.18(8)$, N5–Cu2–N10 $96.46(9)$, N2–Cu1–N7 $96.91(8)$.

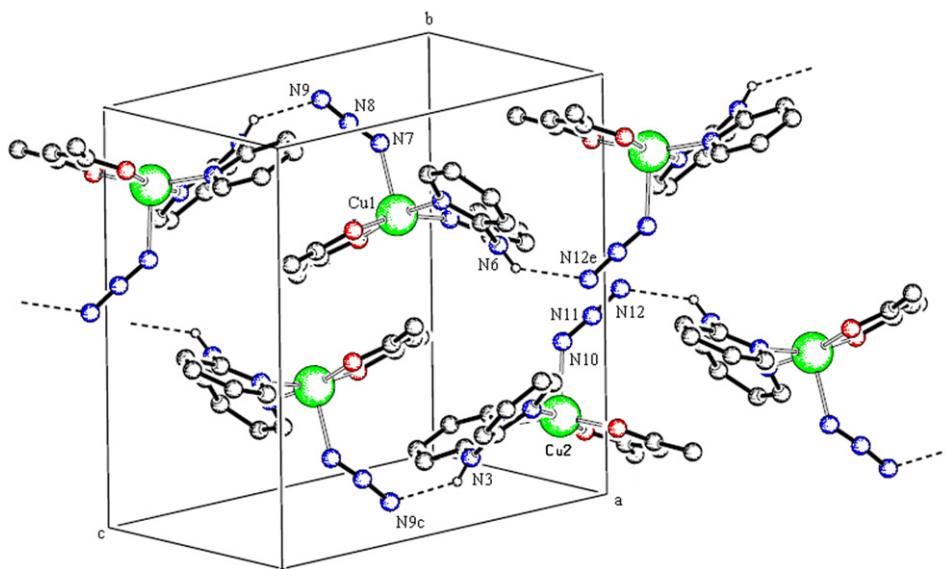


Fig. 2. Packing diagram of **1** with hydrogen bond (dash-lines), showing the one-dimensional structure.

the usual 100–107° range found for Cu(II), Ni(II) and Mn(II) azido compounds [28]. It is interesting to note that the “EO” azido nitrogen atom assumes an asymmetric equatorial–axial disposition between the two Cu(II) ions in the dinuclear unit, with the axial Cu–N(azido) distance

being significantly shorter than the equatorial Cu–N(azido) one. The dpyam ligand is non-planar, a small dihedral angle of 14.5(1)° occurs between the individual pyridine rings and the dpyam bite angle is 90.6(1)°. The intermolecular hydrogen-bonding interactions between the amide nitrogen and nitrogen atom of a neighboring azido ligand [N–N = 2.914 Å] are forming a one-dimensional lattice (Fig. 4).

The diffuse reflectance spectrum of compound **1** involves a broad band at 15,870 cm^{−1}, this spectral character is consistent with the distorted square pyramidal geometry. The transitions may be assigned as the d_{xy} , d_{xz} , d_{yz} , $d_{z^2} \rightarrow d_{x^2-y^2}$ transition. For compound **2**, the spectrum displays a broad band centered at 11,190 cm^{−1}. This spectrum is typical for distorted trigonal-bipyramidal geometry and assigned to the d_{xy} , d_{xz} , d_{yz} , $d_{x^2-y^2} \rightarrow d_{z^2}$ transition.

In the IR the typical anion bands are observed for compound **1** at 2028 cm^{−1} for the azide stretching vibration and for compound **2** the typical dicyanamide vibrations [29,30] are observed as strong bands at 2298 cm^{−1} ($\nu_{s(C-N)} + \nu_{as(C-N)}$) and at 2236, 2165 cm^{−1} ($\nu_{as(C\equiv N)} + \nu_{s(C\equiv N)}$), while the azide vibration is observed at 2053 cm^{−1}.

The EPR spectrum of compound **1** at RT is isotropic ($g_1 = 2.13$), giving no information regarding to the electronic ground state. The EPR spectrum of compound **2** was recorded at RT and 77 K and shows both at RT and 77 K an extremely broad band centered around $g = 2.22$ and a weaker band at low field ($g = 7-9$). No half-field signal could be observed due to the broadness of the band. No separate half field signal and no zero-field splitting parameters could be observed due to the broad band.

The magnetic susceptibility of dinuclear compound **2** has been measured from 5 to 250 K. The magnetic properties of the compound are depicted in Fig. 5 in the form of μ_{eff} versus T plot for one Cu(II) ion. At 250 K the μ_{eff} is 1.75 μ_B per Cu ion, which is about the spin-only value calculated for an uncoupled spin $S = 1/2$ Cu(II) centre. Upon

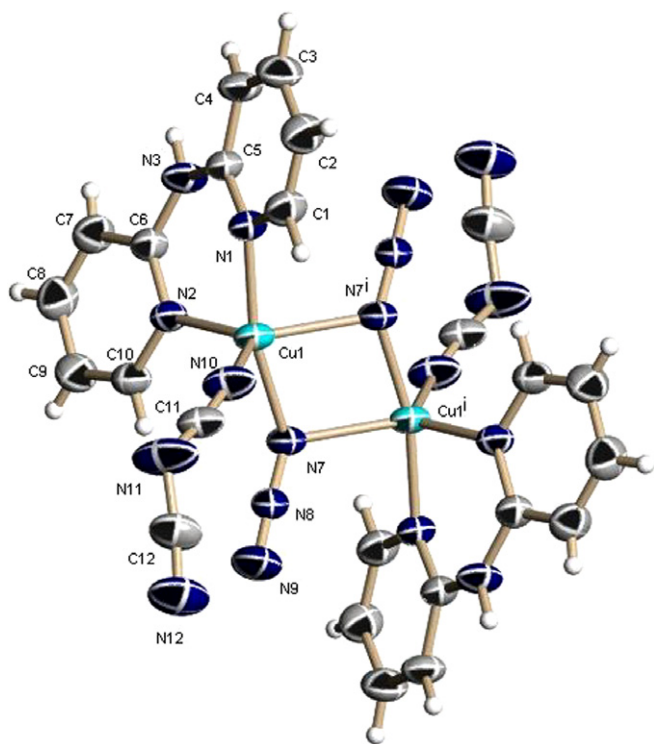


Fig. 3. The molecular structure of **2** with 30% probability displacement ellipsoids. Selected bond lengths (Å) and angles (°): Cu1–N1 1.9903(15), Cu1–N2 2.0456(16), Cu1–N7 1.9990(16), Cu1–N7ⁱ 2.1906(18), Cu1–N10 2.0085(18), N1–Cu1–N7 166.02(7), N10–Cu1–N2 122.22(8), N1–Cu1–N10 95.23(7), N1–Cu1–N7ⁱ 88.09(6), N7–Cu1–N10 92.70(8), N7–Cu1–N7ⁱ 78.00(7), N1–Cu1–N2 90.58(6), N10–Cu1–N7ⁱ 118.65(8), N7–Cu1–N2 94.91(7), N2–Cu1–N7ⁱ 118.96(7) Symmetry codes: (i) $-x + 1, -y + 2, -z$.

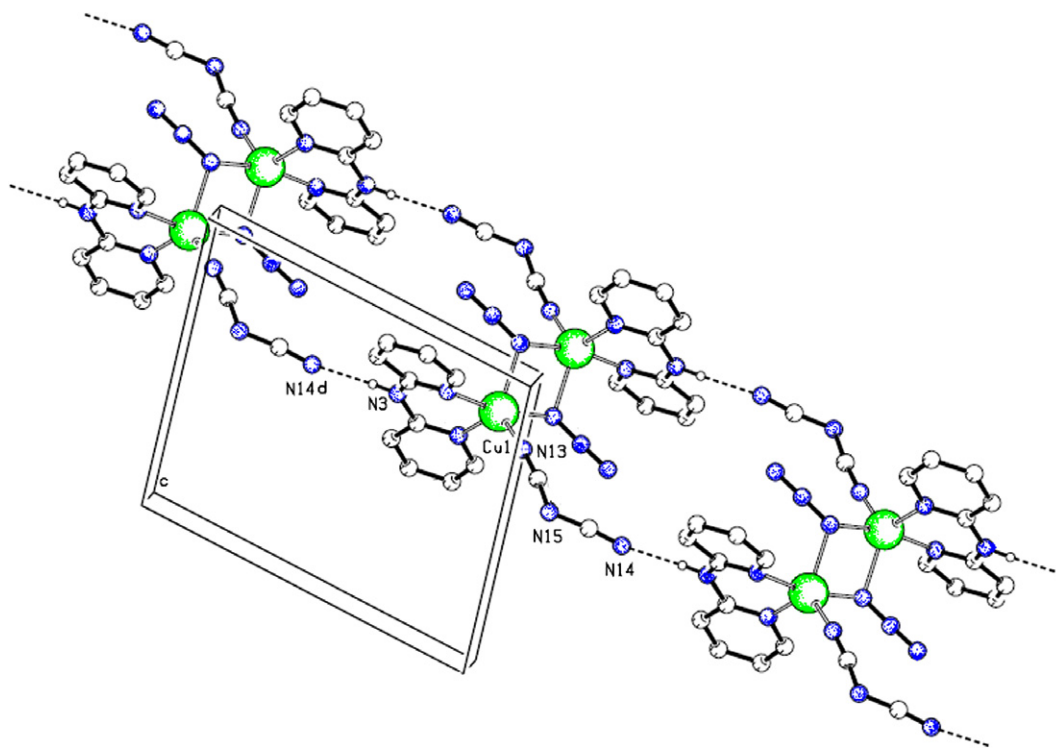


Fig. 4. Packing diagram of **2** with hydrogen bond (dash-lines), showing the one-dimensional structure.

cooling, this value stays almost constant till about 50 K, where it increases gradually to reach $1.84 \mu_B$, at 7 K and then decreases to $1.82 \mu_B$ at 5 K. This magnetic behaviour is typical for very weak ferromagnetically coupled Cu(II) ions in a dinuclear compound.

The theoretical expression for the magnetic susceptibility is based on the general Hamiltonian [31] is: $H_{\text{ex}} = -JS_1S_2$, in which the exchange parameter J , is negative for antiferromagnetic and positive for ferromagnetic interactions. The magnetic data were fitted to the equation given in the literature for dinuclear copper compounds [31]:

$\chi_m = (2Ng^2\beta^2)[kT - (2zJ'/(3 + \exp(-J/kT)))]^{-1} [3 + \exp(-J/kT)]^{-1} + \text{TIP}$, in which N , g , β , k and T have their usual meanings. The parameter zJ' denotes the interaction between neighbouring dinuclear identities. A temperature independent paramagnetism (TIP) was also considered and fixed at 60×10^{-6} per copper ion. The fit was accomplished by minimization of $R = \sum (\chi_m \cdot T_{\text{calc}} - \chi_m \cdot T_{\text{obs}})^2 / (\chi_m \cdot T_{\text{obs}})^2$ by least-squares procedure.

The best fit was obtained for compound **2** with values of $J = +5.8 \text{ cm}^{-1}$, $g = 2.02$, $zJ' = -2.8 \text{ cm}^{-1}$, $p = 0.06$, with a final R of 9×10^{-4} (see solid line in Fig. 5). These values are in agreement with the structural results. These values are also in accordance with another azido/dpyam compound, $[\text{Cu}_2(\text{N}_3)_2(\text{O}_2\text{CCH}_2\text{CH}_3)_2(\text{dpyam})_2]$, which has a J of $+5.1 \text{ cm}^{-1}$, although the structural parameter τ is 0.30 in this case and the Cu–N–Cu angle differs (96.3° against 102.0° for compound **2**).

A number of non symmetrical double “EO” azido-bridged dinuclear Cu(II) compounds have been structurally and magnetically described. Some selected structural and magnetic data for these compounds are summarized in Table 1. In most of these compounds, the metal ion assumes a penta-coordinated square pyramidal coordination geometry with different degrees of distortion towards trigonal bipyramidal geometry, and the azido bridge adopts a basal–apical asymmetric disposition between metal ions. Although the Cu–N–Cu angles (86 – 105°) for all these compounds are smaller than 108° , the magnetic interactions between Cu(II) ions vary from antiferromagnetic to ferromagnetic, suggesting that the angular dependence proposed for symmetric azido bridges with basal–basal configuration

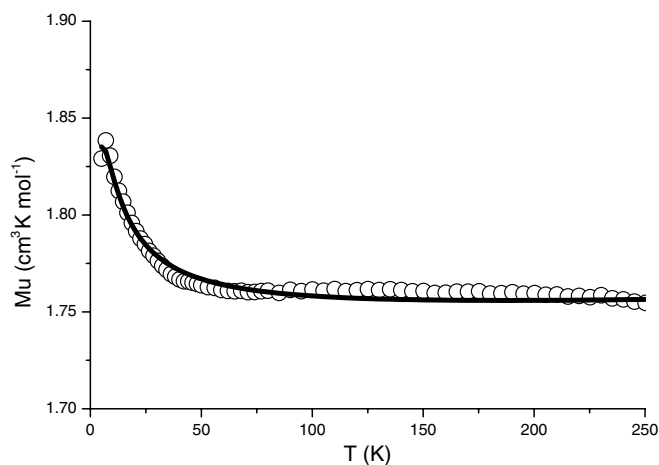


Fig. 5. A plot of the temperature dependence of μ_{eff} versus T per Cu(II) ion for compound **2**. The solid line represents the calculated curve (see text).

Table 1

Selected magneto-structural data for non-symmetrical double end-on azido-bridged dinuclear copper(II) compounds

Dinuclear compounds ^a	Geometry ^b	τ	Configuration mode of the bridge ^c	Cu–Cu (Å)	Cu–N(azido) (Å)	Cu–N–Cu (°)	J (cm ^{−1})	Ref.
[Cu ₂ (N ₃) ₂ (L) ₂]	SP	0.177	ax–eq	3.166	2.551, 2.019	86.9	24	[32]
[Cu ₂ (N ₃) ₄ (phen) ₂] _n	SP	0.068	ax–eq	3.396	2.449, 1.994	99.19	12.76	[13]
[Cu ₂ (N ₃) ₂ (phen) ₂](μ-ta)	SP	0.088	ax–eq	2.737	2.461, 1.984	94.89	12.36	[36]
[Cu ₂ (N ₃) ₂ (L [−]) ₂](ClO ₄) ₂	SP	0.015	ax–eq	3.391		96.7	Weak F	[37]
[Cu ₂ (N ₃) ₄ (aepl) ₂]	SP	0.15	ax–eq	3.348	2.381, 2.016	98.84	−3.06	[35]
[Cu ₂ (N ₃) ₂ L ^a ₂]	SP	0.177	ax–eq	3.181	2.505, 1.998	89.1	−8.5	[18]
[Cu ₂ (N ₃) ₄ (L ₁) ₂]	SP	0.26	ax–eq	3.318	2.475, 2.060	93.60	2.9	[19]
[Cu ₂ (N ₃) ₄ (L ₂) ₂]	SP	0.02	ax–eq	3.193	2.440, 2.039	90.50	−1.8	[19]
[Cu ₂ (N ₃) ₄ (L ₃) ₂]	SP	0.17	ax–eq	3.161	2.546, 2.020	86.82	−3.1	[19]
[Cu ₂ (N ₃) ₄ (L ¹) ₂]	SP	0.13	ax–eq	3.106	2.443, 1.999	88.3	−2.63	[33]
[Cu ₂ (N ₃) ₄ (L ²) ₂]	SP	0.23	ax–eq	3.232	2.447, 1.985	93.0	−1.79	[33]
[Cu ₂ (N ₃) ₄ (L ³) ₂]	SP	0.21	ax–eq	3.273	2.550, 2.016	90.8	−5.37	[33]
[Cu ₂ (N ₃) ₂ (Medien) ₂](ClO ₄) ₂	SP	0.367	ax–eq	3.343	2.513, 2.098	92.5	−16.8	[34]
[Cu ₂ (N ₃) ₂ (O ₂ CCH ₂ CH ₃) ₂ (dpyam) ₂]	SP	0.30	ax–eq	3.25	2.348, 2.006	96.3	+5.1	[23]
[Cu ₂ (N ₃) ₄ (DMP) ₂]	TBP	0.64	ax–eq	3.32	2.245, 1.996	103.05	−27.6	[20]
[Cu ₂ (N ₃) ₂ (C ₂ N ₃) ₂ (dpyam) ₂] (2)	TBP	0.73	ax–eq	3.258	2.191, 1.999	102.0	+5.8	This work
[Cu ₂ (N ₃) ₂ (O ₂ CH) ₂ (dpyam) ₂]	SP	0.38	eq–eq	3.19	2.143, 1.991	101.1	+63.3	[23]
[Cu ₂ (N ₃) ₂ (O ₂ CCH ₃) ₂ (dpyam) ₂]	SP	0.48	eq–eq	3.20	2.143, 1.997	101.2	+63.8	[23]

^a L = 7-amino-4-methyl-5-aza-3-hepten-2-onato(1[−]); phen = 1,10-phenanthroline; ta = terephthalato dianion; L[−] = 1-(imidazol-4-yl)-2-([2-pyridylmethylene]amino)ethane; aepl = 1-(2-aminoethyl)piperidine; L^a = 1-(*N*-salicylideneamino)-2-aminoethane; L₁ = 8-amino-4-methyl-5-azaoct-3-en-2-one; L₂ = *N*-(3-aminopropyl)salicylaldimine; L₃ = 7-amino-4-methyl-5-azahept-3-en-2-one; HL¹ = *N*-[2-(ethylamino)ethyl]salicylaldimine; HL² = 7-(ethylamino)-4-methyl-5-azahept-3-en-2-one; HL³ = 7-amino-4-methyl-5-azaoct-3-en-2-one; Medien = methyldiethylenetriamine; DMP = 2-(3,5-dimethylpyrazol-1-ylmethyl)pyridine.

^b SP = square pyramid, TBP = trigonal bipyramid.

^c eq = equatorial, ax = axial.

is not valid for asymmetric bridges with basal–apical disposition.

In summary, a new “EO” azido-bridged Cu(II) dinuclear compound with the trigonal bipyramidal geometry was obtained, with a weak ferromagnetic interaction between the Cu(II) ions. From this study and also from the related compounds [32–37] in Table 1, it can be concluded that compounds with a distorted trigonal bipyramidal geometry and a basal–apical disposition could also exhibit the magnetic interaction between Cu(II) ions vary from weak antiferromagnetic to weak ferromagnetic and there is no direct correlation visible between the J value and the structural parameters, except for the case where azide is bridging equatorial to both Cu(II) ions, where J ca. +63 cm^{−1}.

Supplementary material

Solid-state (diffuse reflectance) electronic spectra were measured as polycrystalline samples on a Perkin–Elmer Lambda2S spectrophotometer, in the range of 8000–18,000 cm^{−1}. The X-band powder EPR spectra were obtained as polycrystalline samples with a JEOL RE2X electron spin resonance spectrophotometer with DPPH ($g = 2.0036$) as a reference. Magnetic susceptibility measurements (5–250 K) were carried out using a Quantum design MPMS-5S SQUID magnetometer (measurements carried out at 0.1 mT). Data were corrected for magnetization of the sample holder and for diamagnetic contributions, which were estimated from the Pascal constants. CCDC

630417 and 630418 contain the supplementary crystallographic data for **1** and **2**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

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- [25] *Synthesis of the compounds*: Compound **1** was obtained as a side product in the preparation of $[\{\text{Cu}(\text{acac})\text{dpyam}\}_2(\mu\text{-N}_3)]_3 \cdot (\text{ClO}_4)$ by adding $[\text{Cu}(\text{acac})(\text{dpyam})(\text{OH}_2)_2] \cdot \text{ClO}_4$ (1.0 mmol) to a warm solution of NaN_3 (0.5 mmol) in DMF (5 ml). The resulting green solution was allowed to evaporate slowly at room temperature. After several days, green crystals were formed. Anal. Calcd. for $\text{C}_{15}\text{H}_{16}\text{CuN}_6\text{O}_2$: C, 47.93; H, 4.29; N, 22.36. Found: C, 47.82; H, 4.18; N, 22.40. Compound **2** was prepared by stirring for 5 min a solution containing $\text{Cu}(\text{ClO}_4) \cdot 6\text{H}_2\text{O}$ (0.5 mmol), di-2-pyridylamine (0.5 mmol), $\text{NaN}(\text{CN})_2$ (0.5 mmol) and NaN_3 (0.5 mmol) in a methanol/DMF mixture (20 ml, 1:1 v:v). Then 5 ml of DMF was added to the resulting solution and the solution was allowed to stand for slow evaporation at room temperature. After 3 days, brown crystals were formed. Anal. Calcd. for $\text{C}_{24}\text{H}_{18}\text{Cu}_2\text{N}_{18}$: C, 42.00; H, 2.65; N, 36.77. Found: C, 41.87; H, 2.54; N, 37.02.
- [26] *X-ray crystallography*: Crystal data for **1**: $\text{C}_{15}\text{H}_{16}\text{CuN}_6\text{O}_2$ ($M_w = 375.88$), Triclinic, $P\bar{1}$, $a = 9.2707(3)$, $b = 13.2133(4)$, $c = 13.9036(5)$ Å, $\alpha = 83.986(1)^\circ$, $\beta = 77.018(1)^\circ$, $\gamma = 80.910(1)^\circ$, $V = 1634.52(9)$ Å³, $T = 273(2)$ K, $Z = 4$, $D_c = 1.527$ mg/m³, $m = 1.36$ mm⁻¹, $F(000) = 772$, $k(\text{Mo K}\alpha) = 0.71073$ Å, 11,916 reflections measured ($1.51 < h < 30.45^\circ$), 9935 unique ($R_{\text{int}} = 0.016$), $R1 = 0.0360$, $wR2 = 0.0936$. For **2**: $\text{C}_{24}\text{H}_{18}\text{Cu}_2\text{N}_{18}$ ($M_w = 685.64$), Triclinic, $P\bar{1}$, $a = 6.91490(10)$, $b = 9.54880(10)$, $c = 11.4267(2)$ Å, $\alpha = 2.3960(10)^\circ$, $\beta = 75.7700(10)^\circ$, $\gamma = 75.1120(10)^\circ$, $V = 683.347(17)$ Å³, $T = 293(2)$ K, $Z = 1$, $D_c = 1.527$ mg/m³, $m = 1.36$ mm⁻¹, $F(000) = 346$, $k(\text{Mo K}\alpha) = 0.71073$ Å, 4963 reflections measured ($1.90 < h < 30.46^\circ$), 4149 unique ($R_{\text{int}} = 0.015$), $R1 = 0.0314$, $wR2 = 0.0876$. Reflection data for the two compounds were collected on a 1 K Bruker SMART CCD area-detector diffractometer. Data reduction and cell refinements were performed using the program SAINT [Bruker, 1997b. SAINT (Version 4.05). Bruker AXS Inc., Madison, Wisconsin, USA]. An empirical absorption correction by using the SADABS [G.M. Sheldrick, 2000. SADABS. University of Göttingen, Germany] program was applied, which resulted in transmission coefficients ranging from 0.575 to 1.000 and 0.708 to 1.000 for **1** and **2**, respectively. The structure was solved by direct methods and refined by full-matrix least-squares method on $(F_o)^2$ with anisotropic thermal parameters for all non-hydrogen atoms using the SHELXTL-PC [G.M. Sheldrick, 2000. SHELXTL. Version 6.12. Bruker AXS Inc., Madison, Wisconsin, USA] software package. In compound **1**, the H atoms attached to C13 and C28 were located in a difference Fourier map and were refined with a DFIX restraint of C–H = 0.92 (1) Å. The other H atoms were placed in idealized positions and constrained to ride on their parent atoms, with C–H distances in the range of 0.93–0.96 Å and N–H distance of 0.86 Å. The N12 of the azido group found to be disordered; the occupancies of the disordered positions were initially refined and later fixed at 0.5 and 0.5. In compound **2**, the H atom attached to the N atom of amide was located in a difference Fourier map and was refined with a DFIX restraint of N–H = 0.87 (1) Å. The other H atoms were placed in idealized positions and constrained to ride on their parent atoms, with C–H distances of 0.93 Å. The molecular graphics were created by using SHELXTL-PC.
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Crystal structures, spectro-structural correlation and structural pathways of eight $[\text{Cu}(\text{dpyam})_2(\text{NCO})][\text{Y}]$ complexes (dpyam = di-2-pyridylamine), $\text{Y} = \text{Br}^-$, CF_3SO_3^- , $\text{BF}_4^- \cdot \text{dpyam}$, $\text{Cl}^- \cdot 4\text{H}_2\text{O}$, NO_3^- , PF_6^- , ClO_4^- and BPh_4^-

Sujittra Youngme^{a,*}, Jaturong Phatchimkun^a, Unchulee Suksangpanya^a,
Chaveng Pakawatchai^b, Narongsak Chaichit^c, Palangpon Kongsaree^d,
Jurek Krzystek^e, Brian Murphy^f

^a Department of Chemistry, Faculty of Science, Khon Kaen University, Khon Kaen 40002, Thailand

^b Department of Chemistry, Faculty of Science, Prince of Songkla University, Hatyai, Songkla 90112, Thailand

^c Department of Physics, Faculty of Science and Technology, Thammasat University Rangsit, Pathumthani 12121, Thailand

^d Department of Chemistry, Faculty of Science, Mahidol University, Bangkok 10400, Thailand

^e National High Magnetic Field Laboratory, Florida State University, Tallahassee, FL 32310, United States

^f Department of Chemistry, College of Science, United Arab Emirates University, P.O. Box 17551, Al-Ain, United Arab Emirates

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Abstract

The crystal structures of eight new $[\text{Cu}(\text{dpyam})_2(\text{NCO})][\text{Y}]$ complexes which $\text{Y} = \text{Br}^-$ (**1**), CF_3SO_3^- (**2**), $\text{BF}_4^- \cdot \text{dpyam}$ (**3**), $\text{Cl}^- \cdot 4\text{H}_2\text{O}$ (**4**), NO_3^- (**5**), PF_6^- (**6**), ClO_4^- (**7**) and BPh_4^- (**8**), respectively have been determined by X-ray crystallography. Five of the complexes, **1–5** ($\tau = 0.09\text{--}0.30$) have a $\text{CuN}_4\text{N}'$ chromophore with a trigonal bipyramidal distorted square based pyramidal (TBDSBP) stereochemistry, **6** and **7** ($\tau = 0.53\text{--}0.54$) involve an intermediate five-coordinate stereochemistry, while **8** ($\tau = 0.76$) involves a square base pyramidal distorted trigonal bipyramidal (SBPDTB) stereochemistry. The structures of **1–8** are compared by scatter-plot analysis with $[\text{Cu}(\text{dpyam})(\text{NCO})][\text{SO}_4]_{0.5} \cdot \text{dpyam} \cdot 0.5\text{H}_2\text{O}$ (**9**), the only complex of known crystal structure within this series reported to date. Scatter plots of the cations distortion isomers of the $[\text{Cu}(\text{dpyam})_2(\text{NCO})][\text{Y}]$ series of complexes suggests that all nine complexes lie on a common structural pathway, involving a mixture of symmetric, ν_{sym} , C_2 mode and asymmetric, ν_{asym} , non- C_2 modes of vibration of the $\text{CuN}_4\text{N}'$ chromophore. The resulting linear and parallel structural pathways are consistent with the *direct* observation of the effect of vibronic coupling on the stereochemistries of the complexes, which can range from SBPDTB to TBDSBP which correlate with electronic spectral data. The EPR spectra (K-band and V-band) of complexes **1–7** are in rhombic type, while complex **8** is axial with $g_{\perp} = 2.185$ and $g_{\parallel} = 2.005$, consistent with a $d_{x^2-y^2}$ ground state for the approximately trigonal bipyramidal stereochemistry of the $\text{CuN}_4\text{N}'$ chromophore. These are in agreement with electronic reflectance spectra of the complexes and correspond to their stereochemistries.
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Keywords: Crystal structures; Copper(II); Five-coordinate; Scatter-plot; EPR

1. Introduction

One of the consequences of the Jahn-Teller theorem [1] in the stereochemistry of the copper(II) ion has been termed the plasticity effect [2] which suggests that the various distortion isomers of the copper(II) ion are related

* Corresponding author. Fax: +66 43 202 373.

E-mail address: sujittra@kku.ac.th (S. Youngme).

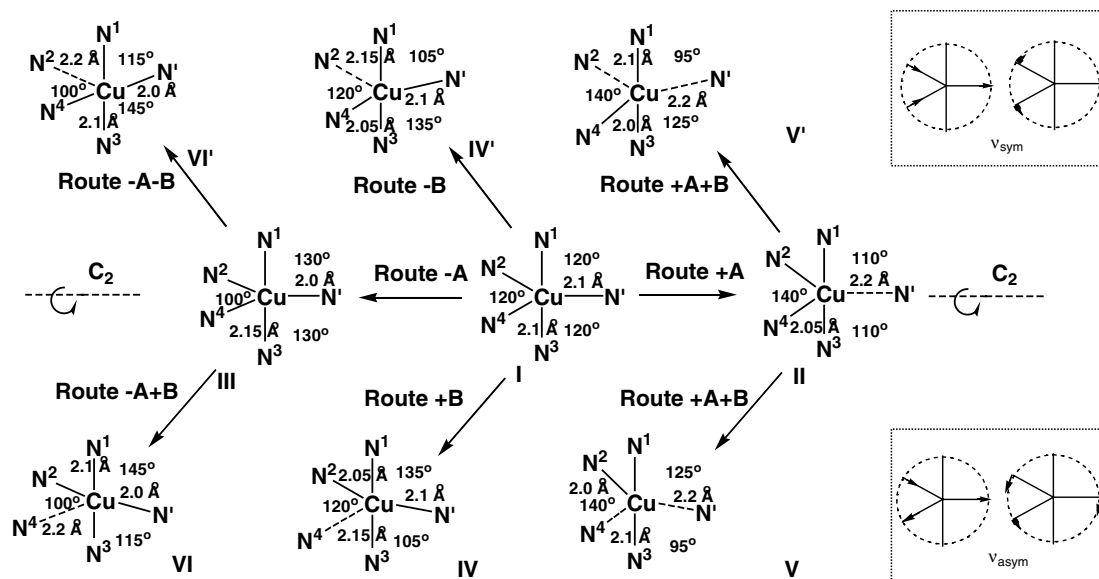


Fig. 1. The forms of distortion of the RTB $\text{CuN}_4\text{N}'$ chromophore involving the $\pm A$, $\pm B$ and $\pm A \pm B$ routes.

by soft modes of vibration of the more regular stereochemistries. Hence, the concept of a structural pathway [3–5], Fig. 1, for $[\text{Cu}(\text{chelate})_2\text{X}][\text{Y}]$ type complexes has been developed.

In 1984, Addison, Reedijk and co-workers introduced a very useful parameter, τ , which provides a measure of the degree of square-based pyramidal (SBP) versus trigonal bipyramidal (TBP) geometry adopted by five-coordinate $\text{Cu}(\text{II})$ complexes [6]. This parameter provides a convenient tool for comparing structures of similar five-coordinate $\text{Cu}(\text{II})$ complexes. The parameter τ is defined as $(\beta - \alpha)/60$, where β and α are the largest coordination angles, and its value varies from 0 (in regular SBP) to 1 (in regular TBP). The molecular structures of five-coordinate copper(II) complexes range extensively from regular trigonal bipyramidal (RTBP, D_{3h}) to regular square based pyramidal (RSBP, C_{4v}) with most complexes falling between these two stereochemistries [7], somewhere along the classical Berry pathway [6,8]. This feature can be useful in probing the relationships between structural correlations and the respective structural pathway involving vibronic type coupling.

In the majority of $[\text{Cu}(\text{chelate})_2\text{X}][\text{Y}]$ complexes the differences in stereochemistry may be associated with the differences in the ligands present i.e. chelate = 2,2'-bipyridine (bipy), 1,10-phenanthroline (phen) and di-2-pyridylamine (dpyam) and $\text{X} = \text{Cl}^-$, Br^- , I^- or H_2O , respectively. A number of structural pathways of various copper(II) five-coordinate series, $[\text{Cu}(\text{bipy})_2\text{X}][\text{Y}]$ and $[\text{Cu}(\text{phen})_2\text{X}][\text{Y}]$ have now been reported in the literature [3,9]. These systems represent various types of structural pathways and such structural correlations have been found to be consistent with spectroscopic data involving EPR and electronic reflectance spectra. However, structural studies and structural correlations involving five-coordinate complexes containing the more flexible dpyam ligand and a

pseudohalide, such as NCO^- have not been reported to date in the literature. Moreover, the square pyramidal geometry in new dpyam complexes is inherently different than previously reported five-coordinate square pyramidal geometries involving copper(II) and other chelate ligands [3,9]. The axial position of the square pyramid in this complex series is the occupied by dpyam nitrogen which is different from those of the bipy and phen series to which the halide or H_2O is occupied. Hence, it is of interest to look at potential structural correlations and investigate the existence of a potential structural pathway for the series of five-coordinate copper(II) complexes of the type, $[\text{Cu}(\text{dpyam})_2(\text{NCO})][\text{Y}]$.

2. Experimental

2.1. General

The ligand, di-2-pyridylamine and all reagents are commercial grade materials and were used without further purification. IR spectra were recorded on a Perkin–Elmer Spectrum One FT-IR spectrophotometer as KBr disc in the 450–4000 cm^{-1} spectral range. Solid-state (diffuse reflectance) electronic spectra were measured as polycrystalline samples on a Perkin–Elmer Lambda 2S spectrometer, over the range 8000–18000 cm^{-1} . X-band electron paramagnetic resonance (EPR) measurements were performed at room temperature on a JEOL RE2X spectrometer, using DPPH ($g = 2.0036$) as a standard. Higher EPR frequencies were employed in experiments conducted at 77 K: K-band (~ 27 GHz), V-band (~ 54 GHz) and W-band (~ 100 GHz). In this case a transmission single-pass home-made spectrometer based on a superconducting magnet was used [10]. Elemental analyses (C, H, N) were determined on a Perkin–Elmer PE2400 CHNS/O.

$[Cu(dpyam)_2(NCO)](Br)$ (**1**): A warm solution of di-2-pyridylamine (0.171 g, 1.0 mmol) in methanol (15 cm³) was added to a hot aqueous solution (15 cm³) of CuBr₂ (0.071 g, 0.5 mmol). Solid KNCO (0.162 g, 2.0 mmol) was then added to the reaction mixture. The solution was allowed to evaporate at room temperature in air. Dark green needle-like crystals of **1** deposited after three days. The crystals were filtered off, washed with mother liquor and air-dried. Yield: ca. 95%. *Anal.* Calc. for C₂₁H₁₈N₇CuOBr: C, 47.78; H, 3.44; N, 18.57. Found: C, 47.84; H, 3.35; N, 18.70%.

$[Cu(dpyam)_2(NCO)](CF_3SO_3)$ (**2**): A warm solution of di-2-pyridylamine (0.171 g, 1.0 mmol) in methanol (15 cm³) was added to a hot aqueous solution (15 cm³) of Cu(CF₃SO₃)₂ (0.181 g, 0.5 mmol). An aqueous solution (20 cm³) of KNCO (0.162 g, 2.0 mmol) was then added. The green solution was slowly evaporated at room temperature. After several days, dark green needle-like crystals of **2** formed. The crystals were filtered off, washed with mother liquor and air-dried. Yield: ca. 60%. *Anal.* Calc. for C₂₂H₁₈N₇CuO₄F₃S: C, 44.26; H, 3.03; N, 16.42. Found: C, 43.98; H, 2.98; N, 16.29%.

$[Cu(dpyam)_2(NCO)](BF_4) \cdot dpyam$ (**3**): A warm solution of di-2-pyridylamine (0.171 g, 1.0 mmol) in methanol (15 cm³) was added to a hot aqueous solution (15 cm³) of Cu(BF₄)₂ · nH₂O (0.118 g, 0.5 mmol). An aqueous solution (10 cm³) of KNCO (0.081 g, 1.0 mmol) was then added to the reaction mixture. The green solution was slowly evaporated at room temperature. Green needle-like crystals of **3** deposited after several days. The crystals were filtered off, washed with mother liquor and air-dried. Yield: ca. 75%. *Anal.* Calc. for C₃₁H₂₇N₁₀CuOBF₄: C, 52.74; H, 3.85; N, 19.84. Found: C, 53.08; H, 4.00; N, 19.67%.

$[Cu(dpyam)_2(NCO)](Cl) \cdot 4H_2O$ (**4**): A warm solution of di-2-pyridylamine (0.171 g, 1.0 mmol) in methanol (15 cm³) was added to a boiling aqueous solution (15 cm³) of CuCl₂ · 2H₂O (0.085 g, 0.5 mmol). KNCO (0.041 g, 0.5 mmol) was then added to the reaction mixture. The green solution was slowly evaporated at room temperature. After two weeks, green needle-like crystals of **4** formed. The crystals were filtered off, washed with mother liquor and air-dried. Yield: ca. 78%. *Anal.* Calc. for C₂₁H₂₆N₇CuO₅Cl: C, 45.41; H, 4.71; N, 17.65. Found: C, 45.28; H, 4.57; N, 17.67%.

$[Cu(dpyam)_2(NCO)](NO_3)$ (**5**): A warm solution of di-2-pyridylamine (0.171 g, 1.00 mmol) in methanol (15 cm³) was added to a hot aqueous solution (10 cm³) of Cu(NO₃)₂ · 3H₂O (0.121 g, 0.5 mmol). Solid KNCO (0.081 g, 1.0 mmol) was then added. The green solution was slowly evaporated at room temperature. After several days dark green-like rod-shaped crystals of **5** formed. The crystals were filtered off, washed with mother liquor and air-dried. Yield: ca. 88%. *Anal.* Calc. for C₂₁H₁₈N₈CuO₄: C, 52.80; H, 3.32; N, 20.05. Found: C, 52.56; H, 3.24; N, 20.17%.

$[Cu(dpyam)_2(NCO)](PF_6)$ (**6**): A warm solution of di-2-pyridylamine (0.17 g, 1.00 mmol) in methanol (15 cm³)

was added to a hot aqueous solution (10 cm³) containing Cu(CH₃COO)₂ · nH₂O (0.091 g, 0.5 mmol) and KNCO (0.081 g, 1.0 mmol). An aqueous solution (15 cm³) of KPF₆ (0.184 g, 1.0 mmol) was then added. The green solution was slowly evaporated at room temperature. After several days, green rod-shaped crystals of **6** formed. The crystals were filtered off, washed with mother liquor and air-dried. Yield: ca. 90%. *Anal.* Calc. for C₂₁H₁₈N₇CuO · PF₆: C, 45.83; H, 2.88; N, 15.59. Found: C, 45.65; H, 2.77; N, 15.46%.

$[Cu(dpyam)_2(NCO)](ClO_4)$ (**7**): A warm solution of di-2-pyridylamine (0.171 g, 1.0 mmol) in methanol (15 cm³) was added to a hot aqueous solution (10 cm³) of Cu(ClO₄)₂ · nH₂O (0.185 g, 0.5 mmol). An aqueous solution (15 cm³) of KNCO (0.081 g, 1.0 mmol) was then added. The dark green solution was slowly evaporated at room temperature. After a week, dark green needle-like crystals of **7** formed. The crystals were filtered off, washed with mother liquor and air-dried. Yield: ca. 75%. *Anal.* Calc. for C₂₁H₁₈N₇CuO₅Cl: C, 49.41; H, 3.11; N, 16.80. Found: C, 49.58; H, 2.99; N, 16.68%. *Caution:* perchlorates are explosive!

$[Cu(dpyam)_2(NCO)](BPh_4)$ (**8**): A warm solution of di-2-pyridylamine (0.171 g, 1.0 mmol) in methanol (15 cm³) was added to a hot aqueous solution (10 cm³) of Cu(CH₃COO)₂ · nH₂O (0.091 g, 0.5 mmol). Solid KNCO (0.081 g, 1.00 mmol) and solid of NaBPh₄ (0.342 g, 1.0 mmol) were then added to the reaction mixture. The green solution was slowly evaporated at room temperature. After two weeks, green rod-shaped crystals of **8** formed. The crystals were filtered off, washed with mother liquor and air-dried. Yield: ca. 80%. *Anal.* Calc. for C₄₅H₃₈N₇CuOB: C, 70.45; H, 4.99; N, 12.78. Found: C, 70.47; H, 5.00; N, 13.01%.

2.2. Crystallography

The X-ray single-crystal data of complexes **1–3** and **5–8** were collected at 293 K on a 4 K Bruker SMART CCD area-detector diffractometer rotating anode, graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å) using the SMART program [11]. Data reduction and cell refinements were performed using the program SAINT [12]. An empirical absorption correction was applied using the SADABS [13] program, which resulted in transmission coefficients ranging from 0.854 to 1.000 for **1**, 0.402 to 1.000 for **2**, 0.774 to 1.000 for **3**, 0.811 to 1.000 for **5**, 0.890 to 1.000 for **6**, 0.834 to 1.000 for **7** and 0.898 to 1.000 for **8**. The unit-cell parameters of complex **4** were determined and the intensity data collected on an Enraf-Nonius MACH3 diffractometer with Mo K α radiation ($\lambda = 0.70183$ Å) at 298 K. An absorption correction was performed using the ψ -scan program, which resulted in transmission coefficients ranging from 0.904 to 1.000.

All eight structures were solved by direct methods and refined by full-matrix least-squares method on (F_{obs})² with

anisotropic thermal parameters for all nonhydrogen atoms using the SHELXTL-PC V 6.12 [14] software package. All hydrogen atoms in **1–8** were located by difference synthesis and refined isotropically, except the hydrogen atoms of the water molecules in **4**, which we were unable to locate and not fix. The molecular graphics were created using SHELXTL-PC. The O atom in isocyanato group of **2** and **3** showed disorder; the occupancies of the disordered positions were initially refined and later fixed at 0.5 and 0.5 for **2** and 0.7 and 0.3 for **3**. The F and O atoms of the trifluoromethanesulfonate group of **2** showed disorder; the occupancies of the disordered positions were initially refined and later fixed at 0.5 and 0.5, respectively. The F atoms of the tetrafluoroborate group of **3** and hexafluorophosphate group of **6** also showed disorder. They were divided into two sets with occupancies of 0.5 and 0.5. The O atoms of the perchlorate group of **7** showed disorder; the occupancies of the disordered positions were initially refined and later fixed at 0.5 and 0.5, respectively. The crystal and refinement details for complexes **1–8** are listed in Table 1. Selected bond lengths and bond angles are given in Table 2. Fig. 2 shows a representative molecular structure for the $[\text{Cu}(\text{dpyam})_2(\text{NCO})]^+$ cation, the atomic numbering scheme and the angle notation used.

3. Results and discussion

3.1. Crystal structures

The asymmetric unit of complexes **1–8** involves a $[\text{Cu}(\text{dpyam})_2(\text{NCO})]^+$ cation and Br^- , CF_3SO_3^- , BF_4^- , dpyam , $\text{Cl}^- \cdot 4\text{H}_2\text{O}$, NO_3^- , PF_6^- , ClO_4^- and BPh_4^- anions, respectively in the lattice. In addition, **3** and **4** involve one dpyam molecule and four water molecules in the unit cell, respectively. None of the anions or water molecules is close enough ($<3.0 \text{ \AA}$) to be considered even weakly semi-coordinated to the copper(II) cation [15]. The structure of the cations all involve a five-coordinate $\text{CuN}_4\text{N}'$ chromophore, with a square pyramidal stereochemistry having a trigonal bipyramidal distorted square based pyramidal stereochemistry (TBDSBP) in **1–5**, an intermediate five-coordinate stereochemistry for **6** and **7**, and a square based pyramidal distortion (SBPDTB) for **8**. All eight complexes are further examples of distortion isomers of the $[\text{Cu}(\text{dpyam})_2(\text{NCO})]^+$ cation, whose stereochemistries are related by the structural pathways of Fig. 1. No attempt will be made to describe the individual structures of complexes **1–8**, Table 2, but scatter-plot analysis will be used to compare their structures with that of $[\text{Cu}(\text{dpyam})_2(\text{NCO})(\text{SO}_4)_{0.5} \cdot \text{dpyam} \cdot 0.5\text{H}_2\text{O}$ (**9**) the only other complex of known crystal structure [16]. Table 2 summarises the selected bond lengths and angles of all eight complexes, sequenced in order of their τ values, where $\tau = (\alpha_8 - \alpha_1)/60$ [6], and Table S1 summarises the maximum, minimum, difference (Δ) and average bond length and bond angle values for the series of nine $[\text{Cu}(\text{dpyam})_2-$

$(\text{NCO})][\text{Y}]$ complexes. Table S3 gives the sums of the in-plane bond angles, and bond distances, $\text{Cu}-\text{N}(2)$, $\text{Cu}-\text{N}(4)$ and $\text{Cu}-\text{N}'$, respectively.

3.2. The $[\text{Cu}(\text{dpyam})_2(\text{NCO})][\text{Y}]$ data

The structures of the nine five-coordinate $\text{CuN}_4\text{N}'$ chromophores vary from TBP to near SBP, reflected in a range of τ values of 0.76–0.09, $\Delta\tau = 0.67$. This is a substantial variation in τ , the largest seen to date for the cation distortion isomers of the $[\text{Cu}(\text{dpyam})_2\text{X}][\text{Y}]$ series of complexes [17]. None of the complexes has a near RTB (regular trigonal bipyramidal) stereochemistry or lies on a twofold axis of symmetry. Six complexes (**1–5** and **9**) have τ values in the more limited range of 0.09 to 0.31 and their stereochemistries are best described as TBDSBP. Complexes **6** and **7** have τ values of 0.53 and 0.54 and their stereochemistries are best described as intermediate five coordinate. Complex **8** has a τ value of 0.76 and its stereochemistry is best described as SBPDTB.

Relative to a RTB stereochemistry, the out-of-plane distances, Table 2, show only small differences, Table S1, with $\Delta\text{Cu}-\text{N}(1) = 0.030 \text{ \AA}$ and $\Delta\text{Cu}-\text{N}(3) = 0.044 \text{ \AA}$. The largest variations in bond lengths are present in the equatorial bond distances $\text{Cu}-\text{N}(4)$, $\text{Cu}-\text{N}'$ and $\text{Cu}-\text{N}(2)$, respectively. The $\text{Cu}-\text{N}(4)$ distances show the largest variation ranging from 2.089(1) to 2.283(3) $\text{\AA}$, with $\Delta = 0.194 \text{ \AA}$ and with an average value = 2.182(3) $\text{\AA}$. The $\text{Cu}-\text{N}(2)$ distances vary from 2.014(10) to 2.074(2) $\text{\AA}$, with $\Delta = 0.060 \text{ \AA}$ and with a mean value = 2.044(2) $\text{\AA}$. The $\text{Cu}-\text{N}'$ distances range from 1.903(3) to 1.984(1) $\text{\AA}$, with $\Delta = 0.081 \text{ \AA}$ and with an average value = 1.947(1) $\text{\AA}$. The average of the in-plane $\text{Cu}-\text{N}(2,4,\text{N}')$ distances, 2.057(2) $\text{\AA}$, is greater than the average of the axial $\text{Cu}-\text{N}(1,3)$ distances, 2.015(1) $\text{\AA}$, by 0.042 $\text{\AA}$, consistent with a TB stereochemistry and slightly lesser than the difference of 0.1 $\text{\AA}$ normally observed [18]. The out-of-plane bond angles, Table 2, show only small differences, Table S1, with $\Delta\alpha_{4-7}$ and $\Delta\alpha_{8-10}$ ranging from 3.6° to 6.5° and 6.2–15.4°, respectively. The α_1 in-plane angles show the largest variation ranging from 124.7(2)° to 167.1(1)°, with $\Delta = 42.4^\circ$ and with a mean value = 151.8(1)°. The α_2 angles show the smallest variation ranging from 98.8(2)° to 119.4(1)°, with $\Delta = 20.6^\circ$ and average = 108.4(1)°. The α_3 angles vary from 93.7(1)° to 115.9(1)°, with $\Delta = 22.6^\circ$ and with an average value = 99.3(1)°. From Table 2 it is noticeable that within the range of τ values of 0.76–0.09, there is slight gap of 0.22 in τ value between the value of 0.54 for **7** to the next value of 0.76 for **8**. This gap corresponds with a change in the ratio of the α_9 and α_{10} angles, for τ values >0.54 , $\alpha_9 > \alpha_{10}$, but for τ values <0.54 , $\alpha_9 < \alpha_{10}$. These relatives have been used to suggest a structural pathway from a regular trigonal bipyramidal to a distorted square-based pyramidal stereochemistry and suggest that, **1–9** form a point in a more extensive structural pathway for the $\text{CuN}_4\text{N}'$ chromophore.

Table 1
Crystallographic and structure refinement data for eight [Cu(dpyam)₂(NCO)]⁺[Y[−]] complexes

	1	2	3	4	5	6	7	8
Formula	C ₂₁ H ₁₈ N ₇ CuOBr	C ₂₂ H ₁₈ N ₇ CuO ₄ F ₃ S	C ₃₁ H ₂₇ N ₁₀ CuOBF ₄	C ₂₁ H ₂₆ N ₇ CuO ₅ Cl	C ₂₁ H ₁₈ N ₈ CuO ₄	C ₂₁ H ₁₈ N ₇ CuOPF ₆	C ₂₁ H ₁₈ N ₇ CuO ₅ Cl	C ₄₅ H ₃₈ N ₇ CuOB
<i>M</i>	527.87	597.03	705.98	555.48	509.97	592.93	547.38	767.22
Crystal system	monoclinic	orthorhombic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>Pbca</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> (Å)	10.9720(1)	15.8752(2)	19.9263(6)	7.1030(3)	11.0911(2)	8.3080(1)	8.1782(6)	13.2229(1)
<i>b</i> (Å)	16.5463(1)	16.7884(2)	7.6268(3)	27.9710(2)	16.323(3)	20.2070(3)	20.1466(1)	9.7836(7)
<i>c</i> (Å)	12.0719(1)	18.6085(3)	22.7070(9)	12.6930(8)	11.8435(2)	14.0520(2)	13.9620(9)	29.805(2)
α (°)	90	90	90	90	90	90	90	90
β (°)	98.492(2)	90	112.410(1)	96.899(3)	99.934	91.061(3)	91.8200(1)	101.8880(1)
γ (°)	90	90	90	90	90	90	90	90
<i>V</i> (Å ³)	2167.6(3)	4959.5(1)	3190.3(2)	2503.6(2)	2112.1(6)	2358.6(6)	2299.3(3)	3773.1(5)
<i>Z</i>	4	8	4	4	4	4	4	4
<i>D</i> _c (g cm ^{−3})	1.618	1.599	1.470	1.452	1.604	1.670	1.581	1.351
μ (mm ^{−1})	2879	1.032	0.752	1.024	1.083	1.072	1.115	0.625
<i>F</i> (000)	1060	2424	1444	1116	1044	1196	1116	1596
Crystal size (mm)	0.20 × 0.16 × 0.04	0.38 × 0.28 × 0.25	0.25 × 0.15 × 0.10	0.43 × 0.20 × 0.18	0.15 × 0.12 × 0.06	0.26 × 0.08 × 0.06	0.16 × 0.13 × 0.08	0.39 × 0.19 × 0.13
Number of reflection collected	18832	33809	22102	8129	11204	20607	14511	32358
Number of unique reflections (<i>R</i> _{int})	5169 (0.0542)	7225 (0.0384)	9087 (0.0804)	3869 (0.0394)	3846 (0.0478)	5657 (0.0572)	5436 (0.0381)	9035 (0.0284)
Data/restraints/parameter	5169/0/352	7225/0/422	9087/0/582	3869/0/389	3846/0/380	5657/0/461	5436/0/396	9035/0/648
Goodness-of-fit	1.030	1.027	1.010	1.105	1.018	1.029	1.035	1.054
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0514, <i>wR</i> ₂ = 0.1023	<i>R</i> ₁ = 0.0587, <i>wR</i> ₂ = 0.1493	<i>R</i> ₁ = 0.0789, <i>wR</i> ₂ = 0.1010	<i>R</i> ₁ = 0.0472, <i>wR</i> ₂ = 0.1318	<i>R</i> ₁ = 0.0405, <i>wR</i> ₂ = 0.0884	<i>R</i> ₁ = 0.0541, <i>wR</i> ₂ = 0.1065	<i>R</i> ₁ = 0.0649, <i>wR</i> ₂ = 0.1611	<i>R</i> ₁ = 0.0471, <i>wR</i> ₂ = 0.1117
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0898, <i>wR</i> ₂ = 0.1151	<i>R</i> ₁ = 0.0827, <i>wR</i> ₂ = 0.1662	<i>R</i> ₁ = 0.2606, <i>wR</i> ₂ = 0.1453	<i>R</i> ₁ = 0.0768, <i>wR</i> ₂ = 0.1655	<i>R</i> ₁ = 0.0583, <i>wR</i> ₂ = 0.095	<i>R</i> ₁ = 0.0944, <i>wR</i> ₂ = 0.1197	<i>R</i> ₁ = 0.0966, <i>wR</i> ₂ = 0.1790	<i>R</i> ₁ = 0.0636, <i>wR</i> ₂ = 0.1201
Largest differential peak and hole (e Å ^{−3})	0.489, −0.481	0.728, −0.674	0.208, −0.223	0.515, −0.583	0.362, −0.308	0.317, −0.371	0.799, −0.452	0.349, −0.395

Table 2
Selected bond lengths (Å) and angles (°) for the $[\text{Cu}(\text{dpyam})_2(\text{NCO})][\text{Y}]$

Y	Br^- (1)	CF_3SO_3^- (2)	$\text{BF}_4^- \cdot \text{dpyam}$ (3)	$\text{Cl}^- \cdot 4\text{H}_2\text{O}$ (4)	NO_3^- (5)	$(\text{SO}_4)_{0.5}^{2-} \cdot \text{dpyam} \cdot 0.5\text{H}_2\text{O}$ (9 ¹¹)	PF_6^- (6)	ClO_4^- (7)	BPh_4^- (8)
$\text{Cu-N}'$	1.945(3)	1.949(3)	1.933(4)	1.955(5)	1.950(3)	1.903(13)	1.949(3)	1.952(4)	1.984(1)
$\text{Cu-N}(1)$	2.030(3)	2.029(3)	2.000(4)	2.008(3)	2.008(2)	2.028(10)	2.008(2)	2.002(3)	2.017(1)
$\text{Cu-N}(3)$	2.045(3)	2.025(3)	2.001(3)	2.012(3)	2.008(3)	2.012(10)	2.013(2)	2.013(3)	2.018(1)
$\text{Cu-N}(2)$	2.021(3)	2.047(2)	2.025(3)	2.016(4)	2.043(2)	2.014(10)	2.074(2)	2.068(3)	2.072(1)
$\text{Cu-N}(4)$	2.283(3)	2.245(3)	2.157(4)	2.181(3)	2.185(2)	2.162(10)	2.169(3)	2.167(3)	2.089(1)
α_1	167.1(1)	159.4(1)	156.2(1)	157.9(1)	157.3(1)	154.7(5)	144.6(1)	144.1(2)	124.7(2)
α_2	98.8(2)	102.8(2)	104.4(1)	104.0(1)	109.1(1)	104.6(5)	116.9(1)	115.6(1)	119.4(1)
α_3	94.1(2)	97.8(1)	99.3(1)	98.1(1)	93.7(1)	100.7(5)	98.5(1)	100.2(1)	115.9(1)
α_4	92.7(1)	94.2(2)	90.4(1)	89.4(1)	92.5(1)	90.1(5)	89.6(1)	89.6(1)	94.9(1)
α_5	92.4(1)	92.4(1)	87.8(1)	88.3(1)	91.8(1)	90.0(5)	88.0(2)	87.4(1)	94.7(1)
α_6	86.2(1)	86.2(1)	87.5(1)	86.6(1)	86.4(1)	85.5(4)	87.7(1)	88.3(1)	89.1(1)
α_7	82.2(1)	85.3(1)	88.7(1)	86.0(1)	86.1(1)	85.9(5)	87.2(2)	87.7(1)	88.5(1)
α_8	172.8(1)	173.1(1)	170.0(2)	173.7(1)	175.3(1)	173.0(5)	176.2(1)	176.2(1)	170.3(2)
α_9	89.9(1)	88.3(1)	90.2(1)	93.3(1)	88.9(1)	91.5(4)	92.6(1)	92.7(1)	86.2(1)
α_{10}	92.0(1)	91.3(1)	101.3(1)	100.3(1)	94.2(1)	100.9(5)	96.5(1)	95.7(1)	85.9(1)
τ	0.09	0.23	0.23	0.26	0.30	0.31	0.53	0.54	0.76

3.3. Scatter-plot analysis for the $[\text{Cu}(\text{dpyam})_2(\text{NCO})][\text{Y}]$ series of complexes

This section presents the data for the $[\text{Cu}(\text{dpyam})_2(\text{NCO})][\text{Y}]$ series of complexes, Table 2, using scatter-plot analysis. The scatter plots (Fig. 3) discussed are as follows: (a) τ versus Cu–N(4), (b) α_3 versus α_1 , (c) α_3 versus Cu–N' and (d) Cu–N(2) versus Cu–N(4). An overview of the range of stereochemistries is provided by the plot of τ versus Cu–N(4). However, as τ involves two simultaneous angle changes, it will not be used further. A number of suggested extreme data points, Table S2, are included in the plots, with the geometry of the extreme seesaw stereochemistry illustrated in Fig. S1. The nine data points in Fig. 3(a) vary from trigonal bipyramidal, TB, to near regular square-based pyramidal, RSBP, with the τ values decreasing from 0.76 to 0.09, respectively as the Cu–N(4) distances increase from 2.089(1) to 2.283(3) Å. The data points show a broad *inverse* trend, and clearly do not cluster around the RTB geometrical point. This plot provides an overview of the observed stereochemistries of the $[\text{Cu}(\text{dpyam})_2(\text{NCO})][\text{Y}]$ series of complexes. There is one data point, **1**, at near SBP with $\tau = 0.09$, but there are no data points at RTB ($\tau = 1.0$). Five of the nine data points have τ values in the range 0.23–0.31 with stereochemistries best described as TBDSBP. Two data points **6** and **7** lie on the main correlation trend-line containing the RTB and RSBP data points. Two data points, **4** and **8** lie on a parallel correlation, with the remaining one data point, **9** lying nearby. Data points **1** and **2** lie off the RTB → RSBP trendline, due to their slightly long Cu–N(4) bond distances, which are ≈ 0.1 Å greater than expected [16].

The data points in Fig. 3(b) show the α_3 values decreasing from $115.9(1)^\circ$ to $94.1(2)^\circ$ as the α_1 values concomitantly increase from $124.7(2)^\circ$ to $167.1(1)^\circ$. All eight data points have α_1 values $>120^\circ$ and α_3 values $<120^\circ$, Table 2. Eight data points are found in the $-A + B$ section of the graph. The exception is data point, **1**, which lies close to the RSBP reference point. It is noticeable that within the α_1 and α_3 data set, point **1** has greater α_1 and α_3 values compared to those of a RSBP stereochemistry. There is no data points, which lies on the RTB → RSBP ($-A + B$) distortion pathway. Four data points, **2**, **3**, **4** and **9**, and the SBP data point, show an *inverse* trend, with each of these data points having α_2 $105 \pm 2^\circ$. The remaining data points, **8**, **7** and **5**, lie on two possible parallel correlations (---) displaying α_2 values of $120 \pm 2^\circ$, $115 \pm 2^\circ$ and $110 \pm 1^\circ$, respectively. This series of three possible parallel correlations have the same gradients. The data points show a SBP distortion, but only the correlation containing the data points corresponding to an α_2 value of 105° can end up at RSBP. For each parallel correlation, the α_2 values remain constant, therefore $\Delta\alpha_1 \uparrow \approx \Delta\alpha_3 \downarrow$ as $\alpha_1 + \alpha_2 + \alpha_3 = 360^\circ$, Table S3, and possibly suggesting the occurrence of preferred or magic angles [19]. The % $-A$ and % $+B$ distortion values calculated from the in-plane α_1 and α_3 bond angle data of Fig. 3(b) are given in Table 3.

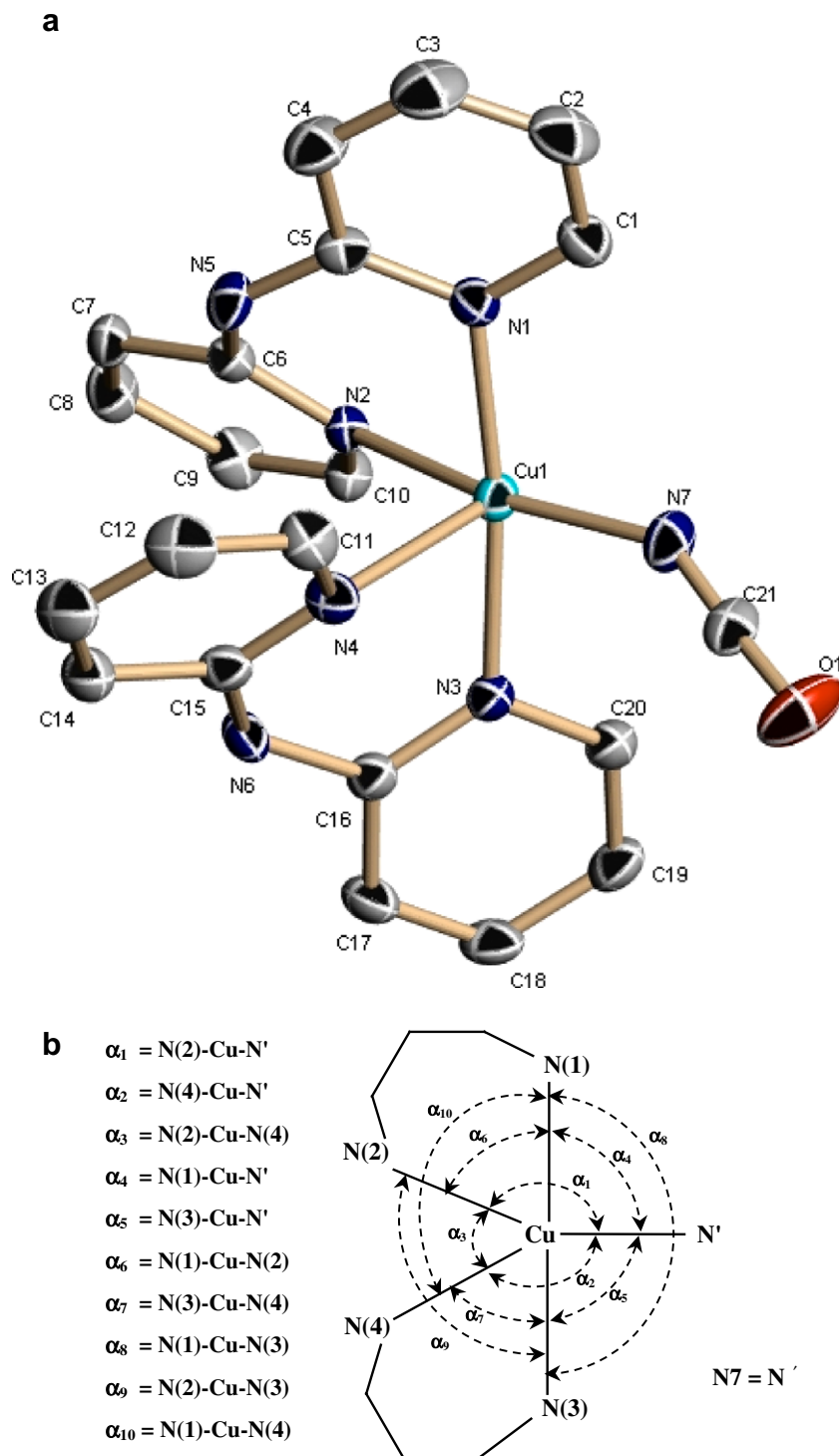


Fig. 2. (a) The molecular structure of the $[\text{Cu}(\text{dpyam})_2(\text{NCO})]^+$ cation of complex **1**, (b) the atom numbering scheme and α_n notation for the $\text{CuN}_4\text{N}'$ chromophore.

The nine data points in Fig. 3(c) show the α_3 values decreasing from $115.9(1)^\circ$ to $94.1(2)^\circ$, $\Delta\alpha_3 = 21.8^\circ$ as the $\text{Cu--N}'$ distances decrease from $1.984(1)$ to $1.903(13)$ Å, $\Delta\text{Cu--N}' = 0.081$ Å. All data points have α_3 values $<120^\circ$ and $\text{Cu--N}'$ distances <2.092 Å, suggesting $-A$ route distortion. Data point, **8** lies well off the $-A \rightarrow \text{RTB} \rightarrow +A$ pathway, with $\text{Cu--N}'$ distances significantly shorter, ≈ 0.08 Å,

than predicted from its corresponding α_3 values, while data points **1–7** also seem to have slightly shorter $\text{Cu--N}'$ distances, ≈ 0.05 Å, than expected from their corresponding α_3 values. There are no data points connecting the RTB data point to the extreme ‘see saw’ data point (the $-A$ route distortion, SSDTB in Fig. S1) There are two possible higher parallel trend lines involving one data point **8**, and two data

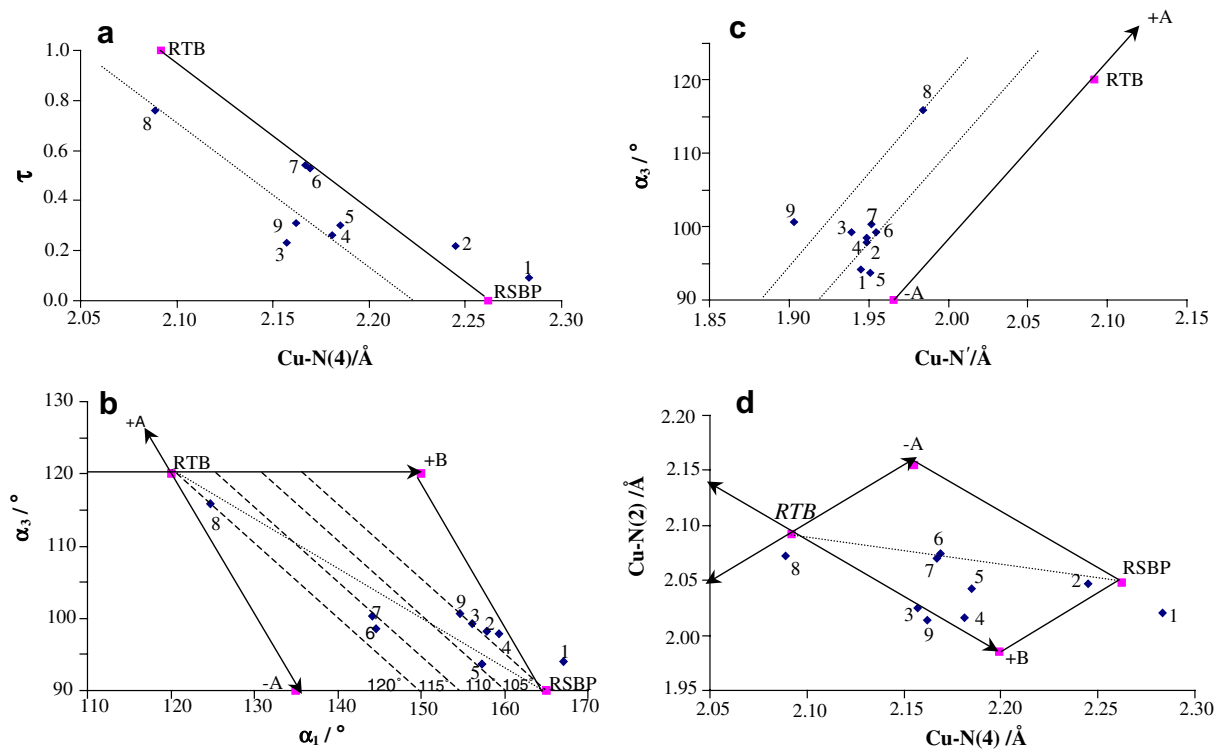


Fig. 3. Standard scatter plots for the $[\text{Cu}(\text{dpyam})(\text{NCO})]\text{Y}$ complexes.

points, 2 and 6 with 1, 3, 4, 5 and 7 lying close by. These linear correlations do not have enough data points to be convincing. However, it is significant that the three correlations involve approximately equal separations between the lines of either $\approx 11^\circ$ in the α_3 values or of $\approx 0.040 \text{ \AA}$ in the $\text{Cu-N}'$ distances. If the data of Fig. 3(c)

are related to those of Fig. 1, then both the α_3 angles and the $\text{Cu-N}'$ distances correspond to a pure $-A$ route distortion of the RTB stereochemistry. In practice, the α_1 and α_2 angles are not even approximately equal, varying from $\Delta(\alpha_1 - \alpha_2) = 5.3\text{--}68.3^\circ$, Table 2. The extreme $-A$ route distortion is clearly five-coordinate, with three short bonds,

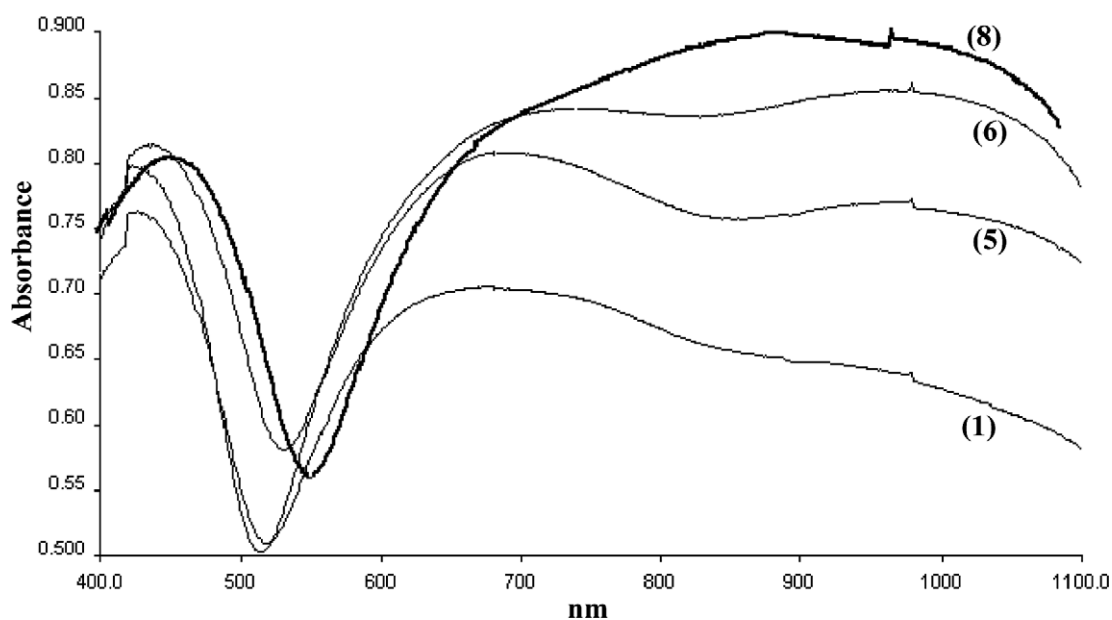


Fig. 4. Electronic reflectance spectra of representative $[\text{Cu}(\text{dpyam})_2(\text{NCO})]\text{Y}$ complexes with different τ values: $\tau = 0.09$ for (1), 0.30 for (5), 0.53 for (6) and 0.76 for (8).

Table 3

The % $-A$ and % $+B$ route distortion values of the complexes calculated using the in-plane angle data of Fig. 3(b)

	Complex								
	1	2	3	4	5	9	6	7	8
% $-A$		82.0	77.3	81.2	97.9	71.7	80.0	73.2	15.3
% $+B$		94.4	85.8	89.6	80.7	83.0	46.1	47.2	8.8

$\text{Cu}-\text{N}(1) = \text{Cu}-\text{N}(3) \approx 2.0 \text{ \AA}$, $\text{Cu}-\text{N}' \approx 1.95 \text{ \AA}$, and two longer bonds, $\text{Cu}-\text{N}(2) = \text{Cu}-\text{N}(4) \approx 2.15 \text{ \AA}$, with in-plane angles of $\alpha_1 = \alpha_2 = 135^\circ$ and $\alpha_3 = 90^\circ$.

The data points in Fig. 3(d) show the $\text{Cu}-\text{N}(2)$ distances decreasing from 2.074(2) to 2.014(10) $\text{\AA}$, while the $\text{Cu}-\text{N}(4)$ distances increase from 2.089(1) to 2.283(3) $\text{\AA}$. Five data points, 2, 4–7 are observed in the $-A + B$ quadrant of the graph, with points 1, 3, 8 and 9 lying outside this quadrant. There are no data points on the $\text{RTB} \rightarrow \pm A$ trendline, but there is one data point, 3 which lies directly on the $\text{RTB} \rightarrow +B$ route pathway. There are two data points 6 and 7 which also lie precisely on the $\text{RTB} \rightarrow \text{RSBP}$ ($-A + B$) pathway, with data point 2, lying close by. Table 4 shows the % $-A$ and % $+B$ distortion values of the complexes calculated using the in-plane $\text{Cu}-\text{N}(2)$ and $\text{Cu}-\text{N}(4)$ distance data. The values are closely comparable to those in Table 3 using the corresponding in-plane bond angle data. In general, Tables 3 and 4 show a large % $-A$ and a large % $+B$ distortion. Data point 8 is exceptional because it shows a few % $-A$ and % $+B$ distortion values.

3.4. General conclusions and comparison of the $[\text{Cu}(\text{dpyam})_2(\text{NCO})][\text{Y}]$ series with other $[\text{Cu}(\text{chelate})_2(\text{X})][\text{Y}]$ series of complexes

The information obtained from the scatter-plot analysis of this series of nine $[\text{Cu}(\text{dpyam})_2(\text{NCO})][\text{Y}]$ complexes can be summarised as follows:

- (1) The distribution of the data points is not random, with respect to the RTB and RSBP data points. They involve a significant spread of 42° and 0.19 $\text{\AA}$, Table S1.
- (2) The τ plot is consistent with a SBP distortion of the RTB $\text{CuN}_4\text{N}'$ chromophore, but with neither the RTB or RSBP structures present. Data point, 1, has extreme to near RSBP geometry with a τ value of 0.09. Five complexes have τ values in the range of 0.23–0.31. Data points, 6 and 7, have an intermediate τ values of 0.53 and 0.54, respectively. Data point, 8, has an exceptional τ value of 0.76, which equates with an unusual SBPDTB stereochemistry for a $[\text{Cu}(\text{dpyam})_2(\text{NCO})][\text{Y}]$ complex.

- (3) The plot of α_3 versus α_1 shows data points lying on parallel correlations, with fixed α_2 values of $120 \pm 5^\circ$, 10° or 15° , suggesting the existence of preferred or magic angles, consistent with $\alpha_1 + \alpha_2 + \alpha_3 = 360^\circ$, Table S3.
- (4) The $\pm A$ and $\pm B$ axes of Fig. 1 can be superimposed on the plots. All data points lie in the $-A + B$ section of the graphs except data point 1 which lies close to the RSBP stereochemistry. Tables 3 and 4 show the % $-A$ and % $+B$ distortion values of the complexes calculated from the in-plane angle and distance data and show large % values of both $-A$ and $+B$ distortion.
- (5) The five-coordinate structures of the dpyam series are comparable to the five-coordinate copper(II) complexes $[\text{Cu}(\text{chelate})_2(\text{X})][\text{Y}]$ when chelate = bipy and phen and $\text{X} = \text{Cl}^-$, Br^- , I^- and H_2O . Those of the bipy and phen families also show distortions ranging from RTB to RSBP, but differ in two aspects. First, almost all the τ values in the corresponding bipy and phen complexes range between intermediate to near RTB, $[\text{Cu}(\text{phen})_2\text{Cl}][\text{Y}]$ [9a] (0.56–0.81), $[\text{Cu}(\text{phen})_2\text{Br}][\text{Y}]$ [9b] (0.72–0.95), $[\text{Cu}(\text{phen})_2\text{I}][\text{Y}]$ [9b] (0.84–1.06), $[\text{Cu}(\text{bipy})_2\text{Cl}][\text{Y}]$ [3,9d] (0.53–1.00), $[\text{Cu}(\text{bipy})_2\text{Br}][\text{Y}]$ [9b,9d] (0.49–0.91), $[\text{Cu}(\text{bipy})_2\text{I}][\text{Y}]$ [9b] (0.80–0.90) and $[\text{Cu}(\text{chelate})_2(\text{OH}_2)][\text{Y}]_2$ [9c] (0.53–0.89), which differ significantly from the dpyam series of complexes where most τ values = 0.09–0.54 due to the more flexible dpyam ligand. Secondly, the distortion structural pathway in the dpyam series involves a $-A + B$ route (Fig. 1), which is different from that of the higher symmetry with twofold axis of $[\text{Cu}(\text{chelate})_2(\text{OH}_2)][\text{Y}]_2$ series which involves, a unique $\pm A$ route.

The stereochemistries of the $[\text{Cu}(\text{chelate})_2(\text{OH}_2)][\text{Y}]_2$ complexes differ from that of the dpyam complexes in having a crystallographic twofold axis of symmetry and hence are best described as having a pure $\pm A$ route distortion, which involves the pure $\nu_{\text{sym}}^{\text{str}}$ and $\nu_{\text{sym}}^{\text{bend}}$ modes of vibration. The $[\text{Cu}(\text{dpyam})_2(\text{NCO})][\text{Y}]$ complexes in contrast, with their slight contraction along the $\text{Cu}-\text{N}'$ distance (opposite α_3), their non-equivalence of the α_1 and α_2 angles without a

Table 4

The % $-A$ and % $+B$ route distortion values of the complexes calculated using the in-plane distance data of Fig. 3(d)

	Complex								
	1	2	3	4	5	9	6	7	8
% - <i>A</i>		82.5		7.9	28.6		46.0	38.1	
% + <i>B</i>		91.8	60.9	76.8	66.5	69.3	45.9	44.0	8.4

twofold axis of symmetry are considered to involve a $-A + B$ route distortion with the obvious domination of $+B$ over $-A$, involving all the four modes of vibration $\nu_{\text{sym}}^{\text{str}}$, $\nu_{\text{sym}}^{\text{bend}}$, $\nu_{\text{asym}}^{\text{str}}$ and $\nu_{\text{asym}}^{\text{bend}}$, namely the molecular structure **VI** of Fig. 1. Alternatively, the precise coordination geometry displayed may be interpreted [9b] as an effect of vibronic coupling of a linear combination of the nuclear modes of vibrations ν_{sym} , a symmetric C_2 mode, and ν_{asym} , an asymmetric non- C_2 mode, of the $\text{CuN}_4\text{N}'$ chromophore.

3.5. IR, electronic properties and EPR of the $[\text{Cu}(\text{dpyam})_2(\text{NCO})][\text{Y}]$ complexes

The infrared spectra display a strong band at 2214 and 2180 cm^{-1} for **1**, 2214 cm^{-1} for **2**, 2209 cm^{-1} for **3**, 2220 cm^{-1} for **4**, 2219 and 2202 cm^{-1} for **5**, 2222 cm^{-1} for **6**, 2214 cm^{-1} for **7** and 2218 cm^{-1} for **8**, which can be assigned to the $\nu_{\text{asym}}(\text{NCO})$ absorption band. The spectrum of **2** also displays a broad and intense band at approximately 1280–1040 cm^{-1} , consistent with the characteristic peak $\nu_4(\text{SO}_3)$ of CF_3SO_3^- anion. The spectrum of **3** displays a broad and intense band at approximately 1074–1014 cm^{-1} , consistent with the characteristic peak of BF_4^- anion. The spectrum of **5** displays an intense band at approximately 1384 and 1307 cm^{-1} , consistent with the characteristic peak of $\nu_{\text{as}}(\text{NO})$ and $\nu_{\text{s}}(\text{NO})$ of NO_3^- anion. The spectrum of **6** displays a broad and intense band at approximately 845–837 cm^{-1} , consistent with the characteristic peak of PF_6^- anion. The spectrum of **7** displays a broad and intense band at approximately 1166–1076 cm^{-1} , consistent with the characteristic peak of ClO_4^- anion.

The polycrystalline electronic reflectance spectra of complexes **1**, **5**, **6** and **8** are represented in Fig. 4. For **8** a single $d \rightarrow d$ transition occurs at 11420 cm^{-1} (876 nm), with some evidence of an unresolved high-energy shoulder at 12880 cm^{-1} (776 nm), consistent with near TB stereochemistry ($\tau = 0.76$). The one-electron ground-state configuration is $d_{z^2} > d_{xy} \approx d_{x^2-y^2} > d_{xz} \approx d_{yz}$. The principal absorption may be assigned as a $d_{x^2-y^2} \rightarrow d_{z^2}$ transition, with the low-energy assigned as a $d_{xz} \approx d_{yz} \rightarrow d_{z^2}$ transition. The electronic spectrum of **8** is comparable to those of complexes with similar Cu(II) environment $[\text{Cu}(\text{phen})_2\text{Cl}][\text{Y}]$, $\text{Y} = \text{BF}_4 \cdot 0.5\text{H}_2\text{O}$, PF_6 and ClO_4 [9a],

$[\text{Cu}(\text{phen})_2\text{Br}][\text{Y}]$, $\text{Y} = \text{Br} \cdot \text{H}_2\text{O}$, ClO_4 and PF_6 [9b]. The spectra of **6** and **7**, $\tau = 0.53$ and 0.54, respectively, both having an intermediate stereochemistry between RTB and RSBP, involve two clearly resolved peaks at 10330 cm^{-1} (968 nm) and 13870 cm^{-1} (721 nm) for **6** and 10350 (966 nm) and 13800 cm^{-1} (725 nm) for **7**, with the lower-energy peak showing a slightly greater intensity, consistent with the intermediate five-coordinate geometry. The one-electron ground-state configuration is $d_{x^2-y^2} > d_{z^2} > d_{xy} > d_{xz} \approx d_{yz}$. The transitions may be assigned as the $d_{z^2} \rightarrow d_{x^2-y^2}$ transition for the low-energy peak and the $d_{xz} \approx d_{yz} \rightarrow d_{x^2-y^2}$ transition for the high-energy peak. The electronic spectra of **6** and **7** are comparable to those of complex with similar environment $[\text{Cu}(\text{phen})_2\text{Cl}][\text{CF}_3\text{SO}_3] \cdot \text{H}_2\text{O}$ [9a]. Complexes **1–5**, $\tau = 0.09–0.31$, which have a TBDSBP stereochemistry, involve high-energy, high-intensity peak at 14510 cm^{-1} (689 nm), 14420 cm^{-1} (694 nm), 14240 cm^{-1} (702 nm), 14200 cm^{-1} (704 nm) and 13930 cm^{-1} (718 nm), respectively, with low-energy, low-intensity shoulder at 10150 cm^{-1} (985 nm), 10180 cm^{-1} (982 nm), 10220 cm^{-1} (978 nm), 10350 cm^{-1} (966 nm) and 10270 cm^{-1} (974 nm), respectively. The one-electron ground state configuration is $d_{x^2-y^2} > d_{z^2} > d_{xy} > d_{xz} \approx d_{yz}$. The transitions may be assigned as the $d_{z^2} \rightarrow d_{x^2-y^2}$ transition for the low-energy shoulder and the $d_{xz} \approx d_{yz} \rightarrow d_{x^2-y^2}$ transition for the high-energy peak. The electronic spectra of **1–5** are comparable to those of complexes with similar environment $[\text{Cu}(\text{phen})_2\text{Cl}][\text{BPh}_4]$ [9a] and $[\text{Cu}(\text{phen})_2\text{Br}][\text{BPh}_4]$ [9b].

The corresponding spectro-structural correlation plots (Fig. S2) reveal that ΔE values increase with increasing τ values for the low-energy peak and the reverse result has been found for the higher-energy peaks. It is evident from Fig. S3, that the basal angles themselves correlate very well with the ΔE values. This plot clearly indicates that a linear correlation between τ and the ΔE values exists in the set of **1–8** where α and β have been defined consistently.

The polycrystalline X-band EPR spectrum at room temperature of complexes **1–8** is isotropic (Table 5), yielding no information in relation to the electronic ground state. Low-temperature (77 K) EPR spectra were performed at higher frequencies (K-band and V-band) than X-band, both on polycrystalline samples, and DMSO solutions, in

Table 5
Consensus g -values for all 8 complexes from EPR

Complex	1	2	3	4	5	6	7	8
<i>X-band</i>								
g_i (RT)	2.1515	2.1576	2.1157	2.1154	2.1084	2.0982	2.1079	2.1324
<i>K and V-band</i> ^a								
g_x	2.05	2.04	2.05	2.030	2.03	2.05	2.04	2.185
g_y	2.05	2.10	2.08	2.075	2.09	2.13	2.08	2.185
g_z	2.27	2.17	2.28	2.245	2.17	2.20	2.24	2.005

^a Estimated error: ± 0.01 for samples 4 and 8, ± 0.02 for all others.

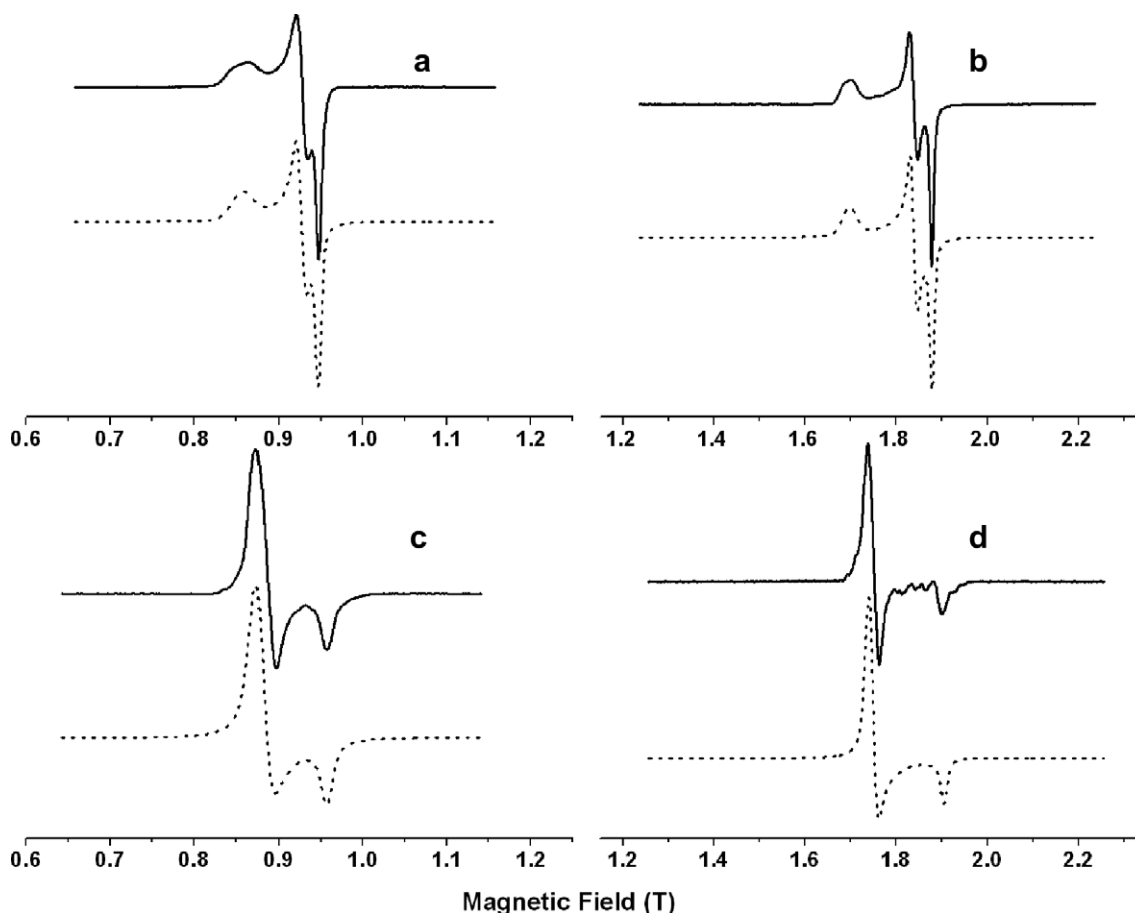


Fig. 5. Experimental (solid line) and simulated (dash line) EPR spectra of complex **4** (a and b) and complex **8** (c and d) at K-band (26.8 GHz, left side) and V-band (53.6 GHz, right side). Simulation parameters: (a) $g_x = 2.022$, $g_y = 2.067$, $g_z = 2.235$; (b) $g_x = 2.037$, $g_y = 2.082$, $g_z = 2.255$; (c) $g_{\perp} = 2.185$, $g_{\parallel} = 2.005$; (d) $g_{\perp} = 2.193$, $g_{\parallel} = 2.010$. Temperature: 77 K; magnetic field sweep rate: 2 mT/s; magnetic field modulation: frequency 40 kHz, amplitude 1 mT.

order to increase the g -value resolution, and possibly also resolve hyperfine structure. Indeed, Q-band (34 GHz) spectra of frozen DMSO solutions showed nicely resolved parallel and perpendicular g components, with a hyperfine structure due to the nuclear $I = 3/2$ spin characteristic for Cu^{2+} observed on top of the parallel component (not shown), this was expected to study the correlation between the five-coordinate geometries and the hyperfine splitting ($A_{\parallel}$ values). However, an analysis of the solution spectra revealed that the complexes under study are decomposed, or otherwise altered in these conditions. These studies were consequently abandoned. Instead, EPR on polycrystalline samples at K-band (27 GHz) and V-band (54 GHz) was successful in fully resolving g -values. Fig. 5 shows spectra of **4** and **8** at both frequencies, accompanied by powder simulations using g -values as in Table 5. Table 5 also presents g -values for the remaining complexes under study. The EPR spectra of complexes **1–7** are in rhombic type [4,7] and three g -factors are obtained as in Table 5, with the lowest g -values > 2.0 which is consistent with the $d_{x^2-y^2}$ ground state, while the EPR spectrum of complex **8** is axial with $g_{\perp} = 2.185$ and $g_{\parallel} = 2.005$, consistent with a d_{z^2} ground state for the approximately trigonal bipyrami-

dal stereochemistry of the $\text{CuN}_4\text{N}'$ chromophore present, $g_{\perp} \gg g_{\parallel} > 2.0$.

4. Conclusions

The present report describes the preparation, crystal structure determination, spectroscopic properties and structural pathway of the five-coordinate copper(II) complexes with pseudohalide ligand, NCO^- . The structure of the $[\text{Cu}(\text{dpyam})_2(\text{NCO})]^+$ cations all involve a five-coordinate $\text{CuN}_4\text{N}'$ chromophore with TBDSBP in **1–5** and **9** ($\tau = 0.09$ – 0.31 , respectively). Complexes **6** and **7** exhibit an intermediate five-coordinate, slightly distorted toward TBP ($\tau = 0.53$ and 0.54 , respectively). The complex **8** shows SBPDTB with a τ value of 0.76 . The detailed structure of a five-coordinate copper(II) complex is dependent upon the type of counter anion in the lattice, due to the ‘Plasticity Effect’, showing how the same complex in different crystal modifications, can have slightly different structures. In the present work the ‘Plasticity Effect’ has been considerably extended by reference to cation distortion isomers, in which the structures of a given cation is modified in the presence of different counter anions. The relatively small structural

differences produced have been correlated to suggest the existence of a continuous ‘Structural Pathway’, connecting the extreme structures, with the individual structures linked by a soft mode of vibration. All data points are found in the $-A + B$ section of the graph, except a data point **1**, which is closed to RSBP. It is noticeable that the α_1 and α_3 of **1** are greater than the usual values of α_1 and α_3 usually found for RSBP complexes, leading to this deviation. Moreover, this structure is the most extreme RSBP known of five-coordinate with dpyam ligand.

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Appendix A. Supplementary material

CCDC numbers 295201, 295202, 295203, 295204, 295205, 295206, 295207 and 295208 contain the supplementary crystallographic data for **1**, **2**, **3**, **4**, **5**, **6**, **7** and **8**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.poly.2006.09.027](https://doi.org/10.1016/j.poly.2006.09.027).

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PUBLICATION PAPERS OF PART II

Hexa- and polynuclear copper(II) coordination compounds based on the carbonato bridge: Synthesis, crystal structures and magnetic properties

Sujittra Youngme^{a,*}, Nanthawat Wannarit^a, Tawun Remsungnen^b,
Narongsak Chaichit^c, Gerard A. van Albada^d, Jan Reedijk^d

^a Department of Chemistry, Faculty of Science, Khon Kaen University, Khon Kaen 40002, Thailand

^b Department of Mathematics, Faculty of Science, Khon Kaen University, Khon Kaen 40002, Thailand

^c Department of Physics, Faculty of Science and Technology, Thammasat University, Rangsit, Pathumthani 12121, Thailand

^d Gorlaeus Laboratories, Leiden Institute of Chemistry, Leiden University, P.O. Box 9502, 2300 RA Leiden, The Netherlands

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Abstract

The crystal structures of polynuclear copper(II) complexes containing the bidentate bpy ligand (bpy = 2,2'-bipyridine) with varied coordination modes of the carbonato bridging ligand, a hexanuclear compound $[\text{Cu}_6(\text{bpy})_{10}(\mu\text{-OH})_2(\mu\text{-CO}_3)_2](\text{CF}_3\text{SO}_3)_6(\text{DMF})_2(\text{H}_2\text{O})_4$ (**1**) and a polymeric compound $\{[\text{Cu}_3(\text{bpy})_3(\mu\text{-OH})_2(\mu\text{-CO}_3)_2](\text{H}_2\text{O})_{6.5}\}_n$ (**2**) are described. Compound **1** consists of the di- μ -hydroxido-bis(2,2'-bipyridine)copper(II) groups coordinated with *trans*-axially at each copper atom by $[\mu\text{-carbonato-bis}(\text{bpy})\text{copper(II)}]$ moieties, forming a hexanuclear copper(II) compound. Each copper(II) ion has a distorted square-pyramidal environment in which three Cu(II) atoms are linked through oxygen atoms of the bridged ligand by the $\mu_3\text{-}\eta^2\text{:}\eta^1\text{-CO}_3$ coordinated mode. Compound **2** consists of two independent di- μ -hydroxido-bis(2,2'-bipyridine)copper(II) dinuclear units which are connected to the central moiety by two different coordination modes of the carbonate bridging ligands, $\mu\text{-}\eta^1\text{:}\eta^1$ (*anti-anti*) and $\mu\text{-}\eta^2\text{:}\eta^1\text{-CO}_3$ configurations. Each Cu(II) ion has a distorted square-pyramidal geometry. The repeating units give rise to a one-dimensional chain along *b*-axis. The lattice structures are stabilized by stacking interaction between pyridine groups of bpy chelated ligands of different units. The spectroscopic properties (IR, Reflectance and EPR spectra) and the magnetic susceptibility data of both compounds are investigated.

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Keywords: Carbonate chemistry; Copper(II) complexes; Crystal structure; EPR; Magnetism

Over the years a great deal of interest has been focused on the copper(II)-carbonato coordination chemistry in which the carbonate anion can act as bridging ligand with a very high structural versatility especially in complexation of copper(II) metal dimers [1], trimers [2], tetramers [3], one- or two-dimensional system [4]. More recently inspiration for this field was drawn from bioinorganic chemistry [5] and from the relationship between the coordination modes of carbonato ligand and the magnetic properties [1–4]. Besides, several polynuclear carbonato bridged

copper(II) compounds also resulted from CO₂ fixation of hydroxido bridged species in air [5b,5c]. From the magnetic point of view, the literature available for magneto-structural studies of the polynuclear copper(II)-carbonato compounds are extremely versatile in which the magnetic properties depend on its coordination mode and symmetry conditions [1–8]. With the aim of the study of the synthetic methods and magnetochemistry of the μ -carbonato bridged coordination compounds with the 2,2'-bipyridine, a number of the diverse carbonato polynuclear copper(II) compounds, $[\text{Cu}_2(\text{bpy})_4(\mu\text{-CO}_3)](\text{PF}_6)_2(\text{DMF})_2$ [1a], $[\text{Cu}_3(\text{bpy})_6(\mu_3\text{-CO}_3)](\text{BF}_4)_4(\text{H}_2\text{O})_2(\text{C}_2\text{H}_6\text{O})$ [2a], $[\text{Cu}_6(\text{bpy})_{10}(\mu\text{-CO}_3)_2(\mu\text{-OH})_2](\text{ClO}_4)_6(\text{H}_2\text{O})_4$ [1a] and $\{[\text{Cu}_3\text{-}$

* Corresponding author. Fax: +66 4320 2373.

E-mail address: sujittra@kku.ac.th (S. Youngme).

(bpy)₃(μ-OH)₂(μ-CO₃)₂(H₂O)₁₁}_n [4i] have been reported with different type of coordination modes of the carbonate bridge and the range of magnetic behavior from antiferromagnetic to moderate ferromagnetic couplings. We now extended the studies towards the new polynuclear copper(II) compounds with cooperative carbonate and hydroxido bridges [9], a hexanuclear [Cu₆(bpy)₁₀(μ-OH)₂(μ-CO₃)₂](CF₃SO₃)₆ (DMF)₂ (H₂O)₄ (**1**) and a polynuclear {[Cu₃(bpy)₃(μ-OH)₂(μ-CO₃)₂](H₂O)_{6.5}}_n (**2**).

The crystal structure of compound **1** consists of the [di-μ-hydroxido-bis(2,2'-bipyridine)copper(II)] moieties, coordinated *trans*-axially at each copper atom by μ-carbonato-bis(2,2'-bipyridine)copper(II) moieties (Fig. 1). The compound **1** also contains six trifluoromethanesulfonate counteranions, two *N,N*-dimethylformamide (abbreviation as DMF) molecules and nine lattice water [10]. The Cu(3)–Cu(3)A separation of 2.844(2) Å and Cu(3)–O(4)–Cu(3)A bridging angle of 94.3(3)° fall within the range found for similarly coordinated di-μ-hydroxidocopper(II) dimers [11–14]. The environment of central copper atoms are nearly regular square-pyramidal geometry, being coordinated by two nitrogen donors from the bpy ligand and two oxygen atoms from the bridging hydroxido group, forming the CuN₂O₂ chromophores with distances ranging 1.934(7)–1.997(8) Å, an apical position is occupied by O(1) from the bridging carbonate species at a distance of 2.341(6) Å. The corresponding τ value [15] for the square-pyramidally disposed Cu(3) atom is 0.10. The Cu(3) atom lies 0.07, above the basal plane toward O(1). The carbonate to oxygen O(1) bridging atom also coordinates with Cu(1), forming an asymmetric monoatomic bridge between Cu(3) and Cu(1); Cu(3)–O(1) 2.341(6) Å, Cu(1)–O(1) 2.037(6) Å, with a Cu(3)–O(1)–Cu(1) bridging angle of 132.6(3)°. The coordination geometry around Cu(1) is best described as being pyramidal with distortion toward trigonal bipyramidal ($\tau = 0.42$). The basal plane consists of three nitrogen atoms of bpy ligands and an O(1) atom of carbonate bridging ligand with distances ranging from 1.990(8) to 2.089(9) Å. The apical position is occupied by N(2) atom of bpy ligand with a bond length of 2.183(10) Å. The Cu(1) atom lies 0.28, above the basal plane toward N(2). Moreover, this carbonate group so also linked to Cu(2) through O(2) at a distance of 1.958(6) Å, forming a triatomic bridge between Cu(1) and Cu(2) (*anti, anti*) and likewise between Cu(2) and Cu(3) (*syn, anti*). The environment geometry of Cu(2) can be described with a distorted pyramidal geometry ($\tau = 0.40$). The basal plane contains three nitrogen atoms of bpy ligands and an oxygen atom of carbonate ligand with distances ranging 1.958(6)–2.075(8) Å. The fifth position is occupied by N(8) atom of bpy ligand with 2.199(9) Å. The Cu(2) atom lies 0.23, above the basal plane toward N(8). The tetrahedral twists of the square bases defined by dihedral angles between two trigonal planes are 30.87, 28.19 and 7.5°, for Cu(1), Cu(2) and Cu(3), respectively. The carbonate moieties coordinate to three copper(II) atoms with $\mu_3\text{-}\eta^2\text{:}\eta^1\text{-CO}_3$ coordinated fashion [Cu(1)–Cu(2) 5.091, Cu(2)–Cu(3) 5.321 and Cu(1)–Cu(3)

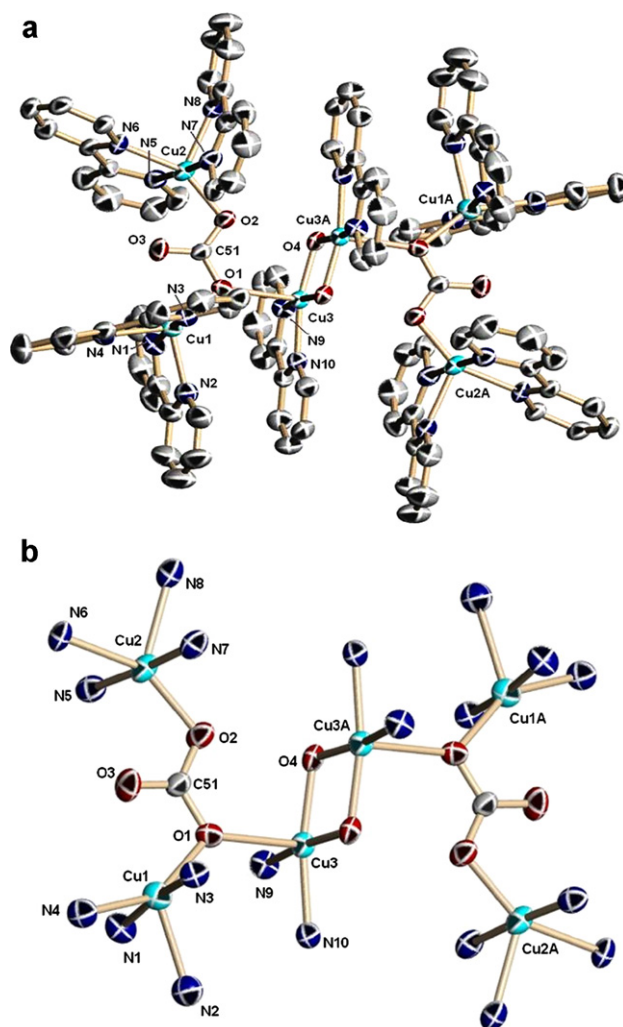


Fig. 1. (a) Molecular structure and atomic numbering scheme for compound **1** (Thermal ellipsoids are drawn at 30% level). Hydrogen atoms, triflate anions, DMF and water molecules are omitted for clarity. “A” symmetry transformations used to generate equivalent atoms $-x, -y + 1, -z$. (b) Figure showing the copper(II) chromophores. Selected bond lengths (Å) and angles (°): Cu(1)–N(3) 1.990(8), Cu(1)–N(1) 1.990(9), Cu(1)–O(1) 2.037(6), Cu(1)–N(4) 2.089(9), Cu(1)–N(2) 2.183(10), Cu(2)–O(2) 1.958(6), Cu(2)–N(5) 1.979(9), Cu(2)–N(7) 2.004(9), Cu(2)–N(6) 2.075(8), Cu(2)–N(8) 2.199(9), Cu(3)–O(4) 1.934(7), Cu(3)–N(10) 1.980(8), Cu(3)–N(9) 1.997(8), Cu(3)–O(1) 2.341(6), Cu(3)–Cu(3)A 2.844(2), and N(3)–Cu(1)–N(1) 173.4(4), O(1)–Cu(1)–N(4) 149.4(3), N(5)–Cu(2)–N(7) 176.6(3), O(2)–Cu(2)–N(6) 150.9(3), O(4)–Cu(3)–N(10) 166.2(3), O(4)A–Cu(3)–N(9) 172.5(3).

4.011 Å]. The centrosymmetric nature of the complex results in the above array being repeated at Cu(1)A, Cu(2)A and Cu(3)A center atoms. The influence of intra- and intermolecular bpy–bpy π -stacking interactions has been considered to play a role in this molecular structure. Inspection of the bipyridine rings show that they are essentially parallel to each other, corresponding to the incorporation of the N(1)–N(2), N(9)–N(10) and N(8)A rings (3.671–3.983 Å) within the molecules. The intermolecular π – π interactions with the face-to-face distance being 3.619 Å form a 1D chain is stacked along the *b*-axis, as

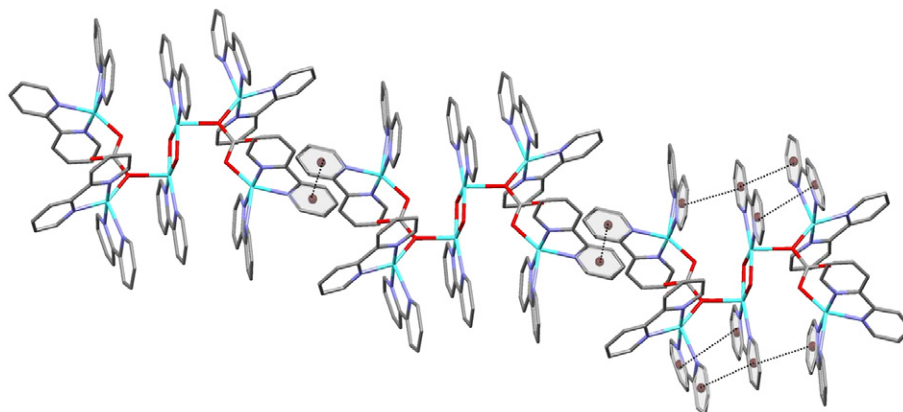


Fig. 2. Packing diagram of **1** with π – π interaction along the b -axis, showing the one-dimensional chain. Hydrogen atoms, triflate anions, DMF and water molecules are omitted for clarity.

illustrated in Fig. 2. The molecular structure of compound **1** is very similar to that of the closely related compound $[\text{Cu}_6(\text{bpy})_{10}(\mu\text{-OH})_2(\mu\text{-CO}_3)_2](\text{ClO}_4)_6(\text{H}_2\text{O})_4$ [**1a**] with comparable τ values of 0.41, 0.23 and 0.05 for Cu(1), Cu(2) and Cu(3), respectively (see Table 1).

The crystal structure of compound **2** [10] involves a polymeric chain of the asymmetric repeating units, $[\text{Cu}_3(\text{bpy})_3(\mu\text{-OH})_2(\mu\text{-CO}_3)_2]_n$. This compound consists of two independent di- μ -hydroxido-bis(2,2'-bipyridine)copper(II) dinuclear moieties, $[\text{Cu}(1)/\text{Cu}(1)\text{A}]$ and $[\text{Cu}(3)/\text{Cu}(3)\text{B}]$, each connected to the central Cu(2) unit via two carbonate bridges with different bridging modes, resulting to the pentanuclear unit (Fig. 3). These pentanuclear units are repeated to form one-dimensional chain along the b -axis (Fig. 3). The central Cu(2) atom is coordinated by two nitrogen atoms from a bpy ligand and two oxygen atoms from two different carbonate bridges with the $\mu\text{-}\eta^1\text{:}\eta^1$ - and $\mu\text{-}\eta^2\text{:}\eta^1\text{-CO}_3$ coordination modes, forming a square base with distances ranging 1.938(7)–2.018(7) Å. The axial position is then occupied by another oxygen atom of the latter carbonate bridge with Cu–O distance of 2.419(6) Å, giving a distorted square–pyramidal geometry with a τ value of 0.22. Consequently, the latter carbonate bridge is bidentately coordinated to Cu(2) center and monodentately coordinated to Cu(3) atom. A dihedral angle between the CuN_2 and CuO_2 planes is 20.2(4)° and the Cu(2) atom lies 0.21 Å above the basal plane toward the apical site. The di- μ -hydroxido-bis(2,2'-bipyridine)copper(II) moiety, $[\text{Cu}(1)/\text{Cu}(1)\text{A}]$ is a dinuclear unit, copper(II) ions are solely bridged with two hydroxido ligands. Each copper(II) ion is five-coordinate with N_2O_3 donor set. The square base consists of two nitrogen atoms from bpy ligand and two oxygen atoms from each bridging hydroxido group, with bond distances varying from 1.939(5) to 2.035(7) Å. The apical position is then occupied by O(2) from the $\mu\text{-}\eta^1\text{:}\eta^1$ carbonate bridging ligand with a distance of 2.175(6) Å. The τ value of 0.16 corresponds to a distorted square–pyramidal geometry. The Cu–Cu separation within the dinuclear unit is 2.913(2) Å and the bridging Cu(1)–O(1)–Cu(1)A angle is 96.8(2)°. These features are very close to those

observed in the corresponding di- μ -hydroxido bridged copper(II) dimers [11–14]. The di- μ -hydroxido-bis(2,2'-bipyridine)copper(II) moiety, $[\text{Cu}(3)/\text{Cu}(3)\text{B}]$ is structurally similar to that of the $[\text{Cu}(1)/\text{Cu}(1)\text{A}]$ moiety ($\tau = 0.16$), bond distances of the square base vary from 1.920(7) to 2.025(8) Å. The apical position is occupied by O(6) of the $\mu\text{-}\eta^2\text{:}\eta^1$ carbonate bridging ligand with a distance of 2.199(6) Å. The Cu–Cu separation within the dinuclear unit is 2.875(2) Å and the bridging Cu(3)–O(8)–Cu(3)B angle is 96.8(3)°. The dihedral angles between trigonal planes of the square bases are 19.8, 20.2 and 15.6°, for Cu(1), Cu(2) and Cu(3), respectively. Moreover, there are the intramolecular interactions, π – π stacking between the neighboring pyridine groups of Cu(2) and Cu(3) chromophores (ring to ring distance 3.691 Å) as shown in Fig. 3. The adjacent Cu chains interdigitate through π – π interaction, which involve each bpy ligand (3.309 Å as closest contacts) and leads to formation of 2D sheets (Fig. 4). The lattice is further stabilized by relatively hydrogen bonds between the water molecules and the carbonate and hydroxido oxygen atoms of the adjacent layers, leading to three-dimensional infinite framework. The structure of compound **2** is very similar to that of the closely related compound $\{[\text{Cu}_3(\text{bpy})_3(\mu\text{-OH})_2(\mu\text{-CO}_3)_2](\text{H}_2\text{O})_{11}\}_n$ [**4i**] with τ values of 0.16, 0.22 and 0.00 for Cu(1), Cu(2) and Cu(3), respectively.

The electronic reflectance spectra of both compounds show two broad, not well-resolved bands at approximately 14,000 and 10,220 cm^{-1} for **1** and 14,080 and 10,140 cm^{-1} for **2**, assigned to the d_{xy} , d_{yz} , $d_{zx} \rightarrow d_{x^2-y^2}$ and $d_{z^2} \rightarrow d_{x^2-y^2}$ transitions, respectively, for each compound. This spectral character of the compounds is consistent with a distorted square–pyramidal geometry.

The IR spectra of **1** and **2** display a strong and broad bands centered at *ca.* 3504 and 3463 cm^{-1} , respectively, which are consistent with the presence of bis- μ -hydroxido species and water molecules. The bands at 1500 and 1330 cm^{-1} for **1** and 1583 and 1348 cm^{-1} for **2** correspond to anti- and symmetric carbonate stretching vibrations, respectively.

Table 1
X-ray structure parameters, spectral data and magnetism for polynuclear μ -CO₃ copper(II) compounds and some related compounds

Compound ^a	Geometry ^b	τ Cu1,Cu2,Cu3	Bridging configuration of the bridge ^c	Bridging mode of CO ₃ ²⁻	Cu–OH–Cu (θ)/°	Coupling constant (cm ⁻¹)	Ref.
<i>Binuclear</i>							
[Cu ₂ (bpy) ₄ (μ -CO ₃)](PF ₆) ₂ (DMF) ₂	Sq. Py.	0.20	eq–eq	μ - η^1 : η^1	–	–70.2	[1a]
[Cu ₂ (dpyam) ₄ (μ -CO ₃)](BF ₄) ₂ (H ₂ O) ₄	Sq. Py.	0.13, 0.29	eq–eq	μ - η^1 : η^1	–	–88.2	[1b]
[Cu ₂ (dpyam) ₄ (μ -CO ₃)](ClO ₄) ₂ (H ₂ O) ₄	Sq. Py.	0.13, 0.30	eq–eq	μ - η^1 : η^1	–	–90.4	[1c]
[Cu ₂ (bpy) ₂ (μ -OH) ₂](SO ₄)(H ₂ O) ₅	Sq. Py.	–	–	–	97.0	+49	[11]
[Cu ₂ (bpy) ₂ (μ -OH) ₂](ClO ₄) ₂	Oct.	–	–	–	96.6	+93	[12]
[Cu ₂ (bpy) ₂ (μ -OH) ₂](NO ₃) ₂	Sq. Py.	–	–	–	95.5	+172	[13]
<i>Hexanuclear</i>							
[Cu ₆ (bpy) ₁₀ (μ -CO ₃) ₂ (μ -OH) ₂](ClO ₄) ₆ (H ₂ O) ₄	Sq. Py.	0.41, 0.23, 0.05	eq–eq (μ -CO ₃) ax–eq (μ -CO ₃) ax–eq (μ -CO ₃) eq–eq (μ -OH)	μ_3 - η^2 : η^1	95.1	+2.75 (μ -CO ₃) +3.25 (μ -CO ₃) +2.75 (μ -CO ₃) +24 (μ -OH)	[1a]
[Cu ₆ (bpy) ₁₀ (μ -CO ₃) ₂ (μ -OH) ₂](CF ₃ SO ₃) ₆ (DMF) ₂ (H ₂ O) ₄ (1)	Sq. Py.	0.42, 0.40, 0.10	eq–eq (μ -OH)	μ_3 - η^2 : η^1	94.3	–	This work
<i>Chain like structure</i>							
Cu(NH ₃) ₂ CO ₃	Sq. Py.	–	ax–eq	μ - η^1 : η^1	–	–5.2, –2.6	[4a,4b]
Na ₂ Cu(CO ₃) ₂	Sq. Py.	–	ax–eq	μ - η^1 : η^1	–	+4.1	[4c,4d]
Na ₂ Cu(CO ₃) ₂ (H ₂ O) ₃	Sq. Py.	–	ax–eq	μ - η^1 : η^1	–	+0.6	[4e]
[Cu(μ -CO ₃)(4-apy)](H ₂ O)	Sq. Planar	–	eq–eq	μ - η^1 : η^1	–	+11	[4f]
[Cu(dpyam)(μ -CO ₃)](H ₂ O) ₃	Sq. Py.	–	ax–eq	μ - η^1 : η^1 : η^1	–	–	[4g,4h]
{[Cu ₃ (bpy) ₂ (μ -OH) ₂ (μ -CO ₃) ₂](H ₂ O) ₁₁ } _n	Sq. Py.	0.16, 0.22, 0.00	eq–eq (μ -OH) eq–eq (μ -OH)	μ - η^1 : η^1 , μ - η^2 : η^1	94.6, 96.5	+154 (μ -OH), +135 (μ -OH)	[4i]
{[Cu ₃ (bpy) ₂ (μ -OH) ₂ (μ -CO ₃) ₂](H ₂ O) _{6.5} } _n (2)	Sq. Py.	0.16, 0.22, 0.00	eq–eq (μ -OH) eq–eq (μ -OH)	μ - η^1 : η^1 , μ - η^2 : η^1	96.8, 96.8	–	This work

^a bpy = 2,2'-bipyridine, dpyam = 2,2'-dipyridylamine, 4-apy = 4-aminopyridine.

^b Sq. Py. = distorted square–pyramidal geometry, Oct. = octahedral geometry, Sq. Planar = square planar geometry.

^c ax = axial, eq = equatorial, – = not given.

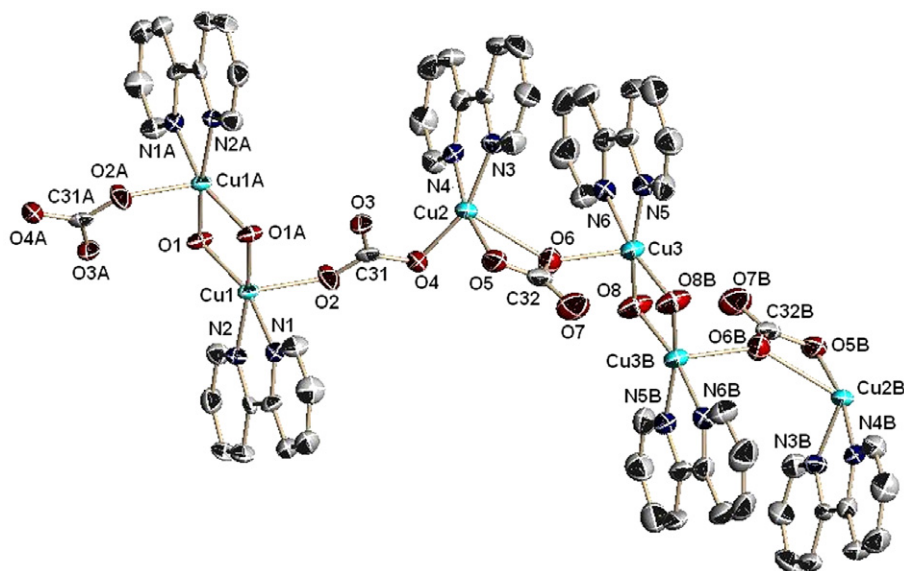


Fig. 3. Crystal structure and atomic numbering scheme for compound **2** (Thermal ellipsoids are drawn at 50% level). Hydrogen atoms and water molecules are omitted for clarity. Selected bond lengths (Å) and angles (°). Selected bond lengths (Å) and angles (°): Cu(1)–N(1) 2.035(7), Cu(1)–N(2) 2.012(7), Cu(1)–O(1) 1.939(5), Cu(1)–O(1A) 1.956(5), Cu(1)–O(2) 2.175(6), Cu(2)–N(3) 2.018(7), Cu(2)–N(4) 2.004(8), Cu(2)–O(4) 1.939(6), Cu(2)–O(5) 1.938(7), Cu(2)–O(6) 2.419(6), Cu(3)–N(5) 2.025(8), Cu(3)–N(6) 2.005(8), Cu(3)–O(6) 2.199(6), Cu(3)–O(8) 1.920(7), Cu(3)–O(8B) 1.927(6), Cu(1)···Cu(1A) 2.913(2), Cu(3)···Cu(3B) 2.875(2) and O(1)–Cu(1)–N(1) 161.3(3), N(2)–Cu(1)–O(1A) 170.8(3), O(4)–Cu(2)–N(3) 160.6(3), O(5)–Cu(2)–N(4) 167.7(3), O(8)–Cu(3)–N(5) 168.2(3), O(8B)–Cu(3)–N(5) 168.2(3). Symmetry codes A = (−x + 1, −y + 1, −z + 1) and B = (−x + 1, −y, −z + 2), respectively.

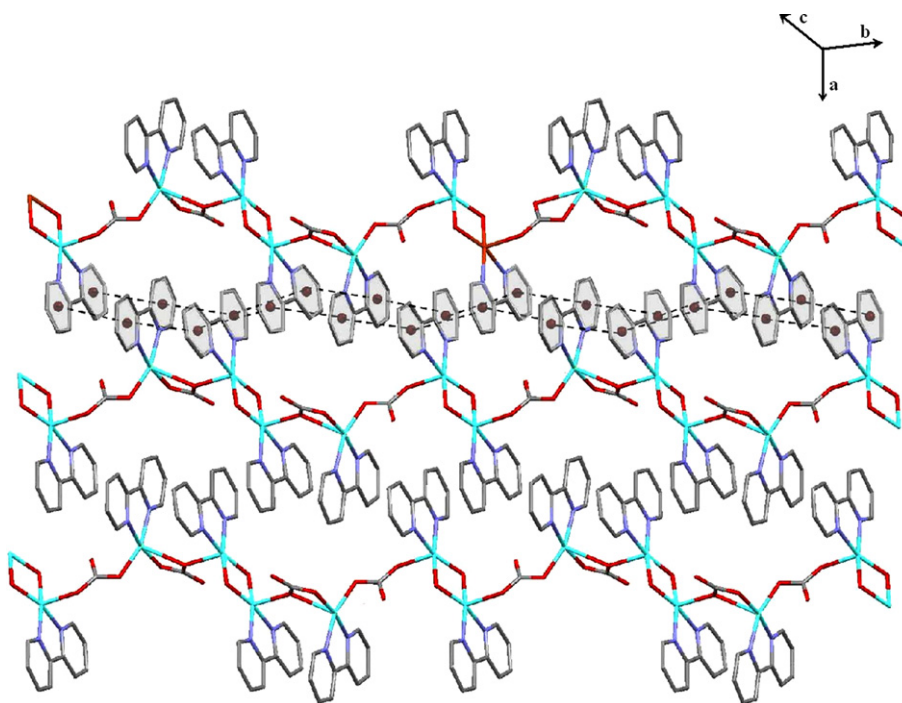


Fig. 4. Packing diagram of **2** showing the two-dimensional sheet formed by adjacent chains through π – π interactions. Hydrogen atoms and water molecules are omitted for clarity.

The polycrystalline EPR spectra (see Figs. S1 and S3) of compounds **1** and **2** are very similar both at RT and at 77 K. The spectrum of **1** shows signals at $g = 2.46$, 2.11 and 1.77, which are values attributed to the a monomeric impurity and also a half-field signal is observed at

$g = 4.44$ (155 mT), which supports the existence of a weak coupling between copper ions. The spectrum of **2** shows a signal of a monomeric impurity at ~ 3300 G and a half-field signal at ~ 1600 G, indicative for a weak coupling between the copper ions.

The magnetic susceptibility data of compounds **1** (5–300 K) and **2** (5–250 K) are reported as a preliminary result, as shown in a plot of $\chi_M T$ versus T for one Cu(II) ion (see Figs. S2 and S4). At 300 K for **1** the μ_B is $1.75 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ per Cu ion, which is about the spin-only value calculated for an uncoupled spin $S = 1/2$ Cu(II) center (for compound **2** this value is somewhat lower, due to the uncertainty in the measurement). Upon cooling, the value slightly increases to a value of $2.35 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at $\sim 5 \text{ K}$ for **1** and $0.87 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at $\sim 7 \text{ K}$ for **2**, then tend to decrease. This magnetic behavior is typical for weakly ferromagnetically coupled copper(II) ions. Some selected structural and magnetic data for polynuclear carbonate bridged Cu(II) compounds are summarized in Table 1. The overall ferromagnetic interaction of the previously studied compounds [1a,4i] containing both the carbonate and di- μ -hydroxido bridges, dominantly result from di- μ -hydroxido copper(II) species. For the planar bis- μ -hydroxido copper(II) species, an antiferromagnetic character is found for complexes with θ larger than 97.5° , while ferromagnetism appears for smaller values of θ [16]. The structure of compound **1** is similar to that of the perchlorate analogue (Table 1) containing both the di- μ -hydroxido Cu(II) entity and the $\text{Cu}_2(\mu\text{-CO}_3)$ unit. The di- μ -hydroxido moiety of compound **1** has the bridging angle of $94.3(3)^\circ$ suggesting a comparable ferromagnetic interaction. However, the predicted coupling constant calculated using Hodgson and Hatfield correlation is $+241.82 \text{ cm}^{-1}$. A very weak ferromagnetic interaction is also expected for the carbonate bridged Cu(II) moiety containing $\mu_3\text{-}\eta^2\text{:}\eta^1\text{-CO}_3$ coordinated fashion in the eq–eq and ax–eq configurations [1a]. Compound **2** is a polymeric chain structure containing the di- μ -hydroxido bridge and two different types of CO_3 coordination modes, $\mu\text{-}\eta^1\text{:}\eta^1$ (*anti-anti*) and $\mu\text{-}\eta^2\text{:}\eta^1$ in ax–eq configuration. The hydroxido bridging angles of 96.8° suggest the ferromagnetic coupling with the predicted coupling parameter of $+55.50 \text{ cm}^{-1}$ as compared to those of the closely related $\{[\text{Cu}_3(\text{bpy})_3(\mu\text{-OH})_2(\mu\text{-CO}_3)_2](\text{H}_2\text{O})_{11}\}_n$ [4i] (Table 1). Both CO_3 bridges with different modes in **2** link the Cu(II) ions in the axial–equatorial/axial–axial configurations, and so a weak ferromagnetic or antiferromagnetic interaction would be expected.

From the synthetic point of view, the strategy to achieve polynuclear carbonate bridged copper(II) compounds **1** and **2** is the use of a Cu(II) salt of a poorly coordinating anion, trifluoromethanesulfonate with the carbonate salt, Na_2CO_3 in a mixture of H_2O –DMF and a mixture of H_2O –MeOH for **1** and a mixture of H_2O –DMF for **2** using the directly prepared method. In such a basic solution, the di- μ -hydroxido species are usually stabilized to mutually occur, forming the polynuclear copper(II) compounds containing both a carbonate and dihydroxido bridges. The magnetic behaviors of the present compounds have been preliminarily investigated in relation with the geometry, bridging configuration and bridging mode of the CO_3^{2-} group, and also the bridging angle of the di- μ -hydroxido entities.

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Appendix A. Supplementary material

CCDC 668013 and 668014 contain the supplementary crystallographic data for structures **1** and **2**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Solid-state (diffuse reflectance) electronic spectra were measured as polycrystalline samples on a Perkin–Elmer Lambda2S spectrophotometer, in the range of $8000\text{--}18,000 \text{ cm}^{-1}$. The X-band powder EPR spectra were obtained as polycrystalline samples with a JEOL RE2X electron spin resonance spectrophotometer with DPPH ($g = 2.0036$) as a reference. Magnetic susceptibility measurements (5–250 K) were carried out using a Quantum design MPMS-5S SQUID magnetometer (measurements carried out at 0.1 mT). Data were corrected for magnetization of the sample holder and for diamagnetic contributions, which were estimated from the Pascal constants. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.inoche.2007.12.004](https://doi.org/10.1016/j.inoche.2007.12.004).

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- [9] *Synthesis*: Compound **1** was prepared by adding a warm solution (10 ml) of bpy (0.312 g, 2.0 mmol) in DMF into an aqueous solution (10 ml) of $\text{Cu}(\text{CF}_3\text{SO}_3)_2$ (0.362 g, 1.0 mmol). After that an aqueous solution (10 ml) of Na_2CO_3 (0.052 g, 0.5 mmol) was added. On slow evaporate in air, for several days the suitable greenish-blue crystals for X-ray analysis were obtained. Yield ca. 66%. Compound **1** was also prepared by the same method and starting materials with the mole ratio of 1:2:0.3 in mixed H_2O – MeOH (15:5 mL). Up on standing for a week, greenish-blue crystals of **1** were deposited. Yield ca. 60%. $\text{C}_{114}\text{H}_{96}\text{Cu}_6\text{N}_{22}\text{O}_{32}\text{F}_{18}\text{S}_6$; *Anal. Calc.*: C 43.1; H 3.1; N 9.4 Found: C 43.0; H 3.1; N 9.3%. Compound **2** was prepared by adding a warm solution (10 ml) of bpy (0.312 g, 2.0 mmol) in DMF, to a warm aqueous solution (10 ml) of $\text{Cu}(\text{CF}_3\text{SO}_3)_2$ (0.362 g, 1.0 mmol) and then 0.052 g of Na_2CO_3 (0.5 mmol) was added. Green crystals of **2** formed after two weeks. Yield ca. 50%. $\text{C}_{32}\text{H}_{31}\text{Cu}_3\text{N}_6\text{O}_{14.25}$ asymmetric unit; *Anal. Calc.*: C 41.7; H 4.2; N 9.1. Found: C 41.5; H 4.0; N 9.1.
- [10] *X-ray crystallography*; *Compound 1*: $\text{C}_{114}\text{H}_{96}\text{Cu}_6\text{N}_{22}\text{O}_{32}\text{F}_{18}\text{S}_6$ ($M_w = 3201.85$), triclinic, $P\bar{1}$, $a = 14.9173(3)$ Å, $b = 16.4162(3)$ Å, $c = 17.6015(3)$ Å, $\alpha = 65.62^\circ$, $\beta = 85.7130(10)^\circ$, $\gamma = 65.4680(10)^\circ$, $V = 3547.31(11)$ Å³, $T = 273(2)$ K, $Z = 1$, $D_c = 1.550$ g cm⁻³, $\mu = 1.079$ mm⁻¹, $F(000) = 1680$, 15,999 reflections measured ($1.50 < h < 27.88^\circ$), 5129 unique ($R_{\text{int}} = 0.0717$), $R_1 = 0.1003$, $wR_2 = 0.2390$. *Compound 2*: $\text{C}_{32}\text{H}_{31}\text{Cu}_3\text{N}_6\text{O}_{14.25}$ asymmetric unit (Formula weight = 922.26), triclinic, $P\bar{1}$, $a = 8.6769(2)$ Å, $b = 11.8993(3)$ Å, $c = 17.42770(10)$ Å, $\alpha = 91.7940(10)^\circ$, $\beta = 91.2320(10)^\circ$, $\gamma = 97.33^\circ$, $V = 1783.23(6)$ Å³, $T = 273(2)$ K, $Z = 2$, $D_c = 1.708$ g cm⁻³, $\mu = 1.852$ mm⁻¹, $F(000) = 926$, 10,132 reflections measured ($1.73 < h < 26.02^\circ$), 6812 unique ($R_{\text{int}} = 0.0644$), $R_1 = 0.0768$, $wR_2 = 0.1586$. Reflection data were collected on a 4 K Bruker SMART APEX CCD area-detector diffractometer (rotating anode, graphite-monochromated Mo K α radiation, $\lambda = 0.71073$ Å) using SMART program [Bruker, SMART (version 5.6)]. Raw data frame integration was performed with SAINT [Siemens. SAINT, Version 4], which also applied correction for Lorentz and Polarization effects. An empirical absorption correction by using the SADABS [G.M. Sheldrick, SADABS, Program for empirical absorption correction of area-detector data, University of Göttingen, Göttingen, Germany] program was applied, which resulted in transmission coefficients ranging from 1.000 to 0.747 for **1** and from 1.000 to 0.537 for **2**. The structures were solved by direct methods and refined by full-matrix least-squares method on $(F_{\text{obs}})^2$ with anisotropic thermal parameters for all non-hydrogen atoms using the SHELXTL-PC V 6.12 [Bruker, SHELXTL, Version 6.12, Bruker AXS Inc., Madison, Wisconsin, USA] software package. Compound **1**, all hydrogen atoms were introduced in calculated positions and refined with fixed geometry with respect to their carrier atoms except H(51) of the hydroxido bridge. Two triflate groups, one DMF molecule and one water molecule are disordered with site occupancies of 0.5. The third triflate group was also disordered and attempts have been made in range possibilities to locate disordered atoms but unsuccessful. Finally, we decide to refine as the ordered molecule with quite high but reliable temperature factors. The bond distances of DMF and some distances of the triflate molecules were restrained with the DFIX 1.47(1), 1.35(1) and 1.23(1) commands for N–C(methyl), N–C(C=O) and C=O bonds, respectively in DMF and the DFIX 1.57(1), 0.5(1), 1.86(1) and 1.32(1) commands for the S(2)–O(10)A, F(2)–F(2)A, C(54)–S(3) and C–F bond lengths, respectively in the triflate molecules. All non-hydrogen atoms were refined anisotropically except one C, four F and four O atoms of the triflate molecules and one C atom of DMF. The remaining four oxygen atoms of water molecules were refined with site occupancies of 0.25. The quite high R value of compound **1** is attributed to these disordered molecules with some restrained distances and isotropic refinement of some non-hydrogen atoms which is usually found. In compound **2**, all hydrogen atoms were geometrically fixed and allowed to ride on attached atoms except those of water molecules, H(31), H(32), H(33), H(34) and H(35). These hydrogen atoms were located by difference synthesis and refined isotropically on three oxygen water atoms, while the other hydrogen atoms of the remaining three water molecules could not be located. Three water oxygen atoms in the latter case were modeled as disordered and two of those were refined with site occupancies of 0.5 and another one with site occupancies of 0.7 and 0.3 for both conformers. The molecular graphic were created by using SHELXTL-PC.
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A novel octanuclear copper(II) compound: Synthesis, crystal structure and magnetic properties

Sujittra Youngme^{a,*}, Nanthawat Wannarit^a, Tawun Remsungnen^b, Chaveng Pakawatchai^c, Narongsak Chaichit^d, Chainarong Engkagul^d, Gerard A. van Albada^e, Jan Reedijk^e

^a Department of Chemistry, Faculty of Science, Khon Kaen University, Khon Kaen 40002, Thailand

^b Department of Mathematic, Faculty of Science, Khon Kaen University, Khon Kaen 40002, Thailand

^c Department of Chemistry, Faculty of Science, Prince of Songkhla University, Hat Yai, Songkhla 90112, Thailand

^d Department of Physics, Faculty of Science and Technology, Thammasat University, Rangsit, Pathumthani 12121, Thailand

^e Gorlaeus Laboratories, Leiden Institute of Chemistry, Leiden University, P.O. Box 9502, 2300 RA Leiden, The Netherlands

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Abstract

The crystal structure of a novel octanuclear copper(II) complex containing the bidentate 1,10-phenanthroline ligand (abbreviated as phen) with cooperative carbonato and hydroxido bridging ligands, $[\text{Cu}_8(\text{phen})_{12}(\mu_3\text{-OH})_2(\mu\text{-OH})_2(\mu_3\text{-CO}_3)_2](\text{CF}_3\text{SO}_3)_8(\text{DMF})_2(\text{H}_2\text{O})_{0.5}$ (**1**) (when DMF = *N,N*-dimethylformamide) is described. Compound **1** consists of two symmetry-related di- μ -hydroxido-bis(1,10-phenanthroline)copper(II) groups which held together by long Cu–O(H) bonds, creating a $\text{Cu}_2(\text{OH})_2$ core of a tetranuclear hydroxido-bridged copper(II) unit, further coordinated with *trans*-axially at Cu(3) and Cu(3)A by $[\mu_3\text{-carbonato-tetrakis(phen)dicopper(II)}]$ moieties. The di- μ -hydroxidocopper(II) species play an important role for the apparent ferromagnetic interaction with the Cu–OH–Cu angles (θ) of $95.8(2)^\circ$ and $93.5(1)^\circ$. The spectroscopic properties (IR, reflectance and EPR spectra) and the magnetic susceptibility data of this compound are investigated and compared with other related polynuclear copper(II) compounds.

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An extensive magneto-structural study of the carbonato-bridged copper(II) polynuclear compounds has shown the versatile properties of the bridging carbonato ligand leading to a wide variety of magnetic behavior from strong to moderate or weak coupling which is either antiferromagnetic or ferromagnetic [1–4]. The carbonate anion is flexible in its coordination modes, with a nuclearity varying from dinuclear to tetranuclear [1–4]. The richness contrasts with the paucity of the magnetic properties of the cooperation with hydroxido-bridged copper(II) dinuclear units, forming higher nuclearity copper(II) compounds [1d]. The hexanuclear $\text{Cu}_6(\text{bpy})_{10}(\mu\text{-OH})_2(\mu\text{-CO}_3)_2(\text{ClO}_4)_6(\text{H}_2\text{O})_4$ was suc-

cessfully synthesized by Kruger and co-workers [1c], exhibiting the overall ferromagnetic interaction. Recently, Doyle and co-workers [5k] have prepared an alternating carbonato/hydroxido-bridged copper(II) polymeric chain compound, $\{[\text{Cu}_3(\text{bpy})_3(\mu\text{-OH})_2(\mu\text{-CO}_3)_2](\text{H}_2\text{O})_{11}\}_n$ revealing a strong ferromagnetic exchange coupling. The magnetic exchange interaction of these compounds through the di- μ -hydroxido bridges masks the carbonate superexchange pathway which is ferromagnetic in nature.

A family of the di- μ -hydroxido copper(II) dinuclear complexes [6–10] form the best understood examples in the magneto-structural correlation studied by Hatfield and Hodgson [11]. An antiferromagnetic character is found for complexes with Cu–OH–Cu angle (θ) values larger than 97.5° , while ferromagnetism appears for smaller values of θ . Ruiz and co-workers [12] later expanded the study by

* Corresponding author. Fax: +66 4320 2373.

E-mail address: sujittra@kku.ac.th (S. Youngme).

incorporating the out-of-plane displacement angle (γ) of the hydrogen atom of the hydroxido group and showed that for values of θ below 97.5° greater γ shifts reduce the antiferromagnetic component, the ferromagnetic character dominates when γ increases above a threshold value of $\gamma = 50^\circ$. So far, the number of X-ray structures of the polynuclear copper(II) compounds with the cooperative carbonato and hydroxido bridges is very limited, considering the extensive research known with the ligand 1,10-phenanthroline (phen). We report herein the synthesis [13], crystal structure [14], spectroscopic properties (IR, reflectance and EPR) and the magnetic investigation of a novel octanuclear copper(II) phen compound, $[\text{Cu}_8(\text{phen})_{12}(\mu_3\text{-OH})_2(\mu\text{-OH})_2(\mu_3\text{-CO}_3)_2](\text{CF}_3\text{SO}_3)_8(\text{DMF})_2(\text{H}_2\text{O})_{0.5}$ (**1**).

The overall molecular structure of **1** consists of eight trifluoromethanesulfonate counteranions, two *N,N*-dimethylformamide (DMF) molecules and a half of lattice water molecule. A centrosymmetric $[\text{Cu}_8(\text{phen})_{12}(\mu_3\text{-OH})_2(\mu\text{-OH})_2(\mu_3\text{-CO}_3)_2]^{8+}$ unit (Fig. 1 and Fig. S1a) contains two [di- μ -hydroxido-bis(1,10-phenanthroline)dicopper(II)] moieties, phen-Cu-(OH)₂-Cu-phen moieties which are held together by long Cu–O(H) bonds, creating Cu₂(OH)₂ core of tetranuclear hydroxido-bridged copper(II) unit. These dihydroxido-bridged copper(II) units are further coordinated *trans*-axially at Cu(3) and Cu(3A) to two [μ_3 -carbonato-tetrakis(1,10-phenanthroline)dicopper(II)] moieties. Within the dinuclear dihydroxido-bridged copper(II) unit, the Cu(3)–Cu(4) separation of 2.853(1) Å, the Cu(3)–O(4)–Cu(4) and Cu(3)–O(5)–Cu(4) bridging

angles of $95.8(2)^\circ$ and $93.5(1)^\circ$ fall within the range found for similarly coordinated di- μ -hydroxido copper(II) dinuclear compounds [6–10]. The environment of two crystallographically independent copper atoms is in a nearly regular square-pyramidal geometry, $\tau = 0.19$ and 0.05 [15] with an apical distances of Cu(3)–O(3) 2.156(4) Å and Cu(4)–O(5A) 2.493(1) Å. Consequently, the phen-Cu-(OH)₂-Cu-phen moieties held together by long Cu–O(H) bonds at 2.493(1) Å, the two copper centers and two oxygen atoms of bridging hydroxido ligands are placed on the vertices of a rectangle, creating a Cu₂(OH)₂ core of tetranuclear hydroxido-bridged copper(II) unit (Fig. S1b). The Cu(3) and Cu(4) atoms lie 0.13 and 0.06, above the basal planes toward O(3) and O(5A), respectively.

The Cu(3) and Cu(3A) centers of di- μ -hydroxido copper(II) moieties are further linked to two symmetry-related [μ -carbonato-tetrakis(1,10-phenanthroline)dicopper(II)] units via the $\mu_3\text{-}\eta^1\text{:}\eta^1\text{:}\eta^1\text{-CO}_3$ coordination mode of carbonate bridging ligand, giving a triangular array of copper atoms. The Cu(1) and Cu(2) of this unit are in an intermediate five-coordinate geometry with a τ values of 0.59 and 0.33, respectively. However, the coordination geometry around Cu(1) is slightly distorted towards a trigonal bipyramid via a Berry-Twist process [16] with the trigonal planar distances of Cu–N(1) 2.175(5), Cu–N(4) 2.129(5) and Cu–N(3) 2.000(5) Å and the axial distances of Cu–O(1) 1.949(4) and Cu–N(2) 1.996(5) Å. This is typical for the trigonal-bipyramidal geometry [17]. While the environment geometry around Cu(2) is slightly distorted towards a

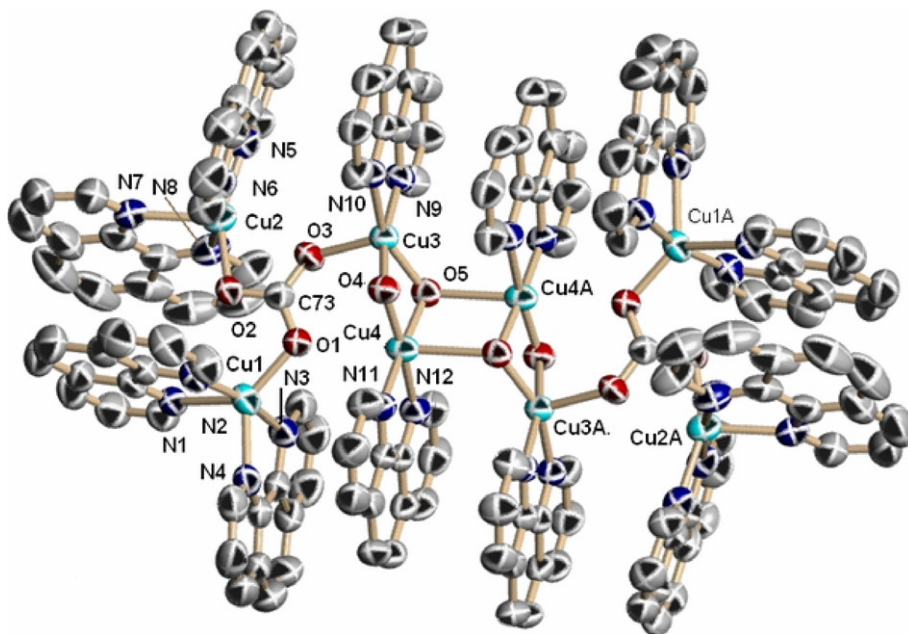


Fig. 1. Molecular structure and atomic numbering scheme for **1**. Thermal ellipsoids are shown at 30% probability level. Hydrogen atoms, triflate anions, DMF and water molecules are omitted for clarity. “A” symmetry transformations are used to generate equivalent atoms $1-x$, $1-y$, $-z$. Selected bond lengths (Å) and angles ($^\circ$): Cu(1)–N(1) 2.175(5), Cu(1)–N(2) 1.996(5), Cu(1)–N(3) 2.000(5), Cu(1)–N(4) 2.129(5), Cu(1)–O(1) 1.949(4), Cu(2)–N(5) 2.054(5), Cu(2)–N(6) 2.000(5), Cu(2)–N(7) 2.246(6), Cu(2)–N(8) 1.998(6), Cu(2)–O(2) 1.956(4), Cu(3)–N(9) 2.019(5), Cu(3)–N(10) 2.025(5), Cu(3)–O(3) 2.156(4), Cu(3)–O(4) 1.925(5), Cu(3)–O(5) 1.974(4), Cu(3)–Cu(4) 2.8526(10), N(2)–Cu(1)–N(3) $167.2(2)^\circ$, O(1)–Cu(1)–N(4) $132.0(1)^\circ$, N(6)–Cu(2)–N(8) $173.9(2)^\circ$, O(2)–Cu(2)–N(5) $154.2(1)^\circ$, N(9)–Cu(3)–O(4) $167.3(2)^\circ$, N(10)–Cu(3)–O(5) $155.8(2)^\circ$, N(11)–Cu(4)–O(5) $177.6(2)^\circ$ and N(12)–Cu(4)–O(4) $174.6(2)^\circ$.

square pyramid ($\tau = 0.33$) with the apical distance of Cu–N(7) 2.246(6) Å. The crystal structure was stabilized by the intermolecular hydrogen-bonding interactions between the oxygen atom of the hydroxido bridges and the oxygen atom of triflate molecules [O(4)···O(7) = 3.040 Å, H(4)···O(7) = 2.464 Å, and O(4)–H(4)···O(7) = 164.36° ($-x+1, -y+1, -z+1$) and O(5)···O(9) = 3.146 Å, H(5)···O(9) = 2.527 Å, and O(5)–H(5)···O(9) = 170.32° ($x, y, z+1$)]. These interactions displace the hydrogen atoms of the hydroxido groups out of the Cu–O–Cu plane by $\gamma = 55.4^\circ$ and 47.0° , respectively. The influence of intramolecular phen–phen π -stacking interactions has been considered to play a role in this molecular structure. The adjacent molecules are interlocked through π – π interactions involving the phen ligand and also play a role in the apparent molecular structure of the present complex, thus favor its formation. These intermolecular π – π interactions with separation of ca. 3.714 Å, form a 2D sheet within the crystallographic bc -plane as shown in Fig. 2.

The EPR spectra of the title compound was recorded as a polycrystalline powder at RT and at 77 K from 0 to 600 mT at X-band frequency ($h\nu = 0.325 \text{ cm}^{-1}$). The EPR spectra at RT and at 77 K were found to be the same and the spectrum (Fig. 3) consists of a very broad and strong signal centered around 320 mT. Furthermore, a weak signal was observed at about 368 mT, which can be assigned to $S = 1$ triplet signals, other triplet signals seem to be obscured by the broad signal at 320 mT. The signal at around 160 mT can be assigned to the forbidden half-field signal ($\Delta M_s = \pm 2$).

The magnetic susceptibility of a powdered sample was measured from 5 to 300 K and the magnetic properties of the title compound are depicted in Fig. 4 in the form of

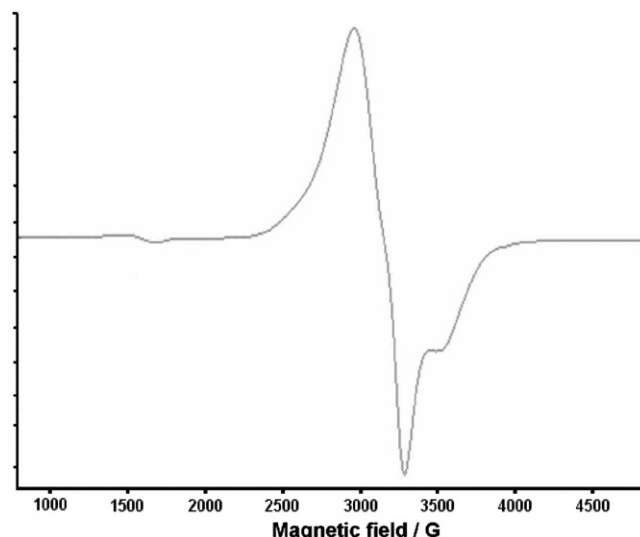


Fig. 3. The EPR spectrum of compound **1** at room temperature.

$\chi_M T$ vs. T for one Cu(II) ion. At 300 K the $\chi_M T$ product has a value of $0.355 \text{ cm}^3 \text{ K mol}^{-1}$, which is close to the spin-only value for one non-interacting Cu(II) ion ($0.375 \text{ cm}^3 \text{ K mol}^{-1}$ at RT). From 300 K the $\chi_M T$ product increases gradually to a value of $0.556 \text{ cm}^3 \text{ K mol}^{-1}$ at 5 K. This magnetic behavior agrees with a weak ferromagnetic interaction. Due to the preliminary nature and the complicated structure, fitting against magnetic parameters was not possible at this moment.

A number of polynuclear carbonato-bridged Cu(II) compounds have been structurally and magnetically described. Some selected structural and magnetic data for these compounds are summarized in Table 1. Compound **1** has the trinuclear carbonato-bridged triangular Cu(II)

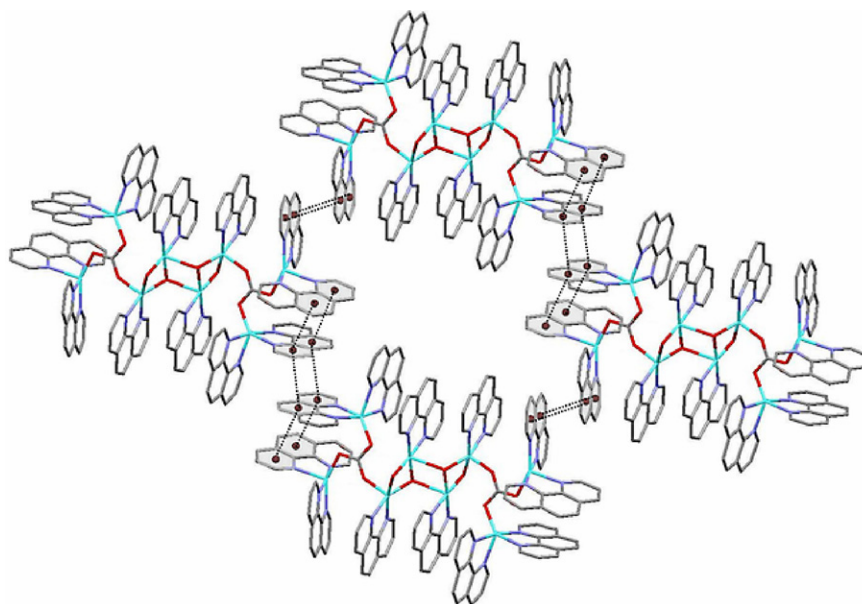


Fig. 2. Packing diagram of **1** showing the two-dimensional sheet formed by adjacent chains through π – π interactions within a crystallographic bc -plane. Hydrogen atoms, triflate anions, DMF and water molecules are omitted for clarity.

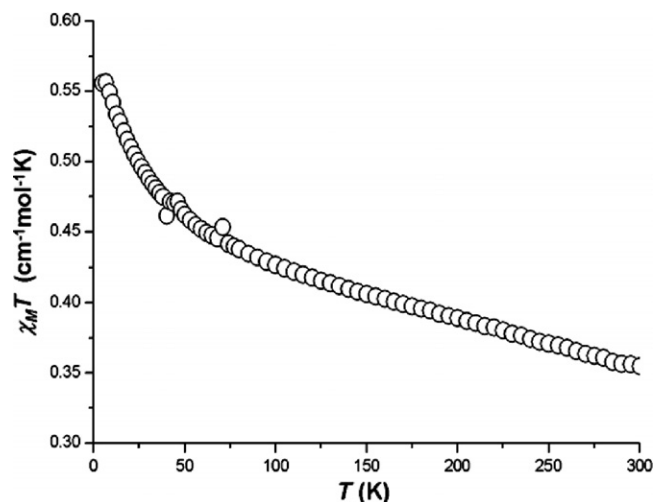


Fig. 4. A plot of $\chi_M T$ vs. T per Cu(II) ion for compound **1**.

units with $\mu_3\text{-}\eta^1\text{:}\eta^1\text{:}\eta^1\text{-CO}_3$ coordination mode, which usually performed the magnetic interaction ranging between weak antiferromagnetic to weak ferromagnetic interaction [3]. The dominant coupling between copper atoms of compound **1** is investigated in a similar trend to that of the previously reported compound, $\{[\text{Cu}_3(\text{bpy})_3(\mu\text{-OH})_2(\mu\text{-CO}_3)_2](\text{H}_2\text{O})_{11}\}_n$ [5k] which revealed the strong ferromagnetic exchange coupling with $J_{(\mu\text{-OH})} = +154$ and $+135 \text{ cm}^{-1}$ for the two independent di- μ -hydroxido copper(II) moieties with $\theta = 94.6^\circ$, 96.5° and $\gamma = 68.3^\circ$, 59.0° . Strong ferromagnetic couplings are predicted through the di- μ -hydroxido pathway because of the values of the bridging angles of **1** are 95.8° and 93.5° corresponding to the ferromagnetic interactions with the singlet–triplet energy gap (J value) [11] of $+130.0$ and $+301.4 \text{ cm}^{-1}$, respectively whereas extremely weak magnetic interactions are expected through the two carbonato bridges (equatorial–equatorial $[\text{Cu}(1)\text{-O}(1)\text{-C}(73)\text{-O}(2)\text{-Cu}(2)]$ and equatorial–axial $[\text{Cu}(1)\text{-O}(1)\text{-C}(73)\text{-O}(3)\text{-Cu}(3)]$ and $[\text{Cu}(2)\text{-O}(2)\text{-C}(73)\text{-O}(3)\text{-Cu}(3)]$ pathways with small values of the spin densities in the O(3) and O(3A) axially coordinated atoms). However, a slight distortion from planarity of two independent di- μ -hydroxido copper(II) units may play a minor influence in the decrease of the magnetic interactions, then providing the overall moderate to strong ferromagnetic interaction. The expected weak magnetic interactions of two terminal trinuclear units are comparable to those of the closely relative trinuclear compounds (Table 1).

In summary, a novel octanuclear copper(II) compound has been synthesized and reported in this study together with its spectroscopic and magnetic results. The present compound contains both carbonato and hydroxido bridges between Cu(II) ions and also have coordinated the ligand phen. The magnetic behavior has shown that the apparent ferromagnetic magnetic interaction might be determined by the hydroxido-bridged copper(II) species and has less by the carbonato-bridged copper(II) units.

Table 1
X-ray structure parameters and magnetism for some related polynuclear carbonato- and hydroxido-bridged copper(II) compounds

Compound ^a	Geometry/ Cu ^b	τ Cu1, Cu2, Cu3, Cu4	Cu–O(CO ₃)/ Å	Cu–O(H)/ Å	Cu...Cu/ Å	Cu–O(H)– Cu/ °	Coupling constant/ cm^{-1}	Ref.
Trinuclear								
$[\text{Cu}_3(\text{bpy})_6(\mu_3\text{-CO}_3)](\text{BF}_4)_4(\text{H}_2\text{O})_2(\text{C}_2\text{H}_6\text{O})$	Sq. Py., TBP	0.21, 0.10, 0.66	1.969–2.055	–	–	–	+10.6	[3a]
$[\text{Cu}_3(\text{dmbpy})_6(\mu_3\text{-CO}_3)](\text{BF}_4)_4(\text{C}_2\text{H}_5\text{OH})(\text{H}_2\text{O})$	Sq. Py., TBP	0.43, 0.26, 0.71	1.963–2.009	–	–	–	+9.3	[3c]
Tetranuclear								
$[\text{Cu}_4(\text{dmbpy})_4(\mu_3\text{-OH})_2(\mu\text{-OH})_2](\text{BF}_4)_4(\text{H}_2\text{O})_4$	Sq. Py.	0.24, 0.17	–	1.953	2.940	97.1, 98.2	+31.1	[3c]
Hexanuclear								
$[\text{Cu}_6(\text{bpy})_{10}(\mu\text{-CO}_3)_2(\mu\text{-OH})_2](\text{ClO}_4)_6(\text{H}_2\text{O})_4$	Sq. Py.	0.41, 0.23, 0.05	1.942–2.002	1.922	2.845	95.1	+2.75 ($\mu\text{-CO}_3$), +3.25 ($\mu\text{-CO}_3$) +2.75 ($\mu\text{-CO}_3$), +24 ($\mu\text{-OH}$)	[1c]
Octanuclear								
$[\text{Cu}_8(\text{phen})_{12}(\mu_3\text{-OH})_2(\mu_3\text{-OH})_2(\mu\text{-OH})_2(\mu\text{-CO}_3)_2](\text{CF}_3\text{SO}_3)_{18}(\text{DMF})_2(\text{H}_2\text{O})_{0.5}$	TBP, Sq. Py.	0.59, 0.33, 0.19, 0.05	1.949–2.156	1.940	2.853	93.5, 95.8	–	This work
Polynuclear								
$\{[\text{Cu}_3(\text{bpy})_2(\mu\text{-OH})_2(\mu\text{-CO}_3)_2](\text{H}_2\text{O})_{11}\}_n$	Sq. Py.	0.16, 0.22, 0.00	–	1.950	2.897	94.6, 96.5	+154 ($\mu\text{-OH}$), +135 ($\mu\text{-OH}$)	[5k]

– = Not given.

^a bpy = 2,2'-bipyridine, dmbpy = 4,4'-dimethyl-2,2'-bipyridine, phen = 1,10-phenanthroline, DMF = N,N-dimethylformamide.

^b TBP = trigonal bipyramidal geometry, Sq. Py. = square pyramidal geometry.

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Appendix A. Supplementary material

IR spectra were recorded with a Biorad FTS-7/PC FTIR spectrophotometer as KBr pellets and/or as nujol mulls in the 4000–450 cm^{-1} spectral range. Solid-state (diffuse reflectance) electronic spectra were measured as polycrystalline samples on a Perkin–Elmer Lambda2S spectrophotometer, in the range of 8000–18,000 cm^{-1} . X-band powder EPR spectra were obtained on a Bruker-EMXplus electron spin resonance spectrometer (Field calibrated with DPPH ($g = 2.0036$)). Magnetic susceptibility measurements (5–300 K) were carried out using a Quantum design MPMS-5S SQUID magnetometer (measurements carried out at 0.1 mT). Data were corrected for magnetization of the sample holder and for diamagnetic contributions, which were estimated from the Pascal constants.

CCDC No. 668093 for structure **1** contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.inoche.2008.01.011](https://doi.org/10.1016/j.inoche.2008.01.011).

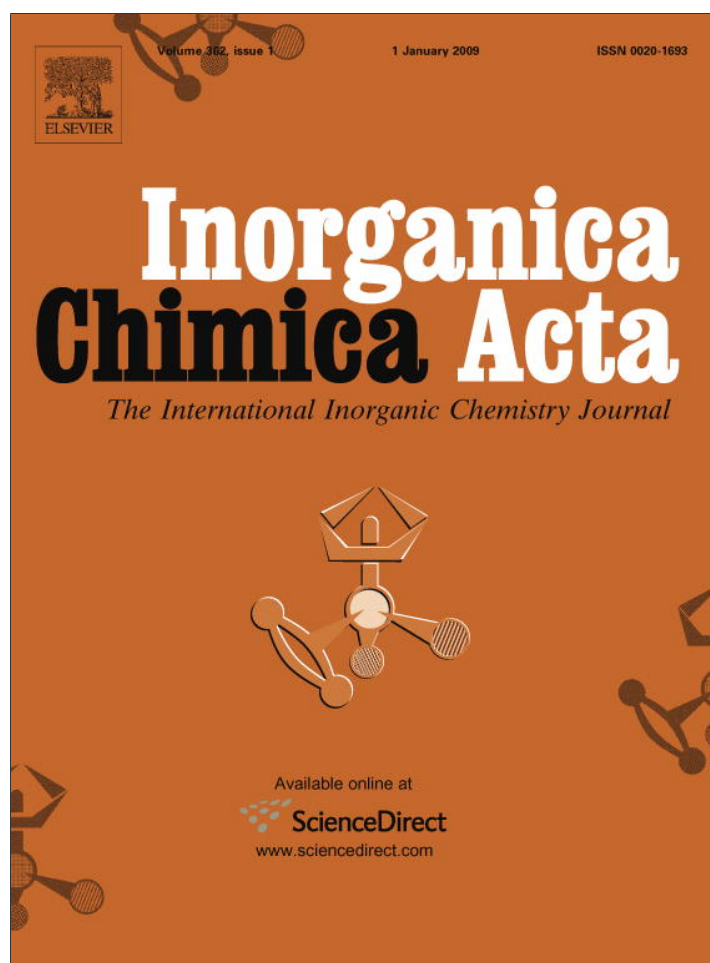
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- [13] *Synthesis of compound 1*: A warm solution (5 ml) of phen (0.199 g, 1.0 mmol) in 3:2 ratio of ethanol:dimethylformamide (DMF) was added to a warm aqueous solution (5 ml) of $\text{Cu}(\text{CF}_3\text{SO}_3)_2$ (0.182 g, 0.5 mmol) and then a warm aqueous solution (5 ml) of Na_2CO_3 (0.026 g, 0.25 mmol) was added. On slow evaporation in air, only green crystals of **1** were formed after a week. Yield ca. 80%. $\text{C}_{157}\text{H}_{100}\text{Cu}_8\text{N}_{25}\text{O}_{35.5}\text{F}_{24}\text{S}_8$; Anal. Calc.: C, 45.7; H, 2.4; N, 8.5. Found: C, 45.6; H, 2.8; N, 8.6. To study the pH effect, the pH of solution was adjusted in a range of 8.5–12.0 with a NaOH solution, resulted the green crystals of **1** with some side product $[\text{Cu}(\text{phen})_3](\text{CF}_3\text{SO}_3)_2$ for high pH (10.0–12.0) were also obtained. IR data for **1** (KBr, cm^{-1}): 3435 $\nu(\text{OH})$, 1357 $\nu_{\text{as}}(\text{CO}_3)$, 1277s $\nu_{\text{as}}(\text{S}-\text{O})$, 1155m $\nu_{\text{as}}(\text{C}-\text{F})$, 1030s $\nu_{\text{as}}(\text{S}-\text{O})$, 774 $\delta_{\text{s}}(\text{CO}_3)$, 755w $\delta_{\text{as}}(\text{CF}_3)$, 637m $\delta_{\text{as}}(\text{SO}_3)$, 573w $\delta_{\text{s}}(\text{CF}_3)$ and 519w $\delta_{\text{s}}(\text{SO}_3)$. Solid-state (diffuse reflectance) electronic spectrum: a broad band from 14970 to 10240 cm^{-1} .
- [14] *X-ray crystallography; crystal data for 1*: $\text{C}_{157}\text{H}_{100}\text{Cu}_8\text{N}_{25}\text{O}_{35.5}\text{F}_{24}\text{S}_8$ (Mw = 4125.59), Triclinic, $P\bar{1}$, $a = 13.9420(6)$ Å, $b = 16.7236(7)$ Å, $c = 19.2163(8)$ Å, $\alpha = 69.1980(10)^\circ$, $\beta = 78.5660(10)^\circ$, $\gamma = 78.5660(10)^\circ$, $V = 4065.1(3)$ Å³, $T = 293(2)$ K, $Z = 1$, $D_c = 1.688$ g cm⁻³,

$\mu = 1.241 \text{ mm}^{-1}$, $F(000) = 2081$, 55,557 reflections measured ($1.32^\circ < 2\theta < 28.05^\circ$), 19,676 unique ($R_{\text{int}} = 0.0470$), $R_1 = 0.0882$, $wR_2 = 0.2554$. The X-ray single-crystal data were collected at 273 K for compounds **1** on a 4 K Bruker SMART APEX CCD area-detector diffractometer (rotating anode, graphite-monochromated $\text{Mo K}\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$) using SMART program [Bruker, SMART (version 5.6)]. Raw data frame integration was performed with SAINT [Siemens, SAINT, Version 4], which also applied correction for Lorentz and Polarization effects. An empirical absorption correction by using the SADABS [G.M. Sheldrick, SADABS, Program for Empirical Absorption correction of Area Detector Data, University of Göttingen, Göttingen, Germany] program was applied, which resulted in transmission coefficients ranging from 1.000 to 0.844 for **1**. The structure was solved by direct methods and refined by full-matrix least-squares method on $(F_{\text{obs}})^2$ with anisotropic thermal parameters for all non-hydrogen atoms using the SHELXTL-PC V 6.12 [Bruker, SHELXTL, Version 6.12, Bruker AXS Inc., Madison, Wisconsin, USA] software package. All hydrogen atoms of phen ligands in **1** were geometrically fixed and allowed to ride on attached atoms except H(4) and H(5) of the hydroxide bridge. The first three triflate molecules are modeled as disordered forms with site occupancies of 0.5 with reasonable bond

lengths and bond angles and a few DFIX treatments of bond distances (C–F 1.340(1) Å). Additionally, isotropic refinement of some atoms was introduced. The fourth triflate and a DMF molecule were also disordered and attempts have been made in many possibilities to locate disordered atoms, but unsuccessful. Finally, we decide to refine as the ordered molecules with restrained bond distances (C–S 1.800(1), C–F 1.340(1), S–O 1.400(1) Å for a triflate molecule and N–C_{methyl} 1.470(1), N–C_{carbonyl} 1.350(1), C=O 1.230(1) Å for a DMF molecule). Additionally, the isotropic refinement of some atoms was introduced, leading to the quite high temperature factor of some atoms and an unreasonable N–C–O angle (77.80°) of a DMF molecule. Hydrogen atoms of a DMF could not be fixed and located. A water oxygen atom was located with an isotropic refinement and site occupancy of 0.25 without located hydrogen atoms. The molecular structure picture was created by using SHELXTL-PC.

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Structural aspects of some 2:1 dipyridylamine complexes of some copper(II) salts: An interesting new polymorph of the binuclear carbonate/perchlorate tetrahydrate adduct

Chaveng Pakawatchai^a, Brian W. Skelton^b, Allan H. White^b, Sujittra Youngme^{c,*}

^a Department of Chemistry, Prince of Songkla University, Hatyai 90112, Thailand

^b Chemistry M313, School of Biomedical, Biomolecular and Chemical Sciences, The University of Western Australia, Crawley, WA 6009, United States

^c Department of Chemistry, Faculty of Science, Khon Kaen University, Khon Kaen 40002, Thailand

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ABSTRACT

Recent work has described the structural characterization of the complexes $\text{Cu}_2(\text{CO}_3)\text{X}'_2\cdot\text{dpyam}\cdot\text{H}_2\text{O}$ (1:4:4), $\text{X}' = \text{ClO}_4, \text{BF}_4$, 'dpyam' = dipyridylamine, as a pair of triclinic $Z = 1$ isomorphs, the cations being modelled in terms of pairs of copper atoms bridged by a carbonate ion disordered about a crystallographic inversion centre. This work has been revisited in the course of describing a new polymorph of the perchlorate in a triclinic cell of twice the size, in which the carbonate unit, now non-disordered, bridges a pair of crystallographically independent copper atoms which display distinctly different coordination environments, one close to the square-pyramidal norm, the other not. Studies of adducts of the form $[(\text{dpyam})_2\text{CuX}]\text{X}'(\cdot n\text{H}_2\text{O})$ are also recorded. The $\text{X}/\text{X}' = \text{propionate/iodide}$ adduct is found to be isomorphous with its acetate/ BF_4 but, interestingly, *not* its propionate/ Cl counterpart. 'Low'-temperature redeterminations of the $\text{NCO}/\text{Cl} \cdot 4\text{H}_2\text{O}$ and nitrite/ ClO_4 adducts are also recorded, enabling definition of the hydrogen-bonding scheme in the former.

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1. Introduction

In recent years publications by Youngme and associates have conducted a systematic study of the metal atom coordination environments in 1:2 complexes of copper(II) salts with dipyridylamine ('dpyam'), using single crystal X-ray diffraction studies as a basis for diverse spectroscopic studies. The majority take the form $[(\text{dpyam}-N,N')_2\text{CuX}]\text{X}'$, in which the copper(II) atoms are usually found to lie in essentially five-coordinate environments, each made up of a pair of bidentate dpyam donors and unidentate X (which may differ from X'). A number of the underpinning X-ray studies were undertaken in diverse venues, resulting in some duplication, as evidenced in the present results; the diversity of venues also resulted in some diversity in conditions and description of the various results, nearly all of those described in the present work being derivative of 'low'-temperature studies, resulting in diminished displacement parameters and enhanced precision, some of the consequences being of considerable interest, which we report herein.

Present interest, in particular, concerns the reports of a pair of isomorphous salts of the form $\text{Cu}_2(\text{CO}_3)\text{X}'_2\cdot\text{dpyam}\cdot\text{H}_2\text{O}$ (1:4:4),

$\text{X}' = \text{BF}_4$ [1], ClO_4 [2,3], both described in terms of a triclinic $Z = 1$ form, entailing, in each case, the adoption of a centrosymmetric model in space group $P\bar{1}$, a pair of symmetry related $[(\text{dpyam})_2\text{Cu}]$ units being linked by a carbonate group modelled as disposed about a crystallographic inversion centre. A parallel determination of the perchlorate carried out in a different venue produced a result at variance with this, the compound still being a tetrahydrate, but with an unambiguously fully ordered triclinic $P1$ model in a cell of twice the volume, with a pair of independent copper atoms in distinctly different environments. This led us to question whether the earlier model may have been inadequate (e.g.) in terms of an over-looked superlattice (etc.) or whether the difference was real and so the two studies were repeated, this time at (ca.) 100 K instead of room-temperature; the results of these studies essentially confirmed the key features of the reported models, showing the result of the duplicate study to define a new (and interesting) polymorph, which we record herein.

A related series of studies concerned adducts of the form $[(\text{dpyam})_2\text{CuX}]\text{X}'(\cdot n\text{H}_2\text{O})$, a number of those having been defined for $\text{X} = \text{carboxylate}$ systems. Of particular interest are those for $\text{X}/\text{X}' = \text{acetate/tetrafluoroborate}$ [1], and for propionate/chloride (monohydrate) [4] (not isomorphous). Surprisingly, a study described herein of the propionate/iodide complex, shows it to be anhydrous and isomorphous with its acetate/tetrafluoroborate counterpart.

* Corresponding author. Tel.: +66 4320 2222; fax: +66 4320 2373.

E-mail address: sujittra@kku.ac.th (S. Youngme).

Finally, also relevant to the latter form, we also record (low-temperature) studies of the cyanate/chloride (tetrahydrate) and nitrite/perchlorate adducts, previously the subject of room-temperature studies ([5,6], respectively), defining the hydrogen-bonding network in the former and the nature of the coordinated nitrite anion more precisely in the latter. The impact of these studies on the associated spectroscopies is discussed.

2. Experimental

2.1. Syntheses

The compound $[(\text{dpyam})_2\text{Cu}(\text{O}_2\text{Cet})]\text{I}$ (i.e. $\text{X/X}' = \text{O}_2\text{Cet/I}$) was prepared by adding a warm solution of dpyam (0.342 g, 2.0 mmol) in ethanol (30 ml) to a warm aqueous solution (20 ml) of $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2 \cdot \text{H}_2\text{O}$ (0.119 g, 0.5 mmol). A solid of NaO_2Cet (0.384 g, 4.0 mmol) and KI (0.166 g, 1.0 mmol) was then added, giving a green solution. The resulting solution was evaporated slowly at room-temperature. After several days, green prism-shaped crystals of this compound were formed and filtered off, washed with mother liquor and air-dried (yield ca. 80%). *Anal. Calc.* for $\text{C}_{23}\text{H}_{23}\text{CuIN}_6\text{O}_2$: C, 45.52; H, 3.84; N, 13.88. Found: C, 45.58; H, 3.79; N, 13.87%. IR (KBr, disc) $\nu_{\text{as}}(\text{COO})$ 1584 cm^{-1} , $\nu_{\text{s}}(\text{COO})$ 1474 cm^{-1} . The compounds $[(\text{dpyam})_2\text{Cu}(\text{ONO})](\text{ClO}_4)$ ($\text{X/X}' = \text{NO}_2/\text{ClO}_4$) [6], $[(\text{dpyam})_2\text{Cu}(\text{NCO})]\text{Cl} \cdot 4\text{H}_2\text{O}$ ($\text{X/X}' = \text{NCO/Cl}$) [5], $[(\text{dpyam})_2\text{Cu}(\text{O} \cdot \text{CO} \cdot \text{O})_{(2/2)}\text{Cu}(\text{dpyam})_2](\text{BF}_4)_2 \cdot 4\text{H}_2\text{O}$ ($\text{X/X}' = (1/2)\text{CO}_3/\text{BF}_4$) [1] and $[(\text{dpyam})_2\text{Cu}(\text{O} \cdot \text{CO} \cdot \text{O})_{(2/2)}\text{Cu}(\text{dpyam})_2](\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ ($\text{X/X}' = (1/2)\text{CO}_3/\text{ClO}_4$) [2,3] were prepared following the previous literature procedures.

2.2. Structure determinations

With one exception (see below), full spheres of 'low'-temperature CCD area-detector diffractometer data were measured (monochromatic Mo K α radiation, $\lambda = 0.71073$ Å; ω -scans) yielding $N_{\text{t}}(\text{total})$ reflections, these merging to N unique (R_{int} cited) after 'empirical'/multiscan absorption corrections (proprietary software), N_0 with $I > 2\sigma(I)$ being considered 'observed'. All reflections were used in the full-matrix refinements on F^2 , refining anisotropic displace-

ment parameter forms for the non-hydrogen atoms, hydrogen atom treatments following a riding model except for those associated with the water molecules which were refined in $(x,y,z,U_{\text{iso}})_{\text{H}}$. Reflection weights were $(\sigma^2(F^2) + (aP)^2 + (bP))^{-1}$. Neutral atom complex scattering factors were employed within the context of the SHELXL-97 program [7]. Pertinent results are given below and in the tables and figures, which show 50% probability amplitude displacement envelopes for the non-hydrogen atoms, hydrogen atoms having arbitrary radii of 0.1 Å. The crystal and refinement details for all complexes are listed in Table 1.

2.2.1. Variata

$(\text{X/X}')=\text{O}_2\text{Cet/I}$. A unique data set was measured at room-temperature using a single counter instrument; an analytical absorption correction was applied. The pendant methyl substituent of the propionate group was modelled as disordered over two sets of sites, set at equal occupancy after trial refinement, the disorder perhaps reflected further afield in the somewhat anomalous displacement ellipsoid(s) of the associated C(21) (and 22) (see Table 2).

$\text{O}_2\text{N/ClO}_4$. As recorded in the room-temperature study [6], the perchlorate group is rotationally disordered about one of the Cl–O bonds over two sets of sites, occupancies in the original report set at 0.5. In the present study, refinement of site occupancies converged at 0.647(4) and complement; in an early inferior study on an independent specimen, also executed at ca. 153 K, the value was 0.646(6).

$(1/2)\text{CO}_3/\text{BF}_4](\text{ClO}_4(\alpha))$. In the previous models for both BF_4^- and ClO_4^- salts, the carbon atoms of the central carbonate units were located at crystallographic centres of symmetry, resulting in unrealistic associated geometries; in the present studies, the carbon atoms were located at general positions, resulting in more 'normal' geometries for the carbonate groups (CO_3^{2-} having site occupancy 0.5). In the room-temperature determinations, the tetrahedral counterion peripheral atoms were modelled as disordered over two sets of sites; in the present studies, no disorder was found, although displacement parameters were somewhat greater than those of the general body of each structure. However, of the two independent water molecules, one was assigned full site occu-

Table 1
Crystal/refinement data

$[(\text{dpyam})_2\text{CuX}](\text{X}' \cdot n\text{H}_2\text{O})$	$[(\text{dpyam})_2\text{Cu}]_2(\text{CO}_3)_2 \cdot 4\text{H}_2\text{O}$					
$\text{X/X}'(/n)$	$\text{O}_2\text{Cet/I}$	$\text{O}_2\text{N/ClO}_4$	$\text{NCO/Cl}(4)$	$(1/2)\text{CO}_3/\text{BF}_4(4)$	$(1/2)\text{CO}_3/\text{ClO}_4(4)(\alpha)$	$(1/2)\text{CO}_3/\text{ClO}_4(4)(\beta)$
Formula	$\text{C}_{23}\text{H}_{23}\text{CuIN}_6\text{O}_2$	$\text{C}_{20}\text{H}_{18}\text{ClCuN}_7\text{O}_6$	$\text{C}_{21}\text{H}_{26}\text{ClCuN}_7\text{O}_5$	$\text{C}_{41}\text{H}_{44}\text{B}_2\text{Cu}_2\text{F}_8\text{N}_{12}\text{O}_7$	$\text{C}_{41}\text{H}_{44}\text{Cl}_2\text{Cu}_2\text{N}_{12}\text{O}_{15}$	$\text{C}_{41}\text{H}_{44}\text{Cl}_2\text{Cu}_2\text{N}_{12}\text{O}_{15}$
M_r (Da)	605.9	551.4	555.5	1117.6	1142.9	1142.9
Crystal system	monoclinic	monoclinic	monoclinic	triclinic	triclinic	triclinic
Space group	$P2_1/c$ (#14)	$P2_1/c$ (#14)	$P2_1/c$ (#14)	$P1$ (#2)	$P1$ (#2)	$P1$ (#2)
a (Å)	13.445(4)	13.736(1)	7.0010(10)	9.4090(10)	9.506(2)	9.5080(10)
b (Å)	8.471(3)	7.6610(10)	27.675(4)	10.840(3)	10.938(2)	13.903(2)
c (Å)	21.715(7)	22.228(4)	12.681(4)	12.013(5)	12.1570(10)	18.520(3)
α (°)				74.47(3)	73.63(1)	83.756(2)
β (°)	91.82(3)	92.380(3)	97.037(2)	78.90(2)	78.95(1)	75.569(2)
γ (°)				77.98(2)	77.89(1)	89.820(2)
V (Å ³)	2472	2337	2439	1142	1174	2356
D_{calc} (g cm ^{−3}) (Z)	1.628(4)	1.567(4)	1.513(4)	1.624(1)	1.617(1)	1.611(2)
μ_{Mo} (mm ^{−1})	2.2	1.10	1.05	1.03	1.10	1.10
Specimen (mm)	0.44, 0.35, 0.12	0.50, 0.50, 0.40	0.35, 0.14, 0.10	0.18, 0.11, 0.05	0.28, 0.19, 0.13	0.35, 0.25, 0.15
$T_{\text{min/max}}$	0.65	0.83	0.72	0.96	0.86	0.84
$2\theta_{\text{max}}$ (°)	50	58	52	62	75	58
N_{t}	4866	27296	27769	16278	55478	27340
N (R_{int})	4337 (0.020)	5939 (0.033)	4795 (0.070)	6932 (0.050)	11826 (0.037)	11446 (0.020)
N_0	3580	4317	3353	3452	7280	8919
$R1$	0.033	0.038	0.062	0.041	0.042	0.038
wR_2 (a, b)	0.078 (0.021, 5.56)	0.108 (0.065)	0.18 (0.086, 3.47)	0.078 (0.022)	0.13 (0.072)	0.12 (0.08)
S	1.09	1.01	1.07	0.92	1.04	1.06
$ \Delta\rho_{\text{max}} $ (e Å ^{−3})	0.67	0.71	1.04	0.77	1.30	1.28
T (K)	295	153	153	100	100	153

Table 2
Selected cation geometries, [(dpyam)₂CuX](X')

X/X'	O ₂ CET/I, O ₂ CMe/BF ₄ , O ₂ CET/Cl ^a	O ₂ N/CIO ₄ ^b	NCO/Cl ^c
T (K)	293, 293, 293	153, 293	153, 293
<i>Distances (Å)</i>			
Cu–N(1)	1.979(3), 2.000(2), 1.993(2)	1.977(2), 1.979(2)	1.999(4), 2.008(3)
Cu–N(2)	2.031(3), 2.026(2), 2.023(2)	2.011(2), 2.038(5)	2.022(4), 2.016(4)
Cu–N(4)	2.004(3), 2.002(2), 2.032(2)	2.001(2), 2.001(3)	2.007(4), 2.012(8)
Cu–N(5)	2.140(3), 2.158(2), 2.186(3)	2.130(2), 2.117(3)	2.163(4), 2.181(3)
Cu–X	2.019(3), 2.017(2), 1.992(2)	2.096(2), 2.179(3)	1.971(4), 1.955(5)
<i>Angles (°)</i>			
N(1)–Cu–N(2)	88.7(1), 88.4(1), 89.1(1)	88.53(7), 88.5(3)	87.0(2), 86.6(1)
N(4)–Cu–N(5)	86.5(1), 87.4(1), 86.3(1)	87.94(8), 87.8(3)	86.7(2), 86.0(1)
X–Cu–N(1)	88.3(1), 88.4(1), 88.3(1)	88.44(7), 88.2(3)	89.5(2), 89.4(1)
X–Cu–N(2)	153.0(1), 160.4(1), 158.8(1)	157.68(7), 157.2(7)	158.0(2), 157.9(1)
X–Cu–N(4)	84.2(1), 87.5(1), 85.4(1)	86.83(7), 86.3(2)	88.2(2), 88.3(1)
X–Cu–N(5)	107.0(1), 102.7(1), 100.7(1)	99.73(7), 100.7(2)	103.4(2), 104.0(1)
N(1)–Cu–N(4)	171.7(1), 173.3(1), 172.1(1)	171.82(8), 172.7(2)	174.2(1), 173.7(1)
N(1)–Cu–N(5)	99.0(1), 98.6(1), 99.6(1)	99.46(7), 97.9(3)	99.0(1), 100.3(1)
N(2)–Cu–N(4)	96.4(1), 93.9(1), 95.1(1)	93.31(8), 94.7(3)	93.1(2), 93.3(1)
N(2)–Cu–N(5)	100.0(1), 96.9(1), 100.4(1)	102.58(8), 102.1(2)	98.6(1), 98.1(1)
<i>Distortion parameter</i>			
τ	0.31, 0.21, 0.22	0.24, 0.26	0.27, 0.27

^a Data from this work, Refs. [1,4], respectively; Cu–O(2) are 2.682(3), 2.706(2), 2.640(4); Cu–O(1)–C(21) are 111.0(2), 107.9(2), 106.4(3); O(11,12)–C are 1.267(4), 1.306(5); 1.264(3), 1.241(4); 1.228(5), 1.261(5) Å.

^b Data from this work, Ref. [6], respectively; Cu–O(2) are 2.560(2), 2.459(3); Cu–O(1)–N is 107.3(1), 104.2(2) and O(1)–N–O(2) 113.3(2), 111.6(2); N–O(1,2) are 1.295(3), 1.228(3); 1.272(4), 1.224(4) Å.

^c Data from this work, Ref. [5], respectively; Cu–N–C are 152.5(4), 152.4(5); N–C–O are 179.1(5), 177.3(1)°. C–N are 1.129(6), 1.137(6); C–O are 1.220(6), 1.193(6) Å.

pancy (O(8)), associated hydrogen atoms being refinable in each case; the other was modelled as disordered over a pair of sites in each case (no associated hydrogen atoms located), site occupancies set at 0.5 in the BF₄[−] salt after trial refinement (O···O 1.53(1) Å), refining to 0.716(5) and complement in the ClO₄[−] salt (O···O 1.814(7) Å).

(1/2)CO₃/ClO₄(β). The model refined smoothly without disorder, only excepting the fourth water molecule, modelled in terms of two residues (set at equal occupancy (0.5) after trial refinement (O(4,5); O(4)···O(5) 1.65(1) Å)) for which no associated hydrogen atoms were located; (x,y,z,U_{iso})_H were refinable for hydrogen atoms in association with O(1–3).

3. Results and discussion

3.1. Structural results

(Despite the primary focus of this paper on the results of the carbonate system we introduce that by dealing with the simpler mononuclear systems first.)

Interest in the [(dpyam)₂CuX]⁽⁺⁾ systems (Table 2) focusses on the differing distortions found in their five-coordinate stereochemistry between the ideal 'trigonal bipyramidal' (TBP) and 'square-based pyramidal' (SBP) extremes, the distortion sometimes quantified in terms of $\tau = (\beta - \alpha)/60$ where β and α (°) are the largest coordination angles ($\tau = 0$ (SBP) – 1 (TBP)) [8]. A number of such systems with X = O-unidentate carboxylate have been defined; the present example takes the ionic form [(dpyam)₂Cu(O-propionato)]⁺ (Fig. 1), one formula unit, devoid of crystallographic symmetry comprising the asymmetric unit of the structure, as is the case in all three present structures of this type. Hydrogen-bonding is found from the central NH hydrogen atoms of the dpyam ligands, within the asymmetric unit, to the uncoordinated carboxylate oxygen atom O(2) (x, y, z) and iodide anion I (x, y, z) at N,H···O 2.775(4), 2.1; N,H···I 3.679(3), 2.9 Å, respectively. Interestingly, the structure is isomorphous with the acetate/tetrafluoroborate analogue [1], rather than the propionate/chloride counterpart [4], which is a monohydrate. The coordination geometries of the three complexes are compared

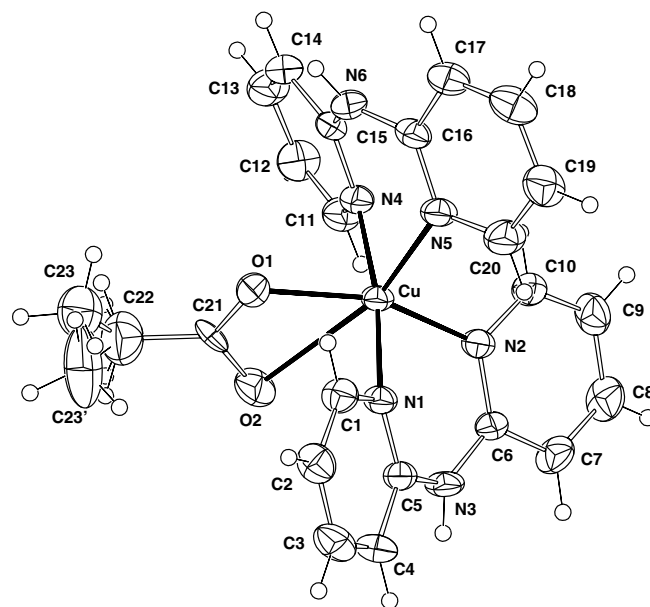


Fig. 1. Projection of the cation of [(dpyam)₂Cu(O₂CET)]⁺, showing the disorder of the pendant ethyl group (20% ellipsoids).

in Table 2; they are similar, that of the present being the most deviant from the SBP norm, and, in all cases, Cu–N(5) – the apical distance – being the longest distance therein. Cu···O(2) distances are similar throughout.

In the cyanato/chloride adduct, studied at low-temperature, the observed coordination geometry is harmonious with that recorded in the room-temperature study [5]. The hydrogen-atoms, not located for the water molecules in the room-temperature study, are now well-resolved, now defining an interesting hydrogen-bonded network, summarized in Table 3, and shown in Fig. 2, the water molecules and counterions being disposed in columns parallel to *a*, through the lattice, linking peripherally to one of the central dpyam NH hydrogen atoms, and to the NCO oxygen atoms (Fig. 2B).

Table 3
Hydrogen-bonding in $[(\text{dpym})_2\text{Cu}(\text{NCO})]\text{Cl} \cdot 4\text{H}_2\text{O}$

Atoms	Parameter
<i>(a) The central dpym ligand NH groups</i>	
$\text{N}(3), \text{H}(3) \cdots \text{Cl}$	$0.88(-); 3.220(4), 2.4_7; 143(-)$
$\text{N}(6), \text{H}(6) \cdots \text{Cl}^{\text{I}}$	$0.88(-); 3.232(4), 2.4_0; 158(-)$
<i>(b) The water molecules</i>	
$\text{O}(1), \text{H}(1\text{A}) \cdots \text{O}(2)$	$0.87(2); 2.787(5), 1.93(2); 167(5)$
$\text{H}(1\text{B}) \cdots \text{O}(4)$	$0.86(5); 2.723(6), 1.86(5); 175(5)$
$\text{O}(2), \text{H}(2\text{A}) \cdots \text{Cl}$	$0.84(3); 3.104(4), 2.27(3); 172(4)$
$\text{H}(2\text{B}) \cdots \text{O}(4^{\text{ii}})$	$0.82(2); 2.783(5), 1.99(2); 160(4)$
$\text{O}(3), \text{H}(3\text{A}) \cdots \text{O}$	$0.87(2); 2.805(6), 1.95(2); 168(5)$
$\text{H}(3\text{B}) \cdots \text{Cl}^{\text{I}}$	$0.85(3); 3.203(5), 2.37(3); 167(5)$
$\text{O}(4), \text{H}(4\text{A}) \cdots \text{O}(3^{\text{iii}})$	$0.85(3); 2.802(6), 1.96(3); 170(6)$
$\text{H}(4\text{B})$	$0.84(3);$

The four values in order are X–H; X $\cdots$ Y, H $\cdots$ Y (Å); X–H $\cdots$ Y (°).

Transformations of the asymmetric unit: (i) $x, y, z - 1$; (ii) $1 - x, \bar{y}, 1 - z$; (iii) $x, y, \bar{z}$.

The results of the present low-temperature study of the nitrito/perchlorate adduct are essentially harmonious with those of the room-temperature study (Table 2) *except* in respect of the nitrite ligand disposition, where significant differences are found, which, in view of the notorious behaviour of nitrite groups in structural studies, would most probably seem consequent on lack of libration correction to the data of the room-temperature study; in the pres-

ent study, nitrite displacement parameters are in keeping with those of the remainder of the structure (the perchlorate group excepted). Hydrogen-bonds from the central NH groups of the ligands are $\text{N}, \text{H} \cdots \text{O}(4') (1 - x, 2 - y, \bar{z})$ (to the minor component of the disordered counterion) $2.975(5), 2.2$ (est.) Å, $\cdots \text{O}(6) (1 - x, 2 - y, \bar{z})$ (to the major component) $2.912(4), 2.2$ (est.) Å, and the other, $\text{N}, \text{H} \cdots \text{O}(1) (\bar{x}, y - 1/2, 1/2 - z)$ $2.922(3), 2.1$ (est.) Å.

The present initial study of the carbonate/perchlorate complex produced a result at variance with the previous room-temperature studies recorded for that salt and its tetrafluoroborate counterpart, the two structures being isomorphous. Accordingly, redeterminations were undertaken on two freshly prepared samples, producing results (Table 4) which were broadly harmonious with the previous room-temperature studies, most particularly in terms of assignment of the unit cells. The hydrogen-bonding is limited and clear-cut: the central ligand NH groups contact the well-defined water molecule oxygen O(8) (ligand 1): $\text{N}, \text{H} \cdots \text{O}(8) (1 - x, \bar{y}, 1 - z)$ $2.817(3), 1.98(4) (\text{BF}_4); 2.833(2), 2.08(4)$ Å (ClO_4), the other interacting with F/O(7) of the counterion: $\text{N}, \text{H} \cdots \text{X}(7) (1 - x, 1 - y, 1 - z)$ $3.005(3), 2.04(2) (\text{BF}_4); 3.065(2), 2.30(3)$ Å (ClO_4). The water molecule hydrogen atoms interact, one with F/O(4) of the counterion: $\text{O}(8), \text{H}(8\text{B}) \cdots \text{X}(4)$ $2.947(3), 2.16(2) (\text{BF}_4); 2.999(2), 2.30(3)$ Å (ClO_4), and the other with carbonate components, $\text{O}(8), \text{H}(8\text{A}) \cdots \text{O}(1)$ (note Cu–O long in this orientation, i.e. O(1) uncoordinated) $2.683(5), 1.88(4) (\text{BF}_4); 2.704(3), 1.94(4) (\text{ClO}_4)$ or $\text{O}(8), \text{H}(8\text{A}) \cdots \text{O}(3) (1 - x, 1 - y, 1 - z)$ $2.810(6), 1.98(4)$

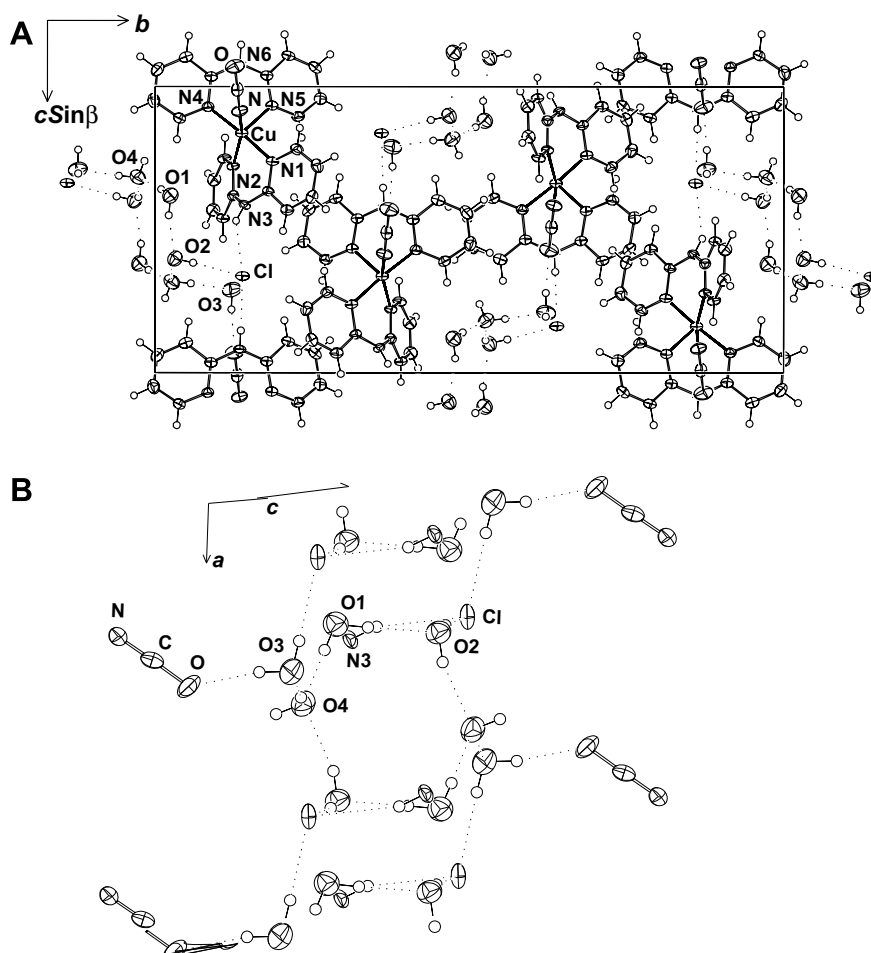


Fig. 2. (A) Unit cell contents of $[(\text{dpym})_2\text{Cu}(\text{NCO})]\text{Cl} \cdot 4\text{H}_2\text{O}$ projected down a , showing the columns of hydrogen-bonded water molecules. (B) The hydrogen-bonded anions and water molecules.

Table 4
Selected cation geometries, [(dpyam)₂CuO · CO · OCu(dpyam)₂](X')₂ · 4H₂O

X	BF ₄	ClO ₄ (α-form)	ClO ₄ (β-form) ^a	
<i>Distances (Å)</i>				
Cu–N(1)(ax)	1.989(2)	2.003(1)	2.004(2)	2.006(2)
Cu–N(2)(eq)	2.084(2)	2.092(1)	2.160(2)	2.029(2)
Cu–N(4)(ax)	1.994(2)	2.014(1)	1.998(2)	2.027(2)
Cu–N(5)(eq)	2.099(2)	2.115(2)	2.057(2)	2.184(2)
Cu–O(1)	2.015(3)	2.029(2)	1.971(2)	
Cu–O(2 ⁱ)	1.931(3)	1.940(2)		1.970(2)
C–O(1)	1.284(8)	1.299(4)	1.298(3)	
C–O(2)	1.323(9)	1.302(4)	1.314(3)	
C–O(3)	1.245(5)	1.270(5)	1.249(3)	
<i>Angles (°)</i>				
N(1)–Cu–N(2)	89.37(8)	89.11(5)	88.25(6)	89.87(6)
N(4)–Cu–N(5)	88.14(8)	88.21(5)	88.86(68)	87.45(6)
O(1)–Cu–N(1)	88.6(1)	88.38(7)	87.87(6)	
O(1)–Cu–N(2)	106.3(1)	106.62(2)	106.50(6)	
O(1)–Cu–N(4)	85.5(1)	85.57(7)	88.00(6)	
O(1)–Cu–N(5)	156.6(1)	155.68(7)	155.81(6)	
N(1)–Cu–N(4)	173.52(7)	173.52(5)	174.02(6)	172.44(6)
N(1)–Cu–N(5)	96.31(8)	96.38(5)	93.15(6)	99.15(6)
N(2)–Cu–N(4)	94.81(8)	94.86(5)	97.07(6)	93.05(6)
N(2)–Cu–N(5)	96.64(7)	97.31(5)	97.69(6)	96.53(3)
O(2 ⁱ)–Cu–N(1)	89.4(1)	89.63(7)		91.91(6)
O(2 ⁱ)–Cu–N(2)	171.3(1)	171.23(7)		169.65(6)
O(2 ⁱ)–Cu–N(4)	85.7(1)	85.68(7)		84.00(6)
O(2 ⁱ)–Cu–N(5)	92.1(1)	91.45(7)		93.25(5)
O(1)–Cu–O(2 ⁱ)	65.0(1)	64.67(9)		
O(1)–C–O(2)	115.3(4)	116.3(3)	115.1(2)	
O(1)–C–O(3)	123.0(6)	122.8(3)	122.9(2)	
O(2)–C–O(3)	121.7(5)	120.9(3)	122.0(2)	
<i>Distortion parameter</i>				
τ	0.28/0.04	0.30/0.04	0.30/0.05	

The two values in each entry for the β-form are for the environments of Cu(1,2), respectively.

Transformation (i) (BF₄, ClO₄(α) only) is 1 – x, 1 – y, 1 – z.

'ax' and 'eq' are *ad hoc* descriptors, treating the array as distorted toward the trigonal bipyramidal norm, the largest angle (invariably N–Cu–N) defining the 'axis' of that putative array.

^a Associated Cu–O–C are 115.5(1), 113.8(1)°.

Table 5
Hydrogen-bonding in β-[(dpyam)₂Cu₂CO₃](ClO₄)₂ · 4H₂O (presentation as in Table 3)

Atoms	Parameter
<i>(a) The central NH groups of the dpyam ligands (H est.)</i>	
N(13), H(13) ··· O(2 ⁱ)	0.88(1); 2.828(2), 2 ₁ ; 138(–)
N(16), H(16) ··· O(11)	0.88(1); 3.126(4), 2 ₄ ; 141(–)
O(12)	0.88(–); 3.086(3), 2 ₃ ; 158(–)
N(23), H(23) ··· O(1 ⁱ)	0.88(–); 2.858(2), 2 ₂ ; 132(–)
N(26), H(26) ··· O(22)	0.88(–); 3.119(3), 2 ₃ ; 169(–)
<i>(b) The water molecules</i>	
O(1), H(1A0) ··· O(11)	0.82(2); 3.070(3), 2.32(3); 146(5)
H(1B0) ··· O(103)	0.82(2); 2.782(2), 2.00(2); 166(5)
O(2), H(2A0) ··· O(101)	0.83(3); 2.719(2), 1.89(2); 161(5)
H(2B0) ··· O(21)	0.81(2); 2.959(3), 2.30(3); 140(5)
O(3), H(3A0)	0.82(3);
H(3B0) ··· O(5 ⁱⁱ)	0.93(2); 2.719(7), 2.30(3); 102(4)

O(4) ··· O(1,3,5) are 2.929(4), 2.872(4), 1.66(1) Å.

Transformations of the asymmetric unit: (i) 2 – x, 1 – y, z; (ii) x – 1, y, z.

(BF₄); 2.815(4), 2.08(4) Å (ClO₄). Calculation of the distortion parameter τ (Table 4) for each compound, shows, in each case, coordination geometries, one close to square-pyramidal in the case of one carbonate donor component, the other less so (τ 0.04, 0.29 ()), in each case (see Table 5).

The second 'β'-form of the latter (CO₃/ClO₄) derivative also has triclinic symmetry and a short (a) axial length very similar to those of the CO₃/BF₄, ClO₄ (α) phase. Unit cell contents for the two forms

of the perchlorate are shown in projection down *a* in Fig. 3, showing the component dispositions in the two structures (redefining the cell of one or the other appropriately as the *bc* diagonal) to be very similar. The cell volume of the β-form (Fig. 3B) is twice that of the α-form (Fig. 3A), the asymmetric unit now comprising the complete formula unit, disorder now being confined to one only of the four water molecules, hydrogen atoms being located and refined for all of the remainder. Interactions of the NH hydrogen atoms are to the anion and water molecule oxygen atoms (Table 5), those of the water molecules to the anion and carbonate oxygen atoms (all of the latter interacting), although there is also a probable interaction from O(3) to the disordered water molecule component O(4). The disposition of the central carbonate component vis-a-vis its pair of pendant dpyam units is of considerable interest. Whereas with the α-form (and the BF₄[–] analogue), the disordered carbonate presents as a bidentate donor to the copper atom (and is tabulated as such), in reality it can only bond through one oxygen atom or the other at any given location, so that the copper atom must remain five-coordinated. Such is the case in the present, but it clearly emerges now that, at least in the β-form, the environments of the two copper atoms have changed considerably, with τ for Cu(1) being 0.30 (angles 155.81(6), 174.02(6)°) and that for Cu(2) 0.05 (angles 169.64(6), 172.44(6)°), i.e. the Cu(2) environment is much closer to the square-pyramidal norm, resolving components very similar to those of the composites in the α-phase and the BF₄ salt.

Table 6 presents data for the present array comparatively with that for other simple *N'**N* systems, these being for *N'**N* = 2,2'-bipyridyl ('bpy') and 1,10-phenanthroline ('phen'), ligands which form five- rather than six-membered chelate rings; in all systems listed, the apical atom is the nitrogen atom, with the longest Cu–N distance. For these systems, with one exception, τ values lie within boundaries established by the more distorted array (0.30) and the square-pyramidal limit, with no discernible trend, other than the change in ligand 'bite' which may be attributed to the effect of the latter.

3.2. Spectroscopic properties

3.2.1. Electronic spectra

The electronic reflectance spectrum of [(dpyam)₂Cu(O₂CET)]I consists of main peaks at 14200 cm^{–1} and 9200 cm^{–1}, ΔE 5000 cm^{–1}, comparable to those of the compound [(dpyam)₂Cu(O–NO)](ClO₄) (14970, 10000 cm^{–1}, ΔE 4970 cm^{–1}), corresponding to a typical feature of the markedly unsymmetrical *cis*-distorted octahedral geometry [9]. That of the compound [(dpyam)₂Cu(N–CO)]Cl · 4H₂O shows the high-energy peak at 14200 cm^{–1} and a low-energy peak at 10350 cm^{–1}, ΔE 3850 cm^{–1} consistent with the distorted square-pyramidal geometry. An energy difference of 3850 cm^{–1} is significantly less than that for the typical *cis*-distorted octahedral dpyam complexes (4800–5600 cm^{–1}) [1]. These spectral features are reasonably assigned as the d_{xy}, d_{yz}, d_{zx} → d_{x²–y²} and d_{z²} → d_{x²–y²} transitions for the high-energy and lower-energy bands, respectively.

No significant distinction in infrared and solid state visible spectra is expected for the binuclear carbonato-bridged complex with ClO₄ anion (α- and β-forms). Both BF₄ and ClO₄ compounds display two broad bands with almost comparable intensity at ca. 15200 and ca. 10800 cm^{–1}, ΔE 4420 cm^{–1}, for the BF₄ derivative and ca. 15200 and ca. 10780 cm^{–1}, ΔE 4420 cm^{–1}, for the ClO₄ compound. This suggests that the coordination geometry is close to the square-pyramidal geometry and both bands are assigned as the d_{xy}, d_{yz}, d_{zx} → d_{x²–y²} and d_{z²} → d_{x²–y²} transitions, respectively, with the spectral features of these compounds harmonious with those recorded in the room-temperature studies of Refs. [1–3,5,6].

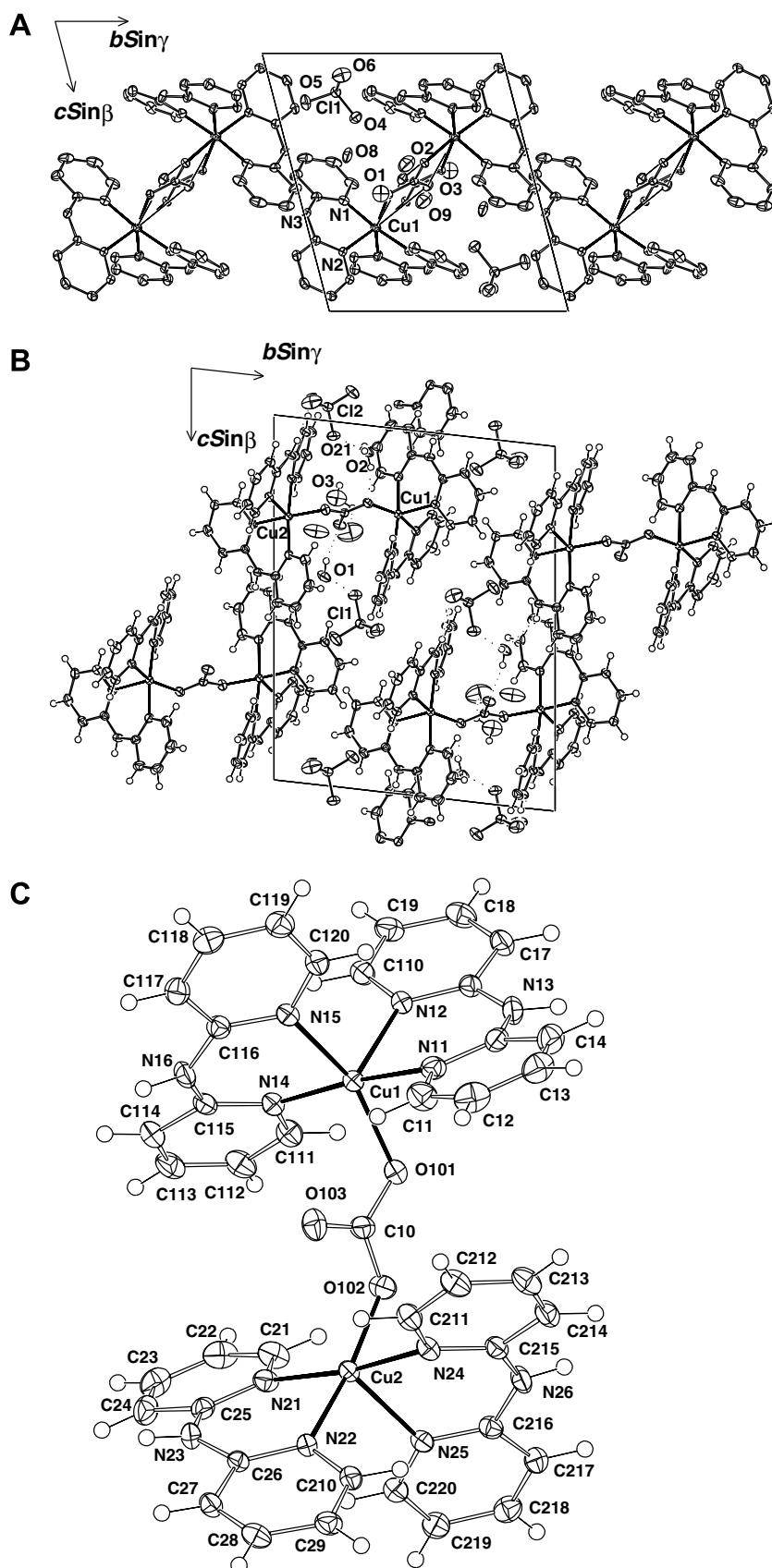


Fig. 3. Unit cell contents of (A) the α - and (B) the β -forms of $[(\text{dpyam})_2\text{Cu}]_2\text{CO}_3[(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}]$, both projected down their a axes. (C) The cation of the β -form.

Table 6
Comparative geometries in ordered $[(N'N)_2Cu(OCO_2)](A)$ and $[[[(N'N)_2Cu]_2(O \cdot CO \cdot O)](X')_2(-nS)](B)$ systems

N'/N/system	Phen/A		bpy/B	Phen/B		dpyam/B
X'/(n)S	-/7H ₂ O ^a	-/11H ₂ O ^a	Br/MeCN · H ₂ O ^b	ClO ₄ /dmf ^a	ClO ₄ /H ₂ O (mois. 1,2) ^a	ClO ₄ /H ₂ O ^c
<i>Distances (Å)</i>						
Cu–N(ax)	2.034(3)	2.021(2)	2.036(6), 2.005(5)	2.013(4), 2.030(4)	2.027(7), 2.016(7); 1.99(1), 2.030(9)	1.998(2), 2.006(2)
	2.030(3)	2.010(2)	2.011(5), 2.037(5)	2.039(4), 2.036(4)	2.020(8), 2.047(7); 2.00(1), 2.010(9)	2.004(2), 2.027(2)
Cu–N(eq)	2.243(3)	2.250(2)	2.191(6), 2.229(5)	2.215(4), 2.258(4)	2.241(3), 2.263(8); 2.13(1), 2.13(1)	2.160(2), 2.184(2)
(<i>trans</i> to O)	2.071(3)	2.056(2)	2.035(5), 2.036(6)	2.045(4), 2.029(4)	2.033(8), 2.029(7); 2.16(1), 2.16(1)	2.057(2), 2.029(2)
Cu–O	1.972(3)	1.964(2)	1.944(4), 1.928(4)	1.933(3), 1.938(3)	1.951(6), 1.925(6); 2.30(2), 2.19(1)	1.971(2), 1.970(2)
Cu–O'	2.421(3)	2.557(3)	2.808(5), 2.779(5)	2.844(3), 2.694(3)	2.565(7), 3.067(9); 2.44(1), 2.44(1)	2.933(2), 2.890(2)
<i>Angles (°)</i>						
O–Cu–N(eq)	88.98(9)	94.50(8)	98.1(2), 101.39(9)	90.7(2), 105.6(2)	97.6(3), 92.3(3); 131.0(4), 100.2(3)	106.50(6), 93.25(6)
	164.8(1)	171.43(8)	163.4(2), 159.4(2)	174.0(2), 162.2(2)	161.4(3), 174.0(3); 131.8(4), 166.2(3)	155.81(6), 169.65(6)
O–Cu–N(ax)	92.7(1)	94.22(8)	92.2(2), 90.7(2)	93.5(2), 91.0(2)	91.1(3), 93.2(3); 88.8(4), 92.2(4)	88.00(6), 91.91(6)
	94.4(1)	93.27(8)	92.2(2), 93.4(2)	93.2(1), 91.2(2)	94.7(3), 90.6(3); 97.7(4), 94.6(3)	87.87(6), 84.00(6)
N–Cu–N(bite)	78.8(1)	81.18(9)	78.1(2), 80.6(2)	87.5(2), 78.0(2)	78.3(3), 78.8(3); 80.3(4), 79.9(4)	88.86(6), 89.87(6)
	80.6(1)	78.80(8)	80.5(2), 78.0(2)	78.9(2), 81.2(2)	81.5(3), 80.7(3); 80.0(4), 79.8(3)	88.25(6), 87.45(6)
N–Cu–N(ax)	170.8(1)	172.50(8)	175.5(2), 172.3(2)	164.0(2), 176.7(2)	170.7(3), 174.5(3); 171.0(4), 173.2(4)	174.02(6), 172.44(6)
Cu–O–C	103.0(2)	107.2(2)	112.0(4), 111.4(4)	114.0(2), 107.4(2)	108.3(6), 120.7(6); 97.8(9), 99.1(9)	115.5(1), 113.8(1)
O–C–O	125.2(3)	123.6(3)	122.2(6) (122.8(6))	122.7(4) (121.8(4))	123.2(9) (122.3(10)) 117(1), (124(1))	122.0(2) (122.9(2))
O–C–O	115.1(3)	116.4(2)	122.8(6), (122.2(6))	121.8(4), (122.7(4)),	122.3(10), (123.2(9)); 124(1), (117(1))	122.9(2), (122.0(2))
	119.6(3)	120.0(3)	115.1(6), (115.1(6))	115.5(4) (115.5(4))	114.5(9), (114.5(9); 119(1), (119(1)))	115.1(2) (115.1(2))
O'	'bonded'	'bonded'	non-bonded	non-bonded	non-bonded; 'bonded'	non-bonded
<i>Distortion parameter</i>						
τ	0.10	0.02	0.20, 0.22	0.17, 0.24	0.16, 0.01; 0.65, 0.12	0.30, 0.05

^a Ref. [10].
^b Ref. [11].
^c The angle 'trans' to the coordinated oxygen.

Acknowledgement

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PUBLICATION PAPERS OF PART III

Polynuclear paddle-wheel copper(II) propionate with di-2-pyridylamine or 1,10-phenanthroline: Preparation, characterization and X-ray structure

Sujittra Youngme ^{a,*}, Achareeya Cheansirisomboon ^a, Chanaiporn Danvirutai ^a,
 Chaveng Pakawatchai ^b, Narongsak Chaichit ^c

^a Department of Chemistry, Faculty of Science, Khon Kaen University, Khon Kaen 40002, Thailand

^b Department of Chemistry, Faculty of Science, Prince of Songkla University, Hatyai, Songkla 90112, Thailand

^c Department of Physics, Faculty of Science and Technology, Thammasat University Rangsit, Pathumthani 12121, Thailand

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Abstract

The synthesis, spectroscopic, magnetic and structural characterization of two new polynuclear copper(II) propionate are described. Both compounds exhibit the typical paddle-wheel type structure. The complex $[\text{Cu}_4(\text{dpyam})_2(\text{OCOC}_2\text{H}_5)_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)_6(\text{H}_2\text{O})_2][\text{Cu}_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)_4(\text{H}_2\text{O})_2] \cdot (\text{DMF})_2$ **1**; where dpyam = di-2-pyridylamine, the “outer” Cu ions, with a $\text{CuN}_2\text{O}_2\text{O}'$ chromophore, have an intermediate five-coordinate geometry. The “inner” Cu ions, with a $\text{CuO}_4\text{O}'$ chromophore, have a square pyramidal geometry. The two Cu(II) ions in the inner unit are bridged by four *syn, syn*- $\eta^1:\eta^1:\mu$ propionates, showing the paddle-wheel cage type. The “outer” and “inner” linked by propionate bridges showing *syn, anti*- $\eta^1:\eta^1:\mu$ coordination mode. The 1D structure of complex $[\text{Cu}_6(\text{phen})_2(\text{H}_2\text{O})_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)_{12}]_n[\text{Cu}_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)_4(\text{H}_2\text{O})_2]_{2n} \cdot (\text{H}_2\text{O})_{0.5n}$ **2**; where phen = 1,10-phenanthroline, consists of zig-zag chains of mononuclear $\text{Cu}(\mu\text{-O}_2\text{CC}_2\text{H}_5)_2(\text{H}_2\text{O})(\text{phen})$ repeating units running along the *b*-axis, which are connected along the unit cell diagonal via $\text{Cu}_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)_4$ paddle-wheel dinuclear units. Within mononuclear and dinuclear units, the Cu(II) ions have a square pyramidal geometry. However, the outer sphere of both compounds consists of the $\text{Cu}_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)_4(\text{H}_2\text{O})_2$ paddle-wheel molecule in which Cu(II) ions involve a square pyramidal geometry.

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Keywords: Copper(II); Di-2-pyridylamine; 1,10-Phenanthroline; Crystal structures; μ -Propionato bridges; EPR

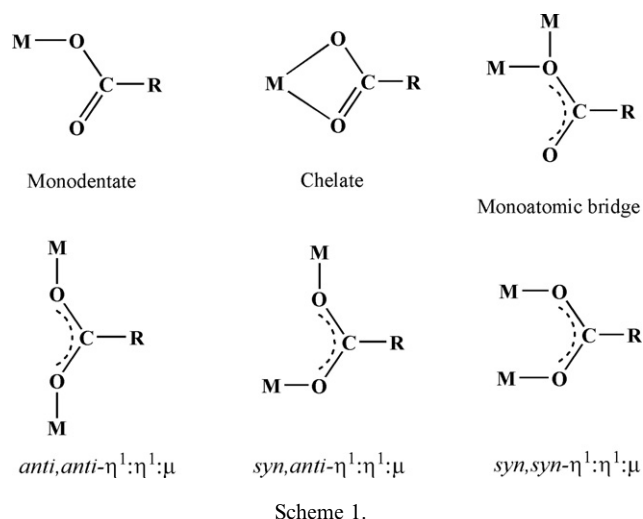
The coordination chemistry of the copper(II) complexes with various carboxylates has been investigated for a long time. Dimeric and polynuclear copper(II) carboxylates have received great attention in the studies of exchange-coupling interactions between adjacent metal centers, as well as for their special bioactive and biocatalytic functions [1–7]. In addition, carboxylate anions exhibit a versatile coordination behavior displaying distinct bonding modes toward metal cations, such as monodentate and chelate, as well as $\eta^1:\eta^1:\mu$ bridging ligands in *syn, syn*, *syn, anti*, and *anti, anti* conformations. Another type of coordination

mode is the monoatomic bridge in which two metal ions are connected by a single oxygen atom of a carboxylate group. This diversity of coordination modes assumed by carboxylate ligands is shown in Scheme 1.

A large number of paddle-wheel type dimeric copper(II) carboxylate adducts, $[\text{Cu}_2(\text{RCO}_2)_4\text{L}_2]$, where L is an apical ligand with an oxygen or a nitrogen atom, have been reported in an effort to clarify the factors influencing the magnitude of the intramolecular magnetic exchange interaction which occurs between two Cu(II) ions of a paddle-wheel moiety in these compounds [1,8–10]. The polynuclear copper(II) carboxylates were found to exhibit three classes of local paddle-wheel structure: (A) stepped polymeric structure with the second lone pair is donated to a metal

* Corresponding author. Fax: +66 43 202373.

E-mail address: sujittra@kku.ac.th (S. Youngme).



ion of another paddle-wheel unit [8]; (B) stepped without additional ligands with polymeric structures can also be obtained by means of ligands which are able to bridge between dinuclear units [9]; (C) the bridging ligand coordinates axially to a Cu ion and at the same time interacts with a carboxylate oxygen atom of another paddle-wheel unit [10]. An example of each class is presented in Scheme 2.

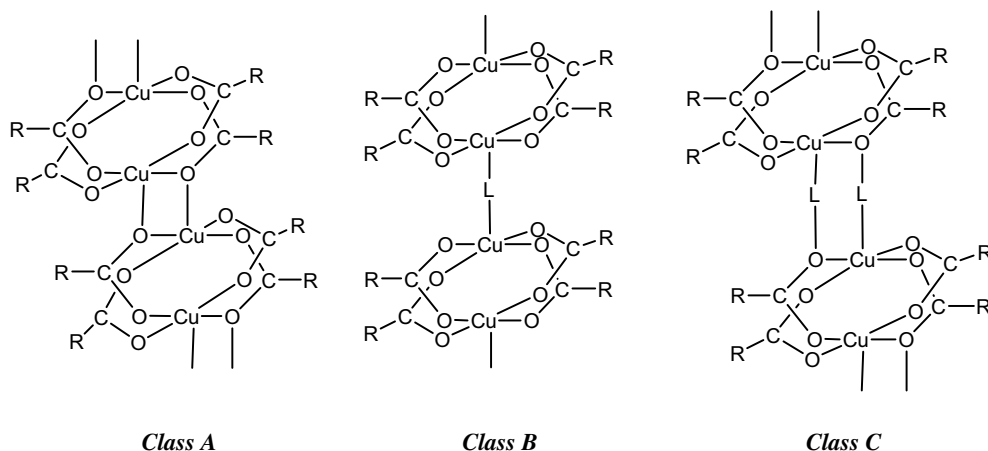
The present work focused on observing the difference between chelate function dpyam (di-2-pyridylamine) and phen (1,10-phenanthroline), and the coordination mode of carboxylate ligands is responsible for the structure of these complexes. For this purpose the compounds $[\text{Cu}_4(\text{dpyam})_2(\text{OCOC}_2\text{H}_5)_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)_6(\text{H}_2\text{O})_2][\text{Cu}_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)_4(\text{H}_2\text{O})_2] \cdot (\text{DMF})_2$ **1** and $[\text{Cu}_6(\text{phen})_2(\text{H}_2\text{O})_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)_{12}][\text{Cu}_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)_4(\text{H}_2\text{O})_2]_{2n} \cdot (\text{H}_2\text{O})_{0.5n}$ **2** are synthesized [11], characterized by spectroscopy and X-ray crystallography [12].

The crystal structure of **1** consists of a centrosymmetric tetranuclear $[\text{Cu}_4(\text{dpyam})_2(\text{OCOC}_2\text{H}_5)_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)_6(\text{H}_2\text{O})_2]$, noncoordinating $[\text{Cu}_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)_4(\text{H}_2\text{O})_2]$ and DMF molecules. The “outer” Cu ions (Cu(1), Cu(1)A), with a $\text{CuN}_2\text{O}_2\text{O}'$ chromophore, have an intermediate geometry

(Fig. 1). The Cu(II) atom is five-coordinated with a basal plane consisting of two N atoms (Cu(1)–N(1), 1.983(3), Cu(1)–N(2), 2.033(3) Å) of dpyam and two O atoms (Cu(1)–O(2), 1.942(2), Cu(1)–O(4), 1.963(2) Å) of two different propionate ligands. The coordinated water molecule O(1) occupies the apical position at a distance of 2.259(2) Å. The CuN_2O_2 chromophore is non-planar with tetrahedral twist of 31.2(1)°. The copper line above this plane, 0.252(1) Å is toward O(1). The copper chromophore can be described as having an intermediate geometry. The distortion of intermediate geometry can be best described by the structural parameter τ ($\tau = 0$ for square pyramid and $\tau = 1$ for trigonal bipyramid[13]), within this case is 0.483.

The “inner” Cu ions (Cu(2), Cu(2)A) involve a five-coordinate $\text{CuO}_4\text{O}'$ chromophore, four oxygens of four different carboxylate groups coordinate to Cu(2) in equatorial positions, at mean distance of 1.967(3) Å. Another propionate O atom coordinate at the apical position, at 2.100(2) Å, completing the square pyramidal coordination geometry with τ value of 0.003. Four propionate anions bridge two copper ions in a $\text{syn,syn-}\eta^1:\eta^1:\mu$ showing the paddle-wheel unit with Cu··Cu distance of 2.632(1) Å. The basal plane is non-planar with a slight tetrahedral twist of 16.5(1)° at Cu(2). The Cu metal atom lies 0.202(1) Å above the basal plane toward the axial site. The “outer” and “inner” units are linked by propionate bridges showing $\text{syn,anti-}\eta^1:\eta^1:\mu$ coordination mode from an axial position of one chromophore to an equatorial position of the other one.

An uncoordinate molecule of $[\text{Cu}_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)_4(\text{H}_2\text{O})_2]$ similar to the “inner”, involves a centrosymmetric dinuclear paddle-wheel unit in which four propionate groups are bridging the two Cu atoms, in a $\text{syn,syn-}\eta^1:\eta^1:\mu$ disposition. An O atom of water molecule occupies the axial position of each Cu atom at a distance of 2.156(2) Å, completing the square pyramidal coordination geometry with τ value of 0.001. The Cu(3)··Cu(3)A distance is 2.647(1) Å. The basal plane is non-planar with a



Scheme 2.

slight tetrahedral twist of $17.2(1)^\circ$ at Cu(3). The Cu metal atoms lies $0.210(1)$ Å above the basal plane toward the axial site. The structural parameters of compound **1** are in the normal ranges found for the paddle-wheel copper(II) dimers statistically analyzed [14].

The lattice structure is stabilized by a complicated hydrogen bonding network between the oxygen atom of the non-bridged propionato ligand and nitrogen atom of amine with $N\cdots O$ distance of $2.790(1)$ Å; between the water oxygen atom of uncoordinated dinuclear paddle-wheel unit and the oxygen atom of *syn,syn*- $\eta^1:\eta^1:\mu$ bridged propionato ligand and non-bridged propionato ligand ($O\cdots O$ distances of $2.861(1)$ and $2.832(1)$ Å, respectively); between the water oxygen atom of “outer” molecule and the oxygen atom of *syn,syn*- $\eta^1:\eta^1:\mu$, *syn,anti*- $\eta^1:\eta^1:\mu$ bridged propionato ligands and water oxygen atom of uncoordinated dinuclear paddle-wheel unit ($O\cdots O$ distances of $2.970(1)$, $3.002(1)$ and $2.829(1)$ Å, respectively).

It is already seen and quite obvious in the experimental part [11] that the formation of the compounds is pH-dependent, where different amounts of propionic acid results in two different structures. The interesting role of oxygen O(3) in compound **1** is obvious, although it is a weak but important interaction with Cu(1). When the solution gets more acidic, the water molecules were attacked by the normal copper paddle-wheel dimer $[Cu_2(\mu-O_2CC_2H_5)_4(H_2O)_2]$ then oxonium cations (OH_3^+) were released. Consequently, the copper atom will be attacked to O(3) leading toward the structure of compound **2**.

The asymmetric unit of **2** consists of a hexanuclear $[Cu_6(phen)_2(H_2O)_2(\mu-O_2CC_2H_5)_{12}]$, a dinuclear $[Cu_2(\mu-O_2CC_2H_5)_4(H_2O)_2]$, two halves of two independent dinuclear $[Cu_2(\mu-O_2CC_2H_5)_4(H_2O)_2]$ units, and a half of water molecule. Compound **2** involves one-dimensional structure arising from the hexanuclear unit and consists of zig-zag

chains of mononuclear $Cu(\mu-O_2CC_2H_5)_2(H_2O)(phen)$ repeating units running along the *b*-axis, which are connected along the unit cell diagonal via $Cu_2(\mu-O_2CC_2H_5)_4$ paddle-wheel dinuclear units (Fig. 2). Both mononuclear and dinuclear units are linked by the syn-anti, triatomic propionato bridge in an axial-equatorial configuration which are consistent with the *class B* (Scheme 2). There are four outer distinct $Cu\cdots Cu$ separations along the *b*-axis which alternate according to the sequence ABCD, where (using the viewpoint of Fig. 3) $A = Cu(1)\cdots Cu(2) = 5.074(1)$ Å; $B = Cu(3)\cdots Cu(4) = 4.287(1)$ Å; $C = Cu(4)\cdots Cu(5) = 5.077(1)$ Å; $D = Cu(6)\cdots Cu(1') = 4.293(1)$ Å. The inner distinct $Cu(2)\cdots Cu(3) = 2.621(1)$ Å; $Cu(5)\cdots Cu(6) = 2.621(1)$ Å.

The paddle-wheel dinuclear $Cu_2(\mu-O_2CC_2H_5)_4$ units in the chain contain four bridging propionates in the *syn,syn*- $\eta^1:\eta^1:\mu$ coordination mode, as found in $[Cu_2(O_2CC_2H_5)_4(H_2O)_2]$ [15] and complex **1**. Square pyramidal coordination at Cu(2), Cu(3), Cu(5) and Cu(6) are completed by oxygen atoms of another propionate bridging molecules at distances of $2.132(2)$, $2.129(2)$, $2.127(3)$ and $2.126(3)$ Å, with the τ values of 0.045 , 0.053 , 0.046 and 0.048 , respectively. The basal planes have a slight tetrahedral twist of $17.1(1)$, $15.9(1)$, $16.8(1)$ and $15.9(1)^\circ$ at Cu(2), Cu(3), Cu(5) and Cu(6), respectively. The Cu atoms are displaced from the basal planes at distances of $0.204(1)$, $0.190(1)$, $0.202(1)$ and $0.191(1)$ Å for Cu(2), Cu(3), Cu(5) and Cu(6), respectively. The $Cu(2)\cdots Cu(3)$ and $Cu(5)\cdots Cu(6)$ separations [$2.621(1)$ and $2.621(1)$ Å] are slightly longer than the $2.611(2)$ Å separation in $[Cu_2(O_2CC_2H_5)_4(H_2O)_2]$ and almost identical to that in **1**.

The mononuclear $Cu(\mu-O_2CC_2H_5)_2(H_2O)(phen)$ units (Cu(1), Cu(4)), with a CuN_2O_2O' chromophore, have a square pyramidal geometry with the small τ values of 0.017 and 0.015 for Cu(1) and Cu(4), respectively, in

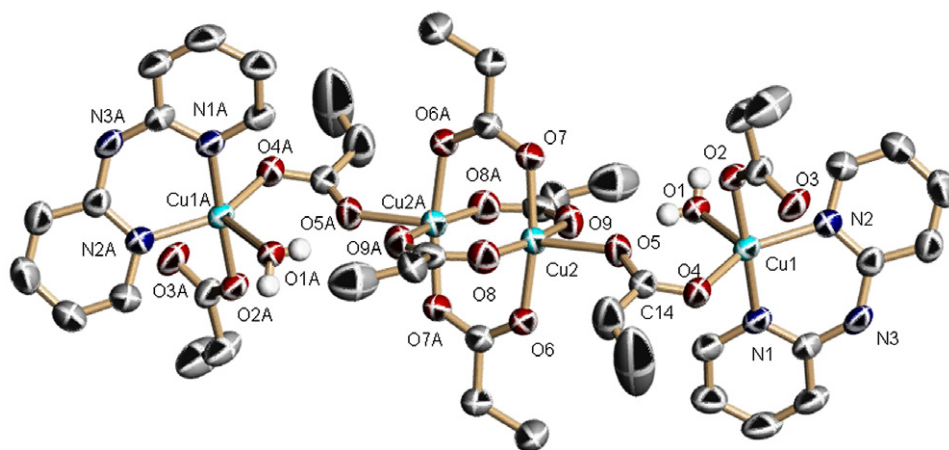


Fig. 1. Plot of tetranuclear $[Cu_4(dpyam)_2(OCOC_2H_5)_2(\mu-O_2CC_2H_5)_6(H_2O)_2]$ unit of **1**. Hydrogen atoms in dpyam and propionato ligands are omitted for clarity. Selected bond lengths (Å) and angles ($^\circ$): $Cu(1)-N(1)$ $1.983(3)$, $Cu(1)-N(2)$ $2.033(3)$, $Cu(1)-O(1)$ $2.259(3)$, $Cu(1)-O(2)$ $1.942(2)$, $Cu(1)-O(4)$ $1.963(2)$, $Cu(2)-O(5)$ $2.100(2)$, $Cu(2)-O(6)$ $1.973(2)$, $Cu(2)-O(7)$ $1.976(2)$, $Cu(2)-O(8)$ $1.960(3)$, $Cu(2)-O(9)$ $1.958(3)$, $Cu(1)-Cu(2)$ $4.919(2)$, $Cu(2)-Cu(2)A$ $2.632(1)$, and $N(1)-Cu(1)-N(2)$ $88.7(1)$, $N(1)-Cu(1)-O(1)$ $88.9(1)$, $N(1)-Cu(1)-O(2)$ $177.7(1)$, $N(1)-Cu(1)-O(4)$ $88.3(1)$, $N(2)-Cu(1)-O(1)$ $98.5(1)$, $N(2)-Cu(1)-O(2)$ $93.0(1)$, $N(2)-Cu(1)-O(4)$ $148.7(1)$, $O(1)-Cu(1)-O(2)$ $89.3(1)$, $O(1)-Cu(1)-O(4)$ $112.6(1)$, $O(2)-Cu(1)-O(4)$ $91.0(1)$, $O(5)-Cu(2)-O(6)$ $97.2(1)$, $O(5)-Cu(2)-O(7)$ $94.2(1)$, $O(5)-Cu(2)-O(8)$ $104.2(1)$, $O(5)-Cu(2)-O(9)$ $87.5(1)$, $O(6)-Cu(2)-O(7)$ $168.1(1)$. Symmetry code: $A = -x + 2, -y + 1, -z + 1$.

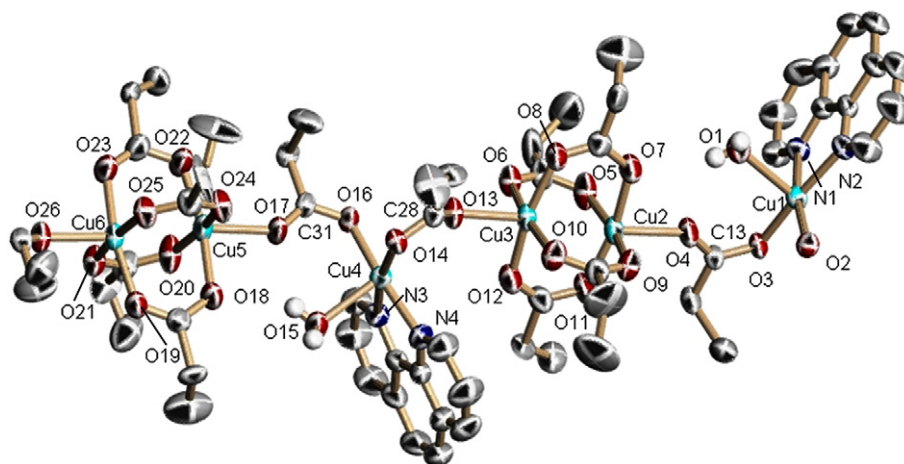


Fig. 2. Plot of hexanuclear $[\text{Cu}_6(\text{phen})_2(\text{H}_2\text{O})_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)_{12}]$ unit of **2**. Hydrogen atoms in phen, propionato ligands and H_2O are omitted for clarity. Selected bond lengths (Å) and angles are in [Supplementary material \(Table S1\)](#).

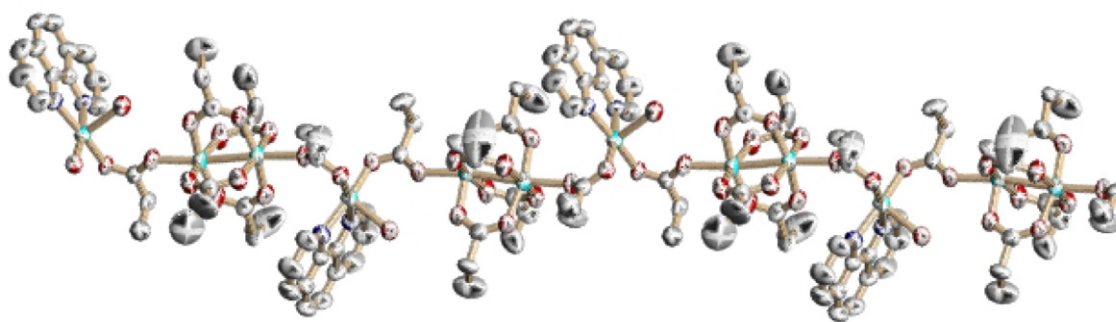


Fig. 3. View of the 1-D polymeric chain in compound **2** along the crystallographic b -axis.

contrast to those of compound **1** ($\tau = 0.483$). The basal plane of a square pyramidal chromophore consists of two N atoms of phen and two O atoms of two different propionate bridges. The coordinated water molecules (O(1), O(15)) occupy the apical positions at distances of 2.342(3) and 2.346(3) Å for Cu(1) and Cu(4), respectively. The CuN_2O_2 chromophores are non-planar with a slight tetrahedral twist of $10.8(1)^\circ$ and $10.9(1)^\circ$, for Cu(1) and Cu(4), respectively. The Cu(1) and Cu(4) line above the basal planes, 0.135 and 0.136 Å toward O(1) and O(15), respectively. The compounds together with a number of related paddle-wheel copper(II) compounds are listed in [Table 1](#) showing the different structure types.

Three discrete independent $[\text{Cu}_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)_4(\text{H}_2\text{O})_2]$ units also involve the dinuclear paddle-wheel unit with comparable structural data to those of another paddle-wheel units of compounds **1** and **2**. The square pyramidal coordinations are completed by oxygen atoms of water molecules at the axial distances of 2.164(3) and 2.159(3) Å at Cu(7) and Cu(8), 2.156(3) Å at Cu(9) and 2.141(3) Å at Cu(10), with the τ values of 0.077, 0.076, 0.001 and 0.061, respectively. The basal planes are non-planar with a slight tetrahedral twist of $17.2(1)^\circ$ and $17.3(1)^\circ$ at Cu(7) and Cu(8), $16.6(1)^\circ$ at Cu(9) and $16.9(1)^\circ$ at Cu(10). The Cu atoms are lifted above the basal planes at distances of

0.206(1), 0.207(1), 0.202(1) and 0.202(1) Å for Cu(7), Cu(8), Cu(9) and Cu(10), respectively. The Cu···Cu distances are 2.636(1) Å for Cu(7)···Cu(8), 2.632(1) Å for Cu(9)···Cu(9A) and 2.627(1) Å for Cu(10)···Cu(10A). The structural parameters of compound **2** are in the normal ranges found for the paddle-wheel copper(II) dimers statistically analyzed [14].

The lattice structure is stabilized by a complicated hydrogen bonding network between the water oxygen atoms of independent, uncoordinated dinuclear paddle-wheel units and the oxygen atoms of *syn,syn*- $\eta^1:\eta^1:\mu$ bridged propionate ligands (O···O distances vary from 2.793(1) to 2.990(1) Å); between the coordinated water oxygen atoms and the oxygen atoms of *syn,syn*- $\eta^1:\eta^1:\mu$, *syn,anti*- $\eta^1:\eta^1:\mu_2$ bridged propionate ligands and water oxygen atoms of discrete dinuclear paddle-wheel units (O···O distances vary from 2.844(1) to 3.011(1) Å).

The IR spectra of compounds **1** and **2** exhibit the anti-symmetric and symmetric carboxylate stretching vibrations at 1588 (**1**), 1591 (**2**) and 1468 (**1**), 1467 (**2**), respectively. These bands are assigned to the stretching modes of the tri-atomic carboxylate bridges [16].

The electronic reflectance spectrum of compound **1** consists of a single broad peak centered at $13\,860\text{ cm}^{-1}$, resulting from the overlap of two nearly equal energy peaks, a

Table 1
Structural data and EPR properties of paddle-wheel polynuclear copper(II) complexes

Complex ^a	Type	Chromophore	Geometry ^b	Polycrystalline EPR spectrum			Cu···Cu (Å)	References
				g_x	g_y	g_z		
[Cu ₄ (dpyam) ₂ (OCOC ₂ H ₅) ₂ (μ-O ₂ CC ₂ H ₅) ₆ (H ₂ O) ₂][Cu ₂ (μ-O ₂ CC ₂ H ₅) ₄ (H ₂ O) ₂](DMF) ₂ (1)	Tetranuclear	CuO ₄ O', CuN ₂ O ₂ O'	SP	–	2.09 ^c	–	2.632	This work
[Cu ₆ (phen) ₂ (H ₂ O) ₂ -(μ-O ₂ CC ₂ H ₅) ₁₂] _n [Cu ₂ -(μ-O ₂ CC ₂ H ₅) ₄ (H ₂ O) ₂] _n ·(H ₂ O) _{0.5n} (2)	Class B	CuO ₄ O', CuN ₂ O ₂ O'	SP	–	2.12 ^c	–	2.621, 4.293, 4.287, 5.077	This work
[Cu ₄ L ₂ (CH ₃ COO) ₆]	Tetranuclear	CuO ₄ O'	SP	–	–	–	2.631	[8m]
[{Cu ₂ (OOCCH ₂ H ₁₁) ₄ (urea)} ₂]	Tetranuclear	CuO ₄ O'	SP	–	–	–	2.6061	[8k]
[Cu ₂ (Me ₃ CCO ₂) ₄ (NITmPy)] _n	Class B	CuO ₄ N	SP	–	–	–	2.610, 2.608	[8h]
[Cu ₂ (O ₂ sCMe) ₄ (btd) ₂] _n	Class B	CuO ₄ N	SP	–	–	–	2.582	[8g]
[{Cu ₆ (O ₂ CMe) ₈ (OMe) ₄ (btd) ₂ }] _n	Class B	CuO ₄ N	SP	2.08	2.08	2.38	2.589, 3.502, 4.074, 6.762	[8g]
[Cu ^I Cu ^I (ip)(ipH)(4,4'-sbipy) _{3/2}] _n	Class B	CuO ₄ N	SP	2.118	–	2.413	2.647	[8i]
				2.090		2.287		
[Cu ₂ (O ₂ CC ₅ H ₁₁) ₄] _n	Class A	CuO ₄ O'	SP	–	–	–	2.579	[8k]
[{Cu ₂ (C ₁₄ H ₁₁ O ₂) ₂](C ₁₄ H ₁₁ O ₂) _{2n}]	Class A	CuO ₄ O'	SP	2.07	2.02	2.33	2.594	[8l]
[Cu ₂ (μ-O ₂ CCH ₃) ₄ (OCH ₃) ₂] _n	Class C	CuO ₄ O'	SP	–	–	–	2.617	[10]

^a Abbreviations: L = 1-(5-bromosalicylaldimino)-3-(2-methylpiperidino)propane, NITmPy = 2-(3-pyridyl)-4,4,5,5-tetramethyl-4,5-dihydroxo-1*H*-imidazolyl-1-oxyl-3-oxide, btd = 2,1,3-benzothiadiazole, ipH₂ = isophthalic acid and 4,4'-bipy = 4,4'-bipyridine.

^b SP: square pyramidal geometry.

^c g_{iso} (determined from pseudo-isotropic spectra).

higher energy peak of the square pyramidal chromophore and a lower energy peak of intermediate five-coordinate chromophore. The one-electron ground state configuration is $d_{x^2-y^2} > d_{z^2} > d_{xy} > d_{xz} \approx d_{yz}$. The transitions may be assigned as the $d_{xy}, d_{xz}, d_{yz}, d_{z^2} \rightarrow d_{x^2-y^2}$ [17] for both distorted geometries. The spectrum of compound **2** consists of a single broad peak at 13,800 cm⁻¹. This spectral character is consistent with the square pyramidal geometry. The transition may be assigned as the $d_{xy}, d_{xz}, d_{yz}, d_{z^2} \rightarrow d_{x^2-y^2}$.

The polycrystalline EPR spectra of compounds **1** and **2** are isotropic at room temperature with $g_{iso} = 2.09$ and 2.12, respectively, giving no information regarding the electronic ground state; at liquid nitrogen temperature (77 K) these values are just slightly increased.

Acknowledgements

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Appendix A. Supplementary material

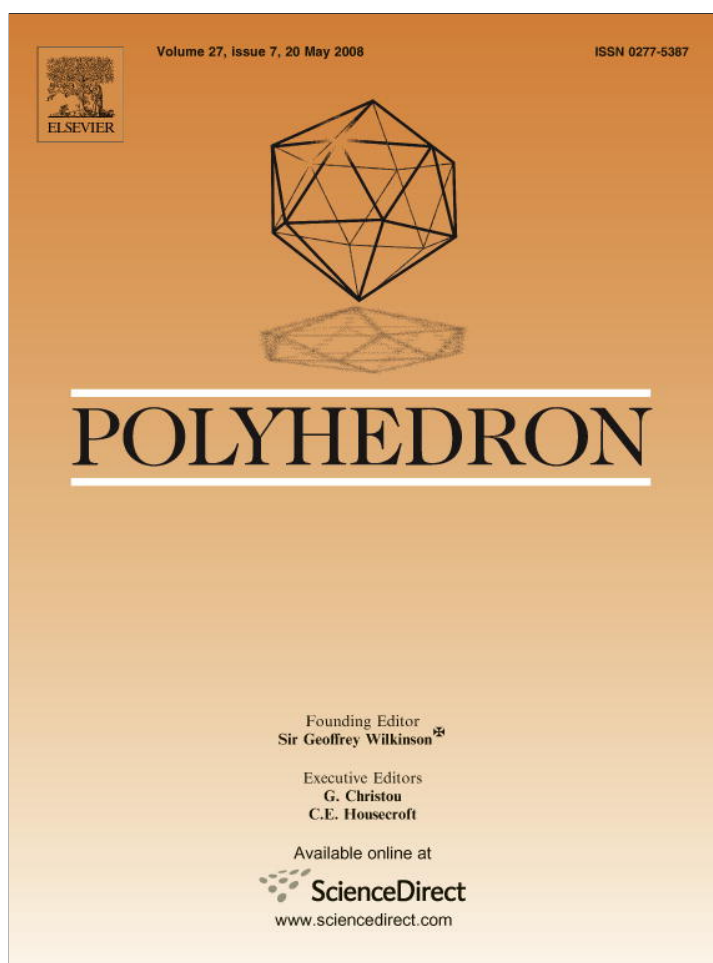
CCDC Nos. 647984 and 647985 for compounds **1** and **2**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via. These data can be obtained free of charge from The Cambridge Crystallo-

graphic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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- [11] Compound **1** was obtained as a mixing solution of dpyam (0.171 g, 1.0 mmol) in DMF: ethanol (20:10 ml) was added to a warm aqueous solution (10 ml) of $\text{Cu}(\text{CO}_3) \cdot \text{Cu}(\text{OH})_2 \cdot n\text{H}_2\text{O}$ (0.332 g, 1.5 mmol). Then an aqueous solution (10 ml) of $\text{NaO}_2\text{CCH}_2\text{CH}_3$ (0.144 g, 1.5 mmol) was added to the mixture yielding a blue solution and the blue precipitate formed in a few minutes. Its color became light blue by slow addition of the concentrate propionic acid (5 ml) yielding a clear, light blue solution. After a month, blue polygon-shaped crystals of compound **1** were obtained which were filtered off, washed with the mother liquid and air-dried. Yield ca. 65%. $\text{C}_{62}\text{H}_{102}\text{Cu}_6\text{N}_8\text{O}_{30}$: *Anal. Calc.* C 40.90; H 5.65; N, 6.15 Found: C 40.50; H 5.61; N, 6.04%. Compound **2** was obtained as a mixing solution of phen (0.198 g, 1.0 mmol) in acetonitrile: ethanol (20:10 ml) was added to a warm aqueous solution (10 ml) of $\text{Cu}(\text{CO}_3) \cdot \text{Cu}(\text{OH})_2 \cdot n\text{H}_2\text{O}$ (0.332 g, 1.5 mmol). Then an aqueous solution (10 ml) of $\text{NaO}_2\text{CCH}_2\text{CH}_3$ (0.144 g, 1.5 mmol) was added to the mixture yielding a blue solution and the blue precipitate formed in a few minutes. The resulting solution became clear and light blue in color by slow addition of the concentrate propionic acid (7 ml). After a month, blue polygon-shaped crystals of compound **2** were obtained which were filtered off, washed with the mother liquid and air-dried. Yield ca. 50%. $\text{C}_{168}\text{H}_{254}\text{Cu}_{20}\text{N}_8\text{O}_{93}$: *Anal. Calc.* C 39.22; H 4.98; N, 2.17 Found: C 39.05; H 4.41; N, 2.01%.
- [12] *Crystal data for 1*: $\text{C}_{62}\text{H}_{102}\text{Cu}_6\text{N}_8\text{O}_{30}$ ($M_w = 1820.76$), Triclinic, $P-1$, $a = 12.1045(11) \text{ \AA}$, $b = 13.3062(12) \text{ \AA}$, $c = 13.7269(12) \text{ \AA}$, $\alpha = 86.735(2)^\circ$, $\beta = 84.440(21)^\circ$, $\gamma = 69.1920(10)^\circ$, $V = 2056.4(3) \text{ \AA}^3$, $T = 293(2) \text{ K}$, $Z = 1$, $D_c = 1.470 \text{ Mg/m}^3$, $\mu = 1.604 \text{ mm}^{-1}$, $F(000) = 944$, $k(\text{Mo K}\alpha) = 0.71073 \text{ \AA}$, 18,126 reflections measured ($1.51 < h < 30.45^\circ$), 9487 unique ($R_{\text{int}} = 0.0210$), $R_1 = 0.0459$, $wR_2 = 0.1141$. For **2**: $\text{C}_{168}\text{H}_{254}\text{Cu}_{20}\text{N}_8\text{O}_{93}$ ($M_w = 5135.73$), Triclinic, $P-1$, $a = 10.474(3) \text{ \AA}$, $b = 22.769(6) \text{ \AA}$, $c = 24.364(6) \text{ \AA}$, $\alpha = 77.490(4)^\circ$, $\beta = 77.670(5)^\circ$, $\gamma = 89.896(5)^\circ$, $V = 5536(3) \text{ \AA}^3$, $T = 293(2) \text{ K}$, $Z = 1$, $D_c = 1.543 \text{ Mg/m}^3$, $\mu = 1.967 \text{ mm}^{-1}$, $F(000) = 2642$, $k(\text{Mo K}\alpha) = 0.71073 \text{ \AA}$, 41,289 reflections measured ($1.90 < h < 30.46^\circ$), 21,468 unique ($R_{\text{int}} = 0.0542$), $R_1 = 0.0438$, $wR_2 = 0.0668$. Reflection data for the two compounds were collected on a 1 K Bruker SMART CCD area-detector diffractometer. Data reduction and cell refinements were performed using the program SAINT [Siemens. SAINT, Version 4 Software Reference Manual, Siemens Analytical X-ray Systems, Inc., Madison, WI, USA, 2000]. An empirical absorption correction by using the SADABS [G.M. Sheldrick, SADABS, Program for Empirical Absorption correction of Area Detector Data, University of Göttingen, Göttingen, Germany, 2000] program was applied, which resulted in transmission coefficients ranging from 0.575 to 1.000 and 0.708 to 1.000 for **1** and **2**, respectively. The structure was solved by direct methods and refined by fullmatrix least-squares method on $(F_{\text{obs}})^2$ with anisotropic thermal parameters for all nonhydrogen atoms using the SHELXTL-PC [Siemens. SHELXTL. 2000, Version 6.12 Reference Manual, Siemens Analytical X-ray Systems, Inc., Madison, WI, USA, 2000] software package. The H atoms were introduced in calculated positions and refined with fixed with respect to their carrier atoms. For the structure determination of compound **1**, one of propionate groups showed disorder; the occupancies of the disordered positions were initially refined and later fixed at 0.50. The DMF group is disordered with site occupancies of 0.50. All hydrogen atoms of the dpyam and propionate ligands in **1** were fixed and allowed to ride on the attached atoms, hydrogen atoms of coordinated water molecules were located geometrically and refined isotropically. For the structure determination of compound **2**, eighteen of propionate groups showed disorder; the occupancies of the disordered positions were initially refined and later fixed at 0.50 for both conformers. All hydrogen atoms of the phen ligand in **2** were fixed and allowed to ride on the attached atoms, while hydrogen atoms of coordinated water molecules were located geometrically and refined isotropically. The molecular graphics were created by using SHELXTL-PC. CCDC Nos. 647984 and 647985 for compounds **1** and **2**, respectively. See <http://www.ccdc.cam.ac.uk> for crystallographic data in CIF format.
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Three new polynuclear tetracarboxylato-bridged copper(II) complexes: Syntheses, X-ray structure and magnetic properties

Sujittra Youngme^{a,*}, Achareeya Cheansirisomboon^a, Chanaiporn Danvirutai^a, Chaveng Pakawatchai^b, Narongsak Chaichit^c, Chainarong Engkagul^c, Gerard A. van Albada^d, José Sánchez Costa^d, Jan Reedijk^d

^a Department of Chemistry, Faculty of Science, Khon Kaen University, Khon Kaen 40002, Thailand

^b Department of Chemistry, Faculty of Science, Prince of Songkla University, Hat Yai, Songkla 90112, Thailand

^c Department of Physics, Faculty of Science and Technology, Thammasat University Rangsit, Pathumthani 12121, Thailand

^d Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden University, P.O. Box 9502, 2300 RA Leiden, The Netherlands

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ABSTRACT

The synthesis, crystal structure and magnetic measurements of three new polynuclear tetracarboxylato-bridged copper(II) complexes, *i.e.* $\{[\text{Cu}_4(\text{phen})_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)_8] \cdot (\text{H}_2\text{O})\}_n$ (**1**), $[\text{Cu}_2(\mu\text{-O}_2\text{CC}_6\text{H}_4\text{OH})_4(\text{C}_7\text{H}_7\text{NO})_2] \cdot 6\text{H}_2\text{O}$ (**2**) and $[\text{Cu}_2(\mu\text{-O}_2\text{CCH}_3)_4(\text{C}_7\text{H}_7\text{NO})_2]$ (**3**) (phen = 1,10-phenanthroline, $\text{O}_2\text{CC}_6\text{H}_4\text{OH}$ = 3-hydroxy benzoate, $\text{C}_7\text{H}_7\text{NO}$ = 4-acetylpyridine) are reported. All compounds consist of dinuclear units, in which two Cu(II) ions are bridged by four *syn,syn*- $\eta^1:\eta^1:\mu$ carboxylates, showing a paddle-wheel cage type with a square-pyramidal geometry, arranged in different ways. The structure of compound **1** consists of an one-dimensional structure generated by an alternating classical dinuclear paddle-wheel unit and an unusual dinuclear $\text{Cu}_2(\mu\text{-OCOC}_2\text{H}_5)_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)_2(\text{phen})_2$ unit, which are connected to each other via a *syn,anti*-triatom propionato bridge in an axial-equatorial configuration. The adjacent chains are connected to generate a 2D structure through the face-to-face $\pi\text{-}\pi$ interaction between phen rings. Structures of compounds **2** and **3** both consist of a symmetric dinuclear Cu(II) carboxylate paddle-wheel core and pyridyl nitrogen atoms of 4-acetylpyridine ligand at the apical position, and just differ in the substituents of the equatorial ligands.

The magnetic properties have been measured and correlated with the molecular structures. It is found that in the two classical paddle-wheel compounds the Cu(II) ions are strongly antiferromagnetically coupled with $J = -278.5$ and -287.0 cm^{-1} for complexes **2** and **3**, respectively. In compound **1** the magnetic susceptibility could be fitted with two different, independent Cu(II) units, one strongly coupled and one weakly coupled; the paddle-wheel dinuclear unit has the strongest antiferromagnetic coupling with a value for J of -299.5 cm^{-1} , whereas the Cu(II) ions in the propionato-bridged dinuclear unit of **1** display a very weak antiferromagnetic coupling with a value for $J = -0.75 \text{ cm}^{-1}$, due to the orthogonality of the magnetic orbitals. Also the exchange within the chain is therefore very weak. The magneto-structural correlations for complexes **1**, **2**, and **3** are discussed on the basis of the structural parameters and magnetic data for the complexes.

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1. Introduction

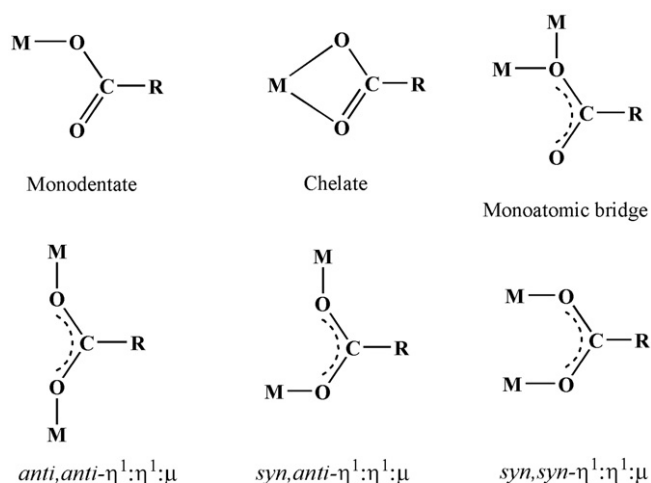
Copper(II) complexes with carboxylate ligands have been of interest for some decades now, as they can contain two or more antiferromagnetically coupled metal centers [1–9]. Carboxylate anions are versatile ligands, because each carboxylate oxygen atom carries two lone pairs. In most dinuclear structures only one of the lone pairs of each oxygen atom is involved in coordination, like in the dinuclear paddle-wheel structure. However, if the second lone pair is donated to a metal ion of another paddle-wheel structure,

this may result in polymeric structures. In addition, carboxylate anions exhibit a versatile coordination behavior displaying distinct bonding modes toward metal cations, such as monodentate and chelate, as well as $\eta^1:\eta^1:\mu$ bridging ligands in *syn*, *syn*, *syn*, *anti*, and *anti*, *anti* conformations. Another type of coordination mode is the monoatomic bridge, in which two metal ions are connected by a single oxygen atom of a carboxylate group. This diversity of coordination modes assumed by carboxylate ligands is shown in Scheme 1.

A large number of paddle-wheel type dinuclear copper(II) carboxylate adducts, $[\text{Cu}_2(\text{RCO}_2)_4\text{L}_2]$, where L is an apical ligand with an oxygen or a nitrogen atom, have been reported in an attempt to clarify the factors influencing the magnitude of the intramolecular

* Corresponding author. Fax: +66 43 202373.

E-mail address: sujittra@kku.ac.th (S. Youngme).



magnetic exchange interaction which occurs between two Cu(II) ions of a paddle-wheel moiety [10–29].

In the present paper, we report the synthesis, crystal structure, spectroscopic and magnetic properties of three copper(II) compounds, i.e. a polynuclear $\{[\text{Cu}_4(\text{phen})_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)_8] \cdot (\text{H}_2\text{O})\}_n$ (**1**) and two dinuclear compounds, $[\text{Cu}_2(\mu\text{-O}_2\text{CC}_6\text{H}_4\text{OH})_4(\text{C}_7\text{H}_7\text{NO})_2] \cdot 6\text{H}_2\text{O}$ (**2**) and $[\text{Cu}_2(\mu\text{-O}_2\text{CCH}_3)_4(\text{C}_7\text{H}_7\text{NO})_2]$ (**3**). The magnetism of the polynuclear compound can be understood on the basis of two species, i.e. 50% paddle-wheel (strongly coupled) and 50% dinuclear-propionate bridged (weakly coupled).

2. Experimental

2.1. Materials and measurements

The ligands 1,10-phenanthroline, propionic acid, 3-hydroxybenzoic acid and 4-acetylpyridine were purchased as commercial chemicals from Aldrich. All other reagents are commercial grade materials and were used without further purification. Elemental analyses (C, H, N) were determined on a Perkin–Elmer PE 2400 CHNS/O Analyzer.

IR spectra were recorded on a Perkin–Elmer Spectrum One FT-IR spectrophotometer as KBr disc in the 4000–450 cm^{-1} spectral range. Solid-state (diffuse reflectance) electronic spectra were measured as polycrystalline samples on a Perkin–Elmer Lambda2S spectrophotometer. X-band powder EPR spectra were obtained on a Bruker-EMXplus electron spin resonance spectrometer (Field calibrated with DPPH ($g = 2.0036$)). Magnetic susceptibility measurements (2–320 K for **1** and 5–350 K for **2** and **3**) were carried out using a Quantum design MPMS-5 S SQUID magnetometer (measurements carried out at 0.1 mT). Data were corrected for magnetization of the sample holder and for diamagnetic contributions, which were estimated from the Pascal constants.

2.2. Syntheses

2.2.1. $\{[\text{Cu}_4(\text{phen})_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)_8] \cdot (\text{H}_2\text{O})\}_n$ (**1**)

A hot aqueous solution (10 ml) of $\text{Cu}(\text{CO}_3) \cdot \text{Cu}(\text{OH})_2$ (0.22 g, 1.0 mmol) was stirred and a blue precipitate formed within a few minutes. The resulting suspension became clear and light blue in color by slow addition of the concentrate propionic acid (2 ml) and stirred for 1 h. A solution of phen (0.20 g, 1.0 mmol) in acetonitrile: ethanol (20:10 ml) was added to the mixture, followed by addition of an aqueous solution of $\text{NaO}_2\text{CCH}_2\text{CH}_3$ (0.10 g,

1.0 mmol) with continuous stirring. After a month, blue polygon-shaped crystals of compound **1** were obtained which were filtered off, washed with the mother liquid and air-dried. Yield, ca. 70%. IR (KBr, cm^{-1}): ν : 3435 s, 1632 s, 1588 s, 1567 s, 1465 m, 1426 s, 1372 m, 1301 m, 1262 m, 1078 m, 848 m, 811 w, 723 m. The electronic diffuse reflectance spectrum of **1** exhibits a broad band centered at 13510 cm^{-1} . These features are consistent with the square-pyramidal based geometry and all d_{xy} , d_{yz} , d_{xz} , $d_{z^2} \rightarrow d_{x^2-y^2}$ transitions are assigned to this broad band. *Anal. Calc.* for $\text{C}_{48}\text{H}_{56}\text{Cu}_4\text{N}_4\text{O}_{17}$: C, 47.4; H, 4.7; N, 4.6. Found: C, 47.3; H, 4.7; N, 4.6%.

2.2.2. $[\text{Cu}_2(\mu\text{-O}_2\text{CC}_6\text{H}_4\text{OH})_4(\text{C}_7\text{H}_7\text{NO})_2] \cdot 6\text{H}_2\text{O}$ (**2**)

A warm solution of 3-hydroxybenzoic acid (0.14 g, 1.0 mmol) in methanol (20 ml) was added to a hot aqueous solution (10 ml) of $\text{Cu}(\text{BF}_4)_2$ (0.24 g, 1.0 mmol). An aqueous solution (10 ml) of 4-Acetylpyridine (0.12 g, 1.0 mmol) was then added. The light blue solution was slowly evaporated at room temperature. After several days, green rod crystals of **2** were formed. The crystals were filtered off, washed with mother liquid and air-dried. Yield, ca. 80%. IR (KBr, cm^{-1}): ν : 3292 s, 1698 m, 1578 s, 1451 m, 1400 s, 1360 m, 1258 m, 1215 w, 1051 w, 938 w, 822 w, 802 m, 767 m. The electronic diffuse reflectance spectrum of **2** exhibits a broad band centered at 13460 cm^{-1} . These features are consistent with the square-pyramidal based geometry and all d_{xy} , d_{yz} , d_{xz} , $d_{z^2} \rightarrow d_{x^2-y^2}$ transitions are assigned to this broad band. *Anal. Calc.* for $\text{C}_{42}\text{H}_{46}\text{Cu}_2\text{N}_2\text{O}_{20}$: C, 49.2; H, 4.5; N, 2.7. Found: C, 51.0; H, 4.2; N, 2.8%.

2.2.3. $[\text{Cu}_2(\mu\text{-O}_2\text{CCH}_3)_4(\text{C}_7\text{H}_7\text{NO})_2]$ (**3**)

The ligand 4-acetylpyridine (0.12 g, 1.0 mmol), dissolved in acetonitrile (10 ml) and a warm solution of $\text{Cu}(\text{CH}_3\text{COO})_2$ (0.18 g, 1.0 mmol) were mixed together. The blue solution was slowly evaporated at room temperature until dark blue crystals of **3** separated. Yield ca. 70%. IR (KBr, cm^{-1}): ν : 1697 s, 1625 s, 1433 s, 1366 m, 1261 s, 1060 w, 834 w, 684 w. The electronic diffuse reflectance spectrum of **3** exhibits a broad band centered at 14470 cm^{-1} . These features are consistent with the square-pyramidal based geometry and all d_{xy} , d_{yz} , d_{xz} , $d_{z^2} \rightarrow d_{x^2-y^2}$ transitions are assigned to this broad band. *Anal. Calc.* for $\text{C}_{22}\text{H}_{26}\text{Cu}_2\text{N}_2\text{O}_{10}$: C, 43.6; H, 4.3; N, 4.6. Found: C, 43.4; H, 4.1; N, 4.6%.

2.3. Crystallography

The X-ray single-crystal data for the three compounds were collected at 273 K for compounds **1** and at 293 K for **2**, **3**, respectively, on a 1 K Bruker SMART CCD area-detector diffractometer using graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å) at a detector distance of 4.5 cm and swing angle of -30° . A hemisphere of the reciprocal space was covered by combination of three sets of exposures; each set had a different ϕ angle (0° , 88° , 180°) and each exposure of 40 s covered 0.3° in ω . Data reduction and cell refinements were performed using the program SAINT [30]. An empirical absorption correction by using the SADABS [31] program was applied, which resulted in transmission coefficients ranging from 0.624 to 1.000 for compound **1**, 0.845 to 1.000 for compound **2** and 0.695 to 1.000 for compound **3**. The structures were solved by direct methods and refined by full matrix least-squares method on $(F_{\text{obs}})^2$ with anisotropic thermal parameters for all non-hydrogen atoms using the SHELXTL-PC V 6.12 software package [32]. All hydrogen atoms were located in a difference Fourier map and refined isotropically, except the H atoms of the propionate groups in **1**, which were fixed geometrically with the HFIX utility and the hydrogen atoms of one water molecule in **1** and four water molecules in **2**, which we were unable to locate and also could not be located at fixed positions. The terminal C atom in three propionate groups of **1** showed disorder; the occupancies of the

Table 1
Crystal and refinement data for complexes **1**, **2** and **3**

Complex	1	2	3
Molecular formula	C ₄₈ H ₅₄ Cu ₄ N ₄ O ₁₇	C ₄₂ H ₄₁ Cu ₂ N ₂ O ₂₀	C ₂₂ H ₂₆ Cu ₂ N ₂ O ₁₀
Molecular weight	1213.11	1020.85	605.53
T (K)	273(2)	293(2)	293(2)
Crystal system	triclinic	monoclinic	monoclinic
Space group	P1	P2 ₁ /n	P2 ₁ /c
a (Å)	10.2456(3)	9.1164(6)	11.7573(6)
b (Å)	12.0032(3)	22.2155(14)	12.9823(6)
c (Å)	13.0657(3)	10.9944(7)	8.6637(4)
α (°)	100.4180(10)	90.00	90.00
β (°)	106.09	93.921(2)	105.6180(10)
γ (°)	114.5540(10)	90.00	90.00
V (Å ³)	1321.29(6)	2221.4(2)	1273.57(11)
Z	1	2	2
D _c (g cm ⁻³)	1.525	1.536	1.579
μ (mm ⁻¹)	1.660	1.041	1.726
F(000)	622	1050	620
Crystal size (mm)	0.18 × 0.38 × 0.88	0.17 × 0.08 × 0.03	0.30 × 0.27 × 0.09
Number of reflection collected	9503	2435	12607
Number of unique reflections [R _{int}]	6926 [0.0238]	4064 [0.0514]	3078 [0.0291]
Data/restraints/parameter	6926/0/416	4064/0/391	3078/0/182
Goodness-of-fit	1.012	1.089	1.046
Final R indices [I > 2σ(I)]	R ₁ = 0.0497, wR ₂ = 0.1285	R ₁ = 0.0399, wR ₂ = 0.0898	R ₁ = 0.0255, wR ₂ = 0.0744
R indices (all data)	R ₁ = 0.0849, wR ₂ = 0.1544	R ₁ = 0.0526, wR ₂ = 0.0952	R ₁ = 0.0285, wR ₂ = 0.0761
Largest difference in peak and hole (e Å ⁻³)	0.53 and -0.65	0.36 and -0.23	0.30 and -0.24

$$R = \sum \|F_o\| - |F_c| / \sum \|F_o\|, R_w = \left[\sum w(F_o - F_c)^2 / \sum wF_o^2 \right]^{1/2}.$$

disordered positions were initially refined and later fixed at 0.5. The molecular graphics were created by using SHELXTL-PC [32] package. The crystal and refinement details for the three compounds are listed in Table 1.

3. Results and discussion

3.1. Crystal structure of $\{[Cu_4(phen)_2(\mu-O_2CC_2H_5)_8] \cdot (H_2O)_n\}_n$ (**1**)

The structure of compound **1** involves a one-dimensional overall structure constructed from tetranuclear units and consists of chains of dinuclear $Cu_2(\mu-OCOC_2H_5)_2(\mu-O_2CC_2H_5)_2(phen)_2$ repeating units which are connected to each other along the unit cell diagonal by $Cu_2(\mu-O_2CC_2H_5)_4$ paddle-wheel dinuclear units. This structure is depicted in Fig. 1 together with the numbering scheme. Selected distances and angles are listed in Table 2. The two dinuclear units are linked by the *syn,anti*-triatom propionato bridge in an axial-equatorial configuration. The polynuclear copper(II) carboxylates are known to exhibit three classes of local paddle-wheel structure. Compound **1** has a structure derived from class B, with a dinuclear molecule bridging two dinuclear units [9].

The paddle-wheel dinuclear $Cu_2(\mu-O_2CC_2H_5)_4$ unit in the chain contains four bridging propionates in the *syn,syn-η¹:η¹*:μ coordination mode, as known for the compound $[Cu_2(\mu-O_2CC_2H_5)_4(H_2O)_2]$ [33]. The geometry around the Cu(2) and Cu(2)A atoms can be considered as square-pyramidal with a τ value of 0.005 (in which the structural parameter τ describes the relative amount of trigonality; τ = 0 for square pyramid and τ = 1 for trigonal bipyramidal [34]) arising from five oxygen atoms of five different propionate groups. The corresponding Cu–O distances in the basal plane are in the range 1.952(3)–1.962(3)(2) Å. An O atom of a bridging propionate molecule occupies the axial position at a distance of 2.120(2) Å.

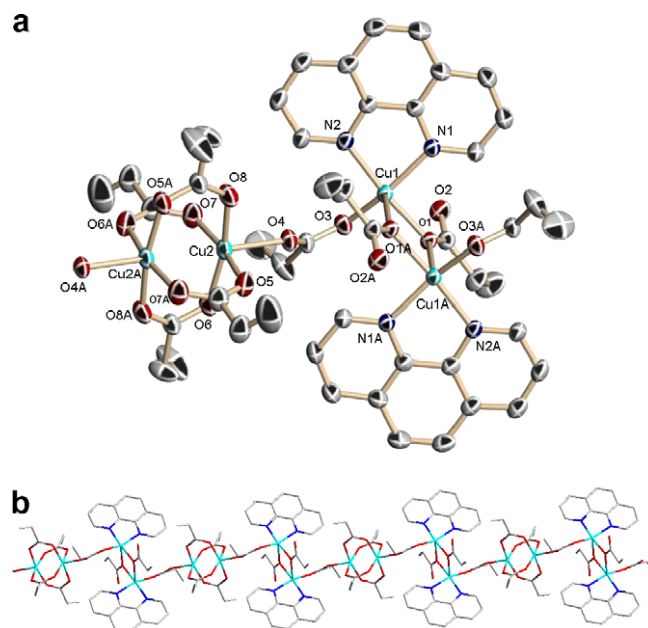


Fig. 1. (a) Thermal ellipsoid (30% probability) plot of $\{[Cu_4(phen)_2(\mu-O_2CC_2H_5)_8] \cdot (H_2O)_n\}_n$ (**1**). Hydrogen atoms and water molecules are omitted for clarity. (b) View of the 1-D polymeric chain.

Table 2
Selected bond lengths (Å) and angles (°) of $\{[Cu_4(phen)_2(\mu-O_2CC_2H_5)_8] \cdot (H_2O)_n\}_n$ (**1**)

Cu(1)–N(1)	2.031(3)	Cu(2)–O(4)	2.120(2)
Cu(1)–N(2)	2.044(3)	Cu(2)–O(5)	1.952(3)
Cu(1)–O(1)	1.960(2)	Cu(2)–O(6)	1.962(3)
Cu(1)–O(1)A	2.354(2)	Cu(2)–O(7)	1.960(3)
Cu(1)–O(3)	1.931(3)	Cu(2)–O(8)	1.962(3)
Cu(1)–Cu(1)A	3.408(1)	Cu(2)–Cu(2)A	2.623(8)
N(1)–Cu(1)–N(2)	80.4(1)	O(4)–Cu(2)–O(5)	94.5(1)
N(1)–Cu(1)–O(1)	94.5(1)	O(4)–Cu(2)–O(6)	99.5(1)
N(2)–Cu(1)–O(1)	101.8(1)	O(4)–Cu(2)–O(7)	97.2(1)
O(1)–Cu(1)–N(1)	93.5(1)	O(4)–Cu(2)–O(8)	92.5(1)
O(1)–Cu(1)–N(2)	173.4(1)	O(5)–Cu(2)–O(6)	89.1(1)
O(1)–Cu(1)–O(1)A	76.0(1)	O(5)–Cu(2)–O(8)	89.3(1)
O(1)–Cu(1)–O(3)	90.2(1)	O(6)–Cu(2)–O(7)	90.2(1)
O(3)–Cu(1)–N(1)	155.9(1)	O(7)–Cu(2)–O(5)	168.3(1)
O(3)–Cu(1)–N(2)	96.5(1)	O(7)–Cu(2)–O(8)	88.9(1)
O(3)–Cu(1)–O(1)A	109.5(1)	O(8)–Cu(2)–O(6)	167.9(1)
Cu(1)–O(1)–Cu(1)A	103.9(1)		

The basal planes have a slight tetrahedral twist of 16.72(1)°. The Cu atoms are displaced from the basal planes at distances of 0.003 Å. The Cu(2)–Cu(2)A distance is 2.623(1) Å and is slightly longer than the Cu···Cu distance in $[Cu_2(\mu-O_2CC_2H_5)_4(H_2O)_2]$ (2.611(2) Å) [33].

The dinuclear $[Cu_2(\mu-OCOC_2H_5)_2(\mu-O_2CC_2H_5)_2(phen)_2]$ unit has a CuN_2O_2O' chromophore and the geometry around the Cu(II) ions (Cu(1) and Cu(1)A) is distorted square pyramidal with a τ value of 0.290. The basal plane of CuN_2O_2O' chromophore consists of two N atoms from the phen ligand and two O atoms from two different propionate bridging molecules and is non-planar with a slight tetrahedral twist of 24.05(1)°. An O atom of a propionate bridging ligand occupies the axial position with a distance of 2.354(2) Å. The Cu atom is situated above the basal planes, 0.215 Å toward the axial sites. Both Cu(1) and Cu(1)A are linked by doubly bridged monoatomic propionato molecules in an axial-equatorial configuration with a Cu···Cu distance of 3.408(1) Å. The structural parameters of compound **1** are compared with some related compounds in Table 5.

The interplanar distances between the phen rings of two adjacent chains are 3.488–3.494 Å, indicating suggests π -stacking interactions. The π - π interaction between parallel phen rings of different chains are shown in Fig. 2. The 2D layer resulting from stacks in the crystal is presented in Fig. 2.

3.2. Crystal structure of $[\text{Cu}_2(\mu\text{-O}_2\text{CC}_6\text{H}_4\text{OH})_4(\text{C}_7\text{H}_7\text{NO})_2] \cdot 6\text{H}_2\text{O}$ (**2**)

The structure of compound **2** consists of centrosymmetric dinuclear paddle-wheel unit. The structure is depicted in Fig. 3 together with the numbering scheme. Selected distances and angles are listed in Table 3. Both Cu(II) ions are linked by four carboxylato groups of the 3-hydroxybenzoate ligand in a *syn,syn*- $\eta^1:\eta^1:\mu$ disposition. The pyridyl nitrogen atom of 4-acetylpyridine is axially coordinated, completing the square-pyramidal coordination geometry with a τ value of 0.002. The Cu–O distances are ranging from 1.958 to 1.970 Å and the Cu–N distance is 2.181(2) Å. The Cu...Cu distance is 2.654(1) Å. The basal plane is non-planar with a slight tetrahedral twist of 17.2(1)° and the Cu atoms lie 0.001 Å above the basal plane toward the axial sites. The structural parameters of compound **2** are in the normal range found for other paddle-wheel copper(II) dinuclear units [35], as shown in Table 5.

The crystal lattice is stabilized by hydrogen bonding between the O atom of uncoordinated water and an O atom of neighbouring carboxylato group; between the O atom of uncoordinated water and O atom of neighbouring hydroxy group of 3-hydroxybenzoate

Table 3

Selected bond lengths (Å) and angles (°) of $[\text{Cu}_2(\mu\text{-O}_2\text{CC}_6\text{H}_4\text{OH})_4(\text{C}_7\text{H}_7\text{NO})_2] \cdot 6\text{H}_2\text{O}$ (**2**)

Cu(1)–N(1)	2.181(2)	Cu(1)–O(3)	1.969(2)
Cu(1)–O(1)	1.970(2)	Cu(1)–O(4)	1.958(2)
Cu(1)–O(2)	1.962(2)	Cu(1)–Cu(1)A	2.654(6)
O(1)–Cu(1)–N(1)	95.2(1)	O(4)–Cu(1)–N(1)	97.9(1)
O(2)–Cu(1)–N(1)	95.0(1)	O(3)–Cu(1)–O(1)	167.2(1)
O(2)–Cu(1)–O(1)	89.8(1)	O(4)–Cu(1)–O(1)	89.2(1)
O(2)–Cu(1)–O(3)	89.0(1)	O(4)–Cu(1)–O(2)	167.0(1)
O(3)–Cu(1)–N(1)	97.6(1)	O(4)–Cu(1)–O(3)	89.1(1)
Hydrogen bonds			
	D–H	H...A	D...A
O(6)–H(19)...	0.564	2.313	2.874
O(8)–H(21)...	0.739	2.549	3.257
O(8)–H(21)...	0.739	2.631	3.191
O(10)–H(11)...	0.738	1.860	2.591
O(9)–H(16)...	0.752	2.025	2.774
O(7)–H(18)A...	0.664	2.109	2.769
O(8)–H(20)...	0.631	2.211	2.835

ⁱ $[x+1, y, z]$.

ⁱⁱ $[x+1/2, -y+3/2, z-1/2]$.

ⁱⁱⁱ $[-x+3/2, y-1/2, -z+1/2]$.

^{iv} $[x, y, z+1]$.

^v $[-x+1, -y+1, -z+2]$.

ligand (O...O distances vary from 2.591(1) to 3.257(1) Å) leading to the formation of a one-dimensional chain in the lattice. Details of the hydrogen bonding are listed in Table 3.

3.3. Crystal structure of $[\text{Cu}_2(\mu\text{-O}_2\text{CCH}_3)_4(\text{C}_7\text{H}_7\text{NO})_2]$ (**3**)

Compound **3** consists of centrosymmetric dinuclear units, similar to other copper acetate derivatives, in which four acetate groups are bridging two Cu atoms and 4-acetylpyridine as a ligand occupies the axial position, giving a CuO_4N chromophore. This structure is depicted in Fig. 4 together with the numbering scheme. Selected distances and angles are listed in Table 4. Each copper atom has a square-pyramidal geometry, with four oxygen atoms in a basal plane (Cu–O distances vary from 1.965(1) to 1.972(1) Å); the fifth coordination position is occupied by the nitrogen of a 4-acetylpyridine ligand with a distance of 2.198(1) Å. The CuO_4N chromophore

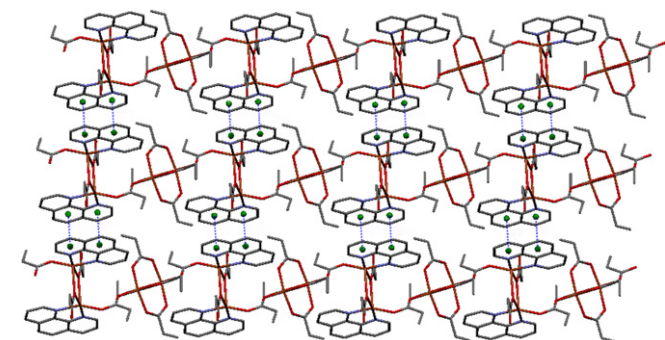


Fig. 2. 2D structure of compound **1** connected by face-to-face π - π interaction between pyridine rings of phen ligand. Hydrogen atoms and non-coordinating H_2O are omitted for clarity.

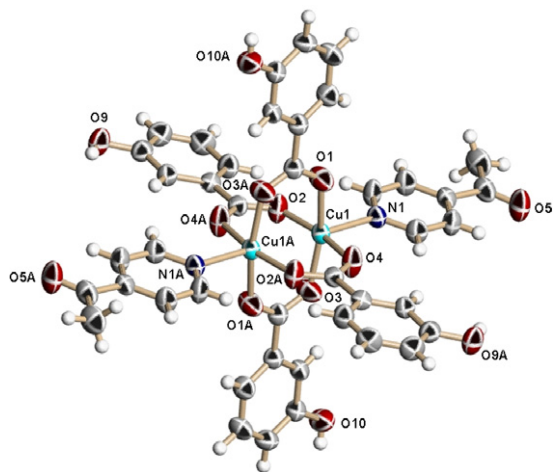


Fig. 3. Thermal ellipsoid (50% probability) plot of $[\text{Cu}_2(\mu\text{-O}_2\text{CC}_6\text{H}_4\text{OH})_4(\text{C}_7\text{H}_7\text{NO})_2] \cdot 6\text{H}_2\text{O}$ (**2**). The water molecules are omitted for clarity.

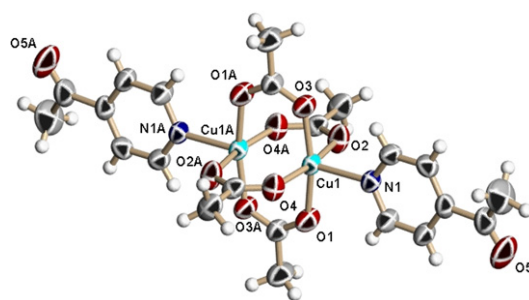


Fig. 4. Thermal ellipsoid (50% probability) plot of $[\text{Cu}_2(\mu\text{-O}_2\text{CCH}_3)_4(\text{C}_7\text{H}_7\text{NO})_2]$ (**3**).

Table 4

Selected bond lengths (Å) and angles (°) of $[\text{Cu}_2(\mu\text{-O}_2\text{CCH}_3)_4(\text{C}_7\text{H}_7\text{NO})_2]$ (**3**)

Cu(1)–N(1)	2.198(13)	Cu(1)–O(4)	1.968(12)
Cu(1)–O(1)	1.972(12)	Cu(1)–O(3)	1.965(12)
Cu(1)–O(2)	1.968(12)	Cu(1)–Cu(1)A	2.631(4)
O(1)–Cu(1)–N(1)	94.3(1)	O(3)–Cu(1)–O(2)	89.2(1)
O(2)–Cu(1)–N(1)	97.1(1)	O(3)–Cu(1)–O(4)	89.5(1)
O(2)–Cu(1)–O(1)	89.5(1)	O(4)–Cu(1)–N(1)	94.7(1)
O(3)–Cu(1)–N(1)	97.6(1)	O(4)–Cu(1)–O(1)	89.5(1)
O(3)–Cu(1)–O(1)	168.1(1)	O(4)–Cu(1)–O(2)	168.2(1)

is non-planar with tetrahedral twist of $18.15(1)^\circ$. The copper atoms are displaced by $0.001 \text{ \AA}$ from the basal planes toward the apical positions. The value of τ is 0.002 , corresponds to a square-pyramidal coordination [34]. Four acetate anions bridge two copper ions in a *syn,syn*- $\eta^1:\eta^1:\mu$ showing a paddle-wheel unit with a Cu...Cu distance of $2.631(4) \text{ \AA}$. The structural parameters of compound **3** compare well with some related compounds, as shown in Table 5.

3.4. EPR and magnetic properties

The EPR spectra of the compounds were recorded as a polycrystalline powder at RT and at 70 K (compound **2** also 120 K) from 0 to 800 mT at X-band frequency ($h\nu = 0.325 \text{ cm}^{-1}$). The EPR spectrum of compound **1** is rather complicated and consists at RT of a very broad and strong signal centered around 290 mT and a shoulder at 249 mT (see Fig. 5A). Furthermore weak signals are observed at about 15, 369, 469 and 532 mT, which can be assigned to $S = 1$ triplet signals [36,37]. The signal at 159 mT can be assigned to the forbidden half-field signal ($\Delta M_s = \pm 2$). At 70 K the signal decreases in intensity (see Fig. 5B), due to the depopulation of the triplet state and in this case at 325 mT the $S = 1/2$ resonance from a mononuclear impurity, which usually is present in dinuclear Cu(II) compounds, becomes visible. At RT this band is hidden under the strong resonance at 290 mT. The g values calculated from the EPR spectrum (considering the fact that the lines are broad and not resolved) is estimated as $g_{xy} = 2.06$ and $g_z = 2.25$, values considered normal for a Cu(II) signal.

As compounds **2** and **3** are almost isostructural, also the EPR spectra of both compounds are very similar as expected. The EPR spectrum of compound **2** is shown in Fig. 6 at RT, 120 and 70 K (the EPR spectrum of compound **3** is given as Supplementary material). The spectrum at RT (Fig. 6A) shows three bands at 23, 470 and 600 mT (that last band is only partly visible due to the limitations of the EPR magnetic field). These bands are typical for a triplet state of a copper(II) acetate hydrate type [11,24–27,36–39] with three resonance lines ($H_{z1}, H_{\perp}, H_{z2}$). At 120 K (Fig. 6B) the H_{z1} signal splits, due to hyperfine interaction of the unpaired electron within the dinuclear unit ($A = 6.2 \text{ mT}$). The small feature at around 320 mT is from a monomeric impurity, which is in most cases always present in dinuclear bulk material. At 70 K the triplet signal becomes very weak (Fig. 6C), and therefore the monomeric impurity at 320 mT appears as relatively very strong. This behaviour is consistent with the magnetic susceptibility of these compounds (see magnetism below). The same type of signals was observed for compound **3** (see Supplementary material). Similar spectra with the same type of bands are observed for the compounds $[\text{Cu}_2(\text{OOC}-$

$\text{C}_5\text{H}_{11})_4(\text{urea})_2]$ [11] and $\{[\text{Cu}_2(\beta\text{-alanine})_4(\text{H}_2\text{O})_2](\text{NO}_3)_4(\text{H}_2\text{O})_4\}$ [26]. For these compounds the zero-field splitting parameter D was calculated as being 0.34 cm^{-1} , so we can estimate that the value of D is also around 0.34 cm^{-1} for compound **2** and **3**.

The magnetic susceptibility of a powdered sample of compound **1** was measured from 2 to 320 K under a constant magnetic field of 0.1 T. The magnetic properties are depicted in Fig. 7 in the form of $\chi_M T$ versus T for four Cu(II) ions. At 320 K the $\chi_M T$ product has a value of $1.60 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$, which is just a little higher than the value expected for four uncorrelated Cu(II) ions ($1.40 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$ for $g = 2$) showing at best a very weak interaction between the metallic centers at 320 K. Upon cooling the $\chi_M T$ product gradually decreased as the temperature was lowered and reached a value of $1.05 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}$ at 75 K, stays constant till about 20 K, where it decreases till it reached a value of $0.98 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}$ at 2 K. This magnetic behaviour agrees with a overall strong antiferromagnetic interaction, at least for part of the Cu(II) ions.

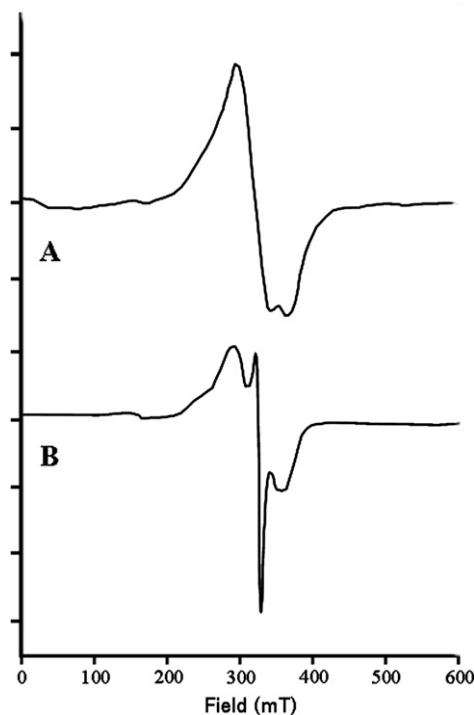


Fig. 5. X-band powder EPR spectrum of compound **1** at RT (A) and at 70 K (B).

Table 5
Structural data and magnetic properties for some relevant paddle-wheel copper(II) complexes^a

Complex ^b	Structure type	Chromophore	τ^c	Cu...Cu (Å)	J (cm^{-1})	Refs.
$[\{\text{Cu}_4(\text{phen})_2(\mu\text{-O}_2\text{CC}_6\text{H}_5)_8\} \cdot (\text{H}_2\text{O})_n]$ (1)	1D	CuO_5	0.005	2.623	−299.5	this work
$[\text{Cu}_2(\mu\text{-O}_2\text{CC}_6\text{H}_4\text{OH})_4(\text{C}_7\text{H}_7\text{NO})_2] \cdot 6\text{H}_2\text{O}$ (2)	dinuclear	CuO_4N	0.002	2.654	−278.5	this work
$[\text{Cu}_2(\mu\text{-O}_2\text{CCH}_3)_4(\text{C}_7\text{H}_7\text{NO})_2]$ (3)	dinuclear	CuO_4N	0.002	2.631	−287.0	this work
$[\text{Cu}_2(\mu\text{-O}_2\text{CH})_4(\text{DMF})_2]$ (4)	dinuclear	$\text{CuO}_4\text{O}'$	0	2.651	−470	[37e]
$[\text{Cu}_2(\mu\text{-O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2]$ (5)	dinuclear	$\text{CuO}_4\text{O}'$		2.620	−299	[24]
$[\text{Cu}_2(\mu\text{-O}_2\text{CCH}_3)_4(\text{NH}_3)_2]$ (6)	dinuclear	CuO_4N		2.620	−284	[24]
$[\text{Cu}_2(\mu\text{-O}_2\text{CCH}_3)_4(\text{MeNHpy})_2]$ (7)	dinuclear	CuO_4N	0.004	2.272	−285	[37d]
$[\text{Cu}_2(\mu\text{-O}_2\text{CCH}_3)_4(\text{NITpPy})_2]$ (8)	dinuclear	CuO_4N		2.622	−172	[12]
$[\text{Cu}_2(\mu\text{-O}_2\text{CC}(\text{CH}_3)_3)_4(\text{NITpPy})_2](\text{C}_6\text{H}_6)$ (9)	dinuclear	CuO_4N		2.614	−192	[12]
$[\text{Cu}_2(\mu\text{-O}_2\text{CC}_6\text{H}_5)_4(\text{H}_2\text{O})_2]$ (10)	dinuclear	$\text{CuO}_4\text{O}'$		2.575	−311	[33]
$[\text{Cu}_2(\mu\text{-DMB})_4(\text{H}_2\text{O})_2]$ (11)	dinuclear	$\text{CuO}_4\text{O}'$		2.619	−325	[25]
$[\text{Cu}_2(\mu\text{-DMB})_2(\mu\text{-O}_2\text{CCH}_3)_2(\text{H}_2\text{O})_2]$ (12)	dinuclear	$\text{CuO}_4\text{O}'$		2.597	−250	[25]

^a All with square-pyramidal geometry and an equatorial–equatorial configuration.

^b Abbreviation: MeNHpy, 2-methylaminopyridine; NITpPy, 4,4,5,5-tetramethyl-2-(4-pyridyl)-2-imidazoline- N^1 -oxyl N^3 -oxide and DMB, 2,6-dimethoxybenzoate.

^c τ : calculated from structural data.

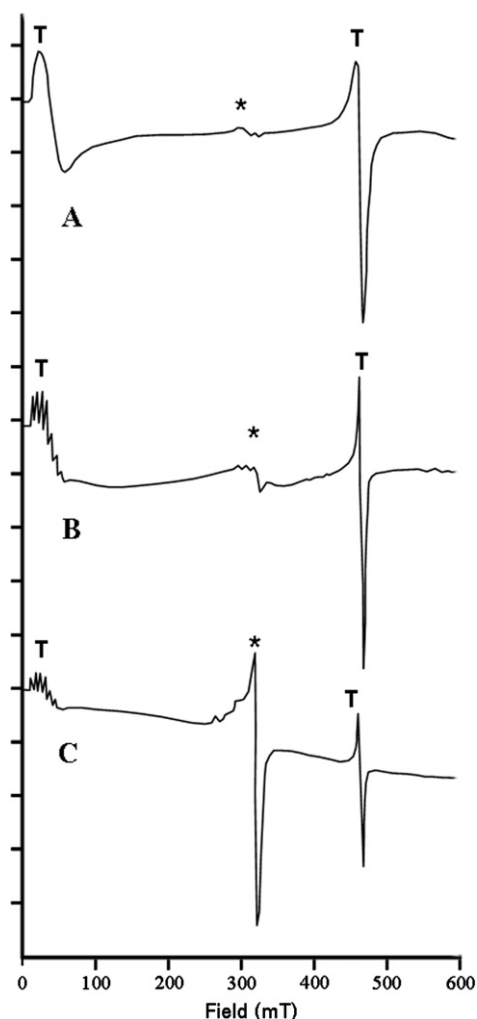


Fig. 6. X-band powder EPR spectrum of compound **2** at RT (A), at 120 K (B) and at 70 K (C). (*) = signal of the mononuclear signal; T = triplet signal).

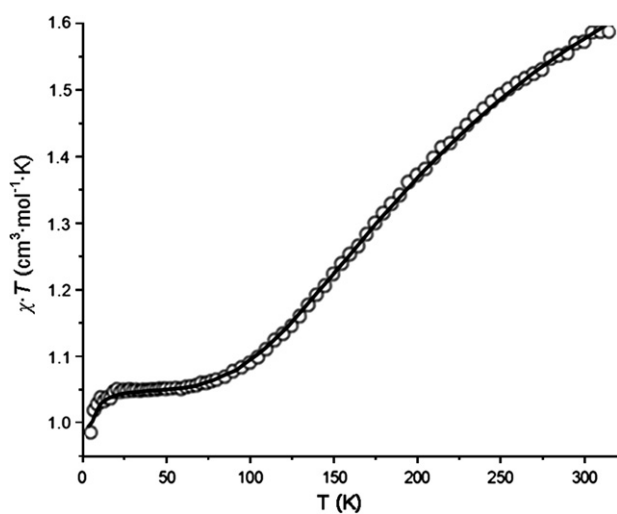


Fig. 7. A plot of the temperature dependence of $\chi_M T$ vs. T for compound **1** in the range 2–320 K.

parameter J , is negative for antiferromagnetic and positive for ferromagnetic interaction.

To simplify the expression for the susceptibility it was decided to use a combination of a two term contribution, i.e. $\chi = \chi_{Cu(1)} + \chi_{Cu(2)}$, in which

$$\chi_{Cu(1)} = 2Ng_1^2\beta^2[kT(3 + \exp(-J_1/kT))]^{-1} \quad \text{and}$$

$$\chi_{Cu(2)} = 2Ng_2^2\beta^2[kT(3 + \exp(-J_2/kT))]^{-1}$$

In these expressions J_1 and J_2 corresponds to the singlet–triplet energy gap for the two dinuclear sub-units in compound **1** (J_1 for the Cu(1)–Cu(1)A unit; J_2 for the Cu(2)–Cu(2)A unit), and N , g , β , k and T have their usual meanings [40]. The best-fit parameters, depicted in Fig. 7 as a solid line, were: $g_1 = 2.35$, $g_2 = 2.22$, $J_1 = -0.75 \text{ cm}^{-1}$, $J_2 = -299.5 \text{ cm}^{-1}$, with $R = 5 \times 10^{-5}$, the agreement factor defined as $\sum_i(\chi_{\text{calcd}} - \chi_{\text{obs}})^2 / \sum_i(\chi_{\text{obs}})^2$. In a first approximation the g values obtained by EPR have been used to properly fit the magnetic behavior, however, a poor result was achieved likely due to the fact that the formula of the magnetic susceptibility is of course based on a number of approximations.

The magnetic susceptibility of powdered samples of compounds **2** and **3** were measured from 5 to 350 K. As the two compounds are structural similar, also the magnetic properties are similar. The magnetic properties of the compounds are depicted in Fig. 8 for compound **2** and in Fig. S3 for compound **3** in the form of $\chi_M T$ versus T for two Cu(II) ions. At 350 K the $\chi_M T$ product of **2** has a value of $0.575 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ ($0.554 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ for **3**), which is below the spin-only value for two non-interacting Cu(II) ions ($0.75 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at RT). From 350 K the $\chi_M T$ product decreases gradually to a value of $0.014 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ for compound **2** at 50 K ($0.006 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ for **3**) and stays constant till 5 K. This magnetic behaviour agrees with a strong antiferromagnetic interaction.

The theoretical expression for the magnetic susceptibility for two interacting $S = 1/2$ centres, which is based on the general Hamiltonian [40] is: $H_{\text{ex}} = -JS_1S_2$, in which the exchange parameter J , is negative for antiferromagnetic and positive for ferromagnetic interaction. The magnetic data were fitted to the equation given in the literature [40] for dinuclear copper compounds:

$$\chi_M = (2Ng^2\beta^2)[kT - (2zJ'/(3 + \exp(-J/kT)))]^{-1} \times [3 + \exp(-J/kT)]^{-1}(1 - p) + \chi_p p,$$

in which N , g , β , k and T have their usual meanings [40]. The parameter p denotes the fraction of paramagnetic impurity in the sample and zJ' the interaction between neighbouring dinuclear identities. The fit was accomplished by minimisation of $R = (\chi_M T_{\text{calc}} - \chi_M T_{\text{obs}})^2$.

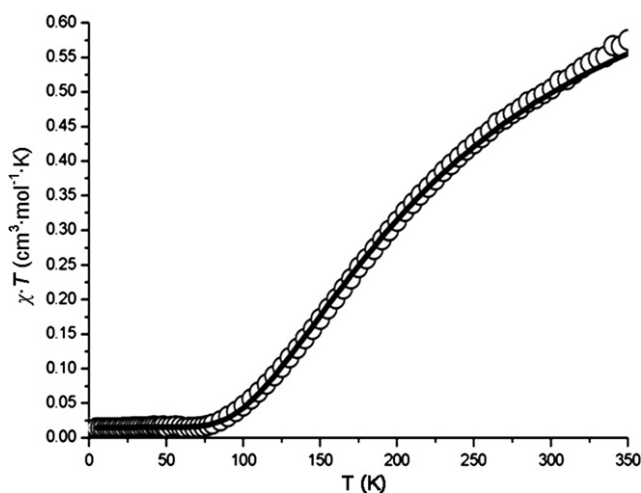


Fig. 8. A plot of the temperature dependence of $\chi_M T$ vs. T for compound **2**.

To explain the magnetic interaction of compound **1** the general Heisenberg Hamiltonian [40] $H_{\text{ex}} = -JS_1S_2$, in which the exchange

$T_{\text{obs}})^2/(\chi_{\text{M}}T_{\text{obs}})^2$ by a least-squares procedure. The best fit for compound **2**, depicted in Fig. 8 as a solid line, was obtained for $J = -278.5 \text{ cm}^{-1}$, $g = 2.15$, $zJ' = -26.3 \text{ cm}^{-1}$, $p = 0.02$, with a final R of 1.5×10^{-2} . The best fit for compound **3**, depicted in Fig. S3 as a solid line, was obtained for $J = -287.0 \text{ cm}^{-1}$, $g = 2.15$, $zJ' = -24.7 \text{ cm}^{-1}$, $p = 0.01$, with a final R of 1.5×10^{-2} . The R values appear a bit high, but can be ascribed to the fact that susceptibility measurements above 300 K are less accurate due to a reduced accuracy in temperature, in fact when only the temperature range of 5–280 K is considered the R -value is much better, i.e. 3×10^{-3} .

Recently, Rodríguez-Forde et al. [24] have reported a density functional study of the exchange coupling in carboxylato-bridged dinuclear copper(II) compounds. They compared the J values for several substituents in $[\text{Cu}_2(\mu\text{-RCOO})_4\text{L}_2]$ and concluded that the electron-withdrawing groups reduce the strength of the exchange coupling. Another factor is the Cu–O bridging bond in copper(II) carboxylate dinuclear units, which is considered to be quite important in the super-exchange mechanism; it is the basis for the super-exchange pathway of the Cu–O–C(R)–O–Cu fragments. When R is strongly σ -bonded to the carboxylate carbon, the strong coordination of the Cu–O bonds in the CuO_4 basal plane will become stronger, in order to maintain the electron neutrality over the whole molecule. Thus, the J value increases when the Cu–O bond length decreases. In addition the coupling constant is weakly dependent on the Cu···Cu distance. If the Cu···Cu distance increases, the overlap of the δ -bonding between the two Cu atoms decreases and the J value would be slightly lower.

The structure of compound **1** is compared with the most related carboxylato-bridged compound $[\text{Cu}_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)_4(\text{H}_2\text{O})_2]$ **10** ($J = -311 \text{ cm}^{-1}$) in Table 5. When water molecules in axial positions of compound **10** are replaced by propionate bridges (compound **1**), the average Cu–O distance is 1.959 Å and the Cu···Cu distance is 2.623 Å, which both are longer than those of the corresponding compound **10** (1.948 and 2.575 Å, respectively). Thus, the strong Cu–O bonds in the CuO_4 basal plane of **1** will become weaker than those of compound **10**; this may result in a decreased $-J$ value. In addition, a longer Cu···Cu distance would lead to a smaller $-J$ value (in this case -299 cm^{-1}). Nevertheless, it should be mentioned that the approximation used to obtain the Hamiltonian to calculate the J value is somewhat simplified, which can explain that the g values are somewhat higher than expected for Cu(1) and Cu(2). Indeed, it was observed that below 50 K the magnetism of compound **1** can be depicted as a unidimensional assembly of antiferromagnetically coupled $S = 1/2$ spins. Confirmation of this magnetic chain behaviour is seen from the linear $\ln \chi_{\text{M}}T$ versus T^{-1} curve in this temperature range (Fig. S4) [41]. In addition, the value of the dinuclear coupling via Cu(1)···Cu(1)A for compound **1** is expected to be small, as predicted by the theoretical calculation. The Cu(1)–O(1)–Cu(1)A pathway involve the d_{z^2} and $d_{x^2-y^2}$ orbital for Cu(1) and for Cu(1)A, therefore and because of the copper symmetry, the unpaired electron around copper(II) are described mainly by a magnetic orbital built from the $d_{x^2-y^2}$, confirming the theoretical result.

Complexes with the $\text{Cu}_2(\mu\text{-O}_2\text{CCH}_3)_4$ basic unit all have relatively high negative magnetic exchange coupling constants. For $[\text{Cu}_2(\mu\text{-O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2]$ **5** with a coupling constant J of -299 cm^{-1} , water molecules in axial positions are replaced by NH_3 for compound **6** [24], or MeNHpy for compound **7** [37] the coupling constant is slightly less negative of -284 and -285 cm^{-1} , respectively. It is indicating that the change of the axial ligand induces smaller variations in the coupling constant. Consequently, compound **3** with the axial 4-acetylpyridine ligands, the slightly decreased $-J$ value is expected. When the acetate groups in compound **3** are replaced by 3-hydroxybenzoate groups (compound **2**), which is a stronger electron-donating group, the increased $-J$ value is expected. According to that, it is reasonable

to imply that the 3-hydroxybenzoate bridge in **2** should provide a somewhat larger exchange coupling than the acetate bridge in compound **3**. However, the experimental results are almost the same ($J = -278.5$ and -287.0 cm^{-1} for complexes **2** and **3**, respectively) and lie almost in the experimental deviation for such large values.

4. Conclusion

We have presented the synthesis and magnetic study of three new polynuclear tetracarboxylato-bridged copper(II) complexes. Four carboxylate ligands bridge two copper ions in a *syn,syn*- $\eta^1:\eta^1:\mu$ showing the paddle-wheel unit. Compound **1** exhibits an one-dimensional chain structure build from two different dinuclear units. The adjacent chains are connected to form a 2D structure through the π – π interaction. Both compounds **2** and **3** are dinuclear with a paddle-wheel structure with 4-acetylpyridine at the apical position. The coordination geometry around each copper(II) ion is (distorted) square-pyramidal for all three compounds. All compounds show a strong antiferromagnetic interaction between the Cu(II) magnetic centres of the dinuclear units, with different magnitude of J values mainly depending on substituents of the carboxylate groups. The observed J values correspond nicely with values found in the literature for other carboxylato-bridged dinuclear units (see Table 5).

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Appendix A. Supplementary data

CCDC 674731, 674732 and 674733 contain the supplementary crystallographic data for **1**, **2** and **3**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.poly.2008.02.023](https://doi.org/10.1016/j.poly.2008.02.023).

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Two new oxalato-bridged dinuclear copper(II) complexes with di-2-pyridylamine: crystal structures, spectroscopic and magnetic properties

Sujittra Youngme ^{a,*}, Achareeya Cheansirisomboon ^a, Chanaiporn Danvirutai ^a,
Narongsak Chaichit ^b, Chaveng Pakawatchai ^c, Gerard A. van Albada ^d, Jan Reedijk ^d

^a Department of Chemistry, Faculty of Science, Khon Kaen University, Khon Kaen 40002, Thailand

^b Department of Physics, Faculty of Science and Technology, Thammasart University Rangsit, Pathumthani 12120, Thailand

^c Department of Chemistry, Faculty of Science, Prince of Songkla University, Hatyai, Songkla 90112, Thailand

^d Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden University, P.O. Box 9502, 2300 RA Leiden, The Netherlands

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Abstract

Two dinuclear Cu(II) complexes of formula $[\text{Cu}_2(\text{dpyam})_2(\mu\text{-C}_2\text{O}_4)(\text{Cl})_2]$ (**1**) and $[\text{Cu}_2(\text{dpyam})_2(\mu\text{-C}_2\text{O}_4)(\text{CF}_3\text{SO}_3)_2]$ (**2**) (dpyam = di-2-pyridylamine) have been synthesized and their spectroscopic and magnetic properties characterized. The structure of **1** is made up of the centrosymmetric dinuclear $[\{\text{Cu}(\text{dpyam})(\text{Cl})\}_2(\mu\text{-C}_2\text{O}_4)]$ units, while **2** contains chains of the dimeric $[\text{Cu}_2(\text{dpyam})_2(\mu\text{-C}_2\text{O}_4)(\text{CF}_3\text{SO}_3)_2]$ units linked by the triflate anions. The two copper atoms in both compounds are linked through a bis-didentate oxalato group leading to a metal–metal separation of 5.526(1) and 5.228(3) Å. The stereochemistry of the Cu(II) chromophore in **1** is approximately square pyramidal, while compound **2** displays an elongated octahedral Cu(II) environment. The IR, ligand field and EPR measurements are in agreement with the structures found. The magnetic susceptibility measurements, measured from 5 to 350 K, revealed a very strong antiferromagnetic interaction between the Cu(II) atoms with a singlet–triplet energy gap (J) of -274 and -342 cm^{-1} , for compounds **1** and **2**, respectively, in agreement with the coplanarity of the magnetic orbitals.

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Keywords: Copper(II); Crystal structure; μ -oxalato bridges; Magnetic properties; EPR

Polynuclear metal complexes are of considerable current interest in relation to the nature of magnetic exchange interactions between metal ions through bridging ligands [1–4], and the oxalate ion is well known to be an appropriate bridging ligand to design magnetic materials and many oxalato-bridged complexes have been prepared and characterized [5–22]. Eight different bridging modes have been observed for the oxalato group in the oxalato copper(II) complexes [21]. A number of dinuclear copper complexes with an oxalato bridge, generally formulated as $[(\text{NN})_{1\text{or}2}\text{Cu}(\mu\text{-C}_2\text{O}_4)\text{-Cu}(\text{NN})_{1\text{or}2}]\text{X}_n$, where NN is a chelating ligand, and X is a counter anion or a solvent molecule, have been structurally characterized [11–16] in the past decades.

In our previous reports the crystal structures, spectroscopic properties and magneto-structural correlation of the complexes $[\text{Cu}_2(\text{dpyam})_4(\mu\text{-C}_2\text{O}_4)](\text{ClO}_4)_2(\text{H}_2\text{O})_3$, $[\text{Cu}_2(\text{dpyam})_4(\mu\text{-C}_2\text{O}_4)](\text{BF}_4)_2(\text{H}_2\text{O})_3$, $[\text{Cu}_2(\text{dpyam})_2(\mu\text{-C}_2\text{O}_4)(\text{NO}_3)_2(\text{DMSO})_2]$ [21], $[\text{Cu}_2(\text{dpyam})_4(\mu\text{-C}_2\text{O}_4)](\text{PF}_6)_2(\text{H}_2\text{O})_2$ and $[\text{Cu}_2(\text{dpyam})_2(\mu\text{-C}_2\text{O}_4)(\text{NO}_3)_2((\text{CH}_3)_2\text{NCOH})_2]$ [22] have been described. The exchange interaction between the copper ions via the oxalate bridge is known to be strongly dependent on the geometry around the copper ions, depending on the nature of counter anions and the terminal ligands.

To extend the understanding of magneto-structural correlation of the oxalato-bridged dinuclear copper(II) complexes with other copper(II) stereochemistry and bridging configuration, further research was undertaken to synthesize new

* Corresponding author. Fax : +66 43 202373.

E-mail address: sujittra@kku.ac.th (S. Youngme).

oxalate-bridged compounds by modifying to other counter ions and compare the magnetic results. In this paper we report the synthesis [23] of two new μ -oxalato copper(II) complexes, $[\text{Cu}_2(\text{dpyam})_2(\mu\text{-C}_2\text{O}_4)(\text{Cl})_2]$ (**1**) and $[\text{Cu}_2(\text{dpyam})_2(\mu\text{-C}_2\text{O}_4)(\text{CF}_3\text{SO}_3)_2]_n$ (**2**), together with the IR-spectroscopic and magnetic analysis.

The molecular structure [24] of compound **1** consists of centrosymmetric dinuclear $[\text{Cu}_2(\text{dpyam})_2(\mu\text{-C}_2\text{O}_4)(\text{Cl})_2]$ units. A picture of the dinuclear structure together with the labeling scheme is shown in Fig. 1. Two copper atoms are linked through a bis-didentate oxalato molecule with a Cu–Cu separation of 5.256(1) Å. The coordination stereochemistry of the $\text{CuN}_2\text{O}_2\text{Cl}$ chromophore is distorted square pyramidal with a τ value = 0.15 ($\tau = 0$ for square pyramidal and $\tau = 1$ for trigonal bipyramidal geometry) [25]. The basal coordination positions are occupied by two oxalato oxygen atoms, O(1) and O(2), and two nitrogen atoms of the dpyam ligand N(1) and N(2). The Cu–N and Cu–O bond distances range from 1.987(4) to 2.025(1) Å. The apical position is occupied by the chloride ion at a larger distance (Cu–Cl = 2.492(1) Å). The four basal atoms are coplanar showing a slight but significant tetrahedral distortion with tetrahedral twist between CuN_2 and CuO_2 planes of 18.8(4)°. The copper atom is 0.22 Å out of that plane toward the apex. The Cu–Cl distances are in the range observed for the copper(II) compounds having Cl at the axial side [26]. The Cu–O(oxalato) distances and the O–Cu–O angles in the five-membered rings of the bis-didentate oxalato molecule are close to those reported for other oxalato bridged Cu(II) dinuclear complexes [7–10].

The lattice structure is stabilized by hydrogen bonding between the amine-N and the Cl (N–Cl distances 3.230(6) Å).

The structure [24] of compound **2** consists of centrosymmetric $[\text{Cu}_2(\text{dpyam})_2(\mu\text{-C}_2\text{O}_4)(\text{CF}_3\text{SO}_3)_2]$ units. This unit is depicted in Fig. 2 together with the numbering scheme. The

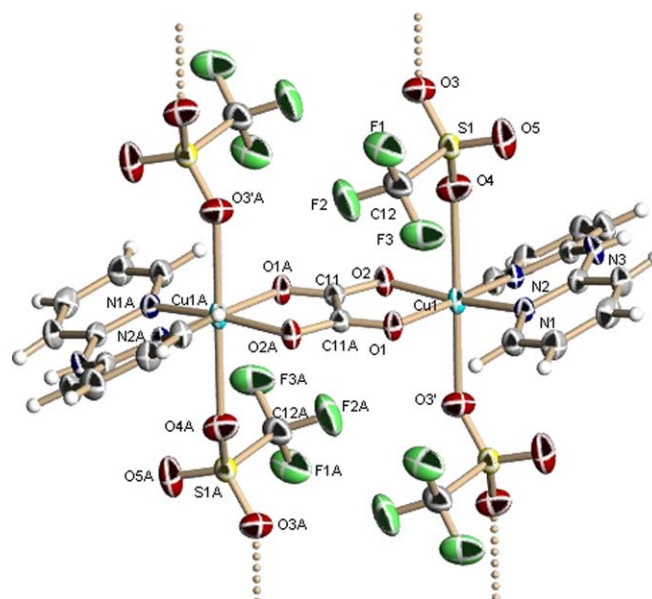


Fig. 2. ORTEP 50% probability plot of the cation in $[\text{Cu}_2(\text{dpyam})_2(\mu\text{-C}_2\text{O}_4)(\text{CF}_3\text{SO}_3)_2]$ (**2**). Atoms with an “A” are generated by a mirror plane. Selected bond lengths (Å) and angles (°): Cu(1)–N(1) 1.975(1), Cu(1)–N(2) 1.971(1), Cu(1)–O(1) 1.986(1), Cu(1)–O(2) 2.001(1), Cu(1)–O(3) 2.443(1), Cu(1)–O(4) 2.596(1), Cu(1)–Cu(1A) 5.228(3) and O(1)–Cu(1)–O(2) 82.9(1), N(1)–Cu(1)–N(2) 91.8(2), O(1)–Cu(1)–N(1) 93.7(1), O(1)–Cu(1)–N(2) 174.2(1), O(2)–Cu(1)–N(1) 172.0(1), O(2)–Cu(1)–N(2) 91.8(1), O(3)–Cu(1)–N(1) 97.3(4), O(3)–Cu(1)–N(2) 88.6(1), O(3)–Cu(1)–O(1) 89.1(1), O(3)–Cu(1)–O(2) 89.9(1), O(4)–Cu(1)–N(1) 84.1(1), O(4)–Cu(1)–N(2) 90.4(1), O(4)–Cu(1)–O(1) 91.8 (1), O(4)–Cu(1)–O(2) 88.7(2), O(3)–Cu(1)–O(4) 178.3(1). $A = -x + 1, -y + 1, -z + 1$.

geometry around the copper atom can be considered as an elongated tetragonal octahedral environment with the equatorial plane formed by two nitrogen atoms of dpyam ligand and two oxygen atoms of the oxalate bridge (Cu–N/O distances vary from 1.971(1) to 2.001(1) Å). These basal planes are linked into an infinite chain by the didentate bridging trifluoromethanesulfonate group. The two donor atoms from the non-symmetrically bridging trifluoromethanesulfonate groups occupy the axial positions above and below the CuN_2O_2 planes, with a Cu–O distances of 2.443(1) and 2.596(1) Å, yielding a $\text{CuN}_2\text{O}_2\text{O}'\text{O}''$ chromophore. Both copper atoms are linked through an oxalate bridge, with a Cu–Cu distance of 5.228(3) Å. The axial O(3)–Cu–O(4) angle is 178.3(1)° and the four donor atoms on the equatorial plane are not perfectly planar, showing a small tetrahedral distortion, with a dihedral angle of 7.6(1)° formed between the O–Cu–O and N–Cu–N planes.

The lattice structure is stabilized by hydrogen bonding between the amine-N and the O(CF_3SO_3) (N–O distances 2.846(1) Å).

The IR spectra of both compounds show characteristic bands of the oxalate bridging ligand [13–15]: $\nu_{\text{asym}(\text{C}-\text{O})}$ at 1669s, $\nu_{\text{sym}(\text{C}-\text{O})}$ at 1375m and $\delta_{(\text{O}-\text{C}-\text{O})}$ at 843m cm^{-1} for compound **1**; $\nu_{\text{asym}(\text{C}-\text{O})}$ at 1664s, $\nu_{\text{sym}(\text{C}-\text{O})}$ at 1370m and $\delta_{(\text{O}-\text{C}-\text{O})}$ at 845m cm^{-1} for compound **2**. The vibrations of the triflate anion, which are known to be very sensitive

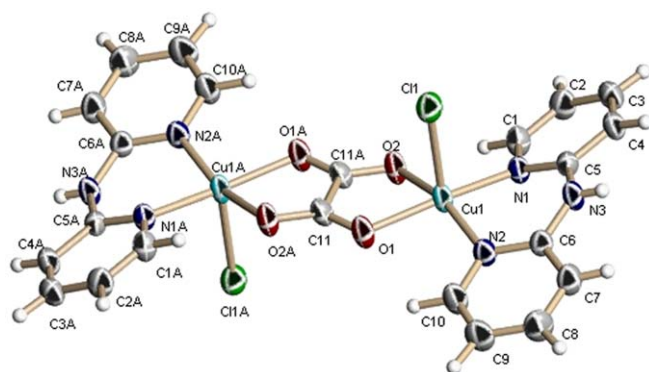


Fig. 1. ORTEP 50% probability plot of the cation in $[\text{Cu}_2(\text{dpyam})_2(\mu\text{-C}_2\text{O}_4)(\text{Cl})_2]$ (**1**). Atoms with an “A” are generated by a mirror plane. Selected bond lengths (Å) and angles (°): Cu(1)–N(1) 1.987(4), Cu(1)–N(2) 1.995(1), Cu(1)–O(1) 2.004(1), Cu(1)–O(2) 2.025(1), Cu(1)–Cl(1) 2.492(6), Cu(1)–Cu(1A) 5.256(1) and O(1)–Cu(1)–O(2) 81.8(4), N(1)–Cu(1)–N(2) 92.0(1), O(1)–Cu(1)–N(1) 170.8(1), O(1)–Cu(1)–N(2) 91.9(1), O(2)–Cu(1)–N(1) 92.0(1), O(2)–Cu(1)–N(2) 161.7(4), Cl(1)–Cu(1)–N(1) 93.8(1), Cl(1)–Cu(1)–N(2) 101.6(5), Cl(1)–Cu(1)–O(1) 93.6(1), Cl(1)–Cu(1)–O(2) 95.9(1). $A = -x, -y + 1, -z + 2$.

to small changes in the coordination are observed as strong bands for compound **2** at 1260, 1248 ($\nu_{\text{as}}\text{S-O}$), 1227 ($\nu_{\text{s}}\text{C-F}$), 1160 ($\nu_{\text{as}}\text{C-F}$) and 1033 cm^{-1} ($\nu_{\text{s}}\text{S-O}$). All these bands are in agreement with the literature for didentate and/or H-bonded triflate absorptions [27–30].

The diffuse reflectance spectrum of **1** displays a broad asymmetric band at 13770 cm^{-1} which is typical for the slightly distorted square pyramidal environment. While, the diffuse reflectance spectrum of **2** consists of a broad peak centered at 15770 cm^{-1} , corresponding to an elongated octahedral geometry. These observations suggest the assignment of the band as the $d_{xz}, d_{yz}, d_{xy}, d_{z^2} \rightarrow d_{x^2-y^2}$ transition for both compounds [31,32].

The X-band EPR spectra measured on polycrystalline samples displays, for both compounds a very broad asymmetric absorption with a centre at approx. $g = 2.08 - 2.11$, at room temperature. No half-field signal was observed at RT. Both compounds were also measured as solids at 77 K, in which cases the signal appears better resolved with $g_{\perp} = 2.05$, $g_{\parallel} = 2.25$ and a weak $A_{\parallel} = 15.5 \pm 5$ mT for compound **1**, which is typical for a $d_{x^2-y^2}$ spectrum, which is attributed to the monomeric impurity in the bulk compound. A weak absorption at 345 mT was clearly observed which is one of the absorptions of the triplet $S = 1$ spectrum of the dinuclear identity. The other triplet bands are broad and obscured by the monomeric impurity signal. A very weak half-field signal was observed at 165 mT. Compound **2** shows at 77 K a typical $S = 1$ triplet spectrum with strong resonance absorptions at 285, 310 and 338 mT. From these absorptions an axial zero-field splitting factor (D) of about 0.05 cm^{-1} could be estimated [33]. The absorption at 323 mT is most likely from the monomeric impurity. A half-field signal, expected for an $S = 1$ system, could not be detected with our equipment.

The magnetic susceptibility of the powdered compounds were measured from 5 to 350 K. The temperature dependence of the molar magnetic susceptibility $\chi_M \cdot T$ of compound **1** is shown in Fig. 3 and for compound **2** in Fig. 4, down to 5 K. At 350 K, $\chi_M \cdot T$ is equal to 0.57 $\text{cm}^3 \text{mol}^{-1}$ in both compounds and decreases when cooling down and reaches almost zero at about 50 K and stays constant till 5 K. This behaviour is typical for a strong antiferromagnetically coupled Cu(II) dinuclear compound. To reproduce this behaviour the theoretical expression of the magnetic susceptibility of spin = 1/2, arising from the Hamiltonian $H = -JS_1 \cdot S_2$, has been considered, including possible intermolecular interactions, in the molecular-field approximation [4, p. 132]:

$$\chi_m = (2Ng^2\beta^2)[kT - (2zJ'/(3 + \exp(-J/kT)))]^{-1} \\ [3 + \exp(-J/kT)]^{-1}(1 - p) + \chi_p p$$

where J is the singlet–triplet energy gap (negative value for antiferromagnetic and positive value for ferromagnetic interaction) and N , g , β , k and T have their usual meanings. The parameter p denotes the molar fraction of paramag-

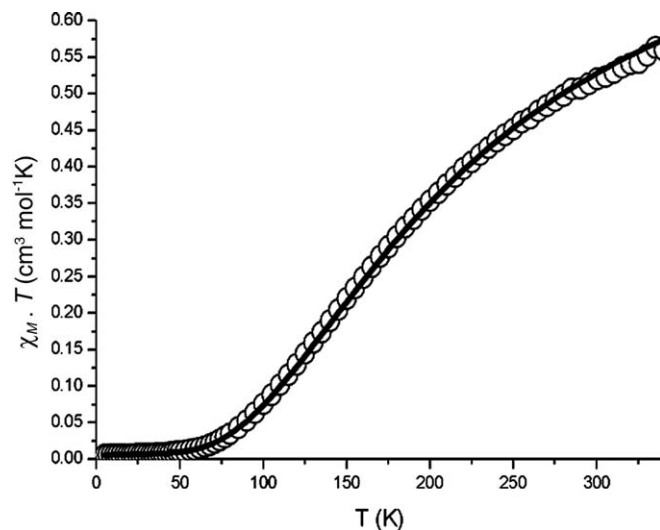


Fig. 3. Temperature dependence of $\chi_M \cdot T$ vs. T for compound (**1**). The solid lines represent the calculated curve (see text).

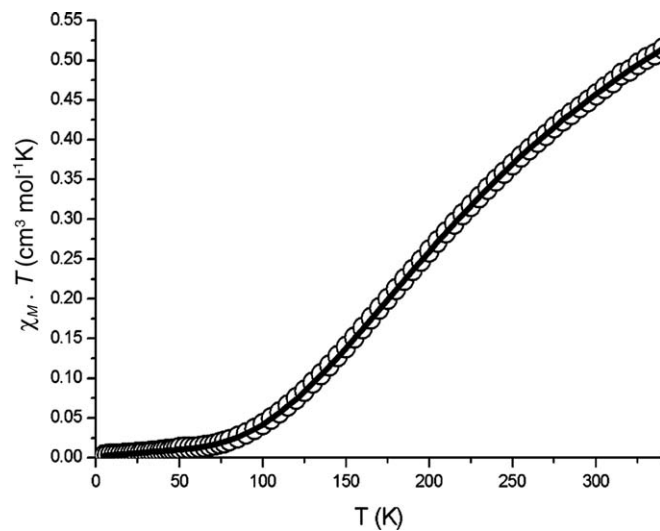


Fig. 4. Temperature dependence of $\chi_M \cdot T$ vs. T for compound (**2**). The solid lines represent the calculated curve (see text).

netic impurity in the sample [4, p. 107] and zJ' the interaction between neighbouring dinuclear identities.

Minimisation of the expression $R = \sum(\chi_{\text{obs}} - \chi_{\text{calc}})^2 / \sum \chi_{\text{obs}}^2$, resulted in the best-fit parameters $J = -274.3 \text{ cm}^{-1}$, $g = 2.13$ and $zJ' = 0.06$ and $p = 0.01$ with $R = 8.0 \times 10^{-2}$ for compound **1** (see solid line Fig. 3) and $J = -342.5 \text{ cm}^{-1}$, $g = 2.10$ and $zJ' = 0.02$ and $p = 0$ with $R = 2.8 \times 10^{-2}$ for compound **2** (see solid line in Fig. 4), which confirms the strong antiferromagnetic type of the intramolecular interaction.

These results are comparable with some other oxalate-bridged Cu(II) dinuclear compounds in the literatures, like the compounds $[\text{Cu}_2(\text{phen})_2(\mu\text{-C}_2\text{O}_4)(\text{NO}_3)_2]$ [19], $[\text{Cu}_2(\text{d-pyam})_2(\mu\text{-C}_2\text{O}_4)(\text{NO}_3)_2(\text{CH}_3)_2\text{SO})_2]$ [21], $[\text{Cu}_2(\text{bpy})_2(\text{C}_2\text{O}_4)(\text{NO}_3)_2(\text{H}_2\text{O})_2]$ [12], $[\text{Cu}_2(N,N\text{-diethylethane-1,2-diamine})_2(\mu\text{-C}_2\text{O}_4)(\text{ClO}_4)_2(\text{H}_2\text{O})_2]$ [15], with a J of -330 , -305 , -382 and -300 cm^{-1} , respectively.

In conclusion we can observe that compound **2** has an elongated tetragonal octahedral geometry with a nearly symmetric oxalato bridge and display a strong antiferromagnetic interaction. The structure and structural distortions of compound **1** are very comparable to that of compound **2**. This strong interaction arises from the non-orthogonality between the $d_{x^2-y^2}$ magnetic orbitals and the orbital of the oxalate group in a distorted square pyramidal geometry; the unpaired electrons are located in $d_{x^2-y^2}$ orbitals. Therefore a strong antiferromagnetic interaction is expected, which is confirmed by the magnetic susceptibility measurements.

Supplementary material

IR spectra were recorded with a Biorad FTS-7/PC FTIR spectrophotometer as KBr pellets and/or as nujol mulls in the 4000–450 cm^{-1} spectral range. Solid-state (diffuse reflectance) electronic spectra were recorded as polycrystalline samples on a Perkin–Elmer Lambda2S spectrophotometer over the range 8000–18,000 cm^{-1} . X-band powder EPR spectra were obtained on a Jeol RE2x electron spin resonance spectrometer using DPPH ($g = 2.0036$) as a standard. Magnetic susceptibility measurements (5–350 K) were carried out using a Quantum Design MPMS-5 S SQUID magnetometer (measurements carried out at 1000 Gauss). Data were corrected for magnetization of the sample holder and for diamagnetic contributions, which were estimated from the Pascal constants.

Acknowledgements

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- [23] Syntheses: $[\text{Cu}(\text{dpyam})_2(\mu\text{-C}_2\text{O}_4)(\text{Cl})_2]$ (**1**): Compound **1** was prepared by adding a hot dimethylformamide solution (20 ml) of dpyam (0.34 g, 2.0 mmol) to hot aqueous solution (40 ml) of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.34 g, 1.0 mmol). The mixture was heated at ca. 100 °C with continuous stirring for 15 min, then the solid $\text{H}_2\text{C}_2\text{O}_4$ (0.06 g, 0.5 mmol) was added. After standing at room temperature for a week, green needle-like crystals of $[\text{Cu}_2(\text{dpyam})_2(\mu\text{-C}_2\text{O}_4)(\text{Cl})_2]$ (**1**) were obtained. Yield ca. 75%. Anal. Calc. for $\text{C}_{22}\text{H}_{18}\text{N}_6\text{Cu}_2\text{O}_4\text{Cl}_2$: C, 42.05; H, 2.89; N, 13.73. Found: C, 42.69; H, 2.60; N, 13.61%. $[\text{Cu}_2(\text{dpyam})_2(\mu\text{-C}_2\text{O}_4)(\text{CF}_3\text{SO}_3)_2]$ (**2**): A solution containing dpyam (0.17 g, 1.0 mmol) in mixing methanol/acetonitrile (20/20 ml) and $\text{Na}_2\text{C}_2\text{O}_4$ (0.07 g, 0.5 mmol) in water (5 ml) was added to a solution of $\text{Cu}(\text{CF}_3\text{SO}_3)_2$ (0.36 g, 1.0 mmol) in methanol (30 ml). The resulting green solution was allowed to evaporate at room temperature. After one week, green crystals of $[\text{Cu}_2(\text{dpyam})_2(\mu\text{-C}_2\text{O}_4)(\text{CF}_3\text{SO}_3)_2]$ (**2**) were obtained which were filtered off, washed with water and were dried in air. Yield ca. 65%. Anal. Calc. for $\text{C}_{24}\text{H}_{18}\text{N}_6\text{Cu}_2\text{O}_{10}\text{S}_2\text{F}_6$: C, 33.69; H, 2.12; N, 9.82. Found: C, 34.12; H, 2.42; N, 10.05 %.
- [24] *Crystal data for compound 1*: $\text{C}_{22}\text{H}_{18}\text{N}_6\text{Cu}_2\text{O}_4\text{Cl}_2$ ($M_w = 628.42$), Triclinic, $P\bar{1}$, $a = 7.4122(6)$ Å, $b = 8.6586(7)$ Å, $c = 9.8002(8)$ Å, $\alpha = 87.9000(10)^\circ$, $\beta = 72.0220(10)^\circ$, $\gamma = 71.8450(10)^\circ$, $V = 567.24(8)$ Å³, $T = 293(2)$ K, $Z = 1$, $D_c = 1.840$ Mg/m³, $\mu = 2.156$ mm⁻¹, $F(000) = 316$, 6459 reflections measured ($2.48 < 2\theta < 27.48^\circ$), 2613 unique ($R_{\text{int}} = 0.0208$), $R_1 = 0.0304$, $wR_2 = 0.0821$. *Crystal data for compound 2*: $\text{C}_{24}\text{H}_{18}\text{N}_6\text{Cu}_2\text{O}_{10}\text{S}_2\text{F}_6$ ($M_w = 855.64$), Monoclinic, $P2(1)/c$, $a = 9.6684(7)$ Å, $b = 7.3752(5)$ Å, $c = 20.9665(14)$ Å, $\beta = 102.3550(10)^\circ$, $V = 1460.42(17)$ Å³, $T = 293(2)$ K, $Z = 4$, $D_c = 1.946$ Mg/m³, $\mu = 1.707$ mm⁻¹, $F(000) = 856$, 12,365 reflections measured ($1.99 < 2\theta < 28.25^\circ$), 3505 unique ($R_{\text{int}} = 0.0230$), $R_1 = 0.0367$, $wR_2 = 0.0863$. CCDC Nos. 603978–603979 for **1** and **2**, respectively. See <http://www.ccdc.cam.ac.uk> for crystallographic data in CIF format.
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Polynuclear copper(II) carboxylates with 2,2'-bipyridine or 1,10-phenanthroline: Synthesis, characterization, X-ray structures and magnetism

Jaurusup Boonmak^a, Sujittra Youngme^{a,*}, Thidarat Chotkhun^a, Chainarong Engkagul^b, Narongsak Chaichit^b, Gerard A. van Albada^c, Jan Reedijk^c

^a Department of Chemistry and Center of Excellence for Innovation in Chemistry, Faculty of Science, Khon Kaen University, Khon Kaen 40002, Thailand

^b Department of Physics, Faculty of Science and Technology, Thammasat University Rangsit, Pathumthani 12121, Thailand

^c Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden University, P.O. Box 9502, 2300 RA Leiden, The Netherlands

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ABSTRACT

[Cu₂(phen)₂(μ-O₂CH)₂(O₂CH)₂]_n (**1**) and [Cu₆(bpy)₆(μ-O₂CC₂H₅)₇(H₂O)₂](PF₆)₅ · 2H₂O (**2**) were synthesized and characterized by elemental analyses, electronic and EPR spectra and X-ray structure analyses. Compound **1** consists of four independent polymeric chains of dinuclear [Cu₂(phen)₂(μ-O₂CH)₂(O₂CH)₂] subunits with the asymmetric bidentate bridging formate groups linking Cu atoms in an *anti-anti* configuration. All Cu(II) ions are in a distorted square-pyramidal geometry. The hexanuclear copper(II) molecule of compound **2** is constructed from three different dinuclear units connected to each other via two *syn-anti*-μ₃-η¹;η² carboxylato bridges. All copper(II) ions are in the distorted square-pyramidal geometry. Two terminal dinuclear units are similar in structure in which both Cu(II) ions are doubly bridged by the *syn-syn* carboxylato anions, while those of the central dinuclear entity are triply bridged by two μ₃-η¹;η² carboxylato anions via monoatomic bridging fashion and one *syn-syn* carboxylato anion. The magnetic susceptibility (5–350 K) of compound **2** was measured and agree with a weak anti-ferromagnetic interaction between the Cu(II) centers.

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The chemistry of copper carboxylates has been extensively investigated since many years due to their relevance for certain copper-containing enzymes [1–7] and has their interesting magneto-structural correlations which focus on the effects of the structural and chemical factors to control the exchange coupling interactions between paramagnetic centers through mono- and multiatomic bridges [7–11]. Furthermore, the diverse coordination modes of carboxylato anions largely contribute to the formation of various structural types for copper carboxylates, such as mononuclear, dinuclear and polynuclear structural units [1,11–13]. Carboxylato anions can bind toward metal cations in various ways: monodentate, chelate, monoatomic bridges, bridging bidentate (μ-η¹;η¹), bridging tridentate (μ₃-η¹;η²), as well as less common multiple bridges [13–16], as shown in Scheme 1.

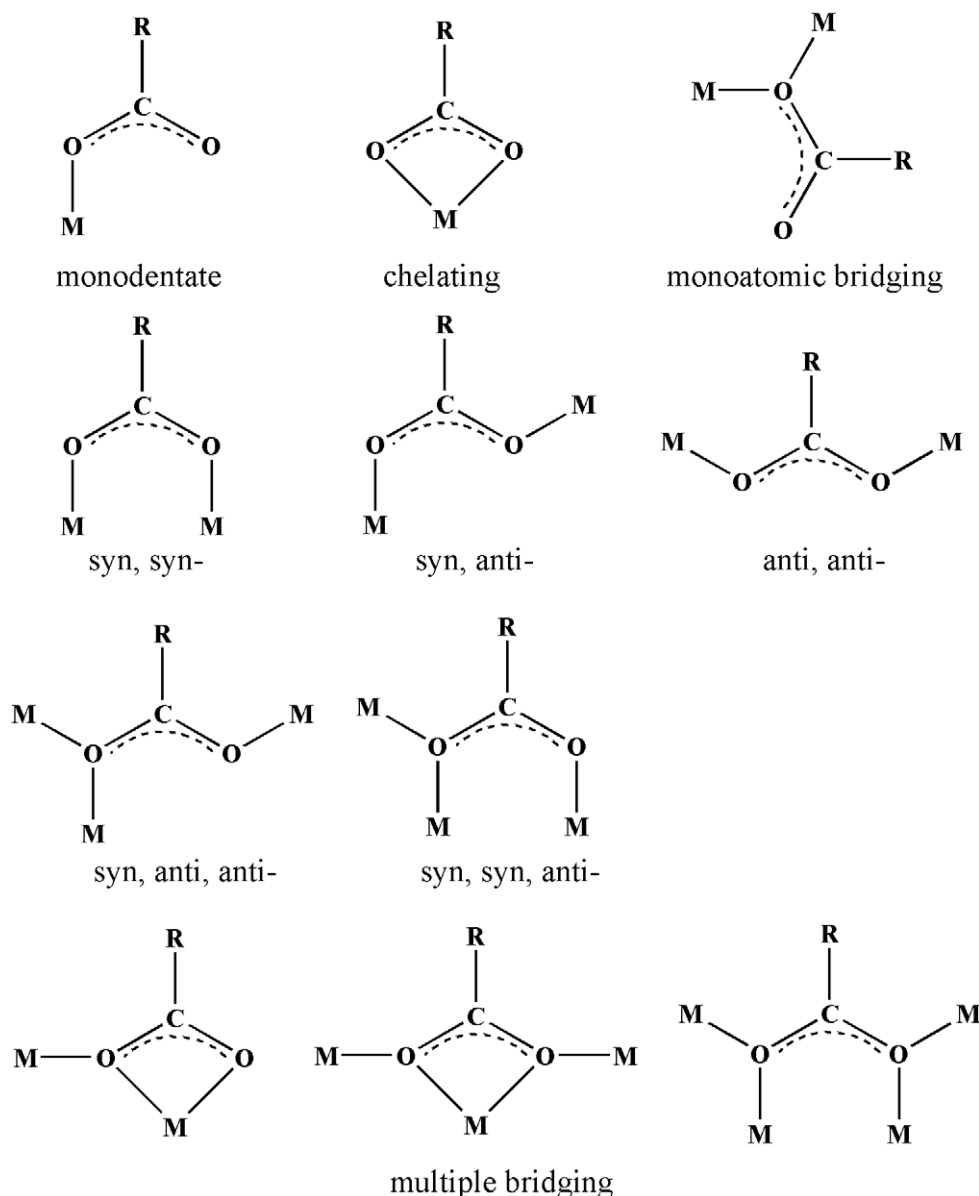
The formate (HCO₂[−]) anion which is the simplest carboxylate with the smallest steric effect, has been used as an effective bridging ligand to form many multidimensional coordination polymers [13,17–19]. Strikingly, it has attracted little attention contrary to acetate (CH₃CO₂[−]), which possesses potentially biscoordinating oxygen atoms tending to favor the formation of transition metal-dimer motifs, i.e. *paddle-wheel*-type complexes such as found in Cu₂(CH₃CO₂)₄ · 2H₂O and in related compounds [20–22]. The higher steri-

cally crowded carboxylato, propionato (CH₃CH₂CO₂[−]) anion, generally shows the same coordination behavior as acetates; however, its tendency to bind between metals is lower due to the higher steric effect [20]. Both 2,2'-bipyridine (bpy) and 1,10-phenanthroline (phen) are examples of alpha-diimine chelating bidentates, which play a key role in these studies, and because of their rigidity and planarity these efficiently provide π-π stacking interactions among their aromatic moieties, which are either intra- or intermolecular. This feature potentially contributes the stability of polynuclear structures as well as the formation of extended supramolecular structures with bridging anionic ligands [10,23–26]. Herein, we report the syntheses [27], crystal structures, and spectroscopic properties of two novel compounds, i.e. a polynuclear [Cu₂(phen)₂(μ-O₂CH)(O₂CH)₃]_n (**1**) and a unique hexanuclear [Cu₆(bpy)₆(μ-O₂CC₂H₅)₇(H₂O)₂](PF₆)₅ · 2H₂O (**2**) along with the magnetic behavior of the latter compound.

The crystal structure [28] of **1** consists of four independent polymeric chains constructed from four similar crystallographically independent dinuclear [Cu₂(phen)₂(μ-O₂CH)₂(O₂CH)₂] subunits (Fig. 1). For each chain, the dinuclear subunits are linked by an asymmetric bidentate bridging formate group in an *anti-anti* configuration, resulting in a polymeric zigzag chain structure. Within each dinuclear subunit, both Cu(II) ions are also bridged by a formate group in an *anti-anti* arrangement. Each Cu atom exhibits a distorted square-pyramidal CuN₂O₃ chromophore. The

* Corresponding author. Fax: +66 43 202 373.

E-mail address: sujittra@kku.ac.th (S. Youngme).



Scheme 1.

coordination around all copper atoms consists of two nitrogen atoms of the phen ligand with Cu–N distances ranging from 2.020(6) to 2.045(6) Å and two oxygen atoms of two different formate ligands, a monodentate group and a bidentate bridging group, with Cu–O distances ranging from 1.947(5) to 1.964(6) Å, located in the basal plane. The axial position of each Cu atom is occupied by an oxygen atom from another bidentate bridging formate group with elongated Cu–O distances ranging from 2.221(6) to 2.252(5) Å. The Cu···Cu distances are varied between 5.703(1) and 5.769(1) Å, which are shorter by 0.2 Å than the corresponding one in the similarly *anti-anti* formate group bridging between the Cu centers [29]. The phen ligands of each polymeric zigzag chain are assembled by the aromatic neighbors of the adjacent chains extended to form two-dimensional layers. The interplanar distances between the phen rings are in a range of 3.694–3.820 Å, indicating definite π – π stacking interaction in a parallel-displaced arrangement [30], as shown in Fig. 2.

Interestingly, although four independent infinite-zigzag polymeric chains are arranged in the same configuration; however, their arrangement directions are distinct in the packing motif. Both

a and *d* chains extend along the crystallographic *a* axis in face to face arrangements (Fig. S1), which are inserted by other two (*b*, *c*) zigzag chains similarly outspreading along the crystallographic *b*-axis (Fig. S2). Consequently, the one-dimensional chains of *a* and *d* are stacked via π – π interaction along the crystallographic *a*-axis, leading to the two-dimensional *a*- and *d*-type sheets. Similarly, extension occurs for the *b* and *c* chains, along the crystallographic *b*-axis, resulting the two-dimensional *b*- and *c*-type sheets, which are inserted between *a*- and *d*-type sheets (Fig. S3). Each sheet is assembled together by weak C–H···O hydrogen bonds, resulting from the –CH groups on the aromatic rings of phen ligands weakly interacting to the uncoordinated formate O atoms for *a*–*b* and *c*–*d* double sheets, and weakly interacting to bridging formate O atoms between the opposed sides of *b*- and *c*-type sheets. Because of these structural features, the supramolecular assembly of the 2-D layers is achieved via weak C–H···O hydrogen bonds in an alternating *abcdabcd* pattern (Fig. S4).

The crystal structure [28] of the hexanuclear copper(II) compound **2** is shown in Fig. 3. It is constructed from three different dinuclear units connecting to each other via the carboxylato

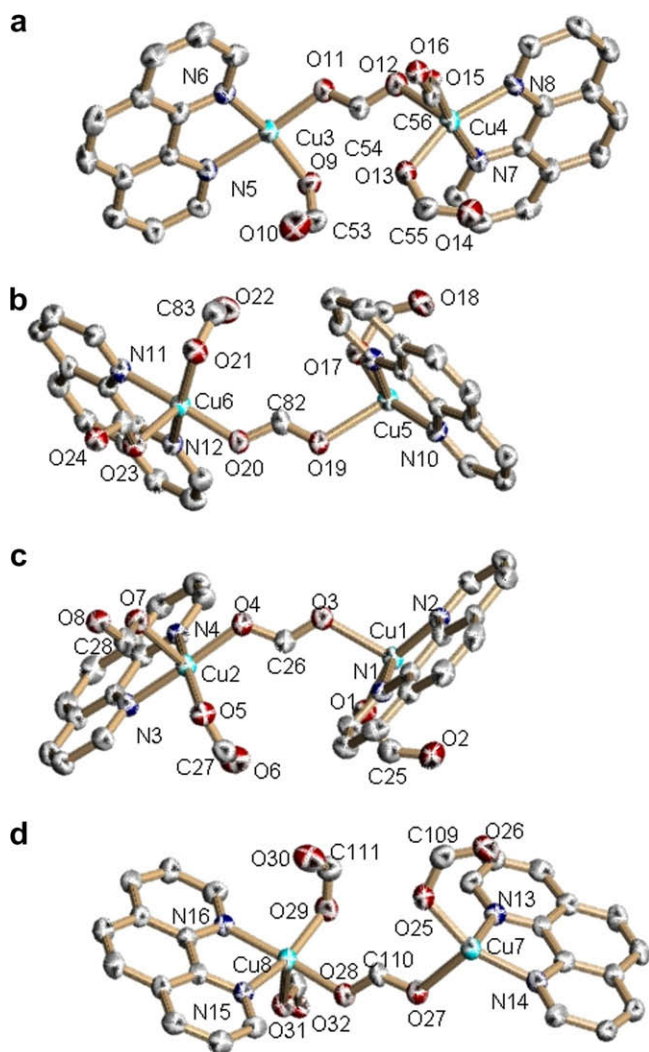


Fig. 1. The crystal structure of four independent dinuclear subunits (a, b, c, d) in the polymeric chains of **1**. All hydrogen atoms are omitted for clarity. Selected bond lengths and angles are given in Supplementary material (Table S1).

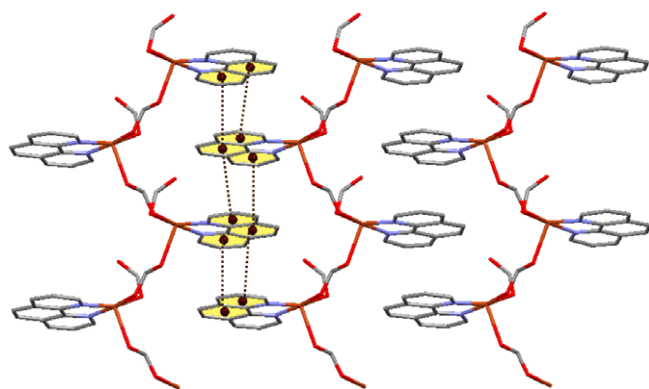


Fig. 2. Fragment of the packing in **1**, highlighting the π - π interactions, generating the two-dimensional layer for each independent chain.

groups in a *syn-anti* arrangement and an axial-equatorial coordination mode with two water molecules occupied as the axial positions of two terminal copper atoms. All copper(II) ions are in the distorted square-pyramidal geometry. The two terminal dinuclear units are similar in structure, both copper atoms in each dinuclear

unit are doubly bridged by carboxylato groups in a *syn-syn* configuration and an equatorial-equatorial conformation in the basal planes of the square-pyramidal $\text{CuN}_2\text{O}_2\text{O}'$ chromophores, the other two positions of each square base are occupied by two nitrogen atoms from a phen ligand. The axial position of each terminal, square-pyramidal copper(II) chromophore is occupied by a water molecule at distances of 2.249(5) Å for Cu(1) and 2.271(5) Å for Cu(6), while those of other copper(II) chromophores (of the terminal dinuclear moieties) are occupied by the bridging oxygen atoms of the carboxylato bridges with distances of 2.159(4) Å for Cu(2) and 2.166(1) Å for Cu(5). The Cu...Cu distances in both terminal dinuclear units are 3.074(4) and 3.050(4) Å, which are larger than those of the common paddle-wheel-type complexes (2.58–2.65 Å) [2,20,31] but they are nearly close to that of $[\text{Cu}(\text{CH}_3\text{COO})(\text{phen})(\text{H}_2\text{O})]_2(\text{NO}_3)_2$, which has a similar *syn-syn*, doubly bridged carboxylato configuration (3.063 Å) [10].

For the central dinuclear unit, both copper atoms are triply bridged by three different carboxylates, a triatomic bridge linking in a *syn-syn*, equatorial-equatorial configuration and two monoatomic bridges linking in an axial-equatorial configuration. The latter two bridging carboxylates also act as the bidentate triatomic bridges linking between the central and terminal dinuclear units. Consequently, these two carboxylates are the tridentate bridging ligand, which bidentately coordinated to both Cu atoms through an oxygen atom with Cu–O–Cu bridging angles of 90.3(3)° and 91.7(3)°, and monodentately coordinated to a Cu atom of the terminal dinuclear units via another oxygen atom in an axial-equatorial conformation. The square pyramidal environment for both copper atoms comprises two nitrogen atoms from a bpy ligand and two oxygen atoms from two different carboxylato bridges, forming a square base and an oxygen atom from the third carboxylato occupying the axial position with distances of 2.353(4) Å for Cu(3) and 2.377(5) Å for Cu(4) with a longer Cu(3)...Cu(4) distance of 3.121(4) Å. Consequently, three independent dinuclear moieties are linked to each other by two tridentate propionato bridges in the *syn-anti* configuration with the longest Cu(2)...Cu(3) and Cu(4)...Cu(5) distances of 4.322(4) and 4.299(4) Å, respectively. The intraplanar distances among the aromatic moieties of chelating bpy ligands are in a range of 3.570–3.926 Å, indicative of the intramolecular π - π stacking interactions which stabilize the hexanuclear compound of **2** (Fig. S5).

The EPR spectra [32] of compound **2** were recorded from a polycrystalline powder at RT and 77 K from 0 to 700 mT at X-band frequency ($h\nu = 0.325 \text{ cm}^{-1}$). At RT, it displays a triplet-like $S = 1$ spectrum with broad unresolved peaks (Fig. S6), which is sharpened up a little at 77 K (Fig. S7). The signal at around 160 mT can be assigned to the forbidden half-field signal ($\Delta M_s = \pm 2$). The bands are too broad for an accurate assignment of the spectrum.

The magnetic susceptibility of a powdered sample of compound **2** was measured from 5 to 350 K, and the magnetic properties of the title compound are depicted in Fig. 4 in the form of $\chi_M T$ versus T for one Cu(II) ion. At 350 K, the $\chi_M T$ product has a value of $0.360 \text{ cm}^3 \text{ K mol}^{-1}$, which is close to the spin-only value for one non-interacting Cu(II) ion ($0.375 \text{ cm}^3 \text{ K mol}^{-1}$ at RT). From 350 K the $\chi_M T$ product stays almost constant and from about 100 K onwards it decreases gradually to a value of $0.005 \text{ cm}^3 \text{ K mol}^{-1}$ at 5 K. This behavior agrees with a weak antiferromagnetic interaction between the Cu(II) ions in compound **2**, which is usually found for the *syn-syn*, equatorial-equatorial arrangement of the carboxylato bridges within each dinuclear moiety [8,10,11].

Due to the preliminary nature and the complicated structure, fitting against magnetic parameters was not possible at this moment. Unfortunately, so far compound **1** could not be produced in sufficient pure amounts to perform EPR and magnetic studies.

In summary, two unique examples of copper(II) compounds with the bpy and phen ligands with formulae $[\text{Cu}_2(\text{phen})_2(\mu\text{-O}_2\text{-O}_2\text{-O}_2)]$

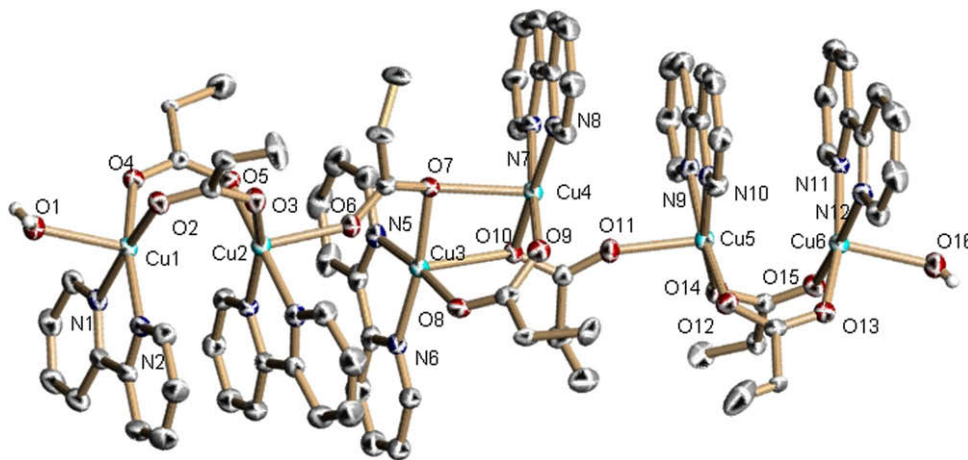


Fig. 3. Plot of $[\text{Cu}_6(\text{bpy})_6(\mu\text{-O}_2\text{CC}_2\text{H}_5)_7(\text{H}_2\text{O})_2](\text{PF}_6)_5 \cdot 2\text{H}_2\text{O}$ (**2**). Hydrogen atoms in bpy and the non coordinating anions and water molecules are omitted for clarity. Selected bond lengths and angles are given in Supplementary material (Table S2).

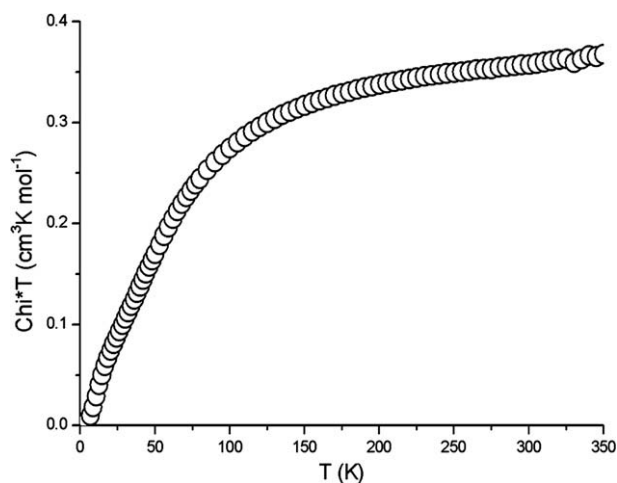


Fig. 4. A plot of $\chi_M T$ versus T per one Cu(II) ion for compound **2**.

$\text{CH}_2(\text{O}_2\text{CH})_2)_n$ (**1**) and $[\text{Cu}_6(\text{bpy})_6(\mu\text{-O}_2\text{CC}_2\text{H}_5)_7(\text{O}_2\text{H})_2](\text{PF}_6)_5 \cdot \text{H}_2\text{O}$ (**2**) are reported. Compound **1** exhibits an one-dimensional zigzag chain structure with the rare *anti-anti-μ-η¹;η¹* formate bridge, linking neighboring copper(II) ions. Compound **2** is a hexanuclear chain molecule containing three different dinuclear units with the *syn-syn-μ-η¹;η¹* and *syn-anti-μ₃-η¹;η²* propionate bridges. All copper(II) ions in both compounds display a distorted square-pyramidal geometry and either intra- or intermolecular π – π stacking interactions among the aromatic moieties remarkably play a key role to stabilize the polynuclear structure of **1** and **2**. Variable temperature magnetic measurements of compound **2** exhibit a weak antiferromagnetic interaction between the Cu(II) ions.

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Appendix A. Supplementary material

CCDC 663088 and 663089 for compounds **1** and **2** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2008.07.015.

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- [27] Compound **1** was obtained when $\text{Cu}(\text{O}_2\text{CH})_2 \cdot 6\text{H}_2\text{O}$ (0.307 g, 2 mmol) was added to a solution of phen (0.198 g, 1 mmol) in a mixed solvent of MeOH (10 mL) and dimethylformamide (10 mL). The reaction mixture was stirred for 2 h. and then the green precipitate was filtered off. The resulting clear-blue filtrate was allowed to stand for one week at room temperature to give a small amount of greenish-blue crystals of **1**. Found: C, 49.9%; H, 3.0%; N, 8.9%. Anal. Calc. for $\text{C}_{28}\text{H}_{20}\text{Cu}_2\text{N}_4\text{O}_8$: C, 50.4%; H, 3.0%; N, 8.4%. Main FT-IR data (KBr, cm^{-1}): ν_{COO} , 1601(vs), 1579(vs). UV-vis (diffuse reflectance, cm^{-1}): 14 640. Compound **2** was obtained when a methanolic solution (10 mL) of bpy (0.156 g, 1 mmol) was added to a mixture of $\text{Cu}(\text{OH})_2$ (0.076 g, 1 mmol) and KPF_6 (0.184 g, 1 mmol) in 10 mL of water. Then, 6 mL (78.82 mmol) of 98% propionic acid was dropped slowly into this mixture under stirring, and was heated for an hour resulting a deep blue solution. On slow evaporation for two weeks deep blue crystals of **2** were obtained. Suitable single-crystals for X-ray diffraction were collected by filtration. Yields ca. 55% (based on $\text{Cu}(\text{OH})_2$). Found: C, 36.8%; H, 3.3%; N, 6.6%. Anal. Calc. for $\text{C}_{81}\text{H}_{91}\text{Cu}_6\text{F}_{30}\text{N}_{12}\text{O}_{18}\text{P}_5$: C, 37.0%; H, 3.5%; N, 6.4%. Main FT-IR data (KBr, cm^{-1}): ν_{COO} , 1603(vs), 1548(vs); ν_{PF_6} , 843(s). UV-vis (diffuse reflectance, cm^{-1}): 15,700, 13,180(sh).
- [28] Crystal data for **1**: $\text{C}_{28}\text{H}_{20}\text{Cu}_2\text{N}_4\text{O}_8$ (M_w = 667.56), triclinic, $P1$, a = 9.5508(1) Å, b = 9.6096(2) Å, c = 28.5572(2) Å, α = 84.7560(10)°, β = 85.2430(10)°, γ = 89.63°, V = 2601.0(6) Å³, T = 293(2) K, Z = 4, D_c = 1.670 g cm⁻³, μ = 1.696 mm⁻¹, $F(000)$ = 1348, 18,898 reflections measured, 16,048 unique (R_{int} = 0.0265), Final R indices [$I > 2\sigma(I)$]: R_1 = 0.0523, wR_2 = 0.1183; R indices [all data]: R_1 = 0.0804, wR_2 = 0.1333, GOF = 1.037. For **2**: $\text{C}_{81}\text{H}_{91}\text{Cu}_6\text{F}_{30}\text{N}_{12}\text{O}_{18}\text{P}_5$ (M_w = 2622.78), Triclinic, $P1$, a = 13.3168(5) Å, b = 16.6044(6) Å, c = 24.9404(8) Å, α = 90.8900(10)°, β = 101.7370(10)°, γ = 97.9890(10)°, V = 5341.6(3) Å³, T = 293(2) K, Z = 2, D_c = 1.631 g cm⁻³, μ = 1.366 mm⁻¹, $F(000)$ = 2640, 28,221 reflections measured, 19,543 unique (R_{int} = 0.0188), final R indices [$I > 2\sigma(I)$]: R_1 = 0.0672, wR_2 = 0.1608; R indices [all data]: R_1 = 0.0942, wR_2 = 0.1845, GOF = 1.066.
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- [32] X-band powder EPR spectra were obtained on a Jeol RE2x electron spin resonance spectrometer using DPPH (g = 2.0036) as a standard. Magnetic susceptibility measurements (5–350 K) were carried out using a Quantum design MPMS-5S SQUID magnetometer (measurements carried out at 0.1 mT). Data were corrected for magnetization of the sample holder and for diamagnetic contributions, which were estimated from the Pascal constants.

Publication papers of miscellaneous result

Dinuclear triply bridged copper(II)-carboxylato compounds with different bischelating ligands: Synthesis, crystal structure, spectroscopic and magnetic properties

Chatkaew Chailuecha ^a, Sujittra Youngme ^{b,*}, Chaveng Pakawatchai ^c,
Narongsak Chaichit ^d, Gerard A. van Albada ^e, Jan Reedijk ^e

^a Department of Chemistry, The School of Science and Technology, Naresuan University Phayao Campus, Phayao 56000, Thailand

^b Department of Chemistry, Faculty of Science, Khon Kaen University, Khon Kaen 40002, Thailand

^c Department of Chemistry, Faculty of Science, Prince of Songkla University, Hatyai, Songkla 90112, Thailand

^d Department of Physics, Faculty of Science and Technology, Thammasart University Rangsit, Pathumthani 12120, Thailand

^e Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden University, P.O. Box 9502, 2300 RA Leiden, The Netherlands

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Abstract

Three new triply bridged dinuclear copper(II) compounds containing carboxylato bridges, $[\text{Cu}_2(\mu\text{-CH}_3\text{COO-}\kappa\text{-O}^1, \text{O}^2)(\mu\text{-CH}_3\text{COO-}\kappa\text{-O}^1)(\text{dpyam})_2](\text{BF}_4)$ (**1**), $[\text{Cu}_2(\mu\text{-CH}_2\text{CH}_3\text{COO-}\kappa\text{-O}^1, \text{O}^2)(\mu\text{-OH})(\mu\text{-OH}_2)(\text{bpy})_2](\text{ClO}_4)_2$ (**2**) and $[\text{Cu}_2(\mu\text{-CH}_3\text{COO-}\kappa\text{-O}^1, \text{O}^2)(\mu\text{-OH})(\mu\text{-OH}_2)(\text{phen})_2](\text{ClO}_4)_2$ (**3**) (in which dpyam = di-2-pyridylamine, bpy = 2,2-bipyridine, phen = phenanthroline), have been synthesized in order to investigate the magnetic super-exchange pathway between coupled copper(II) centres. All three compounds display a distorted square-pyramidal arrangement around each copper(II) ion with a CuN_2O_3 chromophore. Compound **1** has three acetato bridges, two of which connect each square pyramid at two equatorial sites in a triatomic bridging mode and the third acetato bridge acts at the apical site in the monoatomic bridging mode. The structures of compounds **2** and **3** are mutually similar. In each dinuclear unit, both copper(II) ions are linked at two equatorial positions through a hydroxo bridge and a triatomic carboxylato bridge and at the axial position through a water molecule.

The magnetic susceptibility measurements, measured from 5 to 300 K, revealed an antiferromagnetic interaction between the Cu(II) ions in compound **1** and a ferromagnetic interaction for compounds **2** and **3** with singlet–triplet energy gaps (J) of -56 , 149 and 120 cm^{-1} , for compounds **1**, **2** and **3**, respectively.

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Keywords: Copper(II) complexes; EPR; Crystal structure; Carboxylato-bridged; Triply bridged complex; Magnetism

1. Introduction

Triply bridged dinuclear copper(II) compounds with one or more carboxylate moieties have received considerable attention [1–11], due to the various possible super-exchange pathways between coupled copper(II) centres. The magnetic exchange interactions depend on the coor-

dination geometry around the copper(II) centres and coordination mode of the bridging ligand [1–11]. Structurally, the triply bridged dinuclear copper(II) carboxylato compounds with didentate chelating ligands and a five coordination of the Cu(II) ion show an extensive range of compounds with a distortion between regular trigonal bipyramidal and regular square-based pyramidal. This feature can be useful for understanding the relationships between structural features and the value of the intramolecular magnetic exchange interaction in the dinuclear unit.

* Corresponding author. Fax: +66 43 202373.

E-mail address: sujittra@kku.ac.th (S. Youngme).

Our previous reports [10,11] dealt with the distortion of the geometries ranging between regular trigonal bipyramidal and regular square-based pyramidal, and the structurally dependent magnetic properties displayed by the five-coordinate dinuclear copper(II) ions. The structures of complexes $[\text{Cu}_2(\mu\text{-O}_2\text{CH})(\mu\text{-OH})(\mu\text{-Cl})(\text{dpyam})_2](\text{PF}_6)$, $[\text{Cu}_2(\mu\text{-O}_2\text{CH})_2(\mu\text{-OH})(\text{dpyam})_2](\text{PF}_6)$, $[\text{Cu}_2(\mu\text{-O}_2\text{C-CH}_2\text{CH}_3)_2(\mu\text{-OH})(\text{dpyam})_2](\text{ClO}_4)$ and $[\text{Cu}_2(\mu\text{-O}_2\text{CH})(\mu\text{-OH})(\mu\text{-Cl})(\text{dpyam})_2](\text{ClO}_4) \cdot 0.5\text{H}_2\text{O}$ (in which dpyam = di-2-pyridylamine) reveal a distorted trigonal bipyramidal stereochemistry, with a d_{22} ground state and thus the major lobe of the magnetic orbital will be axially directed toward a single bridging ligand: the hydroxo anion in these cases [10,11]. This feature contributes to the observed ferromagnetic coupling between copper(II) magnetic centres.

To extend the understanding of magneto-structural correlation of the triply bridged dinuclear copper(II) carboxylato complexes with other copper(II) stereochemistry and bridging configuration, three further new triply bridged dinuclear copper(II) compounds with hydroxo, acetato and propionato bridges and different chelating ligands $[\text{Cu}_2(\mu\text{-CH}_3\text{COO-}\kappa\text{-O}^1, \text{O}^2)_2(\mu\text{-CH}_3\text{COO-}\kappa\text{-O}^1)(\text{dpyam})_2](\text{BF}_4)$ (**1**), $[\text{Cu}_2(\mu\text{-CH}_2\text{CH}_3\text{COO-}\kappa\text{-O}^1, \text{O}^2)(\mu\text{-OH})(\mu\text{-OH}_2)(\text{bpy})_2](\text{ClO}_4)_2$ (**2**) and $[\text{Cu}_2(\mu\text{-CH}_3\text{COO-}\kappa\text{-O}^1, \text{O}^2)(\mu\text{-OH})(\mu\text{-OH}_2)(\text{phen})_2](\text{ClO}_4)_2$ (**3**) have been synthesized and characterized by X-ray crystallography, IR, EPR and electronic spectra. Also the magnetic susceptibility at low T will be discussed in comparison with other relevant compounds.

2. Experimental

2.1. Materials and measurements

2,2'-Dipyridylamine (di-2-pyridylamine), 2,2'-bipyridyl and 1,10-phenanthroline were purchased as commercial chemicals from Aldrich. All reagents are commercial grade materials and were used without further purification. Elemental analyses (C, H, N) were determined on a Perkin–Elmer PE 2400 CHNS/O Analyzer.

The IR spectra were recorded on a Perkin–Elmer Spectrum One FT-IR spectrophotometer, as KBr disc in the $4000\text{--}450\text{ cm}^{-1}$ spectral range. A solid-state (diffuse reflectance) electronic spectrum was measured as polycrystalline samples on a Perkin–Elmer Lambda2S spectrophotometer, in the range $8000\text{--}18000\text{ cm}^{-1}$. The X-band powder EPR spectra at RT and at 77 K were obtained as polycrystalline samples with a JEOL RE2X electron spin resonance spectrophotometer with DPPH ($g = 2.0036$) as a reference. Magnetic susceptibility measurements (5–300 K) were carried out using a Quantum design MPMS-5S SQUID magnetometer (measurements carried out at 0.1 mT). Data were corrected for magnetization of the sample holder and for diamagnetic contributions, which were estimated from the Pascal constants.

2.2. Syntheses

2.2.1. $[\text{Cu}_2(\mu\text{-CH}_3\text{COO-}\kappa\text{-O}^1, \text{O}^2)_2(\mu\text{-CH}_3\text{COO-}\kappa\text{-O}^1)(\text{dpyam})_2](\text{BF}_4)$ (**1**)

A warm (about 40°C) ethanol solution (5 ml) of dpyam (0.34 g, 2.0 mmol) was added to a hot (about 80°C) aqueous solution (10 ml) of $\text{Cu}_2(\text{O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2$ (0.40 g, 1.1 mmol), yielding a green solution. Then solid NaBF_4 (0.11 g, 0.1 mmol) was added to the solution. A green powder was immediately formed, after which the mixture was heated and 99% CH_3COOH (0.5 ml) was added, yielding a clear green solution. After two weeks, dark green crystals of compound **1** were obtained, filtered off, washed with the mother liquid and air-dried. Yield ca. 70%. *Anal.* Calc. for $\text{C}_{26}\text{H}_{27}\text{Cu}_2\text{BF}_4\text{N}_6\text{O}_6$: C, 42.58; H, 3.71; N, 11.46. Found: C, 42.45; H, 3.40; N, 11.23%. IR (KBr, cm^{-1}): 3343 m, 3219 w, 3068 w, 3019 w, 1644 s, 1627 s, 1600 s, 1532 m, 1486 s, 1439 s, 1374 m, 1315 m, 1239 m, 1161 m, 1081 s, 1018 m, 911 w, 844 w, 775 s, 663 m, 619 w, 533 w.

2.2.2. $[\text{Cu}_2(\mu\text{-CH}_2\text{CH}_3\text{COO-}\kappa\text{-O}^1, \text{O}^2)(\mu\text{-OH})(\mu\text{-OH}_2)(\text{bpy})_2](\text{ClO}_4)_2$ (**2**)

A warm (about 40°C) ethanol solution (10 ml) of bpy (0.16 g, 1.0 mmol) was added to a hot (about 80°C) aqueous solution (10 ml) of $\text{Cu}(\text{ClO}_4)_2(\text{H}_2\text{O})_6$ (0.371 g, 1.0 mmol), after which solid $\text{CH}_3\text{CH}_2\text{COONa}$ (0.38 g, 4.0 mmol) was added. The resulting dark blue solution was allowed to evaporate at room temperature. After one week, green crystals of compound **2** were obtained, which were filtered off, washed with the mother liquid and air-dried. Yield ca. 65%. *Anal.* Calc. for $\text{C}_{23}\text{H}_{24}\text{Cl}_2\text{Cu}_2\text{N}_4\text{O}_{12}$: C, 37.01; H, 3.24; N, 7.51. Found: C, 36.80; H, 3.16; N, 7.30%. IR (KBr, cm^{-1}): 3534 m, 1610 s, 1588 m, 1547 s, 1429 m, 1384 m, 1370 s, 1343 m, 1146 m, 1115 s, 855 s, 779 m, 729 s, 681 m, 624 s.

2.2.3. $[\text{Cu}_2(\mu\text{-CH}_3\text{COO-}\kappa\text{-O}^1, \text{O}^2)(\mu\text{-OH})(\mu\text{-OH}_2)(\text{phen})_2](\text{ClO}_4)_2$ (**3**)

A warm methanol solution (25 ml) of phen (0.40 g, 2.0 mmol) was added to a hot (about 80°C) aqueous solution (10 ml) of $\text{Cu}_2(\text{O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2$ (0.40 g, 1.1 mmol), followed by addition of solid KClO_4 (0.14 g, 1.0 mmol). The resulting dark blue solution was allowed to evaporate at room temperature. After one week, dark blue crystals of compound **3** were obtained which were filtered off, washed with the mother liquid and air-dried. Yield ca. 62%. *Anal.* Calc. for $\text{C}_{26}\text{H}_{22}\text{Cl}_2\text{Cu}_2\text{N}_4\text{O}_{12}$: C, 40.01; H, 2.84; N, 7.18. Found: C, 39.85; H, 2.74; N, 7.09%. IR (KBr, cm^{-1}): 3392 m, 1651 m, 1555 s, 1519 s, 1429 s, 1384 s, 1343 m, 1146 m, 1105 s, 851 s, 779 m, 724 s, 681 m, 623 m, 521 m.

2.3. Crystallography

The X-ray single-crystal data of compounds **1–3** were collected at 293 K on a 1 K Bruker SMART CCD area-detector diffractometer using graphite monochromated

Mo K α radiation ($\lambda = 0.71073$ Å) at a detector distance of 4.5 cm and swing angle of -35° . A hemisphere of the reciprocal space was covered by a combination of three sets of exposures; each set had a different ϕ angle (0° , 88° , 180°) and each exposure of 40 s covered 0.3° in ω . Data reduction and cell refinements were performed using the program SAINT [12]. An empirical absorption correction by using the SADABS [13] program was applied, which resulted in transmission coefficients ranging from 0.811 to 1.000 for **1**, 0.897 to 1.000 for **2** and 0.796 to 1.000 for **3**.

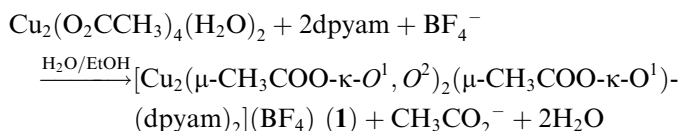
The structures were solved by direct methods and refined by full matrix least-squares method on $(F_{\text{obs}})^2$ with anisotropic thermal parameters for all non-hydrogen atoms using the SHELXTL-PC V 6.12 software package [14]. All hydrogen atoms were located and refined isotropically except two hydrogen atoms from the pyridyl ring and one acetato group in **1** and hydrogen atoms of the propionato group in **2** which were fixed and allowed to ride on attached atoms. While all hydrogen atoms from pyridyl rings in **3** were fixed and allowed to ride on attached atoms. The BF_4^- anion in **1** was found to be disordered over two positions and has an occupancy factor of 0.50. The ClO_4^- anions in **2** and **3** are disordered and both conformers have been used with an occupancy factor of 0.50. Also the CH_3 group and the O4 atom in **1** were found to be disordered and were refined with population parameters of 0.50. The molecular graphics were created by using SHELXTL-PC [14] package. The crystal and refinement details for compounds **1**, **2** and **3** are listed in Table 1.

3. Results and discussion

3.1. Synthesis

A triply acetato bridged dinuclear copper(II) compound $[\text{Cu}_2(\mu\text{-CH}_3\text{COO-}\kappa\text{-O}^1, \text{O}^2)_2(\mu\text{-CH}_3\text{COO-}\kappa\text{-O}^1)(\text{bpy})_2](\text{ClO}_4)$ [1] was previously reported with an intramolecular ferromagnetic coupling between the Cu(II) ions. In order to extend the investigation on magneto-structural correlation of the triply acetato bridging system with different copper(II) geometries, new dinuclear copper(II) compounds with the more flexible ligand dpyam were synthesized.

Treatment of $\text{Cu}_2(\text{O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2$ in water with two equivalent of dpyam in EtOH was followed by addition of NaBF_4 obtaining a green suspension. The reaction mixture was heated and a small amount of concentrated CH_3COOH was added, obtaining a homogeneous green solution, in which dark green crystal, were formed with formula $[\text{Cu}_2(\mu\text{-CH}_3\text{COO-}\kappa\text{-O}^1, \text{O}^2)_2(\mu\text{-CH}_3\text{COO-}\kappa\text{-O}^1)(\text{dpyam})_2](\text{BF}_4)$ (**1**). Its formation can be summarized as



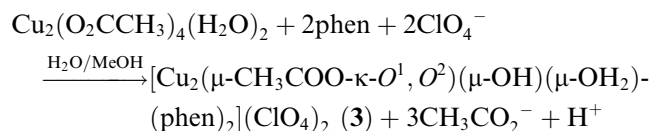
In another synthesis, similar to the above one, the ligand phen was used instead of dpyam. An aqueous solution of $\text{Cu}_2(\text{O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2$ was treated with two equivalent of phen in MeOH and addition of KClO_4 provided dark blue crystals with formula $[\text{Cu}_2(\mu\text{-CH}_3\text{COO-}\kappa\text{-O}^1, \text{O}^2)(\mu\text{-OH})-$

Table 1
Crystal and refinement data for complexes **1**, **2** and **3**

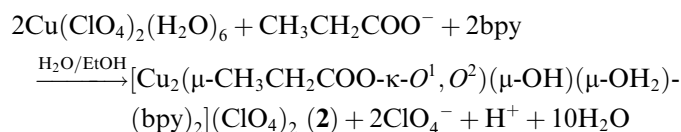
Complex	1	2	3
Formula	$\text{C}_{26}\text{H}_{27}\text{Cu}_2\text{BF}_4\text{N}_6\text{O}_6$	$\text{C}_{23}\text{H}_{24}\text{Cl}_2\text{Cu}_2\text{N}_4\text{O}_{12}$	$\text{C}_{26}\text{H}_{22}\text{Cl}_2\text{Cu}_2\text{N}_4\text{O}_{12}$
Molecular weight	733.45	746.44	780.46
<i>T</i> (K)	293(2)	293(2)	293(2)
Crystal system	orthorhombic	triclinic	orthorhombic
Space group	<i>Pnma</i>	<i>P</i> $\bar{1}$	<i>P2</i> ₁ <i>2</i> ₁
<i>a</i> (Å)	18.2898(9)	8.1858(6)	8.3526(5)
<i>b</i> (Å)	17.0002(9)	11.2941(9)	17.8236(12)
<i>c</i> (Å)	9.3243(5)	16.9046(13)	19.9074(13)
α (°)		90	71.1670(10)
β (°)	90	81.2180(10)	90
γ (°)	90	76.5120(10)	90
<i>V</i> (Å ³)	2899.2(3)	1433.29(19)	2963.7(3)
<i>Z</i>	4	2	4
<i>D</i> _{calc} (g cm ³)	1.513	1.730	1.749
μ (mm ^{−1})	1.529	1.739	1.687
<i>F</i> (000)	1340	756	1576
Crystal size (mm)	0.40 × 0.33 × 0.24	0.23 × 0.15 × 0.06	0.28 × 0.22 × 0.09
Number of reflections collected	17710	10694	18975
Number of unique reflections [<i>R</i> _{int}]	3630 [0.0211]	5209 [0.0224]	6554 [0.0310]
Data/restraints/parameters	3630/0/269	5209/0/498	6554/0/471
Goodness-of-fit	1.062	1.045	1.029
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0481, <i>wR</i> ₂ = 0.1399	<i>R</i> ₁ = 0.0496, <i>wR</i> ₂ = 0.1211	<i>R</i> ₁ = 0.0448, <i>wR</i> ₂ = 0.1098
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0563, <i>wR</i> ₂ = 0.1485	<i>R</i> ₁ = 0.0608, <i>wR</i> ₂ = 0.1280	<i>R</i> ₁ = 0.0587, <i>wR</i> ₂ = 0.1175
Largest difference in peak and hole (e Å ^{−3})	0.919 and −0.844	0.746 and −0.462	0.501 and −0.366

$$R = \sum |F_o| - |F_c| / \sum |F_o|, R_w = [\sum w\{|F_o| - |F_c|\}^2 / \sum w|F_o|^2]^{1/2}.$$

(μ -OH₂)(phen)₂](ClO₄)₂ (**3**). Its formation can be summarized as



To investigate the change in geometry when using the ligand bpy and try to obtain a propionato bridge, the following reaction was carried out: one equivalent of bpy and Cu(ClO₄)₂(H₂O)₆ in H₂O/EtOH was followed by addition of CH₃CH₂COONa and green crystals were obtained with the formula, [Cu₂(μ -CH₃CH₂COO- κ -O¹, O²)(μ -OH)(μ -OH₂)(bpy)₂](ClO₄)₂ (**2**). Its formation can be summarized as



3.2. Description of the crystal structures

3.2.1. Description of [Cu₂(μ -CH₃COO- κ -O¹, O²)₂(μ -CH₃COO- κ -O¹)(dpyam)₂](BF₄) (**1**)

Compound **1** is made up of one half of [Cu₂(μ -CH₃-COO- κ -O¹, O²)₂(μ -CH₃COO- κ -O¹)(dpyam)₂]⁺ moiety, the other half of which was symmetry related via a mirror plane and a BF₄[−] anion. This dinuclear unit is depicted in Fig. 1 together with the numbering scheme, with selected distances and angles are listed in Table 2. The copper(II)

ions are bridged by three acetato groups. Two of the acetate ligands are in a didentate κ -O¹, O² bridging mode and the third is in a rare monoatomic κ -O¹ bridging mode, albeit disordered over two positions due to the symmetry plane. A terminal dpyam molecule completes the five-coordination (4 + 1 type) at each Cu(II) ion, which has a slightly distorted square pyramidal geometry of the CuN₂O₃ chromophore (see Fig. 2). The percentage of distortion of this square pyramidal stereochemistry towards a trigonal bipyramidal is obtained from the value of $\tau = 0.07$ ($\tau = (\beta - \alpha)/60$), where β and α are the largest coordination angles [15,16]. The basal plane consists of two nitrogen atoms of a dpyam ligand (Cu(1)–N(1) and Cu(1)–N(2) distances of 2.004(2) and 1.990(2) Å, respectively) and two oxygen atoms of two didentate acetato groups (Cu(1)–O(1) and Cu(1)–O(2) distances of 1.972(2) and 1.965(2) Å, respectively). The fifth apical coordination site of each Cu(II) ion is occupied by the disordered monoatomic acetato bridge (Cu(1)–O(3) distance of 2.144(2) Å). The basal planes deviate from planarity with a distinct tetrahedral twist as evident from the dihedral angle of 32.1(1)° between the CuN₂ and CuO₂ planes. The Cu(II) ion lies at 0.392(1) Å from the equatorial plane towards O(3) atom. The dihedral angle between the two basal planes is 59.9(1)°. Both of these planes are linked together through two of *syn, syn* (acetato- κ -O¹, O²) bridges giving a Cu···Cu distance of 3.402(1) Å. The bridging Cu(1)–O(3)–Cu(1A) angle is 105.0(1)°. The planes drawn through the dpyam ligands are essentially planar with a dihedral angle of 22.4(1)° between the individual pyridine rings. The crystal lattice is stabilized by hydrogen bonding between the amine

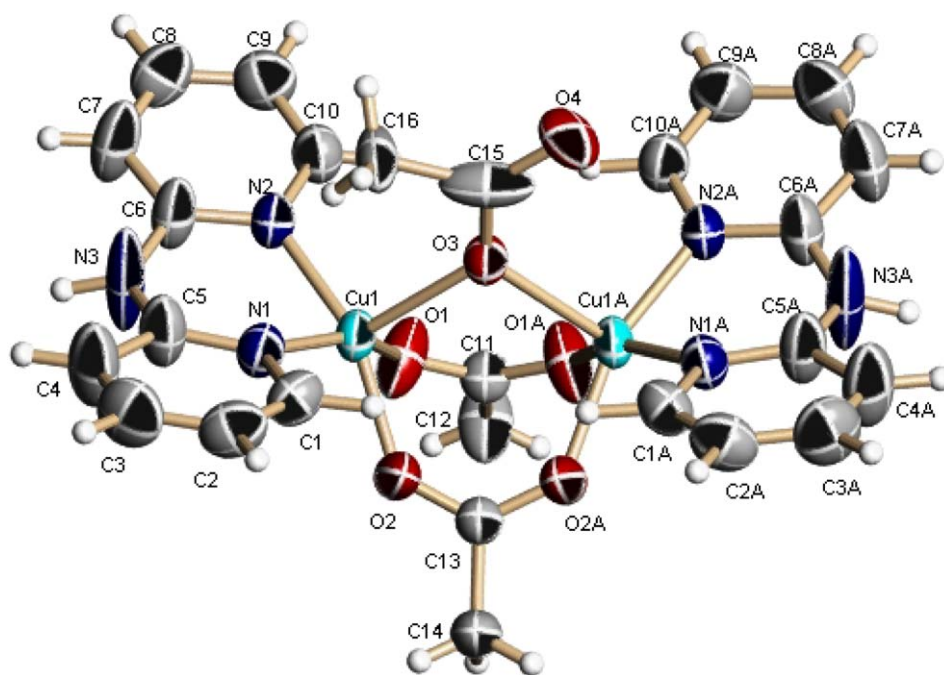


Fig. 1. ORTEP 50% probability plot of the cation in [Cu₂(μ -CH₃COO- κ -O¹, O²)₂(μ -CH₃COO- κ -O¹)(dpyam)₂](BF₄) (**1**). Atoms with an “A” are generated by a mirror plane. The disordered BF₄ molecule is omitted for clarity. Only one conformer of the disordered CH₃ group and O4 atom of the acetate molecule are shown.

Table 2

Selected bond lengths (Å) and angles (°) with e.s.d.s. in parentheses of $[\text{Cu}_2(\mu\text{-CH}_3\text{COO-}\kappa\text{-O}^1, \text{O}^2)_2(\mu\text{-CH}_3\text{COO-}\kappa\text{-O}^1)(\text{dpyam})_2](\text{BF}_4)$ (1)

Cu(1)–N(1)	2.004(2)	Cu(1)–O(1)	1.972(2)
Cu(1)–N(2)	1.990(2)	Cu(1)–O(2)	1.965(2)
Cu(1)–O(3)	2.144(2)	Cu(1)–Cu(1A)	3.402(1)
O(1)–Cu(1)–O(2)	86.7(2)	O(2)–Cu(1)–O(3)	98.5(1)
O(1)–Cu(1)–N(1)	154.9(2)	N(1)–Cu(1)–N(2)	89.4(1)
O(1)–Cu(1)–N(2)	88.3(1)	N(1)–Cu(1)–O(3)	105.1(1)
O(1)–Cu(1)–O(3)	99.9(3)	N(2)–Cu(1)–O(3)	102.2(2)
O(2)–Cu(1)–N(1)	86.8(2)	Cu(1)–O(3)–Cu(1A)	105.0(2)
O(2)–Cu(1)–N(2)	159.3(2)		

A = $[x, 1/2 - y, z]$.

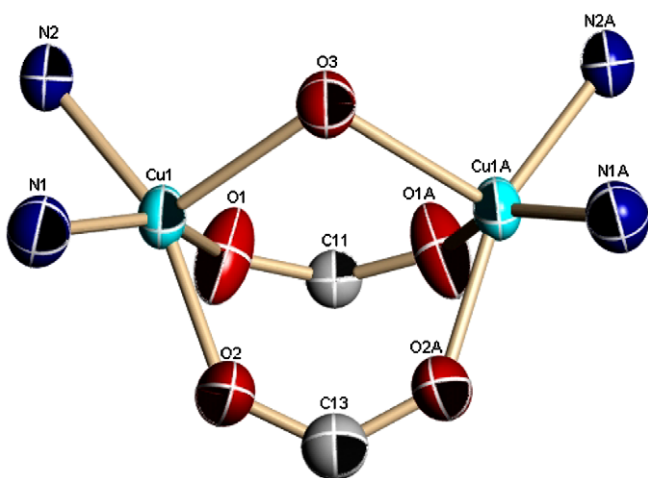


Fig. 2. The chromophore of $[\text{Cu}_2(\mu\text{-CH}_3\text{COO-}\kappa\text{-O}^1, \text{O}^2)_2(\mu\text{-CH}_3\text{COO-}\kappa\text{-O}^1)(\text{dpyam})_2](\text{BF}_4)$ (1).

N and the fluoride atom of BF_4^- anion with a $\text{N}\cdots\text{F}$ distance of 2.871(3). Due to the disorder of the BF_4 group, not all H-bonds could be located.

3.2.2. Description of $[\text{Cu}_2(\mu\text{-CH}_3\text{CH}_2\text{COO-}\kappa\text{-O}^1, \text{O}^2)(\mu\text{-OH})(\mu\text{-OH}_2)(\text{bpy})_2](\text{ClO}_4)_2$ (2)

The dinuclear Cu(II) unit of compound **2** is bridged by three different ligands and consists of a dinuclear $[\text{Cu}_2(\mu\text{-CH}_3\text{CH}_2\text{COO-}\kappa\text{-O}^1, \text{O}^2)(\mu\text{-OH})(\mu\text{-OH}_2)(\text{bpy})_2]^{2+}$ cation with two ClO_4^- anions. This unit is depicted in Fig. 3 together with the numbering scheme. The selected distances and angles are listed in Table 3.

Each Cu(II) ion has a distorted square pyramidal environment ($\tau = 0.20$ and 0.16 for Cu(1) and Cu(2), respectively). The basal plane of CuN_2O_3 chromophore (see Fig. 4) comprises two nitrogen atoms of a terminal bpy ligand (Cu–N distances range between 1.995(3) and 2.005(4) Å), an oxygen atom of the didentate $\kappa\text{-O}^1, \text{O}^2$ bridging propionato ligand (Cu(1)–O(3) and Cu(2)–O(4) distances of 1.942(3) and 1.923(3) Å, respectively) and an oxygen atom of the hydroxo ligand (Cu(1)–O(1) and Cu(2)–O(1) distances of 1.921(3) and 1.920(3) Å, respectively). The coordination at the apical position is completed by the oxygen atom of the aqua ligand (Cu–O

distance of 2.382(4) Å for both Cu(1) and Cu(2)). The discrimination between OH^- and H_2O was made from the Cu–O distances. The basal planes are slightly deviated from planarity with a tetrahedral twist of 15.0(1)° for Cu(1) and 10.9(2)° for Cu(2). The dihedral angle between the two equatorial planes is 59.9(2)°. The copper atoms are displaced 0.136(1) Å for Cu(1) and 0.106(1) Å for Cu(2) from its individual plane. The Cu $\cdots$ Cu separation within the dinuclear unit is 3.037(1) Å, while the bridging Cu(1)–O(1)–Cu(2) angle is 104.5(3)°. The bpy ligands are essentially planar, with only a dihedral angle of 1.2(1)° and 3.2(1)° between the individual pyridine rings, and a dihedral angle of 53.6(2)° occurs between both bpy ligands.

The lattice is further stabilized by moderate to weak hydrogen bonding between the hydroxo oxygen and the oxygen atom of the ClO_4^- anion with a $\text{O}\cdots\text{O}$ distance of 3.033 Å; between the oxygen atom of bridging aqua group and the oxygen atom of perchlorate molecule with $\text{O}\cdots\text{O}$ contacts of 2.869–3.201 Å. Due to the disorder of the ClO_4 groups not all H-bonds could be located.

3.2.3. Description of $[\text{Cu}_2(\mu\text{-CH}_3\text{COO-}\kappa\text{-O}^1, \text{O}^2)(\mu\text{-OH})(\mu\text{-OH}_2)(\text{phen})_2](\text{ClO}_4)_2$ (3)

The structure of compound **3** consists of a dinuclear $[\text{Cu}_2(\mu\text{-CH}_3\text{COO-}\kappa\text{-O}^1, \text{O}^2)(\mu\text{-OH})(\mu\text{-OH}_2)(\text{phen})_2]^{2+}$ unit and two uncoordinating ClO_4^- anions. This unit is depicted in Fig. 5 together with the numbering scheme and selected distances and angles are listed in Table 3. Both Cu(II) ions in the dinuclear unit are linked through a hydroxo, an aqua and a didentate $\kappa\text{-O}^1, \text{O}^2$ bridging acetato ligand resulting in a similar structure to that of compound **2**. The coordination environment around each Cu(II) ion can be best described as weakly distorted square pyramidal, with a CuN_2O_3 chromophore (see Fig. 6) and the $\tau = 0.02$ for Cu(1) and 0.14 for Cu(2). Two nitrogen atoms of the phen ligand (Cu–N distances range between 2.007(4) and 2.020(4) Å), an oxygen atom of the hydroxo bridge (Cu–O distances 1.933(3) Å for both Cu(1) and Cu(2)) and an oxygen atom of the didentate acetato bridge (Cu–O distances 1.930(3) and 1.925(3) Å for Cu(1) and Cu(2), respectively) form the square basal plane. The axial site of each Cu(II) ion is occupied by an oxygen atom of the aqua bridge (Cu–O distances 2.360(4) and 2.375(4) Å for Cu(1) and Cu(2), respectively). The Cu $\cdots$ Cu separation is 2.989(1) Å. The discrimination between OH^- and H_2O was made from the Cu–O distances. The four basal atoms are most planar, showing a slightly tetrahedral distortion with dihedral angles of 16.4(1)° and 8.2(1)° for Cu(1) and Cu(2), respectively. The copper atoms are displaced by 0.122(1) and 0.087(1) Å from the individual basal planes. The dihedral angle between the two equatorial planes is 66.2(1)° and the bridging Cu(1)–O(1)–Cu(2) angle is 101.3(1)°.

The lattice is further stabilized by hydrogen bonding between the hydroxo oxygen and the oxygen atom of ClO_4^- anion with an $\text{O}\cdots\text{O}$ distance of 3.038 Å; between the oxygen atom of bridging water molecule and the oxygen atom of perchlorate molecule with an $\text{O}\cdots\text{O}$ contact

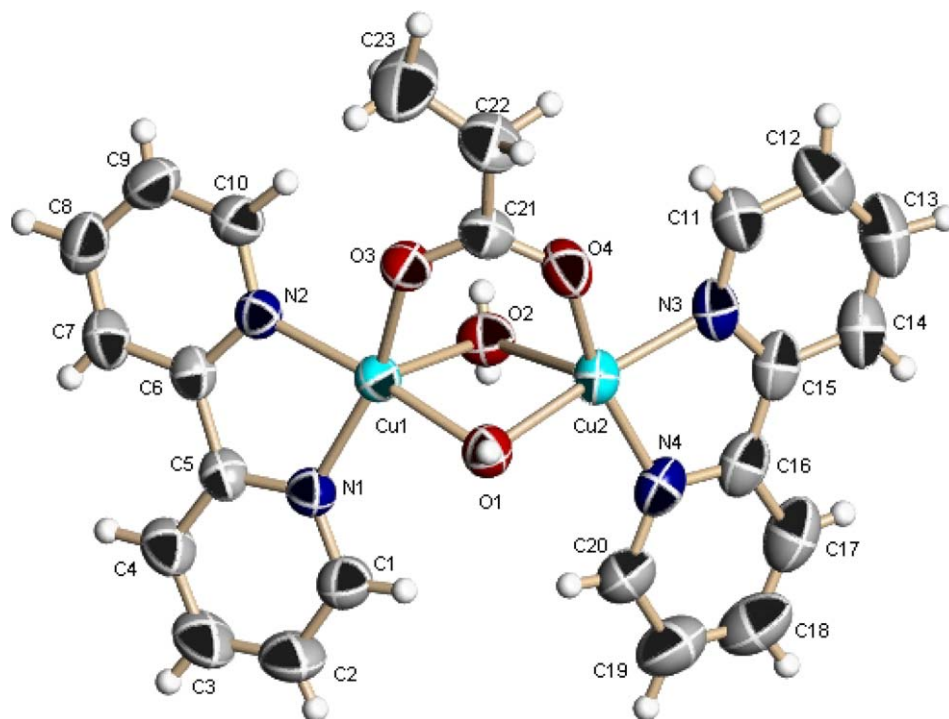


Fig. 3. ORTEP 50% probability plot of the cation in $[\text{Cu}_2(\text{bpy})_2(\mu\text{-OH})(\mu\text{-OH}_2)(\mu\text{-O}_2\text{CCH}_2\text{CH}_3)](\text{ClO}_4)_2$ (**2**). The perchlorate molecules are omitted for clarity.

Table 3

Selected bond lengths (Å) and angles (°) with e.s.d.s. in parentheses of $[\text{Cu}_2(\mu\text{-CH}_2\text{CH}_3\text{COO-}\kappa\text{-O}^1, \text{O}^2)(\mu\text{-OH})(\mu\text{-OH}_2)(\text{bpy})_2](\text{ClO}_4)_2$ (**2**) and $[\text{Cu}_2(\mu\text{-CH}_3\text{COO-}\kappa\text{-O}^1, \text{O}^2)(\mu\text{-OH})(\mu\text{-OH}_2)(\text{phen})_2](\text{ClO}_4)_2$ (**3**)

Compound	2	3	2	3
Cu(1)–N(1)	1.995(3)	2.007(4)	Cu(1)–O(1)	1.921(3)
Cu(1)–N(2)	1.997(3)	2.015(4)	Cu(1)–O(2)	2.382(4)
Cu(1)–O(3)	1.942(3)	1.930(3)	Cu(1)–Cu(2)	3.037(1)
Cu(2)–N(3)	2.001(4)	2.020(4)	Cu(2)–O(1)	1.920(3)
Cu(2)–N(4)	2.005(4)	2.018(4)	Cu(2)–O(2)	2.415(4)
Cu(2)–O(4)	1.923(3)	1.925(3)		
O(1)–Cu(1)–O(2)	81.4(2)	84.8(1)	N(1)–Cu(1)–N(2)	80.7(1)
O(1)–Cu(1)–N(1)	94.1(1)	92.7(1)	N(1)–Cu(1)–O(3)	162.3(1)
O(1)–Cu(1)–N(2)	174.8(1)	173.9(1)	N(2)–Cu(1)–O(3)	89.7(2)
O(1)–Cu(1)–O(3)	95.2(1)	95.7(1)	O(1)–Cu(2)–O(2)	80.5(2)
O(2)–Cu(1)–N(1)	100.4(2)	104.1(1)	O(1)–Cu(2)–N(3)	175.4(2)
O(2)–Cu(1)–N(2)	99.8(2)	94.0(1)	O(1)–Cu(2)–N(4)	94.6(2)
O(1)–Cu(2)–O(4)	94.5(1)	93.6(1)	O(1)–Cu(2)–O(4)	94.5(2)
N(3)–Cu(2)–N(4)	81.0(2)	81.2(1)	O(2)–Cu(2)–N(3)	101.1(2)
N(3)–Cu(2)–O(4)	90.0(1)	89.2(1)	O(2)–Cu(2)–N(4)	95.3(2)
N(4)–Cu(2)–O(4)	165.7(2)	167.7(1)	Cu(1)–O(1)–Cu(2)	104.5(3)
			Cu(1)–O(2)–Cu(2)	78.6(3)

of 2.798–3.233 Å. Due to the disorder of the ClO_4 groups, not all H-bonds could be located.

3.3. Structure comparisons

The compounds are compared in Table 4 together with a number of related dinuclear triply bridged copper(II) compounds. The molecular structures and the copper(II) chromophores of $[\text{Cu}_2(\mu\text{-O}_2\text{CCH}_3)_2(\mu\text{-OCOCH}_3)(\text{bpy})_2](\text{ClO}_4)$ (**4**) ($\tau = 0.14$ and 0.47) [1], $[\text{Cu}_2(\mu\text{-O}_2\text{CCH}_3)_2(\mu\text{-OCH}_3)$

$(\text{bpy})_2](\text{PF}_6)$ (**5**) ($\tau = 0.59$ and 0.66) [3] and $[\text{Cu}_2(\mu\text{-O}_2\text{CCH}_3)_2(\mu\text{-OCH}_2\text{CH}_3)(\text{bpy})_2](\text{PF}_6)$ (**6**) ($\tau = 0.10$ and 0.23) [3] are comparable to that of compound **1** ($\tau = 0.07$) (see Table 4). These complexes all involve two didentate carboxylato triatomic bridges and one monoatomic bridge with a variety of geometries ranging from distorted square pyramidal ($\tau = 0.07$ for **1**) to distorted trigonal bipyramidal ($\tau = 0.59, 0.66$ for **5**).

Triply bridged copper(II) dinuclear compounds are uncommon for three carboxylato ligands and also the

magnetic properties are not available as compared to the second type of complexes. Complexes **7–12** (Table 4) have one carboxylato triatomic bridge and two monoatomic bridges, comparable to those of complexes **2** and **3**. This type of complexes involves a wide range of five-coordinate geometries, from distorted square pyramidal ($\tau = 0.72$ for **12**) depending on the types of monoatomic and triatomic bridges and also the packing forces. The structures of compounds **2** ($\tau = 0.20$ and 0.16) and **3** ($\tau = 0.02$ and 0.14) show some similarity to those of $[\text{Cu}_2(\mu\text{-O}_2\text{CCH}_3)(\mu\text{-OH})-$

$(\mu\text{-OH}_2)(\text{bpy})_2](\text{ClO}_4)_2$ (**7**) ($\tau = 0.14$ and 0.25) [1], $[\text{Cu}_2(\mu\text{-O}_2\text{CCH}_2\text{CH}_3)(\mu\text{-OH})(\text{dpyam})_2](\text{ClO}_4)_2$ (**8**) ($\tau = 0.22$ and 0.43) [11], $[\text{Cu}_2(\mu\text{-O}_2\text{CH})(\mu\text{-OH})(\mu\text{-OCH}_3)(\text{dpyam})_2](\text{ClO}_4)_2$ (**9**) ($\tau = 0.65$) [5], $[\text{Cu}_2(\mu\text{-O}_2\text{CH})(\mu\text{-OH})(\mu\text{-Cl})(\text{dpyam})_2](\text{ClO}_4) \cdot 0.5\text{H}_2\text{O}$ (**10**) ($\tau = 0.67$) [5], $[\text{Cu}_2(\mu\text{-O}_2\text{CH})_2(\mu\text{-OH})(\text{dpyam})_2](\text{PF}_6)_2$ (**11**) ($\tau = 0.71$) [11] and $[\text{Cu}_2(\mu\text{-O}_2\text{CH})(\mu\text{-OH})(\mu\text{-Cl})(\text{dpyam})_2](\text{PF}_6)_2$ (**12**) ($\tau = 0.72$) [11], in which two copper(II) atoms are bridged through three different bridging ligands. The carboxylate bridges in these compounds are in the common $\kappa\text{-O}^1, \text{O}^2$ bridging mode. However, the

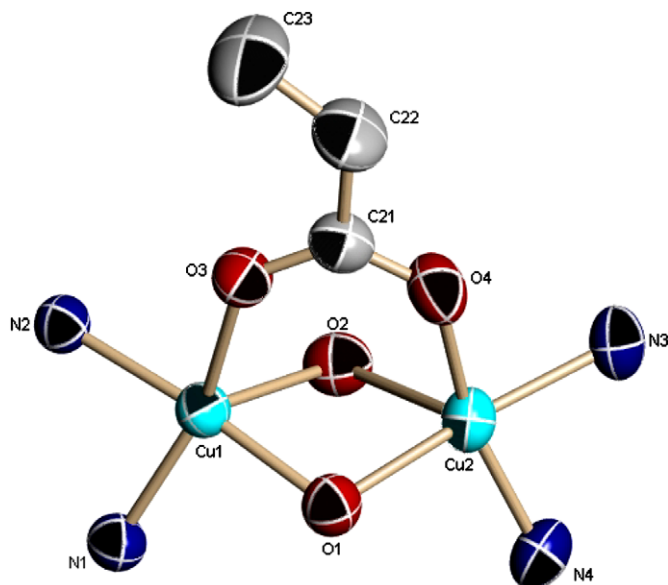


Fig. 4. The chromophore of $[\text{Cu}_2(\text{bpy})_2(\mu\text{-OH})(\mu\text{-OH}_2)(\mu\text{-O}_2\text{CCH}_2\text{CH}_3)](\text{ClO}_4)_2$ (**2**).

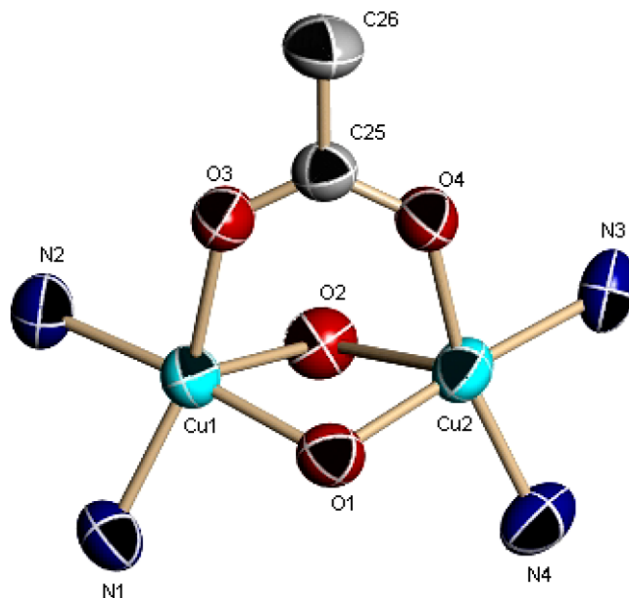


Fig. 6. The chromophore of $[\text{Cu}_2(\text{phen})_2(\mu\text{-OH})(\mu\text{-OH}_2)(\mu\text{-O}_2\text{CCH}_3)](\text{ClO}_4)_2$ (**3**).

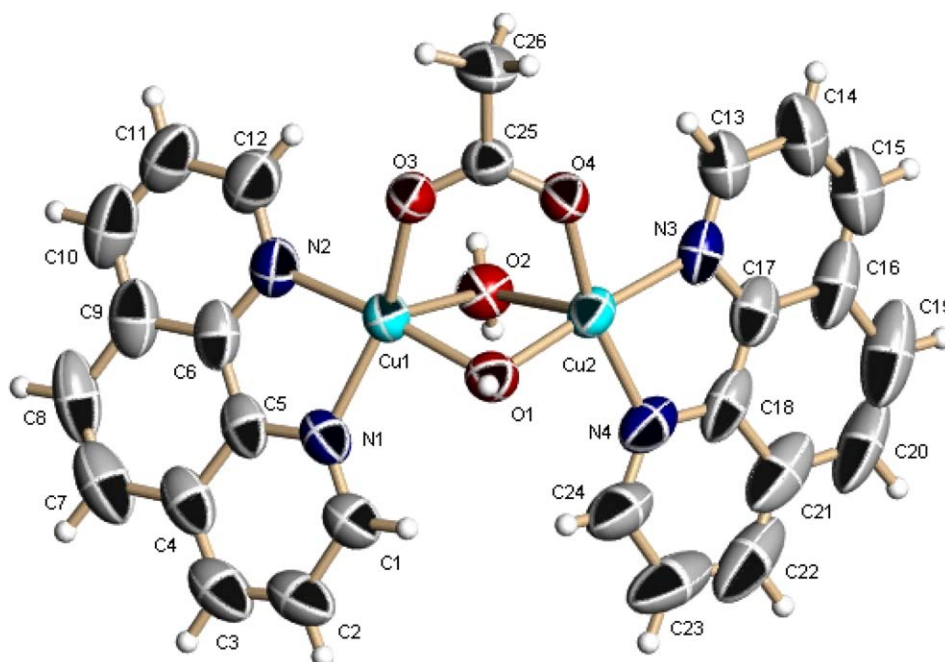


Fig. 5. ORTEP 50% probability plot of the cation in $[\text{Cu}_2(\text{phen})_2(\mu\text{-OH})(\mu\text{-OH}_2)(\mu\text{-O}_2\text{CCH}_3)](\text{ClO}_4)_2$ (**3**). The perchlorate molecules are omitted for clarity.

Table 4
Structural and magnetic data for triply bridged dinuclear copper(II) carboxylato compounds

Compound ^a	Coordination geometry ^b	τ	Chromophore	Cu...Cu	Cu–O		J (cm ^{−1})	Cu–X–Cu (Å)	References
					Axial	Equatorial			
[Cu ₂ (μ-O ₂ CCH ₃) ₂ (μ-OCOCH ₃)(dpyam) ₂](BF ₄) (1)	dist. spy.	0.07	CuN ₂ O ₂ O'	3.402	2.144	1.967–2.002	−55.9	105.0(OCOCH ₃)	this work
[Cu ₂ (μ-O ₂ CCH ₃) ₂ (μ-OCOCH ₃)(bpy) ₂](ClO ₄) (4)	dist. spy., intermediate	0.14, 0.47	CuN ₂ O ₂ O' CuN ₂ O ₂ O'	3.392	2.238 2.169	1.939–1.977 1.930–1.974	3.6	109.8(OCOCH ₃)	[1]
[Cu ₂ (μ-O ₂ CCH ₃) ₂ (μ-OMe)(bpy) ₂](PF ₆) (5)	dist. TBP	0.59, 0.66	CuN ₂ O ₃	3.093	1.922–1.931	1.933–2.099	^c	106.8(OMe)	[3]
[Cu ₂ (μ-O ₂ CCH ₃) ₂ (μ-OEt)(bpy) ₂](PF ₆) (6)	dist. spy.	0.23, 0.10	CuN ₂ O ₂ O'	3.230	2.155, 2.164	1.939–1.982	^c	112.1(OEt)	[3]
[Cu ₂ (μ-O ₂ CCH ₂ CH ₃)(μ-OH)(μ-OH ₂)(bpy) ₂](ClO ₄) ₂ (2)	dist. spy.	0.20, 0.16	CuN ₂ O ₂ O'	3.037	2.382, 2.415	1.920–2.005	148.9	104.5(OH) 78.6(OH ₂)	this work
[Cu ₂ (μ-O ₂ CCH ₃)(μ-OH)(μ-OH ₂)(phen) ₂](ClO ₄) ₂ (3)	dist. spy.	0.02, 0.14	CuN ₂ O ₂ O'	2.989	2.360, 2.375	1.933–2.020	120.0	101.3(OH) 78.3(OH ₂)	this work
[Cu ₂ (μ-O ₂ CCH ₃)(μ-OH)(μ-OH ₂)(bpy) ₂](ClO ₄) ₂ (7)	dist. spy.	0.14, 0.25	CuN ₂ O ₂ O'	3.035	2.379, 2.405	2.006–2.010	19.3	103.8(OH) 78.7(OH ₂)	[1]
[Cu ₂ (μ-O ₂ CCH ₂ CH ₃)(μ-OCOCH ₂ CH ₃)(μ-OH)(dpyam) ₂](ClO ₄) (8)	dist. spy., intermediate	0.22, 0.43	CuN ₂ O ₂ O'	3.006	2.236–2.318	1.931–1.959	24.1	101.8(OH) 86.4(OCOCH ₂ CH ₃)	[11]
[Cu ₂ (μ-O ₂ CH)(μ-OH)(μ-OMe)(dpyam) ₂](ClO ₄) (9)	dist. TBP	0.65	CuN ₂ O ₃	3.023	1.918	2.169–2.175	62.5	104.0(OH) 88.3(OMe)	[5]
[Cu ₂ (μ-O ₂ CH)(μ-OH)(μ-Cl)(dpyam) ₂](ClO ₄) · 0.5H ₂ O (10)	dist. TBP	0.67	CuN ₂ O ₂ Cl	3.036	1.916	2.158	79.1	104.8(OH) 75.6(Cl)	[5]
[Cu ₂ (μ-O ₂ CH)(μ-OCOH)(μ-OH)(dpyam) ₂](PF ₆) (11)	dist. TBP	0.71	CuN ₂ O ₃	3.113	1.934	2.144–2.200	47.8	107.2(OH) 93.1(OCOH)	[11]
[Cu ₂ (μ-O ₂ CH)(μ-OH)(μ-Cl)(dpyam) ₂](PF ₆) (12)	dist. TBP	0.72	CuN ₂ O ₂ Cl	3.061	1.918	2.183	79.7	105.8(OH) 77.3(Cl)	[11]

^a Abbreviations. bpy = 2,2'-bipyridine; dpyam = di-2-pyridylamine; phen = 1,10'-phenanthroline.

^b dist. spy. = distorted square pyramidal, dist. TBP = distorted trigonal.

^c Not given.

molecular structure and copper(II) chromophores of compounds **2** and **3** are closely related to that of compound **7**, as all of them have distortion towards the square pyramidal geometry.

3.4. Spectral characterization

The infrared spectra of compounds **2** and **3** exhibit intense bands at 1547 and 1555 cm^{-1} , respectively, corresponding to the $\nu_{\text{as}}(\text{COO}^-)$ vibration and the intense bands at 1370 and 1429 cm^{-1} , respectively, corresponding to the $\nu_{\text{s}}(\text{COO}^-)$ vibration of the didentate bridging coordination mode of the carboxylate group within a dinuclear species [5,10,11]. Owing to the presence of two different coordination modes of acetato bridges in compound **1**, two broad and strong $\nu_{\text{as}}(\text{COO}^-)$ (1627 and 1600 cm^{-1}) and $\nu_{\text{s}}(\text{COO}^-)$ (1439 and 1374 cm^{-1}) bands are observed. The bands at 1627 and 1374 cm^{-1} ($\Delta = 253 \text{ cm}^{-1}$) are assigned to the stretching modes of the monoatomic carboxylato bridges. The vibrations observed at 1600 and 1439 cm^{-1} ($\Delta = 161 \text{ cm}^{-1}$) are consistent with the triatomic carboxylato bridges [1,8,11]. Moreover, the spectra of compounds **2** and **3** show the very broad band about 3534 and 3392 cm^{-1} , respectively, which can be assigned to the bridging OH vibration of the hydroxo bridge. The broad and intense band at 1000–1081 cm^{-1} for compound **1** is assigned to the characteristic vibration of non-coordinated BF_4^- group, while the bands at 1115–1033 and 1119–1087 cm^{-1} for compounds **2** and **3**, respectively, correspond to ClO_4^- anion. The sharp band at ca. 3300 cm^{-1} for compound **1** is attributed to the presence of N–H stretching vibrations.

The reflectance spectrum of **1** displays a broad asymmetric band at 14100 cm^{-1} which is typical for Cu(II) in a slightly distorted square pyramidal environment with a small elongation in axial position, tetragonality (T) 0.925. ($T = \text{the average four-in-plane distance/the axial out-of-plane distance}$). Compounds **2** and **3** exhibit a broad band at 16860 and 16310 cm^{-1} with a lower energy shoulder at the frequencies of 14080(sh) and 13070(sh) cm^{-1} , respectively. These features are consistent with the distorted square pyramidal geometry with a much larger elongation in the axial position, $T = 0.825$ and 0.824 for **2**; and 0.835 and 0.825 for **3** and the $d_{xy}, d_{yz} \rightarrow d_{x^2-y^2}$ and $d_{xz}, d_{z^2} \rightarrow d_{x^2-y^2}$ transitions are assigned for a broad band and a lower energy shoulder, respectively [17].

3.5. EPR and magnetic properties

The X-band EPR measured on polycrystalline samples at RT and 77 K showed for compound **1** at 77 K a typical $S = 1$ triplet signal with $\Delta M_s = \pm 2$ transition band at 110 mT, and other signals at 195, 243, 335 mT and a weak shoulder at 350 mT, which can be attributed to the H_{z1} , H_{xy1} , H_{xy2} and H_{z2} signals, respectively. These values correspond to a zero-field splitting of about $D = 0.15 \text{ cm}^{-1}$ [18,19]. Also a band at 280 mT is observed which originates

most likely from the $S = 1/2$ spectrum of a mononuclear impurity. Detailed study would require EPR measurements at other frequencies, which is outside the scope of this study.

Compounds **2** and **3** show a quite different pattern of which the spectrum of compound **2** is very weak both at RT and 77 K. For both compounds only a few very broad bands are observed both at RT and 77 K, typical for $S = 1$ with a large zero field splitting. Compound **2** shows broad weak signals at around 185 and 680 mT and compound **3** shows broad signals at around 180, 525 (very weak) and 655 mT. These occurrences of other peaks at high field indicate that the axial zero-field splitting parameter D is larger than the EPR quantum (ca. 0.3 cm^{-1}) and can be estimated as $D \approx 0.4 \text{ cm}^{-1}$ [1,18,20–23]. Detailed study is not possible as the signals are too weak at 77 K, and 4 K EPR is not available.

To investigate the magnetic behaviour in more detail, we undertook magnetic susceptibility measurements from 5 to 300 K. The magnetic properties of the compounds are depicted in Figs. 7–9, for compounds **1**, **2** and **3**, respectively, in the form of μ_{eff} versus T plots for two Cu(II) ions. At 300 K the μ_{eff} is $2.40 \mu_{\text{B}}$ per 2 Cu ions for compound **1**, which is somewhat below the spin-only value calculated for two uncoupled spin $S = 1/2$ Cu(II) centres. Upon cooling, this value stays almost constant till about 60 K, where it decreases gradually to reach $0.1 \mu_{\text{B}}$ at 5 K (see Fig. 7). This magnetic behaviour is typical for antiferromagnetically coupled Cu(II) ions in a dinuclear compound.

Both compounds **2** and **3** show a very similar behaviour. At 300 K the μ_{eff} is $2.85 \mu_{\text{B}}$ per 2 Cu ions for compound **2** ($2.72 \mu_{\text{B}}$, for **3**), which agrees reasonably with the spin-only value calculated for two uncoupled spin $S = 1/2$ Cu(II) centres. Upon cooling it raises gradually to reach 3.02 and $2.88 \mu_{\text{B}}$, at around 30 K, for compounds **2** and **3**, respectively. This behaviour is typical for a ferromagnetically coupled Cu(II) dinuclear compound. Below that tem-

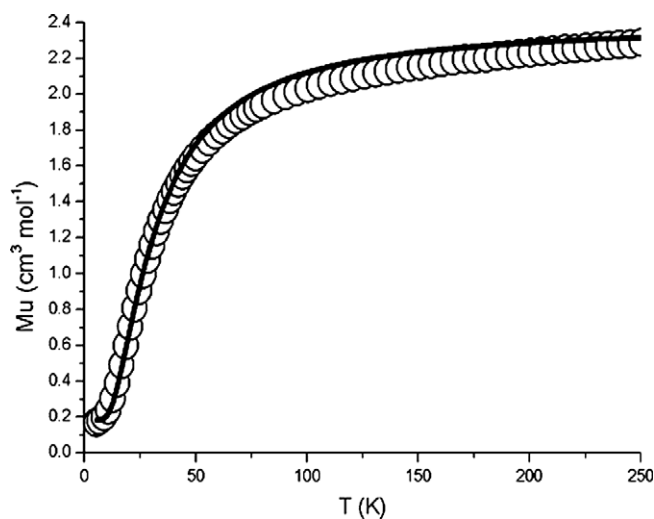


Fig. 7. A plot of the temperature dependence of μ_{eff} vs. T for compound **1**. The solid line represents the calculated curve (see text).

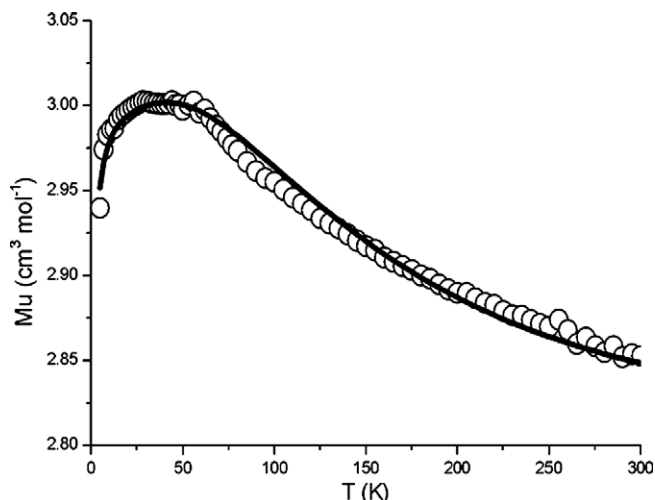


Fig. 8. A plot of the temperature dependence of μ_{eff} vs. T for compound **2**. The solid line represents the calculated curve (see text).

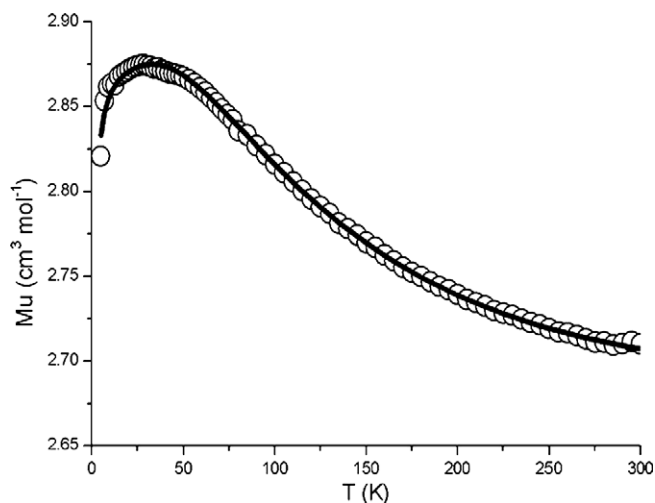


Fig. 9. A plot of the temperature dependence of μ_{eff} vs. T for compound **3**. The solid line represents the calculated curve (see text).

perature, μ_{eff} then diminishes till a value of around $2.94 \mu_{\text{B}}$ for compound **2** ($2.82 \mu_{\text{B}}$ for **3**) at 5 K for the two compounds, which may originate from intermolecular antiferromagnetic interactions, or from zero-field splitting of the $S = 1$ state of the dinuclear species. The theoretical expression for the magnetic susceptibility for two interacting $S = 1/2$ centres based on the general Hamiltonian [24] is $H_{\text{ex}} = -JS_1S_2$, in which the exchange parameter J is negative for antiferromagnetic and positive for ferromagnetic interaction. The magnetic data were fitted to the equation given in the literature for dinuclear copper compounds [24, p. 132].

$\chi_{\text{m}} = (2Ng^2\beta^2)[kT - (2zJ'/(3 + \exp(-J/kT)))]^{-1} [3 + \exp(-J/kT)]^{-1}(1 - p) + \chi_{\text{p}}p + \text{TIP}$, in which N , g , β , k and T have their usual meanings. The parameter p denotes the fraction of paramagnetic impurity in the sample and zJ'

the interaction between neighbouring dinuclear identities. A temperature independent paramagnetism (TIP) was also considered and fixed at 60×10^{-6} per copper ion. The fit was accomplished by minimisation of $R = \sum (\chi_{\text{m}} \cdot T_{\text{calc}} - \chi_{\text{m}} \cdot T_{\text{obs}})^2 / (\chi_{\text{m}} \cdot T_{\text{obs}})^2$ by least-squares procedure.

The best fit was obtained for compound **1** with the following values: $J = -55.9 \text{ cm}^{-1}$, $g = 1.98$, $zJ' = 0 \text{ cm}^{-1}$, $p = 0.05$, with a final R of 2.0×10^{-2} (see solid line in Fig. 7). For compound **2** these values are $J = 148.9 \text{ cm}^{-1}$, $g = 2.14$, $zJ' = -0.88 \text{ cm}^{-1}$, $p = 0.06$, with a final R of 9.0×10^{-4} (see solid line in Fig. 8). For compound **3** these values are $J = 120.0 \text{ cm}^{-1}$, $g = 2.05$, $zJ' = -0.82 \text{ cm}^{-1}$, $p = 0.06$, with a final R of 2.0×10^{-4} (see solid line in Fig. 9).

4. Concluding remarks

Three new triply bridged dinuclear Cu(II) compounds with three different didentate chelating ligands, dpyam, bpy and phen, are synthesized, characterized and the magnetic interaction is studied. The bridges in compound **1** are formed by three acetate molecules of which two are in a didentate and one in a monodentate fashion, compound **2** is bridged by a propionato, a hydroxo and a water molecule, while compound **3** is bridged by acetate, a hydroxo and a water molecule. The coordination geometry around each copper(II) ion is (slightly distorted) square pyramidal for all three compounds.

For planar dinuclear bis-hydroxo-bridged compounds, a correlation is known [25] between J and the Cu–O–Cu angle; an antiferromagnetic interaction was found when the Cu–O–Cu angle is larger than 97.5° , but when the Cu–O–Cu angle is smaller than 97.5° a ferromagnetic interaction would be expected [25]. In compound **1** the oxygen atom of the monodentate acetate molecule is the only bridging moiety with an angle of 105.0° , but it is located in the axial position of the square pyramid and this should be disregarded for its antiferromagnetic contribution. Therefore, an antiferromagnetic interaction in **1** is occurred via both triatomic acetato bridges which link two Cu(II) centres in an eq-eq configuration as found for the typical $\text{Cu}_2(\text{O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2$ family [24]. In Table 4, it can be observed that the geometry of compounds **1** and **4** is significantly different, a moderate antiferromagnetic interaction in compound **1** and a very weak ferromagnetic interaction in compound **4** are observed. The reason for this behaviour is quite clear, the distorted square pyramidal geometry ($\tau = 0.14$) and the intermediate five-coordinate geometry ($\tau = 0.47$) within a dinuclear unit of **4** lead to the partial overlap between the magnetic orbitals which usually contribute to a weak ferromagnetic interaction and are confirmed by a weak ferromagnetic interaction of the corresponding compound **8** (Table 4). Of course some differences are present in the geometry (in some cases, a distorted trigonal bipyramidal geometry with d_{z^2} magnetic orbitals) and in the ligand which also has an influence on the geometry

and therefore on the magnetic orbitals and consequently on the superexchange properties of the bridging atom(s) [26,27]. Also it is known that a change in electron density of the magnetic orbital can have a pronounced effect on the sign and magnitude of a magnetic exchange interaction [28,29].

Compounds **2**, **3** and **7** are almost similar in geometry, but the antiferromagnetic interaction energies differ from 148.9, 120.0 cm⁻¹ (for compounds **2** and **3**) and 19.3 cm⁻¹ for compound **7** [1]. The reason for this difference is not really clear as the Cu–O–Cu angles are 104.5°, 101.3° and 103.8°, respectively. However, it must be noted that the magnetic susceptibility in compound **7** was measured from 5 to 200 K and the Bleaney–Bowers fit was accomplished from 50 to 200 K (see Fig. 8 in [1]). For a real comparison, compound **7** should be remeasured in the same conditions as compounds **2** and **3**. All three compounds clearly show that, depending on the used ligand and co-ligands, a large variety of carboxylate-bridged Cu(II) compounds exist with interesting, new magnetic properties. Future studies will focus on variations in both the ligands and the carboxylates.

5. Supplementary material

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary Publication Nos. CCDC-600945, 600945 and 600947 for compounds **1**, **2** and **3**, respectively. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (internat.) +44 1223 336 033, e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgements

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Structural diversities and spectroscopic properties of bis and tris(1,10-phenanthroline)copper(II) complexes

Sujittra Youngme^{a,*}, Nanthawat Wannarit^a, Chaveng Pakawatchai^b, Narongsak Chaichit^c,
Eakasit Somsook^d, Urho Turpeinen^e, Ilpo Mutikainen^e

^a Department of Chemistry, Faculty of Science, Khon Kaen University, Khon Kaen 40002, Thailand

^b Department of Chemistry, Faculty of Science, Prince of Songkla University, Hatyai, Songkla 90112, Thailand

^c Department of Physics, Faculty of Science and Technology, Thammasat University Rangsit, Pathumthani 12121, Thailand

^d Department of Chemistry, Faculty of Science, Mahidol University, Bangkok 10400, Thailand

^e Laboratory of Inorganic Chemistry, Department of Chemistry, P.O. Box 55 (A.I. Virtasen aukio 1), 00014 University of Helsinki, Finland

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Abstract

The crystal structures of four new compounds containing bis and tris(1,10-phenanthroline)copper(II) complex units have been determined by X-ray crystallographic methods; $[\text{Cu}(\text{phen})_3](\text{S}_4\text{O}_6)(\text{S}_8)$ (**1**), $[\text{Cu}(\text{phen})_3](\text{BF}_4)_2$ (**2**), $[\text{Cu}(\text{phen})_2(\text{OS}_2\text{O}_7)]$ (**3**) and $[\text{Cu}(\text{phen})_2(\text{FBF}_3)](\text{BF}_4)$ (**4**). The crystal structures of **1** and **2** are composed of discrete $[\text{Cu}(\text{phen})_3]^{2+}$ cations, $(\text{S}_4\text{O}_6)^{2-}$ and BF_4^- anions. The Cu(II) ion is octahedrally coordinated by the three phen ligands. As a consequence of the Jahn-Teller effect, the two axial Cu–N bonds are longer than the equatorial Cu–N bonds and the CuN_6 chromophores appear to be elongated rhombic octahedral with tetragonalities of 0.892 and 0.886 for **1** and **2**, respectively. Complexes **3** and **4** consist of mononuclear units, the 5-coordinate Cu(II) environment being distorted square pyramidal ($\tau = 0.31$) and distorted trigonal bipyramidal ($\tau = 0.66$), respectively. The unidentate $\text{S}_2\text{O}_8^{2-}$ anion in **3** occupies the axial position, while the unidentate BF_4^- anion in **4** is coordinated in the trigonal plane. The crystal structures and their electronic properties including IR and EPR spectra are discussed and compared to other relevant complexes based on the Jahn-Teller effect.

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1. Introduction

We have been interested in the coordination properties of some sulfur oxoanions (such as SO_4^{2-} , $\text{S}_2\text{O}_3^{2-}$, $\text{S}_2\text{O}_6^{2-}$, $\text{S}_3\text{O}_6^{2-}$, $\text{S}_4\text{O}_6^{2-}$ and $\text{S}_2\text{O}_8^{2-}$) and some weak or non-coordinating anions (such as BF_4^- , ClO_4^- or PF_6^-) with the equivalent didentate chelate ligands. In this context, the reactions between Cu^{2+} and $\text{S}_2\text{O}_3^{2-}$ in the presence of phenanthroline (phen) and di-2-pyridylamine (dpyam) have been found to be very prolific, with structurally diverse compounds being generated, depending on the reaction

conditions and the nature of the chelate ligands. In particular, when the conditions favour the redox reaction between the thiosulfate or tetrathionate with the metal ion, compounds containing the $\text{S}_4\text{O}_6^{2-}$ and SO_4^{2-} [1] anions were isolated for reaction containing phen and dpyam, respectively [2]. These oxoanions can adopt a variety of different coordination modes, namely monodentate, chelate [3], bridging polymeric (along or across the anion) or non-coordinating counter anion, giving rise to a variety of different geometries in metal complexes with two or three equivalent chelate ligands [4].

Monomeric tris-chelate copper(II) complexes involving *N,N* donors are uncommon due to pronounced Jahn-Teller distortions. The examples of tris-chelated Cu(II) complexes of neutral *N,N*-donors are limited. The examples [5–7] are

* Corresponding author. Fax: +66 43 202373.

E-mail address: sujittra@kku.ac.th (S. Youngme).

$[\text{Cu}(\text{en})_3]^{2+}$ (en = 1,2-ethanediamine), $[\text{Cu}(\text{OMPA})_3]^{2+}$ (OMPA = octamethylpyrophosphoramidate), $[\text{Cu}(\text{bpy})_3]^{2+}$ (bpy = 2,2'-bipyridyl) and $[\text{Cu}(\text{phen})_3]^{2+}$ (phen = 1,10-phenanthroline). Within the copper chromophore, complexes containing three equivalent didentate chelate ligands, $[\text{Cu}(\text{en})_3]\text{SO}_4$ [5] and $[\text{Cu}(\text{OMPA})_3](\text{ClO}_4)_2$ [6], have been found to involve D_3 site symmetry with six apparently equivalent bonds as a consequence of the dynamic Jahn-Teller effect [8–12] and show partially statically and dynamically distorted CuN_6 octahedra for the lower symmetry C_2 or C_1 complexes. The most likely form of the vibronically induced distortion or dynamic Jahn-Teller distortion consistent with C_2 symmetry is the elongated tetragonal distortion [13], producing the most common type of static stereochemistry of the copper(II) ion, namely elongated rhombic or tetragonal octahedral.

In cases of copper(II) complexes with two equivalent didentate chelate ligands and some sulfur oxoanions including those of the ClO_4^- , BF_4^- and PF_6^- anions, the structures displayed four-, five- or six-coordinated chromophores with the monodentate, chelate, didentate polymeric bridge (along the anion) or non-coordinating natures of these anions depending on the nature of the chelate ligands. The examples are $[\text{Cu}(\text{dpyam})_2](\text{ClO}_4)_2$ [14], $[\text{Cu}(\text{dpyam})_2](\text{BF}_4)_2$ [15], $[\text{Cu}(\text{dpyam})_2](\text{PF}_6)_2$ [present work], $[\text{Cu}(\text{bpy})_2(\text{OH}_2)](\text{S}_2\text{O}_6)$ [16], $[\text{Cu}(\text{dpyam})_2(\text{OH}_2)](\text{S}_4\text{O}_6)$ [17], $[\text{Cu}(\text{bpy})_2(\text{O}_2\text{ClO}_2)](\text{ClO}_4)$ [18], $[\text{Cu}(\text{bpy})_2(\text{F}_2\text{BF}_2)](\text{BF}_4)$ [18,19], $[\text{Cu}(\text{bpy} \text{ or } \text{phen})_2(\text{OS}_4\text{O}_7)]$ [20], $[\text{Cu}(\text{bpy})_2(\text{S}_3\text{O}_6)]$ [20,21] and $[\text{Cu}(\text{bpy})_2(\text{OS}_2\text{O}_7)]\text{H}_2\text{O}$ [16]. In order to continue the investigation on the coordination properties and the correlation of the stereochemistry and electronic properties of the tris and bis-chelate copper(II) complexes with these anions, the structures and electronic properties of two new tris-chelate complexes, $[\text{Cu}(\text{phen})_3](\text{S}_4\text{O}_6)(\text{S}_8)$ (**1**) and $[\text{Cu}(\text{phen})_3](\text{BF}_4)_2$ (**2**), and two new bis-chelate complexes, $[\text{Cu}(\text{phen})_2(\text{OS}_2\text{O}_7)]$ (**3**) and $[\text{Cu}(\text{phen})_2(\text{FBF}_3)](\text{BF}_4)$ (**4**), are now reported and discussed in comparison with other relevant complexes. The latter two complexes display some differences in Cu(II) environment and binding modes of $\text{S}_2\text{O}_8^{2-}$ and BF_4^- anions.

2. Experimental

2.1. General

The ligand 1,10-phenanthroline and all reagents are commercial grade materials and were used without further purification. Elemental analyses (C, H, N) were determined on a Perkin-Elmer PE 2400 CHNS Analyzer.

IR spectra were recorded on a Perkin-Elmer Spectrum One FT-IR spectrophotometer as KBr discs in the 4000–450 cm^{-1} spectral range. Solid-state (diffuse reflectance) electronic spectra were measured as polycrystalline samples on a Perkin-Elmer Lambda2S spectrophotometer, within the range 8000–18000 cm^{-1} . ESR spectra were recorded using a Bruker ESR-300 X-band instrument operating at room temperature with DPPH ($g = 2.0036$) as a reference.

2.2. Syntheses of the compounds

2.2.1. $[\text{Cu}(\text{phen})_3](\text{S}_4\text{O}_6)(\text{S}_8)$ (**1**)

A hot DMF solution (10 ml) of phen (0.198 g, 1.0 mmol) was added to a warm aqueous solution (10 ml) of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (0.241 g, 1.0 mmol). Then an aqueous solution (10 ml) of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ (0.248 g, 1.0 mmol) was added to the mixture, yielding a brown solution. After a month, blue polygon-shaped crystals of compound **1** were obtained which were filtered off, washed with the mother liquid and air-dried. Yield ca. 60%. $\text{C}_{36}\text{H}_{24}\text{CuN}_6\text{O}_{18}$: *Anal.* Calc. C, 45.20; H, 2.53; N, 8.79. Found: C, 45.50; H, 2.61; N, 8.84%.

2.2.2. $[\text{Cu}(\text{phen})_3](\text{BF}_4)_2$ (**2**)

This compound was prepared by adding a hot ethanol solution (10 ml) of phen (0.198 g, 1.0 mmol), to a warm aqueous solution (5 ml) of $\text{Cu}(\text{BF}_4)_2 \cdot n\text{H}_2\text{O}$ (0.118 g, 0.5 mmol). The resulting blue solution was allowed to evaporate at room temperature. After two weeks, needle blue crystals of compound **2** were obtained which were filtered off, washed with the mother liquid and air-dried. Yield ca. 85%. $\text{C}_{36}\text{H}_{24}\text{CuF}_8\text{N}_6\text{B}_2$: *Anal.* Calc. C, 55.59; H, 3.11; N, 10.81. Found: C, 55.62; H, 3.25; N, 10.67%.

2.2.3. $[\text{Cu}(\text{phen})_2(\text{OS}_2\text{O}_7)]$ (**3**)

Compound **3** was prepared by adding an aqueous solution (10 ml) of $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot n\text{H}_2\text{O}$ (0.091 g, 0.5 mmol) to a solution of phen (0.198 g, 1.0 mmol) in acetonitrile (20 ml), then an aqueous solution (5 ml) of $\text{K}_2\text{S}_2\text{O}_8$ (0.109 g, 1.0 mmol) was added, yielding a blue solution. The solution was allowed to evaporate at room temperature. After a week, bluish green rod crystals of compound **3** were formed. They were filtered off, washed with the mother liquid and air-dried. Yield ca. 92%. $\text{C}_{24}\text{H}_{16}\text{S}_2\text{CuN}_4\text{O}_8$: *Anal.* Calc. C, 46.79; H, 2.61; N, 9.10. Found: C, 46.45; H, 2.54; N, 9.14%.

2.2.4. $[\text{Cu}(\text{phen})_2(\text{FBF}_3)](\text{BF}_4)$ (**4**)

Compound **4** was prepared by adding an aqueous solution (20 ml) of $\text{Cu}(\text{BF}_4)_2 \cdot n\text{H}_2\text{O}$ (0.236 g, 1.0 mmol) to a solution of phen (0.346 g, 2.5 mmol) in ethanol (20 ml), yielding a blue solution. The solution was allowed to evaporate at room temperature. After a week, bluish green crystals of compound **4** were formed. They were filtered off, washed with the mother liquid and air-dried. Yield ca. 74%. $\text{C}_{24}\text{H}_{16}\text{B}_2\text{CuN}_4\text{F}_8$: *Anal.* Calc. C, 48.25; H, 2.70; N, 9.38. Found: C, 48.18; H, 2.61; N, 9.45%.

2.3. Crystallography

The X-ray single-crystal data were collected at 293 K for compounds **1–4** on a 4K Bruker SMART APEX CCD area-detector diffractometer (rotating anode, graphite-monochromated Mo $\text{K}\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$) using the SMART program [22]. Raw data frame integration was performed with SAINT [23], which also applied correction

for Lorentz and polarization effects. An empirical absorption correction using the SADABS [24] program was applied, which resulted in transmission coefficients ranging from 1.000 to 0.733 for **1**, 1.000 to 0.739 for **2**, 1.000 to 0.768 for **3** and 1.000 to 0.740 for **4**.

The structures were solved by direct methods and refined by the full matrix least-squares method on $(F_{\text{obs}})^2$ with anisotropic thermal parameters for all non-hydrogen atoms, except disordered F atoms of the BF_4^- groups in **2**, using the SHELXTL-PC V 6.12 software package. For the structure determination of compound **1**, the sulfur atoms of the S_8 group showed disorder; the occupancies of the disordered positions were initially refined and later fixed at 0.50 and 0.50. The two F atoms of each BF_4^- group in **2** showed disorder, with occupancies of 0.5. All hydrogen atoms of the phen ligand in **1** were fixed and allowed to ride on the attached atoms, while those of compounds **2–4** were located geometrically and refined isotropically. The molecular structure pictures were created by using the SHELXTL-PC package [25]. The crystal and refinement details for compounds **1–4** are listed in Table 1.

3. Results and discussion

3.1. Description of $[\text{Cu}(\text{phen})_3](\text{S}_4\text{O}_6)(\text{S}_8)$ (**1**) and $[\text{Cu}(\text{phen})_3](\text{BF}_4)_2$ (**2**)

The asymmetric unit of complexes **1** and **2** involves $[\text{Cu}(\text{phen})_3]^{2+}$ cations and $\text{S}_4\text{O}_6^{2-}$ and BF_4^- anions, respec-

tively. In addition, **1** has S_8 molecules in the lattice. The ORTEP views of the asymmetric units of **1** and **2** are shown in Fig. 1, together with the numbering scheme. Selected bond distances and angles are listed in Table 2. The cationic species $[\text{Cu}(\text{phen})_3]^{2+}$ in **1** and **2** are similar in stereochemistry, in which the copper(II) ion is six-coordinated by six nitrogen atoms from three phenanthroline ligands. The coordination geometry around the copper ion can be described as elongated rhombic octahedral with four equatorial Cu–N bond distances being markedly different in the case of **1** (2.026(3) to 2.115(3) Å, $\Delta N_{\text{in}} = 0.089(3)$ Å) as compared to those of **2** (2.031(3) to 2.054(3) Å, $\Delta N_{\text{in}} = 0.023(3)$ Å), with the remaining two nitrogens occupying the apical sites at significantly larger distances (2.295(4) and 2.328(4) Å for **1**; 2.269(3) and 2.346(4) Å for **2**). This leads to a slight difference in tetragonality (T), 0.892 for **1** and 0.886 for **2** ($T = \text{the average four-in-plane distance/the axial out-of-plane distance}$ [26]), the tetragonality increasing with increasing in-plane bond distances. Compound **1** has a high ΔN_{in} value of 0.089 Å, corresponding to a high in-plane rhombic distortion, and there is very little in-plane rhombic distortion in **2**, attributed to a low ΔN_{in} value of 0.023 Å. The basal CuN_4 planes of both compounds are slightly twisted, with dihedral angles ($\text{CuN}_2/\text{CuN}_2$) of $20.4(1)^\circ$ for **1** and $19.3(1)^\circ$ for **2**. The phenanthroline moieties do not display any unusual features with regard to bond lengths and angles in either of the two compounds studied compared with the free molecule [27]. However, they do exhibit meaningful deviations from

Table 1
Crystal and refinement data for complexes **1**, **2**, **3** and **4**

Complex	1	2	3	4
Molecular formula	$[\text{Cu}(\text{phen})_3](\text{S}_4\text{O}_6)(\text{S}_8)$	$[\text{Cu}(\text{phen})_3](\text{BF}_4)_2$	$[\text{Cu}(\text{phen})_2(\text{OS}_2\text{O}_7)]$	$[\text{Cu}(\text{phen})_2(\text{FBF}_3)](\text{BF}_4)$
Molecular weight	956.63	777.77	616.07	597.57
T/K	293(2)	293(2)	293(2)	293(2)
Crystal system	monoclinic	monoclinic	triclinic	triclinic
Space group	$P2(1)/n$	$P2(1)/n$	$P\bar{1}$	$P\bar{1}$
a (Å)	17.1531(9)	9.3179(5)	7.6058(14)	7.4427(2)
b (Å)	13.3857(7)	30.0654(17)	9.6820(18)	10.8338(3)
c (Å)	18.7461(10)	12.8879(7)	15.577(3)	16.1079(3)
α (°)	90.0000	90.0000	79.244(3)	98.8740(10)
β (°)	114.1690(10)	110.4250(10)	81.927(3)	102.8510(10)
γ (°)	90.0000	90.0000	83.155(3)	105.7510(10)
V (Å ³)	3926.9(4)	3383.5(3)	1168.1(3)	1186.43(5)
Z	4	4	2	2
D_c (g cm ^{−3})	1.618	1.527	1.752	1.673
μ/mm^{-1}	1.037	0.727	1.176	1.006
$F(000)$	1948	1572	626	598
Crystal size/mm	$0.25 \times 0.14 \times 0.11$	$0.38 \times 0.23 \times 0.13$	$0.28 \times 0.12 \times 0.03$	$0.38 \times 0.23 \times 0.13$
Number of reflection collected	32558	29647	10356	8932
Number of unique reflections $[R_{\text{int}}]$	8606 [0.0492]	8137 [0.0534]	5404 [0.0256]	6495 [0.0150]
Data/restraints/parameters	8606/12/646	8137/0/647	5404/0/418	6495/0/416
Goodness-of-fit	1.048	1.049	1.050	1.072
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0677$, $wR_2 = 0.1526$	$R_1 = 0.0663$, $wR_2 = 0.1325$	$R_1 = 0.0502$, $wR_2 = 0.1012$	$R_1 = 0.0526$, $wR_2 = 0.1176$
R indices (all data)	$R_1 = 0.0962$, $wR_2 = 0.1676$	$R_1 = 0.1185$, $wR_2 = 0.1529$	$R_1 = 0.0734$, $wR_2 = 0.1103$	$R_1 = 0.0734$, $wR_2 = 0.1308$
Largest difference peak and hole (e Å ^{−3})	0.814, −0.523	0.319, −0.308	0.503, −0.351	0.474, −0.620

$$R = \sum \|F_o\| - \|F_c\| / \sum \|F_o\|, R_w = [\sum w\{|F_o\| - \|F_c\|\}^2 / \sum w\|F_o\|]^2 / 2.$$

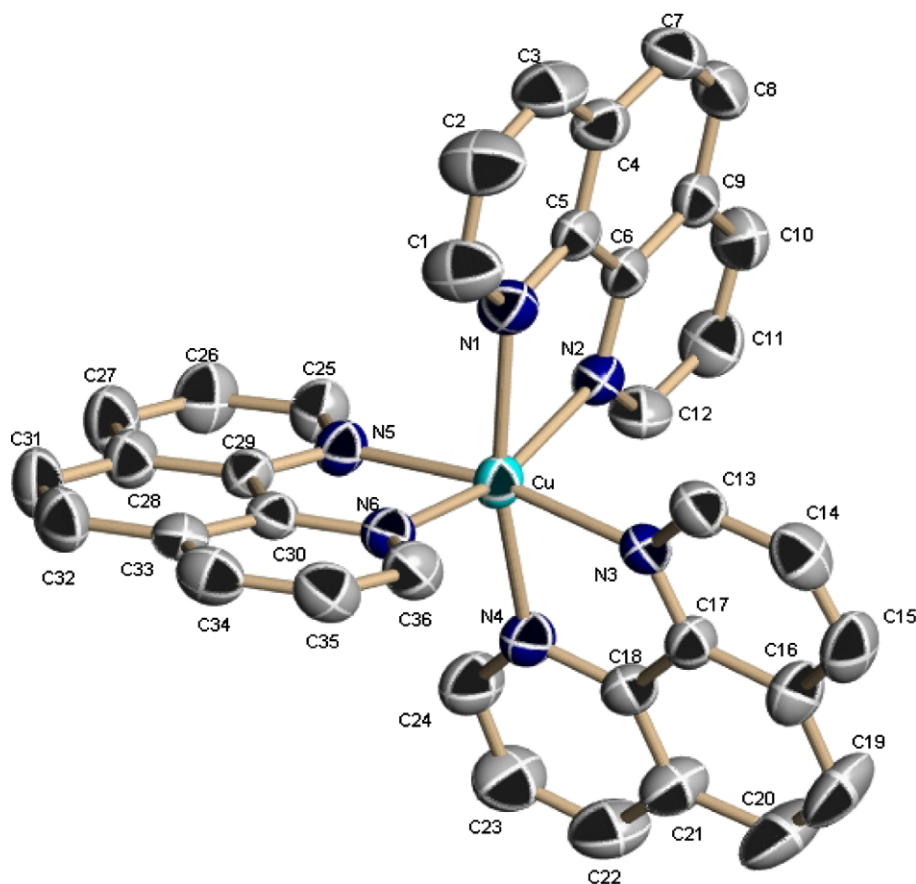


Fig. 1. The representative structure of $[\text{Cu}(\text{phen})_3]^{2+}$ in $[\text{Cu}(\text{phen})_3](\text{S}_4\text{O}_6)(\text{S}_8)$ (**1**) and $[\text{Cu}(\text{phen})_3](\text{BF}_4)_2$ (**2**). Hydrogen atoms are omitted for clarity.

Table 2

Selected bond lengths (Å) and angles (°) with e.s.d.s. in parentheses of $[\text{Cu}(\text{phen})_3](\text{S}_4\text{O}_6)(\text{S}_8)$ (**1**) and $[\text{Cu}(\text{phen})_3](\text{BF}_4)_2$ (**2**)

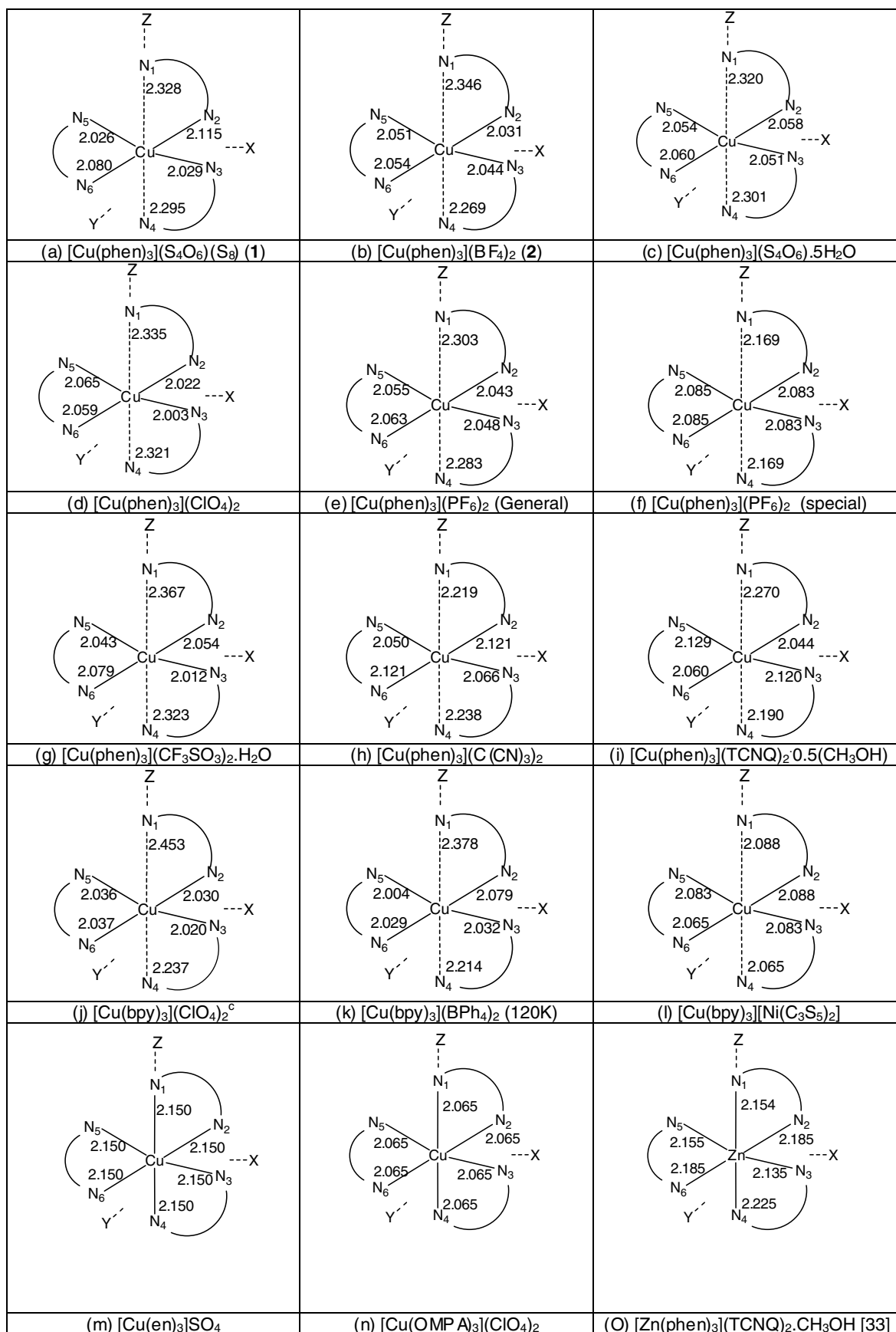
	1	2
Cu–N(1)	2.328(4)	2.346(3)
Cu–N(2)	2.115(3)	2.031(3)
Cu–N(3)	2.029(3)	2.044(3)
Cu–N(4)	2.295(4)	2.269(3)
Cu–N(5)	2.026(3)	2.051(3)
Cu–N(6)	2.080(3)	2.054(3)
N(1)–Cu–N(2)	75.8(1)	76.4(1)
N(1)–Cu–N(3)	97.1(1)	103.1(1)
N(1)–Cu–N(4)	167.0(1)	178.6(1)
N(1)–Cu–N(5)	93.8(1)	87.1(1)
N(1)–Cu–N(6)	87.2(1)	87.0(1)
N(2)–Cu–N(3)	92.5(1)	91.7(1)
N(2)–Cu–N(4)	92.4(1)	102.5(1)
N(2)–Cu–N(5)	95.4(1)	163.3(1)
N(2)–Cu–N(6)	162.4(1)	95.8(1)
N(3)–Cu–N(4)	97.7(1)	77.6(1)
N(3)–Cu–N(5)	167.9(1)	94.1(1)
N(3)–Cu–N(6)	94.2(1)	168.6(1)
N(4)–Cu–N(5)	92.7(1)	94.1(1)
N(4)–Cu–N(6)	105.0(1)	92.3(1)
N(5)–Cu–N(6)	81.0(1)	81.1(1)

Table 3

Selected bond lengths (Å) and angles (°) with e.s.d.s. in parentheses of $[\text{Cu}(\text{phen})_2(\text{OS}_2\text{O}_7)]$ (**3**) and $[\text{Cu}(\text{phen})_2(\text{F}_3\text{BF}_3)](\text{BF}_4)$ (**4**)

	3	4
Cu–N(1)	2.027(3)	2.060(2)
Cu–N(2)	2.002(2)	1.999(2)
Cu–N(3)	1.985(2)	2.078(2)
Cu–N(4)	2.034(3)	2.019(2)
Cu–X(1)	2.353(2)	2.184(2)
Cu–X(2)	3.182(2)	3.110(2)
N(1)–Cu–N(2)	82.4(1)	81.8(1)
N(1)–Cu–N(3)	100.2(1)	137.5(1)
N(1)–Cu–N(4)	148.6(1)	100.1(1)
N(2)–Cu–N(3)	167.0(1)	98.5(1)
N(2)–Cu–N(4)	102.1(1)	177.0(1)
N(3)–Cu–N(4)	82.4(1)	81.7(1)
X(1)–Cu–N(1)	109.4(1)	122.7(1)
X(1)–Cu–N(2)	84.5(1)	89.3(1)
X(1)–Cu–N(3)	82.7(1)	99.8(1)
X(1)–Cu–N(4)	101.9(1)	87.7(1)
X(2)–Cu–N(1)	79.0(1)	68.3(1)
X(2)–Cu–N(2)	88.5(1)	75.6(1)
X(2)–Cu–N(3)	104.5(1)	70.7(1)
X(2)–Cu–N(4)	70.1(1)	107.3(1)
X(1)–Cu–X(2)	168.1(1)	160.3(1)

X = O and F for **3** and **4**, respectively.

Fig. 2. Comparison of [M(phen)₃]²⁺ coordination geometries.

planarity, as measured by the dihedral angle between opposite pyridine groups [2.3(1)°, 3.0(1)° and 3.8(1)° for **1** and 2.4(1)°, 3.9(1)° and 1.3(1)° for **2**]. The angles between the least-square phenanthroline planes are [phen(N(1)–N(2))–phen(N(3)–N(4))] = 85.9(1)°, [phen(N(1)–N(2))–phen(N(5)–N(6))] = 82.3(1)° and [phen(N(3)–N(4))–phen(N(5)–N(6))] = 68.4(1)° for **1** and [phen(N(1)–N(2))–phen(N(3)–N(4))] = 87.3(1)°, [phen(N(1)–N(2))–phen(N(5)–N(6))] = 75.1(1)° and [phen(N(3)–N(4))–phen(N(5)–N(6))] = 81.4(1)° for **2** (See Table 3).

Complexes **1** and **2** are the most common type of tris-chelate copper(II) complexes with three equivalent ligands. The appearance of regular CuN₆ or CuO₆ are rare and are found in few complexes: [Cu(en)₃](SO₄) [5], K₂Pb[Cu(NO₂)₆] [28] and [Cu(OMPA)₃](ClO₄)₂ [6] in which their Cu(II) chromophore has either *D*₃ or *T*_d site symmetries, in apparent violation of the Jahn-Teller theorem due to the dynamic Jahn-Teller effect. Complexes **1** and **2** exhibit lower symmetry of *C*₁, distorted from the parent dynamic Jahn-Teller complex *D*₃ symmetry, and produce the most common type of static stereochemistry (*T* < 0.9) [26], an elongated rhombic octahedron. The elongated octahedral CuN₆ chromophores in **1** and **2** are somewhat different; **1** is much more rhombic and only a few examples have been observed with this feature, Fig. 2h and i. This can be rationalized using the approximate forms of the *Q_e* and *Q_θ* components of the JT active e vibration of a trigonal tris-chelate [Cu(chelate)₃]²⁺ chromophore with *D*₃ symmetry and a ²E electronic ground state and *a*_{2u} [12], as shown in Fig. 3. For both compounds a linear combination of the separate *Q_e* and *Q_θ* components of the JT active e vibration is in operation for which the *Q_e* component in **1** is big when compared to that of **2**. The *Q_e* component can introduce a rhombic distortion of the CuN₆ chromophore, although the component itself is small as compared to *Q_θ*. A distortion along the *Q_θ* component results in a tetragonally distorted CuN₆ octahedron for both compounds. In addition, the molecule of both compounds distorts along the *a*_{2u} coordinate, resulting in the unequivalent Cu–N_{ax} bond distances. The most relevant complexes to **1** and **2** are

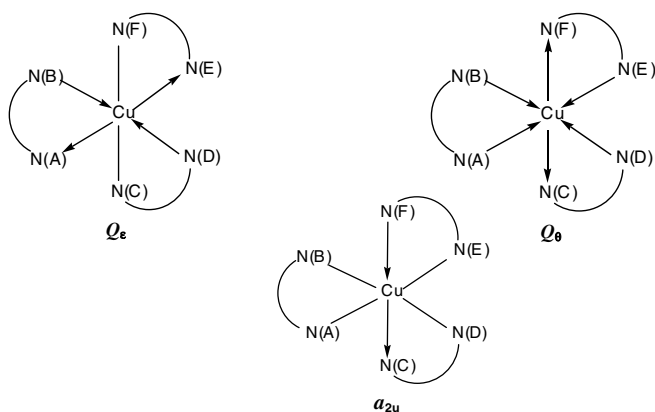


Fig. 3. The approximate forms of *Q_e* and *Q_θ* components of the active JT e vibration of the trigonal tris-chelate [Cu(chelate)₃]²⁺ chromophore. *D*₃ symmetry: chelate = (N–N) or (O–O), and *a*_{2u}.

found in the elongated rhombic octahedral complexes [Cu(phen)₃]X₂ where X = (S₄O₆^{2−})_{0.5} · 5H₂O [2], C(CN)₃[−] [29], ClO₄[−] [30], CF₃SO₃[−] · H₂O [31], PF₆[−] [32] and TCNQ[−] · (CH₃OH)_{0.5} [33]; [Cu(bipy)₃](ClO₄)₂ [34–36], [Cu(bipy)₃](BPh₄)₂ [3], [Cu(bpy)₃][Ni(C₃S₅)₂] [37] and {C₁₄H₁₉N₂}[Cu(hfacac)₃] [38]; the copper(II) chromophores are compared in Table 4 and Fig. 2.

The lattice of compound **1** is stabilized by hydrogen bonding between the amine-C and O(S₄O₆^{2−}) (C...O distances 3.030(1)–3.367(2) Å). For compound **2**, the lattice is stabilized by hydrogen bonding between the amine-C and F(BF₄[−]) (C...F distances 3.094(1)–3.321(2) Å).

3.2. Description of [Cu(phen)₂(OS₂O₇)] (**3**) and [Cu(phen)₂(FBF₃)](BF₄) (**4**)

The structures of **3** and **4** consist of chains of [Cu(phen)₂(OS₂O₇)] and [Cu(phen)₂(FBF₃)]⁺ units, parallel to an axis, respectively with uncoordinated, disordered BF₄[−] anions for **4**. The copper(II) ions are linked into infinite chains by the asymmetrically bridging peroxodisulfato groups (Cu–O 2.353(2), Cu–O' 3.182(2) Å) in **3** across the anion, and the asymmetrically bridging tetrafluoroborate groups (Cu–F 2.184(2), Cu–F' 3.110(2) Å) in **4**. However, the sixth axial coordination sites of the bridging S₂O₈^{2−} in **3** and BF₄[−] in **4** are too long to be considered even as semi-coordination to the Cu(II) ion, 3.182(2) and 3.110(2) Å for **3** and **4**, respectively. Consequently, the local molecular structure of both compounds, Figs. 4 and 5, involves five-coordinate CuN₄O and CuN₄F chromophores, which can be best described as having a distorted square pyramidal geometry with *τ* = 0.31 for **3** and a distorted trigonal bipyramidal geometry with *τ* = 0.66 for **4** (*τ* = (β − α)/60, *τ* = 0 for square pyramid and *τ* = 1 for trigonal bipyramidal) [39]. In **3** the equatorial Cu–N distances are not significantly different, ranging from 1.985(2) to 2.034(3) Å. The axial position is occupied by an O atom of the peroxodisulfate at 2.353(2) Å. The CuN₄ chromophore is non-planar with a marked tetrahedral twist of 36.0(1)°. The Cu atom lies above the basal CuN₄ plane, 0.162(1) Å toward the O atom of peroxodisulfate. The Cu...Cu distance is 7.540(3) Å. The bonding parameters for the S₂O₈ ligand are very close to those found for a previously reported coordinated peroxodisulfate group [18]. The bond lengths in the terminal SO₃ groups are 1.415(3)–1.440(3) Å, the longest, S(1)–O(1) = 1.440(3) Å, is significantly longer than the rest, consistent with the involvement of O(1) in semi-coordination to the Cu(II) atom at 2.353(2) Å [40]. The lattice of compound **3** is stabilized by hydrogen bonding between the amine-C and OS₂O₈^{2−} (C...O distances 3.137(1)–3.444(2) Å) and a very weak interaction between the Cu atom and O' atom of the neighbouring S₂O₈^{2−} group (Cu–O', 3.182(2) Å).

In the case of **4**, the local molecular structure involves a five-coordinate CuN₄F chromophore with a distorted trigonal bipyramidal geometry, *τ* = 0.66, Fig. 5. The out of trigonal plane Cu–N(2) and Cu–N(4) distances are only just

Table 4
Structural data and electronic spectra of tris(chelate)copper(II) complexes

Complex	Cu–N1/Å (ax.)	Cu–N4/Å (ax.)	Cu–N2/Å (eq.)	Cu–N3/Å (eq.)	Cu–N5/Å (eq.)	Cu–N6/Å (eq.)	T^e	Band maxima (kK) ^f	Polycrystalline e.s.r. spectrum			Reference
									g_1	g_2	g_3	
[Cu(phen) ₃](S ₄ O ₆)(S ₈) (1)	2.328(4)	2.295(4)	2.115(3)	2.029(3)	2.026(3)	2.080(3)	0.892	14.57, 8.63		2.108 ^h		this work
[Cu(phen) ₃](BF ₄) ₂ (2)	2.346(3)	2.269(3)	2.031(3)	2.044(3)	2.051(3)	2.054(3)	0.886	14.86, 8.62		2.098 ^h		this work
[Cu(phen) ₃](S ₄ O ₆) · 5H ₂ O	2.320(4)	2.301(4)	2.058(4)	2.051(4)	2.054(4)	2.060(4)	0.890	15.74, 10.66	2.310		2.054	[2]
[Cu(phen) ₃](ClO ₄) ₂	2.335(12)	2.321(11)	2.022(13)	2.003(13)	2.065(12)	2.059(14)	0.875	14.23, 10.63		2.083 ^h		[30]
[Cu(phen) ₃](PF ₆) ₂ (general)	2.303(9)	2.283(10)	2.043(9)	2.048(9)	2.055(9)	2.063(10)	0.895	14.97, 7.73 ^g				[32]
[Cu(phen) ₃](PF ₆) ₂ (special)	2.169(10)	2.169(10)	2.083(11)	2.083(11)	2.085(10)	2.085(10)	0.961					[32]
[Cu(phen) ₃](CF ₃ SO ₃) ₂ · H ₂ O	2.367(3)	2.323(3)	2.054(3)	2.012(3)	2.043(2)	2.079(3)	0.873	14.68, 7.84 ^g				[31]
[Cu(phen) ₃](C(CN) ₃) ₂	2.219(3)	2.238(3)	2.121(3)	2.066(3)	2.121(3)	2.050(3)	0.938					[29]
[Cu(phen) ₃](TCNQ) ₂ · 0.5(CH ₃ OH)	2.270(10)	2.190(10)	2.044(9)	2.120(9)	2.129(9)	2.060(10)	0.936					[33]
[Cu(bpy) ₃](ClO ₄) ₂ ^a	2.450(7)	2.226(7)	2.026(5)	2.030(8)	2.034(8)	2.035(3)	0.869	14.23, 10.63 ^g		2.083 ^h		[34]
[Cu(bpy) ₃](ClO ₄) ₂ ^b	2.469(6)	2.222(7)	2.020(5)	2.018(6)	2.027(6)	2.037(5)	0.864					[37]
[Cu(bpy) ₃](ClO ₄) ₂ ^c	2.453(3)	2.237(3)	2.030(3)	2.020(3)	2.036(3)	2.037(3)	0.866					[36]
[Cu(bpy) ₃](BPh ₄) ₂ (120 K)	2.378(6)	2.214(6)	2.079(5)	2.032(5)	2.004(5)	2.029(5)	0.887	15.01, 7.97 ^g				[3]
{C ₁₄ H ₁₉ N ₂ }[Cu(hfacac) ₃]	2.156(1) ^d	2.201(1) ^d	1.981(1) ^d	2.028(1) ^d	2.002(1) ^d	2.035(1) ^d	0.923					[38]
[Cu(bpy) ₃][Ni(C ₅ S ₅) ₂]	2.088(2)	2.065(2)	2.088(2)	2.083(2)	2.083(2)	2.065(2)	1.002					[37]
[Cu(OMPA) ₃](ClO ₄) ₂	2.065(2)	2.065(2)	2.065(2)	2.065(2)	2.065(2)	2.065(2)	1.000					[6]
[Cu(en) ₃]SO ₄	2.150(2)	2.150(2)	2.150(2)	2.150(2)	2.150(2)	2.150(2)	1.000					[5]

When^{a–c} carried out in temperature range 283–303 K.

ax., axial; eq., equatorial.

^a $R1 = 0.091$.

^b $R1 = 0.062$.

^c $R1 = 0.035$.

^d Cu–O distances.

^e T , tetragonality.

^f $kK = 1000\text{ cm}^{-1}$.

^g Present work at room temperature.

^h g_1 (determination from pseudo-isotropic spectra).

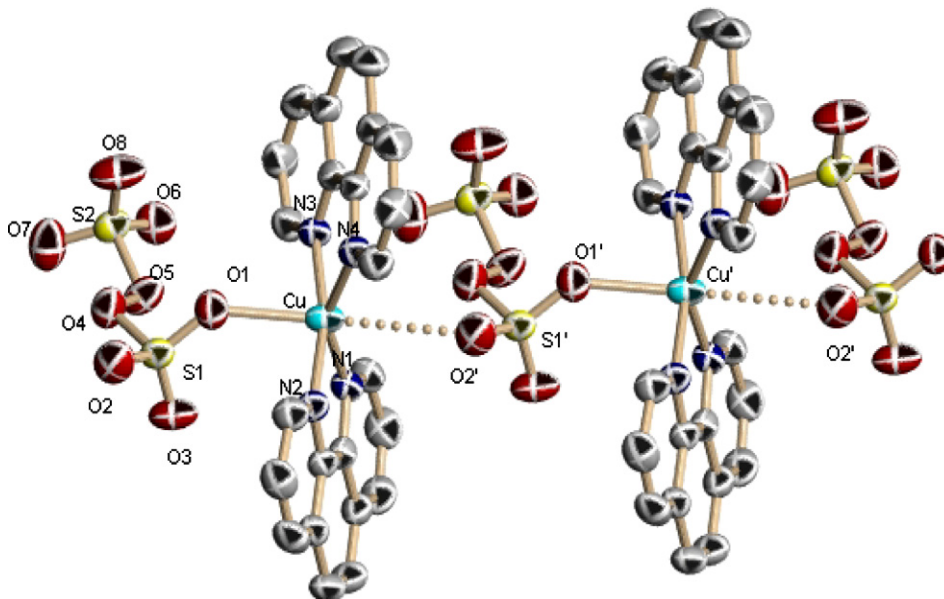


Fig. 4. Thermal ellipsoid (50% probability) plot of $[\text{Cu}(\text{phen})_2(\text{OS}_2\text{O}_7)](\text{S}_2\text{O}_8)$ (**3**). Hydrogen atoms are omitted for clarity.

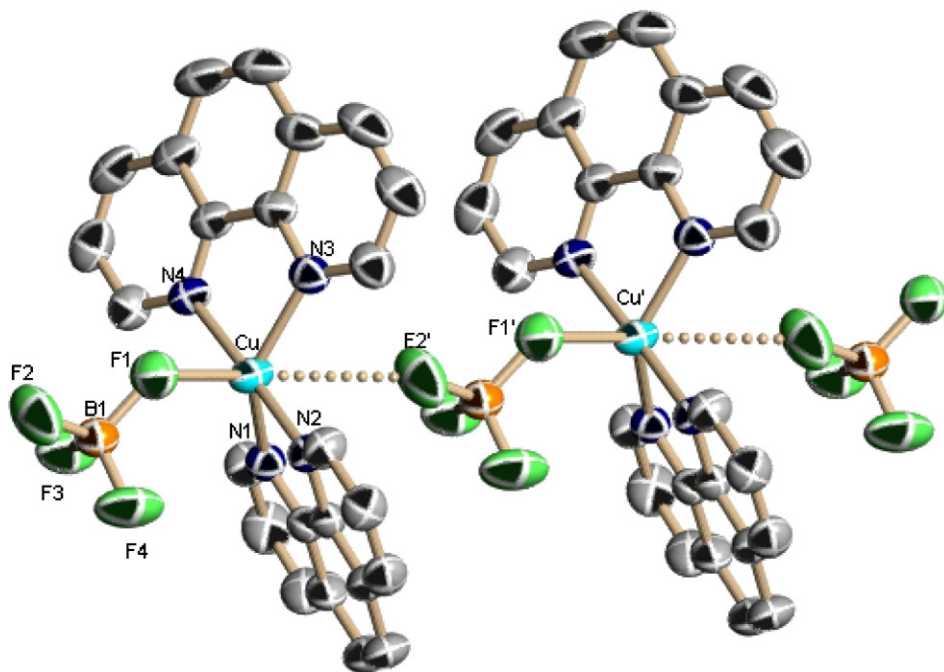


Fig. 5. Thermal ellipsoid (50% probability) plot of $[\text{Cu}(\text{phen})_2(\text{FBF}_3)](\text{BF}_4)$ (**4**). Hydrogen atoms and uncoordinating BF_4^- are omitted for clarity.

significantly different (2.019(2) and 1.999(2) Å) and are almost linear, with $\text{N}(2)\text{--Cu--N}(4) = 177.0(1)^\circ$. The three in-plane Cu–N distances are significantly different (2.060(2), 2.078(2) and 2.184(2) Å) and longer than the out of plane Cu–N distances by 0.060 Å, only slightly less than the difference of 0.1 Å previously observed in trigonal-bipyramidal Cu(II) complexes [41]. The much shorter in-plane Cu–F(1) distance of 2.184(2) Å suggests the non-involvement in axial sites of the typical elongated octahedral geometry as compared with the elongated, previously observed, Cu–F distance of 2.560(2) Å in $[\text{Cu}(\text{bpy})_2\text{--}$

$(\text{F}_2\text{BF}_2)](\text{BF}_4)$ [19]. The octahedral units in this analogous compound are linked into infinite chains by the bridging didentate tetrafluoroborate group. For compound **4**, the lattice is stabilized by hydrogen bonding between the amine-C and $\text{F}(\text{BF}_4^-)$ ($\text{C}\cdots\text{F}$ distances 3.107(4)–3.345(1) Å) and a very weak interaction between Cu atoms and F' atoms of the neighbouring BF_4^- groups (Cu– F' , 3.110(2) Å).

The coordination geometries of the corresponding $\text{Cu}(\text{chelate})_2\text{X}_2$ or, $\text{Cu}(\text{chelate})_2\text{Y}$, where chelate = phen [42–44], dpyam [16,44,45] or bpy [13,20]; $\text{X} = \text{BF}_4^-$,

Table 5
Structural data and electronic spectra of bis(chelate)copper(II) complexes

Complex	Chromophore	Coordination number and geometry	T^a	τ^b	Band maxima (kK^c)	Polycrystalline e.s.r. spectrum			Reference
						g_1	g_2	g_3	
[Cu(phen) ₂ (OS ₂ O ₇)] (3)	CuN ₄ O	5, SPy		0.31	13.48	2.210		2.062	this work
[Cu(phen) ₂ (FBF ₃)](BF ₄) (4)	CuN ₄ F	5, TBP		0.66	12.82, 10.07(sh)		2.180 ^d		this work
[Cu(phen) ₂ (S ₄ O ₆)]	CuN ₄ O ₂	6, Oct	0.81						[4]
[Cu(bpy) ₂ (OS ₂ O ₇)] · H ₂ O	CuN ₄ O	5, interm.		0.52	13.62				[16]
[Cu(bpy) ₂ (S ₄ O ₆)]	CuN ₄ O ₂	6, Oct	0.760		14.70	2.062 ^e	2.067 ^e	2.228 ^e	[20]
[Cu(bpy) ₂ (O ₂ ClO ₂)](ClO ₄)	CuN ₄ O ₂	6, Oct	0.757		15.10	2.054 ^e	2.065 ^e	2.255 ^e	[18]
[Cu(bpy) ₂ (F ₂ BF ₂)](BF ₄)	CuN ₄ F ₂	6, Oct	0.763		15.20	2.055 ^e	2.070 ^e	2.243 ^e	[18,19]
[Cu(bpy) ₂ (OH ₂)](S ₂ O ₆)	CuN ₄ O	5, TBP		0.92	12.45	2.011	2.158	2.225	[16,18]
[Cu(dpyam) ₂](ClO ₄) ₂	CuN ₄	4, Tet			18 120, 15 500(sh), 13 160(sh), 10 420 18 180, 15 630(sh), 13 330(sh), 10 530 18 050, 15 920(sh) 13 050(sh), 10 390				[14]
[Cu(dpyam) ₂](BF ₄) ₂	CuN ₄	4, Tet				2.29	2.29	2.07	[15]
[Cu(dpyam) ₂](PF ₆) ₂ ^f	CuN ₄	4, Tet							
[Cu(dpyam) ₂ (OH ₂) ₂](SO ₄) · 7H ₂ O	CuN ₄ O ₂	6, Oct	0.81		17.52, 1450				[15]
[Cu(dpyam) ₂ (OH ₂) ₂](S ₄ O ₆)	CuN ₄ O ₂	6, Oct	0.82		17.98, 14.79	2.26		2.09	[17]
[Cu(dpyam) ₂ (SO ₄)]Cu(dpyam) ₂ -(OH ₂) ₂ (PF ₆) ₂ · 2H ₂ O	CuN ₄ O ₂	6, <i>cis</i> -Oct ^g			14.97, 10.13	2.47		2.08	[17]

^a T , tetragonality.

^b τ , trigonal distortion index ($\tau = (\beta - \alpha)/60$).

^c $kK = 1000 \text{ cm}^{-1}$.

^d g_1 (determination from pseudo-isotropic spectra).

^e Single crystal e.s.r. values.

^f Present work.

^g The first chromophore, SPy, square pyramidal; TBP, trigonal bipyramidal; Oct, octahedral; Tet, tetrahedral; interm, intermediate geometry between SPy and TBP.

ClO₄[−] and PF₆[−] and Y = S₄O₆^{2−}, S₂O₆^{2−}, S₃O₆^{2−} and S₂O₈^{2−}, are compared with those of the title complexes as in Table 5. The binding behaviour of the anions and the geometries are different depending on types of the chelate ligands.

3.3. Spectral characterization

The IR spectra of compounds **1–4** show broad and intense bands of the ionic S₄O₆^{2−} (1249 and 1215 cm^{−1} for **1**), S₂O₈^{2−} (1285 cm^{−1} for **3**) and BF₄[−] anions (1059 cm^{−1} for **2** and 1066 cm^{−1} for **4**). The electronic reflectance spectra of compounds **1** and **2** show two well-resolved bands with nearly equal intensity at approximately 14 570 and 8630 cm^{−1} for **1**; 14 860 and 8620 cm^{−1} for **2**, which are assigned as the d_{z²} → d_{xy} and d_{xz} ≈ d_{yz} ≈ d_{x²−y²} → d_{xy} transitions, respectively, corresponding to an elongated octahedral geometry with high tetragonality of ca. 0.89. This yields a tentative one-electron orbital sequence of d_{xy} > d_{z²} > d_{xz} ≈ d_{yz} ≈ d_{x²−y²}, an order which is comparable to that previously deduced for the elongated octahedral complexes [38,46]. The electronic reflectance spectrum of **3** consists of a single broad peak at 13 820 cm^{−1}. This spectral character of the compound is consistent with the distorted square pyramidal geometry ($\tau = 0.31$), but with a slightly lower energy than expected due to a high tetrahedral twist of the square base (36.0°) [15]. The one-electron ground state configuration is

d_{x²−y²} > d_{z²} > d_{xy} > d_{xz} ≈ d_{yz}. The transition may be assigned as d_{xy}, d_{xz}, d_{yz}, d_{z²} → d_{x²−y²}. Complex **4** with $\tau = 0.66$ displays a single d → d transition at 12 820 cm^{−1}, with some evidence for a possible low-energy shoulder at 10 700 cm^{−1}, consistent with a distorted TBP stereochemistry [46]. The one-electron ground-state configuration is d_{z²} > d_{xy} ≈ d_{x²−y²} > d_{xz} ≈ d_{yz} and the principal absorption may be assigned as a d_{xz} ≈ d_{yz} → d_{z²} transition, with the low-energy shoulder assigned as a d_{xy} ≈ d_{x²−y²} → d_{z²} transition.

The polycrystalline ESR spectrum of **3** is axial with $g_{\parallel} \gg g_{\perp} > 2.0 = 2.210 \gg 2.062 > 2.0$, consistent with a d_{x²−y²} ground state for the distorted square-based pyramidal geometry of the CuN₄O' chromophore [46]. However, X-band EPR measured on polycrystalline samples of **1**, **2** and **4** at RT showed a broad isotropic signal with a g_{iso} at around 2.108, 2.098 and 2.180, respectively which give no information regarding to the electronic ground state.

4. Supplementary material

CCDC 616539, 616540, 616541 and 616542 contain the supplementary crystallographic data for **1**, **2**, **3** and **4**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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New ferromagnetic dinuclear triply-bridged copper(II) compounds containing carboxylato bridges: Synthesis, X-ray structure and magnetic properties

Sujittra Youngme^{a,*}, Jaturong Phatchimkun^a, Nanthawat Wannarit^a,
Narongsak Chaichit^b, Siwaporn Meejoo^c, Gerard A. van Albada^d, Jan Reedijk^d

^a Department of Chemistry, Faculty of Science, Khon Kaen University, Khon Kaen 40002, Thailand

^b Department of Physics, Faculty of Science and Technology, Thammasat University Rangsit, Pathumthani 12121, Thailand

^c Department of Chemistry, Faculty of Science, Mahidol University, Bangkok 10400, Thailand

^d Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden University, P.O. Box 9502, 2300 RA Leiden, The Netherlands

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Abstract

The new triply-bridged dinuclear copper(II) complexes, $[\text{Cu}_2(\mu\text{-O}_2\text{CH})(\mu\text{-OH})_2(\text{dpyam})_2](\text{ClO}_4) \cdot \text{H}_2\text{O}$ (**1**), $[\text{Cu}_2(\mu\text{-O}_2\text{CCH}_3)(\mu\text{-OH})(\mu\text{-OH}_2)(\text{dpyam})_2](\text{S}_2\text{O}_8)$ (**2**), $[\text{Cu}_2(\mu\text{-O}_2\text{CCH}_3)(\mu\text{-OH})(\mu\text{-OH}_2)(\text{bpy})_2](\text{NO}_3)_2$ (**3**), $[\text{Cu}_2(\mu\text{-O}_2\text{CCH}_3)(\mu\text{-OH})(\mu\text{-OH}_2)(\text{phen})_2](\text{BF}_4)_2 \cdot 0.5\text{H}_2\text{O}$ (**4**), $[\text{Cu}_2(\mu\text{-O}_2\text{CCH}_2\text{CH}_3)(\mu\text{-OH})(\mu\text{-OH}_2)(\text{phen})_2](\text{NO}_3)_2$ (**5**) and $[\text{Cu}_2(\mu\text{-O}_2\text{CCH}_3)(\mu\text{-OH})(\mu\text{-Cl})(\text{bpy})_2]\text{Cl} \cdot 8.5\text{H}_2\text{O}$ (**6**) (dpyam = di-2-pyridylamine, bpy = 2,2'-bipyridine, phen = 1,10-phenanthroline), have been synthesized and characterized crystallographically and also their spectroscopic and magnetic properties have been studied. A structural classification of this type of dimers, based on the data obtained from X-ray diffraction analysis in the present work and those reported in the literature has been performed. In these complexes, the local geometry around the copper centre is generally a distorted square pyramid and distorted trigonal bipyramid with different degrees of distortion. The global geometry of the dinuclear complexes can be described in terms of the relative arrangement of the two five-coordinate environments, giving rise to different classes (A–F) of complexes. The most logical explanations have been provided for each class describing different magnetic interactions. Practically, there is a clear correlation between structural data and J values of the class B complexes. Extended Hückel calculations were performed for the present complexes **1–6**, as well as for some other class B complexes, showing the different molecular orbitals involved in their corresponding frontier orbitals, together with their energy. The results are found to be useful for the proper interpretation and correlation of the magnetic data and the dinuclear structure of the present complexes.

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1. Introduction

Dinuclear copper(II) carboxylates with a pair of copper atoms held by carboxylato-O,O' bridges are of interest toward understanding intramolecular magnetic exchange phenomena and for deriving magneto-structural correla-

tions [1–12]. The magnetic interaction in the triply-bridged dinuclear copper(II) complexes can occur via bridging ligands in various pathways [2,7,13–15], which depends on the coordination geometry of copper(II) ion, the Cu···Cu separation, the bond angles at the bridging atoms, the dihedral angle between the planes containing the copper(II) ions and the copper-bridging ligand bond lengths. Structurally, the triply-bridged dinuclear copper(II) carboxylato compounds with didentate chelating ligands and a five coordination of the Cu(II) ion show an extensive

* Corresponding author. Fax: +66 043 202373.

E-mail address: sujittra@kku.ac.th (S. Youngme).

range of compounds with a distortion between regular trigonal bipyramidal and regular square-based pyramidal. This feature can be useful for understanding the relationships between structural features and the value of the intramolecular magnetic exchange interaction in the triply-bridged dinuclear unit.

Our previous reports [10–12] dealt with the distortion of the geometries ranging between regular trigonal bipyramidal and regular square-based pyramidal, and the structurally dependent magnetic properties displayed by the five-coordinate dinuclear copper(II) ions. The structures of complexes $[\text{Cu}_2(\mu\text{-O}_2\text{CH})(\mu\text{-OH})(\mu\text{-Cl})(\text{dpyam})_2](\text{PF}_6)$, $[\text{Cu}_2(\mu\text{-O}_2\text{CH})_2(\mu\text{-OH})(\text{dpyam})_2](\text{PF}_6)$, $[\text{Cu}_2(\mu\text{-O}_2\text{CH})(\mu\text{-OH})(\mu\text{-Cl})(\text{dpyam})_2](\text{ClO}_4) \cdot 0.5\text{H}_2\text{O}$ [10,11] reveal a distorted trigonal bipyramidal stereochemistry, with a d_{z^2} ground state and thus the major lobe of the magnetic orbital will be axially directed towards a single bridging ligand: the hydroxido anion in these cases. This feature contributes to the observed ferromagnetic coupling between copper(II) magnetic centres. However, the structures of complexes $[\text{Cu}_2(\mu\text{-O}_2\text{CCH}_2\text{CH}_3)_2(\mu\text{-OH})(\text{dpyam})_2](\text{ClO}_4)$ [11], $[\text{Cu}_2(\mu\text{-O}_2\text{CCH}_2\text{CH}_3)(\mu\text{-OH})(\mu\text{-OH}_2)(\text{bpy})_2](\text{ClO}_4)_2$ [12] and $[\text{Cu}_2(\mu\text{-O}_2\text{CCH}_3)(\mu\text{-OH})(\mu\text{-OH}_2)(\text{phen})_2](\text{ClO}_4)_2$ [12], reveal a square-pyramidal stereochemistry with a $d_{x^2-y^2}$ ground state and the ferromagnetic coupling is still observed between copper(II) magnetic centres. On the contrary, the complex $[\text{Cu}_2(\mu\text{-O}_2\text{CCH}_3)_2(\mu\text{-OCOCH}_3)(\text{dpyam})_2](\text{BF}_4)$ [12], which has a square-pyramidal stereochemistry with a $d_{x^2-y^2}$ ground state, reveals an antiferromagnetic interaction between the Cu(II) ions. For a better understanding of the magneto-structural correlation of the triply-bridged dinuclear copper(II) carboxylato complexes with different copper(II) environment and bridging configuration now an additional six new triply-bridged dinuclear copper(II) compounds are reported with different degrees of distortion, i.e. $[\text{Cu}_2(\mu\text{-O}_2\text{CH})(\mu\text{-OH})_2(\text{dpyam})_2](\text{ClO}_4) \cdot \text{H}_2\text{O}$ (**1**), $[\text{Cu}_2(\mu\text{-O}_2\text{CCH}_3)(\mu\text{-OH})(\mu\text{-OH}_2)(\text{dpyam})_2](\text{S}_2\text{O}_8)$ (**2**), $[\text{Cu}_2(\mu\text{-O}_2\text{CCH}_3)(\mu\text{-OH})(\mu\text{-OH}_2)(\text{bpy})_2](\text{NO}_3)_2$ (**3**), $[\text{Cu}_2(\mu\text{-O}_2\text{CCH}_3)(\mu\text{-OH})(\mu\text{-OH}_2)(\text{phen})_2](\text{BF}_4)_2 \cdot 0.5\text{H}_2\text{O}$ (**4**), $[\text{Cu}_2(\mu\text{-O}_2\text{CCH}_2\text{CH}_3)(\mu\text{-OH})(\mu\text{-OH}_2)(\text{phen})_2](\text{NO}_3)_2$ (**5**) and $[\text{Cu}_2(\mu\text{-O}_2\text{CCH}_3)(\mu\text{-OH})(\mu\text{-Cl})(\text{bpy})_2]\text{Cl} \cdot 8.5\text{H}_2\text{O}$ (**6**). The compounds have been characterized by X-ray crystallography, IR, EPR and electronic spectra. The results of magnetic susceptibility measurements of compounds **1–6** from 5 to 250 K are investigated and discussed in relation with those of other relevant compounds. We have also undertaken a theoretical calculation using Extended Hückel methods on the different degree of structural distortion that influence their electronic and magnetic properties.

2. Experimental

2.1. Materials and measurements

1,10-Phenanthroline, 2,2'-bipyridyl and di-2-pyridylamine were purchased as commercial chemicals from Aldrich. All reagents are commercial grade materials and

were used without further purification. Elemental analyses (C, H, N) were determined on a Perkin–Elmer PE 2400 CHNS/O Analyzer. IR spectra were recorded on Spectrum One FT-IR spectrophotometer as KBr disc in the 4000–450 cm^{-1} spectral range. Solid-state (diffuse reflectance) electronic spectra were measured as polycrystalline samples on a Perkin–Elmer Lambda2S spectrophotometer, over the range 8000–18000 cm^{-1} . The X-band powder EPR spectra were recorded using a Bruker ESR-300 X-band instrument operating at room temperature with DPPH ($g = 2.0036$) as a reference. Magnetic susceptibility measurements (5–250 K) were carried out using a Quantum Design MPMS-5 5T SQUID magnetometer (measurements carried out at 0.1 T). Data were corrected for magnetisation of the sample holder and for diamagnetic contributions, which were estimated from the Pascal constants.

Molecular orbital calculations have been carried out with the CACAO (computer-aided composition of atomic orbitals) program [16], which is a program based on extended Hückel (EH) type of analysis, using the crystallographic coordinates. This approach was followed to obtain a better idea on how geometric distortion and the disposition of the magnetic orbitals of each Cu(II) ion influence their electronic and magnetic properties and to compare the magnitude of the ferromagnetic interaction of complexes within the same class. The present work has focused on class B complexes **2–6**, **8** and **9**, as well as class A complex **1**.

2.2. Synthesis

2.2.1. $[\text{Cu}_2(\mu\text{-O}_2\text{CH})(\mu\text{-OH})_2(\text{dpyam})_2](\text{ClO}_4) \cdot \text{H}_2\text{O}$ (**1**)

A hot methanol solution (10 ml) of dpyam (0.171 g, 1.0 mmol) was added to a hot aqueous solution (20 ml) of $\text{Cu}(\text{O}_2\text{CH})_2$ (0.154 g, 1.0 mmol). Then solid HCOONa (0.204 g, 3.0 mmol) was added, followed by solid NaClO_4 (0.195 g, 1.0 mmol). A green powder immediately formed, after which the mixture was warmed with adding methanol (10 ml) and water (10 ml), yielding a clear green solution. On slow evaporation at room temperature for two weeks product **1** was isolated as blue rod-shape crystals. They were filtered off, washed with the mother liquor and air-dried. Yield: ca. 30%. *Anal.* Calc. for $\text{C}_{21}\text{H}_{23}\text{ClCu}_2\text{N}_6\text{O}_9$: C, 37.87; H, 3.48; N, 12.62. Found: C, 37.59; H, 3.33; N, 12.53%.

2.2.2. $[\text{Cu}_2(\mu\text{-O}_2\text{CCH}_3)(\mu\text{-OH})(\mu\text{-OH}_2)(\text{dpyam})_2](\text{S}_2\text{O}_8)$ (**2**)

A hot methanol solution (10 ml) of dpyam (0.171 g, 1.0 mmol) was added to a hot methanol solution (20 ml) of $\text{Cu}(\text{O}_2\text{CCH}_3)_2 \cdot \text{H}_2\text{O}$ (0.181 g, 1.0 mmol). Then a hot aqueous solution (10 ml) of $\text{Na}_2\text{S}_2\text{O}_8$ (0.119 g, 0.5 mmol) was added to the mixture, yielding a green solution. After two weeks, green-square crystals of compound **2** were obtained. The crystals were filtered off, washed with mother liquor and air-dried. Yield: ca. 60%. *Anal.* Calc.

for $C_{22}H_{24}Cu_2N_6O_{12}S_2$: C, 34.97; H, 3.20; N, 11.12. Found: C, 34.91; H, 3.09; N, 11.42%.

2.2.3. $[Cu_2(\mu-O_2CCH_3)(\mu-OH)(\mu-OH_2)(bpy)_2](NO_3)_2$ (**3**)

The warm methanol solution (20 ml) of bpy (0.156 g, 1.0 mmol) was added to a warm aqueous solution (5 ml) of $Cu(O_2CCH_3)_2 \cdot H_2O$ (0.181 g, 1.0 mmol). Then solid $NaNO_3$ (0.043 g, 0.5 mmol) was added to the mixture, yielding a clear blue solution. After one week, blue needle-shaped crystals of compound **3** were obtained. The crystals were filtered off, washed with mother liquor and air-dried. *Anal.* Calc. for $C_{22}H_{22}Cu_2N_6O_{10}$: C, 40.18; H, 3.37; N, 12.78. Found: C, 40.10; H, 3.31; N, 12.97%.

2.2.4. $[Cu_2(\mu-O_2CCH_3)(\mu-OH)(\mu-OH_2)(phen)_2](BF_4)_2 \cdot 0.5H_2O$ (**4**)

The warm methanol solution (20 ml) of phen (0.198 g, 1.0 mmol) was added to a warm aqueous solution (5 ml) of $Cu(O_2CCH_3)_2 \cdot H_2O$ (0.181 g, 1.0 mmol). Then solid $NaBF_4$ (0.055 g, 0.5 mmol) was added to the mixture, yielding a clear greenish-blue solution. After one week, violet-coloured crystals of compound **4** were obtained as needles. The crystals were filtered off, washed with mother liquor and air-dried. *Anal.* Calc. for $C_{26}H_{24}B_2Cu_2F_8N_4O_{4.5}$: C, 40.81; H, 3.16; N, 7.32. Found: C, 40.88; H, 2.91; N, 7.49%.

2.2.5. $[Cu_2(\mu-O_2CCH_2CH_3)(\mu-OH)(\mu-OH_2)(phen)_2](NO_3)_2$ (**5**)

The warm methanol solution (20 ml) of phen (0.198 g, 1.0 mmol) was added to a warm aqueous solution (5 ml) of $Cu(NO_3)_2 \cdot 3H_2O$ (0.241 g, 1.0 mmol). Then solid $NaO_2CCH_2CH_3$ (0.047 g, 0.5 mmol) was added to the mixture, yielding a blue solution. On slow evaporation, its color became greenish-blue. After one week, greenish-blue crystals of compound **5** were obtained. The crystals were filtered off, washed with mother liquor and air-dried. *Anal.* Calc. for $C_{27}H_{24}Cu_2N_6O_{10}$: C, 45.07; H, 3.36; N, 11.68. Found: C, 45.01; H, 3.25; N, 11.83%.

2.2.6. $[Cu_2(\mu-O_2CCH_3)(\mu-OH)(\mu-Cl)(bpy)_2]Cl \cdot 8.5H_2O$ (**6**)

The warm methanol solution (20 ml) of bpy (0.156 g, 1.0 mmol) was added to a warm aqueous solution (5 ml) of $Cu(O_2CCH_3)_2 \cdot H_2O$ (0.181 g, 1.0 mmol). Then solid $NaCl$ (0.029 g, 0.5 mmol) was added to the mixture, yielding a clear blue solution. After one week, greenish-blue crystals of compound **6** were obtained. The crystals were filtered off, washed with mother liquor and air-dried. *Anal.* Calc. for $C_{22}H_{37}Cl_2Cu_2N_4O_{11.5}$: C, 35.72; H, 5.05; N, 7.57. Found: C, 35.55; H, 5.24; N, 7.61%.

2.3. Crystallography

The X-ray single-crystal data for all compounds were collected at 298 K on a 1 K Bruker SMART CCD area-

detector diffractometer using graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at a detector distance of 4.5 cm and swing angle of -35° . A hemisphere of the reciprocal space was covered by combination of three sets of exposures; each set had a different ϕ angle (0, 88, 180°) and each exposure of 40 s covered 0.3° in ω . Data reduction and cell refinements were performed using the program SAINT [17]. An empirical absorption correction by using the SADABS [18] program was applied, which resulted in transmission coefficients ranging from 0.683 to 1.000 for compound **1**, 0.862–1.000 for compound **2**, 0.679–1.000 for compound **3**, 0.744–1.000 for compound **4**, 0.764–1.000 for compound **5** and 0.581–1.000 for compound **6**.

The structures were solved by direct methods and refined by full-matrix least-squares method on $(F_{obs})^2$ with anisotropic thermal parameters for all non-hydrogen atoms using the SHELXTL-PC V 6.12 software package [19]. All hydrogen atoms in **1**, **2**, **3** and **5** were located geometrically and refined isotropically while all hydrogen atoms in **4** and **6** were fixed and allowed to ride on attached atoms. A water molecule in **4** was located with an occupancy of 0.5. For the best results of the refinement of the structure of **6** the oxygen atoms of the overall 8.5 water molecules were refined without hydrogen atoms except a few of them. Two water molecules are disordered with site occupancy of 0.5 for both conformers and two water molecules are located with site occupancies 0.25. All non-H atoms in **6** were refined anisotropically except three oxygen atoms of water molecules. The ClO_4^- anion in **1**, $S_2O_8^{2-}$ in **2**, NO_3^- in **3** and **5**, and BF_4^- in **4** showed disorder; the occupancies of the disordered positions were initially refined and later fixed at 0.5. These disordered counterions have some unreasonable Cl/S/N...O distances with quite high U_{eq} values, which are usually found for the disordered groups. However, the average Cl/S/N...O distances are not significantly different from the normal ordered ones (ClO_4 (**1**), 1.334–1.460 $\text{\AA}$, $d_{av} = 1.408 \text{ \AA}$ (1.414 $\text{\AA}$); S_2O_8 (**2**), 1.344–1.671 $\text{\AA}$, $d_{av} = 1.470 \text{ \AA}$ (1.472 $\text{\AA}$); NO_3 (**3**), 1.072–1.350 $\text{\AA}$, $d_{av} = 1.222 \text{ \AA}$ (1.239 $\text{\AA}$); NO_3 (**5**), 1.069–1.350 $\text{\AA}$, $d_{av} = 1.208 \text{ \AA}$ (1.239 $\text{\AA}$)).

The molecular graphics were created by using the SHELXTL-PC [19] package. The crystal and refinement details for compounds **1–6** are listed in Table 1. Selected bond lengths and angles are given in Tables S4 and S5.

3. Results and discussion

3.1. Description of the crystal structures

3.1.1. Crystal structure of $[Cu_2(\mu-O_2CH)(\mu-OH)_2(dpyam)_2](ClO_4) \cdot H_2O$ (**1**)

The structure of **1** consists of a symmetric dinuclear $[Cu_2(\mu-O_2CH)(\mu-OH)_2(dpyam)_2]^+$ cation, with ClO_4^- counter anions. This unit is depicted in Fig. 1, together with the numbering scheme. Both copper(II) ions of the complex cation are linked through a double hydroxido

Table 1
Crystal and refinement data for complexes 1–6

Complex	1	2	3	4	5	6
Empirical formula	C ₂₁ H ₂₃ ClCu ₂ N ₆ O ₉	C ₂₂ H ₂₄ Cu ₂ N ₆ O ₁₂ S ₂	C ₂₂ H ₂₂ Cu ₂ N ₆ O ₁₀	C ₂₆ H ₂₄ B ₂ Cu ₂ F ₈ N ₄ O _{4.5}	C ₂₇ H ₂₄ Cu ₂ N ₆ O ₁₀	C ₂₂ H ₃₇ Cl ₂ Cu ₂ N ₄ O _{11.5}
Formula weight	664.0	755.67	657.54	1526.35	719.62	730.40
T/K	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)
Crystal system	monoclinic	monoclinic	triclinic	orthorhombic	monoclinic	triclinic
Space group	<i>C2/m</i>	<i>P2₁/m</i>	<i>P</i> $\bar{1}$	<i>P2₁2₁2₁</i>	<i>P2₁/n</i>	<i>P</i> $\bar{1}$
<i>a</i> (Å)	14.3312(5)	8.6702(2)	7.756	8.34520(10)	8.00060(10)	7.4607(2)
<i>b</i> (Å)	16.8446(7)	17.3735(4)	11.417	17.7730(2)	18.4031(2)	13.6636(3)
<i>c</i> (Å)	12.4728(5)	10.07380(10)	15.9420(2)	19.84770(10)	19.3110(3)	17.4330(4)
α (°)	90	90	74.8150(10)	90	90	83.2120(10)
β (°)	120.9700(10)	112.8730(10)	81.2370(10)	90	97.9530(10)	83.3470(10)
γ (°)	90	90	73.24	90	90	78.6260(10)
<i>V</i> (Å ³)	2581.72(17)	2470.85(5)	1299.939(16)	2943.80(5)	2815.92(6)	1722.17(7)
<i>Z</i>	4	2	2	2	4	2
<i>D</i> _{calc} (g cm ^{−3})	1.708	1.795	1.680	1.722	1.697	1.409
μ (mm ^{−1})	1.813	1.745	1.703	1.539	1.581	1.446
<i>F</i> (000)	1344	768	668	1528	1464	736
Crystal size (mm)	0.05 × 0.20 × 0.25	0.125 × 0.125 × 0.125	0.325 × 0.225 × 0.075	0.425 × 0.175 × 0.150	0.300 × 0.225 × 0.050	0.500 × 0.250 × 0.200
Number of reflection collected	8117	7984	9432	18402	20148	9219
Number of unique reflections (<i>R</i> _{int})	3810 (0.0165)	2854 (0.0315)	7804 (0.0168)	3672 (0.0281)	8570 (0.0677)	6282 (0.0395)
Data/restraints/parameter	3810/0/219	2843/0/284	6895/0/503	6504/0/504	7983/0/556	6158/0/422
Goodness-of-fit	1.048	1.031	1.049	1.028	1.058	1.004
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0525, <i>wR</i> ₂ = 0.1455	<i>R</i> ₁ = 0.0344, <i>wR</i> ₂ = 0.0816	<i>R</i> ₁ = 0.0380, <i>wR</i> ₂ = 0.0902	<i>R</i> ₁ = 0.0371, <i>wR</i> ₂ = 0.0812	<i>R</i> ₁ = 0.0670, <i>wR</i> ₂ = 0.0943	<i>R</i> ₁ = 0.0582, <i>wR</i> ₂ = 0.1462
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0708, <i>wR</i> ₂ = 0.1594	<i>R</i> ₁ = 0.0523, <i>wR</i> ₂ = 0.0894	<i>R</i> ₁ = 0.0518, <i>wR</i> ₂ = 0.0988	<i>R</i> ₁ = 0.0522, <i>wR</i> ₂ = 0.0883	<i>R</i> ₁ = 0.1540, <i>wR</i> ₂ = 0.1162	<i>R</i> ₁ = 0.0809, <i>wR</i> ₂ = 0.1591
Largest difference in peak and hole (e Å ^{−3})	0.992 and −0.827	0.638 and −0.677	0.447 and −0.717	0.248 and −0.282	0.327 and −0.379	0.888 and −1.109

$$R = \sum \|F_o\| - |F_c| / \sum \|F_o\|, R_w = [\sum w\{\|F_o\| - |F_c|\}^2 / \sum w\|F_o\|^2]^{1/2}.$$

and a formato bridge, leading to a Cu–Cu distance of 2.902(1) Å. The coordination environment around each copper(II) ion can be best described as tetrahedrally distorted square pyramidal CuN₂O₂O' chromophore with a τ value of 0.27, the structure index is defined as $\tau = (\beta - \alpha)/60$, where β and α are the largest coordination angles, $\tau = 0$ for square pyramidal (SP) and $\tau = 1$ for trigonal bipyramidal (TBP) geometry [20]. The four shorter bonds in the basal plane involve two nitrogen atoms of the dpym ligand (Cu–N 2.005(3) and 2.030(3) Å), two oxygen atoms of bridging hydroxido ligands (Cu–O 1.952(3) and 1.955 Å). An oxygen atom of the triatomic bridging formato ligand completes the five-coordination

at Cu(1) atom (Cu–O(3) 2.345(3) Å), consistent with the typical square-pyramidal geometry. The four basal atoms are not coplanar, showing a significant tetrahedral distortion with a dihedral angle of 23.8° formed between CuO₂ and CuN₂ planes and the copper atom is displaced by 0.189 Å from the basal plane toward the O(3) atom. The dinuclear unit is nearly planar and the dihedral angle between the basal N₂O₂ planes is 165.6°. The bridging angles in the equatorial positions, Cu(1)–O(1)–Cu(1A) and Cu(1)–O(2)–Cu(1A) are 95.8(1)° and 96.0(1)°, respectively. This structural feature is comparable to the planar dihydroxido-copper(II) complexes to which their structures and magnetic properties are well characterized

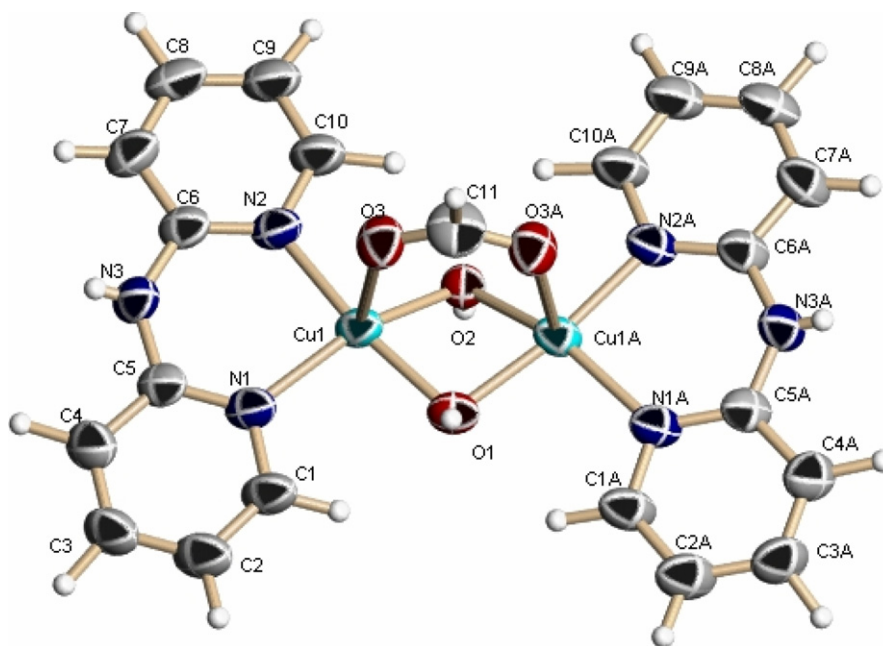


Fig. 1. ORTEP 50% probability plot of the cation in $[\text{Cu}_2(\mu\text{-O}_2\text{CH})(\mu\text{-OH})_2(\text{dpyam})_2](\text{ClO}_4) \cdot \text{H}_2\text{O}$ (**1**), atoms with an “A” are generated by a mirror plane. The uncoordinating anion and water molecules are omitted for clarity.

experimentally and theoretically [21–28]. The dpyam ligands are essentially planar with small dihedral angles of 6.6° between the individual pyridine rings. The bite angles of the dpyam ligands (N–Cu–N, $91.9(1)^\circ$) are only slightly greater than 90° .

The lattice is further stabilized by a hydrogen bonding between the amine N and the oxygen atom of formate group with $\text{N} \cdots \text{O}$ contact of $2.796(1) \text{ \AA}$; between the oxygen atom of bridging hydroxido group and the oxygen atom of lattice water molecules with $\text{O} \cdots \text{O}$ contacts of $2.865(1) \text{ \AA}$; between the oxygen atom of bridging of both hydroxido groups $\text{O} \cdots \text{O}$ contacts of $2.855(1) \text{ \AA}$ along *a*- and *b*-axes, leading to a two dimensional supramolecular structure (see Fig. 2).

3.1.2. Crystal structures of $[\text{Cu}_2(\mu\text{-O}_2\text{CCH}_3)(\mu\text{-OH})(\mu\text{-OH}_2)(\text{dpyam})_2](\text{S}_2\text{O}_8)$ (2**), $[\text{Cu}_2(\mu\text{-O}_2\text{CCH}_3)(\mu\text{-OH})(\mu\text{-OH}_2)(\text{bpy})_2](\text{NO}_3)_2$ (**3**), $[\text{Cu}_2(\mu\text{-O}_2\text{CCH}_3)(\mu\text{-OH})(\mu\text{-OH}_2)(\text{phen})_2](\text{BF}_4)_2 \cdot \text{H}_2\text{O}$ (**4**), $[\text{Cu}_2(\mu\text{-O}_2\text{CCH}_2\text{CH}_3)(\mu\text{-OH})(\mu\text{-OH}_2)(\text{phen})_2](\text{NO}_3)_2$ (**5**)**

The structure of compounds **2–5** are made up of a dinuclear $[\text{Cu}_2(\mu\text{-O}_2\text{CCH}_3/\text{O}_2\text{CCH}_2\text{CH}_3)(\mu\text{-OH})(\mu\text{-OH}_2)(\text{dpyam}/\text{bpy} \text{ or } \text{phen})_2]^+$ cation, an uncoordinated $\text{S}_2\text{O}_8^{2-}$, NO_3^- , BF_4^- and NO_3^- anion, respectively. This unit is depicted in Fig. 3 for complex **2** and Figs. S1–S3 for complexes **3–5**, together with the numbering scheme, with selected distances and angles listed in Tables S4 and S5. In complexes **2–5**, both Cu(II) ions in the dinuclear unit are linked through a hydroxido, an aqua and a didentate

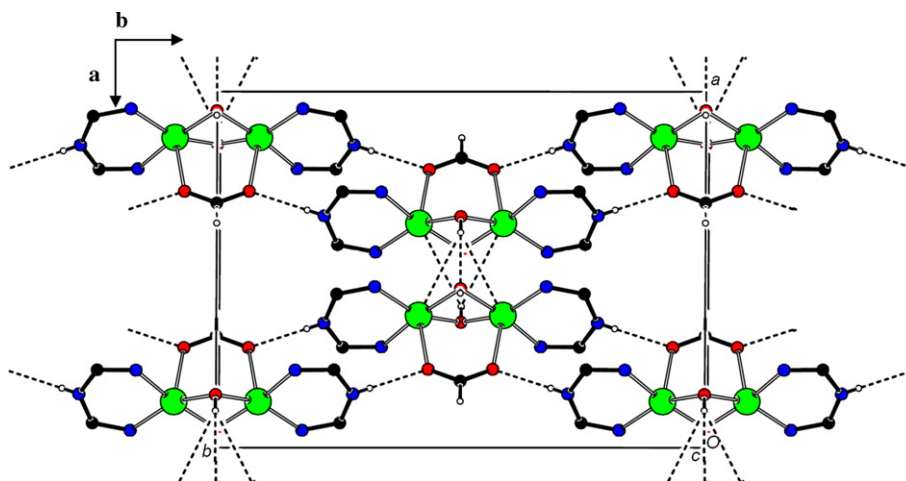


Fig. 2. H-bond system providing an two-dimensional array of complex **1**.

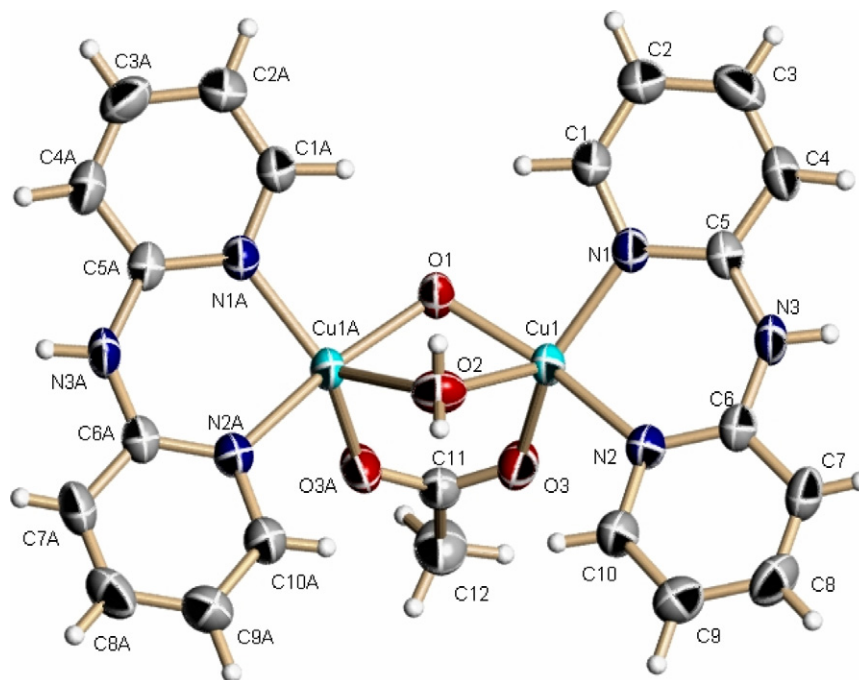


Fig. 3. ORTEP 50% probability plot of the cation in $[\text{Cu}_2(\mu\text{-O}_2\text{CCH}_3)(\mu\text{-OH})(\mu\text{-OH}_2)(\text{dpyam})_2](\text{S}_2\text{O}_8)$ (**2**), atoms with an “A” are generated by a mirror plane. The uncoordinating anion is omitted for clarity.

$\kappa\text{-O}^1, \text{O}^2$ bridging carboxylate ligand resulting in a five-coordinate species at each copper atom. The coordination environment around each Cu(II) ion can be best described as distorted square pyramidal, with a $\text{CuN}_2\text{O}_2\text{O}'$ chromophore (see Fig. 3 and Figs. S1–S3) and the τ values of 0.43 for **2**, 0.21 and 0.19 for **3**, 0.21 and 0.16 for **4** and 0.08 and 0.19 for **5**. The carboxylate groups are in the didentate $\eta^1:\eta^1$ - μ -bridging mode, locating in the equatorial positions. The fifth axial position is occupied by a bridging water molecule at a longer distance of 2.414(2) Å for **2**, 2.347(1) and 2.460(2) Å for **3**, 2.374(3) and 2.390(3) Å for **4** and, 2.344(4) and 2.368(4) Å for **5**. The copper atoms are displaced from the basal plane towards the apical O atom of aqua by 0.225(4) Å for **2**, 0.152(2) and 0.115(1) Å for **3**, 0.124(1) and 0.090(1) Å for **4** and 0.147(1) and 0.148(1) Å for **5**. The CuN_2O_2 chromophores are non-planar with dihedral angles of 40.4(1)° for **2**, 14.5(1) and 11.6(1)° for **3**, 17.0(1)° and 8.6(1)° for **4** and 14.6(1)° and 12.2(1)° for **5**, between the CuN_2 and CuO_2 planes. The dihedral angle between the basal planes is 164.4(1)° for **2**, 120.5(1)° for **3**, 114.6(3)° for **4** and 122.3(2)° for **5**.

For compound **2**, the lattice is stabilized by a hydrogen bonding between the amine N and the oxygen atom of S_2O_8 with $\text{N}\cdots\text{O}$ distance of 2.799–2.919 Å and between the oxygen atom of bridging hydroxido/aqueous groups and the oxygen atoms of S_2O_8 with $\text{O}\cdots\text{O}$ contacts of 2.659–3.364 Å parallel to *a*- and *b*-axes, leading to a two-dimensional supramolecular structure (see Fig. 4).

For compounds **3** and **5**, the lattice is stabilized by a hydrogen bonding between the oxygen atom of bridging

hydroxido/aqueous groups and the oxygen atoms of NO_3^- with $\text{O}\cdots\text{O}$ contacts of 2.712–3.020 Å for **3** and 2.785–3.168 Å for **5**. That of compound **4** is stabilized by a hydrogen bonding between the oxygen atom of bridging hydroxido/aqueous groups and fluoride atoms of BF_4^- with $\text{O}\cdots\text{F}$ contacts of 2.744–3.390 Å.

3.1.3. Crystal structure of $[\text{Cu}_2(\mu\text{-O}_2\text{CCH}_3)(\mu\text{-OH})(\mu\text{-Cl})(\text{bpy})_2]\text{Cl}\cdot 8.5\text{H}_2\text{O}$ (**6**)

The structure of compound **6** consists of a dinuclear $[\text{Cu}_2(\mu\text{-OH})(\mu\text{-O}_2\text{CCH}_3)(\mu\text{-Cl})(\text{bpy})]^{2+}$ cation, with Cl^- counter anions and 8.5 molecules of lattice water. This cation is depicted in Fig. 5, together with the numbering scheme, with selected distances and angles listed in Table S5. Each copper(II) ion has a distorted square pyramidal geometry of the $\text{CuN}_2\text{O}_2\text{Cl}$ chromophore, with a τ value of 0.41 and 0.28 for Cu1 and Cu2, respectively. Two nitrogen atoms of the bpy ligand, two oxygen atoms of the bridging acetato and hydroxido ligands form the square bases. The axial site of each copper(II) atom is occupied by a chlorido ligand at distances of 2.632 and 2.657 Å. The *syn,syn*-coordinated acetato ligand bridges the two equatorial planes, giving a Cu–Cu distance of 3.040(1) Å. The CuN_2O_2 chromophore are non-planar with dihedral angles of 27.4(1)° and 18.9(1)° for **6**, between the CuN_2 and CuO_2 planes. The dihedral angle between the equatorial planes is 123.0(4)° for Cu1 and Cu2. The bridging angles (Cu(1)–O(1)–Cu(2) and Cu(1)–Cl(1)–Cu(2)) are 103.3(1)° and 70.2(1)°, respectively.

The lattice is further stabilized by hydrogen bonding between the hydroxido O and the chloride anion with a short $\text{O}\cdots\text{Cl}$ contact of 2.910(1) Å.

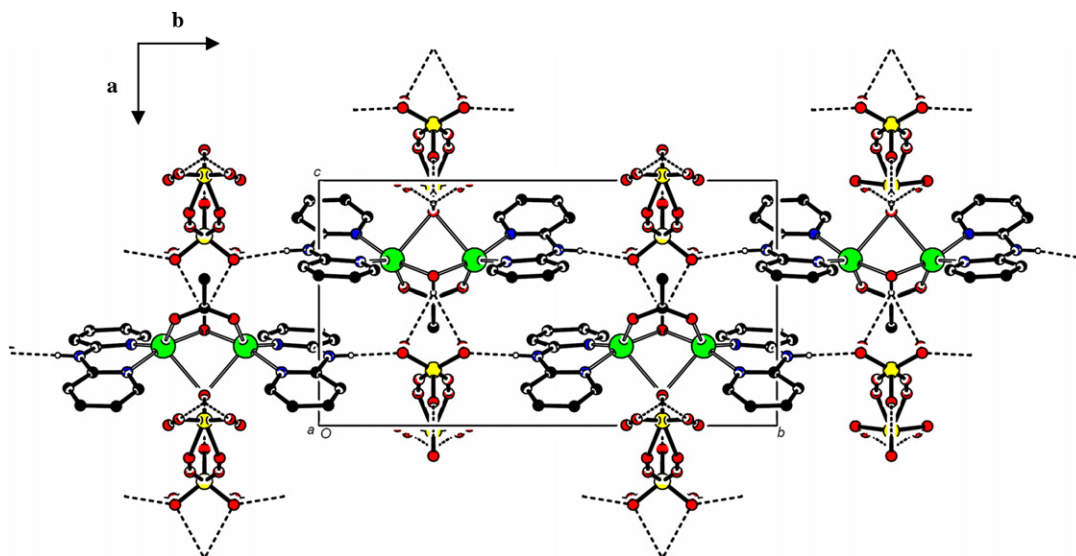


Fig. 4. H-bond system providing an two-dimensional array of complex 2.

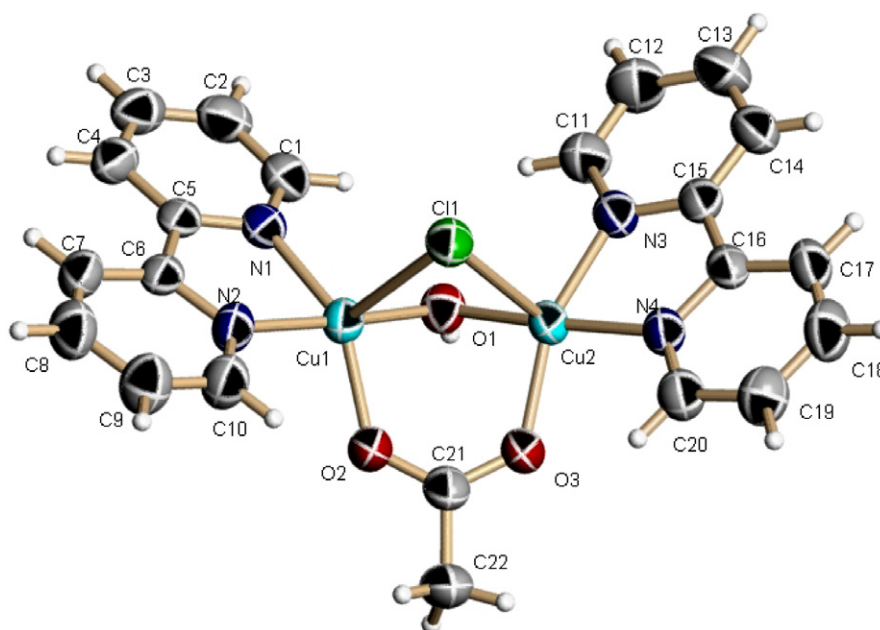


Fig. 5. ORTEP 50% probability plot of the cation in $[\text{Cu}_2(\mu\text{-O}_2\text{CCH}_3)(\mu\text{-OH})(\mu\text{-Cl})(\text{bpy})_2]\text{Cl} \cdot 8.5\text{H}_2\text{O}$ (6). The uncoordinating anion and water molecules are omitted for clarity.

3.2. Structure comparison

The several structural and magnetic parameters of the compounds, together with those of a number of related dinuclear triply-bridged copper(II) compounds are listed in Table 2 and Fig. 6. The arrangement of the five-coordinate chromophores in the triply-bridged dinuclear copper(II) complexes containing a carboxylato bridge may be represented in six different classes (Scheme 1): (A) coplanar bases with a square pyramidal geometry for both Cu(II) environments and two dihydroxido bridges lying in the equatorial positions; (B) non-coplanar bases with a square pyramidal geometry for both Cu(II) ions, triatomic

carboxylato and hydroxido bridges in the equatorial positions; (C) non-coplanar bases with a square pyramidal geometry for both Cu(II) ions and two triatomic carboxylato bridges lying in the equatorial positions; (D) non-coplanar bases with a square pyramidal geometry for both Cu(II) ions, one single-atom or triatomic bridge in an equatorial–equatorial configuration and two carboxylato (two triatomic or monoatomic/triatomic) bridges in an axial–equatorial configuration; (E) non-coplanar with a trigonal bipyramidal geometry for both Cu(II) ions and one hydroxido bridge in an axial–axial configuration; (F) non-coplanar bases with square pyramidal and trigonal bipyramidal geometries and two bridges, which occupy

Table 2
Structural and magnetic data for triply-bridged dinuclear copper(II) carboxylato compounds

Compound ^a	Coordination geometry ^b	τ	Angle between basal plane (°)	Tetrahedral twist (°)	Mode	Cu···Cu (Å)	Cu–X		J (cm ^{−1}) ^c	Cu–X–Cu (Å)	Reference
							Axial	Equatorial			
[Cu ₂ (μ-O ₂ CH)-(μ-OH) ₂ (dpyam) ₂](ClO ₄) · H ₂ O (1)	Dist. Spy.	0.27	165.6	23.8	A	2.903	2.345	1.952–2.005	112.7	95.89 (OH) 96.09 (OH)	this work
[Cu ₂ (μ-O ₂ CCH ₃)(μ-OH)-(μ-OH ₂)(dpyam) ₂](S ₂ O ₈) (2)	Dist. Spy.	0.43	164.4	40.4	B	3.124	2.414	1.911–2.023	n.d.	109.64 (OH) 80.66 (OH ₂)	this work
[Cu ₂ (μ-O ₂ CCH ₃)(μ-OH)-(μ-OH ₂)(bpy) ₂](NO ₃) ₂ (3)	Dist. Spy.	0.21, 0.19	120.5	14.5, 11.6	B	3.049	2.347, 2.460	1.938–2.017	n.d.	103.97 (OH) 78.70 (OH ₂)	this work
[Cu ₂ (μ-O ₂ CCH ₃)(μ-OH)-(μ-OH ₂)(phen) ₂](BF ₄) ₂ · 0.5H ₂ O (4)	Dist. Spy.	0.21, 0.16	114.6	17.0, 8.6	B	3.002	2.374, 2.390	1.925–2.008	120.8	102.07 (OH) 78.12 (OH ₂)	this work
[Cu ₂ (μ-O ₂ CCH ₂ CH ₃)(μ-OH)-(μ-OH ₂)(phen) ₂](NO ₃) ₂ (5)	Dist. Spy.	0.08, 0.19	122.3	14.6, 12.2	B	3.026	2.344, 2.368	1.925–2.029	n.d.	103.58 (OH) 79.90 (OH ₂)	this work
[Cu ₂ (μ-O ₂ CCH ₃)(μ-OH)-(μ-OH ₂)(bpy) ₂](ClO ₄) ₂ (7)	Dist. Spy.	0.14, 0.25	118.1		B	3.035	2.379, 2.405	2.006–2.010	19.3	103.8 (OH) 78.7 (OH ₂)	[1]
[Cu ₂ (μ-O ₂ CCH ₃)(μ-OH)-(μ-OH ₂)(phen) ₂](ClO ₄) ₂ (8)	Dist. Spy.	0.02, 0.14	113.8	16.4, 8.2	B	2.989	2.360, 2.375	1.933–2.020	120.0	101.3 (OH) 78.3 (OH ₂)	[12]
[Cu ₂ (μ-O ₂ CCH ₂ CH ₃)(μ-OH)-(μ-OH ₂)(bpy) ₂](ClO ₄) ₂ (9)	Dist. Spy.	0.20, 0.16	120.1	15.0, 10.9	B	3.037	2.382, 2.415	1.920–2.005	148.9	104.5 (OH) 78.6 (OH ₂)	[12]
[Cu ₂ (μ-O ₂ CCH ₃)(μ-OH)-(μ-Cl)(bpy) ₂](Cl) · 8.5H ₂ O (6)	Dist. Spy.	0.41, 0.28	123.0	27.4, 18.9	B	3.040	2.632, 2.657	1.936–2.029	145.3	103.3 (OH)	this work
[Cu ₂ (μ-O ₂ CH)(μ-OH)-(μ-Cl)(dpyam) ₂](ClO ₄) · 0.5H ₂ O (10)	Dist. TBP.	0.67	90.0		E	3.036	1.916	1.975–2.158	79.1	104.8 (OH) 75.6 (Cl)	[10]
[Cu ₂ (μ-O ₂ CH)(μ-OH)-(μ-Cl)(dpyam) ₂](PF ₆) (11)	Dist. TBP.	0.72	93.2		E	3.061	1.918	1.983–2.183	79.7	105.8 (OH) 77.3 (Cl)	[11]
[Cu ₂ (μ-O ₂ CH)(μ-OH)-(μ-OMe)(dpyam) ₂](ClO ₄) (12)	Dist. TBP.	0.65			E	3.023	1.918	2.169–2.175	62.5	104.0 (OH) 88.3 (OMe)	[10]
[Cu ₂ (μ-O ₂ CH)(μ-OH)-(μ-OCOH)(dpyam) ₂](PF ₆) (13)	Dist. TBP.	0.71	89.7		E	3.113	1.934	2.144–2.200	47.8	107.2 (OH) 93.1 (O ₂ CH)	[11]
[Cu ₂ (μ-O ₂ CCH ₃)(μ-OH)-(μ-OCOCH ₃)(dpyam) ₂](PF ₆) · H ₂ O (14)	Dist. Spy., Dist. TBP.	0.32, 0.51		25.32	F	2.988	2.313, 1.900	1.928–2.087 2.014–2.262	10.13	102.7 (OH) 86.8 (OCOCH ₃)	[27]

$[\text{Cu}_2(\mu\text{-O}_2\text{CC}_2\text{H}_5)(\mu\text{-OCOC}_2\text{H}_5)(\mu\text{-OH})(\text{dpyam})_2](\text{ClO}_4)$ (15)	Dist. Spy.	0.22, 0.43	25.7, 34.4	D	3.006	2.236, 2.318	1.931–1.959	24.1	101.8 (OH) 86.4 ($\text{O}_2\text{CCH}_2\text{CH}_3$)	[11]
$[\text{Cu}_2(\mu\text{-O}_2\text{CCCH}_3)_2(\mu\text{-OCOCCH}_3)(\text{dpyam})_2](\text{BF}_4)$ (16)	Dist. Spy.	0.07	120.1	C	3.402	2.144	1.967–2.002	–55.9	105.0 (OCOCCH_3)	[12]
$[\text{Cu}_2(\mu\text{-O}_2\text{CCCH}_3)_2(\mu\text{-OCOCCH}_3)(\text{bpy})_2](\text{ClO}_4)$ (17)	Dist. Spy.	0.14, 0.47		D	3.392	2.238, 1.930	1.939–1.977 1.974–2.169	3.6	109.8 (OCOCCH_3)	[1]
$[\text{Cu}_2\text{L}(\mu\text{-O}_2\text{CCCH}_3)_2](\text{ClO}_4) \cdot 3\text{H}_2\text{O}$ (18)	Dist. Spy.			D	3.263	2.169	1.942–2.046	–72	113.7 (OPh)	[32]

^a Abbreviations: bpy = 2,2'-bipyridine; dpyam = di-2-pyridylamine; phen = 1,10'-phenanthroline; L = 2,6-bis(*N*-methylpiperazino)methyl-4-chlorophenol, n.d. = not determined.

^b Dist. Spy. = distorted square pyramidal, Dist. TBP = distorted trigonal bipyramidal.

^c *J* = singlet–triplet energy gap.

the axial–equatorial positions, the other one is in an equatorial–equatorial configuration. An example of each class is presented in Fig. 6.

3.3. Spectral characterization

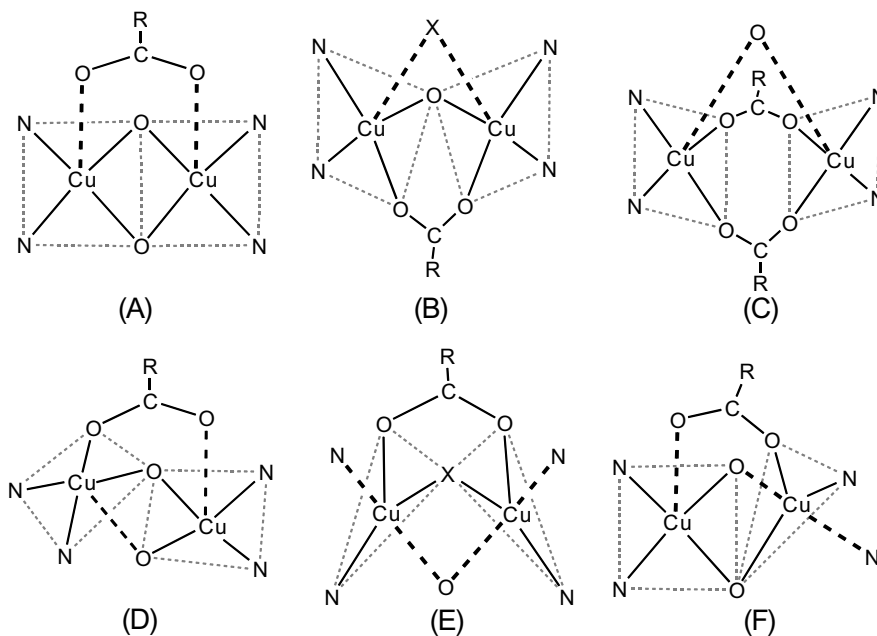
The infrared spectra display a broad band at $\sim 3500\text{ cm}^{-1}$, which can be assigned to the bridging OH vibration of the hydroxido ligands and/or lattice water. The spectrum in complex **1** also exhibits a broad and intense band at 1570 cm^{-1} , corresponding to the $\nu_{\text{as}}(\text{COO}^-)$ vibration and a medium broad band at 1350 cm^{-1} , corresponding to the $\nu_{\text{s}}(\text{COO}^-)$ vibration, the difference Δ [$\Delta = \nu_{\text{as}}(\text{COO}^-) - \nu_{\text{s}}(\text{COO}^-)$; 220 cm^{-1}] is close to that of NaO_2CH (201 cm^{-1}) as expected for the tri-atomic bridging coordination mode of the formate anion within a dinuclear species [1,21]. Owing to the presence of two different coordination modes of carboxylate bridges in **2–6**, $\nu_{\text{as}}(\text{COO}^-)$ and $\nu_{\text{s}}(\text{COO}^-)$ bands are observed in their IR spectra (1556 and 1385 cm^{-1} bands for **2**, 1558 and 1384 cm^{-1} bands for **3**, 1559 and 1396 cm^{-1} bands for **4**, 1553 and 1395 cm^{-1} bands for **5** and 1549 and 1384 cm^{-1} for **6**). The IR spectra of compounds **1–5** show broad and intense bands of the ionic ClO_4^- anion (1089 – 1100 cm^{-1} for **1**), ionic $\text{S}_2\text{O}_8^{2-}$ (1232 – 1280 cm^{-1} for **2**), ionic NO_3^- anion (1365 – 1386 cm^{-1} for **3** and 1362 – 1384 cm^{-1} for **5**) and ionic BF_4^- anion (1084 – 1100 cm^{-1} for **4**) [29].

The electronic diffuse reflectance spectra of **1** and **2** show a single broad band centered at 14000 and 13300 cm^{-1} . This observed single broad peak is consistent with the tetrahedrally-distorted square pyramidal stereochemistry and assigned to be the $d_{z^2}, d_{xy}, d_{xz}, d_{yz} \rightarrow d_{x^2-y^2}$ transition [30].

The diffuse reflectance spectra of **3–6** display a broad band (16500 , 16200 , 16100 and 15600 cm^{-1} for **3**, **4**, **5** and **6**, respectively) and a lower energy shoulder (14200 , 14100 , 13600 and 13200 cm^{-1} for **3**, **4**, **5** and **6**, respectively), the relatively higher energy of this triply-bridged dinuclear species is unusual for the square-pyramidal geometry. However, they are consistent with those observed for the related dpyam, bpy and phen complexes [10–12] and the $d_{xy}, d_{yz} \rightarrow d_{x^2-y^2}$ and $d_{xz}, d_{yz} \rightarrow d_{x^2-y^2}$ transitions are assigned for a broad band and a lower energy shoulder, respectively.

3.4. EPR and magnetic properties

The X-band EPR was measured on polycrystalline samples at RT and 77 K for all six compounds. All compounds (except compound **2**) showed at RT and at 77 K broad bands at the high field and at the low field side both at RT and 77 K , typical for triplet $S = 1$ signal with a large zero-field splitting. The occurrence of other peaks at high field indicates that the axial zero-field splitting parameter *D* is larger than the EPR quantum (ca. 0.3 cm^{-1}). No attempts were undertaken to determine the value of the zero-field splitting. Compound **1** shows,



Scheme 1.

however, a somewhat more complicated $S = 1$ signal, which is stronger and more pronounced at 77 K (see Figs. S6 and S7), while compound **2** shows a peculiar, very broad signal at $g = 2.08$ and a small hump at $g = 2.4$ (see Fig. S8). All spectra also contain at around 320 mT a weak signal which arises from a monomeric impurity, which is almost always present in dinuclear compounds. In compound **6** this signal is rather strong and sharp. Detailed analysis is not possible as the signals are too weak and too broad at 77 K, and as EPR at 4 K is not available. The same type of spectra was also observed for other triply-bridged compounds [10–12].

To investigate the magnetic behavior in more detail we undertook magnetic susceptibility measurements from 5 to 250 K for a selection of compounds, i.e. **1**, **4** and **6**. The susceptibility measurements from the other three compounds (**2**, **3** and **5**) did not give clear data, probably due to the fact that the structure gradually changes upon cooling and/or losing solvent in the lattice. The magnetic properties are depicted in Figs. 7–9, for compounds **1**, **4** and **6**, respectively, in the form of μ_{eff} versus T plots for two Cu(II) ions. All three compounds show a similar behaviour. At 250 K the μ_{eff} is $2.75 \mu_{\text{B}}$ per 2 Cu ions for compound **1** ($2.64 \mu_{\text{B}}$, for **4** and $2.68 \mu_{\text{B}}$, for **6**) which agrees reasonable with the spin-only value calculated for two uncoupled spin $S = 1/2$ Cu(II) centres. Upon cooling μ_{eff} raises gradually to reach 2.87, 2.81 and $2.79 \mu_{\text{B}}$, at around 30 K, for compounds **1**, **4** and **6**, respectively. This behaviour is typical for a ferromagnetically coupled Cu(II) dinuclear compounds. Below that temperature, μ_{eff} then diminishes till a value around $2.47 \mu_{\text{B}}$ for compound **1** ($2.77 \mu_{\text{B}}$ for **4** and $2.73 \mu_{\text{B}}$ for **6**) at 5 K for the three compounds, which may originate from intermolecular antiferromagnetic interactions, and/or from zero-field splitting

of the $S = 1$ state of the dinuclear species. The theoretical expression for the magnetic susceptibility for two interacting $S = 1/2$ centres, based on the general Hamiltonian [31] is: $H_{\text{ex}} = -JS_1S_2$, in which the exchange parameter J , is negative for antiferromagnetic and positive for ferromagnetic interaction. The magnetic data were fitted to the equation given in the literature for dinuclear copper compounds [31]: $\chi_{\text{m}} = (2Ng^2\beta^2)[kT - (2zJ'/(3 + \exp(-J/kT)))]^{-1} [3 + \exp(-J/kT)]^{-1}(1 - p) + \chi_{\text{p}}p + \text{TIP}$, in which N , g , β , k and T have their usual meanings [31]. The parameter p denotes the fraction of paramagnetic impurity in the sample and zJ' the interaction between neighbouring dinuclear identities. A temperature independent paramagnetism (TIP) was also considered and fixed at 60×10^{-6} per copper ion. The fit was accomplished by minimisation of $R = \sum(\chi_{\text{m}} \cdot T_{\text{calc}} - \chi_{\text{m}} \cdot T_{\text{obs}})^2 / (\chi_{\text{m}} \cdot T_{\text{obs}})^2$ by least-squares procedure.

The best fit was obtained for compound **1** with the following values: $J = 112.7 \text{ cm}^{-1}$, $g = 2.09$, $zJ' = -10.0 \text{ cm}^{-1}$, $p = 0.06$, with a final R of 2.0×10^{-3} (see solid line in Fig. 7). For compound **4** these values are $J = 120.8 \text{ cm}^{-1}$, $g = 1.98$, $zJ' = -0.21 \text{ cm}^{-1}$, $p = 0.0$, with a final R of $2.0 \cdot 10^{-3}$ (see solid line in Fig. 8). For compound **6** these values are $J = 145.3 \text{ cm}^{-1}$, $g = 1.98$, $zJ' = -0.8 \text{ cm}^{-1}$, $p = 0.06$, with a final R of 4.0×10^{-4} (see solid line in Fig. 9).

4. Magneto-structural correlation

For planar dihydroxido-bridged copper(II) dinuclear species, a linear correlation between the Cu–O–Cu bridging angle and the singlet–triplet energy gap (J) was first observed by Hodgson and co-workers [22,23]. An antiferromagnetic interaction is found when the Cu–O–Cu angle is larger than 97.5° , but when the Cu–O–Cu angle is smaller than 97.5° , a ferromagnetic interaction would be

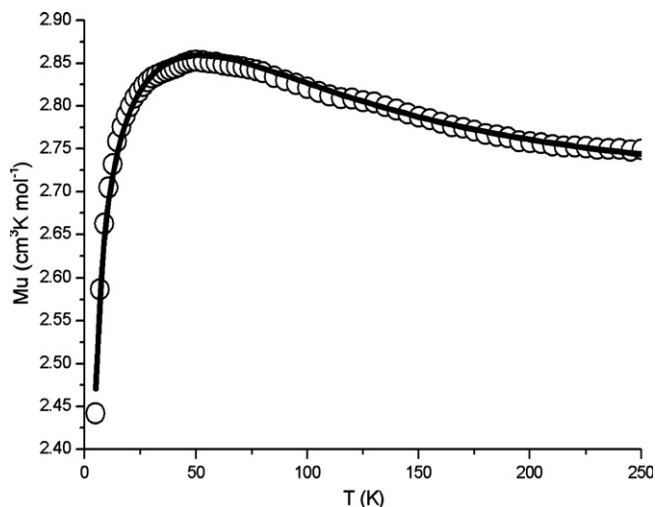


Fig. 7. A plot of the temperature dependence of μ_{eff} vs. T for compound **1**. The solid line represents the calculated curve (see text).

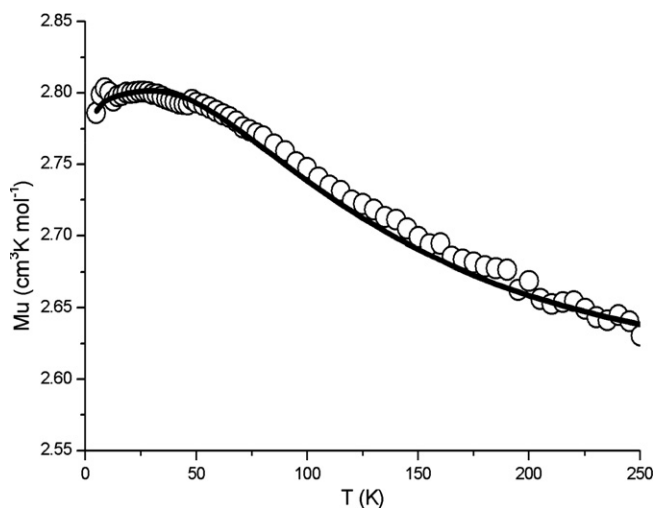


Fig. 8. A plot of the temperature dependence of μ_{eff} vs. T for compound **4**. The solid line represents the calculated curve (see text).

expected. Several theoretical approaches were applied to understand the behavior of the antiferromagnetic and ferromagnetic interaction of such dihydroxido-bridged copper(II) dinuclear species [22–27]. In this case, complex **1** can be analyzed using Hodgson and Hatfield's linear relationship to predict the magnetic properties in complex **1**.

Complex **1** exhibits a distorted square pyramidal geometry (class A), in which the unpaired electron is located in a $d_{x^2-y^2}$ type orbital. The $d_{x^2-y^2}$ magnetic orbital in **1** is directed toward the dihydroxido bridges, the Cu–O–Cu angles of 95.9° and 96.0°. For these bridging angles, a moderate ferromagnetic coupling ($J = 122.5 \text{ cm}^{-1}$) should be expected following Hodgson and Hatfield's linear relationship [22,23]. However, the tetrahedral distortion of the square bases may slightly reduce the magnitude of interaction. In fact, this feature can be predicted from the

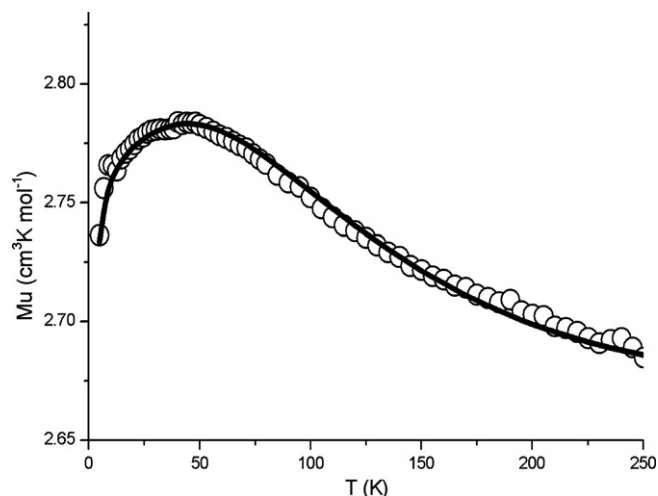


Fig. 9. A plot of the temperature dependence of μ_{eff} vs. T for compound **6**. The solid line represents the calculated curve (see text).

HOMO–LUMO energy gap using extended Hückel molecular orbital (EHMO) calculation (see Section 5).

Complexes **2–6** are classified in class B, Scheme 1 and Table 2, together with few relevant complexes with their previously reported J values, therefore the correlation between structure and magnetic exchange interaction can be performed for class B complexes with four data points (complexes **4**, **6**, **8**, **9**). These complexes offer the clear linear correlations in the plots of J versus Cu–OH–Cu (Fig. 10), J versus angle between basal planes (Fig. S9) and J versus Cu–Cu distance (Fig. S10). The J value increases upon increasing these structural parameters. Consequently, the J values of complexes **2**, **3** and **5** could be predicted to be 205.2, 146.1 and 142.0 cm^{-1} , respectively, following the J versus Cu–OH–Cu plot (see Fig. 10). However, a large number of the detailed structures and their magnetic properties are required for a clear correlation to be observed. An explanation for such a trend can be made in term of countercomplementary effect between the hydroxido bridge which generates ferromagnetic interaction due to the orbital orthogonality and one triatomic bridge in *syn-syn* equatorial–equatorial configuration which usually contributes a weak antiferromagnetic interaction.

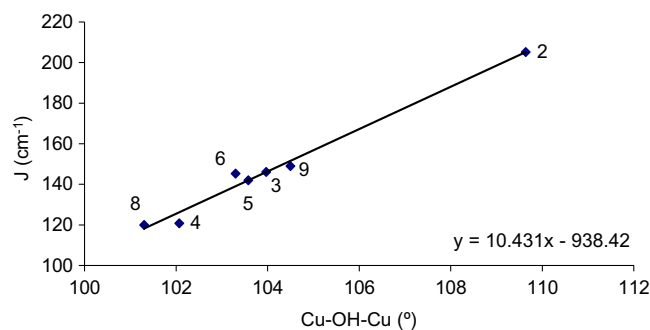


Fig. 10. Plot of J (cm^{-1}) vs. Cu–OH–Cu (°) for class B, the data points of complexes **2**, **3** and **5** are expected from this linear correlation.

Table 3
Energies and participation of atomic orbitals in HOMO and LUMO orbitals calculated for complexes **1–6**

Compound	1	2	3	4	5	6
Energy GAP between HOMO and LUMO orbitals (eV)	0.55	0.005	0.115	0.147	0.134	0.019
HOMO Cu d orbitals participation (%)	30	32	35	34	37	25
HOMO N p orbitals participation (%)	22	22	25	20	18	4
HOMO bridge O p orbitals participation (%)	8	3	2	2	5	12
LUMO Cu d orbitals participation (%)	4	32	34	36	34	28
LUMO N p orbitals participation (%)	20	21	18	15	14	5
LUMO bridge O p orbitals participation (%)	<1	<1	2	3	2	12

Class C complex **16** (see Table 2) revealed a moderate antiferromagnetic interaction with a J value of -55 cm^{-1} , a similar trend found for the classical dinuclear paddle-wheel copper(II) species with four bridges, but with a different number of carboxylate bridges in complex **16**, leading to a smaller J value compared to those of the dinuclear paddle-wheel copper(II) species ($J = -142$ to -300 cm^{-1}).

A possible magnetic exchange pathway for class-D complexes (see Fig. 6 and Table 2) is a single Cu–OH–Cu (101.8°) unit for complex **15** and a triatomic carboxylato bridge for complex **17** which links Cu(II) centres in an equatorial–equatorial configuration. This structure can occur with less electron density due to the nearly intermediate geometry ($\tau = 0.43$ for **15** and 0.47 for **17**) of one Cu(II) centre. Consequently, another possible pathway with less electron density is the triatomic carboxylato bridge for **15** and the monoatomic carboxylato Cu–O–Cu unit (109.8°) for **17**. Hence, a small J value (24.5 cm^{-1} for **15** and 3.6 cm^{-1} for **17**) observed for both complexes may result from a countercomplementary effect between the monoatomic bridge with a small bridging angle which usually contributes the ferromagnetic interaction due to the orthogonality between the copper magnetic orbitals and the oxygen p-orbital, and the triatomic carboxylato bridge which usually contributes to an antiferromagnetic interaction. Another unique orientation of three bridges in the class-D complex was found in $[\text{Cu}_2\text{L}(\mu\text{-O}_2\text{CCH}_3)_2](\text{ClO}_4) \cdot 3\text{H}_2\text{O}$ (**18**) where $\text{LH} = 2,6\text{-bis}(N\text{-methylpiperazino})\text{methyl-4-chlorophenol}$ (see Fig. 6 and Table 2) in which a possible pathway occurs via the Cu–O–Cu unit with an equatorial–equatorial configuration and a large bridging angle of 113.7° , leading to a negative J value of -72 cm^{-1} [32]. It is quite clear that the antiferromagnetic contribution increases upon increasing this bridging angle, thus allowing electron delocalization along the Cu–O–Cu unit. The remaining two triatomic carboxylato bridges which link Cu(II) centres in an axial–equatorial configuration provide a minor influence on the magnetic exchange interaction of the compound.

Class E complexes have a moderate ferromagnetic interaction. The superexchange mechanism for these complexes may be described in term of orbital orthogonality between the copper magnetic orbitals and oxygen p-orbital via Cu–OH–Cu unit allowing two unpaired electrons spins paralleled. As a result, it seems to be reliable to mention that

the dominant ferromagnetic interaction increases with increasing in bridging angle Cu···Cu distance (compounds **10–12**, Table 2) till a certain maximum value, then decreases (compounds **10–13**, Table 2). However, no clear correlation has been observed for class E complexes reported in the literature. Hence, more detailed structures and magnetic properties are required to study the magneto-structural correlation in class E complexes.

A class F complex revealed a weak ferromagnetic nature. The τ values of 0.32 and 0.51 of Cu centres indicate magnetic orbital mainly to be $d_{x^2-y^2}$ and intermediate between $d_{x^2-y^2}$ and d_{z^2} , respectively. This situation usually results in a weak ferromagnetic interaction. Additionally, the presence of the $\eta^1:\eta^1:\mu$ -carboxylate with axial–equatorial configuration may lead to countercomplementary effect giving rise to a small J value, Table 2.

5. Theoretical calculations

Extended Hückel molecular orbital (EHMO) calculations have been carried out on complexes **1–6**, **8** and **9** (see Table 2) with the CACAO program [16], keeping the overall molecular structure unchanged to establish the mechanism of magnetic superexchange interaction through the triple bridges. The singlet–triplet energy gap could decrease with decrease in antiferromagnetic interaction. As the results, the calculated HOMO–LUMO energy gap are 0.55, 0.005, 0.115, 0.147, 0.134, 0.133, 0.162 and 0.111 eV for **1–6**, **8** and **9**, respectively. The results imply that a small difference in energy gap has a large influence on the magnetic interactions, the overall ferromagnetic interaction increases with decrease in energy gap as show in Fig. S11. This plot can confirm the predicted J value for class B complexes. The HOMO and LUMO of class B complexes (**2–6**, **8** and **9**) are close in energy while the energy gap of **1** is significantly larger. The complexes **1–6** are clarified drawing the two corresponding molecular orbitals (Figs. S12–S17). In both MOs the magnetic orbitals are mainly centered in the $d_{x^2-y^2}$ copper orbitals, in agreement with the geometry of the metal ions. The HOMO of **1** is delocalized on the atomic orbitals of both hydroxido bridging ligands, no overlapping through both hydroxido bridges is observed for the LUMO. The important contribution of each Cu(II) ion of 15% is found in the HOMO and a few contribution (2%) of each Cu(II) ion is found in LUMO orbitals. A possible reason of the large

HOMO–LUMO energy gap is the determining factor for the antiferromagnetic contribution to J (singlet–triplet energy difference) of compound **1**. This is in agreement with the large singlet–triplet energy difference observed for planar hydroxido-bridged copper(II) complexes [33].

The HOMO and LUMO of **2** are slightly different in energy and the overlap through the OH and carboxylate bridges is small, resulting ferromagnetic interaction. In complex **2**, the important contribution of each copper(II) ion of 16% is found in HOMO orbital (see Table 3).

The HOMO and LUMO of **3–6** are delocalized on the atomic orbital of hydroxido and O of carboxylate bridging and absent in the OH₂ (complexes **3–5**) or Cl (complex **6**) bridging which are in the axial position for each complex (see Table 3). In complexes **3–6**, the important contribution in HOMO of one of the copper(II) ions (21%, 23%, 21%, 18% in **3–6**, respectively) and smaller contribution to the other one (14%, 11%, 16%, 7% in **3–6**, respectively) are found. The HOMO and LUMO are slightly different in energy and the overlap through the OH and carboxylate bridges is small. This feature should result in a ferromagnetic interaction that can occur through this bridging ligand, as there is the orthogonality between the copper molecular orbital and the oxygen orbital of the OH bridge. A summary of the results obtained from EH analysis performed for **1–6** is shown in Table 3. However, DFT calculations have generally superseded EHMO, but if the results are not significantly different then EHMO is sufficient and faster. The theoretical investigation of magnetic properties are well studied for the dihydroxido-bridged [28], paddle-wheel carboxylato-bridged [34] and azido-bridged [35] dinuclear copper(II) complexes while that for the triply-bridged dinuclear copper(II) complexes has not been reported so far.

6. Conclusions

As a summary, a family of dinuclear triply-bridged copper(II) complexes bearing carboxylato bridges has been classified in terms of their relative arrangements of both local copper(II) chromophores, geometries and carboxylate bridging modes into different classes (A–F) and the efforts have been made to develop the magneto-structural correlation. The most logical explanation for their different magnetic behaviors have been provided in order to gain better understanding in the influence of various types of structures on the sign and magnitude of magnetic exchange interaction in this family of complexes. The results obtained from the EH calculations have proven to be useful for the proper interpretation and correlation of the magnetic and structural data. Linear correlations have been found for class B complexes and revealed that small geometric deviations may produce large energy gaps and therefore significant differences in the magnitude of the magnetic exchange interaction. So, more compounds with a careful inspection of structural parameters combined with their magnetic properties are demanded for both

experimental and theoretical analyses which may lead to a very good magneto-structural correlation and using also the more accurate DFT calculations. A better understanding of factors that favor ferromagnetism in this family of complexes is expected to be useful for the design of novel ferromagnetic materials.

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Appendix A. Supplementary material

CCDC 654135, 654136, 654137, 654138, 654139 and 654140 contain the supplementary crystallographic data for **1**, **2**, **3**, **4**, **5** and **6**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.poly.2007.09.009](https://doi.org/10.1016/j.poly.2007.09.009).

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Aqua(2,2'-bipyridyl)chloronitratocopper(II)

Sujitra Youngme, Jaturong Phatchimkun and Narongsak Chaichit

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Aqua(2,2'-bipyridyl)chloronitrato-copper(II)

Sujittra Youngme,^{a*} Jaturong Phatchimkun^a and
Narongsak Chaichit^b^aDepartment of Chemistry, Faculty of Science, Khon Kaen University, Khon Kaen 40002, Thailand, and ^bDepartment of Physics, Faculty of Science and Technology, Thammasat University Rangsit, Pathumthani 12121, Thailand
Correspondence e-mail: sujittra@kku.ac.th

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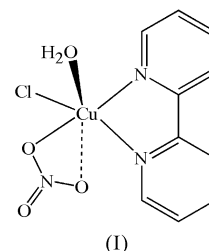
Online 10 November 2006

In a new hydrogen-bonded three-dimensional complex, $[\text{CuCl}(\text{NO}_3)(\text{C}_{10}\text{H}_8\text{N}_2)(\text{H}_2\text{O})]$, the Cu atom has an elongated tetragonal octahedral environment, with two 2,2'-bipyridyl N atoms, one nitrate O atom and one Cl atom forming the equatorial plane, and a second O atom of the nitrate anion and a water molecule in the axial positions. The complex molecules are linked to form a three-dimensional supramolecular array by hydrogen-bonding interactions both between the water O atom and nitrate O atoms, and between the water O atom and the Cl atom of a neighboring molecule.

Comment

In the past decade, the design and synthesis of metal-organic compounds based on the principles of crystal engineering have made rapid progress (Li *et al.*, 2006). Furthermore, the rational design and construction of specific architectures are beneficial for preparing functional materials. Self-assembly of metal compounds by hydrogen bonds into one-, two- and three-dimensional supramolecular architectures connects with biological chemistry, materials chemistry (such as organic films and magnetic materials) and supramolecular chemistry (Chen *et al.*, 2001). Hydrogen bonds play vital roles in highly efficient and specific biological reactions, and are essential for molecular recognition and self-organization of molecules in supramolecular chemistry. Copper complexes have been studied extensively in recent years. Their flexibility, facility of preparation and capacity for stabilizing unusual oxidation states can explain their successful performance in mimicking peculiar geometries around the metal, leading to very interesting spectroscopic properties and varied reactivities (Hathaway, 1987). Moreover, copper complexes have been used extensively as catalysts for a wide variety of reactions, including olefin polymerization (Killian *et al.*, 1996) and oxygen activation (Jung *et al.*, 1996). The stereochemistry of a series of mono(chelate) copper(II) complexes containing an

oxoanion and a halide is currently of interest to us. With the flexible di-2-pyridylamine (dpyam) ligand, the complexes $[\text{CuCl}(\text{NO}_3)(\text{dpyam})] \cdot 0.5\text{H}_2\text{O}$ (Mathews & Manohar, 1991), $[\text{CuCl}(\text{O}_2\text{CCH}_3)(\text{dpyam})]$ (Ugozzoli *et al.*, 1997) and $[\text{CuCl}(\text{O}_2\text{CCH}_2\text{CH}_3)(\text{dpyam})] \cdot \text{H}_2\text{O}$ (Youngme *et al.*, 1999) have been found so far. The former involves a polymeric structure bridged by a chloride ion, while the latter two compounds exhibit monomeric units. In the present paper, we report the crystal structure of the less flexible 2,2'-bipyridyl (bpy) complex $[\text{CuCl}(\text{NO}_3)(\text{bpy})(\text{H}_2\text{O})]$, (I), in which a three-dimensional supramolecular array is formed by hydrogen-bonding interactions. Structural comparison with related complexes has been made and the spectroscopic properties of the complexes are discussed.



The structure of (I) is made up of discrete $[\text{CuCl}(\text{NO}_3)(\text{bpy})(\text{H}_2\text{O})]$ units. The Cu atom is six-coordinated in a distorted octahedral arrangement (Table 1), with two N atoms of the bpy ligand, one O atom of the nitrate anion (atom O2) and a chloride anion forming the equatorial plane, while a second nitrate O atom $[\text{Cu1}-\text{O3} = 2.6262(16) \text{ \AA}]$ and a water O atom occupy the tetragonal positions, thus giving an elongated octahedral geometry with tetragonality ($T = \text{mean in-plane distance}/\text{mean out-of-plane distance}$) of 0.84. The tetragonal octahedral arrangement is typical and expected for Cu^{II} in view of the Jahn-Teller effect (Jahn & Teller, 1937). However, the title compound is further distorted with regard to the coordination of atom O3 from the nitrate ligand, which occupies the off-axis tetragonal position with an axial $\text{O1}-\text{Cu1}-\text{O3}$ angle much less than 180° [$144.17(1)^\circ$], leading to semicoordination to the Cu^{II} ion. The equatorial plane shows a

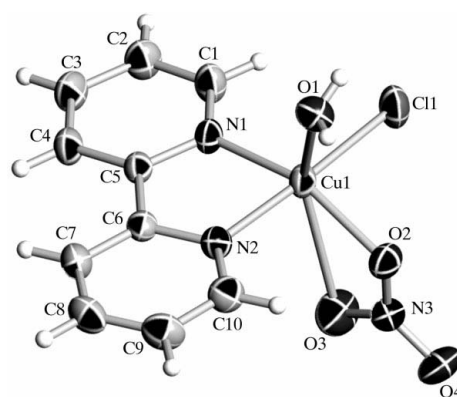


Figure 1
The molecular structure of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme.

slight tetrahedral twist, as is evident from the dihedral angle of $10.0(1)^\circ$ at which the N1/Cu1/N2 and Cl1/Cu1/O2 planes cross. The local molecular geometry of (I) is best described as elongated octahedral with a long off-axis axial bond giving a $(4+1+1')$ structure. The equatorial Cu—Cl distance is normal, in agreement with a previous report (Hathaway, 1987).

The structure of the title complex is found to be different from that of the closely related dpyam complex $[\text{CuCl}(\text{NO}_3)(\text{dpyam})] \cdot 0.5\text{H}_2\text{O}$ (Mathews & Manohar, 1991). This compound consists of polymeric $[\text{CuCl}(\text{NO}_3)(\text{dpyam})]_n$ zigzag chains with monodentate nitrate and bridging chloride ligands and involves a distorted square-based pyramidal geometry. The copper environment in (I) is also different from those of the related dpyam complexes with monovalent acetate and propionate oxoanions, viz. $[\text{CuCl}(\text{O}_2\text{CCH}_3)(\text{dpyam})]$ (Ugozzoli, *et al.*, 1997) and $[\text{CuCl}(\text{O}_2\text{CCH}_2\text{CH}_3)(\text{dpyam})] \cdot \text{H}_2\text{O}$ (Youngme *et al.*, 1999), which comprise mononuclear units with bidentate acetate or propionate ligands and, in the latter, an uncoordinated water molecule, giving a distorted square-based pyramidal geometry. The most similarity to compound (I) is found in the square-pyramidal complex $[\text{Cu}(\text{NCS})(\text{O}_2\text{CCH}_3)(\text{dpyam})(\text{H}_2\text{O})]$ (Youngme *et al.*, 2006), containing a pseudohalide, a coordinated water molecule and a monodentate acetate ligand. The second O atom of the acetate anion coordinates to the Cu^{II} ion in a similar fashion to that of the nitrate in compound (I), but with a very long Cu—O distance [$3.064(1) \text{ \AA}$]. These observations

indicate that both the chelate function of the bpy and dpyam ligands, and the coordination nature of oxoanions, are responsible for the structure of this complex system. This implies that the more flexible dpyam ligand results in a greater variety of geometries and structures (Amournjarusiri & Hathaway, 1991).

The electronic reflectance spectrum of (I) involves a single broad peak at $13\,850 \text{ cm}^{-1}$, corresponding to an elongated tetragonal octahedral geometry with off-axial-direction coordination from the normal to the N1/N2/O2/Cl1 plane (Procter *et al.*, 1972). The electronic spectrum of (I) is similar to those found in complexes with similar Cu^{II} environments, viz. $[\text{Cu}(\text{O}_2\text{CCH}_3)_2(\text{dpyam})] \cdot 2\text{H}_2\text{O}$ ($13\,510 \text{ cm}^{-1}$), $[\text{Cu}(\text{NO}_2)(\text{O}_2\text{CCH}_3)(\text{dpyam})] \cdot \text{H}_2\text{O}$ ($13\,880 \text{ cm}^{-1}$), $[\text{Cu}(\text{NO}_2)_2(\text{dpyam})]$ ($13\,890 \text{ cm}^{-1}$), $[\text{Cu}(\text{NO}_3)_2(\text{dpyam})] \cdot 2\text{H}_2\text{O}$ ($13\,580 \text{ cm}^{-1}$) (Youngme *et al.*, 2002) and $[\text{Cu}(\text{NCS})(\text{O}_2\text{CCH}_3)(\text{dpyam})(\text{H}_2\text{O})]$ ($15\,980 \text{ cm}^{-1}$) (Youngme *et al.*, 2006). The symmetric and antisymmetric NO stretchings appear as strong bands at 1310 and 1384 cm^{-1} , respectively, consistent with the asymmetric bidentate nitrate group (Lewis *et al.*, 1972). The complex molecules are linked to form a three-dimensional supramolecular array by hydrogen-bonding interactions between the water molecule and the coordinated nitrate O atoms and Cl atom of neighboring molecules (Table 2 and Fig. 2).

Experimental

The title complex was prepared by adding a warm solution containing $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (0.241 g, 1.0 mmol) in water (5 ml) to a warm solution of 2,2'-bipyridine (0.156 g, 1.0 mmol) in ethanol (20 ml), followed by the addition of solid NaCl (0.029 g, 0.5 mmol). The resulting blue solution was evaporated slowly at room temperature. After several days, blue–green crystals were formed. The crystals were filtered off, washed with mother liquor and air-dried.

Crystal data

$[\text{CuCl}(\text{NO}_3)(\text{C}_{10}\text{H}_8\text{N}_2)(\text{H}_2\text{O})]$
 $M_r = 335.20$
 Monoclinic, $P2_1/n$
 $a = 10.8944(3) \text{ \AA}$
 $b = 10.6760(3) \text{ \AA}$
 $c = 11.0496(3) \text{ \AA}$
 $\beta = 106.860(1)^\circ$
 $V = 1229.92(6) \text{ \AA}^3$

$Z = 4$
 $D_x = 1.810 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 $\mu = 2.01 \text{ mm}^{-1}$
 $T = 273(2) \text{ K}$
 Rhombus, blue–green
 $0.43 \times 0.35 \times 0.28 \text{ mm}$

Data collection

Siemens SMART CCD area-detector diffractometer
 ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 2000a)
 $T_{\min} = 0.441$, $T_{\max} = 0.576$

7471 measured reflections
 2718 independent reflections
 2466 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.016$
 $\theta_{\max} = 27.1^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.024$
 $wR(F^2) = 0.066$
 $S = 1.09$
 2718 reflections
 180 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0371P)^2 + 0.3286P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.30 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.63 \text{ e \AA}^{-3}$

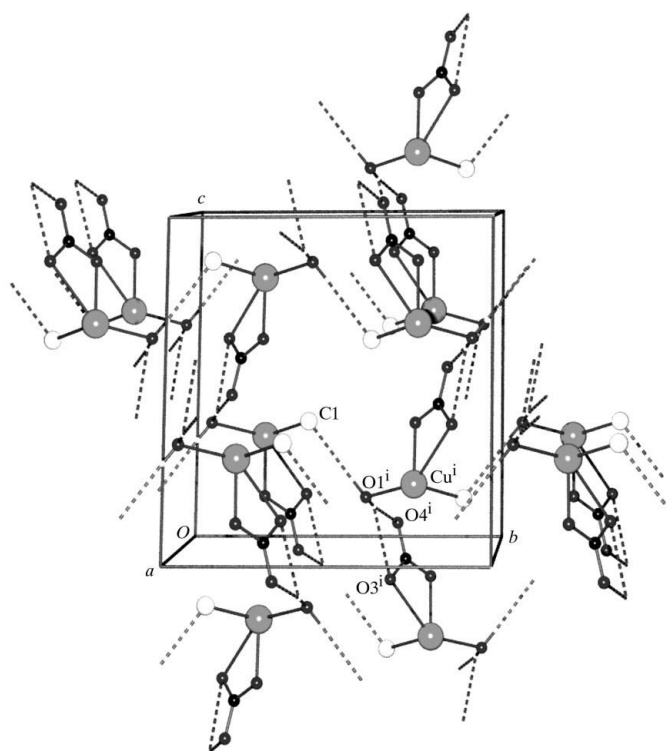


Figure 2

The packing of (I), with hydrogen bonds shown as dashed lines, showing the two-dimensional structure along the a axis. The bpy ligand has been omitted for clarity. [Symmetry code: (i) $\frac{5}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$.]

Table 1

Selected geometric parameters (Å, °).

Cu1—N2	2.0110 (14)	Cu1—Cl1	2.2581 (5)
Cu1—N1	2.0161 (14)	Cu1—O1	2.3040 (13)
Cu1—O2	2.0296 (13)		
N2—Cu1—N1	81.03 (6)	O2—Cu1—Cl1	91.49 (4)
N2—Cu1—O2	91.60 (6)	N2—Cu1—O1	86.15 (5)
N1—Cu1—O2	158.17 (6)	N1—Cu1—O1	108.23 (5)
N2—Cu1—Cl1	176.88 (4)	O2—Cu1—O1	91.60 (5)
N1—Cu1—Cl1	95.91 (4)	Cl1—Cu1—O1	94.22 (4)

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O1—H11...O3 ⁱ	0.82 (2)	2.54 (2)	3.165 (2)	134 (2)
O1—H11...O4 ⁱ	0.82 (2)	2.13 (2)	2.941 (2)	171 (2)
O1—H12...Cl1 ⁱⁱ	0.84 (2)	2.36 (2)	3.1918 (15)	173 (2)
C1—H1...Cl1	0.93	2.68	3.265 (2)	122
C10—H10...O2	0.93	2.57	3.064 (2)	114

Symmetry codes: (i) $x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$; (ii) $-x + \frac{5}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$.

H atoms in the bpy ligand were placed in idealized positions and constrained to ride on their parent atoms, with C—H distances of 0.93 Å and $U_{\text{iso}}(\text{H})$ values of $1.2U_{\text{eq}}(\text{C})$. H atoms bonded to the water O atom were visible in a difference map and were refined with a DFIX (*SHELXTL*; Sheldrick, 2000b) restraint of O—H = 0.85 (1) Å and with $U_{\text{iso}}(\text{H})$ values refined freely.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2000b); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

The authors gratefully acknowledge the Thailand Research Fund (grant Nos. RTA 4880008 and BRG 4980007), Khon

Kaen University, and the Higher Education Development Project: Postgraduate Education and Research Program in Chemistry, Thailand, for support.

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Acta Crystallographica Section C

**Crystal Structure
Communications**

ISSN 0108-2701

Editor: **George Ferguson**

Aqua(di-2-pyridylamine- $\kappa^2 N, N'$)(malonato- $\kappa^2 O, O'$)copper(II) monohydrate

Sujitra Youngme, Jaturong Phatchimkun and Narongsak Chaichit

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Aqua(di-2-pyridylamine- κ^2N,N')-(malonato- κ^2O,O')copper(II) monohydrate

Sujittra Youngme,^{a*} Jaturong Phatchimkun^a and Narongsak Chaichit^b

^aDepartment of Chemistry, Faculty of Science, Khon Kaen University, Khon Kaen 40002, Thailand, and ^bDepartment of Physics, Faculty of Science and Technology, Thammasat University Rangsit, Pathumthani 12121, Thailand
Correspondence e-mail: sujittra@kku.ac.th

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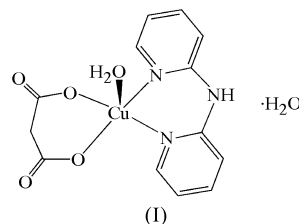
Online 22 November 2006

In the structure of the title complex, $[\text{Cu}(\text{C}_3\text{H}_2\text{O}_4)(\text{C}_{10}\text{H}_8\text{N}_3)(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}$ or $[\text{Cu}(\text{mal})(\text{dpyam})(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}$, where mal is malonate and dpyam is di-2-pyridylamine, the Cu^{II} atom displays square-pyramidal geometry, being coordinated by two N atoms from the dpyam ligand, two O atoms from the mal group and one O atom of a water ligand. The complex molecules are linked to form a three-dimensional network by hydrogen-bonding interactions between coordinated/uncoordinated water molecules and the uncoordinated malonate N and O atoms of neighboring molecules.

Comment

There has been considerable interest in the design and syntheses of transition metal complexes with the malonate ligand in coordination chemistry, owing to the fact that this type of complex has potential application in molecular-based magnets (Rodríguez-Martín *et al.*, 2001). The malonate dianion generally exhibits bi-, tri- or tetradentate coordination modes (Shen *et al.*, 2000). Although some complexes containing mixed malonate and nitrogen-donor ligands have been synthesized and characterized, complexes containing mixed malonate (mal) and di-2-pyridylamine (dpyam) ligands have not been reported. To the best of our knowledge, there are only four reports on structures with malonate and nitrogen-donor ligands, such as phen (1,10-phenanthroline), bpy (2,2'-bipyridyl) and bpym (2,2'-bipyrimidine), namely $[\text{Cu}(\text{mal})(\text{phen})(\text{H}_2\text{O})]\cdot 1.5\text{H}_2\text{O}$, (II) (Kwik *et al.*, 1986), $[\text{Cu}(\text{mal})(\text{bpym})(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}$, (III) (Rodríguez-Martín *et al.*, 2001), $[\text{Cu}(\text{mal})(\text{bpy})(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}$, (IV) (Suresh & Bhadbhade, 1997), and $[\text{Cu}(\text{mal})(\text{bpy})(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}$, (V) (Shen *et al.*, 2000). The first three compounds exhibit mononuclear structures, while the last compound involves a dinuclear unit. In this paper, we report the crystal structure of $[\text{Cu}(\text{mal})(\text{dpyam})(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}$, (I), in which the three-dimensional network is formed by hydrogen bonds. The dpyam ligand has been

selected primarily because of the fact that it also has an NH hydrogen-bond donor function that might form one-, two- or three-dimensional supramolecular architectures. The structure of complex (I) consists of neutral mononuclear $[\text{Cu}(\text{mal})(\text{dpyam})(\text{H}_2\text{O})]$ units (see Fig. 1) and crystallization water molecules. The Cu atom exhibits a slightly distorted square-pyramidal environment, the geometric τ value (Addison *et al.*, 1984) being only 0.045. The Cu^{II} ion is bonded to two dpyam N atoms and two carboxylate O atoms from the malonate ligand in the basal plane, and to a water molecule in the apical position (Table 1 and Fig. 1). The Cu atom is displaced by 0.257 (1) Å from the mean basal plane towards the apical position. In the Cu unit, the dihedral angle between the N1/Cu1/N2 and O1/Cu1/O2 planes is 21.3°. The dpyam ligands are not planar, with a dihedral angle of 22.9° between the pyridine planes. Other related examples including malonate are compounds (II)–(V). In each of these, the Cu^{II} atom exhibits a slightly distorted square-pyramidal geometry, with τ values of 0.057 for (II), 0.006 for (III), 0.061 for (IV) and 0.040 for (V).



The electronic reflectance spectrum of (I) involves two bands at 15 800 and 11 000 cm^{-1} ; this spectral character of the compound is consistent with the distorted square-pyramidal geometry and $\tau = 0.045$. The transitions may be assigned as the $d_{z^2} \rightarrow d_{x^2-y^2}$ transition for the low-energy peak and the $d_{xz} \simeq d_{yz} \rightarrow d_{x^2-y^2}$ transition for the high-energy peak. The electronic spectrum of (I) is similar to that found in a complex with similar Cu^{II} environment, *viz.* compound (V) (15 400 and 11 000 cm^{-1}). The IR spectrum of (I) exhibits several characteristic strong bands in the range 1670–1600 cm^{-1} , which are attributed to C=O stretching modes. The complex molecules are linked to form a three-dimensional network by hydrogen-bonding interactions between the NH group of the dpyam group and the uncoordinated water molecule, and between the

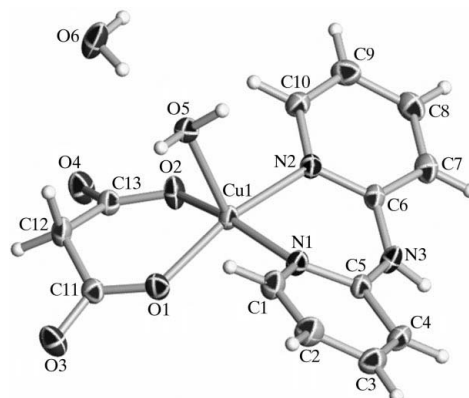


Figure 1
The molecular structure of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme.

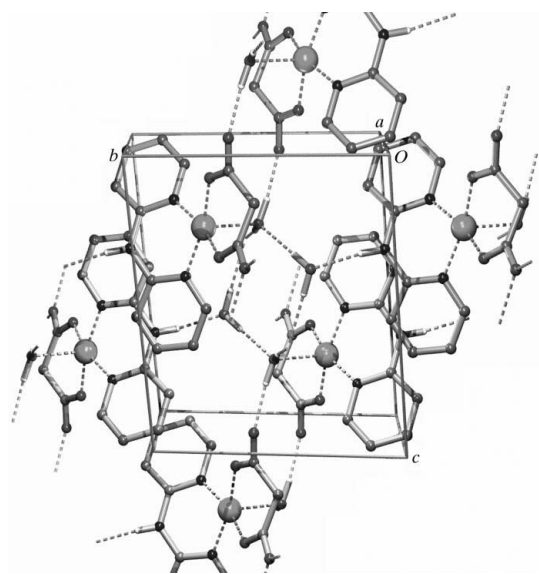


Figure 2
The packing of (I), with hydrogen bonds indicated by dashed lines, showing the three-dimensional structure.

coordinated water molecule and the uncoordinated malonate O atoms (Table 2 and Fig. 2). All available hydrogen-bonding donors take part in hydrogen bonds.

Experimental

A warming solution of copper(II) acetate monohydrate (0.181 g, 1.0 mmol) in water (10 ml) was added to a warming solution of di-2-pyridylamine (0.171 g, 1.0 mmol) in methanol (15 ml), and then solid disodium malonate monohydrate (0.084 g, 0.5 mmol) was added. The resulting green solution was evaporated slowly at room temperature. After several days, blue-green crystals had formed, and these were filtered off, washed with mother liquor and air-dried.

Crystal data

$[\text{Cu}(\text{C}_3\text{H}_2\text{O}_4)(\text{C}_{10}\text{H}_8\text{N}_3)(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$	$\gamma = 74.8440 (10)^\circ$
$M_r = 372.82$	$V = 730.46 (2) \text{ \AA}^3$
Triclinic, $P\bar{1}$	$Z = 2$
$a = 7.2409 (1) \text{ \AA}$	$D_x = 1.695 \text{ Mg m}^{-3}$
$b = 9.6351 (2) \text{ \AA}$	Mo $K\alpha$ radiation
$c = 11.43800 (1) \text{ \AA}$	$\mu = 1.53 \text{ mm}^{-1}$
$\alpha = 87.8150 (10)^\circ$	$T = 293 (2) \text{ K}$
$\beta = 71.7000 (10)^\circ$	Plate, blue-green
	$0.33 \times 0.32 \times 0.10 \text{ mm}$

Data collection

Siemens SMART CCD area-detector diffractometer	5409 measured reflections
ω scans	4432 independent reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 2000a)	3443 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.599$, $T_{\max} = 0.858$	$R_{\text{int}} = 0.018$
	$\theta_{\max} = 30.4^\circ$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2 + (0.0652P)^2 + 0.0267P)]$
$R[F^2 > 2\sigma(F^2)] = 0.034$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.101$	$(\Delta/\sigma)_{\max} = 0.001$
$S = 1.05$	$\Delta\rho_{\max} = 0.37 \text{ e \AA}^{-3}$
3945 reflections	$\Delta\rho_{\min} = -0.53 \text{ e \AA}^{-3}$
224 parameters	
H atoms treated by a mixture of independent and constrained refinement	

Table 1

Selected geometric parameters ($\text{\AA}$, $^\circ$).

Cu—O2	1.9368 (15)	Cu—N1	2.0002 (17)
Cu—O1	1.9396 (15)	Cu—O5	2.2722 (15)
Cu—N2	1.9929 (16)		
O2—Cu—O1	91.84 (7)	N2—Cu—N1	88.10 (7)
O2—Cu—N2	87.37 (7)	O2—Cu—O5	97.62 (7)
O1—Cu—N2	166.18 (7)	O1—Cu—O5	94.39 (7)
O2—Cu—N1	163.51 (7)	N2—Cu—O5	99.39 (6)
O1—Cu—N1	88.80 (7)	N1—Cu—O5	98.76 (6)

Table 2

Hydrogen-bond geometry ($\text{\AA}$, $^\circ$).

$D\cdots H\cdots A$	$D\cdots H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N3—H5 $\cdots$ O6 ⁱ	0.86	2.04	2.836 (3)	155
O5—H13 $\cdots$ O4 ⁱⁱ	0.85 (3)	1.86 (3)	2.702 (3)	173 (2)
O5—H14 $\cdots$ O3 ⁱⁱⁱ	0.89 (2)	1.82 (2)	2.706 (2)	173 (2)
O6—H15 $\cdots$ O4 ^{iv}	0.89 (2)	2.00 (2)	2.885 (3)	174 (2)
O6—H16 $\cdots$ O5	0.89 (4)	1.99 (4)	2.874 (3)	177 (2)

Symmetry codes: (i) $x, y+1, z$; (ii) $x+1, y, z$; (iii) $-x+1, -y+1, -z$; (iv) $-x, -y+1, -z+1$.

Water H atoms were visible in a difference map and were refined with a *DFIX* (*SHELXTL*; Sheldrick, 2000b) restraint [$\text{O—H} = 0.90 (1) \text{ \AA}$]. Other H atoms were placed in idealized positions and constrained to ride on their parent atoms, with $\text{C—H} = 0.93\text{--}0.97 \text{ \AA}$ and $\text{N—H} = 0.86 \text{ \AA}$ [$U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$].

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2000b); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SF3018). Services for accessing these data are described at the back of the journal.

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Acta Crystallographica Section E

Structure Reports

Online

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Acetatoaqua(di-2-pyridylamine)isothiocyanatocopper(II)

Sujittra Youngme, Thidarat Chotkhun and Narongsak Chaichit

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Acetatoaqua(di-2-pyridylamine)isothiocyanatocopper(II)

Sujittra Youngme,^{a*} Thidarat Chotkhun^a and Narongsak Chaichit^b^aDepartment of Chemistry, Faculty of Science, Khon Kaen University, Khon Kaen, 40002, Thailand, and ^bDepartment of Physics, Faculty of Science and Technology, Thammasat University Rangsit, Pathumthani, 12121, Thailand

Correspondence e-mail: sujittra@kku.ac.th

Key indicators

Single-crystal X-ray study

T = 273 K

Mean $\sigma(\text{C}-\text{C}) = 0.003 \text{ \AA}$

R factor = 0.020

wR factor = 0.051

Data-to-parameter ratio = 17.2

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

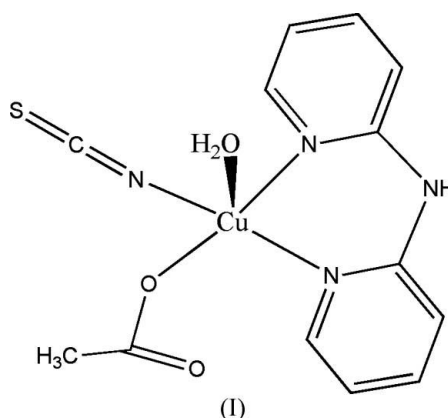
In the structure of the title complex, $[\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)(\text{NCS})-(\text{C}_{10}\text{H}_9\text{N}_3)(\text{H}_2\text{O})]$, the Cu^{II} atom displays a square-pyramidal geometry, coordinated by two N atoms of the di-2-pyridylamine ligand, the N atom from the isothiocyanate ligand and two O atoms from the acetate group and the water molecule. The structure displays intermolecular hydrogen bonding.

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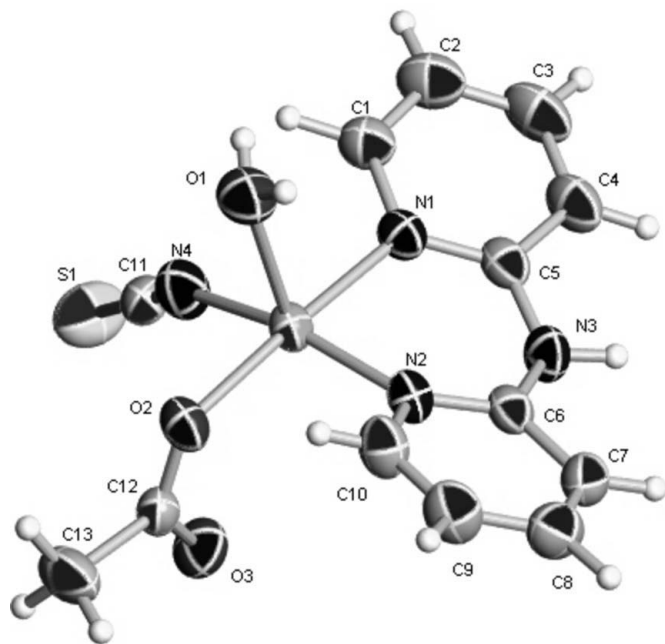
Accepted 4 July 2006

Comment

Copper(II) complexes are known to display a large variety of non-regular stereochemistries (Hathaway, 1987). A large number of $[\text{Cu}(\text{chelate})(\text{OXO})(\text{OYO})]^+$ cations, where the chelate is 2,2'-bipyridyl (bpy), 1,10-phenanthroline (phen) or di-2-pyridylamine (dpyam) and OXO and OYO are monovalent oxyanions, e.g. ONO^- , HCO_2^- , CH_3CO_2^- or $\text{CH}_3\text{CH}_2\text{CO}_2^-$, are well known and have been characterized as having distorted octahedral stereochemistry (Youngme *et al.*, 1998). However, very few complexes containing mixed pseudohalide and carboxylate ligands have been reported in the literature. In this study, we present the five-coordinate copper(II) complex acetatoaqua(di-2-pyridylamine)isothiocyanatocopper(II), (I).



The molecular structure of (I) is shown in Fig. 1. The coordination geometry around the Cu^{II} atom is distorted square pyramidal with a CuN_3O_2 chromophore ($\tau = 0.19$). The structure index is defined as $\tau = (\beta - \alpha)/60$, where β and α are the largest coordination angles; $\tau = 0$ for square pyramidal (SP) and $\tau = 1$ for trigonal bipyramidal (TBP) geometry (Addison *et al.*, 1984). The four shorter bonds in the basal plane involve two N atoms of the dpyam ligand, an O atom from an acetate anion and an N atom from an isothiocyanate anion. A coordinated water molecule occupies the axial positions with a longer Cu—O bond distance (Table 1). The Cu atom is displaced 0.166 (1) Å from its basal plane. The

**Figure 1**

The molecular structure of (I) with 50% probability displacement ellipsoids (arbitrary spheres for H atoms).

dihedral angle between the pyridine rings is 20.4 (1)°, and that between the N1—Cu—N2 and N4—Cu—O3 planes is 15.7 (1)°.

An intermolecular hydrogen-bonding network is present in the crystal structure of (I) (Table 2).

Experimental

The title complex was obtained as a side product in the preparation of $[\text{Cu}(\text{dpyam})_4(\mu\text{-NCS})_6(\text{OOCCH}_3)]$ by adding a warm solution of di-2-pyridylamine (0.171 g, 1.0 mmol) in methanol (20 ml) to a hot aqueous solution (10 ml) of $\text{Cu}(\text{CH}_3\text{COO})_2$ (0.182 g, 1.0 mmol) and KSCN (0.041 g, 0.5 mmol). An aqueous solution (5 ml) of NaOH (0.021 g, 0.5 mmol) was then added. The resulting green solution was allowed to evaporate slowly at room temperature. After several days, blue crystals of (I) formed. The crystals were filtered off, washed with mother liquor and dried in air.

Crystal data

$[\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)(\text{NCS})(\text{C}_{10}\text{H}_9\text{N}_3)(\text{H}_2\text{O})]$
 $M_r = 369.88$
 Orthorhombic, $P2_12_12_1$
 $a = 6.97420$ (10) Å
 $b = 13.2883$ (1) Å
 $c = 17.0472$ (2) Å
 $V = 1579.85$ (3) Å³

$Z = 4$
 $D_x = 1.555$ Mg m⁻³
 Mo $K\alpha$ radiation
 $\mu = 1.53$ mm⁻¹
 $T = 273$ (2) K
 Rod, blue
 $0.48 \times 0.30 \times 0.23$ mm

Data collection

Siemens SMART CCD area-detector diffractometer
 ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 2000a)
 $T_{\min} = 0.596$, $T_{\max} = 0.709$

11607 measured reflections
 4384 independent reflections
 4133 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.016$
 $\theta_{\max} = 30.4^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.020$
 $wR(F^2) = 0.051$
 $S = 1.05$
 4384 reflections
 255 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0328P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.24$ e Å⁻³
 $\Delta\rho_{\min} = -0.27$ e Å⁻³
 Absolute structure: Flack (1983),
 1666 Friedel pairs
 Flack parameter: 0.20 (2)

Table 1

Selected geometric parameters (Å, °).

O1—Cu1	1.9615 (10)	O3—Cu1	2.2937 (13)
N4—C11	1.153 (2)	Cu1—N1	2.0129 (12)
N4—Cu1	1.9794 (14)	Cu1—N2	2.0141 (12)
C11—S1	1.6237 (16)		
O1—Cu1—N4	88.74 (6)	N1—Cu1—N2	89.39 (5)
O1—Cu1—N1	90.41 (5)	O1—Cu1—O3	90.07 (5)
N4—Cu1—N1	164.83 (6)	N4—Cu1—O3	97.81 (7)
O1—Cu1—N2	176.11 (5)	N1—Cu1—O3	97.34 (6)
N4—Cu1—N2	90.43 (6)	N2—Cu1—O3	93.81 (5)

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O3—H12W ⁱ ...O2 ⁱ	0.81 (3)	1.98 (3)	2.782 (3)	171 (4)
O3—H11W ⁱ ...S1 ⁱ	0.77 (3)	2.72 (2)	3.436 (3)	166 (4)
N3—H5...O2 ⁱⁱ	0.87 (1)	1.96 (1)	2.831 (2)	176 (1)
C8—H8...O1 ⁱⁱⁱ	0.93 (1)	2.52 (1)	3.378 (1)	155 (1)

Symmetry codes: (i) $x + 1, y, z$; (ii) $x + \frac{1}{2}, -y + \frac{1}{2}, -z$; (iii) $-x + \frac{1}{2}, -y + 1, z - \frac{1}{2}$.

The H atoms of the dpyam ligand and coordinated water molecule were located in a difference Fourier map and refined isotropically, while the methyl H atoms were positioned geometrically, with C—H = 0.96 Å, and the torsion angle was refined to fit the electron density, $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$.

Data collection: SMART (Bruker, 2000); cell refinement: SAINT (Bruker, 2000); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Sheldrick, 2000b); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

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Acta Crystallographica Section E

Structure Reports

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***N*-(1-Phenyl-1,2-dihydro-2-pyridyl)pyridin-2-amine tetraphenylborate**

Sujittra Youngme, Nanthawat Wannarit and Narongsak Chaichit

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N*-(1-Phenyl-1,2-dihydro-2-pyridyl)pyridin-2-amine tetraphenylborate*Sujittra Youngme,^{a*} Nanthawat Wannarit^a and Narongsak Chaichit^b**^aDepartment of Chemistry, Faculty of Science, Khon Kaen University, Khon Kaen 40002, Thailand, and ^bDepartment of Physics, Faculty of Science and Technology, Thammasat University Rangsit, Pathumthani 12121, Thailand

Correspondence e-mail: sujittra@kku.ac.th

Key indicators

Single-crystal X-ray study

T = 273 KMean $\sigma(\text{C}—\text{C})$ = 0.003 Å*R* factor = 0.049*wR* factor = 0.125

Data-to-parameter ratio = 14.3

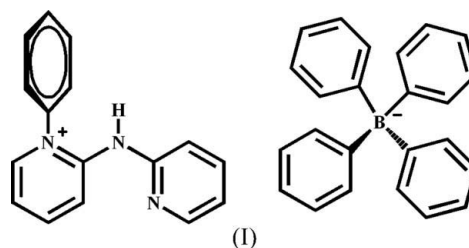
For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.In the title compound, $\text{C}_{16}\text{H}_{14}\text{N}_3^+ \cdot \text{C}_{24}\text{H}_{20}\text{B}^-$, both the cation and the anion are involved in intermolecular $\text{C}—\text{H} \cdots \pi(\text{arene})$ interactions as donors and acceptors.

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Comment

The tetraphenylborate ion $[\text{BPh}_4]^-$ has been widely used as a counter-ion in metal complexes (Kiviniemi *et al.*, 2001) as it can interact with cation centers *via* its phenyl groups. A strong cation– $\pi(\text{arene})$ interaction can arise (when the cation is a transition metal complex) as a metal ligand aromatic cation– π (MLAC π) interaction (Zarić *et al.*, 2000). Moreover, in recent years, much attention has been directed at $\text{C}—\text{H} \cdots \pi(\text{arene})$ interactions between organic cations and phenyl rings from the $[\text{BPh}_4]^-$ anion, and this is often an important factor in the crystal packing (Thalladi *et al.*, 2000; Suezawa *et al.*, 2001). We report here the $\text{C}—\text{H} \cdots \pi$ interactions in the crystal structure of *N*-(1-phenyl-1,2-dihydro-2-pyridyl)pyridin-2-amine tetraphenylborate, (I) (Fig. 1). The N-heteroaromatic cation consists of dpyam and phenyl rings connected to each other *via* a pyridine N atom of a dpyam ring; the dihedral angle between the phenyl ring and mean plane of dpyam is 81.4 (1)°.



The crystal packing in (I) involves $\text{C}—\text{H} \cdots \pi(\text{arene})$ interactions (Table 1) as depicted in Fig. 2, leading to two-dimensional layers. The N-heteroaromatic cation is situated between two $[\text{BPh}_4]^-$ anions and this orientation is stabilized *via* $\text{C}—\text{H} \cdots \pi(\text{arene})$ interactions (Table 1). The $[\text{BPh}_4]^-$ angles $\text{B1}—\text{C29} \cdots \text{C32} = 172.4$ (1)° and $\text{B1}—\text{C23} \cdots \text{C26} = 172.8$ (1)° of the $[\text{BPh}_4]^-$ anion deviate from linearity with a sizeable distortion as both phenyl rings involve shorter $\text{C}—\text{H} \cdots \pi(\text{arene})$ interactions compared with the other two phenyl rings and internal steric effects within the $[\text{BPh}_4]^-$ anion [angles $\text{B1}—\text{C17} \cdots \text{C20} = 175.1$ (1)° and $\text{B1}—\text{C35} \cdots \text{C38} = 173.5$ (1)°]. The $\text{C}—\text{H} \cdots \pi(\text{arene})$ interactions in (I) correspond to type I MLAC π interactions (Milčić *et al.*, 2004), where a donor H atom of an aromatic ring interacts with a pyridine or phenyl group. The $\text{C} \cdots \pi_c$ (π_c is the center of an aromatic ring) centroid distances are mainly above 3.5 Å and comparable to $\text{X} \cdots \pi_c$ centroid distances for the MLAC π interactions in metalloproteins and

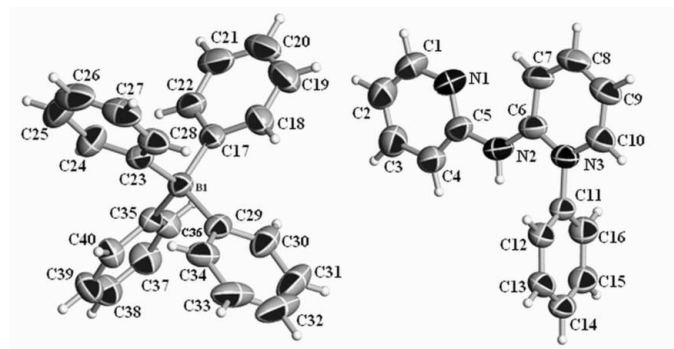


Figure 1
The molecular structure of (I) with 50% probability displacement ellipsoids and the atom numbering scheme.

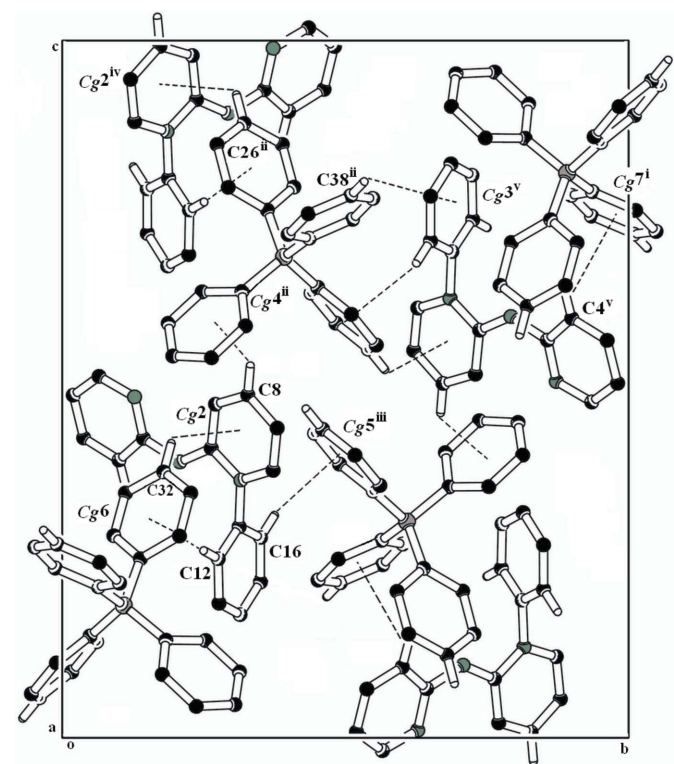


Figure 2
The two shortest C—H... π (arene) interactions (dashed lines) of (I) involving C12/H12 and C16/H16 from the cation with the phenyl rings of two neighboring [BPh₄][−] anions (atoms drawn as their van der Waals spheres).

about 0.2 Å longer than the intermolecular MLAC π interactions in metal complexes involving [BPh₄][−] anions (Milčič *et al.*, 2004).

Experimental

Compound (I) was obtained as a side product in the preparation of [Cu(dpyam)₂](BPh₄)₂. To an acetonitrile (20 ml) solution of dpyam (0.086 g, 0.5 mmol), Cu(BF₄)₂·*n*H₂O (0.118 g, 0.5 mmol) and NaBPh₄ (0.171 g, 0.5 mmol) were added and the mixture was stirred. The

precipitate was removed by filtration. The solvent was evaporated *in vacuo*; after several days, yellow crystals suitable for X-ray analysis were obtained by vapor diffusion using diethyl ether (25%) (m.p. 425 K).

Crystal data

C₁₆H₁₄N₃⁺·C₂₄H₂₀B[−]
M_r = 567.51
Monoclinic, *P*2₁/*c*
a = 9.0635 (2) Å
b = 16.7776 (1) Å
c = 20.8156 (4) Å
 β = 97.096 (1)°
V = 3141.05 (9) Å³

Z = 4
D_x = 1.20 Mg m^{−3}
Mo *K*α radiation
 μ = 0.07 mm^{−1}
T = 273 (2) K
Block, yellow
0.50 × 0.35 × 0.25 mm

Data collection

Siemens SMART CCD area-detector diffractometer
 ω scans
Absorption correction: multi-scan (SADABS; Sheldrick, 2000a)
*T*_{min} = 0.879, *T*_{max} = 0.983

16573 measured reflections
5722 independent reflections
4154 reflections with *I* > 2σ(*I*)
*R*_{int} = 0.025
 $\theta_{\max}$ = 25.4°

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.049
wR(*F*²) = 0.125
S = 1.07
5722 reflections
401 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0481P)^2 + 0.729P]$
where $P = (F_o^2 + 2F_c^2)/3$
(Δ/σ)_{max} < 0.001
 $\Delta\rho_{\max} = 0.15$ e Å^{−3}
 $\Delta\rho_{\min} = -0.16$ e Å^{−3}

Table 1

The C—H... π (arene) interactions and contact geometries (Å, °).

The centroids of the pyridine rings N1/C1–C5 and N3/C6–C10 are defined as Cg1 and Cg2, while those of the phenyl rings for C11–C16, C17–C22, C23–C28, C29–C34 and C35–C40 are defined as Cg3, Cg4, Cg5, Cg6 and Cg7, respectively.

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C4—H4...Cg7 ⁱ	0.93	2.78	3.408 (3)	123
C8—H8...Cg4 ⁱⁱ	0.93	2.81	3.506 (2)	131
C12—H12...Cg6	0.93	2.70	3.645 (2)	167
C16—H16...Cg5 ⁱⁱⁱ	0.93	2.72	3.642 (2)	153
C26—H26...Cg2 ^{iv}	0.93	2.88	3.457 (2)	120
C32—H32...Cg2	0.93	2.82	3.346 (3)	114
C38—H38...Cg3 ^v	0.93	2.90	3.532 (2)	125

Symmetry codes: (i) $x - 1, y, z$; (ii) $x, -y - \frac{1}{2}, z - \frac{1}{2}$; (iii) $-x + 1, y + \frac{1}{2}, -z + \frac{1}{2}$; (iv) $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$; (v) $-x + 2, y - \frac{1}{2}, -z + \frac{1}{2}$.

H atoms attached to the phenyl rings and pyridine rings were placed in calculated positions, with C—H distances of 0.93 Å and *U*_{iso}(H) = 1.2*U*_{eq}(C). The H atom bonded to pyridine atom N2 was refined with a distance restraint of N—H = 0.86 (1) Å.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2000b); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Acta Crystallographica Section C

**Crystal Structure
Communications**

ISSN 0108-2701

Editor: **George Ferguson**

**μ -Acetato-1:2 $\kappa^2 O:O'$ -diacetato-1 $\kappa^2 O,O'$;2 κO -bis(di-2-pyridylamine)-
1 $\kappa^2 N,N'$;2 $\kappa^2 N,N'$ -isothiocyanato-2 κN -dicopper(II)**

Sujittra Youngme, Thidarat Chotkhun and Narongsak Chaichit

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μ -Acetato-1:2 κ^2 O:O'-diacetato-1 κ^2 O,O';2 κ O-bis(di-2-pyridylamine)-1 κ^2 N,N';2 κ^2 N,N'-isothiocyanato-2 κ N-dicopper(II)Sujittra Youngme,^{a*} Thidarat Chotkhun^a and Narongsak Chaichit^b^aDepartment of Chemistry, Faculty of Science, Khon Kaen University, Khon Kaen 40002, Thailand, and ^bDepartment of Physics, Faculty of Science and Technology, Thammasat University Rangsit, Pathumthani 12121, Thailand
Correspondence e-mail: sujittra@kku.ac.th

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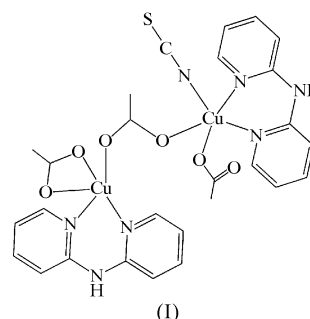
Online 23 January 2007

In the title dinuclear acetate-bridged complex, $[\text{Cu}_2(\text{C}_2\text{H}_3\text{O}_2)_3(\text{NCS})(\text{C}_{10}\text{H}_9\text{N}_3)_2]$, the two Cu atoms are five-coordinated, with a basal plane consisting of two N atoms of a di-2-pyridylamine (dpyam) ligand and two O atoms of two different acetate ligands. The axial positions of these Cu atoms are coordinated to N and O atoms from thiocyanate and acetate molecules, respectively, leading to a distorted square-pyramidal geometry with τ values of 0.30 and 0.22. Both Cu^{II} ions are linked by an acetate group in the equatorial-equatorial positions and have *syn-anti* bridging configurations. Hydrogen-bond interactions between the amine H atom and the coordinated and uncoordinated O atoms of the acetate anions generate an infinite one-dimensional chain.

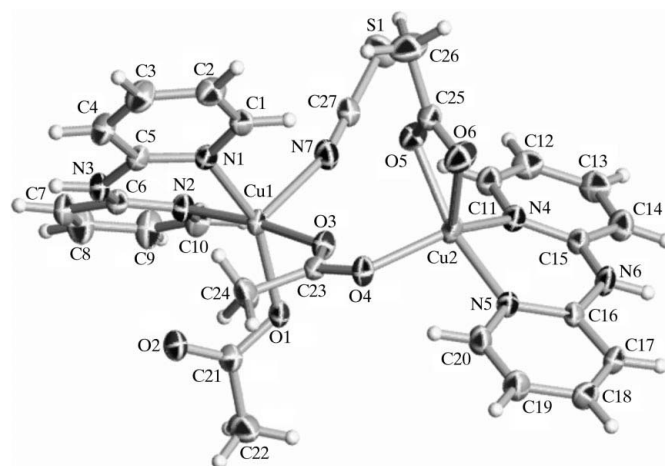
Comment

The coordination chemistry of copper(II) complexes with various carboxylates has been investigated for many years. Carboxylate chemistry is interesting for two reasons. Firstly, carboxylates play a vital role as ligands in biochemical systems involving mono-, di- or polynuclear active sites, and secondly, polynuclear carboxylates are very good probes for exchange-coupling interactions between adjacent metal ions. Carboxylate groups are known to assume different bridging conformations and the important types are *syn-syn*, *anti-anti* and *syn-anti* (Colacio *et al.*, 1993). It may be noted that structurally characterized examples of *syn-anti* configuration are far less numerous than those with the *syn-syn* configuration (Sen *et al.*, 1998). We report here the synthesis and crystal structure of a new acetate-bridged complex with a *syn-anti* configuration, $[\text{Cu}_2(\mu\text{-O}_2\text{CCH}_3)(\text{O}_2\text{CCH}_3)_2(\text{NCS})(\text{dpyam})_2]$ (dpyam is di-2-pyridylamine), (I).

The structure of (I) consists of a dinuclear $[\text{Cu}_2(\mu\text{-O}_2\text{CCH}_3)(\text{O}_2\text{CCH}_3)_2(\text{NCS})(\text{dpyam})_2]$ unit. The Cu atoms are bridged unsymmetrically by an acetate group in a *syn-anti* arrangement (Fig. 1). Atoms Cu1 and Cu2 are five-coordinated, with a basal plane consisting of two N atoms of the dpyam ligand and two O atoms of two different acetate ligands. The axial positions of Cu1 and Cu2 are coordinated by N and O atoms from thiocyanate and acetate ligands, respectively (Table 1), leading to a square-pyramidal geometry. The square bases of the copper chromophores are non-planar, with tetrahedral twists of 25.7 (1) and 43.7 (1)° for Cu1 and Cu2, respectively. The Cu atoms lie above the basal plane, at 0.280 (1) Å towards N7 for Cu1 and 0.112 (1) Å towards O6 for Cu2.



The distortion of a square pyramid can be best described by the structural parameter τ ($\tau = 0$ for a square pyramid and $\tau = 1$ for a trigonal bipyramid; Addison *et al.*, 1984), which in this case has values of 0.30 and 0.22 for Cu1 and Cu2, respectively. The copper chromophores can be described as having a distorted square-pyramidal geometry, with a high tetrahedral twist of the square bases. The $\text{Cu} \cdots \text{Cu}$ distance is 4.800 (3) Å. The dihedral angles between the pyridine rings of the dpyam ligands are 20.9 (1)° for Cu1 and 12.0 (1)° for Cu2. The molecular structure and bridging configuration of (I) are very

**Figure 1**

The molecular structure of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme. H atoms are represented as spheres of arbitrary radii.

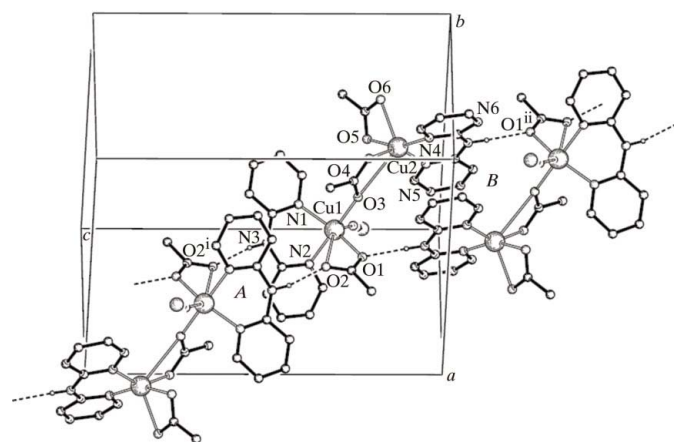


Figure 2

A view of the packing structure of (I), showing the hydrogen-bonding interactions (dashed lines). The hydrogen-bonded rings A and B are defined in the *Comment*. H atoms not involved in hydrogen bonding have been omitted for clarity. [Symmetry codes: (i) $2 - x, 1 - y, 1 - z$; (ii) $1 - x, 1 - y, -z$.]

similar to those of the closely related complexes $[\text{Cu}(\mu\text{-O}_2\text{CH})(\text{dpyam})(\text{HO}_2)]_n(\text{NO}_3)_n$ (Youngme *et al.*, 2005) and $[\text{Cu}(\mu\text{-O}_2\text{CCH}_3)(\text{dpa})](\text{ClO}_4) \cdot 0.5\text{THF}]_n$ [dpa is *N,N*-bis(2-pyridylmethyl)amine] with a single carboxylate bridge (Tanase *et al.*, 2005).

Analysis of the crystal packing of (I) shows hydrogen-bonding interactions between the NH group of the amide and the coordinated and uncoordinated O atoms of the acetate anions, with $\text{N}-\text{H} \cdots \text{O}$ contacts of 2.915 (3) and 2.862 (3) Å. A plot of the hydrogen-bond system forming a one-dimensional structure is given in Fig. 2 and details are given in Table 2. Classical $\text{N}3-\text{H}5 \cdots \text{O}2^{\text{i}}$ [symmetry code: (i) $-x + 2, -y + 1, -z + 1$] and $\text{N}6-\text{H}15 \cdots \text{O}1^{\text{ii}}$ [symmetry code: (ii) $-x + 1, -y + 1, -z$] intermolecular hydrogen bonds between adjacent dimeric units link them into a one-dimensional chain. The resulting motifs, A and B, in the formalism of graph-set analysis of hydrogen-bond patterns (Etter *et al.*, 1990), are characterized as $R_2^2(15)$ (N3, H5, O2ⁱ, C21ⁱ, O1ⁱ, Cu1ⁱ, N1ⁱ, C5ⁱ, N3ⁱ, H5ⁱ, O2, C21, Cu1, N1 and C5) and $R_2^2(20)$ (N6, H15, O1ⁱⁱ, Cu1ⁱⁱ, O3ⁱⁱ, C23ⁱⁱ, O4ⁱⁱ, Cu2ⁱⁱ, N4ⁱⁱ, C15ⁱⁱ, N6ⁱⁱ, H15ⁱⁱ, O1, Cu1, O3, C23, O4, Cu2, N4 and C15), respectively.

Experimental

The title complex was obtained as a by-product in the preparation of $[\text{Cu}_3(\mu\text{-OOCCH}_3)_4(\mu\text{-NCS})_2(\text{dpyam})_2]$ by adding $\text{Cu}(\text{O}_2\text{CCH}_3)_2 \cdot n\text{H}_2\text{O}$ (1.5 mmol) to a warm solution of dpyam (1.0 mmol) in dimethylformamide (DMF) (10.0 ml). A solution of NaNCS (1.0 mmol) in DMF (5.0 ml) was then added and the resulting green solution was allowed to evaporate slowly at room temperature. After several days, green crystals of (I) were formed. The crystals were filtered off, washed with mother liquor and dried in air. IR data (KBr, ν , cm^{-1}): 2084 (vs), 1654 (s), 1589 (s), 1556 (s), 1486 (vs), 1424 (s), 1237 (m), 1160 (m), 1019 (m), 784 (m).

Crystal data

$[\text{Cu}_2(\text{C}_2\text{H}_3\text{O}_2)_3(\text{NCS})(\text{C}_{10}\text{H}_9\text{N}_3)_2]$
 $M_r = 704.70$
 Triclinic, $P\bar{1}$
 $a = 9.6949$ (2) Å
 $b = 10.4915$ (2) Å
 $c = 16.9001$ (2) Å
 $\alpha = 97.6450$ (10)°
 $\beta = 101.4580$ (10)°
 $\gamma = 113.2150$ (10)°

$V = 1505.09$ (4) Å³
 $Z = 2$
 $D_x = 1.555$ Mg m⁻³
 Mo $K\alpha$ radiation
 $\mu = 1.54$ mm⁻¹
 $T = 273$ (2) K
 Polygon, green
 $0.30 \times 0.18 \times 0.08$ mm

Data collection

Siemens SMART CCD area-detector diffractometer
 ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 2000a)
 $T_{\text{min}} = 0.732$, $T_{\text{max}} = 0.891$

8178 measured reflections
 5440 independent reflections
 4510 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.021$
 $\theta_{\text{max}} = 25.4^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.038$
 $wR(F^2) = 0.099$
 $S = 1.05$
 5440 reflections
 399 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0423P)^2 + 1.2895P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.34$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.49$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Cu1—O3	1.996 (2)	Cu2—N4	1.976 (3)
Cu1—N2	2.011 (3)	Cu2—N5	1.976 (3)
Cu1—O1	2.013 (2)	Cu2—O5	1.989 (2)
Cu1—N1	2.030 (3)	Cu2—O4	1.999 (2)
Cu1—N7	2.150 (3)	Cu2—O6	2.339 (3)
O3—Cu1—N2	173.03 (10)	N4—Cu2—N5	92.41 (11)
O3—Cu1—O1	86.58 (9)	N4—Cu2—O5	95.05 (11)
N2—Cu1—O1	90.75 (10)	N5—Cu2—O5	156.16 (11)
O3—Cu1—N1	91.91 (10)	N4—Cu2—O4	142.76 (10)
N2—Cu1—N1	87.77 (10)	N5—Cu2—O4	94.46 (10)
O1—Cu1—N1	154.89 (10)	O5—Cu2—O4	93.21 (10)
O3—Cu1—N7	93.57 (11)	N4—Cu2—O6	120.17 (11)
N2—Cu1—N7	93.31 (11)	N5—Cu2—O6	96.50 (10)
O1—Cu1—N7	103.31 (10)	O5—Cu2—O6	60.28 (9)
N1—Cu1—N7	101.80 (11)	O4—Cu2—O6	95.34 (10)

Table 2

Hydrogen-bond geometry (Å, °).

$D-\text{H} \cdots A$	$D-\text{H}$	$\text{H} \cdots A$	$D \cdots A$	$D-\text{H} \cdots A$
$\text{N}3-\text{H}5 \cdots \text{O}2^{\text{i}}$	0.852 (18)	2.022 (18)	2.862 (3)	168.40
$\text{N}6-\text{H}15 \cdots \text{O}1^{\text{ii}}$	0.860 (18)	2.055 (18)	2.915 (3)	177.80

Symmetry codes: (i) $-x + 2, -y + 1, -z + 1$; (ii) $-x + 1, -y + 1, -z$.

H atoms attached to atoms N3 and N6 were located in difference Fourier maps and refined with a DFIX (*SHELXTL*; Sheldrick, 2000b) restraint of $\text{N}-\text{H} = 0.86$ (1) Å. All H atoms attached to C atoms were fixed geometrically and treated as riding, with $\text{C}-\text{H} = 0.93$ (aromatic) or 0.96 Å (methyl), and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{aromatic C})$ or $1.5U_{\text{eq}}(\text{methyl C})$.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve

structure: *SHELXTL* (Sheldrick, 2000*b*); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL* (Sheldrick 2000*b*) and *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DN3030). Services for accessing these data are described at the back of the journal.

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**Crystal Structure
Communications**

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**(Azido- κ N)bis(di-2-pyridylamine)copper(II) hexafluorophosphate and
(azido- κ N)bis(di-2-pyridylamine)copper(II) chloride tetrahydrate**

**Sujitra Youngme, Jaturong Phatchimkun, Chaveng Pakawatchai, Samran Prabpai
and Palangpon Kongsaree**

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(Azido- κ N)bis(di-2-pyridylamine)-copper(II) hexafluorophosphate and (azido- κ N)bis(di-2-pyridylamine)-copper(II) chloride tetrahydrateSujittra Youngme,^{a*} Jaturong Phatchimkun,^a Chaveng Pakawatchai,^b Samran Prabpai^c and Palangpon Kongsaree^c^aDepartment of Chemistry, Faculty of Science, Khon Kaen University, Khon Kaen 40002, Thailand, ^bDepartment of Chemistry, Faculty of Science, Prince of Songkla University, Hatyai, Songkla 90112, Thailand, and ^cDepartment of Chemistry, Faculty of Science, Mahidol University, Bangkok 10400, Thailand

Correspondence e-mail: sujittra@kku.ac.th

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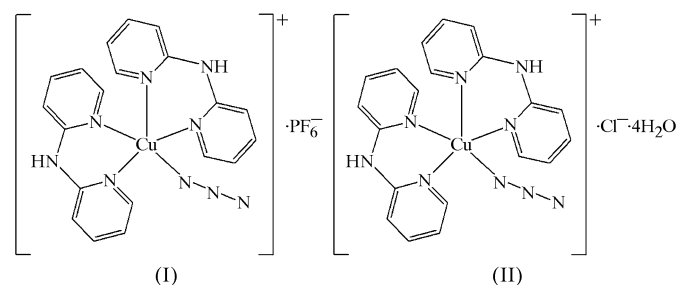
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The two new title complexes, $[\text{Cu}(\text{N}_3)(\text{dpyam})_2]\text{PF}_6$ (dpyam is di-2-pyridylamine, $\text{C}_{10}\text{H}_{11}\text{N}_3$), (I), and $[\text{Cu}(\text{N}_3)(\text{dpyam})_2]\text{Cl}\cdot 4\text{H}_2\text{O}$, (II), respectively, have been characterized by single-crystal X-ray diffraction. Both complexes display a distorted square-pyramidal geometry. Each Cu atom is coordinated in the basal plane by three dpyam N atoms and one azide N atom in equatorial positions, and by another N atom from the dpyam group in the apical position. In complex (I), the one-dimensional supramolecular architecture is assembled *via* hydrogen-bonding interactions between the amine N atom and terminal azide N atoms and the F atoms of the PF_6^- anion. For complex (II), hydrogen-bonding interactions between the amine N atom, the Cl^- anion and water O atoms result in a two-dimensional lattice.

Comment

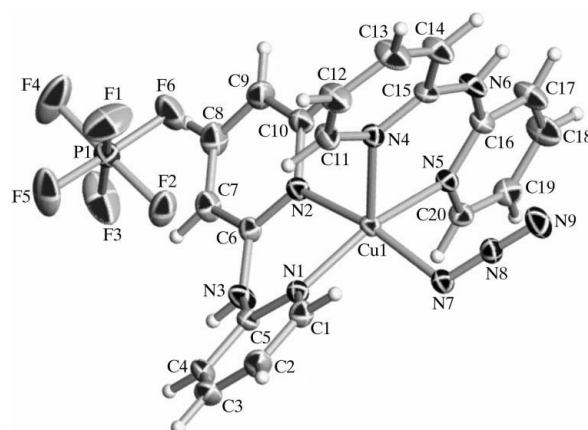
The synthesis of pseudohalide-bridged complexes continues to be a subject of much interest, and intensive investigations have taken place as a result of their diverse structures and potential



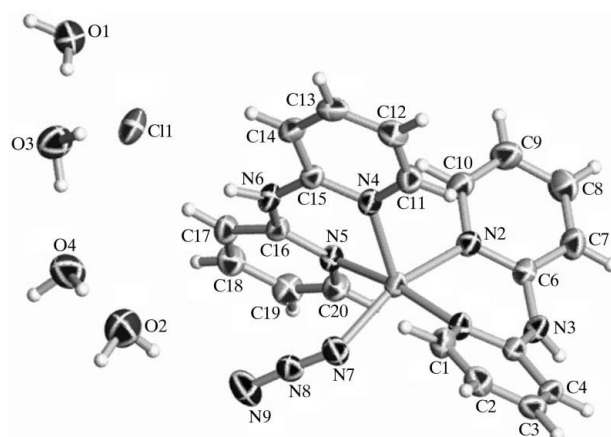
applications in magnetic materials. Pseudohalide ligands (OCN^- , SCN^- , N_3^- , *etc.*) can coordinate to transition metal

atoms in different ways, for example, as a terminal ligand or as a bridge (Talukder *et al.*, 2004). One-, two- or three-dimensional supramolecular architectures assembled *via* intermolecular non-covalent interactions are of considerable interest for the crystal engineering of new functional solid-state materials, as well as for their fascinating structures (Gao *et al.*, 2001). Hydrogen bonding, which combines directionality, selectivity and strength, has been noted as the most versatile organizing force for supramolecular assembly (Chen *et al.*, 2001). We report here the two new title complexes, $[\text{Cu}(\text{N}_3)(\text{dpyam})_2]\text{PF}_6$, (I), and $[\text{Cu}(\text{N}_3)(\text{dpyam})_2]\text{Cl}\cdot 4\text{H}_2\text{O}$, (II). The dpyam ligand has been selected primarily because it also has an N—H hydrogen-bond donor function that might produce one-, two- or three-dimensional supramolecular architectures.

The crystal structures of (I) and (II) (Figs. 1 and 2) consist of a $[\text{Cu}(\text{N}_3)(\text{dpyam})_2]^+$ cation and PF_6^- and Cl^- anions,

**Figure 1**

The molecular structure of (I), showing 30% probability displacement ellipsoids and the atom-numbering scheme. H atoms are shown as small spheres of arbitrary radii. Only one of the disordered components of the PF_6^- anion is shown.

**Figure 2**

The molecular structure of (II), showing 30% probability displacement ellipsoids and the atom-numbering scheme. H atoms are shown as small spheres of arbitrary radii.

respectively. The Cu atoms of both molecules exhibit five-coordination of the $\text{CuN}_4\text{N}'$ chromophore (see scheme). The coordination around each Cu atom consists of three dpyam N atoms and one azide N atom in equatorial positions, and another N atom from dpyam in the apical position. Both complexes exhibit a slightly distorted square-pyramidal environment, the geometric τ values (Addison *et al.*, 1984) being 0.061 for (I) and 0.148 for (II). The average Cu—N distances (Tables 1 and 3) in the equatorial positions are 2.017 (1) Å for (I) and 2.009 (1) Å for (II). The axial Cu—N distances are longer, at 2.153 (2) Å for (I) and 2.169 (2) Å for (II). The Cu atoms are displaced by 0.264 (1) Å for (I) and 0.255 (1) Å for (II) from the mean basal plane towards the apical position. The dpyam ligands are not planar, with dihedral angles between the two pyridine rings of 34.4 (1) and 16.1 (1)° for (I), and 35.3 (1) and 14.6 (1)° for (II).

There are extensive hydrogen-bonding interactions in both structures. In complex (I), intermolecular N—H...F and N—H...N(azide) hydrogen-bonding interactions (Table 2) produce a one-dimensional chain (Fig. 3). The crystal packing of complex (II) is stabilized by intermolecular N—H...Cl, O—H...N(azide), O—H...Cl and O—H...O hydrogen

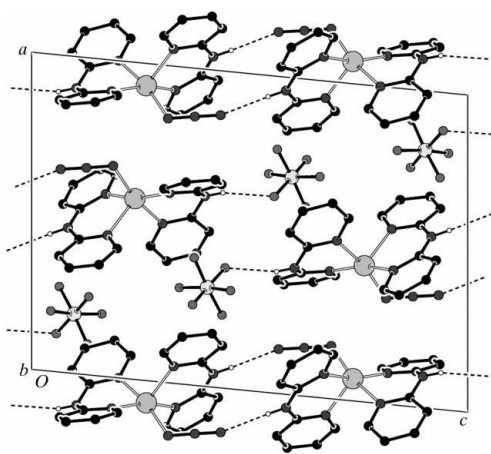


Figure 3
A packing diagram for (I), with hydrogen bonds (dashed lines), showing the one-dimensional structure.

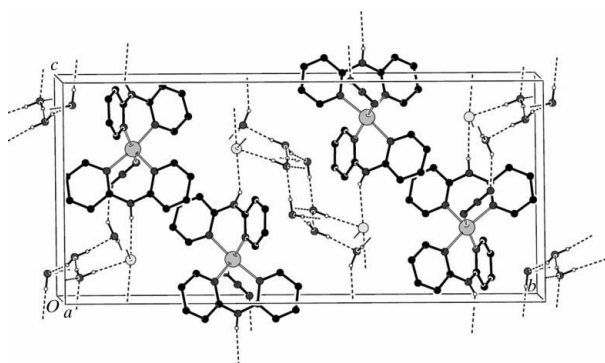


Figure 4
A packing diagram for (II), with hydrogen bonds (dashed lines), showing the two-dimensional structure.

bonds (Table 4), leading to a two-dimensional supramolecular structure (Fig. 4).

The chromophores of (I) and (II) are very similar except for the four additional water molecules in the structure of complex (II), which create a two-dimensional hydrogen-bonded network in (II).

Experimental

Complex (I) was prepared by adding a warm solution of di-2-pyridylamine (0.17 g, 1.00 mmol) in methanol (15 ml) to a hot aqueous solution (10 ml) containing $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ (0.091 g, 0.5 mmol) and NaN_3 (0.065 g, 1.0 mmol). An aqueous solution (15 ml) of KPF_6 (0.184 g, 1.0 mmol) was then added, giving a clear green solution. The resulting solution was evaporated slowly at room temperature. After several days, green needle-shaped crystals of (I) which had formed were filtered off, washed with mother liquor and air-dried (yield *ca* 90%). Green needle-shaped crystals of (II) were obtained by adding a warm solution of di-2-pyridylamine (0.171 g, 1.0 mmol) in methanol (15 ml) to a boiling aqueous solution (15 ml) of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.085 g, 0.5 mmol). NaN_3 (0.130 g, 2.0 mmol) was then added to the reaction mixture. After several days, crystals of (II) which had formed were filtered off, washed with mother liquor and air-dried (yield *ca* 85%). The electronic reflectance spectra of both complexes involve main peaks at 14 050 and 14 000 cm^{-1} , and lower energy shoulders at 11 010 and 11 110 cm^{-1} for (I) and (II), respectively. These spectroscopic characteristics of the compounds are consistent with a distorted square-pyramidal geometry with a small τ value. The transitions may be assigned as the $d_{z^2} \rightarrow d_{x^2-y^2}$ transition for the low-energy shoulder and the $d_{xz} \sim d_{yz} \rightarrow d_{x^2-y^2}$ transition for the high-energy peak. The strongest intensity features in the spectra of (I) and (II) appear at 2042 and 2040 cm^{-1} , respectively, together with sharp and medium intensity peaks at 2035 and 2034 cm^{-1} , respectively, attributed to $\nu_{\text{as}}(\text{N}_3)$. For the IR spectrum of sodium azide, a single strong peak at 2033 cm^{-1} is observed. Hence, in the present compounds, the shift towards higher wavenumbers of the ν_{as} stretching of the azide indicates that it must be coordinated.

Compound (I)

Crystal data

$[\text{Cu}(\text{N}_3)(\text{C}_{10}\text{H}_{11}\text{N}_3)_2]\text{PF}_6$
 $M_r = 592.94$
 Monoclinic, $P2_1/n$
 $a = 14.1074$ (8) Å
 $b = 8.5839$ (5) Å
 $c = 19.4144$ (11) Å
 $\beta = 95.6350$ (10)°
 $V = 2339.7$ (2) Å³

$Z = 4$
 $D_x = 1.683$ Mg m⁻³
 Mo $K\alpha$ radiation
 $\mu = 1.08$ mm⁻¹
 $T = 298$ (2) K
 Needle, green
 0.31 × 0.21 × 0.11 mm

Data collection

Siemens SMART CCD area detector diffractometer
 ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 2000a)
 $T_{\text{min}} = 0.769$, $T_{\text{max}} = 0.884$

19955 measured reflections
 5804 independent reflections
 4381 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.027$
 $\theta_{\text{max}} = 28.3^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.043$
 $wR(F^2) = 0.111$
 $S = 1.05$
 5635 reflections
 397 parameters
 H atoms: see below

$w = 1/[\sigma^2(F_o^2) + (0.0547P)^2 + 0.9007P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.39$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.22$ e Å⁻³

Table 1

Selected geometric parameters (Å, °) for (I).

Cu1—N1	2.0046 (19)	Cu1—N5	2.0361 (19)
Cu1—N7	2.009 (2)	Cu1—N4	2.1534 (19)
Cu1—N2	2.0166 (19)		
N1—Cu1—N7	88.15 (8)	N2—Cu1—N5	89.82 (8)
N1—Cu1—N2	88.00 (8)	N1—Cu1—N4	108.15 (8)
N7—Cu1—N2	166.76 (8)	N7—Cu1—N4	96.51 (8)
N1—Cu1—N5	163.10 (8)	N2—Cu1—N4	96.73 (8)
N7—Cu1—N5	90.18 (8)	N5—Cu1—N4	88.75 (8)

Table 2

Hydrogen-bond geometry (Å, °) for (I).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N3—H5...F3 ⁱ	0.86 (2)	2.20 (2)	3.045 (12)	168 (2)
N3—H5...F3A ⁱ	0.86 (2)	2.14 (2)	2.963 (8)	161 (2)
N6—H15...N9 ⁱⁱ	0.86 (2)	2.27 (2)	3.130 (3)	179 (3)

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $-x+1, -y+1, -z$.**Compound (II)***Crystal data*

[Cu(N₃)(C₁₀H₁₁N₃)₂]Cl·4H₂O
M_r = 555.49
 Monoclinic, *P*₂₁/*c*
a = 7.0560 (2) Å
b = 27.8360 (13) Å
c = 12.8780 (6) Å
 β = 99.009 (2)°
V = 2498.18 (18) Å³

Z = 4
D_x = 1.477 Mg m⁻³
 Mo *K*α radiation
 μ = 1.03 mm⁻¹
T = 298 (2) K
 Needle, green
 0.50 × 0.20 × 0.15 mm

Data collection

Enraf–Nonius MACH3
 diffractometer
 ψ scan
 12357 measured reflections

6685 independent reflections
 4900 reflections with *I* > 2σ(*I*)
*R*_{int} = 0.032
 $\theta_{\max}$ = 29.1°

Refinement

Refinement on *F*²
 $R[F^2 > 2\sigma(F^2)] = 0.046$
 $wR(F^2) = 0.147$
S = 1.10
 6407 reflections
 348 parameters
 H atoms: see below

$w = 1/[\sigma^2(F_o^2) + (0.0828P)^2 + 0.2714P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.012$
 $\Delta\rho_{\max} = 0.46$ e Å⁻³
 $\Delta\rho_{\min} = -0.82$ e Å⁻³

In (I), H atoms attached to N3 and N6 were located in a difference Fourier map and refined with a DFIX (*SHELXTL*; Sheldrick, 2000*b*) restraint of N—H = 0.86 (1) Å. The remaining H atoms were placed in idealized positions and constrained to ride on their parent atoms, with C—H = 0.93 Å and *U*_{iso}(H) = 1.2*U*_{eq}(C). The F atoms of the hexafluorophosphate group showed disorder; the occupancies of the disordered positions were initially refined and later fixed at 0.5. In (II), H atoms attached to water O atoms were located in difference Fourier maps and refined with a DFIX restraint of O—H = 0.90 (1) Å. The remaining H atoms were placed in idealized positions and constrained to ride on their parent atoms, with C—H = 0.93 Å and N—H = 0.86 Å, and with *U*_{iso}(H) = 1.2*U*_{eq}(C,N).

Data collection: *SMART* (Bruker, 2000) for (I); *MACH3* (Enraf–Nonius, 1993) for (II). Cell refinement: *SAINT* (Bruker, 2000) for (I);

Table 3

Selected geometric parameters (Å, °) for (II).

Cu1—N1	1.999 (2)	Cu1—N2	2.028 (2)
Cu1—N5	2.003 (2)	Cu1—N4	2.169 (2)
Cu1—N7	2.007 (2)		
N1—Cu1—N5	169.35 (9)	N7—Cu1—N2	160.47 (10)
N1—Cu1—N7	86.36 (9)	N1—Cu1—N4	102.54 (8)
N5—Cu1—N7	88.99 (9)	N5—Cu1—N4	87.86 (8)
N1—Cu1—N2	87.37 (8)	N7—Cu1—N4	103.42 (10)
N5—Cu1—N2	93.91 (8)	N2—Cu1—N4	95.99 (8)

Table 4

Hydrogen-bond geometry (Å, °) for (II).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O1—H1W...O3	0.90 (3)	1.96 (3)	2.855 (4)	172 (1)
O1—H2W...O3 ⁱ	0.90 (2)	1.95 (2)	2.847 (4)	178 (1)
O2—H3W...Cl1 ⁱⁱ	0.90 (3)	2.30 (3)	3.203 (4)	174 (1)
O2—H4W...N9	0.91 (4)	2.12 (4)	2.964 (5)	153 (5)
O3—H5W...O4	0.92 (4)	1.84 (4)	2.751 (4)	171 (4)
O3—H6W...Cl1	0.89 (3)	2.27 (3)	3.151 (3)	170 (3)
O4—H7W...O2	0.89 (3)	1.96 (3)	2.843 (5)	174 (3)
O4—H8W...O1 ⁱⁱ	0.90 (4)	1.89 (4)	2.768 (4)	164 (1)
N3—H5...Cl1 ⁱⁱⁱ	0.86	2.56	3.256 (2)	139
N6—H15...Cl1	0.86	2.49	3.297 (2)	157

Symmetry codes: (i) $-x+2, -y, -z$; (ii) $x-1, y, z$; (iii) $x, y, z+1$.

MACH3 for (II). Data reduction: *SAINT* for (I); *MolEN* (Fair, 1990) for (II). For both compounds, program(s) used to solve structure: *SHELXTL* (Sheldrick, 2000*b*); program(s) used to refine structure: *SHELXTL*; molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SF3027). Services for accessing these data are described at the back of the journal.

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Five-coordinate copper(II) complexes: crystal structures, spectroscopic properties and new extended structural pathways of $[\text{Cu}(\text{chelate})_2\text{X}]\text{Y}$, where chelate = dpyam, phen and bipy; X = pseudohalide ligands

Sujittra Youngme, Pongthipun Phuengphai, Chaveng Pakawatchai,
Palangpon Kongsaree and Narongsak Chaichit

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Five-coordinate copper(II) complexes: crystal structures, spectroscopic properties and new extended structural pathways of $[\text{Cu}(\text{chelate})_2\text{X}]\text{Y}$, where chelate = dpyam, phen and bipy; X = pseudohalide ligands

Sujittra Youngme,^{a,*} Pongthipun Phuengphai,^{a,b} Chaveng Pakawatchai,^c Palangpon Kongsaree^d and Narongsak Chaichit^e

^aDepartment of Chemistry, Faculty of Science, Khon Kaen University, Khon Kaen 40002, Thailand, ^bChemistry Program, Faculty of Science and Technology, Surindra Rajabhat University, Surin 32000, Thailand, ^cDepartment of Chemistry, Faculty of Science, Prince of Songkla University, Hatyai, Songkla 90112, Thailand, ^dDepartment of Chemistry, Faculty of Science, Mahidol University, Bangkok 10400, Thailand, and ^eDepartment of Physics, Faculty of Science and Technology, Thammasat University Rangsit, Pathumthani 12121, Thailand

Correspondence e-mail: sujittra@kku.ac.th

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Dedicated to Professor Jan Reedijk on the occasion of his 65th birthday and retirement

The crystal structures of four distortion isomers of the $[\text{Cu}(\text{chelate})_2\text{X}]^+$ cation, where chelate = 2,2-bipyridine (bipy), 1,10-phenanthroline (phen) and di-2-pyridylamine (dpyam), X = a pseudohalide ligand (NCO, NCS, N_3 and C_2N_3), have been compared by scatterplot analysis with 25 $[\text{Cu}(\text{chelate})_2\text{X}]\text{Y}$ complexes of known crystal structure. The four new complexes $[\text{Cu}(\text{phen})_2\text{NCO}]\text{Br}$ (1), $[\text{Cu}(\text{phen})_2\text{N}_3]\text{BPh}_4\cdot\text{H}_2\text{O}$ (2), $[\text{Cu}(\text{dpyam})_2(\text{N}_3)]\text{NO}_3\cdot\text{H}_2\text{O}$ (3) and $[\text{Cu}(\text{dpyam})_2(\text{N}_3)]\text{ClO}_4$ (4) involve a near regular square-based pyramidal stereochemistry (RSBP). The structures of complexes (1) and (2) are of the rare cases found for the phen analogue. Scatterplots of the 29 cation distortion isomers of the $[\text{Cu}(\text{chelate})_2\text{X}]\text{Y}$ series of complexes suggest that most of the 29 complexes lie on a common structural pathway, involving a mixture of the symmetric, C_2 , and the asymmetric, non- C_2 , in-plane modes of vibration of the $\text{CuN}_4\text{N}'$ chromophore. Some datapoints are found to lie on extended routes. The resulting structural pathways are consistent with the direct observation of the effect of the modes of vibration on the stereochemistries of the complexes. A comparison of the trends in the 29 datasets suggests a size effect of the phen, bipy and dpyam ligands.

1. Introduction

One of the consequences of the Jahn–Teller theorem (Jahn & Teller, 1937; Bersuker, 2001) in the stereochemistry of the copper(II) ion has been termed the plasticity effect (Gazo *et al.*, 1976), which suggests that the various distortion isomers of the copper(II) ion are related by soft modes of vibration of the more regular stereochemistries. Hence the concept of a structural pathway (Nagle *et al.*, 1990; Hathaway, 1984; Burgi & Dunitz, 1983; Dunitz, 1979) for $[\text{Cu}(\text{chelate})_2\text{X}]\text{Y}$ -type complexes has been developed (Fig. 1).

In 1984, Addison, Reedijk and co-workers introduced a very useful parameter, τ , which provides a measure of the degree of square-based pyramidal (SBP) *versus* trigonal bipyramidal (TBP) geometry adopted by five-coordinate copper(II) complexes (Addison, Rao, Reedijk *et al.*, 1984). This parameter provides a convenient tool for comparing structures of similar five-coordinate copper(II) complexes. The parameter τ is defined as $(\beta - \alpha)/60$, where β and α are the largest coordination angles, and its value varies from 0 (in regular SBP) to 1 (in regular TBP). The molecular structures of five-coordinate copper(II) complexes range extensively from regular trigonal bipyramidal (RTBP, D_{3h}) to regular

square-based pyramidal (RSBP, C_{4v}), see Fig. 2, with most complexes falling between these two stereochemistries (Hathaway & Billing, 1970; Reinen & Friebe, 1984) somewhere along the classical Berry pathway (Addison, Rao & Sinn, 1984). This feature can be useful in probing the rela-

tionships between structural correlations and the respective structural pathway involving vibronic-type coupling.

In the majority of $[\text{Cu}(\text{chelate})_2X]Y$ complexes the differences in stereochemistry may be associated with the differences in the ligands present, *i.e.* chelate = 2,2-bipyridine (bipy), 1,10-phenanthroline (phen) and di-2-pyridylamine (dpyam), and $X = \text{Cl}^-$, Br^- , I^- or H_2O , respectively. Five-coordinated copper(II) coordination compounds of the general formula $[\text{Cu}(\text{dpyam})_2\text{NCO}]Y$ (Youngme, Phatchimkun, Suksangpanya *et al.*, 2007) have been previously reported with the limited number of datasets available. Therefore, it is of interest to extend and develop the structural correlations and investigate the existence of a structural pathway (Fig. 3) for the series of five-coordinate copper(II) complexes of the type $[\text{Cu}(\text{chelate})_2X]Y$, where chelate = phen, bipy or dpyam, and X is an anion of the pseudohalide ligand (NCO, NCS, N_3 and C_2N_3 ; Youngme, Phatchimkun, Suksangpanya *et al.*, 2007; Akhter & Hathaway, 1991; McAuliffe *et al.*, 1992; Munno *et al.*, 1998; Potočník *et al.*, 1995, 1996*a,b*, 1998*a,b*, 2001, 2002, 2003, 2005). In Fig. 3 the new extended structural pathways and distortion of α_8 (N1—Cu—N3) are presented and investigated. To obtain this extended database of 29 complexes, the crystal structures of four new compounds, $[\text{Cu}(\text{phen})_2\text{NCO}]\text{Br}$ (1), $[\text{Cu}(\text{phen})_2\text{N}_3]\cdot\text{BPh}_4\cdot\text{H}_2\text{O}$ (2), $[\text{Cu}(\text{dpyam})_2(\text{N}_3)]\text{NO}_3\cdot\text{H}_2\text{O}$ (3) and $[\text{Cu}(\text{dpyam})_2(\text{N}_3)]\text{ClO}_4$ (4), have been determined and are now reported.

- $\alpha_1 = \text{N2-Cu-N}'$
- $\alpha_2 = \text{N4-Cu-N}'$
- $\alpha_3 = \text{N2-Cu-N4}$
- $\alpha_4 = \text{N1-Cu-N}'$
- $\alpha_5 = \text{N3-Cu-N}'$
- $\alpha_6 = \text{N1-Cu-N2}$
- $\alpha_7 = \text{N3-Cu-N4}$
- $\alpha_8 = \text{N1-Cu-N3}$
- $\alpha_9 = \text{N2-Cu-N3}$
- $\alpha_{10} = \text{N1-Cu-N4}$

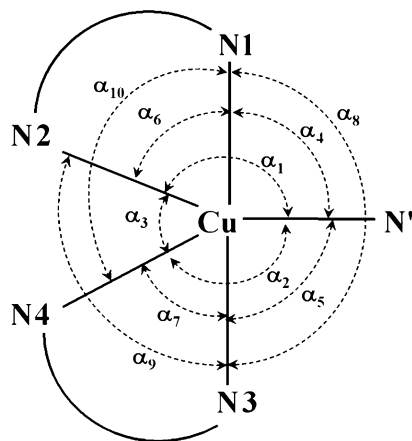


Figure 1

The atom-numbering scheme and α_n notation for the $\text{CuN}_4\text{N}'$ chromophore.

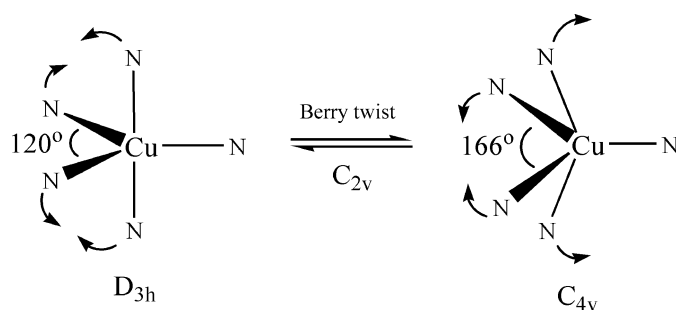


Figure 2

The Berry twist mechanism for interconversion of a regular trigonal bipyramid to square pyramid.

2. Experimental

All reagents were commercial-grade and were used without further purification. Elemental analyses (C, H and N) were performed on a Perkin–Elmer PE2400 CHNS/O analyzer. The IR spectra were recorded on a Spectrum One Perkin–Elmer FT-IR spectrophotometer as KBr pellets in the $4000\text{--}450\text{ cm}^{-1}$ region. Solid-state (diffuse reflectance) electronic spectra were recorded as polycrystalline samples on a Perkin–Elmer Lambda2S spectrophotometer over the range $8000\text{--}18\,000\text{ cm}^{-1}$.

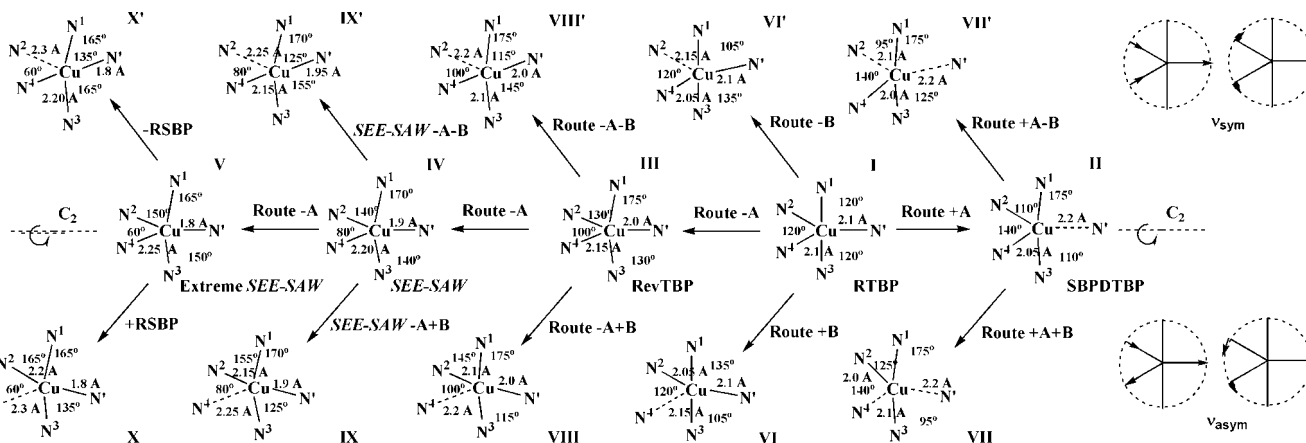


Figure 3

The forms of distortion of the RTBP $\text{CuN}_4\text{N}'$ chromophore involving the $\pm A$, $\pm B$ and $\pm A \pm B$ routes.

Table 1

Crystal and refinement data for (1)–(4).

	(1)	(2)	(3)	(4)
Crystal data				
Chemical formula	C ₂₅ H ₁₆ BrCuN ₅ O	C ₄₈ H ₃₆ BCuN ₇ O	C ₂₀ H ₂₀ CuN ₁₀ O ₄	C ₂₀ H ₁₈ ClCuN ₉ O ₄
<i>M_r</i>	545.88	801.19	528.00	547.42
Cell setting, space group	Triclinic, <i>P</i> $\bar{1}$	Triclinic, <i>P</i> $\bar{1}$	Triclinic, <i>P</i> $\bar{1}$	Monoclinic, <i>P</i> 2 ₁ / <i>c</i>
Temperature (K)	293 (2)	293 (2)	293 (2)	293 (2)
<i>a</i> , <i>b</i> , <i>c</i> (Å)	8.9141 (18), 10.448 (2), 12.291 (3)	10.2373 (4), 11.3628 (4), 19.1037 (7)	7.7515 (6), 9.9160 (8), 15.2750 (12)	13.4360 (5), 8.3880 (3), 22.5750 (5)
α , β , γ (°)	78.688 (4), 81.562 (4), 72.798 (3)	86.6970 (10), 75.8840 (10), 67.7440 (10)	100.0100 (10), 103.3470 (10), 99.5270 (10)	90.00, 118.1471 (19), 90.00
<i>V</i> (Å ³)	1067.4 (4)	1993.07 (13)	1098.78 (15)	2243.35 (13)
<i>Z</i>	2	2	2	4
<i>D_x</i> (Mg m ^{−3})	1.698	1.335	0.798	1.621
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α
μ (mm ^{−1})	2.92	0.60	0.52	1.14
Crystal form, colour	Prismatic, green	Prismatic, blue	Prismatic, blue–green	Prismatic, blue–green
Crystal size (mm)	0.19 × 0.09 × 0.03	0.38 × 0.20 × 0.10	0.24 × 0.18 × 0.10	0.15 × 0.12 × 0.05
Data collection				
Diffractionmeter	Bruker SMART CCD	Bruker SMART CCD	Bruker SMART CCD	Bruker SMART CCD
Data collection method	ω scans	ω scans	ω scans	ω scans
Absorption correction	Semi-empirical <i>SADABS</i>	Semi-empirical <i>SADABS</i>	Semi-empirical <i>SADABS</i>	Semi-empirical <i>SADABS</i>
<i>T_{min}</i>	0.657	0.689	0.842	0.657
<i>T_{max}</i>	1.000	1.000	1.000	1.000
No. of measured, independent and observed reflections	10 680, 3901, 3161	10 733, 7178, 4805	12 952, 5157, 4510	19 249, 4240, 3248
Criterion for observed reflections	<i>I</i> > 2σ(<i>I</i>)	<i>I</i> > 2σ(<i>I</i>)	<i>I</i> > 2σ(<i>I</i>)	<i>I</i> > 2σ(<i>I</i>)
<i>R_{int}</i>	0.030	0.033	0.021	0.058
$\theta_{\max}$ (°)	25.4	25.4	28.3	25.8
Refinement				
Refinement on	<i>F</i> ²	<i>F</i> ²	<i>F</i> ²	<i>F</i> ²
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.039, 0.093, 1.04	0.069, 0.182, 1.13	0.036, 0.092, 1.04	0.045, 0.125, 1.03
No. of reflections	3901	7178	5157	4240
No. of parameters	298	532	423	417
H-atom treatment	Mixture of independent and constrained refinement	Mixture of independent and constrained refinement	Mixture of independent and constrained refinement	Mixture of independent and constrained refinement
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0476P)^2 + 0.2281P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0671P)^2 + 1.4556P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0507P)^2 + 0.2291P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.066P)^2 + 1.310P]$, where $P = (F_o^2 + 2F_c^2)/3$
(Δ/σ) _{max}	0.005	0.005	0.013	0.042
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ^{−3})	0.41, −0.29	0.42, −0.48	0.32, −0.24	0.40, −0.48

Computer programs used: *SMART* (Bruker, 2001b), *SAINT* (Bruker, 2001a), *SHELXS97*, *SHELXL97* (Sheldrick, 2008), *SHELXTL* (Bruker, 2000).**2.1. Preparation of (1)–(4)**

[Cu(phen)₂NCO]Br (1): A warm solution of phen (0.198 g, 1.0 mmol) in methanol (15 cm³) was added to a hot aqueous solution (15 cm³) of CuBr₂ (0.112 g, 0.5 mmol). An aqueous solution (10 cm³) of KNCO (0.081 g, 1.0 mmol) was then added to the reaction mixture. The green solution was slowly evaporated at room temperature. Green crystals of (1) deposited after several days. The crystals were filtered off, washed with mother liquor and air-dried. Yield *ca* 65%. Analysis: calc. for C₂₅H₁₆BrCuN₅O (%): C 55.00, H 2.95, N 12.83; found: C 55.08, H 3.02, N 13.07.

[Cu(phen)₂N₃]BPh₄·H₂O (2): A warm solution of phen (0.198 g, 1.0 mmol) in methanol (15 cm³) was added to a hot aqueous solution (15 cm³) of Cu(O₂CCH₃)₂·H₂O (0.091 g, 0.5 mmol). An aqueous solution (10 cm³) of NaN₃ (0.065 g, 1.0 mmol) was then added to the reaction mixture. Then solid NaBPh₄ (0.171 g, 0.5 mmol) was added and the reaction

mixture was stirred continuously. The green solution was slowly evaporated at room temperature. Green crystals of (2) deposited after several days. The crystals were filtered off, washed with mother liquor and air-dried. Yield *ca* 80%. Analysis: calc. for C₄₈H₃₆BCuN₇O (%): C 71.95, H 4.52, N 12.23; found: C 72.07, H 4.39, N 12.31.

[Cu(dpyam)₂N₃]NO₃·H₂O (3): A warm solution of dpyam (0.171 g, 1.0 mmol) in methanol (15 cm³) was added to a hot aqueous solution (15 cm³) of Cu(NO₃)₂·3H₂O (0.121 g, 0.5 mmol). An aqueous solution (10 cm³) of NaN₃ (0.065 g, 1.0 mmol) was then added to the reaction mixture. The green solution was slowly evaporated at room temperature. Dark green crystals of (3) deposited after several days. The crystals were filtered off, washed with mother liquor and air-dried. Yield *ca* 75%. Analysis: calc. for C₂₀H₂₀CuN₁₀O₄ (%): C 45.50, H 3.82, N 26.52; found: C 45.63, H 3.76, N 26.51.

[Cu(dpyam)₂N₃]ClO₄ (4): A warm solution of dpyam (0.171 g, 1.0 mmol) in methanol (15 cm³) was added to a hot

Table 2Selected bond lengths (Å) and angles (°) for [Cu(L)₂(X)]Y.

$L = \text{dpyam}$										$L = \text{phen}$	$L = \text{bipy}$	
$Y =$	Br^-	CF_3SO_3^-	$\text{BF}_4^- \cdot \text{dpyam}$	$\text{Cl}^- \cdot 4\text{H}_2\text{O}$	NO_3^-	$(\text{SO}_4)_{0.5}^{2-} \cdot \text{dpyam} \cdot 0.5\text{H}_2\text{O}$	PF_6^-	ClO_4^-	BPh_4^-	Br^-	ClO_4^-	$\text{C}(\text{CN})_3^-$
	(5) ^a	(6) ^a	(7) ^a	(8) ^a	(9) ^a	(10) ^b	(11) ^a	(12) ^a	(13) ^a	(1) ^c	(19) ^d	(20) ^e
(a) $X = \text{NCO}$												
$\text{Cu}-\text{N}'$	1.945 (3)	1.949 (3)	1.933 (4)	1.955 (5)	1.950 (3)	1.903 (13)	1.949 (3)	1.952 (4)	1.984 (1)	1.948 (3)	1.961 (8)	1.949 (4)
$\text{Cu}-\text{N1}$	2.030 (3)	2.029 (3)	2.000 (4)	2.008 (3)	2.008 (2)	2.028 (10)	2.008 (2)	2.002 (3)	2.017 (1)	2.029 (3)	2.007 (9)	1.983 (3)
$\text{Cu}-\text{N3}$	2.045 (3)	2.025 (3)	2.001 (3)	2.012 (3)	2.008 (3)	2.012 (10)	2.013 (2)	2.013 (3)	2.018 (1)	2.047 (3)	1.981 (8)	2.003 (3)
$\text{Cu}-\text{N2}$	2.021 (3)	2.047 (2)	2.025 (3)	2.016 (4)	2.043 (2)	2.014 (10)	2.074 (2)	2.068 (3)	2.072 (1)	2.039 (3)	2.095 (8)	2.054 (3)
$\text{Cu}-\text{N4}$	2.283 (3)	2.245 (3)	2.157 (4)	2.181 (3)	2.185 (2)	2.162 (10)	2.169 (3)	2.167 (3)	2.089 (1)	2.345 (3)	2.111 (7)	2.158 (3)
α_1	167.1 (1)	159.4 (1)	156.2 (1)	157.9 (1)	157.3 (1)	154.7 (5)	144.6 (1)	144.1 (2)	124.7 (2)	170.9 (1)	133.2 (1)	141.7 (2)
α_2	98.8 (2)	102.8 (2)	104.4 (1)	104.0 (1)	109.1 (1)	104.6 (5)	116.9 (1)	115.6 (1)	119.4 (1)	100.2 (1)	121.6 (1)	114.5 (1)
α_3	94.1 (2)	97.8 (1)	99.3 (1)	98.1 (1)	93.7 (1)	100.7 (5)	98.5 (1)	100.2 (1)	115.9 (1)	87.6 (1)	105.2 (1)	103.8 (1)
α_4	92.7 (1)	94.2 (2)	90.4 (1)	89.4 (1)	92.5 (1)	90.1 (5)	89.6 (1)	89.6 (1)	94.9 (1)	94.5 (1)	93.4 (1)	95.1 (1)
α_5	92.4 (1)	92.4 (1)	87.8 (1)	88.3 (1)	91.8 (1)	90.0 (5)	88.0 (2)	87.4 (1)	94.7 (1)	93.6 (1)	92.5 (1)	93.0 (1)
α_6	86.2 (1)	86.2 (1)	87.5 (1)	86.6 (1)	86.4 (1)	85.5 (4)	87.7 (1)	88.3 (1)	89.1 (1)	80.8 (1)	79.5 (1)	80.2 (1)
α_7	82.2 (1)	85.3 (1)	88.7 (1)	86.0 (1)	86.1 (1)	85.9 (5)	87.2 (2)	87.7 (1)	88.5 (1)	76.3 (1)	79.5 (1)	78.3 (1)
α_8	172.8 (1)	173.1 (1)	170.0 (2)	173.7 (1)	175.3 (1)	173.0 (5)	176.2 (1)	176.2 (1)	170.3 (2)	164.9 (1)	173.7 (1)	171.6 (1)
α_9	89.9 (1)	88.3 (1)	90.2 (1)	93.3 (1)	88.9 (1)	91.5 (4)	92.6 (1)	92.7 (1)	86.2 (1)	92.8 (1)	94.8 (1)	94.8 (1)
α_{10}	92.0 (1)	91.3 (1)	101.3 (1)	100.3 (1)	94.2 (1)	100.9 (5)	96.5 (1)	95.7 (1)	85.9 (1)	89.7 (1)	99.3 (1)	96.3 (1)
τ	0.09	0.23	0.23	0.26	0.30	0.31	0.53	0.54	0.76	0.10	0.68	0.50
$L = \text{dpyam}$										$L = \text{phen}$	$L = \text{bipy}$	
$Y =$	$\text{NO}_3^- \cdot \text{H}_2\text{O}$ (3) ^c			ClO_4^- (4) ^c		PF_6^- (14) ^f		$\text{Cl}^- \cdot 4\text{H}_2\text{O}$ (15) ^f		$\text{BPh}_4^- \cdot \text{H}_2\text{O}$ (2) ^c	ClO_4^- (23) ^g	
(b) $X = \text{N}_3$												
$\text{Cu}-\text{N}'$	2.020 (1)			2.016 (3)		2.009 (2)		2.007 (2)		1.980 (4)		1.971 (5)
$\text{Cu}-\text{N1}$	2.001 (1)			1.995 (3)		2.005 (2)		1.999 (2)		2.006 (4)		2.001 (4)
$\text{Cu}-\text{N3}$	2.016 (1)			2.027 (3)		2.036 (2)		2.003 (2)		2.022 (4)		2.019 (4)
$\text{Cu}-\text{N2}$	2.022 (1)			2.017 (3)		2.016 (2)		2.028 (2)		2.045 (4)		2.030 (5)
$\text{Cu}-\text{N4}$	2.158 (1)			2.165 (3)		2.153 (2)		2.169 (2)		2.242 (4)		2.218 (5)
α_1	160.5 (1)			168.2 (1)		166.8 (1)		160.5 (1)		166.7 (1)		164.4 (2)
α_2	98.8 (1)			95.2 (1)		96.5 (1)		103.4 (1)		100.6 (1)		105.4 (2)
α_3	100.7 (1)			96.6 (1)		96.7 (1)		96.0 (1)		92.2 (1)		90.0 (2)
α_4	89.1 (1)			88.7 (1)		88.2 (1)		86.4 (1)		90.3 (1)		92.2 (2)
α_5	88.5 (1)			89.6 (1)		90.2 (1)		89.0 (1)		91.5 (1)		89.2 (2)
α_6	87.0 (1)			88.5 (1)		88.0 (1)		87.4 (1)		81.4 (1)		80.5 (2)
α_7	88.0 (1)			89.5 (1)		88.8 (1)		87.9 (1)		78.2 (1)		77.7 (2)
α_8	165.8 (1)			161.7 (1)		163.1 (1)		169.4 (1)		170.4 (1)		173.3 (1)
α_9	90.8 (1)			89.5 (1)		89.8 (1)		93.9 (1)		94.9 (1)		96.6 (2)
α_{10}	106.2 (1)			108.9 (1)		108.2 (1)		102.5 (1)		110.8 (1)		108.2 (2)
τ	0.09			0.11		0.06		0.15		0.06		0.15
$L = \text{bipy}$		$L = \text{dpyam}$		$L = \text{phen}$		$L = \text{phen}$				$L = \text{bipy}$		
$Y =$	$\text{C}(\text{CN})_3^-$ (22) ^h	$\text{NCS} \cdot 0.5\text{DMSO}$ (16) ⁱ	$\text{ONC}(\text{CN})_2^-$ (21) ^j	ClO_4^- (17) ^k	$\text{C}(\text{CN})_3^-$ (18) ^l	ClO_4^- (24) ^m	CF_3SO_3^- (25) ⁿ	$\text{C}(\text{CN})_3^-$ (26) ^o	PF_6^- (27) ^p	ClO_4^- (28) ^q	BF_4^- (29) ^r	
(c) $X = \text{NCS}$												
$\text{Cu}-\text{N}'$	1.978 (4)	1.976 (4)	1.963 (3)	2.005 (5)	1.984 (4)	2.033 (6)	1.990 (2)	1.982 (4)	1.983 (3)	1.995 (3)	2.015 (3)	
$\text{Cu}-\text{N1}$	1.970 (3)	1.997 (3)	1.980 (3)	2.004 (4)	1.987 (3)	1.996 (5)	1.995 (2)	1.977 (4)	2.003 (3)	1.992 (1)	1.998 (3)	
$\text{Cu}-\text{N3}$	1.979 (3)	2.017 (3)	1.994 (3)	1.999 (4)	2.000 (3)	2.001 (5)	1.990 (2)	1.981 (3)	1.986 (3)	2.003 (1)	2.006 (3)	
$\text{Cu}-\text{N2}$	2.064 (3)	2.017 (3)	2.080 (3)	2.089 (4)	2.078 (3)	2.086 (4)	2.108 (2)	2.064 (3)	2.100 (3)	2.040 (1)	2.043 (3)	
$\text{Cu}-\text{N4}$	2.094 (3)	2.164 (3)	2.101 (3)	2.113 (4)	2.112 (3)	2.087 (5)	2.141 (2)	2.112 (4)	2.122 (3)	2.146 (1)	2.142 (3)	
α_1	126.3 (1)	158.6 (1)	128.0 (1)	126.0 (1)	126.6 (1)	118.4 (1)	135.3 (1)	133.6 (2)	133.3 (1)	146.7 (1)	145.0 (1)	
α_2	117.9 (1)	103.9 (1)	115.8 (1)	118.0 (2)	113.2 (1)	115.2 (1)	121.2 (1)	115.7 (2)	122.4 (1)	108.5 (1)	108.6 (1)	
α_3	115.8 (1)	97.4 (1)	116.2 (1)	116.1 (1)	120.2 (1)	126.4 (2)	103.5 (1)	110.7 (1)	104.3 (1)	104.9 (1)	106.4 (1)	
α_4	93.1 (1)	88.9 (1)	93.6 (1)	92.8 (2)	92.8 (1)	90.4 (2)	91.9 (1)	93.4 (2)	90.6 (1)	92.5 (1)	92.4 (1)	
α_5	92.6 (1)	88.1 (1)	93.9 (1)	92.2 (2)	93.2 (1)	90.4 (2)	93.1 (1)	91.4 (2)	93.7 (1)	90.3 (1)	90.0 (1)	
α_6	80.0 (1)	87.4 (1)	80.9 (1)	80.6 (2)	80.8 (1)	80.8 (2)	81.1 (1)	80.8 (1)	80.8 (1)	80.5 (1)	80.5 (1)	
α_7	79.6 (1)	89.0 (1)	80.5 (1)	80.4 (2)	80.5 (1)	80.7 (1)	80.4 (1)	80.7 (1)	80.6 (1)	78.8 (1)	79.1 (1)	
α_8	174.2 (1)	166.2 (1)	172.3 (1)	174.8 (2)	174.0 (1)	179.1 (2)	175.0 (1)	175.1 (1)	175.3 (1)	177.2 (1)	177.5 (1)	
α_9	97.5 (1)	90.5 (1)	95.9 (1)	97.6 (1)	96.6 (1)	98.6 (2)	95.1 (1)	95.2 (1)	94.8 (1)	96.9 (1)	97.2 (1)	
α_{10}	96.7 (1)	104.9 (1)	94.6 (1)	95.9 (2)	96.0 (1)	99.0 (1)	97.2 (1)	98.0 (1)	98.7 (1)	100.8 (1)	100.8 (1)	
(d) $X = \text{C}_2\text{N}_3$												
$\text{Cu}-\text{N}'$	1.978 (4)	1.976 (4)	1.963 (3)	2.005 (5)	1.984 (4)	2.033 (6)	1.990 (2)	1.982 (4)	1.983 (3)	1.995 (3)	2.015 (3)	
$\text{Cu}-\text{N1}$	1.970 (3)	1.997 (3)	1.980 (3)	2.004 (4)	1.987 (3)	1.996 (5)	1.995 (2)	1.977 (4)	2.003 (3)	1.992 (1)	1.998 (3)	
$\text{Cu}-\text{N3}$	1.979 (3)	2.017 (3)	1.994 (3)	1.999 (4)	2.000 (3)	2.001 (5)	1.990 (2)	1.981 (3)	1.986 (3)	2.003 (1)	2.006 (3)	
$\text{Cu}-\text{N2}$	2.064 (3)	2.017 (3)	2.080 (3)	2.089 (4)	2.078 (3)	2.086 (4)	2.108 (2)	2.064 (3)	2.100 (3)	2.040 (1)	2.043 (3)	
$\text{Cu}-\text{N4}$	2.094 (3)	2.164 (3)	2.101 (3)	2.113 (4)	2.112 (3)	2.087 (5)	2.141 (2)	2.112 (4)	2.122 (3)	2.146 (1)	2.142 (3)	
α_1	126.3 (1)	158.6 (1)	128.0 (1)	126.0 (1)	126.6 (1)	118.4 (1)	135.3 (1)	133.6 (2)	133.3 (1)	146.7 (1)	145.0 (1)	
α_2	117.9 (1)	103.9 (1)	115.8 (1)	118.0 (2)	113.2 (1)	115.2 (1)	121.2 (1)	115.7 (2)	122.4 (1)	108.5 (1)	108.6 (1)	
α_3	115.8 (1)	97.4 (1)	116.2 (1)	116.1 (1)	120.2 (1)	126.4 (2)	103.5 (1)	110.7 (1)	104.3 (1)	104.9 (1)	106.4 (1)	
α_4	93.1 (1)	88.9 (1)	93.6 (1)	92.8 (2)	92.8 (1)	90.4 (2)	91.9 (1)	93.4 (2)	90.6 (1)	92.5 (1)	92.4 (1)	
α_5	92.6 (1)	88.1 (1)	93.9 (1)	92.2 (2)	93.2 (1)	90.4 (2)	93.1 (1)	91.4 (2)	93.7 (1)	90.3 (1)	90.0 (1)	
α_6	80.0 (1)	87.4 (1)	80.9 (1)	80.6 (2)	80.8 (1)	80.8 (2)	81.1 (1)	80.8 (1)	80.8 (1)	80.5 (1)	80.5 (1)	
α_7	79.6 (1)	89.0 (1)	80.5 (1)	80.4 (2)	80.5 (1)	80.7 (1)	80.4 (1)	80.7 (1)	80.6 (1)	78.8 (1)	79.1 (1)	
α_8	174.2 (1)	166.2 (1)	172.3 (1)	174.8 (2)	174.0 (1)	179.1 (2)	175.0 (1)	175.1 (1)	175.3 (1)	177.2 (1)	177.5 (1)	
α_9	97.5 (1)	90.5 (1)	95.9 (1)	97.6 (1)	96.6 (1)	98.6 (2)	95.1 (1)	95.2 (1)	94.8 (1)	96.9 (1)	97.2 (1)	
α_{10}	96.7 (1)	104.9 (1)	94.6 (1)	95.9 (2)	96.0 (1)	99.0 (1)	97.2 (1)	98.0 (1)	98.7 (1)	100.8 (1)	100.8 (1)	

Table 2 (continued)

$L = \text{bipy}$		$L = \text{dpyam}$	$L = \text{phen}$			$L = \text{phen}$				$L = \text{bipy}$	
$Y =$	$\text{C}(\text{CN})_3^-$ (22) ^{<i>b</i>}	$\text{NCS} \cdot 0.5\text{DMSO}$ (16) ^{<i>i</i>}	$\text{ONC}(\text{CN})_2^-$ (21) ^{<i>j</i>}	ClO_4^- (17) ^{<i>k</i>}	$\text{C}(\text{CN})_3^-$ (18) ^{<i>l</i>}	ClO_4^- (24) ^{<i>m</i>}	CF_3SO_3^- (25) ^{<i>n</i>}	$\text{C}(\text{CN})_3^-$ (26) ^{<i>o</i>}	PF_6^- (27) ^{<i>p</i>}	ClO_4^- (28) ^{<i>q</i>}	BF_4^- (29) ^{<i>r</i>}
τ	0.80	0.13	0.74	0.81	0.79	0.88	0.66	0.69	0.70	0.51	0.54

References: (a) Youngme, Phatchimkun, Suksangpanya *et al.* (2007), (b) Akhter & Hathaway (1991), (c) this work, (d) McAuliffe *et al.* (1992), (e) Potočník *et al.* (1998a), (f) Youngme, Phatchimkun, Pakawatchai *et al.* (2007), (g) Munno *et al.* (1998), (h) Potočník *et al.* (1998b), (i) Youngme *et al.* (2002), (j) Potočník *et al.* (1995), (k) Parker *et al.* (1994), (l) Potočník *et al.* (1996a), (m) Burčák *et al.* (2004), (n) Potočník *et al.* (2003), (o) Potočník *et al.* (1996b), (p) Potočník *et al.* (2005), (q) Potočník *et al.* (2002), (r) Potočník *et al.* (2001).

aqueous solution (15 cm³) of Cu(ClO₄)₂·4H₂O (0.185 g, 0.5 mmol). An aqueous solution (10 cm³) of NaN₃ (0.065 g, 1.0 mmol) was then added to the reaction mixture. The green solution was slowly evaporated at room temperature. Green crystals of (4) deposited after several days. The crystals were filtered off, washed with mother liquor and air-dried. Yield ca 90%. Analysis: calc. for C₂₀H₁₈ClCuN₉O₄ (%): C 43.88, H 3.31, N 23.03; found: C 43.96, H 3.23, N 23.11.

2.2. Crystallography

Reflection data for (1)–(4) were collected at 293 K on a 4 K Bruker SMART CCD area-detector diffractometer using graphite-monochromated Mo *K* α radiation (λ = 0.71073 Å) at a detector distance of 6.0 cm and swing angle of -28° . A hemisphere of the reciprocal space was covered by a combination of three sets of exposures; each set had a different φ angle (0, 88, 180°) and each exposure of 10 s for (1)–(4) covered 0.3° in ω . Data reduction and cell refinements were performed using the program *SAINT* (Siemens, 1996). An empirical absorption correction was applied using the *SADABS* (Sheldrick, 1996) program. The structure was solved by direct methods and refined by the full-matrix least-squares method on (F_{obs})² with anisotropic displacement parameters for all non-H atoms using the *SHELXTL-PC* (Siemens, 1997) software package.

The NO₃[−] anion in (3) and ClO₄[−] anion in (4) are disordered with site occupancies of 0.50 for both conformers. The molecular graphics were created using *SHELXTL-PC*. The crystal and refinement details for (1)–(4) are listed in Table 1.¹ Selected bond lengths and angles are given in Table 2.

3. Results and discussion

3.1. Crystal structures

Fig. 1 shows a representative molecular structure for the [Cu(chelate)₂*X*] cation, with atom numbering and the angular notation schemes used. The crystallographic and refinement data for the four new complexes reported are given in Table 1. Table 2(a) reports the Cu–*L* distances and α_{1-10} angles of the 12 [Cu(chelate)₂NCO]*Y* complexes (1), (5)–(13) and (19)–(20). Table 2(b) lists the corresponding data for the six

[Cu(chelate)₂N₃]⁺ cations (2)–(4), (14)–(15) and (23). Table 2(c) lists the data for the five [Cu(chelate)₂NCS]⁺ cations (16)–(18), (21) and (22), and Table 2(d) lists the data for the six [Cu(chelate)₂C₂N₃]⁺ cations (24)–(29), thus extending the database to 29 [Cu(chelate)₂(*X*)]⁺ cations. The corresponding τ values, where $\tau = (\alpha_8 - \alpha_1)/60$ (Addison, Rao, Reedijk *et al.*, 1984), are listed, with $\tau = 1.00$ for an RTBP and $\tau = 0.00$ for an RSBP. Table 3 reports the maximum and minimum values of the Cu–*L* distances and α_n angles, their differences and average values. In Table 2, the axial positions, N1 and N3, are defined as the largest N–Cu–N angle of ca 180°, usually $\alpha_8 > \alpha_1$ except complexes (1), (4) and (14). The longest in-plane distance, Cu–N4, is defined as opposite the largest in-plane angle α_1 , with $\alpha_1 > \alpha_2 > \alpha_3$, except the complexes (3), (4), (14), (18), (21) and (24), $\alpha_2 < \alpha_3$. These are due to the flexibility of the molecular structures. The Cu–N' distances observed appear to be shorter than the in-plane Cu–N_{2,4} distances. The results for the new structures will not be compared in detail, but compared with earlier data by scatterplot analysis.

3.2. The [Cu(chelate)₂*X*]*Y* data

For the 29 [Cu(chelate)₂*X*]*Y* complexes, where chelate = phen, bipy or dpyam and *X* is an anion of a pseudohalide ligand (NCO, NCS, N₃ and C₂N₃; Table 2), the structure of the five-coordinate CuN₄N' chromophore varies from square-based pyramidal distorted trigonal bipyramidal, SBPDTBP, for (24) ($\tau = 0.88$) to the near RSBP for (2) ($\tau = 0.06$) and $\Delta\tau = 0.82$. This is a large variation in τ , the largest seen to date for the cation distortion isomers of the [Cu(chelate)₂*X*]*Y* series of complexes (Camus *et al.*, 1999; Johnson & Jacobson, 1973; Jensen & Jacobson, 1981). None of the complexes have a near RTBP (regular trigonal bipyramidal) stereochemistry or lies on a twofold axis of symmetry. There are 14 complexes [(1)–(10), (14)–(16) and (23)] which have τ values in the more limited range 0.06–0.31 and their stereochemistries are best described as TBPDSBP. Five complexes [(11)–(12), (20) and (28)–(29)] have τ values of 0.50–0.54 and their stereochemistries are best described as intermediate five-coordinate. Ten complexes [(13), (17)–(19), (21)–(22), (24)–(27)] have τ values in the range 0.66–0.88 and their stereochemistries are best described as SBPDTBP. Table 3 reports the maximum and minimum values of the Cu–*L* distances and α_n angles, their differences and average values for [Cu(chelate)₂*X*]*Y* complexes. Relative to a RTBP stereochemistry, the out-of-plane distances (Table 2) show only small differences (Table 3)

¹ Supplementary data for this paper are available from the IUCr electronic archives (Reference: BP5008). Services for accessing these data are described at the back of the journal.

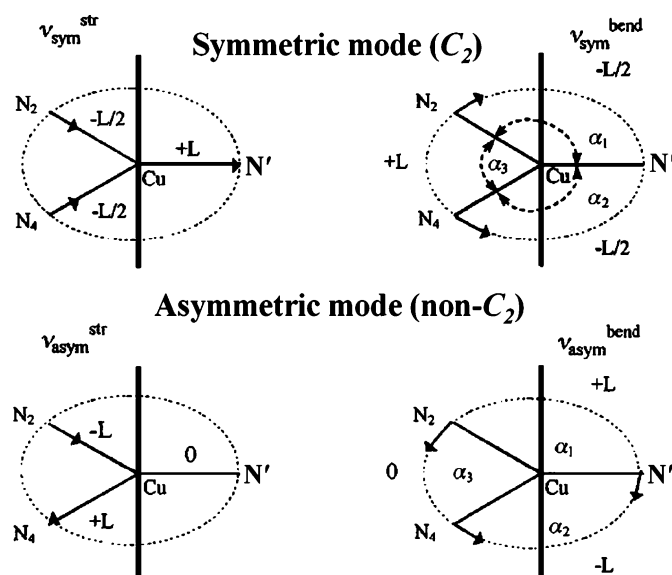
Table 3Maxima, minima, difference (Δ) and average values of the bond lengths ($\text{\AA}$) and angles ($^\circ$) for the $[\text{Cu}(\text{chelate})_2\text{X}]\text{Y}$ complexes.

	Out-of-plane bond lengths		In-plane bond lengths				
	Cu—N1	Cu—N3	Cu—N'	Cu—N2	Cu—N4	τ	
Maximum	2.030 (1)	2.047 (1)	2.033 (6)	2.108 (2)	2.345 (3)	0.88	
Minimum	1.970 (1)	1.979 (1)	1.903 (13)	2.014 (10)	2.087 (5)	0.06	
Δ	0.060	0.068	0.130	0.094	0.258	0.82	
Average	1.998 (1)	2.006 (1)	1.975 (1)	2.052 (1)	2.162 (1)		

	In-plane angles			Out-of -plane angles						
	α_1	α_2	α_3	α_4	α_5	α_6	α_7	α_8	α_9	α_{10}
Maximum	170.9 (1)	122.4 (1)	126.4 (1)	95.1 (1)	94.7 (1)	89.1 (1)	89.5 (1)	179.1 (1)	98.6 (1)	110.8 (1)
Minimum	118.4 (1)	95.2 (1)	87.6 (1)	86.4 (1)	87.4 (1)	79.5 (1)	76.3 (1)	161.7 (2)	86.2 (1)	85.9 (1)
Δ	52.5	27.2	38.8	8.7	7.3	9.6	13.2	17.4	12.4	24.9
Average	147.5 (1)	109.4 (1)	103.1 (1)	91.5 (1)	91.0 (2)	83.8 (1)	83.2 (1)	172.2 (1)	93.4 (1)	99.0 (1)

with $\Delta\text{Cu—N1} = 0.060 \text{ \AA}$ and $\Delta\text{Cu—N3} = 0.068 \text{ \AA}$. The largest variations in bond lengths are present in the equatorial bond distances Cu—N4, Cu—N' and Cu—N2, respectively. The Cu—N4 distances show the largest variation ranging from 2.087 (5) to 2.345 (3) $\text{\AA}$, with $\Delta = 0.258 \text{ \AA}$ and with an average value of 2.162 (1) $\text{\AA}$. The Cu—N2 distances vary from 2.014 (10) to 2.108 (2) $\text{\AA}$, with $\Delta = 0.094 \text{ \AA}$ and with a mean value of 2.052 (1) $\text{\AA}$. The Cu—N' distances range from 1.903 (13) to 2.033 (6) $\text{\AA}$, with $\Delta = 0.130 \text{ \AA}$ and with an average value of 1.975 (1) $\text{\AA}$. The average of the in-plane Cu—N(2, 4, N') distances, 2.063 (1) $\text{\AA}$, is greater than the average of the axial Cu—N(1,3) distances [2.005 (1) $\text{\AA}$], by 0.058 $\text{\AA}$, consistent with a TBP stereochemistry and slightly less than the difference of 0.1 $\text{\AA}$ normally observed (Huq & Shapski, 1971). The out-of-plane bond angles (Table 2) show only small differences, Table 3, with $\Delta\alpha_{4-7}$ and $\Delta\alpha_{8-10}$ ranging from 7.3 to

13.2 and 12.4 to 24.9 $^\circ$, respectively. The α_1 in-plane angles show the largest variation ranging from 118.4 (1) to 170.9 (1) $^\circ$, with $\Delta = 52.5^\circ$ and with a mean value of 147.5 (1) $^\circ$. The α_2 angles show the smallest variation ranging from 95.2 (1) to 122.4 (1) $^\circ$, with $\Delta = 27.2^\circ$ and an average value of 109.4 (1) $^\circ$. The α_3 angles vary from 87.6 (1) to 126.4 (1) $^\circ$, with $\Delta = 38.8^\circ$ and an average value of 103.1 (1) $^\circ$. From Table 2 it is noticeable that within the τ value range of 0.88–0.06 there is a slight gap of 0.04 between the value of 0.70 for (27) to the next value of 0.74 for (21). This gap corresponds to a change in the ratio of the α_9 and α_{10} angles, for τ values > 0.70 , $\alpha_9 > \alpha_{10}$, but for τ values < 0.70 , $\alpha_9 < \alpha_{10}$. These relations have been used to suggest a structural pathway from regular trigonal bipyramidal to distorted square-based pyramidal and suggest that (1)–(29) lie in a more extensive structural pathway for the $\text{CuN}_4\text{N}'$ chromophore.

**Figure 4**

The symmetric and asymmetric modes of vibration for the five-coordinate $\text{CuN}_4\text{N}'$ chromophore, including the relative magnitudes (L).

	E''	B	B_2	A	E
		B	B_1	A	
	E'	A	A_2	A	B_2
		A	A_1	A	B_1
	A_1'	A	A_1	A	A_1

	C_2	C_1
Symmetry	$D_{3h} \longleftrightarrow C_{2v} \longleftrightarrow C_{4v}$	
Jahn-Teller active	No	No
Pseudo J. T. $v_s(C_2)$	Yes	Yes
Active $v_{as}(\text{non-}C_2)$	No	Yes

Figure 5

The one-electron orbital levels of the RTBP stereochemistry and their symmetries in various point groups.

Table 4Limiting values for $\pm A$, $+B$, $-A + B$ and $+A + B$ route distortions.

	RTBP	+A (RSBP)	-A (SEESAW)	+B	-B	-A + B (SBP)	+A + B (SBP)
α_1 ($^\circ$)	120	97.5	135	150	90	165	105
α_2 ($^\circ$)	120	97.5	135	90	150	105	90
α_3 ($^\circ$)	120	165	90	120	120	90	165
Cu—N4 ($\text{\AA}$)	2.092	1.998	2.155	2.199	1.985	2.262	2.025
Cu—N2 ($\text{\AA}$)	2.092	1.998	2.155	1.985	2.199	2.048	1.971
Cu—N' ($\text{\AA}$)	2.092	2.280	1.966	2.092	2.092	1.966	2.280

3.3. Interpretation of the $\pm A$ and $\pm B$ route distortions in terms of modes of vibration

In the distortion of RTBP to RSBP stereochemistry the modes of vibration of the in-plane $\text{CuN}_2\text{N}'$ portion of the chromophore involved are $\nu_{\text{sym}}^{\text{str}}$, $\nu_{\text{sym}}^{\text{bend}}$, $\nu_{\text{asym}}^{\text{str}}$ and $\nu_{\text{asym}}^{\text{bend}}$ (Fig. 4). These senses of distortion can be conveniently described in terms of the $\pm A$ and $\pm B$ routes of Fig. 5. The $\pm A$ route of distortion involves solely $\nu_{\text{sym}}^{\text{str}}$ and $\nu_{\text{sym}}^{\text{bend}}$ modes of vibration, both of which retain the C_2 symmetry of the $\text{CuN}_4\text{N}'$ chromophore. On the other hand, the $\pm B$ route of distortion is determined by the $\nu_{\text{asym}}^{\text{str}}$ and $\nu_{\text{asym}}^{\text{bend}}$ modes, both of which lower the symmetry of the $\text{CuN}_4\text{N}'$ chromophore to C_1 . In practice, the $\text{CuN}_4\text{N}'$ chromophores display no elements of symmetry, *i.e.* they have C_1 symmetry (Table 2 and Fig. 5). Thus, the $[\text{Cu}(\text{chelate})_2X]Y$ series of complexes are described with $-A$ route distortion, which also involves a significant $+B$ route distortion. The pure $-A$ route distortion with C_2 symmetry is represented by the left horizontal distortion through the RTBP stereochemistry in Fig. 5, as a *reversed* trigonal bipyramidal (RevTBP) stereochemistry, implying that the pure $+A$ route distortion (illustrated by the right horizontal distortion in Fig. 5) is referred to as SBPDTPB. However, as the actual datapoints rarely involve pure $\pm A$ or $\pm B$ route distortions, all four modes are generally involved in the distortion of each complex. As the α_3 angles are nearly 40° less than the 120° of the RTBP stereochemistry, it is inappropriate to describe them

as RevTBP and so the term *SEESAW* distorted trigonal bipyramidal (SSDTPB) has been introduced to describe their geometries; however, it should be noted that the distinction between these two geometries is only arbitrary.

3.4. Scatterplot analysis for the $[\text{Cu}(\text{chelate})_2X]Y$ series of complexes

This section presents the data for the $[\text{Cu}(\text{chelate})_2X]Y$ series of complexes (Table 2) using scatterplot analysis. The scatterplots (Figs. 6–12) discussed are as follows: τ versus Cu—N4 (Fig. 6), α_1 versus α_3 (Fig. 7), Cu—N2 versus Cu—N4 (Fig. 8), α_2 , α_1 versus α_3 (Fig. 9), Cu—N' versus Cu—N4 (Fig. 10), Cu—N4 versus Cu—N' (Fig. 11a), Cu—N4 versus Cu—N2 (Fig. 11b) and α_3 versus Cu—N' (Fig. 12). A general discussion on the use of scatterplots has been previously reported (Youngme, Phatchimkun, Suksangpanya *et al.*, 2007) and will now be applied to the 29 $[\text{Cu}(\text{chelate})_2X]^+$ cations. Using the suggested limiting values (Table 4) for the $\pm A$, $\pm B$ and $\pm A \pm B$ route distortions illustrated in Fig. 5, the angle versus angle plots and distance versus distance plots can be divided to represent $\pm A$, $\pm B$ axes and $\pm A \pm B$ sections (Figs. 6–12).

An overview of the range of stereochemistries is provided by the plot of τ versus Cu—N4 in Fig. 6. However, as τ involves two simultaneous angle changes, it will not be used further. A number of suggested extreme datapoints, Table 4, are included in the plots, with the geometry of the extreme *SEESAW* stereochemistry illustrated in Fig. 5. The 29 datapoints in Fig. 6 vary from trigonal bipyramidal (TBP) to near regular square-based pyramidal (RSBP) with the τ values decreasing from 0.88 to 0.06 as the Cu—N4 distances increase from 2.087 (5) to 2.345 (3) $\text{\AA}$, respectively. The datapoints show a broad *inverse* trend and clearly do not cluster around the RTBP geometrical point. This plot provides an overview of the observed stereochemistries of the $[\text{Cu}(\text{chelate})_2X]Y$ series of complexes. Two possible parallel pathways pass through or close to seven and nine datapoints, respectively, and two datapoints lying nearby. Three of the remaining datapoints lie

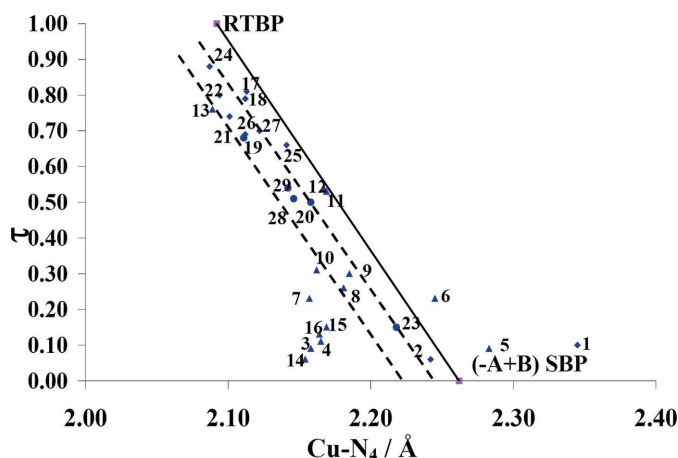


Figure 6
Plot of τ versus Cu—N4: $\blacktriangle$ dpyam, $\bullet$ bipy, $\blacklozenge$ phen.

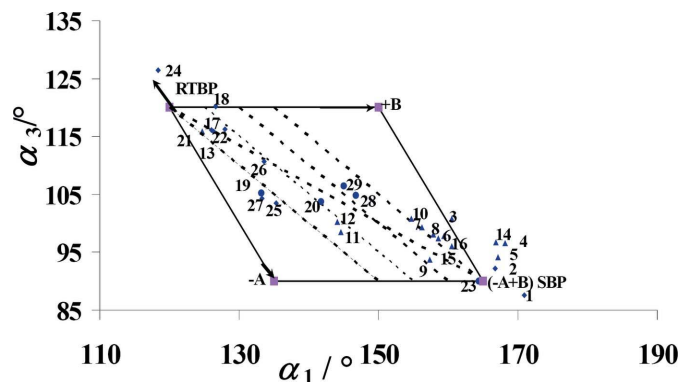


Figure 7
Plot of α_1 versus α_3 : $\blacktriangle$ dpyam, $\bullet$ bipy, $\blacklozenge$ phen.

above the RTBP $\rightarrow$ RSBP pathway and eight dpyam/pseudohalide datapoints clearly lie below the two parallel pathways, which differ significantly from the phen and bipy series in the τ values of complexes owing to the more flexible dpyam ligand. The five bipy/pseudohalide datapoints clearly overlap the phen/pseudohalide datapoints, but are shifted to slightly lower τ and higher Cu—N4 values. The highest τ value is the 0.88 datapoint, which involves the lowest τ value of 0.06 and Cu—N4 distances ranging from 2.242 to 2.087 Å. Both datapoints are in the phen/pseudohalide series. In contrast, the five bipy/pseudohalide datapoints show a much more limited range, with τ ranging from 0.80 to 0.15 and Cu—N4 distances ranging from 2.218 to 2.094 Å.

The datapoints in Fig. 7 show the α_3 values decreasing from 126.4 (1) to 87.6 (1)° as the α_1 values concomitantly increase from 118.4 (1) to 170.9 (1)°. There are 29 datapoints which have α_1 values $> 120^\circ$ and α_3 values $< 120^\circ$, except datapoint (24) (Table 2). There are 21 datapoints found in the $-A + B$ section of the graph. The exceptions are the seven datapoints (1)–(5), (14) and (24), which are in the $-A + B$ section, with a small $+A + B$ (24) route sense of distortion. It is noticeable that within the α_1 and α_3 datasets, these datapoints have greater α_1 and α_3 values compared with those of the RSBP and RTBP stereochemistry. There is only one datapoint (18),

which lies on the RTBP $\Rightarrow +B$ distortion pathway. There are also four datapoints [(17), (22), (23) and (26)], which lie on the RTBP $\Rightarrow$ RSBP ($-A + B$) distortion pathway. Four datapoints [(7), (8), (10) and (16)] and the RSBP datapoint are on the line and show an *inverse* trend, with each of these datapoints having $\alpha_2 = 105 \pm 2^\circ$. The remaining datapoints, three [(9), (28) and (29)], three [(12), (20) and (21)] and one (13), lie on three possible parallel correlations (---) displaying α_2 values of 110 ± 2 , 115 ± 1 and $120 \pm 1^\circ$, respectively. This series of four possible parallel correlations have the same gradients. The datapoints show an SBP distortion, but only the correlation containing the datapoints corresponding to an α_2 value of 105° can contribute to RSBP. For each parallel correlation the α_2 values remain constant, therefore $\Delta\alpha_1 \uparrow \simeq \Delta\alpha_3 \downarrow$ as $\alpha_1 + \alpha_2 + \alpha_3 = 360^\circ$, possibly suggesting the occurrence of preferred or magic angles (Murphy & Hathaway, 2003*a,b*; Murphy, Aljabri, Light & Hursthouse, 2004; Murphy, Roberts, Tyagi & Hathaway, 2004).

The datapoints in Fig. 8 show the Cu—N2 distances decreasing from 2.108 (1) to 2.014 (1) Å, while the Cu—N4 distances increase from 2.089 (1) to 2.345 (1) Å. There are 14 datapoints observed in the $-A + B$ quadrant of the graph, with seven points [(1), (5), (10), (13), (14), (22), (26)] lying outside this quadrant. There are six datapoints [(3), (4), (7), (21), (28), (29)] on the RTBP $\Rightarrow +B$ trendline, and there is one datapoint (24) which lies directly on the RTBP $\Rightarrow \pm A$ route pathway. There is only one datapoint (11), which also lies precisely on the RTBP $\Rightarrow$ RSBP ($-A + B$) pathway, with datapoints (2), (6) (12) and (17) lying close by.

The dataplot of $a_{2,1}$ versus a_3 in Fig. 9 involves $a_{2,1}$ angles ranging from 171 to 94° and a_3 angles from 127 to 87° , and indicates a general increase in the separation of a_2 and a_1 angles from high to low a_3 angles. At high a_3 angles, 127 – 119° , the spread in $\Delta a_{2,1}$ is small, 14° , as $a_1 + a_2 + a_3 = 360^\circ$, but at lower a_3 angles, 116 – 95° , the spread increases to a maximum of 73° at 96.6° of datapoint (4) and then decreases 2.3° at a_3 angles of 93 – 87° [datapoint (1)]. The average $a_{2,1}$ angle of 120° at an a_3 angle of 120° increases to 138.5° ($-A$ route) at an a_3 angle of 95° , and corresponds to the effect of pure $v_{\text{sym}}^{\text{bend}}$ on the a_3 angle. Within the a_3 range 120 – 87° , the values of the indi-

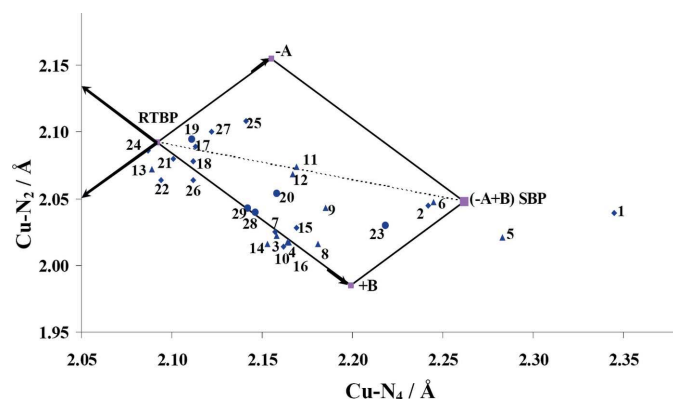


Figure 8
Plot of Cu—N2 versus Cu—N4: $\blacktriangle$ dpyam, $\bullet$ bipy, $\blacklozenge$ phen.

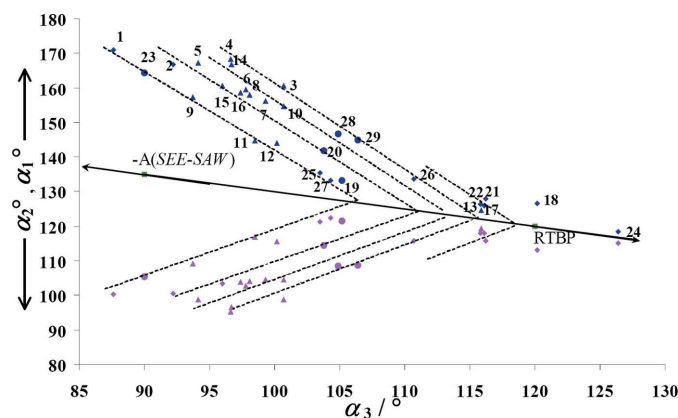


Figure 9
Plot of α_2 , α_1 versus α_3 : $\blacktriangle$ dpyam, $\bullet$ bipy, $\blacklozenge$ phen.

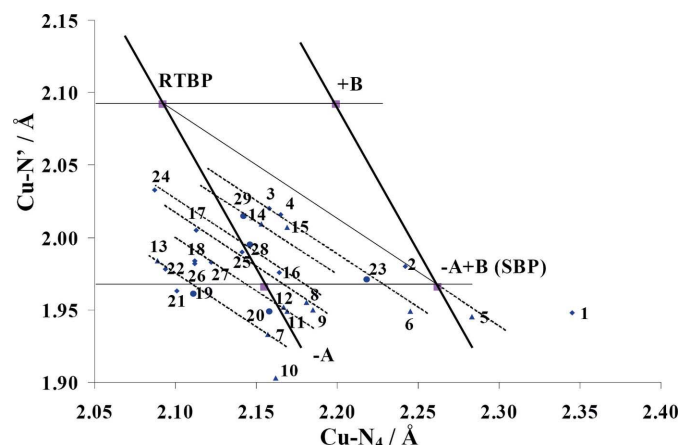


Figure 10
Plot of Cu—N' versus Cu—N4: $\blacktriangle$ dpyam, $\bullet$ bipy, $\blacklozenge$ phen.

vidual a_1 and a_2 angles are evenly distributed about the mean $a_{2,1}$ line. This corresponds to the effect of a pure $\nu_{\text{sym}}^{\text{bend}}$ mode of vibration superimposed onto the pure $\nu_{\text{asym}}^{\text{bend}}$ mode of vibration. The symmetric nature of the data of Fig. 9 about the RTBP $\rightarrow -A$ route dataline and the restriction to the $\Delta a_{2,1}$ angle at high and low a_3 angles suggests a strong link of the $\nu_{\text{sym}}^{\text{bend}}$ and the $\nu_{\text{asym}}^{\text{bend}}$ modes of vibration. The seesaw structure ($a_1 = a_2 = 135^\circ$ and $a_3 \simeq 90^\circ$) is consistent with the formation of a pure $-A$ route distortion (Murphy, Nagle, Murphy & Hathaway, 1997; Murphy *et al.*, 1998, 2003), where the effect of $\nu_{\text{asym}}^{\text{bend}}$ is reduced to zero.

A feature of Fig. 9 is the formation of a number of interpenetrating right-pointing arrowhead structures, generated by reasonably linear correlations of the separate a_1 and a_2 datapoints against the a_3 datapoints. Within the arrowhead the spread in the $\Delta a_{2,1}$ angles and the range in the a_3 angles are limited to < 73 and 10° , respectively, and the tip of the arrow lies on the RTBP $\rightarrow -A$ route pathway. This suggests that as a_3 decreases there is a limit to the spread in $\Delta a_{2,1}$ and the a_3 angle flips to a lower value. Thus, Fig. 9 presents a clear visual

picture of the combined effect of the $\nu_{\text{sym}}^{\text{bend}}$ and the $\nu_{\text{asym}}^{\text{bend}}$ modes of vibration on the in-plane a_{1-3} angles.

The 29 datapoints in Fig. 10 range from 1.903 to 2.033 Å in the Cu—N' distance and from 2.087 to 2.345 Å in the Cu—N4 distance, with a slight gap in the Cu—N' datapoints from 1.97 to 2.03 Å, but not in the Cu—N4 distance. There are no datapoints lying near the RTBP datapoint, in contrast, almost all the datapoints are around the $-A$ route distortion. Correlations may be drawn in the data parallel to the RTBP $\rightarrow$ RSBP pathway, through five, four, three and two datapoints, but these are significantly displaced from the main pathway (RTBP $\rightarrow$ RSBP). This displacement is most noticeable at the lower Cu—N' distances, suggesting that the Cu—N4 distances are more associated with the RTBP $\rightarrow -A$ route pathway of the 'SEESAW' type (IV) structure of Fig. 5. The displacement of the Cu—N4 distances to lower values can be understood in terms of a progression of the pure $\nu_{\text{asym}}^{\text{str}}$ modes of vibration, giving an association of the Cu—N4 distances with the RTBP $\rightarrow -A$ route distortion.

Fig. 11(a) shows the RTBP $\rightarrow -A$ route distortion of 29 datapoints, while Fig. 11(b) shows the RTBP $\rightarrow +B$ route distortion. Consequently, Fig. 12 has been simplified in order to qualitatively determine the directions of distortion along the $\pm A \pm B$ routes of the structural pathways.

Fig. 12 is modified from Fig. 5 in order to clearly visualize the distortion route of a given compound which is the best representation of all the datapoints in the structural pathways. The RTBP is the reference point of all routes, the other routes represent the in-plane distortion from RTBP, both in angles and distances (120, 120 and 120° for in-plane angles and 2.1, 2.1 and 2.1 Å for in-plane distances), which consider vibrational modes ($\nu_{\text{sym}}^{\text{str}}$, $\nu_{\text{sym}}^{\text{bend}}$, $\nu_{\text{asym}}^{\text{str}}$ and $\nu_{\text{asym}}^{\text{bend}}$). Thus, the standard uncertainties of angles and distances are essential in determining the magnitude of distortion for the other routes which are distorted from RTBP. The datapoints of the standard uncertainties of the distances and angles of the other routes are shown in Table 5. The standard uncertainties in SBPDTBP, RevTBP, SEESAW and Extreme SEESAW routes are only considered in angles which correspond to the pure $\nu_{\text{sym}}^{\text{bend}}$ in Fig.

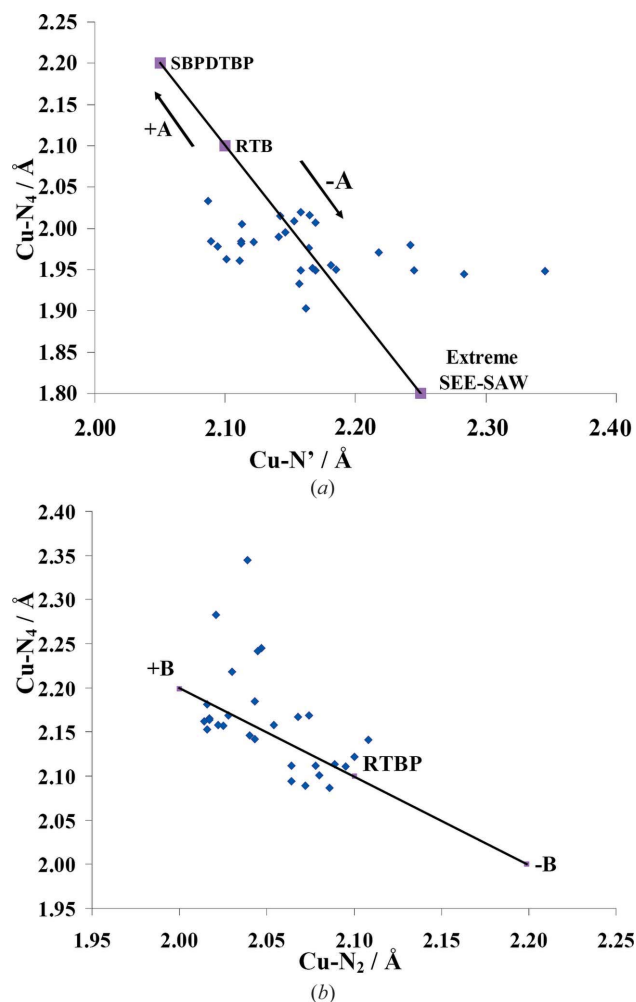


Figure 11
Plots of (a) Cu—N' versus Cu—N4 and (b) Cu—N2 versus Cu—N4: ▲ dpyam, ● bipy, ◆ phen.

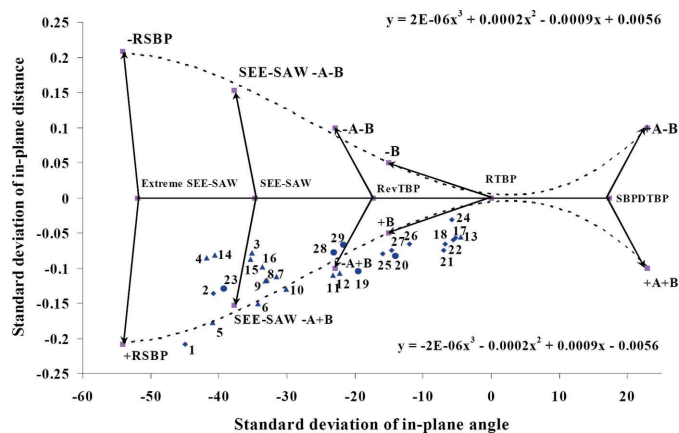


Figure 12
Plot of standard deviation of the in-plane angle versus standard deviation of the in-plane distance of the total data following the structural pathway shown in Fig. 3: ▲ dpyam, ● bipy, ◆ phen.

Table 5

The standard uncertainties (s.u.) in the in-plane angles and distances of other routes and sample datapoints.

	S.u. in angle		S.u. in distance		
	0		0		RTBP (I)
	17.32051		0		SBPDTBP (II)
	−17.3205		0		RevTBP (III)
	−34.641		0		SEESAW (IV)
	−51.9615		0		Extreme-SEESAW (V)
	−15	−0.05			+B (VI)
	22.91288	−0.1			+A + B (VII)
	−22.9129	−0.1			−A + B (VIII)
	−37.7492	−0.15275			SEESAW −A + B (IX)
	−54.0833	−0.20817			+RSBP (X)
	−15	0.05			−B (VI')
	22.91288	0.1			+A − B (VII')
	−22.9129	0.1			−A − B (VIII')
	−37.7492	0.15275			SEESAW −A − B (IX')
	−54.0833	0.20817			−RSBP (X')

	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)	(1)
S.u. in distance	−0.17732	−0.15079	−0.11259	−0.11692	−0.11835	−0.12994	−0.11034	−0.10761	−0.05636	−0.20798
S.u. in angle	−40.85743	−34.21286	−31.48243	−32.95467	−33.17971	−30.11428	−23.20582	−22.27338	−4.43058	−44.90015

	(19)	(20)	(3)	(4)	(14)	(15)	(2)	(23)	(21)	(22)
S.u. in distance	−0.08237	−0.1045	−0.0791	−0.08574	−0.08119	−0.0881	−0.13643	−0.12899	−0.07436	−0.06021
S.u. in angle	−14.06840	−19.53945	−35.08689	−41.74829	−40.53011	−35.29736	−40.80445	−39.27153	−6.93109	−5.55608

	(16)	(17)	(18)	(24)	(25)	(26)	(27)	(28)	(29)
S.u. in distance	−0.09886	−0.05671	−0.0663	−0.03089	−0.07939	−0.06574	−0.07472	−0.07753	−0.06673
S.u. in angle	−33.61493	−5.25389	−6.70224	−5.76888	−15.93393	−12.04035	−14.64821	−23.16405	−21.67856

5. For the remaining routes, the standard deviations are considered in both distances and angles. The polynomial fitting curves are displayed in the equations presented in Fig. 12. There are 29 sample datapoints in Fig. 12 which show distortion from RTBP to $-A + B$ and continue to +RSBP. There is not even one datapoint distorted from RTBP to $+A$ and/or $-B$. This is explained as the inherent feature of five-coordinate copper(II) complexes with a pseudohalide ligand system. In this system most datapoints lie below and above the polynomial curve, but are spread over a wide range of distortions from RTBP $\rightarrow$ RSBP. Datapoint (1) is distorted to near +RSBP, which is the most distorted from RTBP found so far for this family of complexes. Most of the datapoints of phen/pseudohalide lie below the polynomial curve and are distorted from RTBP to $-A + B$. Only datapoint (2) lies above the polynomial curve and is found to be distorted from SEESAW $-A + B$ to +RSBP. Thus, (1) and (2) show extremely distorted stereochemistries, which is unusual for the phen analogue as most of the phen/pseudohalide are usually found in RTBP $\rightarrow -A + B$. Additionally, complex (1) has a Cu–N4 distance of 2.345 Å, which is the longest Cu–N distance for a phen chelate attached to Cu. The datapoints of the dpyam/pseudohalide point towards $-A + B$ to +RSBP owing to the more flexible dpyam ligand; only datapoint (13) ($\tau = 0.76$) points to RTBP $\rightarrow +B$ which equates to an unusual SBPDTBP stereochemistry for dpyam/pseudohalide. The datapoints of bipy/pseudohalide are usually found in RTBP $\rightarrow -A + B$; only

datapoint (23) shows the distortion from SEESAW $-A + B$ to +RSBP.

3.5. General conclusions from the $[\text{Cu}(\text{chelate})_2\text{X}]\text{Y}$ series scatterplot data

The information obtained from the scatterplot analysis of this series of 29 $[\text{Cu}(\text{chelate})_2\text{X}]\text{Y}$ complexes with a pseudohalide ligand can be summarized as follows:

(i) The data refer to a total of 29 chelate/pseudohalide single-crystal structures of the $[\text{Cu}(\text{chelate})_2\text{X}]^+$ cation distortion isomers, where $X = \text{NCO}$ (12 complexes), N_3 (six complexes), NCS (five complexes) and C_2N_3 (six complexes), in lattices of different Y^- anions.

(ii) The stereochemistry of the phen/pseudohalide series has τ values in the range 0.88–0.06, while those of the bipy/pseudohalide series are in the range 0.80–0.15 and those of the dpyam/pseudohalide series appear in the range 0.76–0.09. However, the dpyam/pseudohalide series of complexes show a clear difference from the phen and bipy series that most τ values appear in the range 0.09–0.54, while those of the bipy, phen/pseudohalide are found in the range 0.88–0.51 owing to the more flexible dpyam ligand. The phen complex (2) has a τ value of 0.06, which indicates the most RSBP found so far in a series of five-coordinate copper(II) complexes with a pseudohalide ligand.

Table 6Electronic reflectance data for $[\text{Cu}(\text{dpyam})_2\text{X}]\text{Y}$ complexes.

Complex	τ	Peak energy (10^3 cm^{-1})
(3)	0.09	14.49, 10.17
(4)	0.11	14.45, 10.42
(5)	0.09	14.51, 10.15
(6)	0.23	14.42, 10.18
(7)	0.23	14.24, 10.22
(8)	0.26	14.20, 10.35
(9)	0.30	13.93, 10.27
(10)	0.31	14.23, 10.63
(11)	0.53	13.87, 10.33
(12)	0.54	13.80, 10.35
(13)	0.76	12.88, 11.42
(14)	0.06	14.05, 11.01
(15)	0.15	14.00, 11.11
(16)	0.13	15.74, 10.66
RTBP	1.00	12.00

(iii) Of the 29 datapoints, three lie above the RTBP–RSBP line and eight lie below the RTBP–RSBP line in Fig. 6, in a random distribution. For the remaining 18 datapoints, the distribution is not random and there is clear evidence of linear pathways (Bersuker, 2001), significantly parallel to the RTBP $\rightarrow$ RSBP ($-A + B$) route distortions associated with the structural pathways of Fig. 5.

(iv) Within the two scatterplots of Figs. 7 and 10, significant parallel correlations are observed. Most of the datapoints are in the range $-A + B$ and the correlation can be understood in terms of coupling into linear progressions (Nakamoto, 1978) the four in-plane modes of vibration of the $\text{CuN}_4\text{N}'$ chromophore (Bacci, 1986; Holmes *et al.*, 1969), all of which are of A symmetry (Reinen, 1983; Reinen & Atanasov, 1991) in the C_1 point group (Fig. 5).

(v) Within the scatterplot of Fig. 9, there is clear evidence for a right-pointing arrowhead structure which has limited ranges of a_3 angles. The ‘flips’ to adjacent arrowheads are associated with progressions in the pure $n\nu_{\text{sym}}^{\text{bend}}$ modes of vibration and are related to the individual parallel pathways of Fig. 7.

(vi) Together the scatterplots of Figs. 6–10 present the most convincing evidence for the involvement of the four in-plane

modes of vibration of the $\text{CuN}_4\text{N}'$ chromophore (Fig. 2) in determining the direction of the distortion along the $\pm A \pm B$ routes of the structural pathways of Fig. 5.

(vii) The best scatterplot (Fig. 12) is introduced to determine the directions and magnitude of distortion in the structural pathways, compared with the results from Figs. 7 and 10 which involve the distortion from RTBP $\rightarrow -A + B$ route.

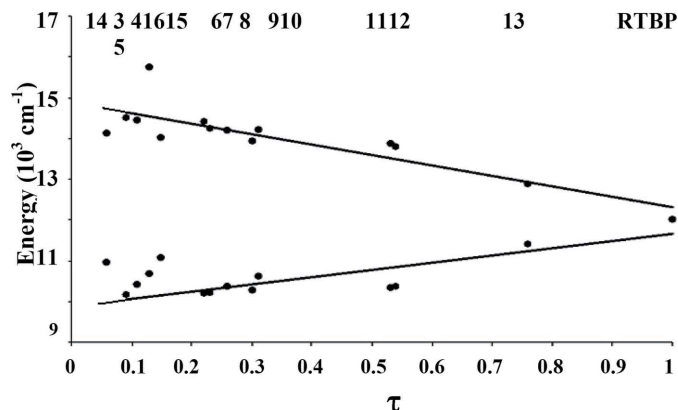
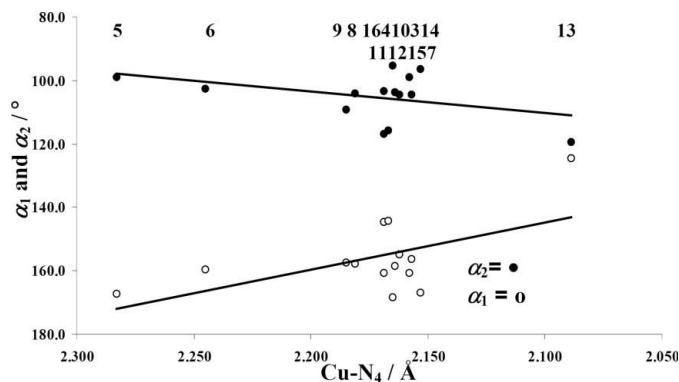
(viii) The present structural pathway (Fig. 5) is modified from the previously reported pathway (Youngme, Phatchimkun, Suksangpanya *et al.*, 2007). The extended routes are Extreme *SEESAW*, +RSBP and –RSBP, in order to explore the distortion of all the datapoints available for the dpyam, phen and bipy/pseudohalides series.

(ix) A new modification has been made to the $\text{N1} - \text{Cu} - \text{N3}$ angle (α_8) in order to obtain $\tau = 0$ for RSBP (Fig. 5).

3.6. IR and electronic properties of the $[\text{Cu}(\text{chelate})_2\text{X}]\text{Y}$ complexes

The IR spectra display a strong band at 2213 cm^{-1} for (1), 2221 cm^{-1} for (2), which can be assigned to the $\nu_{\text{asym}}(\text{NCO})$ absorption band, and a strong band at 2042 cm^{-1} for (3) and 2038 cm^{-1} for (4), which can be assigned to the $\nu_{\text{asym}}(\text{N}_3)$ absorption band. The spectrum of (3) displays intense bands at approximately 1384 and 1323 cm^{-1} , consistent with the characteristic peaks of $\nu_{\text{as}}(\text{NO})$ and $\nu_{\text{t}}(\text{NO})$ of the NO_3^- anion. The spectrum of (4) displays a broad and intense band at approximately 1106 – 1060 cm^{-1} , consistent with the characteristic peak of the ClO_4^- anion.

The polycrystalline electronic reflectance spectra of some representative complexes are shown in Table 6 (Harrison *et al.*, 1981; Nagle *et al.*, 1990) as illustrated examples. Complexes (1)–(4), $\tau = 0.10, 0.06, 0.09$ and 0.11 , which have a TBDSBP stereochemistry, involve a high-energy, high-intensity peak at $13\,570 \text{ cm}^{-1}$ for (1), $14\,400 \text{ cm}^{-1}$ for (2), $14\,490 \text{ cm}^{-1}$ for (3) and $14\,450 \text{ cm}^{-1}$ for (4), with a low-energy, low-intensity shoulder at $11\,140 \text{ cm}^{-1}$ for (1), $10\,110 \text{ cm}^{-1}$ for (2), $10\,170 \text{ cm}^{-1}$ for (3) and $10\,420 \text{ cm}^{-1}$ for (4). The one-electron ground-state configuration is $d_{x^2-y^2} > d_{z^2} > d_{xy} > d_{xz} \simeq d_{yz}$, and the transitions may be assigned as the $d_{z^2} \Rightarrow d_{x^2-y^2}$ transition

**Figure 13**Plot of τ value versus electronic energies for $[\text{Cu}(\text{dpyam})_2\text{X}]\text{Y}$ complexes.**Figure 14**Plot of the two basal angles α_1 and α_2 versus the $\text{Cu}-\text{N}_4$ values for $[\text{Cu}(\text{dpyam})_2\text{X}]\text{Y}$.

for the low-energy shoulder and the $d_{xz} \simeq d_{yz} \Rightarrow d_{x^2-y^2}$ transition for the high-energy peak.

The corresponding spectro-structural correlation plots (Fig. 13) reveal that ΔE values increase with increasing τ values for the low-energy peak and the reverse result has been found for the higher-energy peak. It is evident from Fig. 14 that the basal angles themselves have a similar trend to the ΔE values. This plot clearly indicates that a linear correlation between τ and the ΔE values exists in (3)–(16).

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