[6] S. Youngme, P. Phuengphai, N. Chaichit, G.A. van Albada, O. Roubeau, J. Reedijk, Inorg. Chim. Acta 7 (2004) 3603.
[7] S. Youngme, P. Phuengphai, N. Chaichit, G.A. van Albada, O. Roubeau, J. Reedijk, Inorg. Chim. Acta 358 (2005) 2262.
[8] S. Youngme, P. Phuengphai, N. Chaichit, G.A. van Albada, O. Roubeau, J. Reedijk, Inorg. Chim. Acta 358 (2005) 849.
[9] S. Youngme, P. Phuengphai, C. Pakawatchai, G.A. van Albada, S. Tanase, I. Mutikainen, U. Turpeinen, J. Reedijk, Inorg. Chem. Commun. 8 (2005) 335.
[10] Z.-E. Lin, J. Zhang, Y.-Q. Sun, G.-Y. Yang, Inorg. Chem. 43 (2004) 797.
[11] R.C. Finn, J. Zubieta, J. Phys. Chem. Solids 62 (2001) 1513.
[12] A.W. Addison, T.N. Rao, J. Reedijk, J. van Rijn, G.C. Verschoor, J. Chem. Soc., Dalton Trans. (1984) 1349.
[13] A.M. Krogh Andersen, P. Norby, J.C. Hanson, T. Vogt, Inorg. Chem. 37 (1998) 876.
[14] B.J. Hathaway, in: G. Wilkinson, R.D. Gill, J.A. McCleverty (Eds.), Comprehensive Coordination Chemistry, vol. 5, Pergamon Press, Oxford, 1987 (Chapter 53).
[15] O. Kahn, Molecular Magnetism, VCH Publishers, New York, 1993.
[16] Siemens, SAINT 1996, Version4 Software Reference Manual, Siemens Analytical X-Ray Systems, Inc., Madison, WI, USA, 1996.
[17] Siemens, SHELXTL 1996, Version 5 Reference Manual, Siemens Analytical X-Ray Systems, Inc., Madison, WI, USA, 1996.

PUBLICATION PAPERS OF PART III

ELSEVIER

Available online at www.sciencedirect.com
SCIENCE DIRECT®

Polyhedron 23 (2004) 1641–1647

POLYHEDRON
www.elsevier.com/locate/poly

The novel dinuclear doubly and triply bridged copper(II) compound with monoatomic bridges

Sujittra Youngme [a,*], Chatkaew Chailuecha [a], Narongsak Chaichit [b]

[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*

Received 8 January 2004; accepted 29 March 2004

Abstract

The planar dihydroxo-bridged $[Cu_2(dpyam)_2(\mu\text{-}OH)_2I_2]\cdot 2H_2O$ **(1)** and the roof-shaped trihydroxo-bridged $[Cu_2(dpyam)_2(\mu\text{-}OH)_3]Cl\cdot 3H_2O$ **(2)** (in which dpyam = di-2-pyridylamine) dinuclear copper(II) compounds have been synthesized and their crystal structures determined by X-ray crystallographic methods. All of compounds are being centrosymmetric molecule. Compound **1** contains a dinuclear $[I(dpyam)Cu(\mu\text{-}OH)_2Cu(dpyam)I]^+$ unit with a strictly planar CuO_2 network, dihedral angle between the CuO_2 planes of 180°. Each copper(II) ion is in a tetrahedrally distorted square pyramidal coordination geometry of the CuN_2O_2I chromophore with a dihedral angle 19.3° between the CuN_2 and CuO_2 planes. In the dinuclear $[(dpyam)Cu(\mu\text{-}OH)_3Cu(dpyam)]^+$ unit of compound **2**, the triply bridged Cu(II) ions show a distorted square pyramidal coordination. The fifth apical ligand is a longer bonded bridging OH^- group, at distance of 2.433(4) Å, which joins the basal CuN_2O_2 planes in a roof-shaped configuration with a dihedral angle of 142.5°. The Cu–Cu distance is 2.803(7) Å.

Keywords: Copper(II) complexes; Crystal structure; Dihydroxo-bridged; Roof-shaped; Triply bridged

---

1. Introduction

In the last three decades, the dinuclear doubly bridged copper(II) compounds with nitrogen donor ligand and monoatomic bridges have been received much attention especially the di-μ-hydroxo-bridged copper(II) systems which have been studied widely both from experimental and theoretical points of view, since the magnetostructural correlations described by Hatfield et al. [1] for the Cu–O–Cu bridging angle and spin coupling constant ($2J$) between the metal centers. More recently, these correlations have been extended by Ruiz et al. [2,3]. However, the structure characterized of the triply bridged copper(II) compounds containing nitrogen donor didentated chelate ligand and monoatomic bridges are less reported. So far only a few closely related structures, $[Cu_2(dpyam)_2(\mu\text{-}OH)_2(\mu\text{-}OH_2)]Cl_2\cdot 2H_2O$ [4], $[Cu_2(dpyam)_2(\mu\text{-}OMe)_2(\mu\text{-}Cl)]Cl\cdot MeOH$ [5] and $[Cu_2(dpyam)_2(\mu\text{-}OH)_2(\mu\text{-}OH_2)]Br_2\cdot 2H_2O$ [6] (in which dpyam = di-2-pyridylamine) are reported in the literature. In order to extend the investigation on this series of compounds an attempt has been made to prepare the novel planar di-μ-hydroxo-bridged copper(II) compound, $[Cu_2(dpyam)_2(\mu\text{-}OH)_2I_2]\cdot 2H_2O$ **(1)**, and the novel dinuclear copper(II) compounds containing three monoatomic bridges with homospecies, $[Cu_2(dpyam)_2(\mu\text{-}OH)_3]Cl\cdot 3H_2O$ **(2)**. Their IR, EPR and electronic spectra have been investigated and discussed, along with structural and spectral comparisons with those of other relevant compounds.

2. Experimental

2.1. Materials and measurements

Di-2-pyridylamine were purchased as commercial chemicals from Aldrich. All reagents are commercial grade

---

* Corresponding author. Tel.: +66-043-20222241; fax: +66-043-202373.
E-mail address: sujittra@kku.ac.th (S. Youngme).

0277-5387/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.poly.2004.03.021

materials and were used without further purification. Elemental analyses (C, H, N) were determined on a Perkin–Elmer PE 2400 CHNS/O Analyzer by Microanalytical Service of Science and Technological Research Equipment Center, Chulalongkorn University.

IR spectra were recorded on a Biorad FTS-7/PC FT-IR and a Perkin–Elmer Spectrum One FT-IR spectrophotometer for compounds **1** and **2**, respectively 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 obtained on polycrystalline samples at room temperature and 77 K with a JEOL RE2X electron spin resonance spectrometer by Microanalytical Service of Science and Technological Research Equipment Center, Chulalongkorn University.

2.2. *Synthesis of compound 1*

2.2.1. *[$Cu_2(dpyam)_2(\mu\text{-}OH)_2I_2$]·$2H_2O$ (1)*

The hot aqueous solution (5 ml) of KI (0.166 g, 1.0 mmol) was added to a hot aqueous solution (5 ml) of $Cu(NO_3)_2 \cdot 3H_2O$ (0.121 g, 0.5 mmol). Then a hot acetone solution (8 ml) of dpyam (0.086 g, 0.5 mmol) was added to the mixture yielding a green solution. Its color became greenish-blue by slow addition of an aqueous solution (10 ml) of NaOH (0.020 g, 0.5 mmol) and the blue precipitate formed in a few minutes. The precipitate was filtered off and recrystallized in a hot aqueous solution. After two weeks, blue-plate crystals of compound **1** were obtained. *Anal.* Calc. for $C_{20}H_{24}Cu_2I_2N_6O_4$: C, 30.28; H, 3.05; N, 10.59. Found: C, 30.35; H, 3.12; N, 10.40%.

2.3. *Synthesis of compound 2*

2.3.1. *[$Cu_2(dpyam)_2(\mu\text{-}OH)_3$]Cl·$3H_2O$ (2)*

This compound was prepared by adding a hot acetone solution (10 ml) of dpyam (0.171 g, 1.0 mmol) to a hot aqueous solution (30 ml) of $CuCl_2 \cdot 2H_2O$ (0.170 g, 1.0 mmol) yielding a turquoise green solution. Its color became blue by slow addition of an aqueous solution (10 ml) of NaOH (0.039 g, 1.0 mmol). This solution was allowed to evaporate at room temperature. After several days, bluish-purple crystals of compound **2** were obtained which were filtered off, washed with mother liquor and air-dried. *Anal.* Calc. for $C_{20}H_{27}ClCu_2N_6O_6$: C, 41.70; H, 4.72; N, 14.59. Found: C, 41.67; H, 4.81; N, 14.53%.

2.4. *Crystallography*

The X-ray single-crystal data for two compounds were collected at 298 and 293 K for compounds **1** and **2**, respectively on a 1 K Bruker SMART CCD area-detector diffractometer using graphite monochromated Mo Kα 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 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 [7]. An empirical absorption correction by using the SADABS [8] program was applied, which resulted in transmission coefficients ranging from 0.741 to 1.000 for compound **1**, 0.752 to 1.000 for compound **2**.

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 [9]. All hydrogen atoms were located geometrically and refined isotropically except those of a hydroxo group and two molecules of lattice water for **2**.

The molecular graphics were created by using SHELXTL-PC [9] package. The crystal and refinement details for compounds **1** and **2** are listed in Table 1. Selected bond lengths and angles are given in Tables 2 and 3.

3. Results and discussion

3.1. *Crystal structure of [$Cu_2(dpyam)_2(\mu\text{-}OH)_2I_2$]·$2H_2O$ (1)*

The structure of compound **1** consists of a centrosymmetric dinuclear [$Cu_2(dpyam)_2(\mu\text{-}OH)_2I_2$] unit and two molecules of lattice water. This unit is depicted in Fig. 1, together with the numbering scheme, with selected distances and angles listed in Table 2. Both copper(II) atoms of the complex are linked through the double hydroxo bridges. Each copper(II) atom has a distorted square pyramidal coordination, $\tau = 0.04$ (the structure index is defined as $\tau = (\beta - \alpha)/60$, where β and α are the largest coordination angles [10,11]), with the basal plane, CuN_2O_2 chromophore, comprised of two nitrogen atoms from a terminal dpyam ligand (Cu(1)–N(1) distance of 2.007(3) and Cu(1)–N(2) distance of 2.006(3) Å) and two oxygen atoms from two hydroxo groups (Cu(1)–O(1) distance of 1.967(2) and Cu(1)–O(1A) distance of 1.960(2) Å). The fifth apical coordination site of each copper(II) atom is occupied by an I atom (Cu–I distance of 3.040 Å) to complete the distorted square pyramidal CuN_2O_2I chromophore. However, the Cu–I distance is too long for even weak semi-coordination. The basal planes are slightly deviated from planarity with a distinct tetrahedral twist, evident from the dihedral angle of 19.3° between CuN_2 and CuO_2 planes. The Cu–Cu separation within the dinuclear unit is 2.988(7) Å, while the bridging Cu(1)–

Table 1
Crystal and refinement data for complexes 1and 2

Complex	(1)	(2)
Molecular formula	[$Cu_2(dpyam)_2(\mu\text{-}OH)_2I_2$] · $2H_2O$	[$Cu_2(dpyam)_2(\mu\text{-}OH)_3$]Cl · $3H_2O$
Molecular weight	793.33	610.02
T (K)	293(2)	293(2)
Crystal system	triclinic	orthorhombic
Space group	$P\bar{1}$	$Cmc2_1$
a (Å)	9.191	15.690
b (Å)	9.440(2)	8.629
c (Å)	9.472(2)	18.249
α (°)	111.54	90
β (°)	97.08(10)	90
γ (°)	108.84(10)	90
V (Å^1)	695.66(2)	2470.85(5)
Z	1	4
D_{calc} (g cm ^{3})	1.980	1.626
μ (mm ^{1})	3.792	1.877
$F(000)$	402	1228
Crystal size (mm)	0.05 × 0.20 × 0.25	0.23 × 0.45 × 0.10
Number of reflections collected	5226	9012
Number of unique reflections [R_{int}]	3810 [0.0165]	3593 [0.0408]
Data/restraints/parameter	3810/0/219	3593/1/181
Goodness-of-fit	1.012	1.123
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0345$, $wR_2 = 0.0824$	$R_1 = 0.0408$, $wR_2 = 0.1386$
R indices (all data)	$R_1 = 0.0483$, $wR_2 = 0.0904$	$R_1 = 0.0453$, $wR_2 = 0.1427$
Largest difference peak and hole (e Å$_3$)	0.963, −1.010	1.539, −0.402

Table 2
Selected bond lengths [Å] and angles [°] with e.s.d.s. in parentheses of [$Cu_2(dpyam)_2(\mu\text{-}OH)_2I_2$] · $2H_2O$ **(1)**

Bond lengths			
Cu(1)–N(1)	2.007(3)	Cu(1)–O(1)	1.967(2)
Cu(1)–N(2)	2.006(3)	Cu(1)–O(1A)	1.960(2)
Cu(1)–I(1)	3.040(5)	Cu(1)–Cu(1A)	2.988(7)
Bond angles			
O(1)–Cu(1)–O(1A)	80.93(11)	O(1A)–Cu(1)–I(1)	99.75(9)
O(1)–Cu(1)–N(1)	93.51(10)	N(1)–Cu(1)–N(2)	89.31(11)
O(1)–Cu(1)–N(2)	166.55(12)	N(1)–Cu(1)–I(1)	95.83(8)
O(1)–Cu(1)–I(1)	97.48(8)	N(2)–Cu(1)–I(1)	95.30(9)
O(1A)–Cu(1)–N(1)	164.oo(12)	Cu(1)–O(1)– Cu(1A)	99.07(11)
O(1A)–Cu(1)–N(2)	92.82(10)		

Hydrogen bonds	D-H	H...A	D...A	D-H...A
N(3) – H(5)...O(3)[a]	0.79	2.13	2.9156	173
O(1) – H(10)...O(2)[b]	0.53	2.25	2.7500	157
O(3) – H(13)...O(1)[c]	0.62	2.40	2.8474	130

$A = -x, -y+1, -z$.
[a] $[1-x, 2-y, -z]$.
[b] $[-x, 1-y, -z]$.
[c] $[1-x, 1-y, -z]$.

O(1)–Cu(1A) angle is 99.1(11)°. Each copper atom is displaced toward the apical I atom of 0.243 Å from the basal N_2O_2 plane. The dinuclear unit is exactly planar, a dihedral angle between two CuO_2 planes is 180° and that between the basal N_2O_2 planes is 180° (see Fig. 3). The bite angle of the dpyam ligand N(1)–Cu(1)–N(2) of 89.3(11)° is only slightly less than 90° but the O(1)–Cu(1)–O(1A) angle of 80.9(11)° is significantly less than 90°. The individual pyridine rings are planar, and the dpyam ligand is non-planar, dihedral angle of 27.2° occurs between the individual pyridine rings.

The lattice is further stabilized by a hydrogen bonding between the amine N and the oxygen atom of lattice water molecule with N···O contact of 2.916 Å ; between the oxygen atom of bridging hydroxo group and the oxygen atom of lattice water molecules with O···O contacts of 2.750–2.847 Å.

Table 3
Selected bond lengths [Å] and angles [°] with e.s.d.s. in parentheses of $[Cu_2(dpyam)_2(\mu\text{-}OH)_3]Cl\cdot 3H_2O$ (**2**)

Bond lengths			
Cu(1)–N(1)	1.995(3)	Cu(1)–O(1)	1.942(3)
Cu(1)–N(2)	2.006(3)	Cu(1)–O(2)	1.953(3)
Cu(1)–O(3)	2.433(4)	Cu(1)–Cu(1A)	2.803(7)
Bond angles			
O(1)–Cu(1)–O(2)	81.1(2)	N(1)–Cu(1)–N(2)	91.79(13)
O(1)–Cu(1)–O(3)	78.8(2)	N(1)–Cu(1)–O(3)	102.05(14)
O(1)–Cu(1)–N(1)	174.6(2)	N(2)–Cu(1)–O(3)	104.44(14)
O(1)–Cu(1)–N(2)	93.17(14)	Cu(1)–O(1)–Cu(1A)	92.4(2)
O(2)–Cu(1)–O(3)	76.4(2)	Cu(1)–O(2)–Cu(1A)	91.7(2)
O(2)–Cu(1)–N(1)	93.88(14)	Cu(1)–O(3)–Cu(1A)	70.34(13)
O(2)–Cu(1)–N(2)	174.0(2)		

Hydrogen bonds	D-H	H...A	D...A	D-H...A
N(3) – H(5)...Cl(1)[a]	0.86	2.39	3.2518	176
O(2) – H(11)...Cl(1)[b]	0.63	2.59	3.2283	178
O(3) – H(12)...Cl(1)	0.52	2.66	3.1756	174

$A = -x+2, y, z$.
[a] $[x, -1+y, z]$.
[b] $[1/2+x, -1/2+y, z]$.

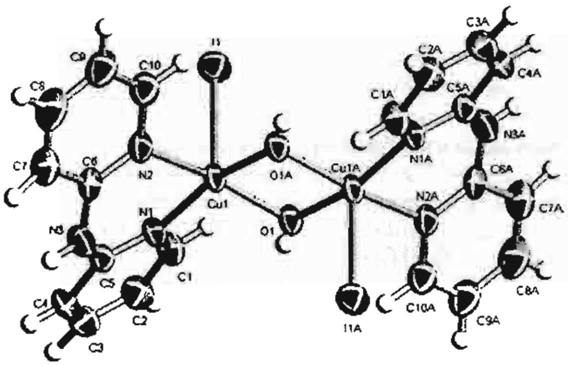


Fig. 1. ORTEP 50% probability plot of the cation in $[Cu_2(dpyam)_2(\mu\text{-}OH)_2I_2]\cdot 2H_2O$ (**1**) Atoms with an "A" are generated by a mirror plane.

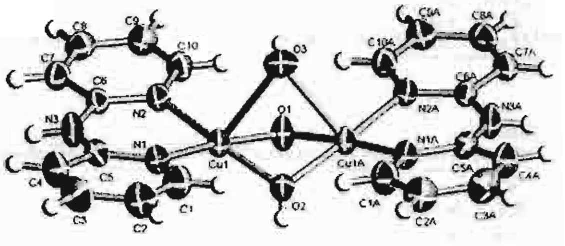


Fig. 2. ORTEP 50% probability plot of the cation in $[Cu_2(dpyam)_2(\mu\text{-}OH)_3]Cl\cdot 3H_2O$ (**2**) Atoms with an "A" are generated by a mirror plane.

3.2. Crystal structure of $[Cu_2(dpyam)_2(\mu\text{-}OH)_3]Cl\cdot 3H_2O$ (2)

The structure of compound **2** is made up of a dinuclear $[Cu_2(OH)_3(dpyam)]^+$ cation, an uncoordinated Cl^- anion and three crystallisation water molecules. This unit is depicted in Fig. 2, together with the numbering scheme, with selected distances and angles listed in Table 3. The cation is located on a mirror plane through the three bridging OH^- groups. The whole cationic unit and the copper environment are the rooftop configuration. Compound **2** involves a triplyhydroxo-bridged structure with a square pyramidal CuN_2O_2O' chromophore, the fifth axial position is occupied by a longer bonded bridging OH^- group with a distance of 2.433(3) Å. The copper atom is displaced from the basal plane towards the apical oxygen by 0.035 Å. The Cu(1)–N(1) and Cu(1)–N(2) distances are

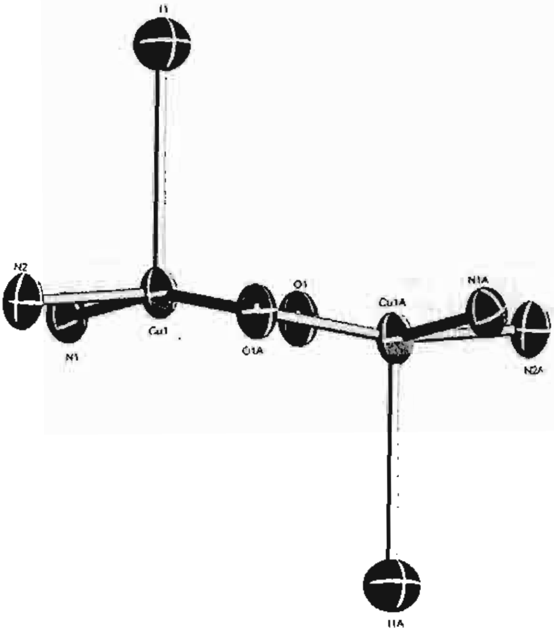


Fig. 3. The chromophore of $[Cu_2(dpyam)_2(\mu\text{-}OH)_2I_2]\cdot 2H_2O$ (**1**).

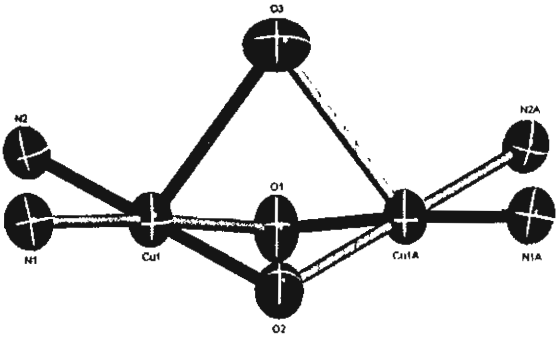


Fig. 4. The chromophore of $[Cu_2(dpyam)_2(\mu\text{-}OH)_3]Cl \cdot 3H_2O$ (2).

1.995(3) and 2.006(3) Å, respectively. The average Cu–O (hydroxo bridge) distance of 1.948 Å is slightly shorter and very close to those observed in the corresponding di-hydroxo bridged copper(II) dimers [5,6,12,13]. The CuN_2O_2 chromophore is planar with a slight tetrahedral twist, dihedral angle of 2.8° between the CuN_2 and CuO_2 planes, but the Cu_2O_2 network is not planar, a dihedral angle between the CuO_2 planes is 142.5° (see Fig. 4). The Cu–Cu distance is 2.803(1) Å. The bridging Cu–O(1)–Cu and Cu–O(2)–Cu angles are 92.4(2)° and 91.7(2)°, respectively, which are not in the range normally found for the planar dihydroxo-bridged copper(II) dimers. The dpyam ligand as a whole is nearly planar and involves a dihedral angle of 9.1° between the individual pyridine rings.

The lattice is stabilized by a hydrogen bonding between the amine N and the chloride atom with N ⋯ Cl distance of 3.252 Å and between the oxygen atom of bridging hydroxo group and the chloride atom with O ⋯ Cl contacts of 3.176–3.228 Å.

3.3. Spectral characterization

The infrared spectra of compounds **1** and **2** show a broad band at 3460 and 3400 cm^{-1}, respectively which can be assigned to the bridging OH vibrations of the hydroxo bridge and/or lattice water.

The electronic diffuse reflectance spectrum of compound **1** shows a broad band centered at 15 120 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 [14,15]. The reflectance spectrum of **2** displays a broad band and a lower energy shoulder at the frequencies of 17 800 and 14 600(sh) cm^{-1}. The relatively higher energy of this triply bridged dimer is unusual for the square pyramidal geometry. However, they are consistent with those observed for the relevant bipy complexes [16] 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.

The X-band polycrystalline EPR spectrum of compound **1**, at room temperature, displays a weak signal at ~320 mT ($g_i = 2.078$), while a triplet state signal at ~100–160 mT ($g_i = 6.964$) is not observed properly. The former feature is most certainly from a monomeric Cu(II) impurity, which is always present in dinuclear species. Compound **2** exhibits an intense signal at ~101 mT ($g_i = 6.695$) and a weaker signal at ~307 mT ($g_i = 2.220$). The latter is attributed to the monomeric impurity while the former is usually attributed to intramolecular exchange interaction between copper(II) ions, $\Delta Ms = \pm 2$ transition [17,18].

Compound **1** is planar (dihedral angle of 180° between the CuO_2 planes) and involves the Cu–O–Cu angle of 99.1° expecting a moderate antiferromagnetic coupling ($J = -116$ cm^{-1}) following Hodgson and Hatfield's linear relationship [1,18]. However, the experimental value of singlet-triplet energy gap ($2J$) would be smaller than the predicted value. The difference could be due to the deviation from planarity of the CuN_2O_2 plane with a tetrahedral twist between CuN_2 and CuO_2 planes, which may reduce the orthogonality of the copper(II) $d_{x^2-y^2}$ (or d_{xy}) orbital with the bridging hydroxo groups [4]. The most relevant compound $[Cu_2(dpyam)_2(\mu\text{-}OH)_2Br_2] \cdot 4H_2O$ also involves a double hydroxo bridge and an observed J value of −48.6 cm^{-1}, while the predicted value was as high as −116 cm^{-1} [6]. On the other hand compound **2** has the roof-shaped hydroxo bridge network with a dihedral angle of 142.5° between the CuO_2 planes and the Hatfield's linear relationship, which arises from studies of planar $Cu_2(OH)_2$ cores, is not valid then. The related structure, $[Cu_2(dpyam)_2(\mu\text{-}OH)_2(\mu\text{-}OH_2)]Br_2 \cdot 2H_2O$ compound exhibits $J = -0.6$ cm^{-1}.

3.4. Structure comparison

There are five dihydroxo-bridged copper(II) dimers containing the dpyam ligand: $[Cu_2(dpyam)_2(\mu\text{-}OH)_2Br_2] \cdot 4H_2O$ **(3)**, $[Cu_2(dpyam)_2(\mu\text{-}OH)_2(FBF_3)_2]$ **(4)**, $[Cu_2(dpyam)_2(\mu\text{-}OH)_2(ONO_2)_2]$ **(5)**, $[Cu_2(dpyam)_2(\mu\text{-}OH)_2(\mu\text{-}OH_2)]Cl_2 \cdot 2H_2O$ **(6)** and$[Cu_2(dpyam)_2(\mu\text{-}OH)_2(\mu\text{-}OH_2)]Br_2 \cdot 2H_2O$ **(7)** have been structurally reported [4–6,12]. In the known dimer structures, three copper environments are observed: rhombic coplanar [19], CuN_2O_2, square-based pyramidal, CuN_2O_2X [18,20], and elongated rhombic octahedral [21,22], $CuN_2O_2X_2$. Compounds **1**, **3**, **4** and **5** involve the planar dihydroxo-bridged copper(II) dimer, all exhibit the square pyramidal CuN_2O_2X chromophore geometry. Compound **1** involves the square-based pyramidal CuN_2O_2I chromophores which are very comparable to the CuN_2O_2Br, CuN_2O_2F and CuN_2O_2O' chromophores in **3**, **4** and **5**, respectively. The fifth axial distances of 3.040(5) Å in compound **1** are much longer than those of 2.803(2) and 2.804(2), 2.745(7), 2.400(1) and 2.500(1) Å in compounds **3**, **4** and **5**, respectively. The marked tetrahedral twists of the CuN_2O_2 chromophores in compound **1** and also in compounds **3**, **4** and **5** (dihedral angle of 19.3°, 21.8° and 21.4°, 24.0°, 20.7° and 16.7°, respectively) are less usual. However, the Cu_2O_2 network in these compounds is planar and the planarities of both the CuN_2O_2 chromophore and the Cu_2O_2 unit for each compound are not many different. Consequently, the Cu–Cu separation of 2.988(7) Å in compound **1** is more similar in compounds **3**, **4** and **5** (2.993(2); 2.919(5) and 2.954(2) Å, respectively). The Cu–O–Cu bridging angle of 99.1 Å in compound **1** is comparable to that of compounds **3**, **4** and **5** (98.1° and 100.1°, 99.3°, 99.4° and 98.9°, respectively). There are a significant difference observed in the Cu to N_2O_2 mean plane distances, those of compounds **1** and **3** (0.243, 0.273 Å, respectively) are longer than those of compounds **4** and **5** (0.022; 0.079 and 0.142 Å, respectively) arising from a very weak interaction in the sixth position of the chromophore provided from the other F atom of the BF_4^- group in compound **4** and the other O atom of the NO_3^- group in compound **5**. However, these sixth distances are between 3.0–4.0 Å. The structural data of compounds **1**, **3**, **4** and **5** have revealed that the bigger in the bite N–Cu–N angle (98.3°, 88.6° and 88.9°, 99.3°, 98.9° and 99.4°, respectively), the bigger the bridging Cu–O–Cu angle is observed. Consequently, the Cu–O–Cu angles in the parent dpyam complexes are bigger (>97.5°) than those of the corresponding bipy complexes (<97.5°). This feature is also observed in other corresponding dimers involving the other terminal ligand. This concludes that the terminal ligand other than the anion and solvent molecule influences the magnitude of the Cu–O–Cu angle.

The most interesting and unusual feature in structure of compound **2** is that this is the triply bridged dinuclear compound with a roof-shaped bridge, the dihedral angle between the CuO_2 planes is far from 180°. Each hydroxo group is symmetrically bound, with Cu–O(1) bond slightly shorter than Cu–O(2) bond. The bridging angles in compound **2** are significantly less than those found in the planar dihydroxo-bridged copper (II) dimers and are not in the usual range 95°–105°, normally found for these dimers [23–25]. So far, compound **2** represents the second structurally characterized examples of a triply bridged dinuclear copper(II) compound containing three monoatomic bridges with homospecies. The first one has been pointed out for the known $Cs_3[Cu_2Cl_7(H_2O)_2]$ compound [26], containing three Cl^- anions bridging two copper atoms separated by 3.45 Å. The related structures of the roof-shaped dinuclear copper(II) containing three monoatomic bridges are $[Cu_2(dpyam)_2(\mu\text{-}OH)_2(\mu\text{-}OH_2)]Cl_2 \cdot 2H_2O$ **(6)** and $[Cu_2(dpyam)_2(\mu\text{-}OH)_2(\mu\text{-}OH_2)]Br_2 \cdot 2H_2O$ **(7)** and $[Cu_2(dpyam)_2(\mu\text{-}OMe)_2(\mu\text{-}Cl)]Cl \cdot MeOH$ **(8)**. The cations present in compounds **2**, **6**, **7** and **8** show a similar structure, they exhibit the metal centres in a square pyramidal configuration with in-plane configuration of a dpyam ligand and of two bridging O atoms and involve in similar CuO_2Cu roof-top angles (142.5°, 140.6°, 135.8°, 144.3°, respectively). Also the in-plane Cu–N and Cu–O distances are similar to each other and the Cu–Cu separations are quite comparable (2.803, 2.797, 2.849, 2.792 Å, respectively). The cations differ, however, in the nature of the fifth bridging ligand, which is a hydroxo group in compound **2**, a water molecule in compounds **6** and **7**, and a bigger chloride anion in compound **8**.

4. Conclusion

In comparison to the planar di-μ-hydroxo-bridged complexes significant differences are observed. The dihedral angle between the CuO_2 planes of the dihydroxo-bridged dimers becomes near 180°, while their CuN_2O_2 chromophores are not planar with a distinct tetrahedral twist (except that for the octahedral geometry). On the other hand, the planarity of the square planes for each CuN_2O_2 chromophore with a slight tetrahedral twist is observed in the triply bridged dimers. Due to bending in the molecule, the Cu–Cu distances (2.792–2.849 Å) in the triply bridged complexes are significantly shorter than those of the planar dihydroxo-bridged complexes (2.870–3.000 Å). However, these distances are typical in the range previously observed, 2.80–3.00 Å [1,27]. There is an additional remarkable difference observed, the bridging Cu–O–Cu angles (91.0°–94.7°) in the roof-shaped dimers are significantly smaller than 95.0° while in the planar dihydroxo-bridged dimers, these angles are in the range 95.0°–104.1°.

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 no.CCDC-223620, 223621, for structures **1** and **2**, respectively. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (international) +44-1223-336-033, e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

The authors would like to thank The Thailand Research Fund and Khon Kaen University for research grant. Support of the Postgraduate Education and Research Program in Chemistry is also gratefully acknowledged.

References

[1] V.H. Crawford, H.W. Richardson, J.R. Wasson, D.J. Hodgson, W.E. Hatfield, Inorg. Chem. 15 (1976) 2107.

[2] E. Ruiz, P. Alemany, S. Alvarez, J. Cano, Inorg. Chem. 36 (1997) 3683.

[3] E. Ruiz, P. Alemany, S. Alvarez, J. Cano, J. Am. Chem. Soc. 119 (1997) 1297.

[4] L.P. Wu, M.E. Keniry, B.J. Hathaway, Acta Cryst. C48 (1992) 35.

[5] N. Marsich, A. Camus, F. Ugozzoli, A.M.M. Lanfredi, Inorg. Chim. Acta 236 (1995) 117.

[6] S. Youngme, G.A. van Albada, O. Roubeau, C. Pakawatchai, N. Chaichit, J. Reedijk, Inorg. Chim. Acta 342 (2003) 48.

[7] Siemens. SAINT. 1996, Version4 Software Reference Manual, Siemens Analytical X-Ray Systems, Inc., Madison, WI, USA.

[8] G.M. Sheldrick, SADABS, Program for Empirical Absorption correction of Area Dectector Data, University of Göttingen, Göttingen, Germany, 1996.

[9] Bruker. XSHELL. 1999, Version 6.12 Reference Manual, Bruker AXS, Inc., Madison, WI, USA.

[10] A.W. Addison, T.N. Rao, J. Reedijk, J. van Rijn, G.C. Verschoor, J. Chem. Soc., Dalton Trans. (1984) 1349.

[11] M. Brophy, G. Murphy, C. O'Sullivan, B. Hathaway, B. Murphy, Polyhedron 18 (1999) 611.

[12] S. Youngme, W. Somjitsripunya, K. Chinnakali, S. Chantrapromma, H.K. Fun, Polyhedron 18 (1999) 857.

[13] S. Youngme, G.A. van Albada, H. Kooijman, O. Roubeau, W. Somjitsripunya, A.L. Spek, C. Pakawatchai, J. Reedijk, Eur. J. Inorg. Chem. (2002) 2367.

[14] G. Murphy, C. Murphy, B. Murphy, B. Hathaway, J. Chem. Soc., Dalton Trans. (1997) 2653.

[15] G. Murphy, C. O'Sullivan, B. Murphy, B. Hathaway, Inorg. Chem. 37 (1998) 240.

[16] C.M. Harris, E. Sinn, W.R. Walker, P.R. Woolliams, Aust. J. Chem. 21 (1968) 631.

[17] G. De Munno, M. Julve, F. Lloret, J. Faus, M. Verdaguer, A. Caneschi, Inorg. Chem. 34 (1995) 157.

[18] G.A. van Albada, I. Mutikainen, W.J.J. Smeets, A.L. Spek, U. Turpeinen, J. Reedijk, Inorg. Chim. Acta 327 (2002) 134.

[19] M.F. Charlot, S. Jeannin, Y. Jeannin, O. Kahn, J. Lucrece-Abaul, J. Martin-Frere, Inorg. Chem. 18 (1979) 1675.

[20] J.M. Seco, U. Amador, M.J. González Garmendia, Polyhedron 18 (1999) 3605.

[21] G.A.van Albada, I. Mutikainen, U. Turpeinen, J. Reedijk, Inorg. Chim. Acta 324 (2001) 273.

[22] S. Amani Komaei, G.A. van Albada, J.G. Haasnoot, H. Kooijman, A.L. Spek, J. Reedijk, Inorg. Chim. Acta 286 (1999) 24.

[23] I. Castro, M. Julve, G.D. Munno, G. Bruno, J.A. Real, F. Lloret, J. Faus, J. Chem. Soc., Dalton Trans. (1992) 1739.

[24] I. Castro, M. Julve, G.D. Munno, G. Bruno, J.A. Real, F. Lloret, J. Faus, J. Chem. Soc., Dalton Trans. (1992) 47.

[25] P.J. Hay, J.C. Thibeault, R. Hoffmann, J. Am. Chem. Soc. 97 (1975) 4884.

[26] V.W. Vogt, H. Haas, Acta Cryst., Sect. B. (1971) 1521.

[27] B.J. Hathaway, Comprehensive co-ordination chemistry. in: G. Wilkinson (Editor in Chief), R.D. Gillard, J.A. McCleverty (Executive Editors), The Synthesis, Reactions, Properties and Applications of Co-ordination Compounds, vol. 5, Sec. 53, Pergamon Press, Oxford, 1987; pp. 533–774.

Available online at www.sciencedirect.com
SCIENCE DIRECT
Inorganica Chimica Acta 357 (2004) 2532–2542
Inorganica Chimica Acta
www.elsevier.com/locate/ica

Synthesis, crystal structure, spectroscopic and magnetic properties of doubly and triply bridged dinuclear copper(II) compounds containing di-2-pyridylamine as a ligand ☆

Sujittra Youngme [a,*], Chatkaew Chailuecha [a], Gerard A. van Albada [b], Chaveng Pakawatchai [c], Narongsak Chaichit [d], Jan Reedijk [b]

[a] *Department of Chemistry, Faculty of Science, Khon Kaen University, Khon Kaen 40002, Thailand*
[b] *Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden University, P.O. Box 9502, 2300 RA Leiden, The Netherlands*
[c] *Department of Chemistry, Faculty of Science, Prince of Songkla University, Hatyai, Songkla 90112, Thailand*
[d] *Department of Physics, Faculty of Science and Technology, Thammasat University Rangsit, Pathumthani 12121, Thailand*

Received 8 October 2003; accepted 21 January 2004
Available online 19 March 2004

Abstract

The dihydroxo-bridged dinuclear copper(II) compound $[Cu_2(dpyam)_2(\mu\text{-}OH)_2]I_2$ (**1**) and the triply bridged dinuclear copper(II) compounds with a formato bridge $[Cu_2(dpyam)_2(\mu\text{-}O_2CH)(\mu\text{-}OH)(\mu\text{-}OMe)](ClO_4)$ (**2**) and $[Cu_2(dpyam)_2(\mu\text{-}O_2CH)(\mu\text{-}OH)(\mu\text{-}Cl)](ClO_4)\cdot 0.5H_2O$ (**3**) (in which dpyam = di-2-pyridylamine) have been synthesized and their crystal structures determined by X-ray crystallographic methods. All three compounds are either centrosymmetric, or have a symmetry plane in the molecule. Compound **1** contains the $[Cu_2(dpyam)_2(\mu\text{-}OH)_2]^+$ unit and iodide anions. Each copper(II) ion is in a slightly tetrahedrally distorted square planar coordination with the square plane consisting of two nitrogen atoms of the dpyam ligand and two bridging hydroxo groups. The Cu–I distances of 3.321 Å are quite long and only involve a weak semi-coordination. Compound **2** contains a triply bridged dinuclear copper(II) species, the coordination environment around each copper(II) ion involves a distorted trigonal-bipyramidal CuN_2O_3 chromophore. In the dinuclear unit of compound **3**, the triply bridged copper(II) ions show a distorted trigonal-bipyramidal coordination of the CuN_2O_2Cl chromophore. The Cu–Cu distances are 2.933(2), 3.023(1) and 3.036(1) Å for compounds **1**, **2** and **3**, respectively.

The magnetic susceptibility measurements, measured from 5 to 280 K, revealed a weak antiferromagnetic interaction between the Cu(II) atoms for compound **1** with a singlet–triplet energy gap (J) of $-15.3\ cm^{-1}$, whereas compounds **2** and **3** are ferromagnetic with $J = 62.5$ and $79.1\ cm^{-1}$, respectively.

Keywords: Copper(II) complexes; Crystal structure; Formato-bridged; Triply bridged; Magnetic properties

1. Introduction

The magneto-structural characterization of ligand-bridged dinuclear copper(II) compounds have received much attention during the past several years [1,2]. The planar dihydroxo-bridged and the triply bridged copper(II) dinuclear species are extensively studied, because of the magnetic interaction between two unpaired electrons [3–19]. For the dihydroxo-bridged copper(II) dinuclear species, the linear correlation between the Cu–O–Cu bridging angle and the singlet–triplet energy gap (J) was first observed by Hodgson and co-workers [3]. 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 expected. Several theoretical approaches were applied to understand the behavior of the antiferromagnetic and ferromagnetic interaction of such dihydroxo-bridged copper(II) dinuclear species [4–11].

☆ Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2004.01.039.

* Corresponding author. Fax: +66-43-243-338.
E-mail address: sujittra@kku.ac.th (S. Youngme).

0020-1693/$ - see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.ica.2004.01.039

The magnetic interaction in the triply bridged dinuclear copper(II) complexes can occur via bridging ligands in various pathways, which depend on the type of the bridging ligand, monoatomic and polyatomic bridge for example, and the coordination geometry of the copper(II) center [12–19]. For the square-pyramidal geometry, the magnetic orbital for the copper(II) center is the $d_{x^2-y^2}$ orbital which lies along the basal plane. Therefore, a superexchange interaction between two copper(II) ions is usually observed through the ligands which are located in the same equatorial plane. If the geometry of the copper(II) ion is trigonal-bipyramidal the unpaired spin density is along the *z*-axis, i.e., in the d_{z^2} orbital, that can overlap with the apical-positioned bridging ligands. The magnitude of magnetic interaction is primarily governed by an overlap of two magnetic orbitals centered on the nearest-neighbour copper(II) ions. The present work is focused on the various types of overlapping interactions between the ligand atomic orbital and the copper(II) d orbitals. For this purpose, a dihydroxo-bridged $[Cu_2(dpyam)_2)(\mu\text{-}OH)_2]I_2$ (**1**) and two triply bridged dinuclear copper(II) compounds $[Cu_2(dpyam)_2(\mu\text{-}O_2CH)(\mu\text{-}OH)(\mu\text{-}OMe)](ClO_4)$ (**2**) and $[Cu_2(dpyam)_2(\mu\text{-}O_2CH)(\mu\text{-}OH)(\mu\text{-}Cl)](ClO_4)\cdot 5H_2O$ (**3**) are synthesized with the ligand di-2-pyridylamine and characterized by spectroscopy and X-ray crystallography; also magnetic measurements are performed on the compounds.

2. Experimental

2.1. Reagents and physical measurements

The ligand di-2-pyridylamine 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/O Analyzer by Microanalytical Service of Science and Technological Research Equipment Center, Chulalongkorn University.

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, within the range 8000–18 000 cm^{-1}. 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 with DPPH ($g = 2.0036$) as a reference. Magnetic susceptibility measurements (5–280 K) were carried out using a Quantum design MPMS-5 5T SQUID magnetometer (measurements carried out at 1000 Gauss) performed at Leiden University. 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. $[Cu_2(dpyam)_2(\mu\text{-}OH)_2]I_2$ (1)

A hot aqueous solution (5 ml) of KI (0.166 g, 1.0 mmol) was added to a hot aqueous solution (5 ml) of $Cu(NO_3)_2\cdot 3H_2O$ (0.121 g, 0.5 mmol). Then, a hot acetone solution (10 ml) of dpyam (0.086 g, 0.5 mmol) was added to the mixture yielding a green solution. Its color became greenish-blue by slow addition of an aqueous solution (10 ml) of NaOH (0.020 g, 0.5 mmol) and a blue precipitate formed within a few minutes. The precipitate was filtered off and recrystallized from a hot aqueous solution. After a month, blue crystals of compound **1** were obtained. *Anal.* Calc. for $C_{20}H_{20}Cu_2I_2N_6O_2$: C, 31.7; H, 2.7; N, 11.1. Found: C, 31.9; H, 2.4; N, 11.3%.

2.2.2. $[Cu_2(dpyam)_2(\mu\text{-}O_2CH)(\mu\text{-}OH)(\mu\text{-}OMe)](ClO_4)$ (2)

This compound was prepared by adding a hot ethanolic solution (10 ml) of dpyam (0.171 g, 1.0 mmol) to a hot aqueous solution (10 ml) of $Cu(ClO_4)\cdot 6H_2O$ (0.371 g, 1.0 mmol), after which solid HCOONa (0.272 g, 4.0 mmol) was added. The resulting green 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. *Anal.* Calc. for $C_{22}H_{23}ClCu_2N_6O_8$: C, 39.9; H, 3.5; N, 12.7. Found: C, 39.8; H, 3.6; N, 12.9%.

2.2.3. $[Cu_2(dpyam)_2(\mu\text{-}O_2CH)(\mu\text{-}OH)(\mu\text{-}Cl)](ClO_4)\cdot 0.5H_2O$ (3)

A hot DMF solution (20 ml) of dpyam (0.171 g, 1.0 mmol) was added to a hot aqueous solution (10 ml) of $CuCl_2$ (0.135 g, 1.0 mmol). Then, a hot aqueous solution (10 ml) of HCOONa (0.136 g, 2.0 mmol) was added to the mixture yielding a dark green solution, after which the solid $KClO_4$ (0.416 g, 3.0 mmol) was added. The resulting dark green solution was allowed to evaporate at room temperature. After a month, dark green crystals of compound **3** were formed which were filtered off, washed with the mother liquid and air-dried. *Anal.* Calc. for $C_{21}H_{21}Cl_2Cu_2N_6O_{7.5}$: C, 37.3; H, 3.1; N, 12.4. Found: C, 37.7; H, 3.4; N, 12.5%.

2.3. Crystallography

The X-ray single-crystal data for three compounds were collected at 293 K on a 1 K Bruker SMART CCD area-detector diffractometer using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at a detector distance of 4.5 cm and swing angle of −35°. Data reduction and cell refinements were performed using the program SAINT [20]. An empirical absorption correction by using the SADABS [21] program was applied, which resulted in transmission coefficients ranging from 0.701 to 1.000 for **1**, 0.654 to 1.000 for **2** and 0.773 to 1.000 for **3**.

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 except O atoms of the disordered perchlorate group in **2** using the SHELXTL-PC V 6.12 software package [22]. The O atoms of the perchlorate group of **2** showed high disorder; the occupancies of the disordered positions were initially refined and later fixed at 0.45 and 0.55, respectively. The O atoms of the percholrate group of **3** also showed disorder. Attempts to model disordered positions into two sets are unsuccessful. However, their thermal parameters are substantially reasonable. All hydrogen atoms in **1** and **3** were located geometrically and refined isotropically. In **2**, all hydrogen atoms of the formate and dpyam ligands were geometrically fixed and allowed to ride on the attached atoms, those of the bridging hydroxo and bridging methoxo groups were located geometrically.

The molecular structure pictures were created by using SHELXTL-PC [22] package. The crystal and refinement details for compounds **1**, **2** and **3** are listed in Table 1.

3. Results and discussion

3.1. Description of $[Cu_2(dpyam)_2(\mu\text{-}OH)_2]I_2$ (1)

The structure of compound **1** consists of a centrosymmetric dinuclear $[Cu_2(dpyam)_2(\mu\text{-}OH)_2]^{2+}$ cation, with iodide counter anions. This unit is depicted in Fig. 1, together with the numbering scheme, with selected distances and angles listed in Table 2. Both copper(II) ions of the complex cation are linked through the double hydroxo bridges, leading to a Cu–Cu distance of 2.933(2) Å. Each copper(II) ion is in a tetrahedrally distorted square-planar coordination environment consisting of a CuN_2O_2 chromophore, which has two bridging hydroxo groups and a terminal dpyam ligand coordinated through their nitrogen atoms. A dihedral angle of 21.9° is present between the CuO_2 and CuN_2 planes. The apical Cu–I distance (3.321(5) Å) is too long to be considered as coordination (semi-coordination only). The fact that the copper(II) ions are lifted from the N_2O_2 planes, toward the I^- ions by 0.122 Å is a further indication for the semi-coordination. The Cu–O distances (1.935(5) and 1.937(5) Å) are slightly shorter than the Cu–N distances (2.006(5) and 2.007(5) Å). The bridging Cu–O–Cu angles are 98.5(2)°, greater than 97.5°, hence an antiferromagnetic coupling between copper(II) ions is predicted from Hodgson and Hatfield equation [3]. The dpyam ligands are essentially planar

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

Complex	**1**	**2**	**3**
Molecular formula	$[Cu_2(dpyam)_2(\mu\text{-}OH)_2]I_2$	$[Cu_2(dpyam)_2(\mu\text{-}O_2CH)(\mu\text{-}OH)(\mu\text{-}OMe)](ClO_4)$	$[Cu_2(dpyam)_2(\mu\text{-}O_2CH)(\mu\text{-}OH)(\mu\text{-}Cl)](ClO_4)\cdot 0.5H_2O$
Molecular weight	757.30	661.99	675.43
T (K)	293(2)	293(2)	273(2)
Crystal system	triclinic	orthorhombic	orthorhombic
Space group	$P\bar{1}$	$Cmc2_1$	$Cmc2_1$
a (Å)	7.28690(10)	16.7872(13)	16.8229(3)
b (Å)	9.3274(3)	8.0793(7)	7.8066(2)
c (Å)	9.5968(3)	18.7410(15)	19.2753(0)
α (°)	101.345(2)	90	90
β (°)	96.997(2)	90	90
γ (°)	109.985(2)	90	90
V (Å^3)	588.23(3)	2541.8(4)	2531.42(10)
Z	1	4	4
D_c (g cm^3)	2.138	1.693	1.749
μ (mm^{-1})	4.462	1.837	1.946
$F(000)$	362	1312	1344
Crystal size (mm)	0.08 × 0.08 × 0.20	0.08 × 0.20 × 0.30	0.13 × 0.33 × 0.40
Number of reflections collected	4407	10 804	9109
Number of unique reflections	3210 ($R_{int} = 0.0246$)	3124 ($R_{int} = 0.0226$)	3640 ($R_{int} = 0.0208$)
Data/restraints/parameter	3210/0/185	3124/1/206	3640/1/230
Goodness-of-fit	1.089	1.095	1.007
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0542$, $wR_2 = 0.0972$	$R_1 = 0.0571$, $wR_2 = 0.1668$	$R_1 = 0.0278$, $wR_2 = 0.0707$
R indices (all data)	$R_1 = 0.0965$, $wR_2 = 0.1168$	$R_1 = 0.0625$, $wR_2 = 0.1734$	$R_1 = 0.0322$, $wR_2 = 0.0731$
Largest difference peak and hole (e Å^3)	1.182, −0.894	0.979, −0.419	0.388, −0.373

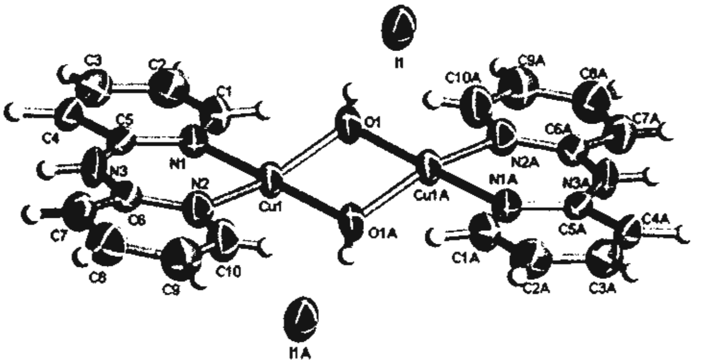


Fig. 1. ORTEP 50% probability plot of the cation in $[Cu_2(dpyam)_2(\mu\text{-}OH)_2]I_2$ (**1**) Atoms with an "A" are generated by a mirror plane.

Table 2
Selected bond lengths (Å) and angles (°) with e.s.d.s. in parentheses of $[Cu_2(dpyam)_2(\mu\text{-}OH)_2]I_2$ (**1**)

Cu(1)–N(1)	2.006(5)	Cu(1)–O(1)	1.937(5)
Cu(1)–N(2)	2.007(5)	Cu(1)–O(1A)	1.935(5)
Cu(1A)····I(1)	3.321(5)	Cu(1)–Cu(1A)	2.933(2)
O(1)–Cu(1)–N(1)	94.2(2)	O(1A)–Cu(1)–O(1)	81.5(2)
O(1)–Cu(1)–N(2)	158.6(3)	N(1)–Cu(1)–Cu(1A)	134.5(4)
O(1)–Cu(1)–Cu(1A)	40.7(2)	N(1)–Cu(1)–N(2)	92.6(2)
O(1A)–Cu(1)–N(1)	171.7(2)	N(2)–Cu(1)–Cu(1A)	131.3(2)
O(1A)–Cu(1)–N(2)	94.0(2)	Cu(1A)–O(1)–Cu(1)	98.5(2)
O(1A)–Cu(1)–Cu(1A)	40.7(2)		

A, $[-x+1,\ -y+1,\ -z+1]$.

with small dihedral angles of 4.8° between the individual pyridine rings. The bite angles of the dpyam ligands (N–Cu–N, 92.6(2)°) are only slightly greater than 90°.

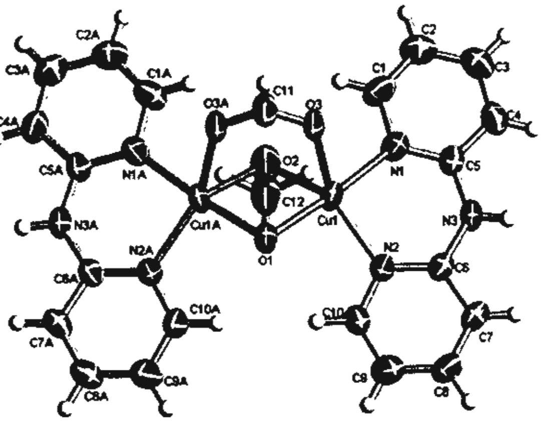


Fig. 2. ORTEP 50% probability plot of the cation in $[Cu_2(dpyam)_2(\mu\text{-}O_2CH)(\mu\text{-}OH)(\mu\text{-}OMe)](ClO_4)$ (**2**) Atoms with an "A" are generated by a mirror plane.

3.2. Description of $[Cu_2(dpyam)_2(\mu\text{-}O_2CH)(\mu\text{-}OH)(\mu\text{-}OMe)](ClO_4)$ (2)

Compound **2** is a dinuclear unit copper(II) complex bridging by three different ligands. The structure of compound **2** consists of symmetric dinuclear $[Cu_2(dpyam)_2(\mu\text{-}O_2CH)(\mu\text{-}OH)(\mu\text{-}OMe)]^+$ cations with a single ClO_4^- counteranion. This unit is depicted in Fig. 2 together with the numbering scheme, with selected distances and angles listed in Table 3. Each copper(II) ion involves a CuN_2O_3 chromophore. The coordination geometry around each copper(II) ion is distorted trigonal-bipyramidal ($\tau = 0.65$). The structure index is defined as $\tau = (\beta - \alpha)/60$, where β and α are the largest coordination angles [23,24]. The three longer bonds in the trigonal planar plane are a nitrogen atom of the dpyam ligand (Cu–N(2) distance 2.010(4) Å), an oxygen atom of the bridging formato ligand (Cu–O(3) distance 2.175(3) Å) and an oxygen atom of the bridging methoxo ligand (Cu–O(2) distance 2.169(5) Å). The two shorter bonds in the axial positions involve the other nitrogen atom of the dpyam ligand (Cu–N(1) distance 1.961(4) Å) and an oxygen atom of the bridging hydroxo ligand (Cu–O(1) distance 1.918(4) Å). This is typical for the trigonal-bipyramidal geometry [25]. The formate anion bridges two copper atoms in a *syn–syn* arrangement [26,27]. The Cu–Cu distance is 3.023(1) Å. The bridging Cu(1)–O(1)–Cu(1A) and Cu(1)–O(2)–Cu(1A) angles are 104.0(3)° and 88.3(2)°, respectively. The dpyam ligands are essentially planar, with only a dihedral angle of 6.9° between the individual pyridine rings. The bite angles of the dpyam ligands (N–Cu–N, 91.4(2)°) are only slightly greater than 90°. The lattice is further stabilized by hydrogen bonding between the amine N and the oxygen atom of bridging formato group with a N···O contact of 2.869 Å. Details of the hydrogen bonding are also listed in Table 3.

3.3. Description of $[Cu_2(dpyam)_2(\mu\text{-}O_2CH)(\mu\text{-}OH)(\mu\text{-}Cl)](ClO_4)\cdot 0.5H_2O$ (3)

The structure of compound **3** consists of symmetric dinuclear $[Cu_2(dpyam)_2(\mu\text{-}O_2CH)(\mu\text{-}OH)(\mu\text{-}Cl)]^+$

Table 3
Selected bond lengths (Å) and angles (°) with e.s.d.s. in parentheses of $[Cu_2(dpyam)_2(\mu\text{-}O_2CH)(\mu\text{-}OH)(\mu\text{-}OMe](ClO_4)$ (2)

Cu(1)–N(1)		1.961(4)	Cu(1)–O(2)	2.169(5)
Cu(1)–N(2)		2.010(4)	Cu(1)–O(3)	2.175(3)
Cu(1)–O(1)		1.918(4)	Cu(1)–Cu(1A)	3.023(1)
O(1)–Cu(1)–O(2)		81.9(2)	N(1)–Cu(1)–Cu(1A)	138.2(1)
O(1)–Cu(1)–O(3)		88.5(2)	N(1)–Cu(1)–N(2)	91.1(2)
O(1)–Cu(1)–N(1)		174.8(2)	N(2)–Cu(1)–O(2)	133.0(3)
O(1)–Cu(1)–N(2)		93.7(2)	N(2)–Cu(1)–O(3)	135.7(2)
O(1)–Cu(1)–Cu(1A)		38.0(1)	N(2)–Cu(1)–Cu(1A)	125.3(1)
O(2)–Cu(1)–O(3)		91.1(2)	Cu(1)–O(1)–Cu(1A)	104.0(3)
O(2)–Cu(1)–Cu(1A)		45.8(1)	Cu(1)–O(2)–Cu(1A)	88.3(2)
O(3)–Cu(1)–Cu(1A)		79.7(1)	C(11)–O(3)–Cu(1)	126.5(3)
N(1)–Cu(1)–O(2)		95.6(2)	O(3)–C(11)–O(3A)	126.6(6)
N(1)–Cu(1)–O(3)		86.9(2)		
Hydrogen bonds	D–H	H···A	D···A	D–H···A
N(3)–H(5)···O(3)B	0.86	2.12	2.869	146

A, [−x, y, z]; B, [1/2 − x, 1/2 + y, z].

cation, a ClO_4^- counter anion and half a molecule of lattice water. This unit is depicted in Fig. 3 together with the used numbering scheme, with selected distances and angles listed in Table 4. In the dinuclear unit, the copper(II) ions are triply bridged through three different ligands, i.e., formate, chloride and hydroxide anions. Each copper(II) center is coordinated by two oxygen atoms and an chloride atom of the triple bridges and two nitrogen atoms of a dpyam ligand, leading to the five-coordinated, distorted trigonal-bipyramidal geometry with CuN_2O_2Cl chromophore ($\tau = 0.67$). The trigonal plane consists of a nitrogen atom of the dpyam ligand (Cu–N(2) distance 2.027(2) Å), a bridging chloro ligand (Cu–Cl(1) distance 2.478(2) Å) and an oxygen atom of the bridging formato ligand (Cu–O(2) distance 2.158(1) Å). The apical coordination sites are occupied by another nitrogen atom of the dpyam ligand (Cu–N(1) distance 1.975(1) Å) and an oxygen atom of the bridging hydroxo group (Cu–O(1) distance 1.916(1) Å). The Cu–Cu distance is 3.036(1) Å. The bridging Cu(1)–O(1)–Cu(1A) and Cu(1)–Cl(1)–Cu(1A) angles are 104.8(1)° and 75.6(1)°, respectively. The dpyam ligands are planar, the dihedral angle between the individual pyridine rings is as low as 6.6°.

The lattice is further stabilized by hydrogen bonding between the amine N and the oxygen atom of bridging formato group with a N···O distance of 2.864 Å; between the oxygen atom of bridging hydroxo group and

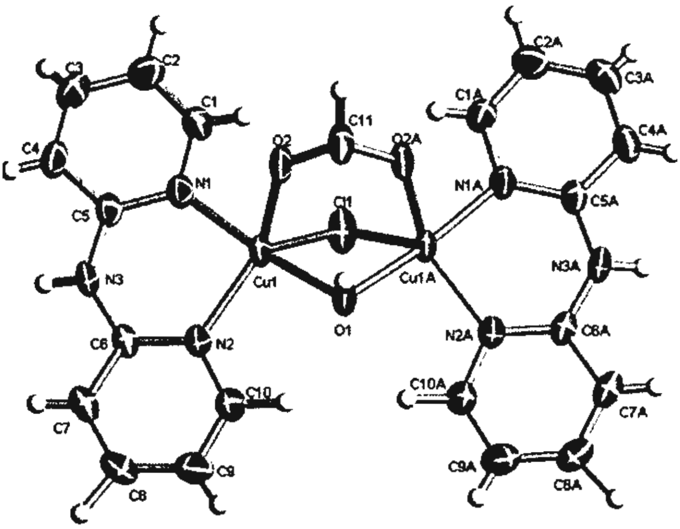


Fig. 3. ORTEP 50% probability plot of the cation in $[Cu_2(dpyam)_2(\mu\text{-}O_2CH)(\mu\text{-}OH)(\mu\text{-}Cl)](ClO_4)\cdot 0.5H_2O$ (3) Atoms with an "A" are generated by a mirror plane.

Table 4
Selected bond lengths (Å) and angles (°) with e.s.d.s. in parentheses of $[Cu_2(dpyam)_2(\mu\text{-}O_2CH)(\mu\text{-}OH)(\mu\text{-}Cl)](ClO_4) \cdot 0.5H_2O$ (3)

Cu(1)–N(1)		1.975(1)	Cu(1)–O(1)	1.916(2)
Cu(1)–N(2)		2.027(2)	Cu(1)–O(2)	2.158(1)
Cu(1)–Cl(1)		2.478(2)	Cu(1)–Cu(1A)	3.036(1)
O(1)–Cu(1)–N(1)		173.8(1)	N(1)–Cu(1)–Cl(1)	96.4(1)
O(1)–Cu(1)–N(2)		94.1(1)	N(1)–Cu(1)–Cu(1A)	138.0(1)
O(1)–Cu(1)–O(2)		88.1(1)	N(2)–Cu(1)–O(2)	133.6(1)
O(1)–Cu(1)–Cl(1)		82.5(1)	N(2)–Cu(1)–Cl(1)	119.1(1)
O(1)–Cu(1)–Cu(1A)		37.6(1)	N(2)–Cu(1)–Cu(1A)	126.3(1)
O(2)–Cu(1)–Cl(1)		107.2(1)	Cu(1)–O(1)–Cu(1A)	104. 8(1)
O(2)–Cu(1)–Cu(1A)		79.4(1)	Cu(1)–Cl(1)–Cu(1A)	75.6(1)
N(1)–Cu(1)–N(2)		91.7(1)	C(11)–O(2)–Cu(1)	126.8(1)
N(1)–Cu(1)–O(2)		86.4(1)	O(2)–C(11)–O(2A)	127.1(3)
Hydrogen bonds	D–H	H···A	D···A	D–H···A
N(3)–H(5)···O(2)B	0.83	2.06	2.864	164
O(1)–H(12)···O(4)C	0.66	2.33	2.922	151

A, $[-x+2,\ y,\ z]$; B, $[1/2-x,\ 1/2+y,\ z]$; C, $[-x,\ 1-y,\ 1/2+z]$.

the oxygen atom of perchlorate molecule with an O···O contact of 2.922 Å. Details of the hydrogen bondings are also listed in Table 4.

3.4. Structure comparison

Compound **1** involves a tetrahedrally distorted square-planar species with CuN_2O_2 chromophore. The Cu_2O_2 network is exactly planar (dihedral angle between CuO_2 and CuO_2, 180.0°), however, the marked tetrahedral twist in the CuN_2O_2 chromophore (dihedral angle between CuN_2 and CuO_2, 21.9°) is less common. Both dihedral angles are compared to those of the other dihydroxo compounds in the literature, as summarized in Table 5. The non-planarity of the CuN_2O_2 group reduces the antiferromagnetic character that causes the J value in this compound to be smaller.

The cationic unit of the compounds **2** and **3** consist of a triply bridged pair of five-coordinated copper(II) ions. Each copper(II) ion is in a distorted trigonal-bipyramidal geometry. The copper(II) orbital ground state for this geometry is based on the orbital d_{z^2} with the z-axis aligned along the axial direction. The d_{z^2} orbitals, one on each copper(II) center, are more favorably positioned to overlap directly in a σ fashion with the hydroxo bridging. So an exchange interaction becomes possible between the unpaired electron via the σ orbital of the hydroxo bridge. The comparable exchange parameters, J, are shown in Table 5.

3.5. IR and electronic spectra

The infrared spectra of compounds **1**, **2** and **3** show a broad band at 3460, 3467 and 3449 cm^{-1}, respectively, which can be assigned to the bridging OH vibrations of the hydroxo bridge and/or lattice water. For compounds **2** and **3**, the spectra also exhibit the broad and intense band at 1570 cm^{-1} correspond to the $\nu_{as}(COO^-)$ vibration and a medium broad band at 1435 and 1434 cm^{-1} correspond to the $\nu_s(COO^-)$ vibration of the didentate bridging coordination mode of the formate group within a dinuclear species. Moreover, the spectra of compounds **2** and **3** exhibit the broad and strong band about 1104–1082 cm^{-1} correspond to the characteristic vibration of non-coordinated ClO_4^- group [28].

The electronic diffuse reflectance spectrum of compound **1** shows a broad band centered at 16 750 cm^{-1}. The relatively low energy of the spectrum may be associated with the slight tetrahedral twist of the CuN_2O_2 chromophore. This observed single broad peak is consistent with the tetrahedrally distorted square planar stereochemistry and assigned to be the d_{z^2}, d_{xy}, d_{xz}, d_{yz}, $\rightarrow d_{x^2-y^2}$ transition. The reflectance spectra of compounds **2** and **3** display a broad band centered at 12 740 and 12 610 cm^{-1}, respectively. These spectra are typical for the distorted trigonal-bipyramidal geometry and the bands are assigned to be the $d_{x^2-y^2}$, d_{xy}, d_{xz}, $d_{yz} \rightarrow d_{z^2}$ transition. A regular trigonal-bipyramidal geometry is usually characterized by an asymmetric broad peak at ≈11 500 cm^{-1} with a possible high-energy shoulder at ≈14 500 cm^{-1}. The principal absorption may be assigned as a $d_{x^2-y^2} \rightarrow d_{z^2}$ transition, with the high-energy shoulder assigned as a $d_{xz} \approx d_{yz} \rightarrow d_{z^2}$ [29,30].

3.6. EPR and magnetic properties

For all three compounds, the X-band EPR spectra (measured on polycrystalline samples at r.t. and 77 K) in all cases are either very weak (some of them show a g_{par} at 2.07) or broad (g_{iso} at 2.11), and no hyperfine is resolved. Therefore, magnetic susceptibility studies were undertaken.

Table 5
Structural and magnetic data for planar dihydroxo-bridged dinuclear copper(II) compounds

Compound[a]	Coordination geometry[b]	Chromophore	CuN_2/CuO_2 (°)	CuO_2/CuO_2 (°)	Axial distance (Å)	Cu–O–Cu (°)	J (cm^{-1})	Reference
Planar dihydroxo-bridged								
$[Cu_2(dpyam)_2(OH)_2]I_2$ (1)	Sq.	CuN_2O_2	21.9	180.0	–	98.5, 98.5	−15.3	this work
$[Cu_2(dpyam)_2(OH)_2(NO_3)_2]$	Spy.	CuN_2O_2O'	16.7, 20.7	173.3	2.400, 2.500	98.9, 99.4	[c]	[35]
$[Cu_2(dpyam)_2(OH)_2Br_2](H_2O)_4$	Spy.	CuN_2O_2Br	21.8, 21.4	179.9	2.803, 2.804	98.1, 100.1	−48.6(5)[f]	[36]
$[Cu_2(dpyam)_2(OH)_2(BF_4)_2]$	Spy.	CuN_2O_2F	24.0	[c]	2.745, 2.745	99.3	[c]	[37]
$[Cu_2(dpyam)_2(OH)_2(ClO_4)_2]$	Oct.	$CuN_2O_2O'_2$	22.6	180.0	2.725,2.725	99.4, 99.4	−37.2/29.3[d]	[38]
$[Cu_2(dpyam)_2(OH)_2(CF_3\ SO_3)_2]$	Oct.	$CuN_2O_2O'_2$	10.2, 10.0	174.8	2.698, 2.894	100.7, 97.8	82.5(1)/84.7(2)[e]	[36]
$[Cu_2(C_6H_{11}NH_2)_4(OH)_2](ClO_4)_2$	Sq.	CuN_2O_2	[c]	147.5	–	96.6, 99.7	−256	[39]
$[Cu_2(ampym)_4(OH)_2(CF_3SO_3)_2](ampym)_2$	Spy.	CuN_2O_2O'	[c]	[c]	2.503, 2.503	97.96	−7.2	[40]
$[\{Cu(bipy)(PhNHpy)\}_2(OH)_2](PF_6)_2$	Spy.	CuO_2N_2N'	[c]	180.0	2.28, 2.28	98.7	−12.1	[41]
$[Cu_2(dmbipy)_2(OH)_2(CF_3SO_3)_2]$	Oct.	$CuN_2O_2O'_2$	[c]	[c]	2.578, 2.666	94.5	148	[42]
$[Cu_2L_4(OH)_2(ClO_4)_2]$	Oct.	$CuN_2O_2O'_2$	14.7	180.0	2.602, 2.673	99.30	−34.1	[43]

[a] *Abbreviations*: dpyam, di-2-pyridylamine; $C_6H_{11}NH_2$, cyclohexylamine; ampym, 2-aminopyrimidine; bipy, 2,2′-bipyridine; PhNHpy, *N*-phenyl-2-pyridinamine, dmbipy, 4,4′-dimethyl-2,2′-bipyridine; L, 2-amino-4-methylpyrimidine.

[b] Sq., square planar; Spy., square-pyramidal; Oct., octrahedral.

[c] Not reported.

[d] This compound has a crystallographic phase transition. The values correspond with the different temperature ranges.

[e] Depending on the fitting procedure.

[f] No accurate fitting could be performed, as the compound contained a mixture of two species, see [36].

The magnetic susceptibility of a powdered sample of compound **1** was measured from 5 to 280 K. The magnetic property of **1** is depicted in Fig. 4 in the form of μ_{eff} versus T for two Cu(II) ions. At 280 K, the μ_{eff} starts at a value of about $2.43\mu_B$ (this values is close to what is expected for two spin = 1/2 uncoupled centres). Upon cooling, the effective moment of **1** stays almost constant and at about 50 K is started to decrease to reach the value of $1.07\mu_B$ at 5 K. This behaviour is typical for a weak antiferromagnetic interaction.

The theoretical expression for the magnetic susceptibility for two interacting $S = 1/2$ centres, which is based on the general Hamiltonian [2], 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 compounds [2, p. 132]:

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

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$R = \sum(\chi_m \cdot T_{calc} - \chi_m \cdot T_{obs})^2/(\chi_m \cdot T_{obs})^2$ by least-squares procedure. The best fit was obtained for $J = -15.3$ cm^{-1}, $g = 1.98$, $zJ' = 0.56$ cm^{-1}, $p = 0.06$, with a final R of 4.2×10^{-2} (see Fig. 4). The antiferromagnetic behavior nicely corresponds to the structural data, i.e., with a Cu–O–Cu angle larger than 97.5°.

The magnetic properties of compounds **2** and **3** mutually show a very similar behaviour and are depicted in Figs. 5 and 6, respectively, also in the form of μ_{eff} versus T for two Cu(II) ions. At 280 K, μ_{eff} is $2.56\mu_B$ for compound **2** ($2.78\mu_B$ for compound **3**) which agrees well with the spin-only value of Cu(II) calculated for two uncoupled spin = 1/2 centres. Upon cooling, it raises gradually to reach $2.74\mu_B$ and 2.97 at 30 K, for compounds **2** and **3**, respectively. This is typical for a ferromagnetically coupled Cu(II) dinuclear compound. Below that temperature, μ_{eff} then diminishes till a value of $2.63\mu_B$ at 5 K for compound **2** (2.76 for compound **3**), which may originate from intermolecular antiferromagnetic interactions, or from zero-field splitting of the $S = 1$ state of the dinuclear species.

The best fit was obtained for compound **2** with the following values: $J = 62.5$ cm^{-1}, $g = 1.99$, $zJ' = -3.80$ cm^{-1}, $p = 0.06$, with a final R of 1.4×10^{-3} (see Fig. 5). For compound **3**, these values are $J = 79.1$ cm^{-1},

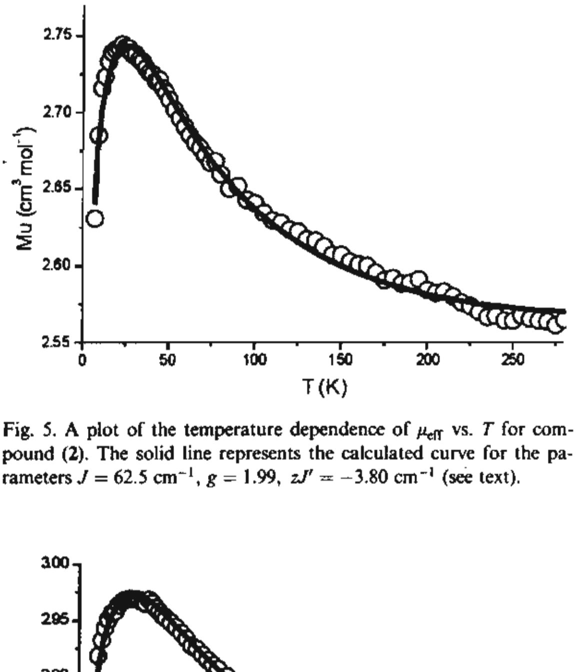


Fig. 5. A plot of the temperature dependence of μ_{eff} vs. T for compound (**2**). The solid line represents the calculated curve for the parameters $J = 62.5$ cm^{-1}, $g = 1.99$, $zJ' = -3.80$ cm^{-1} (see text).

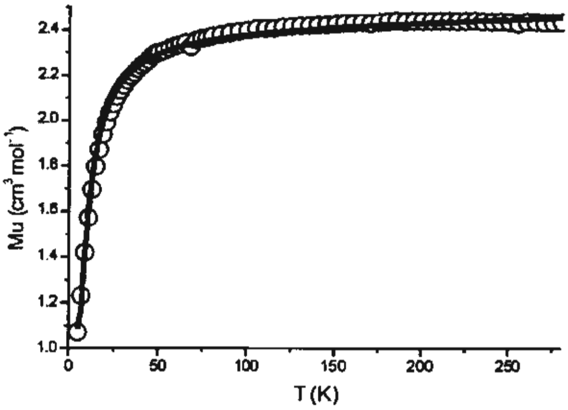


Fig. 4. A plot of the temperature dependence of μ_{eff} vs. T for compound (**1**). The solid line represents the calculated curve for the parameters $J = -15.3$ cm^{-1}, $g = 1.98$, $zJ' = 0.56$ cm^{-1} (see text).

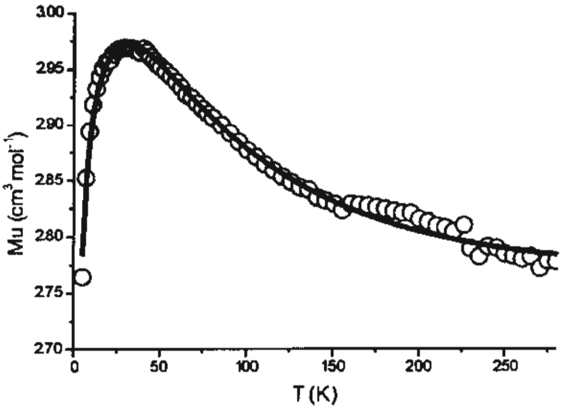


Fig. 6. A plot of the temperature dependence of μ_{eff} vs. T for compound (**3**). The solid line represents the calculated curve for the parameters $J = 79.1$ cm^{-1}, $g = 2.14$, $zJ' = -4.27$ cm^{-1} (see text).

Table 6
Structural and magnetic data for singly and triply bridged dinuclear copper(II) compounds

Compound[a]	Coordination geometry[b]	τ	Chromophore	μ-OH position[c]	Cu–OH–Cu (°)	J (cm^{-1})	Reference
Triply bridged							
$[Cu_2(dpyam)_2(O_2CH)(OH)(OMe)](ClO_4)$ (**2**)	Dist. TBP	0.65	CuN_2O_3	Axial/Axial	88.6, 104.5	62.5	this work
$[Cu_2(dpyam)_2(O_2CH)(OH)(Cl)](ClO_4) \cdot 0.5H_2O$ (**3**)	Dist. TBP	0.67	CuN_2O_2Cl	Axial/Axial	104.8	79.1	this work
$[Cu_2(bpy)_2(\mu\text{-}O_2CCH_3)_3](ClO_4)$	Dist. Spy., Intermediate	0.14[e], 0.47[e]	CuN_2O_3, CuN_2O_3	–	–	3.6	[34]
$[Cu_2(bpy)_2(OH)(H_2O)(O_2CCH_3)](ClO_4)_2$	Dist. Spy.	0.14, 0.25[e]	CuN_2O_3	Eq./Eq	78.7, 103.8	19.3	[34]
$[Cu_2(EtBITP)(OH)Cl_3] \cdot DMF$	Dist. TBP	0.58, 0.55[e]	CuN_2Cl_2O	Axial/Axial	104.7	−260	[44]
$[Cu_2(PTP)(OH)Cl_3] \cdot 2CH_3CN$	Intermediate	0.51	CuN_2Cl_2O	–	106.2	−296	[45]
$[Cu_2(PAP)(OH)(IO_3)_3] \cdot 4H_2O$	Dist. Spy.[d]	0.40[d]	CuN_2O_3	Axial/Axial	113.8	−283	[45–47]
$[Cu_2(PAP)(OH)Cl(SO_4)] \cdot 2H_2O$	Dist. Spy.	0.35, 0.37[e]	CuN_2O_3	Eq./Eq	115.5	−532	[48]
Singly bridged							
$[Cu_2(bpy)_2(OH)](ClO_4)_3$	Dist. TBP	0.32, 0.71[e]	CuN_4O	Eq./Eq.	141.6	−322	[31]
$[Cu_2(LL)(OH)](BF_4)_3$	Dist. Sq.	0.13[e]	CuS_2ON	Eq./Eq.	132.2	−820	[48,49]

[a] *Abbreviations*: dpyam, di-2-pyridylamine; bpy, 2,2′-bipyridine; EtBITP, 3,6-bis(2-benzimidazolylthio)pyridazine; PTP, 3,6-bis(2-pyridylthio)phthalazine; PAP, 1,4-bis-(2-pyrodyl amino)phthalazine); LL, 1,4-bis((1-oxa-4,10-dithia-7-azacyclododecan-7-yl)methyl)benzene).

[b] Dist. TBP, distorted trigonal-bipyramidal, Dist. Spy., distorted square-pyramidal.

[c] Eq., equatorial.

[d] Average trigonality (τ_{av}). According to the τ value of 0.40, the preferred geometry should be intermediate towards distorted square-pyramidal.

[e] Calculated from the known structural parameters.

$g = 2.14$, $zJ' = -4.27$ cm^{-1}, $p = 0.025$, with a final R of 1.6×10^{-3} (see Fig. 6).

These J values do not correspond to the values expected from the correlation of J and Cu–O–Cu angle for dihydroxo-bridged species. Two origins are to be held responsible for this. The copper(II) ions in both compounds have a five-coordinate trigonal-bipyramidal geometry with the d_{z^2} ground state, whereas the dihydroxo-bridged copper(II) complexes are square-pyramidal with $d_{x^2-y^2}$ ground state. A change in electron density of the magnetic orbital can have a pronounced effect on the sign and magnitude of a magnetic exchange interaction [31,32]. In this case, for both complexes, a single pathway via (Cu–OH–Cu) is possible for the electron delocalization via the d_{z^2} magnetic orbitals, corresponding to the weak, or intermediately strong, ferromagnetic interaction. Secondly, also the formato bridge plays a role in the magnetic interaction, a fact already described earlier in the literature as a so-called "countercomplementary effect" [2,34,50–52].

The obvious explanation for the single hydroxo-bridged and triply bridged dinuclear copper(II) complexes lies in the fact that the most complexes have an intermediate geometry between the square-pyramidal and trigonal-bipyramidal extremes [31–33,44–49]. It should be noted that when the copper(II) geometry is close to regular square-pyramidal, an often strong antiferromagnetic interaction will be predominant, but a reduction of an antiferromagnetic contribution will be observed when the geometry becomes closer to trigonal-bipyramidal (see Table 6).

It is somewhat surprising that compounds **2** and **3** exhibit a moderately strong ferromagnetic interaction which may originate from the triply bridged nature of both compounds. So far only a few closely related structures in the triply bridged copper(II) compounds have reported ferromagnetic properties, examples being $[Cu_2(bpy)_2(\mu\text{-}O_2CCH_3)_3](ClO_4)_2$ and $[Cu_2(bpy)_2(\mu\text{-}OH)(\text{-}OH_2)(\mu\text{-}O_2CCH_3)](ClO_4)_2$ with $J = 3.6$ and 19.3 cm^{-1}, respectively [34]. The comparison of the trigonality, the parameter τ, and exchange parameter, J, are summarized in Table 6.

4. Conclusions

The structure of the dihydroxo-bridged compound **1** displays a strictly planar Cu_2O_2 network of copper(II) dinuclear species. Each copper(II) ion is in a tetrahedrally distorted square planar geometry with the unpaired electron occupying the $d_{x^2-y^2}$ orbital. However, the value of singlet–triplet energy gap ($J = -15.3$ cm^{-1}) is noticeably smaller than the value calculated from the correlation of Hatfield and Hodgson for the hydroxo-bridged compounds for a bridging angle of 98.5(2)° ($J = -71$ cm^{-1}). Such a deviation is not uncommon (see Table 5) and the tetrahedral distortion is to be held responsible for this significant deviation of the magnetic behaviour.

Compounds **2** and **3** contain a triply bridged dinuclear copper(II) unit both with a hydroxo and a formato bridge. The coordination geometry around each copper(II) ion is slightly distorted trigonal-bipyramidal. A strong magnetic interaction requires both good σ orientation of the magnetic orbitals and good superexchange properties of the bridging atom(s) [2,52]. The magnetic orbital is d_{z^2} for both copper(II) centers with lobes directed toward the bridging hydroxo ligand, but also the formato bridge cannot be excluded as a countercomplementary effect. Further it must be kept in mind that both compounds have a third bridging molecule, i.e., a methoxo group and chloride for compounds **2** and **3**, respectively. Therefore, the "overall" effect is in this case a moderate ferromagnetic exchange.

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 no. CCDC-219202-04 for structures **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

The authors thank The Thailand Research Fund and Khon Kaen University for research grant. Support of the Postgraduate Education and Research Program in Chemistry is also gratefully acknowledged. The work described in the present paper has been supported by the Leiden University Study group WFMO (Werkgroep Fundamenteel Materialen Onderzoek). Support of the NRSC Catalysis (a Research School Combination of HRSMC and NIOK) is kindly acknowledged.

References

[1] O. Kahn, Y. Pei, Y. Journaux, in: Q.W. Bruce, D.D. O'Hare (Eds.), Inorganic Materials, Wiley, Chichester, UK, 1992.

[2] O. Kahn, Molecular Magnetism, VCH Publishers, New York, 1993.

[3] V.H. Crawford, H.W. Richardson, J.R. Wasson, D.J. Hodgson, W.E. Hatfield, Inorg. Chem. 15 (1976) 2107.

[4] J.A. Barnes, D.J. Hodgson, W.E. Hatfield, Inorg. Chem. 11 (1972) 144.

[5] P.J. Hay, J.C. Thibeault, R. Hoffmann, J. Am. Chem. Soc. 97 (1975) 4884.

[6] A. Bencini, D. Gatteschi, Inorg. Chim. Acta 31 (1978) 11.

[7] L. Banci, A. Bencini, D. Gatteschi, J. Am. Chem. Soc. 105 (1983) 761.

[8] O. Kahn, M.F. Charlot, Inorg. Chem. 19 (1980) 1410.

[9] E. Ruiz, P. Alemany, S. Alvarez, J. Cano, Inorg. Chem. 36 (1997) 3683.

[10] E. Ruiz, P. Alemany, S. Alvarez, J. Cano, J. Am. Chem. Soc. 119 (1997) 1297.

[11] B. Graham, M.T.W. Hearn, P.C. Junk, C.M. Kepert, F.E. Mabbs, B. Moubaraki, K.S. Murray, L. Spiccia, Inorg. Chem. 40 (2001) 1536.

[12] A. Yatani, M. Fujii, Y. Nakao, S. Kashino, M. Kinoshita, W. Mori, S. Suzuki, Inorg. Chim. Acta 316 (2001) 127.

[13] T.M. Rajendiran, R. Kannappan, R. Venkatesan, P.S. Rao, M. Kandaswamy, Polyhedron 18 (1999) 3085.

[14] S.P. Perlepes, J.C. Huffman, G. Christou, Polyhedron 10 (1991) 2301.

[15] V. McKee, M. Zvagulis, C.A. Reed, Inorg. Chem. 24 (1985) 2914.

[16] W.B. Tolman, R.L. Rardin, S.J. Lippard, J. Am. Chem. Soc. 111 (1989) 4532.

[17] B. Żurowska, J. Mroziński, Inorg. Chim. Acta 342 (2003) 23.

[18] A. Neels, H. Stoeckli-Evans, A. Escuer, R. Vicente, Inorg. Chim. Acta 260 (1997) 189.

[19] M. Julve, M. Verdaguer, A. Gleizes, M. Philoche-Levisalles, O. Kahn, Inorg. Chem. 23 (1984) 3808.

[20] Siemens, SAINT, Version 4 Software Reference Manual, Siemens Analytical X-Ray Systems, Inc., Madison, WI, USA, 1996.

[21] G.M. Sheldrick, SADABS, Program for Empirical Absorption correction of Area Dectector Data, University of Göttingen, Göttingen, Germany, 1996.

[22] Bruker, XSHELL, Version 6.12, Reference Manual, Bruker AXS, Inc., Madison, WI, USA, 1999.

[23] A.W. Addison, T.N. Rao, J. Reedijk, J. van Rijn, G.C. Verschoor, J. Chem. Soc., Dalton Trans. (1984) 1349.

[24] M. Brophy, G. Murphy, C. O'Sullivan, B. Hathaway, B. Murphy, Polyhedron 18 (1999) 611.

[25] G. Murphy, P. Nagle, B. Murphy, B. Hathaway, J. Chem. Soc., Dalton Trans. (1997) 2645.

[26] D.K. Towle, S.K. Hoffmann, W.E. Hatfield, P. Singh, P. Chaudhuri, Inorg. Chem. 27 (1988) 394.

[27] W.A. Wojtczak, M.J. Hampden-Smith, E.N. Duesler, Inorg. Chem. 37 (1998) 1781.

[28] V.H. Crawford, H.W. Richardson, J.R. Wasson, D.J. Hodgson, W.E. Hatfield, Inorg. Chem. 15 (1976) 2107.

[29] G. Murphy, C. Murphy, B. Murphy, B. Hathaway, J. Chem. Soc., Dalton Trans. (1997) 2653.

[30] G. Murphy, C. O'Sullivan, B. Murphy, B. Hathaway, Inorg. Chem. 37 (1998) 240.

[31] M.S. Haddad, S.R. Wilson, D.J. Hodgson, D.N. Hendrickson, J. Am. Chem. Soc. 103 (1981) 384.

[32] M.S. Haddad, D.N. Hendrickson, Inorg. Chim. Acta 28 (1978) L121.

[33] T.R. Felthouse, E.J. Laskowski, D.N. Hendrickson, Inorg. Chem. 16 (1977) 1077.

[34] G. Christou, S.P. Perlepes, E. Libby, K. Folting, J.C. Huffman, R.J. Webb, D.N. Hendrickson, Inorg. Chem. 29 (1990) 3657.

[35] S. Youngme, W. Somjitsripunya, K. Chinnakali, S. Chantrapromma, H.K. Fun, Polyhedron 18 (1999) 857.

[36] S. Youngme, G.A. van Albada, O. Roubeau, C. Pakawatchai, N. Chaichit, J. Reedijk, Inorg. Chim. Acta 342 (2003) 48.

[37] L.-P. Wu, M.E. Keniry, B.J. Hathaway, Acta Crystallogr., Sect. C 48 (1992) 35.

[38] S. Youngme, G.A. van Albada, H. Kooijman, O. Roubeau, W. Somjitsripunya, A.L. Spek, C. Pakawatchai, J. Reedijk, Eur. J. Inorg. Chem. (2002) 2367.

[39] M.F. Charlot, S. Jeannin, Y. Jeannin, O. Kahn, J. Lucrece-Abaul, J. Martin-Frere, Inorg. Chem. 18 (1979) 1675.

[40] G.A. van Albada, I. Mutikainen, W.J.J. Smeets, A.L. Spek, U. Turpeinen, J. Reedijk, Inorg. Chim. Acta 327 (2002) 134.

[41] J.M. Seco, U. Amador, M.J. González Garmendia, Polyhedron 18 (1999) 3605.

[42] G.A. van Albada, I. Mutikainen, U. Turpeinen, J. Reedijk, Inorg. Chim. Acta 324 (2001) 273.

[43] S. Amani Komaei, G.A. van Albada, J.G. Haasnoot, H. Kooijman, A.L. Spek, J. Reedijk, Inorg. Chim. Acta 286 (1999) 24.

[44] L.K. Thompson, S.K. Mandal, L. Rosenberg, Inorg. Chim. Acta 133 (1987) 81.
[45] L. Chen, L.K. Thompson, J.N. Bridson, Inorg. Chim. Acta 244 (1996) 87.
[46] L.K. Thompson, F.L. Lee, E.J. Gabe, Inorg. Chem. 27 (1988) 39.
[47] L.K. Thompson, Can. J. Chem. 61 (1983) 579.
[48] L.K. Thompson, A.W. Hanson, B.S. Ramaswamy, Inorg. Chem. 23 (1984) 2459.
[49] P.L. Burk, J.A. Osborn, M.T. Youinou, J. Am. Chem. Soc. 103 (1981) 1273.
[50] Y. Nishida, S. Kida, J. Chem. Soc., Dalton Trans. (1986) 2633.
[51] V. McKee, M. Zvagulis, C.A. Reed, Inorg. Chem. 24 (1985) 2914.
[52] V. McKee, M. Zvagulis, J.V. Dagdigian, M.G. Patch, C.A. Reed, J. Am. Chem. Soc. 106 (1984) 4765.

Available online at www.sciencedirect.com

SCIENCE @ DIRECT®

Inorganica Chimica Acta 358 (2005) 1068–1078

Inorganica Chimica Acta

www.elsevier.com/locate/ica

Dinuclear triply-bridged copper(II) compounds containing carboxylato bridges and di-2-pyridylamine as a ligand: synthesis, crystal structure, spectroscopic and magnetic properties

Sujittra Youngme [a,*], Chatkaew Chailuecha [a], Gerard A. van Albada [b], Chaveng Pakawatchai [c], Narongsak Chaichit [d], Jan Reedijk [b]

[a] *Department of Chemistry, Faculty of science, Khon Kaen University, Khon Kaen 40002, Thailand*
[b] *Gorlaeus Laboratories, Leiden Institute of Chemistry, Leiden University, P.O. Box 9502, 2300 RA Leiden, The Netherlands*
[c] *Department of Chemistry, Faculty of Science, Prince of Songkla University, Hatyai, Songkla 90112, Thailand*
[d] *Department of Physics, Faculty of Science and Technology, Thammasat University Rangsit, Pathumthani 12121, Thailand*

Received 26 August 2004; accepted 10 November 2004

Abstract

Three new triply-bridged dinuclear copper(II) compounds with carboxylato bridges, $[Cu_2(\mu\text{-}O_2CH)(\mu\text{-}OH)(\mu\text{-}Cl)(dpyam)_2](PF_6)$ (**1**), $[Cu_2(\mu\text{-}O_2CH)_2(\mu\text{-}OH)(dpyam)_2](PF_6)$ (**2**) and $[Cu_2(\mu\text{-}O_2CCH_2CH_3)_2(\mu\text{-}OH)(dpyam)_2](ClO_4)$ (**3**) (dpyam = di-2-pyridylamine) have been synthesized and characterized crystallographically and spectroscopically. Compound **1** consists of a dinuclear unit in which both copper(II) ions are bridged by three different ligands, i.e., formate, chloride and hydroxide anions, providing a distorted trigonal bipyramidal geometry with a CuN_2O_2Cl chromophore. Compounds **2** and **3** have two bridging formato ligands and two bridging propionato ligands, respectively, together with a hydroxo bridge. The carboxylato ligands in both compounds **2** and **3** exhibit different coordination modes. One is in a syn, syn $\eta^1:\eta^1:\mu_2$ bridging mode and the other is in a monoatomic bridging mode. The structure of compound **2** involves a dinuclear unit, with a distorted trigonal bipyramidal geometry around each Cu(II) ion with a CuN_2O_3 chromophore. Compound **3** contains a non-centrosymmetric unit; the coordination environment around Cu(1) is a distorted square–pyramidal geometry and an intermediate geometry of sp and tbp around the Cu(II) ion. The Cu···Cu separations are 3.061, 3.113 and 3.006 Å for compounds **1**, **2** and **3**, respectively. The EPR spectra of all three compounds show a broad isotropic signal with a *g* value around 2.10.

The magnetic susceptibility measurements, measured from 5 to 280 K, revealed a moderate ferromagnetic interaction between the Cu(II) ions with a singlet–triplet energy gap (*J*) of 79.7, 47.8 and 24.1 cm^{-1}, for compounds **1**, **2** and **3**, respectively. Also a very weak intermolecular antiferromagnetic interaction was observed between the dinuclear units.

Keywords: Copper carboxylate complexes; Copper(II) complexes; Crystal structures; EPR spectra; Magnetic properties; Triply-bridged dinuclear copper(II) complexes; Carboxylato-bridged

1. Introduction

Triply-bridged dinuclear copper(II) compounds with one or more carboxylate moieties have recently received considerable attention [1–9], due to the various possible super-exchange pathways between coupled copper(II) centers. The magnetic exchange interactions are depending on the coordination geometry around the copper(II) centers. Structurally, the triply-bridged dinuclear copper(II) carboxylato compounds with didentate chelating ligands and a five coordination of the Cu(II) ion, show

---

[*] Corresponding author. Tel.: +664320222241; fax : +6643202373.
E-mail address: sujittra@kku.ac.th (S. Youngme).

0020-1693/$ - see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.ica.2004.11.019

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.

With the ligand 2,2′-bipyridine (abbreviated as bpy) a number of carboxylated triply-bridged dinuclear copper(II) compounds, $[Cu_2(\mu\text{-}O_2CCH_3)_3(bpy)_2](ClO_4)$ [1]; $[Cu_2(\mu\text{-}O_2CCH_3)(\mu\text{-}OH)(\mu\text{-}OH_2)(bpy)_2](ClO_4)_2$ [1]; $[Cu_2(\mu\text{-}O_2CCH_3)(\mu\text{-}OH)(\mu\text{-}Cl)(bpy)_2](ClO_4)\cdot H_2O$ [2]; $[Cu_2(\mu\text{-}O_2CCH_3)_2(\mu\text{-}OEt)(bpy)_2](PF_6)$ [3] and $[Cu_2(\mu\text{-}O_2CCH_3)_2(\mu\text{-}OMe)(bpy)_2](PF_6)$ [3] have been reported in the literature [1–3]. These compounds exhibit many types of bridging conformations of the carboxylato molecule and various geometries of the Cu(II) ions. However, compounds with formate and propionate as bridging molecules, in contrary to acetate bridges, have rarely been reported for bpy and related ligands. To obtain more insight into the geometries displayed by the Cu(II) ion in connection with the magnetic properties we now use the ligand dpyam (dpyam = di-2-pyridylamine).

In this study three new triply-bridged dinuclear copper(II) compounds with hydroxo, formato and propionato bridges, $[Cu_2(\mu\text{-}O_2CH)(\mu\text{-}OH)(\mu\text{-}Cl)(dpyam)_2](PF_6)$ (**1**), $[Cu_2(\mu\text{-}O_2CH)_2(\mu\text{-}OH)(dpyam)_2](PF_6)$ (**2**) and $[Cu_2(\mu\text{-}O_2CCH_2CH_3)_2(\mu\text{-}OH)(dpyam)_2](ClO_4)$ (**3**) have been synthesized and characterized by X-ray crystallography, IR, EPR and electronic spectra. Also the magnetic susceptibility has been investigated and will be discussed in comparison with other relevant compounds.

2. Experimental

2.1. General

The ligand di-2-pyridylamine 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 by Microanalytical Service of Science and Technological Research Equipment Center, Chulalongkorn University.

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, within the range 8000–18000 cm^{-1}. 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 with DPPH ($g = 2.0036$) as a reference. Magnetic susceptibility measurements (5–280 K) were carried out using a Quantum design MPMS-5 5T SQUID magnetometer (measurements carried out at 1000 Gauss) performed at Leiden University. Data were corrected for magnetization of the sample holder and for diamagnetic contributions, which were estimated from the Pascal constants.

2.2. Syntheses of the compounds

2.2.1. $[Cu_2(\mu\text{-}O_2CH)(\mu\text{-}OH)(\mu\text{-}Cl)(dpyam)_2](PF_6)$ (1)

A hot DMF solution (10 ml) of dpyam (0.171 g, 1.0 mmol) was added to a hot DMF solution (10 ml) of $CuCl_2\cdot 2H_2O$ (0.171 g, 1.0 mmol). Then solid HCOONa (0.136 g, 2.0 mmol) was added to the mixture yielding a brown solution. Its color became green by addition of an aqueous solution (5 ml) of KPF_6 (0.184 g, 1.0 mmol). After a month, green polygon-shape crystals of compound **1** were obtained which were filtered off, washed with the mother liquid and air-dried. *Anal.* Calc. for $C_{21}H_{20}ClCu_2F_6N_6O_3P$: C, 35.4; H, 2.8; N, 11.8. Found: C, 35.5; H, 2.5; N, 11.6%.

2.2.2. $Cu_2(\mu\text{-}O_2CH)_2(\mu\text{-}OH)(dpyam)_2](PF_6)$ (2)

This compound was prepared by adding a hot DMSO solution (5 ml) of dpyam (0.171 g, 1.0 mmol), to a hot aqueous solution (10 ml) of $Cu(COOH)_2$ (0.154 g, 1.0 mmol), after which a hot methanol solution (10 ml) of KPF_6 (0.184 g, 1.0 mmol) was added. The resulting green solution was allowed to evaporate at room temperature. After two weeks, needle green crystals of compound **2** were obtained which were filtered off, washed with the mother liquid and air-dried. *Anal.* Calc. for $C_{22}H_{21}Cu_2F_6N_6O_5P$: C, 36.6; H, 2.9; N, 11.7. Found: C 36.1; H 2.6; N, 11.8%.

2.2.3. $[Cu_2(dpyam)_2(\mu\text{-}O_2CCH_2CH_3)_2(\mu\text{-}OH)](ClO_4)$ (3)

Compound **3** was prepared by adding an aqueous solution (10 ml) of $Cu(ClO_4)_2\cdot 6H_2O$ (0.370 g, 1.0 mmol) to a solution of dpyam (0.171 g, 1.0 mmol) in acetone (10 ml), then a solution of CH_3CH_2COONa (0.384 g, 4.0 mmol) in ethanol (10 ml) was added, yielding a bluish-green solution. The solution was allowed to evaporate at room temperature. After a week, bluish-green hexagon crystals of compound **3** were formed. They were filtered off, washed with mother liquid and air-dried. *Anal.* Calc. for $C_{26}H_{29}ClCu_2N_6O_9$: C, 42.7; H, 4.0; N, 11.5. Found: C, 42.4; H, 4.1; N, 11.3%.

2.3. Crystallography

The X-ray single-crystal data were collected at 293 K for compounds **1** and **2** and 100 K for compound **3** on a 4 K Bruker SMART APEX CCD area-detector diffractometer (rotating anode, graphite-monochromated Mo Kα radiation, $\lambda = 0.71073$ Å) using SMART program [10]. Raw data frame integration was performed with SAINT [11], which also applied correction for Lorentz and polarization effects. An empirical absorption correction by using the SADABS [12] program was applied, which resulted in transmission coefficients ranging from 1.000 to 0.733 for **1**, 1.000 to 0.800 for **2**, 1.000 to 0.801 for **3**.

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 except disordered F atoms of the PF_6^- groups in **1** using the SHELXTL-PC v 6.12 software package. For the structure determination of compound **1** and **2**, the two F atoms of each PF_6^- group showed disorder; the occupancies of the disordered positions were initially refined and later fixed at 0.49 and 0.51 for compound **1** and 0.47 and 0.53 for compound **2**. Furthermore, for compound **2**, one O atom of a formato group is also disordered and refined with site occupancies of 0.5. Three O atoms of the ClO_4^- anion in compound **3** found also to be disordered and were refined into two sets with occupancies of 0.49 and 0.51. All hydrogen atoms in **1**, **2** and **3** were located geometrically and refined isotropically, except for nine H atoms of the dpyam ligand in **2** which were fixed and allowed to ride on the attached atoms. The molecular structure pictures were created by using SHELXTL-PC package [13]. The crystal and refinement details for compounds **1**, **2** and **3** are listed in Table 1.

3. Results and discussion

3.1. Synthesis

Reaction of $CuCl_2 \cdot 2H_2O$ with one equivalent of dpyam in DMF/H_2O followed by addition of HCOONa and KPF_6 led to the very rare example of a triply-bridged dinuclear copper(II) complexes, $[Cu_2(O_2CH)(OH)Cl(dpyam)_2](PF_6)$ (**1**) containing three different anionic bridging ligands. Its formation can be summarized in Eq. (1).

$$2CuCl \cdot 2H_2O + 2dpyam + HCO_2^- + PF_6^- \xrightarrow{DMF/H_2O} [Cu_2(O_2CH)(OH)Cl(dpyam)_2](PF_6) + 3Cl^- + H^+ \quad (1)$$

Treatment of $Cu(O_2CH)_2$ in water with one equivalent of dpyam in DMSO followed by addition of KPF_6 in MeOH (Eq. (2)) gave a clear green solution, from which pure, highly crystalline $[Cu_2(O_2CH)_2(OH)(dpyam)_2](PF_6)$ (**2**) can be obtained.

$$2Cu(O_2CH)_2 + 2dpyam + PF_6^- \xrightarrow{DMSO/H_2O/MeOH} [Cu_2(O_2CH)_2(OH)(dpyam)_2](PF_6) + 2HCO_2^- + H^+ \quad (2)$$

In a similar fashion, treatment of $Cu(ClO_4)_2 \cdot 6H_2O$ in water with one equivalent of dpyam in acetone and CH_3CH_2COONa in EtOH led to the triply-bridged dinuclear complex $[Cu_2(O_2CCH_2CH_3)(OH)(dpyam)_2](ClO_4)$ (**3**). The reaction stoichiometry is presented in Eq. (3).

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

Complex	1	2	3
Molecular formula	$[Cu_2(\mu\text{-}O_2CH)(\mu\text{-}OH)(\mu\text{-}Cl)(dpyam)_2](PF_6)$	$[Cu_2(\mu\text{-}O_2CH)_2(\mu\text{-}OH)(dpyam)_2](PF_6)$	$[Cu_2(\mu\text{-}O_2CCH_2CH_3)_2(\mu\text{-}OH)(dpyam)_2](ClO_4)$
Molecular weight	711.94	721.50	732.08
T (K)	293(2)	293(2)	100(2)
Crystal system	orthorhombic	orthorhombic	monoclinic
Space group	$Cmc2_1$	$Cmc2_1$	$P2_1/c$
a (Å)	16.8665(1)	17.011(4)	11.0890(7)
b (Å)	7.829	8.031(2)	16.7467(11)
c (Å)	19.4941(1)	19.258(5)	16.1864(10)
β (°)	90	90	107.7110(10)
V (Å^3)	2574.22(2)	2631.1(11)	2863.4(3)
Z	4	4	4
D_c (g cm^3)	1.837	1.821	1.698
μ (mm^{-1})	1.900	1.767	1.644
$F(0\,0\,0)$	1424	1448	1496
Crystal size (mm)	0.13 × 0.28 × 0.33	0.25 × 0.12 × 0.05	0.26 × 0.20 × 0.09
Number of reflection collected	9380	11 030	16 907
Number of unique reflections (R_{int})	3725 (0.0224)	3180 (0.0355)	6660 (0.0380)
Data/restraints/parameter	3725/1/234	3180/1/234	6660/0/541
Goodness-of-fit	1.033	1.022	1.039
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0387$, $wR_2 = 0.1073$	$R_1 = 0.0515$, $wR_2 = 0.1194$	$R_1 = 0.0440$, $wR_2 = 0.0857$
R indices (all data)	$R_1 = 0.0441$, $wR_2 = 0.1115$	$R_1 = 0.0699$, $wR_2 = 0.1296$	$R_1 = 0.0618$, $wR_2 = 0.0916$
Largest differential peak and hole (e Å^3)	0.651 and −0.672	0.669 and −0.468	0.519 and −0.464

$$2Cu(ClO_4)_2\cdot 6H_2O + 2dpyam + 2CH_3CH_2CO_2^- \xrightarrow{EtOH/H_2O/acetone} [Cu_2(O_2CCH_2CH_3)_2(OH)(dpyam)_2](PF_6) + 3ClO_4^- + H^+ \quad (3)$$

3.2. Description of structures

3.2.1. Description of [$Cu_2(\mu\text{-}O_2CH)(\mu\text{-}OH)(\mu\text{-}Cl)(dpyam)_2](PF_6)$ (1)

The structure of compound 1 consists of a dinuclear [$Cu_2(\mu\text{-}O_2CH)(\mu\text{-}OH)(\mu\text{-}Cl)(dpyam)_2]^+$ cation and a disordered PF_6^- counteranion. This unit is depicted in Fig. 1 together with the numbering scheme. Selected distances and angles are listed in Table 2. Each copper(II) ion has a distorted trigonal bipyramidal geometry ($\tau = 0.72$, the structure index is defined as $\tau = (\beta - \alpha)/60$, where β and are the largest coordination angles, $\tau = 0$ for square pyramidal (SP) and $\tau = 1$ for trigonal bipyramidal (TBP) geometry) [14], of the CuN_2O_2Cl chromophore, with a nitrogen atom of the dpyam ligand (Cu(1)–N(1) 2.031(3) Å), an oxygen atom of the bridging formato ligand (Cu(1)–O(1) 2.183(2) Å) and a bridging chloro ligand (Cu(1)–Cl(1) 2.451(1) Å) forming the trigonal plane. The axial site of each copper(II) atom is occupied by another nitrogen atom of the dpyam ligand (Cu(1)–N(2) 1.983(2) Å) and an oxygen atom of the hydroxo ligand (Cu(1)–O(2) 1.918(2) Å), which are shorter than those of the equatorial plane corresponding to the typical environment of the trigonal bipyramidal geometry [15]. The symmetric syn,syn-coordinated formato ligand bridges the two equatorial planes, giving a Cu···Cu distance of 3.061(5) Å. The dihedral angle between the equatorial planes is 86.8°. The bridging angles (Cu(1)–O(2)–Cu(1)A and Cu(1)–Cl(1)–Cu(1)A are 105.9(1) and 77.2(1)°, respectively. The dpyam ligands are essentially planar, with only a dihedral angle of 4.4° between the individual pyridine rings.

The crystal lattice is stabilized by hydrogen bonding between the amine N and the oxygen atom of bridging formato group with a N···O distance 2.860(3) Å and between the oxygen atom of bridging hydroxo group and the fluoride atom of PF_6^- anion with O···F contact of 2.954(7) Å. Details of the hydrogen bonding are listed in Table 2.

3.2.2. Description of [$Cu_2(\mu\text{-}O_2CH)_2(\mu\text{-}OH)(dpyam)_2](PF_6)$ (2)

Compound 2 is made up of one-half [$Cu(\mu\text{-}O_2CH)_2(\mu\text{-}OH)(dpyam)]^+$ moiety, which the other half being symmetry related via a mirror plane and a disordered PF_6^- anion. This unit is depicted in Fig. 2 together with the numbering scheme. Selected distances and angles are listed in Table 3. The formato ligands, one of which is in a disordered position, in compound 2 exhibit a different coordination mode. Both copper(II) ions within the dinuclear unit are bridged by three ligands, i.e., a hydroxo group and two formato ligands, of which one formato ligand is in a didentate syn,syn $\eta^1:\eta^1:\mu_2$-bridging mode [16,17] and the other is in the disordered monoatomic bridging mode. A terminal dpyam ligand completes the five coordination at each copper atom, which has a distorted trigonal bipyramidal geometry ($\tau = 0.71$) of the CuN_2O_3 chromophore. An oxygen atom of the monoatomic bridged formato ligand (Cu(1)–O(2) 2.144(6) Å), an oxygen atom of the $\eta^1:\eta^1:\mu_2$-bridging formato ligand (Cu(1)–O(4) 2.200(3) Å) and a nitrogen atom of the dpyam ligand (Cu(1)–N(2) 2.029(4) Å) comprise the trigonal plane. These equatorial distances are considerably longer than the two axial bonds occupied by an oxygen atom of the

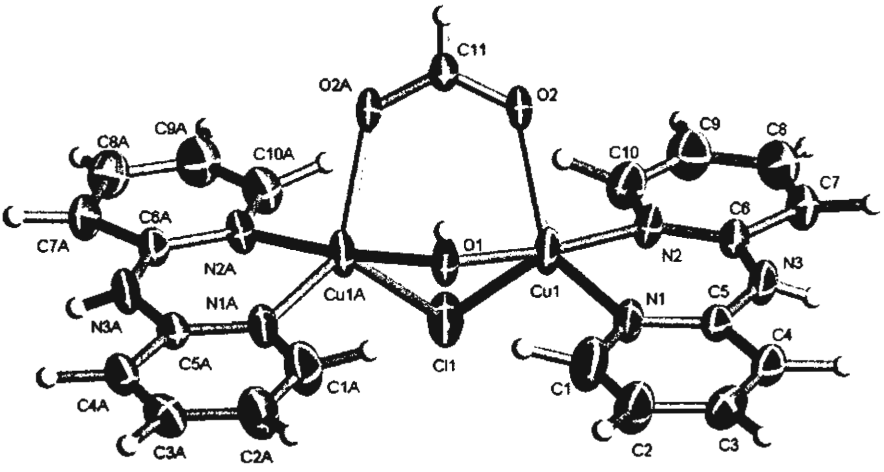


Fig. 1. Thermal ellipsoid (50% probability) plot of [$Cu_2(\mu\text{-}O_2CH)(\mu\text{-}OH)(\mu\text{-}Cl)(dpyam)_2](PF_6)$ (1). Atoms with an "A" are generated by a mirror plane. The uncoordinated PF_6 anion is omitted for clarity.

Table 2
Selected bond lengths (Å) and angles (°) of [Cu_2(μ-O_2CH)(μ-OH)(μ-Cl)(dpyam)$_2$](PF_6) (**1**)

Cu(1)–N(1)		2.031(3)	Cu(1)–O(1)	2.183(2)
Cu(1)–N(2)		1.983(2)	Cu(1)–O(2)	1.918(2)
Cu(1)–Cl(1)		2.451(1)	Cu(1)–Cu(1)A	3.061(5)
O(1)–Cu(1)–N(1)		130.6(1)	N(1)–Cu(1)–Cl(1)	124.1(1)
O(1)–Cu(1)–N(2)		86.7(1)	N(2)–Cu(1)–O(2)	173.8(1)
O(1)–Cu(1)–O(2)		87.3(1)	N(2)–Cu(1)–Cl(1)	97.7(1)
O(1)–Cu(1)–Cl(1)		104.8(1)	Cu(1)–O(2)–Cu(1)A	105.9(1)
O(2)–Cu(1)–Cl(1)		82.3(1)	Cu(1)–Cl(1)–Cu(1)A	77.2(1)
N(1)–Cu(1)–N(2)		91.8(1)	C(11)–O(1)–Cu(1)	127.5(2)
N(1)–Cu(1)–O(2)		93.2(1)	O(1)–C(11)–O(1)A	126.5(4)
Hydrogen bonds	D–H	H···A	D···A	D–H···A
N(3)–H(5)···O(1) [1/2 − x, 1/2 + y, z]	0.81(3)	2.08(3)	2.860(3)	162(3)
O(2)–H(12)···F(6) [−1/2 − x, −1/2 + y, z]	0.81(8)	2.18(7)	2.954(7)	159(7)

e.s.d.s. in parentheses.
A = [−x + 1, y, z].

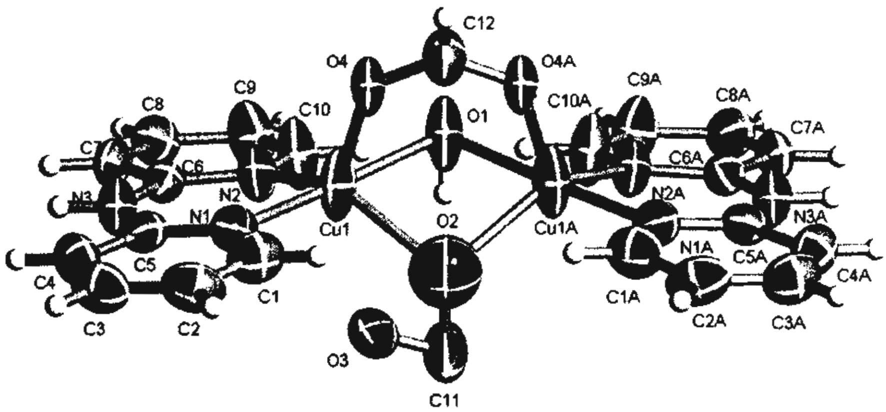


Fig. 2. Thermal ellipsoid (50% probability) plot of [Cu_2(μ-O_2CH)$_2$(μ-OH)(dpyam)$_2$](PF_6) (**2**). Atoms with an "A" are generated by a mirror plane. The uncoordinated PF_6 anion is omitted for clarity. Only one site occupancy of the disordered formato molecule is shown.

Table 3
Selected bond lengths (Å) and angles (°) of [Cu_2(μ-O_2CH)$_2$(μ-OH)(dpyam)$_2$](PF_6) (**2**)

Cu(1)–N(1)	1.972(4)	Cu(1)–O(2)	2.144(6)	
Cu(1)–N(2)	2.029(4)	Cu(1)–O(4)	2.200(3)	
Cu(1)–O(1)	1.934(5)	Cu(1)–Cu(1)A	3.113(5)	
Cu(1)–O(3)	2.246(5)			
O(1)–Cu(1)–O(2)	78.2(2)	N(1)–Cu(1)–O(2)	100.5(2)	
O(1)–Cu(1)–O(4)	96.6(2)	N(1)–Cu(1)–O(4)	87.2(1)	
O(1)–Cu(1)–N(1)	173.6(2)	N(1)–Cu(1)–N(2)	91.7(1)	
O(1)–Cu(1)–N(2)	93.3(2)	N(2)–Cu(1)–O(2)	138.3(3)	
O(2)–Cu(1)–O(4)	89.7(3)	N(2)–Cu(1)–O(4)	130.9(1)	
C(12)–O(4)–Cu(1)	127.4(4)	O(4)–C(12)–O(4)A	127.5(7)	
Cu(1)–O(1)–Cu(1)A	107.2(4)	Cu(1)–O(2)–Cu(1)A	93.1(4)	
Hydrogen bonds	D–H	H···A	D···A	D–H···A
N(3)–H(5)···O(4) [3/2 − x, −1/2 + y, z]	0.86	2.15	2.917(5)	148

e.s.d.s. in parentheses.
A = [−x + 2, y, z].

bridging hydroxo ligand (Cu(1)–O(1) 1.934(5) Å) and another nitrogen atom of the dpyam ligand (Cu(1)–N(1) 1.972(4) Å) corresponding to the typical environment of the trigonal bipyramidal geometry [15]. The Cu···Cu separation is 3.113(5) Å. The bridging Cu(1)–O(1)–Cu(1)A, Cu(1)–O(2)–Cu(1)A angles are 107.2(4), 93.1(4)°, respectively. The dihedral angle between the two equatorial planes is 90.3°. The dpyam ligands are essentially planar, with only very small dihedral angles varies for individual pyridine rings.

The crystal lattice is stabilized by hydrogen bonding between the amine N and the oxygen atom of bridging formato group with a N···O contact of 2.917(5) Å. Details of the hydrogen bonding are listed in Table 3.

3.2.3. Description of [$Cu_2(\mu$-$O_2CCH_2CH_3)_2(\mu$-$OH)(dpyam)_2](ClO_4)$ (3)

The structure of 3 consists of a dinuclear [$Cu_2(\mu$-$O_2CCH_2CH_3)_2(\mu$-OH)(dpyam)$_2]^+$ cation and a disordered uncoordinated ClO_4^- anion. This unit is depicted in Fig. 3, together with the numbering scheme used. Selected distances and angles are listed in Table 4. The Cu(II) ions are triply bridged by two propionate ligands and a hydroxo group. One of the propionato ligands is in the didentate syn,syn η^1:η^1:μ_2-bridging mode and the other is in the monoatomic bridging mode, similar to those of the formato ligands in compound **2**. The Cu···Cu separation is 3.006(2) Å. The coordination environment around Cu(1) can be best described as distorted square pyramidal, with a CuN_2O_2O chromophore and a τ value of 0.22. The four shorter bonds in the basal plane involve two nitrogen atoms of the dpyam ligand (Cu–N 1.985(2) and 2.018(2) Å), an oxygen atom of the bridging hydroxo ligand (Cu(1)–O(1) 1.931(2) Å) and an oxygen atom of the didentate bridging propionato ligand (Cu(1)–O(3) 1.959(2) Å). An oxygen atom of the monoatomic bridging propionato ligand completes the five-coordination of Cu(1) (Cu–O(4) 2.318(2) Å), consistent with a square–pyramidal geometry [18]. The four basal atoms are not coplanar, showing a significant tetrahedral distortion with a dihedral angle of 25.7° formed between CuO_2 and CuN_2 planes and the copper atom is displaced by 0.112 Å from the basal plane towards the O(4) atom.

The geometry around Cu(2) is an intermediate between a trigonal bipyramid and a square pyramid which is distorted via a Berry–Twist process [19], with a τ value of 0.43.The basal plane comprises of two nitrogen atoms of the dpyam ligand (Cu–N 1.986(2) and 2.010(2) Å), an oxygen atom of the bridging hydroxo ligand (Cu(2)–O(1) 1.942(2) Å) and an oxygen atom of the monoatomic bridging propionato ligand (Cu(2)–O(4) 2.065(2) Å). The fifth apical coordination site is occupied by an oxygen atom of the didentate-bridging

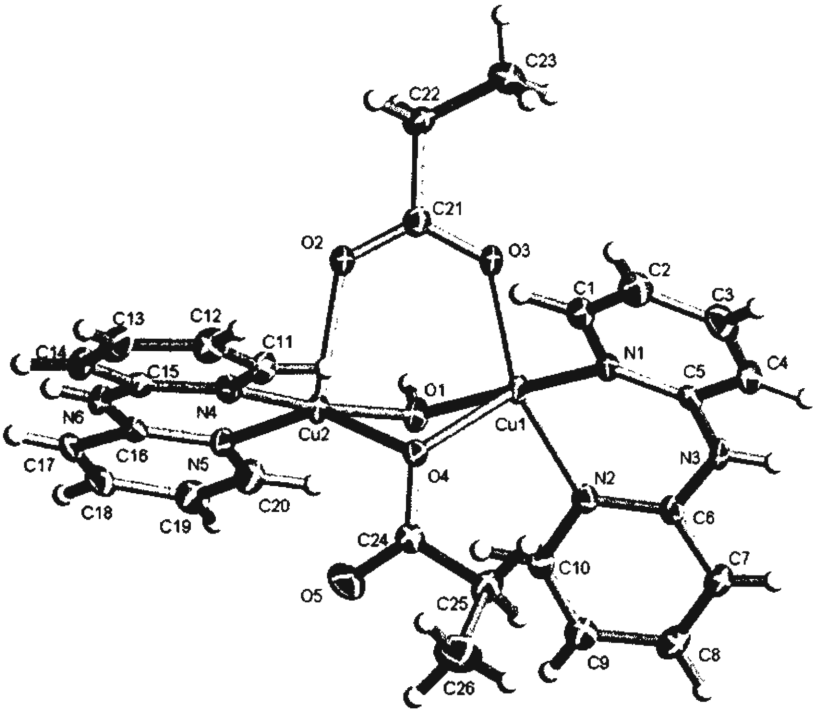


Fig. 3. Thermal ellipsoid (50% probability) plot of [$Cu_2(\mu$-$O_2CCH_2CH_3)_2(\mu$-OH)(dpyam)$_2](ClO_4)$ (3). The uncoordinated ClO_4 anion is omitted for clarity.

Table 4
Selected bond lengths (Å) and angles (°) of [$Cu_2(\mu\text{-}O_2CCH_2CH_3)_2(\mu\text{-}OH)(dpyam)_2$]($ClO_4$) (3)

Cu(1)–N(1)	1.985(2)	Cu(2)–N(4)	1.986(2)
Cu(1)–N(2)	2.018(2)	Cu(2)–N(5)	2.010(2)
Cu(1)–O(1)	1.931(2)	Cu(2)–O(1)	1.942(2)
Cu(1)–O(3)	1.959(2)	Cu(2)–O(2)	2.236(2)
Cu(1)–O(4)	2.318(2)	Cu(2)–O(4)	2.065(1)
Cu(1)–Cu(1)A	3.006(5)		
O(1)–Cu(1)–O(3)	93.0(1)	O(1)–Cu(2)–O(2)	88.4(1)
O(1)–Cu(1)–O(4)	75.9(1)	O(1)–Cu(2)–O(4)	82.0(1)
O(1)–Cu(1)–N(1)	169.2(1)	O(1)–Cu(2)–N(4)	171.9(2)
O(1)–Cu(1)–N(2)	93.4(1)	O(1)–Cu(2)–N(5)	95.3(7)
O(3)–Cu(1)–O(4)	104.3(1)	O(2)–Cu(2)–O(4)	100.3(1)
N(1)–Cu(1)–O(3)	87.6(1)	N(4)–Cu(2)–O(2)	85.4(1)
N(1)–Cu(1)–O(4)	93.5(1)	N(4)–Cu(2)–O(4)	94.0(1)
N(1)–Cu(1)–N(2)	90.4(1)	N(4)–Cu(2)–N(5)	91.8(1)
N(2)–Cu(1)–O(3)	156.0(1)	N(5)–Cu(2)–O(2)	113.4(1)
N(2)–Cu(1)–O(4)	99.6(1)	N(5)–Cu(2)–O(4)	146.2(1)
C(21)–O(3)–Cu(1)	129.7(1)	Cu(1)–O(1)–Cu(2)	101.8(1)
C(21)–O(2)–Cu(2)	126.0(1)	Cu(1)–O(4)–Cu(2)	86.4(1)
O(2)–C(21)–O(3)	125.1(3)		

Hydrogen bonds	D–H	H···A	D···A	D–H···A
O(1)–H(21)···O(8) [x, 1/2 − y, −1/2 + z]	0.75(3)	2.23(3)	2.986(3)	176(3)
N(3)–H(5)···O(5) [x, 1/2 − y, −1/2 + z]	0.83(3)	1.95(3)	2.763(3)	165(3)
N(6)–H(15)···O(2) [1 − x, −y, 1 − z]	0.75(4)	2.10(4)	2.827(3)	165(5)

e.s.d.s. in parentheses.
A = [x, 1/2 − y, −1/2 + z].

propionato ligand with a Cu(2)–O(2) distance of 2.236(2) Å, providing a distorted square-pyramidal CuN_2O_2O' chromophore with a marked tetrahedral twist, 34.4° between CuN_2 and CuO_2 planes. The copper atom is displaced 0.246 Å from the basal plane toward O(2) atom. The bridging Cu(1)–O(1)–Cu(2) and Cu(1)–O(4)–Cu(2) angles are 101.8(1)° and 86.4(1)°, respectively.

The crystal lattice is stabilized by a hydrogen bonding between the amine N and an oxygen atom of bridging propionato group with N···O contacts of 2.763(3)–2.827(3) Å and between the oxygen atom of bridging hydroxo group and the oxygen atom of ClO_4^- anion with a distance of 2.986(3) Å. Details of the hydrogen bonding are listed in Table 4.

3.3. Structure comparison

The compounds together with a number of related dinuclear triply-bridged copper(II) compounds are listed in Table 5. The molecular structures and the copper(II) chromophores of [$Cu_2(\mu\text{-}O_2CCH_3)(\mu\text{-}OH)(\mu\text{-}Cl)(bpy)_2$]($ClO_4$) · H_2O **(8)** ($\tau = 0.40$) [2] and [$Cu_2(\mu\text{-}O_2CH)(\mu\text{-}OH)(\mu\text{-}Cl)(dpyam)_2$]($ClO_4$) · $0.5H_2O$ **(11)** ($\tau = 0.67$) [5] are comparable to that of compound **1** ($\tau = 0.72$) (see Table 5), in which two copper(II) atoms are bridged through three different bridging ligands: carboxylate, hydroxide and chloride anions. The carboxylate bridges in these three compounds display the same syn, syn η^1:η^1:μ_2-bridging mode. However, the coordination geometry of compound **8** is slightly different in distortion towards the square pyramid geometry ($\tau = 0.40$), presumably due to the more flexibility of the dpyam ligand.

The structure of compound **2** ($\tau = 0.71$) shows some similarity to those of [$Cu_2(\mu\text{-}O_2CCH_3)_2(\mu\text{-}OCH_3)(bpy)_2$]($PF_6$) **(9)** ($\tau = 0.66$ and 0.59) [3] and [$Cu_2(\mu\text{-}O_2CH)(\mu\text{-}OH)(\mu\text{-}OCH_3)(dpyam)_2$]($ClO_4$) **(10)** ($\tau = 0.65$) [5], all of which involve a distorted trigonal bipyramidal geometry with a CuN_2O_3 chromophore (see Table 5). Compounds **10** and **2** have two monoatomic bridges, which one connects two apical sites of the trigonal bipyramidal copper(II) chromophores whereas, compound **9** has only one monoatomic bridge (a methoxo group), which connects two apical sites of the trigonal bipyramidal geometry.

The copper(II) environments of compound **3** ($\tau = 0.22$ and 0.43) are related to those of the known dinuclear structures, [$Cu_2(\mu\text{-}O_2CCH_3)_2(\mu\text{-}OEt)(bpy)_2$]($PF_6$) **(4)** ($\tau = 0.23$ and 0.10) [3], [$Cu_2(\mu\text{-}OH)(\mu\text{-}O_2CH)_2(bpy)_2$]($BF_4$) **(5)** ($\tau = 0.11$ and 0.43) [4], [$Cu_2(\mu\text{-}O_2CCH_3)_3(bpy)_2$]($ClO_4$) **(6)** ($\tau = 0.14$ and 0.47) [1] and [$Cu_2(\mu\text{-}O_2CCH_3)(\mu\text{-}OH)(\mu\text{-}H_2O)(bpy)_2$]($ClO_4$)$_2$ **(7)** ($\tau = 0.14$ and 0.25) [1] (see Table 5). The apical distances in these compounds are typical Cu–O distances of 2.2–2.7 Å [20]. The molecular structure

Table 5
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)	Reference
					Axial	Equatorial			
$[Cu_2(\mu\text{-}O_2CCH_3)_2(\mu\text{-}OEt)(bpy)_2](PF_6)$ **(4)**	Dist. Spy.	0.23, 0.10	CuN_2O_2O'	3.230	2.155–2.164	1.939–1.982		112.1(OEt)	[3]
$[Cu_2(\mu\text{-}OH)(\mu\text{-}O_2CH)_2(bpy)_2](BF_4)$ **(5)**	Dist. Spy., intermediate	0.11[c], 0.43[c]	CuN_2O_3, CuN_2O_3	3.171	2.140 2.190	1.927–2.029 1.928–2.012	99.0	110.7(OH)	[4]
$[Cu_2(\mu\text{-}O_2CCH_3)_3(bpy)_2](ClO_4)$ **(6)**	Dist. Spy., Intermediate[d]	0.14[c], 0.47[c]	CuN_2O_2O' CuN_2O_3	3.392	2.238 1.930	1.939–1.977 1.974–2.169	3.6	109.8(O_2CCH_3)	[1]
$[Cu_2(\mu\text{-}O_2CCH_3\mu\text{-}OH)(\mu\text{-}H_2O)(bpy)_2](ClO_4)_2$ **(7)**	Dist. Spy.	0.14[c], 0.25[c]	CuN_2O_2O'	3.035	2.379–2.405	2.006–2.010	19.3	103.8(OH) 78.7(H_2O)	[1]
$[Cu_2(\mu\text{-}O_2CCH_3\mu\text{-}OH)(\mu\text{-}Cl)(bpy)_2](ClO_4)\cdot H_2O$ **(8)**	Dist. Spy.	0.40	CuN_2O_2Cl	2.957		1.920–1.971		100.7(OH) 70.6(Cl)	[2]
$[Cu_2(\mu\text{-}O_2CCH_3)_2(\mu\text{-}OCH_3)(bpy)_2](PF_6)$ **(9)**	Dist. TBP.	0.66, 0.59	CuN_2O_3	3.093	1.922–1.931	1.933–2.099		106.8(OCH_3)	[3]
$[Cu_2(\mu\text{-}O_2CH)(\mu\text{-}OH)(\mu\text{-}OCH_3)(dpyam)_2](ClO_4)$ **(10)**	Dist. TBP.	0.65	CuN_2O_3	3.023	1.918	2.169–2.175	62.5	104.0(OH) 88.3(OCH_3)	[5]
$[Cu_2(\mu\text{-}O_2CH)(\mu\text{-}OH)(\mu\text{-}Cl)(dpyam)_2](ClO_4)\cdot 0.5H_2O$ **(11)**	Dist. TBP.	0.67	CuN_2O_2Cl	3.036	1.916	2.158	79.1	104.8(OH) 75.6(Cl)	[5]
$[Cu_2(\mu\text{-}O_2CH)(\mu\text{-}OH)(\mu\text{-}Cl)(dpyam)_2](PF_6)$ **(1)**	Dist. TBP.	0.72	CuN_2O_2Cl	3.061	1.918	2.183	79.7	105.8(OH) 77.3(Cl)	This work
$[Cu_2(\mu\text{-}O_2CH)_2(\mu\text{-}OH)(dpyam)_2](PF_6)$ **(2)**	Dist. TBP.	0.71	CuN_2O_3	3.113	1.934	2.144–2.200	47.8	107.2(OH) 93.1(O_2CH)	This work
$[Cu_2(\mu\text{-}O_2CCH_2CH_3)_2(\mu\text{-}OH)(dpyam)_2](ClO_4)$ **(3)**	Dist. Spy.,	0.22,	CuN_2O_2O'	3.006	2.236–2.318	1.931–1.959	24.1	101.8(OH)	This work
	Intermediate	0.43	CuN_2O_3					86.4($O_2CCH_2CH_3$)	

[a] Abbreviations: bpy = 2,2′-bipyridine; bppz = 2,5-bis(2-pyridyl)pyrazine; dpyam = di-2-pyridylamine.

[b] Dist. Spy. = distorted square pyramidal, Dist. TBP = distorted trigonal bipyramidal.

[c] Calculated from the known structural parameters.

[d] The original paper describes as Dist. TBP. for the calculated τ value of 0.47.

and the copper(II) chromophores of compound **3** are very comparable to that of compound **7**, both of them have two monoatomic bridges and a triatomic bridge.

3.4. Spectral characterization and EPR measurements

The IR spectra of compounds **1**, **2** and **3** show broad and intense bands of the ionic PF_6^- anion (843 cm^{-1} for **1** and 842 cm^{-1} for **2**) and ionic ClO_4^- anion (1086 cm^{-1} for **3**). The spectra also exhibit a broad band at 3563, 3580 and 3750 cm^{-1} for compounds **1**, **2** and **3**, respectively, which can be assigned to the bridging OH group. The broad and intense bands at 1571 and 1396 cm^{-1} in compound **1** correspond to the $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ vibration of the didentate bridging coordination mode of the carboxylate group within a dinuclear species [5]. Owing to the presence of two different coordination modes of carboxylate bridges in **2** and **3**, two $\nu_{as}(COO^-)$ and two $\nu_s(COO^-)$ bands are observed in its IR spectrum (1619 and 1385 cm^{-1} bands for compound **2** and 1600 and 1392 cm^{-1} for compound **3**). These bands are assigned to the stretching modes of the monoatomic carboxylate bridges [1,8]. The vibrations observed at 1603 and 1436 cm^{-1} for compound **2** and 1556 and 1435 cm^{-1} for compound **3** are consistent with the triatomic carboxylate bridge [1,8].

The electronic reflectance spectrum of compound **1** shows a broad asymmetric band at ≈11 800 cm^{-1} with a high-energy shoulder at ca. 14 600 cm^{-1} consistent with a distorted trigonal bipyramidal geometry [21,22]. Compound **2** has a very broad band centered at ca. 12 810 cm^{-1}. Compound **3** exhibits a broad asymmetric band centered at ca. 12 810 cm^{-1} with a high-energy shoulder at ca. 14 710 cm^{-1}, which would be consistent with two different metal geometries ($\tau = 0.22$ and 0.43) within the complex.

The X-band EPR measured on polycrystalline samples at RT and 77 K showed in all three compounds a broad isotropic signal with a g_{iso} at around 2.10 and no hyperfine is resolved. To have more insight into the magnetic behaviour magnetic susceptibility studies were undertaken of a powdered sample from 5 to 280 K (see below).

3.5. Magnetic properties

The magnetic properties of the compounds are depicted in Figs. 4–6, for compounds **1**, **2** and **3**, respectively, in the form of μ_{eff} versus T plots for two Cu(II) ions.

The magnetic properties of all three compounds show a very similar behaviour. At 280 K the μ_{eff} is 2.75 μ_B for compound **1** (2.40 $_B$ and 2.60 μ_B, for **2** and **3**) which agrees reasonable with the spin-only value calculated for two uncoupled spin = 1/2 Cu(II) centers. Upon cooling it raises gradually to reach 3.02, 2.68 and 2.78 μ_B, at

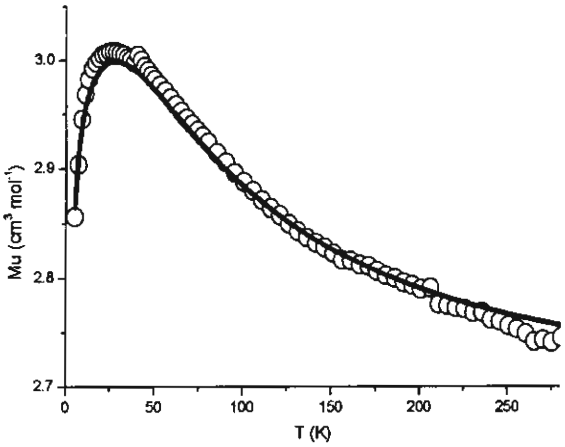


Fig. 4. A plot of the temperature dependence of μ_{eff} vs. T for compound **1**. The solid line represents the calculated curve (see text).

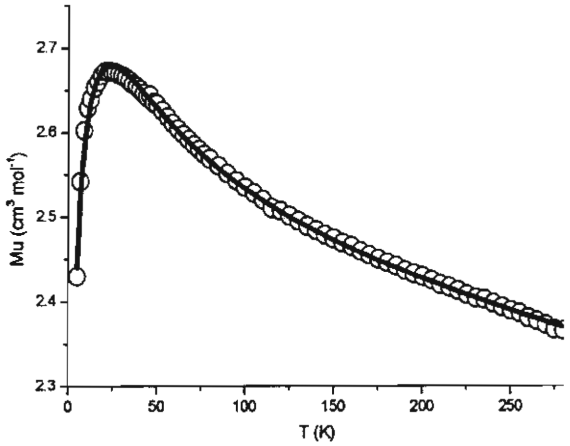


Fig. 5. A plot of the temperature dependence of μ_{eff} vs. T for compound **2**. The solid line represents the calculated curve (see text).

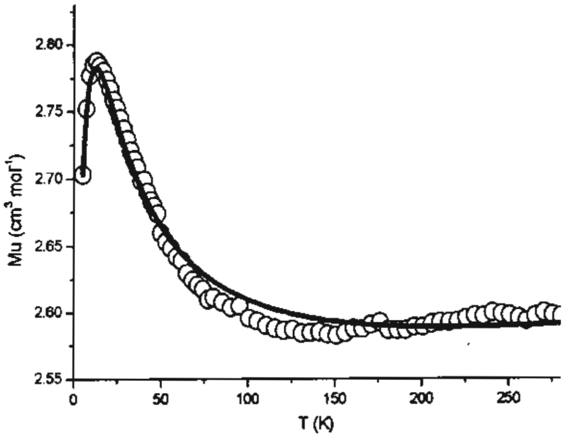


Fig. 6. A plot of the temperature dependence of μ_{eff} vs. T for compound **3**. The solid line represents the calculated curve (see text).

around 30 K, for compounds **1**, **2** and **3**, respectively. This behaviour is typical for a ferromagnetically coupled Cu(II) dinuclear compound. Below that temperature, μ_{eff} then diminishes till a value around 2.85–2.45 μ_B at 5 K for the three 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 $S = 1/2$ centers, which is based on the general Hamiltonian [23] 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 [23, p. 132].

$\chi_m = (2Ng^2\beta^2)[kT - (2zJ'/(3 + \exp(-J/kT)))]^{-1}[3 + \exp(-J/kT)]^{-1}(1 - p) + \chi_p p + \text{TIP}$, 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 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 **1** with the following values: $J = 79.7$ cm^{-1}, $g = 2.15$, $zJ' = -2.9$ cm^{-1}, $p = 0.0$, with a final R of 1.0×10^{-3} (see Fig. 4). For compound **2** these values are $J = 47.8$ cm^{-1}, $g = 1.99$, $zJ' = -7.6$ cm^{-1}, $p = 0.002$, with a final R of $1.6 \cdot 10^{-3}$ (see Fig. 5). For compound **3** these values are $J = 24.1$ cm^{-1}, $g = 2.05$, $zJ' = -3.4$ cm^{-1}, $p = 0.0$, with a final R of 1.2×10^{-3} (see Fig. 6).

This overall ferromagnetic behaviour has been observed earlier for many other triply-bridged dpyam compounds, also containing a hydroxo bridge [5], i.e., compounds **10** and **11** in Table 5. For dinuclear bis-hydroxo-bridged compounds a correlation is known 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 [24]. In this study the angles vary between 101.8° and 107.2° and by neglecting the other bridges an antiferromagnetic exchange would have been expected. However, the difference between the compounds with only hydroxo bridges and the triply bridges is great. The copper(II) ions in compounds **1**–**3** (and also **10** and **11** in Table 5) have a five-coordinate (more or less distorted) trigonal bipyramidal geometry with the d_{z^2} ground state, whereas the dihydroxo-bridged copper(II) complexes are square pyramidal with $d_{x^2-y^2}$ ground states. 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 [25,26]. In this case, for compounds **1**–**3**, a single pathway via the unit (Cu–OH–Cu) is possible for the electron delocalization via the d_{z^2} magnetic orbitals, corresponding to the weak, or intermediate, ferromagnetic interaction. Secondly also the carboxylato bridge plays a role in the magnetic interaction, which was described in the literature as a so-called "countercomplementary effect" [23,27–29]. This effect cannot be quantitated, however.

From Table 5 it can anyway be noted that for almost all triply bridges Cu(II) dinuclear compounds, when the copper(II) geometry is (distorted) trigonal bipyramidal a moderate overall ferromagnetic interaction is observed (compounds **10**, **11**, **1** and **2**) and when the geometry becomes more distorted to square pyramidal (compounds **6**, **7** and **3**) the overall ferromagnetic interaction becomes, in general, weaker.

4. Conclusions

Three new triply-bridged compounds with dpyam are synthesized, characterized and their magnetic interaction studied. All three compounds contain a dinuclear copper(II) unit with a hydroxo and a formato/chloride bridge (compound **1**), two formato bridges (compound **2**) and two propionato bridges (compound **3**). The coordination geometry around each copper(II) ion is slightly distorted trigonal bipyramidal for **1** and **2** and an intermediate between SP and TBP for **3**. A strong magnetic interaction requires both good σ orientation of the magnetic orbitals and good superexchange properties of the bridging atom(s) [23,29]. The magnetic orbital is d_{z^2} for the copper(II) centers with lobes (more or less) directed toward the bridging hydroxo ligand, but also the formato/propionato/chloride bridge(s) cannot be excluded as a countercomplementary contribution. Therefore the "overall" effect is in this case a moderate ferromagnetic exchange, as can be seen for compounds **10**, **11**, **1** and **2** with the same type of geometry, while in compounds **3**, **6** and **7** the distortion is large, the overlap of the orbitals becomes weaker and also the ferromagnetic interaction becomes weaker. An exception appears to be compound **5**, but in this compound, both Cu(II) ions have differently distorted 5 coordinated geometries and a fairly large Cu–O–Cu angle.

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 243062–64 for structures **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.ac.uk].

Acknowledgements

The authors thank The Thailand Research Fund and Khon Kaen University for research grant. Support of the Postgraduate Education and Research Program in Chemistry is also gratefully acknowledged. The work described in the present paper has been supported by the Leiden University Study group WFMO (Werkgroep Fundamenteel Materialen Onderzoek). Support of the NRSC Catalysis (a Research School Combination of HRSMC and NIOK) is kindly acknowledged.

References

[1] G. Christou, S.P. Perlepes, E. Libby, K. Folting, J.C. Huffman, R.J. Webb, D.N. Hendrickson, Inorg. Chem. 29 (1990) 3657.

[2] S.P. Perlepes, J.C. Huffman, G. Christou, Polyhedron 10 (1991) 2301.

[3] S.P. Perlepes, J.C. Huffman, G. Christou, S. Paschalidou, Polyhedron 14 (1995) 1073.

[4] T. Tokii, M. Nagamatsu, H. Hamada, M. Nakashima, Chem. Lett. (1992) 1091.

[5] (a) S. Youngme, C. Chailuecha, G.A. van Albada, C. Pakawatchai, N. Chaichit, J. Reedijk, Inorg. Chim. Acta 357 (2004) 2532; (b) W. Huang, D. Hu, S. Gou, H. Qian, H.-K. Fun, S.S.S. Raj, Q. Meng, J. Mol. Struct. 649 (2003) 269.

[6] B. Graham, M.T.W. Hearn, P.C. Junk, C.M. Kepert, F.E. Mabbs, B. Moubaraki, K.S. Murray, L. Spiccia, Inorg. Chem. 40 (2001) 1536.

[7] T.M. Rajendiran, R. Kannappan, R. Venkatesan, P.S. Rao, M. Kandaswamy, Polyhedron 18 (1999) 3085.

[8] I. Chadjistamatis, A. Terzis, C.P. Raptopoulou, S.P. Perlepes, Inorg. Chem. Commun. 6 (2003) 1365.

[9] M. Lubben, R. Hage, A. Meetsma, K. Bÿma, B.L. Feringa, Inorg. Chem. 34 (1995) 2217.

[10] Bruker, SMART (version 5.6), Bruker AXS Inc., Madison, Wisconsin, USA, 2000.

[11] Bruker, SAINT (version 5.6), Bruker AXS Inc., Madison, Wisconsin, USA, 2000.

[12] Bruker, SADABS (version 5.6), Bruker AXS Inc., Madison, Wisconsin, USA, 2000.

[13] Bruker, SHELXTL (version 6.12), Bruker AXS Inc., Madison, Wisconsin, USA, 2000.

[14] A.W. Addison, T.N. Rao, J. Reedijk, J. van Rijn, G.C. Verschoor, J. Chem. Soc., Dalton Trans. (1984) 1349.

[15] F. Huq, A.C. Shapski, J. Chem. Soc. A (1971) 1927.

[16] D.K. Towle, S.K. Hoffmann, W.E. Hatfield, P. Singh, P. Chaudhuri, Inorg. Chem. 27 (1988) 394.

[17] W.A. Wojtczak, M.J. Hampden-Smith, E.N. Duesler, Inorg. Chem. 37 (1998) 1781.

[18] S. Youngme, G.A. van Albada, O. Roubeau, C. Pakawatchai, N. Chaichit, J. Reedijk, Inorg. Chim. Acta 342 (2003) 48.

[19] S. Berry, J. Chem. Phys. 32 (1960) 933.

[20] S. Youngme, W. Somjitsripunya, K. Chinnakali, S. Chantrapromma, H.K. Fun, Polyhedron 18 (1999) 857.

[21] G. Murphy, C. Murphy, B. Murphy, B. Hathaway, J. Chem. Soc., Dalton Trans. (1997) 2653.

[22] G. Murphy, P. Nagle, B. Murphy, B. Hathaway, J. Chem. Soc., Dalton Trans. (1997) 2645.

[23] O. Kahn, Molecular Magnetism, VCH Publishers, New York, 1993.

[24] V.H. Crawford, H.W. Richardson, J.R. Wasson, D.J. Hodgson, W.E. Hatfi eld, Inorg. Chem. 15 (1976) 2107.

[25] M.S. Haddad, S.R. Wilson, D.J. Hodgson, D.N. Hendrickson, J. Am. Chem. Soc. 103 (1981) 384.

[26] M.S. Haddad, D.N. Hendrickson, Inorg. Chim. Acta 28 (1978) L121.

[27] Y. Nishida, S. Kida, J. Chem. Soc., Dalton Trans. (1986) 2633.

[28] V. McKee, M. Zvagulis, C.A. Reed, Inorg. Chem. 24 (1985) 2914.

[29] V. McKee, M. Zvagulis, J.V. Dagdigian, M.G. Patch, C.A. Reed, J. Am. Chem. Soc. 106 (1984) 4765.

Available online at www.sciencedirect.com

SCIENCE @ DIRECT®

Inorganica Chimica Acta 358 (2005) 3267–3271

Inorganica Chimica Acta

www.elsevier.com/locate/ica

Note

Synthesis, crystal structure and magnetic properties of a polynuclear Cu(II) complex: *catena*-poly-[aqua(di-2-pyridylamine)copper(II)(μ-formato-*O*,*O′*)nitrate]

Sujittra Youngme [a,*], Pongthipun Phuengphai [a], Narongsak Chaichit [b], Gerard A. van Albada [c], Stefania Tanase [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] *Gorlaeus Laboratories, Leiden Institute of Chemistry, Leiden University, P.O. Box 9502, 2300 RA Leiden, The Netherlands*

Received 11 November 2004; accepted 28 December 2004

Abstract

The synthesis, X-ray structure, spectroscopic and magnetic properties of a zig-zag formato-bridged chain complex with the formula $[Cu(dpyam)(\mu\text{-}O_2CH)(OH_2)]_n(NO_3)_n$ (**1**) (in which dpyam = di-2-pyridylamine) is described.

The geometry of the copper(II) ion is distorted square pyramidal with a basal plane consisting of two nitrogen atoms of the dpyam ligand (Cu–N distances 1.987(3) and 2.010(3) Å) and two oxygen atoms of two different formato ligands (Cu–O distances 1.974(2) and 1.975(2) Å). A coordinated water molecule occupies the axial position at a distance of 2.222(3) Å. The copper atoms are bridged unsymmetrically by a formato anion in a syn-anti arrangement, resulting in a polymeric zig-zag chain structure.

The magnetic susceptibility measurements (5–280 K) agree with a very weak ferromagnetic chain interaction between the Cu centres with a J value of $0.75\ cm^{-1}$.

Keywords: Copper(II) complex; Di-2-pyridylamine; Magnetic properties; Crystal structure

---

1. Introduction

Reported complexes of copper(II) and didentate mono(chelating) ligands with monovalent oxoanions may be grouped in several classes for each type of oxoanion, depending on coordinating nature. Complexes with monovalent oxoanions formulated as $Cu(LL)(anion1)_2 \cdot nH_2O$, or $Cu(chelate)(anion1)(anion2) \cdot nH_2O$, (in which anion1 and/or anion2 = NO_2^-, NO_3^-, ClO_4^-, $CH_3CH_2COO^-$, CH_3COO^- or $HCOO^-$ and LL = didentate chelating ligand), were found to exhibit four types of local molecular structures: (A) mononuclear tetrahedrally-distorted elongated octahedral units with an extremely asymmetric didentate coordination of both oxoanions [1]; (B) polymeric elongated tetragonal (or rhombic) octahedral units with the nearly symmetric didentate coordination of a basal oxoanion and the bridging didentate coordination in the axial positions of the second one [2]; (C) polymeric tetrahedrally distorted square pyramid with non-bridging monodentate and bridging didentate oxoanions [3,4]; (D) dinuclear tetrahedrally distorted square pyramidal with non-bridging monodentate and bridging didentate oxoanions [5,6]. An example of each class is presented in Scheme 1.

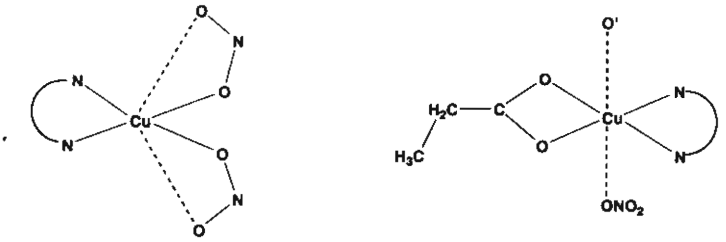
X-ray studies of polynuclear formato-bridged Cu(II) compounds with N-donor ligands are relatively rare

---

[*] Corresponding author. Tel.: +66 43 202 222 41; fax: +66 43 202 373.

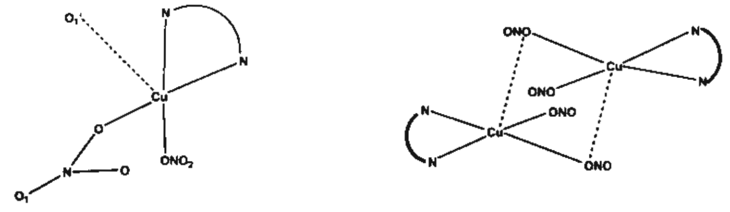
E-mail address: sujittra@kku.ac.th (S. Youngme).

0020-1693/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.ica.2004.12.032



Class A: [Cu(dpyam)(NO$_2$)$_2$][26]

Class B: [Cu(dpyam)(NO$_3$)(O$_2$CCH$_2$CH$_3$)] [2]



Class C: [Cu(Prdpa)(NO$_3$)$_2$] [3,4]

Class D: [Cu$_2$(dpyam)$_2$(ONO)$_2$(μ-ONO)$_2$]·2CH$_3$CN [5]

Scheme 1.

[7–12] and the number of magnetic studies undertaken with these compounds is even more scarce [7,8]. Also polynuclear Cu(II) compounds with the ligand used in this study, di-2-pyridylamine (abbreviated as dpyam) are relatively rare, as only a few are reported to date [1,3,22–25]. With the ligand dpyam and formato as a bridging ligand only one dinuclear compound, [Cu$_2$(dpyam)$_2$(μ-O$_2$CH)(O$_2$CH)$_3$(H$_2$O)](H$_2$O), has been reported [6].

In this study we describe the synthesis, spectroscopic properties, magnetic study and EPR of a chain-type formato-bridged Cu(II) compound, [Cu(dpyam)(μ-O$_2$CH)(H$_2$O)]$_n$(NO$_3$)$_n$ (1).

2. Experimental

2.1. Synthesis of [Cu(dpyam)(μ-O$_2$CH)(H$_2$O)]$_n$ (NO$_3$)$_n$ (1)

Solid NaHCOO (0.136 g, 2.0 mmol) dissolved in water (10 ml) was added to a warm solution of di-2-pyridylamine (0.171 g, 1.0 mmol) in methanol (10 ml) yielding a pale-yellow solution. Its colour became greenish by slow addition of an aqueous solution (10 ml) of Cu(NO$_3$)$_2$ · 2.5H$_2$O (0.232 g, 1.0 mmol). The resulting green solution was allowed to evaporate at room temperature. After several days, blue-green crystals of **1** were deposited. Yield: ca. 60%. *Anal.* Calc. for $C_{11}H_{12}CuN_4O_6$: C, 36.7; H, 3.4; N, 15.6. Found: C, 36.3; H, 3.3; N, 15.4%. IR (KBr; cm^{-1}): ν_{as}(C–O) 1591(s), ν_{as}(N–O) 1384(s), ν_s(C–O) 1354(s), ν_s(N–O) 1340(s) and δ (O–C–O) 906(w).

2.2. Physical measurements

Elemental analyses (C, H, N) were determined on a Perkin–Elmer PE2400 CHNS/O Analyzer by the Microanalytical Service of Science and Technological Research Equipment Center, Chulalongkorn University, Thailand. IR spectrum was recorded on a Spectrum One Perkin–Elmer FT-IR spectrophotometer as KBr pellets in the 4000–450 cm^{-1} spectral range. Diffuse reflectance measurement from 9000 to 20 000 cm^{-1} was recorded as polycrystalline samples using a Perkin–Elmer Lambda 2S spectrophotometer equipped with an integrating sphere attachment. Barium sulfate was used as the reflectance standard. X-band powder EPR spectrum was recorded on a JEOL RE2x electron spin resonance spectrometer using DPPH ($g = 2.0036$) as a standard. Magnetic susceptibility measurements (5–300 K) were carried out using a Quantum Design MPMS-5 5T SQUID magnetometer (measurements carried out at 1000 G) performed at Leiden University. Data were corrected for magnetisation of the sample holder and for diamagnetic contributions, which were estimated from Pascal constants.

2.3. Crystallography

Reflection data were collected at 293 K on a 1 K Bruker SMART CCD area-detector diffractometer using graphite monochromated Mo Kα 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 15 s for **1**, covered 0.3° in ω. Data reduction and cell refinements were performed using the program SAINT [13]. An empirical absorption correction by using the SADABS [14] program was applied, which resulted in transmission coefficients ranging from 0.7662 to 1.0000 for **1**. 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 6.1 [15] software package. All hydrogen atoms in **1** were located by difference synthesis and refined isotropically. The nitrate group is disordered with site occupancies of 0.50 for both conformers and the average bond length, 1.216(6) Å and bond angle, 119.8(3)° are within the typical values for the uncoordinated nitrate group [16]. The molecular graphics were created by using SHELXTL-PC. The crystal and refinement details are listed in Table 1.

3. Results and discussion

3.1. Description of the structure

A plot of the structure together with the used numbering system is shown in Fig. 1 with selected bond distances and angles given in Table 2. The structure of **1** consists of a polynuclear $[Cu(dpyam)(\mu\text{-}O_2CH)(H_2O)]^+$ cation, and an uncoordinated disordered NO_3^- anion.

Table 1
Crystal and refinement data of $[Cu(dpyam)(\mu\text{-}O_2CH)(OH_2)]_n(NO_3)_n$

Molecular formula	$C_{11}H_{12}CuN_4O_6$
Molecular weight	359.79
T (K)	293(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	9.7179(2)
b (Å)	19.06310(10)
c (Å)	7.5064(2)
β (Å)	94.8530(10)
V (Å^3)	1385.60(5)
Z	4
D_{calc} (Mg m^{-3})	1.725
μ (mm^{-1})	1.613
Crystal size (mm)	0.05 × 0.13 × 0.38
θ Range (°)	2.10–30.47
Number of reflections collected	10 187
Number of unique reflections	3941 ($R_{int} = 0.0462$)
Goodness-of-fit	1.042
Final R indices [$I > 2\sigma(I)$], $wR_2 = 0.0752$	$R_1 = 0.0541$; $wR_2 = 0.0971$
R indices (all data)	$R_1 = 0.1057$; $wR_2 = 0.1147$
Largest difference peak and hole (e Å^{-3})	0.538, −0.461

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

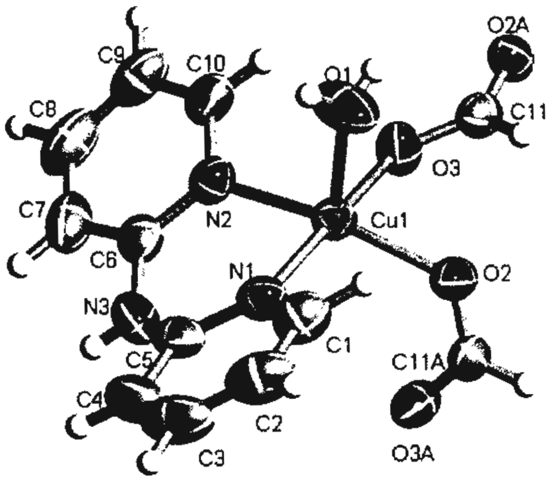


Fig. 1. Thermal ellipsoid plot (50% probability) of $[Cu(dpyam)(\mu\text{-}O_2CH)(H_2O)]_n(NO_3)_n$ (**1**). The uncoordinated nitrate anion has been omitted for clarity.

The copper atoms are bridged unsymmetrically by a formate group in a syn-anti arrangement [17], resulting in a polymeric zig-zag chain structure (Fig. 2). The Cu(II) atom is five-coordinated with a basal plane consisting of two nitrogen atoms of the dpyam ligand (Cu–N distances 1.987(3) and 2.010(3) Å) and two oxygen atoms of two different formato ligands (Cu–O distances 1.974(2) and 1.975(2) Å). The coordinated water molecule occupies the axial position at a distance of 2.222(3) Å. The CuN_2O_2 chromophore is non-planar with a tetrahedral twist of 14.4(1)°. The Cu atom lies above this plane, 0.202 Å toward O(1). The copper chromophore can be described as having a slightly distorted square pyramidal geometry. The distortion of square pyramidal can be best described by the structural parameter τ ($\tau = 0$ for square pyramid and $\tau = 1$ for trigonal bipyramidal [18]), which in this case is 0.11. The Cu···Cu distance is 4.881(3) Å.

The lattice structure is stabilised by a hydrogen-bonding network between the N–H atom of the ligand and oxygen atoms of the nitrate anion with N–H···O contacts of 2.839(8)–3.072(17) Å and between the hydrogen of water oxygen atom and the nitrate oxygen atoms with O–H···O contacts of 2.617(12)–3.096(16) Å. A plot of the hydrogen bond system is given in Fig. 3 and details are given in Table 2.

3.2. EPR and magnetic measurements

The polycrystalline EPR spectrum of **1**, at both room temperature and liquid nitrogen temperature (77 K) shows a rhombic spectrum with $g_1 = 2.06$, $g_2 = 2.15$ and $g_3 = 2.21$, consistent with the $d_{x^2-y^2}$ ground state for the square pyramidal geometry of the $CuN_2O_2(O)$ chromophore [19]. No hyperfine splitting is resolved.

Table 2
Selected bond lengths (Å) and angles (°) with e.s.d. in parentheses of compound **1**

Cu(1)–O(3)	1.975(2)	Cu(1)–O(2)	1.974(2)
Cu(1)–N(1)	1.987(3)	Cu(1)–N(2)	2.010(3)
Cu(1)–O(1)	2.222(3)	Cu(1)···Cu(1A)	4.881(3)
O(3)–Cu(1)–O(2)	90.8(1)	O(3)–Cu(1)–N(1)	173.3(1)
O(2)–Cu(1)–N(1)	91.4(1)	O(3)–Cu(1)–N(2)	87.3(1)
O(2)–Cu(1)–N(2)	166.8(1)	N(1)–Cu(1)–N(2)	89.0(1)
O(3)–Cu(1)–O(1)	95.1(1)	O(2)–Cu(1)–O(1)	94.9(1)
N(1)–Cu(1)–O(1)	90.8(1)	N(2)–Cu(1)–O(1)	98.1(1)

D-H···A (°)	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A
Hydrogen-bonding parameters				
N(3)–H(5)···*O(4) [$-1+x,y,-1+z$]	0.75(4)	2.37(4)	3.072(17)	154(4)
N(3)–H(5)···*O(6A) [$-1+x,y,-1+z$]	0.75(4)	2.13(4)	2.839(8)	157(4)
O(1)–H(11)···*O(4) [$1-x,-y,1-z$]	0.82(6)	2.32(6)	3.050(16)	149(5)
O(1)–H(11)···*O(4A) [$1-x,-y,1-z$]	0.82(6)	1.98(6)	2.790(11)	168(5)
O(1)–H(11)···*O(5) [$1-x,-y,1-z$]	0.82(6)	2.33(6)	3.096(16)	156(5)
O(1)–H(12)···*O(5)	0.68(6)	2.00(6)	2.617(12)	153(6)
O(1)–H(12)···*O(5A)	0.68(6)	2.08(6)	2.749(8)	170(6)

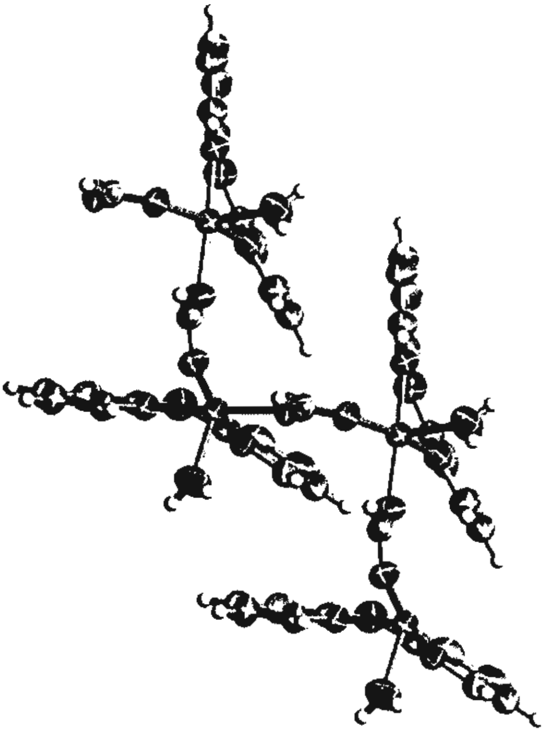


Fig. 2. The polymeric zig-zag chain of $[Cu(dpyam)(\mu\text{-}O_2CH)(H_2O)]_n$-$(NO_3)_n$. The uncoordinated nitrate anion has been omitted for clarity.

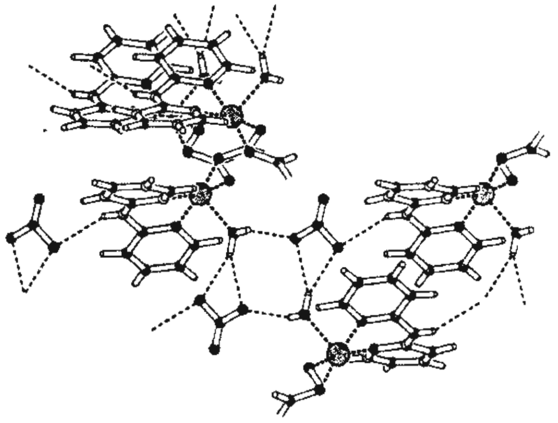


Fig. 3. A plot showing the H-bond system. Only one conformation of the disordered nitrate anion is showing here.

The EPR recorded in a frozen solution (DMF) at 77 K reveal a well-resolved axial spectrum with a $g_\perp$ of 2.05 a $g_\parallel$ of 2.28 and with an $A_\parallel$ of 16.5 mT, indicating that in solution the geometry around the Cu(II) ion has been changed. These solution EPR values have also observed for another formato-bridged Cu(II) compound with an $CuN_2O_2(O)$ chromophore [7] and indicate that also the DMF molecule plays an important role in the coordination.

The magnetisation of a powdered sample of **1** was measured from 5 to 300 K in an applied field of 0.1 T. The resulting molar magnetic susceptibility, χ_M, and the product $\chi_M T$ are plotted in Fig. 4. At around 300 K, the compound exhibits a $\chi_M T$ value of 0.34 $cm^3\,mol^{-1}\,K$, which is close to the theoretical value expected for one non-coupled Cu(II) centre with $S = 1/2$ ($\chi_M T = 0.375\ cm^3\,mol^{-1}\,K$). On lowering the temperature, the $\chi_M T$ value stays almost constant till around 50 K when it start to increase until it reaches a value of about 0.68 $cm^3\,mol^{-1}\,K$ at 5 K, a behaviour indicative of a weak ferromagnetic coupling between Cu centres.

The temperature dependence of χ_m has been fitted using the equation [20] derived from the Heisenberg exchange Hamiltonian for an uniformly spaced chain of spins with $S = 1/2$: $H = -J\sum_{i=1}^{n-1} S_{A_i} \cdot S_{A_{i+1}}$ (in which A_i

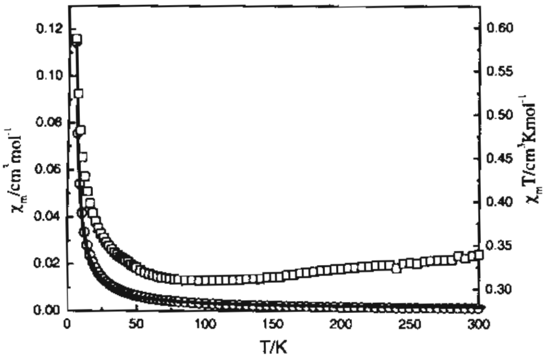


Fig. 4. A plot of temperature dependence of X_MT vs. T (□) and X_M vs. T (○) for compound **1**. The solid line for X_M vs. T represents the calculated curve for the parameters $J = 0.75\ \text{cm}^{-1}$, $g = 2.00$ (see text).

are the nearest neighbour Cu(II) ions and the exchange parameter J is positive for ferromagnetic and negative for an antiferromagnetic interaction). A Temperature Independent Paramagnetism (TIP) of $60 \times 10^{-6}\ \text{cm}^3\ \text{mol}^{-1}$ per Cu(II) ion has been used. The best fit of the experimental magnetic susceptibility data for a chain (solid line in Fig. 3) was obtained using the magnetic parameters $g = 2.00$, $J = 0.75\ \text{cm}^{-1}$, with $R = 1.09 \times 10^{-6}$. As the Cu···Cu distance is fairly large (4.881(3) Å) this very weak ferromagnetic interaction most likely occurs via the Cu–O–C–O–Cu pathway. Similar cases have been observed in the literature [8], although in one example even no interaction was found at all for such a bridge [7]. Such a weak ferromagnetic interaction has also been observed for a number of polynuclear malonate-bridged Cu(II) compounds [21].

4. Supplementary material

Crystallographic data for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publication CCDC No. 240813 for structure **1**. Copies of the data can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

Acknowledgements

The authors thank The Thailand Research Fund and Khon Kaen University for a research grant. Support of the Postgraduate Education and Research Program in Chemistry (Thailand) is also gratefully acknowledged. The work described in the present paper has been supported by the Leiden University Study group WFMO (Werkgroep Fundamenteel MaterialenOnderzoek).

References

[1] S. Youngme, N. Chaichit, K. Damnatara, Polyhedron 21 (2002) 943 (references cited therein).
[2] S. Youngme, C. Pakawatchai, H.K. Fun, Acta Crystallogr. Sect. C 54 (1998) 451.
[3] T.D. Coombs, B.J. Brisdon, C.P. Curtis, M.F. Mahon, S.A. Brewer, C.R. Willis, Polyhedron 20 (2001) 2935.
[4] S. Youngme, P. Phuengphai, N. Chaichit, C. Pakawatchai, G.A. van Albada, O. Roubeau, J. Reedijk, Inorg. Chim. Acta 357 (2004) 3603.
[5] A. Camus, N. Marsich, A.M.M. Lanfredi, F. Ugozzoli, C. Massera, Inorg. Chim. Acta 309 (2000) 1.
[6] S. Youngme, W. Somjitsripunya, K. Chinnakali, S. Chantrapromma, H.K. Fun, Polyhedron 18 (1999) 857.
[7] G.A. van Albada, S. Amani Komaei, H. Kooijman, A.L. Spek, J. Reedijk, Inorg. Chim. Acta 287 (1999) 226.
[8] J.L. Manson, J.G. Lecher, J. Gu, U. Geiser, J.A. Schlueter, R. Henning, X. Wang, A.J. Schultz, H.-J. Koo, M.-H. Whangbo, J. Chem. Soc., Dalton Trans. (2003) 2905.
[9] G. Davey, F.S. Stephens, J. Chem. Soc. A (1971) 103.
[10] B.A. Cartwright, L. Couchman, A.C. Skapski, Acta Crystallogr., Sect. B 35 (1979) 824.
[11] M.A. Bernard, M.M. Borel, F. Busnot, A. Leclaire, Rev. Chim. Miner. 16 (1979) 124.
[12] M. Bukowska-Strzyzewska, A. Tosik, Acta Crystallogr., Sect. C 39 (1983) 203.
[13] Siemens. SAINT 1996, Version 4 Software Reference Manual, Siemens Analytical X-Ray Systems, Inc., Madison, WI, USA, 1996.
[14] G.M. Sheldrick, SADABS, Program for Empirical Absorption Correction of Area Dectector Data, University of Göttingen, Göttingen, Germany, 1996.
[15] Siemens. SHELXTL 1996, Version 5 Reference Manual, Siemens Analytical X-Ray Systems, Inc., Madison, WI, USA, 1996.
[16] C.C. Addison, N. Logan, S.C. Wallwork, C.D. Garner, Q. Rev. Chem. Soc. 25 (1971) 289.
[17] G. Davey, F.S. Stephens, J. Chem. Soc. A (1971) 103.
[18] A.W. Addison, T.N. Rao, J. Reedijk, J. van Rijn, G.C. Verschoor, J. Chem. Soc., Dalton Trans. (1984) 1349.
[19] B.J. Hathaway, in: G. Wilkinson, R.D. Gill, J.A. McCleverty (Eds.), Comprehensive Coordination Chemistry, vol. 5, Pergamon Press, Oxford, 1987.
[20] O. Kahn, Molecular Magnetism, VCH Publication, New York, 1993, p. 253.
[21] J. Pasán, F.S. Delgado, Y. Rodríguez-Martín, M. Hernández-Molina, C. Ruiz-Pérez, J. Sanchiz, F. Lloret, M. Julve, Polyhedron 22 (2003) 2143.
[22] S. Youngme, N. Chaichit, C. Pakawatchai, S. Booncoon, Polyhedron 21 (2002) 1279.
[23] S. Youngme, C. Pakawatchai, H.K. Fun, K. Chinnakali, Acta Crystallogr., Sect. C 54 (1998) 1586.
[24] N. Ray, S. Tyagi, B.J. Hathaway, Acta Crystallogr., Sect. B 38 (1982) 1574.
[25] J. Sletten, Acta Chem. Scand., Sect. A 38 (1984) 491.
[26] S. Youngme, S. Tonpho, K. Chinnakali, S. Chantrapromma, H.-K. Fun, Polyhedron 18 (1999) 851.