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The coordination chemistry of mono(di-2-pyridylamine) copper(II) complexes with monovalent and divalent oxoanions: crystal structure, spectroscopic and magnetic properties of dinuclear $[Cu(L)(\mu\text{-}H_2PO_4)(H_2PO_4)]_2$ and polynuclear $[Cu(L)(\mu_3\text{-}HPO_4)]_n$

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Abstract

The crystal structures of two copper(II) complexes containing the ligand di-2-pyridylamine (dpyam) with monovalent $H_2PO_4^-$ and divalent HPO_4^{2-} oxoanions, $[Cu(dpyam)(\mu\text{-}H_2PO_4\text{-}O,O')(H_2PO_4)]_2$ (**1**) and $[Cu(dpyam)(\mu_3\text{-}HPO_4\text{-}O,O',O'')]_n$ (**2**), are reported and determined by X-ray crystallography. The dinuclear Cu(II) complex **1** was obtained by the reaction of dpyam with $Cu(NO_3)_2 \cdot 3H_2O$ and KH_2PO_4 in a water–ethanol (45/55) mixture. The molecules are linked into dinuclear units by two bridging didentate dihydrogenphosphate groups (*endo*/*exo*) in an equatorial–equatorial configuration giving a slightly distorted square pyramidal stereochemistry. The Cu–Cu contact distance of 5.136(2) Å is unusually large due to the *exo*/*endo* binding of the phosphate bridges. Complex **2** is a polymeric copper(II) derivative with helical $[Cu(HPO_4)]_3$ units surrounded by dpyam ligands and stabilized by intermolecular hydrogen bonds. Two nearest Cu(II) ions are bridged by a tridentate hydrogenphosphate group which is didentately coordinated to one copper(II) ion, and monodentately coordinated to another in an equatorial–equatorial configuration in an unusual bridging coordination mode. Each copper(II) ion in **2** exhibits a tetrahedrally distorted square-based geometry with the third oxygen atom (Cu–O = 2.719(3) Å), from the hydrogenphosphate group weakly bound in an approximately axial position giving an extremely tetrahedrally distorted square-based pyramidal CuN_2O_2O' chromophore. The magnetic susceptibility measurements (5–300 K) reveals an antiferromagnetic interaction with J values of −2.85(1) and −26.20(2) cm^{-1} for complexes **1** and **2**, respectively. Some magneto-structural trends are discussed, along with their EPR and electronic reflectance spectra and compared with those of related complexes.

Keywords: Crystal structures; Copper(II) complexes; Dihydrogenphosphate complexes; Di-2-pyridylamine complexes

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1. Introduction

The variety of complexes of copper(II) and didentate mono(chelating) ligand with monovalent and divalent oxoanions may be grouped in many classes for each type of oxoanions depending on the coordinating nature [1–23]. Complexes with monovalent oxoanions formulated as $Cu(chelate)(anion1)_2(H_2O)_n$ or $Cu(chelate)(anion1)(anion2)(H_2O)_n$ (in which anion1 and/or anion2 = NO_2^-, NO_3^-, ClO_4^-, $CH_3CH_2COO^-$, CH_3COO^- or $HCOO^-$) were found to exhibit four classes of local molecular structures, as summarized in

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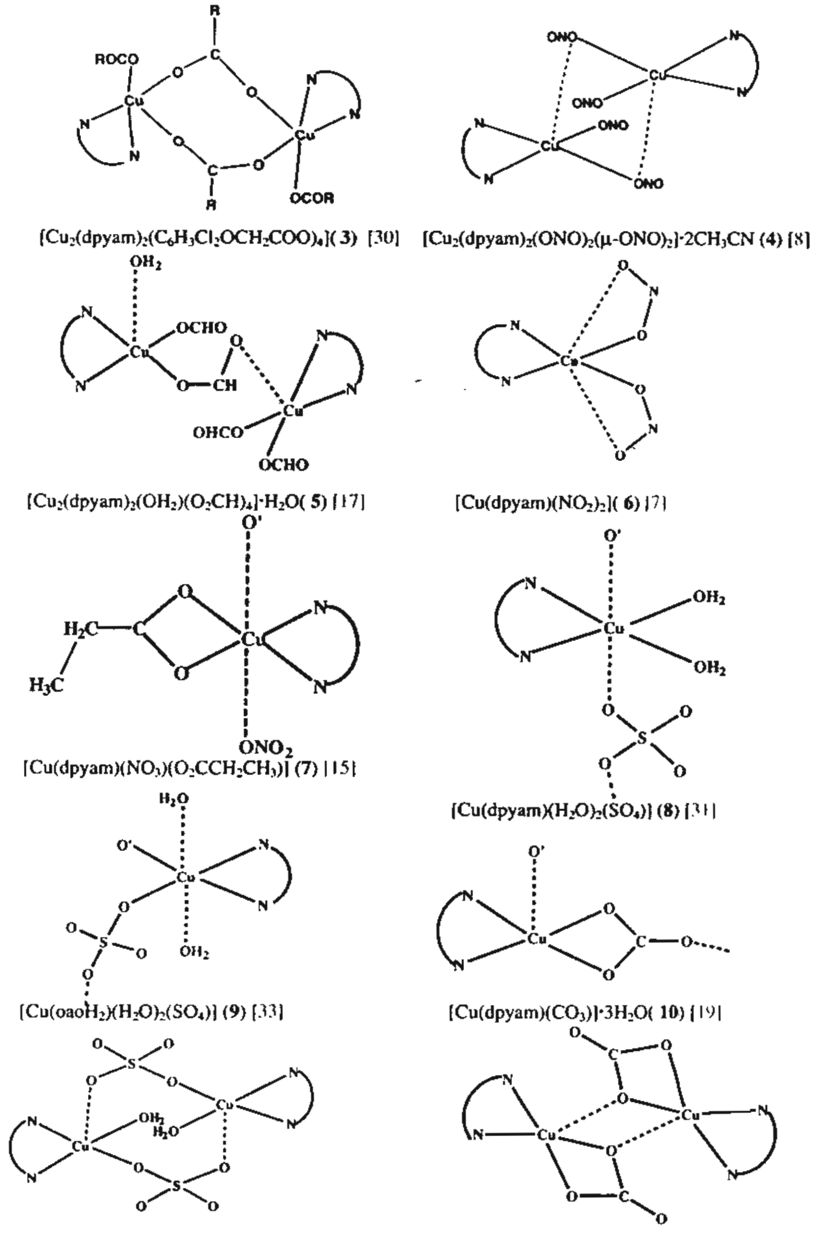
Scheme 1. These four classes can be described as follows: Class A: monomeric tetrahedrally distorted elongated octahedron with an extremely asymmetric didentate coordination of both oxoanions [1–12]; Class B: polymeric elongated tetragonal (or rhombic) octahedron with the nearly symmetric didentate coordination of a basal oxoanion and the bridging didentate coordination in the axial positions of the second one [12–15]; Class C: polymeric tetrahedrally distorted square pyramid with non-bridging monodentate and bridging didentate oxoanions [16] and Class D: dinuclear tetrahedrally distorted square pyramid with non-bridging monodentate and bridging didentate oxoanions [8,17].

Complexes with divalent oxoanions formulated as Cu(chelate)(anion)(H_2O)$_n$ (in which anion = CO_3^{2-} and



[Cu_2(dpyam)$_2$($C_6H_3Cl_2OCH_2COO$)$_4$](**3**) [30]

[Cu_2(dpyam)$_2$(ONO)$_2$(μ-ONO)$_2$]·2CH_3CN (**4**) [8]

[Cu_2(dpyam)$_2$(OH_2)(O_2CH)$_4$]·H_2O(**5**) [17]

[Cu(dpyam)(NO_2)$_2$](**6**) [7]

[Cu(dpyam)(NO_3)($O_2CCH_2CH_3$)] (**7**) [15]

[Cu(dpyam)(H_2O)$_2$(SO_4)] (**8**) [31]

[Cu(oaoH_2)(H_2O)$_2$(SO_4)] (**9**) [33]

[Cu(dpyam)(CO_3)]·3H_2O(**10**) [19]

[Cu_2(oaoH_2)$_2$(H_2O)$_2$(SO_4)$_2$](**11**) [32]

[Cu_2(dpyam)$_2$(CO_3)$_2$]·H_2O(**12**) [23]

Scheme 1. Representation of the coordination modes described to date for the mono(chelate) copper(II) complexes with monovalent and divalent oxoanions.

SO_4^{2-}) exhibit five classes of local molecular structures, namely: Class A: monomeric distorted square-based pyramid with didentate oxoanion [18]; Class B: polymeric distorted square-based pyramid with bridging tridentate oxoanions [19]; Class C: monomeric square-based pyramid with monodentate oxoanion [20]; Class D: polymeric elongated octahedron with bridging didentate oxoanions [21,22]; Class E: dinuclear distorted square-based pyramid with double bridges of tridentate oxoanions [23].

We now extended our studies towards mono-, di- and trivalent tetraoxophosphate anions. In this study, the compounds [Cu(dpyam)(μ-H_2PO_4-O,O′)(H_2PO_4)]$_2$ (1) and [Cu(dpyam)(μ_3-HPO_4-O,O′,O″)]$_n$ (2) have been synthesized and characterized. They contain monovalent $H_2PO_4^-$ and divalent HPO_4^{2-} oxoanions and their X-ray structures, spectroscopic properties and magnetic behaviour are investigated and discussed in the context of a magneto-structural correlation study. These two structures appear to belong to class D and class B, for **1** and **2**, respectively.

2. Experimental

2.1. General

All reagents were commercial grade materials and were used without further purification. 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 Centre, Chulalongkorn University.

2.2. Syntheses of the compounds

2.2.1. [Cu(dpyam)(μ-H_2PO_4-O,O′)(H_2PO_4)]$_2$ (1) and [Cu(dpyam)(μ_3-HPO_4-O,O′,O″)]$_n$ (2)

An aqueous solution (30 ml) of $Cu(NO_3)_2 \cdot 3H_2O$ (0.241 g, 1.0 mmol) was added to a solution of dpyam (0.171 g, 1.0 mmol) in ethanol (15 ml) and followed by an aqueous solution (20 ml) of potassium dihydrogenphosphate (0.272 g, 2.0 mmol). The resulting green solution was allowed to evaporate at room temperature. After several days, dark green crystals of [Cu(dpyam)(μ_3-HPO_4-O,O′,O″)]$_n$ (2) (*Anal.* Calc. for $C_{10}H_{10}CuN_3O_4P$: C, 36.32; H, 3.05; N, 12.71. Found: C, 36.25; H, 2.98; N, 12.67%) were deposited. Yield: ca. 40%. Subsequently, green needle crystals of [Cu_4(dpyam)$_4$(μ_3,η^3-HPO_4)$_2$(NO_3)$_2$(H_2O)$_2$](NO_3)$_2 \cdot 2H_2O$ (*Anal.* Calc. for $C_{40}H_{46}Cu_4N_{16}O_{24}P_2$: C, 33.13; H, 3.19; N, 15.45. Found: C, 33.20; H, 3.04; N, 15.52%) were deposited in the second crystallization. Yield: ca. 30%. This complex was obtained as a side product and has also been characterized crystallographically (to be published separately). Greenish-blue crystals of [Cu(dpyam)(μ-H_2PO_4-O,O′)(H_2PO_4)]$_2$ (1) were obtained in the final crystallization. They were filtered off, washed with the

Table 1
Crystal and refinement data for complexes 1 and 2

Complex	1	2
Molecular formula	$C_{20}H_{26}Cu_2N_6O_{16}P_4$	$C_{10}H_{10}CuN_3O_4P$
Molecular weight	857.44	330.72
T (K)	293(2)	293(2)
Crystal system	triclinic	trigonal
Space group	$P\bar{1}$	$P3/2$
a (Å)	8.0347(1)	9.6644(1)
b (Å)	10.0264(1)	9.6644(1)
c (Å)	10.5912(1)	10.6841(2)
α (°)	83.217(1)	90
β (°)	70.490(1)	90
γ (°)	69.356(1)	120
V (Å^3)	752.58(2)	864.21(2)
Z	2	2
D_{calc} (g cm^{-3})	1.892	1.271
μ (mm^{-1})	1.712	1.365
$F(000)$	434	334
Crystal size (mm)	0.15×0.35×0.50	0.28×0.30×0.20
θ Range (°)	2.04–30.48	2.43–30.48
Number of reflections collected	5631	6496
Number of unique reflections	4101	3042
Data/restraints/parameter	4101/0/269	3042/1/212
Goodness-of-fit	1.065	1.030
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0261$, $wR_2 = 0.0752$	$R_1 = 0.0186$, $wR_2 = 0.0451$
R indices (all data)	$R_1 = 0.0281$, $wR_2 = 0.0759$	$R_1 = 0.0192$, $wR_2 = 0.0452$
Largest difference peak and hole (e Å^{-3})	0.580 and −0.509	0.252 and −0.321

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

mother liquid and dried in air. Yield: ca. 20%. (*Anal.* Calc. for $C_{20}H_{26}Cu_2N_6O_{16}P_4$: C, 28.05; H, 3.03; N, 9.80. Found: C, 28.14; H, 2.93; N, 9.74%).

2.3. Crystal structure analyses

Reflection data for complexes **1** and **2** were collected at 293 K on a 1K Bruker SMART CCD area-detector diffractometer using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Data reduction and cell refinements were performed using the program SAINT [24]. An empirical absorption correction by using the SADABS [25] program was applied, which resulted in transmission coefficients ranging from 0.790 to 1.000 for **1** and from 0.854 to 1.000 for **2**. The structures ware 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 [26] software package. All hydrogen atoms in **1** and **2** were located by difference synthesis and refined isotropically. The molecular graphics were created by using SHELXTL-PC. The crystal and refinement details for **1** and **2** are listed in Table 1.

2.4. Physical measurements

IR spectra were recorded on a Spectrum One Perkin–Elmer FT-IR spectrophotometer as KBr pellets in the 4000–450 cm^{-1} spectral range. Diffuse reflectance measurements from 9090 to 20 000 cm^{-1} were recorded as polycrystalline samples using a Perkin–Elmer Lambda 2S spectrophotometer equipped with an intergrating sphere attachment. Barium sulfate was used as the reflectance standard. X-band powder EPR spectra were 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 magnetization of the sample holder and for diamagnetic contributions, which were estimated from the Pascal constants.

3. Results and discussion

3.1. Description of the crystal structures

3.1.1. $[Cu(dpyam)(\mu\text{-}H_2PO_4\text{-}O,O')(H_2PO_4)]_2$ (1)

The structure is depicted in Fig. 1 together with the numbering scheme. Selected bond distances and angles are listed in Table 2. The centrosymmetric dinuclear compound consists of two $[Cu(dpyam)(\mu\text{-}H_2PO_4\text{-}O,O')(H_2PO_4)]$ units being doubly bridged by two didentate dihydrogenphosphato anions. The local molecular structure of the copper atom involves a square pyramidal CuN_2O_2O' chromophore. The basal plane consists of two oxygen atoms of the two bridging dihydrogenphosphato groups, O(5) and O(8A) and of dpyam ligand coordinated through two nitrogen atoms. The dpyam ligand chelates in the square plane, almost symmetrically, with Cu–N distances of 1.991(1) and 1.997(1) Å and a bite angle of 88.1(1)°. The equatorial Cu(1)–O(8A) and Cu(1)–O(5) bond distances are slightly shorter with values of 1.964(1) and 1.987(1) Å. The fifth axial coordination site is occupied by one oxygen atom of non-bridging monodentate dihydrogenphosphato group at the Cu–O distance of 2.271(1) Å. The four in-plane atoms, N(1), N(2), O(5) and O(8A) are essentially planar (r.m.s. deviation 0.0598 Å), with a slightly tetrahedral twist (dihedral angles between the CuN_2 and CuO_2 planes = 14.0°). The Cu atom lies 0.16 Å above this plane towards O(1). The tetragonality, $T = 0.874$ based on the changes in bond lengths ($T =$ the mean in-plane bond length/the mean out-of-plane bond length). The τ-value

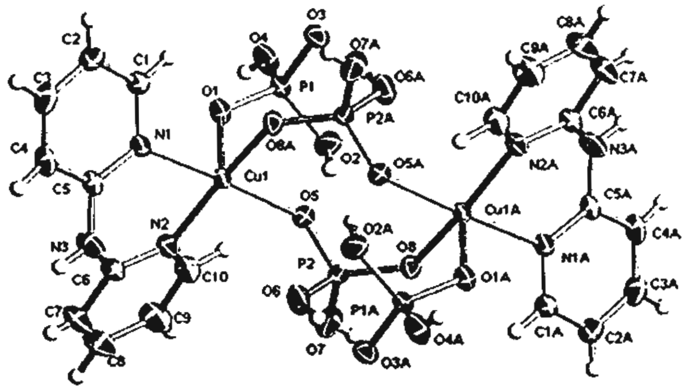


Fig. 1. ORTEP 50% probability plot of $[Cu(dpyam)(\mu\text{-}H_2PO_4)(H_2PO_4)]_2$ (1). H-atoms are omitted for clarity. Atoms with an "A" are generated by an inversion centre.

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

Bond lengths				
Cu(1)–O(8)A	1.964(1)	Cu(1)–O(5)	1.987(1)	
Cu(1)–N(1)	1.991(1)	Cu(1)–N(2)	1.997(1)	
Cu(1)–O(1)	2.271(1)	P(1)–O(1)	1.512(1)	
P(1)–O(3)	1.519(1)	P(1)–O(4)	1.558(1)	
P(1)–O(2)	1.581(1)	P(2)–O(8)	1.506(1)	
P(2)–O(5)	1.518(1)	P(2)–O(7)	1.558(1)	
P(2)–O(6)	1.564(1)	Cu(1)–Cu(1)A	5.136(2)	
Bond angles				
O(8)A–Cu(1)–O(5)	89.7(1)	O(8)A–Cu(1)–N(1)	89.0(1)	
O(5)–Cu(1)–N(1)	174.1(1)	O(8)A–Cu(1)–N(2)	167.0(1)	
O(5)–Cu(1)–N(2)	91.8(1)	N(1)–Cu(1)–N(2)	88.1(1)	
O(8)A–Cu(1)–O(1)	96.0(1)	O(5)–Cu(1)–O(1)	91.9(1)	
N(1)–Cu(1)–O(1)	94.1(1)	N(2)–Cu(1)–O(1)	96.8(1)	
O(1)–P(1)–O(3)	115.1(1)	O(1)–P(1)–O(4)	112.2(1)	
O(3)–P(1)–O(4)	106.9(1)	O(1)–P(1)–O(2)	109.2(1)	
O(3)–P(1)–O(2)	108.5(1)	O(4)–P(1)–O(2)	104.1(1)	
O(8)–P(2)–O(5)	115.6(1)	O(8)–P(2)–O(7)	109.6(1)	
O(5)–P(2)–O(7)	105.9(1)	O(8)–P(2)–O(6)	112.6(1)	
O(5)–P(2)–O(6)	105.6(1)	O(7)–P(2)–O(6)	106.8(1)	
P(2)–O(5)–Cu(1)	130.9(1)	P(1)–O(1)–Cu(1)	122.9(1)	
D–H···A (°)	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)
Hydrogen-bonding parameters				
N(3)–H(5)···O(3) [$x, 1+y, z$]	0.82(2)	2.362(19)	3.1603(19)	165(2)
O(4)–H(41)···O(1) [$-x, 1-y, 2-z$]	0.57(3)	2.02(3)	2.5825(18)	169(6)
O(6)–H(61)···O(3) [$1-x, 1-y, 1-z$]	0.79(3)	1.84(3)	2.631(2)	172(3)
O(7)–H(71)···O(3) [$1+x, y, z$]	0.62(4)	2.05(4)	2.648(2)	164(5)

Symmetry code: A, $-x+1, -y+1, -z+1$.

defined to describe the degree of trigonal distortion is 0.12 (τ describes the relative amount of trigonality; $\tau = 0$ for square pyramid and $\tau = 1$ for trigonal bipyramid) [27], so the geometry around the Cu(II) atom can be best described as square-based pyramidal, with only a slight trigonal distortion. The Cu–Cu distance is 5.136(2) Å.

The O(8)–P(2)–O(5) bridging angle of 115.7(1)° is larger than 109.5° of the ideal tetrahedral geometry, and the remaining angles involve less deviation from 109.5° [O(5)–P(2)–O(7) 105.9(1)°, O(5)–P(2)–O(6) 105.6(1)°, O(7)–P(2)–O(6) 106.8(1)° and O(8)–P(2)–O(6) 112.6(1)°]. The coordinated P–O bonds, 1.518(1) and 1.506(1) Å, are shorter than the uncoordinated P–OH bonds, 1.564(1) and 1.559(1) Å. These differences are normally found for the two-coordinate bridging coordination of the dihydrogenphosphate anion [28]. The non-bridging monodentate dihydrogenphosphato group involves O–P–O angles ranging from 104.1(1)° to 115.1(1)°. The P–OH bonds, 1.558(1) and 1.581(1) Å, are longer than the P=O bonds, 1.512(1) and 1.519(1) Å, which is in usual observation. The uncoordinated P=O bond distance, 1.519(1) Å, is slightly longer than the coordinated one, 1.511(1) Å, which is unusual. This difference arises from the hydrogen bond involved to the uncoordinated P=O bond. The P=O distances in both the monodentate dihydrogenphosphato group and the dihydrogenphosphato bridge are ranging from 1.506(1) to 1.519(1) Å, while the P–OH bond distances vary from 1.558(1) to 1.581(1) Å. This behaviour is consistent with the general observation that P–OH bonds are longer than P=O bonds in primary and secondary phosphates [28].

The lattice structures are stabilized by a hydrogen bonding network between the amine N and the oxygen atom of the non-bridged dihydrogenphosphate anion with a distance of 3.160(1) Å, and between oxygen atoms of different dihydrogenphosphate groups (O···O distances vary from 2.582(1) to 2.648(2) Å). Details of hydrogen bonding are given in Table 2 and a projection of the lattice is shown in Fig. 2.

3.1.2. [Cu(dpyam)(μ_3-HPO$_4$-O,O′,O″)]$_n$ (2)

The structure is depicted in Fig. 3 together with the numbering scheme. Selected bond distances and angles are listed in Table 3. The structure consists of a neutral and polymeric chains of [Cu(dpyam)(μ_3-HPO$_4$-O,O′,O″)] bridged by tridentate hydrogenphosphato ligands. The local molecular structure of the copper atom involves square pyramidal CuN$_2$O$_2$O′ chromophore in an equatorial–equatorial configuration. The basal plane consists of two oxygen atoms from two equivalent bridging hydrogenphosphato groups and of a dpyam ligand coordinated through two nitrogen atoms. The dpyam ligand chelates in the tetragonal plane, almost symmetrically, with Cu–N distances of 1.969(1) and

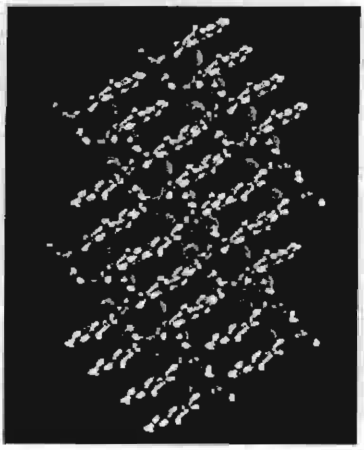


Fig. 2. Showing the lattice structure of complex 1.

1.994(1) Å, and a bite angle of 92.0(6)°. The equatorial Cu(1)–O(1) and Cu(1)–O(4) bond distances are slightly shorter with values of 1.946(1) and 1.919(1) Å. The third oxygen atom from hydrogenphosphate group is bent towards the Cu atom to complete a fifth coordination site in an axial position at a much longer distance of 2.719(2) Å, generating a distorted square-based pyramidal stereochemistry. The four in-plane atoms, N(1), N(2), O(1) and O(4) are not planar (r.m.s. deviation 0.562 Å) and display a marked tetrahedral twist (dihedral angles between the CuN_2 and CuO_2 planes amounts to 45.56°). The Cu atom lies 0.202 Å above this plane towards O(2A). The copper chromophore can be described as having an extremely tetrahedrally distorted square pyramidal geometry with the tetragonality, T of 0.720 and τ-value of 0.12. The Cu–Cu distance is 5.955(2) Å.

The hydrogenphosphato group in this compound involves a quite unusual tridentate μ-κ-O,O′,O″ coordination mode: didentately coordinated to one copper chromophore and monodentately bonded to another. To the best of our knowledge, this coordination mode of the bridging hydrogenphosphate present in complex **2** is unique for the transition metal complexes.

The coordinated P=O bonds, 1.519(1), 1.510(2) and 1.531(1) Å, are shorter than the uncoordinated P–OH bond, 1.588(2) Å. This is usually found for the three-coordinate bridging coordination of the hydrogenphosphate anion [29]. The tridentate hydrogenphosphato group involves O–P–O angles ranging from 101.9(1)° to 111.7(1)°. The lattice structure is stabilized by a hydrogen-bonding network between the amine N and an oxygen atom of the hydrogenphosphate group with a short contact distance of 2.663(3) Å and between the oxygen atom of the hydrogenphosphate group to the oxygen atom of another hydrogenphosphato group with a contact distance of 2.528(3) Å. The structure contains chains of Cu ions in the c-direction bridged by the HPO_4^{2-} ions in a trigonal way. Two nearest Cu(II) ions are bridged by a tridentate hydrogenphosphate group which is didentately coordinated to one copper(II) ion, and monodentately coordinated to another in an equatorial–equatorial configuration in an unusual bridging coordination mode. The helical arrangement of the Cu–HPO_4 chain is clearly visible in Fig. 4 with the N ligands at the outside stacked in the direction of the three-fold screw axis.

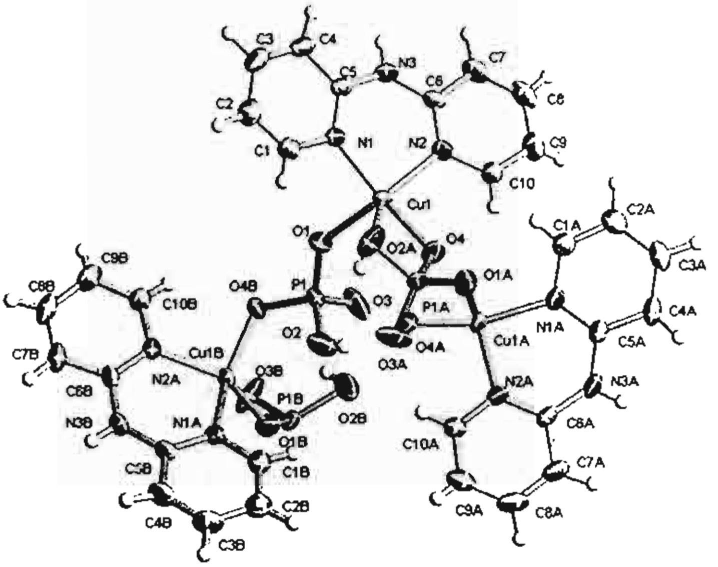


Fig. 3. ORTEP 50% probability plot of the cation in $[Cu(dpyam)(\mu_3\text{-}HPO_4)]_n$ (**2**). H-atoms are omitted for clarity. Atoms with an "A" and "B" are generated by symmetry operations.

Table 3
Selected bond lengths (Å) an angles (°) with e.s.d.s. in parentheses of compound **2**

Bond lengths			
Cu(1)–O(4)	1.919(1)	Cu(1)–O(1)	1.946(1)
Cu(1)–N(1)	1.969(1)	Cu(1)–N(2)	1.994(1)
P(1)–O(3)	1.510(1)	P(1)–O(1)	1.519(1)
P(1)–O(4)A	1.531(1)	P(1)–O(2)	1.588(2)
Cu(1)–O(2)A	2.719(3)	Cu(1)–Cu(1)A	5.955(2)
Bond angles			
O(4)–Cu(1)–O(1)	101.6(1)	O(4)–Cu(1)–N(1)	149.7(1)
O(1)–Cu(1)–N(1)	91.4(1)	O(4)–Cu(1)–N(2)	93.6(1)
O(1)–Cu(1)–N(2)	142.6(1)	O(1)–Cu(1)–N(2)	92.0(1)
O(3)–P(1)–O(1)	111.7(1)	O(3)–P(1)–O(4)A	111.1(1)
O(1)–P(1)–O(4)A	111.6(1)	O(3)–P(1)–O(2)	110.7(1)
O(1)–P(1)–O(2)	109.3(1)	O(4)A–P(1)–O(2)	101.9(1)

Symmetry code: A, $x+y+1, -x+1, z+1/3$.

3.2. Structural comparison

The square pyramidal CuN_2O_2O' chromophore of complex **1** corresponds to the square pyramidal CuN_2O_2O' chromophore observed from the copper environments of the known dinuclear structures; $[Cu_2(dpyam)_2(C_6H_3Cl_2OCH_2\text{-}COO)_4]$ (**3**) [30], $[Cu_2(dpyam)_2(ONO\text{-}O,O')_2(\mu\text{-}ONO\text{-}O)_2]\cdot 2CH_3CN$ (**4**) [8] and $[Cu_2(dpyam)_2(OH_2)(O_2CH)_4]\cdot H_2O$ (**5**) [17] (Table 4 and Scheme 1). The structure of **1** and **3**, confirms the two-coordinate bridging coordination of oxoanions in equatorial–equatorial and axial–equatorial configurations, respectively. Additionally, there are some differences in the five-coordinate distortion ($\tau = 0.12$ and 0.48 for **1** and **3**, respectively), along with the tetragonality $T = 0.874$ and 0.897 for **1** and **3**, respectively. The CuN_2O_2O' chromophore of **1** is best described as square-based pyramidal with a slight trigonal distortion, while that of **3** can be described as having an intermediate geometry between regular square pyramid and trigonal bipyramidal. The nitrite groups in **4** act as two non-bridging monodentate anions and two bridging monodentate anions while the formate groups in **5** act as three non-bridging monodentate anions and a single bridging didentate anion. The copper atoms in **4** and **5** are bridged by oxoanion in an axial–equatorial configuration that is different from the equatorial–equatorial configuration in **1**. The monomeric Cu(II) complexes shows tetrahedrally distorted elongated tetragonal-octahedral geometry with the long off-the-z-axis coordination of the second oxygen atoms from each OXO^- ligand in the axial positions (complex **6**). While an important feature of the structures of polymeric complexes is the two-coordinate bridging coordination of the oxoanion, which shows an unsymmetrical bonding to the Cu atom in the elongated rhombic octahedral configuration (complex **7**).

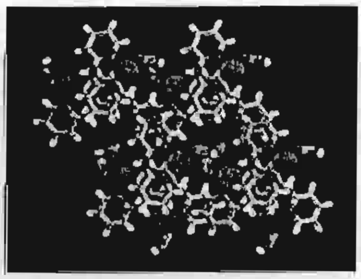


Fig. 4. Showing the lattice structure of complex **2**.

The polymeric structure of complex **2** is comparable to those of complexes with divalent sulfate anion $[Cu(dpyam)(H_2O)_2(SO_4)]$ (**8**) [31], $[Cu(en)(H_2O)_2(SO_4)]$ [21], $[Cu(bpy)(H_2O)_2(SO_4)]$ [22], $[Cu(phen)(H_2O)_2(SO_4)]$ [32], and $[Cu(oaoH_2)(H_2O)_2(SO_4)]$ (**9**) [33] all having a polymeric structure with bridging didentate sulfate groups and coordinated water and are also comparable to the compound with a divalent carbonate group $[Cu(dpyam)(CO_3)]\cdot 3H_2O$ (**10**) [34] (see Scheme 1 and Table 5). The Cu atoms in **10** are bridged by the carbonate anion in an axial–equatorial configuration, while in complex **2** the Cu atoms are bridged by the HPO_4^{2-} oxoanion in an equatorial–equatorial configuration. However, they differ from the square-pyramidal monomeric complexes, $[Cu(tmen)(H_2O)_2(SO_4)]\cdot H_2O$ [20], $[Cu(dpyam)(CO_3)(H_2O)]\cdot 2H_2O$ [18] which contains a monodentate sulfate and didentate carbonate anion, respectively. The dinuclear complexes $[Cu(oaoH_2)(H_2O)(SO_4)]_2$ (**11**) [33] and $[Cu(dpyam)(CO_3)]_2(H_2O)$ (**12**) [23] have a square pyramidal structure with bridging didentate sulfate and carbonate groups in an axial–equatorial configuration.

3.3. EPR spectra and magnetic properties

The polycrystalline EPR spectrum of compound **1** reveals at room temperature and at 77 K an axial signal with $g_{\parallel} = 2.32$ and $g_{\perp} = 2.07$. For compound **2** at room temperature an unresolved isotropic signal is obtained with $g = 2.13$. At 77 K a more resolved signal is obtained for compound **2** with $g_{\parallel} = 2.29$ and $g_{\perp} = 2.08$. The signals for both compounds are consistent with the $d_{x^2-y^2}$ ground state and a distorted square-based pyramidal geometry. No triplet signal has been observed. Apparently, the dinuclear units in **1** are not isolated from one another, resulting in exchange narrowing.

The magnetic susceptibility of powdered samples were measured from 5 to 300 K. The magnetic properties of compound **1** are given in Fig. 5 in the form of χ_M and $\chi_M T$ versus T plots. The $\chi_M T$ value at 300 K of 0.805 $cm^3\ mol^{-1}$ K, is in agreement with uncoupled spin 1/2 centres (0.375 $cm^3\ mol^{-1}$ K per centre with $g = 2$). Decrease of $\chi_M T$ is observed upon lowering the temperature starting from 50 K down to 0.69 $cm^3\ mol^{-1}$ K at 5 K, which is indicative for a very weak antiferromagnetic interaction.

Table 4
Structural data and electronic spectra of complex **1** and relevant complexes

Complex	Coordination geometry	τ	Chromophore	Tetragonality	Tetrahedral twist (°)	Bridging configuration	J value (cm^{-1})	References
Dinuclear								
$[Cu(dpyam)(\mu\text{-}H_2PO_4\text{-}O,O')(H_2PO_4)]_2$ (**1**)	dinuclear SP	0.120	CuN_2O_3	0.874	14.00	equatorial–equatorial	−2.85(1)	this work
$[Cu(dpyam)(C_6H_3Cl_2OCH_2COO)_2]_2$ (**3**)	dinuclear dist.SP	0.480	CuN_2O_3	0.897		axial–equatorial	−0.8	[30]
$[Cu(dpyam)(ONO\text{-}O,O)(\mu\text{-}ONO\text{-}O)]_2\cdot 2CH_3CN$ (**4**)	dinuclear dist.SP	0.000	CuN_2O_3	0.813		axial–equatorial		[8]
$[Cu_2(dpyam)_2(O_2CH)_4(OH_2)]\cdot H_2O$ (**5**)	dinuclear dist.SP	0.113, 0.096	CuN_2O_3	0.841	16.01, 19.35	axial–equatorial		[17]
Monomeric								
$[Cu(dpyam)(NO_2)_2]$ (**6**)	monomeric dist.oct.	0.020	$CuN_2O_2O'_2$	0.813	31.16			[7]
$[Cu(dpyam)(O_2CCH_3)_2]\cdot 2H_2O$	monomeric dist.oct.		$CuN_2O_2O'_2$	0.764	34.38			[6]
$[Cu(bpy)(NO_3)_2]$	monomeric dist.oct		$CuN_2O_2O'_2$	0.776	27.7			[9]
$[Cu(TIMM)(NO_2)_2]$	monomeric dist.oct		$CuN_2O_2O'_2$	0.792				[11]
$[Cu(BimOBz)(NO_3)_2]$	monomeric dist.oct		$CuN_2O_2O'_2$	0.779	15.6			[12]
Polymeric								
$[Cu(dpyam)(NO_3)_2]$	polymeric elong.oct.		$CuN_2O_2O'_2$	0.824, 0.817	7.00, 3.80			[10]
$[Cu(dpyam)(NO_3)(O_2CCH_2CH_3)]$ (**7**)	polymeric elong.oct.		$CuN_2O_2O'_2$	0.753		axial–equatorial		[15]
$[Cu(dpyam)(O_2CCH_3)(O_2ClO_2)]\cdot H_2O$	polymeric elong.oct.		$CuN_2O_2O'_2$	0.765		axial–axial		[13]

dpyam, di-2-pyridylamine; bpy, 2,2′-bipyridine; TIMM, Tris[2-(1-methyl)imidazolyl]methoxymethane; BimOBz, bis(1-methyl-4,5-diphenylimidaz-2-oyl)(benzyloxy)methane; dist.oct., distorted octahedral; dist.SP, distorted square pyramidal; elong.oct., elongated octahedral.

The magnetic data were fitted for two interacting $S = 1/2$ centres, based on the general Hamiltonian [34a]: $H = -JS_1 \cdot S_2$, in which the exchange parameter J is negative for antiferromagnetic and positive for ferromagnetic interaction. The data were fitted to the equation given in the literature [34a]. Also a temperature independent paramagnetism (TIP) of the Cu(II) ions has been considered. The resulting best fit parameters, corresponding to the full lines in Fig. 5, were $J = -2.85(1)$ cm^{-1} and $TIP = 0.85 \times 10^{-5}$ cm^3 mol^{-1} with g fixed to 2.00.

The magnetic properties of compound **2** are given in Fig. 6 in the form of χ_M and $\chi_M T$ versus T plots. From 300 K onwards the magnetism is steadily decreasing down to 0.01 cm^3 mol^{-1} K at 5 K, indicative for a medium antiferromagnetic coupling between neighbouring Cu(II) ions. The maximum in χ_M, expected for such couplings, is observed at 45 K, and a small Curie tail indicative of paramagnetic impurity is detected below 15 K. The data were fitted using the theoretical expression for a uniform Heisenberg chain [34]. The possibility of a percentage of paramagnetic impurity (p) and the TIP of the Cu(II) ions have been also taken into account. The resulting best fit parameters, corresponding to the full lines in Fig. 6 were $J = -26.20(2)$ cm^{-1}, $g = 1.98(1)$, $TIP = 1 \times 10^{-5}$ cm^3 mol^{-1} and $p = 0.3(1)\%$.

Because of the square pyramidal geometry in compounds **1** and **2** the spin density is mostly in the $d_{x^2-y^2}$ orbitals of the copper(II) ions. The $H_nPO_4^{(3-n)-}$ bridges, joining the copper atoms in an equatorial–equatorial configuration, the superexchange coupling through the phosphate anion (Cu–O–P–O–Cu) can be expected to be non-negligible. The antiferromagnetic couplings found in compounds **1** and **2** are thus in agreement with this structural feature and the large Cu–Cu distances.

3.4. Electronic and IR spectra

The electronic diffuse reflectance spectrum of **1** shows a broad band at 14.9×10^3 cm^{-1}. This observed single broad peak is consistent with the square pyramidal stereochemistry and assigned to be d_{z^2}, d_{xy}, d_{xz}, $d_{yz} \rightarrow d_{x^2-y^2}$ transition. Complex **2** exhibits a main peak at 14.4×10^3 cm^{-1} with a shoulder at 11.2×10^3 cm^{-1}. The transitions may be assigned as the d_{xy}, $d_{z^2} \rightarrow d_{x^2-y^2}$ transition for the low-energy peak and the d_{xz}, $d_{yz} \rightarrow d_{x^2-y^2}$ transition for the high-energy peak.

Table 5
Structural data and electronic spectra of complex **2** and relevant complexes

Complex	Coordination geometry	τ	Chromophore	Tetragonality	Tetrahedral twist (°)	Configuration	*J* value (cm^{-1})	References
Polymer								
[Cu(dpyam)(μ_3-HPO$_4$-O,O′,O″)]$_n$ (**2**)	polymeric dist.SP	0.120	CuN_2O_3	0.720	45.5	equatorial–equatorial	−26.20(2)	this work
Cu(dpyam)(CO$_3$)·3H$_2$O (**8**)	polymeric dist. SP	0.003	CuN_2O_2O'	0.861		axial–equatorial		[19]
[Cu(dpyam)(H$_2$O)$_2$(SO$_4$)] (**9**)	polymeric elong.oct		$CuN_2O_2O'_2$	0.815	15.8	axial–axial		[31]
[Cu(phen)(H$_2$O)$_2$(SO$_4$)]	polymeric elong. oct		$CuN_2O_2O'_2$	0.808		axial–axial	−3.8	[32]
[Cu(oaoH$_2$)(H$_2$O)$_2$(SO$_4$)] (**10**)	polymeric dist.oct		$CuN_2O_2O'_2$	0.832		axial–equatorial	−1.0	[33]
Monomer								
[Cu(dpyam)(CO$_3$)(H$_2$O)]·2H$_2$O	monomeric dist.SP	0.096	CuN_2O_3	0.899	50.3			[18]
[Cu(tmen)(H$_2$O)$_2$(SO$_4$)]·H$_2$O	monomeric dist.SP	0.085	CuN_2O_3	0.908				[20]
Dimer								
[Cu(oaoH$_2$)(H$_2$O)(SO$_4$)]$_2$ (**11**)	dinuclear dist.TP	0.145	CuN_2O_3	0.774		axial–equatorial	−1.27	[33]
[Cu(dpyam)(CO$_3$)]$_2$·H$_2$O (**12**)	dinuclear dist.SP	0.220	CuN_2O_3	0.815	5.9[a], 5.1[b]	axial–equatorial	−9.9	[23]

dpyam, di-2-pyridylamine; bpy, 2,2′-bipyridine; phen, 1,10-phenanthroline; oaoH$_2$, oxamide oxime; tmen, *N,N,N′,N′*-tetramethylethylenediamine; dist.oct., distorted octahedral; dist.SP, distorted square pyramidal; dist.TP, distorted tetragonal pyramidal.

[a] Chromophore A.

[b] Chromophore B.

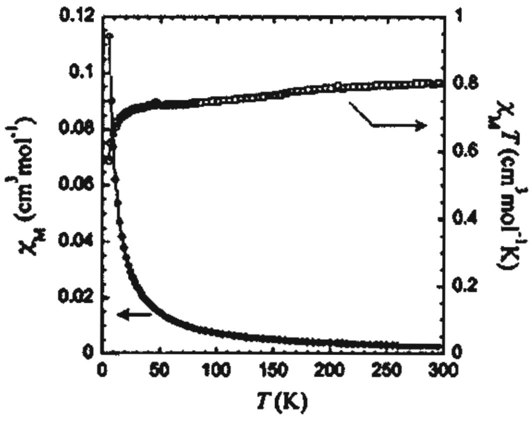


Fig. 5. Plots of temperature dependence of the molar magnetic susceptibility χ_M (○) and the $\chi_M T$ product (□) for compound **1**. The solid lines represent the calculated curves for the parameters $J = -2.85(1)$ cm^{-1} (see text).

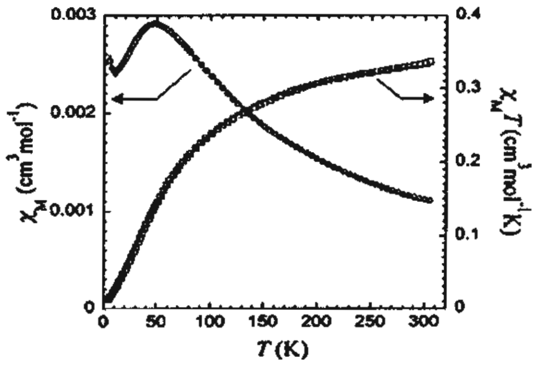


Fig. 6. Plots of temperature dependence of the molar magnetic susceptibility χ_M (○) and the $\chi_M T$ product (□) for compound **2**. The solid lines represent the calculated curves for the parameters $J = -26.20(2)$ cm^{-1}, $g = 1.98(1)$ (see text).

The infrared spectrum of complex **1** shows bands at ca. 1353; 1330, 1112 and 1049; 975 and 881 cm^{-1} and a broad band at ca. 522–488 cm^{-1} characteristic of P–O–H in-plane deformation, ν(P–O), ν(P–O–(H)) and δ(O–P–O), respectively, which corresponds to the literature [28,35–38]. The IR spectrum of complex **2** shows two strong and one medium band at 1092, 1056 and 968 cm^{-1}, characteristic of a ν(P–O). The δ(O–P–O) vibrations are found at 585 and 555 cm^{-1} [39–41].

4. Conclusions

In this study, two Cu(II) compounds with the ligand dipyam containing phosphato bridges are synthesized and characterized and have both a weakly distorted square pyramidal geometry. Compound **1** is a dinuclear compound bridged by two phosphato anions. The Cu–Cu interaction is very weak antiferromagnetic ($J = -2.85(1)\ \mathrm{cm}^{-1}$) and is generated via the phosphato bridge. Compound **2** is a polynuclear compound bridged by a phosphato group which is didentately coordinated to one copper atom and monocoordinated to the next copper atom. The magnetic interaction is weak antiferromagnetic ($J = -26.20(2)\ \mathrm{cm}^{-1}$) and occurs also via the phosphato group in the Cu chain.

5. Supplementary material

Crystallographic data for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC Nos. 230043 and 230044 for structures **1** and **2**, respectively. 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, www:http://www.ccdc.cam.ac.uk).

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Note

An unprecedented tetranuclear Cu(II) cluster, exclusively bridged by two μ_3,η^3-hydrogenphosphate anions: synthesis, structure, and magnetic properties

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Abstract

A novel tetranuclear μ_3,η^3-HPO_4^{2-} Cu(II) complex with a new coordination mode of a hydrogenphosphato bridge, $[Cu_4(\text{di-2-pyridylamine})_4(\mu_3,\eta^3\text{-}HPO_4)_2(H_2O)_2(NO_3)_2](NO_3)_2(H_2O)_2$ has been synthesised and characterised structurally, spectroscopically and magnetically. The geometry around the Cu(II) ions is distorted square pyramidal for Cu1 and an intermediate between square pyramidal and trigonal pyramidal. The magnetic susceptibility measurements have been fit for a weak antiferromagnetic interaction of $J = -10.3(1)$ cm^{-1} between outer Cu ions and $J = -5.3(2)$ cm^{-1} between inner Cu atoms.

Keywords: Tetranuclear complexes; Copper(II) cluster; Hydrogenphosphate complexes; Di-2-pyridylamine; Magnetism

1. Introduction

In the past few years, the design and synthesis of inorganic–organic hybrid materials have been increasingly developed for their potential application in the fields of catalysts, biology, electrical conductivity, magnetism and photochemistry [1]. A number of polynuclear hydrogenphosphate-bridged metal systems have been structurally characterised [2] in relation to bioinorganic models [3] and the relationship between the hydrogenphosphato bridging mode and magnetic properties [4]. In recent years, many researches have focused on the synthesis of inorganic–organic hybrid frameworks containing the phosphate anion (and derivatives) in a bridging mode [5–9]. Very recently, a tetranuclear compound with 2,2′-bipyridine and a μ_4-PO_4 bridging mode was published; however, the bridge also contained a bridging carbonate anion [10].

To obtain more insight into bridging phosphate anions, we now extended that study using the ligand di-2-pyridylamine (abbreviated as dpyam). In the present study, an unprecedented hydrogenphosphato-bridging Cu(II) complex, $[Cu_4(dpyam)_4(\mu_3,\eta^3\text{-}HPO_4)_2(H_2O)_2(NO_3)_2](NO_3)_2(H_2O)_2$ (**1**), with different coordination geometries of the hydrogenphosphato bridges, is described and investigated structurally and magnetically. To the best of our knowledge, this is also the first Cu(II) tetranuclear compound with a (μ_3,η^3-HPO_4-O′,O′,O″) phosphate binding mode.

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2. Experimental

2.1. Materials and measurements

All reagents were commercial grade materials and were used without further purification. Elemental analyses (C, H, N) were determined on a Perkin–Elmer PE2400 CHNS/O Analyser. IR spectra were recorded on a Spectrum One Perkin–Elmer FT-IR spectrophotometer as KBr pellets in the 4000–450 cm^{-1} spectral range. Diffuse reflectance measurements from 9090 to 20 000 cm^{-1} were 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 spectra were 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 Gauss). Data were corrected for magnetisation of the sample holder and for diamagnetic contributions, which were estimated from the Pascal constants.

2.2. Synthesis of the compound 1

2.2.1. $[Cu_4(dpyam)_4(\mu_3,\eta^3\text{-}HPO_4)_2(NO_3)_2(H_2O)_2](NO_3)_2(H_2O)_2$

An aqueous solution (30 ml) of $Cu(NO_3)_2{\cdot}3H_2O$ (0.24 g, 1.0 mmol) was added to a solution of di-2-pyridylamine (0.17 g, 1.0 mmol) in ethanol (15 ml) and followed by an aqueous solution (20 ml) of potassium dihydrogenphosphate (0.27 g, 2.0 mmol). The green solution was allowed to slowly evaporate at room temperature. After several days, dark green crystals were deposited, which have been characterised as being the compound $[Cu(dpyam)(\mu\text{-}HPO_4)]_n$. After filtration, the remaining solution was allowed to evaporate in the open air and after a few days green needle shaped crystals of complex 1 were deposited in a yield of 56%. The crystals were filtered, washed with the mother liquid and dried in air. Elemental *Anal.* Calc. for $C_{40}H_{46}Cu_4N_{16}O_{24}P_2$: C, 33.13; H, 3.19; N, 15.45. Found: C, 33.20; H, 3.04; N, 15.52%. The infrared spectrum of 1 exhibits strong bands at 1384 cm^{-1} [$\nu_{as}(NO)$], 1313 cm^{-1} [$\nu(NO)$] and 1111, 1056 and 1012 cm^{-1} [$\nu(P\text{–}O)$].

2.3. Crystallography

Crystal data: $C_{40}H_{42}Cu_4N_{16}O_{24}P_2$, monoclinic, space group *C2/c*, $a = 28.4236(1)$, $b = 9.7305(1)$, $c = 22.7510(2)$ (Å), $\beta = 118.183(10)°$, $V = 5546.38(9)$ Å^3, $\mu = 1.667$ mm^{-1}, $Z = 4$ and $R1 = 0.051$ for 7885 reflections. Reflection data for complex 1 were collected at 273 K on a 1K Bruker SMART CCD area-detector diffractometer. Data reduction and cell refinements were performed using the program SAINT [11]. 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 [12] software package. All hydrogen atoms were located by difference synthesis and refined isotropically except for the lattice water hydrogen atoms (4 H atoms), which could not be located and are also not fixed. The molecular graphics were created by using SHELXTL-PC [12]. CCDC Reference No. 233865. See http://www.ccdc.cam.ac.uk for crystallographic data in CIF format.

3. Results and discussion

3.1. Crystal structure of $[Cu_4(dpyam)_4(\mu_3,\eta^3\text{-}HPO_4)_2(NO_3)_2(H_2O)_2](NO_3)_2(H_2O)_2$ (1)

A plot of the structure is depicted in Fig. 1 with selected bond distances and angles in Table 1. The crystal structure obtained consists of a centrosymmetric tetranuclear $[Cu_4(dpyam)_4(\mu_3,\eta^3\text{-}HPO_4)_2(NO_3)_2(H_2O)_2]^{2+}$ cation, two non-coordinating NO_3^- anions and two molecules of lattice water. The four copper ions of the tetranuclear identity are linked through a double hydrogenphosphate bridge, with internal Cu···Cu distances varying from 4.136(2) to 7.833(2) Å. The cation is located on an inversion centre located in between the two bridging HPO_4^{2-} groups. The coordination mode of HPO_4^{2-} is tridentate bridging, each anion is bonded monodentately to two Cu(II) ions and didentately coordinated to a third Cu ion resulting in a novel μ_3,η^3 coordination mode. The two different Cu ions have a different chromophore (CuN_2O_2O' chromophore for Cu1 and a CuN_2O_3 chromophore for Cu2).

The geometry around Cu1 can be best described as distorted square pyramidal with the basal plane formed by 2 nitrogen atoms of a dpyam ligand (Cu–N distances 1.967(3) and 2.001(3) Å) and two oxygen atoms from different bridging hydrogenphosphato groups (Cu–O distances 1.968(2) and 1.972(2) Å). The apical position is occupied by an oxygen atom of one of the bridging hydrogenphosphate groups (Cu1–O7 2.497(2) Å). The angles of the basal plane are 161.77(12) and 142.43(12)°, while the four in-plane atoms (N1, N2, O4 and O6) are not planar (rms deviation of 0.473 Å) and have a marked tetrahedral twist (dihedral angles between the CuN_2 and CuO_2 planes) of 41.2°. The Cu ion lies 0.163 Å above this plane towards O(7). The distortion parameter τ, defined to describe the degree of trigonal distortion is 0.32 (a regular trigonal bipyramid (TBP) and square-based pyramid (SP) have τ values of 1.00 and 0.00, respectively [13]). The two Cu1 ions are doubly bridged by a HPO_4^{2-} anion in an equatorial–

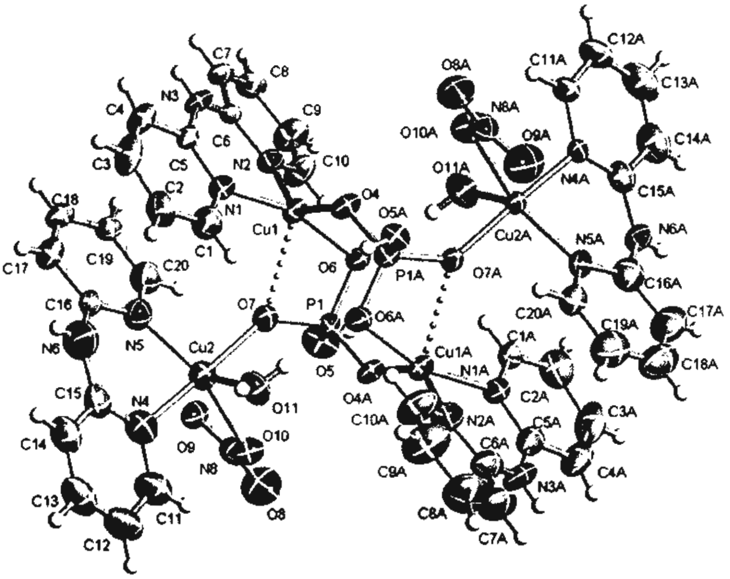

Fig. 1. Thermal ellipsoid plot (50% probability) of **1**. Atoms with an "A" are generated by symmetry operation $-x+2$, $-y$, $-z+1$. The uncoordinating nitrate anions and lattice water molecules are omitted for clarity.

Table 1
Selected bond lengths (Å) and angles (°) with esd in parentheses of compound **1**

Cu(1)–O(6)	1.972(2)	Cu(1)–O(4)	1.968(2),
Cu(1)–N(1)	1.967(2)	Cu(1)–N(2)	2.001(3)
Cu(1)–O(7)	2.497(2)	Cu(2)–O(7)	1.933(2)
Cu(2)–N(5)	2.013(3)	Cu(2)–N(4)	1.979(3)
Cu(2)–O(10)	2.145(2)	Cu(2)–O(11)	2.152(3)
Cu(2)–O(9)	2.743(2)	Cu(1)–Cu(2)	4.136(2)
Cu(1)–Cu(2)A	4.895(2)	Cu(1)–Cu(1)A	4.560(2)
Cu(2)–Cu(2)A	7.833(2)		
N(1)–Cu(1)–O(6)	161.7(1)	O(4)–Cu(1)–N(2)	142.4(1)
O(6)–Cu(1)–O(7)	110.4(1)	O(7)–Cu(1)–N(2)	106.2(1)
N(5)–Cu(2)–O(10)	137.6(1)	N(5)–Cu(2)–O(11)	131.1(1)
N(4)–Cu(2)–O(7)	168.6(1)		

Hydrogen-bonding parameters

D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)
N(3)–H(5)···O(4) [$-x$, $1-y$, $1-z$]	0.77(5)	2.26(5)	2.918(4)	144(5)
N(6)–H(15)···O(2) [$1/2-x$, $3/2-y$, $1-z$]	0.73(4)	2.18(4)	2.904(6)	172(4)
O(11)–H(21)···O(1) [x, $2-y$, $1/2+z$]	0.65(6)	2.22(6)	2.813(5)	153(7)
O(11)–H(22)···O(6) [$-x$, $2-y$, $1-z$]	0.79(6)	1.93(6)	2.718(5)	175(5)
O(5)–H(23)···O(1W) [$-1+x$, $1+y$, z]	0.79(5)	1.82(5)	2.608(5)	173(5)

equatorial configuration. Cu2 is linked to Cu1 via O7 of P1.

The geometry around the Cu2 ion is distorted TBP with the trigonal plane formed by the nitrogen atom of a dpyam ligand (Cu–N distance 2.013(3) Å) and two oxygen atoms, one from a water molecule and one from a coordinating nitrate anion (Cu–O distances 2.145(3), 2.152(4) Å). The angles of the trigonal plane are 137.56(11) and 131.15(12)°. The apical positions are occupied by a N-atom of the dpyam ligand (Cu–N 1.979(3) Å) and an oxygen atom of a bridging hydrogenphosphato group (Cu–O 1.933(2) Å) with an angle of 168.64(12)°. These shorter distances as compared to those in the trigonal plane are typical for TBP geometry. The distortion parameter τ for Cu2 is 0.49, so in fact it is an intermediate between TBP and SP.

The lattice structure is stabilised by a hydrogen-bonding network between the N atom of the dpyam ligand and oxygen atoms of a hydrogenphosphato group and a nitrate anion (N···O distances 2.918(4), 2.904(6) Å); between the coordinated water oxygen atom and the oxygen atoms of a hydrogenphosphato

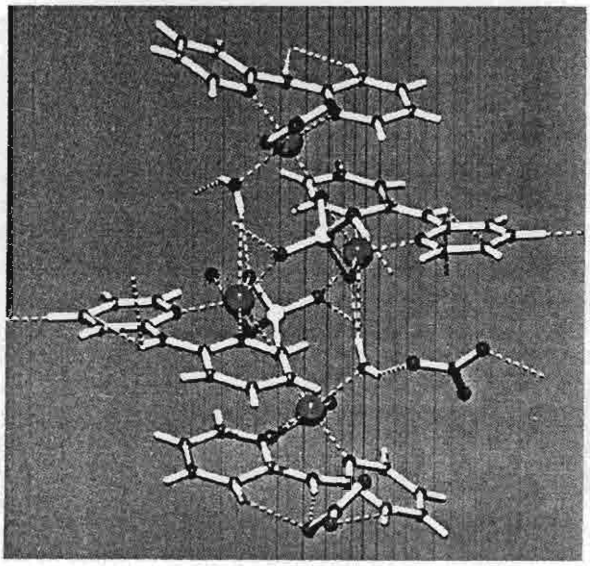

Fig. 2. Hydrogen bonding of 1.

group and a nitrate anion (O···O distances 2.813(5), 2.718(5) Å) and finally a quite strong bond between an oxygen atom of a hydrogenphosphato group and the oxygen atom of the non-coordinated water molecule (O···O distance only 2.608(5) Å). Details of the hydrogen bonds are given in Table 1 and a H-bonding picture is presented in Fig. 2.

3.2. Spectroscopy and magnetism

The diffuse reflectance spectrum of 1 measured as a solid shows a broad split band with a maximum at 11.4 and 13.9×10^3 cm^{-1}, which can be considered as normal transitions for TBP to SP geometries [14].

The polycrystalline EPR spectrum of compound 1 reveals a very broad isotropic signal with g at around 2.11 (RT and 77 K). This broad unresolved signal can be due to exchange narrowing and also to the fact that the compound contains two different copper sites. No signals for triplet species are observed.

The magnetic susceptibility of a powdered sample was measured from 5 to 300 K. The magnetic properties of the complex are depicted in Fig. 3 in the form of χ_m versus T and $\chi_m T$ versus T. Fig. 4 shows the magnetic interaction scheme, which was used for the fitting procedure and is based on the assumption that the magnetic coupling between outer and inner Cu ions is identical for all Cu1–Cu2, Cu1–Cu2A, Cu1A–Cu2A and Cu1A–Cu2 pairs. This is understandable, as the Cu–Cu distances and the O–P–O bridging pathway are very similar. The corresponding Hamiltonian is then

$$H = -J_1(S_{\mathrm{Cu1}}\cdot S_{\mathrm{Cu2}} + S_{\mathrm{Cu1}}\cdot S_{\mathrm{Cu2A}} + S_{\mathrm{Cu1A}}\cdot S_{\mathrm{Cu2}} + S_{\mathrm{Cu1A}}\cdot S_{\mathrm{Cu2}}) - J_2(S_{\mathrm{Cu1}}\cdot S_{\mathrm{Cu1A}}).$$

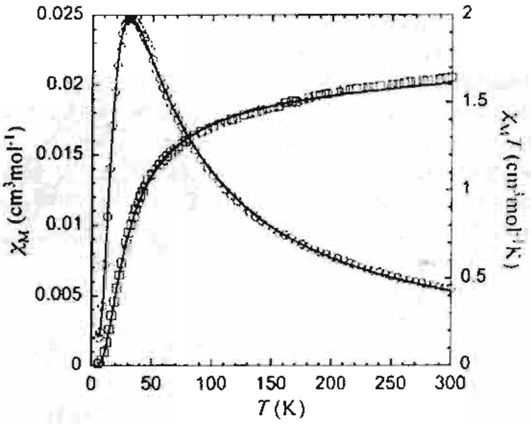

Fig. 3. Temperature dependence of the molar magnetic susceptibility χ_M (○) and the $\chi_M T$ product (□) for compound 1. The solid lines represent the calculated curves for $J_1 = -10.3(1)$ cm^{-1}, $J_2 = -5.3(2)$ cm^{-1} (see text).

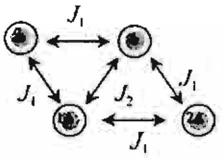

Fig. 4. Scheme of the magnetic interactions used in the calculations, using atom labelling from the structural data (see text).

Applying the Kambe vector coupling method with $S_A = S_{\mathrm{Cu2}} + S_{\mathrm{Cu2A}}$ and $S_B = S_{\mathrm{Cu1}} + S_{\mathrm{Cu1A}}$ (J_1 represents the Cu–Cu outer–inner magnetic interaction and J_2 the Cu–Cu inner–inner magnetic interaction, see Fig. 4) yields the following expression for the energy levels:

$$E(S_T,S_A,S_B) = -\frac{J_1}{2}(S_T(S_T+1) - S_A(S_A+1) - S_B(S_B+1)) - \frac{J_2}{2}(S_B(S_B+1))$$

and after inserting in the van Vleck equation [15] the expression for the molar susceptibility

$$\chi_{\mathrm{tetra}} = (1-p)\frac{Ng^2\beta^2}{k_BT} \times \frac{\left[2+2\exp\left(\frac{J_2}{k_BT}\right)+10\exp\left(\frac{(J_1+J_2)}{k_BT}\right)\right]}{\left[4+3\exp\left(\frac{J_2}{k_BT}\right)+5\exp\left(\frac{(J_1+J_2)}{k_BT}\right)+\exp\left(\frac{-2J_1+J_2}{k_BT}\right)\right]} + \frac{4\times0.375\times p}{T} + \mathrm{TIP},$$

which includes terms to take into account the temperature independent paramagnetism (TIP) and a monomeric paramagnetic impurity (p). Fitting the experimental data to this expression yields the full lines in Fig. 3 corresponding to the parameters $g = 2.01(1)$,

$J_1 = 10.3(1)$ cm^{-1}, $J_2 = -5.3(2)$ cm^{-1} and $p = 0.060(3)\%$. The TIP was kept at a constant of 2.0×10^{-4} cm^3 mol^{-1}. The fitted g value does not correspond completely with the g value obtained by EPR, but as the EPR gives a very broad unresolved signal no accuracy can be given on that observed EPR g value.

The phosphate bridges in the title compound are all in an equatorial–equatorial mode, (type I) for Cu1–Cu1A, SP–SP geometry; an equatorial–axial mode (type II) for Cu1–Cu2A and Cu1A–Cu2, SP–TBP geometry; and an axial–axial mode (type III) for Cu1–Cu2 and Cu1A–Cu2A, SP–TBP geometry, while the unpaired electron is usually in the $d_{x^2-y^2}$ for SP geometry and delocalised in d_z^2 for the TBP geometry. The delocalised efficiency of the unpaired electrons expected for inner Cu-ions (Cu1–Cu1A, SP geometry) and outer Cu ions (Cu2, Cu2A, TBP geometry) is remarkably diminished due to the distorted SP with a remarkable tetrahedral twist of the square base for the inner Cu-ions and the significantly distorted TBP (in fact an intermediate five-coordinated geometry) for the outer Cu-ions, resulting in a weaker overlap between magnetic orbitals, and therefore in a weaker antiferromagnetic interaction. The fact that $J_1 > J_2$ is thus due to differences in the Cu–O–P–O–Cu pathways and therefore the type II pathway seems slightly more efficient. However, the precise geometry of the phosphate bridge is likely to have an influence on the exchange parameters. Moreover, indeed the shortest Cu–Cu distance between inner Cu ions (4.56 Å) is larger than that between inner and outer Cu ions (4.13 Å). Detailed correlation of these structural effects with the magnetic exchange parameters requires other comparable compounds with phosphate bridges, which is under current investigation.

4. Conclusions

A tetranuclear Cu(II) compound with an unique (μ_3,η^3-HPO_4–O′,O′,O″) binding mode has been described. The compound shows a weak antiferromagnetic interaction. Parameters determined for the exchange intercation between the outer Cu ions are $J = -10.3(1)$ cm^{-1} and $J = -5.3(2)$ cm^{-1} for the inner Cu ions.

Acknowledgements

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Note

A novel polymeric trinuclear-based μ_3-phosphato-bridged Cu(II) complex containing two different types of monophosphate. Synthesis, structure and magnetism of $\{[Cu_3(\text{di-2-pyridylamine})_3(\mu_3,\eta^3\text{-}HPO_4)(\mu_3,\eta^4\text{-}PO_4)(H_2O)]\text{-}(PF_6)(H_2O)_3\}_n$

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Abstract

A novel trinuclear-based polymeric Cu(II) complex with uniquely bridged $H_xPO_4^{(3-x)-}$ anions, $[Cu_3(\text{di-2-pyridylamine})_3(\mu_3,\eta^3\text{-}HPO_4)(\mu_3,\eta^4\text{-}PO_4)(H_2O)](PF_6)(H_2O)_3\}_n$ **1** has been synthesized and characterised. Each Cu(II) ion in the polynuclear unit is linked by hydrogenphosphato and phosphato bridges showing μ_3, η^3-$HPO_4^{2-}$and an unprecedented μ_3, η^4-PO_4^{3-} coordination mode. Two different coordination geometries around the Cu(II) ions are found in the polynuclear unit: an intermediate geometry between square pyramidal and trigonal bipyramidal and a tetrahedrally distorted square-based pyramidal geometry. The Cu ··· Cu distances vary from 4.408(3) to 5.942(3) Å. From variable magnetic susceptibility measurements (5–250 K) a weak antiferromagetic interactions between the Cu(II) ions in the trinuclear unit with an exchange parameter of $J = -4.98$ cm^{-1} and a very weak antiferromagnetic interaction between neighbouring units with $zJ' = -1.49$ cm^{-1} are observed.

Keywords: Copper(II) complexes; Hydrogenphosphate complexes; Di-2-pyridylamine; Magnetism

1. Introduction

Recently, many research activities have focused on the synthesis of new open-framework metal phosphates, owing to their diverse structural chemistry and potential applications [1–3]. In the context of building open frameworks, it is also possible to use organic molecules in the skeleton. As compared with inorganic phosphates, the organic molecules have larger sizes of polyhedral centres and a wide variety of means of intramolecular connection. The organic components can greatly affect the connecting patterns of inorganic polyhedra, thus providing a method for the synthesis of new materials [4–6]. The synthesis of metal–phosphate complexes containing organic didentate chelating ligands has been investigated recently [7,8]. We have now extended the study by using the didentate ligand di-2-pyridylamine (abbreviated dpyam) and $H_nPO_4^{(3-n)-}$ oxoanions, to obtain complexes with different nuclearity and different

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coordinating and bridging modes of $H_xPO_4^{(3-x)-}$ ion. In the present study the synthesis, structural characterisation and magnetic properties of the polynuclear compound $\{[Cu_3(dpyam)_3(\mu_3,\eta^4\text{-}PO_4)(\mu_3,\eta^3\ HPO_4)(H_2O)](PF_6)(H_2O)_3\}_n$ (**1**) is reported. The unique 1-D structure is built up from the copper(II) ion, dpyam and two different $H_xPO_4^{(3-x)-}$ bridges with a novel coordination mode.

2. Experimental

2.1. Experimental

An aqueous solution (30 ml) of $Cu(COOCH_3)_2$ (0.18 g, 1.0 mmol) was added to a solution of di-2-pyridylamine (0.17 g, 1.0 mmol) in ethanol (15 ml) and followed by an aqueous solution (20 ml) of potassium dihydrogenphosphate (0.27 g, 2.0 mmol) and an aqueous solution (10 ml) of potassium hexafluorophosphate (0.18 g, 1.0 mmol). The resulting green solution was allowed to evaporate at room temperature for 2 weeks, producing dark green needle crystals of **1** (*Anal.* Calc. for $C_{30}H_{36}Cu_3F_6N_9O_{12}P_3$: C, 32.4; H, 3.3; N, 11.3. Found: C, 32.7; H, 3.3; N, 11.4%). IR (KBr; cm^{-1}): 3411 m, 1195 s, 1100 s, 1074 s, 1015 m, 984 w, 842 s, 768 s, 558 m, 499 w. X-band powder EPR spectrum was obtained on a JEOL RE2X electron spin resonance spectrometer with DPPH ($g = 2.0036$) as a reference. Magnetic susceptibility measurements were carried out using a Quantum design MPMS-5 5T SQUID magnetometer (measurements carried out at 1000 G). Data were corrected for magnetization of the sample holder and for diamagnetic contributions, which were estimated from the Pascal constants.

2.1.1. Crystal data

$C_{30}H_{36}Cu_3F_6N_9O_{12}P_3$, triclinic, space group $P\bar{1}$, $a = 7.4301(5)$, $b = 15.9715(10)$, $c = 17.4521(11)$ (Å), $\alpha = 67.9970(10)°$, $\beta = 85.2240(10)°$, $\gamma = 79.7430(10)°$, $V = 1889.2(2)$ (Å^3), $\mu = 1.955$ Mg/m^3 and $R_1 = 0.0458$ for 7116 reflections. Reflection data for complex **1** were collected on a 1K Bruker SMART CCD area-detector diffractometer. Data reduction and cell refinements were performed using the program SAINT [9]. The structure was solved by direct methods and refined by full-matrix least-squares method on $(F_{obs})^2$ with anisotropic thermal parameters for all non-hydrogen atoms using the SHELXTL-PC V 6.12 [10] software package. All hydrogen atoms were located by difference synthesis and refined isotropically. The molecular graphics were created by using SHELXTL-PC [10]. CCDC reference number 240395 (see crystallographic data in CIF format, e-mail: deposit@ccdc.cam.ac.uk, www: http://www.ccdc.cam.ac.uk).

3. Results and discussion

The structure of **1** (Fig. 1) consists of a polynuclear infinite chain structure of $[Cu_3(dpyam)_3(\mu_3,\eta^4\text{-}PO_4)(\mu_3,\eta^3\text{-}HPO_4)(H_2O)]^+$ cations, uncoordinated PF_6^- anions and lattice water molecules.

The Cu atoms are bridged unsymmetrically through mixed tridentate hydrogenphosphate and tetradentate phosphate ligands. The tridentate HPO_4^{2-} anion coordinates monodentately to three different Cu(II) ions, resulting in a μ_3,η^3 coordination mode. The tetradentate PO_4^{3-} anion coordinates didentately to two different Cu(II) ions and monodentately to a third Cu(II) ion, resulting in a μ_3,η^4 coordination mode.

The five-coordinated CuN_2O_3 chromophore around the Cu1 ion is obtained by two nitrogen atoms of a dpyam ligand (Cu–N distances 2.008(3), 2.027(3) Å), two oxygen atoms of two different hydrogenphosphate anions (Cu–O distances 1.957(2), 1.942(2) Å) and an oxygen of a coordinated water molecule (Cu–O distance 2.191(3) Å). The largest angle (O1–Cu1–N1) is 166.93(11)°, while the angles of the trigonal plane are 132.82(12)°, 119.12(11)° and 107.70(12)°.

The distortion of a square pyramidal coordination sphere can be described by the structural parameter τ, which indicates the relative amount of trigonality ($\tau = 0$ for a pure square pyramid (sp) and $\tau = 1$ for a trigonal bipyramid (tbp) [11]). In this case $\tau = 0.57$, so the geometry can be described as an intermediate between sp and tbp.

The other two Cu(II) ions have both a distorted square-pyramidal geometry. The basal plane of Cu2 consists of two oxygen atoms from different bridging $\mu_3,\eta^3\text{-}HPO_4$ and $\mu_3,\eta^4\text{-}PO_4$ anions (Cu–O distances 1.929(2), 1.920(2) Å) and two nitrogen atoms from a dpyam ligand (Cu–N distances 1.991(3), 1.978(3) Å). The apical position is formed by an oxygen atom from a didentate coordinated phosphate group at a semi-coordination distance of 2.912(1) Å. The basal angles are 150.69(12)° and 140.26(12)°, resulting in a τ value of 0.17.

The geometry of Cu3 is almost the same as Cu2 with the basal plane consisting of two oxygen atoms from different bridging $\mu_3,\eta^3\text{-}HPO_4$ and $\mu_3,\eta^4\text{-}PO_4$ anions (Cu–O distances (1.924(2), 1.908(2) Å) and two nitrogen atoms from a dpyam ligand (Cu–N distances 1.976(3), 1.985(3) Å). The apical position is formed by an oxygen atom from a didentate coordinated phosphate group at a semi-coordination distance of 2.989(1) Å. The basal angles are 155.82(11)° and 148.04(12)°, resulting in a τ value of 0.13. The square-pyramidal geometry is quite distorted as the four in-plane atoms (N4, N5, O2A, O7 for Cu2 and N7, N8, O4A, O5 for Cu3) are not planar with an extremely high r.m.s. deviations of 0.804 and 0.598 Å, respectively. The Cu ion lies 0.079 Å for Cu2 and 0.062 Å for Cu3 above this plane towards

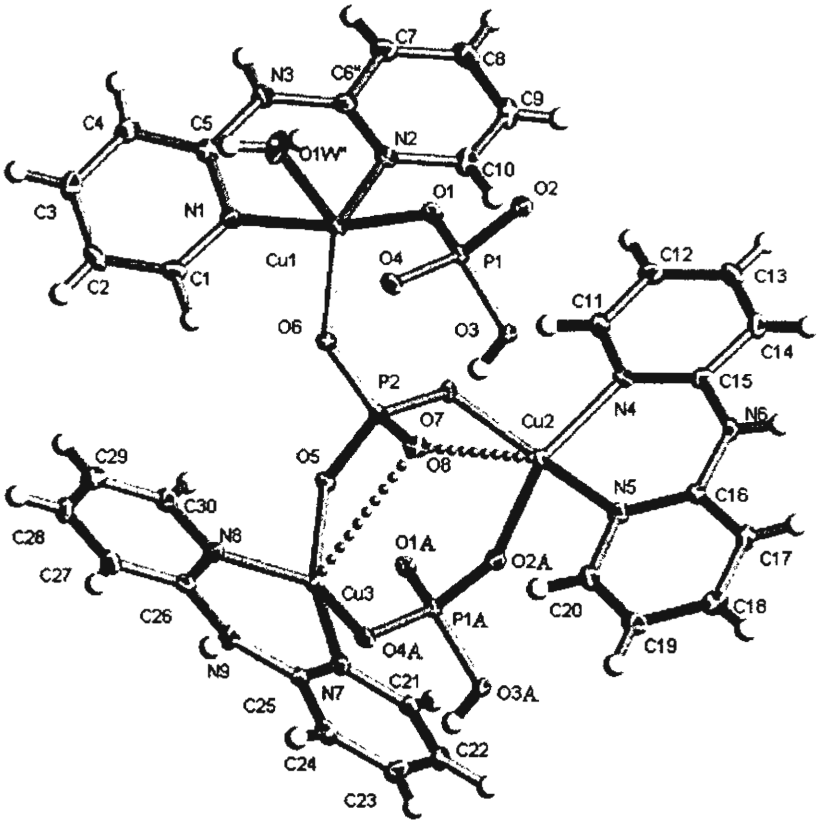

Fig. 1. Thermal ellipsoid (50% probability) plot of the title compound. The uncoordinating PF_6 anion and the lattice water molecules are omitted for clarity. Selected bond lengths (Å) and angles (°) Cu(1)–O(6) 1.942(2), Cu(1)–O(1) 1.957(2), Cu(1)–N(1) 2.008(3), Cu(1)–N(2) 2.027(3), Cu(1)–O(1W) 2.191(3), Cu(2)–O(2A) 1.920(2), Cu(2)–O(7) 1.929(2), Cu(2)–N(5) 1.978(3), Cu(2)–N(4) 1.991(3), Cu(2)–O(8) 2.912(1), Cu(3)–O(4A) 1.908(2), Cu(3)–O(5) 1.924(2), Cu(3)–N(8) 1.976(3), Cu(3)–N(7) 1.985(3), Cu(3)–O(8) 2.989(1), O(6)–Cu(1)–O(1) 97.3(1), O(1)–Cu(1)–N(1) 166.9(1), O(6)–Cu(1)–N(2) 132.8(1), O(6)–Cu(1)–O(1W) 119.1(1), N(2)–Cu(1)–O(1W) 107.6(1), O(7)–Cu(2)–N(5) 150.6(1), O(2A)–Cu(2)–N(4) 140.2(1), O(4A)–Cu(3)–N(8) 148.0(1), O(5)–Cu(3)–N(7) 155.8(1), Cu1–Cu2 5.218, Cu1–Cu3 5.942, Cu2–Cu3 4.407(7). $A = -x + 2, -y, -z + 1$.

O8. The origin of this distortion is the small value for the angles O5–Cu3–O8 and O7–Cu2–O8 (56.61° and 58.09°, respectively).

The lattice structure is stabilised by a hydrogen-bonding network interaction with N···O distances of 2.807–2.914 Å, O···O distances of 2.544–2.982 Å and O···F distances from 2.936 to 3.113 Å.

The diffuse reflectance spectrum of **1** measured as a solid shows a broad band centred at about 12.5×10^3 cm^{-1}, which can be considered as normal for the presence of both trigonal bipyramidal to square-pyramidal geometries [12].

The polycrystalline EPR spectrum of compound **1** reveals at RT and 77 K a very broad isotropic signal with $g = 2.12$. This single signal may be due to exchange narrowing and also to the fact that the compound contains three different copper sites, with different g-tensor orientations.

The magnetic susceptibility of a powdered sample was measured from 5 to 250 K. The magnetic properties

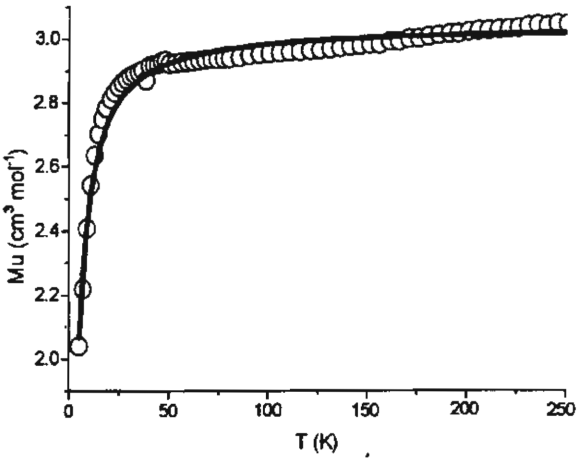

Fig. 2. A plot for compound **1** of temperature dependence of μ_{eff} vs. T is shown; the solid line represents the calculated curve for the parameters $J = -4.98$ cm^{-1}, $g = 2.03$ and $zJ' = -1.49$ cm^{-1}, see text.

of the complex are depicted in Fig. 2 in the form of μ_{eff} versus T for three Cu(II) ions.

From 250 K to about 30 K the μ_{eff} stays almost constant between 3.1–2.90 BM. This value is somewhat lower than the spin-only value of three uncoupled copper(II) $S = 1/2$ ions (theoretical value for $g = 2$, $\mu_{\mathrm{eff}} = 3.88$ BM). At about 30 K the μ_{eff} starts to decrease slightly to a value of 1.95 BM at 5 K. This overall behaviour indicates a very weak antiferromagnetic interaction between the Cu(II) ions. The magnetic data were fitted to the theoretical expression for the magnetic susceptibility of a triangular trinuclear system, considering the following Hamiltonian for the description of the magnetic interactions: $\mathrm{H} = -J_{12}\,(\mathrm{S}_1 \cdot \mathrm{S}_2) - J_{13}(\mathrm{S}_1 \cdot \mathrm{S}_3) - J_{23}\,(\mathrm{S}_2 \cdot \mathrm{S}_3)$.

Although the Cu(II) triangle in compound **1** is not strictly equilateral, we considered identical g tensors and exchange integrals J_{ij} for the three copper(II) ions. This is because using the general expression for an asymmetrical triangular system does not give direct access to the exchange parameters [13], they are then related to each other, without increasing the quality of the fit in this particular case. The expression for the molar susceptibility is then derived from the above Hamiltonian as used before in the literature [14–16].

The common exchange parameter is denoted as J and parameter zJ' introduces intercluster magnetic interactions, with z nearest neighbours. A Temperature Independent Paramagnetism (TIP) was also considered and fixed at 60×10^{-6} per copper. Minimising the function $R = \sum(\chi_{\mathrm{obs}} - \chi_{\mathrm{calc}})^2 / \sum \chi_{\mathrm{obs}}^2$, the best fit was obtained for $J = -4.98\ \mathrm{cm}^{-1}$, $g = 2.03$ and $zJ' = -1.49\ \mathrm{cm}^{-1}$, with $R = 8 \times 10^{-3}$.

The phosphate bridges in the title compound are in an equatorial–equatorial mode for Cu1–Cu2 and Cu1–Cu3, TBP-SP and the hydrogenphosphate links Cu2 and Cu3 in an equatorial-equatorial mode of the square pyramidal environment. The unpaired electron is usually in the $d_{x^2-y^2}$ for the square pyramidal geometry and delocalized in d_z^2 for the trigonal bipyramidal environment. As the Cu1 environment is extremely distorted trigonal bipyramidal (in fact an intermediate five-coordinated geometry) and Cu2 and Cu3 are in an extremely tetrahedral distorted square-based pyramidal environment, hence remarkable diminish the delocalized efficiency of the unpaired electrons resulting from a weaker overlap between magnetic orbitals, and therefore a weaker antiferromagnetic interaction is observed. Moreover, the three Cu ions are far away from each other (distances vary from 4.407 to 5.942 Å).

So far such Cu(II) compounds with phosphato bridges of which also the magnetic interaction reported have been rare and more examples will be required for magneto-structural correlations in such compounds.

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A novel tetranuclear hydrogenphosphate-bridged Cu(II) cluster. Synthesis, structure, spectroscopy and magnetism of $[Cu_4(dpyam)_4(\mu_4,\eta^3\text{-}HPO_4)_2(\mu\text{-}X)_2]X_2(H_2O)_6$ (X = Cl, Br)

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Abstract

Two novel tetranuclear $\mu_4,\eta^3\text{-}HPO_4^{2-}$-Cu(II) compounds with an unprecedented mode of a hydrogenphosphato bridge, $[Cu_4(dpyam)_4(\mu_4,\eta^3\text{-}HPO_4)_2(\mu\text{-}X)_2]^{2+}$ (in which dpyam = di-2-pyridylamine and X = Cl (**1**), Br (**2**)) have been synthesised and characterised structurally and magnetically. The Cu(II) ions in the structures each display a square-pyramidal geometry, with two tridentate hydrogenphosphato groups bridging four copper atoms in a μ_4,η^3 coordination mode which is rarely found in hydrogenphosphate metal compounds. Each (different) pair of Cu(II) ions is additionally bridged by halide ions, with relatively long Cu–X distances (2.551(3)–2.604(3) Å for **1** and 2.707(1)–2.766(2) Å for **2**) and subsequently also a small Cu–X–Cu angle (65.7(1)° and 65.1(1)° for **1** and 61.6(1)° and 62.4(1) for **2**) and a large Cu–X–Cu angle (95.5(1)° and 96.5(1)° for **1** and 91.1(1)° and 92.6(1)° for **2**). Cu···Cu distances in the tetranuclear units varies from 2.802(3) to 5.232(3) Å for **1** and from 2.834(1) to5.233(1) Å in **2**. The lattice structures are stabilised by extensive intermolecular hydrogen bonds. The magnetic susceptibility measurements down to 5 K revealed a weak ferromagnetic interaction between the outer pairs of Cu(II) ions which vary from 22 to 46 cm^{-1} in **1** and 12 to 33 cm^{-1} in **2** and a moderately strong antiferromagnetic interaction between the inner Cu(II) ions of $-79\ cm^{-1}$ in **1** and $-83\ cm^{-1}$ in **2**, via the Cu–O–P–O–Cu pathway.

Keywords: Tetranuclear complexes; Copper (II) cluster; Hydrogenphosphate complexes; Di-2-pyridylamine; Magnetism

1. Introduction

The synthesis of open-framework metal phosphates has been a subject of intense research owing to their interesting structural chemistry and potential applications as ion-exchangers, catalysts and adsorbents [1–3]. A large number of these materials are synthesised in the presence of organic amines as structure directing (templating) agents. Recently, many research activities have focused on the synthesis of organic–inorganic hybrid frameworks, such as phosphates of transition metals [4–7]. As compared with organic ligands, the advantage of using inorganic multidentate anionic ligands in combination with organic polar molecules and ligands is the efficacy of rational design of crystalline solids through their coordinating properties and geometries. So far the most extensively studied bridging

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organic ligand with transition metals and phosphate is 4,4′-bipyridine with a number of one-, two- and three-dimensional structures [4–8]. With ligands like 2,2′-bipyridine [9] and 1,10-phenanthroline [10] the number of such new organic–inorganic hybrid compounds are rare. Now we have extended this research by using the ligand di-2-pyridylamine (abbreviated as dpyam) and have isolated several new phases in such organic–inorganic metal-phosphate systems. In the present study, two novel examples of the dpyam-phosphate system, $[Cu_4(dpyam)_4(\mu_4,\eta^3\text{-}HPO_4)_2(\mu\text{-}Cl)_2]Cl_2(H_2O)_6$ (**1**) and $[Cu_4(dpyam)_4(\mu_4,\eta^3\text{-}HPO_4)_2(\mu\text{-}Br)_2]Br_2(H_2O)_6$ (**2**) are reported.

Both compounds were prepared as green crystals from potassium dihydrogenphosphate, dpyam and copper halide in ethanol under ambient conditions and characterised by elemental analysis and infrared spectroscopy. Also the magnetic susceptibility has been studied. The two new compounds have a μ_4-HPO_4 bridging system, which is to the best of our knowledge only reported once [11] and in that case the copper (II) atoms are also bridged by a carbonato ligand. This is the first case reported for a tetranuclear Cu(II) system bridged only by μ_4-HPO_4 and halide anions.

2. Experimental

2.1. Synthesis of the compounds

Solid KH_2PO_4 (0.27 g, 2.0 mmol) dissolved in water (20 ml) was added to a warm solution of di-2-pyridylamine (0.17 g, 1.0 mmol) in ethanol (15 ml) yielding a pale-yellow solution. The colour became greenish by slow addition of an aqueous solution (30 ml) of $CuCl_2 \cdot 2H_2O$ (0.17 g, 1.0 mmol). The resulting green solution was allowed to evaporate at room temperature. After several days, green crystals of **1** were deposited. They were filtered off, washed with the mother liquid and air-dried. Compound **2** was prepared similarly to that of **1** using $CuBr_2$ (0.22 g,1.0 mmol) as starting material. Yield approx. 67%. Elemental analyses of the bulk powders, as used for the measurements: Compound **1** $(Cu_4(dpyam)_4(HPO_4)_2(Cl)_2](Cl)_2(H_2O)_{5.5})$: *Anal.* Calc. for $C_{40}H_{49}Cu_4N_{12}O_{13.5}Cl_4P_2$: C, 35.02; H, 3.60; N, 12.25. Found: C, 34.88; H, 3.42; N, 12.13%. Compound **2**: $Cu_4(dpyam)_4(HPO_4)_2(Br)_2](Br)_2(H_2O)_{5.5}$; *Anal.* Calc. for $C_{40}H_{49}Cu_4N_{12}O_{13.5}$ Br_4P_2: C, 31.00; H, 3.18; N, 10.84. Found: C, 31.61; H, 2.96; N, 10.79%.

2.2. Physical measurements

IR spectra were recorded on a Spectrum One Perkin–Elmer FT-IR spectrophotometer as KBr pellets in the 4000–450 cm^{-1} spectral range. Diffuse reflectance measurements from 9090 to 20 000 cm^{-1} were 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 spectra were recorded on a JEOL RE2x electron spin resonance spectrometer using DPPH ($g = 2.0036$) as a standard. Magnetic susceptibility measurements (5–350 K) were carried out using a Quantum Design MPMS-5 5T SQUID magnetometer (measurements carried out at 0.1 T). Data were corrected for magnetisation of the sample holder and for diamagnetic contributions, which were estimated from the Pascal constants.

2.3. Crystal structure analyses

Reflection data for complexes **1** and **2** were collected at 293 K on a 1K Bruker SMART CCD area-detector diffractometer using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Data reduction and cell refinements were performed using the program SAINT [12]. 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 [13] software package. All hydrogen atoms in **1** were located by difference synthesis and refined isotropically except H(22), H(29), H(42), H(52) and H(58). These hydrogen atoms were geometrically fixed and allowed to ride on attached atoms. One water hydrogen atom and one hydrogenphosphate hydrogen atom of **1** were unable to locate and also not fixed. For **2**, all hydrogen atoms were located and refined isotropically except five water hydrogen atoms, which were unable to locate and also not fixed. Two water oxygen atoms of both compounds were disordered and were refined with site occupancies of 0.5. Moreover, two water oxygen atoms of both compounds were refined with site occupation factor of 0.5. The molecular graphics were created by using SHELXTL-PC [13]. Crystallographic data for both structures are presented in Table 1.

3. Results and discussion

3.1. Description of the structures

The asymmetric unit of **1** and **2** consists of one and a half units of $[Cu_4(dpyam)_4(\mu_4,\eta^3\text{-}HPO_4)_2(\mu\text{-}X)_2]X_2$ (X = Cl, Br) and 12 lattice water molecules, two of which having site occupation factor of 0.5. Both structures are isostructural. Structures **1** and **2** involve two crystallographically independent, but very similar tetranuclear units of $[Cu_4(dpyam)_4(\mu_4,\eta^3\text{-}HPO_4)_2(\mu\text{-}X)_2]^{2+}$. One unit of each structure with the atomic numbering system is presented in Figs. 1 and 2, for compounds **1** and **2**, respectively. The second unit of compounds **1**

Table 1
Crystallographic data for compounds **1** and **2**

Complex	**1**	**2**
Molecular formula	$[Cu_4(dpyam)_4(HPO_4)_2(Cl)_2](Cl)_2(H_2O)_6$	$[Cu_4(dpyam)_4(HPO_4)_2(Br)_2](Br)_2(H_2O)_6$
Empirical formula	$C_{60}H_{79}Cu_6N_{18}O_{23}Cl_6P_3$	$C_{60}H_{79}Cu_6N_{18}O_{23}Br_6P_3$
Formula weight	2107.26	2374.02
T (K)	273(2)	273(2)
Crystal system	monoclinic	monoclinic
Space group	*Cm*	*Cm*
a (Å)	16.3150(2)	16.4716(3)
b (Å)	48.2777(1)	49.3270(4)
c (Å)	12.5824(1)	12.6314(2)
β (°)	125.9980(10)	126.2060(10)
V (Å^3)	8017.99(12)	8281.1(2)
Z	4	4
D_{cal} (g cm^{-3})	1.746	1.904
μ (mm^{-1})	1.907	4.548
$F(0\,0\,0)$	4280	4712
Crystal size (mm)	0.33 × 0.45 × 0.75	0.23 × 0.24 × 0.35
θ (°)	1.60–30.55	1.59–30.43
Number of reflections collected	30 204	31 126
Number of unique reflections	17 411	18 172
Number of observed references [$I > 2\sigma(I)$]	11 833	10 280
T_{max} and T_{min}	1.000 and 0.712	1.000 and 0.709
Data/restraints/parameter	17 411/2/1306	18 172/2/1090
Goodness-of-fit	1.044	1.019
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0364$, $wR_2 = 0.0914$	$R_1 = 0.0796$, $wR_2 = 0.1949$
R indices (all data)	$R_1 = 0.0448$, $wR_2 = 0.0981$	$R_1 = 0.1148$, $wR_2 = 0.2255$
Largest difference peak and hole (e Å^{-3})	1.981 and −0.604	6.603 and −1.298

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

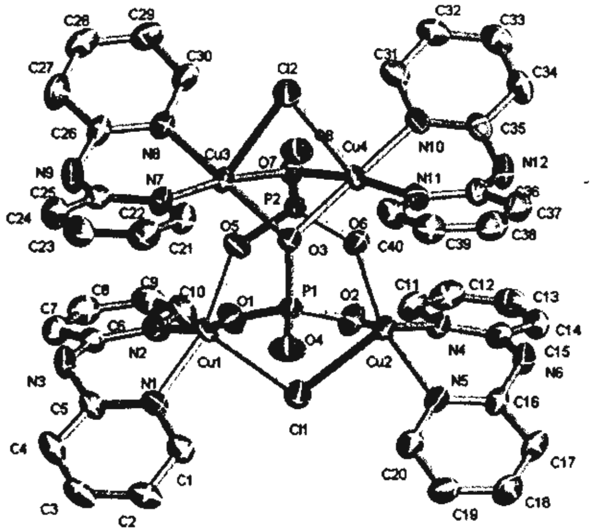

Fig. 1. Thermal ellipsoid plot of the first unit of compound **1** with labeling scheme. Hydrogen atoms, the uncoordinating chloride atoms and the lattice water molecules are omitted for clarity.

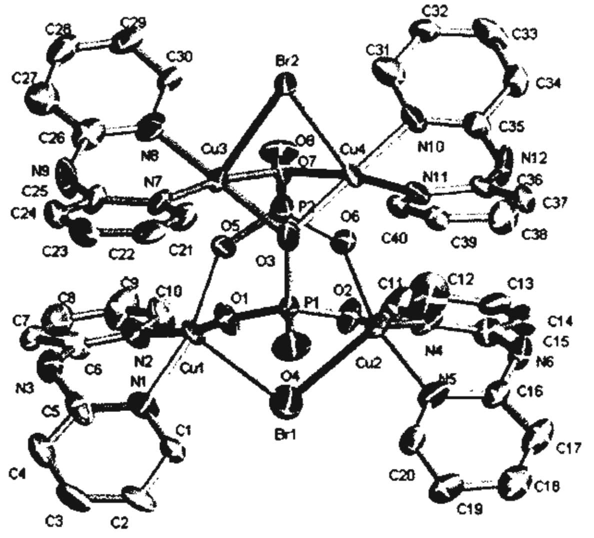

Fig. 2. Thermal ellipsoid plot of the first unit of compound **2** with labeling scheme. Hydrogen atoms, the uncoordinating bromide atoms and the lattice water molecules are omitted for clarity.

and **2** is given as supplementary material (Figs. S1 and S2). Selected bond lengths and angles are given in Table 2. The first unit of each compound is situated on a general position, whereas the second unit is situated on a mirror plane. The unit cell contains four molecules on general positions and two molecules on special positions.

Each tetranuclear unit of both compounds consists of two pairs of five-coordinated copper (II) ions bridged by two tetrahedral tridentate hydrogenphosphato groups in

Table 2
Selected distances and angles for compounds **1** and **2**

	1	**2**
Bond lengths		
Cu(6)–N(17)	1.962(4)	1.977(9)
Cu(6)–N(16)	1.965(4)	1.960(9)
Cu(6)–O(9)	2.011(3)	2.045(7)
Cu(6)–O(12)	2.021(3)	2.039(8)
Cu(6)–X(4)	2.604(1)	2.766(2)
Cu(5)–O(10)	1.947(3)	1.937(9)
Cu(5)–O(13)	1.966(3)	1.974(9)
Cu(5)–N(14)	1.993(4)	2.008(10)
Cu(5)–N(13)	2.012(4)	2.019(10)
Cu(5)–X(3)	2.560(1)	2.708(1)
Cu(4)–N(10)	1.970(4)	1.981(10)
Cu(4)–N(11)	1.982(4)	1.998(10)
Cu(4)–O(7)	2.012(3)	2.005(7)
Cu(4)–O(3)	2.026(3)	2.029(8)
Cu(4)–X(2)	2.592(1)	2.745(1)
Cu(3)–N(8)	1.971(4)	1.984(10)
Cu(3)–N(7)	1.981(4)	2.005(10)
Cu(3)–O(7)	2.012(3)	1.993(7)
Cu(3)–O(3)	2.030(3)	2.033(8)
Cu(3)–X(2)	2.598(1)	2.757(1)
Cu(2)–O(6)	1.950(3)	1.979(8)
Cu(2)–O(2)	1.969(3)	1.970(8)
Cu(2)–N(5)	1.996(4)	1.987(10)
Cu(2)–N(4)	2.009(4)	2.023(9)
Cu(2)–X(1)	2.556(1)	2.720(1)
Cu(1)–O(5)	1.948(3)	1.988(8)
Cu(1)–O(1)	1.965(3)	1.974(7)
Cu(1)–N(1)	1.993(3)	2.003(10)
Cu(1)–N(2)	2.001(4)	2.021(10)
Cu(1)–X(1)	2.551(1)	2.715(1)
Cu(1)–Cu(2)	3.781(1)	3.881(1)
Cu(3)–Cu(4)	2.816(1)	2.851(1)
Cu(2)–Cu(4)	4.027(3)	4.028(1)
Cu(1)–Cu(3)	4.069(3)	4.036(1)
Cu(5)–Cu(6)	4.072(3)	4.035(1)
Cu(5)–Cu(5A)	3.820(1)	3.918(1)
Cu(5A)–Cu(6A)	5.224(1)	5.234(1)
Cu(6)–Cu(6A)	2.802(1)	2.834(1)
Bond angles		
N(16)–Cu(6)–O(9)	171.7(2)	173.2(4)
N(17)–Cu(6)–O(12)	172.9(2)	173.1(4)
O(10)–Cu(5)–N(14)	164.0(2)	165.0(4)
O(13)–Cu(5)–N(13)	162.5(2)	163.3(4)
N(11)–Cu(4)–O(7)	171.6(2)	170.8(4)
N(10)–Cu(4)–O(3)	173.3(2)	174.2(4)
N(7)–Cu(3)–O(7)	171.7(2)	170.8(4)
N(8)–Cu(3)–O(3)	173.4(2)	175.1(4)
O(6)–Cu(2)–N(5)	162.6(2)	164.5(4)
O(2)–Cu(2)–N(4)	164.8(2)	164.9(4)
O(5)–Cu(1)–N(1)	164.5(2)	165.3(4)
O(1)–Cu(1)–N(2)	161.3(2)	162.3(4)
Cu(1)–X(1)–Cu(2)	95.5(1)	91.1(1)
Cu(3)–X(2)–Cu(4)	65.7(1)	62.4(1)
Cu(5)–X(3)–Cu(5A)	96.5(1)	92.6(1)
Cu(6)–X(4)–Cu(6A)	65.1(1)	61.6(1)

Symmetry code: $A = -x, -y + 1, -z$, and X = Cl and Br for **1** and **2**, respectively.

each molecule. Both HPO_4^{2-} groups coordinate monodentately to one copper (II) ion and bridging via one oxygen to two other Cu(II) ions, yielding a very rare μ_4,η^3 coordination mode. Each copper ion has a planar square base with a CuN_2O_2X chromophore consisting of two oxygen atoms of two bridging HPO_4^{2-} groups (Cu–O distances vary from 1.947(3) to 2.030(3) Å) and two nitrogen atoms of a dpyam ligand (Cu–N distances vary from 1.962(4) to 2.012(4) Å). The axial position is occupied by a bridging halide anion (Cu–Cl distances vary from 2.559(1) to 2.604(1) Å and Cu–Br distances vary from 2.708(1) to 2.766(2) Å), thus giving a slightly tetrahedrally distorted square-based pyramidal CuN_2O_2X chromophore for both units in compounds **1** and **2**.

Consequently, all copper (II) ions are linked to each other via double-bridged HPO_4^{2-} groups in an equatorial–equatorial configuration. Each copper atom is displaced 0.072 to 0.340 Å and 0.069 to 0.337 Å for Cu(1) to Cu(6) of **1** and **2**, respectively, from the basal plane (N_2O_2) towards the apical halide ion. The τ value (τ describes the relative amount of trigonality; $\tau = 0$ for square pyramid and $\tau = 1$ for trigonal bipyramidal [14]) vary from 0.020 to 0.053 and 0.001 to 0.071 for compounds **1** and **2**, respectively, indicating a nearly perfect square-based pyramidal geometry for all CuN_2O_2X chromophores.

The Cu···Cu distances in the tetranuclear units vary from 2.802(1) to 5.224(1) Å in **1** and from 2.834(2) to 5.234(1) Å in compound **2**.

Each tetranuclear unit has a unique structure with a short Cu–Cu distance (2.816(1) and 2.802(1) Å for **1** and 2.834(1) and 2.851(1) Å for**2**) and a long Cu–Cu distance (3.781(1) and 3.820(1) Å for **1** and 3.881(1) and 3.918(1) for **2**). Consequently, the units have also a small Cu–X–Cu angle (65.7(1)° and 65.1(1)° for **1** and 61.6(1)° and 62.4(1) for **2**) and a large Cu–X–Cu angle (95.5(1)° and 96.5(1)° for **1** and 91.1(1)° and 92.7(1)° for **2**). See Table 2 for details.

The lattice structure is stabilised by a complicated hydrogen-bonding network between oxygen atoms of the hydrogenphosphato groups and oxygen atoms of uncoordinated water molecules (O···O distances vary from 2.587(1) to 2.639(1) Å for **1**, and from 2.587(1) to 2.591(1) Å for **2**) and between oxygen atoms of different water molecules (O···O distances vary from 2.664(1) to 2.845(1) Å for **1** and from 2.588(1) to 2.695(1) Å for **2**). Also hydrogen bond contacts are observed between the O and N atoms and the halide ions (distances vary from 3.139(1) to 3.420(1) Å for **1** and from 3.276(1) to 3.542(1) Å for **2**).

3.2. Electronic and infrared spectra

The electronic diffuse reflectance spectra of **1** and **2** consist of an unsymmetrical, broad band centred around 15.0×10^3 and $14.9 \times 10^3\ cm^{-1}$, respectively, consistent with the square-pyramidal stereochemistry [15].

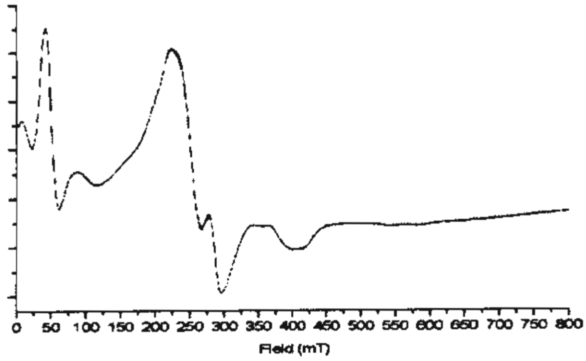

Fig. 3. X-band EPR spectrum (solid) of **1** measured at 77 K.

The infrared spectra of both compounds exhibit strong bands for the phosphato anions [16,17] at 1159, 1098 and 980 cm^{-1} [ν(P–O)] and 529 and 511 cm^{-1} [δ(O–P–O)] for **1** and 1159, 1096 and 976 cm^{-1} [ν(P–O)] and 529 and 511 cm^{-1} [δ(O–P–O) for **2**.

3.3. EPR spectroscopy

The X-band polycrystalline powder EPR spectra of compound **1**, measured from 0 to 800 mT at 77 K (see Fig. 3), revealed a triplet spectrum with some large and less large features at about 50, 90, 225, 280 and 350 mT. Also two very weak signals occur at about 540 and 580 indicating that different Cu(II) species are present. This type of spectrum can be compared with some other tetranuclear copper (II) compounds with a $D > h\nu$ (about 0.3 cm^{-1}) [18,19]. The absorption at low field is most probably the $\Delta M_s = \pm 2$ transition, while the absorption around 280 mT can be attributed to the $\Delta M_s = \pm 1$ transition. For such complicated tetranuclear species, a single-crystal EPR analysis would be required to establish the exact zero-field splitting parameters; this is outside the scope of this investigation. The EPR spectrum of **2** at 77 K and both spectra at RT are presented as supplementary material as Figs. S3, S4 and S5, respectively.

3.4. Magnetic susceptibility

The magnetisation of powdered samples of **1** and **2** were measured from 5 to 350 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 Figs. 4 and 5 for compounds **1** and **2**, respectively.

In both cases χ_M gradually increases upon lowering temperature from values at high temperatures in agreement with four uncoupled spin = 1/2 centres. A maximum is reached around 55 K, at which temperature χ_M decreases sharply. This behaviour is indicative of an antiferromagnetic coupling between some of the copper ions in **1** and **2**. For simplicity, the two similar tetranuclear units contained in the structures **1** and **2** will be considered as identical for the rationalisation of these magnetic properties. Moreover, the diagonal coupling pathways through phosphato groups (J_3 in Fig. 6) will also be assumed identical. These approximations result in the magnetic coupling scheme proposed in Fig. 6, in which the letters A, B, C and D correspond to the structural labelling of the Cu atoms (see Figs. 1 and 2). The $\mathrm{Cu_A}$–$\mathrm{Cu_B}$ (J_2) interaction (Cu3–Cu4 in Fig. 1 with the Cu–O–Cu bridge) represents the shortest distance (about 2.8 Å), the $\mathrm{Cu_C}$–$\mathrm{Cu_D}$ (J_4) interaction (Cu1–Cu2 in Fig. 2 with the Cu–O–P–O–Cu bridge) represents the long distance (about 3.8 Å), while the $\mathrm{Cu_A}$–$\mathrm{Cu_C}$ and $\mathrm{Cu_B}$–$\mathrm{Cu_D}$ (J_1) interaction (Cu3–Cu1 and

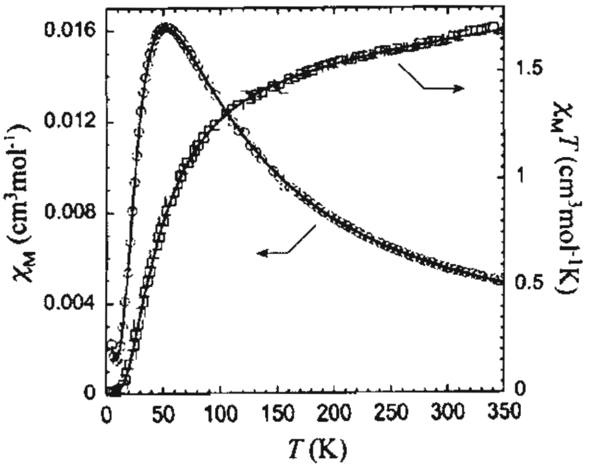

Fig. 4. Plots of temperature dependence of the molar magnetic susceptibility χ_M (○) and the $\chi_M T$ product (□) for compound **1**. The solid lines represent the calculated curves (see text).

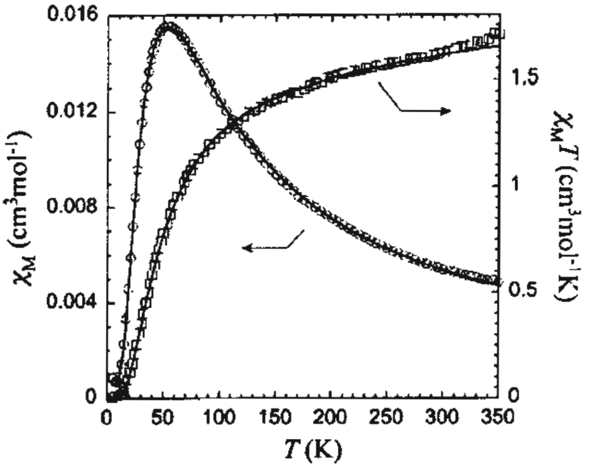

Fig. 5. Plots of temperature dependence of the molar magnetic susceptibility χ_M (○) and the $\chi_M T$ product (□) for compound **2**. The solid lines represent the calculated curves (see text).

Cu4–Cu2, respectively, in Fig. 1) have the longest distance of about 4.07 Å.

The corresponding Hamiltonian writes:

$$H = -2J_1(S_A \cdot S_C + S_B \cdot S_D) - 2J_2(S_A \cdot S_B) - 2J_3(S_B \cdot S_C + S_A \cdot S_D) - 2J_4(S_C \cdot S_D). \quad (1)$$

Although the topologies of the compounds differ, this Hamiltonian is identical to one solved for a linear tetranuclear copper compound [20,21].

The energy levels and their spin quantum numbers (used in the fitting procedure) which were derived are as follows:

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

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

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

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

$$S_5 = 0: \quad E_5 = J_1 + J_3 + (J_2 + J_4)/2 + \left[4(J_1^2 + J_3^2) + J_2^2 + J_4^2 - 2J_1(J_2 + 2J_3 + J4) - 2J_2(J_3 - J_4) - 2J_3J_4\right]^{1/2},$$

$$S_6 = 0: \quad E_6 = J_1 + J_3 + (J_2 + J_4)/2 - \left[4(J_1^2 + J_3^2) + J_2^2 + J_4^2 - 2J_1(J_2 + 2J_3 + J4) - 2J_2(J_3 - J_4) - 2J_3J_4\right]^{1/2}.$$

Considering also that the g values are identical for all copper ions, the molar magnetic susceptibility is then

$$\chi_M = \frac{N_A g^2 \beta^2}{3k_B T} \frac{\sum_i S_i(S_i + 1)(2S_i + 1)\exp(-E_i/k_B T)}{\sum_i (S_i + 1)\exp(-E_i/k_B T)}. \quad (2)$$

A term taking into account a small monomeric paramagnetic impurity was added to this expression and evaluated from the low temperature data as little as 0.05% and 0.06% for **1** and **2**, respectively. To avoid over-parameterisation, these terms were held constant during the fitting procedure as well as the g value, which was fixed at 2; this is a quite normal value for Cu(II) species. For both compounds, the experimental data were first fitted to Eq. (2) letting the coupling constants vary by groups of 2 and 3 and holding the other(s) to 0. In this way, it was found first that J_3 had to be negative (antiferromagnetic) of the order of $-60\,\mathrm{cm}^{-1}$, and secondly, that the other coupling constants should be positive (ferromagnetic) with J_1 and J_2 of the same order, to obtain a good fit. At this point, one has to remark that these findings are in correct agreement with the structural data. Indeed, apart for the Cu_A–Cu_C and Cu_B–Cu_D pairs, the basal planes of the other pairs of copper ions are almost perpendicular to each other. This geometry indicates that the overlap between the spin-rich d_{x2-y2} orbitals of these copper ions cannot be expected to be important. In addition, Cu_A–O–Cu_B angles are close to 90°, a value yielding ferromagnetic interaction in dinuclear alkoxo- or hydroxo-bridged copper dimers [22,23]. Finally, halide bridges between Cu_A and Cu_B and Cu_C and Cu_D correspond to the axial coordination site of the copper ions where the spin density is negligible. Therefore, the participation of this pathway to the interactions should be negligible.

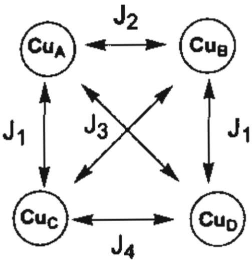

Fig. 6. Scheme of the magnetic interactions used in the calculations (see text).

So with the initial experiments stated above the data were fit by forcing $J_1 = J_2$ and letting the three remaining coupling constants free, starting from $J_3 < 0$ and J_1 and $J_4 > 0$. The two sets of best fit parameters, corresponding to the full lines in Figs. 4 and 5 were obtained as $2J_1 = 2J_2 = 22(2)\,\mathrm{cm}^{-1}$, $2J_3 = -79(1)\,\mathrm{cm}^{-1}$, $2J_4 = 46(4)\,\mathrm{cm}^{-1}$ and $2J_1 = 2J_2 = 33(1)\,\mathrm{cm}^{-1}$, $2J_3 = -83(1)\,\mathrm{cm}^{-1}$, $2J_4 = 12(3)\,\mathrm{cm}^{-1}$, for compounds **1** and **2**, respectively. Their magnetic behaviour is thus dominated by a medium antiferromagnetic interaction occurring through the diagonal phosphato bridges (J_3), resulting in a singlet ground state with a first excited triplet state at, e.g., 76 and $84\,\mathrm{cm}^{-1}$ above it (see energy-level scheme above).

4. Conclusions

In summary, two novel tetranuclear μ_4,η^3-HPO_4^{2-}-bridged copper(II) complexes have been synthesised and reported in this study. These structures show a μ_4,η^3-bridging coordination mode which is rarely found in hydrogenphosphate metals compounds and these are the first structures reported with a μ_4-HPO_4 and halide system and these systems provide a new opportunity to study the coordination mode of hydrogenphosphate groups in relation with the magnetic behaviour. The magnetic properties are dominated by a moderately strong antiferromagnetic interaction via the Cu–O–P–O–Cu pathway between the diagonal (inner) Cu ions (Cu_1–Cu_4, Cu_2–Cu_3 pairs), but a weak ferromagnetic interaction is observed between the outer Cu ions (Cu_3–Cu_4 and Cu_1–Cu_2 pairs).

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Appendix A. Supplementary data

The thermal ellipsoid plots of the second crystallographic units of compound **1** and compound **2** and their EPR spectra of **2** at 77 K and of **1** and **2** at RT are presented as supplementary material. Crystallographic data for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC Nos. 233926 and 233927 for structures **1** and **2**, respectively. 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, www: http://www.ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2005.01.019.

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A copper(II) chain compound with hydrogenphosphate bridges organized in a double-chain structure. Synthesis, structure and magnetic properties of $[Cu(1,10\text{-phenanthroline})(\mu\text{-}HPO_4)(H_2O)_2]_n$

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Abstract

A new Cu(II) chain compound, $[Cu(1,10\text{-phenanthroline})(\mu\text{-}HPO_4)(H_2O)_2]_n$ 1 has been synthesized hydrothermally and structurally characterized by elemental analysis, IR, EPR spectrum and single-crystal X-ray diffraction. The Cu(II) ion is tetragonally coordinated with a phen ligand and two aqua ligands in the equatorial plane (Cu–N distance 2.006(2) Å and Cu–O distance 1.969(2) Å) and hydrogenphosphates as axial ligands (Cu–O distance 2.470(2) Å), thereby forming a linear chain. The crystal lattice is formed from antiparallel chains, kept together by relatively strong phosphate–water H-bonds (intra- and intermolecular) with O···O contacts of 2.615(3) and 2.672(3) Å and by interpenetrated stacking of the phen ligands with other chains. The magnetic susceptibility measurements (5–300 K) agrees with a weak antiferromagnetic chain interaction between the Cu centers with *J* value of $-5.86\ cm^{-1}$.

Keywords: Hydrothermal synthesis; Copper(II); Polymeric; One-dimensional chain; Magnetic properties

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Open-framework materials have been of interest because of their traditional use in catalysis, separation, and ion exchange and their potential applications as hybrid composite materials in nonlinear optical and sensing applications [1]. Recently much research has focused on the synthesis of inorganic–organic hybrid frameworks using HPO_4^{2-} and derivative ions as bridging [2,3] and both monodentate coordinating and bridging modes of HPO_4^{2-} and derivative ions have been investigated. Complexes of copper(II) and didentate mono(chelate) ligand with divalent oxoanions may be grouped in classes for each type of oxoanions depending on the coordinating nature. Complexes with divalent oxoanions formulated as $Cu(LL)(A)(H_2O)_n$, where LL = chelating didentate ligand and $A = CO_3^{2-}$ and SO_4^{2-} have been divided into five classes of local molecular structures, viz.: (I) mononuclear distorted square-based pyramids with a didentate oxoanion [4]; (II) polymeric distorted square-based pyramids with a bridging tridentate oxoanion [5]; (III) mononuclear

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square-based pyramids with a monodentate oxoanion [6]; (IV) polymeric elongated octahedron with bridging didentate oxoanions [7–10]; (V) dinuclear distorted square-based pyramid with double bridges of tridentate oxoanions [11]. With 2,2′-bipyridine (bipy) [12,13] or 1,10-phenanthroline (phen) [14] as the chelating ligand LL, such organic–inorganic hybrid compounds have hardly been synthesized so far. Since some copper(II) complexes with phen ligands have shown to be of interest to catalysis and biochemistry [15], it appeared of interest to prepare Cu(II)–phen coordination polymers with phosphates. So far the presence of one-dimensional interdigitation by phen stacks structures in a copper(II) coordination polymer has been rarely reported [16,17]. In this study we describe the hydrothermal synthesis and crystal structure of a double-chain coordination polymer with the formula $[Cu(phen)(H_2O)_2(\mu\text{-}HPO_4)]_n$ **1**. The spectroscopic properties and magnetic behavior are investigated and discussed.

Compound **1** was synthesized from the reaction mixture of $Cu(NO_3)_2 \cdot 3H_2O$ (0.241 g, 1.0 mmol), 1,10-phenanthroline (0.198 g, 1.0 mmol), $NaH_2PO_4 \cdot H_2O$ (0.175 g, 1.0 mmol) and H_2O (12 ml). The resulting solution was stirred in air for 5 min and transfer into a reactor bomb and heated at 160 °C for 120 h. Blue crystals of **1** were recovered in 55% yield after filtration, washing with water and drying on air. Anal. Calc. for $C_{12}H_{13}CuN_2O_6P$: C, 38.36; H, 3.46; N, 7.45%. Found: C, 38.41; H, 3.53; N, 7.48%. FT-IR data (cm^{-1}): 3415(m), 3051(w), 1601(m), 1497(w), 1474(m), 1447(s), 1319(w), 1250(w), 1176(s), 1076(s), 1032(w), 1001(m), 959(s), 888(s), 772(s), 730(m), 637(w), 618(w), 510(s) cm^{-1}.

A plot of the structure together with the numbering system is shown in Fig. 1. The structure of **1** consists of a chain of $[Cu(phen)(H_2O)_2(\mu\text{-}HPO_4)]$ units. The geometry around the copper(II) ion, which has a $CuN_2O_2O'_2$ chromophore, can be best described as tetragonally distorted octahedral. The basal plane consists of two pyridyl nitrogen atoms from the phen ligand (Cu–N distance 2.006(2) Å) and two oxygen atoms from a water molecule (Cu–O distance 1.969(2) Å). These basal planes are linked into an infinite chain by the didentate bridging hydrogenphosphate group. The two donor atoms from the almost symmetrically bridging hydrogenphosphate groups occupy the axial positions above and below the CuN_2O_2 planes, with a Cu–O distance of 2.470(2) Å. The axial O–Cu–O angle is 178.48(6)°.

The most interesting feature of **1** is its one-dimensional double chain structure. These two one-dimensional chains are antiparallel to each other along the a axis of the cell. Relatively strong hydrogen bonds exist between the oxygen atoms of the phosphate anions and the oxygen atoms of different water molecules with O···O distance of 2.615(3) and 2.672(3) Å, thereby keeping the chains together in pairs. See also Table 1 and Fig. 2 for details.

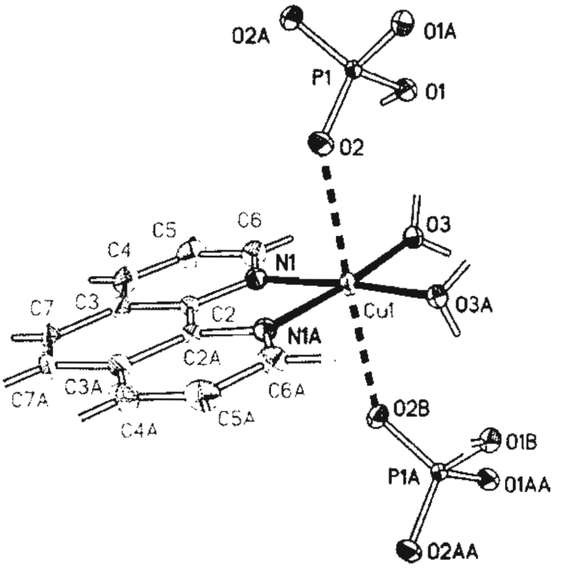

Fig. 1. Thermal ellipsoid plot (50% probability) of $[Cu(phen)(H_2O)_2(\mu\text{-}HPO_4)]_n$ **1**. Atoms marked with an "A", "B" or "AA" are generated by an inversion centre. Selected bond lengths (Å) and angles (°): Cu(1)–O(2) 2.470(2), Cu(1)–O(3) 1.969(2), Cu(1)–N(1) 2.006(2), P(1)–O(1) 1.484(2), P(1)–O(2) 1.461(2) and O(2)–Cu(1)–O(3) 86.09(8), O(2)–Cu(1)–N(1) 88.83(8), O(2)–Cu(1)–O(2B) 178.48(6), O(2)–Cu(1)–O(3A) 92.88(8), O(2)–Cu(1)–N(1A) 92.32(8), O(3)–Cu(1)–N(1) 91.99(9), O(3)–Cu(1)–O(3A) 94.11(8), O(3)–Cu(1)–N(1A) 173.76(9), N(1)–Cu(1)–N(1A) 81.94(9). Symmetry codes B: $-x$, y, $1/2-z$.

Table 1
The geometry of hydrogen bonding (Å, °)

D–H···A	D–H	H···A	D···A	D–H···A
O(3)–H(31)···O(1)	0.857	1.759	2.615(3)	179.0
O(3)–H(32)···O(1) [$x,-y,1/2+z$]	0.846	1.844	2.672(3)	165.8

It appears that the hydrogen bonding between the two chains plays an important role in the formation of this double-chain structure.

The phen ligands are located nearly parallel to the equatorial plane of copper(II) center and perpendicular to the chain extension direction. The distance between the closest two phen planes on a mono-chain is 7.022 Å. In the lattice, each phen ligand on a mono-chain is interpenetrated into the interspaces of the closest two phen ligands of another chain. Obviously, the lattice structure in **1** results in that all molecular planes of phen are nearly parallel in stacks. The shortest distance between two phen rings in **1** is 3.533 Å.

The polymeric structure of **1** is comparable to those of complexes with a carbonate anion $[Cu(dpyam)(CO_3)](H_2O)_3$ (in which dpyam = di-2-pyridylamine) [5] or with a sulfate group as an anion, like $[Cu(dpyam)(H_2O)_2(SO_4)]$ [9], $[Cu(ethylenediamine)(H_2O)_2(SO_4)]$ [7], $[Cu(bpy)(H_2O)_2(SO_4)]$ [8], $[Cu(oxamideoxime)(H_2O)_2(SO_4)]$ [18] and completely isomorphous with

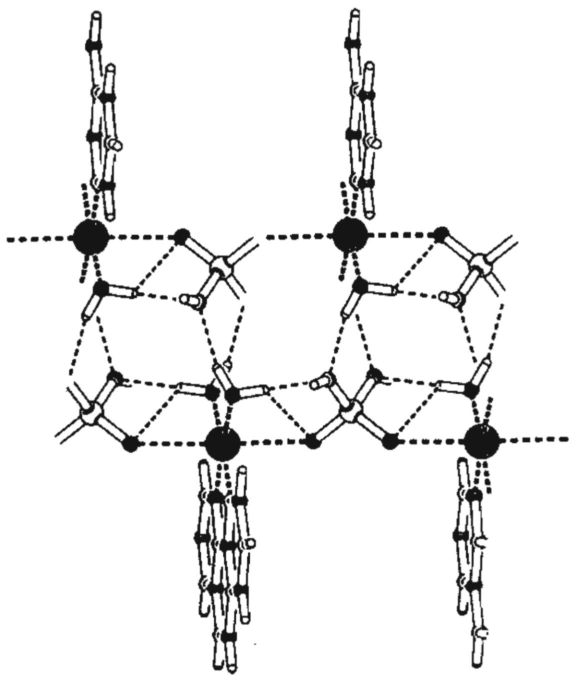

Fig. 2. View of the hydrogen bond system.

the compound $[Cu(phen)(H_2O)_2(SO_4)]$ [10]. The only difference is the phosphate group, which has a H donor atom present.

The EPR spectrum of compound **1** reveals, at RT and at 77 K, the same axial signal with a $g_\perp$ of 2.08 and $g_\parallel$ of 2.24, which is in agreement with a (distorted) octahedral geometry [19]. No hyperfine splitting is resolved.

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 $\chi_M \times T$ are plotted in Fig. 3. At 300 K, the compound exhibits a $\chi_M T$ value of 0.369 $cm^3 mol^{-1}$ K, which is close to the theoretical value expected for one noncoupled Cu(II) center with $S = 1/2$ ($\chi_M T =$ 0.375 $cm^3 mol^{-1}$ K). On lowering the temperature, the $\chi_M T$ value decreases until it reaches a value of about 0.03 $cm^3 mol^{-1}$ K, a behavior indicative of an antiferromagnetic coupling between two Cu centers.

The temperature dependence of χ_M was then fitted using the equation for a uniformly spaced copper(II) linear chain [20]. A Temperature Independent Paramagnetism (TIP) of 60×10^{-6} $cm^3 mol^{-1}$ per Cu(II) ion has been used. The best fit of the experimental magnetic susceptibility data (solid line in Fig. 3) was obtained using the magnetic parameters $g = 2.00$, $J = -5.86$ cm^{-1}, with $R = 1.6 \times 10^{-5}$.

Any magnetic interaction via the phosphate O–P–O bridge should be very weak, also because the unpaired electrons are in orbitals perpendicular to the chain.

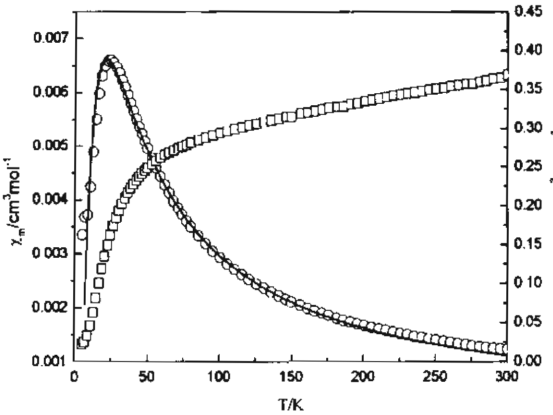

Fig. 3. A plot of temperature dependence of $\chi_M T$ vs. T [□] and χ_M vs. T [○] for compound **1**. The solid lines represents the calculated curve for the parameters $J = -5.86$ cm^{-1}, $g = 2.00$ (see text).

The present value may in addition have contributions from the hydrogen bonds. The J value found is in agreement with the weak antiferromagnetic interaction observed in the related compounds $[Cu(phen)(H_2O)_2(SO_4)]$ [10] and $[Cu(oxamideoxime)(H_2O)_2(SO_4)]$ [18], which have a sulfate O–S–O bridge in the axial direction and which have J values of −3.8 and −1.0 cm^{-1}, respectively.

Supplementary material

Crystal data for **1**: $C_{12}H_{13}CuN_2O_6P$, Monoclinic, $C2/c$ (No.15), $a = 14.870(2)$, $b = 13.83304(18)$, $c = 7.0220(9)$ Å, $\beta = 108.630(2)$ Å, $V = 1368.5(3)$ Å^3, $T = 293(2)$ K, $Z = 4$, $D_c = 1.824$ Mg m^{-3}, $\mu = 1.745$ mm^{-1}, $F(0\,0\,0) = 764$, k(Mo Kα) = 0.71073 Å. A total of 5,776 reflections were measured in the setting angles $2.06° < h < 28.28°$ by x scan method, of which 1633 were independent reflections. The crystal structure was solved by direct method, and refined by full-matrix least squares on F^2. Empirical absorption corrections were applied, which resulted in transmission coefficients ranging from 0.7403 to 1.000 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 nonhydrogen atoms using the SIR2002 and SHELXL-97 software package, and converging to $R_1 = 0.0388$ and $wR_2 = 0.0944$ $[I > 2\sigma(I)]$. CCDC-256479 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Center (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223 336033; e-mail: deposit@ccdc.cam.ac.uk].

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INORGANIC CHEMISTRY COMMUNICATIONS

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Synthesis, crystal structure and magnetic properties of an unexpected new coordination Cu(II) compound, containing two different phosphato-bridged dinuclear units; $[Cu_2(phen)_2(\mu\text{-}H_2PO_4\text{-}O,O')_2(H_2PO_4)_2][Cu_2(phen)_2(\mu\text{-}H_2PO_4\text{-}O,O')(\mu\text{-}H_2PO_4\text{-}O)(\mu\text{-}HPO_4\text{-}O)]_2(H_2O)_9$(phen = 1,10-phenanthroline)

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Abstract

The crystal structure of a copper(II) complex containing the ligand 1,10-phenanthroline (phen) with mono- and di-dentate $H_2PO_4^-$ and monodentate HPO_4^{2-} oxoanions, $[Cu_2(phen)(\mu\text{-}H_2PO_4\text{-}O,O')_2(H_2PO_4)_2][Cu_2(phen)_2(\mu\text{-}H_2PO_4\text{-}O,O')(\mu\text{-}H_2PO_4\text{-}O)(\mu\text{-}HPO_4\text{-}O)]_2(H_2O)_9$, is reported and determined by X-ray crystallography. Two crystallographically independent dinuclear units with different bridging properties of (di)hydrogenphosphato anions are found in this compound.

The two Cu(II) ions in the first unit, $[Cu_2(phen)(\mu\text{-}H_2PO_4\text{-}O,O')_2(H_2PO_4)_2]$, are bridged by two didentate bridging dihydrogenphosphato monoanions and also contains two non-bridging monovalent dihydrogenphosphato anions. The geometry of the Cu(II) ions is square pyramidal with a Cu–Cu distance of 5.043(3) Å.

The two Cu(II) ions in the second unit, $[Cu_2(phen)_2(\mu\text{-}H_2PO_4\text{-}O,O')(\mu\text{-}H_2PO_4\text{-}O)(\mu\text{-}HPO_4\text{-}O)]$, are bridged by three different hydrogenphosphate anions; a didentate bridging dihydrogenphosphate monoanion, a monodentate dihydrogenphosphate bridging monoanion and a monodentate hydrogenphosphate dianion. This bridging mode is unique and has not been reported so far for dinuclear Cu(II) compounds. The geometry of the Cu(II) ions in this second unit is distorted square pyramidal and the Cu–Cu distance is 3.074(3) Å.

The magnetic susceptibility measurement (5–300 K) have been fitted with two different J values. A weak antiferromagnetic interaction between the Cu ions in one dinuclear unit with $J_1 = -8.2\ \mathrm{cm}^{-1}$ and a very weak ferromagnetic interaction between the Cu ions in the other dinuclear unit with $J_2 = 0.96\ \mathrm{cm}^{-1}$, allow an acceptable fit.

Keywords: Crystal structure; Copper(II); Dihydrogenphosphate complex; Magnetic properties

Open-framework materials are of considerable interest due to their rich structural chemistry and potential applications in catalysis, separation and ion exchange [1,2]. One class of these materials concerns aluminophosphates, commonly known as AlPOs [3]. Many of these compounds exhibit novel microporous structures. Two notable recent examples are VPI-5 and JDF-20, containing extra-large 18- and 20-ring channels, respectively [4,5]. Recently, others and we have focused on the synthesis of inorganic–organic hybrid compounds by incorporating organic ligands in the structure of copper phosphates [6–11]. Compared with

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inorganic ligands, organic multidentate ligands possess more rich coordination sites and a wide variety of shapes.

To obtain more insight into bridging phosphate anions, we have extended our study using the ligand 1,10-phenanthroline (abbreviated as phen). In the present study, a mixed hydrogenphosphato-bridging Cu(II) complex, [Cu$_2$(phen)(μ-H$_2$PO$_4$-*O*,*O*′)$_2$(H$_2$PO$_4$)$_2$][Cu$_2$(phen)$_2$(μ-H$_2$PO$_4$-*O*,*O*′) (μ-H$_2$PO$_4$-*O*)(μ-HPO$_4$-*O*)]$_2$(H$_2$O)$_9$, containing two crystallographically independent molecules with different coordination modes of (di)hydrogenphosphato bridges, is described and investigated structurally and magnetically. The unit cell of the title compound contains two crystallographically independent dinuclear units, one unit [Cu$_2$(phen)$_2$(μ-H$_2$PO$_4$)$_2$(H$_2$PO$_4$)$_2$] (unit A) and two units of [Cu$_2$(phen)$_2$(μ-H$_2$PO$_4$)$_2$(μ-HPO$_4$)]$_2$ (unit B). Also nine water molecules, of which one is disordered, are present in the unit cell. The dihydrogenphosphato bridges in the two crystallographically independent units are totally different in coordination modes. The first dinuclear moiety, [Cu$_2$(phen)(μ-H$_2$PO$_4$-*O*,*O*′)$_2$(H$_2$PO$_4$)$_2$] (unit A, Fig. 1(a))

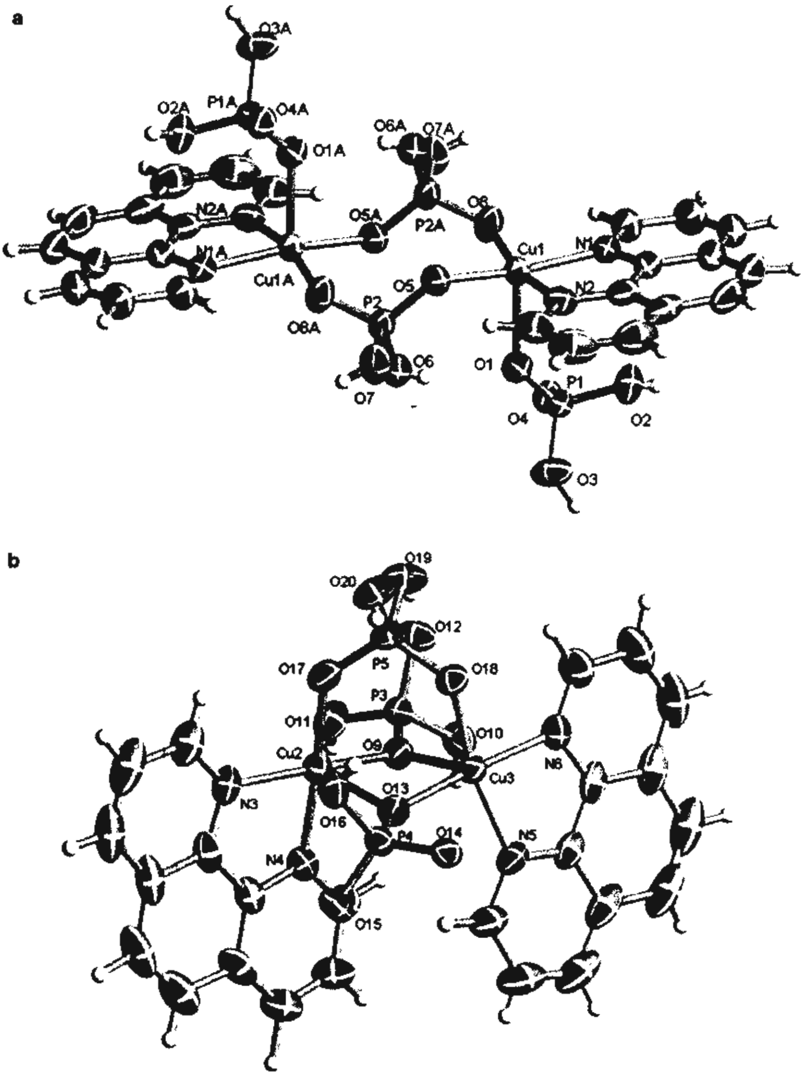

Fig. 1. The molecular structure of [Cu$_2$(phen)(μ-H$_2$PO$_4$*O*,*O*′)$_2$(H$_2$PO$_4$)$_2$][Cu$_2$(phen)$_2$(μ-H$_2$PO$_4$-*O*,*O*′)(μ-H$_2$PO$_4$-*O*)(μ-HPO$_4$-*O*)]$_2$(H$_2$O)$_8$, the uncoordinating water molecules are omitted for clarity. (a) The structure of [Cu$_2$(phen)(μ-H$_2$PO$_4$*O*,*O*′)$_2$(H$_2$PO$_4$)$_2$] (unit A). Selected bond distances (Å) and angles: Cu(1)–N(1) 2.015(3), Cu(1)–N(2) 2.021(3), Cu(1)–O(1) 2.230(3), Cu(1)–O(5) 1.949(3), Cu(1)–O(8) 1.928(3), Cu(1)–Cu(1A) 5.043(3), O(1)–Cu(1)–O(5) 94.0(1), O(1)–Cu(1)–O(8) 99.9(1), O(1)–Cu(1)–N(1) 96.5(1), O(1)–Cu(1)–N(2) 92.4(1), O(5)–Cu(1)–O(8) 94.9(1), O(5)–Cu(1)–N(1) 167.8(1), O(5)–Cu(1)–N(2) 91.8(1), O(8)–Cu(1)–N(1) 89.6(1), O(8)–Cu(1)–N(2) 165.6(1). $A = -x + 2, -y + 2, -z$. (b) The structure of [Cu$_2$(phen)$_2$(μ-H$_2$PO$_4$-*O*,*O*′)(μ-H$_2$PO$_4$-*O*)(μ-HPO$_4$-*O*)] (unit B). Selected bond distances (Å) and angles (°): Cu(2)–N(3) 1.996(3), Cu(2)–N(4) 1.997(3), Cu(2)–O(9) 2.288(3), Cu(2)–O(13) 1.930(2), Cu(2)–O(17) 1.950(2), Cu(3)–N(5) 2.011(3), Cu(3)–N(6) 1.995(3), Cu(3)–O(9) 1.945(2), Cu(3)–O(13) 2.261(3), Cu(3)–O(18) 1.937(3), Cu(2)–Cu(3) 3.074(3), O(9)–Cu(2)–O(13) 84.0(1), O(9)–Cu(2)–O(17) 93.0(1), O(9)–Cu(2)–N(3) 95.8(1), O(9)–Cu(2)–N(4) 98.9(1), O(13)–Cu(2)–O(17) 91.8(1), O(13)–Cu(2)–N(3) 176.0(1), O(13)–Cu(2)–N(4) 93.5(1), O(17)–Cu(2)–N(3) 92.2(1), O(17)–Cu(2)–N(4) 167.5(1), O(9)–Cu(3)–O(13) 84.4(1), O(9)–Cu(3)–O(18) 92.4(1), O(9)–Cu(3)–N(5) 93.2(1), O(9)–Cu(3)–N(6) 171.4(1), O(13)–Cu(3)–O(18) 92.6(1), O(13)–Cu(3)–N(5) 86.6(1), O(13)–Cu(3)–N(6) 102.5(1), O(18)–Cu(3)–N(5) 174.2(1), O(18)–Cu(3)–N(6) 92.4(1), Cu(2)–O(9)–Cu(3) 92.8(1), Cu(2)–O(13)–Cu(3) 94.0(1). $A = -x + 2, -y + 2, -z$

is doubly bridged by two didentate dihydrogenphosphato anions. The geometry of the Cu(II) ions is square pyramidal (τ value of 0.04; the τ value describes the relative amount of trigonality; $\tau = 0$ for square pyramid and $\tau = 1$ for trigonal bipyramidal) [12]. The basal plane of CuN_2O_2O' chromophore consists of two oxygen atoms of the two bridging dihydrogenphosphato groups, O(5) and O(8) (Cu–O distances of 1.949(3) and 1.928(3) Å) and two nitrogen atoms of a phen ligand (Cu–N distances of 2.015(3), 2.021(3) Å). The fifth axial coordination site is occupied by one oxygen atom of non-bridging monodentate dihydrogenphosphato group at the Cu–O(1) distance of 2.230(3) Å. The basal angles are 167.8(1)° and 165.6(1)°. The four in-plane atoms, N(1), N(2), O(5) and O(8) are essentially planar (r.m.s. deviation 0.098 Å), with a slightly tetrahedral twist (dihedral angles between the CuN_2 and CuO_2 planes 16.1°). The Cu atom lies 0.197 Å above this plane towards O(1). The Cu···Cu distance is 5.043(3) Å. The coordinated P–O bonds, 1.498(3) and 1.502(3) Å, are shorter than the uncoordinated P–OH bonds, 1.548(3) and 1.567(3) Å. These differences are normally found for the two-coordinate bridging coordination of dihydrogenphosphate anion [13]. The non-bridging monodentate dihydrogenphosphato group involves O–P–O angles ranging from 106.7(1) to 115.3(1) Å. The P–OH bonds, 1.563(3) and 1.572(3) Å, are longer than the P=O bonds, 1.495(3) and 1.570(3) Å, which is in usual observation.

The second unit, $[Cu_2(phen)_2(\mu\text{-}H_2PO_4\text{-}O,O')(\mu\text{-}H_2PO_4\text{-}O)(\mu\text{-}HPO_4\text{-}O)]$ (unit B, Fig. 1(b)), is slightly asymmetric and bridged by three different hydrogenphosphate anions: a didentate bridging dihydrogenphosphate anion, a monodentate bridging dihydrogenphosphate anion and a monodentate bridging hydrogenphosphate anion. This mode is unique and not reported so far for dinuclear Cu(II) compounds.

The geometry of the Cu(II) ions is distorted square pyramidal (τ value of 0.14 and 0.004 for Cu2 and Cu3, respectively) and the Cu–Cu distance is 3.074(3) Å. The basal plane of the CuN_2O_2O' chromophore of each Cu(II) ion consists of two nitrogen atoms of a phen ligand (Cu–N distances vary from 1.995(4) to 2.011(3) Å), one oxygen atom of a didentate bridging dihydrogenphosphato anion (Cu–O distances 1.937(3), 1.950(3) Å) and an oxygen atom of a monodentate bridging dihydrogenphosphato anion (Cu(3)–O(9) distance 1.945(3) Å) or of a monodentate bridging hydrogenphosphato anion (Cu(2)–O(13) distance 1.930(2) Å). The basal angles are 167.5(1)°, 176.0(1)° and 171.4(1)°, 174.2(1)° for Cu2 and Cu3, respectively. The fifth axial coordination site is occupied by an oxygen atom of monodentate hydrogenphosphato anion (Cu(3)–O(13) distance 2.261(3) Å) or of a monodihydrogenphosphato anion (Cu(2)–O(9) distance 2.288(3) Å). The four basal atoms show a small tetrahedral distortion with a dihedral angle of 11.5° and 7.5° formed between CuO_2 and CuN_2 planes and the copper atoms are displaced by −0.095 and −0.047 Å from the basal plane towards the O(9) and O(13) atoms.

The lattice structure is stabilized by a complicated hydrogen bonding network between the oxygen atom of the non-bridged dihydrogenphosphate anion and oxygen atoms of the bridged dihydrogenphosphate anion in unit A and unit B ($O_{(H2PO4)}\cdots O_{(\mu\text{-}H_2PO4)}$ distances 2.602(1), 2.532–2.692(1) Å, respectively); between oxygen atom of dihydrogenphosphate group of unit A and water oxygen atom ($O_{(\mu\text{-}H_2PO4)}\cdots O_{(water)}$ distance 2.564(1) Å); between oxygen atoms of different dihydrogenphosphate groups of unit B ($O_{(\mu\text{-}H_2PO4)}\cdots O_{(\mu\text{-}H_2PO4)}$ distance 2.547(1) Å) and between oxygen atoms of dihydrogenphosphate groups and hydrogenphosphate group of unit B ($O_{(\mu\text{-}H_2PO4)}\cdots O_{(\mu\text{-}HPO_4)}$ distances 2.461(1)–2.584(1) Å). The unique bridging mode using three different phosphates is clearly stabilized by this H bonding pattern.

The electronic diffuse reflectance spectrum shows a broad band at 14,400 cm^{-1}. This single broad peak is consistent with the square pyramidal stereochemistry and assigned to be d_{z^2}, d_{xy}, d_{xz}, $d_{yz} \rightarrow d_{x^2y}{}^2$ transition [14].

The polycrystalline EPR spectrum of the powdered compound reveals at room temperature and at 77 K an axial signal with $g_\parallel = 2.27$ and $g_\perp = 2.05$, respectively. These signals are consistent with the $d_{x^2-y}{}^2$ ground state and resulting from a distorted square-based pyramidal geometry. No strong triplet signals have been observed. However, at around 160 mT a very weak "half-field" signal is observed, indicative for dinuclear compounds.

The magnetic susceptibility of a powdered sample was measured from 5 to 250 K. The magnetic properties are given in Fig. 2 in the form of a χT vs. T (a) and χ vs. T plots (b). In the χT curve, at 250 K, the χT value is 2.088 $cm^3\,mol^{-1}\,K$, close to that expected for six uncoupled copper centres ($\chi T = 2.25\ cm^3\,mol^{-1}\,K$, $g = 2$). As the temperature is decreased the value remains constant until 50 K, where a decrease begins, pointing at a weak antiferromagnetic interaction. This is confirmed by the fact that no maximum is observed in the χ vs. T plot.

Two crystallographically different dinuclear units form the unit cell with a total of six coppers, 2 in unit A and

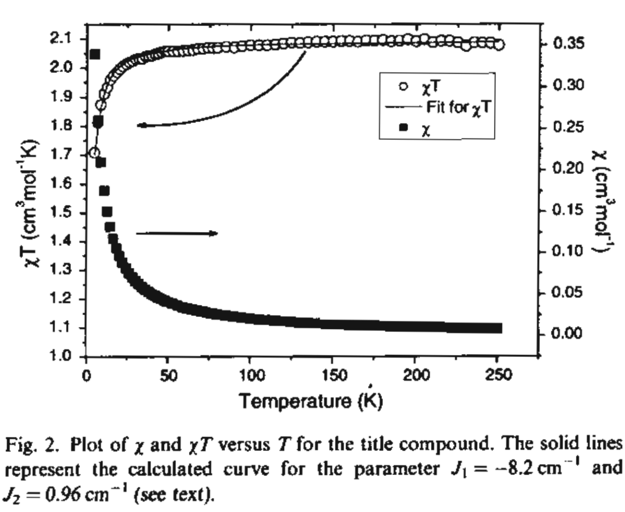

Fig. 2. Plot of χ and χT versus T for the title compound. The solid lines represent the calculated curve for the parameter $J_1 = -8.2\ cm^{-1}$ and $J_2 = 0.96\ cm^{-1}$ (see text).

2×2 in unit B. The following Hamiltonian was considered to fit the magnetic data: $H = -J_1 \mathrm{S_a S_b} - 2 \cdot J_2 \mathrm{S_c S_d}$, in which J_1 is the interaction in the dinuclear unit A and J_2 that in the dinuclear unit B. As they are independent units, each may have its own coupling constant. Considering an identical g value for the four different coppers and including standard temperature independent paramagnetism, the molar magnetic susceptibility is, based on a Bleaney–Bowers equation [15], described by

$$\chi = 2N_\mathrm{A} g^2 \beta^2 / 3k_\mathrm{B} T[1/(3 + \exp(-J_1/K_\mathrm{B}T)) + 2/(3 + \exp(-J_2/K_\mathrm{B}T))] + \mathrm{TIP}.$$

The best set of parameters that fits the magnetic data are: $J_1 = -8.2\ \mathrm{cm}^{-1}$, $J_2 = 0.96\ \mathrm{cm}^{-1}$ and $g = 1.92$. TIP was kept constant with a value of 60×10^{-4} per copper atom. The g value is somewhat lower than expected. This may be due to the small quantity of the sample which was measured. The low values for the coupling constants indicate very weak interactions between the coppers in both dinuclear units. For the unit bridged by two dihydrogenophosphate anions (unit A), the negative value of J_1 implies that the interaction is antiferromagnetic. As the two coppers have a square pyramidal (SP) geometry, their magnetic orbital is $d_{x^2-y^2}$. The angle between these orbitals is about 180°. This and the fact that they are both in the same plane explain the antiferromagnetic interaction. The weakness of the interaction can also be due to the long distance between the two coppers. J_2 (unit B) is on the contrary positive. The magnetic orbitals of the coppers are again $d_{x^2-y^2}$, as the coppers have SP geometry. One of the anions is bridging the two coppers through their magnetic orbitals, but in this case, they are parallel to each other, thus no interaction is expected. A rather complicated explanation of the ferromagnetic interaction alights and DFT calculations will be needed for a better comprehension of this parameter.

The very weak (anti)ferromagnetic couplings found in the title compound is in agreement with this structural feature and the large Cu–Cu distances and is also in agreement with the earlier observed compound, $[\mathrm{Cu(dpyam)}(\mu\text{-}\mathrm{H_2PO_4})(\mathrm{H_2PO_4})]_2$, with a J_1 value of $-8.2\ \mathrm{cm}^{-1}$ [6]. The unusual ferromagnetism observed for the second unit could be further investigated with DFT calculations, which is out of the scope of this study.

Supplementary material

Crystal data: $\mathrm{C_{72}H_{71}Cu_6N_{12}O_{49}P_{10}}$ ($M_\mathrm{w} = 2579.4$), Monoclinic, $P2(1)/n$, $a = 11.9784(5)$, $b = 31.1685(14)$, $c = 13.3329(6)$ Å, $\beta = 101.5570(10)°$, $V = 4876.9(4)$ Å^3, $T = 293(2)$ K, $Z = 2$, $D_\mathrm{c} = 1.757$;Mg/m^3, $\mu = 1.553\ \mathrm{mm}^{-1}$, $F(000) = 2606.0$, $k(\mathrm{Mo\ K\alpha}) = 0.71073$ Å, 42,866 reflections measured ($3.07° < h < 25.03°$), 11,666 unique ($R_\mathrm{int} = 0.0578$), $R_1 = 0.0497$, $wR_2 = 0.1240$. Reflection data were collected on a 1K Bruker SMART CCD area-detector diffractometer. Data reduction and cell refinements were performed using the program SAINT [16]. The structure was solved by direct methods and refined by full-matrix least-squares method on $(F_\mathrm{obs})^2$ with anisotropic thermal parameters for all non-hydrogen atoms using the SHELXTL-PC [17] software package. All hydrogen atoms were located and refined isotropically except 13 water hydrogen atoms, which were unable to locate and also not fixed. One water oxygen atom was disordered and refined with site occupancies of 0.50 and 0.50. The location of the H20O belonging to O20 is influenced by the disordered atom O3W (two positions, no hydrogen atoms could be located nor fixed) to which it forms weak hydrogen bonds. The molecular graphics were created by using SHELXTL-PC [17]. CCDC No. 284274. See http://www.ccdc.cam.ac.uk for crystallographic data in CIF format.

Synthesis: The compound was synthesized by adding an aqueous solution (15 ml) of $\mathrm{Cu(ClO_4)_2(H_2O)_6}$ (0.19 g, 0.5 mmol) to a solution of phen (0.10 g, 0.5 mmol) in ethanol (10 ml) and followed by an aqueous solution (10 ml) of potassium dihydrogenphosphate (0.14 g, 1.0 mmol). The resulting blue-green solution was allowed to evaporate at room temperature. After several days, bluish-green crystals were deposited. Yield: ca. 55%. They were filtered off, washed with the mother liquid and dried in air. Anal Calc. for $\mathrm{C_{72}H_{84}Cu_6N_{12}O_{49}P_{10}}$ (M_w: 2592.5): C, 33.4; H, 3.3; N, 6.5. Found: C, 32.9; H, 3.0; N, 6.5%. FT-IR data (cm^{-1}): 1167s, 1109s and 1078(s), ν_as(P–O); 946s, ν_s(P–O); 893m, 886m and 856s, δ (P–O(H)) out-of-plane deformation; 596m, 535s, and 509s, δ (O–P–O).

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Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2005.10.020.

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