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A new one-dimensional coordination polymer and a new supramolecular dimer made of trinuclear copper(II) complexes: crystal structure and magnetic properties

En-Qing Gao,[ab] **Qi-Hua Zhao,**[a] **Jin-Kui Tang,**[a] **Dai-Zheng Liao,***[ac] **Zong-Hui Jiang**[a] **and Shi-Ping Yan**[a]

[a] *Department of Chemistry, Nankai University, Tianjin, 300071, P.R. China.*
E-mail: coord@nankai.edu.cn
[b] *Department of Chemistry, Qufu Normal University, Qufu, 273165, P.R. China*
[c] *State Key Laboratory of Structural Chemistry, Institute of Research on Structures of Matter, Fuzhou, 350002, P.R. China*

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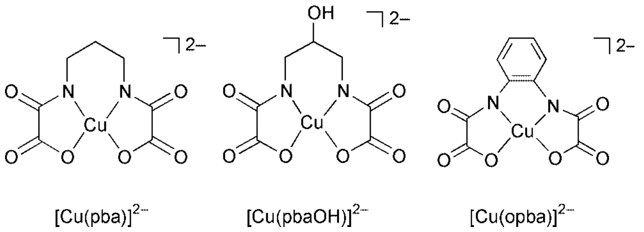
Two oxamato-bridged copper(II) complexes of formula $[Cu_3(pbaOH)(tmen)_2(H_2O)(ClO_4)]_n[ClO_4]_n\cdot nH_2O$ **1** and $[Cu_3(opba)(tmen)_2(H_2O)_3][Cu_3(opba)(tmen)_2(H_2O)_2][ClO_4]_4\cdot 3H_2O$ **2** have been synthesized and characterized by IR, ESR, electronic spectra and X-ray crystallographic analyses, where $pbaOH^{4-}$ = 2-hydroxyl-*N*,*N′*-trimethylenebis(oxamate), $opba^{4-}$ = *N*,*N′*-*o*-phenylenebis(oxamate), tmen = *N*,*N*,*N′*,*N′*-tetramethylethylenediamine. Both complexes consist of cationic trinuclear entities, in which copper atoms reside in square-planar (4) or square-pyramidal (4+1) environments. In complex **1** the hydroxyl group of one trinuclear entity coordinates to a terminal copper atom of another, thus forming an unusual one-dimensional chain. In **2** two neighboring trinuclear cations interact to form an interesting supramolecular (or "supracationic") dimer. The magnetic properties of the two complexes have been investigated, indicating that two copper(II) ions bridged by the oxamato bridge interact antiferromagnetically with $J = -334.4\ cm^{-1}$ for **1** and $-356.6\ cm^{-1}$ for **2** (based on $\hat{\boldsymbol{H}} = -\boldsymbol{J}\hat{\boldsymbol{S}}_1\cdot\hat{\boldsymbol{S}}_2$).

Introduction

Molecular magnetism has seen a rapid development in the last two decades or so.[1–3] It is now well established that the $C_2X_2Y_2^{2-}$ (X, Y = O, N or S) bridging ligands are efficient mediators for magnetic interactions.[4–8] By using the N,N′-substituted bis(oxamato)copper(II) complexes, such as $[Cu(pba)]^{2-}$, $[Cu(pbaOH)]^{2-}$ and $[Cu(opba)]^{2-}$ (Scheme 1), as bridging ligands to link another two copper(II) ions Ribas and co-workers prepared a number of trinuclear copper(II) complexes.[9–13] It has been shown that the magnetic interaction within these trinuclear species can be tuned by choosing appropriate terminal ligands, which are said to act as "adjusting screws". However, only a limited number of such complexes, most of which consist of isolated trinuclear species,[11,12] have been characterized structurally. Recently, by using NCS^- as the bridge between Cu^{II}_3 entities, a one-dimensional chain compound has been prepared.[13] Here we report two interesting structures made of trinuclear copper(II) complexes, of formulae $[Cu_3(pbaOH)(tmen)_2(H_2O)(ClO_4)]_n[ClO_4]_n\cdot nH_2O$ **1** and $[Cu_3(opba)(tmen)_2(H_2O)_3][Cu_3(opba)(tmen)_2(H_2O)_2][ClO_4]_4\cdot 3H_2O$ **2**. Complex **1** consists of one-dimensional chains and **2** of interesting supramolecular dimers formed *via* π–π interactions. The magnetic properties of the two complexes are also reported.



Scheme 1

Experimental

Materials

All the starting chemicals were of A. R. grade and used as received. The mononuclear precursors, $Na_2[Cu(pbaOH)]\cdot 3H_2O$[14] and $Na_2[Cu(opba)]\cdot 3H_2O$,[15] were prepared as described.

Synthesis

An aqueous solution (5 cm^3) of tmen (1 mmol) was added to a stirred aqueous solution (10 cm^3) of $Cu(ClO_4)_2\cdot 6H_2O$ (1 mmol). To the resulting solution was added dropwise an aqueous solution (20 cm^3) of $Na_2[Cu(pbaOH)]\cdot 3H_2O$ or $Na_2[Cu(opba)]\cdot 3H_2O$ (0.5 mmol) with constant stirring. The mixture was stirred for 10 min and then filtered to remove any possible precipitate. Slow evaporation of the filtrate at room temperature afforded greenish blue crystals in two months. Calc. for $[Cu_3(pbaOH)(tmen)_2(H_2O)(ClO_4)]_n[ClO_4]_n\cdot nH_2O$ **1**, $C_{19}H_{40}Cl_2Cu_3N_6O_{17}$: C, 25.75; H, 4.55; N, 9.48. Found: C, 25.50; H, 4.65; N, 9.41%. Calc. for $[Cu_3(opba)(tmen)_2(H_2O)_3][Cu_3(opba)(tmen)_2(H_2O)_2][ClO_4]_4\cdot 3H_2O$ **2**, $C_{44}H_{88}Cl_4Cu_6N_{12}O_{36}$: C, 28.05; H, 4.71; N, 8.92. Found: C, 28.41; H, 4.58; N, 9.16%. Main IR bands (KBr, cm^{-1}): **1**, 3400s (br), 3250sh, 2900w, 1635vs, 1600vs, 1460m, 1320m, 1105s, 1050sh, 805m, 760w; **2**, 3400m (br), 2900w, 1620vs, 1590vs, 1460m, 1425m, 1355m, 1275w, 1100s, 1080s, 945w, 865w, 802m, 760m.

Physical measurements

Elemental analyses (C, H, N) were performed on a Perkin-Elmer 240 analyser. IR spectra were recorded on a Shimadzu

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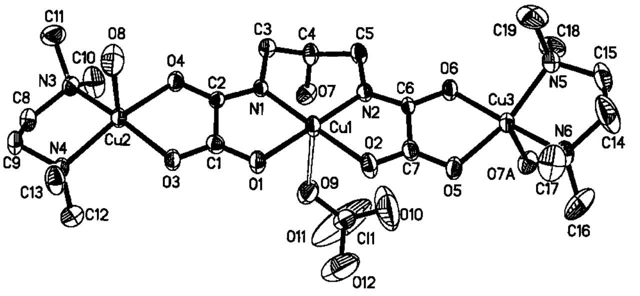

Fig. 1 An ORTEP[18] view of the trinuclear unit in **1**. The thermal ellipsoids are drawn at the 30% probability level.

IR-408 spectrometer as KBr pellets, electronic spectra on a Shimadzu UV-2101PC UV-VIS scanning spectrophotometer in acetonitrile, and X-band ESR spectra on a Bruker ER 200 D-SRC ESR spectrometer. Variable-temperature magnetic susceptibilities were measured on a Quantum Design MPMS-7 SQID magnetometer. Diamagnetic corrections were made with Pascal's constants for all the constituent atoms.[16]

Crystallographic studies

Diffraction intensity data for single crystals of **1** and **2** were collected at room temperature on a Bruker Smart 1000 CCD area detector equipped with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). Empirical absorption corrections were applied using the SADABS program.[17a] The structure was solved by the direct method and refined by full-matrix least squares on F^2 with anisotropic thermal parameters for all non-hydrogen atoms.[17b] The hydrogen atoms of solvent molecules were not added, and the other hydrogen atoms located geometrically and refined isotropically. Pertinent crystallographic data and structure refinement parameters are summarized in Table 1.

CCDC reference numbers 155651 and 155652.

See http://www.rsc.org/suppdata/dt/b1/b100142f/ for crystallographic data in CIF or other electronic format.

Results and discussion

Description of the structure of 1

The structure of complex **1** consists of one-dimensional chains derived from $[(H_2O)(tmen)Cu\{Cu(pbaOH)(ClO_4)\}Cu(tmen)]^+$ cationic units, non-coordinated water molecules and perchlorate ions. A perspective view of the trinuclear unit is depicted in Fig. 1 and selected bond lengths and angles are listed in Table 2.

In the trinuclear unit the neighboring copper atoms are bridged by oxamato groups. All copper atoms are in a 4 + 1 environment with a square-pyramidal geometry. The basal plane of the central Cu1 atom is formed by the two deprotonated amido nitrogens and the two carboxylato oxygens from the $pbaOH^{4-}$ ligand, and the apical position is occupied by an oxygen atom (O9) from one perchlorate anion at 2.684(6) Å. The basal positions of the terminal copper atoms are occupied by two oxygen atoms from the oxamato bridge and two nitrogen atoms from the tmen ligand. The coordination polyhedron of Cu2 is completed by a water molecule (Cu2–O8, 2.28 Å), and that of Cu3 by a hydroxyl oxygen atom of the $pbaOH^{4-}$ ligand from another trinuclear entity (Cu3–O7A, 2.453 Å). As a result of this coordination one of the terminal copper atoms in a trinuclear entity is linked to the central copper atom that arises from another trinuclear entity generated by a 2_1 operation, thus leading to a cationic one-dimensional helix chain around the screw axis. The structure is reminiscent of that of $[(SCN)(tmen)Cu\{Cu(pba)(ClO_4)\}Cu(tmen)(\mu\text{-}NCS)]_n\cdot 3nH_2O$.[13] In this compound a terminal copper atom of a trinuclear entity and the central one of another trinuclear entity are bridged by a NCS^- ligand, leading to a neutral one-dimensional system that is very similar to that in **1**.

Table 1 Summary of crystallographic data for complexes **1** and **2**

	1	2
Formula	$C_{19}H_{40}Cl_2Cu_3N_6O_{17}$	$C_{44}H_{88}Cl_4Cu_6N_{12}O_{36}$
Formula weight	886.09	1884.30
Crystal system	Orthorhombic	Monoclinic
Space group	$Pca2_1$	$P2_1/n$
a/Å	21.2818(11)	20.2579(13)
b/Å	12.8206(7)	17.1410(11)
c/Å	12.6462(7)	22.1609(14)
β/°		102.6130(10)
V/Å^3	3450.5(3)	7509.5(8)
Z	4	4
μ(Mo-Kα)/mm^{-1}	2.065	1.905
T/K	293(2)	298(2)
Independent reflections (R_{int})	5353 (0.0368)	13088 (0.0308)
$R1$, $wR2$ [$I > 2\sigma(I)$]	0.0403, 0.0989	0.0509, 0.1321
$R1$, $wR2$ (all data)	0.0516, 0.1069	0.0828, 0.1560

Table 2 Selected bond distances (Å) and angles (°) for **1**

Cu(1)–N(1)	1.930(4)	Cu(1)–N(2)	1.933(4)
Cu(1)–O(1)	1.973(4)	Cu(1)–O(2)	1.989(5)
Cu(1)–O(9)	2.684(6)	Cu(2)–O(4)	1.961(4)
Cu(2)–O(3)	1.998(4)	Cu(2)–N(3)	2.027(5)
Cu(2)–N(4)	2.028(4)	Cu(2)–O(8)	2.285(5)
Cu(3)–O(6)	1.964(4)	Cu(3)–O(5)	1.984(4)
Cu(3)–N(5)	2.004(5)	Cu(3)–N(6)	2.009(5)
Cu(3)–O(7A)	2.453(4)	C(1)–C(2)	1.538(7)
O(1)–C(1)	1.250(7)	O(3)–C(1)	1.231(7)
O(4)–C(2)	1.273(6)	N(1)–C(2)	1.299(7)
O(2)–C(7)	1.253(7)	O(5)–C(7)	1.242(7)
O(6)–C(6)	1.287(6)	N(2)–C(6)	1.288(7)
C(6)–C(7)	1.541(7)		

N(1)–Cu(1)–N(2)	94.84(18)	N(1)–Cu(1)–O(1)	85.07(17)
N(2)–Cu(1)–O(1)	179.6(2)	N(1)–Cu(1)–O(2)	178.0(2)
N(2)–Cu(1)–O(2)	85.32(17)	O(1)–Cu(1)–O(2)	94.75(16)
N(1)–Cu(1)–O(9)	91.49(18)	N(2)–Cu(1)–O(9)	90.4(2)
O(1)–Cu(1)–O(9)	90.0(2)	O(2)–Cu(1)–O(9)	90.5(2)
O(4)–Cu(2)–O(3)	83.99(16)	O(4)–Cu(2)–N(3)	92.90(18)
O(3)–Cu(2)–N(3)	166.8(2)	O(4)–Cu(2)–N(4)	167.61(19)
O(3)–Cu(2)–N(4)	92.91(17)	N(3)–Cu(2)–N(4)	87.39(18)
O(4)–Cu(2)–O(8)	91.59(19)	O(3)–Cu(2)–O(8)	91.5(2)
N(3)–Cu(2)–O(8)	101.4(2)	N(4)–Cu(2)–O(8)	100.5(2)
O(6)–Cu(3)–O(5)	84.30(16)	O(6)–Cu(3)–N(5)	92.1(2)
O(5)–Cu(3)–N(5)	159.3(2)	O(6)–Cu(3)–N(6)	171.8(2)
O(5)–Cu(3)–N(6)	92.54(19)	N(5)–Cu(3)–N(6)	88.1(2)
O(6)–Cu(3)–O(7A)	91.60(17)	O(5)–Cu(3)–O(7A)	104.47(19)
N(5)–Cu(3)–O(7A)	96.0(2)	N(6)–Cu(3)–O(7A)	96.52(19)

Symmetry transformation used to generate equivalent atoms: A $-x + 1, -y + 1, z + \frac{1}{2}$.

Within a trinuclear entity the dihedral angles between the central Cu1 and the terminal Cu2 and Cu3 basal planes are 8.6 and 24.3°, respectively. The Cu1 ··· Cu2 and Cu1 ··· Cu3 distances are 5.180 and 5.161 Å, respectively. The shortest metal-to-metal separation between trinuclear entities is 5.916 Å (Cu3 ··· Cu1A).

In the lattice the non-coordinated water molecule and perchlorate ion lie between chains. The water molecule forms two hydrogen bonds: one with a carboxylato oxygen atom [O2 ··· O17($-x + \frac{3}{2}$, $y - 1$, $z + \frac{1}{2}$), 2.903 Å] from a chain and the other with the coordinated water molecule [O8 ··· O17 ($x - \frac{1}{2}$, $-y + 1$, z), 2.666 Å] from another chain, thus yielding a two-dimensional hydrogen-bonded supramolecular network.

Description of the structure of 2

The structure of complex **2** consists of two different, but similar, cationic trinuclear entities $[(H_2O)(tmen)Cu\{Cu(opba)(H_2O)\}Cu(tmen)(H_2O)]^{2+}$ (denoted as **2a**) and $[(H_2O)$-

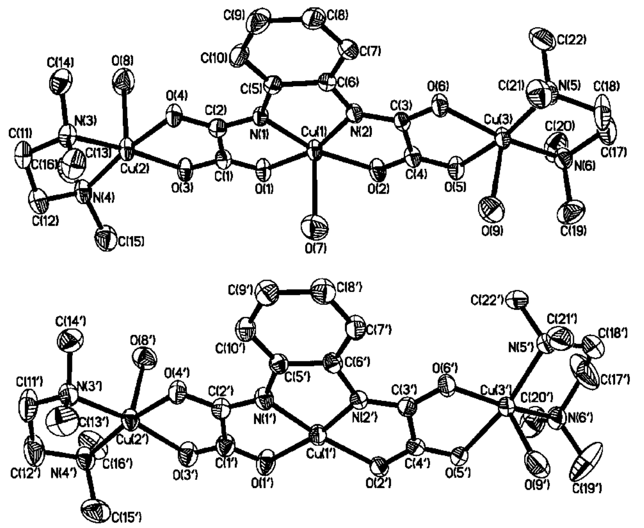

Fig. 2 ORTEP view of the two trinuclear entities in **2**. Details as in Fig. 1.

Table 3 Selected bond distances (Å) and angles (°) for **3**

Cu(1)–N(2)	1.923(4)	Cu(1′)–N(1′)	1.916(4)
Cu(1)–N(1)	1.925(3)	Cu(1′)–N(2′)	1.917(4)
Cu(1)–O(1)	2.005(3)	Cu(1′)–O(1′)	1.967(4)
Cu(1)–O(2)	2.005(3)	Cu(1′)–O(2′)	1.974(3)
Cu(1)–O(7)	2.321(4)		
Cu(2)–O(4)	1.969(3)	Cu(2′)–O(4′)	1.987(3)
Cu(2)–O(3)	1.993(3)	Cu(2′)–O(3′)	1.990(4)
Cu(2)–N(3)	2.016(4)	Cu(2′)–N(3′)	2.016(4)
Cu(2)–N(4)	2.020(4)	Cu(2′)–N(4′)	2.018(4)
Cu(2)–O(8)	2.392(4)	Cu(2′)–O(8′)	2.276(4)
Cu(3)–O(6)	1.977(3)	Cu(3′)–O(6′)	1.980(3)
Cu(3)–O(5)	1.996(3)	Cu(3′)–O(5′)	2.005(3)
Cu(3)–N(5)	2.002(4)	Cu(3′)–N(5′)	2.015(4)
Cu(3)–N(6)	2.006(4)	Cu(3′)–N(6′)	2.029(5)
Cu(3)–O(9)	2.324(4)	Cu(3′)–O(9′)	2.288(4)
N(2)–Cu(1)–N(1)	82.21(15)	N(1′)–Cu(1′)–N(2′)	82.88(16)
N(2)–Cu(1)–O(1)	163.43(15)	N(1′)–Cu(1′)–O(1′)	84.74(15)
N(1)–Cu(1)–O(1)	83.61(13)	N(2′)–Cu(1′)–O(1′)	167.57(15)
N(2)–Cu(1)–O(2)	84.05(14)	N(1′)–Cu(1′)–O(2′)	166.98(15)
N(1)–Cu(1)–O(2)	165.19(14)	N(2′)–Cu(1′)–O(2′)	84.49(14)
O(1)–Cu(1)–O(2)	109.02(12)	O(1′)–Cu(1′)–O(2′)	107.81(14)
O(4)–Cu(2)–O(3)	84.27(12)	O(4′)–Cu(2′)–O(3′)	84.28(14)
O(4)–Cu(2)–N(3)	92.16(14)	O(4′)–Cu(2′)–N(3′)	93.04(15)
O(3)–Cu(2)–N(3)	169.80(15)	O(3′)–Cu(2′)–N(3′)	167.52(18)
O(4)–Cu(2)–N(4)	170.81(7)	O(4′)–Cu(2′)–N(4′)	168.27(18)
O(3)–Cu(2)–N(4)	94.18(15)	O(3′)–Cu(2′)–N(4′)	92.80(16)
N(3)–Cu(2)–N(4)	87.83(16)	N(3′)–Cu(2′)–N(4′)	87.37(17)
O(4)–Cu(2)–O(8)	90.81(16)	O(4′)–Cu(2′)–O(8′)	91.39(15)
O(3)–Cu(2)–O(8)	89.36(15)	O(3′)–Cu(2′)–O(8′)	91.76(16)
N(3)–Cu(2)–O(8)	100.26(16)	N(3′)–Cu(2′)–O(8′)	100.51(17)
N(4)–Cu(2)–O(8)	98.24(18)	N(4′)–Cu(2′)–O(8′)	100.07(18)
O(6)–Cu(3)–O(5)	84.52(12)	O(6′)–Cu(3′)–O(5′)	84.01(13)
O(6)–Cu(3)–N(5)	91.88(14)	O(6′)–Cu(3′)–N(5′)	91.91(16)
O(5)–Cu(3)–N(5)	168.76(17)	O(5′)–Cu(3′)–N(5′)	167.16(16)
O(6)–Cu(3)–N(6)	167.95(17)	O(6′)–Cu(3′)–N(6′)	166.9(2)
O(5)–Cu(3)–N(6)	94.00(14)	O(5′)–Cu(3′)–N(6′)	93.46(17)
N(5)–Cu(3)–N(6)	87.30(16)	N(5′)–Cu(3′)–N(6′)	87.77(19)
O(6)–Cu(3)–O(9)	90.71(15)	O(6′)–Cu(3′)–O(9′)	93.41(18)
O(5)–Cu(3)–O(9)	89.80(15)	O(5′)–Cu(3′)–O(9′)	92.25(15)
N(5)–Cu(3)–O(9)	100.91(16)	N(5′)–Cu(3′)–O(9′)	100.16(17)
N(6)–Cu(3)–O(9)	101.26(17)	N(6′)–Cu(3′)–O(9′)	99.5(2)
N(2)–Cu(1)–O(7)	98.45(16)	O(1)–Cu(1)–O(7)	92.83(15)
N(1)–Cu(1)–O(7)	101.87(16)	O(2)–Cu(1)–O(7)	85.60(16)

(tmen)Cu{Cu(opba)}Cu(tmen)(H_2O)]$^{2+}$ (**2b**), non-coordinated perchlorate ions and water molecules. A perspective view of the two trinuclear entities is depicted in Fig. 2 and selected bond lengths and angles are listed in Table 3.

While the central Cu1′ atom in the **2b** unit resides in a slightly distorted square-planar environment, all other metal atoms have approximately square-pyramidal coordination (4 + 1), the apical positions being occupied by water molecules at 2.29–2.39 Å. The central copper atoms are ligated by two amido nitrogen atoms and two carboxylato oxygen atoms from the oxamato groups, and the terminal copper atoms by two nitrogen atoms from tmen and two carbonyl oxygens of the oxamato bridge. The basal geometry around each copper atom is essentially planar, and the metal atoms are displaced towards the apices by 0.137, 0.165, 0.200, 0.209 and 0.224 Å for Cu1, Cu2, Cu3, Cu2′ and Cu3′, respectively. The dihedral angles between the central Cu1 and the terminal Cu2 and Cu3 basal planes are 17.9 and 3.2°, respectively. The corresponding angles in **2b** are 9.5 and 27.49°. The metal-to-metal distances within each trinuclear entity are 5.179, 5.191, 5.188, 5.143 Å for Cu1 ··· Cu2, Cu1 ··· Cu3, Cu1′ ··· Cu2′ and Cu1′ ··· Cu3′, respectively.

The two different trinuclear cations **2a** and **2b** always appear in pairs, with no counter ions between them. The two central metal atoms, Cu1 and Cu1′, are separated by 4.122 Å, much shorter than intramolecular Cu ··· Cu distances. Thus it seems that the two trinuclear cations form a unique supramolecular or "supracationic" dimer by intermolecular interactions. Further investigation on the crystal structure did not suggest any intercationic hydrogen bond, but there are indications of a weak π–π interaction. The central [Cu(opba)]$^{2-}$ moiety in each trinuclear unit is quite flat, indicating a π conjugating system extended to the CuN_2O_2 chromophore. There is overlap between the two π conjugating systems. The two [Cu(opba)]$^{2-}$ moieties are nearly parallel to each other and the center-to-center separation, where the centers are defined by Cu1, O1, O2, N1, N2, and C1 to C10 in **2a** and the corresponding atoms in **2b**, is 3.491 Å. Although such a weak interaction alone may be insufficient to overcome cation–cation repulsion, it must play an important role in stabilizing the "supracationic" dimeric structure.

Spectral properties

In the IR spectra the broad band at *ca.* 3400 cm^{-1}, which is split in the case of **1**, is attributable to ν(O–H). The strong band observed around 1100 cm^{-1} is indicative of the perchlorate ion.[19] Bands due to ν(C=O) vibrations in the oxamato group appear at 1595–1635 cm^{-1}.[19] The sharp bands at 1300–1460 cm^{-1} may be attributable to the ν(C–N) and ν(C–O) absorptions. The visible spectra of **1** and **2** in acetonitrile exhibit only a very broad band centered at 610 and 625 nm, respectively. It should be attributed to the envelop of the d–d transitions of copper(II) ions in different tetragonal environments.

The X-band powder ESR spectra of **1** and **2** at room temperature are very similar and exhibit only a broad and symmetrical band centered at $g = 2.10$. This value is in good agreement with the average g value obtained by the fitting of magnetic susceptibility data (*vide infra*).

Magnetic properties

The χ_m *versus* T and $\chi_m T$ *versus* T plots for complexes **1** and **2** are shown in Fig. 3. The $\chi_m T$ products at room temperature are 0.60 and 0.58 cm^3 K mol^{-1} for **1** and **2**, respectively. These values are much lower than the spin-only value expected for three uncoupled copper(II) ions (1.13 cm^3 K mol^{-1}). The products decrease smoothly upon cooling and reach an approximate plateau in the 100–20 K range with $\chi_m T$ at about 0.39 cm^3 K mol^{-1}. This value is in the expected range for a spin doublet state. The above features are typical of isolated trinuclear copper(II) species with antiferromagnetic coupling between metal ions. Upon cooling further below 20 K the $\chi_m T$ values decrease rather rapidly towards zero, indicating that the trinuclear units are not well isolated magnetically and that an antiferromagnetic interaction is operative between them.

The spin Hamiltonian appropriate for describing the magnetic properties of isolated trimers is given in eqn. (1) where

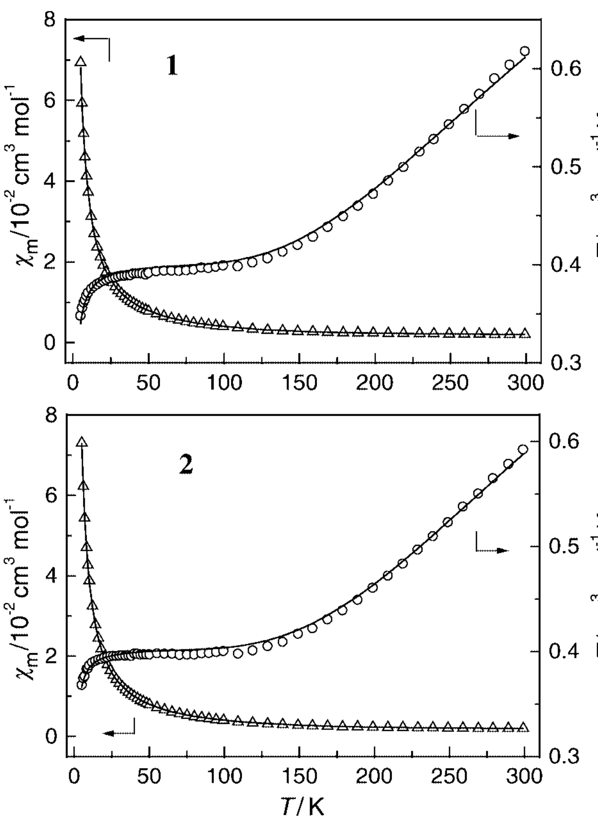

Fig. 3 χ_m *versus* T and $\chi_m T$ *versus* T plots for **1** and **2**.

$$\hat{H} = -J(\hat{S}_c\cdot\hat{S}_{t1} + \hat{S}_c\cdot\hat{S}_{t2}) - j\hat{S}_{t1}\cdot\hat{S}_{t2} \qquad (1)$$

J denotes the exchange parameter between the central and terminal copper(II) ions, and j the parameter between the two terminal copper(II) ions. In eqn. (1) it has been assumed that $J_{Cu1Cu2} = J_{Cu1Cu3} = J$ for the sake of simplicity, although the two bridging networks in each trinuclear entity are not structurally identical. In addition, for compound **2**, due to the presence of two different trinuclear entities, the J factor corresponds to their average. The magnetic susceptibility deduced from the Hamiltonian is as in eqn. (2) where g denotes the average g

$$\chi_m = \frac{Ng^2\beta^2}{4kT}\left[\frac{\exp(-j/kT) + \exp(-J/kJ) + 10\exp(J/2kT)}{\exp(-j/kT) + \exp(-J/kT) + 2\exp(J/2kT)}\right] \qquad (2)$$

factor for the three copper(II) ions. To take into account the interaction between trinuclear entities, the susceptibility can be corrected by the molecular-field approximation[20] (3) where zJ'

$$\chi'_m = \chi_m/[1 - (2zJ'\chi_m/Ng^2\beta^2)] \qquad (3)$$

denotes the intermolecular exchange parameter. The fitting of the experimental data by eqns. (2) and (3) is very insensitive to the value of j, which consequently cannot be determined from the magnetic data. Other studies on trinuclear complexes have also found that this j factor has a negligible effect on magnetic properties.[7,9,21] Excellent agreement between calculated and experimental data has been obtained by assuming $j = 0$. Minimizing $R = \Sigma(\chi_{obsd} - \chi_{calcd})^2/\Sigma\chi_{obsd}^2$ leads to $J = -334.4$ cm^{-1}, $g = 2.08$ and $zJ' = -1.3$ cm^{-1} for **1**, and $J = -356.6$ cm^{-1}, $g = 2.08$ and $zJ' = -0.72$ cm^{-1} for **2**. In both cases R is less than 10^{-4}.

The J values for **1** and **2** are very close to those for other oxamato-bridged trinuclear copper(II) species with diamines as terminal ligands (-330 to -380 cm^{-1}), and much larger than those for similar species with tridentate amines as terminal ligands (-84 to -196 cm^{-1}).[9–13] In the former class, terminal copper(II) ions have square-planar, square-pyramidal (4 + 1) (as observed in **1** and **2**) or axially elongated octahedral (4 + 2) coordination with the oxamato donors in basal or equatorial positions. It follows that the magnetic orbitals around terminal copper(II) ions are markedly delocalized towards the bridge, and have a maximal overlap with that around the central ion, resulting in a strong antiferromagnetic interaction. For the latter class, with tridentate amines as terminal ligands, the coordination geometry around the terminal copper(II) ion varies between trigonal bipyramidal and square pyramidal with one of the oxamato donor atoms in axial positions. The magnetic orbital is less delocalized, the overlap is reduced and the magnitude of the interaction is smaller.[11]

Conclusions

Starting from bis(oxamato)copper(II) complexes that contain the hydroxyl or phenyl group, we obtained an unusual one-dimensional coordination polymer (**1**) and an interesting supramolecular or "supracationic" quasi-dimer (**2**). Both compounds consist of a cationic trinuclear Cu_3 entity. In **1** the hydroxyl group of one Cu_3 entity coordinates to a terminal copper atom of another entity to form a one-dimensional chain. In **2** an unusual type of π–π interaction is operative between two neighboring trinuclear cations. Magnetic studies stress the fact that the oxamato group propagates a strong antiferromagnetic interaction when a 4 or 4 + 1 coordination environment is imposed on copper(II) ions.

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