DALTON
FULL PAPER

Trinuclear copper(II) complexes with bridging (N–N) diazine ligands: structural and magnetic studies

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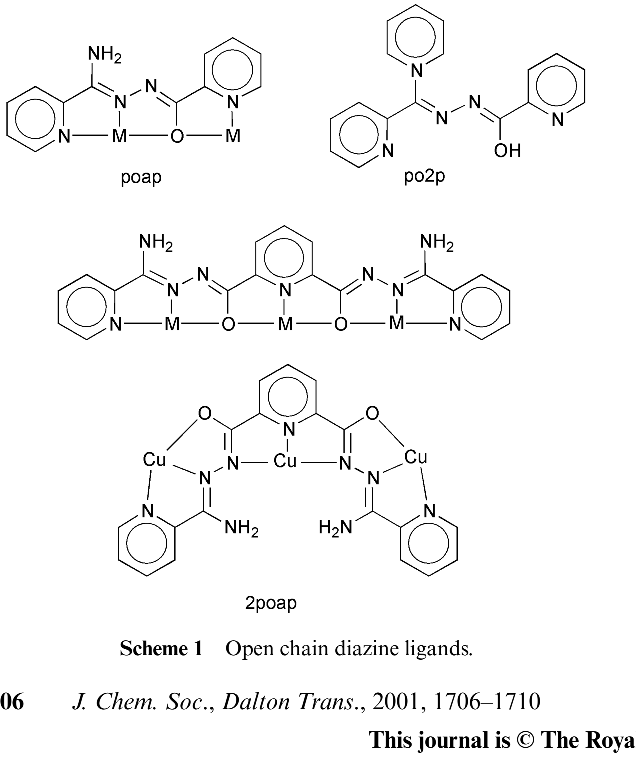
The polytopic ligands 2poap and po2p have a linear disposition of coordination pockets suitably disposed to bind metal ions in close proximity and produce linear trinuclear copper(II) complexes. The complexes $[Cu_3(2poap - 2H)(CH_3CO_2)_4]\cdot 3H_2O$ (**1**), $[Cu_3(2poap - 2H)(H_2O)(DMF)_3(CH_3OH)_2](BF_4)_4$ (**2**), and $[Cu_3(po2p - H)_2(H_2O)_2](ClO_4)_4\cdot 2H_2O$ (**3**) have a linear arrangement of Cu(II) centres linked by a *trans* arrangement of N–N single bonds. Each metal is assigned a $d_{x^2-y^2}$ magnetic ground state, and the *trans* diazine bridging arrangement leads to strong antiferromagnetic coupling in complete agreement with previous magnetostructural correlations relating the twist of the copper magnetic planes around the N–N bond to the exchange integral.

Introduction

Open-chain polydentate diazine ligands based on single N–N bond fragments display several possible mononucleating and dinucleating coordination modes due to the flexibility of the ligand around the N–N single bond.[1–5] Ligands in this class have been found to form mononuclear,[5–8] dinuclear,[9–15] trinuclear[16] and tetranuclear[17,18] copper(II) complexes. Recent studies on dinuclear copper(II) complexes of a series of new open-chain N_4 and N_5 diazine ligands have shown that a variety of geometrical conformations can be created, which depend on co-ligands and reaction conditions, and that a linear relationship exists between the rotation angle and the exchange integral over a 105° range, with ferromagnetic coupling at angles < 80° and antiferromagnetic coupling at angles > 80°.[19–21]

Polytopic ligands which combine a flexible N–N diazine fragment, and potentially bridging alkoxide groups (Scheme 1) generally form self assembled alkoxo-bridged clusters and grids, and the N–N group does not act in a bridging capacity. Square M_4 grids (M = Cu, Co, Ni, Mn),[18,22] and trigonal bipyramidal M_5 clusters (M = Mn, Co)[18,23] form with ligands like poap, while with extended ligands like 2poap nona-nuclear M_9 square grids (M = Mn, Cu)[24,25] have been observed in those reactions where weak potential co-ligands (*e.g.* anion, solvent) are found. In all these cases intramolecular spin coupling is observed, with examples of ferromagnetic (copper) and antiferromagnetic behaviour (other metals). With copper acetate 2poap produces the linear trinuclear complex $[Cu_3(2poap - 2H)(CH_3CO_2)_4]\cdot 3H_2O$ (**1**), involving coordinated acetate, and in the presence of DMF $[Cu_3(2poap - 2H)(H_2O)(DMF)_3(CH_3OH)_2](BF_4)_4$ (**2**) is produced, in which DMF is a ligand. Both involve just N–N bridging between metal ion centers. $[Cu_3(po2p - H)_2(H_2O)_2](ClO_4)_4\cdot 2H_2O$ (**3**) is different in that the three metals are bridged by a roughly linear arrangement of two N–N groups, with a conformationally locked *trans* disposition of the magnetic planes around the N–N single bonds. Fairly strong antiferromagnetic exchange is observed between the copper(II) centres in all cases ($-J > 75\ cm^{-1}$) in agreement with the previous correlations.[19–21]



Scheme 1 Open chain diazine ligands.

Experimental

Materials

Commercially available solvents and chemicals were used without further purification.

Physical measurements

Melting points were measured on a Fisher-Johns melting point apparatus. Electronic spectra were recorded as Nujol mulls using a Cary 5E spectrometer. Infrared spectra were recorded as Nujol mulls using a Mattson Polaris FTIR instrument. Mass spectra were obtained using a VG micromass 7070HS spectrometer. C, H, N analyses on vacuum dried samples (24 h) were performed by the Canadian Microanalytical Service, Delta, B.C., Canada. Variable temperature magnetic data were obtained with a Quantum Design MPMS5S Squid magnetometer operating at 0.1–1.0 T (2–300 K). Calibrations were carried out with a palladium standard cylinder, and temperature errors were determined with $[H_2TMEN][CuCl_4]$ ($H_2TMEN = (CH_3)_2HNCH_2CH_2NH(CH_3)_2^{2+}$).[26]

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Preparations

Ligands. 2poap was prepared as reported previously.[24]

Po2p. 2-Picolinic hydrazide (1.37 g, 0.010 mol) was dissolved in ethanol (40 mL) and a solution of dipyridyl ketone (1.84 g, 0.010 mol) in ethanol (10 mL) added. The resulting clear solution was refluxed for 10 h, and concentrated to a volume of 20 mL. A white crystalline product formed (yield 2.5 g, 83%), mp 162–163 °C (Found: C, 67.38; H, 4.34; N, 23.19. $C_{17}H_{13}N_5O$ requires: C, 67.32; H, 4.32; N, 23.09%); ν_{max}/cm^{-1} (Nujol): 3368 (NH), 1687 (C=O), 1583, 1564 (C=N), 993 (py); *m*/*z* 304 (M + H), 197, 169, 168, 141, 115, 78.

Complexes. *$[Cu_3(2poap - 2H)(CH_3CO_2)_4]\cdot3H_2O$ 1.* 2poap (0.20 g, 0.50 mmol) was added with stirring to a warm solution of $[Cu(OAc)_2(H_2O)]_2$ (0.40 g, 2.0 mmol) dissolved in 20 mL deionized water. The clear green solution was filtered and allowed to stand at room temperature for a few days. Dark yellow-green crystals suitable for structural analysis formed, which were filtered off, washed with ice water and dried in air (yield 46%, 0.20 g) (Found: C, 36.45; H, 3.71; N, 14.21. $[Cu_3(C_{19}H_{15}N_9O_2)(CH_3CO_2)_4]\cdot3H_2O$ requires: C, 36.76; H, 3.77; N, 14.29%). λ_{max}/nm (Nujol) 744; ν_{max}/cm^{-1} (Nujol): 3500 (H_2O), 3320 (NH), 1667, 1641 (C=N) and 1025 (py).

$[Cu_3(2poap - 2H)(H_2O)(DMF)_3(CH_3OH)_2](BF_4)_4$ 2. 2poap (0.40 g, 1.0 mmol) was added to a solution of $Cu(BF_4)_2\cdot6H_2O$ (1.4 g, 4.0 mmol) in MeOH–DMF (10/10 mL) and the mixture stirred at room temperature to give a greenish yellow solution. Green crystals suitable for structure determination were obtained by ether diffusion into the solution. However the crystals were found to be unstable outside the mother liquor. Consequently a sample was stored under mother liquor prior to the structural determination, and a crystal mounted on a quartz fibre quickly using the flash freeze method (yield 42%, 0.48 g) (Found (vacuum dried sample): C, 29.08; H, 2.87; N, 14.72. $[Cu_3(C_{19}H_{15}N_9O_2)(DMF)_3](BF_4)_4$ requires: C, 29.02; H, 3.13; N, 14.51%). λ_{max}/nm (Nujol): 813; ν_{max}/cm^{-1} (crystalline sample; Nujol): 3514 (H_2O), 3440 (MeOH), 1697 (DMF), 1658, 1645 (C=N), 1072 (BF_4) and 1027 (py).

$[Cu_3(po2p - H)_2(H_2O)_2](ClO_4)_4\cdot2H_2O$ 3. p2oap (0.15 g 0.50 mmol) was added with stirring at room temperature to a solution of $Cu(ClO_4)_2\cdot6H_2O$ (0.74 g, 2.0 mmol) in water (20 mL) to give a greenish yellow solution. Dark green, almost black crystals were obtained on standing at room temperature (yield 49%, 0.31 g) (Found: C, 32.02; H, 2.60; N, 11.01. $[Cu_3(C_{17}H_{12}N_5O)_2(H_2O)_2](ClO_4)_4\cdot2H_2O$ requires: C, 32.29; H, 2.55; N, 11.07%). λ_{max}/nm (Nujol): 768; ν_{max}/cm^{-1} (Nujol): 3600, 3450 (H_2O), 1628, 1603, 1591, 1576, 1563 (C=N), 1096, 1051 (ClO_4).

Crystallography

The diffraction intensities of a yellow-green, irregular crystal of **1** were collected with graphite monochromated Mo-Kα X-radiation using a Rigaku AFC6S diffractometer at 299(1) K and the *ω*–*2θ* scan technique. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods.[27,28] All atoms except hydrogens were refined anisotropically. Hydrogen atoms were placed in calculated positions. Neutral atom scattering factors[29] and anomalous-dispersion terms[30,31] were taken from the usual sources. All calculations were performed with the teXsan[32] crystallographic software package using a PC computer. Crystal data collection and structure refinement for **3** were carried out in a similar manner using Cu-Kα radiation. Abbreviated crystal data for **1** and **3** are given in Table 1.

Diffraction data for single crystals of **2** were collected using a Bruker SMART CCD diffractometer, equipped with an Oxford Cryostream N_2 cooling device,[33] with graphite monochromated Mo-Kα radiation. Cell parameters were determined and refined using the SMART software,[34a] raw frame data were integrated using the SAINT program,[34b] and the structure was solved using direct methods and refined by full-matrix least squares on F^2 using SHELXTL.[35] Non-hydrogen atoms were refined with anisotropic atomic displacement parameters (adps). Disorder problems associated with the BF_4^- anions have so far prevented a satisfactory refinement of this structure. Therefore only a preliminary account of the structure of the molecular cation, which is clearly defined, is presented at this time.

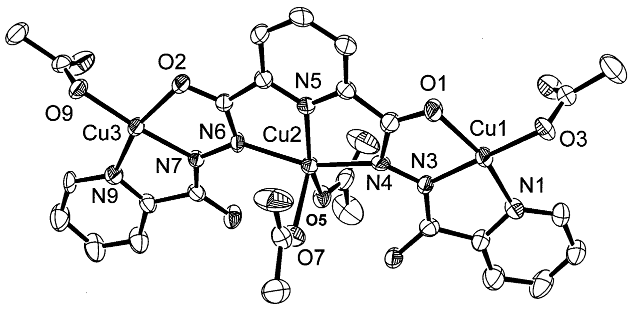

Fig. 1 Structural representation of the trinuclear fragment in $[Cu_3(2poap - 2H)(CH_3CO_2)_4]\cdot3H_2O$ (**1**), (40% probability thermal ellipsoids).

CCDC reference numbers 158370 and 158371.

See http://www.rsc.org/suppdata/dt/b0/b008768h/ for crystallographic data in CIF or other electronic format.

Results and discussion

Structures

Crystal structure of $[Cu_3(2poap - 2H)(CH_3CO_2)_4]\cdot3H_2O$ 1. The main fragment is a trinuclear complex comprising a single nona-dentate ligand bound to three copper centres in an approximately linear array, with all ligand donor sites involved in coordination except the NH_2 groups. The structure of the trinuclear fragment in **1** is depicted in Fig. 1, and selected bond distances and angles are listed in Table 2. The three coppers are directly linked by two almost *trans* diazine (N–N) bridges (torsion angles Cu(2)–N(4)–N(3)–Cu(1) 168.4°, Cu(2)–N(6)–N(7)–Cu(3) 160.7°). Within the trinuclear complex itself the copper–copper distances exceed 4.8 Å (Cu(1)–Cu(2) 4.892(3) Å, Cu(2)–Cu(3) 4.962(3) Å). The central copper (Cu(2)) is five-coordinate with a geometry that is closer to a square-pyramid than a trigonal-bipyramid. The juxtaposition of N(4), N(5) and N(6) and the contiguous five-membered chelate ring combination that involves Cu(2), leads to a somewhat distorted bonding situation around Cu(2). The Cu(2)–N(5) distance is quite short (1.933(5) Å), but the Cu(2)–N(4) and Cu(2)–N(6) distances are much longer (2.080(5) Å and 2.141(5) Å respectively). The basal plane of the square-pyramid is defined by N(4), N(5), N(6) and O(5), with the long axial bond to mono-dentate acetate oxygen O(7). The terminal coppers are nominally four coordinate, square-planar, and bound by an N_2O_2 donor set, including a terminal acetate. However long contacts from Cu(1) and Cu(3) to acetate oxygen atoms on neighbouring trinuclear subunits (Cu(1)–O(9) 2.435(4) Å, Cu(3)–O(3) 2.335(4) Å) actually link the complex into a linear chain, and so these copper centres are in fact square-pyramidal. Fig. 2 illustrates a fragment of this chain showing the Cu(1)–Cu(3) inter-trinuclear connection. This leads to a short inter-trinuclear metal–metal separation (Cu(1)–Cu(3) 3.371(2) Å). However despite this short copper–copper contact *via* the Cu–O–Cu bridges the connection is strictly orthogonal, thus leading to the absence of any anti-ferromagnetic coupling between Cu(1) and Cu(3) (*vide infra*).

The ligand loses two protons, but defining the sites of deprotonation based on a bond distance assessment is not easy. The C–O distances (C(7)–O(1) 1.284(7) Å, C(13)–O(2) 1.281(7) Å)

Table 1 Crystallographic data and refinement details for **1** and **3**

Compound	**1**	**3**
Empirical formula	$C_{27}H_{33}Cu_3N_9O_{13}$	$C_{34}H_{32}Cu_3N_{10}O_{22}Cl_4$
M	882.25	1265.13
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$ (no. 14)	$P\bar{1}$
a/Å	9.722(3)	14.751(2)
b/Å	23.218(3)	17.692(2)
c/Å	15.305(2)	9.773(1)
α/°		93.269(9)
β/°	93.62(2)	101.909(9)
γ/°		110.253(7)
U/Å^3	3448(1)	2318.2(5)
T/K	299(1)	299(2)
Z	4	2
μ/mm^{-1}	1.911	4.563
Reflections collected: total, independent, R_{int}	8628, 8168, 0.042	7209, 6884, 0.055
Final $R1$, $wR2^a$	0.055, 0.054 (R, R_w)	0.067, 0.216

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR2 = [\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w|F_o|^2$; $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $R_w = (\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2)]^{1/2}$.

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

Cu(1)–O(1)	1.975(4)	Cu(3)–O(2)	1.971(4)
Cu(1)–O(3)	1.913(4)	Cu(3)–O(9)	1.929(4)
Cu(1)–N(1)	2.006(5)	Cu(3)–N(7)	1.921(5)
Cu(1)–N(3)	1.920(5)	Cu(3)–N(9)	1.999(5)
Cu(1)–O(9)	2.435(4)	Cu(3)–O(3)	2.335(4)
Cu(2)–O(5)	1.955(4)	Cu(1)–Cu(2)	4.892(3)
Cu(2)–O(7)	2.129(4)	Cu(2)–Cu(3)	4.962(3)
Cu(2)–N(4)	2.080(5)	Cu(1)–Cu(3)	3.371(2)
Cu(2)–N(5)	1.933(5)	N(3)–N(4)	1.388(6)
Cu(2)–N(6)	2.141(5)	N(6)–N(7)	1.409(6)
O(1)–Cu(1)–O(3)	99.7(2)	O(7)–Cu(2)–N(5)	122.9(2)
O(1)–Cu(1)–N(3)	161.2(2)	O(7)–Cu(2)–N(6)	99.1(2)
O(3)–Cu(1)–N(1)	80.8(2)	N(4)–Cu(2)–N(5)	79.1(2)
O(3)–Cu(1)–N(3)	98.8(2)	N(4)–Cu(2)–N(6)	157.9(2)
O(3)–Cu(1)–N(3)	178.8(2)	N(5)–Cu(2)–N(6)	78.9(2)
N(1)–Cu(1)–N(3)	80.7(2)	O(2)–Cu(3)–O(9)	94.9(2)
O(5)–Cu(2)–O(7)	85.9(2)	O(2)–Cu(3)–N(7)	80.0(2)
O(5)–Cu(2)–N(4)	100.1(2)	O(2)–Cu(3)–N(9)	160.4(2)
O(5)–Cu(2)–N(5)	151.2(2)	O(9)–Cu(3)–N(7)	174.8(2)
O(5)–Cu(2)–N(6)	98.1(2)	O(9)–Cu(3)–N(9)	103.8(2)
O(7)–Cu(2)–N(4)	94.6(2)	N(7)–Cu(3)–N(9)	81.2(2)

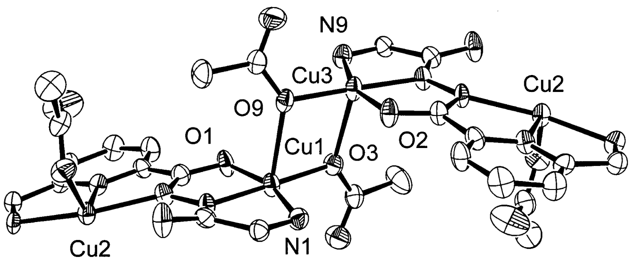

Fig. 2 Structural representation of a chain fragment in $[Cu_3(2poap - 2H)(CH_3CO_2)_4]\cdot 3H_2O$ (**1**) showing the orthogonal connection at Cu(1) and Cu(3) (40% probability thermal ellipsoids).

are quite short and might imply double bond character. If this is the case then the site of deprotonation must occur within the connected O–C–N–N fragments. C–N and N–N distances suggest mostly single bond character in each case and so nitrogens N(3) and N(7) are the likely sites of deprotonation. This is supported by the relatively short distances Cu(3)–N(7) (1.921(5) Å, and Cu(1)–N(3) (1.921(3) Å), but there may be some charge delocalisation over the whole framework.

Crystal structure of $[Cu_3(2poap - 2H)(H_2O)(DMF)_3(CH_3OH)_2](BF_4)_4$ 2. The preliminary structural representation of **2** is depicted in Fig. 3.[36,37] The tricopper(II) cation is similar to **1** and consists of three square-pyramidal copper(II) centers bonded to a single, essentially flat nona-dentate ligand, with one terminal DMF molecule bound equatorially to Cu(1) and Cu(1)′ and one DMF axially to Cu(2) (O(3)). Cu(2) also has an equatorial coordinated water molecule (O(4)). The copper centres are linked by single N–N diazine groups in an almost *trans* configuration, and there are no inter-trinuclear close contacts, as in **1**.

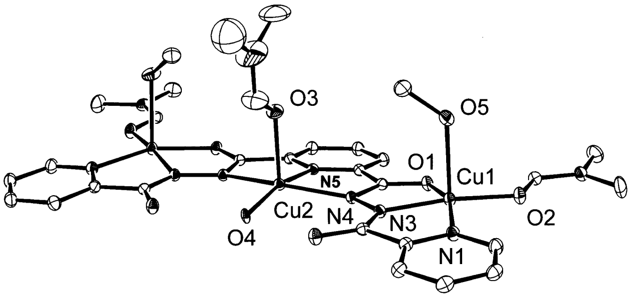

Fig. 3 Preliminary structural representation of the cation in $[Cu_3(2poap - 2H)(H_2O)(DMF)_3(CH_3OH)_2](BF_4)_4$ (**2**) (35% probability thermal ellipsoids).

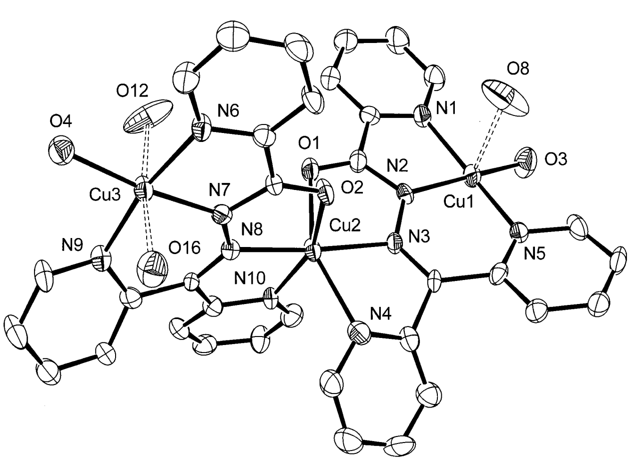

Fig. 4 Structural representation of the cation in $[Cu_3(po2p - H)_2(H_2O)_2](ClO_4)_4\cdot 2H_2O$ (**3**) (40% probability thermal ellipsoids).

Crystal structure of $[Cu_3(po2p - H)_2(H_2O)_2](ClO_4)_4\cdot 2H_2O$ 3. The structure of **3** is depicted in Fig. 4, and selected bond distances and angles are given in Table 3. The trinuclear structure is created by the association of two ligands binding to the same copper centre (Cu(2)) *via* a tridentate N_2O coordination pocket at one end of each ligand. The central copper has an unusual tetragonally elongated CuN_4O_2, six-coordinate stereochemistry. The copper equatorial plane is defined by N(8), N(10), N(3)

Table 3 Selected bond distances (Å) and angles (°) relevant to the copper coordination spheres in **3**

Cu(1)–O(3)	1.95(1)	Cu(3)–O(4)	1.984(9)
Cu(1)–N(1)	2.00(1)	Cu(3)–N(6)	2.03(1)
Cu(1)–N(2)	1.933(9)	Cu(3)–N(7)	1.912(9)
Cu(1)–N(5)	1.97(1)	Cu(3)–N(9)	2.03(1)
Cu(1)–O(8)	2.61(1)	Cu(3)–O(12)	2.51(1)
Cu(2)–O(1)	2.259(9)	Cu(3)–O(16)	2.51(1)
Cu(2)–O(2)	2.057(8)	N(2)–N(3)	1.35(1)
Cu(2)–N(3)	2.05(1)	N(7)–N(8)	1.35(1)
Cu(2)–N(4)	2.24(1)	Cu(1)–Cu(2)	4.790(8)
Cu(2)–N(8)	1.95(1)	Cu(2)–Cu(3)	4.672(7)
Cu(2)–N(10)	2.01(1)		
O(3)–Cu(1)–N(1)	92.2(4)	O(2)–Cu(2)–N(10)	158.8(4)
O(3)–Cu(1)–N(2)	167.0(5)	N(3)–Cu(2)–N(4)	76.1(4)
O(3)–Cu(1)–N(5)	95.9(4)	N(3)–Cu(2)–N(8)	175.1(4)
N(1)–Cu(1)–N(2)	81.5(5)	N(3)–Cu(2)–N(10)	103.2(4)
N(1)–Cu(1)–N(5)	169.8(5)	N(4)–Cu(2)–N(8)	108.2(4)
N(2)–Cu(1)–N(5)	91.8(4)	N(4)–Cu(2)–N(10)	90.1(4)
O(1)–Cu(2)–O(2)	87.0(4)	N(8)–Cu(2)–N(10)	79.4(4)
O(1)–Cu(2)–N(3)	75.3(4)	O(4)–Cu(3)–N(6)	95.3(4)
O(1)–Cu(2)–N(4)	151.3(4)	O(4)–Cu(3)–N(7)	172.9(4)
O(1)–Cu(2)–N(8)	100.5(4)	O(4)–Cu(3)–N(9)	94.1(4)
O(1)–Cu(2)–N(10)	93.4(4)	N(6)–Cu(3)–N(7)	81.1(4)
O(2)–Cu(2)–N(3)	97.4(4)	N(6)–Cu(3)–N(9)	169.5(4)
O(2)–Cu(2)–N(4)	99.7(4)	N(7)–Cu(3)–N(9)	90.1(4)
O(2)–Cu(2)–N(8)	79.7(4)		

and O(2) (Cu–donor distances <2.06 Å), with longer axial contacts to O(1) and N(4). Each ligand has six donors and the second coordination pockets bind another copper completing the trinuclear array. Cu(3) is also a tetragonally distorted six-coordinate centre with long contacts to perchlorate oxygens (Cu(3)–O(12) 2.51(1) Å, Cu(3)–O(16) 2.51(1) Å), while Cu(1) is square-pyramidal with a long contact to perchlorate oxygen O(8) (Cu(1)–O(8) 2.61(1) Å). The overall arrangement of the three coppers is non-linear as a result of the twist of the two N–N fragments about the N(8)–Cu(2)–N(3) axis (N(2)–N(3)–N(8)–N(7) torsional angle 75°) with a Cu(1)–Cu(2)–Cu(3) angle of 142.1°. Copper–copper separations are quite long, as would be expected (Cu(1)–Cu(2) 4.790(8) Å, Cu(2)–Cu(3) 4.672(7) Å). The alkoxide oxygens are nominally considered to be deprotonated, consistent with their role in other cluster complexes of related ligands,[22] but the short C–O distances (C(6)–O(1) 1.23(1) Å, C(23)–O(2) 1.24(1) Å) suggest significant C=O double bond character and that the site of deprotonation exists elsewhere in the O–C–N–N framework. There are no very short Cu–N distances, and intermediate bond distances within the immediate ligand backbone suggest a significant charge redistribution within the ligand itself.

The structures of **1** and **2** are in sharp contrast to other structures involving 2poap, where with $Cu(NO_3)_2$ and $Mn(ClO_4)_2$, which involve weakly coordinating anions, in solvents like aqueous methanol, self assembly reactions occur to produce novel homoleptic Mn_9O_{12}[24] and Cu_9O_{12}[25] square [3 × 3] grid structures with just alkoxide groups bridging the metal centres. In these complexes each ligand coordinates to three metal ion centres and acts in a hepta-dentate fashion (Scheme 1). Clearly for **1** the acetate ion is a strong enough ligand to influence the reaction outcome and prevent the formation of the nona-nuclear grid. With compound **2** the solvent appears to have a significant effect in that DMF acts as a donor and coordinates to all three copper centres, effectively preventing the Cu_9 grid formation.

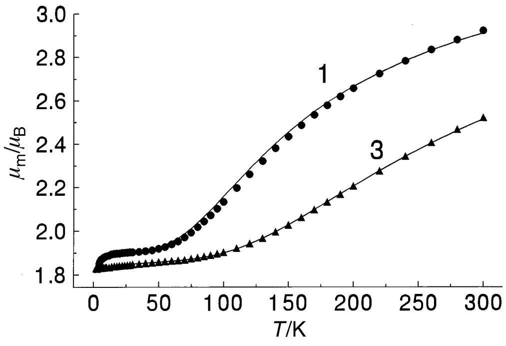

Fig. 5 Variable temperature magnetic data for $[Cu_3(2poap - 2H)(CH_3CO_2)_4]\cdot 3H_2O$ (**1**) and $[Cu_3(po2p - H)_2(H_2O)_2](ClO_4)_4\cdot 2H_2O$ (**3**).

Magnetism

Variable temperature magnetic susceptibility measurements were carried out on powdered samples of all of the complexes, taken from the same uniform batches used for structural determinations, in the temperature range 2–300 K and at field strengths of 0.1 T to 1.0 T. The magnetic moment for complex **1** varies from 2.92 μ_B (per mole) at 300 K to 1.85 μ_B at 4.5 K (Fig. 5). The drop signifies the presence of quite strong antiferromagnetic coupling and the value at low temperature is the result of the residual paramagnetism associated with an odd number of copper(II) centres. The isotropic exchange properties of a symmetrical system with a linear arrangement of three $S = \frac{1}{2}$ spin centres is described by the appropriate exchange Hamiltonian (eqn. (1)). In this case, since the distance between external coppers is so large, J' is assumed to be zero. The variable temperature magnetic data were fitted to eqn. (2) with

$$H_{ex} = -2J[S_1\cdot S_2 + S_2\cdot S_3] - 2J'[S_1\cdot S_3] \qquad (1)$$

$$\chi_m = \frac{Ng^2\beta^2}{3k(T-\theta)}\left[\frac{10e^x + e^{-2x} + 1}{2e^x + e^{-2x} + 1}\right](1-\rho) + \left(\frac{3Ng^2\beta^2}{4kT}\right)\rho + N\alpha \qquad (2)$$

$g = 2.19(1)$, $J = -75.5(2)$ cm^{-1}, $\theta = -0.2$ K, $\rho = 0.015$, $N\alpha = 0.000180$ cm^3 mol^{-1}, $10^2R = 0.6$ ($R = [\Sigma(\chi_{obs} - \chi_{calc})^2/\Sigma\chi_{obs}{}^2]^{1/2}$) and $x = -J/kT$. The solid line in Fig. 5 was calculated using these parameters. The very small θ correction indicates that the chain structure of **1** does not influence the magnetic properties to any significant degree, in keeping with the strictly orthogonal connections between the ends of the trinuclear sub-units, and so the trinuclear model is an accurate one. Variable temperature magnetic data for **2** and **3** show similar profiles of magnetic moment with temperature. Fitting of the data to eqn. (2) gave excellent agreement in both cases with $g = 2.24(1)$, $J = -78.4(2)$ cm^{-1}, $\theta = -0.1$ K, $\rho = 0.029$, $N\alpha = 0.00022$ cm^3 mol^{-1}, $10^2R = 0.61$ (**2**), and $g = 2.12(1)$, $J = -134.6(2)$ cm^{-1}, $\theta = -0.05$ K, $\rho = 0.008$, $N\alpha = 0.00020$ cm^3 mol^{-1}, $10^2R = 0.24$ (**3**). Fig. 5 shows the experimental and theoretical data for **3** calculated with these parameters.

The principal feature responsible for the magnetic properties of these compounds is the single N–N bond which is the only direct linkage between adjacent pairs of copper(II) centres. Previous studies on dinuclear copper(II) complexes have shown clearly that exchange coupling can occur through a single N–N bond bridge and that the extent of exchange coupling is linearly dependent upon the rotational angle of the copper magnetic planes relative to the single bond itself, which is a function of the relative orientation of the nitrogen p orbitals. At large angles approaching a *trans* conformation strong antiferromagnetic coupling is observed, while at low angles the exchange gets weaker with a change-over to ferromagnetic behaviour at acute angles around 80°.[19–21] Compounds **1** and **2** have the same ligand with essentially equal Cu–N–N–Cu torsional angles between the central and outer coppers. Both bonds between the central copper and adjacent diazine nitrogen atoms are fairly long equatorial connections, and so the essentially equivalent exchange integrals are a reflection on the similar rotational angles of the copper magnetic planes with respect to the N–N bonds.

Compound **3** has a different ligand, but a similar magnetic structural element with the three copper centres connected just by N–N bonds. The magnetic plane of the central copper is defined by N(8), N(10), N(3) and O(2) and the two ligands are twisted around the N(8)–Cu(2)–N(3) axis by about 90°. The Cu–N–N–Cu torsional angles are 176.3° and 169.0° (Cu(1) and Cu(3) respectively) resulting in an almost fully *trans* arrangement of the respective copper centres around the N–N bonds. The substantially larger exchange integral in this case is entirely consistent with this conformational feature, in addition to the presence of comparatively shorter overall Cu–N bond lengths to Cu(2).

Compounds **1** and **2** have reasonable structures based on the compartmental nature of the ligand, and one other related ligand type produces a similar linear trinuclear N–N bridged arrangement.[16] In this case the ligands have the same central picolinic dihydrazide core, but have peripheral phenolic groups, which produce terminal six-membered chelate rings rather than the five-membered rings present in the 2poap systems. This effectively prevents the formation of a [3 × 3] grid structure because of the non-linear arrangement of the ligand donor pockets. However the trinuclear subunits have somewhat weaker antiferromagnetic coupling ($-J = 42$–63 cm^{-1}) than that observed in **1** and **2**.

Conclusion

Three new trinuclear complexes are reported with just N–N single bond linkages between the copper(II) centres. The compounds exhibit moderate to strong antiferromagnetic coupling as a result of σ-superexchange *via* the N–N bridges. The magnetic properties are accounted for sensibly on the basis of large rotational angles of the copper magnetic planes about the diazine bridges, in complete agreement with previous studies.

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