

A self-assembled novel octanuclear Cu(II) 'pin-wheel' cluster exhibiting ferromagnetic coupling

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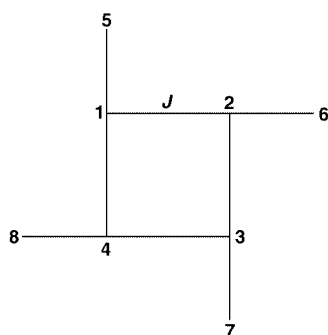
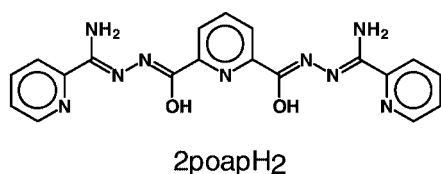
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The heptadentate, 'tritopic' ligand 2poapH₂ reacts with Cu(NO₃)₂ in the presence of Gd(NO₃)₃ to give a novel, self-assembled, ferromagnetically coupled, alkoxide bridged octanuclear Cu(II) cluster in the shape of a pin-wheel, with a central Cu₄[μ-O₄] core, and isolated Gd-like [Gd(NO₃)₄(H₂O)₂]⁻ anions.

Self-assembly reactions with polytopic ligands have led to a number of novel polynuclear cluster complexes, and with the ligand coordination pockets held in a linear array 2D grid structures are produced with tetranuclear,¹⁻⁴ hexanuclear,⁵ nonanuclear,⁶⁻⁹ and hexadecanuclear¹⁰ examples. Interest in such systems stems from their ability to produce high nuclearity metallic clusters with pre-determined geometrical arrangements of closely spaced metal centres. With appropriate bridging groups arranged strategically in the ligand backbone magnetic coupling between the metal ions can occur. Examples of alkoxide bridged nonanuclear grids show antiferromagnetic coupling (M₉(μ-O)₁₂; M = Mn(II), Co(II), Ni(II)), while with copper(II) ferromagnetic exchange prevails due to strict magnetic orbital orthogonality *via* the μ-O bridges.

In an attempt to generate a mixed lanthanide/copper complex of the ligand 2poapH₂ (Scheme 1), with the possibility of enhanced ferromagnetic exchange, Gd(NO₃)₃ and Cu(NO₃)₂ were reacted with the ligand sequentially.† The resulting green complex, [Cu₈(2poap)₄(CH₃OH)₄(CH₃CN)₄][Gd(NO₃)₄(H₂O)₂]₂(NO₃)₆·1.3Cu(NO₃)₂·(H₂O)₁₀ (**1**),‡ has been shown to contain both copper and gadolinium, but the main fragment consists of a self-assembled octanuclear Cu(II)₈ cation accompanied by two isolated [Gd(NO₃)₄(H₂O)₂]⁻ anions, and a fourth component which has been identified crystallographically as a Cu(NO₃)₂ based fragment trapped in the lattice. Fig. 1 shows the octanuclear cation with four opposed ligands in parallel pairs bound *via* terminal coordination pockets to a central square 2 ×



Scheme 1

2 core of four octahedral Cu(II) centres, which are bridged by alkoxide oxygen atoms, in an arrangement common to other [M₄(μ-O)₄] square grids⁴ with the ditopic ligand poapH (M = Mn(II), Co(II), Ni(II), Cu(II), Zn(II)). The other ends of the four ligands radiate from the core to create a pin-wheel structure with the external coppers connected to the core by alkoxide bridges. The external tridentate ligand pockets fill only three copper coordination sites, and other sites at these square pyramidal copper centres are occupied by solvent molecules (CH₃OH, CH₃CN from solvent used to produce crystals). The core structure showing the alkoxide bridging connections is illustrated in Fig. 2. Cu–O–Cu angles overall fall in the range 139.0–142.0°. Cu–Cu distances within the core fall in the range

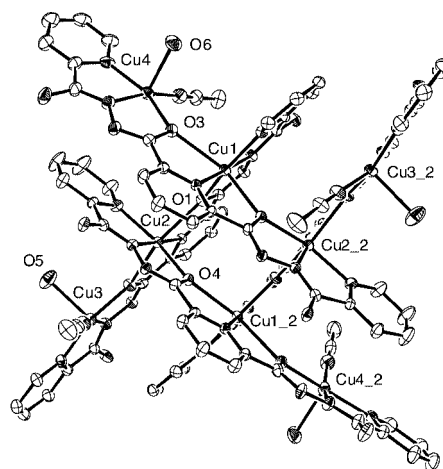


Fig. 1 Structural representation of the cation [Cu₈(2poap)₄(CH₃OH)₄(CH₃CN)₄] in (**1**) (40% probability thermal ellipsoids). Cu(1)–O(4)^{*} 2.307(4), Cu(1)–O(1) 2.020(4), Cu(2)–O(1) 2.283(4), Cu(2)–O(4) 2.030(4), Cu(3)–O(2) 1.969(5), Cu(3)–O(5) 2.215(6), Cu(2)–O(2) 2.340(4), Cu(1)–O(3) 2.404(5), Cu(4)–O(3) 1.983(5), Cu(4)–O(6) 2.224(6), Cu(1)–Cu(2) 4.082(2), Cu(2)–Cu(1)^{*} 4.038(2), Cu(2)–Cu(3) 4.038(2), Cu(1)–Cu(4) 4.151(2), Cu(3)–Cu(3)^{*} 12.805(2), Cu(4)–Cu(4)^{*} 12.676(2) Å; Cu–O–Cu 139.0–142.0°.

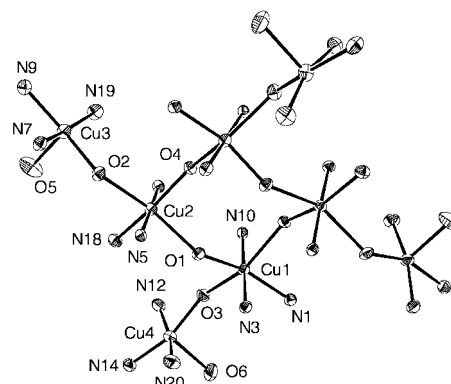


Fig. 2 Structural representation of the octanuclear core in **1**.

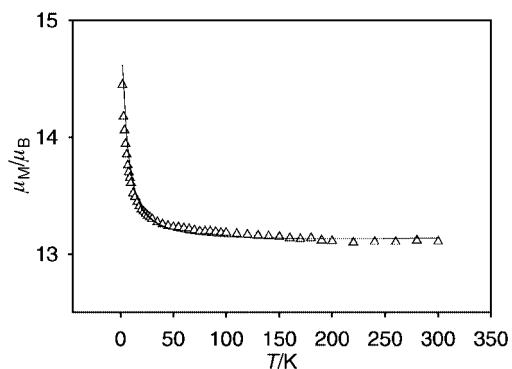


Fig. 3 Magnetic properties of **1** plotted as μ_{mol} vs. temperature. The solid line is the best fit of the data to eqn. (1) (see text for fitting parameters).

4.03–4.09 Å, and in the range 4.03–4.15 Å outside. The diagonal external Cu–Cu distances exceed 12.6 Å. The coppers within the core are six-coordinate, with elongated tetragonal stereochemistry. The long contacts involve all the ring oxygen bridging atoms and all *trans* related oxygens (e.g. Cu(2)–O(1) 2.283(4) Å; Cu(2)–O(2) 2.340(5) Å). The external square pyramidal coppers have short contacts to the oxygen bridges (Cu(3)–O(2) 1.969(5) Å, Cu(4)–O(3) 1.983(5) Å), and long axial contacts to the weakly bound methanol molecules (Cu(3)–O(5) 2.215(6) Å, Cu(4)–O(6) 2.224(6) Å). This leads to a unique arrangement of the copper atoms, in which all the oxygen bridging connections involve strict metal magnetic orbital ($d_{x^2-y^2}$) orthogonality, resulting in unique ferromagnetic properties (*vide infra*). A related, antiferromagnetically coupled complex $[\text{Cu}_8(\text{dpd}-2\text{H})_4(\mu\text{-O}_2\text{CMe})_4\{\text{pyOH}\}_4](\text{ClO}_4)_4$ (**2**) (dpd–2H = dianion from the *gem*-diol (py)₂(OH)₂; pyOH = 2-hydroxypyridine), reported recently has a Cu₄(μ-O)₄ core and four pendant copper centres linked by carboxylate bridges.¹¹

Fig. 3 shows the profile of molar magnetic moment vs. temperature for **1**, with a moment rising slightly from 13.1 μ_B at 300 K to 13.3 μ_B at about 25 K, followed by a sharp rise to a maximum value of 14.5 μ_B at 2 K. § Given the fact that the isolated Gd(III) and Cu(II) centres should behave as Curie components the overall magnetic behaviour of **1** indicates the presence of a ferromagnetically coupled cluster. The magnetic data were fitted to an isotropic exchange expression based on a spin Hamiltonian [eqn. (1); Scheme 1],

$$H = -J(S_1S_2 + S_2S_3 + S_3S_4 + S_1S_4 + S_1S_5 + S_2S_6 + S_3S_7 + S_4S_8) \quad (1)$$

reflecting equivalent exchange interactions (*J*) between adjacent copper(II) centres. The total spin states, and their energies, were calculated using the normal spin vector coupling method,¹² and substituted into the van Vleck equation in the usual way. Curie components corresponding to 2 Gd(III) ions and 1.3 Cu(II) ions identified in the X-ray structure were included. An excellent data fit was obtained using a non-linear regression procedure, and the solid line in Fig. 3 was calculated for $g_{\text{av}} = 2.113(2)$, $J = 5.0(2) \text{ cm}^{-1}$, $\text{TIP} = 0.000500 \text{ emu mol}^{-1}$, $\theta = -0.10 \text{ K}$ ($R = 1.0\%$) (θ is a Weiss-like corrective term, $\text{TIP} = \text{temperature independent paramagnetism}$). The positive *J* confirms the intramolecular ferromagnetic behaviour, with a value comparable to related 2×2 and 3×3 grid systems,^{4,8,9} and illustrates another example in which there appears to be a spontaneous tendency for the closely spaced magnetic planes to tilt away from each other in the alkoxide bridged cluster. Magnetization vs. field data at 2 K showed incomplete saturation at 5 T, with a value of $24.8 N\beta$ at 5 T. This

is consistent with the sum of the ferromagnetically coupled Cu₈ cluster, and the Curie-like Gd(III) and Cu(II) centers.

The novel ferromagnetically coupled Cu₈ pinwheel cluster forms in a mixed metal self-assembly reaction. Gd(III) is assumed to influence the cluster self assembly, possibly by a pre-coordination step at one end of a ligand, prior to formation of the central square core, followed by displacement of the Gd(III) by Cu(II) ions. Similar reactions are being studied with other first row transition metals.

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Notes and references

† 2poapH₂ was synthesized by a published procedure.⁷ 2poapH₂ (0.40 g, 1.0 mmol) was added to a warm methanol solution (25 mL) of Gd(NO₃)₃·6H₂O (0.23 g, 0.5 mmol) and the mixture stirred for several minutes until the ligand dissolved, forming a clear yellowish solution. CH₃CN (20 mL) was added and the solution refluxed, and a warm solution of Cu(NO₃)₂·3H₂O (0.75 g, 3.1 mmol) in methanol (10 mL) added slowly. A brownish powder formed initially, which then dissolved forming a clear deep green solution. Well formed dark green crystals, suitable for X-ray analysis, were produced from the filtered solution after several days (yield 85%). Found (vacuum dried sample): C, 25.87; H, 2.56; N, 19.53. Calc. for (C₁₉H₁₅N₉O₂)₄·Cu₈Gd₂(CH₃CN)₄(CH₃OH)₄(NO₃)₁₄·14H₂O·1.3Cu(NO₃)₂: C, 25.87; H, 2.86; N, 19.41. $\nu_{\text{max}}/\text{cm}^{-1}$ (Nujol) 3436 (H₂O), 3343, 3172 (NH), 1665 (C=N) and 1026 (py). $\lambda_{\text{max}}/\text{nm}$ (Nujol) 700. $\mu_{\text{RT}} = 13.1 \mu_{\text{B}}$ (mol).

‡ Crystal data for $[\text{Cu}_8(2\text{poap})_4(\text{CH}_3\text{OH})_4(\text{CH}_3\text{CN})_4][\text{Gd}(\text{NO}_3)_4(\text{H}_2\text{O})_2(\text{NO}_3)_6 \cdot 1.3\text{Cu}(\text{NO}_3)_2 \cdot (\text{H}_2\text{O})_{10}]$ (**1**): C₄₄H_{52.5}N_{27.5}O_{31.65}Cu_{4.65}Gd₁; $M = 1922.9$, monoclinic, space group C2/c (no. 15), $a = 26.647(1)$, $b = 18.1576(9)$, $c = 30.423(2)$ Å, $\beta = 90.282(1)^\circ$, $U = 14720(1)$ Å³, $Z = 8$, $D_c = 1.735 \text{ g cm}^{-3}$, $T = 193(1) \text{ K}$, $\mu(\text{Mo-K}\alpha) = 23.12 \text{ cm}^{-1}$. 954 parameters were refined with 10976 unique reflections ($I > 2.0\sigma(I)$) to give $R1 = 0.057$, $wR2 = 0.178$ (15062 independent reflections, $R_{\text{int}} = 0.041$) (Bruker P4/CCD with graphite-monochromatized Mo-K α X-radiation, and a rotating anode generator). Hydrogen atoms were introduced in calculated positions with isotropic thermal parameters set 20% greater than bonding partners and were not refined. A total of six hydrogens from the gadolinium waters and the methanol molecules were omitted from the model. One methyl group from a bound methanol was fixed for the final round of refinement. CCDC reference number 160557. See <http://www.rsc.org/suppdata/cc/b1/b101966j/> for crystallographic data in CIF or other electronic format.

§ SQUID magnetometer (Quantum Design MPMS5S) with fields of 0.1–5 T. Diamagnetic corrections for the sample holder and the sample were applied.

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