COMMUNICATION

ChemComm
www.rsc.org/chemcomm

Structural and magnetic properties of a self-assembled spheroidal triakonta-hexanuclear Cu_{36} cluster

Tareque S. M. Abedin, Laurence K. Thompson,* David O. Miller and Erik Krupicka
Deparment of Chemistry, Memorial University, St. John's, NL, Canada A1B 3X7. E-mail: lthomp@mun.ca; Fax: +1 709-737-3702; Tel: +1 709-737-8750

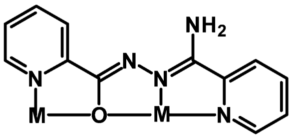
Received (in Cambridge, UK) 18th November 2002, Accepted 4th February 2003
First published as an Advance Article on the web 12th February 2003

An extended tritopic picolinic dihydrazide ligand with terminal oxime groups (dpocco) undergoes spontaneous self-assembly in the presence of copper acetate to produce a unique Cu_{36} cluster exhibiting intramolecular anti-ferromagnetic exchange.

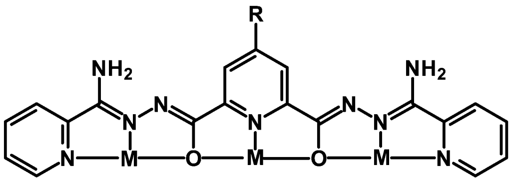
The self-assembly approach to nano-scale poly-metallic clusters has led to the syntheses of high nuclearity species containing up to 24 metal centres (*e.g.* Ni_{24}) with simple ligand mixtures based on *e.g.* Hmpo (3-methyl-3-pyrazolin-5-one),[1] and poly-carboxylic acids (Fe_{17}. Fe_{19})[2,3] as the primary ligand. Other ligands, *e.g.* OH, O^{2-}, H_2O, solvent, acetate, are incorporated into the non-homoleptic cluster as it forms from anionic and solvent fragments. Homoleptic systems are more difficult to create, and require the programming of essential coordinating elements into the ligands themselves. Square, self-assembled tetranuclear [2 × 2] $[M_4(\mu\text{-}O)_4]$ grid-like structures (M_4, M = Mn, Co, Ni, Cu) have been obtained with ditopic ligands like poap, in which the proximity of the metal ions leads to magnetic exchange within the grids.[4–6] Extending the ligands to include an extra pocket (tritopic), *e.g.* R2poap, creates a suitable framework for the formation of [3 × 3] $[M_9(\mu\text{-}O)_{12}]$ homoleptic, square nona-nuclear grids (M_9, M = Mn, Fe, Co, Ni, Cu, Zn) by high yield self-assembly reactions.[7–9] These systems exhibit intramolecular antiferromagnetic (Mn, Co, Ni), and ferromagnetic (Cu) exchange resulting from the close proximity of the alkoxide bridged metal centres. Related Ag_9, and Pb_{16} non-magnetic, homoleptic grids have been produced with polytopic extended pyridazine and pyrimidine ligands.[10,11] These compounds result in a logical and predictable manner because of the geometrical features of the donor groupings that are programmed into the coordination pockets of the ligands.

Tritopic ligands of this type, with a contiguous linear arrangement of coordination pockets, which form five-membered chelate rings, are ideal templates for extension to form larger grids, *e.g.* M_{16}, M_{25} *etc.*, but this has proven to be quite a synthetic challenge. However putting a terminal substituent, with the potential for additional bridging interactions, on the end of the basic ligand framework, *e.g.* an oxime group in dpocco, is straightforward, and presents the possibility of extending the nuclearity of a grid assembly or perhaps linking grid subunits together. Reaction of dpocco with copper acetate in aqueous methanol resulted in the low yield synthesis (12.5%) of a dark green, almost black, crystalline product, $[Cu_{36}(dpocco\text{-}4H)_{12}(\mu_3\text{-}OH)_8]$ $(CH_3COO)_{16}{\cdot}xH_2O$ (**1**),† which has been characterized by structural analysis.‡

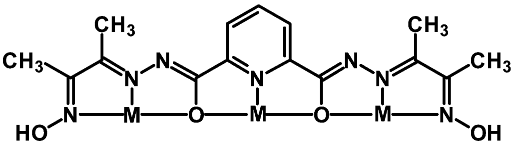
Dpocco, like its R2poap counterparts, can adopt several different conformations, and in **1** the diazine nitrogen atoms bridge a central copper within each ligand to two terminal copper ions, which then form part of a triangle of copper ions bridged by oxime linkages from three interconnecting ligands, with a μ_3-OH bridge at the centre of each triangle (Scheme 1). Fig. 1 illustrates one of the two essentially identical spheroidal



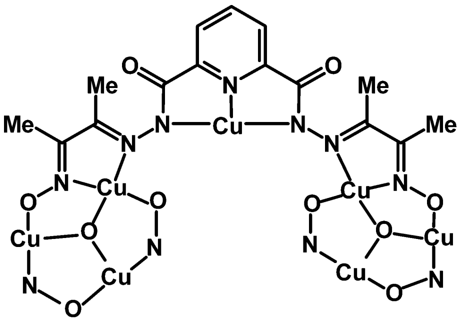
poap



R2poap (R=H,Cl)



dpocco



Scheme 1

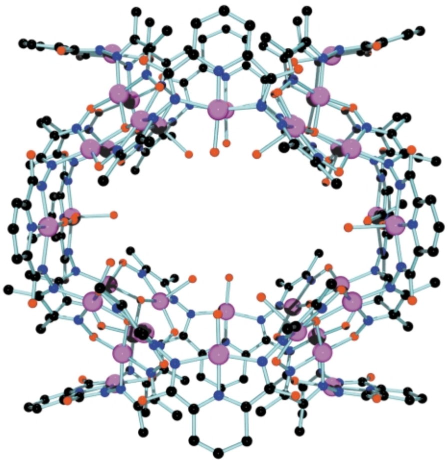


Fig. 1 Structure of $[Cu_{36}(dpocco\text{-}4H)_{12}\ (\mu_3\text{-}OH)_8]^{16+}$; magenta = Cu, red = O, blue = N, black = carbon.

DOI: 10.1039/b211401c

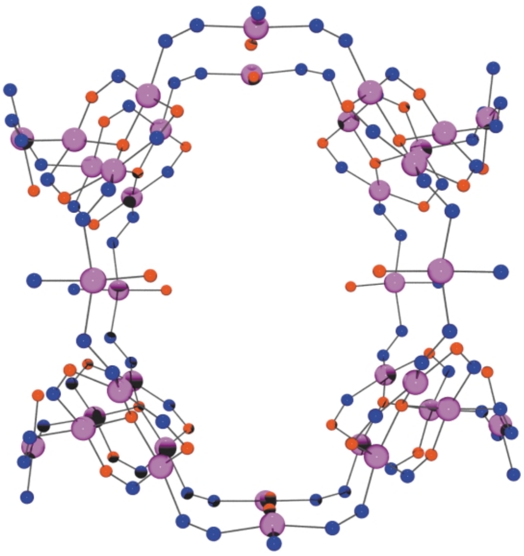


Fig. 2 Core structure for **1**; magenta = Cu, blue = nitrogen, red = oxygen.

clusters in the complex, which are related by an inversion centre, with four [$Cu_3(OH)$] subunits at the top and the bottom of the molecule and with each corner of each triangle linked by a single dpocco ligand, bonded to its central copper ion. The overall structure in each cluster shows a large hole in the centre of the sphere, which contains several coordinated acetate ions, and water molecules. A simplified view is shown in Fig. 2, which highlights the immediate bonding connections between the 36 copper ions. The hole is surrounded by a sheath of coordinated water molecules, butanedione monoxime methyl groups, and acetate groups.

Cu–Cu separations within each triangle fall in the range 3.15–3.30 Å with Cu–OH–Cu angles in the range 110–112°. Within each ligand the copper ions are more widely separated (Cu–Cu 4.25–4.50 Å), with Cu–N–N–Cu torsional angles in the range 77–92°. The μ_3-OH and μ_2-N_2 diazine groups define the magnetic connectivity in the cluster, and based on examples with similar bridging situations global intramolecular anti-ferromagnetic exchange would be anticipated.[12,13] Variable temperature magnetic data were collected (2–300 K) in a 0.1 T external field (Quantum Design MPMS5S SQUID magnetometer), and are shown in Fig. 3, expressed as μ_{mol}.

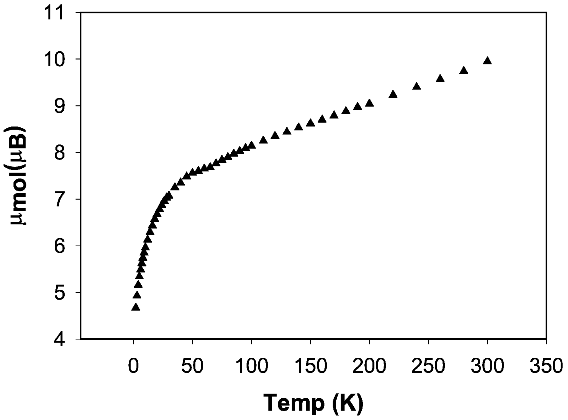


Fig. 3 Plot of temperature variation of magnetic moment per mole for **1**.

The value at 300 K is consistent with the Cu_{36} cluster, and the drop in moment as temperature is lowered is consistent with the expected overall intra-molecular anti-ferromagnetic exchange. In the low temperature limit, each triangular subunit would result in a spin doublet ground state, and would be expected to couple anti-ferromagnetically to the other copper atoms *via* the N–N bridges. This would reasonably lead to a net moment approaching zero at low temperatures. The complexity of the exchange problem presented by this novel polyhedral array of spin centres has thus far prevented an evaluation of the exchange integrals within the fundamental subunits. We are currently approaching the problem on the simplified basis of just two *J* values, one within each triangle, and another through each N–N bridge connection.

We thank Dr R. McDonald, University of Alberta, for structural data, and the Natural Sciences and Engineering Research Council of Canada (NSERC) for financial support.

Notes and references

† Dpocco 0.18 g (0.50 mmol) of was added to a solution of copper acetate 0.40 g (2.0 mmol) in methanol–H_2O (20 : 5 mL) with stirring at room temperature. After stirring for 12 h the solution was filtered. Dark green, almost black crystals suitable for X-ray analysis were obtained after two weeks (12.5% yield). Elemental analysis; Calc. for $(C_{15}H_{15}N_7O_4)_{12}$-$Cu_{36}(OH)_8(CH_3COO)_{16}(H_2O)_{96}$ C, 27.13; H, 4.59; N, 12.54 Found C, 26.83; H, 3.84; N, 12.42%. This analysis indicates a 4^- charge on each ligand, and the presence of eight hydoxide ions.

‡ *Crystal data* **1**: $C_{212}H_{358}O_{149}N_{84}Cu_{36}$, M = 8755.29, triclinic, $P\bar{1}$(#2), a = 26.022(3), b = 26.291(3), c = 42.147(5) Å, α = 80.586(3), β = 84.344(2), γ = 61.558(2)°, V = 25006(5) Å^3, T = 190(1) K, Z = 2, $F(000)$ = 8908, μ(Mo-Kα) = 15.65 cm^{-1}; 101668 data, 82136 unique (R_{int} = 0.078), R_1 = 0.152, wR_2 = 0.467 (34311 with $I > 10\sigma(I)$).

The structural data set would not support full anisotropic refinement of the model, primarily due to weak diffraction and a subsequent low percentage of observed data. A sensible charge balance can be obtained from the elemental analysis, which assumes that each copper triad is bridged by hydroxide. A significant number of acetates are missing from the final structure. However the main Cu_{36} cluster is clearly revealed.

CCDC 198461. See http://www.rsc.org/suppdata/cc/b2/b211401c/ for crystallographic data in CIF format.

1 R. E. P. Winpenny, *J. Chem. Soc., Dalton Trans.*, 2002, 1, and references therein.
2 W. Schmitt, M. Murugesu, J. C. Goodwin, J. P. Hill, A. Mandel, R. Bhalla, C. E. Anson, S. L. Heath and A. K. Powell, *Polyhedron*, 2001, **20**, 1687.
3 J. C. Goodwin, R. Sessoli, D. Gatteschi, W. Wernsdorfer, A. K. Powell and S. L. Heath, *J. Chem. Soc., Dalton Trans.*, 2000, 1835.
4 C. J. Matthews, K. Avery, Z. Xu, L. K. Thompson, L. Zhao, D. O. Miller, K. Biradha, K. Poirier, M. J. Zaworotko, C. Wilson, A. E. Goeta and J. A. K. Howard, *Inorg. Chem.*, 1999, **38**, 5276.
5 L. K. Thompson, C. J. Matthews, L. Zhao, Z. Xu, D. O. Miller, C. Wilson, M. A. Leech, J. A. K. Howard, S. L. Heath, A. G. Whitaker and R. E. P. Winpenny, *J. Solid State Chem.*, 2001, **159**, 308.
6 Z. Xu, L. K. Thompson and D. O. Miller, *J. Chem. Soc., Dalton Trans.*, 2002, 2462.
7 L. Zhao, C. J. Matthews, L. K. Thompson and S. L. Heath, *Chem. Commun.*, 2000, 265.
8 L. Zhao, Z. Xu, L. K. Thompson, S. L. Heath, D. O. Miller and M. Ohba, *Angew. Chem., Int. Ed.*, 2000, **39**, 3114.
9 L. Zhao, Z. Xu, L. K. Thompson and D. O. Miller, *Polyhedron*, 2001, **20**, 1359.
10 P. N. W. Baxter, J.-M. Lehn, B. O. Kneisel and D. Fenske, *Angew. Chem., Int. Ed.*, 1997, **36**, 1978.
11 A. M. Garcia, F. J. Romero-Salguero, D. M. Bassani, J.-M. Lehn, G. Baum and D. Fenske, *Chem. Eur. J.*, 1999, **5**, 1803.
12 D. Datta and A. Chakravorty, *Inorg. Chem.*, 1983, **22**, 1611.
13 L. K. Thompson, Z. Xu, A. E. Goeta, J. A. K. Howard, H. J. Clase and D. O. Miller, *Inorg. Chem.*, 1998, **37**, 3217.