A tetradecanuclear copper dimeric macrocyclic complex with a body-centred heptanuclear core-structure and magnetism

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2,6-Diformyl-4-methylphenol and 1,3-diamino-2-hydroxypropane template condense in the presence of $Cu(NO_3)_2$ and azide to produce a 3 : 3 macrocyclic ring containing an unprecedented grouping of seven copper(II) ions within the macrocyclic cavity, with the seventh metal completing a body-centred heptanuclear lattice.

Template condensation reactions of 2,6-diformyl-4-methylphenol (DFMP) with diamino alcohols are common, and result in mainly (2 + 2) macrocyclic rings encompassing four metals, with examples involving 2,6-diaminomethyl-4-methylphenol (Ni_4, Zn_4) ,[1,2] and 1,5-diamino-3-hydroxypentane [Cu_4, $(Cu_4)_2$].[3–5] In one unusual case, reaction of DFMP with 2,6-diaminomethyl-4-methylphenol with copper acetate led to the formation of an expanded (3 : 3) macrocycle incorporating six metal ions in a distorted boat-shaped cluster.[6] A rational approach to the expanded (3 : 3) macrocycles was devised by using a 'shorter' diaminoalcohol linker subunit, which would effectively prevent (2 : 2) cyclisation because of the steric strain involved. In a novel reaction involving DFMP and 1,3-diamino-2-hydroxypropane, in the presence of copper(II) nitrate, the (3 : 3) macrocycle (L3) was produced, within which six copper(II) ions were incorporated in a novel 'benzene-like' array.[7,8] The six copper centres were bridged alternately by a combination of μ-O (alkoxide), and μ-O_2 (phenoxide/hydroxide) bridging groups leading to strong intramolecular antiferromagnetic exchange. The overall structure consisted of two saucer shaped Cu_6 rings joined at the base by weak axial contacts between copper centres to form a dodecanuclear structure overall. A recent report describes a 3 : 3 condensation of diformyldihydroxybenzene with substituted phenylenediamines, and the incorporation of three Zn(II) ions in the macrocyclic ring, with extra-ring coordination of four additional Zn(II) ions in a heptazinc cluster.[9] Expanded cyclisation to form a closely related 6 : 6 macrocyclic system indicates six potential ring coordination sites, but no complexes are reported.[10]

In the present communication we describe a modification of the earlier template synthesis, which has allowed the unprecedented insertion of a seventh copper ion into the macrocyclic cavity, to effectively fill in the hole at the centre of the hexagonal arrangement of copper ions.† The complex $[(L3 - 6H)Cu_7(\mu_3\text{-}OCH_3)(\mu_3\text{-}OH)_2(CH_3OH)_2(NO_3)(H_2O)(N_3)_2]_2(NO_3)_4\cdot 9H_2O$ (**1**) was obtained as green crystals suitable for X-ray structural determination.‡ The overall molecular structure consists of two heptanuclear halves joined by two μ-1,3-azide bridges. A heptanuclear half is shown in Fig. 1, and the dimeric structure is shown in Fig. 2. Six square or square-pyramidal copper(II) ions (Cu(2)–Cu(7)) are arranged in a hexagonal ring within the macrocyclic ligand, which results from the template condensation of three DFMP and DAP subunits. Cu(3) has an axially bound disordered nitrate, and Cu(7) has an axially bound water (omitted from Fig. 1 and 2). Cu(5) and Cu(6) have axially bound methanol molecules, which are lost on drying.† Within the ring the copper ions are bridged alternately by single and double oxygen bridges from alkoxide (Cu(3), Cu(5); Cu(4), Cu(7); Cu(2), Cu(6)), phenoxide/hydroxide (Cu(4), Cu(6); Cu(5), Cu(7)) and phenoxide/methoxide (Cu(2), Cu(3)) combinations. Alkoxide bridge angles fall in the range 116.9–134.0°, phenoxide bridge angles fall in the range 100.8–101.0°, hydroxide bridge angles within the hexacopper ring are 97.5° and 97.8°, and the Cu(2)–O(10)–Cu(3) methoxide bridge angle is 101.7°. Cu(1) is bridged to Cu(4), Cu(6), Cu(5) and Cu(7) by two μ_3-OH bridges. The solid angles at O(4) and O(5) (326.6 and 327.2°, respectively) indicate significant pyramidal distortion at these bridging centres. The range of oxygen bridge angles as a whole would suggest the presence of dominant intramolecular antiferromagnetic exchange (*vide infra*). Each macrocyclic half has a 'bowl' shape, clearly resulting from strain inherent in the 3 : 3 condensed ring, and the two halves are connected by axial μ_2-1,3-azide bridges *via* Cu(1) to Cu(4) and Cu(7) on the adjacent half (Fig. 2), with the concave faces of the metallocycles in closest contact. This creates a large tetradecanuclear cluster.

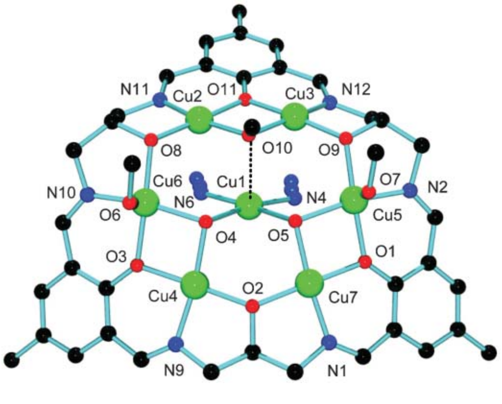

Fig. 1 Structural representation of a heptanuclear half of **1** (hydrogen atoms removed for clarity; black = carbon).

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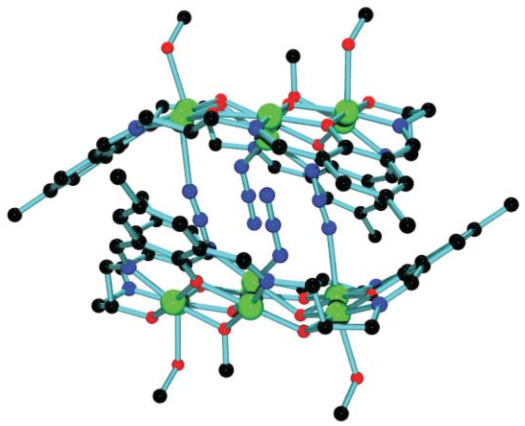

Fig. 2 Dimeric structure of **1** (green = copper, blue = nitrogen, red = oxygen, black = carbon).

The variable-temperature magnetic data for **1** are shown in Fig. 3 as plots of susceptibility and moment per mole (per heptanuclear half). The room-temperature moment (4.1 μ_B; 1.55 μ_B per copper) is consistent with the presence of seven antiferromagnetically coupled Cu(II) ions within each macrocyclic cluster, and drops to 2.03 μ_B at 2 K, consistent with the odd number of metals present. Devising a magnetic exchange model for such a complex system is difficult, but can be approached on the basis of some predictability regarding the type of bridge present, and the magnetic connectivity between the copper ions. Copper atoms Cu(2)–Cu(7), which are directly bound to the macrocyclic ligand, all have planar or square-pyramidal geometries, with in plane connections through the bridging oxygen atoms to neighbours. Based on the Cu–O–Cu bridge angles the six copper ions in the metallocyclic ring would therefore be expected to take part in antiferromagnetic exchange, with stronger exchange *via* the alkoxide bridges, as a result of the larger angles. The central copper Cu(1) has a square-pyramidal geometry with in-plane coordination to O(4) and O(5), but axial coordination to O(10). This means that Cu(1) can be coupled directly to Cu(4), Cu(6), Cu(5) and Cu(7) through magnetic orbital overlap, but not to Cu(2) and Cu(3). The significant pyramidal nature of the OH bridges at O(4) and O(5) suggests relatively weak antiferromagnetic coupling between Cu(1) and these neighbouring centres, but no antiferromagnetic exchange with Cu(2) and Cu(3). The bridging 1,3-N_3 connections between the heptanuclear halves of the Cu_{14} cluster are axial, and so any significant antiferromagnetic exchange between the two subunits would not be expected.

Fig. 4 represents a realistic exchange model for each heptanuclear cluster based on the exchange Hamiltonian (eqn (1)).

$$H_{ex} = -J_1\{S_2{\cdot}S_3 + S_5{\cdot}S_7 + S_4{\cdot}S_6\} - J2\{S_3{\cdot}S_5 + S_4{\cdot}S_7 + S_2{\cdot}S_6\} - J_3\{S_1{\cdot}S_5 + S_1{\cdot}S_7 + S_1{\cdot}S_4 + S_1{\cdot}S_6\} \quad (1)$$

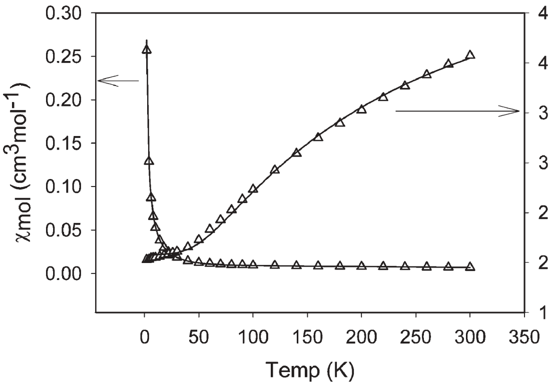

Fig. 3 Variable-temperature magnetism for **1**. See text for fitted parameters.

Fitting the experimental data to this model with three different, and independent J values, in addition to varying 'g', and possibly other parameters, could lead to overparamaterization. Therefore initially the data were fitted to a model for which $J = J_1 = J_2 = J_3$. A reasonable fit was obtained using MAGMUN4.1[11] for g = 2.22(2), $J = -154(4)$ cm^{-1}, TIP = 430(5) $\times$ 10^{-6} cm^3 mol^{-1}, ρ = 0.028 (fraction of Curie-like paramagnetic impurity), R = 0.025 ($R = [\sum(\chi_{obs.} - \chi_{calc.})^2/\sum\chi_{obs}{}^2]^{1/2}$). This J value compares reasonably with the isotropic exchange situation found in the parent hexanuclear macrocyclic complex $[Cu_6]_2$.[7,8] Since the three bridging connections are quite different, models with differing J values were also tried. However it was found that fitting improved only when J_3 was reduced to small values, and ultimately the best model involved eliminating it completely. This is sensible based on the significant pyramidal distortion at O(4) and O(5), which would lead to reduced overlap with the bonded copper magnetic orbitals. The best fit was obtained for g = 2.21(1), $J_1 = J_2 = -224(4)$ cm^{-1}, TIP = 445(5) $\times$ 10^{-6} cm^3 mol^{-1}, ρ = 0.029, R = 0.016. The solid lines in Fig. 3 were calculated with these parameters. The good data fit, and values for J_1 and J_2 which are comparable with the hexanuclear parent $[Cu_6]_2$ complex, indicate a reasonable assessment of the exchange picture. Further discrimination of J_1 and J_2 (*vide supra*) was not attempted, since it seemed unlikely that significantly improved fits would be obtained. Also fine tuning of the exchange model by the introduction of extra parameters to possibly account for inter-dimer coupling was not carried out, because of the approximation of the model as a whole, and the fact that any such interaction would clearly be very small.

The overall magnetic properties of **1** do not differ appreciably from those of the parent $[Cu_6]_2$ cluster,[7,8] except that the ground state (S' = 1/2) is different, due to the presence of the extra copper ion in the centre of the hexacopper ring. The body-centred nature of the Cu_7 macrocyclic subunit is rare, and shows that with this type of ligand an intricate closed lattice arrangement of metals can be generated. The 'bowl' shaped nature of the metallocycle, resulting from inherent strain within the macrocyclic ligand itself, leads to the seventh copper ion protruding slightly from the bowl, such that it becomes tilted slightly out of the central position, thus

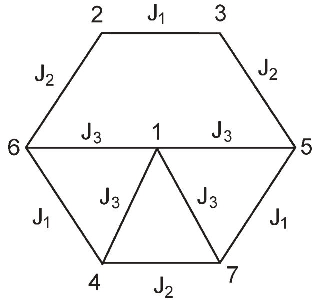

Fig. 4 Magnetic exchange model for **1**.

leading to the unsymmetric exchange situation, and the orthogonal connectivity to Cu(2) and Cu(3). Given the dimensions of the triangular grouping O(4), O(5), O(10) (O(4)–O(10) 3.057 Å, O(5)–O(10) 3.073 Å, O(4)–O(5) 2.771 Å) the incorporation of Cu(1) within the metallocyclic ring might have been expected. The prospect of encouraging other metals to do the same presents some interesting possibilities for the creation of ferrimagnetic systems, and possible novel ground state spin situations. Studies in this area are being pursued.

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Notes and references

† Experimental details: 2,6-diformyl-4-methylphenol (DFMP) (1 mmol, 0.16 g) dissolved in methanol (10 mL) was added to a hot methanolic solution (20 mL) of $Cu(NO_3)_2 \cdot 3H_2O$ (2.5 mmol, 0.60 g) with stirring. A green solution was obtained after refluxing for *ca.* 10 min. A solution of 1,3-diamino-2-hydroxypropane (DAP) (1 mmol, 0.09 g) in methanol was added dropwise over a period of 5 min, followed by triethylamine (2 mmol, 0.20 g) and a solution of sodium azide (1 mmol, 0.06 g) dissolved in 10 mL of hot methanol. The reaction mixture was stirred under reflux for *ca.* 24 h, filtered and the filtrate concentrated using a rotary evaporator to *ca.* 20 mL and kept undisturbed at ambient temperature. After two weeks dark green crystals of **1** suitable for X-ray study were obtained (yield: 0.045 g, 11%). From the mother-liquor a second crop of the compound was also recovered (0.20 g. 50%) which showed a very similar IR spectrum: $\nu(N_3)$ 2102, 2034 (sh) cm^{-1}. Elemental analysis (%) (dried sample). Found: C, 28.05; H, 3.23; N, 13.64. Calc. for $Cu_{14}(C_{36}H_{36}N_6O_6)_2(OCH_3)_2(OH)_4(N_3)_4(NO_3)_6(H_2O)_{14}$: C, 28.61; H, 3.57; N, 13.51.

‡ *Crystal data for* **1**. $C_{78}H_{120}Cu_{14}N_{30}O_{51}$, M = 2797.4(5), triclinic, space group $P\bar{1}$, a = 14.0485(12), b = 15.7647(14), c = 15.772(2) Å, α = 116.174(2), β = 108.739(2), γ = 98.205(2)°, U = 2797.4(5) Å^3, T = 100(2) K, Z = 1, μ(Mo-Kα) = 2.707 mm^{-1}, 22204 reflections measured, 9877 unique, and 6629 ($>2\sigma(I)$) used in the calculations; R_1 = 0.0536, wR_2 = 0.1428. The solvent electron density was modeled using PLATON/SQUEEZE (ver. 1.04), which located a potential solvent volume of 520 Å^3 and an electron count of 185 electrons/cell, consistent with four nitrate molecules and nine water molecules/cell. Four nitrate molecules and nine water molecules were added to the contents of the unit cell during the final refinement to properly calculate the crystal data. CCDC 619927. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b612795a

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11 MAGMUN4.1. MAGMUN4.1/OW01.exe is available as a combined package free of charge from the authors (http://www.ucs.mun.ca/~lthomp/magmun). MAGMUN has been developed by Dr Zhiqiang Xu and OW01.exe by Dr O. Waldmann. We do not distribute the source codes. The programs may be used only for scientific purposes, and economic utilization is not allowed. If either routine is used to obtain scientific results, which are published, the origin of the programs should be quoted.