# A Novel Antiferromagnetically Coupled, Dimeric, Dodecanuclear Copper(II) Complex involving Two Macrocyclic Ligands each with a 'Benzene-like' Arrangement of Six Copper Centres

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Template condensation of 2,6-diformyl-4-methylphenol with 1,3-diamino-2-hydroxypropane, in the presence of copper(II) nitrate and a base, results in the formation of a novel dimeric, dodecacopper(II) complex of a 30-membered macrocyclic ligand ($H_6M$), with a pseudo-hexagonal, 'benzene-like' arrangement of metal centres and an alternating double ($\mu_2$-OPh, $\mu_2$-OH) and single ($\mu_2$-OR) bridge arrangement within each ring.

Polynuclear metal complexes are of great importance as biological models and because of their potential use in catalysis. Frequently such systems result from the organization of several metals into a cluster by the bridging action of *e.g.* oxygen groups, either as hydroxide or as part of an organic ligand. However the organization of a group of metals (*e.g.* three or greater) by a single ligand entity is not common and relies on the availability of suitable repeating building blocks and suitable synthetic routes to the ligands themselves. In previous studies we have described some tetranuclear copper(II) complexes *e.g.* [$Cu_4L(OH)_2(H_2O)_8$]($CF_3SO_3$)$_6$ {L = 1,2,4,5-tetrakis[2-pyridyl(R)amino]benzodipyridazine; R =

H, 4-Me},[1,2] in which one octadentate ligand binds four metal centres. Large polyazacycloalkanes[3,4] have been shown to bind three copper(II) centres, while (2 + 2) template condensations of 2,6-diformyl-4-methylphenol (DFMP) with 2,6-diaminomethyl-4-methylphenol ($Ni_4$, $Zn_4$)[5,6] and 2,6-diformyl-4(R)-phenol (R = Me, $Bu^t$) with 1,5-diamino-3-hydroxypentane [$Cu_4$, ($Cu_4$)$_2$][7–9] produce complexes in which one macrocyclic ligand encompasses four metal centres. In one isolated case involving template condensation of DFMP with 2,6-diaminomethyl-4-methylphenol, in the presence of copper acetate, a (3 + 3) macrocycle formed incorporating six metals in a boat-shaped cluster.[10]

Template condensations of DFMP with 1,3-diamino-2-hydroxypropane (DAHP), in the presence of $Pb^{2+}$, $Mn^{2+}$ and $Ni^{2+}$ ion produced the (2 + 2) macrocycle only and just binuclear complexes in which the secondary alcohol group remained protonated and uncoordinated.[11,12] It is apparent that, unlike the macrocycles involving 1,5-diamino-3-hydroxypentane, these 20-membered macrocycles have a cavity which is too small to accommodate four metals. However, in rare cases higher oligomeric macrocyclic rings can form which bind larger numbers of metals. Template ($Ba^{2+}$) condensation of 2,6-diacetylpyridine with DAHP, followed by trans-metallation, produces the binuclear (2 + 2) $Mn(ClO_4)_2$ complex as the major product, but a tetranuclear (4 + 4) $Mn(ClO_4)_2$ complex as well, which involves proton loss from and coordination of the secondary alcohol groups.[13] With macrocycles involving hydroxypropane bridges the coordination of the secondary alcohol group would therefore seem critical for the formation of large (3 + 3 and higher) macrocyclic rings.

Template condensation of 2,6-diformyl-4(R)phenol (R = Me, $Bu^t$) and DAHP, in the presence of copper(ii) salts alone, produces binuclear (2 + 2) macrocyclic complexes, with no coordination of the secondary alcohol group.[14] However, the reaction of copper(ii) nitrate (4 equiv.), DFMP (2 equiv.), DAHP (2 equiv.) and triethylamine (4 equiv.) in refluxing methanol (24 h), followed by concentration to a small volume produced the dodecanuclear complex $[Cu_6M(\mu_2\text{-}OH)_3]_2(NO_3)_6\cdot10H_2O$ **1**. Crystals suitable for X-ray analysis were obtained from $Me_2SO$–methanol mixture. The structure of **1** has been determined.†

The structure of the dimeric cation (Fig. 1 illustrates the hexanuclear monomer) is unique and consists of two almost flat, hexagonal macrocyclic rings, each involving an array of six nominally pseudo square-planar copper(ii) centres, which are coupled together by an axial bridging interaction in which hydroxide bridges O(7) and O(9) not only bridge copper pairs Cu(1), Cu(2) and Cu(5), Cu(6) respectively within the same ring, but also provide a bridge to copper atoms Cu(4) and Cu(3) respectively on the other macrocyclic ring. The molecular symmetry dictates that this inter-macrocycle bridging also involves the symmetry related atoms and so the two rings are held together by four axial hydroxide bridges. A view of the dodecanuclear dimer is shown in Fig. 2. The relatively short inter-ring hydroxide contacts [Cu(3')-O(9) 2.45(1), Cu(4')-O(7) 2.43(1) Å] indicate a significant axial interaction and so three copper atoms are bridged in a tripodal arrangement by O(7) and O(9) (solid angles approximately 312°) and the geometry at Cu(3) and Cu(4) is square-pyramidal. A pair of symmetrically related, bidentate, nitrate groups, bonded to Cu(1) via O(11) and Cu(2) via O(10), are located on the concave (outer) face of the complex [Cu(1)-O(11) 2.36(2), Cu(2)-O(10) 2.56(2) Å]. A second pair of disordered and poorly refined nitrate groups also bond to the outer faces at Cu(5) and Cu(6). Five pairs of water molecules and two disordered nitrate anions have been located in the lattice.

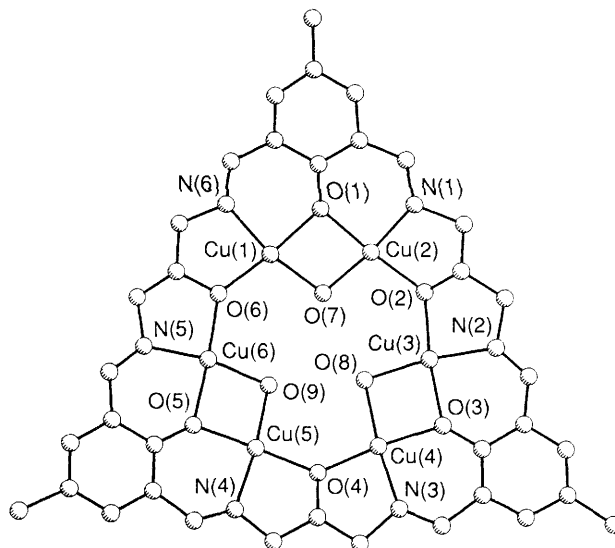The copper atoms are linked within each ring by an alternating single and double bridged arrangement of oxygen

**Fig. 1** Structural view of the $[Cu_6M(\mu_2\text{-}OH)_3]^{3+}$ cation **1**

Bond lengths (Å): Cu(1)–O(1) 1.98(1), Cu(1)–O(6) 1.92(1), Cu(1)–O(7) 1.96(1), Cu(1)–N(6) 1.95(2), Cu(2)–O(1) 1.96(1), Cu(2)–O(2) 1.93(1), Cu(2)–O(7) 1.94(1), Cu(2)–N(1) 1.92(2), Cu(3)–O(2) 1.96(1), Cu(3)–O(3) 1.96(1), Cu(3)–O(8) 1.98(1), Cu(3')–O(9) 2.45(1), Cu(3)–N(2) 1.96(2), Cu(4)–O(3) 1.96(1), Cu(4)–O(4) 1.95(1), Cu(4')–O(7) 2.43(1), Cu(4)–O(8) 1.99(1), Cu(4)–N(3) 1.92(2), Cu(5)–O(4) 1.94(1), Cu(5)–O(5) 1.94(1), Cu(5)–O(9) 1.93(1), Cu(5)–N(4) 1.94(2), Cu(6)–O(5) 1.97(1), Cu(6)–O(6) 1.95(1), Cu(6)–O(9) 1.96(1), Cu(6)–N(5) 1.91(2), Cu(1)–Cu(2) 2.929(3), Cu(2)–Cu(3) 3.544(5), Cu(3)–Cu(4) 2.960(4), Cu(4)–Cu(5) 3.570(4), Cu(5)–Cu(6) 2.937(5), Cu(1)–Cu(6) 3.567(5), Cu(1)–Cu(3) 5.540(6), Cu(3)–Cu(5) 5.680(4), Cu(1)–Cu(5) 5.702(7), Cu(2)–Cu(4) 5.690(7), Cu(4)–Cu(6) 5.554(6), Cu(2)–Cu(6) 5.666(5), Cu(1)–Cu(4) 6.453(8), Cu(2)–Cu(5) 6.644(6), Cu(3)–Cu(6) 6.404(5). Bond angles (°): Cu(1)–O(1)–Cu(2) 96.0(6), Cu(1)–O(7)–Cu(2) 97.3(5), Cu(2)–O(2)–Cu(3) 131.7(6), Cu(3)–O(3)–Cu(4) 97.9(5), Cu(3)–O(8)–Cu(4) 96.3(4), Cu(4)–O(4)–Cu(5) 133.1(8), Cu(5)–O(9)–Cu(6) 98.2(5), Cu(5)–O(5)–Cu(6) 97.3(5), Cu(6)–O(6)–Cu(1) 135.0(6).

atoms (alkoxide and hydroxide plus phenoxide) that resembles a resonance form of benzene. The adjacent copper–copper separations alternate between short (2.92–2.96 Å; double) and long (3.54–3.57 Å; single) contacts. The hexanuclear macrocyclic fragments do not have real mirror planes, but possess three pseudo-mirror planes passing through bridging groups [(O(1), O(7), O(4)), (O(2), O(9), O(5))] and [O(3), O(8), O(6)] and perpendicular to the plane of the six copper atoms (deviations from the least-squares $Cu_6$ plane are $<0.03$ Å for all copper atoms). Each hexanuclear, macrocyclic half is dished slightly in the centre, with the appearance of a shallow bowl, and the two halves are bridged via the convex surfaces. The bridging hydroxides [O(7), O(8), O(9)] appear to be the only species present in the central cavity. The phenoxide and hydroxide bridge angles lie in the ranges 96.0–97.9° and 96.3–98.2° respectively, while the alkoxide bridge angles are much larger (131.7–135.0°). The intra-ring copper–oxygen (1.92–1.98 Å) and copper–nitrogen (1.91–1.96 Å) distances are normal and similar to those reported for other copper(ii) complexes with related dinucleating and tetranucleating macrocyclic ligands.[8,9,12]

The redox chemistry of **1** was studied by cyclic voltammetry ($Me_2SO$–tetraethylammonium perchlorate, Pt, saturated calomel electrode). It exhibits three quasi-reversible redox waves at $E_{1/2}^1 = 0.075$ V ($\Delta E_p = 130$ mV), $E_{1/2}^2 = -0.44$ V ($\Delta E_p = 80$ mV) and $E_{1/2}^3 = -0.92$ V ($\Delta E_p = 100$ mV), which may be associated with $Cu^{II}/Cu^{I}$ reduction. The deposition of metallic copper during electrolysis has, so far, prevented the assignment of these waves to specific redox steps.

Cation **1** has a low room temperature magnetic moment ($\mu_{eff} = 1.37$ BM at 300 K) indicating the presence of net antiferromagnetism in the dodecanuclear copper(ii) species.
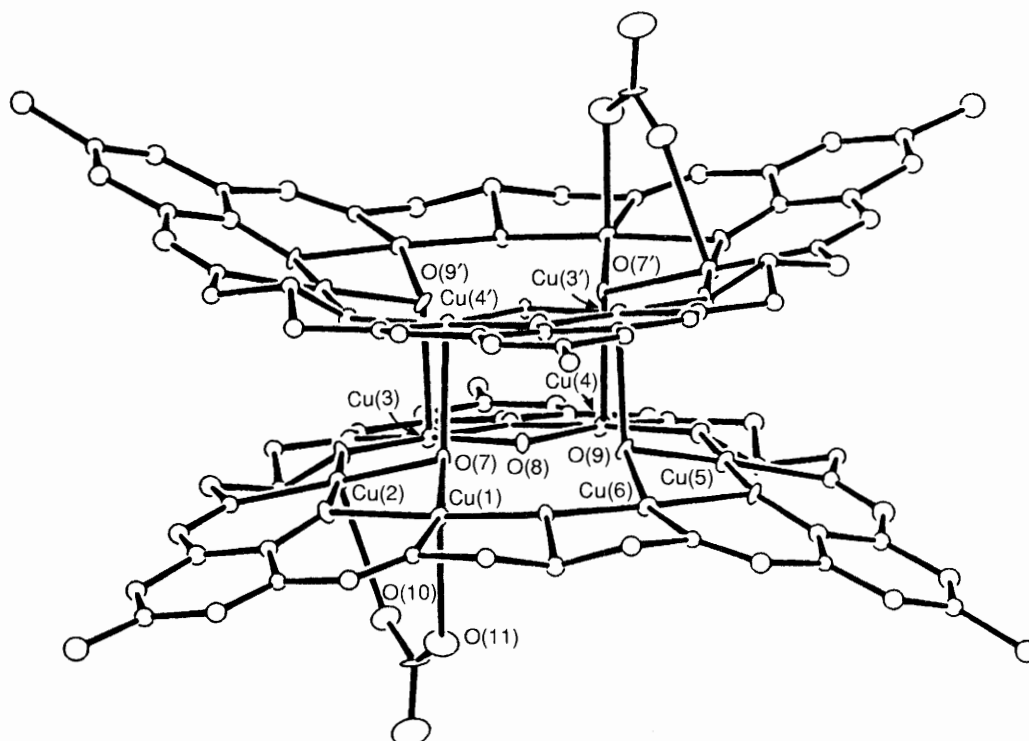
**Fig. 2** Structural view of the $[Cu_6M(\mu_2\text{-OH})_3]_2^{6+}$ dimeric cation **1**

Variable temperature (5–300 K) magnetic data on a powdered sample of **1** show a broad maximum in susceptibility, centred at about 130 K, confirming the presence of dominant antiferromagnetic exchange. The symmetric and alternating arrangement of single and double oxygen bridges, linking all the copper magnetic orbitals within each ring, indicates the likelihood of exchange involving the whole hexanuclear ring. Of the two different bridge groups the single atom, alkoxide bridge (large Cu–O–Cu angle) is considered to dominate the exchange situation. We are in the process of analysing these magnetic data (and data for other related complexes) using an appropriate geometric exchange model in order to evaluate both intra- and inter-ring exchange.

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