The *X*-Ray Crystal Structure and some Properties of a Planar Tetracopper(II) Macrocyclic Complex containing a μ_4-Hydroxo Bridge

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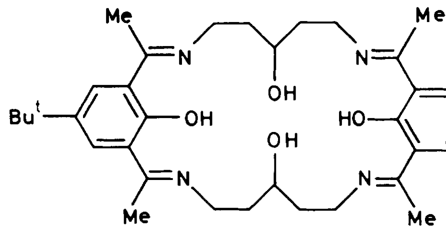
A planar, tetranuclear copper(II) complex of a macrocyclic ligand has been synthesised; the *X*-ray structure shows that the complex also contains a μ_4-hydroxo ligand bound to each of the four copper ions and coplanar with them.

Polynuclear metal complexes are of wide interest both as enzyme models and because of their potential as homogeneous catalysts. We have extended our previous study of polynucleating macrocycles with potentially bridging alcohol groups[1] to include systems incorporating additional endogenous phenol groups. The presence of such bridging groups within the macrocyclic cavity promotes the binding of several metal ions, as well as mediating magnetic and electronic interactions between them.

Complexes of the new ligand H_4L are obtained by Schiff's-base condensation of 2,6-diformyl-4-t-butylphenol with 1,5-diamino-3-hydroxypentane in the presence of a template ion. The macrocycle has two phenol groups and two alcohol groups all of which are capable of bridging metal ions on deprotona-



H_4L

tion; in addition, the ligand contains four imine nitrogen donors. Related ligands[2] incorporating 1,3-diamino-2-hydroxypropane have been shown to be capable of binding either one or two metal ions; use of the longer pentane derivative should significantly expand the macrocyclic ring. The resulting ligand is large enough to bind four transition metal ions, each with approximately square planar geometry and bridged to neighbouring metal ions *via* deprotonated alkoxide and phenoxide donors. In this paper we report the synthesis and characterisation of such a tetrametallic complex, $[Cu_4L(OH)]\cdot3NO_3\cdot3H_2O$, which also contains a μ_4-hydroxo ligand.

The complex was obtained as a dark green powder from a template reaction in which 2,6-diformyl-4-t-butylphenol (2 mmol), 1,5-diamino-3-hydroxypentane (2 mmol), and $Cu(NO_3)_2\cdot3H_2O$ (4 mmol) were refluxed in a methanol–ethanol mixture for 20 h. Formation of the macrocycle was confirmed from the i.r. spectrum in which the carbonyl and amine bands of the reactants were replaced by an imine stretch at 1640 cm^{-1}. Microanalysis figures agree with the formulation $[Cu_4L(OH)]\cdot3NO_3\cdot3H_2O$ and preliminary magnetic measurements (μ_{eff} = 1.36 and 0.92 μ_B per Cu atom at 298 and 93 K, respectively†) revealed quite strong interactions between the metal centres, suggesting a bridged structure. Crystals suitable for *X*-ray study were obtained by ether diffusion into an acetonitrile solution of the complex.

The structure of the $[Cu_4L(OH)]^{3+}$ cation is shown in Figure 1;‡ the molecule is centrosymmetric with the oxygen atom O(x) on a centre of symmetry. Within the macrocyclic ring only the saturated carbon atoms show significant deviation from planarity and, of these, C(12), C(13), and C(15) are disordered, having 50% occupancy of equivalent sites on either side of the macrocyclic plane. Four Cu^{II} ions are bound within the macrocycle, each co-ordinated to an imine nitrogen, one phenoxide oxygen, one alkoxide oxygen, the central hydroxide ion, *i.e.* O(x), and one axial donor (water or nitrate). The macrocyclic oxygen donors are all deprotonated and bridging so that the square plane about each copper shares two edges with the equivalent planes of two neighbouring copper atoms. The Cu–Cu distances [3.000(1) and 2.953(1) Å for Cu(1)–Cu(2) and Cu(1)–Cu(2′), respectively] are quite short but do not represent bonding distances. Bond distances between the copper atoms and the macrocyclic donors are unremarkable; however the longer Cu–O(x) distances of 2.082(1) and 2.127(1) Å for Cu(1) and Cu(2), coupled with the compressed O–Cu–O(x) angles (82.2—83.8°), suggest that this bond is somewhat weaker than the other three. This may be due to a less than perfect fit between metal and ligand. In the case of Cu(2), an axially bonded water molecule is present as a fifth ligand [Cu–O(W1) 2.249(5) Å] while Cu(1) exhibits a longer interaction with a 50/50 disordered water [Cu(1)–O(W2) 2.48(1) Å] or nitrate moiety [Cu(1)–O(22) 2.82(2) Å]. Individual macrocyclic units are linked by hydrogen bonding through the 50% occupancy nitrate group; O(W1) [under transformation (1 + *x*, *y*, *z*)]–O(21) 2.72 Å. There is a second hydrogen bond between O(W1) [under transformation (–*x*,1–*y*,1–*z*)] and O(12) of the non-bonded nitrate (2.86 Å). These interactions presumably determine the unit cell packing.

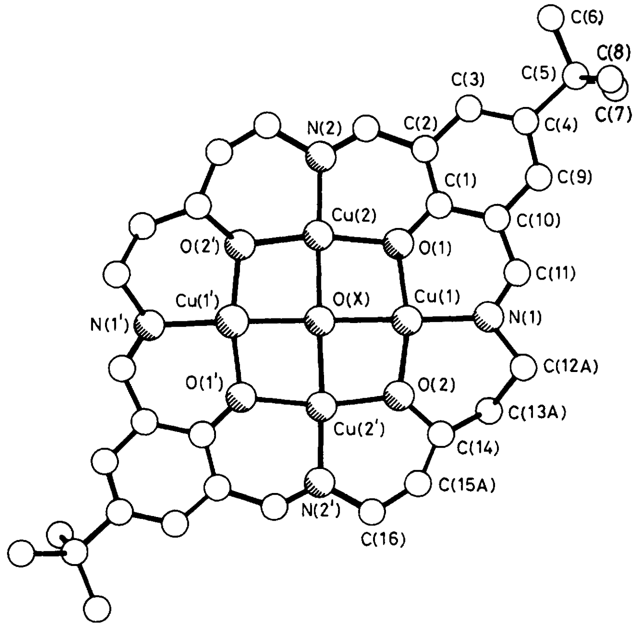


Figure 1. Structure of the $[Cu_4L(OH)]^{3+}$ cation; hydrogen atoms and axial ligands have been omitted and the disordered atoms C(12), C(13), and C(15) are shown in one of the two possible conformations. Selected bond lengths and angles: Cu(1)–Cu(2) 3.000(1), Cu(1)–Cu(2′) 2.953(1), Cu(1)–O(x) 2.082(1), Cu(2)–O(x) 2.127(1), Cu(2)–O(1) 1.915(4), Cu(1)–O(2) 1.883(4), Cu(1)–N(1) 1.940(6), Cu(2)–O(1) 1.916(5), Cu(2)–O(2′) 1.864(5), Cu(2)–N(2) 1.937(5) Å; Cu(1)–O(x)–Cu(2) 90.9(1), Cu(1)–O(x)–Cu(2′) 89.1(1), O(1)–Cu(1)–N(1) 94.5(2), O(1)–Cu(1)–O(2) 167.1(2), O(1)–Cu(1)–O(x) 83.5(1), N(1)–Cu(1)–O(2) 98.4(2), N(1)–Cu(1)–O(x) 175.4(1), O(2)–Cu(2)–O(x) 83.8(2), O(1)–Cu(2)–N(2) 94.42, O(1)–Cu(2)–O(2′) 163.6(2), O(1)–Cu(2)–O(x) 82.2(1), N(2)–Cu(2)–O(2′) 98.5(2), N(2)–Cu(2)–O(x) 167.3(2), O(2′)–Cu(2)–O(x) 83.0(1)°.

The central donor, O(x), which is bound to all four copper atoms is required by stoicheiometry to have one negative charge. Although no hydrogen atom has been located we designate this species as OH^- rather than O^- as the latter would require oxidation of water (or reduction of O_2) to have occurred. If this is the case, the central oxygen atom is five-co-ordinate and (presumably) square pyramidal with the hydrogen disordered above and below the macrocyclic plane.

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† 1 $\mu_B = 9.274 \times 10^{-24}$ J T^{-1}.

‡ *Crystal Data:* $C_{34}H_{51}Cu_4O_{17}$, green crystal, monoclinic, space group $P2_1/a$, $a = 10.384(2)$, $b = 18.515(5)$, $c = 11.264(2)$ Å, $\beta = 107.48°$, $U = 2665(1)$ Å^3, $Z = 2$, $F(000) = 1111.7$, crystal dimensions 0.4 × 0.3 × 0.2 mm. Data collected at 160 K on a Nicolet R3m four-circle diffractometer using graphite monochromated Mo-K_α radiation. Using 1.8° ω-scans with scan rate 3.91° min^{-1}, 3627 unique reflections were collected in the range $4 < 2\theta < 50°$ and 2521 with $I > 3\sigma(I)$ were used for the structural analysis. The structure was solved using Patterson methods and refined to $R = 0.047$, $R_\omega = 0.066$. All programs used in data reduction and structure solution are contained in the SHELXTL (Version 4.1) package (see ref. 7). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

Although, to our knowledge, such geometry has not been observed for hydroxide in first row transition metal complexes, it is not unknown for oxygen in polynuclear systems. Oxo ligands with high co-ordination numbers are quite common in complexes of second and third row transition elements.[4] A number of Cu_4O units have been reported in which the oxygen atom (usually O^{2-}) is bound to four copper centres[5] but the geometry in these cases invariably approximates to tetrahedral. To our knowledge the present complex is the first example in which an hydroxide group is bound to four copper(II) ions in a square planar array. However, a similar $\mu_4(OH)$ unit, in which a disordered hydroxide is bound to three Cu^I centres within a slightly larger Cu_4 array, has been characterised,[6] and a macrocyclic tetranickel(II) complex containing a planar μ_4-hydroxo ligand has been reported very recently.[7]

To date, only the tetra-copper complex has been structurally characterised but preliminary studies have shown that a tetra-manganese(II) complex can also be prepared.[3] It seems likely that a series of structurally related complexes of the other first-row transition metals can be synthesised. These complexes, with four metal ions in close proximity and two relatively open faces may have potential as catalysts, promoting reaction between axially co-ordinated groups. It may also be feasible to replace the μ_4-hydroxo group with other guest molecules and, possibly, to activate these towards further reaction.

We are grateful to the New Zealand University Grants Committee for the award of a postdoctoral fellowship to S. S. T.

Received, 14th September 1987; Com. 1325

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