Synthesis and Crystal Structure of a Complex in which a Single Macrocyclic Ligand binds Six Cu^{II} Centres in a Cyclohexane Boat Arrangement

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The hexa Schiff base macrocycle formed by condensation of three molecules of 2,6-diformyl-4-methylphenol with three molecules of 2,6-bis(aminomethyl)-4-methylphenol binds six copper(II) ions in a cyclohexane boat arrangement with two μ_2-hydroxo groups (O···O separation 3.32 Å) occupying the central cavity.

The organisation provided by ligands capable of binding small groups of metal centres in various pre-determined ways may provide complexes showing structural features and reactivity that would be unlikely or impossible in the absence of that organisation. Many studies of complexes in which pairs of metal centres are secured by binucleating ligands[1] have been reported since the first deliberately designed examples were described twenty years ago.[2] More recently, complexes of a macrocyclic trinucleating ligand[3] and macrocyclic tetranucleating ligands[4] have been reported. We describe here the first example of a complex in which a single macrocyclic ligand binds six copper centres in close proximity.

Reaction between 2,6-bis(aminomethyl)-4-methylphenol monohydrochloride, 2,6-diformyl-4-methylphenol, copper(II) acetate monohydrate, and tetrabutylammonium tetrafluoroborate (1 : 1 : 2 : excess) in boiling methanol gave, after the solution had been concentrated and allowed to stand, a green crystalline product of formula $[LCu_6(MeCO_2)_2(OH)_2(MeOH)_2(H_2O)](BF_4)_2\cdot4.4MeOH$,† where L^{6-} is the macrocyclic hexa Schiff base hexaphenolate ligand described below.

The structure revealed by *X*-ray crystallography‡ consists of discrete hexanuclear cations of formula $[LCu_6(MeCO_2)_2(OH)_2(MeOH)_2(H_2O)]^{2+}$ together with BF_4^- ions and lattice methanol. One view of the cation is shown in Figure 1. Details of the co-ordination environment of the boat shaped Cu_6 core and the atom numbering scheme are shown in Figure 2. The macrocycle results from Schiff base condensation of three diamine units (labelled I in Figure 1) with three dialdehyde units (labelled II in Figure 1).

The macrocyclic C, N, O framework together with the associated six coppers, two acetates, and two hydroxides possesses a pseudo mirror plane passing through O(1) and O(4), perpendicular to the plane of Cu(1), Cu(3), Cu(4), and Cu(6). A true mirror plane does not exist because the pseudo-related Cu(2) and Cu(5) carry co-ordinated methanol and water, respectively, and Cu(4) has a weakly co-ordinated methanol whereas the pseudo-related Cu(3) does not.

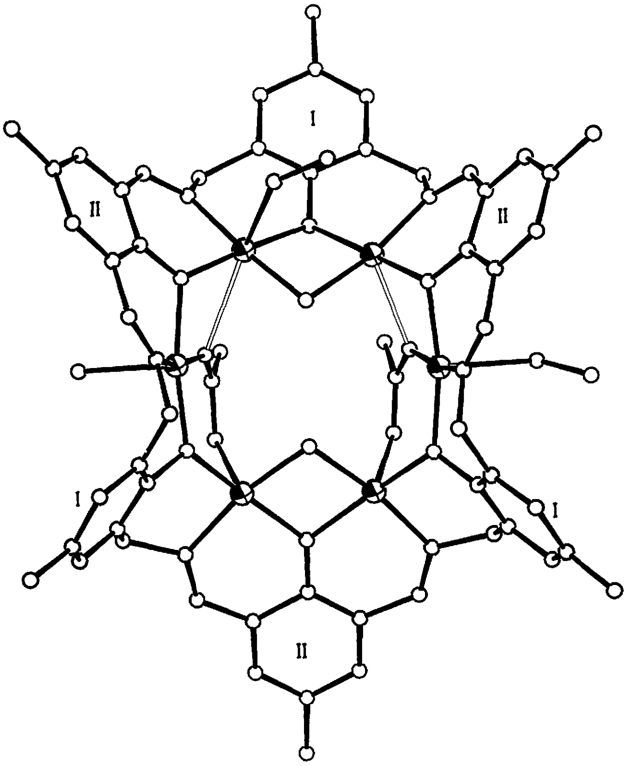

Figure 1. View of the $[LCu_6(MeCO_2)_2(OH)_2(MeOH)_2(H_2O)]^{2+}$ cation. Diamine derived units are labelled I and dialdehyde-derived units are labelled II. The atoms are of arbitrary size, the metal atoms are partly crosshatched.

Two hydroxo groups, located in the pseudo-mirror plane, each bridge a pair of coppers, Cu(1) and Cu(6), which share a diamine-derived phenolate, and Cu(3) and Cu(4), which share a dialdehyde-derived phenolate. These hydroxo groups with an O···O separation of 3.32 Å are the only species within the central cavity formed by the six coppers. The two acetate units, which are approximately but not exactly mirror-related, each bridge two coppers by normal bonds and each associates

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† The crystals used for the *X*-ray analysis were obtained directly from a methanolic reaction mixture which had been evaporated to a concentration appropriate for subsequent slow crystal growth in an enclosed vessel over a period of several days. The crystals degenerated rapidly on exposure to the atmosphere as a result of loss of methanol and were therefore sealed with mother liquor in Lindemann tubes for the *X*-ray analysis. A bulk sample isolated in 30% yield, after being dried under vacuum at 80 °C and then exposed to air had an elemental composition corresponding to $LCu_6(MeCO_2)_2(OH)_2(BF_4)_2\cdot\sim4H_2O$.

‡ *Crystal data* for $[LCu_6(MeCO_2)_2(OH)_2(MeOH)_2(H_2O)](BF_4)_2\cdot4.4MeOH$: $C_{64.4}H_{83.6}B_2Cu_6F_8N_6O_{19.4}$, $M = 1807$, triclinic, space group $P\bar{1}$, $a = 11.283(4)$, $b = 16.652(8)$, $c = 22.127(6)$ Å, $\alpha = 81.65(4)$, $\beta = 80.34(3)$, $\gamma = 74.88(4)°$, $U = 3934(3)$ Å^3, $Z = 2$, $D_m = 1.549(7)$, $D_c = 1.525$ g cm^{-3}, $\mu(\text{Mo-}K_\alpha) = 16.54$ cm^{-1}, $F(000) = 2392$. Intensity data were measured at 295(1) K with Mo-K_α radiation (graphite crystal monochromator) using an Enraf Nonius CAD-4F diffractometer and employing the $\omega/2\theta$ scan method. The structure was solved using a combination of Patterson and direct methods (SHELXS-86) and refined using a blocked full-matrix least-squares procedure (SHELX-76), with anisotropic thermal parameters assigned to all non-hydrogen atoms except those of the methanol molecules of solvation; at convergence $R = 0.083$ and $R_w = 0.080$ for the 5014 reflections with $I > 2\sigma(I)$. All the hydrogen atoms of the macrocycle were included in the model at their calculated positions. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

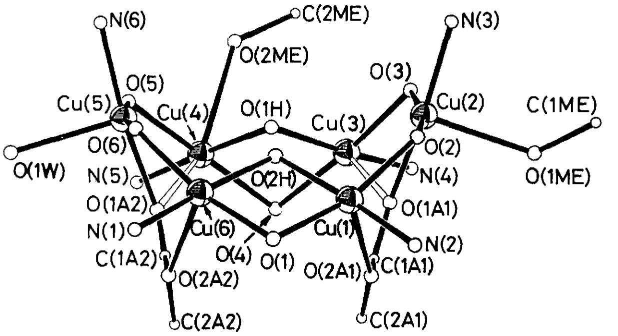

Figure 2. View of the co-ordination environment of the Cu_6 core showing the cyclohexane boat arrangement adopted by the metal atoms and the atomic numbering scheme.

weakly with a third copper [Cu(4)–O(1A2) 2.62(1) Å and Cu(3)–O(1A1) 2.39(1) Å]; the significant difference in the lengths of these two weak bonds presumably arises because Cu(4) has a *trans* co-ordinated methanol whereas Cu(3) has no *trans* ligand.

Five of the coppers are essentially square pyramidal. The only non-pyramidal metal is Cu(4), which has an elongated tetragonal environment with a methanol at 2.60(1) Å and an acetate oxygen [O(1A2)] at 2.62(1) Å along the direction of elongation. The apical ligands within the square pyramidal donor sets of the other five coppers are provided as follows: at Cu(1) an acetate oxygen [O(2A1)], at Cu(2) a methanol, at Cu(3) an acetate oxygen [O(1A1)], at Cu(5) a water, and at Cu(6) an acetate oxygen [O(2A2)]. The bridging acetates are each 'basal' to one square pyramidal copper [Cu(2) and Cu(5)] and are 'apical' to the others.

The separations between adjacent coppers are: Cu(1)···Cu(2) 3.400(3), Cu(2)···Cu(3) 3.176(3), Cu(3)···Cu(4) 2.891(3), Cu(4)···C(5) 3.252(3), Cu(5)···Cu(6) 3.416(3), Cu(6)···Cu(1) 2.974(3) Å. The three 'long diagonals' within the Cu_6 cluster, namely Cu(5)···Cu(2), Cu(6)···Cu(3), and Cu(1)···Cu(4) are 5.925, 6.168, and 6.197 Å, respectively (Figure 2).

In conclusion, this new hexanuclear cluster and related species may provide the opportunity for devising and studying previously unobserved types of molecular trapping and of multi-metal-promoted processes within the central cavity; the associated redox chemistry will clearly be rich and interesting.

Received, 21st December 1989; Com. 9/05459F

References

1 D. E. Fenton, 'Advances in Inorganic and Bioinorganic Mechanisms,' 1983, vol. 2, p. 187; P. Zanello, S. Tamburini, P. A. Vigato, and G. A. Mazzochin, *Coord. Chem. Rev.*, 1987, **77**, 165; D. E. Fenton, U. Casellato, P. A. Vigato, and M. Vidali, *Inorg. Chem. Acta*, 1982, **62**, 57; *Chem. Soc. Rev.*, 1979, **8**, 199.

2 R. Robson, *Inorg. Nucl. Chem. Lett.*, 1970, **6**, 125; *Aust. J. Chem.*, 1970, **23**, 2217.

3 J. Comarmond, B. Dietrich, J.-M. Lehn, and R. Louis, *J. Chem. Soc., Chem. Commun.*, 1985, 74.

4 M. Bell, A. J. Edwards, B. F. Hoskins, E. H. Kachab, and R. Robson, *J. Chem. Soc., Chem. Commun.*, 1987, 1852; V. McKee and S. S. Tandon, *ibid.*, 1988, 385; M. Bell, A. J. Edwards, B. F. Hoskins, E. H. Kachab, and R. Robson, *J. Am. Chem. Soc.*, 1989, **111**, 3603; V. McKee and S. S. Tandon, *J. Chem. Soc., Chem. Commun.*, 1988, 1334; *Inorg Chem.*, 1989, **28**, 2901.