

## Synthesis and Crystal Structure of a Complex of a Tetranucleating Macrocyclic Ligand which binds Four Ni<sup>II</sup> Ions in a Square Arrangement with a $\mu_4$ -Hydroxo Group at the Centre

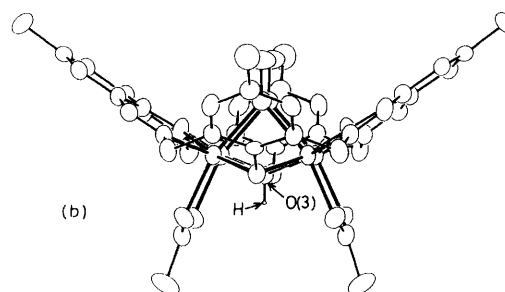
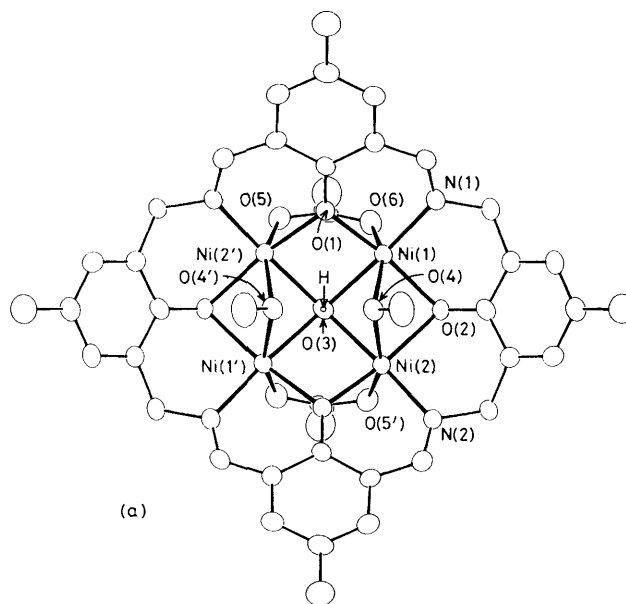
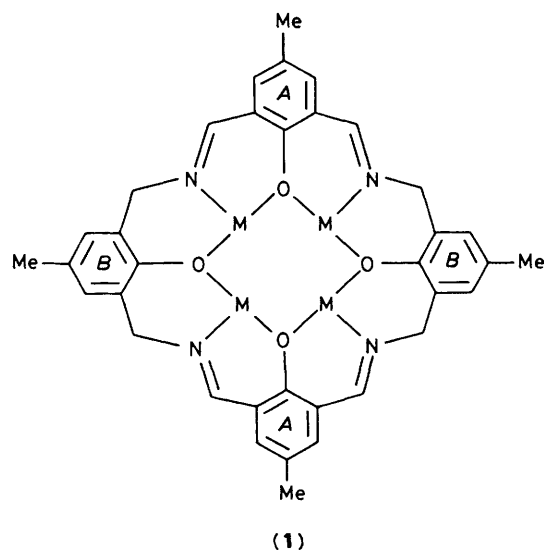
Malcolm Bell, Alison J. Edwards, Bernard F. Hoskins, Edward H. Kachab, and Richard Robson\*

*Department of Inorganic Chemistry, University of Melbourne, Parkville, Victoria 3052, Australia*

The tetra Schiff base macrocycle formed by condensation of two molecules of 2,6-diformyl-5-methylphenol with two molecules of 2,6-bis(aminomethyl)-5-methylphenol binds four nickel(II) ions at the corners of an approximate square of edge 2.8–2.9 Å with an unusual  $\mu_4$ -hydroxo group bound essentially equally to all four metals.

Ligands capable of binding four metal centres in close proximity, in such a way that a central region bounded by the four is accessible to substrate molecules, may afford complexes with unprecedented structures and reactivity. Some of the possibilities offered are the trapping of molecules under

unusual bonding circumstances and their consequent activation, the multi-electron reduction or oxidation of substrates, and new types of reactions between species attached to neighbouring metal centres. We describe here one of several conceivable ways of imposing these circumstances upon four



metal centres, the ligand used being the tetranucleating macrocycle  $L^{4-}$ , illustrated in complex (1).

The ligand was assembled by heating 2,6-diformyl-5-methylphenol,<sup>1</sup> the sodium salt of 2,6-bis(aminomethyl)-5-methylphenol,<sup>†</sup> nickel acetate, sodium acetate, and acetic acid together in methanol in 1:1:2.2:2.7:4.1 proportions, respectively. Addition of hot water followed by partial evaporation at atmospheric pressure gave green plates which were recrystallised from aqueous methanol in the presence of additional nickel acetate to yield  $[LNi_4(MeCO_2)_2(OH)(MeO \cdot H \cdot OMe)] \cdot 4MeOH$  as green monoclinic crystals.

Two views of the molecular structure as revealed by X-ray crystallography‡ are represented in Figure 1. The molecule is situated around a crystallographic 2-fold axis of symmetry and the four nickel ions are located almost at the corners of a square perpendicular to the axis [Ni(1) ··· Ni(2) 2.788(1), Ni(1) ··· Ni(2') 2.936(1), Ni(1) ··· Ni(1') 4.052(1), Ni(2) ··· Ni(2') 4.046(1) Å]. The  $LNi_4$  arrangement is basically as in (1) but the four aromatic rings are inclined, all on the same side of the  $Ni_4$  plane, at considerable angles to that plane, the extent of which is clearly demonstrated in Figure 1(b). The

**Figure 1.** (a) View down the two-fold axis showing the square nature of the central  $Ni_4$  unit and the bridging acetate and methoxy systems. (b) The molecule viewed along the  $O(2) \cdots O(2')$  direction revealing the dish-like conformation of the macrocyclic ligand.

Selected distances (Å) and angles (°): Ni(1)–O(1) 1.980(4), Ni(1)–O(2) 2.094(4), Ni(1)–O(3) 2.113(2), Ni(1)–N(1) 1.979(5), Ni(1)–O(4) 2.146(4), Ni(1)–O(6) 2.086(5), Ni(2)–O(1') 1.982(5), Ni(2)–O(2) 2.095(3), Ni(2)–O(3) 2.109(2), Ni(2)–N(2) 1.979(4), Ni(2)–O(4) 2.145(4), Ni(2)–O(5') 2.053(5); Ni(1)–O(3)–Ni(2) 82.7(2), Ni(1)–O(3)–N(2') 88.1(2), H–O(3)–Ni(1) 106.5(15), H–O(3)–Ni(2) 106.4(15), Ni(1)–O(3)–Ni(1') 147.0(3), Ni(2)–O(3)–Ni(2') 147.2(3).

† Prepared from 2,6-bis(hydroxymethyl)-5-methylphenol<sup>1</sup> by reaction with HCl followed by the Delépine reaction with hexamethylenetetramine.

‡ *Crystal data:*  $C_{46}H_{62}N_4Ni_4O_{15}$ ,  $M = 1145.8$ , monoclinic, space group  $C2/c$ ,  $a = 21.494(2)$ ,  $b = 8.996(1)$ ,  $c = 25.451(3)$  Å,  $\beta = 93.75(1)^\circ$ ,  $U = 4910.7$  Å<sup>3</sup>,  $Z = 4$ ,  $D_m = 1.557(5)$ ,  $D_c = 1.550$  g cm<sup>-3</sup>,  $\mu(Mo-K_\alpha) = 15.57$  cm<sup>-1</sup>,  $F(000) = 2392$ . Intensity data were measured at 295(1) K with Mo- $K_\alpha$  radiation (graphite crystal monochromator) using an Enraf-Nonious CAD-4F diffractometer and employing the  $\omega/2\theta$  scan method. The structure was solved using direct methods (SHELX-86) and a full-matrix least-squares refinement (SHELX-76), with anisotropic thermal parameters assigned to all non-hydrogen atoms, converged with  $R = 0.050$  and  $R_w = 0.048$  for the 2972 observed reflections [ $I \geq 3\sigma(I)$ ]. A difference map revealed all the hydrogen atoms of the macrocyclic ligand which were included in the model at their calculated positions. The hydroxy-hydrogen and that which forms the H-bonding bridge between the two methoxy groups were also clearly evident, and both, situated on the two-fold axis, were included in the model. 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.

dihedral angles between the  $Ni_4$  plane and rings A in (1) are  $34.6^\circ$ , and those between the metal plane and rings B are  $38.3^\circ$ . The two acetate groups bridge the pairs of nickel ions associated with phenoxide residues A in (1) [*i.e.* Ni(1), Ni(2') and Ni(2), Ni(1')]. The acetates are on the side of the  $Ni_4$  plane opposite the macrocycle. On the same side of the  $Ni_4$  plane as the macrocycle are two methoxy units which bridge the nickel pairs not bridged by acetates [*i.e.* Ni(1), Ni(2), and Ni(1'), Ni(2')]. A hydrogen atom is clearly evident on the 2-fold axis between the two methoxy oxygen atoms yielding a hydrogen bonded  $(MeO \cdot H \cdot OMe)^-$  system with a very short oxygen–oxygen separation of 2.509(7) Å. The oxygen centres of the methoxy units and of the phenoxide residues B in (1) are markedly pyramidal [O(2) is 0.67 Å out of the plane of its bonded neighbours] whereas those of phenoxide residues A are almost planar.

A pseudo-octahedral arrangement around each nickel ion is completed by a central  $\mu_4$ -hydroxo group located on the 2-fold axis with its hydrogen pointing away from the  $\text{Ni}_4$  plane [O(3)-H in Figure 1(b)] and with the oxygen essentially equidistant [2.109(2)—2.113(2) Å] from all four metals and 0.60 Å below the  $\text{Ni}_4$  plane as represented in Figure 1(b). This hydroxo group, associating equally with four metal centres

whilst being capable formally of providing only three pairs of electrons, is to our knowledge without precedent.

*Received, 14th August 1987; Com. 1200*

#### Reference

- 1 F. Ullman and K. Brittner, *Chem. Ber.*, 1909, **42**, 2539.
-