X-Ray Structural Analysis of a Tetra-manganese(II) Complex of a new (4 × 4) Schiff-base Macrocycle incorporating a Cubane-like $Mn_4(alkoxy)_4$ Core

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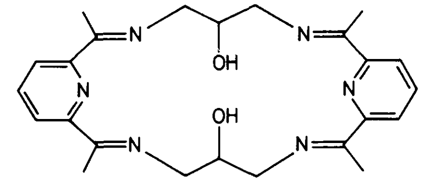
X-Ray structure analysis of the tetranuclear Schiff-base macrocylic complex $[C_{12}H_{14}N_3OMn^{II}]_4(ClO_4)_4$ shows the (4 × 4) macrocycle is folded so that the four alkoxide oxygen atoms cap the faces of a tetrahedral Mn_4 cluster, resulting in a cubane-type stereochemistry.

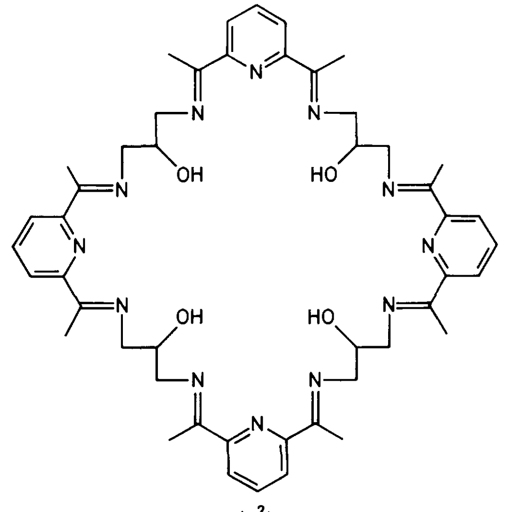
In a previous communication[1] we reported the template synthesis of a barium complex of the (2 × 2) Schiff-base macrocycle L^1 and the subsequent preparation by trans-metallation of a mono-bridged, binuclear copper(II) complex. A similar synthetic route using 2,6-diacetylpyridine, 1,3-diamino-2-hydroxypropane, and Ba^{2+} as template ion, followed by transmetallation with $Mn(ClO_4)_2{\cdot}6H_2O$ in refluxing methanol yields two yellow, crystalline products. The major component is the expected binuclear manganese complex of L^1. The *X*-ray structure of the air-stable minor product revealed it to be $[Mn_4(L^2)]$ $(ClO_4)_4$. The macrocycle L^2 is the product of a new (4 × 4) Schiff-base condensation and the four manganese(II) centres, along with the four deprotonated alkoxy groups of the ligand, form a novel cubane-type cluster.

The structure of the complex is shown in Figure 1 and Figure 2 shows the $Mn_4(alkoxy)_4$ core in the same orientation.† The two halves of the structure are related by a crystallographic two-fold axis of symmetry which passes through the centres of the pseudocubane faces defined by Mn(1), O(2), Mn(1'), and O(2') and by Mn(2), O(1), Mn(2'), and O(1'); in addition, a non-crystallographic S_4 symmetry axis coincides with the C_2. Each manganese atom is seven-co-ordinate with approximate pentagonal bipyramidal geometry. The donors in the pentagonal plane are three nitrogen atoms and two alkoxide oxygen atoms while the axial ligands are a third alkoxide and a semi-co-ordinated perchlorate anion [Mn–$OClO_3$ 2.63(1) Å for both Mn(1) and Mn(2)]. The alkoxide oxygens show distorted tetrahedral geometry with angles in the range 95—127°. Within the cubane core, angles about manganese are all acute (77—83°), while those at oxygen are obtuse (95—102°), as might be expected in view of their respective co-ordination geometries. There is no evidence for any metal–metal bonding; the shortest manganese–manganese distance is 3.32(1) Å [for Mn(1)–Mn(2)].

Formation of the (4 × 4) macrocycle could occur either at the template stage or as a rearrangement[3,4] during the transmetallation reaction. The former route seems more likely, a possible driving force being the preference of the Ba^{2+} template ion for alkoxy donors over the softer pyridine and imine nitrogens. If this is so, it should be possible to isolate complexes of L^2 with other transition metals and preliminary



(L^1)



(L^2)

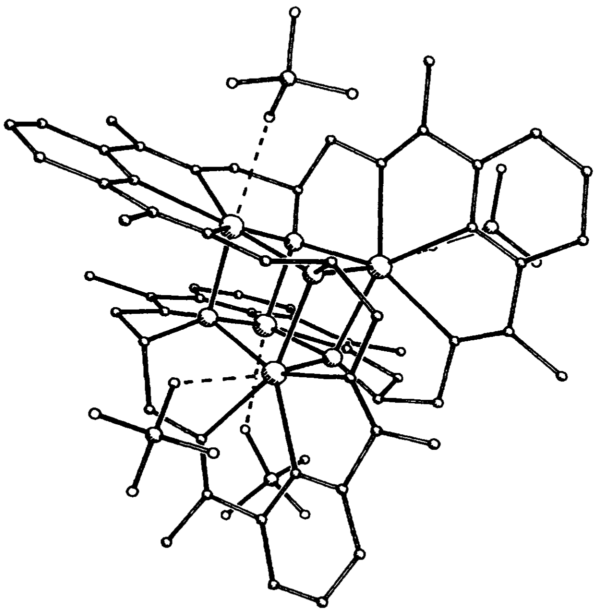


Figure 1. Perspective diagram of the $[Mn_4(L^2)](ClO_4)_4$ unit showing the folding of the macrocycle. Dotted lines represent the long [2.63(1) Å] Mn–$OClO_3$ bonds.

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† *Crystal data*: Orange-yellow monoclinic crystals from MeOH, $C_{48}H_{56}Cl_4Mn_4N_{12}O_{20}$, a = 20.276(6), b = 14.165(6), c = 20.388(7) Å, β = 90.59(3)°; space group $C2/c$, Z = 4. Data were collected at 190 K on a Nicolet R3m four-circle diffractometer using graphite monochromated Mo-K_α radiation. 3831 unique reflections were collected and 1639 with $I > 2.5\sigma(I)$ were used for structural analysis. The structure was solved using direct methods and gave final R 0.091 and R_w 0.084. All programmes used in data reduction and structure solution are contained in the SHELXTL (Version 4.0) package (see ref. 2). Atomic co-ordinates are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

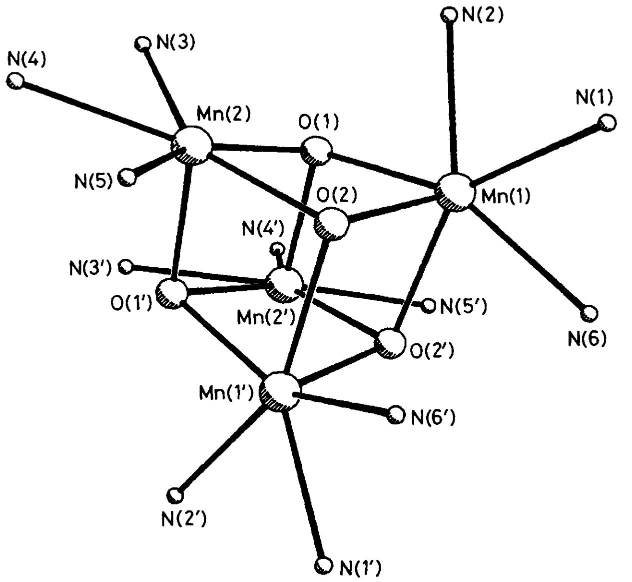

Figure 2. View of the pseudocubane type $Mn_4(alkoxy)_4$ core. The perchlorate anions and the carbon atoms of the macrocycle have been omitted. Selected bond lengths (Å) and angles (°); Mn(1)–N(1) 2.29(1), Mn(1)–N(2) 2.31(1), Mn(1)–N(6) 2.31(1), Mn(1)–O(1) 2.19(1), Mn(1)–O(2) 2.13(1), Mn(1)–O(2') 2.27(1), Mn(2)–N(3) 2.33(1), Mn(2)–N(4) 2.30(1), Mn(2)–N(5) 2.28(1), Mn(2)–O(1) 2.31(1), Mn(2)–O(2) 2.18(1), and Mn(2)–O(1') 2.14(1); O(1)–Mn(1)–O(2) 82.8(5), O(1)–Mn(1)–O(2') 78.7(4), O(2)–Mn(1)–O(2') 77.2(5), O(1)–Mn(2)–O(2) 79.0(4), O(1)–Mn(2)–O(1') 78.2(5), O(2)–Mn(2)–O(1') 81.9(5), Mn(1)–O(1)–Mn(2) 94.8(5), Mn(1)–O(1)–Mn(2') 100.4(5), Mn(2)–O(1)–Mn(2') 101.6(5), Mn(1)–O(2)–Mn(2) 100.5(5), Mn(1)–O(2)–Mn(1') 102.5(5), Mn(2)–O(2)–Mn(1') 96.7(5).

results[5] for Fe^{II} suggest that this is the case. The failure to observe (4 × 4) products in other, similar barium-promoted Schiff base (2 × 2) condensations[3,4] may be ascribed to lack of a suitable hard donor in the macrocyclic systems.

A few manganese(I) cubane structures with formulae $[Mn_4(CO)_{12}(F\ or\ OH)_4]$[6] and $[Mn_4(CO)_{12}(OR)_4]$[7] have been reported previously. To our knowledge, however, the present complex is the first example either in the manganese(II) oxidation state or in the absence of carbonyl ligands. The existence of Mn_4 clusters having similar distorted cubane geometries in different oxidation states is reminiscent of the well studied natural and synthetic Fe_4S_4 clusters.[8] By analogy with the iron systems considerable delocalisation might be expected within the $Mn_4(alkoxy)_4$ system and this may explain the observed stability of the complex towards air oxidation. The properties of macrocyclic complexes containing transition metal cubanes should have relevance to the study of iron–sulphur proteins; in particular, to the influence on redox behaviour of the protein chain, modelled here by the macrocycle.

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References

1 V. McKee and J. Smith, *J. Chem. Soc., Chem. Commun.*, 1983, 1465.
2 G. M. Sheldrick, SHELXTL User Manual, Revision 4, 1984: Nicolet XRD Corporation, Madison, Wisconsin.
3 S. M. Nelson, C. V. Knox, M. McCann, and M. G. B. Drew, *J. Chem. Soc., Dalton Trans.*, 1981, 1669.
4 M. G. B. Drew, J. Nelson, and S. M. Nelson, *J. Chem. Soc., Dalton Trans.*, 1981, 1678.
5 V. McKee, J. Smith, and W. B. Shepard, unpublished results.
6 E. Horn, M. R. Snow, and P. C. Zeleny, *Aust. J. Chem.*, 1980, **33**, 1659.
7 M. Herberhold, G. Suss, J. Ellermann, and H. Gabelein, *Chem. Ber.*, 1978, **111**, 2931.
8 See for example, B. A. Averill and W. H. Orme-Johnson in 'Metal Ions in Biological Systems,' Vol. 7, ed. H. Sigel, 1978, 127; R. H. Holm, *Acc. Chem. Res.*, 1977, **10**, 427.