

## A Novel Series of Planar Pentadentate Macrocyclic Ligands. X-Ray Structure of 10,11,12,13-Tetrahydrodibenzo[*b,k*]pyrido[*g,f*][1,4,7,10,13]penta-azacyclopentadecin-*N*<sup>5</sup>,*N*<sup>10</sup>,*N*<sup>13</sup>,*N*<sup>18</sup>-*N*<sup>19b</sup>-di(perchlorato)manganese

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**Summary** Application of the co-ordination template effect of  $Mn^{II}$  and  $Zn^{II}$  ions has allowed the preparation of complexes of a series of novel pentadentate macrocyclic ligands; an X-ray structure analysis of one of these complexes has shown that the donor atoms in the macrocycle define the five equatorial co-ordination positions of a distorted pentagonal bipyramid.

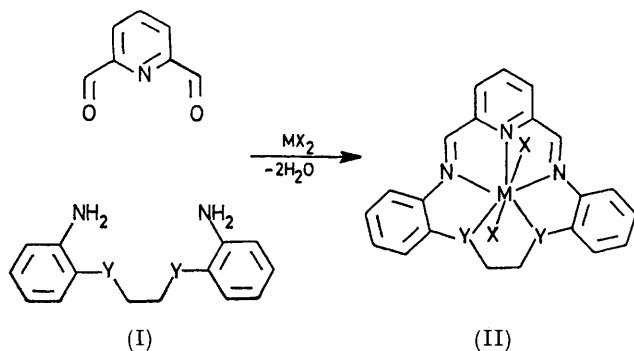
THE use of transition-metal ions to control the stereochemistry of reactions involving the formation of imine groups is well known and is frequently applied to the synthesis of complexes of macrocyclic ligands.<sup>1</sup> There are

('kinetic' or 'thermodynamic template effects')<sup>2</sup> will be less effective for unstable co-ordination geometries of the template ion. It seemed probable that macrocyclic ligands which define unusual co-ordination polyhedra at metal ions are most likely to result when the template ion has a relatively small preference for any particular co-ordination geometry and when the precursors in the ligand synthesis possess rigid stereochemical features which will not allow a more conventional co-ordination polyhedron to be adopted by the template ion.

The successful application of these principles has allowed the synthesis of a unique series of pentadentate macrocyclic ligands which define an equatorial plane in pentagonal bipyramidal complexes of zinc(II) and manganese(II). Condensation of pyridine-2,6-dicarbaldehyde with the primary diamines (I) in methanolic solutions of divalent manganese and zinc salts gave the complexes (II)–(IV) in reasonable yields (25% for  $X = ClO_4$  and  $NO_3$ ). Micro-analysis agreed with the proposed formulae for (II)–(IV) and crystallographic molecular-weight determinations confirmed molecular formulae for (IIa), (IIIa), and (IVb) ( $X = ClO_4$ ).

The complex (IIa) [ $C_{21}H_{19}N_5Mn(ClO_4)_2$ ,  $M = 595.26$ ] crystallized from MeCN as orange monoclinic crystals, space-group  $C2/c$ ,  $a = 14.694(3)$ ,  $b = 11.779(3)$ ,  $c = 16.758(3)$  Å,  $\beta = 127.93(1)^\circ$ ,  $D_m = 1.71$ ,  $D_c = 1.73$  g cm<sup>-3</sup>,  $Z = 4$ . 1300 independent reflections ( $I/\Delta I \geq 2$ ) were collected with a Syntex 4-circle automatic diffractometer using graphite-monochromatised Mo- $K_\alpha$  radiation. Full-matrix least-squares refinement of positional and temperature parameters (Mn and Cl atoms anisotropic) of all non-hydrogen atoms has given a current  $R$  value of 0.09.

The molecule has crystallographic  $C_2$  symmetry with a pentagonal bipyramidal arrangement of the donor atoms



$X = ClO_4$

(IIa)  $Y = NH$ ,  $M = Mn$ ;

(IIIa)  $Y = O$ ,  $M = Mn$ ;

(IVa)  $Y = S$ ,  $M = Mn$ ;

(IIb)  $Y = NH$ ,  $M = Zn$

(IIIb)  $Y = O$ ,  $M = Zn$

(IVb)  $Y = S$ ,  $M = Zn$

very few examples where unusual co-ordination geometries or high co-ordination numbers are involved in such syntheses, presumably because lowering the free energy of the transition state or products of reaction by complexation

(Figure). The co-ordination polyhedron is unusually regular for this geometry with all metal-ligand bond-lengths lying

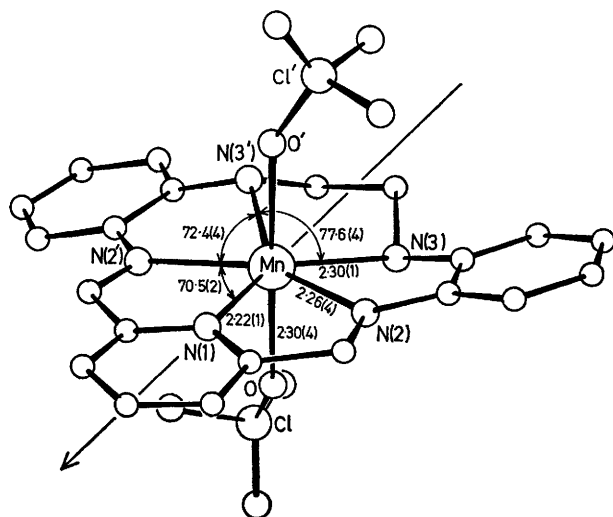


FIGURE. Structure of the pentagonal bipyramidal complex  $C_{21}H_{19}N_5Mn(ClO_4)_2$  showing the principal bond lengths and angles (e.s.d.s in parentheses).

- <sup>1</sup> (a) D. H. Busch, K. Farmery, V. L. Goedken, V. Katovic, A. C. Melnyk, C. R. Sperati, and N. Tokel, *Adv. Chem Ser.*, 1971, **100**, 44; (b) N. F. Curtis, *Coordination Chem. Rev.*, 1968, **3**, 3; (c) L. F. Lindoy, *Quart. Rev.*, 1971, **25**, 379.
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in the range 2.23—2.30 Å. The equatorial 'N<sub>5</sub>' donor set is nearly planar, as might be expected from its rigid conjugated construction, and the maximum deviations from planarity as shown by the nitrogen donors of the saturated chelate ring [N(3) and N(3')] which are displaced equally by 0.31 Å above and below the best plane containing the MnN<sub>5</sub> atoms.

A noteworthy feature of this structure is the very short bond to the co-ordinated perchlorate group [2.30(4) Å]. The strength of complexation of the perchlorate group is also indicated by the considerable splitting of the Cl-O stretching band ( $\nu_3$  in  $T_d$  symmetry) at 1085  $cm^{-1}$  in the i.r. spectrum, showing two bands at 1040 and 1106  $cm^{-1}$  ( $\nu_1$  and  $\nu_4$  in  $C_{3v}$  symmetry).<sup>3</sup>

One other macrocyclic pentadentate ligand<sup>4</sup> has been shown<sup>5</sup> to define the equatorial plane in a pentagonal bipyramidal complex. The pentapyrrole analogues of porphyrins<sup>6</sup> should give similar complexes and are being investigated.

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