Molecular Association without Co-ordination in an Adduct of 1,10-Phenanthroline with a Manganese(II) Macrocyclic Complex; X-Ray Crystal and Molecular Structure

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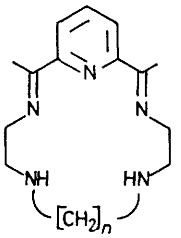
Summary In the 1 : 1 adduct formed between 1,10-phenanthroline and the seven-co-ordinate complex $Mn(232\text{-}N_5)(ClO_4)_2\cdot 2H_2O$ the phenanthroline molecules are not co-ordinated to the metal but are sandwiched between adjacent macrocycle planes in a lamellar structure held together mainly by hydrogen bonds and probably also by π-donor–π-acceptor and dispersion forces.

The property of porphyrins and related planar unsaturated macrocycles, as well as many of their metal complexes, to self-associate and to form molecular complexes with other planar unsaturated molecules is well known.[1] Much of the current interest in such systems relates to the probable importance of donor–acceptor π–π interactions in the biological function of naturally occurring macrocycles. For example, it has been suggested[2] that charge transfer interaction between the dihydroporphyrin ring in chlorophyll and plastoquinone may be implicated in the electron transfer process. Again, there is *X*-ray evidence[3] for a molecular interaction between the porphyrin π-systems in haemoglobin and myoglobin and certain aromatic side chains of the protein which are thought to serve to position the non-covalently held protoporphyrin in the haem cavity. Of particular relevance to the present note are two recent spectroscopic studies[4] of the interaction in solution of iron-(III) porphyrins with, in one case, the electron donor 1,10-phenanthroline and, in another, the acceptor trinitrobenzene In each case the experimental evidence points to an interaction at a point remote from the metal. However, structural information is sparse. We here report the solid-state structure of the product of reaction of 1,10-phenanthroline with a manganese(II) complex of a planar unsaturated macrocyclic ligand in which the phenanthroline molecules are not co-ordinated to the metal but, instead, are sandwiched between adjacent macrocycle planes in a lamellar structure.



(222-N_5), $n = 2$
(232-N_5), $n = 3$

The parent macrocyclic complex is one of a series of seven-co-ordinate complexes of the ligands (222-N_5) and (232-N_5) in which the quinquedentate ligand spans the pentagonal plane and the axial positions are occupied by univalent anions or solvent molecules.[5] Reaction of $[Mn(232\text{-}N_5)Cl(H_2O)]Cl{\cdot}H_2O$ with 1,10-phenthroline hydrate in 1 : 1 to 1 : 3 molar ratios in methanol and recrystallization of the product from ethanol in the presence of $NaClO_4{\cdot}H_2O$ gave crystals of stoicheiometry $Mn(232\text{-}N_5)(ClO_4)_2{\cdot}2H_2O{\cdot}phen{\cdot}\frac{1}{2}$ ethanol. I.r. and u.v.–visible spectra showed no evidence for co-ordination of phenanthroline. Indeed, these and other properties suggested the presence of the pentagonal bipyramidal cation $[Mn(232\text{-}N_5)(H_2O)_2]^{2+}$. In order to determine the structural relationship of the phenanthroline molecule to this cation in the unit cell, a single crystal *X*-ray study was undertaken. The structure is as predicted; the cation is pentagonal bipyramidal with $Mn–N_{eq}$ 2·34(3)—2·41(3) Å and $Mn–O_{ax}$ 2·20(2)—2·24(2) Å. The maximum deviation of a contributing atom from the MnN_5 plane is 0·03 Å.

Crystal data: $C_{29}H_{40}Cl_2MnN_7O_{10\cdot5}$, *M* 780·6, monoclinic, $a = 7{\cdot}490(5)$, $b = 21{\cdot}975(12)$, $c = 21{\cdot}291(12)$ Å, $\beta = 95{\cdot}29(12)$ °, $U = 3489{\cdot}1$ Å^3, $D_m = 1{\cdot}50(2)$, $D_c = 1{\cdot}49$ g cm^{-3}, spacegroup $P2_1/n$, $Z = 4$; $R = 0{\cdot}10$ for 950 independent reflections above background collected on a G.E. XRD 5 diffractometer. Atoms in the unit cell had high thermal motion (U ranging from 0·062 to 0·172 Å^2 for the cation and phen) which led to this small number of observed reflections.†

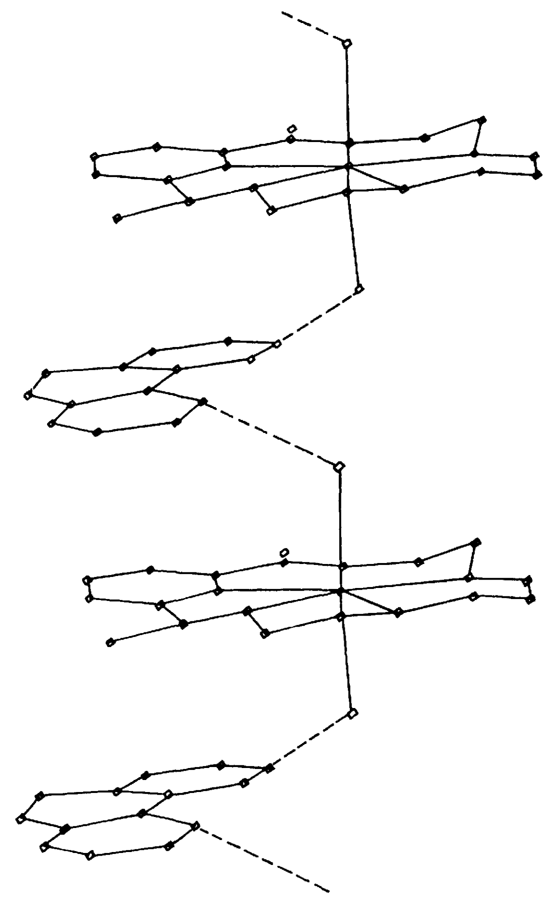


FIGURE. The lamellar structure of $[Mn(232\text{-}N_5)(H_2O)_2]^{2+}$ and 1,10-phenanthroline along the *a* (7·49 Å) axis. Hydrogen bonds are shown as dotted lines.

The phenanthroline molecules are sandwiched between adjacent macrocycle planes in a lamellar structure (Figure), the angle between macrocycle and phenanthroline planes being 2·7°. It is noteworthy that the phenanthroline molecules lie next to the unsaturated (tri-imine) segments of the macrocycles. One nitrogen atom of each phenanthroline is hydrogen-bonded to a co-ordinated water molecule of the complex lying above and the other to a co-ordinated water molecule of the complex lying below (N · · · O 2·78 and 2·74 Å). While the hydrogen bonds constitute a specific linkage between macrocyclic complex and diamine, the lamellar nature of the structure strongly suggests the occurrence of a supplementary interaction having its origin in the delocalized π-systems of the two molecular planes. Most of the inter-planar contacts are in the range 3·5—3·7 Å, *i.e.* at the higher end of the range generally found in lamellar organic molecular complexes and in the relatively few molecular complexes involving planar metal chelates for which structural information exists.[1,6] While we have no means of assessing the relative

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† The atomic co-ordinates for this work 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.

importance of π-donor–π-acceptor, dispersion, and dipole-dipole forces, it seems likely that all contribute to some extent. No new absorption in the electronic spectrum attributable to a charge transfer transition was apparent, however.

The behaviour described contrasts with that of the fully conjugated quadridentate macrocycle formed by condensation of two molecules of 2,6-diacetylpyridine with two molecules of hydrazine. This normally planar macrocycle adopts a folded conformation in the adducts of its Fe^{II} complexes with 1,10-phenanthroline and 2,2′-bipyridine in order to accommodate the *cis*-nitrogen donors.[7]

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