Crystal Structure of Di-μ-hydroxo-bis-[*NN'*-trimethylenebis(salicylaldiminato)-manganese(III)]-Tetrapyridine, a Supposed Oxygen Carrier

By HUGH S. MASLEN and T. NEIL WATERS*
(*Department of Chemistry, University of Auckland, New Zealand*)

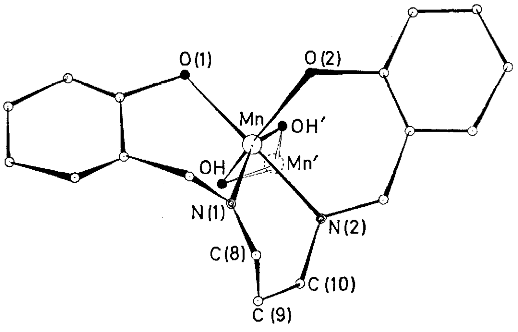
Summary The reaction between molecular oxygen and *NN'*-trimethylenebis(salicylaldiminato)manganese(II), [Mn(salpn)], produces di-μ-hydroxo-bis-(*NN'*-trimethylenebis(salicylaldiminato)manganese(III)-tetrapyridine as an oxidation product.

AN oxygen carrying role for Schiff base complexes of manganese(II) has been suggested,[1,2] metal: dioxygen ratios of 1:1 and 1:0·5 being determined. In one instance dinitrogen and carbon monoxide were also reported to bind reversibly.[1] Suggested structures cover the symmetrical co-ordination of dioxygen as in $IrCl(CO)O_2(PPh_3)_2$,[3] the bridging of metal centres in a peroxide-like fashion or, assuming oxidation, the bridging by a single oxo-link similar to that of $[Fe(salen)]_2O$.[4]

We have prepared black crystals of an oxygenated product of $Mn(salpn)H_2O$ by allowing molecular oxygen to react with a pyridine solution of the complex. The compound, assumed to be product E of ref. 2, has been subjected to *X*-ray analysis.

Crystal data: $C_{34}H_{34}Mn_2N_4O_6,4(C_5H_5N)$, $M = 1021$, triclinic, $P\bar{1}$; $a = 10{\cdot}227(2)$, $b = 14{\cdot}098(3)$, $c = 9{\cdot}011(2)$ Å, $\alpha = 104{\cdot}05(2)$, $\beta = 89{\cdot}32(2)$, $\gamma = 106{\cdot}06(2)°$, $U = 1209$ Å^3, ($\lambda = 0{\cdot}7107$ for Mo-K_α); $Z = 1$.

The molecule is dimeric (see Figure), with each manganese atom bonding octahedrally to two bridging hydroxy-groups, (hydrogen atoms were located) and to a quadridentate organic ligand. Four pyridine molecules are present in the crystal but are not directly bonded to the complex. The compound is thus di-μ-hydroxo-bis-[*NN'*-trimethylenebis(salicylaldiminato)manganese(III)]tetrapyridine and it is clear that an oxidation, rather than dioxygen addition, has taken place. Since, however, the distinction between the relatively non-reactive monohydrate, $Mn(salpn)H_2O$, and the air sensitive Mn(salpn) is lost in pyridine,[2] it is tempting to think that the *cis* positions for the hydroxo-groups imply a reaction proceeding through initial dioxygen addition.



FIGURE

The close (2·72 Å) manganese–manganese distance explains, at least qualitatively, the antiferromagnetic nature of the compound and strongly suggests that the similar behaviour found in the oxygenation product of the ethylene analogue Mn(salen)[4] arises from similar structural causes.

The organic ligand occupies four adjacent octahedral sites, a mode of bonding also observed in an octahedral complex containing a substituted salen group.[5] Such a geometry, although not usual, is compatible with idealised geometries for the three chelate rings formed by complex formation and with normal bond angles about each ligand atom. It is surprising, therefore, to note that each salicylaldiminato-fraction is bent about a line through its oxygen and nitrogen atoms (by dihedral angles of 27° and 33°) and that the chelate ring containing the trimethylene group conforms closely to a boat geometry with N(2) and C(8)—rather than Mn and C(9)—as bow and stern atoms. Steric reasons often put forward to explain folding, or stepping, in salicylaldimine complexes[6] do not seem to apply but a geometrical, rather than electronic, explanation still seems appropriate. The overall boat conformation of the central chelate ring is a consequence of the relative co-ordinating sites of the donor atoms whereas its approximation to ideality must be accompanied by a folding of the salicylaldiminato-residues in the manner found if coplanar bonding is to be maintained about the nitrogens.

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