

## The Multidentate Chemistry of Manganese(II). V. Non-charged Complexes of Salen-type Ligands and Their Reaction with Oxygen

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*The preparation of a series of manganese(II) compounds of the type  $[Mn(\text{ligand})]$  (where ligand = salen, or ethylene-chain substituted salen) is reported.*

*The interaction of oxygen with pyridine solutions of these manganese(II) complexes has been studied in some detail, and it has been shown that in boiling pyridine such reaction yields complexes only of stoichiometry  $[Mn(\text{ligand})OH]$  together with a small amount of  $MnO_2$ . Detailed oxygen uptake measurements indicate that each Mn atom reacts with one O atom.*

*In pyridine solutions at  $-15^\circ C$ , oxygen uptake has been shown to be approx. 0.6 O atoms to each Mn atom, and although  $[Mn(\text{ligand})OH]$  is again the major reaction product, a large proportion of the manganese in the reaction is obtained in an inseparable mixture which appears to contain more than one manganese complex.*

*Oxygenation of the similar  $[Mn^II(\text{ligand})]$  complexes (where ligand = *N,N'*-bis(salicylaldehyde)-*o*-phenylenediamine and *N,N'*-bis(salicylaldehyde)-1,3-propanediimine) have been studied for comparison purposes. Magnetic data are given for all complexes. A comprehensive statement of results of previous workers in the field is given.*

### Introduction

The preparation of  $[Mn(\text{salen})]$  (salen = *N,N'*-bis(salicylaldehyde)ethylenediimine) appears to have been first reported by Pfeiffer *et al.* [1] in 1933. These workers noted that if a chloroform solution of the compound was allowed to stand in air, a red-brown deposit was obtained, which they suggested from analysis was  $[Mn^{III}(\text{salen})OH]$ . One of the co-workers reported [2] this result elsewhere in the following year.

In 1957 Asmussen and Soling [3] reported detailed magnetic studies on  $[Mn(\text{salen})]$  and  $[Mn(\text{salphen})]$  (salphen = *N,N'*-bis(salicylaldehyde)-*o*-phenylenediimine). Both compounds were postulated to possess antiferromagnetic interaction with, for example, the moment of  $[Mn(\text{salen})]$  changing from 5.29 B.M. at 290K to 4.09 B.M. at 85K.

In 1968 Lewis *et al.* [4] repeated the magnetic work of Asmussen and Soling upon  $[Mn(\text{salen})]$ , and also studied magnetic properties of a number of compounds of the  $[Mn(\text{salen})]$  and  $[Mn(\text{salphen})]$  type, in which various substituents were incorporated in the benzene rings of the salicylaldehyde residues. They found that the magnetic properties of  $[Mn(\text{salen})]$  could be explained on the basis of a dimeric structure of the type found in  $[Cu(\text{salen})]$  [5] in which dimerization occurs via the mutual sharing by the copper atoms of one of the oxygen atoms of each ligand; the similarity of the X-ray powder photographs of  $[Mn(\text{salen})]$  and  $[Cu(\text{salen})]_2$  suggested that the compounds were iso-structural.

Lewis *et al.* also noted that the Mn(II) compounds derived from salen-type ligands with substituted salicylaldehyde residues (*viz.* 5-chloro, 5-bromo, 3-nitro) were all monomeric and of the type  $[Mn(\text{subst. salen})(\text{solvent})]$ . It may be surmised that the substituent prevented the dimerization that occurs in  $[Mn(\text{salen})]$  in the solid state, and that thus these compounds readily coordinate a molecule of solvent in a vacant octahedral site, which may indeed act as a weak bridge between adjacent molecules.

The magnetic results of Lewis *et al.* on  $[Mn(\text{salen})]$  were substantially supported by the work of Earnshaw *et al.* [6].

The reaction of  $[Mn(\text{salen})]$  with oxygen has been the subject of some study – much of it inconclusive. Lewis and coworkers [4] agreed with Pfeiffer *et al.* [1] that oxygen attacks  $[Mn(\text{salen})]$  in solution to yield  $[Mn(\text{salen})OH]$  Lewis *et al.* found that this Mn(III) compound was difficult to obtain pure, and that oxidation in pyridine or dimethylformamide solution appeared to give purer specimens than oxidation in either ethanol or benzene. On the basis of its antiferromagnetic behaviour, they suggested that the compound could be formulated as either  $[Mn^{III}(\text{salen})O_{1/2}]_n$  or as  $[Mn^{III}(\text{salen})]_2O \cdot H_2O$ , similar to the corresponding Fe(III) complexes [7]; although they point out that their infrared data does not support this interpretation.

In 1970 Matsushita and coworkers [8] published a note claiming that two types of complex could be

obtained from the oxidation of  $[\text{Mn}(\text{salen})]$ , viz.  $[\text{Mn}^{\text{III}}(\text{salen})]_2\text{O}_2$  and  $[\text{Mn}^{\text{IV}}(\text{salen})\text{O}]_n$ . Further details published by this group [9] in 1973 indicated that the former compound could be obtained in approx. 90% yield from oxidation in a 1:50 =  $\text{O}_2:\text{N}_2$  atmosphere of a dimethylsulphoxide solution of  $[\text{Mn}(\text{salen})]$ , while the latter polymer was obtained, also in 90% yield by oxidation with pure oxygen in pyridine solution. Oxidation of  $[\text{Mn}(\text{salen})]$  in dimethylsulphoxide using a pure oxygen atmosphere appears to yield a mixture of the dichloromethane soluble reddish-brown  $[\text{Mn}(\text{salen})]_2\text{O}_2$ , and the generally insoluble  $[\text{Mn}(\text{salen})\text{O}]_n$  polymer. The Mn(III) compound exhibits a large anti-ferromagnetic interaction and Matsushita *et al.* showed that the magnetic behaviour over a temperature range can be fitted to a binuclear Mn-O<sub>2</sub>-Mn cluster. Both compounds prepared by these workers have magnetic moments of 1.96 to 1.99 B.M. at room temperature.

Recently Taylor *et al.* [10] have reprepared the compounds of Matsushita *et al.* and studied their X-ray photoelectron spectroscopy.

Two other relevant oxidation products of  $[\text{Mn}(\text{salen})]$  have been reported; both obtained by nitric oxide reactions. Earnshaw *et al.* [6] have reported the isolation of  $[\text{Mn}(\text{salen})\text{OAc}]$  from the reaction of Mn(II) acetate with salen in ethanol under nitric oxide gas, while Tamaki and coworkers [11] report that  $[\text{Mn}(\text{salen})]$  reacts in dimethylsulphoxide with NO to yield  $[\text{O}=\text{Mn}(\text{salen})]_2\text{O}_2$ .

We have for some years been studying the reaction of oxygen with quadridentate complexes of manganese(II), and in the light of experience, observe that:

- (i) Reproducible analyses for oxidation products of these systems are difficult to obtain unless one

meticulously observes consistent repeat preparational procedures. Even then analyses cannot distinguish between such claimed species as:

- (a)  $[\text{Mn}(\text{salen})\text{OH}]$   
 (b)  $[\text{Mn}(\text{salen})]_2\text{O}\cdot\text{H}_2\text{O}$   
 (c)  $[\text{Mn}(\text{salen})\text{O}]_n$   
 (d)  $[\text{Mn}(\text{salen})]_2\text{O}_2$   
 (e)  $[\text{Mn}(\text{salen})\text{O}_{1/2}]_n$

- (ii) Magnetic data are open to the widest degree of interpretation.  
 (iii) The problem of  $\text{MnO}_2$  contamination is ever present.  
 (iv) Interpretation of infrared spectra, used by many workers, in the 1000–600  $\text{cm}^{-1}$  region to demonstrate Mn–O vibrations of various types is fraught with problems. For example:  $[\text{Mn}(\text{salpn})]\cdot\text{H}_2\text{O}$  (salpn = N,N'-bis(salicylaldehyde)-1,3-diiminopropane) in HCBD has at least 7 major IR peaks in the region 600–800  $\text{cm}^{-1}$ , while  $[\text{Mn}(\text{salpn})\text{OH}]_2\cdot 4\text{py}$  in HCBD has at least 6 major peaks in this region.

#### Mn(II) Compounds

Whereas Lewis *et al.* [4] studied the manganese(II) compounds of phenyl-ring substituted salen-type ligands, we have prepared Mn(II) compounds of I with substituents on the central ethylene chain of salen. Corresponding compounds of ligands salphen and salpn have also been reprepared [3, 12]. The ligands used in this work are listed in Table I.

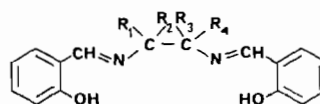


TABLE I. Quadridentate Ligands Studied in This Work.

Ligand	Name	R groups in I				Analysis %		
		R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>	C	H	N
Ia (salen)	N,N'-bis(salicylaldehyde)ethylenediimine	H	H	H	H	Calc. 71.7 Fnd. 71.6	6.0	10.4
Ib	N,N'-bis(salicylaldehyde)meso-2,3-butanediimine	H	CH <sub>3</sub>	H	CH <sub>3</sub>	Calc. 73.0 Fnd. 72.9	6.8	9.4
Ic	N,N'-bis(salicylaldehyde)trans-1,2-diphenylethylenediimine	H	Ph	H	Ph	Calc. 80.0 Fnd. 80.0	5.7	6.7
Id	N,N'-bis(salicylaldehyde)meso-1,2-diphenylethylenediimine	H	Ph	H	Ph	Calc. 80.0 Fnd. 79.9	5.7	6.7
Ie	N,N'-bis(salicylaldehyde)-1,1,2,2-tetramethylethylenediimine	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	Calc. 74.1 Fnd. 73.9	7.5	8.6
salphen	N,N'-bis(salicylaldehyde)o-phenylenediimine					Calc. 76.0 Fnd. 75.9	5.1	8.9
salpn	N,N'-bis(salicylaldehyde)1,3-propanediimine					Calc. 72.4 Fnd. 72.6	6.4	9.9

TABLE II. Mn(II) Compounds

Compound <sup>a,b</sup>		Analysis				Magnetic Moment $\mu_{\text{eff}}$ in B.M. at 298K
		C	H	N	Mn	
[Mn(lig Ia)]	Calc.	59.8	4.4	8.7	17.1	5.25 ± 0.03
<i>i.e.</i> [Mn(salen)]	Fnd.	59.6	4.5	8.7	17.2	
[Mn(lig Ib)]	Calc.	61.9	5.2	8.0	15.8	5.92 ± 0.01
	Fnd.	61.6	5.4	7.9	15.5	
[Mn(lig Ic)]	Calc.	71.0	4.7	5.9	11.6	5.97 ± 0.01
	Fnd.	70.8	4.7	5.8	11.4	
[Mn(lig Id)]	Calc.	71.0	4.7	5.9	11.6	5.83 ± 0.01
	Fnd.	71.0	4.6	6.0	11.7	
[Mn(lig Ie)]	Calc.	63.7	5.8	7.4	14.6	5.98 ± 0.03
	Fnd.	63.6	5.9	7.4	14.5	
[Mn(salphen)] · H <sub>2</sub> O	Calc.	62.0	4.2	7.2	14.2	6.00 ± 0.03
	Fnd.	61.8	4.2	7.2	14.1	
[Mn(salpn)] · H <sub>2</sub> O	Calc.	57.8	5.1	7.9	15.6	6.10 ± 0.04
	Fnd.	57.1	5.2	7.7	15.9	

<sup>a</sup>See Table I for abbreviations for ligands. <sup>b</sup>All compounds are crystalline and coloured from yellow to orange.

The interaction of the sodium salts of the seven ligands of Table I in dry ethanol under nitrogen, with manganese(II) acetate-3-water yielded compounds of formulation [Mn(lig I)], [Mn(salphen) or (salpn)] · H<sub>2</sub>O (See Table II). It has also been noted by Calderazzo *et al.* [13], that the anhydrous compounds [Mn(lig Ia)] and [Mn(salpn)] can be prepared by interaction in dry solvent of the relevant ligand with Mn<sub>2</sub>(CO)<sub>10</sub>. Although we have used this method elsewhere [14], we have not found it essential to do so in this work.

Apart from the compound [Mn(lig Ib)], all the Mn(II) compounds were prepared at least twice, and the analytical figures of Table II are average values. Both [Mn(lig Id)] and [Mn(lig Ie)] separated from solution with approx. 0.5 molecules of water per Mn atom. This was removed by drying under vacuum at 80 °C.

The room temperature magnetic data indicate that only [Mn(lig Ia)] possesses a moment appreciably lower than the spin-only value for high spin Mn(II) of 5.92 B.M. The anti-ferromagnetic nature of this compound has been previously demonstrated [3, 4]. Magnetic data thus suggests that ligands of type I, with substituents on the ethylene moiety, form monomeric Mn(II) compounds, as indeed do ligands of the same type with substituents on the salicylaldehyde rings [4]. This contention is reinforced by the close similarity (suggesting isomorphism) of the X-ray powder photographs of [Mn(ligand Ib)] and [Co(ligand Ib)]; this latter complex being known to be approx. square planar and monomeric [15]. Nevertheless, it should be noted that no conclusive decision can be made about the structure of the compounds [Mn(lig Ic, Id, Ie)]; the binuclear com-

plex bis(N-methylsalicylaldiminato)manganese(II) appears to have no significant antiferromagnetism [16].

#### Oxygenation Reactions of Mn(II) Compounds

All the manganese(II) compounds of Table II were reacted with oxygen under controlled conditions (see Experimental).

The first series of experiments was carried out by bubbling oxygen through boiling pyridine solutions of the [Mn(ligand)] complex. In each case this led to the initial deposition of a major proportion of the manganese as a fairly insoluble dark brown to black complex, which we postulate to be [Mn(ligand)OH]. That [Mn(salpn)OH] is a hydroxy-species has been previously shown [17], and the infrared spectra in the OH stretching region support the presence of hydroxy rather than oxo-groups (see Table V).

In each case for the first series of reactions, a second crop of the same compound (sometimes with a small amount of MnO<sub>2</sub> impurity) could be obtained by partial evaporation of the reaction solution. Finally, evaporation of the solution to dryness in each case yielded impure MnO<sub>2</sub>. The percentage yield for each of the above steps is shown in Table III, and it is clear that all the starting material has been accounted for in each case. Thus, we believe that there is only one major product (apart from MnO<sub>2</sub>) of the oxygenation reactions of all seven Mn(II) complexes in boiling pyridine. This product has the empirical formula [Mn(ligand)OH]. It should however be noted, that the pyridine solvent is particularly difficult to remove from the products in all cases. To obtain reproducible analyses we have vacuum dried to constant weight all analytical samples at 50 °C over P<sub>2</sub>O<sub>5</sub>. Such a process undoubtedly removed all

TABLE III. Summary of Products Obtained from Oxygenation Reactions.

Starting Material	Products <sup>d</sup> found:		Formulation of Products													
	(i) from boiling pyridine		Formula													
	Product	% Yield <sup>a</sup>	Analysis (found %)			Analysis (found %)			Analysis (Calc %)							
		C	H	N	Mn	Yield	C	H	N	Mn	C	H	N	Mn		
[Mn(ligand Ia)]	initial	82	56.8	4.2	8.7	16.0	57	56.7	4.9	8.6	16.0	[Mn(lig and Ia)OH]	56.8	4.5	8.3	16.3
	2nd crop	8	56.5	4.6	8.4	16.1	—	no product				"	—	—	—	63.2 <sup>e</sup>
	residue <sup>b</sup>	9	4.3	0.4	0.8	57.6	41	non-reproducible				see note (b)	—	—	—	—
[Mn(ligand Ib)]	initial	78	59.4	5.4	7.9	15.2	58	59.6	5.7	7.3	15.0	[Mn(ligand Ib)OH]	59.0	5.2	7.6	15.0
	2nd crop	12	58.9	5.2	7.6	15.0	—	no product				"	—	—	—	—
	residue	7	5.8	0.3	0.6	59.1	41	non-reproducible				see note (b)	—	—	—	—
[Mn(ligand Ic)]	initial	79	68.9	4.7	5.9	10.9	55	68.7	4.9	5.9	10.7	[Mn(ligand Ic)OH]	68.6	4.7	5.7	11.2
	2nd crop	8	66.9	4.1	5.1	12.4	—	no product				" + MnO <sub>2</sub>	—	—	—	—
	residue	10	2.1	0.1	0.2	59.6	42	non-reproducible				see note (b)	—	—	—	—
[Mn(ligand Id)]	initial	83	68.7	4.8	5.9	10.8	55	68.9	4.7	5.4	10.9	[Mn(ligand Id)OH]	68.6	4.7	5.7	11.2
	2nd crop	6	66.2	3.9	5.1	12.8	—	no product				" + MnO <sub>2</sub>	—	—	—	—
	residue	9	4.3	0.4	0.5	60.0	45	non-reproducible				see note (b)	—	—	—	—
[Mn(ligand Ie)]	initial	80	60.7	5.7	7.2	13.7	59	61.2	5.7	6.8	14.3	[Mn(ligand Ie)OH]	60.9	5.8	7.1	14.0
	2nd crop	10	60.5	5.3	6.8	13.6	—	no product				"	—	—	—	—
	residue	10	5.0	0.4	0.5	57.6	40	non-reproducible				see note (b)	—	—	—	—
[Mn(salphen)]	initial	75	62.0	3.7	7.0	14.4	54	62.3	3.8	7.0	14.6	[Mn(salphen)OH]	62.2	3.9	7.3	14.2
	2nd crop	8	61.3	3.3	6.4	15.9	—	no product				" + MnO <sub>2</sub>	—	—	—	—
	residue	14	4.8	0.3	0.6	61.0	45	non-reproducible				see note (b)	—	—	—	—
[Mn(salpn)]	initial	76	57.7	4.7	7.6	15.6	60	57.6	4.6	7.6	15.2	[Mn(salpn)OH]	58.0	4.8	7.9	15.6
	2nd crop	12	57.9	4.8	7.4	15.4	—	no product				"	—	—	—	—
	residue	9	3.2	0.3	0.6	62.0	38	non-reproducible				see note (b)	—	—	—	—

<sup>a</sup>% Yield based on starting material.<sup>b</sup> The residue from boiling pyridine reactions is clearly impure MnO<sub>2</sub>; see text for further details. <sup>c</sup> Calculated as MnO<sub>2</sub>. <sup>d</sup> All products are deep brown to black in colour.

TABLE IV. Details of Oxygen Uptake Reactions for [Mn(ligand)].

(a) Uptake Ratios Compound		Uptake Ratio, Mn:O						
		(i) In boiling pyridine			(ii) In pyridine at $-15^{\circ}\text{C}$			
[Mn(lig 1a)]		1.00 : 0.96			1.00 : 0.62			
[Mn(lig 1b)]		1.00 : 1.00			1.00 : 0.66			
[Mn(lig 1c)]		1.00 : 0.93			1.00 : 0.59			
[Mn(lig 1d)]		1.00 : 0.94			1.00 : 0.55			
[Mn(lig 1e)]		1.00 : 0.97			1.00 : 0.64			
[Mn(salphen)]		1.00 : 0.94			1.00 : 0.65			
[Mn(salpn)]		1.00 : 0.94			1.00 : 0.61			

(b) Uptake Rates for [Mn(lig 1a)] and [Mn(lig 1d)]								
Uptake shown in ml of $\text{O}_2$ at S.T.P. (corrected for pyridine uptake)								
Reaction No.		Wt. of Cmpd. in g	Time					
			15 min	30 min	1 hr	2 hr	5 hr	10 hr
(i)	[Mn(lig 1a)]	in boiling pyridine						
	1	0.2674	3.01	5.48	6.79	8.20	10.34	10.86
2	0.2640	4.57	6.20	7.26	8.62	10.63	11.17	
(ii)	[Mn(lig 1a)]	at $-15^{\circ}\text{C}$						
	1	0.2689	2.75	3.44	4.39	5.58	7.10	7.24
2	0.2694	2.70	3.41	4.27	5.38	6.75	6.80	
(iii)	[Mn(lig 1d)]	in boiling pyridine						
	1	0.4760	2.98	4.93	6.29	7.68	9.82	10.26
2	0.4739	4.12	5.55	6.69	8.07	10.18	11.00	
(iv)	[Mn(lig 1d)]	at $-15^{\circ}\text{C}$						
	1	0.4598	2.53	3.30	4.13	5.12	6.04	6.09
2	0.4688	2.41	3.19	4.01	4.99	5.94	5.99	

solvent pyridine, but may also have driven off lattice and coordinated pyridine molecules. Thus it may be that the products listed in Table III actually deposit with pyridine molecules in their structure, as was found to be the case in earlier work on similar reactions [14]. The detailed oxygen uptake measurements for boiling pyridine solutions (see Table IV) support the formation of a compound with Mn:O ratio of 1:1.

A second series of similar experiments was carried out using cold ( $-15^{\circ}\text{C}$ ) pyridine solvent. It was found that in all cases [Mn(ligand)OH] was again obtained. However, at this lower temperature only 50–60% recovery of manganese was achieved in the form of this complex. This initial deposit was the only one obtained from solution. Slow evaporation of the pyridine solution at room temperature yielded no further product until all the solvent had been removed. These final products were shown, in each case, by analysis and X-ray powder photographs, to be non-reproducible mixtures. The general lack of good solubility of the mixtures in organic solvents precluded purification.

The oxygen uptake measurements performed on the cold pyridine solution reactions, indicated that

each Mn atom reacted with approx. 0.6 O atoms. This, coupled with the above results, suggests that a mixture of products is obtained from oxygenation reactions in cold pyridine, although it may be the case that at this temperature not all the [Mn(ligand)] complex reacts.

None of the physical data obtained for the compounds [Mn(ligand)OH] is helpful in interpreting the structure(s). Perhaps the dimeric dihydroxy bridge structure of [Mn(salpn)OH] [17] is present in the other six compounds. Certainly salen-type ligands can deform in the manner of salpn in this compound.

Reversibility of the oxygenation reaction that produced [Mn(ligand)OH] was not found feasible in any case. Thermogravimetric treatment of the compounds could not be interpreted simply, and the weight losses up to the decomposition point varied for each compound.

## Experimental

### Preparation of Ligands

Schiff-base condensation in ethanol of the required proportions of diamine and salicylaldehyde

TABLE V. Infrared and Magnetic Data for Compounds of Mn(III) – [Mn(ligand OH)].

Compound	I.R. OH stretches cm <sup>-1</sup>	$\mu_{\text{eff}}$ in B.M. at 298K
[Mn(lig Ia)OH] <i>i.e.</i> [Mn(salen)OH]	3570 and 3380	2.01
[Mn(lig Ib)OH]	3570 and 3390	2.09
[Mn(lig Ic)OH]	3520 and 3350	2.00
[Mn(lig Id)OH]	3500 and 3370	1.98
[Mn(lig Ie)OH]	3560 and 3400	2.24
[Mn(salphen)OH]	3510 and 3390	2.02
[Mn(salpn)OH]	3520 and 3450	1.94

yielded the ligands, which were recrystallised from ethanol and analysed (see Table I) to ensure purity.

The substituted diamines were prepared by the following methods:

- (i) meso-stilbenediamine – Irving and Parkins [18]
- (ii) ( $\pm$ ) - stilbenediamine – Mills and Quibell [19]
- (iii) 2,3-diaminobutane – Dickery *et al.* [20]
- (iv) 1,1,2,2-tetramethylethylenediamine – Basolo *et al.* [21]
- (v) 3,3-dimethyl-1,2-butane diamine – by Ni/Al alloy reduction of the corresponding oxime in basic solution.

#### Preparation of Mn(II) Complexes – [Mn(ligand)]

A composite method was used, incorporating the methods of Lewis *et al.* [4] and Carter *et al.* [22]. The ligand (4.08 mmol) in absolute ethanol (40 ml) under nitrogen was treated with slightly less than the stoichiometric amount of sodium. The solution was heated to reflux under nitrogen, and manganese(II) acetate-3-water (4.08 mmol; 1 g) in absolute ethanol was added dropwise. Refluxing was continued for up to 5 hr, and the solid present when the reaction mixture was cooled was filtered off, washed with absolute ethanol and ether and vacuum dried over P<sub>2</sub>O<sub>5</sub>. Analyses and magnetic data are shown in Table II. In most cases the values are average values of two preparations, as the method gave reproducible results.

The infrared spectra of all the ligand I complexes showed no peaks in the OH stretch region, but both the salphen and salpn complexes exhibited a broad peak near 3000 cm<sup>-1</sup>, and are thus postulated on this basis, and on the basis of analysis, to possess one molecule of water [12, 23].

#### Oxygenation Reactions

Approx. 1 millimol of the Mn(II) compound was dissolved with stirring in dry pyridine (50 ml) under nitrogen, and treated at the boiling point (series 1) or at –15 °C (series 2) with pure dry oxygen at atmospheric pressure. Details of the method have been given previously [14].

In all cases initial uptake is rapid, falling off after the first hour until in no case was there appreciable oxygen uptake after 10 hr (see Table IVb). Each of the seven Mn(II) compounds was reacted with oxygen at least twice at both temperatures, and the ratios of Mn:O uptake in Table IVa are average values. As previously noted [14], allowance in uptake calculations is made for the small volume of oxygen that dissolves in 50 ml of pyridine (0.26 to 0.30 ml). Detailed rates for two of the uptake reactions are shown in Table IVb.

#### Isolation of Oxygenated Compounds

In all cases the deposit at the completion of oxygenation was removed by filtration and found to be [Mn(ligand)OH] (see Table III). Slow partial evaporation of the pyridine solutions in a desiccator yielded a second crop deposit of this product for reactions carried out in boiling pyridine, but not for reactions done at –15 °C. Evaporation to dryness in the desiccator yielded impure MnO<sub>2</sub> for the boiling pyridine reactions, but analytically non-reproducible mixtures for the reactions at –15 °C.

All the analyses shown in Table III were obtained from samples vacuum dried over P<sub>2</sub>O<sub>5</sub> at 50 °C.

#### Physical Measurements

Infrared spectra in HCBd mulls were recorded on a Perkin–Elmer 457 spectrophotometer, while X-ray powder photographs were taken at 90 min exposures using CuK $\alpha$  radiation.

Magnetic data was obtained on a Gouy balance, while micro-analyses were performed by the University of Queensland Chemistry Department micro-analytical laboratory and the CSIRO Microanalytical Service Melbourne.

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