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The Multidentate Chemistry of Manganese(II).
IV. Non-Charged Complexes of Linear Quadridentate Nitrogenous Ligands and Their Reaction with Oxygen

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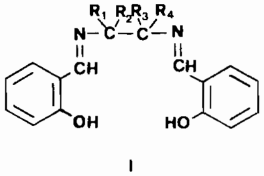
The preparation and properties of the non-charged manganese(II) compounds of formula [$Mn(N_4$ *ligand)*], *in which* (N_4*ligand) is any one of twelve linear quadridentate nitrogeneous ligands derived from the interaction of α-diketones and 2-pyridylhydrazones, are described. The structures of the compounds have been elucidated by reference to similar nickel(II) compounds and to magnetic moment studies.*

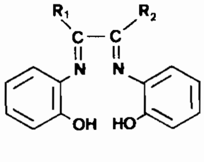
The reaction of these compounds with oxygen in cold pyridine solution has been studied in detail and it has been shown that each manganese atom combines with approx. 1.3 oxygen atoms. Reaction rates have been measured in some cases. This odd manganese to oxygen ratio is explained by the isolation from the oxygenation reactions of four products: (i) MnO_2*; (ii)* $Mn(N_4ligand)(py)OH$*; (iii)* $Mn(N_4ligand)(py)O_2$*; (iv)* $Mn(N_4ligand)(py)O$ *or* $Mn(N_4ligand)(py)O_{1/2}$*;*

Introduction

Uncharged manganese(II) complexes of the planar quadridentate macrocyclic ligand phthalocyanine (pc), and of the long chain quadridentate ligands of the salen (N, N′-ethylenebis(salicylaldimine)) type (I) have been shown to readily take up oxygen [1, 2]. However, while [Mn(pc)] appears to do this reversibly, [Mn(salen)] appears to be irreversibly oxidised upon oxygenation.



I



II

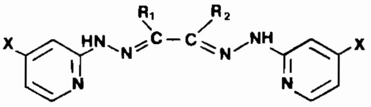
We are currenty studying the structure and oxygenation reactions of the neutral manganese(II) complexes of the general types:

(i) [Mn(salen)] – formula I in which R_1, R_2, R_3 and R_4 are varied from H to Me to Ph.

(ii) [Mn(ligand type II)]

(iii) [Mn(ligand type III)]

(iv) [Mn(macrocyclic ligand with 4 nitrogen donors)]



III

The work described here is concerned only with ligands of general type III. Work upon ligands of type I will be reported shortly [3].

The complexes of a number of transition metals with the ligands of type III have been known for some time [4, 5]. However, it is only recently that manganese(II) complexes have been reported [6]. Such complexes have the formulation Mn(lig III)X_2 (where X = Cl or Br) or $Mn(lig\ III)_2(ClO_4)_2$. Attempts to remove the hydrazine residue protons of these compounds in basic solution – a reaction that proceeds readily to produce the uncharged neutral complex for many other metals – led to a large degree of decomposition, and the neutral Mn(II) compounds to be described here could not in general be obtained pure by this method.

Results and Discussion

Preparation of [*Mn(lig III)*] *Compounds*

Neutral Mn(II) complexes of the above formula have been prepared for twelve ligands of type III, *viz.* IIIa to IIIl (see Table I), by modification of the method of Calderazzo *et al.* [7] for the preparation of [Mn(salen)]. Attempts to prepare these deprotonated neutral compounds from the corresponding protonated compound (Mn(lig III)Cl_2) in dry absolute ethanol by use of sodium ethoxide were generally unsuccessful, as decomposition

TABLE I. Manganese(II) Compounds of Ligands of Type III. Formulation [Mn(lig III)].[a]

Ligand No.	Substituent in III			Analysis					Magnetic Moment		
	R_1	R_2	X		C	H	N	Mn	Cl/Br	B.M. at 293 K	B.M. at 90K
IIIa	H	H	H	Calc.	49.2	3.4	28.7	18.8		4.31	4.72
				Found	49.0	3.4	28.3	18.7			
IIIb	H	Me	H	Calc.	50.8	3.9	27.4	17.9		4.32	
				Found	51.0	4.1	27.4	17.5			
IIIc	Me	Me	H	Calc.	52.3	4.4	26.2	17.1		4.34	4.74
				Found	52.0	4.2	25.9	16.9			
IIId	H	t-Bu	H	Calc.	55.0	5.2	24.1	15.8		4.36	
				Found	55.1	5.4	23.6	15.8			
IIIe	Ph	Ph	H	Calc.	64.7	4.0	18.9	12.4		4.35	
				Found	64.7	3.7	18.7	12.7			
IIIf	cyclohexane ring		H	Calc.	55.3	4.6	24.2	15.9		4.39	
				Found	55.0	5.0	24.6	15.9			
IIIg	H	H	Cl	Calc.	39.8	2.2	23.2	15.7	19.6	3.98	
				Found	39.7	2.0	22.9	14.9	19.0		
IIIh	H	H	Br	Calc.	31.9	1.8	18.6	12.2	35.5	3.99	
				Found	32.0	2.0	19.0	12.0	35.3		
IIIi	H	H	Me	Calc.	52.3	4.4	26.2	17.1		4.03	4.03
				Found	52.1	4.4	26.3	17.6			
IIIj	Me	Me	Cl	Calc.	43.1	3.1	21.5	14.1	18.2	4.00	
				Found	42.8	2.9	21.7	14.4	17.9		
IIIk	Me	Me	Br	Calc.	35.1	2.5	17.5	11.5	33.4	4.05	
				Found	35.3	2.8	17.5	11.4	33.0		
IIIl	Me	Me	Me	Calc.	55.0	5.2	24.1	15.8		4.00	4.02
				Found	55.6	5.2	24.0	16.0			

[a] Abbrev.: Me = methyl; t-Bu = tertiary butyl; Ph = phenyl.

appeared to take place and only in a few cases could (impure) samples of the required neutral compounds be isolated.

The interaction of any of the twelve ligands with decacarbonyldimanganese in refluxing tetrahydrofuran in the presence of ultraviolet radiation and under nitrogen atmosphere yielded from 35% to 50% of the required product. Furthermore, the method yielded analytically pure microcrystalline products provided the ratio of ligand to metal carbonyl was 2 to 1.

All the neutral compounds are deep violet to red (dichroic) in colour. Their analyses and magnetic moments are shown in Table I. They are soluble in most organic solvents (some even moderately soluble in diethyl ether) yielding deep violet solutions. Electronic absorption spectra of dichloromethane solutions of the compounds all showed four intense peaks:

(i) 240 to 250 nm; $\epsilon_0 \approx 2 \times 10^4$
(ii) 280 to 290 nm; $\epsilon_0 \approx 2 \times 10^4$
(iii) 380 to 390 nm; $\epsilon_0 \approx 1 \times 10^4$
(iv) approx. 500 nm; $\epsilon_0 \approx 5 \times 10^3$

It is assumed that in each case these are charge-transfer bands. The lowest energy band is well into the visible region and completely prevents the possibility of seeing the weak forbidden d–d transitions for manganese(II).

The mass spectra of the compounds of ligands IIIa, IIIb, IIIc, IIIe, and IIIf at 70 eV show a very small peak in each case at the atom mass unit corresponding to a dimer structure, *viz.* $[Mn_2(lig)_2]^+$, with a main peak at an a.m.u. corresponding to the monomer. These results can be interpreted, in a manner analogous to that of Miller and Oliver [8] for [Mn(salen)], to indicate that the compound has a dimeric structure in the solid state which readily breaks down under mass spectral analysis. However, there are alternative explanations of these results.

Firstly, it is possible that the complexes deposit from solution as mixtures of dimer and monomer. A sample of $[Ni^{II}(lig\ IIIc)]$ has been shown to possess a monomeric structure, while McKenzie *et al.* [10] have shown by X-ray crystallography that $[Ni^{II}(lig\ IIIf)]$ can possess a dimeric structure in which two ligand moieties bridge two nickel atoms. Furthermore, McKenzie [11] has indicated that a large number of ligands of type III can form both monomeric and dimeric Ni(II) and Pd(II) complexes. Such isomers deposit as mixtures from the reaction solution and can be separated by passage of chloroform solutions down an alumina column.

Secondly, it could be argued that the compounds prepared in this work are monomeric, but that in mass spectrographic analysis a very small amount of dimer formation occurs.

Comparison of X-ray powder photographs of [Mn(lig IIIa, b, c, d, e, g and j)] with the corresponding nickel(II) monomeric compounds obtained by the method of McKenzie [11], indicate that all these Mn(II) and Ni(II) compounds of the same ligand are isomorphous. Thus in these seven cases the Mn(II) compound obtained appears to be (at least very predominantly) monomer. Although this evidence does not indicate the presence of any dimeric Mn(II) compounds in these cases, nor does it preclude the presence of small amounts of dimer. Attempts to ensure that any dimer present was removed by passage of chloroform solutions of the compounds [Mn(lig III)] down alumina columns were unsuccessful as the compounds oxidise very readily.

Comparison of X-ray powder photographs of [Mn(lig IIIf)], [Ni(lig IIIf)] and [Ni_2(lig $IIIf)_2$] indicated that in this case the Mn(II) compound is a mixture of monomer and dimer. This result accords with McKenzie's observation [11], that the dimer species are most readily obtained with ligands of type IIIf in which a cyclic α-diketone is a precursor.

The mass spectra of the Mn(II) compounds derived from the ligands containing 4-substituents on both the pyridine rings, *viz.* [Mn(lig IIIg, h, i, j, k and l)] do not have a peak higher than the monomer mass ion. These six compounds appear to be monomers, and, as will be argued from magnetic moment data, exist as discrete units in the solid state.

Magnetic Properties of Mn(II) Compounds

The room temperature magnetic moments of powder samples of all the manganese(II) compounds are shown in Table I. They appear to fall into two groups: (i) those with moments of approx. 4.3BM from ligands IIIa to IIIf with no substituents on the pyridine rings. (ii) Those with moments of approx. 4.0BM from ligands IIIg to IIIl with 4-substituents on the pyridine rings.

[Ni(lig IIIc)] has been shown to possess a planar structure [9], with weak interaction in the octahedral nickel atom sites with donor nitrogen atoms attached to nickel atoms in molecules above and below the Ni–N_4 plane. Thus a layer structure is present in which the distance between a nickel atom in one layer and the nitrogen in the next is 3.48 Å, and a four-membered ring system Ni–N–Ni–N, vertical to the Ni–N_4 system, is obtained.

This structure is very similar to that of [Ni^{II}(pc)] (pc = phthalocyanine) in which adjacent Ni–N_4 layers are 3.38 Å apart. Thus, the compound [Mn(lig IIIc)], which is isomorphous with [Ni lig IIIc)], is also similar in structure to [Ni(pc)], which has [Mn(pc)] isomorphous to it [12].

We have used this similarity of structure of [Mn(lig IIIc)] and [Mn(pc)] as a basis for the magnetic moment analysis. It should be noted here that it is assumed that all the compounds [Mn(lig a, b, d, e, g, h, i, j, h and l)] are essentially monomeric and have a similar structure to [Mn(lig IIIc)]. [(Mn(lig IIIf)] is apparently a monomer/dimer mixture, and any attempt to offer comment on magnetic properties must await separation of the isomers).

Martin *et al.* [13] have shown that [Mn(pc)] has $\mu_{\parallel}$ = 4.0B.M. over the temperature range 80 to 300K, while the vertical interaction between adjacent molecules raises $\mu_{\perp}$ well above the spin-only value for square planar d^5 (3.88 B.M.) to 4.4 B.M. at 300 K. $\mu_{\perp}$ is temperature dependent, rising to 5.00 B.M. at 90K. Thus, in a powder sample of [Mn(pc)], μ_{eff} (average) is 4.33 B.M. at 300K.

It would appear that complexes of [Mn(lig IIIa, b, c, d and e)] have a basic square planar environment, with some vertical interaction between molecular layers of the type exhibited in [Mn(pc)]. This contention is supported by the fact that both [Mn(lig IIIa and c)] have an increase in the powder sample magnetic moment from 4.31 B.M. and 4.34 B.M. respectively at 293 K to 4.72 B.M. and 4.74 B.M. respectively at 90K. This ferromagnetic interaction is similar to that shown by [Mn(pc)].

The Mn(II) compounds derived from the ligands with a substituent at the 4-position of both pyridine rings all have moments close to 4.0 B.M. at 293K. Studies on the compounds [Mn(lig IIIi)] and [Mn(lig IIIl)] show that this value is virtually unchanged at 90K (see Table I). This behaviour parallels that of $\mu_{\parallel}$ for [Mn(pc)], and can be interpreted to indicate that these compounds do not have interaction between Mn atoms in one molecular layer and donor atoms in an adjacent layer. Presumably the pyridine ring substituents force the layers apart. It was hoped that this property might have an effect upon the type of complex obtained upon oxygenation of the Mn(II) complexes.

Oxygenation Reactions

Early work on the oxygenation reactions of the Mn(II) compounds in pyridine solution at approx. −15 °C led to the isolation of two types of oxygen-containing compounds: (i) those with a Mn:O ratio of 1:1 or 1:0.5, for ligands IIIa to IIIf without pyridine ring substituents, (ii) those with a Mn:O ratio of 1:2 for ligands IIIg to IIIl with pyridine ring substituents, and in an earlier report [14] it was suggested that perhaps a "picket-fence" [15] behaviour of the ligands allowed type (ii) complexes to add molecular oxygen.

However, these early results were based on the isolation of the first deposited product from the oxygenation reaction after the removal of the amorphous black material (impure MnO_2) deposited during reaction (see Table II and Experimental).

Studies undertaken using detailed manometric measurements of oxygen uptake indicate that, under standardized conditions, all the Mn(II) compounds

TABLE II. Initial Compounds Obtained from Oxygen Reaction with Complexes [Mn(lig III)]. Deposited from Pyridine (py) Solution at −15C.

Complex[a]	Uptake of O Mn : O	% Yield[b]	Stoichiometry of Compound[c]	Analysis						Magnetic Moment B.M. at 293K
					C	H	N	Mn	Cl/Br	
[Mn(lig IIIa)]	1.00 : 1.24	35	Mn(lig IIIa)(py)O	Calc.	52.6	3.9	25.3	14.2		3.80
				Found	52.4	3.7	24.9	14.0		
[Mn(lig IIIb)]	1.00 : 1.26	38	Mn(lig IIIb)(py)O	Calc.	53.7	4.2	24.4	13.7		3.66
				Found	53.2	4.6	24.4	13.6		
[Mn(lig IIIc)]	1.00 : 1.35	32	Mn(lig IIIc)(py)O	Calc.	54.8	4.6	23.6	13.2		3.59
				Found	55.1	5.0	24.0	13.4		
[Mn(lig IIId)]	1.00 : 1.40	36	Mn(lig IIId)(py)O	Calc.	56.8	5.2	22.1	12.4		3.62
				Found	56.7	5.2	22.0	12.7		
[Mn(lig IIIe)]	1.00 : 1.26	37	Mn(lig IIIe)(py)O	Calc.	64.4	4.3	18.1	10.2		3.62
				Found	64.0	4.0	18.0	10.0		
[Mn(lig IIIf)]	1.00 : 1.25	30	Mn(lig IIIf)(py)O	Calc.	57.0	4.8	22.2	12.4		3.75
				Found	57.0	4.7	21.9	12.2		
[Mn(lig IIIg)]	1.00 : 1.28	30	Mn(lig IIIg)(py)O_2	Calc.	43.1	2.7	20.7	11.6	15.0	3.88
				Found	43.0	2.5	21.0	12.0	15.4	
[Mn(lig IIIh)]	1.00 : 1.32	36	Mn(lig IIIh)(py)O_2	Calc.	36.4	2.3	17.5	9.8	28.5	3.64
				Found	36.1	2.3	17.4	9.8	28.4	
[Mn(lig IIIi)]	1.00 : 1.40	34	Mn(lig IIIi)(py)O_2	Calc.	52.8	4.4	22.7	12.7		3.77
				Found	52.7	4.4	22.9	12.3		
[Mn(lig IIIj)]	1.00 : 1.20	28	Mn(lig IIIj)(py)O_2	Calc.	45.5	3.4	19.6	11.0	14.2	3.82
				Found	45.0	3.2	19.7	11.4	14.3	
[Mn(lig IIIk)]	1.00 : 1.38	30	Mn(lig IIIk)(py)O_2	Calc.	38.6	2.9	16.6	9.3	27.1	3.81
				Found	38.4	2.7	16.3	9.0	26.5	
[Mn(lig IIIl)]	1.00 : 1.38	32	Mn(lig IIIl)(py)O_2	Calc.	54.8	5.0	21.3	12.0		3.66
				Found	54.5	4.7	21.0	12.3		

[a] See Table I for ligand abbreviations. [b] Based on weight of Mn(II) complex. [c] All compounds deep violet to black in colour. Elemental analyses do not allow distinction between the products formulated as Mn(lig III)(py)O and Mn(lig III)(py)$O_{1/2}$. Calculated figures are shown for the former stoichiometry.

take up oxygen in the ration Mn:O = 1:1.2 to 1.4 (Table II). Thus each compound takes up in excess of 1 atom, but much less than 2 atoms, of oxygen per manganese atom. The actual uptake ratio is reproducible for any given compound with an accuracy of ±5%.

Evidence from the work [3] on oxygenation reactions of Mn(II) complexes of a number of ligands of types I and II indicates that a number of different products can be obtained as the first deposited product (after MnO_2 removal) from the reaction solution, depending upon the ligand being used. These results suggested that the Mn:O uptake ratios in this work were possibly due to the production for any one reaction of a number of oxygenated species in solution.

Accordingly, a study was made of the reaction rate and the products for the reaction of oxygen with the complexes [Mn(lig IIIc and k)] in pyridine solution at approx. −15 °C. In the case of both compounds, use of fractional crystallization and column chromatography allowed the separation from reaction solution of three violet-black compounds of stoichiometry:

(A) Mn(lig III)(py)O_2
(B) Mn(lig III)(py)O or Mn(lig III)(py)$O_{1/2}$
(C) Mn(lig III)(OH)(py)

The physical properties and yields of all six compounds are shown in Table III, while the oxygen uptake rates are in Table IV. The magnetic moments of these complexes are not of use in elucidating their structure, and while mass spectral analysis of all the oxygenated compounds was attempted, this yielded many peaks in each case, and any attempt to analyse this data would be invidious, as would be attempts to "explain" the infrared spectra of any of the oxygenated compounds. Only in the two cases of the hydroxy-compounds, (C), were the infrared spectra of use; both compounds have OH stretching peaks at 3520 ± 5 cm^{-1} and 3450 ± 5 cm^{-1} and an OH bend at 1080 ± 5 cm^{-1}. No similar peaks were present in the infrared spectra of compounds of types (A) and (B).

The claim that in both cases three different pure compounds can be isolated, rests on the reproducibility of the analyses, *viz.* Mn(lig IIIc)(py)O and Mn(lig IIIk)(py)O_2 were both prepared and analysed for C, H, Mn and N five times each, while the other four

TABLE III. Oxygenation Products from Ligands IIIc and IIIk.

Compound[a]	% Yield[b]	Analysis	C	H	N	Mn	Br	Magnetic Moment B.M. at 273k	Infrared OH stretch
Mn(lig IIIc)(py)$O_{1 \text{ or } 1/2}$	40	Calc.	54.8	4.6	23.6	13.2		3.59	No peaks
		Found	55.1	4.4	24.0	13.4			
Mn(lig IIIc)(py)O_2	15–20	Calc.	52.8	4.4	22.7	12.7		3.77	No peaks
		Found	52.6	4.3	22.5	12.7			
Mn(lig IIIc)(py)OH	15–18	Calc.	54.7	4.8	23.5	13.2		3.31	3524 and
		Found	54.5	4.7	23.6	13.3			3447 cm^{-1}
Mn(lig IIIk)(py)$O_{1 \text{ or } 1/2}$	35	Calc.	39.7	3.0	17.1	9.6	27.9	4.00	No peaks
		Found	39.7	2.9	17.0	9.6	27.7		
Mn(lig IIIk)(py)O_2	14–18	Calc.	38.6	2.9	16.6	9.3	27.1	3.81	No peaks
		Found	38.4	2.7	16.3	9.0	26.5		
Mn(lig IIIk)(py)OH	12–15	Calc.	39.6	3.1	17.0	9.6	27.8	3.34	3515 and
		Found	39.5	3.0	17.2	9.7	27.6		3454 cm^{-1}

[a] All compounds deep violet to black in colour. Elemental analyses do not allow distinction between the products formulated as Mn(lig III)(py)O and Mn(lig III)(py)$O_{1/2}$. Calculated figures are shown for Mn(lig III)(py)O. [b] Impure MnO_2 (5–10%) also isolated.

TABLE IV. Rate of Oxygen Uptake for Compounds [Mn(lig IIIc)] and [Mn(lig IIIk)] in Pyridine (50 ml) at –15 °C. Uptake shown in ml (corrected for pyridine absorption of Oxygen) of O_2 at constant pressure of 1 atmosphere.

Reaction No.	Wt. of Cmpd. in g	30 min	1 hr	2 hr	4 hr	6 hr	10 hr
	[Mn(lig IIIc)]						
1	0.3072	6.01	7.79	10.48	13.41	14.09	14.28
2	0.3067	5.98	7.74	10.46	13.27	14.07	14.24
3	0.3070	6.06	8.02	10.44	13.50	14.00	14.00
4	0.3084	6.04	8.00	10.71	13.77	14.04	14.60
5	0.3062	5.79	7.79	9.93	13.04	13.96	14.28
	[Mn(lig IIIk)]						
1	0.4751	6.11	8.00	10.52	13.50	14.31	14.45
2	0.4771	6.42	8.33	10.72	13.90	14.50	14.61
3	0.4820	6.71	8.40	10.52	13.88	14.61	15.04
4	0.4794	6.38	8.07	10.61	13.94	14.93	14.34
5	0.4767	6.38	8.21	10.71	13.76	13.98	14.11

compounds were analysed for these four elements three times each.

Possible Structure of the Oxygenated Compounds Listed in Tables II and III.

(A) [Mn(lig III)(py)O_2]; (B) [Mn(lig III)(py)O] or Mn(lig III)(py)$O_{1/2}$

Ochiai [20] has argued that the first two steps in metal oxygenation are:

(i) $M + O_2 \rightleftarrows MO_2$

(ii) $MO_2 + M \rightleftarrows MO_2M$

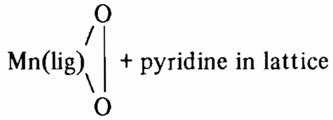
However, he has (cleverly) not discussed likely structures. The results of this work cannot distinguish between the following possible structures for:

(A) (i) py–Mn(lig)–O–O*

(ii) –O–Mn(lig)–O–O–Mn(lig)–O–
+ pyridine in lattice

(iii) O=Mn(lig)–O–O–Mn(lig)=O
+ pyridine in lattice

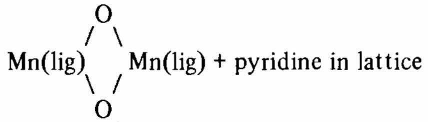
(iv)



$$\mathrm{Mn(lig)}\!\left\langle\begin{matrix}\mathrm{O}\\ |\\ \mathrm{O}\end{matrix}\right. + \text{pyridine in lattice}$$

(B) (i) py–Mn(lig)–O–O–Mn(lig)–py

(ii)



$$\mathrm{Mn(lig)}\langle\begin{matrix}\mathrm{O}\\ \\ \mathrm{O}\end{matrix}\rangle\mathrm{Mn(lig)} + \text{pyridine in lattice}$$

(iii) Py–Mn(lig)=O

(iv) py–Mn(lig)–O–Mn(lig)–py**

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*Mn(lig) is a unit with the Mn atom coordinated to the 4N atoms of the ligand.

**It is not possible to make a distinction between Mn(lig)-(py)O and Mn(lig)(py)$O_{1/2}$ on the basis of elemental analyses. The problem is aptly illustrated by the work in the papers of reference 1.

TABLE V. Physical Properties of Compounds of Formula Mn(lig III)(OH)(py)$_n$.

Compound[a]	Analysis						Infrared Peaks OH Stretch, cm^{-1}
		C	H	N	Mn	Cl/Br	
Mn(lig IIIa(OH)(py)	Calc.	52.4	4.1	25.2	14.1		3520; 3449
	Found	52.5	4.0	25.0	14.3		
Mn(lig IIIb)(OH)(py)	Calc.	53.6	4.5	24.3	13.6		3529; 3442
	Found	53.4	4.2	24.0	13.5		
Mn(lig IIIc)(OH)(py)	Calc.	54.7	4.8	23.5	13.2		3524; 3447
	Found	54.5	4.7	23.6	13.3		
Mn(lig IIId)(OH)(py)	Calc.	56.6	5.4	22.0	12.4		3519; 3450
	Found	56.6	5.2	22.0	12.7		
Mn(lig IIIe)(OH)(py)	Calc.	64.3	4.4	18.1	10.2		3522; 3454
	Found	64.1	4.0	18.0	10.2		
Mn(lig IIIf)(OH)(py)	Calc.	56.9	5.0	22.1	12.4		3527; 3454
	Found	56.8	4.9	21.7	12.0		
Mn(lig IIIg)(OH)(py)$_2$	Calc.	49.2	3.5	20.8	10.2	13.2	3529; 3450
	Found	48.9	3.5	20.9	10.5	12.9	
Mn(lig IIIh)(OH)(py)	Calc.	37.4	2.6	17.9	10.1	29.3	3531; 3456
	Found	37.5	2.7	18.2	9.9	29.0	
Mn(lig IIIi)(OH)(py)$_2$	Calc.	58.1	5.0	22.6	11.0		3520; 3452
	Found	57.9	4.8	22.4	10.7		
Mn(lig IIIj)(OH)(py)	Calc.	46.9	3.7	20.2	11.3	14.6	3518; 2456
	Found	47.2	4.0	20.0	11.0	14.9	
Mn(lig IIIk)(OH)(py)	Calc.	39.6	3.1	17.0	9.6	27.8	3515; 3454
	Found	39.5	3.0	17.2	9.7	27.6	
Mn(lig IIIl)(OH)(py)$_2$	Calc.	59.5	5.5	21.4	10.5		3517; 3450
	Found	59.3	5.4	22.6	10.1		

[a] All compounds deep violet to black in colour.

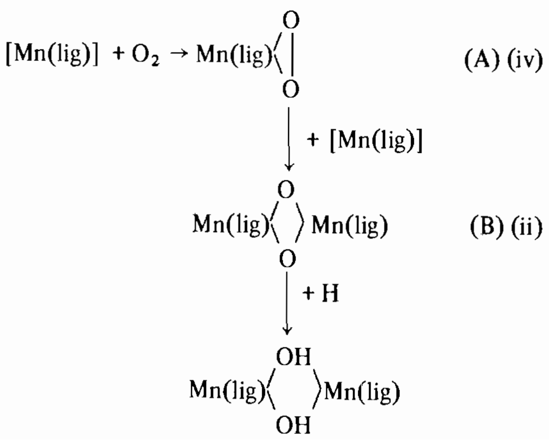
It should be noted that the eight foregoing structures all assume: (a) that the Mn atom is 6-coordinate and (b) that (apart from (A) (iv) and (B) (ii) the ligand moieties are planar with all four donor nitrogens bonding to the metal. McKenzie *et al.* [10] have shown that ligands of type(III) do not have to be planar, and the 6-coordinate nature of the Mn atom cannot be assumed. Thus, there are many more possible structures.

The infrared spectra of all compounds of types (A) and (B) have been done. Although attempts have been made [17, 18] to elucidate the mode of O–Mn or O–O bonding on this basis, we are not prepared to attempt such an analysis from the veritable "jungle" of peaks obtained.

(C) [Mn(lig III)OH](py)

We postulate these compounds to be dimers with a dihydroxy-bridge between the two Mn atoms, and lattice pyridine molecules. This postulate is supported by the OH-stretch peaks in the infrared spectra (see Table III), which occur at similar positions to those of [Mn(salen)(OH]$_2$·(py)$_4$, which has been shown [19] to possess this type of structure. Mass spectral analysis of all the compounds prepared possessing this stoichiometry did not show peaks for the mass ion for [Mn(lig III)OH]$_2^+$, but exhibited a large number of peaks at lower a.m.u. values.

It is of interest to note that if the Mn(II) compound, [Mn(lig III)], for any of the twelve ligands of type III, is reacted in pyridine solution with oxygen at temperatures above 40 °C, the only product (apart from MnO$_2$) to be obtained is [Mn-(lig III)(OH)](py)$_n$ (see Table V). Hopefully, this work has isolated various steps on the road to this compound, and perhaps the reaction to [Mn(lig III)-OH]$_2$ proceeds via (A) (iv) and (B) (ii) above:



Experimental

Preparation of Ligands

This was undertaken as described elsewhere [4, 5] by Schiff-base condensation of one molecular proportion of the required α-diketone with two molecular proportions of the required 2-pyridolhydrazine in ethanol. The exception to this general method was the condensation of benzil with 2-pyridylhydrazine, where the osazone could only be obtained by refluxing the reagents in glacial acetic acid [16].

Preparation of the Manganese(II) Complexes of Formula [Mn(lig III)]

These compounds were prepared by the method of Calderazzo *et al.* [7] for [Mn(salen)], using dry tetrahydrofuran as a solvent and a dry nitrogen atmosphere. Analyses and physical properties of all these compounds are shown in Table I. The compounds are all deep violet to black in colour, and appear stable in dry air. However, in the presence of organic solvents (in which they are very soluble) they take up oxygen readily.

Oxygenation Reactions

Measurement of Oxygen Uptake

Approx. 1 millimole of the Mn(II) compound ([Mn(lig III)]) was dissolved with stirring in dry pyridine (50 ml) under N_2; the flask containing the solution at atmospheric pressure being connected through a closed stopcock to a vacuum line, which had been evacuated and filled with pure dry oxygen at atmospheric pressure. The stopcock was opened and the reaction allowed to proceed at approx. −15 °C.

The uptake of oxygen was followed using a constant pressure mercury manometer. In each case initial uptake was rapid, falling off after the first hour until in all cases no appreciable uptake was noted after 10 hours (see Table IV). Each of the twelve compounds in Table II was oxygenated at least twice, and the ratio of manganese to oxygen taken up is the average of two readings (see Column 2, Table II), excepting the compounds [Mn(lig IIIc and k)], where the average of five uptake measurements is quoted. For these two compounds the uptake reaction was performed five times, and measurements of uptake against time were obtained (see Table IV). The reproducibility of oxygen uptake for any one compound was never worse than ±5%.

A series of five blank reactions in which the above experimental conditions were reproduced in the absence of manganese(II) compound demonstrated that cold pyridine takes up a small volume of oxygen under these conditions. As the manganese(II) compounds are all very soluble in pyridine, a constant volume of pyridine (50 ml) was used in each reaction, and allowance for the oxygen dissolved in the pyridine (0.26 to 0.30 ml) has been made in all the values quoted. In no case was this blank uptake more than 3% of the total uptake value for any manganese(II) compound.

As there was no appreciable colour change of the violet to black solutions of the manganese(II) compounds upon oxygenation, there appeared to be no simple test to see if the oxygenation was reversible. As all the oxygenation reactions yielded an amorphous black deposit, which is assumed to be impure MnO_2(only traces of C, H and N found upon microanalysis), it is clear that deoxygenation must, if it occurred, be less than total.

The solutions obtained from the oxygenation reactions were filtered under oxygen and kept at approx. −15 °C for a week to yield violet to black microcrystalline deposits. These products and their % yields are listed in columns 3 and 4 of Table II.

Detailed Analysis of Oxygenated Products from [Mn(lig IIIc)] and [Mn(lig IIIk)]

[Mn(lig IIIc)]

The oxygenation reaction described above was carried out five times. In each case the initial deposit, after the reaction solution had been kept at −15 °C for one week, was [Mn(lig IIIc) (py)$O_{1 \text{ or } 1/2}$], which was removed by filtration in air. The filtrates obtained were combined into 3 solutions (2 × 2 and 1 × 1) and passed down an alumina column. The solution eluted yielded upon evaporation [Mn(lig IIIc)(py)O_2], while elution of the column with 50/50 benzene/pyridine yielded a solution which deposited [Mn(lig IIIc)(py)OH] upon evaporation. The yields and properties of all three compounds are shown in Table III. % yields, analyses and magnetic moments are all average values.

[Mn(lig IIIk)]

The same experimental method was applied to this compound as described above for [Mn(lig IIIc)]. In this case [Mn(lig IIIk)(py)O_2] separated as the first product and [Mn(lig IIIk)(py)$O_{1 \text{ or } 1/2}$] and [Mn(lig IIIk)(py)OH] were separated on the alumina column. Details of average yields and physical properties are listed in Table III.

Physical Measurements

Ultraviolet–visible spectra and infrared nujol mull spectra were recorded on a Unicam SP 800 and a Perkin–Elmer 457 Spectrophotometer respectively.

X-ray powder photographs were taken at 90 min exposures using CuKα radiation.

Magnetic data was measured on a Faraday variable temperature balance, while microanalyses were performed by the University of Queensland Chemistry

Department microanalytical laboratory and the CSIRO microanalytical service Melbourne.

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