Synthesis and Characterisation of Manganese(III) Unsymmetrical Schiff-base Complexes: a Unique Example of a Cocrystallised Manganese(III) Unsymmetrical Schiff-base Complex, and a Symmetric Schiff-base Complex arising from Rearrangement of the Former†

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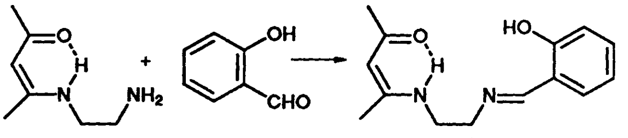
Some manganese(III) complexes with unsymmetrical Schiff bases have been prepared and characterised. The ligands were prepared by condensation of 7-amino-4-methyl-5-azahept-3-en-2-one with salicylaldehyde, 2-hydroxyacetophenone or substituted salicylaldehydes (5-chloro, 5-methoxy, 3-ethoxy or 3,5-dibromo). On reaction with manganese(II) perchlorate in air, manganese(III) Schiff-base complexes are obtained. The crystal structures of two of these have been determined, one being cocrystallised with $[\{Mn(salen)(H_2O)\}_2][ClO_4]_2$ containing the symmetrical salen ligand [*N,N'*-ethane-1,2-diylbis(salicylideneiminate)]. Unlike the dimeric structures previously found for similar complexes, the two structures are monomeric with octahedral MnN_2O_4 co-ordination spheres.

It is well established that manganese plays a central role in some biological systems, *e.g.* in a superoxide dismutase[1] and an azide-insensitive catalase;[2] of greater importance is that it is essential for the oxidation of water to O_2 in the photosynthetic process,[3,4] having been found to be associated with the water-oxidising complex in all O_2-evolving photosynthetic organisms so far studied. Moreover, no other metal has been found to reactivate lost O_2-evolution activity in reconstructed complexes deficient in manganese.

There is currently a great deal of interest in synthesising models of this system based on high-nuclearity manganese complexes, *viz.* Mn_4,[5] Mn_6[6] and Mn_8,[7] but, unfortunately, the absence of water from these systems inevitably render them useless as models for the water oxidising complex, although they may have some validity as models for the post-water-oxidising complex. We[8] and others[9-14] have examined binuclear systems in an attempt to mimic the water photolysis action of photosystem II of the green plant. We have succeeded in generating molecular oxygen and reducing *p*-benzoquinone to hydroquinone by visible irradiation of an aqueous solution of $[\{Mn(salpd)(H_2O)\}_2][ClO_4]_2 \cdot 2H_2O$ [salpd = *N,N'*-propane-1,3-diylbis(salicylideneiminate)]. Recently a quantum-mechanical study of our work was published by Awad and Anderson.[15]

We have sought to extend our work to unsymmetrical tetradentate ligands bound to high-valent manganese. Although such ligands are rare they are not unknown and have been complexed with oxovanadium(IV),[16] copper(II),[17,18] nickel(II)[19] and cobalt(III).[19]

We have previously reported the synthesis of the unsymmetrical Schiff-base ligand H_2L^1 from the reaction of 7-amino-4-methyl-5-azahept-3-en-2-one with salicylaldehyde (Scheme 1) and subsequently prepared the manganese(III) complex $[\{MnL^1(H_2O)\}_2][ClO_4]_2 \cdot 4H_2O$.[20] To our great surprise we found that, upon irradiation of an aqueous solution of this complex with a tungsten lamp for 6 h, ligand rearrangement occurred and the manganese(III) complex of the symmetrical ligand H_2salen $[\{Mn(salen)(H_2O)\}_2][ClO_4]_2 \cdot H_2O$ [salen = *N,N'*-ethane-1,2-diylbis(salicylideneiminate)] was isolated in *ca.* 40% yield; this rearranged complex was characterised by single-crystal X-ray techniques.[20] This is clearly a strange, and possibly important, observation and we have begun an investigation of it. At first we wished to establish that a range of unsymmetrical Schiff-base complexes of manganese(III) can be prepared and isolated. These are reported here. We have also been able to obtain an X-ray crystal structure of a manganese(III) complex of an unsymmetrical Schiff base, as well as of a material which consists of a cocrystallised manganese(III) complex containing symmetrical and unsymmetrical ligands.



Scheme 1

H_2L^1

Results and Discussion

The unsymmetrical Schiff-base ligands are listed in Table 1, together with ^1H NMR data. Details of their preparations and those of their complexes are given in the Experimental section. All of the manganese(III) Schiff-base complexes have the stoichiometry $MnL(ClO_4) \cdot xH_2O$, x = 1–3 (Table 2). In general the complexes exhibit very similar infrared features (Table 3) and the typical bands assigned to Schiff-base ligands are evident. All show a shift to lower energy of the ligand ν(C=N) band on complexation, and a broad absorption centred at *ca.* 3450 cm^{-1},

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

Table 1 Analytical and ^{1}H NMR data for the ligands

	Analysis (%)[a]			^{1}H NMR (δ)[b]						
Ligand	C	H	N	H^1	H^2	H^3	H^4	$H^{5,7}$	H^6	Others
H_2L^1	67.6 (68.3)	7.6 (7.3)	10.9 (11.4)	6.9–7.4	8.35(s)	3.75(t)	3.6(m)	1.9, 2.0(s)	4.95(s)	
H_2L^2	68.4 (69.2)	7.5 (7.6)	10.3 (10.8)	6.8–7.5		3.75(t)	3.6(m)	1.9, 2.0(s)	4.98(s)	2.34(2)
H_2L^3	64.5 (66.2)	7.3 (7.6)	9.4 (9.6)	6.9–6.95	8.34(s)	3.75(t)	3.65(m)	1.9, 2.0(s)	4.92(s)	4.5(m), 1.45(t)
H_2L^4	64.3 (65.2)	7.3 (7.2)	9.2 (10.1)	6.8–6.95	8.32(s)	3.7(t)	3.6(m)	1.9, 2.0(s)	4.95(s)	3.8(s)
H_2L^5	58.3 (59.9)	6.3 (6.1)	9.8 (10.0)	6.9–7.2	8.29(s)	3.7(t)	3.6(m)	1.9, 2.0(s)	4.96(s)	
H_2L^6	40.1 (41.6)	3.7 (4.0)	6.7 (6.9)	7.7, 7.3	8.25(s)	3.75(t)	3.65(m)	1.9, 2.0(s)	4.96(s)	

[a] Calculated values in parentheses. [b] Solvent CD_3OD.

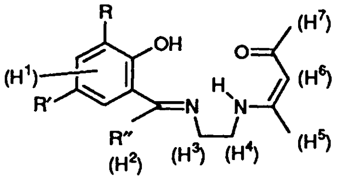
Table 2 Analytical and other data for the complexes

	Analysis (%)[a]					FAB[b]		
Complex	C	H	N	Cl	Mn	*m/z*	μ_{eff}	θ/K
$[MnL^1]ClO_4{\cdot}3H_2O$	37.5 (37.2)	4.6 (4.8)	6.2 (6.2)	8.3 (7.9)		299	5.0	
$[MnL^2]ClO_4{\cdot}H_2O$	41.5 (41.8)	4.5 (4.8)	6.4 (6.5)	7.5 (8.2)	12.1 (12.8)	313	4.88	−16.6
$[MnL^3]ClO_4{\cdot}2H_2O$	40.0 (40.1)	4.9 (5.0)	5.6 (5.8)	7.9 (7.4)	9.4 (11.5)	343	4.8	−15
$[MnL^4]ClO_4{\cdot}2H_2O$	38.4 (38.7)	4.5 (4.7)	5.6 (6.0)	7.8 (7.6)		329	4.7	−20.7
$[MnL^5]ClO_4{\cdot}2H_2O$	35.5 (35.1)	4.2 (4.0)	5.4 (5.8)	16.9 (15.1)	10.2 (11.7)	333	4.7	−27.9
$[MnL^6]ClO_4{\cdot}H_2O$	29.1 (29.2)	2.5 (2.8)	4.4 (4.9)			457		

[a] Calculated values in parentheses. [b] Peaks corresponding to $[MnL]^+$.

Table 3 Important infrared absorptions (cm^{-1}) of the ligands and complexes

Compound	ν(O–H)	ν(O–H)	ν(C=N)	ν(Cl–O)
H_2L^1		2720vw	1630s	
$[MnL^1]ClO_4{\cdot}3H_2O$	3400s (br)	2705vw	1625s	1110vs (br)
H_2L^2		2700w (br)	1615s (br)	
$[MnL^2]ClO_4{\cdot}H_2O$	3450 (vbr)	2707w	1595s	1095vs (br)
H_2L^3			1629vs	
$[MnL^3]ClO_4{\cdot}2H_2O$	3400vs (vbr)		1618vs	1080vs (br)
H_2L^4		2710w	1635s	
$[MnL^4]ClO_4{\cdot}2H_2O$	3500vs (vbr)		1631s	1090vs (vbr)
H_2L^5			1639s	
$[MnL^5]ClO_4{\cdot}2H_2O$	3350vs (vbr)		1627s	1100vs (vbr)
H_2L^6		2720w	1640s	
$[MnL^6]ClO_4{\cdot}H_2O$	3400s (br)		1630s	1100vs (vbr)



	R	R′	R″
H_2L^1	H	H	H
H_2L^2	H	H	Me
H_2L^3	EtO	H	H
H_2L^4	H	MeO	H
H_2L^5	H	Cl	H
H_2L^6	Br	Br	H

assigned to a combination of the ν(O–H) modes of co-ordinated and lattice water. The broad unsplit absorptions at *ca.* 1100 cm^{-1} are indicative of unco-ordinated perchlorate groups.

From mass spectral evidence (Table 2) the structure of the complexes in the solid state is monomeric rather than the dimeric structures we have previously found for similar complexes. The FAB mass spectra for all of these complexes show evidence for the presence of the ion $[MnL]^+$, *i.e.* a monomer.

Conclusive evidence for the monomeric structure comes from the single-crystal X-ray analyses of $[MnL^3(H_2O)_2]ClO_4{\cdot}EtOH$ and $[MnL^1(H_2O)_2]ClO_4$ (see below). These are shown to be monomers with octahedral MnN_2O_4 co-ordination spheres. Although crystal structures are not yet available for the remaining complexes, the similarity in the infrared and FAB mass spectra and the magnetic susceptibility measurements suggests that these too are monomers.

Magnetic measurements on these complexes reveal room-temperature magnetic moments close to 4.9, Table 2, consistent with a high-spin d^4 system with no magnetic interaction between the manganese centres. The magnetic behaviour has been studied in the temperature range 300–77 K, and in the case of $[MnL^4]ClO_4{\cdot}2H_2O$ in the 300–4 K range, Fig. 1(*a*) and 1(*b*), and all complexes are found to obey the Curie–Weiss law. Plots of the reciprocals of the magnetic susceptibilities against absolute temperature are linear, with Weiss constants ranging between −15 and −28 K. These are indicative of very weak antiferromagnetic interactions.

Cyclic Voltammetry Studies.—It is presumed that an intermediate $Mn^{III}Mn^{IV}$ transition state is involved when water is oxidised to oxygen in the natural photosynthetic process. In the 'model' systems which we have previously investigated it has been shown that the photoactivity of the $[\{MnL(H_2O)\}_2]^{2+}$ complex (L = dianion of O_2N_2 tetradentate Schiff base) is critically dependent on the structure of the ligand. Thus, in the present study cyclic voltammetry measurements have been carried out in order to investigate the electrochemistry involved

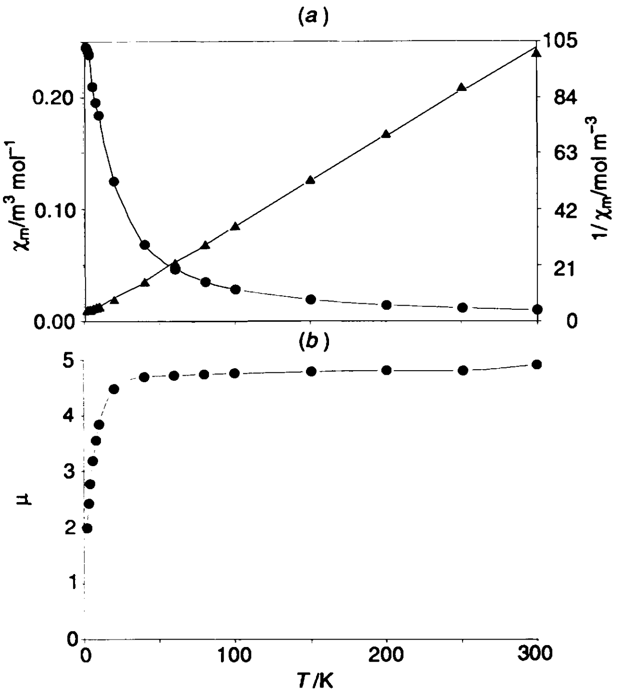


Fig. 1 Plots of (a) $1/\chi_m$ (▲), χ_m (●) and (b) μ vs. temperature for the complex $[MnL^4]ClO_4 \cdot 2H_2O$

Table 4 Electrochemical data for the complexes

Compound	E_p^a/V	E_p^c/V	E/V	$E^{\circ\prime}$/V
$[MnL^1]ClO_4 \cdot 3H_2O$	1.48	1.37	0.11	1.43
	1.17			
$[MnL^2]ClO_4 \cdot H_2O$	1.53	1.25	0.28	1.39
	0.23	−0.41		
$[MnL^4]ClO_4 \cdot 2H_2O$	1.36	1.04	0.32	1.20
	1.14	0.09		
$[MnL^3]ClO_4 \cdot 2H_2O$	1.13	1.02	0.11	1.08
	0.15	−0.36		
$[MnL^5]ClO_4 \cdot 2H_2O$	1.52	1.38	0.14	1.46
	0.23	−0.20		

in the redox process of this transition state. The results are summarised in Table 4.

The voltammograms of most of the complexes showed two oxidation and two reduction peaks, indicating two redox processes, presumably Mn^{III}–Mn^{II} and Mn^{IV}–Mn^{III} couples. None of the complexes showed completely reversible behaviour, but quasi-reversible behaviour (as judged from the peak-current ratios) was observed (E = 0.11–0.32 V). The peak positions are clearly influenced by the particular ligand present. For example, the half-wave potentials ($E^{\circ\prime}$) of the most positive pair of peaks for $[MnL^5]ClO_4 \cdot 2H_2O$ is greater than that for $[MnL^4]ClO_4 \cdot 2H_2O$ (1.46 compared with 1.20 V), as expected from electronic considerations. Unfortunately the solubility of these complexes in common solvents was too low for any meaningful coulometric studies. What we can propose, however, is that the redox processes involve Mn^{III}–Mn^{II} and Mn^{IV}–Mn^{III} couples, the latter being more positive and showing quasi-reversible behaviour, Fig. 2(a) and 2(b).

Stability of the Complexes.—We have previously reported the synthesis of the complex $[MnL^1]ClO_4 \cdot 3H_2O$. After irradiation of an aqueous solution of it with a 300 W tungsten lamp for 6 h a compound was recovered which X-ray studies revealed to be a manganese(III) complex of the symmetrical Schiff-base ligand salen.[20] We are attempting to study this rearrangement and have succeeded in being able to cocrystallise $[MnL^1(H_2O)_2]ClO_4$ and its rearranged product $[\{Mn(salen)(H_2O)\}_2][ClO_4]_2$ from a recrystallisation of $[MnL^1]ClO_4 \cdot 3H_2O$ from anhydrous Pr^iOH in daylight. Whilst this observation does not shed light on the mechanism of the ligand rearrangement it does, nonetheless, offer confirmation that at one point both the complex containing the unsymmetrical ligand and that containing the symmetrical ligand co-exist.

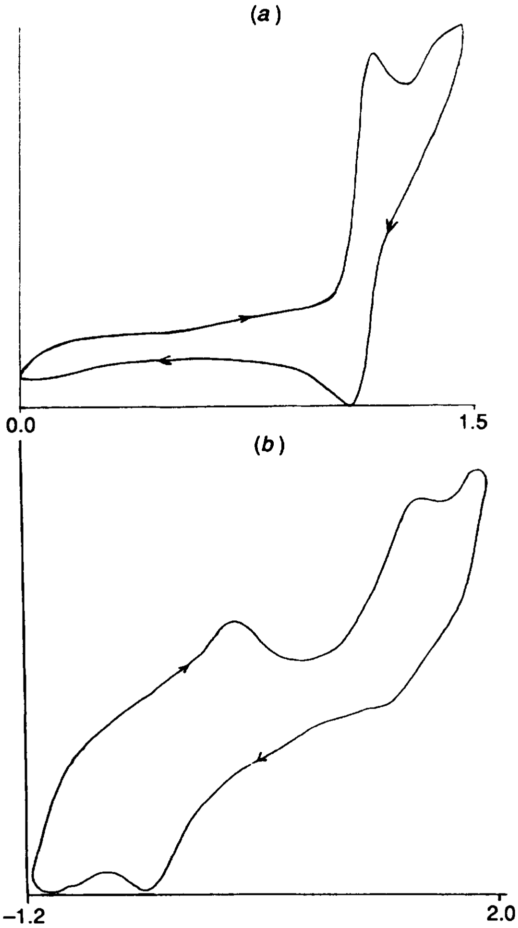


Fig. 2 Cyclic voltammograms for the complexes (a) $[MnL^4]ClO_4 \cdot 2H_2O$ and (b) $[MnL^2]ClO_4 \cdot H_2O$

Crystallographic Studies.—From an ethanol solution of $[MnL^3(H_2O)_2]ClO_4$, crystals suitable for X-ray studies were obtained. The structure of the cation with the atom numbering scheme is shown in Fig. 3. Atomic coordinates and selected bond lengths and angles are given in Tables 5 and 6 respectively. The molecule consists of a monomeric cation with the unsymmetrical Schiff base in the equatorial plane, and two capping water molecules, completing a distorted-octahedral arrangement. There is a molecule of ethanol in the lattice, from the recrystallisation solvent, and a perchlorate is the counter ion.

From an isopropyl alcohol solution of $[MnL^1(H_2O)_2]ClO_4$, crystals suitable for X-ray studies were isolated. Atomic coordinates and selected bond lengths and angles are given in Tables 7 and 8. Two different manganese complexes are present: $[MnL^1(H_2O)_2]ClO_4$, a monomer similar to the compound described above, with the unsymmetrical ligand in the equatorial plane [N–Mn–N 84.7(8)°] and two co-ordinated waters at Mn–O 2.30(2) Å in the apical positions of a distorted-octahedral environment of the metal (Fig. 4); and the centrosymmetric salen manganese dimer $[\{Mn(salen)(H_2O)\}_2][ClO_4]_2$, resulting from the rearrangement described before.[20] One salen oxygen, in addition to contributing to the Schiff-base O–N–N–O square-planar arrangement about manganese,

Table 5 Positional parameters for $[MnL^3(H_2O)_2]ClO_4{\cdot}EtOH$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Mn	0.792 3(1)	0.372 16(6)	0.345 88(7)	C(11)	0.777 4(8)	0.256 5(5)	0.488 8(4)
O(1)	0.479 3(5)	0.312 3(3)	0.314 5(3)	C(12)	0.755 5(8)	0.263 5(5)	0.590 4(4)
O(2)	1.130 5(8)	0.421 5(4)	0.377 1(3)	C(13)	0.742(1)	0.168 9(6)	0.614 7(6)
O(8)	0.760 6(5)	0.527 0(3)	0.410 4(2)	C(14)	0.752(1)	0.062 1(7)	0.539 4(6)
O(11)	0.797 3(5)	0.352 1(3)	0.472 6(2)	C(15)	0.775(1)	0.053 1(6)	0.439 5(6)
O(12)	0.747 0(5)	0.370 1(3)	0.660 0(3)	C(16)	0.774 6(9)	0.464 3(5)	0.076 9(4)
N(2)	0.837 1(7)	0.214 3(4)	0.273 4(3)	C(17)	0.723(1)	0.385 2(7)	0.766 1(5)
N(5)	0.798 8(6)	0.380 8(4)	0.209 0(3)	C(18)	0.715(1)	0.507 1(8)	0.822 8(6)
C(1)	0.824 0(8)	0.135 8(5)	0.309 3(5)	O(20)	0.359 7(6)	0.131 9(4)	0.134 3(3)
C(3)	0.894(1)	0.194 3(5)	0.167 4(4)	C(21)	0.320(1)	0.015 2(7)	0.118 7(6)
C(4)	0.796 9(9)	0.269 4(5)	0.125 5(4)	C(22)	0.314(1)	−0.015(8)	0.213 7(7)
C(6)	0.786 0(7)	0.471 8(5)	0.185 9(4)	Cl	0.222 5(4)	0.199 5(2)	−0.097 9(1)
C(7)	0.774 2(9)	0.578 4(5)	0.265 5(5)	O(3)	0.194(1)	0.103 6(4)	−0.072 1(4)
C(8)	0.759 9(7)	0.602 7(5)	0.367 0(5)	O(4)	0.238(1)	0.162 0(5)	0.200 7(5)
C(9)	0.739(1)	0.717 3(6)	0.440 4(7)	O(5)	0.073(1)	0.264 6(5)	0.078 9(5)
C(10)	0.788 4(8)	0.150 2(5)	0.413 5(4)	O(6)	0.378(1)	0.265 8(6)	−0.046 2(7)

Table 6 Selected interatomic distances (Å) and angles (°) for $[MnL^3(H_2O)_2]^+$

Mn–O(1)	2.265(4)	Mn–O(11)	1.874(4)
Mn–O(2)	2.420(6)	Mn–N(2)	1.970(5)
Mn–O(8)	1.897(3)	Mn–N(5)	1.954(4)
O(1)–Mn–O(2)	175.7(2)	O(8)–Mn–O(11)	91.6(2)
O(1)–Mn–O(11)	90.9(2)	N(2)–Mn–N(5)	83.8(2)
O(1)–Mn–N(2)	88.4(2)		

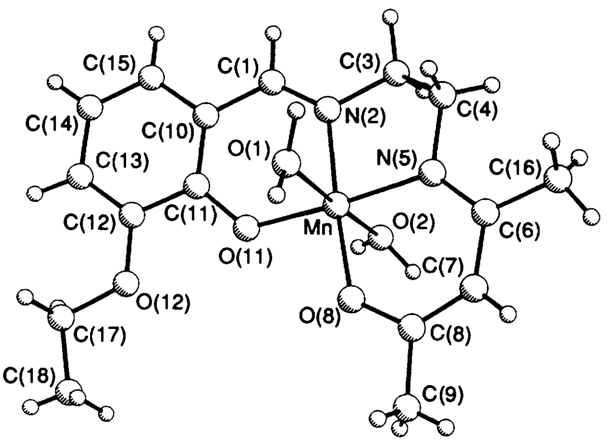


Fig. 3 Structure of the cation $[MnL^3(H_2O)_2]^+$, including the labelling scheme

Mn–O 1.87(1) Å, caps a second manganese, Mn–O 2.36(1) Å, opposite an apical water molecule, Mn–O 2.22(1) Å. The crystal structure is completed by perchlorate anions and Pr^{i}OH of crystallisation, which take part in a complex hydrogen-bonding scheme with alternating monomer and dimers linked into infinite chains by O ··· O separations ranging from 2.71(5) to 2.94(3) Å, see Fig. 5.

Experimental

Ligand Preparation.—The method of preparation of the unsymmetrical Schiff-base ligands is a modification of the method of Costes[19] and is illustrated below.

To the amine 7-amino-4-methyl-5-azahept-3-en-2-one[1] (10 g, 7.0 × 10^{-2} mol) in absolute ethanol (20 cm^3) was added the substituted salicylaldehyde (7.0 × 10^{-2} mol) or 2-hydroxyacetophenone. The mixture was stirred and heated to 40 °C for 10 min, cooled to room temperature, and concentrated under vacuum, where a yellow solid of the unsymmetrical Schiff base, H_2L, precipitated. This was filtered off, washed with ethanol (2 × 20 cm^3), and dried under vacuum at room temperature. The yields were almost quantitative. Analytical and ^{1}H NMR data are given in Table 1.

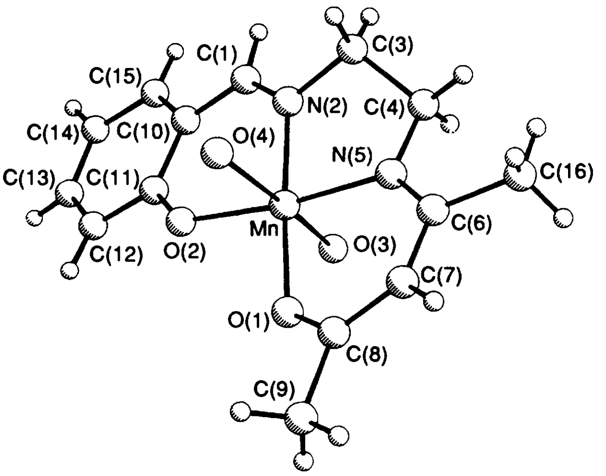


Fig. 4 Structure of the cation $[MnL^1(H_2O)_2]^+$, including the labelling scheme

Complex Preparation.—All the manganese(III) Schiff-base complexes were prepared in an identical manner, employing a modified method originally developed by Boucher and Coe.[21] The general method is outlined below.

To the ligand H_2L (5 mmol), dissolved in ethanol–methanol (1 : 1, 75 cm^3), was added $MnClO_4{\cdot}6H_2O$ (5 mmol). No reaction appeared to occur until the addition of an aqueous solution (2 cm^3) of NaOH (10 mmol), after which the solution progressively darkened. After stirring in the presence of dust-free air for about 5 d a blackish precipitate of manganese oxides and some other side products was filtered off and rejected. The solution was left at room temperature until evaporation resulted in a brown precipitate of the complex. This was washed with cold ethanol (25 cm^3) and dry diethyl ether (2 × 25 cm^3), and dried in vacuum. Yields *ca.* 60%. The crystals of $[MnL^3(H_2O)_2]ClO_4{\cdot}EtOH$ were obtained after recrystallisation from ethanol.

Physical Measurements.—Elemental analyses were performed by the Elemental Analysis Services of the Institute and by the University of Santiago. Infrared spectra were recorded on a Perkin Elmer 180 spectrophotometer. Magnetic susceptibilities were measured in the range 300–70 K by use of a Faraday balance, using a field of 5000 G (0.5 T) and in one case using a

Table 7 Positional parameters for $[MnL^1(H_2O)_2]ClO_4$ and $0.5[\{Mn(salen)(H_2O)\}_2][ClO_4]_2$ with Pr^iOH solvent

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Mn(1)	0.1899(4)	0.4766(3)	0.6265(3)	C(43)	0.183(4)	0.784(3)	0.917(3)
O(1)	0.134(1)	0.456(1)	0.461(1)	Mn(2)	0.0664(4)	0.9291(3)	0.4946(3)
O(2)	0.027(1)	0.378(1)	0.600(1)	O(5)	−0.072(1)	0.830(1)	0.351(1)
O(3)	0.133(1)	0.600(1)	0.646(1)	O(6)	−0.033(1)	0.936(1)	0.561(1)
O(4)	0.232(1)	0.344(1)	0.613(1)	O(7)	0.091(1)	0.808(1)	0.568(1)
N(2)	0.254(2)	0.506(1)	0.798(1)	N(22)	0.184(2)	0.947(1)	0.432(2)
N(5)	0.366(2)	0.573(1)	0.671(2)	N(25)	0.221(2)	1.034(1)	0.635(2)
C(1)	0.190(2)	0.485(2)	0.852(2)	C(21)	0.159(2)	0.910(2)	0.327(2)
C(3)	0.393(3)	0.564(2)	0.865(2)	C(23)	0.318(3)	1.011(2)	0.523(2)
C(4)	0.440(3)	0.632(2)	0.794(3)	C(24)	0.333(2)	1.092(2)	0.622(2)
C(6)	0.414(2)	0.586(2)	0.601(2)	C(26)	0.234(3)	1.054(2)	0.741(2)
C(7)	0.343(2)	0.533(2)	0.484(2)	C(27)	0.033(2)	0.845(2)	0.235(2)
C(8)	0.211(2)	0.473(2)	0.416(2)	C(28)	−0.077(2)	0.806(2)	0.243(2)
C(9)	0.135(3)	0.416(2)	0.282(2)	C(29)	−0.203(2)	0.736(2)	0.146(2)
C(10)	0.059(2)	0.428(2)	0.799(2)	C(30)	−0.210(2)	0.707(2)	0.036(2)
C(11)	−0.025(2)	0.376(2)	0.673(2)	C(31)	−0.103(3)	0.743(2)	0.020(2)
C(12)	−0.157(3)	0.317(2)	0.624(3)	C(32)	0.015(3)	0.809(2)	0.119(3)
C(13)	−0.207(3)	0.314(2)	0.700(3)	C(33)	0.127(2)	0.998(2)	0.760(2)
C(14)	−0.131(3)	0.358(2)	0.819(3)	C(34)	0.003(2)	0.942(2)	0.675(2)
C(15)	0.001(3)	0.420(2)	0.869(2)	C(35)	−0.094(3)	0.892(2)	0.708(2)
C(16)	0.557(3)	0.656(2)	0.644(3)	C(36)	−0.059(3)	0.905(2)	0.826(3)
Cl(1)	0.5481(8)	0.3845(7)	0.7854(8)	C(37)	0.071(3)	0.968(2)	0.915(2)
O(13)	0.482(2)	0.368(2)	0.671(2)	C(38)	0.166(2)	1.015(2)	0.887(2)
O(14)	0.461(2)	0.338(2)	0.829(2)	Cl(2)	0.560(1)	0.935(1)	0.746(1)
O(15)	0.608(3)	0.334(2)	0.805(3)	O(21)	0.504(6)	0.939(4)	0.806(5)
O(16)	0.626(4)	0.485(2)	0.838(3)	O(22)	0.471(4)	0.867(2)	0.643(3)
O(41)	0.276(2)	0.809(1)	0.789(2)	O(23)	0.656(4)	0.921(3)	0.797(5)
C(41)	0.301(3)	0.841(2)	0.910(3)	O(24)	0.610(3)	1.036(2)	0.749(4)
C(42)	0.417(3)	0.834(3)	0.998(3)				

Table 8 Selected interatomic distances (Å) and angles (°) for $[MnL^1(H_2O)_2]^+$ and $[\{Mn(salen)(H_2O)\}_2]^{2+}$

Mn(1)–O(1)	1.91(2)	Mn(2)–O(5)	1.87(1)
Mn(1)–O(2)	1.89(2)	Mn(2)–O(6)	1.87(1)
Mn(1)–O(3)	2.30(2)	Mn(2)–O(6)	2.36(1)
Mn(1)–O(4)	2.30(2)	Mn(2)–O(7)	2.22(1)
Mn(1)–N(2)	1.97(2)	Mn(2)–N(22)	1.96(2)
Mn(1)–N(5)	1.94(2)	Mn(2)–N(25)	1.94(2)
O(1)–Mn(1)–O(2)	92.9(7)	O(2)–Mn(1)–O(4)	88.0(6)
O(1)–Mn(1)–O(3)	93.3(6)	N(2)–Mn(1)–N(5)	84.7(8)
O(1)–Mn(1)–O(4)	89.4(6)	O(5)–Mn(2)–O(6)	95.2(6)
O(1)–Mn(1)–N(2)	176.8(7)	O(5)–Mn(2)–O(7)	92.1(6)
O(1)–Mn(1)–N(5)	93.0(8)	O(5)–Mn(2)–N(22)	90.8(7)
O(2)–Mn(1)–O(3)	86.7(6)	N(22)–Mn(2)–N(25)	82.9(8)

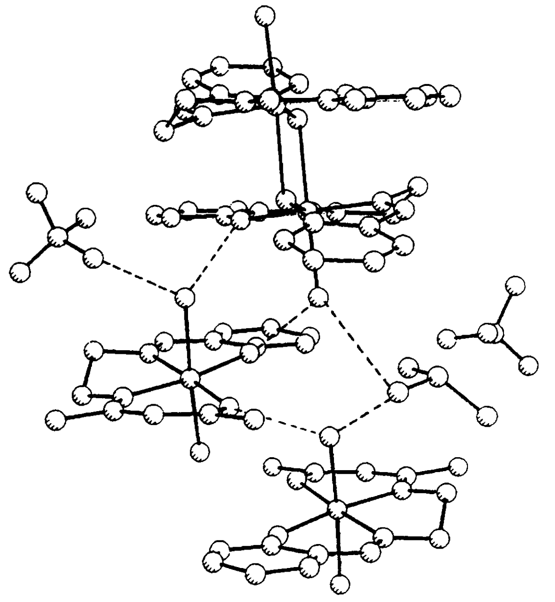


Fig. 5 Crystal structure of the cocrystallised $[MnL^1(H_2O)_2]ClO_4$ and its rearranged product $[\{Mn(salen)(H_2O)\}_2][ClO_4]_2$

SQUID SHE magnetometer in the range 300–2 K. Cyclic voltammetry was performed on a EG and G Princeton Applied Research Corp. Model 362 potentiostat in conjunction with a three-electrode cell fitted with a purge-gas inlet and outlet and consisting of a platinum-wire working electrode, Ag–AgCl reference electrode and a platinum auxiliary electrode, using an acetonitrile solution of the metallic complexes containing 0.2 mol dm^{-3} tetraethylammonium perchlorate as supporting electrolyte. The FAB mass spectra were recorded on a Kratos MS50TC spectrometer connected to a DS 90 data system, using *m*-nitrobenzyl alcohol as solvent.

Crystallographic Measurements.—For the crystals of $[MnL^3(H_2O)_2]ClO_4$ measurements were made on an Enraf-Nonius CAD-4 diffractometer, with monochromated Mo-Kα radiation (λ = 0.710 69 Å) using ω–2θ scans. Structure calculations were performed by direct methods using MITHRIL[22] and 351 parameters were refined by full-matrix least squares with TEXSAN[23] to a final $R = 0.064$, $R' = 0.033$, $w = 1/[\sigma^2(F_o) + 0.03F_o^2]$.

All non-hydrogen atoms were refined anisotropically and hydrogen atoms constrained to chemically reasonable positions. Of the 3743 reflections collected, 3689 were unique (R_{int} = 0.013) and 2334 considered as observed [$F > 3\sigma(F)$]. Residual electron density in the final difference map ranged from −0.40 to 0.65 e $Å^{-3}$.

Crystal data for $[MnL^3(H_2O)_2]ClO_4 \cdot EtOH$, $C_{18}H_{30}ClMnN_2O_{10}$, $M = 524.83$, triclinic, space group $P\bar{1}$ (no. 2), $a = 7.171(3)$, $b = 12.766(5)$, $c = 13.945(6)$, $\alpha = 111.15(3)$, $\beta = 92.88(3)$, $\gamma = 95.78(3)°$, $U = 1179(2)$ Å^3, $Z = 2$, D_c = 1.478 g cm^{-3}, μ(Mo-Kα) = 7.03 cm^{-1}, $F(000) = 548$.

In the case of the crystal with two different manganese complexes the measurements were made on a Rigaku AFC6S diffractometer with monochromated Mo-Kα radiation (λ = 0.710 69 Å) using ω–2θ scans. A total of 6958 reflections were recorded of which 1476 were considered observed [$I > 2\sigma(I)$].

Residual density in the final Fourier difference maps ranged from −0.43 to 0.45 eÅ^{-3}. Structure calculations were performed by direct methods using MITHRIL[22] and refined by full-matrix least squares with TEXSAN[23] to a final $R = 0.075$, $R' = 0.081$, $w = 1/[\sigma^2(F_o) + 0.3F^2]$.

Crystal data. $[\text{MnL}^1(\text{H}_2\text{O})_2]\text{ClO}_4 + 0.5[\{\text{Mn(salen)}(\text{H}_2\text{O})\}_2][\text{ClO}_4]_2 + \text{Pr}^i\text{OH}$ solvent, $C_{33}H_{44}Cl_2Mn_2N_4O_{16}$, $M = 933.51$, triclinic, space group $P\bar{1}$ (no. 2), $a = 13.26(2)$, $b = 15.01(2)$, $c = 13.00(1)$ Å, $\alpha = 95.2(1)$, $\beta = 113.45(8)$, $\gamma = 115.3(1)^\circ$, $U = 2037(2)$ Å^3, $Z = 2$, $D_c = 1.525$ g cm^{-3}, $\mu(\text{Mo-K}\alpha) = 7.98$ cm^{-1}, $F(000) = 968$.

Additional material for both complexes available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

References

1 M. L. Ludwig, K. A. Pattridge and W. C. Stallings, in *Manganese in Metabolism and Enzyme Function*, eds. V. L. Schramm and F. C. Wedler, Academic Press, New York, 1986, ch. 21, p. 405.
2 W. F. Beyer and I. Fridivich, in *Manganese in Metabolism and Enzyme Function*, eds. V. L. Schramm and F. C. Wedler, Academic Press, New York, 1986, ch. 12, p. 193.
3 G. C. Dismukes, in *Manganese in Metabolism and Enzyme Function*, eds. V. L. Schramm and F. C. Wedler, ch. 16, p. 275
4 V. L. Pecoraro, *Photochem. Photobiol.*, 1986, **48**, 249.
5 C. Christmas, J. B. Vincent, J. C. Huffman, G. Christou, H.-R. Chang and D. N. Hendrickson, *J. Chem. Soc., Chem. Commun.*, 1987, 1303.
6 A. R. Schake, J. B. Vincent, Q. Li, P. D. W. Boyd, K. Folting, J. C. Huffman, D. N. Hendrickson and G. Christou, *Inorg. Chem.*, 1989, **28**, 1915.
7 C. Christmas, J. B. Vincent, H.-R. Chang, J. C. Huffman, G. Christou and D. N. Hendrickson, *J. Am. Chem. Soc.*, 1988, **110**, 823.
8 F. M. Ashmawy, C. A. McAuliffe, R. V. Parish and J. Tames, *J. Chem. Soc., Chem. Commun.*, 1984, 14; *J. Chem. Soc., Dalton Trans.*, 1985, 1391.
9 K. Wieghardt, M. Köppen, B. Nuber and J. Weiss, *J. Chem. Soc., Chem. Commun.*, 1986, 1530.
10 K. Wieghardt, U. Bossek, J. Bonvoisin, P. Beauvillain, J.-J. Girerd, B. Nuber, J. Weiss and J. Heinze, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 1030.
11 M. A. Collins, D. J. Hodgson, K. Michelsen and D. K. Towle, *J. Chem. Soc., Chem. Commun.*, 1987, 1659.
12 K. Wieghardt, U. Bossek, L. Zsolnai, G. Huttner, G. Blondin, J.-J. Girerd and F. Babonneau, *J. Chem. Soc., Chem. Commun.*, 1987, 651.
13 H.-R. Chang, H. Diril, M. J. Nilges, X. Zhang, J. A. Potenza, H. J. Schugar, D. N. Hendrickson and S. S. Isied, *J. Am. Chem. Soc.*, 1988, **110**, 625.
14 J. A. Bonadies, M. L. Kirk, M. S. Lah, D. P. Kessissoglou, W. E. Hatfield and V. L. Pecoraro, *Inorg. Chem.*, 1989, **28**, 2037.
15 M. K. Awad and A. B. Anderson, *J. Am. Chem. Soc.*, 1989, **111**, 802.
16 J. P. Costes and G. Cros, *C.R. Hebd. Seances Acad. Sci., Ser. 2*, 1982, **294**, 173.
17 J. P. Costes, *Inorg. Chim. Acta*, 1987, **130**, 17.
18 J. P. Costes and M. I. Fernandez Garcia, *Transition Met. Chem.*, 1988, **13**, 131.
19 J. P. Costes, *Bull. Soc. Chim. Fr.*, 1986, 78.
20 A. Garcia-Deibe, A. Sousa, M. R. Bermejo, P. P. Mac Rory, C. A. McAuliffe, R. G. Pritchard and M. Helliwell, *J. Chem. Soc., Chem. Commun.*, 1991, 728.
21 L. J. Boucher and C. G. Coe, *Inorg. Chem.*, 1975, **14**, 1289.
22 MITHRIL, C. J. Gilmore, *J. Appl. Crystallogr.*, 1984, **17**, 42.
23 TEXSAN-TEXRAY Structure Analysis Package, Molecular Structure Corporation, Houston, TX, 1985.

Received 24*th August* 1992; *Paper* 2/04563J