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Electronic and steric effects in manganese Schiff-base complexes as models for the water oxidation complex in photosystem II. The isolation of manganese-(II) and -(III) complexes of 3- and 3,5-substituted *N*,*N*′-bis(salicylidene)ethane-1,2-diamine (H_2salen) ligands†

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Manganese-(II) and -(III) complexes of substituted *N*,*N*′-bis(salicylidene)ethane-1,2-diamine (H_2salen) ligands H_2L (substituents are in the 3, 5 or 3,5 positions of the phenyl rings of the salen moiety) have been prepared and thoroughly characterised. The reaction of $Mn(ClO_4)_2{\cdot}6H_2O$ with H_2L in ethanol in air normally leads to manganese(III) complexes ligated by both the N_2O_2 ligand and water molecule(s). However, by employing electron-withdrawing substituents on the ligand, *e.g.* 3-Br,5-NO_2, a manganese(II) complex can be obtained. A 'borderline' ligand is represented by the 5-NO_2 derivative (nsalen), which produces a manganese(II) complex contaminated with a small amount of a manganese(III) species. Using a more rigorous oxidising agent in the synthesis, $[Fe(\eta\text{-}C_5H_5)_2][FeCl_4]$, drives the reaction totally to a manganese(III) complex [Mn(nsalen)Cl(H_2O)]. In addition to magnetic susceptibility studies, cyclic voltammetry has been employed. All the complexes exhibit an oxidation and reduction peak, the reversible character being confirmed by pulse voltammetry. Pulse voltammetry also confirmed the nature of the manganese(II) species [Mn(bnsalen)(H_2O)$_2$]·2H_2O [H_2bnsalen = *N*,*N*′-bis(3-bromo-5-nitrosalicylidene)ethane-1,2-diamine] and that a slight amount of a manganese(III) species is present in [Mn(nsalen)(H_2O)$_2$]·2H_2O. Six complexes have been crystallographically characterised. Despite the retention of an octahedral manganese environment in all of them, the supramolecular structures exhibit a wide diversity. The 3,5-dichloro and 5-bromo salen complexes containing co-ordinated water display combined π and hydrogen bonding, as well as dimerisation. The complex [{Mn(μ-dbsalen)(μ-O)}$_2$] (dbsalen = 3,5-dibromo derivative) offers an alternative bridging arrangement, and [Mn(bsalen)(MeOH)($OClO_3$)]·H_2O (bsalen = 5-bromo derivative) highlights the versatility of the manganese centre in these systems where, unexpectedly, perchlorate is co-ordinated in place of a lattice water. A more subtle rearrangement of supramolecular structure is obtained in [Mn(nsalen)Cl(H_2O)] where the usual combination of π- or hydrogen-bonding interaction is modified by the corresponding ability of the 5-NO_2 substituent.

The continuing interest in the co-ordination chemistry of manganese is still largely driven by the desire to prepare functional models of manganese-containing biological systems.[1,2] Arguably the greatest success in these studies has been achieved in the preparation of a number of functional non-haem catalase mimics,[3] whilst the dreams of many bioinorganic chemists lie in the preparation of functional models of the oxygen-evolving complex (OEC) found within photosystem II of green plants and cyanobacteria. A wealth of biophysical data has been obtained for these systems and has been used for the basis of these model studies resulting in the explosion in the co-ordination chemistry of manganese over the last ten years. Much of this work has been reviewed extensively in a number of excellent book and review articles.[2,4–7] These ongoing studies continue to produce compounds of exceptional interest. Two notable recent examples include Mn_4 cubanes containing extremely rare examples of monodentate μ_3-N_3^- and -OCN^- groups[8] and an octadecanuclear manganese cluster with an unexpected $S = 0$ ground state.[9]

Our own studies in this area were initiated by Calvin's flawed report of the photolytic activity of binuclear manganese systems,[10] the so-called minimal model. The rationale for this model is that the oxidation of water is a four-electron process and thus the minimum requirement for this is two manganese ions cycling between the +II and +IV states. With this in mind we sought to prepare complexes of manganese with tetradentate N_2O_2 donor set Schiff-base ligands employing the poorly co-ordinating perchlorate counter-ion, to enable water to complete the co-ordination sphere of manganese. We hoped that there would be a degree of intermolecular interaction between these species leading to dimers. These compounds did indeed prove to possess the ability to activate water co-ordinated to manganese, in the presence of photoactivated *p*-benzoquinone, to produce oxygen.[11] However, it was not until another seven years that we were able crystallographically to characterise such an aqua-linked dimeric species and finally propose a mechanism for oxygen evolution from these compounds.[12]

Owing to the enormous potential of our findings we have continued our studies and have begun to investigate the effects on structure and oxidation level in the resultant manganese complexes of varying substituents about the aromatic ring of the Schiff-base ligands.[13] Herein we report the preparation and

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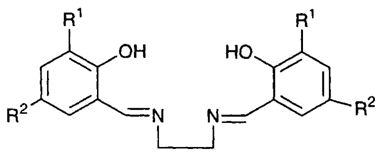
† Dedicated to The Royal University of Santiago de Compostela in the year of its 500th Anniversary.

Non-SI units employed: $\mu_B \approx 9.27 \times 10^{-24}$ J T^{-1}, G = 10^{-4} T.

Table 1 Analytical and other data for the complexes

Complex	Analysis (%)[a] C	H	N	μ_{eff}/μ_B	FAB[b] m/z	$E^{\circ c}$
$[Mn(salen)(H_2O)_2]ClO_4 \cdot H_2O$	41.1 (40.5)	3.6 (4.2)	5.5 (5.9)	4.8	321	−0.225
$[Mn(eosalen)(H_2O)_2]ClO_4$	44.3 (44.4)	4.9 (4.8)	5.1 (5.2)	4.8	409	−0.209
$[Mn(csalen)(H_2O)_2]ClO_4$	38.6 (36.5)	2.5 (3.0)	5.5 (5.3)	4.9	390	−0.136
$[Mn(bsalen)(H_2O)_2]ClO_4$	31.1 (31.1)	1.9 (2.6)	4.5 (4.5)	4.8	479	−0.134
$[Mn(dcsalen)(H_2O)_2]ClO_4$	32.8 (32.2)	2.5 (2.4)	4.5 (4.7)	4.7	459	0.031
$[Mn(dbsalen)(H_2O)_2]ClO_4$	25.3 (24.8)	1.0 (1.8)	3.3 (3.6)	5.0	637	−0.118
$[Mn(bcsalen)(H_2O)_2]ClO_4$	30.2 (28.1)	2.2 (2.0)	4.0 (4.1)	4.7	547	0.035
$[Mn(bmosalen)(H_2O)_2]ClO_4 \cdot 2H_2O$	30.5 (30.4)	2.5 (3.4)	3.9 (3.9)	4.7	539	—
$[Mn(nsalen)(H_2O)_2] \cdot 2H_2O$	40.0 (39.8)	3.0 (4.1)	11.1 (11.6)	5.4	411	0.093
$[Mn(bnsalen)(H_2O)_2] \cdot 2H_2O$	28.2 (27.3)	2.1 (2.0)	8.3 (8.0)	5.7	569	0.267

[a] Found (calculated). [b] Peaks corresponding to $[MnL]^+$. [c] Electrode potentials (V *vs.* SCE) for $Mn^{II} \longrightarrow Mn^{III}$.



H_2salen	$R^1 = R^2 = H$
H_2eosalen	$R^1 = EtO, R^2 = H$
H_2csalen	$R^1 = H, R^2 = Cl$
H_2bsalen	$R^1 = H, R^2 = Br$
H_2dcsalen	$R^1 = R^2 = Cl$
H_2dbsalen	$R^1 = R^2 = Br$
H_2bcsalen	$R^1 = Br, R^2 = Cl$
H_2bmosalen	$R^1 = MeO, R^2 = Br$
H_2nsalen	$R^1 = H, R^2 = NO_2$
H_2bnsalen	$R^1 = Br, R^2 = NO_2$

remarkable structural chemistry of a series of complexes prepared from such substituted derivatives of *N*,*N*′-bis(salicylidene)ethane-1,2-diamine (H_2salen).

Results and Discussion

The tetradentate Schiff bases, H_2L, used in this study readily react with manganese perchlorate, in the presence of sodium hydroxide and air, to give compounds which can be formulated as $[MnL(H_2O)_2]ClO_4 \cdot nH_2O$, where L signifies the ligand in its dianionic form. However, when a nitro substituent *para* to the phenolic oxygen is present complexes formulated as $[MnL(H_2O)_2] \cdot 2H_2O$ are isolated indicating that the oxidising conditions involved in the Boucher method[14] are not powerful enough to achieve oxidation to manganese(III). This oxidation, however, can be achieved by other chemical means (see below). Analytical, mass spectral, magnetic susceptibility and electrochemical data for the complexes are given in Table 1. The analytical data for the complexes were sometimes slightly unsatisfactory when compared with the theoretical values. We attribute this to the diverse mixture of structural chemistry together with the mixed oxidation levels possible which must contaminate the compounds (see below). In our experience bulk products from these reactions are normally of the stoichiometry given in Table 1[11–13] and it should be stressed that these data are reproducible indicating that such contamination is a consistent phenomenon.

All compounds exhibit peaks in their fast atom bombardment (FAB) mass spectra relating to fragments of the form $[MnL]^+$ which, in combination with a shift in the imine bands of the complexes in the infrared spectra to lower energy compared with the free base values, indicate that co-ordination has occurred. For all complexes the bands centred at *ca.* 3450 cm^{-1} can be assigned to a combination of the ν(O–H) modes of co-ordinated and lattice water. Broad unsplit bands centred at 1100 cm^{-1} as well as bands at 630 cm^{-1} in the spectra of compounds formulated as $[MnL(H_2O)_2]ClO_4 \cdot nH_2O$ are indicative of the presence of the unco-ordinated perchlorate counter ion.

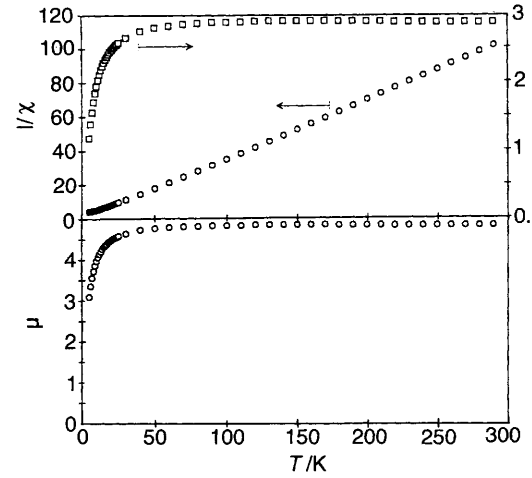


Fig. 1 Plots of $1/\chi$ (○), χT (□) and μ_{eff} *versus* temperature for $[Mn(bsalen)(H_2O)_2]ClO_4$

This is confirmed by magnetic susceptibility measurements on the complexes. Those formulated as $[MnL(H_2O)_2]ClO_4 \cdot nH_2O$ exhibit room-temperature magnetic moments in the range 4.7–5.0 μ_B, close to the spin-only value of 4.9 μ_B expected for a magnetically dilute high-spin d^4 manganese(III) ion. In contrast the complexes of the 5-NO_2-substituted ligands show markedly elevated moments. That of $[Mn(bnsalen)(H_2O)_2] \cdot 2H_2O$ is 5.7 μ_B which is close to the spin-only value of 5.9 μ_B expected for the high-spin d^5 magnetically dilute manganese(II) ion. On the other hand the magnetic moment of $[Mn(nsalen)(H_2O)_2] \cdot 2H_2O$ of 5.4 μ_B is rather low, and is intermediate between the spin-only values of high-spin d^4 and d^5 systems. This may well be a result of a small amount of manganese(III) impurity in the sample* as is indicated by cyclic voltammetry (see below). The temperature-dependent magnetic susceptibility of $[Mn(bsalen)(H_2O)]ClO_4$ was measured in the temperature range 5–299 K. The compound shows behaviour typical of the Curie–Weiss law (Fig. 1) with a value of $\theta = -3.6$ K, showing that there are antiferromagnetic interactions in the solid state.

Electrochemical studies

For all the compounds studied a one-electron reduction–oxidation wave is observed, which at slow scan rates of about

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* A referee pointed out that small contaminants may be the reason for the relatively low magnetic moments.

0.02 V s^{-1} is reversible. A typical voltammogram of $[Mn(dcsalen)(H_2O)_2]ClO_4$ is given in Fig. 2(*a*). The reversible nature of these systems was confirmed by pulse voltammetry [Fig. 2(*b*) and (*c*)]. In all cases except for $[Mn(bnsalen)(H_2O)_2]{\cdot}2H_2O$ and $[Mn(nsalen)(H_2O)_2]{\cdot}2H_2O$, when the initial potentials were more negative than the wave voltage range, anodic and cathodic currents were observed with reference to the current observed without electroactive compounds [Fig. 2(*b*)]. However, when the initial potentials were more positive than the wave range only cathodic currents were observed [Fig. 2(*c*)]. These data show that in solution there are only the oxidised forms of the implied redox systems, *viz.* additional proof that the compounds are of manganese(III).

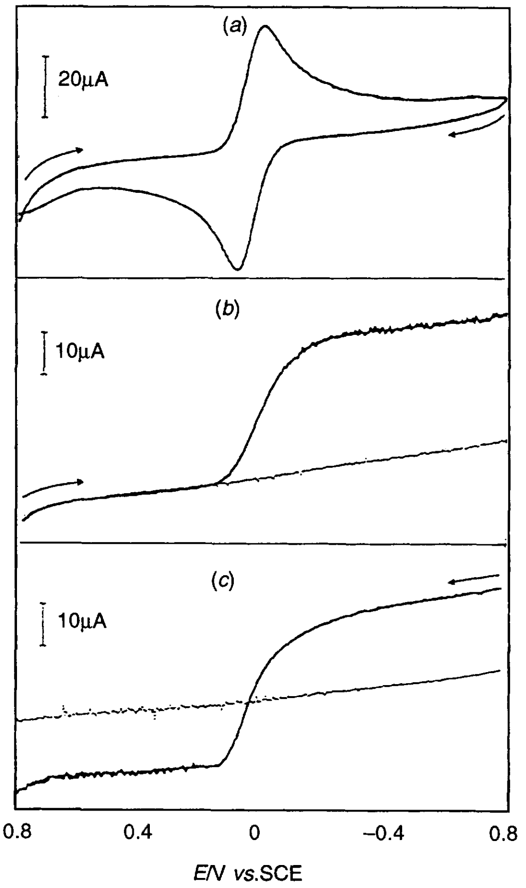

Fig. 2 Voltammograms of $[Mn(dcsalen)(H_2O)_2]ClO_4$, using (*a*) cyclic voltammetry; (*b*) normal pulse voltammetry with a pulse base potential of 0.8 V *versus* the saturated calomel electrode (SCE) and (*c*) normal pulse voltammetry with a pulse base potential of −0.8 V *versus* SCE

In the case of $[Mn(bnsalen)(H_2O)_2]{\cdot}2H_2O$ when an anodic scan was used in normal pulse polarographic voltammetry only an anodic current was recorded. However, when a cathodic potential scan was performed both anodic and cathodic currents were observed [Fig. 3(*a*) and (*b*) respectively]. This indicates a complex of manganese(II). The behaviour of $[Mn(nsalen)(H_2O)_2]{\cdot}2H_2O$ was similar [Fig. 3(*c*) and (*d*)] but the presence of a small cathodic charge during the anodic scan indicates that a small quantity of a manganese(III) species is present. The presence of such a species is easily rationalised by observing the values of the Mn^{II}–Mn^{III} redox potentials for the compounds (Table 1). The effect of varying the substituents about the phenyl ring in the ligands is to produce a window of 492 mV for this redox process. Clearly the borderline for the aerial oxidation of the initially formed manganese(II) complexes to the desired manganese(III) species, involved in the Boucher method,[14] is a Mn^{II}–Mn^{III} couple of the order of 0.093 V. This is based on the observation of slight manganese(III) contamination in the complex formulated as $[Mn(nsalen)(H_2O)_2]{\cdot}2H_2O$. Such changes in the redox potential of manganese complexes have been observed for other complexes containing Schiff-base ligands,[15] and are easily rationalised in terms of the substituents about the phenyl ring. Manganese(II) can be produced by employing strong electron-withdrawing groups *e.g.* nitro, whilst the corollary that strong donor substituents should produce manganese(IV) is yet to be investigated.

Crystal structure of $[\{Mn(dcsalen)(H_2O)_2\}_2][ClO_4]_2$ 1

The structure of complex **1** comprises the planar tetradentate Schiff-base ligands tightly bound to manganese(III) *via* $Mn–N_{imine}$ bonds of 1.963(4) and 1.973(4) Å and $Mn–O_{phenol}$ bonds of 1.889(3) and 1.871(3) Å. The co-ordination spheres of the distorted-octahedral manganese centres are then completed by capping *trans* water molecules $Mn–O_{water}$ 2.220(4) and 2.272(4) Å as shown in Fig. 4. Pairs of these molecules associate *via* a combination of π-aryl stacking interactions and hydrogen bonds between capping water molecules and phenoxy oxygen atoms forming dimers which resemble the bis-μ-aqua-bridged dimers proposed originally by us as the active species in the

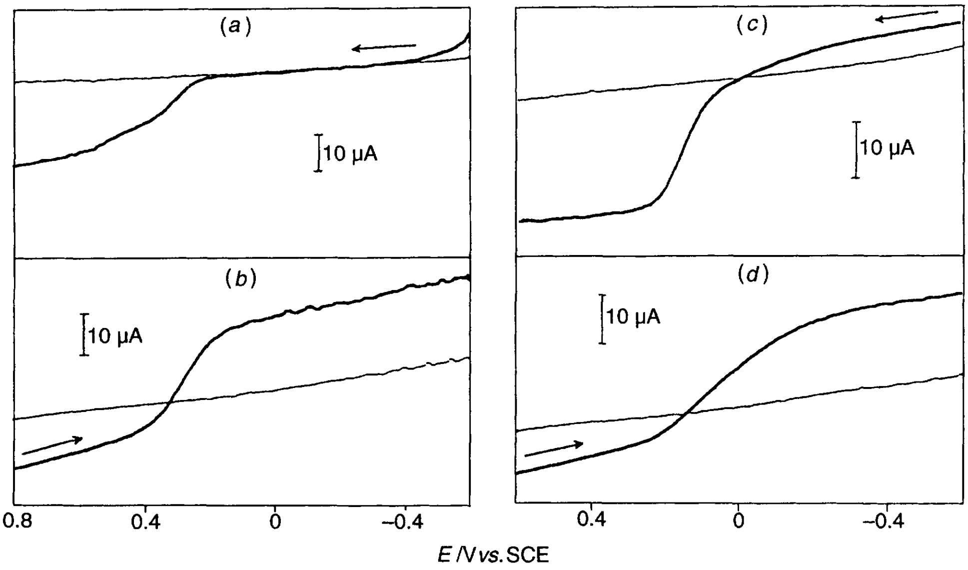

Fig. 3 Pulse voltammograms of $[Mn(bnsalen)(H_2O)_2]$ using pulse base potential of −0.6 (*a*) and 0.6 V (*b*) and of $[Mn(nsalen)(H_2O)_2]$ using pulse base potentials of −0.6 (*c*) and 0.6 V (*d*) *versus* SCE

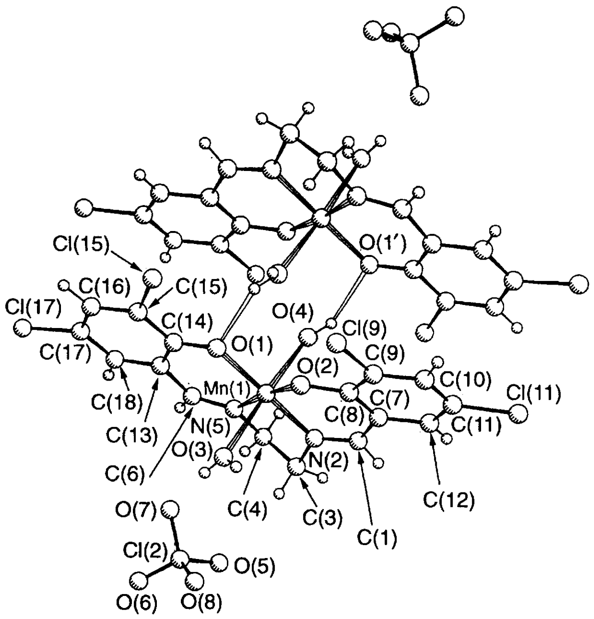

Fig. 4 Crystal structure of $[\{Mn(dcsalen)(H_2O)_2\}_2][ClO_4]_2$ **1**

Table 2 Selected bond lengths (Å) and angles (°) for complex **1** with estimated standard deviations (e.s.d.s) in parentheses

Mn(1)–O(1)	1.889(3)	VMn(1)–N(5)	1.973(4)
Mn(1)–O(2)	1.871(3)	Mn(1)–O(3)	2.272(4)
Mn(1)–N(2)	1.963(4)	Mn(1)–O(4)	2.220(4)
O(1)–Mn(1)–O(2)	93.3(1)	O(2)–Mn(1)–N(5)	174.0(2)
O(1)–Mn(1)–O(3)	92.3(1)	O(3)–Mn(1)–O(4)	175.9(2)
O(1)–Mn(1)–O(4)	91.2(1)	O(3)–Mn(1)–N(2)	90.4(1)
O(1)–Mn(1)–N(2)	173.9(1)	O(3)–Mn(1)–N(5)	87.6(2)
O(1)–Mn(1)–N(5)	92.0(1)	O(4)–Mn(1)–N(2)	85.9(1)
O(2)–Mn(1)–O(3)	89.2(2)	O(4)–Mn(1)–N(5)	90.1(2)
O(2)–Mn(1)–O(4)	92.7(2)	N(2)–Mn(1)–N(5)	82.7(2)
O(2)–Mn(1)–N(2)	92.2(1)		

photolytic splitting of water in these systems.[11] The characterisation of this structure enabled us to propose a mechanism for the evolution of oxygen from these complexes.[12] The bridging hydrogen-bonding scheme involves O···O interactions of 2.901(5), H···O 2.06(7) Å and O–H···O angles of 154(6)°. The overall hydrogen-bonding scheme is completed by two hydrogen bonds from the non-bridging water molecules to neighbouring perchlorate anions, O···O 2.869(8) and 2.740(6) Å, O···H distances of 2.28(9) and 1.94(8) Å and O–H···O angles of 138(9) and 170(6)°. This contrasting water environment is reflected in a significant difference in $Mn-OH_2$ bond lengths, 2.272(4) Å for the water molecule involved in perchlorate hydrogen bonding compared with 2.220(4) Å for the bridging water molecules. Selected bond lengths and angles are given in Table 2.

Crystal structures of $[\{Mn(bsalen)(H_2O)_2\}_2][ClO_4]_2 \cdot 2H_2O$ 2 and $[\{Mn(bsalen)(H_2O)\}_2][ClO_4]_2 \cdot 2H_2O$ 3

Recrystallisation of the species formulated as $[Mn(bsalen)(H_2O)_2]ClO_4$ from MeOH–Pr^{i}OH resulted in the isolation of crystals which contain two independent molecules, **2** and **3**, in the unit cell. We have previously characterised a species in which partial rearrangement of an unsymmetrical tetradentate Schiff base to form its symmetrical analogue resulted in the presence of complexes of both bases in the unit cell.[16] This, however, is the first example of a unit cell containing two distinct molecules as a result of the altered co-ordination properties of the ligand without a chemical change (*e.g.* rearrangement, deprotonation of a further donor atom) in this class of compound.

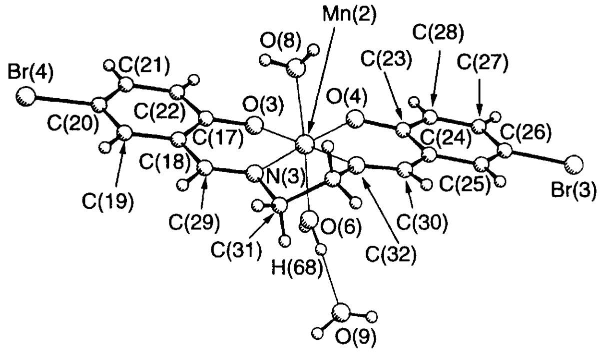

Fig. 5 Crystal structure of $[\{Mn(bsalen)(H_2O)_2\}_2][ClO_4]_2 \cdot 2H_2O$ **2**

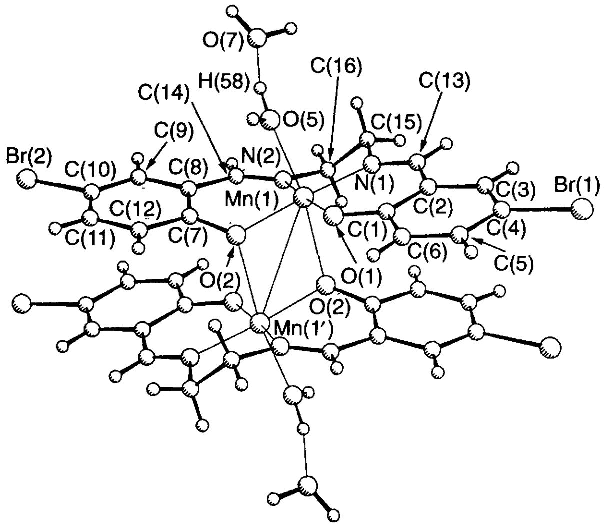

Fig. 6 Crystal structure of $[\{Mn(bsalen)(H_2O)\}_2][ClO_4]_2 \cdot 2H_2O$ **3**

The first molecule, **2**, is shown in Fig. 5 to consist of a 'pseudo' aqua-bridged dimer which is essentially identical to **1**. The $Mn-N_{imine}$ bond lengths of 1.976(8) and 1.977(9) Å together with $Mn-O_{phenol}$ bond lengths of 1.875(7) and 1.877(7) Å are essentially identical, as are $Mn-O_{water}$ bonds of 2.216(7) and 2.228(7) Å. It is interesting that this compound should exist as a dimer as the complex of the related ligand in which the imine nitrogen atoms are linked by a propane rather than an ethane bridge exists as a polymer,[13] as does the related complex of the 5-Cl derivative of propane.[17] This seems to indicate that extremely small ligand changes which have no effect on the 'co-ordination mode' can have quite profound effects on the structural chemistry observed in the resultant complexes. Selected bond lengths and angles for **2** are given in Table 3.

The second molecule **3** is shown in Fig. 6. It consists of a centrosymmetric dimer in which the manganese atoms are linked by μ-phenoxy bridges from one of the phenolic oxygen atoms of each Schiff-base ligand to the opposite metal centre resulting in μ-phenoxy Mn–O bonds of 2.419(7) Å and a Mn···Mn separation of 3.350(3) Å. The co-ordination sphere around each manganese atom is then completed by $Mn-N_{imine}$ bonds of 1.977(8) and 1.983(9) Å, a $Mn-O_{phenol}$ bond of 1.893(7) Å and a capping water molecule $Mn-O_{water}$ bond of 2.143(7) Å. The equatorial atoms about the two manganese atoms are coplanar; the manganese atoms are 0.0952 Å out of this plane, consequently the environment around each manganese atom can be described as a distorted $N_2O_2O'_2$ octahedron. Although we have previously isolated such μ-phenoxy dimers,[13] we have never observed such structural chemistry when large sterically demanding substituents are present about the aryl rings of the Schiff-base ligands. In fact we have even proposed that such substitution prevents the formation of such dimers. The isolation of this compound is thus remarkable, more so for the mixed nature of the molecules in the unit cell. These two distinct species are linked by hydrogen bonds between O(1) and water O(6) and O(3) and water O(5) to form infinite chains of the form **2**···**3**···**2**···**3**···, *etc.*, see Fig. 7.

Crystal structure of [{Mn(μ-dbsalen)(μ-O)}$_2$]2MeCN 4

The structure of complex **4** is shown in Fig. 8 and is quite remarkable. It consists of a binuclear manganese complex bridged by two Schiff-base ligands acting as N,O donors to each manganese centre. To our knowledge there has only been one example of a complex containing a bridging Schiff base of this type reported,[18] [$Mn_2(salpn)_3$] [H_2salpn = *N*,*N*′-bis(salicylidene)propane-1,3-diamine], in which the manganese centres are tethered by the propane backbone between the imine nitrogen donors. Clearly in this case, unlike that in [$Mn_2(salpn)_3$], the manganese centres will not be magnetically independent as the co-ordination spheres of the manganese atoms are completed by two *cis*-bridging μ-oxo groups. The assignment of these bridging atoms as μ-oxo rather than μ-hydroxo, μ-aqua or a mixture of these is based on the bond lengths, angles and symmetry about the central core. The Mn–O(3) bridging bonds of 1.791(4) and 1.806(6) Å, the Mn–O(3)–Mn′ angle of 96.7(2)° and the Mn··· Mn separation of 2.688(1) Å are all consistent with a di-μ-oxo-bridged manganese(IV) complex.[2,18] The co-ordination sphere of each manganese atom is then completed by two dbsalen ligands, each donating half of its N_2O_2 donor set to each of the manganese atoms at *cis* sites. This necessitates a twist in the C–N bonds in the ligands resulting in a dihedral angle between the planes of the phenyl rings of the ligands of 122.1(3)°. Therein lies the remarkable feature of the structure. Previously we had assumed that there was insufficient flexibility in this type of ligand to allow such co-ordination and accepted that such ligands would only occupy the equatorial plane about the manganese atom; clearly this assumption is no longer valid and this alternative structural motif must be considered in future studies. The $Mn-O_{phenol}$ bond lengths of 1.919(6) and 1.923(4) Å and the $Mn-N_{imine}$ bond lengths of 2.003(8) and 2.012(7) Å are typical of such manganese(IV) systems. Other selected bond lengths and angles are given in Table 4.

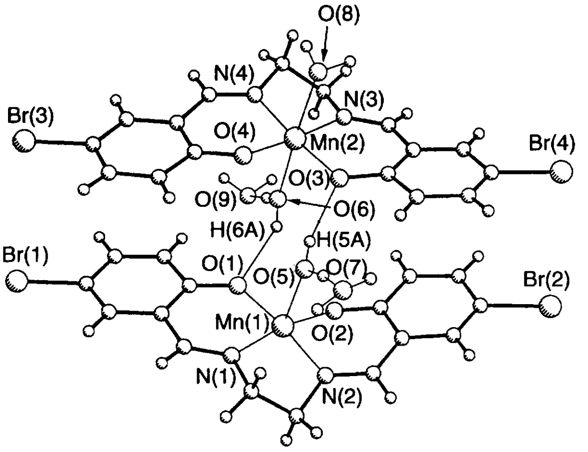

Fig. 7 The unit cell of the species crystallised from [Mn(bsalen)(H_2O)$_2$]ClO_4 showing the hydrogen bonding between **2** and **3**

Crystal structure of [Mn(dbsalen)(MeOH)($OClO_3$)]·H_2O 5

The structure of complex **5** is given in Fig. 9. The molecule comprises a manganese(III) centre co-ordinated by the nearly planar Schiff-base ligand [dihedral angle between the planes of the phenyl rings is 19(1)°] with the $Mn-O_{phenol}$ bond lengths of 1.88(1) and 1.86(2) Å together with $Mn-N_{imine}$ bond lengths of 1.95(1) and 1.97(1) Å, which are unexceptional. The co-

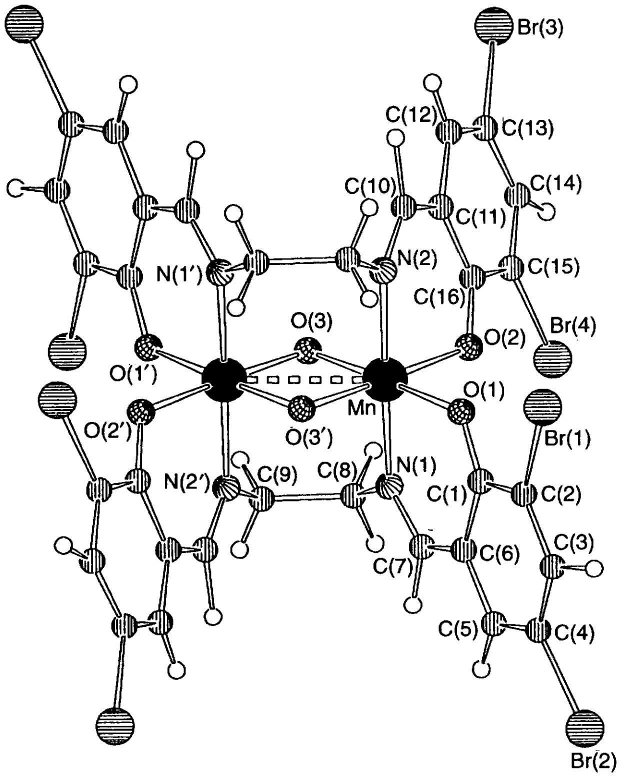

Fig. 8 Crystal structure of [{Mn(μ-dbsalen)(μ-O)}$_2$]·2MeCN **4**

Table 3 Selected bond lengths (Å) and angles (°) for complexes **2** and **3**

2

Mn(2)–O(3)	1.875(7)	Mn(2)–O(8)	2.228(7)
Mn(2)–O(4)	1.877(7)	Mn(2)–N(3)	1.976(8)
Mn(2)–O(6)	2.216(7)	Mn(2)–N(4)	1.977(9)
O(3)–Mn(2)–O(4)	92.4(3)	O(4)–Mn(2)–N(4)	92.0(3)
O(3)–Mn(2)–O(6)	90.7(3)	O(6)–Mn(2)–O(8)	175.6(3)
O(3)–Mn(2)–O(8)	89.4(3)	O(6)–Mn(2)–N(3)	89.0(3)
O(3)–Mn(2)–N(3)	92.7(3)	O(6)–Mn(2)–N(4)	90.9(3)
O(3)–Mn(2)–N(4)	175.3(3)	O(8)–Mn(2)–N(3)	86.6(3)
O(4)–Mn(2)–O(6)	91.5(3)	O(8)–Mn(2)–N(4)	88.7(3)
O(4)–Mn(2)–O(8)	93.0(3)	N(3)–Mn(2)–N(4)	82.9(4)
O(4)–Mn(2)–N(3)	174.9(3)		

3

Mn(1)–O(1)	1.893(7)	Mn(1)–N(1)	1.977(8)
Mn(1)–O(2)	1.906(6)	Mn(1)–N(2)	1.983(9)
Mn(1)–O(5)	2.143(7)		
O(1)–Mn(1)–O(2)	96.0(3)	O(2)–Mn(1)–N(1)	169.1(3)
O(1)–Mn(1)–O(5)	93.4(3)	O(2)–Mn(1)–N(2)	89.8(3)
O(1)–Mn(1)–N(1)	91.8(3)	O(5)–Mn(1)–N(1)	94.4(3)
O(1)–Mn(1)–N(2)	172.8(3)	O(5)–Mn(1)–N(2)	90.5(3)
O(2)–Mn(1)–O(5)	92.7(3)	N(1)–Mn(1)–N(2)	81.9(3)

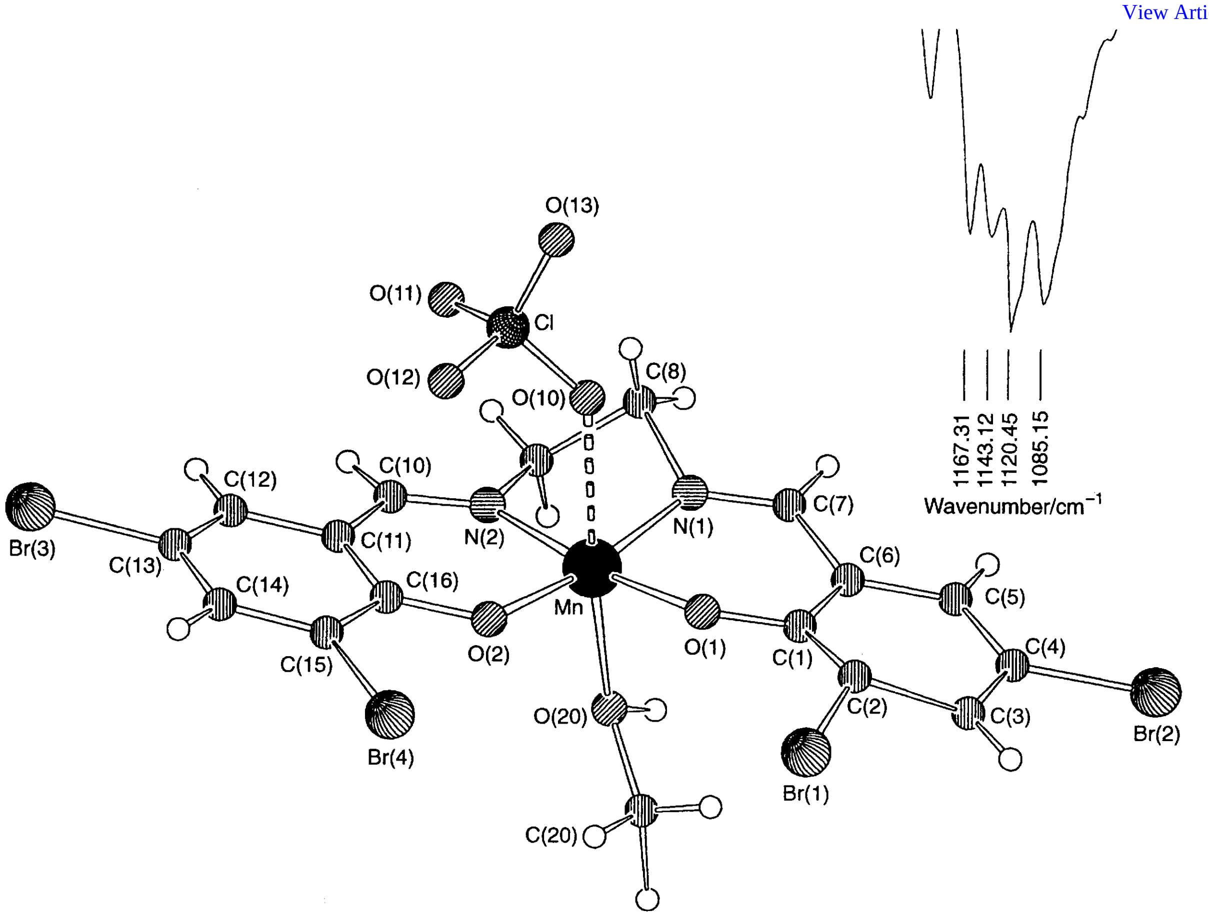

Fig. 9 Crystal structure of [Mn(dbsalen)(MeOH)(OClO$_3$)]·H$_2$O **5**. Inset: the IR spectrum showing the splitting of ν_3(Cl–O)

Table 4 Selected bond lengths (Å) and angles (°) for complex **4**

Mn–O(1)	1.923(4)	Mn–O(3′)	1.806(6)
Mn–O(2)	1.919(6)	Mn–N(1)	2.012(7)
Mn–O(3)	1.791(4)	Mn–N(2)	2.003(8)
O(1)–Mn–O(2)	92.4(2)	O(2)–Mn–N(2)	89.7(3)
O(1)–Mn–O(3)	174.9(3)	O(3)–Mn–O(3′)	83.3(2)
O(1)–Mn–O(3′)	91.7(2)	O(3)–Mn–N(1)	90.3(2)
O(1)–Mn–N(1)	90.8(2)	O(3)–Mn–N(2)	88.9(2)
O(1)–Mn–N(2)	90.2(2)	O(3)–Mn–N(1)	91.7(3)
O(2)–Mn–O(3)	92.6(2)	O(3)–Mn–N(2)	90.7(3)
O(2)–Mn–O(3)	175.8(2)	N(1)–Mn–N(2)	177.4(3)
O(2)–Mn–N(1)	87.8(3)		

ordination sphere of the manganese centre is completed by a methanol molecule [Mn–O$_{\mathrm{methanol}}$ 2.19(2) Å] and most remarkably a perchlorate anion. Although the bond length Mn–OClO$_3$ is long, 2.50(1) Å, the infrared spectrum of the compound clearly shows a splitting of the ν_3(O–Cl) band (see insert in Fig. 9), indicating that it is co-ordinated and no longer possesses tetrahedral symmetry. Thus, the co-ordination sphere about the manganese centre can be described as a distorted MnN$_2$O$_2$O′O″ octahedron. This is a most unusual structure, primarily due to the fact that this is the first experience we have had of perchlorate co-ordination in these systems, as judged from extensive crystallographic[12,13,16,17] and infrared characterisation.* Moreover, the presence of an unco-ordinated water molecule, a better donor, in the unit cell is remarkable. Selected bond lengths and angles are given in Table 5. It is also noteworthy that two such diverse and unusual compounds as **4** and **5** have been isolated from essentially the same reaction procedure.

Crystal structure of [Mn(nsalen)Cl(H$_2$O)] 6

Schiff-base ligands with electron-withdrawing substituents such as 5-NO$_2$ groups appear to favour the stabilisation of manganese(II) rather than manganese(III), when the complexes are prepared under aerobic conditions (see above). However, we have found that it is possible to produce manganese(III) complexes from these manganese(II) species using ferrocenium tetrachloroferrate(III), *viz* equation (1). The crystal structure of

$$[\mathrm{Mn(nsalen)(H_2O)_2}] \xrightarrow{[\mathrm{Fe}(\eta\text{-}\mathrm{C_5H_5})_2][\mathrm{FeCl_4}]} \underset{\mathbf{6}}{[\mathrm{Mn(nsalen)Cl(H_2O)}]} \quad (1)$$

6 is given in Fig. 10 which shows it to consist of a monomeric distorted-octahedral manganese(III) centre. The manganese ion is ligated in the equatorial plane by the Schiff-base ligand with Mn–O$_{\mathrm{phenol}}$ bonds of 1.901(9) and 1.915(8) Å and Mn–N$_{\mathrm{imine}}$ bonds of 2.07(1) and 2.111(9) Å. The four donor atoms of the Schiff base lie within 0.02 Å of the least-squares plane they define, however the manganese atom is shifted out of the plane by 0.17 Å towards the chloride atom. Such behaviour is typical of this class of compound[19] although the Mn–Cl bond length of 2.306 Å is somewhat shorter than those in the related compounds [Mn(acen)Cl],[19a] [Mn(salen)Cl][19b] and [Mn(tetramesalen)-Cl][19c] 2.381(1), 2.461(1) and 2.391(4) Å respectively {acen = *N,N′*-ethylenebis(acetylacetone imine), tetramesalen = the [2:1] Schiff base of 2′-hydroxy-5′-methylacetophenone and 1,2-diaminoethane}, but shows a marked shortening compared

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* In greater than 100 compounds that we have now prepared of this type this represents the only example of splitting of the perchlorate band in the infrared spectra of the compounds, indicating that this is a unique example of perchlorate co-ordination in these systems.

Table 5 Selected bond lengths (Å) and angles (°) for complex **5**

Mn–O(1)	1.88(1)	Mn–O(20)	2.19(2)
Mn–O(2)	1.86(2)	Mn–N(1)	1.95(1)
Mn–O(10)	2.50(1)	Mn–N(2)	1.97(1)
O(1)–Mn–O(2)	93.7(5)	O(2)–Mn–N(2)	91.5(6)
O(1)–Mn–O(10)	89.4(5)	O(10)–Mn–O(20)	172.6(5)
O(1)–Mn–O(20)	91.2(5)	O(10)–Mn–N(1)	82.3(5)
O(1)–Mn–O(1)	91.2(5)	O(10)–Mn–N(2)	85.1(5)
O(2)–Mn–N(2)	172.4(6)	O(20)–Mn–N(1)	90.3(5)
O(2)–Mn–O(10)	89.6(5)	O(20)–Mn–N(2)	93.8(5)
O(2)–Mn–O(20)	97.7(4)	N(1)–Mn–N(2)	93.1(5)
O(2)–Mn–N(1)	170.6(5)		

Table 6 Selected bond lengths (Å) and angles (°) for complex **6**

Mn(1)–Cl(1)	2.306(4)	Mn(1)–O(7)	2.246(9)
Mn(1)–O(1)	1.901(9)	Mn(1)–N(1)	2.07(1)
Mn(1)–O(2)	1.915(8)	Mn(1)–N(2)	2.111(9)
Cl(1)–Mn(1)–O(1)	98.2(3)	O(1)–Mn(1)–N(2)	163.3(4)
Cl(1)–Mn(1)–O(2)	96.1(3)	O(2)–Mn(1)–O(7)	84.6(3)
Cl(1)–Mn(1)–O(7)	175.7(3)	O(2)–Mn(1)–N(1)	163.4(4)
Cl(1)–Mn(1)–N(1)	92.0(3)	O(2)–Mn(1)–N(2)	87.2(4)
Cl(1)–Mn(1)–N(2)	91.9(3)	O(7)–Mn(1)–N(1)	86.2(4)
O(1)–Mn(1)–O(2)	104.9(3)	O(7)–Mn(1)–N(2)	83.9(4)
O(1)–Mn(1)–O(7)	85.7(4)	N(1)–Mn(1)–N(2)	78.1(4)
O(1)–Mn(1)–N(1)	88.2(4)		

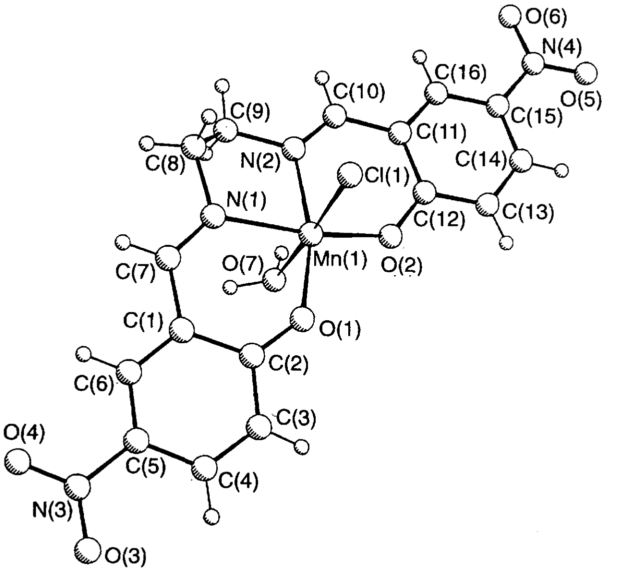

Fig. 10 Crystal structure of [Mn(nsalen)Cl(H_2O)] **6**

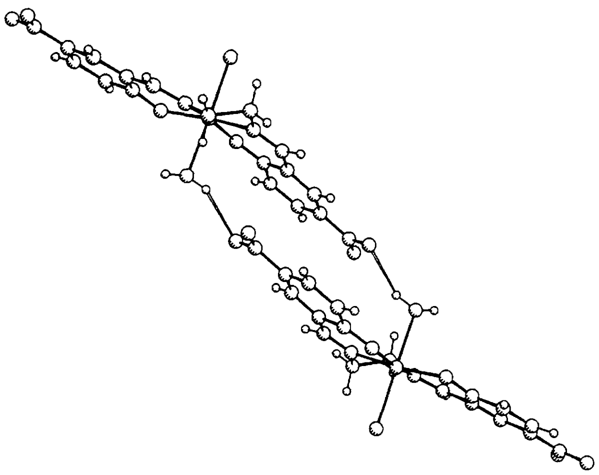

Fig. 11 Crystal structure of **6** showing the dimeric unit

to that in the related [Mn(salpn)Cl(MeOH)] species of 2.493(1).[19d] The distorted octahedron is completed by a water molecule [Mn–O_{water} 2.246(9) Å] which forms a hydrogen bond in the unit cell with the nitro group of an adjacent complex to form a dimer (Fig. 11). Selected bond lengths and angles are given in Table 6.

Conclusion

Fine tuning of tetradentate N_2O_2 donor set Schiff-base ligands is readily achieved by placing varying substituents about their phenyl rings. This has a profound effect upon the complexes formed in this study producing a 492 mV change in the Mn^{II}–Mn^{III} redox couple. It enables the facile preparation of both manganese-(II) and -(III) complexes from the aerial reaction of manganese(II) perchlorate with the dianion of the Schiff base. In one case, with 5-NO_2 substitution a 'borderline' situation is observed in which a manganese(II) complex contaminated with a manganese(III) impurity is obtained.

The structural chemistry reported offers further evidence of the tendency of such complexes to form dimeric species in the solid state. The first three structures **1**–**3** can be regarded as typical examples of square-planar MnONNO in substituted salen systems. Only small differences are seen in the bond lengths, whether the more remote capping oxygen is provided by water or a shared neighbouring phenoxy atom, with the Mn–N bonds in the three manganese centres falling in the range 1.963(4)–1.983(9) and Mn–O 1.871(3)–1.906(6) Å. Even in **5** where the capping Mn–O distances are highly asymmetric [Mn–HOMe 2.19(2) and Mn–$OClO_3$ 2.50(1) Å] the central MnONNO core still retains the standard geometry. It is only when a capping water is replaced by strongly bonding chlorine that the Mn–N bonds show a significant weakening [2.07(1) and 2.111(9) Å]. In one remarkable case a manganese(IV) dimer is obtained in which the manganese centres are bridged not only by μ-oxo groups, but also by μ-dbsalen ligands. This, to our knowledge, is the first example of such ligation by this type of ligand. The diversity in these systems is further emphasised by the isolation of the monomeric species **5**, from essentially the same reaction, in which perchlorate co-ordinates to the manganese centre in preference to lattice water.

Experimental

Chemicals

Salicylaldehydes (Maybridge), 1,2-diaminoethane (Aldrich) and manganese(II) perchlorate hexahydrate (Fluka) were used as received without further purification.

Physical measurements

Elemental analyses were performed on a Carlo Erba Model 1108 CHNS-O elemental analyser. The IR spectra were recorded as KBr discs on a Philips Scientific SP1000 spectrophotometer. ^1H NMR spectra on a Bruker WH spectrometer as $CDCl_3$ solutions using $SiMe_4$ as an internal reference. Magnetic susceptibility measurements in the 5–300 K temperature range were obtained using a SQUID magnetometer operating at 5000 G. Room-temperature magnetic susceptibilities were measured using a Digital Measurement system 1660 vibrating magnetometer operating at 5000 G. The compound $HgCo(NCS)_4$ was employed as a susceptibility standard.

Electrochemical measurements

All measurements were performed using an EG&G PAR model 273 potentiostat, controlled by EG&G PAR model 270 software. A Metrohm model 6.1204.000 graphite disc coupled to a Metrohm model 628–10 rotating electrode device was used as a working electrode. A saturated calomel electrode was used as a reference and a platinum wire as an auxiliary electrode. All measurements were made with *ca.* 10^{-3} mol dm^{-3} solutions of the complexes in dimethylformamide using 0.2 mol dm^{-3} NBu_4PF_6 as a supporting electrode. Cyclic voltammetry measurements were performed with a static graphite electrode, whilst direct-current and pulse voltammograms were recorded with the graphite disc rotating at 2000 revolutions per minute.

Schiff base preparation

The symmetrical Schiff bases were all prepared using a standard methodology which is highlighted by the following. To 1,2-diaminoethane (0.45 g, 7.5 mmol) in absolute alcohol (150 cm^3) was added 3-bromo-5-nitrosalicylaldehyde (3.689 g, 15 mmol). The resultant mixture was refluxed for 3 h after which it was concentrated *in vacuo* to *ca.* 50 cm^3 and the yellow solid filtered off and washed copiously with diethyl ether. Yields were almost quantitative.

H_2salen (Found: C, 71.8; H, 6.1; N, 10.3 Calc. for $C_{16}H_{16}N_2O_2$: C, 71.6; H, 6.0; N, 10.5%): ^{1}H NMR δ 3.94 (s, 2 H), 6.8–7.2 (m, 4 H), 8.36 (s, 1 H) and 13.23 (s, 1 H); IR ν(C=N) 1630 cm^{-1}. H_2eosalen (Found: C, 67.5; H, 7.3; N, 7.4. Calc. for $C_{20}H_{24}N_2O_4$: C, 67.4; H, 6.8; N, 7.9%): ^{1}H NMR δ 1.48 (t, 3 H), 3.95 (s, 2 H), 4.1 (q, 2 H), 6.7–6.9 (m, 3 H), 8.32 (s, 1 H) and 13.62 (s, 1 H); IR ν(C=N) 1625 cm^{-1}. H_2csalen (Found: C, 57.3; H, 4.6; N, 8.4. Calc. for $C_{16}H_{14}Cl_2N_2O_2$: C, 57.0; H, 4.2; N, 8.3%): ^{1}H NMR δ 3.96 (s, 2 H), 6.8–7.2 (m, 3 H), 8.29 (s, 1 H) and 13.13 (s, 1 H); IR ν(C=N) 1625 cm^{-1}. H_2bsalen (Found: C, 45.2; H, 3.5; N, 6.6. Calc. for $C_{16}H_{14}Br_2N_2O_2$: C, 45.1; H, 3.3; N, 6.6%): ^{1}H NMR δ 3.96 (s, 2 H), 6.8–7.4 (m, 3 H), 8.29 (s, 1 H) and 13.16 (s, 1 H); IR ν(C=N) 1630 cm^{-1}. H_2dcsalen (Found: C, 46.6; H, 3.2; N, 6.9. Calc. for $C_{16}H_{12}Cl_4N_2O_2$: C, 47.3; H, 3.0; N, 6.9%): ^{1}H NMR δ 4.01 (t, 2 H), 7.1–7.4 (m, 2 H), 8.28 (s, 1 H) and 14.0 (s, 1 H); IR ν(C=N) 1630 cm^{-1}. H_2dbsalen (Found: C, 33.5; H, 3.4; N, 5.2. Calc. for $C_{16}H_{12}Br_4N_2O_2$: C, 32.9; H, 2.1; N, 4.8%): ^{1}H NMR δ 4.00 (t, 2 H), 7.2–7.6 (m, 2 H), 8.25 (s, 1 H) and 14.1 (s, 1 H); IR ν(C=N) 1630 cm^{-1}. H_2bcsalen (Found: C, 38.8; H, 3.3; N, 6.4. Calc. for $C_{16}H_{12}Br_2Cl_2N_2O_2$: C, 38.8; H, 2.4; N, 5.7%): ^{1}H NMR δ 4.01 (t, 2 H), 7.2–7.5 (m, 2 H), 8.26 (s, 1 H) and 14.1 (s, 1 H); IR ν(C=N) 1630 cm^{-1}. H_2bmosalen (Found: C, 44.4; H, 3.9; N, 5.7 Calc. for $C_{18}H_{16}Br_2N_2O_4$. C, 44.4; H, 3.7; N, 5.8%): ^{1}H NMR δ 3.88 (s, 3 H), 3.97 (t, 2 H), 6.9–7.2 (m, 2 H), 8.24 (s, 1 H) and 13.6 (s, 1 H); IR ν(C=N) 1625 cm^{-1}. H_2nsalen (Found. C, 53.4; H, 3.6; N, 15.3. Calc. for $C_{16}H_{14}N_4O_6$: C, 53.6; H, 3.9; N, 15.6%): ^{1}H NMR δ 4.00 (s, 2 H), 6.9–8.4 (m, 3 H) and 8.80 (s, 1 H); IR ν(C=N) 1610 cm^{-1}. H_2bnsalen (Found: C, 37.3; H, 2.6; N, 10.8. Calc. for $C_{16}H_{12}Br_2N_4O_6$. C, 37.2; H, 2.3; N, 10.9%): ^{1}H NMR δ 4.06 (t, 2 H), 8.3–8.4 (m, 2 H) and 8.76 (s, 1 H); IR ν(C=N) 1590 cm^{-1}.

Complex preparation

All complexes were prepared by the same method, by a modification of the Boucher preparation.[14] A typical procedure is outlined below. To the Schiff base H_2L (5 mmol) in ethanol–methanol (1 : 1, 75 cm^3) was added $Mn(ClO_4)_2 \cdot 6H_2O$ (5 mmol). **CAUTION**: although no problems have been encountered in this work, perchlorates are potentially explosive and should be treated in small quantities with care. No reaction appeared until the addition of an aqueous solution (2 cm^3) of sodium hydroxide (0.4 g, 10 mmol) which caused a rapid darkening of the solution. After stirring in the presence of air for about 4 d a blackish solid was filtered off and rejected. The remaining solution was left to evaporate at room temperature until a dark precipitate of the corresponding complex appeared. The precipitate was filtered off, washed with cold ethanol (25 cm^3 × 2), diethyl ether (25 cm^3 × 2) and then dried *in vacuo*, yield *ca.* 60%.

IR: [Mn(salen)$(H_2O)_2$]$ClO_4 \cdot H_2O$ ν(O–H) 3440, ν(C=N) 1615, ν_3(Cl–O) 1100, ν_4(Cl–O) 640; [Mn(eosalen)$(H_2O)_2$]ClO_4 ν(O–H) 3450, ν(C=N) 1620, ν_3(Cl–O) 1090, ν_4(Cl–O) 635; [Mn(csalen)$(H_2O)_2$]ClO_4 ν(O–H) 3420, ν(C=N) 1620, ν_3(Cl–O) 1095, ν_4(Cl–O) 625; [Mn(bsalen)$(H_2O)_2$]ClO_4 ν(O–H) 3370, ν(C=N) 1620, ν_3(Cl–O) 1100, ν_4(Cl–O) 630; [Mn(dcsalen)$(H_2O)_2$]ClO_4 ν(O–H) 3440, ν(C=N) 1620, ν_3(Cl–O) 1100, ν_4(Cl–O) 630; [Mn(dbsalen)$(H_2O)_2$]ClO_4 ν(O–H) 3440, ν(C=N) 1625, ν_3(Cl–O) 1100, ν_4(Cl–O) 630; Mn(bcsalen) ν(O–H) 3420, ν(C=N) 1620, ν_3(Cl–O) 1100, ν_4(Cl–O) 630; [Mn(bmosalen)$(H_2O)_2$]$ClO_4 \cdot 2H_2O$ ν(O–H) 3420, ν(C=N) 1620, ν_3(Cl–O) 1090, ν_4(Cl–O) 630; [Mn(nsalen)$(H_2O)_2$]$\cdot 2H_2O$ ν(O–H) 3450, ν(C=N) 1600, $\nu_{asym}(NO_2)$ 1470, $\nu_{sym}(NO_2)$ 1300, $\delta(NO_2)$ 840; [Mn(bnsalen)$(H_2O)_2$]$\cdot 2H_2O$ ν(O–H) 3430, ν(C=N) 1580, $\nu_{asym}(NO_2)$ 1480, $\nu_{sym}(NO_2)$ 1315 and $\delta(NO_2)$ 855 cm^{-1}.

In the case of H_2dbsalen, the base (0.5 g, 0.86 mmol) was treated with a solution (2 cm^3) of NaOH (0.07 g, 1.75 mmol) in methanol (75 cm^3). To the resultant solution was added $Mn(ClO_4)_2 \cdot 6H_2O$ (0.37 g, 1.00 mmol) and stirred in air for 24 h. The precipitated solid was filtered off and the filtrate evaporated to dryness. The resultant solid was recrystallised from acetonitrile yielding crystals suitable for X-ray diffraction studies of [{Mn(μ-dbsalen)(μ-O)}$_2$]·2MeCN **4**. Alternatively, if after removal of the precipitated solid the filtrate was allowed to evaporate slowly, crystals suitable for single-crystal studies were obtained of [Mn(dbsalen)(MeOH)$(OClO_3)$]$\cdot H_2O$ **5**.

Oxidation of manganese(II) Schiff-base complexes

A solution of [Mn(nsalen)$(H_2O)_2$]$\cdot 2H_2O$ (0.15 g, 0.35 mmol) in acetonitrile (20 cm^3) was treated with an acetonitrile solution (30 cm^3) of ferrocenium tetrachloroferrate(III) (0.15 g, 0.39 mmol) for 1 h at room temperature. The solution was evaporated to dryness and the resultant solid washed with diethyl ether (2 × 25 cm^3) and recrystallised from methanol–acetonitrile to yield crystals of [Mn(nsalen)Cl(H_2O)] **6** suitable for X-ray diffraction studies.

Crystallography

Crystal data and details of refinement are given in Table 7.

[Mn(dcsalen)$(H_2O)_2$]ClO_4 1. Orange prismatic crystals suitable for single-crystal X-ray studies were obtained by crystallisation from MeOH–Pr^{i}OH. A Siemens R3m/v diffractometer employing graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å) was used for data collection. Lorentz-polarisation corrections were applied but absorption was ignored. The structure was solved by direct methods (SHELXS 86)[20] and refined by full-matrix least squares (TEXSAN)[21] with all non-hydrogen atoms treated anisotropically and hydrogen atoms isotropically.

[Mn(bsalen)$(H_2O)_2$]ClO_4 2 and 3. Suitable crystals were obtained as above. An orange acicular crystal was used for data collection on a Rigaku AFC5R diffractometer using Cu-Kα radiation (λ = 1.541 78 Å) and a 12 kW rotating anode. The intensities of three representative reflections which were measured every 200 declined by 0.16%, showed no significant decrease. An empirical absorption correction using the program DIFABS[22] was applied, resulting in transmission factors ranging from 0.72 to 1.42. Data were corrected for Lorentz-polarisation effects. The structure was solved by direct methods.[20] Non-hydrogen atoms were refined anisotropically, hydrogen atoms were found by Fourier-difference synthesis and apart from those of water were set to idealised positions (C–H 0.95 Å). All calculations were performed using TEXSAN.

[{Mn(μ-dbsalen)(μ-O)}$_2$]·2MeCN 4. A brown prismatic crystal was used for data collection on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo-Kα radi-

Table 7 Crystal data for complexes **1**–**6** and details of refinement *

	1	**2 + 3**	**4**	**5**	**6**
Molecular formula	$C_{16}H_{14}Cl_5MnN_2O_8$	$C_{32}H_{34}Br_4Cl_2Mn_2N_4O_{17}$	$C_{36}H_{26}Br_8Mn_2N_6O_6$	$C_{17}H_{16}Br_4ClMnN_2O_8$	$C_{16}H_{14}ClMnN_4O_7$
M	594.5	1247.04	1387.80	786.35	464.70
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$ (no.14)	$P2_1/n$ (no.14)	$P\bar{1}$	$P2_1/c$	$P2_1/n$ (no.14)
a/Å	12.349(4)	14.088(7)	10.732(1)	14.857(5)	24.259(4)
b/Å	12.880(4)	21.413(5)	11.467(2)	10.436(1)	11.809(3)
c/Å	14.165(5)	14.082(2)	10.351(1)	15.727(5)	6.382(5)
α/°			98.32(1)		
β/°	106.66(2)	95.78(2)	116.38(1)	94.03(2)	90.01(2)
γ/°			97.98(1)		
U/Å^3	2158(2)	4227(2)	1099.1(5)	2432(1)	1828(2)
Z	4	4	1	4	4
D_c/g cm^{-3}	1.829	1.959	2.097	2.147	1.688
F(000)	1192	2456	662	1512	944
μ/cm^{-1}	12.59	112.47	3.90	7.187	8.88
Crystal size/mm	0.30 × 0.30 × 0.15	0.02 × 0.07 × 0.55	0.20 × 0.30 × 0.35	0.35 × 0.15 × 0.10	0.40 × 0.20 × 0.05
$2\theta_{max}$	50.1	120.3	62	56	50.0
Total data measured	4196	6715	7307	6339	3475
No.unique reflections	4015	6431	6621	5893	3459
No.observed reflections [$I > 3\sigma(I)$]	3066	3433	2896	2360	1592
No. parameters	346	550	263	299	263
$\Delta\rho_{min}, \Delta\rho_{max}$/e Å^{-3}	−0.79, 0.45	−0.53, 0.53	−0.76, 0.85	−0.76, 0.82	−1.25, 1.08
Final R	0.045	0.055	0.048	0.069	0.076
Final R'	0.041	0.060	0.051	0.078	0.054

Details in common: weighting scheme $w = 1/[\sigma^2(F) + 0.03F^2]$, $R = \Sigma||F_o| - |F_c||/\Sigma F_o$, $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o{}^2]^{\frac{1}{2}}$

ation (λ = 0.710 73 Å). Corrections were applied for Lorentz-polarisation effects and also for absorption (μ = 3.90 mm^{-1}) (minimum, maximum transmision factors 0.55, 1.15). The structure was solved by Patterson (SHELXS 86[23]) and Fourier methods and refined by full-matrix least squares based on F^2. From residual electron density in an otherwise anomalous void, the existence of a highly disordered molecule of MeCN was deduced. A model based on geometrical criteria was assumed. Despite large correlation factors between the parameters of the three atoms, this model appeared to be the best possible one, and no further attempts were made to improve on it. Most hydrogens were located from the Fourier-difference map [those of acetonitrile were placed at assumed positions (C–H 0.95 Å)]. Correction for extinction was made in the last cycle of refinement; the secondary extinction coefficient refined to g = 7.454 × 10^{-8} $\{F_c = F_c/[1 + g(F_c)^2L_p]\}$.

[Mn(dbsalen)(MeOH)(OClO$_3$)]·H$_2$O 5. A brown prismatic crystal was obtained by slow evaporation of a methanol solution and used for data collection on an Enraf-Nonius CAD4 diffractometer using Mo-Kα radiation (λ = 0.710 73 Å). Direct methods were used for structure solution (SHELXS 86[20]) and all non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms (except those of the water molecules which were located from the Fourier-difference map) were calculated in idealised positions and introduced into structure calculations. Empirical absorption corrections (minimum, maximum transmission factors 0.62, 0.96) and extinction correction (coefficient 3.43 × 10^{-8}) were applied.

[Mn(nsalen)Cl(H$_2$O)] 6. A black plate crystal was used for data collection on a Rigaku AFC6S diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å). The intensities of the three representative reflections declined by 1.50%, accordingly a linear correction factor was applied. An empirical absorption correction was applied using the program DIFABS[22] which resulted in transmission factors ranging from 0.95 to 1.02 (linear absorption coefficient 8.9 cm^{-1}). The data were corrected for Lorentz-polarisation effects and a correction for secondary extinction was applied (coefficient = 0.429 × 10^{-8}). The structure was solved by direct methods.[20] Non-hydrogen atoms were refined anisotropically whilst hydrogen atoms were included in idealised positions. All calculations were performed using TEXSAN.

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/67.

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