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Further attempts to rationalise the co-ordination chemistry of manganese with Schiff base ligands and supplementary carboxylate donors

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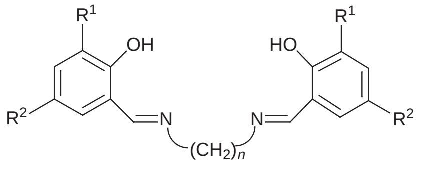
Some manganese(III) complexes of Schiff base ligands with ancillary carboxylate donors have been found to exhibit structural diversity, although some patterns emerged. Thus, when the ligands $3CH_3O$-salen and $3CH_3O$-salpn [$3CH_3O$-salen = dianion of *N*,*N′*-bis(3-methoxysalicylidene)ethane-1,2-diamine, $3CH_3O$-salpn = dianion of *N*,*N′*-bis(3-methoxysalicylidene)propane-1,3-diamine] are used in conjunction with carboxylates RCO_2^- (R = Me, Et, Pr^n or CH_2Ph) unidentate carboxylate bonding occurs as in the crystallographically observed $[Mn(3CH_3O\text{-salen})(O_2CMe)(H_2O)]\cdot 2H_2O$ **1**, $[Mn(3CH_3O\text{-salen})(O_2CCH_2Ph)(H_2O)]\cdot H_2O$ **4**, and $[Mn(3CH_3O\text{-salpn})(O_2CCH_2Ph)(H_2O)]$ **5**. On the other hand, employing the more sterically encumbered carboxylates $Bu^tCO_2^-$ and $Pr^iCO_2^-$, bidentate chelating binding of the carboxylate occurs, as in $[Mn(3CH_3O\text{-salpn})(O_2CBu^t)]$ **2** and $[Mn(3CH_3O\text{-salpn})(O_2CPr^i)]$ **3**. The reactivity of [Mn(salpn)(acac)] (acac = acetylacetonate) with Me_3SiCl and aliphatic carboxylic acids, RCO_2H (R = Me, Et, Pr^n, Bu^n, Pr^i or Bu^t), has also been investigated. A dimer species $[\{Mn(salpn)Cl\}_2]\cdot CH_3CN$ **6** was isolated from the reaction of Me_3SiCl with [Mn(salpn)(acac)] while the carboxylic acids seem to lead to the isolation of monomers, such as $[Mn(salpn)(O_2CPr^i)]$ **7**. This synthetic route has also been applied to the preparation of related complexes, in which the manganese(III) centre is not attainable with reliability *via* the aerobic oxidation of a manganese(II) precursor, although some rare examples have been obtained by the latter method, such as $[Mn(5NO_2\text{-salen})(O_2CMe)(H_2O)]$, **8**, [$5NO_2$-salen = dianion of *N*,*N′*-bis(5-nitrosalicylidene)ethane-1,2-diamine]). Single crystals were grown from a dimethylformamide solution of the material of stoichiometry $Mn(3Br,5NO_2\text{-salpn})(O_2CMe)\cdot H_2O$ [$3Br,5NO_2$-salpn = dianion of *N*,*N′*-bis(3-bromo-5-nitrosalicylidene)propane-1,3-diamine], isolated from this route and found to consist of the unexpected $[\{Mn(\mu\text{-}3Br,5NO_2\text{-salpn})(\mu\text{-}O)\}_2]\cdot 3DMF$ **9**, apparently containing a manganese(IV) species, in spite of the electron withdrawing nature of the substituents on the aromatic rings of the ligand.

Introduction

Much of the recent interest in the co-ordination chemistry of manganese has been driven by the involvement of manganese in a number of biological systems.[1–5] Owing to the strong experimental evidence associated with the presence of a multinuclear cluster of manganese ions within the Oxygen Evolving Complex (OEC) of Photosystem II, and the intrinsic interest in such compounds, inorganic chemists have been enticed into the area, resulting in the preparation of a great number of extremely elegant biomimetic compounds.[6] Such complexes have not been limited to multinuclear cluster complexes, since enzymes such as manganese catalase, ribonucleotide reductase and the xylose isomerases involve two manganese ions which are thought to be associated in a dimer. Thus, great interest has also surrounded the preparation of dinuclear complexes[7] in addition to the higher nuclearity cluster compounds. Dinuclear units in which the manganese ions are linked by two or three ions that include O^{2-} in a bis(μ-oxo) bridge[8] or O^{2-} together with two carboxylates,[9] alkoxides or a combination of alkoxide/phenoxide and carboxylate donors are widely observed and have been well characterised.[10]

Our recent investigations in this area have centred on the preparation of manganese complexes of tetradentate (N_2O_2 donor set) Schiff base ligands with ancillary carboxylate ligands to see whether different structural behaviour in model complexes results through the variation of the carboxylate used, in order to model the aspartate and glutamate side chains of proteins. We have found that changing these carboxylate donors can have a profound effect on the structural chemistry in the resultant complexes. When acetate was employed with the salpn ligand the polymeric complex $[\{Mn(salpn)(O_2CMe)]_2(H_2O)_3\}_n]$ was isolated.[11] Unlike the other rare examples of such polymeric compounds[12] in which the ligands stack on top of one another, there was twist of 90° between adjacent ligands in the polymeric backbone. This results in the polymer having a dimeric, rather than the more usual monomeric, repeat unit. Consequently we extended our investigations to other linear chain carboxylates, butyrate (O_2CPr^n) and valerate (O_2CBu^n), and found that a diverse range of structural chemistry was available.[13] With butyrate and the salen ligand a dinuclear species was characterised, $[Mn_2(salen)_2(O_2CPr^n)(H_2O)(EtOH)][O_2CPr^n]$; an apparent 'snapshot' of polymer formation (the non-co-ordinated carboxylate, when viewed in the crystal packing diagram, appears ideally positioned to bind to the manganese centres and hence allow polymer formation to occur) which, on the basis of cyclic voltammetry studies, maintains its structural integrity in acetonitrile solution. In complete contrast, when the valerate counter ion was used the monomeric species $[Mn(salpn)(O_2CBu^n)]$ was isolated. We have since isolated other monomeric species, together with dimeric and polymeric species, by using other linear, branched chain and aromatic carboxylates. Interestingly, the polymeric species we have isolated can contain either monomeric or dimeric repeat units together with ligation of the carboxylate in the *anti-anti* or *syn-anti* mode.[14] Despite the large number of species we have now structurally characterised, we have been unable, as yet, to establish any pattern in the structural chemistry obtained. We were therefore keen to rationalise this behaviour through the structural characterisation of additional compounds of this type and to establish whether we could prepare a specific structural motif to order. An obvious means of achieving this goal was by attempting to replace a ligand already co-ordinated to a manganese centre whilst maintaining the geometric integrity of that centre. An ideal candidate appeared to be the monomeric species [Mn(salpn)(acac)][15] and herein we report our findings.



H_23CH_3O-salen: $n = 2$, $R^1 = CH_3O$, $R^2 = H$
H_23CH_3O-salpn: $n = 3$, $R^1 = CH_3O$, $R^2 = H$
H_25NO_2-salpn: $n = 3$, $R^1 = H$, $R^2 = NO_2$
$H_23Br,5NO_2$-salpn: $n = 3$, $R^1 = Br$, $R^2 = NO_2$

Results and discussion

Preparation of complexes of $3CH_3O$-salen and $3CH_3O$-salpn with auxiliary carboxylate ligands

All of the complexes were prepared as previously reported[11–14] by the reaction of the ligand with a stoichiometric quantity of the appropriate manganese(II) carboxylate salt in ethanol under aerobic conditions, yielding complexes of stoichiometry $MnL(O_2CR)$ (see Table 1). All complexes show characteristic shifts in their infrared spectra to lower frequency of ν(C=N), *cf.* 'free' ligand values, upon co-ordination to manganese, which together with parent ion peaks in their FAB mass spectra corresponding to $[MnL]^+$ and room temperature magnetic moments typical of such compounds[14] indicate complete co-ordination of the Schiff base ligand. Unfortunately little other information can be deduced without resorting to single crystal X-ray diffraction. In view of our previous interesting findings and our desire to rationalise the structural chemistry in these species further we sought crystals suitable for X-ray diffraction studies.

Crystal structure of $[Mn(3CH_3O\text{-salen})(O_2CMe)(H_2O)]\cdot 2H_2O$ 1

Previously we had proposed that complexes prepared by this method containing the $3CH_3O$-salen ligand and aliphatic carboxylate anions were isostructural.[14] This was based on a comparison of a variety of behaviour, in particular the almost identical fragmentation patterns observed by FAB mass spectroscopy; such a phenomenon has not been observed by us in any other series of these compounds. The crystallographic characterisation of the monomeric species, **1**, indicates that although the co-ordination mode of the carboxylate remains as the unusual unidentate mode when this ligand is used, a slight variation in structure is possible, Fig. 1. The structure is found to consist of a monomeric manganese(III) centre which is ligated in the *xy* plane by the tetradentate Schiff base ligand. The axial co-ordination sites of manganese are filled by a water molecule and a unidentate acetate ligand. This mode of co-ordination of the carboxylate anion was also observed in both of our previous examples of these materials, $[\{Mn(3CH_3O\text{-salen})(O_2CEt^n)\}_2]$ and $[\{Mn(3CH_3O\text{-salen})(O_2CBu^n)\}_2]$,[14] and this perhaps accounts for the unusual similarity in the fragmentation pattern observed in the FAB mass spectra of these complexes. Unlike the previous two structurally characterised complexes, in which the co-ordination sphere was completed by weak μ-phenoxy interactions [*cf.* Mn–O(1*) = 2.559 and 2.771 Å in the propionate and valerate, respectively], the manganese co-ordination sphere in **1** is completed by a water molecule [Mn–O(1w) 2.334(4) Å]. In all other respects the structures are identical and it is perhaps not surprising that we were previously unable to distinguish between these structural motifs. Such subtle differences in solid state structure are also observed in [Mn(salpn)Cl] (see below) and it seems possible that the monomeric *versus* dimeric structure is affected by the solvent used for crystallisation. It is important to stress though that, with the exception of ^iPr and ^tBu (see below), the carboxylate is always co-ordinated in the unidentate mode when a methoxy group is *ortho* to the phenolic oxygen donor. All other bond lengths and angles are typical of such complexes.

Crystal structures of $[Mn(3CH_3O\text{-salpn})(O_2CBu^t)]$ 2 and $[Mn(3CH_3O\text{-salpn})(O_2CPr^i)]$ 3

Both complexes **2** and **3** were found to exist as monomeric species in which the Schiff base ligand affords *cis* sites at the manganese(III) centre for bidentate chelation of the carboxylate ligands. They consist (Fig. 2) of extremely distorted octahedral centres, typical in such complexes.[13,14] The asymmetric nature of the $Mn–N_{imine}$ and $Mn–O_{carboxylate}$ bond lengths is particularly striking, Mn–N(1) 2.150(5) and 2.150(13), Mn–N(2) 1.986(5) and 1.939(15), Mn–O(5) 2.329(5) and 2.372(12) Å; Mn–O(6) 2.071(4) and 2.026(13) Å for **2** and **3**, respectively. The distortion in the octahedral centres is further exemplified by the following angles for **2** and **3**, respectively: O(2)–Mn(1)–O(6) 155.5(2) and 154.8(5), O(2)–Mn(1)–N(1) 110.1(2) and 113.3(5), O(6)–Mn(1)–O(5) 58.7(2) and 58.5(5) and N(1)–Mn(1)–O(5) 153.1(2) and 150.1(5)°.

Such co-ordination is very rare in these compounds with only one example of such a monomeric Schiff base complex in the Cambridge Crystallographic Database,[13] whilst two further examples have also recently been reported by us.[14] The presence of *cis* sites at the metal centre for chelation of the carboxylate results from the flexibility in the trimethylene backbone between the imine nitrogens of the Schiff base ligand; however, such 'flexing' of the ligand backbone is not guaranteed. It is apparent that when sterically demanding carboxylates are employed, such as trimethylacetate and isobutyrate, monomers such as **2** and **3** will prevail, as only monomeric species have been observed with these carboxylates. It therefore seems reasonable to propose that with these sterically demanding carboxylates and a tetradentate N_2O_2 donor set Schiff base ligand with a trimethylene backbone a monomeric complex will result. Nevertheless, steric congestion cannot be the sole reason for the ligand to adopt the strained *cis* conformation, as we have also observed monomers with valerate (O_2CBu^n)[13] and propionate (O_2CEt)[14] anions; the former is the exclusive product whilst a polymeric species, with *trans* sites ligated by an *anti-anti* bridging carboxylates, is also observed for the latter.

Crystal structures of $[Mn(3CH_3O\text{-salen})(O_2CCH_2Ph)(H_2O)]\cdot H_2O$ 4 and $[Mn(3CH_3O\text{-salpn})(O_2CCH_2Ph)(H_2O)]$ 5

The structural characterisation of complex **4**, Fig. 3(a), serves to substantiate further our proviso that only unidentate co-ordination of a carboxylate ligand should be observed with the $3CH_3O$-salen ligand. As in **1** the co-ordination sphere of the octahedral manganese centre consists of the tetradentate Schiff base ligand in the *xy* plane, with the axial sites filled with the unidentate carboxylate O(5) and a water molecule O(1w). A

Table 1 Analytical and some selected data for the manganese(III) carboxylate complexes containing 3CH_3O-salen and 3CH_3O-salpn as ligands

Complex	Analysis (%)[a] C	H	N	Mn	IR/cm^{-1} ν(C=N)	μ_{eff}/μ_B	FAB[b] m/z	Yield[c] (%)
[Mn(3CH_3O-salen)(O_2CPh)]·H_2O	57.1 (57.7)	4.2 (4.8)	5.3 (5.4)		1625	4.8	381	95
[Mn(3CH_3O-salen)(O_2CCH_2Ph)]·2H_2O	56.9 (56.5)	5.0 (5.3)	5.1 (5.1)		1624	4.8	381	82
[Mn(3CH_3O-salpn)(O_2CMe)]	55.2 (55.5)	4.8 (5.1)	6.1 (6.2)	11.8 (12.1)	1616	4.8	395	86
[Mn(3CH_3O-salpn)(O_2CEt)]	56.1 (56.4)	5.2 (5.4)	6.1 (6.0)	11.6 (11.7)	1616	4.6	395	86
[Mn(3CH_3O-salpn)(O_2CPr^n)]	56.9 (57.3)	5.1 (5.6)	5.8 (5.8)	10.9 (11.4)	1616	4.4	395	71
[Mn(3CH_3O-salpn)(O_2CBu^n)]	57.7 (58.1)	6.0 (5.9)	5.5 (5.6)	11.6 (11.1)	1616	4.7	395	68
[Mn(3CH_3O-salpn)(O_2CPr^i)]	57.4 (57.3)	5.6 (5.6)	5.7 (5.8)		1617	4.8	395	76
[Mn(3CH_3O-salpn)(O_2CBu^t)]	58.3 (58.1)	6.3 (5.9)	5.4 (5.6)		1614	4.6	395	94
[Mn(3CH_3O-salpn)(O_2CPh)]	60.5 (60.5)	4.8 (4.9)	5.3 (5.4)		1613	4.9	395	78
[Mn(3CH_3O-salpn)(O_2CCH_2Ph)]	60.5 (61.1)	4.8 (5.1)	5.1 (5.3)		1616	4.9	395	78

[a] Found (calculated). [b] Peaks corresponding to $[ML]^+$. [c] Based on manganese.

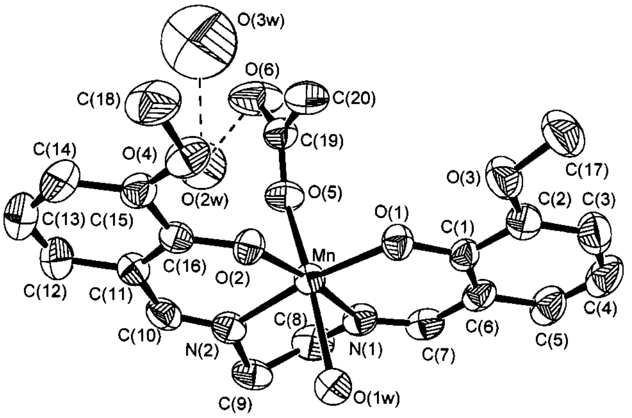


Fig. 1 Molecular structure of [Mn(3CH_3O-salen)(O_2CMe)(H_2O)]·2H_2O **1**. Selected bond lengths (Å) and angles (°) with estimated standard deviations (e.s.d.s) in parentheses: Mn–O(1) 1.891(3), Mn–O(2) 1.885(3), Mn–N(1) 1.988(4), Mn–N(2) 1.986(4), Mn–O(5) 2.130(3) and Mn–O(1w) 2.334(4); O(1)–Mn–O(2) 95.36(13), O(1)–Mn–N(1) 91.0(2), O(1)–Mn–N(2) 171.6(2), O(1)–Mn–O(5) 96.96(14), O(1)–Mn–O(1w) 89.0(2), O(2)–Mn–N(1) 172.9(2), O(2)–Mn–N(2) 91.2(2), O(2)–Mn–O(5) 93.69(13), O(2)–Mn–O(1w) 90.6(2), O(5)–Mn–O(1w) 172.28(14), N(1)–Mn–N(2) 82.2(2), N(1)–Mn–O(5) 88.7(2), N(1)–Mn–O(1w) 86.3(2), N(2)–Mn–O(5) 87.8(2) and N(2)–Mn–O(1w) 85.7(2).

further water molecule of crystallisation O(2w) is hydrogen bonded to O(6). The structural characterisation of **5**, Fig. 3(b), as a related monomer was somewhat surprising. We have only structurally characterised one material containing this carboxylate, which was polymeric,[14] where the carboxylate bridged planar manganese Schiff base centres are in the *syn-anti* mode. The reasons for this bridging mode lay in the steric demands associated with the carboxylate, and we therefore expected **5** to be either a monomeric complex as observed for **2** and **3**, typical of sterically demanding carboxylates, or a polymeric complex as we have previously reported.[14] The isolation of a monomeric species in which the carboxylate is unidentate appears to indicate that the governing factor when the carboxylate is of an intermediate steric nature is the *ortho*-methoxy group, and that provided ^{t}Bu and ^{i}Pr groups are avoided on the carboxylate the unidentate mode of binding will always prevail.

Comparison of the bond lengths about the metal centres in complexes **1**, **4** and **5** reveals some interesting structural differences between the three monomers. In all three structures the Mn–$O_{carboxylate}$ bond lengths are identical (within their e.s.d.s): Mn–O(5) 2.130(3), **1**; Mn(1)–O(5) 2.135(10), **4**; and Mn(1)–O(5) 2.139(7) Å, **5**. Perhaps more interesting are the differences in bond lengths between the manganese ions and the donor atoms of the Schiff base ligands. For **1** and **4** these bond lengths are virtually identical when viewed within the extent of the data limits, with the exception of Mn–N(2) which shows a slight lengthening in **1**. For **5** it is immediately obvious that all these bond lengths are longer than those observed for **1** and **4**: Mn(1)–O(1) 1.912(6), Mn(1)–N(1) 2.026(8), Mn(1)–N(2) 2.050(9) Å for **5**, *cf.* Mn–O(1) 1.891(3), Mn–N(1) 1.988(4), Mn–N(2) 1.986(4) for **1** and Mn–O(1) 1.880(9), Mn–N(1) 1.995(11) and Mn–N(2) 1.971(11) Å for **4**. The lengthening observed in the Mn–$O_{phenolic}$ bond lengths in **5** is not nearly as pronounced as the differences in the Mn–N_{imine} bond length, that of Mn(1)–N(2) being particularly marked. These differences must be accounted for by the change of ligand backbone bridges in **1** and **4**.

Preparation of monomeric manganese Schiff base complexes with chelating carboxylate ligands

The reaction of Me_3SiCl with [Mn(salpn)(acac)]. Our initial reasons for investigating the reactivity of [Mn(salpn)(acac)] with Me_3SiCl were twofold. First, we wished to discover whether it was a straightforward procedure to replace the acetylacetonate ligand, and, secondly, to see whether such a reaction could lead to the formation of cluster compounds. This reagent has previously been employed as an abstractor of carboxylate ligands co-ordinated to metal centres[16] and has subsequently been employed in this manner to prepare manganese clusters.[17] The reaction of [Mn(salpn)(acac)] with Me_3SiCl in dry degassed acetonitrile resulted in the formation of a compound of stoichiometry Mn(salpn)Cl in 61% yield (see Table 2). The positive ion FAB mass spectrum of the complex shows a parent ion peak at m/z 335 which corresponds to a cation of the form $[Mn(salpn)]^+$. No fragments involving chloride co-ordination were observed, indicating that if chloride is ligated to the metal centre in the solid state that this ligation is weak. The absence of bands in the infrared spectrum at 1635 and 1600 cm^{-1}, which we attribute to the acetylacetonate group of the starting material, together with a shift in the imine band from 1615 to 1623 cm^{-1}, indicate that complete displacement of acetylacetonate has occurred, apparently *via* a simple counter ion exchange. In the light of these data, and the only slightly lowered room temperature magnetic moment of 4.5 μ_B, relative to that expected for magnetically dilute d^4 manganese(III), it is reasonable to propose the formation of a five-co-ordinate monomeric species as has previously been observed in related compounds.[18]

Crystals suitable for single crystal X-ray diffraction studies were mounted in an atmosphere of the mother-liquor (since decomposition occurs in the absence of solvent vapour). These were found to consist of the weakly μ-phenoxy bridged dimeric species [{Mn(salpn)Cl}$_2$]·CH_3CN **6**, shown in Fig. 4. The structure is essentially analogous to that found for the related [Mn(salen)Cl][18b] and other species[18a,c–e] however due to the much shorter μ-phenoxy bonds Mn(1)–O(1*) 2.487(4) Å (*cf.* 2.897 Å in a related monomer[18c]) and the roughly octahedral manganese(III) geometry, we thus prefer to present this structure as a dimer rather than a monomer. Indeed such a structure has been postulated by Pecoraro and co-workers,[19]

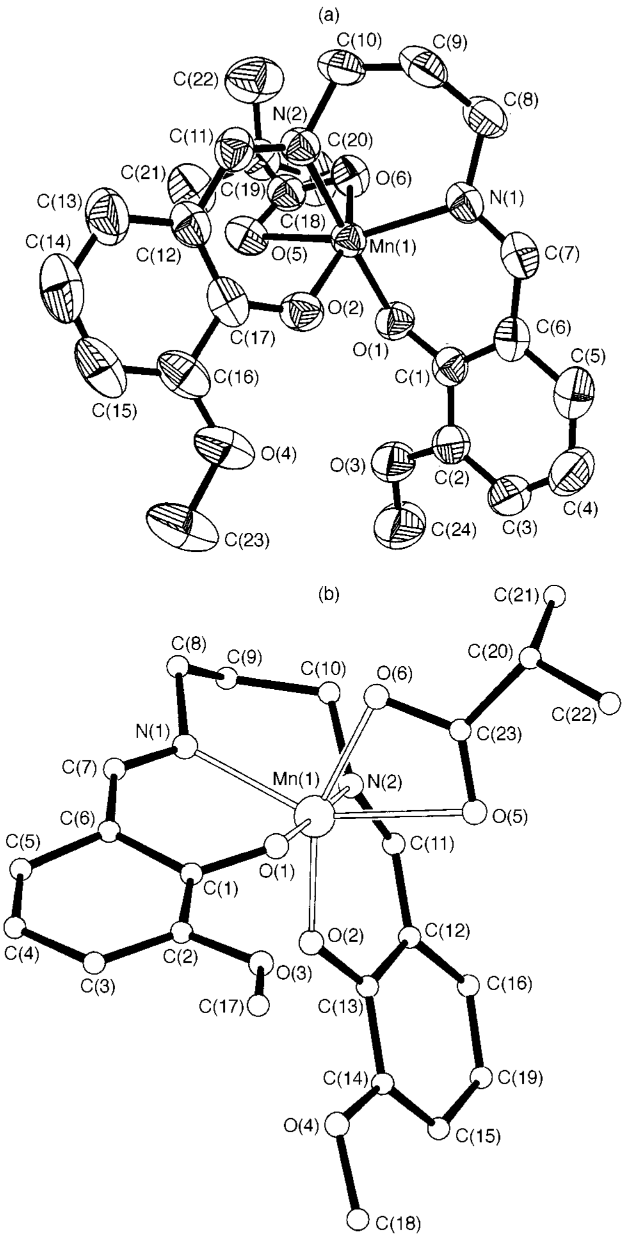


Fig. 2 (a) Molecular structure of [Mn(3CH_3O-salpn)(O_2CBu^t)] **2**. Selected bond lengths (Å) and angles (°) with e.s.d.s in parentheses: Mn(1)–O(1) 1.868(4), Mn(1)–O(2) 1.918(4), Mn(1)–N(1) 2.150(5), Mn(1)–N(2) 1.986(5), Mn(1)–O(5) 2.329(5) and Mn(1)–O(6) 2.071(4); O(1)–Mn(1)–O(2) 91.0(2), O(1)–Mn(1)–N(1) 87.9(2), O(1)–Mn(1)–N(2) 177.3(2), O(1)–Mn(1)–O(5) 94.0(2), O(1)–Mn(1)–O(6) 91.2(2), O(2)–Mn(1)–N(1) 110.1(2), O(2)–Mn(1)–N(2) 88.9(2), O(2)–Mn(1)–O(5) 96.8(2), O(2)–Mn(1)–O(6) 155.5(2), O(5)–Mn–O(6) 58.7(2), N(1)–Mn(1)–N(2) 89.6(2), N(1)–Mn(1)–O(5) 153.1(2), N(1)–Mn(1)–O(6) 94.4(2), N(2)–Mn(1)–O(5) 88.7(2) and N(2)–Mn–O(6) 90.0(2). (b) Molecular structure of [Mn(3CH_3O-salpn)(O_2CPr^i)], **3**. Selected bond lengths (Å) and angles (°) with e.s.d.s in parentheses: Mn(1)–O(1) 1.867(12), Mn(1)–O(2) 1.875(11), Mn(1)–N(1) 2.150(13), Mn(1)–N(2) 1.939(15), Mn(1)–O(5) 2.372(12) and Mn(1)–O(6) 2.026(13); O(1)–Mn(1)–O(2) 90.0(5), O(1)–Mn(1)–N(1) 89.3(6), O(1)–Mn(1)–N(2) 179.0(6), O(1)–Mn(1)–O(5) 93.8(5), O(1)–Mn(1)–O(6) 92.5(5), O(2)–Mn(1)–N(1) 113.3(5), O(2)–Mn(1)–N(2) 89.0(6), O(2)–Mn(1)–O(5) 96.4(5), O(2)–Mn(1)–O(6) 154.8(5), O(5)–Mn–O(6) 58.5(5), N(1)–Mn(1)–N(2) 89.7(6), N(1)–Mn(1)–O(5) 150.1(5), N(1)–Mn(1)–O(6) 91.7(5), N(2)–Mn(1)–O(5) 87.3(5) and N(2)–Mn–O(6) 88.2(6).

who suggested that the absence of solvent molecules capable of co-ordinating to the manganese(III) centre would lead to the formation of **6**, rather than the monomeric octahedral species that have been reported. The remaining bond lengths and angles are unexceptional for such compounds.

The characterisation of complex **6** clearly demonstrates that it is a simple procedure to replace the acetylacetonate ligand.

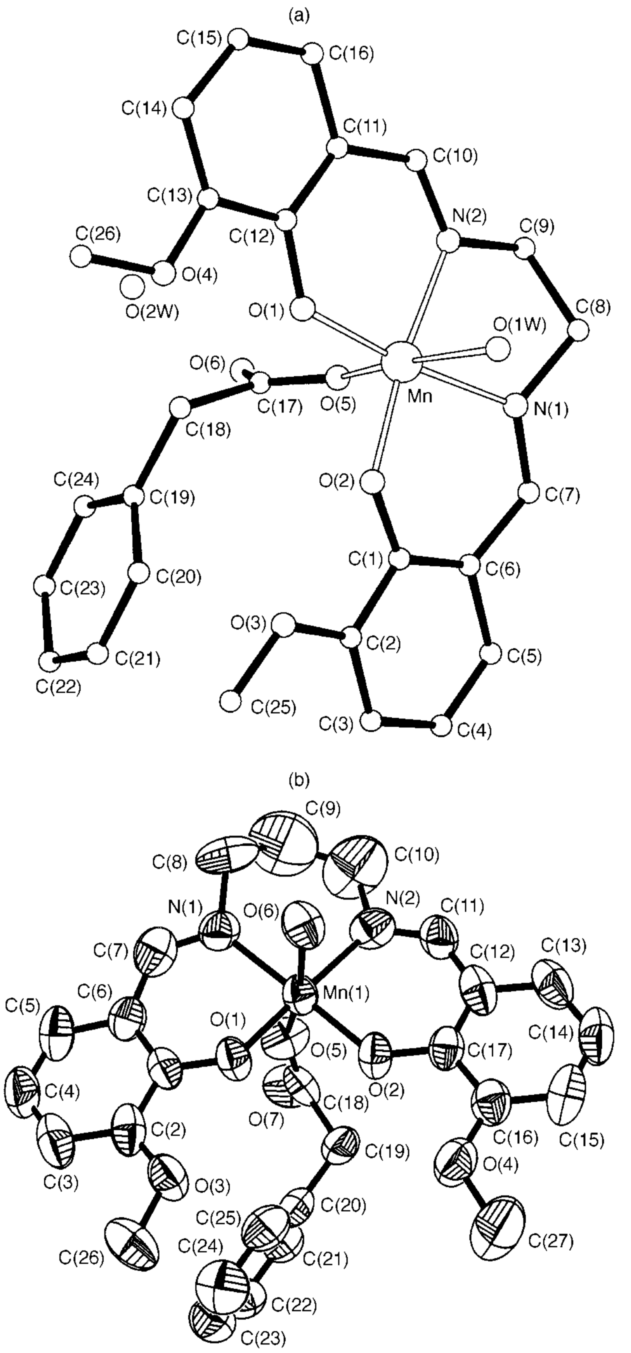


Fig. 3 (a) Molecular structure of [Mn(3CH_3O-salen)(O_2CCH_2Ph)(H_2O)]·H_2O **4**. Selected bond lengths (Å) and angles (°) with e.s.d.s in parentheses: Mn–O(1) 1.880(9), Mn–O(2) 1.887(9), Mn–N(1) 1.995(11), Mn–N(2) 1.971(11), Mn–O(5) 2.135(10) and Mn–O(1w) 2.353(9); O(1)–Mn–O(2) 93.5(4), O(1)–Mn–N(1) 172.5(5), O(1)–Mn–N(2) 92.0(4), O(1)–Mn–O(5) 98.7(4), O(1)–Mn–O(1w) 91.8(4), O(2)–Mn–N(1) 91.7(4), O(2)–Mn–N(2) 172.7(5), O(2)–Mn–O(5) 94.5(4), O(2)–Mn–O(1w) 87.9(4), O(5)–Mn–O(1w) 169.1(3), N(1)–Mn–N(2) 82.4(5), N(1)–Mn–O(5) 86.2(4), N(1)–Mn–O(1w) 83.0(4), N(2)–Mn–O(5) 89.5(4) and N(2)–Mn–O(1w) 87.1(4). (b) Molecular structure of [Mn(3CH_3O-salpn)(O_2CCH_2Ph)(H_2O)] **5**. Selected bond lengths (Å) and angles (°) with e.s.d.s in parentheses: Mn(1)–O(1) 1.912(6), Mn(1)–O(2) 1.914(6), Mn(1)–N(1) 2.026(8), Mn(1)–N(2) 2.050(9), Mn(1)–O(5) 2.139(7) and Mn(1)–O(6) 2.316(6); O(1)–Mn(1)–O(2) 87.0(3), O(1)–Mn(1)–N(1) 89.7(3), O(1)–Mn(1)–N(2) 175.2(3), O(1)–Mn(1)–O(5) 94.3(3), O(1)–Mn(1)–O(6) 87.5(2), O(2)–Mn(1)–N(1) 173.9(3), O(2)–Mn(1)–N(2) 89.8(3), O(2)–Mn(1)–O(5) 100.4(3), O(2)–Mn(1)–O(6) 89.9(3), O(5)–Mn–O(6) 169.6(3), N(1)–Mn(1)–N(2) 93.1(3), N(1)–Mn(1)–O(5) 85.0(3), N(1)–Mn(1)–O(6) 84.7(3), N(2)–Mn(1)–O(5) 89.8(3) and N(2)–Mn–O(6) 88.9(3).

Of interest is the change of geometry at the metal centre in that the *cis*-chelated sites of the “pretemplated” complex do not remain. In **6** *trans* sites are open at the metal centre due to the

Table 2 Analytical and some selected data for the manganese complexes containing salpn, 5NO$_2$-salpn and 3Br,5NO$_2$-salpn as ligands

	Analysis (%)[a]							
Complex	C	H	N	Mn	IR/cm^{-1} ν(C=N)	μ_{eff}/μ_B	FAB[b] m/z	Yield[c] (%)
[Mn(salpn)Cl]	55.0 (55.1)	4.5 (4.3)	7.2 (7.6)	14.3 (14.8)	1623	4.5	335	61
[Mn(salpn)(O$_2$CMe)]·H$_2$O	55.2 (55.3)	5.0 (5.1)	6.6 (6.8)	13.8 (13.4)	1615	4.8	335	57
[Mn(salpn)(O$_2$CEt)]	58.5 (58.8)	5.2 (5.2)	6.7 (6.9)	13.0 (13.5)	1614	4.8	335	58
[Mn(salpn)(O$_2$CPr^n)]	60.0 (59.7)	5.4 (5.5)	6.5 (6.6)	13.1 (13.0)	1614	4.8	335	79
[Mn(salpn)(O$_2$CBu^n)]	60.3 (60.6)	5.8 (5.7)	6.4 (6.4)	12.9 (12.6)	1616	4.5	335	57
[Mn(salpn)(O$_2$CPr^i)]	59.2 (59.7)	5.5 (5.5)	6.2 (6.6)	13.1 (13.0)	1616	4.5	335	66
[Mn(salpn)(O$_2$CBu^t)]	60.2 (60.6)	5.5 (5.7)	6.2 (6.4)	12.8 (12.6)	1614	4.7	335	72
Mn(5NO$_2$-salpn)(H$_2$O)	45.9 (46.0)	3.6 (3.6)	12.2 (12.6)		1622			46
Mn(3Br,5NO$_2$-salpn)	37.0 (36.8)	2.6 (2.5)	10.8 (10.1)		1598			40
[Mn(5NO$_2$-salpn)(O$_2$CMe)]·H$_2$O	45.4 (45.4)	3.8 (3.8)	11.4 (11.2)		1622	4.8	425	59
[Mn(5NO$_2$-salpn)(O$_2$CEt)]	47.6 (48.2)	3.8 (3.8)	11.0 (11.2)		1622	4.7	425	54
[Mn(5NO$_2$-salpn)(O$_2$CPr^n)]·2H$_2$O	45.8 (46.0)	3.9 (4.6)	10.4 (10.2)		1620	4.9	425	47
[Mn(5NO$_2$-salpn)(O$_2$CPr^i)]	48.5 (49.2)	3.9 (4.1)	11.3 (10.9)		1623	4.9	425	62
[Mn(5NO$_2$-salpn)(O$_2$CBu^t)]	49.1 (50.2)	4.2 (4.4)	10.5 (10.6)		1622	5.0	425	58
[Mn(3Br,5NO$_2$-salpn)(O$_2$CMe)]·2H$_2$O	33.6 (33.6)	2.6 (2.8)	8.3 (8.3)		1620	5.0	583	54
[Mn(3Br,5NO$_2$-salpn)(O$_2$CEt)]	36.1 (36.6)	2.6 (2.6)	8.5 (8.5)		1622	4.7	583	57
[Mn(3Br,5NO$_2$-salpn)(O$_2$CPr^n)]·H$_2$O	36.2 (36.6)	2.6 (3.0)	8.7 (8.1)		1626	4.8	581	54

[a] Found (calculated). [b] Peaks corresponding to [ML]$^+$. [c] Based on manganese.

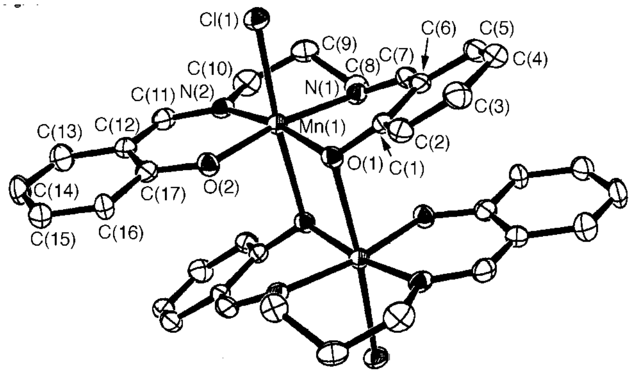


Fig. 4 Molecular structure of [{Mn(salpn)Cl}$_2$]·CH$_3$CN **6**. Lattice acetonitrile is not depicted. Selected bond lengths (Å) and angles (°) with e.s.d.s: Mn(1)–Cl(1) 2.4521(18), Mn(1)–O(1) 1.919(4), Mn(1)–O(2) 1.868(4), Mn(1)–N(1) 2.026(5), Mn(1)–N(2) 2.039(5) and Mn(1)–O(1*) 2.487(4); O(1)–Mn(1)–Cl(1) 99.45(13), O(2)–Mn(1)–Cl(1) 96.78(14), N(1)–Mn(1)–Cl(1) 90.62(14), N(2)–Mn(1)–Cl(1) 91.92(15), O(1)–Mn(1)–O(2) 86.51(17), O(1)–Mn(1)–N(1) 87.16(18), O(1)–Mn(1)–N(2) 168.47(18), O(2)–Mn(1)–N(1) 170.96(19), O(2)–Mn(1)–N(2) 90.36(19) and N(1)–Mn(1)–N(2) 94.6(2).

Schiff base ligand adopting an equatorial position. Larson and Pecoraro[15] have previously employed [Mn(salpn)(acac)] in the preparation of the dinuclear manganese(IV) species [{Mn(salpn)O}$_2$] through peroxide oxidation of the manganese(III) species [Mn(salpn)(acac)] in acetonitrile. In this instance the *cis* sites at the manganese centre, occupied by the acetylacetonate ligand, were replaced directly by the bridging μ-oxo groups in the manganese(IV) complex; this was attributed directly to the pretemplated nature of the manganese(III) species. Refined mechanistic interpretations of this reaction were made which invoked the initial process to be deprotonation of hydrogen peroxide by the acetylacetonate ligand and showed that both the bridging μ-oxo groups originated from the same molecule of hydrogen peroxide. From these results it was therefore apparent that if we used the co-ordinated acetylacetonate as a base, and avoided high thermodynamic driving forces (*e.g.* the formation of Si–O bonds), we would be able directly to replace the acetylacetonate with carboxylate groups through the reaction of carboxylic acids with [Mn(salpn)(acac)] and produce manganese(III) complexes.

The reaction of carboxylic acids with [Mn(salpn)(acac)]. A series of straight- and branched-chain aliphatic carboxylic acids, RCO$_2$H (R = Me, Et, Pr^n, Bu^n, Pr^i or Bu^t), were treated with [Mn(salpn)(acac)] in ethanol affording a succession of compounds of stoichiometry [Mn(salpn)(O$_2$CR)], see Table 2. All compounds exhibit magnetic properties typical of manganese(III) Schiff base compounds of this type[11,13,14] with most magnetic moments being close to the spin only value of 4.9 μ_B expected for magnetically dilute high spin d^4 systems, indicating little or no antiferromagnetic interactions in the solid state. The positive ion FAB mass spectra of the compounds all show parent ion peaks relating to the fragment [Mn(salpn)]$^+$ at m/z 335 and no other fragments relating to carboxylate (or acetylacetonate) co-ordination to a monomeric manganese species. This behaviour is consistent with the other monomeric manganese(III) Schiff base complexes reported herein and those that we have previously reported with bidentate and chelating carboxylates.[13,14] All compounds show a strong band between 1614 and 1616 cm^{-1} in their infrared spectra attributable to ν(C=N). These values are comparable with those of the starting material; however, the complete absence of strong bands at 1635 and 1600 cm^{-1} of the acetylacetonate species indicate that this anion has been replaced by a carboxylate anion. This is substantiated by the presence of bands between 1543 and 1548, 1466 and 1470 and 616 and 622 cm^{-1} which can be assigned to ν_{asym}(OCO), ν_{sym}(OCO) and δ(OCO), respectively. The difference between the asymmetric and symmetric stretching modes of the carboxylate of *ca.* 80 cm^{-1} can be tentatively assigned to the presence of bidentate and chelating carboxylate groups.[13,14]

Electrochemistry of the complexes. The electrochemical behaviour of the complexes was investigated in dichloromethane solution using tetrabutylammonium hexafluorophosphate as a supporting electrolyte. All compounds formulated as [Mn(salpn)(O$_2$CR)] show essentially identical behaviour which is typified by the voltammogram of [Mn(salpn)(O$_2$CBu^n)], in Fig. 5(a). There are two different redox processes occurring. The first process (O$_1$/R$_1$) corresponds to the quasi-reversible manganese(II/III) couple, $E_{1/2} = -0.25$ to -0.30 V (see Table 3 for electrochemical data) whilst the second redox process (O$_2$/R$_2$) is assigned to the sequential oxidation of the species to the manganese(IV) state ($E_{pa} = 0.97$ to 1.00 V). This second process does not show reversible electrochemistry. However, the reductive waves between 0.18 and 0.25 V can be associated with this oxidative process, as the reductive wave is absent when the electrode is rotated and also through alteration of the voltage window, since when a window up to 0.9 V is employed the reductive wave is not observed. It is interesting that cyclic voltammetry serves as a very sensitive test of the purity of these compounds. Despite the apparent purity of the compounds

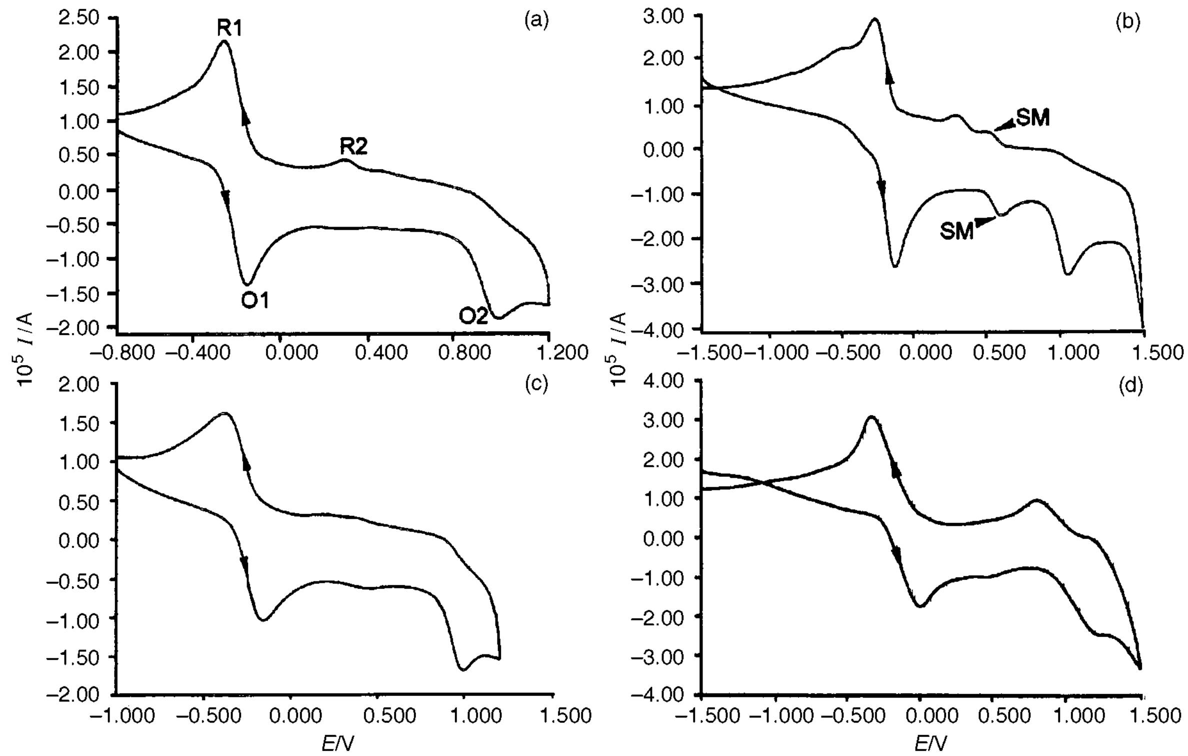


Fig. 5 Cyclic voltammograms of (a) [Mn(salpn)(O_2CBu^n)], (b) [Mn(salpn)(O_2CBu^t)], (c) [Mn(salpn)(O_2CMe)]$_{2n}$(H_2O)$_{3n}$ and (d) [{Mn(salpn)Cl}$_2$] in dichloromethane. Calomel electrode all potentials are *versus* the saturated calomel electrode.

Table 3 Electrochemical data for the complexes *versus* saturated calomel electrode

	Assigned couple (V)					
Compound	$Mn^{II/III}$	$Mn^{III/II}$	$E_{1/2}$	$Mn^{III/IV}$	$Mn^{IV/III}$	$E_{1/2}$
[{Mn(salpn)Cl}$_2$]	0.0	−0.31	−0.16	1.21	1.18	1.20
[Mn(salpn)(O_2CMe)]·H_2O	−0.19	−0.35	−0.27	0.98	0.22	—
[Mn(salpn)(O_2CEt)]	−0.19	−0.35	−0.27	0.98	0.22	—
[Mn(salpn)(O_2CPr^n)]	−0.17	−0.34	−0.25	1.00	0.22	—
[Mn(salpn)(O_2CBu^n)]	−0.19	−0.32	−0.26	0.97	0.25	—
[Mn(salpn)(O_2CPr^i)]	−0.18	−0.42	−0.30	1.00	0.17	—
[Mn(salpn)(O_2CBu^t)]	−0.21	−0.40	−0.30	0.97	0.18	—
[{[Mn(salpn)(O_2CMe)]$_2$(H_2O)$_3$}$_n$]	−0.18	−0.34	−0.26	1.00	—	—

(*viz*. as judged by elemental analyses and infrared spectroscopy, see Table 2) cyclic voltammetry is able to detect the presence of starting material as this species shows a quasi-reversible couple at E_{pa} 0.53 V and E_{pc} 0.45 V. A typical example is given in Fig. 5(b) in which the starting material impurity (labelled SM) is clearly present, in spite of the apparent "purity" of the complex. In these cases further reaction with the appropriate acid until this wave is no longer observed indicates complete displacement of acetylacetonate has occurred.

These voltammetric studies appear to suggest that similar solution species are present. However, as yet we are unable to predict the form these species take in solution, *i.e.* whether they exist as the desired monomers with *cis* chelated carboxylates or as ionised species of the form Mn(salpn)$^+$. We have four reasons to suppose that the solution species are the desired *cis* chelated monomers. First, the subtle changes in the $E_{1/2}$ values of the manganese(II/III) couples indicate that changing the carboxylate auxiliary ligand affects, albeit slightly, the potential at which this process occurs. If the solution species was the cationic Mn(salpn)$^+$ these values would be expected to be identical. Secondly, the cyclic voltammogram of the polymeric species [Mn(salpn)(O_2CMe)]$_{2n}$(H_2O)$_{3n}$ whose structure we have previously reported,[11] in which the manganese centre contains *trans* co-ordinated carboxylates, shows subtle differences electrochemically, Fig. 5(c). As for the species previously described a quasi-reversible manganese(II/III) couple is observed {E_{pa} −0.18 V, E_{pc} −0.34 V, $E_{1/2}$ −0.26 V, *cf.* −0.27 V for [Mn(salpn)(O_2CMe)]}. However, unlike the previous complexes no reversible process relating to the oxidative wave at E_{pa} 1.0 V is observed. Thirdly, when the cyclic voltammogram of **6** was recorded different behaviour was again observed, Fig. 5(d). Two quasi-reversible processes are observed which we assign to the manganese-(II/III) and -(III/IV) couples with $E_{1/2}$ values of −0.16 and 1.20 V, respectively. Li and Pecoraro[18c] have previously reported that the only solution species observed for the structurally related [Mn(salen)Cl][18b] was the Mn(salen)$^+$ cation. It seems reasonable to propose that in solution **6** will behave in a similar manner and that the differences between the voltammogram of **6** and those of the carboxylate complexes prepared are as a result of such ionisation. Finally dichloromethane solutions of the complexes formulated as [Mn(salpn)(O_2CR)] show no conductivity.

X-Ray studies. X-Ray powder diffraction studies of [Mn(salpn)(O_2CBu^n)] and [Mn(salpn)(O_2CBu^t)] indicate that these species are monomeric with *cis*-chelated carboxylates in the solid state. This is based on the identical nature of the powder diffraction patterns with those of the crystallographically characterised monomers derived from our conventional reaction of the appropriate manganese(II) carboxylate salt with the Schiff base ligand.[13,14] These powder diffraction patterns are shown in Fig. 6. Crystals suitable for single crystal X-ray dif-

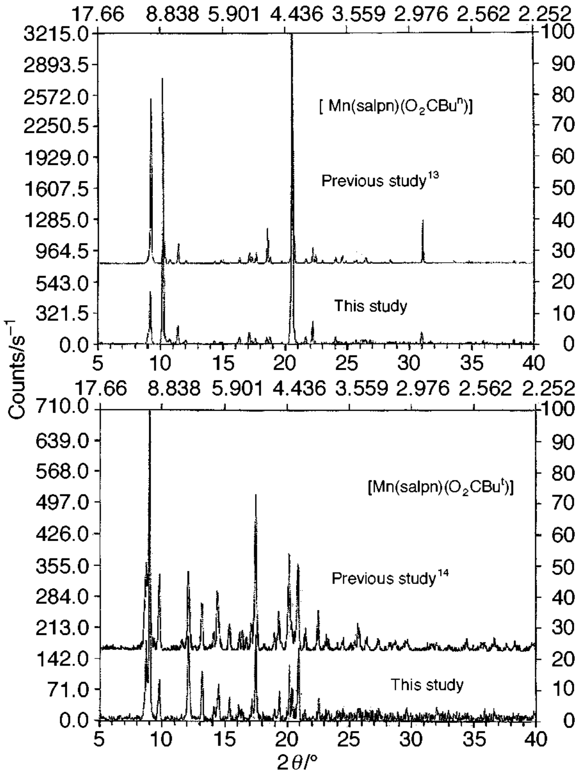


Fig. 6 Powder X-ray diffraction patterns of (a) $[Mn(salpn)(O_2CBu^n)]$ and (b) $[Mn(salpn)(O_2CBu^t)]$ prepared in this study compared with those of their crystallographically characterised monomers.[13,14]

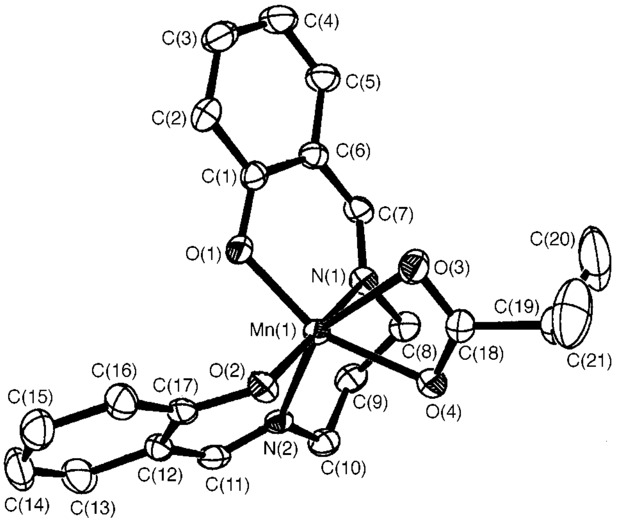


Fig. 7 Molecular structure of $[Mn(salpn)(O_2CPr^i)]$ **7**. Selected bond lengths (Å) and angles (°) with e.s.d.s: Mn(1)–O(1) 1.899(3), Mn(1)–O(2) 1.872(3), Mn(1)–O(3) 2.304(4), Mn(1)–O(4) 2.099(4), Mn(1)–N(1) 1.990(4) and Mn(1)–N(2) 2.128(4), O(1)–Mn(1)–O(2) 89.73(15), O(1)–Mn(1)–N(1) 89.59(15), O(2)–Mn(1)–N(1) 176.21(15), O(1)–Mn(1)–N(2) 112.59(15), O(2)–Mn(1)–N(2) 87.51(15), N(1)–Mn(1)–N(2) 89.31(16), O(3)–Mn(1)–N(2) 153.48(14), O(4)–Mn(1)–N(2) 94.28(14), O(1)–Mn(1)–O(3) 93.90(15), O(1)–Mn(1)–O(4) 153.03(15) and O(4)–Mn(1)–O(3) 59.21(13).

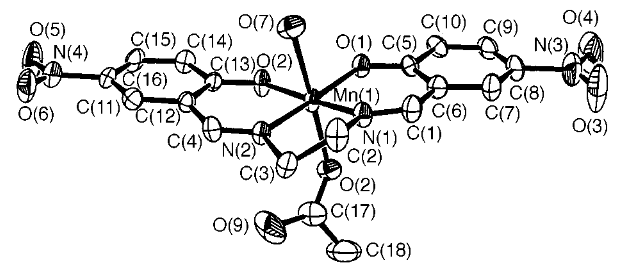


Fig. 8 Molecular structure of $[Mn(5NO_2\text{-salen})(O_2CMe)(H_2O)]$ **8**. Selected bond lengths (Å) and angles (°) with e.s.d.s: Mn(1)–O(1) 1.882(4), Mn(1)–O(2) 1.890(4), Mn(1)–N(1) 1.977(4), Mn(1)–N(2) 1.970(4), Mn(1)–O(7) 2.347(5) and Mn(1)–O(8) 2.123(4); O(1)–Mn(1)–O(2) 91.67(14), O(1)–Mn(1)–N(2) 172.31(17), O(2)–Mn(1)–N(2) 92.81(16), O(1)–Mn(1)–N(1) 91.25(15), O(2)–Mn(1)–N(1) 173.09(17), N(2)–Mn(1)–N(1) 83.63(16), O(1)–Mn(1)–O(8) 92.86(15), O(2)–Mn(1)–O(8) 95.39(16), N(2)–Mn(1)–O(8) 92.93(17), N(1)–Mn(1)–O(8) 90.71(18), O(1)–Mn(1)–O(7) 92.17(17), O(2)–Mn(1)–O(7) 89.94(17), N(2)–Mn(1)–O(7) 81.68(18), N(1)–Mn(1)–O(7) 84.69(19), O(8)–Mn(1)–O(7) 173.26(16).

fraction studies of $[Mn(salpn)(O_2CPr^i)]$ **7** were found to consist, as expected, of a monomeric manganese(III) Schiff base complex with a *cis*-chelated carboxylate ligand, Fig. 7. The distorted N_2O_4 octahedral co-ordination sphere of the manganese centre is essentially identical to those that we have previously characterised in other related monomers.[13,14] The distortion of the manganese centre is as a result of the chelation of the carboxylate. These structures are all typified by asymmetric co-ordination of the carboxylate [in this case Mn(1)–O(3) 2.304(4) and Mn(1)–O(4) 2.099(4) Å]. It is such co-ordination that we have attributed to the absence of fragments relating to the monomeric manganese species $[Mn(salpn)(O_2CR)]^+$ in the FAB mass spectra of the complexes. All other bond lengths and angles are unexceptional.

Preparation of manganese(III) complexes of Schiff base ligands containing electron-withdrawing substituents with ancillary carboxylate donors

In view of the apparent success of the reaction of carboxylic acids with [Mn(salpn)(acac)] for the preparation of complexes of the form $[Mn(salpn)(O_2CR)]$, we wondered whether this synthetic method might access a route to manganese(III) complexes of this stoichiometry with electron withdrawing substituents about the aromatic rings of the Schiff base ligands, *e.g.* $5NO_2$-salpn and 3Br,$5NO_2$-salpn. Our desires for such a route were based on our experiences with the related salen ligands with these substituents[20,21] and the inconsistent nature of the products obtained under our standard aerobic reaction conditions.[11,13,14] We found that aerial oxidation under Boucher conditions[22] does not yield any manganese(III) complex with 3Br, $5NO_2$ substituents and that for $5NO_2$ substituents, although some manganese(III) species could be detected by cyclic voltammetry, the main product of the reaction was a manganese(II) species. Manganese(III) species could be isolated, however, by the chemical oxidation of the manganese(II) species using ferrocenium tetrachloroferrate(III).[20] Furthermore, we have even found that it is possible to isolate manganese(II) species from the reduction of manganese(III) acetate in the presence of 3Br,$5NO_2$-salen.[21] Our attempts to isolate manganese(III) complexes with ancillary carboxylate ligands, as indicated, have been largely unsuccessful, manganese(II) complexes of stoichiometry $Mn(L)\cdot nH_2O$ being isolated routinely. However, on one occasion, in the reaction of $5NO_2$-salpn with manganese(II) acetate tetrahydrate, we have been able to isolate a manganese(III) species from the reaction liquor after removal of the precipitated manganese(II) complex and slow evaporation yielding $[Mn(5NO_2\text{-salpn})(O_2CMe)(H_2O)]$. This is consistent with the isolation of $[Mn(5NO_2\text{-salen})(O_2CMe)(H_2O)]$ **8**, Fig. 8, using $5NO_2$-salen. The structure consists of an octahedrally co-ordinated manganese(III) centre, analogous with **1**, **4** and **5**, in which the *xy* plane of the manganese ion is co-ordinated by the Schiff base ligand and axial sites are filled by water and the acetate ligated in the unidentate mode. The $Mn–O_{phenolic}$ bond lengths are identical with those observed in **1** and **4** indicating that the *ortho*-methoxy group and *para*-nitro group do not affect this bond length in any way. The $Mn–N_{imine}$ bonds are shorter than all of the other bonds in **4** and **5**. The $Mn–O_{carboxylate}$ distance is the shortest of any of these

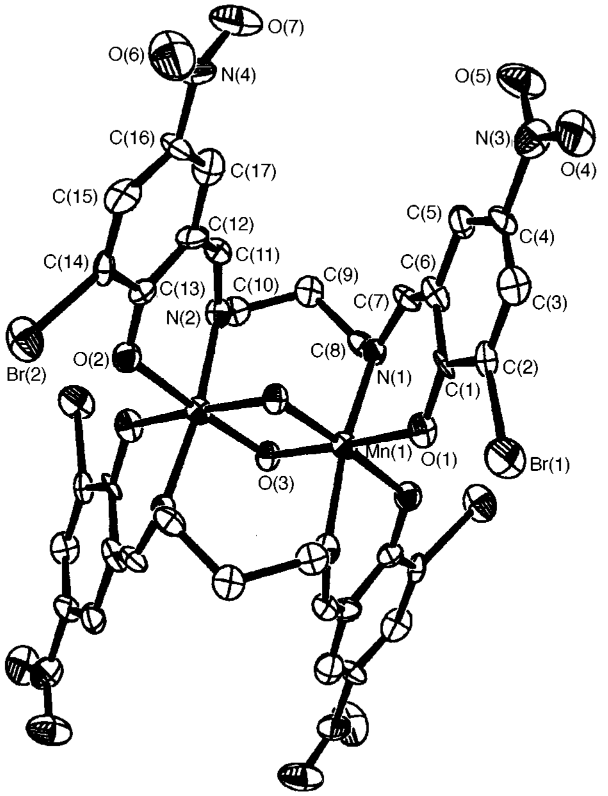


Fig. 9 Molecular structure of $[\{Mn(\mu\text{-}3Br,5NO_2\text{-}salpn)(\mu\text{-}O)\}_2]\cdot 5DMF$ **9**. Selected bond lengths (Å) and angles (°) with e.s.d.s: Mn(1)–Mn(1*) 2.736(2), Mn(1)–O(1) 1.933(5), Mn(1)–O(1*) 1.952(5), Mn(1)–O(3) 1.809(5), Mn(1)–O(3*) 1.797(4), Mn(1)–N(1) 1.997(6) and Mn(1)–N(1*) 1.993(6); O(1)–Mn(1)–O(1*) 93.1(2), O(1)–Mn(1)–O(3) 173.6(2), O(1)–Mn(1)–O(3*) 92.5(2), O(1)–Mn(1)–N(1) 88.4(2), O(1)–Mn(1)–N(1*) 87.5(2), O(1*)–Mn(1)–O(3) 93.2(2), O(1*)–Mn(1)–O(3*) 174.5(2), O(1*)–Mn(1)–N(1) 86.0(2), O(1*)–Mn(1)–N(1*) 87.1(2), O(3)–Mn(1)–O(3*) 81.3(2), O(3)–Mn(1)–N(1) 93.3(2), O(3)–Mn(1)–N(1*) 91.6(2), O(3*)–Mn(1)–N(1) 94.7(2), O(3*)–Mn(1)–N(1*) 92.7(2) and N(1)–Mn(1)–N(1*) 171.7(2).

monomers, Mn–O(8) 2.123(4) Å, whilst the manganese–water distance is intermediate between **1** and **4** at 2.347(5) Å.

In view of the success in the displacement of acetylacetonate with a carboxylate in [Mn(salpn)(acac)] we attempted to apply the same reaction to $[Mn(5NO_2\text{-}salpn)(acac)]$ and $[Mn(3Br,5NO_2\text{-}salpn)(acac)]$ prepared by the same method as [Mn(salpn)(acac)] (see Experimental section).[15] It appears that this does provide a satisfactory route to compounds of stoichiometry $MnL(O_2CR)$, but in much lower yields than the unsubstituted analogue, due to the precipitation of yellow materials of composition $MnL(H_2O)_n$, $n = 0,2$, in up to 50% yield. We have only been able to isolate crystals from one of these complexes, $Mn(3Br,5NO_2\text{-}salpn)(O_2CMe)\cdot 2H_2O$. These were not the expected complex, but rather a di-μ-oxo manganese(IV) species, $[\{Mn(\mu\text{-}3Br,5NO_2\text{-}salpn)(\mu\text{-}O)\}_2]\cdot 5DMF$, **9**, Fig. 9, which is structurally analogous with a related dimer that we have previously reported.[20] In the previous case the remarkable feature of the structure lay in the non-planar nature of the salen ligand. Although this twist is still inherent in **9** it is perhaps less surprising since there is much greater conformational freedom between the imino nitrogen atoms N1 and N2 in this ligand than in a salen-based ligand. The most surprising feature of the compound is the apparent attainment of the +4 oxidation state with this ligand. This assignment is based on the similarity between the bond lengths and angles in the central $Mn–O_2–Mn$ of **9** and other well characterised di-μ-oxo-bridged manganese(IV) species.[20] The Mn–O(3) bridging bonds of 1.797(4) Å and 1.809(5) Å, the Mn–O(3)–Mn′ angle of 98.7(2)° and the $Mn\cdots Mn$ separation of 2.736(2) Å are all typical of such systems.

Conclusion

The co-ordination chemistry of manganese(III) Schiff base complexes with ancillary carboxylate ligands is an area of tremendous variety. Although at times capricious, some obvious patterns are developing. When sterically restricting carboxylates $^{-}O_2CBu^t$ and $^{-}O_2CPr^i$ are employed with salpn based ligands monomers ensue, in which the carboxylate asymmetrically chelates *cis* sites at the metal centre as is observed in complexes **2**, **3**, **7** and previous studies.[13,14] This behaviour appears to be independent of ligand substituents. When tetradentate Schiff base ligands with methoxy groups *ortho* to the phenolic donor atoms are used and sterically very demanding carboxylates are avoided the unique mode of co-ordination of the carboxylate is unidentate, **1**, **4** and **5**. Unlike our previous studies[14] in which the co-ordination spheres of the manganese centres were completed by weak μ-phenoxy bridges to a second metal centre forming dimers, the complexes reported herein are all monomers in which water molecules complete the co-ordination sphere. The differences between these two structural motifs are relatively minor and of greatest significance is the unidentate binding mode of the carboxylate which appears to result exclusively for these systems. A similar binding mode is also observed in **8**.

It is apparent that we are able to prepare monomeric species of stoichiometry $[Mn(salpn)(O_2CR)]$ by the reaction of [Mn(salpn)(acac)] with a variety of aliphatic carboxylic acids. This is substantiated by cyclic voltammetry and X-ray studies. X-Ray powder diffraction shows the products of these reactions with valeric and trimethylacetic acid to be the same as the monomers that we have crystallographically characterised from the reaction of the manganese(II) carboxylate salt and the Schiff base ligand.[13,14] Single crystal studies of **7** further substantiate this view. This methodology is also a relatively satisfactory means of preparing complexes of manganese(III) with electron withdrawing substituents on the aromatic rings of the Schiff base ligands which normally prevent the aerial oxidation of manganese(II) salts.[20] Although manganese(II) side products are also isolated a number of manganese(III) complexes have been isolated in fair yield. On one occasion we have been able to isolate from one of these products single crystals of a manganese(IV) di-μ-oxo dimer in which the manganese centres are also bridged by two ligands, **9**, a further remarkable example of oxidation of manganese to the +4 level with concomitant formation of di-μ-oxo bridges upon recrystallisation from DMF.

We believe these results develop the chemistry of these systems considerably. Clear and predictable patterns have developed, and we hope will continue to develop yet unpredictable and fascinating structures also persist within this niche.

Experimental

All experiments, except for the preparation of complex **6**, were carried out in air. All reagents (Aldrich and Maybridge Chemicals) and solvents were used as received except acetonitrile (for the preparation of **6**) and dichloromethane (for cyclic voltammetry) which were freshly distilled from CaH_2 prior to use.

Physical measurements

Infrared spectra were recorded on a Bruker IFS66V spectrophotometer as KBr discs, FAB mass spectra on a Kratos MS-45 spectrometer with a FAB probe and a xenon reaction gas using a *m*-nitrobenzyl alcohol matrix. Room temperature magnetic moments were measured on a Faraday balance which was calibrated using $HgCo(NCS)_4$. Elemental analyses were performed by the in-house services of the University of Santiago and UMIST. Cyclic voltammetry was performed with a Princeton Applied Research model 270 potentiostat and potential scan-

Table 4 Crystal data and details of refinement

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
Formula	$C_{20}H_{21}MnN_2O_9$	$C_{25}H_{31}Cl_2MnN_2O_6$	$C_{23}H_{27}MnN_2O_6$	$C_{26}H_{27}MnN_2O_8$	$C_{28}H_{32}MnN_2O_8$	$C_{19}H_{19}ClMnN_3O_2$	$C_{21}H_{23}MnN_2O_4$	$C_{18}H_{17}MnN_4O_9$	$C_{49}H_{59}Br_4Mn_2N_{13}O_{19}$
M	488.33	581.36	482.41	550.44	579.50	411.76	422.35	488.30	1563.61
Crystal dimensions/mm	0.45 × 0.38 × 0.12	0.56 × 0.45 × 0.33	0.52 × 0.16 × 0.10	0.40 × 0.27 × 0.12	0.62 × 0.42 × 0.21	0.40 × 0.25 × 0.25	0.35 × 0.30 × 0.20	0.35 × 0.30 × 0.15	0.25 × 0.25 × 0.20
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Orthorhombic	Monoclinic	Monoclinic
Space group	$P2_1/c$ (no. 14)	$P2_1/n$ (no. 14)	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)	$P2_1/n$ (no.14)	*Pbca* (no.61)	$P2_1/c$ (no. 14)	$P2_1/n$ (no. 14)
a/Å	12.053(2)	13.034(3)	9.692(2)	9.927(2)	10.440(6)	10.849(4)	17.844(4)	14.014(2)	12.592(2)
b/Å	19.874(4)	12.111(4)	12.088(2)	13.495(3)	13.647(5)	12.409(5)	18.881(5)	12.086(2)	12.103(3)
c/Å	9.312(2)	18.446(5)	20.027(4)	18.761(4)	19.300(11)	13.610(4)	12.337(3)	13.370(2)	20.266(2)
β/°	99.97(2)	102.760(10)	99.55(3)	95.88(3)	99.33(6)	95.54(3)	90.0	115.71(2)	92.11(2)
V/Å^3	2196.9	2839.9	2313.8	2500.1	2713	1823.6	4156.5	2040.4	3086.7(10)
Z	4	4	4	4	4	4	8	4	2
D_c/g cm^{-3}	1.476	1.360	1.385	1.462	1.419	1.500	1.350	1.590	1.682
F(000)	1008	1208	1008	1160	1212	848	1760	1000	1572
μ/cm^{-1}	6.55	6.93	6.11	5.82	5.40	8.89	6.63	7.07	3.079
$2\theta_{max}$/°	50.10	45.00	44.84	44.90	45.02	50.00	50.00	50.00	50.00
Number of unique data	2166	3679	1097	888	3547	3161	3643	3573	5398
Number of observed data[a]	2166	3679	1097	888	3544	3161	3643	3573	5398
Number of variables	382	325	134	184	343	236	323	357	418
R[b]	0.0433	0.0748	0.1063	0.0541	0.0946	0.0444	0.048	0.0461	0.0430
R'[c]	0.1186	0.2098	0.2957	0.1385	0.2518	0.1057	0.1226	0.1096	0.0817

[a] $I > 2.00\sigma(I)$. [b] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] $R' = [\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma wF_o{}^2)]^{\frac{1}{4}}$.

ning unit with the operating program ECHEM. The electrolytic cell consisted of a METROHM model 6.12404 carbon disc working electrode, a saturated calomel reference electrode and a platinum wire auxiliary electrode. Voltammograms were obtained of *ca.* 1 mM dichloromethane solutions of the complexes using 0.1 M Bu_4NPF_6 as a supporting electrolyte.

Preparations

Schiff base ligands. All ligands were prepared in virtually quantitative yields as previously reported and satisfactorily characterised by elemental analysis, ^{1}H NMR, infrared and FAB mass spectroscopy.[20]

Compounds of stoichiometry [Mn(3CH$_3$O-salen)(O$_2$CR)] and [Mn(3CH$_3$O-salpn)(O$_2$CR)]. All compounds were prepared by the same method as previously reported in high yields (based on manganese).[11,13,14] They were characterised by elemental analysis, infrared, mass spectroscopy, room temperature magnetic moment measurement and FAB mass spectroscopy.

[MnL(acac)] complexes. All complexes were prepared as previously reported[15] by the reaction of [Mn(acac)$_3$] (Aldrich) with the appropriate ligand. The [MnL(acac)] were characterised satisfactorily.

[Mn(salpn)Cl]. Acetonitrile (25 cm^3) was freshly distilled from CaH$_2$ and added to [Mn(salpn)(acac)] (0.5 g, 1.15 mmol) under nitrogen. Chlorotrimethylsilane (0.15 cm^3, 1.15 mmol) was added to the solution which resulted in the immediate formation of an emerald green suspension which rapidly darkened to form a dark solid. The reaction was stirred for 5 min before cooling to 5 °C. The resultant microcrystalline precipitate formed was collected by filtration, washed copiously with diethyl ether and dried *in vacuo*.

Monomeric complexes [Mn(salpn)(O$_2$CR)], by the reaction of carboxylic acids with [Mn(salpn)(acac)]. All the monomeric manganese(III) complexes were prepared similarly, typified by that of [Mn(salpn)(O$_2$CPr^i)]. To an ethanolic solution (25 cm^3) of [Mn(salpn)(acac)] (0.568 g, 1.3 mmol) was added isobutyric acid (1.27 g, 1.4 mmol). The solution was heated to reflux with stirring for 2 h then reduced in volume (*ca.* 4 cm^3) and the complex precipitated in diethyl ether (100 cm^3) from this solution. The green solid thus formed was collected by filtration, washed with diethyl ether (2 × 5 cm^3) and dried *in vacuo*.

Reaction of [Mn(5NO$_2$salpn)(acac)] and [Mn(3Br,5NO$_2$-salpn)(acac)] with carboxylic acids

These reactions were performed in an analogous way to the reactions of carboxylic acids with [Mn(salpn)(acac)] with one modification. Prior to volume reduction the precipitated yellow material was removed by filtration. This material was washed with diethyl ether (20 cm^3) and dried *in vacuo* yielding complexes of stoichiometry MnL(H$_2$O)$_n$ (n = 0–2) in 35–50% yield.

X-Ray diffraction studies

Powder studies. X-Ray powder diffraction patterns were recorded using a Scintag XRD2000 powder diffractometer using Cu-Kα radiation of $\lambda = 1.5481$ Å.

Single crystal studies. Crystals suitable for X-ray studies were obtained in the following ways. Those of complexes **1** and **4** were obtained by slow evaporation of acetonitrile solutions of the complexes. Crystals of **2** and **3** were obtained by layering a concentrated dichloromethane solution of the complexes with *n*-hexane. Crystals of **5** were obtained by slow evaporation of an acetonitrile–ethanol solution of the complexes. Cooling of a saturated acetonitrile solution of the complex at 5 °C for 3 weeks produced crystals of it as its acetonitrile solvate, **6**. Crystals of **7** and **8** were obtained by layering a concentrated ethanolic solution of the complex with *n*-hexane. Crystals of **9** were obtained from a DMF solution of [Mn(3Br,5NO$_2$-salpn)(O$_2$CMe)]·2H$_2$O after several weeks.

Crystal data and experimental conditions are listed in Table 4. All data were collected at ambient temperature with Mo-Kα radiation of $\lambda = 0.71069$ Å on a Nicolet P3, **1** and **3**, a Siemens P4, **2** and **5**, CAD-4, **4**, or Rigaku AFC6S diffractometer, **6**–**9**. The intensities of three representative reflections declined by 14.4% for **7**. A linear correction factor was applied to account for this. All data were corrected for Lorentz-polarisation effects. The structures were solved by direct methods[24,25] and refined using full matrix least squares on F^2. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in idealised positions. All calculations were performed using the TEXSAN[26] crystallographic package.

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See http://www.rsc.org/suppdata/dt/1999/31/ for crystallographic files in .cif format.

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