

Structurally Diverse Manganese(III) Carboxylate Complexes of N₂O₂ Donor Set Symmetrical Schiff Base Ligands

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The isolation of [Mn₂(Salen)₂(O₂CPr)(EtOH)(H₂O)][O₂CPr] and [Mn(salpn)(O₂CBu)] from manganese(II) carboxylates indicates that a diverse range of structural possibilities exist for Schiff base complexes of these salts.

The involvement of manganese in many biological systems is well established. Manganese is essential to superoxide dismutase¹ and an azide insensitive catalase,² but the most important role of manganese in nature is in the water-oxidising complex (WOC) of photosystem II (PSII).^{3,4} It is recognised that four manganese ions are necessary for high rates of dioxygen evolution, but there is some doubt as to their structural role. The manganese ions in PSII are ligated by oxygen and nitrogen donors from amino acid side chains. EXAFS studies have shown that there are two Mn...Mn separations of 2.7 and 3.3 Å,⁵ and a carboxylate bridge between the manganese ions has been postulated for the latter separation. Therefore, the chemistry of multinuclear manganese complexes with ligand donor environment relevant to the biological system is receiving considerable attention.

Studies into the possible manganese binding sites in PS II have excluded sulfur-containing residues such as cysteine and methionine.⁶ Deprotonated alkoxy-type ligands such as serine, threonine and tyrosine residues have also been excluded because they are only stable under alkaline conditions,^{7,8} whereas acidic conditions are known to prevail at the manganese site. Consequently, only nitrogen donor ligands, such as histidine and lysine, carboxylate donors, such as aspartate and glutamate, and primary amides, such as asparagine and glutamine, remain.⁹ Many of the proposed models contain simple nitrogen donor and acetate ligands,^{10–12} and these have been employed as alternatives for the amino acid side groups in the proteins that bind the manganese ions producing a remarkably diverse range of structures.

We have recently reported the first example of a manganese(III) Schiff base polymeric complex containing a dimeric repeat unit,¹³ in [Mn(salpn)(OAc)]_{2n}(H₂O)_{3n} and we have subsequently extended our studies to longer chain carboxylate ligands, which represent better structural models for the carboxylate groups of amino acids. In view of the fascinating diversity of structures associated with the acetate ligand a study involving other carboxylate ligands could produce complexes with interesting structural features. This has indeed proved to be the case and we have isolated dinuclear and monomeric complexes for the butyrate and valerate ligands, respectively.

Both complexes were prepared by the direct reaction of the appropriate manganese(II) carboxylate salt† and the appropriate Schiff base ligand in ethanol. The reactions were refluxed for 2–3 h then the solvent reduced in volume. Crystals of **1**‡ were prepared from the reduced ethanolic solution, which was layered with *n*-hexane at room temperature. After 3–5 days a large crop of dark brown crystals formed at the solution interface. Crystals of **2**‡ were prepared in an analogous manner, except the solution was layered with diethyl ether rather than *n*-hexane.

It was first thought that these complexes would possess polymeric structures, similar to the previously prepared acetate complexes;^{13,15–17} the longer carbon chain of the butyrate and valerate groups should not cause any steric restraints since they are unbranched. This was supported by the elemental analyses which suggested a stoichiometry of Mn(L)(O₂CR) for both complexes, and room temperature

magnetic moments typical of magnetically dilute high-spin manganese(III). However, single crystal X-ray studies revealed the structures to be markedly different.

The complex [Mn(salen)(O₂CPr)] crystallised as the dinuclear complex [Mn₂(salen)₂(O₂CPr)(EtOH)(H₂O)][O₂CPr] **1**, (Fig. 1). The manganese atoms are situated in the equatorial plane of two phenolic oxygen atoms and two imine nitrogen atoms of the salen ligand and are bridged by a single butyrate group. Octahedral co-ordination is completed by an ethanol molecule for Mn(1) and a water molecule for Mn(2). The expected Jahn–Teller elongation is observed along the axial bonds, Mn(1)–O(7), 2.279(7), Mn(1)–O(5), 2.155(8), Mn(2)–O(6), 2.121(8) and Mn(2)–O(8), 2.247(7) Å. The cationic charge of the dinuclear unit [Mn₂(salen)₂–{O₂CPr}(EtOH)(H₂O)]⁺ is balanced by an unco-ordinated butyrate anion. This represents the first example of non-charged donors, such as water and ethanol, co-ordinating to manganese in preference to the strongly co-ordinating carboxylate group, and may well have implications for water co-ordination to manganese in PSII in preference to other more likely donors. IR studies show two stretching frequencies [$\nu_{\text{asym}}(\text{CO}_2)$ 1558, 1542 and $\nu_{\text{sym}}(\text{CO}_2)$ 1403, 1388 cm⁻¹] for both the stretches for the carboxylate groups, an observation we attribute to the two different environments of the carboxylate groups.

The cyclic voltammogram of **1** [Fig. 3(a)], in acetonitrile at 25 °C in the potential range –1.0 to +1.0 V vs. ferrocenium

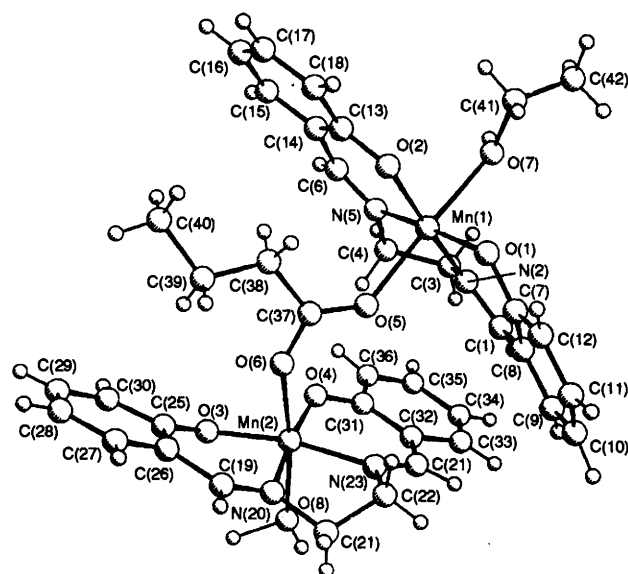


Fig. 1 The crystal structure of [Mn₂(salen)₂(O₂CPr)(EtOH)(H₂O)][O₂CPr]. Selected bond distances (Å) and angles (°): Mn(1)–O(1) 1.890(7), Mn(1)–O(2) 1.876(7), Mn(1)–O(5) 2.155(8), Mn(1)–O(7) 2.279(7), Mn(1)–N(2) 1.959(9), Mn(1)–N(5) 1.969(8), Mn(1)···Mn(2) 5.598(3); O(1)–Mn(1)–O(2) 95.2(3), O(1)–Mn(1)–O(7) 92.5(3), O(1)–Mn(1)–N(2) 90.2(3), O(1)–Mn(1)–N(5) 172.3(4), O(2)–Mn(1)–O(5) 98.1(3), O(2)–Mn(1)–O(7) 88.1(3), O(5)–Mn(1)–N(2) 87.0(3), O(7)–Mn(1)–N(2) 86.4(3), N(2)–Mn(1)–N(5) 82.1(4)

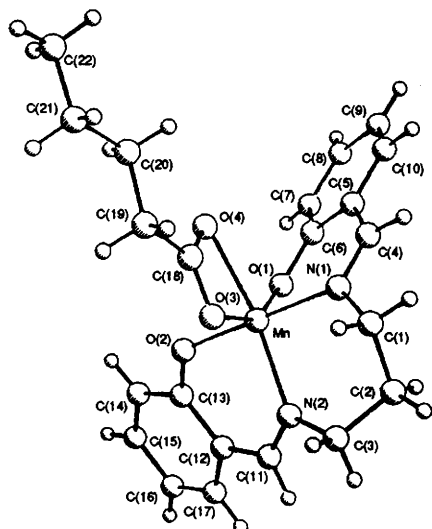


Fig. 2 The crystal structure of $[\text{Mn}(\text{O}_2\text{CBu})(\text{salpn})]$. Selected bond distances (\AA) and angles ($^\circ$): Mn–O(2) 1.868(4), Mn–O(1) 1.910(4), Mn–O(3) 2.120(5), Mn–O(4) 2.294(5), Mn–N(1) 1.970(5), Mn–N(2) 2.119(5); O(4)–Mn–O(1) 94.5(2), O(1)–Mn–N(2) 112.7(2), N(2)–Mn–O(3) 93.5(2), O(3)–Mn–O(4) 59.2(2), N(2)–Mn–N(1) 90.4(2), O(2)–Mn–N(2) 89.0(2)

(Fc⁺)/ferrocene (Fc), exhibits two oxidative peaks at -0.21 and $+0.42$ V which we assign to the $\text{Mn}_2^{\text{III}}/\text{Mn}^{\text{III}}\text{Mn}^{\text{IV}}$ and $\text{Mn}^{\text{III}}\text{Mn}^{\text{IV}}/\text{Mn}_2^{\text{IV}}$ couples respectively. A two electron reduction wave is observed at -0.41 V which we assign to the $\text{Mn}_2^{\text{IV}}/\text{Mn}_2^{\text{III}}$ couple.

The solid-state variable temperature magnetic susceptibility of **1** has been measured from 300 to 5 K. The magnetic moment varies from $4.75 \mu_B$ at 300 K to $3.82 \mu_B$ at 5 K, indicating that there is very little antiferromagnetic coupling between the manganese ions. A degree of antiferromagnetic coupling was detected for the previously reported polymer $[\text{Mn}(\text{salpn})(\text{OAc})]_{2n}(\text{H}_2\text{O})_{3n}$ ($\mu_{\text{eff}} = 4.43 \mu_B$) despite the larger Mn...Mn separation, $6.411(3) \text{\AA}$. This different magnetic and structural behaviour can only be attributed to the different carboxylate group, and it is likely that these differences arise as a result of subtle changes in the $\text{p}K_b$ values of the carboxylate.

In complete contrast to the aforementioned structure and that of the polymeric acetate complex, $[\text{Mn}(\text{O}_2\text{CBu})(\text{salpn})]$, **2**, has a monomeric structure (Fig. 2). This is only the second monomeric manganese complex with nitrogen donor and carboxylate ligands to be crystallographically characterised, the first being $[\text{Mn}(\text{sal})_2(\text{bpy})]^{18}$ ($\text{H}_2\text{sal} = \text{salicylic acid}$, $\text{bpy} = 2,2'$ -bipyridine).

Whilst chelation of the carboxylate ligand is well known in manganese carboxylate salts^{19,20} there is only one other example of a complex containing nitrogen donor ligands in which the carboxylate ligand is chelating,²¹ carboxylate ligands in such complexes are usually chelating and bridging.^{22,23} The chelation of the valerate anion necessarily involves considerable distortion of the manganese centre from ideal geometry. This is clearly illustrated in the bond lengths and angles at the manganese centre, (Fig. 2). IR studies show two $\nu(\text{CO}_2)$ stretches at 1548 and 1469 cm^{-1} , the difference in energy of which is characteristic of a chelating carboxylate group.²⁴

The cyclic voltammogram of **2**, [Fig. 3(b)], in acetonitrile at 25°C , in the potential range -1.0 to $+1.5$ V vs. Fc⁺/Fc, exhibits a quasireversible oxidative peak at $+0.39$ V and a quasireversible reductive peak at $+0.25$ V, which we assign to the $\text{Mn}^{\text{III}}/\text{Mn}^{\text{IV}}$ and $\text{Mn}^{\text{IV}}/\text{Mn}^{\text{III}}$ couples, respectively. The room temperature magnetic moment of **2** is $4.67 \mu_B$, which is typical of magnetically dilute high-spin manganese(III).

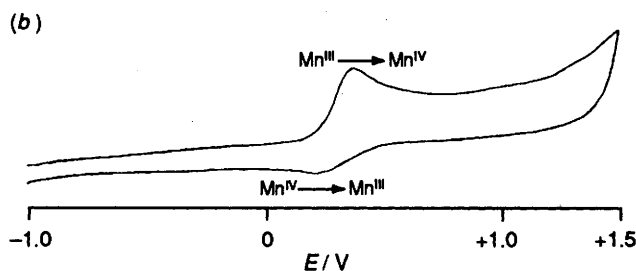
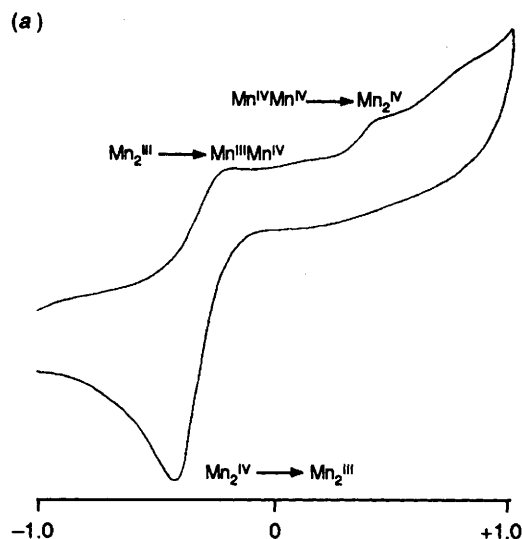


Fig. 3 Cyclic voltammograms of (a) $[\text{Mn}_2(\text{salen})_2(\text{O}_2\text{CPr})(\text{EtOH})(\text{H}_2\text{O})]$ $[\text{O}_2\text{CPr}]$ and (b) $[\text{Mn}(\text{O}_2\text{CBu})(\text{salpn})]$

These studies demonstrate that a wide range of structures may be formed by manganese complexes containing carboxylate ligands, but, more importantly, that the structures and magnetic properties are critically dependent on the nature of the carboxylate ligand used. These facts are crucial in the validity of compounds previously proposed as models of PSII;^{10–12} can these compounds be prepared with these longer chain carboxylate groups and if so do their physical properties still mimic those of PSII?

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Footnotes

† The manganese(II) carboxylate salts were prepared by the direct reaction of manganese(II) carbonate with an excess of the appropriate carboxylic acid in aqueous solution. The reaction was refluxed for 5–6 h and the unreacted manganese carbonate was removed by filtration. The aqueous phase was then washed with diethyl ether to remove any excess acid, and subsequently evaporated to dryness to yield a pale pink solid. This was dried under vacuum at 170°C for 2 h, ground and then dried *in vacuo* over P_2O_5 .

‡ Crystal data: $1 \text{ C}_{42}\text{H}_{50}\text{N}_4\text{O}_{10}\text{Mn}_2$, $M = 880.75$, monoclinic, space group $P2_1/n$ (No. 14), $a = 14.101(5)$, $b = 12.389(4)$, $c = 23.361(6) \text{\AA}$, $\beta = 94.26(3)^\circ$, $V = 4070(4) \text{\AA}^3$, $D_c = 1.437 \text{ g cm}^{-3}$, $Z = 4$ (from least-squares refinement of 20 carefully centred reflections in the range $8.9 < 2\theta < 15.0^\circ$). Employing graphite-monochromated Mo-K α radiation ($\lambda = 0.71069 \text{\AA}$) on a Siemens R3m/V diffractometer

at 233 K producing 7085 unique reflections from 7525 reflections and employing the $\omega/2\theta$ scanning technique ($2\theta_{\max}$ 50.1°). Structure solutions were obtained by direct methods (DIRDIF)¹⁴ with hydrogen atoms constrained to chemically reasonable positions. Final residual factors were $R = 0.071$ and $R_w = 0.060$, respectively. All non-hydrogen atoms were treated anisotropically, giving hydrogen atoms an isotropic parameter common to each molecular ion.

Crystal data: $2\text{C}_{22}\text{H}_{25}\text{N}_2\text{O}_4\text{Mn}$, $M = 436.39$, monoclinic, space group $C2/c$ (No. 15), $a = 21.910(8)$, $b = 11.836(9)$, $c = 18.781(9)$ Å, $\beta = 119.16(3)^\circ$, $V = 4253(8)$ Å³, $D_c = 1.363$ g cm⁻³, $Z = 8$ (from least-squares refinement of 25 carefully centred reflections in the range $14.4 < 2\theta < 20.3^\circ$). Employing graphite-monochromated Mo-K α radiation ($\lambda = 0.71069$ Å) on a Rigaku AFC6S diffractometer producing 3955 unique reflections from 4069 reflections and employing the $\omega/2\theta$ scanning technique ($2\theta_{\max}$ 50.0°). Structure solutions were obtained by direct methods (DIRDIF)¹⁴ with hydrogen atoms constrained to chemically reasonable positions. Final residual factors were $R = 0.049$ and $R_w = 0.058$, respectively. All non-hydrogen atoms were treated anisotropically, giving hydrogen atoms an isotropic parameter common to each molecular ion.

Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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