A New Geometry for Tetramanganese: Fused Open Cubanes

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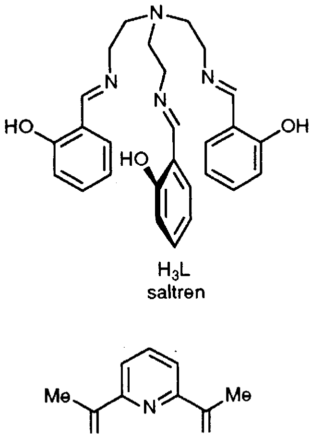
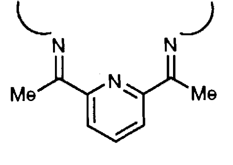
A series of complex ions containing the $[Mn_4O_2(L)_2]^{2+}$ ion have been synthesised and structurally characterised; the Mn_4O_6 cores consist of two incomplete, face-sharing cubanes, EPR spectra are consistent with the Mn^{III} description and complex electrochemsitry is observed.

As knowledge of the structure of the active site of the oxygen-evolving complex (OEC) of Photosystem II advances,[1] it stimulates development of synthetic programmes aimed at matching the known spectroscopic and structural parameters of the biosite. Some of these 'structural' models, it is hoped, may eventually prove capable of mimicking, even in part, the remarkable function of the natural site. The following information is presently available regarding the PSII active site. The four manganese ions are present as an unsymmetrical cluster, incorporating Mn–Mn distances of 2.7 and 3.3 Å; the shorter distance is consistent with a di-μ-oxo bridge, and the longer with a single μ-oxo or a μ-carboxylato-μ-oxo bridge.[2,3] Mn is ligated *via* O- and/or N-donors;[2–4] the N-ligation level appears to be low,[5] possibly involving histidine,[6] while the most likely O-donors are oxo and protein carboxylate. The EPR-active state S_2 is mixed-valence, most probably $Mn^{III}{}_3 Mn^{IV}$, and recent EPR evidence confirms that the Mn^{IV} ion is incorporated in the cluster.[3] Chloride is required for the OEC to function and, although there is currently no convincing evidence for coordination of Cl^- to Mn, a relatively long Mn–Cl bond cannot be ruled out.[4] Many Mn model compounds have been prepared;[7–9] the most appropriate, in terms of ligation and redox state, are those of Christou,[10,11] but none so far shows any photoredox activity.

For some time, we have been interested in di- and poly-manganese complexes of Schiff base macrocycles[12–14] and have come to recognise the tendency of manganese in higher oxidation states (*i.e.* >2) to self-assemble into polynuclear clusters *via* μ-oxo links. Mixed-valence tetramanganese derivatives of L^2 and L^3, incorporating both μ-oxo and μ-carboxylato ligands, have been obtained,[15] but poor crystal



H_3L
saltren



L^2 $n = 3$
L^3 $n = 4$

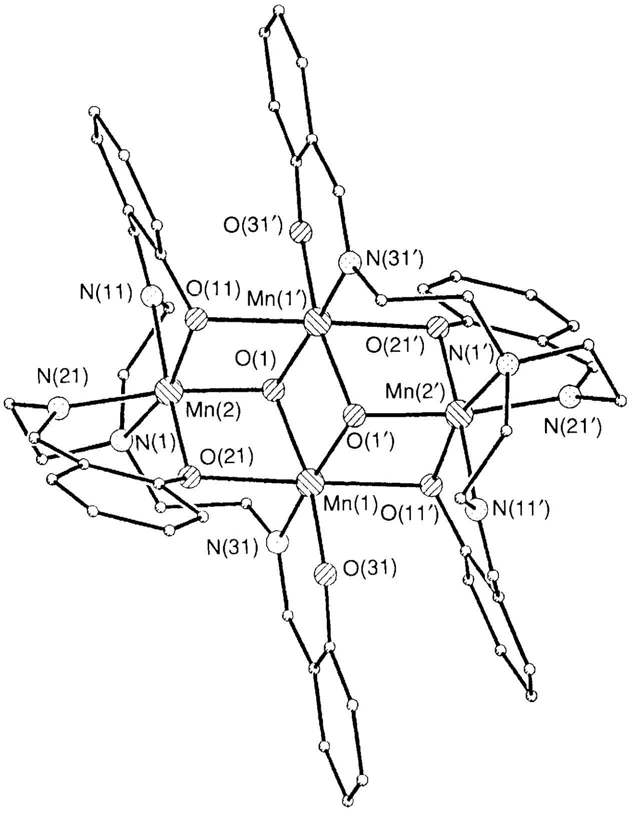


Fig. 1 Perspective view of one of the two independent [Mn$_4$O$_2$(L)$_2$]$^{2+}$ ions

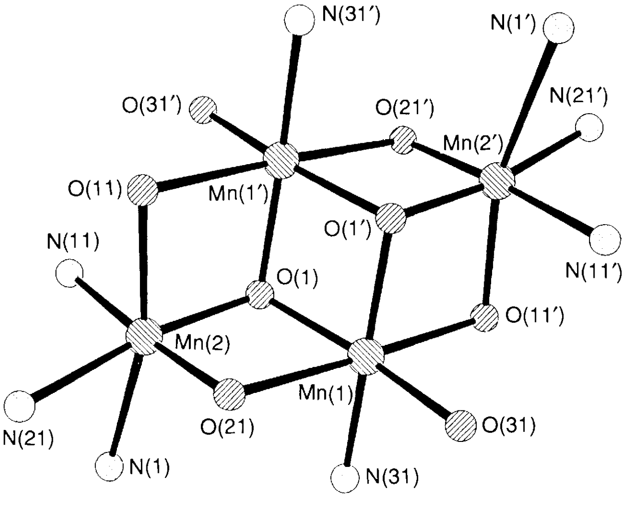


Fig. 2 The coordination spheres of the manganese atoms. Selected interatomic distances (Å) and angles (°): Mn(1)–Mn(2) 2.992(2); Mn(1)–Mn(1′) 2.898(2); Mn(1)–Mn(2′) 3.035(2); Mn(1)–O(1) 1.900(4); Mn(1)–O(1′) 1.944(4); Mn(1)–O(11′) 2.273(3): Mn(1)–O(21) 2.304(3); Mn(1)–O(31) 1.891(4); Mn(1)–N(31) 2.021(5); Mn(2)–O(1) 1.920(3); Mn(2)–O(11) 2.093(4); Mn(2)–O(21) 1.893(4); Mn(2)–N(1) 2.402(6); Mn(2)–N(11) 2.004(5); Mn(2)–N(21) 2.026(4); Mn(1)–O(1)–Mn(1′) 97.9(2); Mn(1)–O(1)–Mn(2) 103.5(1); Mn(2)–O(1)–Mn(1′) 103.5(2).

quality has prevented full refinement of the structures. Preliminary data, however, do show appropriate Mn–Mn distances of 2.7 and *ca.* 3.3 Å (the longer distance being ligand-dependent as it is intramacrocyclic). The average oxidation state of manganese in these complexes is 2.5.

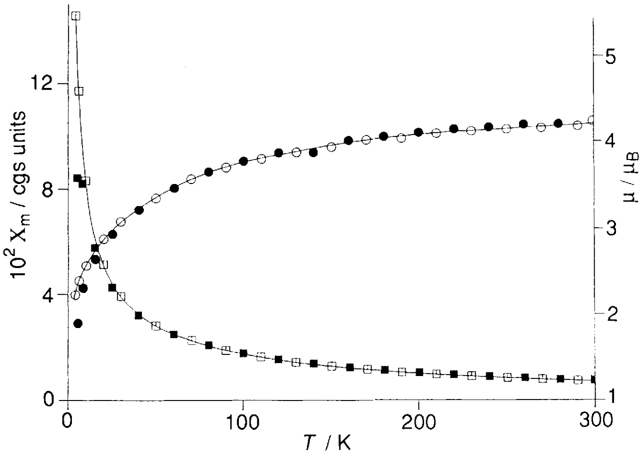


Fig. 3 The variation of molar magnetic susceptibility (□, ■) and magnetic moment (○, ●) per manganese ion for the two salts [Mn$_4$O$_2$L$_2$][ClO$_4$]$_2$ (□) and (○) and [Mn$_4$O$_2$L$_2$][MnCl$_4$]·2MeCN (■) and (●) in the temperature range 300–4.2 K. Alternate data points are plotted so as to display both compounds. The measured magnetic susceptibility of the [MnCl$_4$]$^{2-}$ salt is corrected for an assumed spin-only contribution from this anion. At low temperature, this correction accounts for a significant fraction of the measured susceptibility of the complex salt (*ca.* 75% at 4.2 K) giving rise to appreciable error in the data for this salt, which probably explains the deviation of the two sets of data below 30 K.

In order to increase the level of O-ligation (and, in consequence, the average Mn oxidation state), we made use of the podand ligand, H$_3$L (saltren). Both template condensation of tris(2-aminoethyl)amine with salicylaldehyde and direct treatment of the neutral ligand with Mn^{III} in MeOH–MeCN result in deprotonation of the phenol oxygens and isolation of the tetranuclear di-μ-oxo cluster [Mn$_4$O$_2$(L)$_2$]$^{2+}$ (as [MnCl$_4$]$^{2-}$, ClO$_4$$^-$, CF$_3SO_3$$^-$ or Ph$_4$B$^-$ salts). Identical products were obtained using Mn^{II} salts (after air oxidation of the initial yellow solutions). Dominant in the FAB mass spectra of these products was an isotopic cluster centred around *m/z* 1163, corresponding to [Mn$_4$O$_2$(L)$_2$]$^+$; a weaker peak, with intensity dependent on the counter-ion X, was often observed at *m/z* corresponding to [Mn$_4$O$_2$(L)$_2$X]$^+$. Preliminary crystallographic data on the triflate salt [Mn$_4$O$_2$(L)$_2$][CF$_3$SO$_3$]$_2$·2H$_2$O revealed a cluster almost identical to that in Fig. 1; however paucity of data and triflate disorder prevented refinement of the structure below R = 0.12.

The product of reaction of H$_3$L with excess of MnCl$_2$·4H$_2$O yielded a more satisfactory crystal, with formulation [Mn$_4$O$_2$(L)$_2$][MnCl$_4$]·2MeCN. The FAB mass spectrum of this product showed, in addition to the 1163 *m/z* peak, a weak *m/z* 1198 cluster attributable to [Mn$_4$O$_2$(L)$_2$Cl]$^+$, though the mechanism of Cl$^-$ abstraction in the FAB MS process is not at present clear.

The structure[†] contains discrete [Mn$_4$(L)$_2$(O)$_2$]$^{2+}$ cations and [MnCl$_4$]$^{2-}$ anions; there is no evidence of any interaction between cations and anions or MeCN solvent molecules.

[†] *Crystal data*: C$_{58}$H$_{60}$Cl$_4$Mn$_5$N$_{10}$O$_8$, brown-green dichroic, 0.9 × 0.75 × 0.65 mm, triclinic, space group $P\bar{1}$, a = 11.996(5), b = 13.919(6), c = 29.248(9) Å, α = 94.27, β = 103.32(4), γ = 106.25(3)°, U = 3123(2) Å^3, Z = 2, F(000) = 1470, μ = 1.175 mm^{-1}. Data collected at −100 °C on a Nicolet R3m diffractometer using Mo-Kα radiation. Using 1.6° ω-scans at 4.88° min^{-1}, 12 211 unique reflections were collected (4 < 2θ < 52°) and 9407 with $F > 6\sigma(F)$ were used in the refinement. The structure was solved by Patterson methods and least-squares refinement converged with R = 0.0604, R_w = 0.0805. Hydrogen atoms were inserted at calculated positions with a common, fixed thermal parameter and all non-hydrogen atoms were refined with anisotropic thermal parameters. All programs used in data reduction, solution and refinement are contained in the SHELXTL-PC package.[16] Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

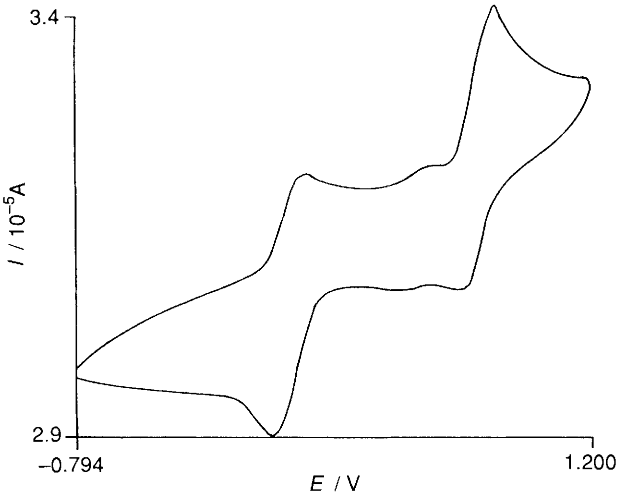


Fig. 4 Cyclic voltammetry of $[Mn_4O_2L_2][ClO_4]_2$ (10^{-3} mol dm^{-3} in propylene carbonate, 10^{-1} mol dm^{-3} in tetrabutylammonium perchlorate); scan rate 50 mV s^{-1}; mV *vs.* Ag/AgCl

There are two independent, centrosymmetric cations in the unit cell and, since these differ only slightly (in the orientation of the phenyl rings), only one is shown in Fig. 1. The Mn coordination geometry is illustrated in Fig. 2. Each Mn atom is six-coordinate, Mn(1) having 'NO_5' donor set while Mn(2) has an 'N_3O_3' set. All of the donors come from the saltren ligands except for the two oxo ions, O(1) and the symmetry-related O(1′), which are separated by 2.54 Å. The oxo and phenoxy groups bridge the four Mn atoms to form two face-sharing incomplete cubanes. The mean planes of Mn(2), O(1), Mn(1′), O(11) and of Mn(1), O(1′), Mn(2′), O(11) are parallel, as are those of Mn(2), O(1), O(21), Mn(1) and O(1′), Mn(2′), Mn(1′), O(21′) and these pairs make angles of 95.1 and 100.2° respectively with the mean plane of Mn(1), Mn(1′), O(1), O(1′). The geometry at the Mn atoms approaches octahedral, although there is a distinct Jahn-Teller distortion about Mn(1) which is not evident about Mn(2). The oxo ligands have pyramidal geometry (Mn–O–Mn angles 96.9–103.6°); this contrasts with the frequently observed $Mn^{III}{}_4$ O_2 'butterfly' configurations where the oxo group shows approximately trigonal planar coordination,[9,17] described as two Mn_3O triangular units sharing an edge. The Mn(1)–Mn(1′) distance [2.898(2) Å] is longer than those observed in the 'butterfly' complexes for di-μ-oxo bridged Mn^{III} (2.79–2.85 Å).[7,9] The remaining intermanganese distances, bridged by μ-oxo and μ-phenoxo, are somewhat longer [2.999(2) and 3.035(2) Å for Mn(1)–Mn(2) and Mn(1)–Mn(2′), respectively].

With the exception of the $[MnCl_4]^{2-}$ salt, which as expected shows a $g = 2$ signal, the complexes are EPR-silent in the solid state, although there is evidence of some disproportionation in the dimethylformamide (DMF) glass spectrum. The temperature dependence of magnetic susceptibility of the cluster in the four salts shows an overall antiferromagnetic interaction, the moment reducing from *ca.* 4.5–4.1 μ_B/Mn ion at 300 K to *ca.* 2 μ_B/Mn at 4.2 K (Fig. 3).

Solution measurements on these clusters are to some extent suspect because of the evidence of disproportionation. Electronic spectra, however, are virtually identical in MeCN solution and in the solid state, so we believe that the moderately intense absorption close to 590 nm (ε *ca.* 400) and weaker *ca.* 1000 nm (ε *ca.* 90) band represent transitions involving the Mn^{III} redox state. Mn^{III} μ-oxo complexes are frequently associated with peaks at *ca.* 600 nm which are too intense to be classified as d–d absorptions and which may originate in $O^{2-} \rightarrow Mn^{3+}$ charge transfer.

Cyclic voltammetric experiments carried out in DMF solution tend towards complex and irreversible behaviour: the best-behaved electrochemistry was observed using freshly-opened propylene carbonate as solvent. A pair of poorly reversible waves at +30 and +780 mV *vs.* Ag/AgCl (Fig. 4) was seen, which by analogy with redox transformations in a similar (but more highly N-ligated) system[18] could be assigned to oxidation of the inner pair of Mn^{III} ions (with 'NO_5' donor set), and the peripheral pair of Mn^{III} ions (with 'N_3O_3' donor set) respectively. Differential pulse voltammetry of the +30 mV process showed a broad and asymmetric profile suggestive of a two-step electron transfer with 80–90 mV separation of individual redox potentials.

We are continuing our study of the electrochemistry of these systems in the hope of confirming these assignments. However, whatever the nature of the redox processes, their easy accessibility is a favourable indicator of the potential value of these new clusters in redox (and possibly even photoredox) catalysis.

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