

Assembly and Structural Characterization of Binuclear μ -Oxo-di- μ -acetato Bridged Complexes of Manganese(III). Analogues of the Di-iron(III) Centre in Hemerythrin

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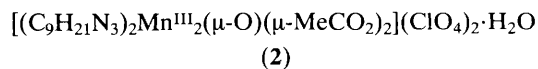
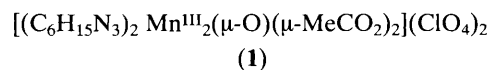
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The complexes $[L_2Mn^{III}_2(\mu-O)(\mu-MeCO_2)_2](ClO_4)_2$, (**1**), and $[L'_2Mn^{III}_2(\mu-O)(\mu-MeCO_2)_2](ClO_4)_2 \cdot H_2O$, (**2**), where L and L' represent the cyclic triamines 1,4,7-triazacyclononane and (*N,N',N''*-trimethyl-1,4,7-triazacyclononane, have been synthesized from $Mn(MeCO_2)_3 \cdot 2H_2O$ in water-ethanol mixtures; characterization by X-ray crystallography showed that both complexes contain a μ -oxo-di- μ -acetato-metal(III) core, as found in hemerythrin, and therefore these complexes may have bioinorganic significance.

The synthesis and properties of a number of binuclear iron(III) complexes that serve as accurate structural, spectroscopic, and chemical models for the μ -(oxo)-bis(μ -carboxylato)-di-iron(III) core¹ of the met forms of the marine invertebrate respiratory protein hemerythrin² have been reported recently. An important aspect of this work has been the demonstration of their ease of formation in solution starting from simple, mononuclear ferric salts ('self-assembly' method).³ The μ -(oxo)-bis(μ -carboxylato)-dimetal(III) moiety is a likely structural unit both in biomolecules and 'inorganic' complexes, therefore it is surprising that this entity has not been discovered previously.⁴ We report here the syntheses of such complexes of manganese(III).

The bioinorganic chemistry of Mn containing enzymes is at present not well understood owing to lack of structural information on the nature of the first co-ordination spheres of the Mn centres involved. It is thought that binuclear or tetranuclear species of Mn^{III} or Mn^{IV} occur in the water oxidation site photosystem II.⁵ Since carboxylate groups and a variety of nitrogen donor atoms are present in proteins, self-assembly of the μ -(oxo)-bis(μ -carboxylato)-dimanganese unit is a distinct possibility in biology. Recent EXAFS studies on the enzyme lend further support to the occurrence of oxo-bridged Mn^{III}/Mn^{IV} centres with O,N-donor atoms rather than sulphur donors in their first co-ordination sphere.^{5c}

When a solution of the respective cyclic triamine 1,4,7-triazacyclononane or *N,N',N''*-trimethyl-1,4,7-triazacyclononane⁶ (1 g) in an ethanol-water mixture (30 ml, 85 vol. %) is treated with $Mn(MeCO_2)_3 \cdot 2H_2O$ ⁷ (0.9 g) and sodium acetate (2 g) at 20 °C, a clear deep-red solution is obtained. After adjusting the pH of this solution to 5 with a few drops of conc. $HClO_4$ and addition of $NaClO_4$ (3 g), black-red crystals of $[(C_6H_{15}N_3)_2Mn^{III}_2(\mu-O)(\mu-MeCO_2)_2](ClO_4)_2$, (**1**), and $[(C_9H_{21}N_3)_2Mn^{III}_2(\mu-O)(\mu-MeCO_2)_2](ClO_4)_2 \cdot H_2O$, (**2**), precipitated. Aqueous solutions of (**1**) and (**2**) decompose within a few hours. Analytically pure crystals, which were suitable for X-ray studies, were grown from more stable acetonitrile solutions of (**1**) and (**2**).



The electronic spectra of (**1**) and (**2**) are very similar. Figure 1 shows the spectrum of (**1**). Interestingly, the two intense bands at 486 and 521 nm are also observed in the spectra of all complexes containing the $Fe^{III}(\mu-O)(\mu-MeCO_2)_2Fe^{III}$ core

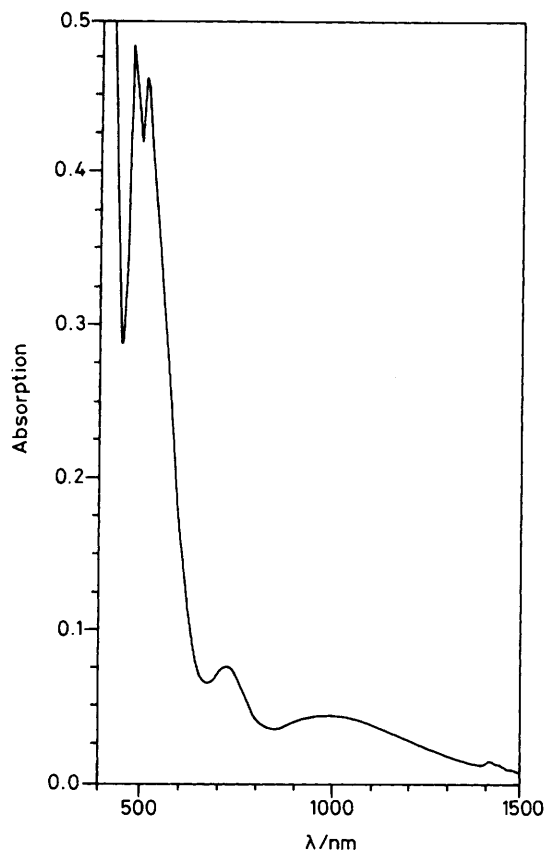


Figure 1. U.v.-visible spectrum of (2) in acetonitrile at 20 °C (7.2×10^{-4} mol dm $^{-3}$, 1 cm cell).

(457 and 492 nm). The exact nature of these transitions is still unknown.^{1b} In the i.r. spectra of (1) and (2) strong bands at 1570, 1450, and 1415 cm $^{-1}$ are indicative of bridging acetato groups and a $\nu(\text{Mn}-\text{O}-\text{Mn})$ band of medium intensity is observed at 730 cm $^{-1}$. Similar behaviour has been reported for the di-iron(III) analogue of (1).^{1c}

Crystal data for (1) [and (2) in brackets] $M = 701.3$ [803.5], tetragonal [orthorhombic], space group $I4_1ca$ [$Amma$], $a = 16.460(6)$ [13.139(5)], $b = 16.460(6)$ [15.143(5)], $c = 24.830(9)$ [17.768(7)], $Z = 8$ [4], $D_m = 1.36$ [1.49], $D_c = 1.385$ [1.509] g cm $^{-3}$, crystal dimensions 0.4 × 0.4 × 0.8 [0.1 × 0.2 × 0.5] mm, $R_w = 0.077$ [0.085] for 1331 [1933] reflections with $I > 2.5 \sigma(I)$ collected at 20 °C on an AED II-Siemens diffractometer, $\theta-2\theta$ scan, $3 > 2\theta > 50^\circ$ [60°] empirical absorption corrections have been carried out.[†]

The structures of the binuclear cations of (1) and (2) are depicted in Figure 2. The cations of (1) and (2) possess crystallographically imposed C_2 and D_{2h} symmetry, respectively. This results in an apparent loss of either the $\lambda\lambda\lambda$ or $\delta\delta\delta$ configuration of the five membered rings, $\text{Mn}-\text{N}-\text{C}-\text{C}-\text{N}$, in (2), which is usually found for octahedral metal complexes

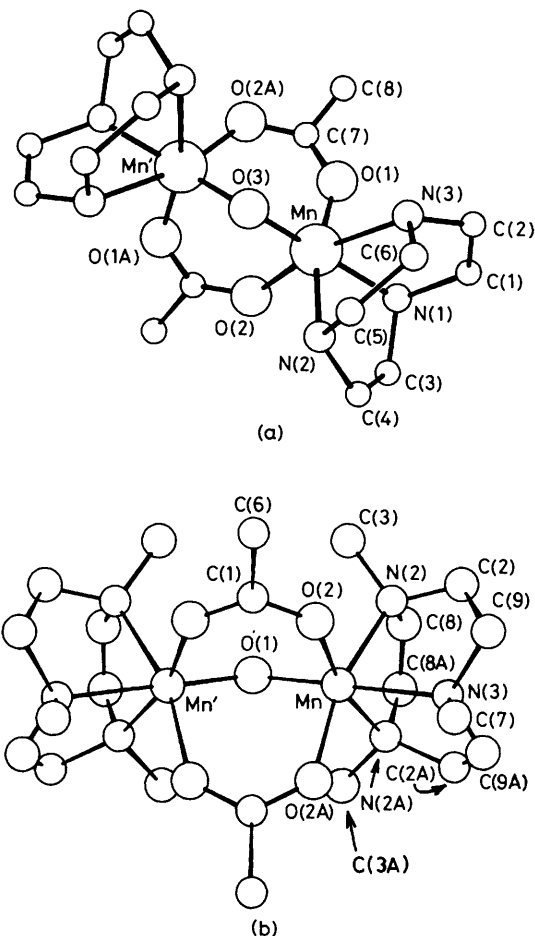


Figure 2. Structures of (1) (a) and (2) (b). Selected bond distances (Å) and angles (°) in (1) and (2) of Mn_2O_3 cores. (1): Mn-Mn' 3.084(3), Mn-O(3) 1.80(1), Mn-N(1) 2.06(1.3), Mn-N(2) 2.25(2), Mn-N(3) 2.22(2), Mn-O(1) 1.94(1.3), Mn-O(2) 2.05(1.3); Mn-O(3)-Mn' 117.9(2), O(3)-Mn-N(1) 170(0.3), O(1)-Mn-O(2) 97(1), O(3)-Mn-O(2) 97(1). (2): Mn-O(1) 1.810(4), Mn-O(2) 2.047(4), Mn-N(2) 2.232(5), Mn-N(3) 2.131(7); Mn-O(1)-Mn' 120.9(1), O(2)-Mn-O(2A) 99.0(3), O(2A)-Mn-N(3) 86.4(3), O(1)-Mn-O(2) 95.6(3).

containing facially co-ordinated triazacyclononane ligands. Unusually large anisotropic temperature factors for the methylenecarbon atoms in (2) suggest that an equal distribution of cations with $\lambda\lambda\lambda$ and $\delta\delta\delta$ configurations of the ligands prevails in the crystals. This, together with, at 20 °C, rotating ClO_4^- anions, is responsible for the relatively large R -factor.

The Mn^{III} ions are in a distorted octahedral environment of three oxygens (one from each symmetric μ -acetato bridge and from the μ -oxo bridge) and three nitrogens of facially co-ordinated cyclic amine ligands. The geometry of the $\text{Mn}_2(\text{O})(\text{MeCO}_2)_2$ core is very similar to that of its iron(III) analogues.¹

The Mn-O distance in the μ -oxo bridge (av. 1.805 Å) is short compared with those of the μ -acetato bridges (av. 2.05 Å).^{9b} In contrast to its Fe^{III} analogue there is no appreciable *trans* influence of the μ -oxo group on the Mn-N bonds in *trans* position (Figure 2).

The magnetism of (1) and (2) are in marked contrast to that of their antiferromagnetic Fe^{III} analogues. In the temperature range 120–298 K magnetic susceptibilities of powdered

[†] The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

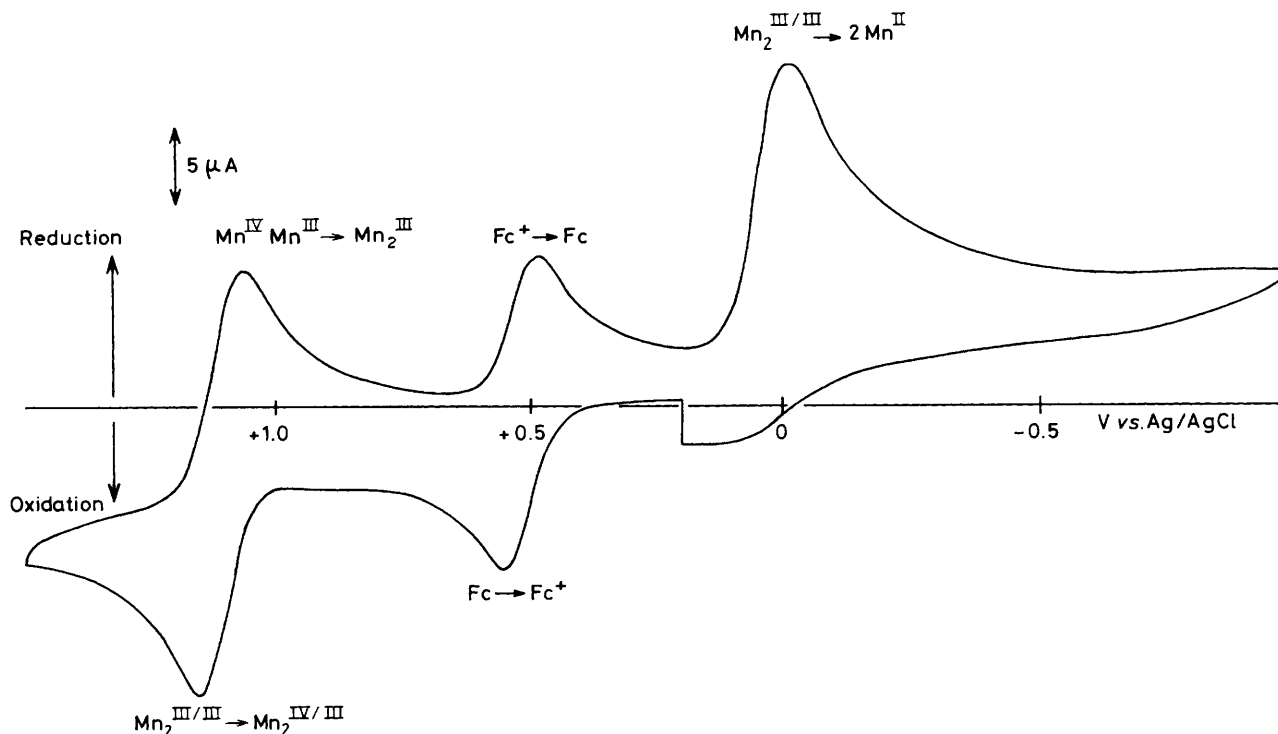
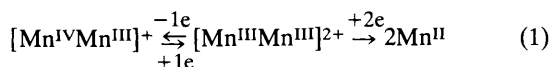


Figure 3. Cyclic voltammogram of (2) in acetonitrile at 25°C [(2)] = 10^{-3} mol dm $^{-3}$, 0.1 mol dm $^{-3}$ NBu $_4$ PF $_6$ supporting electrolyte, Pt-button electrode, scan rate 100 mV s $^{-1}$, internal standard ferrocene.

samples of (1) and (2) (Faraday method) adhere closely to the Curie-Weiss law [(1): $\mu = 5.12 \mu_B$, $\theta = +38$ K; (2): $\mu = 5.28 \mu_B$, $\theta = +28$ K per Mn III]. This indicates high-spin d 4 electronic configuration for Mn III ions. In contrast, other μ -acetato bridged Mn $^{III}_2$ dimers exhibit antiferromagnetic coupling.⁸⁻¹⁰

The cyclic voltammogram of (2) (Figure 3) in acetonitrile at 25 °C, containing NBu $_4$ PF $_6$ as supporting electrolyte, in the potential range 0 to 1.5 V vs. ferrocenium (Fc $^+$)/ferrocene (Fc) exhibits one quasireversible redox reaction at $E_1 + 0.585$ V. Controlled potential coulometry establishes that this wave is a one electron process. At more negative potentials an irreversible two electron reduction of (2) is observed with no corresponding oxidation peak ($E_{p,c} - 0.50$ V vs. Fc $^+$ /Fc). Thus, reduction of (2) is accompanied by chemical decomposition (dissociation to monomers). These reactions are summarized in equation (1). The Mn IV Mn III species of (2)



decomposed in solution within 1 h. The cyclic voltammogram of (1) is very similar. A quasireversible one electron redox process ($E_1 + 0.28$ V vs. Fc $^+$ /Fc) yielding a Mn III Mn IV mixed valence species, and an irreversible two electron reduction wave at ($E_{p,c} - 1.0$ V vs. Fc $^+$ /Fc) are observed. Both potentials exhibit substantial cathodic shifts compared to those of (2). The Mn III Mn IV mixed valence species of (1) is unstable in solution.

Binuclear di- μ -oxo bridged mixed valence Mn III Mn IV complexes containing nitrogen donor ligands (e.g. bipyridine, phenanthroline) are quite common in the chemistry of manganese in its higher oxidation states.¹⁰

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