A Bent Mixed-valence Manganese(III/II/III) Complex: A New Class of Trinuclear, Acetate Bridged Schiff's Base Compounds Exhibiting a $g = 2$ Multiline E.S.R. Signal

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The e.s.r. spectrum of the bent mixed valence Mn(III/II/III)(saladhp)$_2$(OAc)$_4$(MeOH)$_2$[saladhp = 2-(salicylideneaminato)-1,3-dihydroxy-2-methylpropane] in dimethylformamide provides the observation of a multiline e.s.r. signal from a trinuclear mixed-valence manganese complex and allows for the comparison of magnetic and spectroscopic properties of related models for the photosynthetic water oxidizing enzyme.

A detailed definition of the nuclearity, oxidation states, and structure of the active site manganese cluster(s) of the thylakoid membrane associated oxygen evolving complex (OEC) of photosystem II is being vigorously pursued by the characterization of synthetic models prepared recently by a number of research groups.[1] The OEC contains four manganese ions. The available data strongly suggest that at least two, and as many as all four, manganese ions form an e.s.r.-detectable cluster which is believed to be responsible for the water oxidation reaction shown in equation (1). A mixed-valence cluster is the origin of a $g = 2$ multiline signature which is e.s.r. observable in the S$_2$ oxidation level of
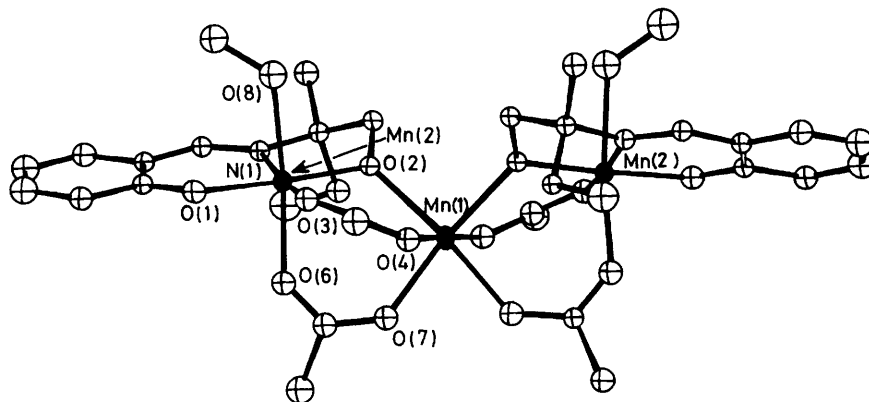
Figure 1. An ORTEP diagram of β-Mn$^{III/II/III}$(saladhp)$_2$(OAc)$_4$(MeOH)$_2$ (**1**) with thermal ellipsoids at 30%. Important distances (Å) and angles (°): Mn(1)–Mn(2), 3.502(2); Mn(2)–Mn(2'), 6.547; Mn(1)–O(2), 2.165(7); Mn(1)–O(4), 2.189(8); Mn(1)–O(7), 2.153(9); Mn(2)–O(1), 1.880(7); Mn(2)–O(2), 1.884(7); Mn(2)–N(1), 1.989(9); Mn(2)–O(3), 1.974(8); Mn(2)–O(6), 2.167(9); Mn(2)–O(8), 2.336(9); Mn(2)–Mn(1)–Mn(2'), 138.5; Mn(1)–O(2)–Mn(2), 119.6(4).
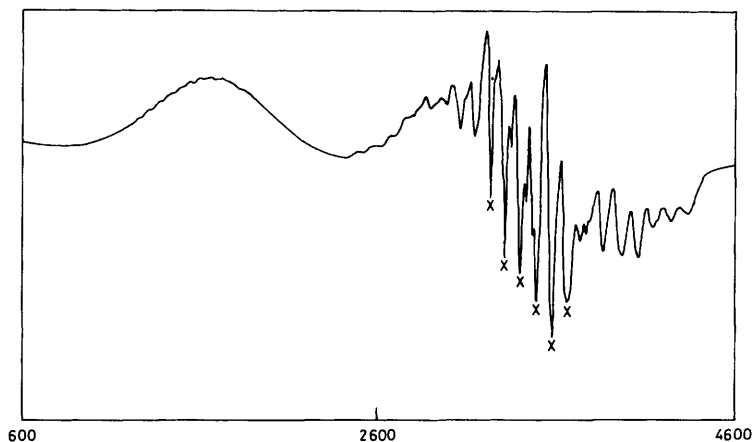
Figure 2. X-Band (9.4227 GHz) e.s.r. spectrum of (**1**) in a DMF glass recorded at 4.5 K. The six resonances marked by X arise from a small amount of Mn^{II} which dissociates from the trinuclear complex in DMF. Power = 100 μW; 100 kHz modulation.

the enzyme.[2] A low field feature ($g \approx 4.1$)[3] in the S_2 e.s.r. spectrum is also thought to arise from manganese. In a single centre proposal, a tetranuclear mixed valence ·cluster is responsible for the $g = 2$ multiline and a conformationally perturbed form of this cluster generates the $g \approx 4.1$ signal.[4] A different hypothesis for metal organization within the OEC invokes two mononuclear centres, one of which is in an electron transfer equilibrium with a binuclear centre.[5] Alternatively, a mononuclear and trinuclear formulation could be consistent with the latter proposal. We now present the isolation and characterization of a bent† trinuclear mixed valence acetate (**1**), β-$Mn^{III/II/III}$-(saladhp)$_2$(OAc)$_4$-(MeOH)$_2$,‡ which is a structural isomer of a recently described linear complex,[6] and report the observation of a $g \approx 2$ multiline signal from a dimethylformamide (DMF) solution of this trinuclear, mixed valence manganese cluster.[7]

$$2 H_2O \rightarrow O_2 + 4H^+ + 4 e^- \qquad (1)$$

Compound (**1**) can be isolated in >80% yield after the linear complex α-$Mn^{III/II/III}$(saladhp)$_2$(OAc)$_4$(MeOH)$_2$ (**2**)[6] and 2 equiv. of 2-hydroxypyridine are dissolved in aceto-nitrile. The X-ray structure of (**1**) (Figure 1) illustrates that the saladhp ligands acts as a tridentate chelating agent using one imine nitrogen and phenolate and alkoxide oxygen atoms to co-ordinate to the metal.§ The alkoxide acts as a bridge

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† The linear or α isomers are those in which the Mn^{III}–Mn^{II}–Mn^{III} angle is 180°. The bent or β isomers have angles less than 180°.

‡ Abbreviations used: saladhp = 2-(salicylideneaminato)-1,3-dihy-droxy-2-methylpropane; OAc = acetate; pyrOH = 2-hydroxypyr-idine; MeOH = methanol.

§ *Crystal data*: $Mn_3C_{52}H_{31}N_6O_{20}$, $M = 1255.4$, monoclinic, space group $C2/c$, $a = 25.049(15)$, $b = 10.160(5)$, $c = 25.763(8)$ Å; β = 117.95(4)°, $U = 5792(5)$ Å^3, $Z = 4$, $D_c = 1.440$ g cm^{-3}, λ(Mo-K_α) = 0.7107 Å, μ(Mo-K_α) = 6.93 cm^{-1}, crystal dimensions 0.16 × 0.10 × 0.24 mm^3. The intensities of 3185 reflections were measured at room temperature ($0 \le 2\theta \le 40°$) on a P2$_1$ diffractometer using Mo-K_α radiation. The structure was solved by direct methods using MULTAN78. Anisotropic thermal parameters were used for the two manganese atoms. Other non-hydrogen atoms were refined isotropic-ally. All calculations were carried out using the SHELX-76 program. For 1458 unique observed reflections [(I) > 3σ(I)], the final R value was 0.062. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors Issue No. 1.

between the central Mn^{II} and the terminal Mn^{III} ions which are separated by 3.50 Å. The cluster is stabilized by two sets of two bridging acetates. The Mn^{III} ions also have co-ordinated methanol. The material is valence-trapped as shown by the long central Mn^{II} to heteroatom bond lengths and by the Jahn–Teller distortion of the high spin Mn^{III} terminal atoms [*e.g.*, Mn(2)–O(6), 2.167 Å *vs.* Mn(2)–O(3), 1.974 Å].

Complexes (**1**) (bent) and (**2**) (linear) are distinguished by a comparison of the central Mn^{II} co-ordination environment and the solvent orientation on the terminal Mn^{III} ions. The bridging alkoxides [O(2)] in (**1**) are bound to the central metal octahedron in a *cis*-configuration. To maintain the Mn(1)–O(2)–Mn(2) angle [119.6(4)°] in (**1**), the Mn(2)–Mn(1)–Mn(2′) angle [138.5 (4)°] must be less than 180° resulting in a bent structure. In contrast, these alkoxide ligands are posi-tioned *trans* in (**2**), which allows for the observed linear Mn(2)–Mn(1)–Mn(2′) arrangement. A further distinction between (**1**) and (**2**) is the orientation of the solvent molecules on the terminal Mn^{III} ions. The two methanols are *cis* in (**1**) while *trans* in (**2**). We are exploring the possibility that (**1**) may exhibit heightened intramolecular reactivity relative to (**2**) because the solvent molecules are on the same side of the molecule in (**1**). A crystallographic result of these structural modifications is that (**1**) contains a crystallographic two-fold axis that bisects O(2)–Mn(1)–O(2′), while Mn(1) sits on an inversion centre in (**2**).

As a result of the obvious angular change, (**1**) and (**2**) exhibit dramatically different terminal manganese separations (6.5 and 7.1 Å, respectively). This spatial perturbation appears to have little consequence for the magnetic properties since variable temperature magnetic studies (4.2—100 K)¶ indicate that both complexes have J values that are very similar [(**1**): J −6.7; (**2**): J −7.1 cm^{-1}]. This might be expected for two reasons. First, the Mn^{III}–O(2)–Mn^{II} distances and angles[8] in (**2**) [Mn^{II}–O(2), 2.144; Mn^{III}–O(2), 1.885 Å; Mn^{III}–O(2)–Mn^{II}, 121.7°] and (**1**) [Mn^{II}–O(2) 2.163; Mn^{III}–O(2), 1.884 Å; Mn^{III}–O(2)–Mn^{II}, 119.6°] are nearly identical. Second, an analysis[6] of (**2**) shows that the data can be fit quite well to a model assuming no exchange interaction between the terminal manganese(III) sites. Incorporation of this exchange parameter in the optimization procedure resulted in a neglible interaction and no improvement in the fit.

The e.s.r. spectrum shown in Figure 2 is obtained when (**1**)

¶ Best fit parameters for (**1**) J_{12} −6.7 cm^{-1}; $J_{22'}$ 0 cm^{-1}; $g_1 = 2.00$ (fixed); $g_2 = 2.03$.

is dissolved in DMF. A six-line component arising from a small amount of dissociated Mn^{II} is seen at $g = 1.99$ ($a = 89$ G; $G = 10^{-4}$ T). In addition, the wings of a multiline signal (19 or 20 lines) centred at $g \approx 2.00$ ($a \sim 95$ G) and extending over a 1900 G range is also present. This compares well with that observed for the OEC.[2] The paramagnetically perturbed ^{1}H n.m.r. spectrum[8] of (1) in DMF demonstrates that the acetate bridges (+47.3 and +36.9 p.p.m.) remain intact in this solvent. Furthermore, the room temperature solution moment is nearly identical (8.4 μ_B) to the room temperature solid state moment (8.2 μ_B). Therefore, we believe that this multiline signal arises either from a perturbed conformation of the trinuclear complex in DMF or a partially dissociated $Mn^{II/III}$ dinuclear species. Studies are in progress to define more precisely the solution species responsible for this multiline signal. The broad low field component is similar to that observed for (2) in CH_2Cl_2/toluene.[6] Examination of (2) in DMF demonstrates that this material also shows a $g = 2$ multiline feature.

The $g = 2$ multiline signal of the S_2 oxidation level of the OEC has provided the basis for much speculation as to the nuclearity and oxidation state(s) of the manganese ions in the oxygen evolving complex. It is now apparent that mixed valence dimer [as $Mn^{III/II}$ or $Mn^{III/IV}$] trinuclear $Mn^{III/II/III}$ and tetranuclear $Mn^{III/III/III/IV}$,[9] complexes exhibit multiline features. Indeed, even the enzymic multiline signal varies depending on the conditions of its generation and observation.[10] Therefore, the simple observation of multiline or $g = 4.1$ signals in a model complex may provide little structural insight for the manganese in the OEC. Factors such as the temperature dependence, power saturation, number of lines, line shapes and widths and relative intensities must also be considered. Only after detailed analysis of these parameters of models and the enzymic systems[5,11] may meaningful structural information from the multiline component be extracted.

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