A Novel Manganese(III) Dimer with an Extremely Long Mn ··· Mn Distance

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The *X*-ray crystal structure of $[Mn_2(salpd)_2(EtOH)_3(H_2O)](BPh_4)_2$ [salpd = propane-1,3-diylbis(salicylideneiminato)] shows it to be a dimer held together by an array of hydrogen bonds; the Mn ··· Mn distance is 5.21(1) Å.

There is increasing interest in high-valent multinuclear manganese complexes. This arises from a recognition of the importance of manganese in biological systems. It is firmly established that manganese is central to a superoxide dismutase[1] and an azide insensitive catalase,[2] but of much greater importance is that manganese is essential for the oxidation of water to O_2 in the photosynthetic process.[3,4] It has been found to be associated with the water-oxidising complex (WOC) in all O_2 evolving photosynthetic organisms studied to date, and no other metal has been found to reactivate lost O_2 evolution activity in reconstructed complexes deficient in manganese. There is widespread agreement that four manganese ions are necessary for high rates of O_2 evolution from photosynthetic membranes of green plants and green, red, and blue-green algae.[3] However, there is some doubt that all four perform the same function, and it is recognised that two of the four differ in terms of their lability;[5,6] it has been suggested that a structural rather than a catalytic function is performed by the loosely bound pair of manganese ions.

Although many of the new species being synthesised contain high-nuclearity manganese, *e.g.*, Mn_4,[7] Mn_6,[8] Mn_9,[9] we[10] and others[11–16] have concentrated on dinuclear complexes in an attempt to develop a model for the water photolysis site in PPS II of the green plant. Moreover, Weighardt[11,17] has drawn attention to the spontaneous self-assembly of dinuclear manganese(III), which he proposes as an indication of their inherent stability.

Indeed, more than simply modelling PPS II, we have been able to mimic it and have been able to generate O_2 and reduce *p*-quinone to hydroxyquinone by visible irradiation of aqueous solutions of $[\{Mn(salpd)(H_2O)\}_2](ClO_4)_2$ (**1**) [salpd = propane-1,3-diylbis(salicylideneiminato)].

Following the simple model for the active O_2 evolving site in PPS II proposed by Calvin[18] our strategy was to produce manganese(III) complexes of N_2O_2 ligands and non-co-ordinating counteranions so that water could bond to, and not be displaced from, the manganese centres. Recently, a mechanistic quantum mechanical study of our work has been published by Awad and Anderson.[19]

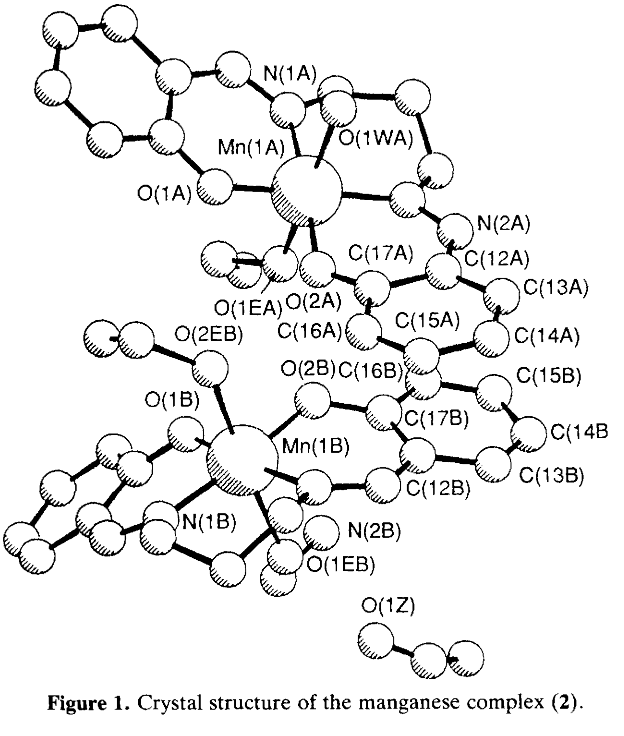

Figure 1. Crystal structure of the manganese complex (**2**).

$$[\{Mn(salpd)(H_2O)\}_2](ClO_4)_2$$
(1)

$$[Mn_2(salpd)_2(EtOH)_3(H_2O)](BPh_4)_2$$
(2)

In view of the importance of (**1**) we have attempted to grow crystals from aqueous solution suitable for single crystal *X*-ray diffraction studies, but this has not proven to be possible. However, we have discovered that a most interesting dimer can be obtained from ethanol solution, the crystal structure of which reveals several novel features and which lends support to Weighardt's dimer self-assembly hypothesis.

A green ethanolic solution was prepared by gently warming (**1**) in aqueous ethanol and in an attempt to precipitate the cation of (**1**) an ethanolic solution of $NaBPh_4$ was added; on standing overnight in the refrigerator small green crystals of $[Mn_2(salpd)_2(EtOH)_3(H_2O)](BPh_4)_2$ (**2**) were deposited. These were filtered off and washed with cold ethanol.

Fundamentally, the dimer is composed of an approximately octahedral $[Mn(salpd)(EtOH)(H_2O)]^+$ (**A**) and $[Mn(salpd)(EtOH)_2]^+$ (**B**) cation with two crystallographically independent BPh_4^- anions and an EtOH of crystallisation completing the crystal structure.† The two cations are associated by two hydrogen bonds formed between the approximately square planar tetradentate ligands and co-ordinated ethanol, which they sandwich, Figure 1, O(2A) $\cdots$ O(2EB) 2.75(3), O(2B) $\cdots$ O(1EA) 2.73(3) Å. The hydrogen bonding scheme also involves the remaining co-ordinated and lattice ethanol, O(1EB) $\cdots$ O(12) 2.57(5) Å. Dimerisation, which has brought the two manganese atoms within 5.21(1) Å of each other, is also facilitated by the π-interaction between the overlapping rings C(12A) $\cdots$ C(17A) and C(12B) $\cdots$ C(17B) interplanar angle 10°, C(17A) $\cdots$ C(17B) 3.65(3) Å.

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† *Crystal data* for $C_{78}H_{88}B_2Mn_2N_4O_9$, $M = 1357.1$, monoclinic, space group $P2_1/c$, $a = 11.960(5)$, $b = 29.235(4)$, $c = 23.551(9)$ Å, $\beta = 104.07(3)°$, $U = 7987.1$ Å^3 (by least squares refinement on diffractometer angles of 25 automatically centred reflexions). Graphite monochromatised Mo-K_α radiation, $\lambda = 0.71069$ Å, $Z = 4$, $D_c = 1.13$ Mg m^{-3}. Crystals were dark green plates (0.4 × 0.4 × 0.02 mm); CAD-4 diffractometer employing $\omega/2\theta$ scans to measure 6529 reflexions ($I > 0$, $1 \leqslant \theta \leqslant 25°$; $+h$, $+k$, $\pm l$) yielding 3363 unique $F \geq 3\sigma(F)$ on merging. Lorentz–polarisation and absorption corrections were applied. Structure solution by direct methods (MULTAN 80). Blocked matrix least squares refinement (SHELX 76) with hydrogen atoms constrained to chemically reasonable positions with the exception of those attached to ethanol and water, which were omitted. A final $R = 0.078$ was attained by treating all non-hydrogen atoms anisotropically and giving the 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 Notice to Authors, Issue No. 1.

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