Modelling the Photosynthetic Water Oxidation Centre: Synthesis, Structure, and Magnetic Properties of $[Mn_4O_2(OAc)_7(bipy)_2](ClO_4)\cdot 3H_2O$ (bipy = 2,2′-Bipyridine)

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The synthesis, structure, and magnetic properties of $[Mn_4O_2(OAc)_7(bipy)_2](ClO_4)\cdot 3H_2O$, bipy = 2,2′-bipyridine) are reported; this complex is the first tetranuclear oxide-bridged manganese(III) species and represents the best available model for the photosynthetic water oxidation centre.

In spite of efforts to elucidate the structure of the Mn centre operating in the photosynthetic water oxidation enzyme of green plants, little is known about the arrangement of the metals or their ligation. It is generally believed that four atoms of Mn per photosystem II (PS II) reaction centre are essential for oxygen evolution[1] and that all are in close proximity to one another.[2—4] The Mn atoms are apparently heterogeneous, being composed of two pools of two similar atoms.[5,6] The Mn aggregate is capable of cycling between five distinct oxidation levels, labelled S_0—S_4 in the pioneering work of Kok,[7] which involve the higher metal oxidation states (II—IV).[8—10] Recent e.x.a.f.s. results have provided important information on the first co-ordination sphere of the Mn in the S_1 level.[11] At least two Mn atoms per PS II reaction centre occur as a binuclear species with a Mn · · · Mn separation of *ca.* 2.7 Å, and low atomic weight atoms at *ca.* 1.75 and 1.98 Å; these values are characteristic of bridging oxide (or hydroxide) and terminal O- or N-based ligands, respectively. The data can also accommodate additional Mn atoms which are further than 3.0 Å from the binuclear centre.[11] No porphyrin has been detected, suggesting amino acid side chain ligation to be involved.

Our objective is the synthesis of an inorganic model of the native Mn complex to assist in elucidating the nature and

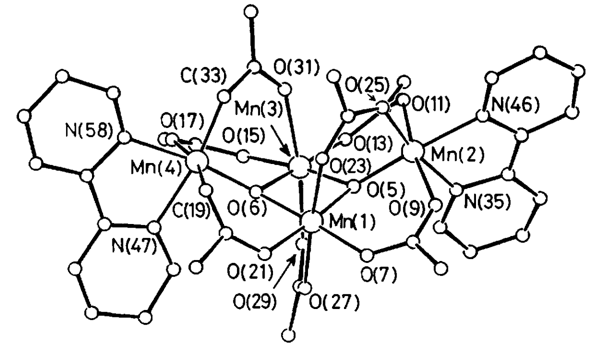

Figure 1. Structure of the $[Mn_4O_2(O_2CMe)_7(bipy)_2]^+$ cation showing the atom labelling scheme. Selected bond lengths (Å) and angles (°) are: Mn(1) · · · Mn(3), 2.848(5); Mn(1) · · · Mn(2), 3.312(5); Mn(1) · · · Mn(4), 3.385(5); Mn(3) · · · Mn(4), 3.299(5); O(5)–Mn(1,2,3), 1.918(12), 1.844(13), 1.889(13), respectively; O(6)–Mn(1,3,4), 1.911(15), 1.930(15), 1.804(16), respectively; Mn–N, 2.021(20)—2.084(18); Mn(1)–O(5)–Mn(2), 123.3(7); Mn(1)–O(5)–Mn(3), 96.8(6); Mn(2)–O(5)–Mn(3), 129.1(7); Mn(1)–O(6)–Mn(3), 95.7(7); Mn(1)–O(6)–Mn(4), 131.3(9); Mn(3)–O(6)–Mn(4), 124.0(8).

mode of action of this unit during water oxidation. A necessary preliminary has been a better development of higher oxidation state Mn chemistry with the type of ligands likely to be bound to the metal within the natural system. This area of Mn chemistry has been poorly explored. We have been investigating the use of $NBu^n{}_4MnO_4$ in non-aqueous solvents as a synthetic route into higher valent Mn.[12] Use of carboxylates and pyridine (pyr) as ligands has led to a series of trinuclear μ_3-oxide-bridged Mn compounds possessing the basic carboxylic structure.[13] We can now report that reaction of 2,2′-bipyridine (bipy) with these complexes leads to higher nuclearity, oxide-bridged species.

Addition of 3.2 equiv. of bipy to 1 equiv. of $[Mn_3O(OAc)_6(pyr)_3](ClO_4)$[13] in MeCN gives a deep red solution. Layering this solution with a mixture of equal volumes of hexanes and Et_2O affords dark red crystals of $[Mn_4O_2(OAc)_7(bipy)_2](ClO_4)\cdot 3H_2O$ (**1**) in *ca.* 70% yield.† The structure of the cation of (**1**) is shown in Figure 1.‡ The complex contains an $[Mn_4O_2]^{8+}$ core with peripheral ligation provided by bridging AcO^- and terminal bipy groups to yield a structure with virtual C_2 symmetry. The core can be thought of as being derived from two edge-sharing Mn_3O units; the resulting arrangement, however, is not planar but has a butterfly structure with a dihedral angle of 135.35°. The μ_3-oxide atoms O(5) and O(6) lie 0.351 and 0.318 Å below their respective Mn_3 planes, unlike the planar arrangement found in the Mn_3O complexes. The metals all possess distorted octahedral geometry and are in the +3 oxidation state. The central Mn(1) · · · Mn(3) distance [2.848(5) Å] is significantly shorter than the other Mn · · · Mn distances [3.299(5)—3.385(5) Å] and is bridged by the unique AcO^- ligand, O(27), and O(29). Complex (**1**) is the first example of an Mn_4O_2 unit in Mn chemistry, although some Fe_4O_2 species have recently been prepared.[14]

Complex (**1**) possesses several features which are similar to those of the enzyme site and which thus make it attractive as a potential model: (a) a metal nuclearity of four; (b) oxide (O^{2-})-bridges between the metal centres; (c) O- and N-based ligation; (d) an average metal oxidation state of +3 (corresponding to the enzyme S_1 state)[8—10,15]; (e) metric parameters which are consistent with, although slightly larger than, the e.x.a.f.s. data on the enzyme {the short Mn · · · Mn and the Mn–μ_3-O distances [mean 1.883(45) Å] are slightly beyond the limits imposed by the e.x.a.f.s. fits, 2.69(3) and 1.75(3) Å, respectively}; and (f) two pairs of inequivalent Mn atoms. Such comparisons emphasise that, although *exact* structural correspondence may not exist, complex (**1**) is nevertheless extremely close to providing the first satisfactory model of the native site (based on available data). Note that the central Mn_2O_2 rhomb of (**1**) is akin to that in $[Mn_2O_2(bipy)_4]^{3+}$ which has often been considered the closest available model.[4,16]

The solid-state variable temperature magnetic susceptibility of (**1**) has been measured from 300.6 to 5.0 K. The effective magnetic moment of the tetranuclear cation gradually varies from 7.96 μ_B at 300.6 K to a relatively constant value of 6.3—6.5 μ_B in the 90—20 K region. A small increase in μ_{eff} is seen below 20 K. If it is assumed that the magnetic exchange interaction between Mn(2) and Mn(4), which is characterised by exchange parameter J_{24}, is negligible and that $J_{12} = J_{23} = J_{34} = J_{41} \equiv J$, then the experimental susceptibility data can be satisfactorily fitted to a theoretical expression involving isotropic pairwise interactions to give $J = -7.6\ cm^{-1}$ and $J_{13} = -22.5\ cm^{-1}$. The constant value of 6.3—6.5 μ_B in the 20—90 K region reflects the fact that several low-lying electronic states encompassing total spins of S = 0, 1, 2, 3, and 4 are accidentally nearly degenerate. The S_2 state of the native Mn site has recently been reported as possessing an $S = 3/2$ ground state[17] but no magnetic data on the S_1 state are currently available.

Investigations of the reactivity characteristics of (**1**) are underway, including attempts to remove the unique AcO^- group bridging Mn(1) and Mn(3) for this may be influencing the Mn(1) · · · Mn(3) separation. This may also liberate potential H_2O-binding sites. Parallel studies are yielding additional species. Reaction under similar conditions of mixed-valence $[Mn_3O(O_2CPh)_6(pyr)_2(H_2O)]$ with 3 equiv. of bipy yields a crystalline material of formulation§ $Mn_4O_2(O_2CPh)_7(bipy)_2$ with an average oxidation level of +2.75 and which may correspond to the enzyme S_0 state. Attempts to characterise structurally this material are in progress.

In summary, synthetic access into tetranuclear oxide-bridged Mn complexes has been achieved and the obtained products found to have several features similar to those in the native enzyme. Availability of these materials should prove invaluable in continuing attempts to elucidate the nature of the native Mn site.

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† A satisfactory analysis has been obtained. Electronic spectrum in CH_2Cl_2, $\lambda_{max.}$/nm (ε_M/Mn, l mol^{-1} cm^{-1}); 243(130 000), 296(9 200), 412(266), 447(268), 504(251).

‡ *Crystal data:* $C_{34}H_{43}N_4O_{23}ClMn_4$, M_r = 1130.96, triclinic, space group $P\bar{1}$, $Z = 2$, a = 21.133(11), b = 11.428(5), c = 11.839(6) Å, α = 102.12(2), β = 119.72(2), γ = 78.20(2)°, U = 2410.61 Å^3, T = −155 °C, crystal dimensions 0.18 × 0.18 × 0.34 mm; data were collected in the range $6 \leq 2\theta \leq 45°$. The structure was solved by a combination of direct methods (MULTAN) and refined by full-matrix least squares. All non-hydrogen atoms were refined with anisotropic thermal parameters except for those of the disordered water molecules which were refined isotropically. Hydrogen atoms were not included. A total of 2434 unique reflections with $F > 2.33\sigma(F)$ were refined to conventional values of R and R_w of 9.05 and 8.94%, respectively. 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.

§ A satisfactory analysis has been obtained. This neutral material is much more soluble in less-polar solvents, including tetrahydrofuran. Electronic spectrum in dimethylformamide $\lambda_{max.}$/nm (ε_M/Mn^{III}, l mol^{-1} cm^{-1}); 279 (15 700), 428 (442), 472 (372).

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