Support from Model Studies for the Proposed Existence of an S_{-1} Oxidation Level in the Manganese Assembly of the Photosynthetic Water Oxidation Centre

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The preparation and properties of the oxide-bridged tetranuclear complex $[Mn_4O_2(OAc)_6(bpy)_2]$ (**1**) (bpy = 2,2′-bipyridine) are reported; the complex has an average metal oxidation state of +2.5, corresponding to the putative S_{-1} oxidation state of the photosynthetic water oxidation centre.

It is generally believed that four atoms of manganese per photosystem II reaction centre are essential for oxygen evolution in green plants and photosynthetic bacteria.[1] The Mn_4 aggregate is capable of cycling amongst five distinct oxidation levels labelled S_n (n = 0—4) involving the 'higher' metal oxidation states (II—IV).[2—5] Recent e.x.a.f.s results on the S_1 level have indicated that two Mn atoms are separated by *ca.* 2.7 Å, with additional Mn atoms at distances greater than 3.0 Å from these two.[6] The e.x.a.f.s data also indicate the Mn atoms to be bridged by oxide (O^{2-}) atoms and to possess peripheral ligation provided by *O*- and/or *N*-based amino acid side chain functions; no porphyrins have been detected.

The possible existence of a 'super-reduced' oxidation level, labelled S_{-1}, has been the subject of several recent reports. Pretreatment of spinach chloroplast particles with H_2O_2 yields a reduced S_{-1} state which requires five rather than three light flashes before maximal O_2 evolution is observed.[7] Similarly, Thibault and his co-workers have shown that the oxygen evolution behaviour of the cyanobacteria *Euglena gracilis* and *Oscillatoria chalybea* as a function of applied light flashes is anomalous when analysed with the usual Kok S_n state model.[8,9] This 'abnormality' vanishes, however, if the existence of an S_{-1} level is included in the model. This conclusion has been further supported by Pistorius and Schmid in studies of the cyanobacterium *Anacystis nidulans.*[10] Evidence for an S_{-1} level is thus continuing to grow.

We recently reported the synthesis of the tetranuclear complexes (**2**) and (**3**), possessing structural parameters and other features consistent with the e.x.a.f.s data for the natural system.[11] These complexes possess average oxidation levels of +2.75 (z = 0) and +3.0 (z = 1), establishing them as models of the S_0 and S_1 states, respectively. We report here that a complex containing the Mn_4O_2 core can be prepared which possesses an average metal oxidation state of +2.50. This would correspond to that of the putative S_{-1} state and provides the first support from established tetranuclear Mn chemistry for the existence of the Mn assembly at this oxidation level in the natural system.

A solution of the mixed-valence trinuclear complex $[Mn_3O(OAc)_6(py)_3](py)$ (0.50 mmol) in MeCN (20 ml) was treated with 2,2′-bipyridine (bpy) (1.60 mmol). Within minutes a fine brown powder precipitated in *ca.* 90% yield. The solid was collected by filtration, washed with Et_2O, and recrystallized from $CHCl_3$/MeCN or $CHCl_3$/hexanes to give

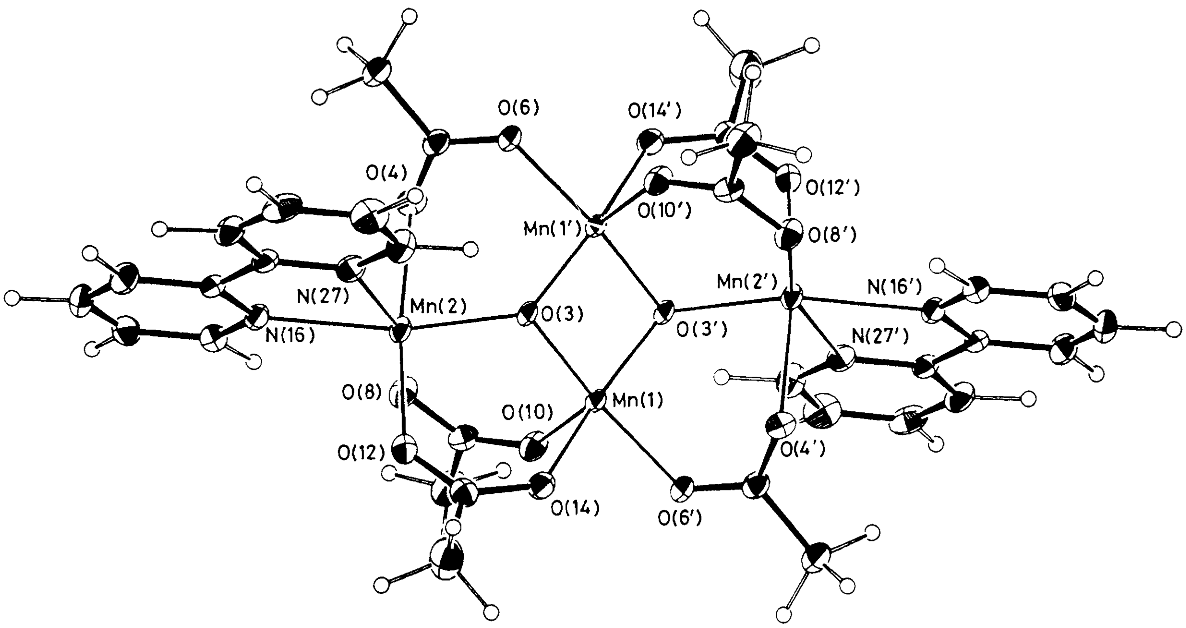

Figure 1. ORTEP projection of $[Mn_4O_2(OAc)_6(bpy)_2]$ (**1**) at the 50% probability level, showing the atom labelling scheme. Selected bond lengths (Å) and angles (°) are: Mn(1) · · · Mn(1′) 2.779(1), Mn(1) · · · Mn(2) 3.288(1), Mn(1) · · · Mn(2′) 3.481(1), Mn(1)–O(3) 1.851(2), Mn(1)–O(3′) 1.856(2), Mn(1)–O(6) 1.980(2), Mn(1)–O(10′) 2.118(2), Mn(1)–O(14′) 1.977(2), Mn(2)–O(3) 2.103(2), Mn(2)–O(4) 2.228(2), Mn(2)–O(8) 2.121(2), Mn(2)–O(12) 2.191(2), Mn(2)–N(16) 2.260(3), Mn(2)–N(27) 2.267(3), O(3)–Mn(1)–O(3′) 82.88(10), O(3)–Mn(1)–O(6′) 169.91(9), Mn(1)–O(3)–Mn(1′) 97.12(10), Mn(1)–O(3)–Mn(2) 122.99(11).

well-formed dark brown crystals of $[Mn_4O_2(OAc)_6(bpy)_2]\cdot 2CHCl_3$ (**1**) suitable for structural studies.† The structure of (**1**) is shown in Figure 1.‡ The molecule lies on a crystallographic inversion centre, resulting in an exactly planar array of four Mn atoms. The metals are bridged by μ_3-O atoms O(3) and O(3′), one above and one below the Mn_4 plane. Peripheral ligation is completed by six bridging OAc^- groups and two terminal bpy groups. Charge considerations necessitate a mixed-valence $Mn^{II,II,III,III}$ oxidation state description; Mn(1) and Mn(1′) are assigned as the Mn^{III} centres, on the basis of consideration of the structural parameters listed in the caption to Figure 1, and comparison of Mn(2) and Mn(2′) bond distances to their *O*- and *N*-based ligands with those in (**3**). Specifically, Mn(2)–O,N lengths (2.121—2.267 Å) are longer on average than the corresponding distances in (**3**) (1.865—2.197 Å), consistent with a lower oxidation state in (**1**) at these metal positions. The five-co-ordination at Mn(1) and Mn(1′) is rare for Mn^{III} with O,N-ligation, which usually adopts octahedral co-ordination. Overall, the structure of (**1**) is thus similar to but not identical with that of (**3**); the latter has a butterfly arrangement of the four Mn atoms, both μ_3-O atoms on the same side of the molecule, all metal centres in octahedral geometry, and seven rather than six bridging OAc^- groups. At present it is difficult to explain why an additional OAc^- group is not bridging Mn(1) and Mn(1′), as seen in (**3**).

$[Mn_4O_2(OAc)_6(bpy)_2]$ (**1**)

$[Mn_4O_2(O_2CR)_7(bpy)_2]^{z+}$
(**2**) $z = 0, R = Ph$
(**3**) $z = 1, R = Me$

The solid-state variable temperature magnetic susceptibility of (**1**) has been measured over the range 300.9—10.0 K. The effective magnetic moment of the tetranuclear unit gradually decreases from 8.61 μ_B at 300.9 K to 4.86 μ_B at 10.0 K. If it is assumed that the magnetic exchange interaction between Mn(2) and Mn(2′), characterized by the exchange parameter $J_{22'}$, is negligible, and that $J_{12} = J_{12'} = J_{1'2} = J_{1'2'} = J$, then the experimental susceptibility data can be satisfactorily fitted to a theoretical expression involving isotropic pairwise interactions ($S_1 = S_{1'} = 2$; $S_2 = S_{2'} = 5/2$) to give $J = -1.97$ and $J_{11'} = -3.12$ cm^{-1}, and no contribution from paramagnetic impurities (PAR = 0%). At present no magnetic data are available on S_{-1} for comparison.

In summary, the characterization of (**1**) now establishes that the discrete $[Mn_4O_2]$ unit, which has been shown to possess several features in common with the enzyme site, can be obtained in three different oxidation levels corresponding to the S_{-1}, S_0, and S_1 states of the native system. This result thus lends support to the current belief that the S_{-1} state corresponds to a reduced form of the Mn_4 aggregate within the water oxidation site. Conversely, the high degree of oxidation state correspondence between these synthetic complexes and the native site further supports our belief that the former may

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† A satisfactory analysis (C, H, N, Mn) has been obtained. Electronic spectrum in CH_2Cl_2: $\lambda_{max.}$/nm (ε_m per Mn^{III}/l mol^{-1} cm^{-1}) 466 (410) and 504 (386).

‡ *Crystal data:* $C_{34}H_{36}Cl_6Mn_4N_4O_{14}$, $M_r = 1157.15$, triclinic, space group $P\bar{1}$, $Z = 1$, $a = 13.883(3)$, $b = 10.592(2)$, $c = 8.848(1)$ Å, $\alpha = 91.18(1)$, $\beta = 72.14(1)$, $\gamma = 71.44(1)°$, $U = 1157.15$ Å^3, $T = -160$ °C, crystal dimensions 0.24 × 0.24 × 0.30 mm; data (Mo-K_α radiation) were collected in the range $6° \leqslant 2\theta \leqslant 45°$. The structure was solved by a combination of direct methods (MULTAN) and refined by full-matrix least-squares techniques. All non-hydrogen atoms were refined with anisotropic thermal parameters. In the latter stages, all hydrogens were located in a difference Fourier analysis and included in the final refinement cycles with isotropic thermal parameters. A total of 2867 unique reflections with $F > 3.00\sigma(F)$ were refined to conventional values of R and R_w of 3.23 and 3.75%, 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.

well represent good structural models of the biological unit, and forms the basis for our incorporation of the Mn_4O_2 structural unit into a mechanistic proposal for the water oxidation cycle.[12]

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