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Toward synthetic models for high oxidation state forms of the Photosystem II active site metal cluster: the first tetranuclear manganese cluster containing a $[Mn_4(\mu\text{-}O)_5]^{6+}$ core†

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The first tetrameric high valent manganese complex consisting of a $Mn^{IV}{}_4(\mu\text{-}O)_5$ bridged core, $[Mn_4(\mu\text{-}O)_5(dmb)_4(dmbO)_2](ClO_4)_4$,‡ was isolated *via* dimanganese (III,IV) and (IV,IV) intermediates in presence of the oxidant *tert*-butyl hydroperoxide and was characterized by X-ray crystallography, electrochemistry, infrared, UV-visible, ^1H NMR, and mass spectroscopy; the structure found differs greatly from a proposal for the putative Mn_4O_5 aggregate found in Photosystem II.

An oxo-bridged tetranuclear manganese aggregate (denoted Mn_4 herein) is generally thought to be responsible for the oxidation of water to molecular oxygen in Photosystem II (PSII).[1] A crystal structure of the *Synechococcus elongatus* PSII dark-adapted state (designated S_1) at 3.8 Å resolution was reported recently.[2] The structure of the four-manganese atom cluster, presumably at the water oxidase (WO) active site, is shown in Fig. 1A. However, WO cofactors chloride and calcium were not located in the aforementioned crystal structure nor were the location of residue side-chain atoms. Although the positions of oxygen atoms that surely bridge Mn atoms have not been determined at this stage, the reported Mn_4 structure appears to resemble B in Fig. 1, which is an isomer of another proposed model (C).[3b] Structure A is quite distinct from one that has received much attention (Fig. 1D), often referred to as the 'Berkeley' model.[3a,b] Advancement from the PSII Kok S_2 to S_3 state[4] is accompanied by changes in the Mn_4 cluster structure as indicated by X-ray absorption spectroscopy.[3c,5] In our opinion, these changes are consistent with a significant cluster structural rearrangement. Thus, when the structure of Mn_4 at the enzyme S_1 oxidation level is determined to high resolution, it will perhaps not represent the structure of the Kok S_3 and S_4 forms.

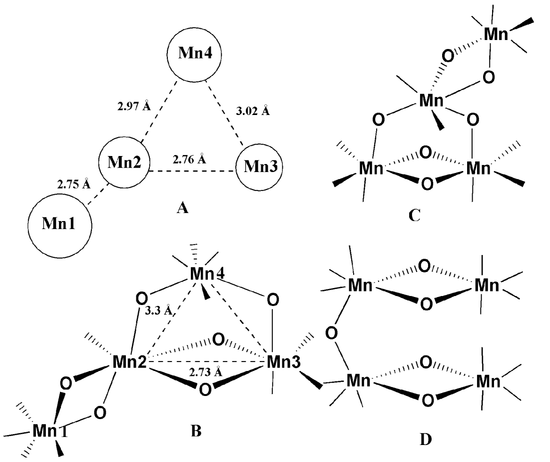
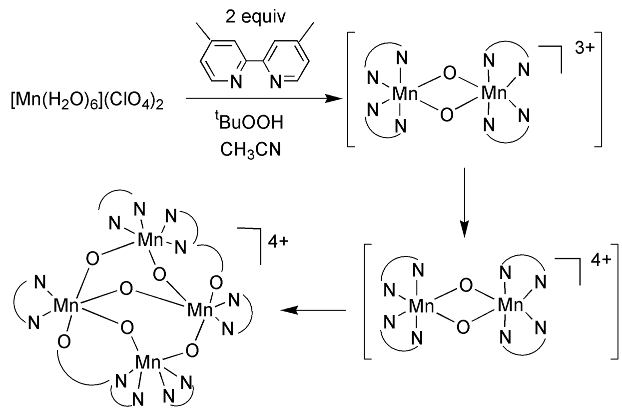


Fig. 1 Selected tetranuclear Mn complexes.

We and others are preparing and characterizing oxo-bridged high valent manganese aggregates *in vitro* in order to test hypotheses concerning the PSII Mn_4 three-dimensional and electronic structure and what role it plays in four-electron water oxidation catalysis. Tetranuclear complexes of varying geometry and containing different numbers of bridging oxo (O^{2-}) ligands have been reported, including species with 'butterfly'-like Mn_4O_2 cores,[6] cubane-shaped Mn_4O_3X[7] and Mn_4O_4 cores,[8] 'dimer-of-dimers' complexes containing two stacked bis-μ-oxo bridged dimanganese units,[9] closed adamantane-shaped Mn_4O_6 cores,[10] and its open Mn_4O_6 geometrical isomer.[11] Based on EXAFS studies of the enzyme active site, Klein, Yachandra and coworkers proposed an open 'dimer-of-dimers' geometry (Fig. 1D) that has a $\{Mn_4(\mu\text{-}O)_5\}$ core for the PSII S_1–S_3 states.[3] Importantly, they allow for other structures consistent with their data.[3b] Thus it is desirable to synthesize molecules with the $Mn_4(\mu\text{-}O)_5$ and other core formulations in order to determine which three-dimensional structures are to be conjectured for the higher manganese oxidation states S_3 and S_4. Here we report the synthesis of a novel manganese complex, $[Mn_4(\mu\text{-}O)_5(dmb)_4(dmbO)_2](ClO_4)_4$ (**1**), which to our knowledge is the first example of a tetranuclear manganese complex that contains five oxo bridges, as proposed by Klein and coworkers.[3] The synthesis and physical characteristics of **1**, and its relevance to Mn_4 in PSII are described herein.

The reaction of $Mn(ClO_4)_2\cdot 6H_2O$ (0.100 g, 0.275 mmol) with 4,4′-dimethyl-2,2′-bipyridine (dmb) (0.102 g, 0.552 mmol) in acetonitrile gives rise to a yellow solution, which changes initially to dark green and finally to a dark brown color upon dropwise addition of 3 ml of a 90% *tert*-butyl hydroperoxide solution over a period of 20 min (Scheme 1). The oxidation of the Mn^{II} species could be stopped at the (III,IV) (**2**) and at the (IV,IV) (**3**) oxidation levels§ by the addition of 1.5 and 2.5 ml, respectively, of the oxidant solution. Microcrystalline **1** was isolated in 53% yield from the brown reaction mixture by vapor diffusion of diethyl ether into acetonitrile at −20 °C.¶ X-Ray quality single crystals were obtained by layering a dilute acetonitrile solution with ether at room temperature. Complex **1**¶ crystallizes in the triclinic space group $P\bar{1}$ with four CH_3CN



Scheme 1

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† Electronic supplementary information (ESI) available: Full ORTEP of cation, ESI mass spectrum and ^1H NMR spectrum. 3D Picture of the crystal structure. See http://www.rsc.org/suppdata/cc/b1/b111554e/

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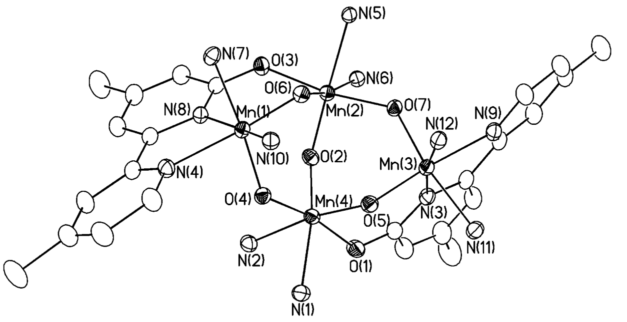

Fig. 2 An ORTEP diagram of complex **1** showing 30% probability thermal ellipsoids (hydrogen atoms and the dmb ligands are omitted for clarity). Selected bond distances (Å) and angles (°): Mn(1)–O(6) 1.757(2), Mn(1)–N(10) 2.016(2), Mn(2)–O(2) 1.788(2), Mn(2)–O(3) 1.956(2), Mn(3)–O(7) 1.762(2), Mn(4)–O(2) 1.788(2), Mn(4)–O(1) 1.938(2), Mn(4)–N(1) 2.073(3); O(6)–Mn(1)–O(4) 98.31(9), O(6)–Mn(1)–N(8) 96.99(9), O(2)–Mn(2)–O(6) 98.80(9), O(2)–Mn(2)–O(3) 91.88(9), O(2)–Mn(2)–N(5) 169.33(9), O(1)–Mn(4)–O(4) 170.30(9), Mn(2)–O(2)–Mn(4) 126.65(11).

molecules in the lattice. The structure, shown in Fig. 2,‖ consists of a rather open arrangement of four Mn atoms and five bridging oxo groups.

The crystallographic asymmetric unit contains the entire Mn_4 aggregate, four ClO_4^- counter-ions and four CH_3CN molecules. Interestingly, two of the six dmb ligands were oxidized selectively at the 6 position and they are designated here as 'dmbO'. These two dmbO ligands bridge a pair of Mn atoms. Because of the manganese–aryloxo bonds, the Mn(1)···Mn(2) and Mn(3)···Mn(4) distances are slightly shorter (av. 3.180 Å) than for Mn(1)···Mn(4) and Mn(2)···Mn(3) (av. 3.277 Å). The average bond distance between Mn and μ-oxo groups is 1.770 Å, whereas the Mn to aryloxo-oxygen bond distances [Mn(4)–O(1) and Mn(2)–O(3)] are 1.938(2) and 1.957(2) Å, respectively. Assuming that both dmbO ligands are deprotonated and singly charged and that all bridging O atoms are oxide groups (O^{2-}) ligands, then all manganese atoms are deduced to be in the +4 formal oxidation state. This oxidation state assignment is supported by the fact that the Mn–ligand bond distances in **1** compare well with those in other reported Mn–oxo complexes.[6–11]

The solution ^1H NMR spectrum of **1** is consistent with two-fold rotation symmetry, with the axis passing through bridging oxygen atom O(2). Six 4,4′ methyl group proton resonances are observed between 8 and 20 ppm. We also find twelve resonances for 3,3′ and 5,5′ protons with integration equaling one third of that for the methyl protons, and five peaks assigned as 6,6′ protons, which are rather broad due to their proximity to the paramagnetic centers. Thus all 23 resonances that are predicted from the crystal structure, assuming pseudo two-fold symmetry, are observed. X-Band EPR studies in frozen (77 K) acetonitrile solution reveal no significant absorption bands. This is likely due to anti-ferromagnetic coupling among the Mn^{IV} ions giving rise to an $S = 0$ ground state and integer spin excited states.** The Mn···Mn distances in **1** rule it out as closely analogous to the PSII Mn_4 complex at the S_1 and S_2 states. However, as mentioned above, recent EXAFS studies show Mn···Mn elongation at the S_3 state.[3c] Thus compound **1** is possibly structurally relevant to the higher Kok S states: S_3 and S_4.

In conclusion, structural characterization of complex **1** reveals the first $\{Mn_4O_5\}$ core type for high-valent tetranuclear Mn clusters, with oxidation states thought by many in the field to correspond to the S_3 state of the PSII water-to-oxygen catalytic cycle. Our ongoing studies focus on the mechanism of formation of the new core as well as its reactivity towards ligand substitution reactions with carboxylate and other donor ligands. Finally, we emphasize that this work addresses, for the first time, the issue of the structural preference for the $[Mn_4(\mu\text{-}O)_5]^{6+}$ core, a point of interest not only for those in the Photosystem II field but also for the basic research field of chalcogenide-bridged metal aggregates.

Notes and references

‡ 'dmb' is 4,4′-dimethyl-2,2′-bipyridyl and 'dmbO' is 4,4′-dimethyl-2,2′-bipyridinyl-6-ol anion.

§ $[Mn_2O_2(dmb)_4](ClO_4)_3$ and $[Mn_2O_2(dmb)_4](ClO_4)_4$: both of the complexes were isolated in high purity and yield and were characterized by NMR, UV-Vis and X-ray crystallography, and will be reported elsewhere.

¶ Purity was confirmed by ^1H NMR. Anal. Calc. for $Mn_4O_{23}N_{12}Cl_4C_{72}H_{70}\cdot 2CH_3CN$: C, 47.31, H, 4.08, N, 10.30, Mn, 11.54, Cl, 7.45. Found: C, 47.41, H, 4.12, N, 10.24, Mn, 11.65, Cl, 7.35%. Electrochemistry: compound **1** shows an irreversible reduction response at –0.50 V with respect to $Ag/Ag(ClO_4)$ in acetonitrile solution with 0.1 M electrolyte (Bu_4NClO_4) concentration. Selected IR bands for **1** (cm^{-1}): 1620 (s), 1560 (m), 1490 (m), 1450 (w), 1410 (m), 1310 (s), 1250 (s), 1220 (s), 1170 (s), 1095 (vs), 922 (m), 831 (s), 800 (m), 636 (s), 521 (m), 515 (m), 450 (w), 420 (m). UV-Vis spectrum for **1** in acetonitrile (λ_{max}/nm ($\varepsilon/10^4$ M^{-1} cm^{-1})): 296 (3.11), 260 (3.06), 230 (2.82), 335 (1.51) (sh). Mass spectral data for **1** in acetonitrile: the positive ion ESI-MS shows $\mathbf{1}(ClO_4)_3^+$ $[(M - ClO_4)^+]$ at m/z 1733.5 and $[(M - 2ClO_4)^{2+}/2]$ at m/z 816.4.

‖ *Crystal data*: $Mn_4O_{23}N_{16}Cl_4C_{80}H_{82}$; triclinic, space group $P\bar{1}$, a = 13.628 (2), b = 16.920 (3), c = 20.279 (4) Å, α = 92.786 (3), β = 99.273 (3), γ = 102.050 (3)°, V = 4496.8 (13) Å^3, Z = 2, D_c = 1.475 Mg m^{-3}, $F(000)$ = 2052, μ(Mo-Kα) = 0.748 mm^{-1}, λ = 0.71073 Å and T = 193 K. 29896 reflections measured, 20802 unique (R_{int} = 0.0376, with no absorption corrections). The final $wR_1(F^2)$ = 0.0775 on all data, conventional R_1 = 0.0495 on $[I > 2\sigma(I)]$. One of the four ClO_4 ions was modelled as being disordered. An ORTEP view of the cation is shown in the ESI.† CCDC reference number 179380. See http://www.rsc.org/suppdata/cc/b1/b111554e/ for crystallographic data in CIF or other electronic format.

** A full investigation of the magnetic properties of **1** is underway.

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