Towards models of the oxygen-evolving complex (OEC) of photosystem II: a Mn$_4$Ca cluster of relevance to low oxidation states of the OEC†

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Synthetic access has been achieved into high oxidation state Mn/Ca chemistry with the 4:1 Mn : Ca stoichiometry of the oxygen-evolving complex (OEC) of plants and cyanobacteria; the anion of (Et$_3$NH)$_2$[Mn$^{III}$Ca(O$_2$CPh)$_4$] has a square pyramidal metal topology and an $S = 0$ ground state.

Among the various reasons for the current intense interest in manganese chemistry is the existence of this metal at the active sites of several redox enzymes,1 the most important of which is the oxygen-evolving complex (OEC) on the donor side of photosystem II (PS II) in green plants, algae and cyanobacteria.2 The OEC catalyses the oxidation of H$_2$O to molecular dioxygen through a four-electron process; the latter involves various oxidation states of the OEC, the so-called Sn Kok states ($n = 0$ to 4), and is the source of essentially all the O$_2$ on this planet.

The OEC has long been known to contain four Mn and one Ca$^{2+}$ ions,3 but the exact metal topology was only recently revealed in detail from the crystal structure of PS II from the cyanobacterium Thermosynechococcus vulcanus at 1.9 Å.5 At this high resolution, it was seen that an oxo-bridged [Mn$_3$CaO$_4$] cubane-like cluster is linked to a fourth, external Mn atom via one of its bridging $\mu_2$-O$^-$ ions, which thus becomes $\mu_3$, as well as via an external $\mu_2$-O$^-$ ion, serving to link one of the cubane Mn atoms to the external Mn atom (Scheme 1). The Mn oxidation states at the various $S_n$ Kok states involve a mixture of Mn$^{III}$ and Mn$^{IV}$; the dark-stable $S_1$ state is 2Mn$^{III}$, 2Mn$^{IV}$, and $S_2$, the most studied Kok state, is Mn$^{III}$, 3Mn$^{IV}$.6 In addition, the presence of a Ca$^{2+}$ ion is vital for the WOC activity; without its existence the OEC could not advance to the $S_1$ state.7

The synthesis and detailed study of synthetic analogues (molecular models) of this [Mn$_4$Ca] cluster would greatly enhance our understanding of the spectroscopic, physical and catalytic properties of the WOC, as well as its reactivity and functional characteristics. Despite the large number of multinuclear, homometallic Mn clusters that have been synthesized at various high oxidation states,8 heterometallic Mn$^{a+}$–Ca ($n \geq 3$) cluster chemistry has been sparingly explored.9

Thus, not only are there currently no structural models of the OEC, in fact there are currently no structurally characterized molecular species in Mn/Ca bioinorganic chemistry exhibiting more than one of the following crucial requirements for modelling the OEC: (i) a Mn$_4$Ca metal stoichiometry; (ii) a distorted cubane unit; and (iii) the preferable Mn oxidation states (III, IV, or mixed-valence III/IV). With this in mind, we started a program aiming at the investigation of heterometallic Mn$^{a+}$–Ca ($n > 2$) chemistry, primarily using the self-assembly synthetic approach comprising simple metal carboxylate reagents and a potentially chelating and/or bridging organic ligand with a known ability to stabilize high metal oxidation states. One such family of ligands is oximes,10 whose oximate group ($>\text{C}==\text{N}−\text{O}^-$) has proved to be extremely versatile for binding to Mn$^{III}$ and Mn$^{IV}$ atoms. In particular, we chose to employ salicylhydroxamic acid (shaH$_2$, Scheme 2), a photosynthetically effective group,11 as a means of obtaining new molecular species containing both Mn and Ca. Note that shaH$_2$ could potentially undergo a metal-assisted amide–iminol tautomerism, and thus transform to salicyldroxime (shiH$_3$, Scheme 2); the latter is an oximate-based ligand with four coordination sites available for binding to both Mn and Ca metal centers.

We herein report the synthesis, structure and physical properties of the first [Mn$^{III}$$_4$Ca$_4$] complex, possessing both the same Mn : Ca ratio as the OEC and all the Mn atoms at a high oxidation state.

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The 1 : 1 : 1 reaction of \(\text{Mn(O}_2\text{CPh})_2\) \(2\text{H}_2\text{O}\) and \(\text{Ca(O}_2\text{CPh})_2\) with \(\text{shaH}_2\), in the presence of three equiv. of \(\text{NEt}_3\), in \(\text{CH}_2\text{Cl}_2\) gave a dark brown solution. This was filtered, and the filtrate was slowly concentrated by evaporation to give dark brown crystals of \((\text{NHEt}_3)_2[\text{Mn}_4\text{Ca(O}_2\text{CPh})_4(\text{shi})_4]\) in 55% yield.† Complex \((\text{NHEt}_3)_2[\text{Mn}_4\text{Ca(O}_2\text{CPh})_4(\text{shi})_4]\) crystallizes in the monoclinic space group \(C2/c\) with the cluster dianion (Fig. 1) in a general position. The core of I consists of four Mn\(^{III}\) and one Ca\(^{II}\) atoms arranged in a slightly distorted square pyramidal topology (Fig. S1, ESI†) with the Ca\(^{II}\) atom at the apical position and the Mn atoms forming the square base. The Mn\(^{III}\) atoms form a near-planar square, with each of the edges bridged by a diatomic oximate group from a \(\text{shi}^3\) ligand, thus giving Mn⋯Mn separations of 4.594–4.627 Å. The essentially ideal planarity of the Mn\(^{III}\) unit is clearly due to the large Mn–N–O–Mn torsion angles, which span the range of 172.5(2)–179.3(2)\(^o\). The linkage between the basal Mn\(^{III}\) atoms and the apical, eight-coordinate, Ca\(^{II}\) atom is provided by the oximate O atoms of \(\text{shi}^3\) ligands (Fig. S2, ESI†) and the four \(\eta^1:\eta^1:\mu^1\) bidentate bridging benzoate groups, causing Ca⋯Mn separations of 3.716–3.749 Å. Ligation around each Mn\(^{III}\) atom is completed by the alkoxide and phenoxide O atoms from \(\text{shi}^3\) groups; the latter are thus \(\eta^1:\eta^1:\eta^2:\mu^3\). The complex therefore contains an overall \([\text{Mn}_4\text{Ca(\mu-NO)}_4]\)^{10+} core (Fig. S1, ESI†).

All Mn\(^{III}\) atoms are five-coordinate with distorted square pyramidal geometry. This is confirmed by analysis of the shape-determining bond angles using the approach of Reedijk and Addison et al.,12 which yields an average value for the trigonality index, \(\tau\), of 0.27 for the four metal ions. The metal oxidation states were established by charge considerations, metric parameters and bond valence sum calculations (BVS),13 the latter giving values of 3.10, 3.04, 3.08 and 3.09 for Mn1, Mn2, Mn3 and Mn4, respectively.

Complex I exhibits a solid-state electronic spectrum typical of a high-spin d\(^4\) electron configuration. The spectrum is characterized by several absorption bands with shoulders in the range of 340–485 nm; these are assigned to LMCT transitions. The absorption bands around 235–300 nm belong to the π–π* transitions within the ligands because of their high intensity. The weaker low-energy absorptions in the range of 550–695 nm are assigned to d–d transitions of the Mn\(^{III}\) ions within I, typical for five-coordinate, square pyramidal Mn\(^{III}\) complexes.14 The cyclic voltammogram (CV) for complex I is shown in Fig. 2. It displays two broad peaks indicative of an irreversible oxidation at 368 mV and an irreversible reduction at –866 mV. This behaviour is consistent with a chemical change occurring after electron transfer.15

Solid-state, direct-current (dc) magnetic susceptibility (\(\chi_M\)) data for air-dried complex 1 \(\text{CH}_2\text{Cl}_2\) were collected in the temperature range of 5.0–300 K in an applied field of 0.1 T. \(\chi_MT\) steadily decreases from 9.30 cm\(^3\) K mol\(^{-1}\) at 300 K to 0.53 cm\(^3\) K mol\(^{-1}\) at 5.0 K (Fig. 3). The 300 K value is much less than the spin-only (\(g = 2\)) value of 12 cm\(^3\) K mol\(^{-1}\) for four non-interacting Mn\(^{III}\) ions. This is indicative of dominant antiferromagnetic exchange interactions between the paramagnetic metal centers, and a resulting \(S = 0\) ground state. The data were fit to the theoretical expression for a Mn\(^{III}\) linear square using the 1-\(J\) model shown in Fig. 3 (inset). The fit (solid blue line in Fig. 3) gave fit parameter values (\(J = -2.39(7)\) cm\(^{-1}\) and \(g = 1.90(3)\)), indicating an \(S = 0\) ground state and an \(S = 1\) first excited

![Fig. 1](image1.png)  
**Fig. 1** Labeled PovRay representation of the molecular structure of the dianion of complex I. Color scheme: Ca, yellow; Mn\(^{III}\), blue; O, red; N, green; C, grey.

![Fig. 2](image2.png)  
**Fig. 2** CV at 100 mV s\(^{-1}\) for complex I containing 0.1 M \(\text{NBu}_4\text{PF}_6\) as a supporting electrolyte. The indicated potentials are vs. \(\text{Fc/Fc}^+\).
state at 6.78 cm\(^{-1}\) higher in energy. A temperature-independent paramagnetism (TIP) term was included, held fixed at \(200 \times 10^{-6}\) cm\(^{-1}\) mol\(^{-1}\). A fit of the data to a 2-J model (i.e., \(J \neq 0\)) gave results of comparable quality (Fig. S3, ESI\(^1\)), but these might lead to overparameterization problems; thus, the long Mn\(^{III}\)\(\cdot\)Mn\(^{III}\) exchange interaction can be ignored. The anti-ferromagnetic interactions are as expected for a system coupled solely through oximate bridges with very large Mn–N–O–M (M = 3d-metal ion) torsion angles.\(^\text{106}\)

The primary purpose of this communication is to report the attainment of I, which has the same Mn\(_2\)Ca content and carboxylate ligation as the OEC. We recognize, however, that within the structure of I the average Mn\(_{\cdot\cdot}\)Mn (between closest neighbours) and Mn\(_{\cdot}\)Ca separations are 4.6 and 3.7 Å, respectively, significantly longer than the corresponding values of 2.7–3.3 and B\(_2\)Mn\(^{III}\) levels, respectively, and an EPR signal assignable to a state of the OEC. Assuming that these involve Mn-based reductions, OEC being at the 2Mn\(^{III}\), 2Mn\(^{IV}\) oxidation level, then the Mn\(^{III}\) exchange interaction within the structure of \(1\) is different from the distorted-cubane core found in the native OEC, but may be relevant to other ways. On the basis of the dark-stable 0 state. Hydrazine groups in the vacant cavity within the \(1\) structure, but may be relevant to S.7 1. It is thus possible that the structure of complex I may be of more relevance to these lower oxidation state forms of the OEC that will have a lower preference for oxide bridges than to the higher oxidation states that have a cubane structure and are involved in the catalytic cycle. Along these lines, the similarity between the oximate N–O bridging unit of \(1\) and the Mn–N–O–M unit seen in hydroxylamine-bridged metal complexes\(^\text{13}\) is intriguing and suggests that I may be providing insights into the kind of subunits that might be generated on reduction of the OEC with hydroxylamine.

In summary, a Mn/Ca species exhibiting the same Mn\(_2\)Ca stoichiometry as the OEC has been prepared at the Mn\(^{III}\)\(^2\) oxidation level. The core of I is different from the distorted-cubane core found in the native OEC, but may be relevant to lower oxidation level species that are intermediates during assembly of the OEC in vivo, or those generated by treatment of the OEC with strong reducing agents. We are now seeking methods to modify the structure of I by introducing O\(^2−\)/OH\(^−\) groups in the vacant cavity within the (Mn\(^{III}\)\(^4\)) planar unit, without altering the metal stoichiometry.

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Notes and references

\[\text{Air-dried solid analyzed (C, H, N) as I-CH}_2\text{Cl}_2. \text{Caled (found): C, 50.72 (51.08); H, 4.32 (4.32); N, 5.14 (4.64%). Crystal data for I-}\] 4CH\(_2\text{Cl}_2; \text{C}_8\text{H}_6\text{Mn}_2\text{CaN}_2\text{O}_4\text{Cl}_6. M_\text{r} = 1944.93, mono clinic, space group C2/c with a = 27.7602(9), b = 27.4448(5), c = 22.1179(6) Å, }\]

\[\text{R} = 96.006(2); V = 16758.4(9) Å^3, T = 150(2) K, Z = 8, D_l = 1.542 g cm^{-3}, \text{92} 210 \text{reflections collected, 16995 unique (R_{int} = 0.0512). }\]

\[\text{R}_I [1 > 2\sigma(I)] = 0.0910, \text{wR}_2 = 0.2788 (F^2, \text{all data). The crystal was twinned with a high mosaicity that made any attempts at twin integration fail. The Fobs values were consistently higher than Fcalc. This unresolved twinning is probably responsible for the residual electron density peaks that are in chemically meaningless positions. Two of the three E\(_{\text{III}}\)NH\(^+\) positions are disordered over inversion centers, and exist at 0.5 occupa} \]

\[\text{cy. The site across the inversion center was occupied by } \text{Et}_3\text{NH}^+ \text{positions are disordered over inversion centers, and exist at 0.5 occupancy. The site across the inversion center was occupied by disordered CH}_2\text{Cl}_2 \text{molecules. Thus, the program SQUEEZE\(_\text{I}\) was used to calculate the solvent disorder area and remove its contribution to the overall intensity data. CCDC 827419.}\]


19 For a recent example, see P. Böing, A. Willner, T. Pape, A. Heppa and N. W. Mistel, Dalton Trans., 2008, 2549, and references therein.