Cite this: Chem. Commun., 2011, 47, 11128–11130

www.rsc.org/chemcomm

COMMUNICATION

Towards models of the oxygen-evolving complex (OEC) of photosystem II: a Mn_4Ca cluster of relevance to low oxidation states of the OEC[†]

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Received 24th June 2011, Accepted 26th August 2011 DOI: 10.1039/c1cc13770k

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 $(Et_3NH)_2[Mn^{III}_4Ca(O_2CPh)_4(shi)_4]$ 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 H₂O to molecular dioxygen through a four-electron process; the latter involves various oxidation states of the OEC, the so-called S_n Kok states (n = 0 to 4),³ and is the source of essentially all the O₂ on this planet.

The OEC has long been known to contain four Mn and one Ca^{2+} ions,⁴ 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 {Mn₃CaO₄} cubane-like cluster is linked to a fourth, external Mn atom *via* one of its bridging μ_3 -O²⁻ ions, which thus becomes μ_4 -, as well as *via* an external μ_2 -O²⁻ 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 Ca²⁺ ion is vital for the WOC activity; without its existence the OEC could not advance to the S_3 state.⁷



Scheme 1 The $\{Mn_4CaO_5\}$ core of the OEC in PS II.⁵

The synthesis and detailed study of synthetic analogues (molecular models) of this {Mn₄Ca} 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 Mnⁿ⁺-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 Mn₄Ca 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^{n+} -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 $(>C=N-O^{-})$ has proved to be extremely versatile for binding to Mn^{III} and Mn^{IV} atoms. In particular, we chose to employ salicylhydroxamic acid (shaH₂, Scheme 2), a photosynthetically effective group,¹¹ as a means of obtaining new molecular species containing both Mn and Ca. Note that shaH₂ could potentially undergo a metal-assisted amide-iminol tautomerism, and thus transform to salicylhydroxime (shiH₃, 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 $\{Mn^{III}_4Ca\}$ 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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[†] Electronic supplementary information (ESI) available. CCDC 827419. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1cc13370k



Scheme 2 Structural formulae and abbreviations of the organic ligands discussed in the text.

The 1:1:1 reaction of Mn(O₂CPh)₂·2H₂O and Ca(O₂CPh)₂ with shaH₂, in the presence of three equiv. of NEt₃, in CH₂Cl₂ gave a dark brown solution. This was filtered, and the filtrate was slowly concentrated by evaporation to give dark brown crystals of (NHEt₃)₂[Mn₄Ca(O₂CPh)₄(shi)₄]·4CH₂Cl₂ (1.4CH₂Cl₂) in 55% yield.[‡] Complex 1.4CH₂Cl₂ crystallizes[‡] in the monoclinic space group C2/c with the cluster dianion (Fig. 1) in a general position. The core of 1 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 shi^{3–} ligand, thus giving Mn···Mn separations of 4.594–4.627 Å. The essentially ideal planarity of the Mn₄ unit is clearly due to the large Mn-N-O-Mn torsion angles, which span the range of $172.5(2)-179.3(2)^{\circ}$, very close to the ideal linearity degree of 180°.

The linkage between the basal Mn^{III} atoms and the apical, eight-coordinate, Ca^{II} atom is provided by the oximate O atoms of shi³⁻ ligands (Fig. S2, ESI†) and the four $\eta^1:\eta^1:\mu$ bidentate bridging benzoate groups, causing $Ca\cdots Mn$ separations of 3.716–3.749 Å. Ligation around each Mn^{III} atom is completed by the alkoxide and phenoxide O atoms from shi³⁻ groups; the latter are thus $\eta^1:\eta^1:\eta^1:\eta^2:\mu_3$. The complex therefore contains an overall $[Mn_4Ca(\mu-NO)_4]^{10+}$ 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, τ , of 0.27 for the four metal ions. The metal oxidation states were established by charge considerations,



Fig. 1 Labeled PovRay representation of the molecular structure of the dianion of complex **1**. Color scheme: Ca, yellow; Mn^{III}, blue; O, red; N, green; C, grey.

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 **1** exhibits a solid-state electronic spectrum typical of a high-spin d⁴ 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 **1**, typical for five-coordinate, square pyramidal Mn(III) complexes.¹⁴ The cyclic voltammogram (CV) for complex **1** 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 ($\chi_{\rm M}$) data for air-dried complex 1·CH₂Cl₂ were collected in the temperature range of 5.0–300 K in an applied field of 0.1 T. $\chi_{\rm M}T$ steadily decreases from 9.30 cm³ K mol⁻¹ at 300 K to 0.53 cm³ 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 cm³ 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}₄ square using the 1-J model shown in Fig. 3 (inset). The fit (solid blue line in Fig. 3) gave fit parameter values ($\mathscr{H} = -2JS_i \cdot S_j$ convention) of J = -3.39(7) cm⁻¹ and g = 1.90(3), indicating an S = 0 ground state and an S = 1 first excited



Fig. 2 CV at 100 mV s⁻¹ for complex 1 containing 0.1 M NBuⁿPF₆ as a supporting electrolyte. The indicated potentials are *vs.* Fc/Fc⁺.



Fig. 3 $\chi_M T vs. T$ plot for 1·CH₂Cl₂. The blue solid line is the fit of the data; see the text for the fit parameters. Inset: 1-*J* coupling scheme for 1.

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state at 6.78 cm⁻¹ higher in energy. A temperatureindependent paramagnetism (TIP) term was included, held fixed at 200 × 10⁻⁶ cm³ 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†), but these might lead to overparameterization problems; thus, the long Mn^{III}...Mn^{III} exchange interaction can be ignored. The antiferromagnetic interactions are as expected for a system coupled solely through oximate bridges with very large M–N–O–M (M = 3d-metal ion) torsion angles.^{10b}

The primary purpose of this communication is to report the attainment of 1, which has the same Mn₄Ca content and carboxylate ligation as the OEC. We recognize, however, that within the structure of 1 the average Mn \cdots Mn (between closest neighbours) and Mn Ca separations are 4.6 and 3.7 Å, respectively, significantly longer than the corresponding values of 2.7–3.3 and \sim 3.4 Å for the OEC in PS II.^{5,6} However, the structure of 1 may be relevant to the OEC in other ways. On the basis of the dark-stable S_1 Kok state of the OEC being at the 2Mn^{III}, 2Mn^{IV} oxidation level, then the Mn^{III}_{4} level of 1 would place it at the S_{-1} state. Hydrazine (N₂H₄) and hydroxylamine (NH₂OH) are known to be able to reduce the OEC to S_{-1} , S_{-2} and even S_{-3} states.¹⁶ These are not involved in the water oxidation catalytic cycle, but may be related to intermediates during the in vivo assembly of the OEC. Assuming that these involve Mn-based reductions, then they would be at the 4Mn^{III}, Mn^{II}, 3Mn^{III} and 2Mn^{II} 2Mn^{III} levels, respectively, and an EPR signal assignable to a $Mn^{II}Mn^{III}$ subunit has been detected for S_{-2} .¹⁷ It is thus possible that the structure of complex 1 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 oximato N-O bridging unit of shi³⁻ within 1 and the M-N-O-M unit seen in hydroxylamine-bridged metal complexes¹⁸ is intriguing and suggests that 1 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 Mn₄Ca stoichiometry as the OEC has been prepared at the Mn^{III}₄ oxidation level. The core of **1** is different from the distortedcubane 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 **1** by introducing O^{2-}/OH^{-} groups in the vacant cavity within the {Mn^{III}₄} planar unit, without altering the metal stoichiometry.

Th.C.S thanks the Royal Society of Chemistry Research Fund for chemical supply. This work was also supported by the National Science Foundation (CHE-0910472 to G.C.). The Advanced Light Source is supported by the Director, Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

Notes and references

‡ Air-dried solid analyzed (C, H, N) as 1-CH₂Cl₂. Calcd (found): C, 50.72 (51.08); H, 4.32 (4.32); N, 5.14 (4.64%). Crystal data for 1-4CH₂Cl₂: C₇₆H₈₄Mn₄CaN₆O₂₀Cl₈, $M_w = 1944.93$, monoclinic, space group C2/c with a = 27.7602(9), b = 27.4445(8), c = 22.1179(6) Å, $\beta = 96.006(2)^\circ$, V = 16758.4(9) Å³, T = 150(2) K, Z = 8, $D_c = 1.542$ g cm⁻³, 92.201 reflections collected, 16.995 unique ($R_{int} = 0.0512$), R_1 [$I > 2\sigma(I)$] = 0.0910, $wR_2 = 0.2788$ (F^2 , all data). The crystal was twinned with a high mosaicity that made any attempts at twin integration fail. The F_{obs} values were consistently higher than F_{calc} . This unresolved twinning is probably responsible for the residual electron density peaks that are in chemically meaningless positions. Two of the three Et₃NH⁺ positions are disordered over inversion centers, and exist at 0.5 occupancy. The site across the inversion center was occupied by disordered CH₂Cl₂ molecules. Thus, the program SQUEEZE¹⁹ was used to calculate the solvent disorder area and remove its contribution to the overall intensity data. CCDC 827419.

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