The first high oxidation state manganese–calcium cluster: relevance to the water oxidizing complex of photosynthesis†

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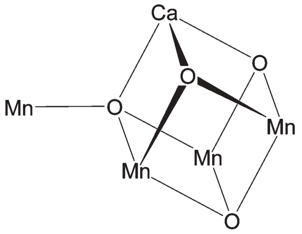
Synthetic entry has been achieved into high oxidation state Mn–Ca cluster chemistry with the preparation of $[Mn_{13}Ca_2O_{10}(OH)_2(OMe)_2(O_2CPh)_{18}(H_2O)_4]$; the structure contains $[Mn_4CaO_4]$ sub-units similar to that found in the photosynthetic water oxidizing complex.

The water oxidizing complex (WOC) near photosystem II (PS II) catalyses the oxidation of H_2O to O_2 gas in green plants and cyanobacteria.[1,2] This four-electron process involves various oxidation levels of the WOC (the so-called S_n states, $n = 0$ to 4),[3] and is the source of essentially all the O_2 on this planet. The WOC has been studied for many years by a variety of spectroscopic and physicochemical techniques, and has long been known to require Ca^{2+} for activity,[4] but it was the recent crystal structure resolution of the PS II of the cyanobacterium *Thermosynechococcus elongatus* at 3.5 Å that finally revealed the details of a heterometallic Mn_4CaO_4 cluster.[5] This comprises a Mn_3CaO_4 cubane, with the fourth Mn atom attached to one of its bridging O^{2-} ions.



The synthesis and detailed study of synthetic analogues (models) of this cluster would greatly enhance our understanding of the spectroscopic, physical and redox properties of the WOC, as well as its reactivity characteristics. However, not only is this heterometallic Mn_4CaO_4 cluster currently unknown in inorganic chemistry, there are no structurally characterized molecular species to our knowledge containing both Ca^{2+} and higher oxidation state Mn^{3+} and/or Mn^{4+} ions. Currently known is a single Mn^{2+}–Ca^{2+} species, which is polymeric,[6] and a salt where the Ca^{2+} is the cation of a Mn_4-containing anion (shortest Mn···Ca separation is 4.895 Å).[7] This is in stark contrast to the many Mn_4 complexes currently known, such as those with butterfly, cubane, and dimer-of-dimer structures.[8] None of these has ever been reported to incorporate calcium. However, we can now report that a synthetic route has been developed into this area of inorganic chemistry.

Various reactions between Mn and Ca sources were explored under many different conditions before the following was developed. The reaction of $(NBu^n_4)[Mn_4O_2(O_2CPh)_9(H_2O)]$[9] with 0.25 equiv. of $Ca(NO_3)_2\cdot 4H_2O$ in MeCN/MeOH (20 : 1 v/v) gave a dark brown solution. This was filtered, and the filtrate slowly concentrated by evaporation to give brown crystals of $[Mn_{13}Ca_2O_{10}(OH)_2(OMe)_2(O_2CPh)_{18}(H_2O)_4]\cdot 10MeCN$ (**1**·10MeCN) in 40% yield. The same product was obtained when $Ca(ClO_4)_2$ or $Ca(O_2CPh)_2$ was used. Complex **1**·10MeCN crystallizes‡ in the triclinic space group $P\bar{1}$ with the cluster on an inversion centre. The structure (Fig. 1) consists of a $[Mn_{13}Ca_2]^{42+}$ core held together by 4 μ_3-O^{2-}, 6 μ_4-O^{2-}, 2 μ_3-HO^- and 2 μ_3-MeO^- ions. It can be described as two Mn_4O_4 cubes attached to a central, planar Mn_3O_4 unit, to which are also attached two Mn–Ca pairs, one above and one below the plane. The cluster is mixed-valent (Mn^{IV}, 10 Mn^{III}, 2 Mn^{II}) with the Mn^{IV} in the centre (Mn2) and the Mn^{II} next to the Ca^{2+} ions (Mn3, Mn3a). Peripheral

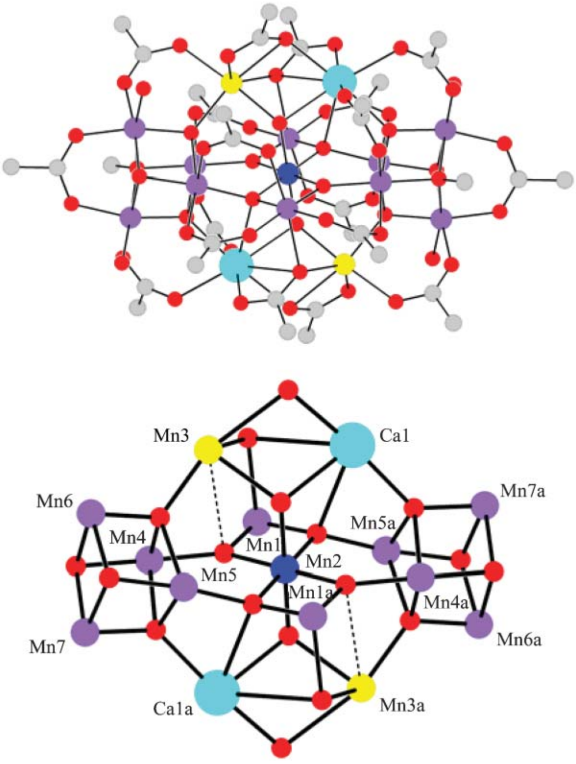


Fig. 1 The centrosymmetric structure of **1** (with the benzoate rings omitted for clarity, except for the *ipso* C atoms) and its core; the dashed lines are the weak Mn–O contacts. Colour code: Ca cyan; Mn^{IV} blue; Mn^{III} violet; Mn^{II} yellow; O red; C grey.

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† Electronic supplementary information (ESI) available: fits of magnetization data. See http://www.rsc.org/suppdata/cc/b4/b413680b/

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ligation is provided by 14 μ-, 2 μ_3- and 2 unusual η^3, η^1, μ_4- bridging benzoate groups, as well as terminal H_2O molecules on Mn6, Mn6a, Mn7, and Mn7a. The metal oxidation states and the protonation levels of O^{2-}, MeO^- and HO^- ions were established by bond-valence sum calculations, charge considerations, inspection of metric parameters and the identification of Mn^{III} Jahn–Teller (JT) elongation axes on all Mn except Mn2, Mn3 and Mn3a. All Mn and the Ca^{2+} ions are six- and eight-coordinate, respectively; seven of the eight Ca–O bonds are in the range 2.297–2.770 Å, but the eighth is longer (Ca1–O2 = 3.039 Å). The Mn3–O5 bond is also very weak (2.998 Å), presumably due to strain in the molecule.

The solid state dc magnetic susceptibility (χ_M) of **1** was measured in the 5.00–300 K range in a 1 kG (0.1 T) field and plotted as $\chi_M T$ *vs.* T in Fig. 2. The $\chi_M T$ value at 300 K of 30.96 $cm^3\ mol^{-1}$ K is much lower than the 40.63 $cm^3\ mol^{-1}$ K value expected for a cluster of Mn^{IV}, 10 Mn^{III}, 2 Mn^{II} non-interacting ions, indicating the presence of strong antiferromagnetic exchange interactions within complex **1**. The $\chi_M T$ value steadily decreases with decreasing temperature to 3.47 $cm^3\ mol^{-1}$ K at 5.00 K, consistent with a small ground-state spin (S) in the S = 5/2 ± 1 region. In order to identify the ground state, magnetization (M) data were collected in the 0.5–5 T and 1.8–8 K ranges. Fitting of the data gave S = 5/2, g = 1.86(5) and D = −1.63(25) cm^{-1}, where D is the axial zero-field splitting parameter.† This ground state S value is supported by ac susceptibility measurements, whose real (in-phase) $\chi_M' T$ signal of ~3.3 $cm^3\ mol^{-1}$ K is consistent with S = 5/2 and $g < 2$, as expected for Mn.

The primary purpose of this communication is to report the development of higher oxidation state Mn–Ca cluster chemistry. The $Mn_{13}Ca_2$ nuclearity of **1** is, of course, much higher than that found in the biological site (Mn_4Ca).[5] Nevertheless, it hasn't escaped our notice that within the structure of **1** is a sub-unit whose structure is intriguing with respect to the WOC, in that it possesses the Mn_3CaO_4 distorted-cubane topology of the native site. In fact there are two types of cubane-containing Mn_4Ca moieties within **1**, and they are shown in Fig. 3. One has the Ca^{2+} ion within the cube, and the other has it outside. The former, on the left of Fig. 3, is the one relevant to the WOC site. The Mn3···O5 contact is weak (2.998 Å), undoubtedly because Mn3 is also attached to O8 from a different unit, but the distorted, heteronuclear Mn_3CaO_4 cubane arrangement is nevertheless clear, its first observation outside the WOC. The Ca–Mn separations are in the range 3.505–3.961 Å, and these would undoubtedly decrease in a discrete version of this unit; for comparison, calcium EXAFS (extended X-ray absorption fine structure) data of the latter indicate the Mn···Ca separation in the WOC to be ~3.4 Å.[10] On the right is a related structure, but with the Ca^{2+} ion attached to an O atom of a Mn_4O_4 cube. Such cubes were never serious structural candidates for the WOC site, based on EXAFS data.[1]

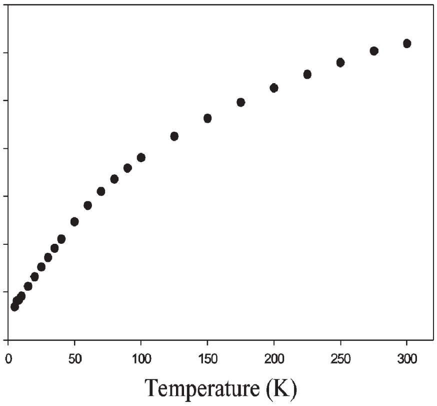

Fig. 2 $\chi_M T$ *vs.* T plot for complex **1**.

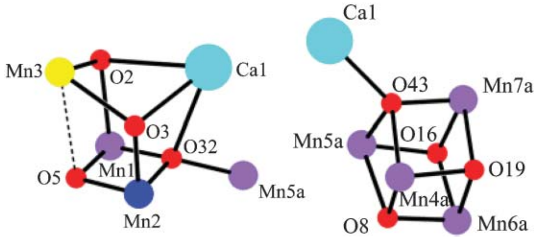

Fig. 3 Two cubane sub-units within **1**. On the left is the Mn_4CaO_4 unit, as found in the WOC; the dashed line indicates the weak Mn–O bond. On the right is a Ca^{2+} ion attached to a Mn_4O_4 cubane.

In summary, the initial example of a higher oxidation state Mn–Ca cluster containing intimately associated Mn and Ca ions has been synthesized. From a bioinorganic perspective, the pentadecanuclearity of **1** is too high to model the WOC, but we nevertheless believe this work provides a foundation from which to tackle the synthesis of the native Mn_4Ca unit responsible for the binding and oxidative coupling of two water molecules to O_2 gas. In this regard, the occurrence within **1** of sub-units with a recognizable structural relationship to the WOC site is encouraging, and suggests that modification of the reaction system to foster lower nuclearity products might possibly yield Mn_3CaO_4 cubane-containing products. An obvious modification is the addition of chelates to the reaction that yields **1**, or alternatively to treat pre-formed **1** with chelates to break it up into smaller nuclearity products. Note that the reaction system for **1** contained no such chelate to limit nuclearity growth, and that it is thus not surprising that a large nuclearity product was obtained. Both the described strategies involving chelates, and others, to obtain lower nuclearity Mn–Ca products are currently under investigation.

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Notes and references

‡ Vacuum-dried solid analyzed (C, H, N) as solvent-free. Crystal structure data for complex **1**·10MeCN: $C_{148}H_{136}Ca_2Mn_{13}N_{10}O_{54}$, M_r = 3713.05, triclinic, $P\bar{1}$, a = 15.0839(17), b = 16.3794(19), c = 17.959(2) Å, α = 112.343(2), β = 103.301(2), γ = 92.272(2)°, Z = 1, V = 3953.9(8) $Å^3$, d_{calc} = 1.559 g cm^{-3}, T = 173 K. The structure was solved by direct methods in *SHELXTL6* and refined on F^2 using full-matrix least squares. The 10 MeCN molecules were disordered and could not be modelled properly, hence the program SQUEEZE[11] was used to calculate the solvent disorder area and remove its contribution to the overall intensity data. The final refinement parameters $R1$ and $wR2$ were 9.06 and 21.68%, respectively. CCDC 249919. See http://www.rsc.org/suppdata/cc/b4/b413680b/ for crystallographic data in .cif or other electronic format.

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