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Evolution of Manganese-Calcium Cluster Structures based on Nitrogen and Oxygen Donor Ligands

S. Melnic,^a S. Shova,^{a*} A. C. Benniston,^{b*} and P. G. Waddell^c

Several X-ray determined structures are described of ditopic clusters based on the $Mn_{(m)}Ca_{(n)}$ motif where $m = 2$, $n = 2$; $m = 6$, $n = 2$. A cuboid arrangement of $Ca_2Mn_2O_6$ is observed in three structures and they vary slightly in terms of Mn-O and Ca-O bond lengths. A “wheel and axle” like motif is observed in the final structure in which a calcium thread resides insided a Mn_6 ring. Crystal packing features are also described for the cuboid structures and subtle structural changes are discussed in the framework of supramolecular chemistry and crystal engineering.

Introduction

The marriage between two earth abundant metal ions is especially highlighted in the structure of the manganese-calcium water oxygen complex of photosystem-II.¹ The complex which is responsible for performing the demanding water oxidation reaction, comprises of four manganese ions and one calcium ion arranged in a cubane arrangement (Mn_4CaO_5).² The central Mn_3CaO_4 cuboidal core is distorted, and the outer manganese is attached via two μ -oxo bridges. High-resolution structures are consistent with four water molecules coordinated to the Mn_4CaO_5 cluster.³ Two water molecules are associated with the Ca^{2+} ion and two further waters are coordinated to the outer manganese ion. There is still some debate of the oxidation states of the manganese ions in its resting state, but two +3 (d^4) and two +4 (d^3) manganese ions seems to be universally recognised.⁴ Even before the definitive X-ray structure determinations by groups such as Barber,⁵ Umena⁶ and more recently Suga,⁷ the quest to produce artificial mimics witnessed several structures that comprised manganese and calcium ions arranged in various structural motifs.⁸ The more recent example mimic structures are certainly more akin to the natural structure. In 2011 and 2012 the groups of Agapie⁹ and Christou¹⁰ reported the first heteropolynuclear Mn-Ca clusters that have approached both geometric and electronic structure of the cubane subunit Mn_3CaO_4 of the OEC. Later, in 2015, Zhang¹¹ and co-workers successfully synthesised the asymmetric cluster as the closest mimic of the full site of the OEC.

From a philosophical point of view it is worth questioning how well the natural complex is optimised for its purpose? Did Nature, once a working system arose from evolutionary processes in the Archean period, which spanned some 1.5 billion years, simply cease to search for further modifications? Certainly comparisons of cyanobacteria, green algae and modern plants reveal a common inorganic core, which would suggest that little change took place over a large time span.¹² The reason for the absence of any evolution of the active site has been put down to the challenging four electron/four proton coupled oxidation reaction; the process is one of the most thermodynamically challenging multi-electron reactions in biology. Whereas ligating groups for metal ion binding in natural enzymes are provided mainly by amino acid residues, the toolkit at the disposal for craftspeople of artificial

assemblies is certainly more varied. Of course, Nature wins out on the structural complexity that peptide scaffolds afford, which can, for instance, serve to protect metal ions and provide intricate pathways for the transport of water molecules.¹³ The common denominator is the coordination chemistry of metal ions, which can interplay between kinetic inertness and lability by a simple change in oxidation state so that structures are fluxional. It is also reasonable to assume that the coordination chemistry of manganese and calcium ions are the same today as they were some 2.5 billion years ago. In this context, if matching the complexity of peptide frameworks is improbable, then spanning the potential structural diversity of mixed-metal complexes appears a more feasible approach. Hence, we have undertaken a study in search for alternative structures to support high-valent manganese centres with proximal calcium ions. The focus is to go beyond truly mimicking precisely the Mn_4CaO_5 arrangement. Our first effort in this regard produced a calcium(II) rod decorated along its periphery with manganese(II) complexes.^{14a} A follow-up publication focused on the magnetic properties of the complex $[Mn_2Ca_2(HMP)_6(H_2O)_4(CH_3CN)_2](ClO_4)_4$.^{14b} Here, we extend the study using the ligand, H-HMP, and various manganese complexes along with a calcium(II) nitrate or perchlorate salt. In three specific cases the $Mn(3+)_2Ca(2+)_2$ core is observed in the structures, whereas a $Mn(3+)_6Ca(2+)_2$ motif is seen in the other case.

Scheme 1. Basic chemical pictures for the prepared manganese-calcium clusters discussed in the text. Note: **H-BA** = benzoic acid, **H-CBA** = 3-chlorobenzoic acid, **H-AC** = acetic acid, **H-DCA** = dichloroacetic acid, **H-HMP** = 2-hydroxymethylpyridine, **bipy** = 2,2'-bipyridine.

Figure 1. Top: Monomeric unit of **1** (left) and the basic coordination about the manganese and calcium ions (right). Bottom: Basic cuboid-like arrangement and bond lengths. Hydrogen atoms and solvent molecules have been omitted for clarity.

Results and discussion

The various synthetic methods for obtaining the mixed-metal cluster complexes are illustrated in Scheme 1, with the top panel highlighting the use of the common featured ligand 2-hydroxymethylpyridine (**H-HMP**) and two simple calcium salts. In the preparation of compounds **2**, **3** and **4** the “Mn₃O” (Mn³⁺/Mn²⁺) core was used with various ligands completing the starting materials’ coordination sphere. The synthesis of **1** involved a Mn³⁺/Mn⁴⁺ dimer complex as the starting material. Samples of **1-4** were obtained as pink coloured crystalline solids in yields ranging from 50-60 %. The FT-IR spectra of samples **2-4** were consistent with the presence of carboxylate moieties; typical CO stretching modes were observed at 1600-1680 cm⁻¹. Additional features in the FT-IR spectrum for **1** included a Cl-O stretch at 1097 cm⁻¹ and an N-O stretch at 1349 cm⁻¹. Elemental analysis of each complex was consistent with its molecular formula. Data pertaining to the crystal structures of **1-4** are collected in Table 1 of the Experimental.

the major occupancy, with the bidentate nitrate, will be discussed.

The six coordinate manganese centre comprises of a N₂O₄ donor set, in which two **HMP** ligands and two μ₃-oxo units bridge two manganese centres and complete the coordination sphere. The oxidation state of the manganese is assigned to +3 by inspection of the molecular formula. The calcium(II) ion is 8-coordinate and comprises a NO₇ donor set, which consists of a bidentate nitrate ion, a unidentate nitrate, two oxygen atoms from the mono-anionic **HMP** ligands, a μ₃-oxo from a **HMP** ligand and a water molecule. The simplified picture of Figure 1 shows the cuboid-like arrangement at the Mn₂Ca₂ core. The calcium ion is connected to the manganese(III) ions via a μ₃-oxo and two μ₂-oxo atoms of **HMP** ligands. The geometry at the manganese ion is best described as a distorted octahedron; the O1-Mn1-O2 bond angle is close to the expected 180° (176.47(10)°). However significant deviations from ideal octahedral geometry are observed due to the bite angle of the **HMP** ligands (*ca.* 80°) forming two five-membered rings, and the attractive electrostatic interaction between the calcium ion and the μ₃ oxygen atom (O3-Ca1: 2.487(2) Å), which causes the angle between the two axial coordination sites to deviate significantly from 180° (O3-Mn1-N1: 165.73(9)°). Noticeable in the cuboid-like arrangement are the two disparate Mn-O bond lengths to the μ₃-oxo (Figure 1 bottom), which is consistent with Jahn-Teller distortion at the Mn³⁺ high-spin d⁴ site; i.e., four short bonds (Mn1-O1, Mn1-O2, Mn1-O3, Mn1-N1) and two long (Mn1-N2, Mn1-O3'). The Mn-Mn and Ca-Ca separation distances within the Mn₂Ca₂ core are 3.2301(7) Å and 6.204(1) Å, respectively.

Analysis of the supramolecular chemistry of **1** reveals a 1-D coordination polymer motif (Figure 2), in which adjacent Mn-Ca clusters are bridged by two nitrate or perchlorate anions between neighbouring calcium ions with an inter-chain Ca-Ca distance of 5.7071(9) Å. The polymeric chain propagates along the crystallographic [100] direction with each polymer unit related to the next by crystallographic inversion symmetry.

Figure 2. Representation of a section of the 1-D coordination polymer for **1** along the *a*-axis showing the bridging nitrate anions. Hydrogen atoms, solvent molecules and the minority-occupancy bridging perchlorate ions have been omitted for clarity.

Crystal Structure of [Mn₂Ca₂(HMP)₆(NO₃)₂(ClO₄)₂(CH₃)₂CO] (**1**)

The complex **1** crystallised in the triclinic space group P-1, and the molecular structure is shown in Figure 1. Collected in Table 2 are selected bond lengths and angles. The structure is a 1-D coordination polymer where the nitrate and perchlorate ions bridging the calcium ions exhibit occupational disorder with *ca.* 60 and 40% occupancies respectively. For simplicity the structure of

Table 2. Selected bond lengths and angles for structure **1**.

Bond Length	Å	Angle	°
Mn1-O1	1.863(2)	O1-Mn1-O2	176.47(10)
Mn1'-O2	1.877(2)	O3-Mn1-N1	165.73(10)
Mn1-O3	1.966(2)	O3'-Mn1-N2	162.73(9)
Mn1-O3'	2.279(2)	O3'-Mn1-O2	83.06(9)
Mn1-N1	2.057(3)	O3'-Mn1-O1	97.30()
Mn1-N2	2.222(3)	O3'-Mn1-O3	81.18(9)
Ca1-Mn1	3.4606(8)	Ca1-O1-Mn1	108.15(10)
Ca1-Mn1'	3.5338(8)	Ca1-O2-Mn1'	111.71(9)
Ca1-O1	2.393(2)	Ca1-O3-Mn1	95.62(7)
Ca1-O2	2.379(2)	Ca1'-O3'-Mn1	101.34(9)
Ca1-O3	2.487(2)	O1-Ca1-O11	159.3(5)
Ca1-O4	2.504(3)	O2-Ca1-O4	147.84(8)
Ca1-O5	2.484(3)	O2-Ca1-O5	161.07(8)
Ca1-O10	2.393(12)	O3-Ca1-O10	143.2(3)
Ca1-O11	2.497(14)	O3-Ca1-O4	133.54(8)
Ca1-N3	2.576(3)	O10-Ca1-N3	152.1(3)

Figure 3. Top: The monomeric unit of **2** showing hydrogen bonding and π - π interactions with carbon-bound hydrogen atoms and counterions omitted for clarity (left) and the basic coordination chemistry about the manganese and calcium ions (right). Bottom: Basic cuboid-like arrangement and bond lengths.**Crystal Structure of $[\text{Mn}_2\text{Ca}_2(\text{HMP})_6(\text{CBA})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ (**2**)**

The complex **2** crystallised in the triclinic space group P-1, and the molecular structure is shown in Figure 3. A collection of selected bond lengths and angles are shown in Table 3. As with **1**, the basic structural motif comprises of a Mn_2Ca_2 unit, with each manganese ion in the +3 oxidation state. The calcium(II) ion is 7-coordinate with a NO_6 donor set, which is made up of a water molecule, two μ_2 -O atoms from **HMP** ligands, a μ_3 -O from a single **HMP**, two oxygen atoms from two separate **CBA** molecules and a pyridine nitrogen of a **HMP** group. The distorted octahedral 6-coordinate manganese(III) ion contains a N_2O_4 donor set, with two μ_3 -O, two μ_2 -O and two N atoms completing the coordination sphere. There is an apparent change in coordination number at the calcium ion compared to that observed for **1**, as this is due to the presence of a monodentate water molecule where there is a bidentate nitrate group in **1**, the cuboid-like arrangement (Figure 3 bottom) of the cores are more or less identical. The Mn-Mn and Ca-Ca separation distances

within the Mn_2Ca_2 core are 3.3025(9) Å and 6.047(1) Å, respectively.

Much like the structure of **1**, **2** also forms a 1-D coordination polymer structure which propagates along the crystallographic [100] direction with each polymer unit related to the next by crystallographic inversion symmetry, as shown in Figure 4. In this case the Mn_2Ca_2 units are linked *via* two **CBA** moieties providing the bridge between the calcium ions; both oxygen atoms of the carboxylate are involved in bonding to adjacent calcium ions with a Ca-Ca distance of 4.689(1) Å, which is significantly shorter than that observed in **1**. Focusing on the bridging section, it can be seen that the link between the clusters is further stabilised by both hydrogen bonding from the water molecules attached to the calcium ions to a proximal oxygen of a carboxylate, and a degree of aryl overlap between an **HMP** group and the bridging **CBA** (3.588(3) Å). A further π - π interaction between two **HMP** moieties on the cluster (3.512(3) Å) leads to the formation of a three-membered stack between the cluster and the bridging **CBA** moiety. These interactions are most likely the cause of the shorter distance between polymeric units in this structure compared to **1**. The π -stacking interaction in particular appears to contract the bridging section as its presence causes the carboxylate moiety to pull the calcium ions closer together. The strain caused by this is attested to by the twist in the plane of the carboxylate group relative to the phenyl group on **CBA** (16.69(15)°). This orientation of the **CBA** also appears to be stabilised by potential Cl- π interactions between the *meta*-chlorine of **CBA** and the aromatic ring of a neighbouring **HMP**.

Figure 4. Representation of a section of the 1-D coordination polymer for **2** along the a-axis showing the bridging carboxylates. Hydrogen atoms and counterions have been omitted for clarity.**Table 3.** Selected bond lengths and angles for structure **2**.

Bond Length	Å	Angle	°
Mn1-O1	1.970(2)	O2-Mn1-O3	175.57(11)
Mn1'-O1	2.298(3)	O1-Mn1-N2	165.09(12)
Mn1-O2	1.862(3)	O1-Mn1-N3	163.54(11)
Mn1-O3	1.874(3)	Ca1-O1-Mn1	100.23(10)
Mn1-N2	2.055(3)	Ca1-O1-Mn1'	94.44(9)
Mn1-N3	2.207(3)	Ca1-O2-Mn1'	107.07(12)
Ca1-Mn1	3.4044(9)	Ca1-O3-Mn1'	109.48(12)
Ca1-Mn1'	3.4852(10)	O1-Ca1-O4	133.27(9)
Ca1-O1	2.448(3)	O2-Ca1-O1W	155.78(10)
Ca1-O2	2.355(3)	O3-Ca1-O5	176.90(10)
Ca1-O3	2.379(3)	O2-Ca1-N1	124.12(10)
Ca1-O4	2.385(3)	O4-Ca1-N1	158.15(11)
Ca1-O1W	2.384(3)	O1W-Ca1-N1	78.49(11)
Ca1-N1	2.593(3)	N1-Ca1-O1	64.85(9)

Figure 5. Top: Monomeric unit of **3** with carbon-bound hydrogen atoms and solvent molecules omitted for clarity (left) and the basic coordination chemistry about the manganese and calcium ions (right). Bottom: The basic cuboid-like arrangement and bond lengths.

Crystal Structure of $[\text{Mn}_2\text{Ca}_2(\text{HMP})_6(\text{DCA})_2(\text{NO}_3)_2(\text{H}_2\text{O})_2]$ (**3**)

The complex **3** crystallised in the monoclinic space group $C2/c$, and the molecular structure is shown in Figure 5. A collection of selected bond lengths and angles are shown in Table 5. The calcium(II) ion is 8-coordinate and comprises a NO_7 donor set, which consists of a bidentate nitrate ion, a unidentate **DCA**, two oxygen atoms from the mono-anionic **HMP** ligands, a μ_3 -oxo from a **HMP** ligand and a water molecule. As observed for the previous structures each manganese(III) ion is Jahn-Teller distorted and consists of a N_2O_4 donor group, with four bridging hydroxyl groups from **HMP** ligands forming a link to the two calcium ions. The general Mn_2Ca_2 core is virtually identical to that of **1** and the Mn-Mn and Ca-Ca distances are 3.238(1) Å and 6.163(2) Å, respectively.

The crystal packing diagram (not shown) demonstrates that the Mn_2Ca_2 units are not linked together as seen for the previous two cases (*cf.* **1** & **2**). In this case, the role of π - π interactions in the formation of the bridging section in the structure of **2** is further illuminated by the inability of the **DCA** groups to do the same. On first inspection one may assume that the hydrogen bond from the calcium-bound water molecule to the carboxylate group is what precludes the formation of bridging interactions in **3** but as this motif exists in **2** this is unlikely to be the case. It is clear that the absence of π - π interactions in **3** prevents the monomer units from aligning in such a way that the carboxylate is able to act as a link between them.

Table 4. Selected bond lengths and angles for structure **3**.

Bond Length	Å	Angle	°
Mn1-O1	1.851(4)	O1-Mn1-O2	177.2(2)
Mn1-O2	1.877(4)	O3-Mn1-N1	164.50(19)
Mn1-O3	1.960(4)	O3'-Mn1-N2	160.53(17)
Mn1-N1	2.065(5)	Ca1-O1-Mn1'	108.5(2)
Mn1-N2	2.220(5)	Ca1-O2-Mn1	112.91(19)
Mn1-O3'	2.284(4)	Ca1-O3'-Mn1	96.35(15)
Ca1-Mn1	3.5324(14)	Ca1-O3'-Mn1'	101.36(17)
Ca1-Mn1'	3.429(2)	O1-Ca1-O1W	152.92(18)
Ca1-O1	2.357(4)	O2-Ca1-O4	151.46(18)
Ca1-O2	2.350(4)	O2-Ca1-O5	158.58(17)
Ca1-O3'	2.454(4)	O3'-Ca1-O7	135.35(16)
Ca1-O4	2.659(6)	O4-Ca1-O5	48.89(17)
Ca1-O5	2.472(6)	O2-Ca1-O3'	69.19(14)
Ca1-O7	2.337(5)	O1-Ca1-O3'	64.87(14)
Ca1-O1W	2.417(5)	O2-Ca1-O7	86.01(16)
Ca1-N3	2.499(6)	O7-Ca1-O1W	76.33(19)

Figure 6. Molecular structure of **4** with hydrogen atoms, counterions and water molecules omitted for clarity (left) and the basic coordination chemistry about the manganese and calcium ions with selected numbering (right).

Crystal Structure of $[\text{Mn}_6\text{Ca}_2(\text{HMP})_6(\text{BA})_6\text{O}_3(\text{H}_2\text{O})_{10}](\text{ClO}_4)_4$ (**4**)

The complex **4** crystallised in the monoclinic space group $C2/c$, and the molecular structure is shown in Figure 6. A collection of selected bond lengths and angles are shown in Table 5. The molecular structure comprises of a hexa-manganese ring capped on each side by a calcium ion giving the impression that a dimeric calcium complex has been threaded into a central cavity. From inspection of the molecular formula each manganese is assigned to the +3 oxidation state. The general feature of the structure is very similar to that reported for $\text{Mn}_6\text{Ca}_2\text{O}_9$ by Zhang and co-workers;¹⁵ the manganese ions in this example are however in the +4 oxidation state. Each manganese ion is six coordinate with a NO_5 ligation set. The Mn1 and Mn2 ions coordination sphere incorporate two μ_3 -O atoms from separate **HMP** ligands, two oxygen atoms from independent **BA** ligands, a pyridine unit (from **HMP**) and a μ_4 -oxo subunit. The coordination chemistry at Mn3 is slightly different and involves two μ_2 -O atoms from separate **HMP** ligands, two oxygen atoms from independent **BA** ligands, a pyridine unit (from **HMP**) and a μ_4 -oxo subunit. Each manganese centre displays typical Jahn-Teller distortion as expected for high-spin Mn^{3+} (d^4) ions. The six **BA** ligands act to bridge between adjacent manganese centres in an

$\mu_2-\eta^1:\eta^1$ fashion. In comparison, **HMP** ligands bridge manganese centres via the hydroxyl group ($\mu_2-\eta^2$). The two calcium ions are both 8-coordinate utilising all oxygen donors from three water molecules, three μ_4 -oxido groups and two hydroxyls from separate **HMP** ligands. The μ_4 -oxo groups link together two manganese and two calcium ions. The Ca-Ca separation distance is 3.5368(11) Å. The Ca-Mn distances fall within a range of *ca.* 3.6–3.7 Å.

The coordination about manganese in this structure is once again distorted octahedron though this distortion is not as pronounced as in the structure of **1**. The O-Mn-O angles between the axial coordination sites range between *ca.* 173–178° in this case. The equatorial plane exhibits the greater departure from idealised geometry due to the *ca.* 80° bite angle of the **HMP** ligand and the discrepancy between the Mn-Mn distances (*ca.* 3.15 Å) *versus* the widths of the carboxylate groups (*ca.* 2.24 Å).

Figure 7 A view highlighting the hydrogen bonding network in which water molecules link the clusters (fine lines) and perchlorate counterions *via* the calcium-bound water molecules.

As the calcium ions are observed to cap a manganese hexamer in this structure it is clear that the orientation of the phenyl groups relative to the calcium ions preclude the formation of a coordination polymer akin to the structure of **2**. What is not immediately obvious is why under very similar reaction conditions **BA** will form these monomeric units and **CBA** will form a polymer. That the supramolecular chemistry of **4** in the solid state appears governed by hydrogen bonding and not polymeric coordination interactions is one reason. This structure highlights the potential structure directing influence of the proposed Cl- π interaction in **2**. Both **BA** and **CBA** are capable of being involved in π - π interactions but as only **CBA** forms a coordination polymer it can be asserted that the Cl- π interaction is key. The aforementioned hydrogen bonding network in **4** links the Ca-OH₂ subunits of one Mn₆Ca₂ moiety to its neighbour *via* hydrogen bonds to the perchlorate anions. Hydrogen bonded water networks involving calcium ions are also observed in the natural OEC structure.⁷

Table 5. Selected bond lengths and angles for structure **4**.

Bond Length	Å	Angle	°
Mn1-O1	1.915(2)	O1-Mn1-O4	165.74(9)
Mn1-O2	2.303(2)	O2-Mn1-O5	177.56(8)
Mn1-O4	1.947(2)	O10-Mn1-N1	168.98(8)
Mn1-O5	2.159(2)	Mn1-O1-Mn2	96.70(9)
Mn1-O10	1.8496(15)	Mn1-O2-Mn2	96.95(8)
Mn1-N1	2.061(2)	O2-Mn2-O6	164.64(9)
Mn2-O1	2.310(2)	O1-Mn2-O8	175.73(8)
Mn2-O2	1.915(2)	O11-Mn2-N2	169.81(9)
Mn2-O6	1.9429(2)	Mn2-O11-Mn3	116.25(10)
Mn2-O8	2.165(2)	O3-Mn3-O9	163.87(9)
Mn2-O11	1.858(2)	O3-Mn3-O7	173.69(8)
Mn2-N2	2.060(3)	O11-Mn3-N3	171.43(10)
Mn3-O3	1.921(2)	O10-Ca1-O11	75.73(6)
Mn3-O3'	2.280(2)	O10-Ca1-O1'	61.13(4)
Mn3-O7	2.169(2)	O10-Ca1-O13	134.98(6)
Mn3-O9	1.939(2)	O12-Ca1-O13	77.78(7)
Mn3-O11	1.846(2)	O12-Ca1-O11	144.32(7)
Mn3-N3	2.051(3)	O12-Ca1-O1'	77.34(7)
Ca1-O1'	2.680(2)	O2-Ca1-O11	126.59(6)
Ca1-O2	2.700(2)	O2-Ca1-O13	142.91(7)
Ca1-O10	2.495(2)	O2-Ca1-O10	65.92(8)
Ca1-O11	2.488(2)	O2-Ca1-O1'	118.32(6)
Ca1-O11'	2.504(2)	O14-Ca1-O1'	145.64(7)
Ca1-O12	2.457(2)	O14-Ca1-O10	141.44(6)
Ca1-O13	2.472(2)	O14-Ca1-O11	132.55(8)
Ca1-O14	2.431(2)	O14-Ca1-O13	77.60(7)

General Discussion

The common feature of the X-ray structures for the complexes **1–3** is the Mn₂Ca₂O₆N₂ motif. The actual core is very reminiscent of Mn₄O₆N₂ structures reported by Clerac *et al.*¹⁷ The formation of the basic structure seems to be quite independent on the synthetic method used. For example, the preparation of **1** used a mixed valent (Mn³⁺/Mn⁴⁺) starting material containing 2,2'-bipyridine ligands that are not incorporated into the final complex.

The effect of the various carboxylic acids used in this study on the supramolecular chemistry of the clusters formed illuminate ways in which these structures may be engineered to produce specific motifs. The structure of **1**, formed without the presence of an acid, forms a polymer where the counterions act to bridge the clusters. Where an acid is present and is involved in the coordination chemistry, the nature of the acid involved dictates whether monomers or a polymer are formed. Comparison of structures **2** and **3** reveals how altering one ligand at the cluster can affect the crystal packing. Even though both clusters exhibit the same core structure, the carboxylate moiety **CBA** within **2** promotes 1-D coordination polymer formation, whereas the **DCA** carboxylate in **3**, also a chlorinated carboxylic acid, does not facilitate intermolecular bridging interactions. Such a sensitive effect may be rather significant in crystal engineering design. Another interesting crystal engineering feature is evident by comparison of structures **2** and **4**. Again, the synthetic methods differ only by the choice of carboxylic acid in the

starting materials: **CBA** in the case of **2** and **BA** for **4**. The two structures are very different in their supramolecular chemistry and although both acids could potentially be involved in the π - π interactions that appear to facilitate the bridging in **2**, the structure of **4** is monomeric. It is clear that the meta chlorine in the benzene ring is rather significant. One potential reason for the disparity in the two structures is the result of chlorine- π interactions.¹⁸ Inspection of the crystal packing diagram for **2** (Figure 8) shows that the chlorine for the bridging **CBA** appears to point toward the centroid of a neighbouring **HMP** ligand. This additional stabilising effect may be enough not only to encourage 1-D polymer formation during crystallisation rather than cyclisation as observed for **BA**, but also to bring the clusters closer together than the bridges formed of counterions in **1**. It is noted that the manganese ions within **2** are all in the +3 oxidation state for an NO_5 donor group, but are in the +4 oxidation state for an analogous structure with an O_6 donor set.¹⁵ The substitution of one nitrogen for the harder oxygen is enough to help stabilise the higher oxidation state.

Figure 8. Partial crystal packing diagram for **2** showing the potential Cl- π interaction with an adjacent **HMP** ligand. Hydrogens bonded to carbon atoms and counterions are omitted for clarity.

Conclusions

Using various starting materials approach we have shown that heterobimetallic complexes incorporating calcium(II) and manganese(III) ions can be prepared. Given that the $\text{Mn}_2\text{Ca}_2\text{O}_6$ moiety is observed in three complexes would suggest it is a low-energy structure that preferentially crystallises from solution. It is worth speculating that one reason why the MnCa cuboid arrangement in the natural OEC arose was driven by the same type of crystallisation process. Initially, a very rudimentary structure may have accumulated as a non-functioning building block which evolved over time to eventually become the cluster capable of performing the water oxidation reaction. We note that the Mn-Ca distances in the cuboid structures presented here (*ca.* 3.5 Å) are very similar to those in the natural system.⁷

In addition to this, the sensitivity of the structures to the ligand system used in the synthesis was illustrated, exemplified by the observation that meta-substituted chlorobenzoic acid may be a suitable unit to promote coordination polymer formation *via* π - π and Cl- π interactions. A similar finding was reported by Sundberg¹⁹ in which it was shown that the position of the chlorine in the aromatic ring determines the packing mode of benzoate anions. The hexa-manganese ring-like structure with its threaded calcium core can be considered to resemble a rotaxane (ring + axle). Such a topologically different approach to mixed manganese-calcium structures may have some merit and open up a new field of study. By variation of the manganese ring size and the calcium core it should be possible to create potential water channels coupled to a redox-active loop. We intend to test the design principles in new supramolecular structures.

Experimental

Synthesis

All chemicals were purchased from commercial sources and used as received. The starting materials $[\text{Mn}(\text{DCA})_2]$, $[\text{Mn}_2\text{O}_2(\text{bipy})_4](\text{ClO}_4)_3$,²⁰ $[\text{Mn}_3\text{O}(\text{CBA})_6(\text{py})_2(\text{H}_2\text{O})]$,²¹ $[\text{Mn}_3\text{O}(\text{BA})_6(\text{py})_2(\text{H}_2\text{O})]$,²² and $[\text{Mn}_{12}\text{O}_{12}(\text{AC})_{12}(\text{DCA})_4]$ ²³ were prepared by literature methods.

Preparation of $[\text{Mn}_2\text{Ca}_2(\text{HMP})_6(\text{NO}_3)_2(\text{ClO}_4)_2(\text{CH}_3)_2\text{CO}]$ (**1**)

To a stirred solution of H-HMP (0.09 g, 0.82 mmol) and $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (0.014 g, 0.07 mmol) in acetone (20 mL) was added solid $[\text{Mn}_2\text{O}_2(\text{bipy})_4](\text{ClO}_4)_3$ (0.126 g, 0.12 mmol). The reaction mixture was stirred for 10 min at 60°C to afford a clear solution. The resulting brown solution was allowed to cool to room temperature and was filtered. The filtrate was left undisturbed to concentrate slowly by evaporation. After 3 days, pink crystals were collected by filtration, washed with Et_2O and dried under vacuum. Elemental analysis calc. for $\text{C}_{39}\text{H}_{42}\text{Ca}_2\text{Cl}_{0.8}\text{Mn}_2\text{N}_{9.2}\text{O}_{19.8}$: C, 39.87; H, 3.60; N, 10.97%. Found: C, 40.02; H 3.83; N, 11.05%. Selected IR data (cm^{-1}): 2844 (w), 1713 (m), 1604 (m), 1436 (m), 1394 (m), 1349 (m), 1310 (s), 1228 (vs), 1119 (s), 1097 (s), 1058 (s), 1043 (s), 981 (s), 824 (m), 761 (s), 721 (m), 657 (s), 621 (m).

Preparation of $\{[\text{MnCa}(\text{HMP})_3(\text{CBA})(\text{H}_2\text{O})]\text{ClO}_4\}_n$ (**2**)

To a stirred solution of H-HMP (0.045 g, 0.41 mmol) and $\text{Ca}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ (0.2 g, 0.64 mmol) in CH_3CN (10 mL) was added a solution of $[\text{Mn}_3\text{O}(\text{CBA})_6(\text{py})_2(\text{H}_2\text{O})]$ (0.10 g, 0.08 mmol) in CH_3CN (10 mL). The reaction mixture was stirred for 1 h at room temperature. The resulting dark pink solution was filtered. X-ray quality pink crystals were grown by vapour diffusion of diethyl ether into the solution of the complex. After 5 days, crystals were collected by filtration, washed with Et_2O and dried under vacuum. Elemental analysis calc. for $\text{C}_{25}\text{H}_{24}\text{CaCl}_2\text{Mn}_3\text{N}_9\text{O}_{9.95}$: C, 43.37; H, 3.49; N, 6.07%. Found: C, 43.09; H 3.12; N, 5.98%. Selected IR data (cm^{-1}): 3459 (b), 3330 (b), 1607 (mb), 1538 (s), 1483 (m), 1435 (s), 1413 (mb), 1374 (m), 1280 (m), 1227 (w), 1058 (s), 1040 (vs), 930 (mb), 820 (w), 757 (s), 716 (mb), 659 (m).

Preparation of $[\text{Mn}_2\text{Ca}_2(\text{HMP})_6(\text{DCA})_2(\text{NO}_3)_2(\text{H}_2\text{O})_2]$ (**3**)

The synthesis of $[\text{Mn}_{12}\text{O}_{12}(\text{AC})_{12}(\text{DCA})_4]$ was carried out by adapting a literature procedure²³ and using $\text{Mn}(\text{DCA})_2$ instead of $\text{Mn}(\text{AC})_2$. The precursor was used as received without any further purification. To a stirred solution of H-HMP (0.09 g, 0.82 mmol) and $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (0.014 g, 0.07 mmol) in acetone (20 mL) was added solid $[\text{Mn}_{12}\text{O}_{12}(\text{AC})_{12}(\text{DCA})_4]$ (0.04 g, 0.02 mmol). The reaction mixture was stirred for 10 min at 60°C to afford a clear solution. The resulting brown solution was allowed to cool to room temperature and was filtered. The filtrate was left undisturbed to concentrate slowly by evaporation. After 3 days, pink crystals were collected by filtration, washed with Et_2O and dried under vacuum. Elemental analysis calc. for $\text{C}_{46}\text{H}_{54}\text{Ca}_2\text{Cl}_4\text{Mn}_2\text{N}_8\text{O}_{20}$: C, 40.30; H, 3.97; N, 8.17%. Found: C, 39.93; H, 3.66; N, 8.50%. Selected IR data (cm^{-1}): 3454 (b), 2842 (w), 1709 (m), 1638 (s), 1602 (m), 1569 (w), 1404 (mb), 1350 (vs), 1222 (m), 1157 (w), 1061 (s), 1044 (vs), 824 (m), 762 (s), 719 (m), 671 (m).

Preparation of $[\text{Mn}_6\text{Ca}_2(\text{HMP})_6(\text{BA})_6\text{O}_3(\text{H}_2\text{O})_6](\text{ClO}_4)_4 \cdot 4\text{H}_2\text{O}$ (**4**)

To a stirred solution of H-HMP (0.045 g, 0.41 mmol) and $\text{Ca}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ (0.2 g, 0.64 mmol) in CH_3CN (10 mL) was added a solution of $[\text{Mn}_3\text{O}(\text{BA})_6(\text{py})_2(\text{H}_2\text{O})]$ (0.09 g, 0.08 mmol) in CH_3CN (10 mL). The reaction mixture was stirred for 1 h at room temperature. The resulting dark pink solution was filtered. X-ray quality pink crystals were grown by vapour diffusion of diethyl ether into the solution of the complex. After 5 days, crystals were collected by filtration, washed and dried under vacuum. Elemental analysis calc. for $\text{C}_{78}\text{H}_{86}\text{Ca}_2\text{Cl}_4\text{Mn}_6\text{N}_6\text{O}_{47}$: C, 38.11; H, 3.50; N, 3.40%. Found: C, 38.69; H, 3.44; N, 3.58%. Selected IR data (cm^{-1}): 3517 (b), 1603 (s), 1567 (s), 1477 (w), 1441 (m), 1381 (vs), 1308 (w), 1282 (m), 1092 (s), 1035 (s), 972 (m), 843 (w), 760 (m), 717 (m), 677 (s), 622 (m).

X-ray Crystallography

Data pertaining to the crystal structures **1-4** are collected in Table 1. X-ray data were collected for complexes **1** and **4** using an Xcalibur, Atlas, Gemini ultra diffractometer equipped with an Oxford Cryosystems CryostreamPlus open-flow N_2 cooling device. Data were collected using copper radiation ($\lambda_{\text{CuK}\alpha} = 1.54184 \text{ \AA}$) and intensities were corrected for absorption using a multifaceted crystal model created by indexing the faces of the crystals for which data were collected.²⁴ X-ray data were collected for complexes **2** and **3** using an Xcalibur Eos diffractometer using molybdenum radiation ($\lambda_{\text{MoK}\alpha} = 0.71073 \text{ \AA}$). Cell refinement, data collection and data reduction were undertaken via the software CrysAlis.²⁵ Intensities were corrected for absorption using CrysAlisPro. Using the Olex2 interface,²⁶ the structures were solved with the ShelXS or ShelXT structure solution program using Direct Methods or intrinsic phasing respectively,²⁷ and refined with the ShelXL refinement package using least-squares minimization.²⁸ All fully-occupied non-hydrogen atoms were refined anisotropically. Hydrogen atoms were positioned with idealized geometry with the exception of those bonded to heteroatoms which were located using peaks in the Fourier

difference map. The atomic displacement parameters of all hydrogen atoms were constrained using a riding model.

Table 1. Crystal structure data for complexes **1-4**.

Compound	1	2	3	4
Empirical Formula	C ₃₉ H ₄₂ Ca ₂ Cl _{0.8} Mn ₂ N _{9.2} O _{19.8}	C ₂₅ H ₂₄ CaCl ₂ MnN ₃ O _{9.95}	C ₄₆ H ₅₄ Ca ₂ Cl ₄ Mn ₂ N ₈ O ₂₀	C ₇₈ H ₈₆ Ca ₂ Cl ₄ Mn ₆ N ₆ O ₄₇
Formula weight	1174.82	691.59	1370.81	2456.17
Temp. / K	150.0(2)	172.95(10)	173.00(14)	150.0(2)
Crystal system	triclinic	triclinic	monoclinic	monoclinic
Space group	P-1	P-1	C2/c	C2/c
a / Å	10.5975(6)	10.4621(5)	24.660(2)	25.8236(3)
b / Å	11.4166(7)	11.6521(5)	11.8933(10)	14.88011(20)
c / Å	11.7527(6)	12.3464(5)	20.3808(14)	27.1462(4)
α / °	61.595(6)	87.205(4)	90	90
β / °	79.180(5)	89.130(4)	107.529(7)	107.2590(14)
γ / °	68.553(5)	88.881(4)	90	90
Volume / Å ³	1163.96(13)	1502.87(12)	5700.0(7)	9961.5(2)
Z	1	2	4	2
ρ_{calc} g/cm ³	1.676	1.528	1.597	1.638
μ / mm ⁻¹	7.555	0.845	0.891	8.766
F(000)	602.0	707.0	2816.0	5020.0
Crystal size / mm ³	0.17 × 0.12 × 0.04	0.4 × 0.2 × 0.1	0.2 × 0.1 × 0.03	0.22 × 0.08 × 0.06
Radiation	CuK α (λ = 1.54184)	MoK α (λ = 0.71073)	MoK α (λ = 0.71073)	CuK α (λ = 1.54184)
2 θ range for data collection / °	8.554 to 134.014	3.3 to 50.06	3.46 to 50.06	6.82 to 133.792
Index ranges	-12 ≤ h ≤ 12, -13 ≤ k ≤ 13, -13 ≤ l ≤ 1	-12 ≤ h ≤ 12, -13 ≤ k ≤ 13, -14 ≤ l ≤ 14	-29 ≤ h ≤ 24, -14 ≤ k ≤ 11, -24 ≤ l ≤ 24	-30 ≤ h ≤ 23, -15 ≤ k ≤ 17, -32 ≤ l ≤ 32
Reflections collected	16519	12990	14020	36746
Independent reflections	4106 [R _{int} = 0.0520, R _{sigma} = 0.0408]	5302 [R _{int} = 0.0379, R _{sigma} = 0.0549]	5019 [R _{int} = 0.0733, R _{sigma} = 0.1149]	8789 [R _{int} = 0.0752, R _{sigma} = 0.0556]
Data/restraints/parameters	4106/412/354	5302/56/401	5019/10/367	8789/1/684
Goodness-of-fit on F ²	1.044	1.037	1.036	1.053
Final R indexes [I ≥ 2 σ (I)]	R ₁ = 0.0459, wR ₂ = 0.1149	R ₁ = 0.0584, wR ₂ = 0.1462	R ₁ = 0.0826, wR ₂ = 0.1918	R ₁ = 0.0384, wR ₂ = 0.0882
Final R indexes [all data]	R ₁ = 0.0549, wR ₂ = 0.1221	R ₁ = 0.0713, wR ₂ = 0.1556	R ₁ = 0.1294, wR ₂ = 0.2199	R ₁ = 0.0555, wR ₂ = 0.0991
Largest diff. peak/hole / e Å ⁻³	0.92/-0.54	1.12/-0.60	0.63/-0.97	0.46/-0.44

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