

Exploiting the multifunctionality of organocations in the assembly of hybrid polyoxometalate clusters and networks†

Chris Ritchie,^a Eric M. Burkholder,^a De-Liang Long,^a David Adam,^a Paul Kögerler^b and Leroy Cronin^{*a}

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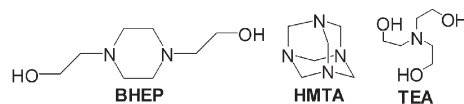
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Assembly of an unprecedented $[(P^V Mn^{II} W^{VI}_{11} O_{39})_2 (PO_4)]^{13-}$ and a $[P_2 Mn_4 W_{18} O_{68}]^{10-}$ cluster have been observed and structurally characterised and cryospray mass spectroscopic ionization (CSI) has been used to observe one of the very reactive building blocks linking solid state with solution studies.

Polyoxometalates (POMs) represent a class of inorganic materials with an almost unmatched range of structure types, combined with a vast range of possible uses and physical properties from materials science to biology.¹⁻⁴ Despite this great range of cluster types and properties, the ability to assemble cluster systems from a variety of known building blocks in a pre-determined way, and hence gain ultimate control over the cluster architecture and their intrinsic properties, still eludes researchers.²⁻⁴ This is because there is a great deal of sensitivity between synthetic conditions and the overall cluster architecture formed. For instance, reaction systems that yield lacunary POMs,⁵ have been shown to self-assemble under conditions where many possible species are present, with factors such as subtle changes in pH,⁵ buffer capacity, ionic strength and cation size and type⁶ having a significant effect on the products isolated. Therefore the engineering of architectures using lacunary POMs is a fantastic challenge.⁷ Herein we present a new approach, utilising the multifunctional ligand *N,N'*-bis(2-hydroxyethyl)piperazine (BHEP) which acts as a buffer, encapsulating cation and as a ligand, that builds on our previous studies which allowed us to isolate a $\{Mo_{16}\}^8 \equiv [H_2 Mo^V_4 Mo^{VI}_{12} O_{52}]^{10-}$, $\{M_{18}\}^9 \equiv [M_{18} O_{54} (SO_3)_2]^{4-}$ ($M \equiv Mo$ or W), $\{W_{19}\}^{10} \equiv [H_4 W_{19} O_{64}]^{6-}$ and $\{W_{36}\}^{11} \equiv [H_{12} W_{36} O_{120}]^{12-}$ using bulky organic cations such as HMTA (hexamethyltetraamine) and TEA (triethanolamine).⁸⁻¹¹ By utilising the multifunctional protonated ligand H_2BHEP^{2+} we have been able to isolate two new POM-based architectures: the unprecedented dimeric cluster unit $[(PMnW_{11}O_{39})_2(PO_4)]^{13-}$ (**1**) and a 2D network based on $[P_2Mn_4W_{18}O_{68}]^{10-}$ anions (**2**) which have been synthesised incorporating the $\{PW_9\}^{12}$ and $\{PW_{11}\}^{13}$ lacunary fragments, respectively; thus demonstrating the multifunctionality of the BHEP ligand. Furthermore each compound is isolated under virtually identical reaction conditions by dissolving Na_2WO_4 in an aqueous solution followed by acidification with nitric acid, addition of BHEP and then phosphoric acid where the

pH is adjusted to 6.05 or 6.80 before the Mn^{2+} salt is added to yield compounds **1** and **2** analytically pure in 25 and 39%, yields respectively.‡ Compound **1** can be formulated as $(H_2BHEP)_5(HBHEP)Na_2[(PMnW_{11}O_{39})_2(PO_4)] \cdot 18H_2O$ and is composed of two α - $[PMnW_{11}O_{39}]^{5-}$ clusters connected by a bridging phosphate unit that links the Mn^{2+} centres that themselves bind to the mono-vacant Keggin entity. It would appear that this moiety is stabilized, in the solid state, by the surrounding four H_2BHEP cations (Fig. 1).§



In compound **1**, the manganese ions are five-coordinate and bind to the cluster through the basal plane of the Mn ion, defined by the $[(W-O)_4-Mn]$ unit where the four (Mn–O distances average 2.10 Å), the fifth coordination site of the Mn ion is coordinated to the bridging phosphate unit, which resides on a two-fold axis (Fig. 2). Characterisation of this linkage with magnetic susceptibility measurements using a SQUID shows that the low-field magnetism of compound **1** is defined by weak intramolecular antiferromagnetic coupling that is typical for such Mn^{II} dimers and an isotropic Heisenberg-type spin Hamiltonian of the type $H = -JS_1S_2$ can be fitted to the susceptibility data to yield $J/k_B = -0.72$ K with $g = 1.985$.

Further, in the solid state the dimeric phosphate-bridged species are connected into two dimensions along the *b* and *c* axes by

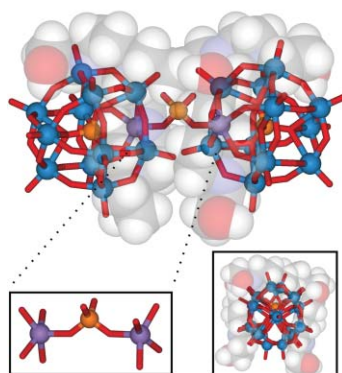


Fig. 1 Representation of the structure of $[(PMnW_{11}O_{39})_2(PO_4)]^{13-}$ (H_2BHEP)₄⁵⁻. POM unit: W: blue, Mn: purple, P: orange, O: red sticks. The H_2BHEP cations are shown as faded CPK representation (C: black, H: red, N: blue) and both a side view (top) and end on view (bottom right) is shown to help demonstrate the encapsulation of the $[Mn\{PO_4\}Mn]^{1+}$ unit (shown bottom left).

^aWestCHEM, Department of Chemistry, University of Glasgow, Joseph Black Building, University Avenue, Glasgow, UK G12 8QQ. E-mail: L.Cronin@chem.gla.ac.uk; Fax: +44 141 330 4888; Tel: +44 141 330 6650

^bAmes Laboratory and Department of Physics and Astronomy, Iowa State University, Ames, IA, 50011, USA

† Electronic supplementary information (ESI) available: crystallographic data, SQUID measurements, synthesis, microanalysis, IR, ³¹P NMR, MS and TGA analysis. See DOI: 10.1039/b612741j

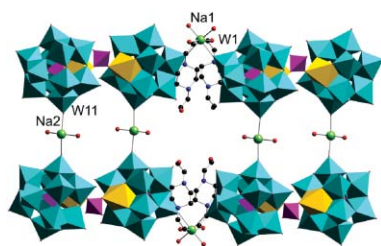


Fig. 2 Graphical representation of **1** showing the cluster connectivity into two dimensions by Na. Additional cationic BHEP and solvent are omitted for clarity. Colour code: W: light blue, Mn: yellow, O: red, P: purple, C: black, N: dark blue, Na: lime.

sodium ions (Fig. 2). Na1 resides on a two fold axis and connects the clusters approximately along the *c* axis through two *cis*-Na–O=W bonds with two BHEP ligands decorating the sodium ion by coordination through their hydroxyl groups. The other ethanol arm of the ligand remains free and is not involved in any coordination mode. Two water molecules complete the octahedral environment of the sodium. Na2 resides on a mirror plane and links the clusters along the *b* axis by coordination with the terminal oxo group of W11 at a distance of 2.36(3) Å. Two water molecules occupy the other remaining positions of the atoms square planar geometry with a bond length of 2.43(7) Å. This geometry, although not unprecedented, is rare for sodium and may be induced due to the local steric interactions between adjacent clusters, and also between the six BHEP ligands that surround each cluster.

Thermogravimetric analysis of **1** shows a multi-step weight loss that correlates with the loss of various components within the crystal structure under oxidizing conditions. An initial weight loss of 4.6% over the temperature range 50–150 °C accounts for solvent water molecules, with an accumulated loss of 16.8% (calc. 16.6%) between 150 and 800 °C equalling the loss of all BHEP present in the structure, in addition to the bridging phosphate unit. By carrying out an identical TGA-MS experiment under a nitrogen atmosphere, the decomposition process involves the loss of an additional 8.1 wt% compared to in the presence of air. This additional mass loss is associated with the decomposition of the metal oxide to accommodate the complete oxidation of residual organic fragments that cannot be oxidised in the absence of air. These observations highlight the robust nature of the POM in air up to 1000 °C.

Although compound **2**, (H₂BHEP)₃Na₄[P₂Mn₄W₁₈O₆₈]·15H₂O, is synthesised using only a slight increase in pH and temperature in comparison to **1**, its structure is entirely different. Compound **2** is composed of two {B–PW₉O₃₄}^{9–} units with four manganese centres sandwiched between these in the well-known belt-like fashion.¹⁴ Many examples of this cluster type can be found in the literature,¹⁴ however to the best of our knowledge this is the first 2D hybrid network involving this cluster unit. Hydroxyl groups of the ligand are involved in Na–BHEP–Na connectivity running parallel to the clusters (Fig. 3), with the sodium ions connecting the clusters through a *trans*-Na–O=W linkage (Na–O: 2.44(8) Å, W–O: 1.73(6) Å) and the Na ion is located on an inversion centre. The remaining two equatorial coordination sites are occupied by the hydroxyl groups of the BHEP ligand and have a slightly shorter contact of 2.37(7) Å (Na–O), with the remaining apical positions occupied by water. Further BHEP cations are located within the interlaminar space along with waters of crystallisation.

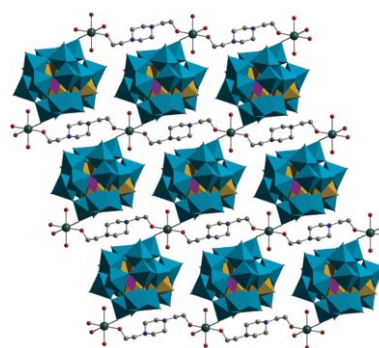


Fig. 3 A view of the packing of **2** showing the connectivity between cluster units by BHEP and Na. Colour code: W: light blue, Mn: yellow, O: red, P: purple, C: black, N: dark blue, Na: lime. Water and additional BHEP are omitted for clarity.

Due to the similar reaction conditions the self-assembly of **1** and **2** was also investigated using ³¹P NMR (Fig. 4, see ESI for details†), since we hypothesised that the formation of the dimer unit found in **1** may occur by insertion of the {(H₂O)₄Mn{PO₄}Mn(H₂O)₄}¹⁺ building block that could be imagined to form readily in solution on addition of Mn²⁺ into the phosphate rich reaction mixture. Formation and insertion of such species have previously yielded tungstosilicate clusters with pendant phosphate groups.^{15,16}

Since the conditions required to form both compounds **1** and **2** are identical, except the pH and reaction temperature which is pH 6.05 and RT for compound **1** and pH 6.8 and 60 °C for compound **2** (before addition of the Mn salts), ³¹P NMR studies were undertaken to examine the formation of these compounds under these conditions. Firstly the NMR of both the reaction solutions (Fig. 4) before addition of the Mn salt at pH 6.05 and 6.8, respectively, are identical between 0 and –12 ppm showing three peaks associated with the free acid H₃PO₄ (–2.211 ppm), the {PW₉} (–10.73) and {PW₁₁} (–11.2). On addition of the Mn(NO₃)₂ salt to the solution at pH 6.05, three peaks are now observed at –2.211, –11.00 and a broad peak spanning –20 to 20 ppm. The first peak can be assigned to H₃PO₄ and the second broad peak corresponds to a mixture of the {PW₁₁O₃₉}^{7–} and

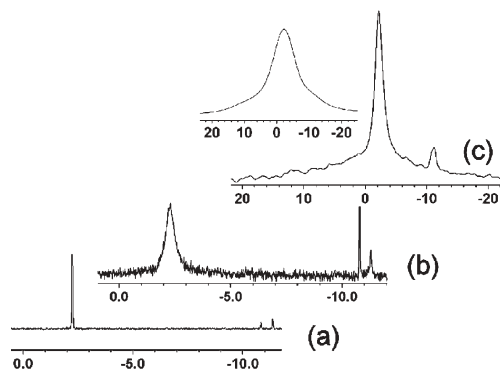


Fig. 4 ³¹P NMR of reaction mixture (RM) at pH 6.05 and 6.8 before the addition of Mn²⁺ ions (a), after the addition of Mn²⁺ to the RM at 6.8 (b), after the addition of Mn²⁺ to the RM at 6.05 with the insert showing the broad peak between ±20 ppm (c). All scales are in ppm. Line broadening parameters were set at 1.00 Hz, but increased to 1000 Hz in order to observe the broad peak that we believe could be associated with the (H₂O)₄MnPO₄Mn(H₂O)₄ species in (1).

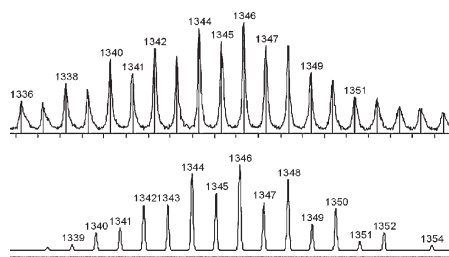


Fig. 5 CSI mass spectrum of the reaction mixture at pH 6.05 shown top and the simulated isotopic pattern, bottom. Mn and W are present in +3 and +6 oxidation states respectively, the Mn^{3+} ion being produced under the MS conditions.

$\{\text{B-PW}_9\text{O}_{34}\}^{9-}$ (which is broad and encompasses both resonances). We therefore assign the extremely broad peak between -20 to 20 ppm to the $\{(\text{H}_2\text{O})_4\text{Mn}\{\text{PO}_4\}\text{Mn}(\text{H}_2\text{O})_4\}^{1+}$ moiety (or a similar unit); the broad nature of the peak is indicative of interaction between the phosphorous centre and the paramagnetic Mn^{2+} ions, or rapid exchange of the phosphate ligand. The first idea is at least partly supported¹⁷ by the observation that this broad peak is not seen in the ^{31}P NMR of the solution at pH 6.8 which gives rise to compound **2** and only shows the presence of H_3PO_4 (-2.211 ppm) and $\{\text{PW}_9\}$ (-10.73 ppm), and $\{\text{PW}_{11}\text{O}_{39}\}^{7-}$ (-11.2 ppm) see (Fig. 4). This study shows that only upon addition of Mn^{2+} salts to the reaction mixture at pH 6.05 can the $\{(\text{H}_2\text{O})_4\text{Mn}\{\text{PO}_4\}\text{Mn}(\text{H}_2\text{O})_4\}^{1+}$ moiety (or a similar unit) be observed. Further evidence supporting the presence of the phosphate bridged Mn species was found by examining the reaction mixture at pH 6.05 using CSI (cryospray mass spectroscopic ionisation) which showed a $\{(\text{PO}_4)[\text{Mn}_1\text{W}_2]\}^+ \equiv \{[\text{Mn}(\text{H}_2\text{O})_2(\text{W}_2\text{O}_6(\text{H}_2\text{O})_4)(\text{PO}_4)[\text{Mn}(\text{H}_2\text{O})_2(\text{W}_2\text{O}_7(\text{H}_2\text{O})_3)]\}^+$ centred at $m/z = 1346$ (Fig. 5).

In summary, POM network structures like those presented here are uncommon since the majority of hybrid POM materials are prepared by deploying organic amines as cations that form hydrogen bonded networks, or transition metal chelate linkers based on pyridyl ligands or derivatives thereof. However, both **1** and **2** are synthesised from the same reaction mixture, with only slight alteration in pH and temperature. It is interesting that only at pH 6.05, the value required for the isolation of **1**, can a broad phosphorus-containing paramagnetic species be observed in solution. Further, it is shown that the BHEP moiety is able to act as a tri-functional species being a cation, ligand and buffer. The *direct* observation of the dimeric, phosphate bridged Mn unit in CSI as $\{(\text{PO}_4)[\text{Mn}_1\text{W}_2]\}^+$ begins to offer a much sought after glimpse of the self-assembly processes occurring in solution. This also could point to the formation of **1** *via* the insertion of this $\{\text{Mn}_1\text{W}_2\}$ unit into a tri-vacant $\{\text{W}_9\}$ species. Further work will examine this possibility as well as extending the use of multi-functional cations to both buffer and structure direct the formation of POM-based architectures *via* a combination of coordinative and supramolecular interactions. Indeed, combining this approach with solution studies such as NMR and CSI provides a powerful approach towards understanding and designing new cluster archetypes thus beginning to bridge the gap in understanding between the solid state architecture and self-assembly processes occurring in solution.

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Notes and references

† **1** $(\text{H}_2\text{BHEP})_5(\text{HBHEP})\text{Na}_2[(\text{PMnW}_{11}\text{O}_{39})_2\{\text{PO}_4\}]\cdot 18\text{H}_2\text{O}$: 1.65 g (5 mmol) $\text{Na}_2\text{WO}_4\cdot 2\text{H}_2\text{O}$ were dissolved in 20 ml aqueous NaCl solution (1 M) and acidified to pH 3.5 with nitric acid (4 M) followed by the addition of 0.84 g (4.82 mmol) BHEP. To this solution 0.446 g phosphoric acid (85%) were added. The solution pH is then adjusted to 6.05 with dilute NaOH. And a solution of 0.1152 g $\text{Mn}(\text{NO}_3)_2$ in 1 ml H_2O is added. This results in a yellow insoluble precipitate that is removed by centrifugation. Large yellow plates crystallise from the clear yellow solution (pH 6.05) and are isolated by filtration after 3 weeks. Yield: 0.403 g (25%). **2** $(\text{H}_2\text{BHEP})_3\text{Na}_4[(\text{P}_2\text{Mn}_4\text{W}_{18}\text{O}_{68})]\cdot 15\text{H}_2\text{O}$: 1.65 g (5 mmol) $\text{Na}_2\text{WO}_4\cdot 2\text{H}_2\text{O}$ were dissolved in 20 ml NaCl (1 M) and acidified to pH 7.5 with nitric acid (4 M) followed by the addition of 0.84 g (4.82 mmol) BHEP. To this solution 0.446 g phosphoric acid (85%) were added, resulting in a white precipitate that re-dissolves upon stirring. The solution was then acidified further to pH 6.8 using dilute nitric acid. Finally, a solution of 0.1152 g $\text{Mn}(\text{NO}_3)_2$ in 1 ml H_2O is added. This results in a yellow insoluble precipitate that is removed by centrifugation. The clear yellow solution is then heated to 60°C for 15 min. Large yellow plates crystallise from the clear yellow solution (pH 6.80) in a yield: 0.62 g (39%). See ESI† for analytical data for **1** and **2**.

§ Crystallographic data: **1**: monoclinic, space group $C2/m$, $a = 12.218(2)$, $b = 55.659(10)$, $c = 23.647(4)$ Å, $\beta = 93.382(6)^\circ$, $V = 16053(5)$ Å³, $Z = 8$, $\mu(\text{Mo-K}\alpha) = 1.229$ cm⁻¹. Final $R1 = 0.0713$ and $wR2 = 0.1909$ (all data). CCDC 619691. **2**: triclinic, space group $P\bar{1}$, $a = 12.5674(5)$, $b = 13.0776(5)$, $c = 17.2042(6)$ Å, $\alpha = 81.738(2)$, $\beta = 80.966(2)$, $\gamma = 67.900(2)^\circ$, $V = 2576.21(17)$ Å³, $Z = 2$, $\mu(\text{Mo-K}\alpha) = 1.229$ cm⁻¹. Final $R1 = 0.0400$ and $wR2 = 0.0990$ (all data). CCDC 606966. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b612741j.

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- This hypothesis will be investigated and reported later.