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

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Assembly of an unprecedented \([\{P(V)^3\text{Mn}^{IV}\text{W}^{VI}\text{O}_{11}\text{Na}_2\}\{P^V\text{O}_4\}]\)^{13—}\nand a \([\{\text{P}_{2}\text{MnW}_{10}\text{O}_{48}\}\{\text{PO}_{4}\}]^{10—}\) 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 uncountable range of structures 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,6 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 \(N,N‘\text{-bis(2-hydroxyethyl)}\) 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 \(\{\text{Mo}_{16}\}\) = \([\text{H}_2\text{Mo}_{9}\text{V}_3\text{Mo}_{11}\text{O}_{39}]^{18—}\) , \(\{\text{Mo}_{15}\}\) = \([\text{Mo}_{13}\text{V}_6\text{O}_{37}(\text{SO}_{3})_2]\)^{24—} (\(\text{M} = \text{Mo or W}\)), \(\{\text{W}_{19}\}\) = \([\text{H}_4\text{W}_{10}\text{O}_{46}]^{6—}\) and \(\{\text{W}_{16}\}\) = \([\text{H}_2\text{W}_{8}\text{O}_{22}]^{12—}\) using bulky organic cations such as HMTA (hexamethyltetramine) and TEA (triethanolamine).8–11 By utilising the multifunctional protonated ligand \(\text{H}_2\text{BHEP}\)^{2+} we have been able to isolate two new POM-based architectures: the unprecedented dimeric cluster unit \([\{\text{PMnW}_{11}\text{O}_{39}\}\{\text{PO}_{4}\}]^{11—}\) (1) and a 2D network based on \([\{\text{P}_{2}\text{MnW}_{10}\text{O}_{48}\}\{\text{PO}_{4}\}]^{10—}\) anions (2) which have been synthesised incorporating the \(\{\text{PW}_{9}\]\^{12—} and \(\{\text{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 Na₃WO₄ 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 \((\text{H}_2\text{BHEP})_5(\text{BHEP})\text{Na}_4(\{\text{PMnW}_{11}\text{O}_{39}\}\{\text{PO}_{4}\})\cdot 18\text{H}_2\text{O}\) and is composed of two \(\{\text{PMnW}_{11}\text{O}_{39}\]\^{11—} 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 \(\text{H}_2\text{BHEP}\) 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 \([\text{W}_3\text{O}_{12}\text{Mn}]\) 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 \(H = -J\text{S}_1\text{S}_2\) can be fitted to the susceptibility data to yield \(\Delta J/k_B = -0.72\) 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

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

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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 decomposition process involving the loss of an additional 8.1 wt% compared to in the absence 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)5Na4[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-PW11O39\}6- units with four manganese centres sandwiched between these in the well-known belt-like fashion.\textsuperscript{14} Many examples of this cluster type can be found in the literature,\textsuperscript{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.

Due to the similar reaction conditions the self-assembly of 1 and 2 was also investigated using \textsuperscript{31}P NMR (Fig. 4, see ESI for details\textsuperscript{14}), 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\}\textsuperscript{4+} building block that could be imagined to form readily in solution on addition of Mn\textsuperscript{2+} into the phosphate rich reaction mixture. Formation and insertion of such species have previously yielded tungstosilicate clusters with pendant phosphate groups.\textsuperscript{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), \textsuperscript{31}P 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 \{PW\textsubscript{11}\} (−10.73) and \{PW\textsubscript{11}\} (−11.2). On addition of the Mn(NO\textsubscript{3})\textsubscript{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 \{PW\textsubscript{11}O\textsubscript{39}\}\textsuperscript{7-} and
Further work will which gives rise to compound Mn2+ ions, or rapid exchange of the phosphate ligand. The first interaction between the phosphorous centre and the paramagnetic a similar unit); the broad nature of the peak is indicative of functional cations to both buffer and structure direct the formation between the solid state architecture and self-assembly processes archetypes thus beginning to bridge the gap in understanding approach towards understanding and designing new cluster spectroscopic ionisation) which showed a {(PO4)[Mn1W2]2}+ the reaction mixture at pH 6.05 using CSI (cryospray mass spectrum of the reaction mixture at pH 6.05 shown top (Mo-Ka) = 1.229 cm⁻¹. Final RI = 1.0527 and wR2 = 0.1989 (all data) CCDC 619691.

1. H2BHEP)5(HBHEP)Na4[(P2Mn4W18O68)2{PO4}]·18H2O: 1.65 g (5 mmol) Na2WO4·2H2O 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, resulting 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 (H2BHEP)Na4[(P2Mn4W18O68)2{PO4}]·15H2O: 1.65 g (5 mmol) Na2WO4·2H2O 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 Mn(NO3)2 in 1 ml H2O 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 6.05) in a yield: 0.62 g (39%). See ESI for analytical data for 1 and 2.

17. This hypothesis will be investigated and reported later.