The trinity of polyoxometalates: connecting {M$_{12}$} Keggin and {M$_{18}$} Dawson clusters to triangles†

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Two topologically equivalent triangular POM aggregates based upon the Keggin (1) and Dawson (2) cluster species, with distinctive double {W–O–M} intra-molecular linkages involving Mn^{III} and Co^{III} ions are presented; both these compounds demonstrate electrocatalytic activity.
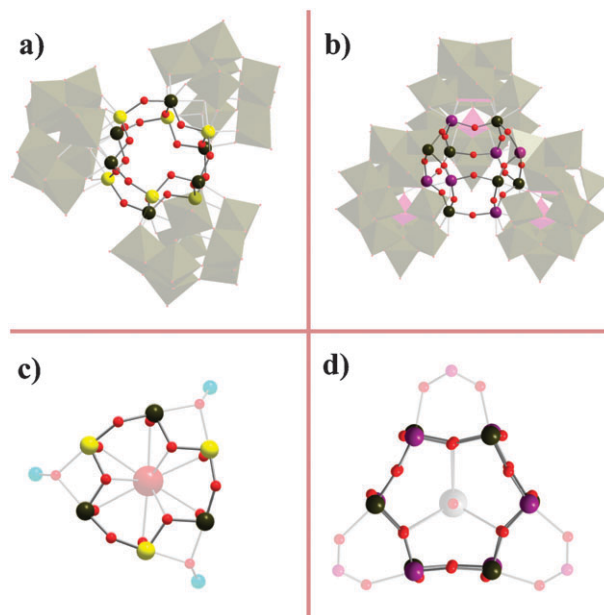
The quest to develop architectural control in the assembly of polyoxometalates (POMs), metal–oxygen clusters of early transition metals,[1,2] has come far during the last decade but the ability to reliably link smaller units together into 'designed' architectures is limited.[2] Despite this it has long been known that mono-, di- and tri-vacant (lacunary) species of the Keggin ($[XM_{12}O_{40}]^{n-}$) and up to hexa-vacant derivatives of the Dawson ($[X_2M_{18}O_{62}]^{n-}$, where X = Si^{IV}, Ge^{IV} etc. and P^{V}, S^{VI} etc., respectively; M = W^{VI,V} Mo^{VI,V} etc.) clusters can act as nucleophilic ligands for transition-metal (TM) or rare-earth cations.[3–7] Furthermore, several recent developments describe improvements that are being made in the condensation of transition metal-substituted polyoxometalate (TMSP)-based building blocks.[8] Clusters such as these may serve as Keggin[9–11] and Wells–Dawson-based[12–14] secondary building units[15] for the synthesis of more complex architectures. In contribution to this body of work, we have recently demonstrated that infinite network arrays of three- and four-{W–O–M}-connected Keggin polyoxoanions are in fact possible.[5]

The principle restriction in the assembly of composite supramolecular POM compounds is the fact that it has been difficult to systematically create a range of well-defined rigid building blocks that can be reliably used in the assembly of larger aggregates (*e.g.* triangles, squares, cubes *etc.*). This means the ability to 'design' predefined topologies can be limited.[16,17] Therefore, the identification of a library of building units with well defined topologies is an important step to gain access to a library of POM building blocks that could be assembled into more complex architectures. For instance a library of POM building blocks could be developed and exploited in similar ways to the metal–ligand systems that have been used for molecular panelling[18a] or open

frameworks.[18b] This is one very promising approach to create POM architectures using geometrically-defined principles.

Herein we present two new POM cluster architectures that start to form one such building block library whereby both share an analogous triangular topology, but are each based upon different building block units: a Keggin-based trimeric cluster aggregate $[Rb \subset (GeW_{10}Mn_2O_{38})_3]^{17-}$ (**1a**) and a Wells–Dawson-based trimeric aggregate $[K \subset (P_2W_{16}Co_2O_{60})_3]^{23-}$ (**2a**). Although these architectures are constructed from two different archetypal POMs, they possess closely-related multiple intra-molecular linkages and structurally-identical topologies relating to the core which connects the three cluster 'arms' in compounds **1** and **2**, see Fig. 1.

Although **1** and **2** have identical topologies, these compounds were synthesized *via* different experimental methods. Reaction of divacant lacunary decatungstogermanate, $[\gamma\text{-}GeW_{10}O_{36}]^{8-}$ with Mn(OAc)$_2$·4H$_2$O and KMnO$_4$ in aqueous medium at ambient temperature and pH *ca.* 4.5 afforded the trimeric Keggin Rb$_{11}$K$_6$[Rb$\subset$(GeW$_{10}$Mn$_2$O$_{38}$)$_3$] cluster (**1**). Correspondingly, the reaction of Dawson

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† Electronic supplementary information (ESI) available: Full experimental and analytical data. CCDC 720569 and 720570. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b903206a
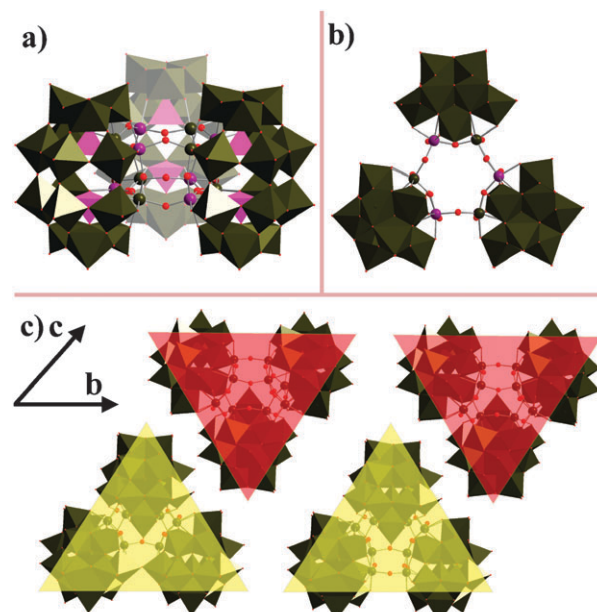‡ These authors contributed equally to this publication.

Fig. 1 Template core units of **1** and **2**. (a) [Rb$\subset$(GeW$_{10}$Mn$_2$O$_{38}$)$_3$]$^{17-}$ (**1a**), (b) [K$\subset$(P$_2$W$_{16}$Co$_2$O$_{60}$)$_3$]$^{21-}$ (**2a**). (c) Isolated core unit of **1**: maroon sphere: Rb (d) isolated core unit of **2**: gray sphere: K. All cations and solvent water molecules are omitted for clarity. Olive polyhedra: WO$_6$; red spheres: oxygen; yellow spheres: Mn; blue spheres: Ge; purple spheres: Co; pink spheres: P.
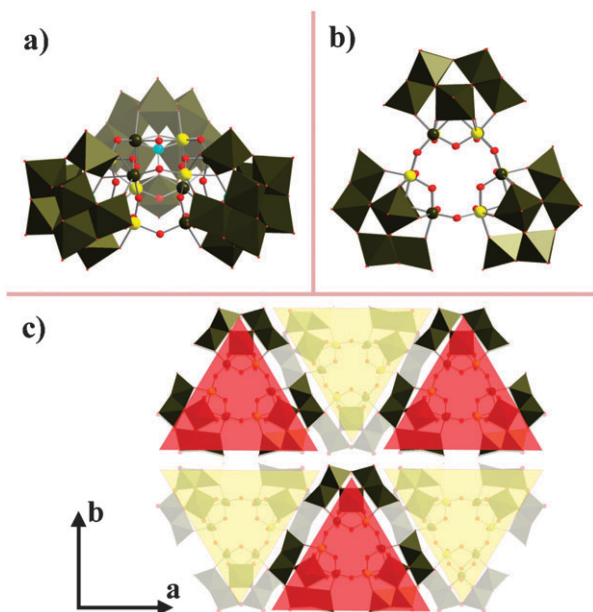
Fig. 2 (a) Side view and (b) top view of the trimeric Mn^{III}-linked Keggin cluster $[(GeW_{10}Mn_2O_{38})_3]^{18-}$ (**1a**). (c) Representation of the packing arrangement of **1a** viewed along the crystallographic c axis. Olive polyhedra: WO$_6$; red spheres: oxygen; yellow spheres: Mn; blue spheres: Ge. All cations and solvent water molecules have been omitted for clarity.

Fig. 3 (a) Side view and (b) top view of the trimeric Co^{III}-linked Dawson cluster $[(P_2W_{16}Co_2O_{60})_3]^{24-}$ (**2a**). (c) Representation of the packing arrangement of **2a** viewed along the crystallographic a axis. Olive polyhedra: WO$_6$; red spheres: oxygen; purple spheres: Co; pink spheres: P. All cations and solvent water molecules have been omitted for clarity.

polyoxoanion $[\alpha\text{-}P_2W_{18}O_{62}]^{6-}$ with CoCl$_2\cdot$6H$_2$O, in the presence of tris(hydroxymethyl) aminomethane and subsequent recrystallization from 1 M NaCl solution, led to the isolation of the trimeric Dawson Na$_{21}$K$_2$[K$\subset$(P$_2$W$_{16}$Co$_2$O$_{60}$)$_3$] cluster (**2**). Both compounds have been characterized by single crystal X-ray diffraction,§ FAAS, TG analysis, IR spectroscopy and CV (ESI†).

The molecular structure of **1**, represented in Fig. 2, consists of three Mn^{III} di-substituted Keggin units linked together through {Mn–O–W}$_2$ connectivities. Alternatively, **1** can also be considered as an assembly of three fused {Ge$_1$Mn$_2$W$_{10}$O$_{38}$} monomers which encapsulates a Rb$^+$ cation inside the cavity (*ca.* 6.72 Å). An important feature is that two Mn^{III} cations reside in the two vacant sites of lacunary {GeW$_{12}$} moieties and both exhibit a distorted octahedral geometry with five O atoms derived from the polyoxoanions and one from the μ_2-oxo ligand. It is interesting to note that two Mn^{III} are connected with two W centers derived from the adjacent {Ge$_1$Mn$_2$W$_{10}$} subunit *via* the μ_2-oxo groups, forming the {Mn–O–W}$_2$ bridges. Thus, three {Ge$_1$Mn$_2$W$_{10}$} building blocks are fused together by six {Mn–O–W} bridges to the trimeric Keggin-type polyoxoanion **1**.

In **1**, the Mn–O–W angles between the adjacent Keggin units are in the range of 134–136°, with the M–O–Mn linkages, over which the tungsten and manganese atoms are statistically disordered, showing an average M–O bond length of *ca.* 1.91 Å. All the tungsten atoms have a disordered octahedral geometry and the bond valence sum (BVS) analysis[19] clearly indicates that all the tungsten atoms are in the +6 oxidation state. Eight of the tungsten centers in each Keggin unit incorporate one terminal oxo group which is located at an average bond distance of *ca.* 1.72 Å (W=O$_t$) and is in accord

with the literature,[19] while all of the bridging oxo atoms have an average bond distance of *ca.* 1.9 Å. Interestingly, the average Mn$\cdots$W separation of *ca.* 3.52 Å *via* {Mn–O–W}$_2$ bridges is similar to that of the Mn$\cdots$W separation in the {W$_{72}$Mn$^{III}_{12}$} framework reported earlier.[5] It must be mentioned that two single W–O–M bridged triangular polyanionic forms, $[Zr_6(O)_2(OH)_6(\gamma\text{-}SiW_{10}O_{36})_3]^{18-}$ and $[(SiW_{11}MnO_{39})_3]^{18-}$, have been reported in the literature.[20] Accordingly, these compounds contain a total of three W–O–M bonds as opposed to six observed in the compounds reported here.

Similarly, the molecular structure of **2**, represented by Fig. 3, consists of three Co^{III} di-substituted Wells–Dawson units linked together in an identical fashion to that of **1** through {Co–O–W}$_2$ connectivities. In a similar analogy, **2** can thus be considered an assembly of three fused {P$_2$Co$_2$W$_{16}$O$_{60}$} monomers templated by a K$^+$ cation encapsulated within the anionic cavity (*ca.* 7.12 Å). **2** can therefore be described as a cyclic trimer of a di-Co-substituted Dawson-type polyoxoanion, representing the first triple-Dawson-type structure in POM chemistry. This divacant species can be formed *via* removal of two adjacent {WO$_6$} octahedra from the "belt" region of its parent Dawson, {P$_2$W$_{18}$}. The Co–O–W angles between the adjacent Dawson units in **2** are in the range of 142–150°. W–O–Co linkages over which tungsten and cobalt atoms are statistically disordered show an average M–O bond length of *ca.* 1.91 Å. The tungsten centers in each Dawson unit are in the +6 oxidation state (BVS analysis[19]) and each unit incorporates one terminal oxo group—located at an average bond distance of *ca.* 1.74 Å (W=O$_t$), similar to that of **1**. Meanwhile bridging oxo atoms have an average bond distance of *ca.* 1.9 Å.