

Formation, self-assembly and transformation of a transient selenotungstate building block into clusters, chains and macrocycles†

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The one-pot syntheses of a series of dimeric and trimeric selenotungstates based on the $[\text{Se}_2\text{W}_{12}\text{O}_{46}]^{12-}$ unit are presented alongside the structure of the tetrameric $[\text{Se}_8\text{W}_{48}\text{O}_{176}]^{32-}$ wheel. Mass spectrometry has probed the stability of these clusters whilst their electronic structure has been contrasted to their known phosphotungstate analogues.

Polyoxometalates (POMs) are a class of polynuclear anionic metal-oxo clusters, formed *via* the condensation of oxometalate units and heteroatom ‘templates’ into a range of nanoscale structures.¹ Recently POM chemistry has developed rapidly thanks, in large part, to the identification of lacunary POM species in which vacancies in the oxometalate framework may be occupied by additional heterometals in order to generate a plethora of new species.² These lacunary ‘secondary building units’ (SBUs) vary in their structure and stability, ranging from the ubiquitous tri-lacunary $\{\text{XW}_9\}$ and $\{\text{X}_2\text{W}_{15}\}$ fragments of the Keggin and Wells-Dawson ions respectively,³ to more chemically complex, metastable lacuna such as the family of silicotungstate species $\{\text{SiW}_{12-x}\}$ ($x = 1-4$) for instance.⁴ One species which has received considerable attention is the hexalacunary $[\text{H}_2\text{P}_2\text{W}_{12}\text{O}_{48}]^{12-}$ fragment⁵ which can form a series of macrocycles based on the same building block, ranging from the $[\text{P}_5\text{W}_{30}\text{O}_{110}]^{15-}$ Preyssler ion,⁶ through the trimeric $[\text{P}_6\text{W}_{39}\text{O}_{147}(\text{H}_2\text{O})_3]^{30-}$ species⁷ up to the extremely well studied tetrameric $[\text{P}_8\text{W}_{48}\text{O}_{184}]^{40-}$ macrocycle.⁸

The key to formation of these lacunary SBUs is the heteroatom template species, which plays a key role in the structure of the final polyanion, whilst additional functionality may also be imparted to the POM *via* the specific properties (*i.e.* electronic structure) of

the heteroatom.⁹ In particular, the Se^{IV} and Te^{IV} ions have been employed to great effect recently as a means of generating a diverse range of lacunary building blocks in solution,¹⁰ leading to the identification of a series high-nuclearity POM architectures.¹¹ In fact, there remains an extremely limited pool of isolated Se^{IV} or Te^{IV} templated lacuna and so the onus remains on synthetic POM chemists to identify new pathways towards their formation and, in particular, identify means by which the *in situ* assembly of these ‘building blocks’ can be controlled and subsequently exploited.

Herein, we present the synthesis of five new selenotungstate species based on the formation and subsequent assembly of the previously unreported $[\text{Se}_2\text{W}_{12}\text{O}_{46}]^{12-}$ building block. This species is directly comparable to the metastable $[\text{H}_2\text{P}_2\text{W}_{12}\text{O}_{48}]^{12-}$ cluster and might also be viewed as an isomerically related lacunary fragment of the previously reported sulphite containing ‘trojan horse’ archetype (Fig. S1†).¹²

Notably, unlike the $\{\text{P}_2\text{W}_{12}\}$ analogue, it has not thus far been possible to isolate this species directly. By exploiting a facile one-pot strategy however, we have successfully isolated the $\{\text{Se}_2\text{W}_{12}\}$ unit within both the Mn-bridged dimeric assemblies; $[\text{Mn}_4\text{Se}_6\text{W}_{24}\text{O}_{94}\text{Cl}(\text{H}_2\text{O})_6]^{13-}$ (**1a**), $[(\text{Mn}_3\text{Se}_6\text{W}_{24}\text{O}_{94}\text{Cl}(\text{H}_2\text{O})_2)]^{15-}$ (**2a**) and the trimeric macrocyclic species $[\text{Se}_6\text{W}_{39}\text{O}_{141}(\text{H}_2\text{O})_3]^{24-}$ (**3a**) and $[\text{PdSe}_6\text{W}_{39}\text{O}_{141}(\text{H}_2\text{O})_5]^{22-}$ (**4a**). Furthermore, we also demonstrate how **3** has been employed as a precursor to the nanoscale macrocyclic tetramer $[\text{Se}_8\text{W}_{48}\text{O}_{176}]^{32-}$ (**5a**).

Compound **1** was synthesised from an acidified mixture of Na_2WO_4 , Na_2SeO_3 and *N*-methyldiethanolamine to which $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ was subsequently added (see ESI†). Crystallographic analysis reveals that **1** assembles such that two $\{\text{Se}_2\text{W}_{12}\}$ anions are directly bridged by two Mn^{II} centres occupying the empty ‘belt’ positions on both lacuna (Fig. 1a). These are in turn linked by a Cl^- ion which lies on the inversion centre of the anion unit. In addition, a third Mn^{II} ion occupies one of the vacant ‘cap’ positions on each $\{\text{Se}_2\text{W}_{12}\}$ unit and forms a secondary Mn–O–Se bridge with a pendant Se^{IV} ion which resides on the remaining lacunary ‘cap’ position on the opposing POM unit. Interestingly, modifying the reaction conditions slightly enabled the isolation of a second product, **2**. In this cluster, the basic dimeric structure of **1** has been retained (with the unique Cl1

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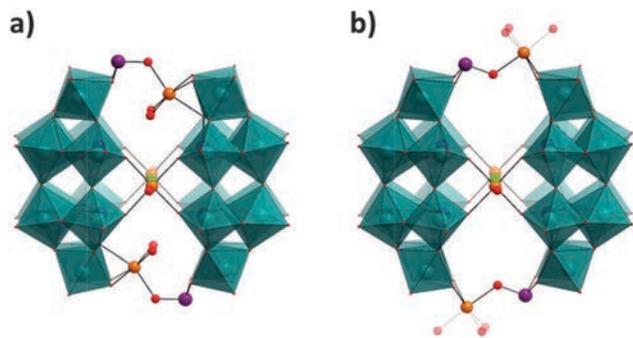


Fig. 1 Combined polyhedral/ball and stick representation of; (a) compound **1**, $[\text{Mn}_4\text{Se}_6\text{W}_{24}\text{O}_{94}\text{Cl}(\text{H}_2\text{O})_6]^{13-}$ and; (b) the repeating unit in the 1D-chain structure of **2**, $([\text{Mn}_3\text{Se}_6\text{W}_{24}\text{O}_{94}\text{Cl}(\text{H}_2\text{O})_2]^{15-})_n$. (Colour code: $\{\text{Se}_2\text{W}_{12}\}$ units = teal polyhedra, Se = purple, Cl = green, Mn = orange, O = red. Cations and water molecules have been omitted for clarity).

atom occupying an inversion centre and the Mn2 position on a twofold axis) though, crucially, the Mn^{II} ions which completed the capping $\{\text{M}_3\}$ triad have rearranged and now coordinate to the POM in a pendant position, whereby they are now forced towards the outside of the core dimeric unit (Fig. 1b). In this way, the cluster is now able to react further with adjacent $\{\text{Mn}_3\text{Se}_6\text{W}_{24}\}$ units *via* these exposed axial Mn^{II} centres which subsequently form both an 'edge-sharing' link to a capping W^{VI} centre on a neighbouring cluster through two shared μ_2 -oxo-bonds and a further Mn–O–Se bridge with a pendant Se^{IV} ion in order to yield an extended 1D-chain structure (Fig. S2†).

When similar synthetic conditions are employed in the absence of a suitable heterometal species, a remarkable new cyclic structure may be obtained (**3**). This $\{\text{Se}_6\text{W}_{39}\}$ wheel is comprised of three $\{\text{Se}_2\text{W}_{12}\}$ units which are linked into a trimeric assembly *via* the addition of three bridging $[\text{WO}(\text{H}_2\text{O})]^{4+}$ groups (Fig. 2a). These unusual linkers presumably perform a charge-balancing role, serving to help stabilise the high negative charge of the $\{\text{Se}_2\text{W}_{12}\}$ lacuna. It is noteworthy that **3** shares the same basic structure as the previously identified $\{\text{P}_6\text{W}_{39}\}$ anion⁷ and furthermore that, despite the presumed relative stability of the $\{\text{P}_2\text{W}_{12}\}$ and $\{\text{Se}_2\text{W}_{12}\}$ building blocks (*i.e.* $\text{P} > \text{Se}$), it has been possible to isolate the 'naked' $\{\text{Se}_6\text{W}_{39}\}$ ring but not the equivalent $\{\text{P}_6\text{W}_{39}\}$ species.

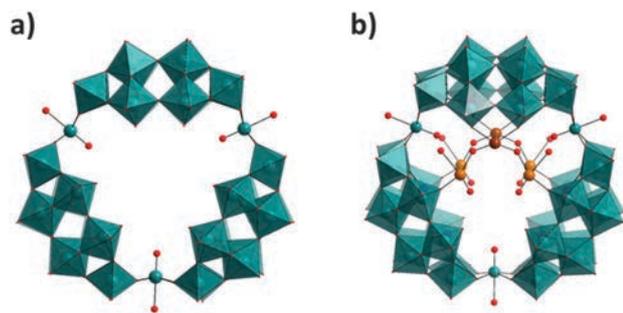


Fig. 2 Combined polyhedral/ball and stick representations showing: (a) the trimeric structure of **3**, $[\text{Se}_6\text{W}_{39}\text{O}_{141}(\text{H}_2\text{O})_3]^{24-}$ and; (b) the structure of **4**, $[\text{PdSe}_6\text{W}_{39}\text{O}_{141}(\text{H}_2\text{O})_5]^{22-}$, showing the disordered positions of the incorporated Pd^{2+} . (Colour code: $\{\text{Se}_2\text{W}_{12}\}$ units = teal polyhedra, Pd (20% occupancy) = brown, Pd (18% occupancy) = tan, O = red. Cations and water molecules have been omitted for clarity).

One obvious advantage of the cyclic, superlacunary structure of **3** is the possibility for further functionalisation *via* introduction of additional heterometals. By retaining the one-pot conditions employed in the synthesis of **3**, subsequent addition of Pd^{2+} ions to the solution allowed us to isolate a Pd-substituted derivative of the $\{\text{Se}_6\text{W}_{39}\}$ wheel (**4**) (Fig. 2b). **4** crystallises in an orthorhombic system with the space group $Cmcm$ in which a single Pd^{2+} ion is disordered over six positions within the cavity of the macrocycle. The charge-balancing Na^+ ions present on the exterior of the POM shell (as observed in **3**) have been displaced by $[\text{Pd}(\text{H}_2\text{O})_4]^{2+}$ whilst the remaining anionic charge is accounted for by $(\text{NH}_4)^+$ cations. This result is particularly encouraging in that it suggests that new architectures based on the cyclic $\{\text{Se}_6\text{W}_{39}\}$ species may be successfully accessed and further work will explore how both bottom-up and top-down approaches to functionalising the wheel might be exploited. Electrospray ionisation mass spectrometry (ESI-MS) was used to attempt to both characterise and probe the solution stability of **1–4**.

Unfortunately, initial attempts to obtain a useful spectrum of **4** were unsuccessful owing to poor ionisation of the analyte, however the spectra of **1–3** were highly revealing: specifically in that no peaks could be identified in any of the measurements which matched the intact cluster. Furthermore, the highest mass fragments (*ca.* 3100–3300 Da) identified in all three cases were found to be very similar and could be identified as corresponding to the $\{\text{Se}_2\text{W}_{12}\}$ building block (see ESI† for more detail). This initial result suggests that compounds **1–3**, whilst stable in the solid state, may be susceptible to decomposition in solution – at least without suitable buffering or the presence of additional electrolyte maintaining a higher ionic strength.

In addition to the one-pot strategy used to isolate **1–4**, we have also been able to identify the Se^{IV} analogue of the well-known $\{\text{P}_8\text{W}_{48}\}$ wheel, $[\text{Se}_8\text{W}_{48}\text{O}_{176}]^{32-}$ (**5**), which was isolated *via* recrystallization of **3** from a Li^+ rich, high ionic strength media. This result agrees with the aforementioned poor solution stability of **3** and, as we employed conditions very close to those used to synthesise the $\{\text{P}_8\text{W}_{48}\}$ wheel, it is conceivable that **3** is acting as a source of the $\{\text{Se}_2\text{W}_{12}\}$ precursor unit. Indeed, **5** which crystallises in a monoclinic system with the space group $C2/m$, closely parallels the structure of the $\{\text{P}_8\text{W}_{48}\}$ wheel, in which four $\{\text{Se}_2\text{W}_{12}\}$ units oligomerise *via* two corner-sharing μ_2 -oxo bonds at the cap positions of each sub-unit (Fig. 3). It is also noticeable that the 'hinge' positions in **5** are fully occupied by one Li^+ cation rather than a K^+ ion disordered over two positions, as in the case of $\{\text{P}_8\text{W}_{48}\}$. Unfortunately, it has been especially challenging to reproduce this result in high yield and with acceptable purity, and so we are currently unable to provide an in-depth analysis of **5**. Given the remarkable stability of the $\{\text{P}_8\text{W}_{48}\}$ anion, especially in comparison to the $\{\text{P}_6\text{W}_{39}\}$ trimer, this observation is somewhat counterintuitive and future work will seek to present a detailed analysis of **5** and obtain a deeper understanding of the means by which it can be assembled.

Initial results on the electronic structure of the three main POM units have been obtained,¹³ considering the highest symmetry for each cluster as C_{2v} for $[\text{Se}_2\text{W}_{12}\text{O}_{46}]^{12-}$, D_{3h} for **3** and D_{4h} for **5** (Fig. 4). The frontier orbitals of these anions are symmetry adapted combinations of 2p (O) and 5d (W) orbitals respectively (as is expected for d^0 POMs)¹⁴ where the HOMO is delocalized around the oxygen and the LUMO around the W^{VI} centres. We have also compared the electronic structure of the analogous phosphate-templated species (see ESI† for

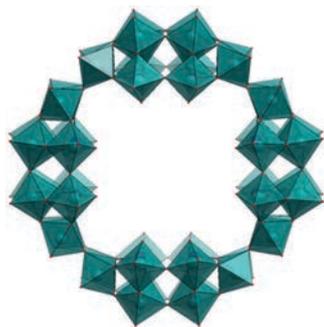


Fig. 3 Polyhedral structure of the tetrameric $[\text{Se}_8\text{W}_{48}\text{O}_{176}]^{32-}$ wheel. (Colour code: $\{\text{Se}_2\text{W}_{12}\}$ units = teal polyhedra. Cations and water molecules have been omitted for clarity).

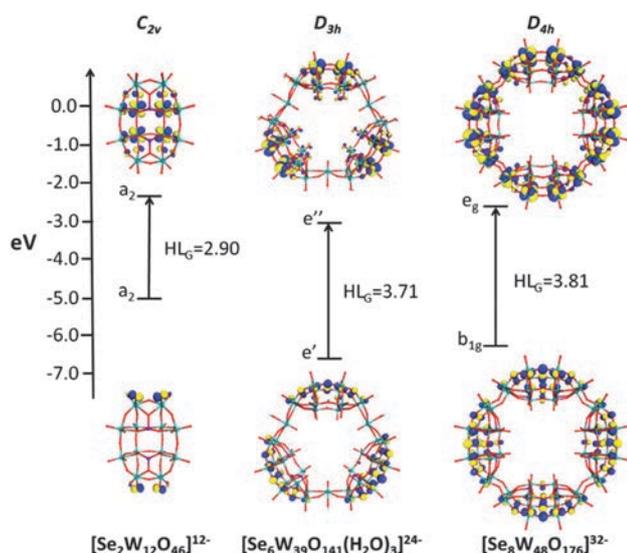


Fig. 4 Comparison of the frontier molecular orbitals of the $\{\text{Se}_2\text{W}_{12}\}$ building block, **3** and **5** showing the positions and energies of the HOMO and LUMO states and the corresponding HOMO–LUMO gap (in eV).

more details). In both cases, the HOMO–LUMO gaps increase on moving from the less stable $\{\text{X}_2\text{W}_{12}\}$ unit through to the $\{\text{X}_8\text{W}_{48}\}$ wheel, though it is interesting to note that the distribution of the delocalized frontier orbitals changes considerably between the Se- and P-based clusters. Also, the energies of the frontier orbitals between the $\{\text{P}_8\text{W}_{48}\}$ and $\{\text{Se}_8\text{W}_{48}\}$ clusters are similar, suggesting that the Se-templated species should be stable, encouraging us and to work for an improved synthesis of **5**.

In summary, we have demonstrated the flexibility of the newly identified $\{\text{Se}_2\text{W}_{12}\}$ unit, with the one-pot syntheses of a series of dimeric and trimeric structures. Further, we have shown the existence of a Se-analogue of the well-known $\{\text{X}_8\text{W}_{48}\}$ POM archetype and future work will elaborate on the synthesis and properties of this species, focusing on the reproducible synthesis of $\{\text{Se}_8\text{W}_{48}\}$ so that we, and others, may explore the host–guest chemistry and anticipated novel REDOX properties.

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