

Self-Assembly of a Nanosized, Saddle-Shaped, Solution-Stable Polyoxometalate Anion Built from Pentagonal Building Blocks: $[H_{34}W_{119}Se_8Fe_2O_{420}]^{54-}$

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Abstract: Precise control of the “one-pot” reaction conditions is employed for the assembly of a nanosized 2.8 nm cluster, $[H_{34}W_{119}Se_8Fe_2O_{420}]^{54-}$ (**1a**), which is templated using eight selenite units and two iron(III) centers. Not only is this cluster characterized structurally using X-ray crystallography, it is the largest polyoxotungstate to be observed intact in solution using ESI-MS, with a molecular mass of ca. 30 000 Da.

Heteropolyoxometalates (HPOMs) have been the subject of a large number of studies due to their nanoscale size and tunable electronic and physical properties, which hold great promise for a variety of applications (catalysis, medicine, and materials science) as well as fundamental studies of self-assembly.¹ These nanosized clusters can be derived from metal oxide cages of the general composition $(MO_n)_x$ that incorporate anion templates, e.g., BO_3^{3-} , PO_4^{3-} , or IO_6^{5-} , resulting in the discovery of a series of new clusters.² However, the mechanism of HPOM formation is still not fully understood, although the key to unlocking this appears to lie in understanding the assembly and linkage of the building blocks.³ For instance, it is widely acknowledged that pentagonal building blocks formed around the pentagonal bipyramidal core $\{MO_7\}$ unit ($M = W, Mo, \text{ or } Nb$) are key in constructing high-nuclearity clusters and a series of iconic $\{MoO_7\}$ -based giant polyanions, e.g., the $\{Mo_{154}\}$ ring and $\{Mo_{132}\}$ ball.⁴ However, until very recently, the use of pentagonal units had been limited to Mo-based clusters, with only a few examples with $\{WO_7\}$ offering the possibility that extremely large clusters similar to those possible with molybdates could also be possible with tungstates.⁵

Herein, we present a nanosized 2.8 nm, solution-stable cluster anion, $[H_{34}W_{119}Se_8Fe_2O_{420}]^{54-}$ (**1a**), in the form $K_{44}Na_{10}[H_{34}W_{119}Se_8Fe_2O_{420}] \cdot 220H_2O$ (**1**), which incorporates pentagonal $\{WO_7\}$ building units and is synthesized in one-pot reaction conditions. A mixture of $Na_2WO_4 \cdot 2H_2O$ (4.5 g, 13.6 mmol), Na_2SeO_3 (0.40 g, 2.3 mmol), and KCl (0.5 g, 6.7 mmol) in 60 mL of water at low pH (1.7) was stirred for 0.5 h in the presence of a small amount of $Fe(NO_3)_3 \cdot 9H_2O$ (0.25 g, 0.62 mmol) under ambient conditions. Evaporation of the solution afforded pale yellow crystals of compound **1** in 4 weeks in ca. 4% yield (based on tungsten), and the compound was characterized by chemical analysis and single-crystal X-ray crystallography.

Analysis of **1a** shows that the cluster contains 121 metal centers, of which 119 are W atoms and 2 are Fe ions. Bond valence sum calculations indicate that the oxidation states of all W, Se, and Fe centers are 6+, 4+, and 3+, respectively. Structural analysis reveals that **1a** is a unique “saddle-shaped” cluster that contains more than 120 metal centers, with a molecular weight over 29 000 (for the anion), as shown in Figure 1. Empirically, our synthetic studies indicate that the correct concentration of selenite and potassium is essential for the formation of building blocks with pentagonal $\{WO_7\}$ units, and the two Fe(III) ions “seed” a linkage that develops

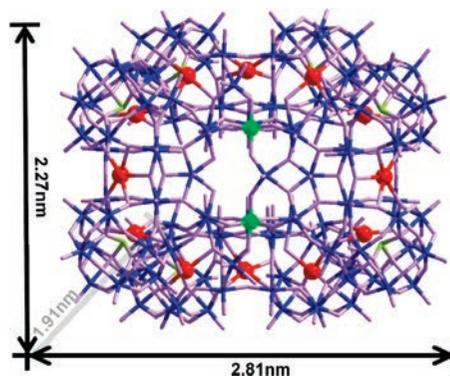


Figure 1. Structure of $[H_{34}W_{119}Se_8Fe_2O_{420}]^{54-}$ (**1a**), with K^+ cations in the cavity (red spheres). The main framework is presented by colored sticks, and the central Fe core is highlighted in green (O, rose; Se, lime; W, blue). The cluster measures 2.8 nm at its widest point.

the overall extremely large cluster structure. The anion consists of four crescent-shaped branches and a $\{W_3Fe_2\}$ core at the center. The “crescent” unit is constructed by two $\{W_9Se\}$ and a pentagonal tungstate-based $\{W(W_4)\}$ body that are linked by six corner-shared octahedral $\{WO_6\}$ linkers separately. The whole branch can be described as an aggregate of 29 tungstate centers enclosing two selenites inside, forming a $\{W_{29}Se_2\}$ secondary building unit, which we have previously presented as a key new building block.^{5d} While these four $\{W_{29}Se_2\}$ units assemble together, two iron(III) atoms and three extra tungsten ions fill the gap between them and form the $\{W_3Fe_2\}$ core, which finally results in the target cluster $[H_{34}W_{119}Se_8Fe_2O_{420}]^{54-}$, as shown in Figure 2.

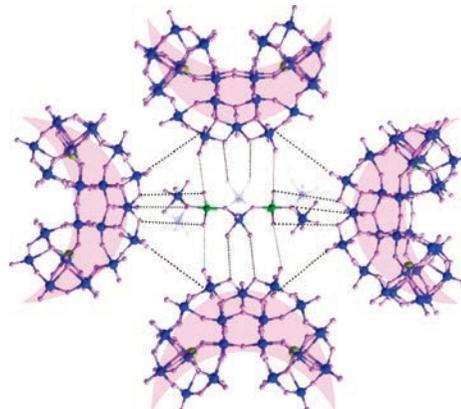


Figure 2. 2D representation of connectivity of the cluster showing the building units in **1a**. The cluster is shown in ball-and-stick mode. The $\{W_{29}Se_2\}$ branches are shown under crescent-shaped shadow (Fe, green; O, rose; Se, lime; W, blue). The links between building blocks are shown as dashed lines and are exaggerated longer to avoid overlapping of the four “crescent” subclusters. The cations are omitted for clarity.

Compound **1** represents the largest polyoxotungstate framework so far containing pentagonal units. The pentagonal $\{WO_7\}$ units here show some unique structural features compared with the previously reported $\{MO_7\}$ ($M = Mo, W, \text{ or } Nb$) in $[Mo_{186}O_{554}(OH)_{10} \cdot (H_2O)_{77}]^{22-}$, $[HNb_{27}O_{76}]^{16-}$, or $[W_{72}Mo_{60}O_{372}(CH_3COO)_{36}(H_2O)_{60}]^{48-6.5a}$. For instance, the four branches are linked together via the $\{W(W_4)\}$ units containing the central pentagonal W center. Although the $W-O$ bond lengths and $O-W-O$ angles within the pentagonal $\{WO_7\}$ moieties are similar to the aforementioned $\{MO_7\}$ units, all previously known pentagonal $\{MO_7\}$ “templates” are complete $\{M(M_5)\}$ pentagonal units.^{5b} In contrast, the $\{WO_7\}$ units found here in **1a** instead adopt a unique $\{W(W_4)\}$ “lacunary” form, where one corner of the pentagonally expanded units is missing (see Figure 3). Thus, we can tentatively suggest that $\{W(W_4)\}$ species can be viewed as a symmetry-breaking unit, giving rise to a saddle-shaped cluster with C_{2v} symmetry which contains both positive and negative curvature, whereas the high-symmetry pentagonal systems can give rise to wheel-shaped and spherical clusters.^{4,8} As such, it is remarkable that all the possible pentagonal building blocks, $\{W(W_5)\}$, the “lacunary” $\{W(W_4)\}$ and $\{W(W_4M)\}$, and a $\{W(W_4)\}$ completed by other transition metals, appear in compound **1**. In detail, two $\{W(W_4)\}$ units are located adjacently at the center of the cluster; the two vacant fifth sites of these two $\{W(W_4)\}$ moieties are only 2.06 Å apart and share the occupancy of a single, disordered W atom. Thus, these two $\{W(W_4)\}$ units can be described as a $\{W(W_4)\}-\{W(W_5)\}$ dimer. The other two $\{W(W_4)\}$ parts are completed by $\{FeO_6\}$ pieces to form $\{W(W_4Fe)\}$ pentagonal-type units, which are located on either side of the aforementioned $\{W(W_4)\}-\{W(W_5)\}$ “dimer” fragment (see Figure 3). All these units make up the cluster core or base of the “saddle”, which is linked further to $\{SeW_6\}$ units, and this “saddle-type” structure defines a bigger surface area compared with that of the closed clusters, cf. $\{Mo_{132}\}$. Also, the Fe-containing $\{W(W_4Fe)\}$ is unique and is able to decrease the net positive charge, cf. site occupancy by Fe^{III} vs W^{VI} , which may help stabilize the secondary building unit and thereby “seed” the formation of the nanosized $\{W_{119}\}$ cluster with the Fe-substituted pentagonal unit.

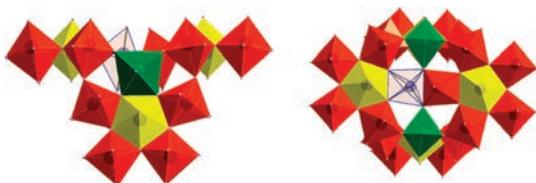


Figure 3. Polyhedral representation of the cluster core in $[H_{34}W_{119}Se_8Fe_2O_{420}]^{54-}$ (**1a**): side view (left) and top view (right). The $\{WO_6\}$ are shown in orange, the $\{FeO_6\}$ in green, and the $\{WO_7\}$ in yellow. The disordered $\{WO_6\}$ is shown as semitransparent polyhedra.

Moreover, ESI-MS was utilized to explore the solution behavior of the compound, and to our surprise we found that cluster **1a** can be observed directly (both as the monomer **1a** and as the dimer $(\mathbf{1a})_2$). This is the heaviest polyoxometalate cluster complex (>30 kDa for the monomer and >60 kDa for the dimer) to be observed directly by electrospray mass spectrometry and is observed as an ensemble of related clusters with differing numbers of cations, as follows with the monomer and dimers of **1a**. For instance, the monomer can be assigned as $\{K_{8+x}Na_{9+y}H_{29+z}[H_{34}W_{119}Se_8Fe_2O_{420}(H_2O)_{34+n}]\}^{(8-x-y-z)-}$ and the dimer as $\{K_{16+x}Na_{19+y}H_{57+z}[(H_{34}W_{119}Se_8Fe_2O_{420})_2(H_2O)_{74+n}]\}^{(16-x-y-z)-}$ (see Figure 4). The direct assignment of **1a** was made possible by its extraordinary high charge, with assignments made via charge deconvolution. This also fits the crystallographic analysis, given the fact that there are at least 12 K^+ cations bound within the cavity of cluster (see Figure S3.2 and Table S3.1 in the Supporting Information).⁷

In conclusion, this work demonstrates that it is possible to assemble $\{WO_7\}$ -based giant heteropolyoxotungstate clusters such

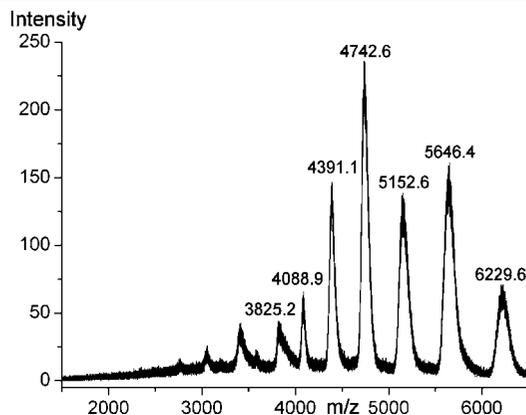


Figure 4. Negative-mode ESI of compound **1** in mixed $H_2O/MeCN$ solvent (5:95). All the peaks shown relate to different charge states of the same basic parent cluster, $[H_{34}W_{119}Se_8Fe_2O_{420}]^{54-}$, which is observed as a monomer or dimer in the gas phase (see Supporting Information).

as $[H_{34}W_{119}Se_8Fe_2O_{420}]^{54-}$ (**1a**) by using a hetero template strategy. Here the Se-based units form the “arms”, and an Fe-based core links the units together. Overall, **1a** has a unique saddle shape and nanoscale size, representing the biggest polyoxotungstate framework containing pentagonal units so far. Furthermore, the flexible assembly of the $\{WO_7\}$ units effectively gives rise to the formation of the unique $\{W(W_4)\}$ building units and the Fe-substituted pentagonal species $\{W(W_4Fe)\}$, which direct the assembly of this gigantic 2.8 nm solution-stable cluster.

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Supporting Information Available: Experimental details including the synthesis and characterization; X-ray crystallographic (CIF) files. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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