# A High-Nuclearity "Celtic-Ring" Isopolyoxotungstate, [H$_{12}$W$_{36}$O$_{120}$]$^{12-}$, That Captures Trace Potassium Ions

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Polyoxometalates have been subjected to a vast number of studies due to their attractive electronic and molecular properties that give rise to a variety of applications, e.g., in catalysis,[1] medicine,[2] and materials science.[3] Their versatile nature originates from the ability to polymerize metal oxide-based polyhedra to form a range of clusters from low to high nuclearities. In particular, the ability for molybdenum-based systems to form very large clusters has been demonstrated by a number of nanosized cluster systems.[4] Therefore, the ability to assemble large cluster systems from smaller known building blocks in a predetermined way is a great challenge, as such routes could be a direct way to systematically control the overall cluster architecture and properties. While developing strategies toward this goal, we recently reported a new family of isopoly-oxomolybdates[5] based on the [H$_2$Mo$_{16}$O$_{52}$]$^{10-}$ framework, and a family of sulfite-based Dawson-type polyoxomolybdates [Mo$_{18}$O$_{54}$-(SO$_3$)$_2$]$^{n-}$ that possess unusual electronic properties and a short S···S interaction between the two sulfite anions inside the cluster.[6] These clusters were "trapped" using an approach that employs bulky organic cations and hence restricts aggregation to the more highly symmetrical clusters, allowing a fundamentally more diverse set of clusters and cluster-based building blocks to be isolated.

In this paper we report the successful extension of this strategy[5] to polyoxotungstate chemistry and the ability to utilize organic-based cations in trapping a {W$_{36}$}-based cluster. This compound was isolated as (TEAH)$_9$Na$_2${(H$_2$O)$_4$K⊂[H$_{12}$W$_{36}$O$_{120}$]}·17 H$_2$O **1** (TEAH = protonated triethanolamine) and includes the 3-fold symmetric cluster anion [H$_{12}$W$_{36}$O$_{120}$]$^{12-}$ **1a** (see Figure 1). Remarkably, the cluster anion represents the largest isopolyoxotungstate so far discovered; cf. the dodecatungstates [H$_2$W$_{12}$O$_{40}$]$^{6-}$, [H$_2$W$_{12}$O$_{42}$]$^{10-}$, and [W$_{24}$O$_{84}$]$^{24-}$.[7] This is interesting as, in contrast to isopolyoxo-tungstates, heteropolyoxotungstates have been observed with higher nuclearities, e.g., [H$_7$W$_{48}$O$_{152}$(PO$_4$)$_8$]$^{33-}$ [8] or [Ce$_{16}$(H$_2$O)$_{36}$W$_{148}$O$_{488}$(AsO$_3$)$_{12}$]$^{76-}$,[9] but they all are exclusively templated by heteroatom anions such as PO$_4$$^{3-}$ and AsO$_3$$^{3-}$, which act as very effective link-ing groups and also affect the nucleophilicity of the heteropoly-oxotungstate cluster framework.

The cluster compound **1** was initially isolated from the reaction system comprising triethanolamine (TEA) (3.0 g, 20 mmol) and Na$_2$WO$_4$·2H$_2$O (1.6 g, 4.9 mmol) dissolved in water (25 mL). The pH was adjusted to 2.0 by the addition of hydrochloric acid (37%) with stirring, followed by the addition of Na$_2$S$_2$O$_4$ (0.11 g, 0.63 mmol). The blue solution was stirred for a further 10 min and then sealed and stored at 4 °C for 1 month. During this time, the blue color faded and the solution finally became colorless, at which point a small amount of colorless needle crystals of **1** gradually appeared in ca. 10% yield (based on tungsten); these were characterized by chemical analysis and single-crystal X-ray crystallography. Al-though no potassium salt was used as a starting material, crystal-
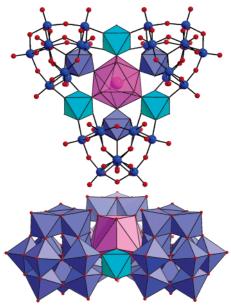


**Figure 1.** Molecular structure of {(H$_2$O)$_4$K⊂[H$_{12}$W$_{36}$O$_{120}$]}$^{11-}$ present in compound **1**. The top view shows a ball-and-stick representation of the W (blue) and O (red) framework. The central 10-coordinate K$^+$ ion is repre-sented by a purple sphere and its coordination environment by a purple polyhedron. The K$^+$ ion is coordinated to the terminal oxygen positions of a {W$_6$O$_6$} moiety, and each of these metal-centered polyhedra are shown in blue or cyan. Below, all the WO-based polyhedra are shown in blue ({W$_1$} linkers in cyan), with potassium in purple and oxygen positions depicted as red spheres. This view also reveals the "cavity" in which the K$^+$ ion resides.

lographic data clearly support the unambiguous assignment of a K$^+$ ion coordinated to the central cavity of the [H$_{12}$W$_{36}$O$_{120}$]$^{12-}$ cluster anion. Furthermore, the small amount of potassium (ca. 0.5 mg) required to produce 135 mg of **1** can therefore be assumed to originate from the reagents used and the glassware, as confirmed by atomic absorption analysis. Subsequent experiments also demon-strated that the addition of Na$_2$S$_2$O$_4$ is necessary for the synthesis of **1**.

The crystallographic studies revealed that **1** has an approximate formula of (TEAH)$_9$Na$_2${(H$_2$O)$_4$K⊂[H$_{12}$W$_{36}$O$_{120}$]}·17H$_2$O. Although the TEAH$^+$, sodium cations, and solvent water molecules are highly disordered, the new cluster anion, [H$_{12}$W$_{36}$O$_{120}$]$^{12-}$ (**1a**), is very well defined and encapsulates a K$^+$ ion. The anion **1a** is approxi-mately C$_{3v}$-symmetric with a Celtic ring-like shape (see Figure 1).

As such, **1a** comprises three {W$_{11}$} cluster subunits linked together by three {W$_1$} bridges (shown as the cyan-colored polyhedra in Figure 1); further, a K$^+$ ion is captured at the center of the {W$_{36}$} cluster in a {W$_6$O$_6$} ring. Notably, the three {W$_{11}$} subunits are analogous to the framework geometry of the [H$_4$W$_{11}$O$_{38}$]$^{6-}$ cluster reported by Lehmann et al.[10] This structure consists of a ring of six basal W positions, an additional W position
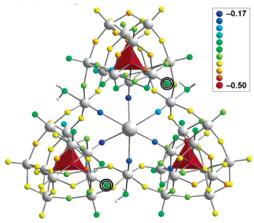
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**Figure 3.** Structural representation of the anionic $\{[K(H_2W_{12}O_{40})]^{5-}\}_\infty$ chain in **2** ($\{WO_6\}$ units shown as blue polyhedra and $K^+$ ions as purple spheres). The $[K(TEAH)_4]^{5+}$ units are omitted for clarity.

also yields **1**, but this must be carefully controlled as the addition of excess KCl to the reaction mixture, followed by heating, instead results in the formation of $\{[K(TEAH)_4][K(H_2W_{12}O_{40})]\}_\infty$ (**2**). Compound **2** contains the previously characterized α-Keggin anion $[H_2W_{12}O_{40}]^{6-}$.[12] However, in this case, compound **2** is composed of discrete $[K(TEAH)_4]^{5+}$ cations and a linear anionic coordination polymer $\{[K(H_2W_{12}O_{40})]^{5-}\}_\infty$, with potassium cations and $[H_2W_{12}O_{40}]^{6-}$ alternating in the chain (Figure 3).

In conclusion, this work demonstrates that it is possible to assemble large $\{W_{36}\}$ isopolyoxotungstate-based clusters such as **1** and the $\{W_{12}\}$ cluster chain **2** by applying a "shrink-wrapping" strategy.[5] Interestingly, the assembly of **1** requires trace amounts of $K^+$ ions to be present as well as the organo cations, and the formation of a $[\{M_6O_6\}K]$ moiety in $\{K \subset W_{36}\}$ appears to be central to the templation of the overall $\{W_{36}\}$ cluster anion; the inclusion of potassium in this moiety is strikingly similar to the inclusion of potassium in $[\{Mo_6O_6\}K]$ motifs that are observed in the spherical $[K_{20} \subset Mo_{80}V_{22}]$ cluster.[13] Furthermore, DFT results suggest that the $\{W_{36}\}$ clusters could themselves be utilized as building blocks for larger architectures with other electrophiles, and it appears that the cluster possess charge density "hotspots" that are the most likely sites of further molecular growth. Future work will aim to realize this architectural strategy as well as focus on the host−guest chemistry of the $\{K \subset W_{36}\}$ cluster in solution.

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

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**Figure 2.** Color-coded distribution of calculated partial atomic charges of the oxygen positions in **1a**, with the ranges of Löwdin charges assigned in the legend. The two terminal oxo positions coordinating to $Na^+$ cations in the crystalline lattice of **1** are encircled in black. The four inner $\mu_{3/4}$-O positions per $\{W_{11}\}$ group, two of which are protonated, span a nearly regular $O_4$ tetrahedron (red polyhedra).

in the center of this ring, and four apical W positions in a butterfly configuration. Every W center has a distorted $WO_6$ octahedral coordination geometry, with one terminal W=O (W−O $\sim$1.70 Å) extending away from the cluster. Within the $\{W_{11}\}$ moieties, two protons form hydrogen bonds between the four central $\mu_{3/4}$-oxo ligands.

The three bridging $\{W_1\}$ groups also display a distorted $WO_6$ octahedral coordination geometry, each sharing four bridging oxo ligands in the equatorial plane with the $\{W_{11}\}$ clusters; one W=$O_{term}$ (W−O $\sim$1.70 Å) points to the central $K^+$ ion, and one water molecule ligand (W−$OH_2 \sim$2.20 Å) points outside the cluster. The $K^+$ ion is 10-fold coordinated to six $O_{term}$ ligands from the tungstate and to four water molecules (K−O distances are in the range between 2.75(2) and 3.03(2) Å). The $K^+$ ion is displaced slightly above the equatorial plane, formed by the six $O_{term}$ ligands, with three water molecules coordinating from above and one below the equatorial plane.

Given the unusual structure of **1a**, density functional theory calculations[11] were performed. They revealed an interesting distribution of partial atomic charges on the oxygen positions of the $\{W_{36}\}$ polyoxoanion whereby the charges significantly deviate from average values (up to 10% for $\mu_2$-oxo groups, and up to 30% for terminal oxo groups). These could be interpreted as possible reactivity "hotspots" toward electrophilic reactants. Indeed, the nucleophilicity of the accessible surface, defined by terminal and $\mu_2$-oxo groups, shows a maximum at the $\mu_2$- and terminal oxo positions binding to the four apical W centers of each $\{W_{11}\}$ unit (Figure 2).

Thus, electrophilic groups such as $M^{2+/3+}$ ions are likely, e.g., to bind to the apical $W_3(\mu_2$-O$)_3$ groups. The $\{W_{36}\}$ anion might hence be regarded as a potential building block for future polyoxotungstate-based frameworks. Interestingly, the sodium cations in the solid-state structure of **1** coordinate to less negative, terminal oxo positions of basal W centers. Of the four inner $\mu_n$-O positions per $\{W_{11}\}$ group that span a nearly regular $O_4$ tetrahedron (O···O distances 2.8−3.0 Å), the $\mu_4$-O and the opposite $\mu_3$-O position (with all W−O−W angles <97°) display the highest negative partial charges and hence are most likely to be protonated. This is in contrast to the similar tetrahedral arrangement of the four central $\mu_3$-oxo positions in $\{H_2W_{12}O_{40}\}$ Keggin structures for which nearly identical partial charges and Bond-Valence Sum (BVS) values are found.

Attempts to repeat the synthesis of **1** by the deliberate addition of a source of $K^+$ (KCl, 13 mg, 0.17 mmol) under similar conditions