Polyyoxometalates 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, medicine, and materials science. 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. 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 isopolyoxomolybdates based on the $[\text{H}_2\text{Mo}_{16}\text{O}_{48}]^{10-}$ framework, and a family of sulfite-based Dawson-type isopolyoxomolybdates that possess unusual electronic properties and a short $S\cdots S$ interaction between the two sulfite anions inside the cluster. 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 to polyoxotungstate chemistry and the ability to utilize organic-based cations in trapping a $[\text{W}_{36}\text{O}_{120}]^{12-}$-based cluster. This compound was isolated from the reaction system comprising triethanolamine (TEA) ($3.0 \text{ g} \ 20 \text{ mmol}$) and $\text{Na}_2\text{WO}_4\cdot2\text{H}_2\text{O}$ ($1.6 \text{ g} \ 4.9 \text{ mmol}$) dissolved in water ($25 \text{ mL}$). The pH was adjusted to $2.0$ by the addition of hydrochloric acid (37%) with stirring, followed by the addition of $\text{Na}_2\text{S}_2\text{O}_5$ ($0.11 \text{ g} \ 0.63 \text{ mmol}$). The blue solution was stirred for a further $10 \text{ min}$ and then cooled and stirred for $1 \text{ month}$. During this time, the blue color of the solution gradually appeared and a small amount of colorless needle crystals of $1$ (see Figure 1). Remarkably, the cluster anion represents the largest isopolyoxotungstate so far discovered; cf. the dodecatungstates $[\text{H}_2\text{W}_{12}\text{O}_{42}]^{10-}$ and $[\text{H}_2\text{W}_{12}\text{O}_{42}]^{10-}$ that possess unusual electronic properties and a short $S\cdots S$ interaction between the two sulfite anions inside the cluster. 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.

The cluster compound $1$ was isolated from the reaction system comprising triethanolamine (TEA) ($3.0 \text{ g} \ 20 \text{ mmol}$) and $\text{Na}_2\text{WO}_4\cdot2\text{H}_2\text{O}$ ($1.6 \text{ g} \ 4.9 \text{ mmol}$) dissolved in water ($25 \text{ mL}$). The pH was adjusted to $2.0$ by the addition of hydrochloric acid (37%) with stirring, followed by the addition of $\text{Na}_2\text{S}_2\text{O}_5$ ($0.11 \text{ g} \ 0.63 \text{ mmol}$). The blue solution was stirred for a further $10 \text{ min}$ and then cooled and stirred for $1 \text{ month}$. During this time, the blue color of the solution gradually appeared and a small amount of colorless needle crystals of $1$ (see Figure 1). Remarkably, the cluster anion represents the largest isopolyoxotungstate so far discovered; cf. the dodecatungstates $[\text{H}_2\text{W}_{12}\text{O}_{42}]^{10-}$ and $[\text{H}_2\text{W}_{12}\text{O}_{42}]^{10-}$ that possess unusual electronic properties and a short $S\cdots S$ interaction between the two sulfite anions inside the cluster. 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.

**Figure 1.** Molecular structure of $[\text{H}_2\text{O}_7\text{K}\text{C}[\text{H}_2\text{W}_{36}\text{O}_{120}]^{12-}]$ present in compound $1$. The top view shows a ball-and-stick representation of the $\text{W}$ (blue) and $\text{O}$ (red) framework. The central $10$-coordinate $\text{K}^{+}$ ion is represented by a purple sphere and its coordination environment by a purple polyhedron. The $\text{K}^{+}$ ion is coordinated to the terminal oxygen positions of a $\text{W}_6\text{O}_{12}$ moiety, and each of these metal-centered polyhedra are shown in blue or cyan. Below, all the $\text{WO}_6$-based polyhedra are shown in blue ($\{\text{W}_6\}$ linkers in cyan), with potassium in purple and oxygen positions depicted as red spheres. This view also reveals the “cavity” in which the $\text{K}^{+}$ ion resides.
in the center of this ring, and four apical W positions in a butterfly configuration. Every W center has a distorted WO6 octahedral coordination geometry, with one terminal W=O (W−O ~1.70 Å) extending away from the cluster. Within the {W11} moieties, two protons form hydrogen bonds between the four central μ3xo-oxo ligands.

The three bridging {W1} groups also display a distorted WO6 octahedral coordination geometry, each sharing four bridging oxo ligands in the equatorial plane with the {W11} clusters; one W=Owern (W−O ~1.70 Å) points to the central K+ ion, and one water molecule ligand (W−OH ~2.20 Å) points outside the cluster. The K+ ion is 10-fold coordinated to six Oterm 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 Oterm ligands, with three water molecules coordinating from above and one below the equatorial plane.

Given the unusual structure of 1a, density functional theory calculations were performed. They revealed an interesting distribution of partial atomic charges on the oxygen positions of the {W16} polyoxoanion whereby the charges significantly deviate from average values (up to 10% for μ2-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 μ2-oxo groups, shows a maximum at the μ2- and terminal oxo positions binding to the four apical W centers of each {W11} unit (Figure 2).

Thus, electrophilic groups such as M2+ ions are likely, e.g., to bind to the apical W3(μ2-O3) groups. The {W16} anion might hence be regarded as a potential building block for future polyoxoantostate-based frameworks. Interestingly, the sodium cations in the solid-state structure of 1a coordinate to less negative, terminal oxo positions of basal W centers. Of the four inner μ2-O positions per {W11} group that span a nearly regular O4 tetrahedron (O−O distances 2.8−3.0 Å), the μ2-O and the opposite μ2-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 μ3-oxo positions in (HW3O9)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 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(H2W12O40)]]∞ (2). Compound 2 contains the previously characterized ε-Keggin anion ([H2W12O40]8−). However, in this case, compound 2 is composed of discrete [K(TEAH)4]3+ cations and a linear anionic coordination polymer {[[K(H2W12O40)]]∞}−, with potassium cations and [H2W12O40]8− alternating in the chain (Figure 3).

In conclusion, this work demonstrates that it is possible to assemble large [W16] isopolyoxoantostate-based clusters such as 1 and the {W11} cluster chain 2 by applying a “shrink-wrapping” strategy. 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 [M2O6K] moiety in [KClW16] appears to be central to the templation of the overall [W16] cluster anion; the inclusion of potassium in this moiety is strikingly similar to the inclusion of potassium in [MoO3K] motifs that are observed in the spherical [K20Mo3V2]3 cluster. Furthermore, DFT results suggest that the [W16] 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 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 [KClW16] cluster in solution.

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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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