

# Capture of Periodate in a $\{W_{18}O_{54}\}$ Cluster Cage Yielding a Catalytically Active Polyoxometalate $[H_3W_{18}O_{56}(IO_6)]^{6-}$ Embedded with High-Valent Iodine\*\*

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The expansion in polyoxometalate (POM) chemistry has accelerated dramatically in recent years.<sup>[1]</sup> Much focus has been on the discovery and assembly of new POM clusters<sup>[2–6]</sup> and/or the use of traditional clusters as building blocks in constructing organic–inorganic hybrid materials.<sup>[7–8]</sup> By using protonated organic amine cations, such as protonated hexamethylenetetraamine and triethanolammonium (TEAH<sup>+</sup>), which can kinetically stabilize and thus help to isolate reactive reduced POM clusters, we have isolated a range of new cluster types, for example,  $[H_2Mo_{16}O_{52}]^{10-}$ , a partially reduced cluster,<sup>[9]</sup> and  $[Mo_{18}O_{54}(SO_3)_2]^{4-/6-}$ , a thermochromic Dawson-like cluster containing nonconventional templates ( $SO_3$ ) inside the cluster shell.<sup>[10]</sup> The extension of this work to tungsten-based systems led to the discovery of new isopolyoxotungstate archetypes,  $[H_{12}W_{36}O_{120}]^{12-}$  and  $[H_4W_{19}O_{62}]^{6-}$ .<sup>[11,12]</sup> The  $[H_4W_{19}O_{62}]^{6-}$  cluster comprises a Dawson-like structure with an additional tungsten site located at the center of the  $\{W_{18}O_{54}\}$  cluster shell, effectively replacing the two heteroanion templates that characterize the conventional Dawson-type structures. Structural analysis of the  $[H_4W_{19}O_{62}]^{6-}$  cluster shows that the cluster can be also described as a  $\{W_{18}O_{54}\}$  cluster shell templated by an octahedral or trigonal prismatic  $WO_6$  unit plus two bridging water ligands.<sup>[12]</sup> Therefore, we thought that it may be possible to replace the central  $WO_6$  moiety with other encapsulated  $XO_6$  species, where for example  $X = Pt^{IV}$ ,  $Sb^V$ ,  $Te^{VI}$ , or  $I^{VII}$ . Herein we have targeted such substitutions, as this route allows the physical properties of the metal-oxide cluster shell

to be modulated. In particular, the encapsulation of templates in very high or very low oxidation states should significantly affect the acidic, catalytic, and redox properties of the resulting cluster systems, and is especially interesting for the encapsulation of high-oxidation state templates.<sup>[13]</sup>

Herein we demonstrate that it is possible to embed iodine(VII) into a Dawson-like  $\{W_{18}O_{54}\}$  matrix as the periodate species  $IO_6^{5-}$  to yield a range of cluster salts,  $K_6[H_3W_{18}O_{56}(IO_6)] \cdot 9H_2O$  **1**,  $(TPA)_6[H_3W_{18}O_{56}(IO_6)]$  **2**, and  $(TBA)_6[H_3W_{18}O_{56}(IO_6)]$  **2'** (TPA = tetrapropylammonium, TBA = tetrabutylammonium). These species have different solubilities in a range of solvents, and all contain the  $[H_3W_{18}O_{56}(IO_6)]^{6-}$  anion. This POM anion represents the first example of a Dawson-type  $\{W_{18}O_{54}\}$  shell templated by a hetero  $XO_6$  moiety, and the first example of a crystallographically characterized tungstatoperiodate. This cluster is catalytically active in oxidations and has unusual redox behavior arising from the encapsulation of the iodine(VII) species.

Compound **1** was prepared by refluxing an aqueous solution containing  $Na_2WO_4$  and  $H_5IO_6$  (molar ratio 14:1) and precipitating with excess KCl as light green crystals. X-ray crystallographic structural analysis<sup>[14]</sup> of **1** reveals a Dawson-type  $D_{3h}$ -symmetric  $\{W_{18}O_{54}\}$  cluster shell enclosing an  $IO_6$  unit with average I–O distance of 1.90(2) Å and an (I)O–W distance of 2.42(2) Å. Two additional interior oxygen positions each bridge one of the two capping  $\{W_3\}$  groups of the clusters, with average O–W distances of 2.23(2) Å. The  $D_{3d}$  symmetry of the  $IO_6$  unit does not match the  $\{W_{18}O_{54}\}$   $D_{3h}$  symmetry of the cluster shell, lowering the symmetry of the complete cluster aggregate to  $C_{3v}$ , and thus representing a  $\beta^*$  isomer in the family of  $\{W_{18}\}$  Dawson structures.<sup>[12]</sup> This is the first time that a  $\beta^*$  isomer has been determined crystallographically; previously known isomers are mostly  $\alpha$  and  $\gamma^*$  types (Figure 1).

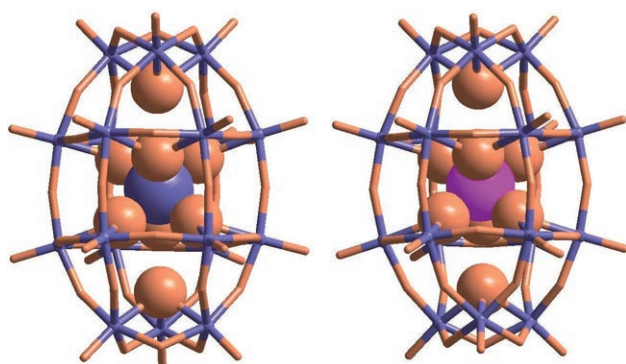
As in the case of the  $[H_4W_{19}O_{62}]^{6-}$  cluster, the two tetrahedral cavities that are usually occupied by heteroatoms in conventional Dawson clusters are vacant, and the apical interior  $\mu_3$ -O positions are protonated, which involves H-bonding between adjacent pairs of oxygen sites within these cavities. The structure of the cluster  $[H_3W_{18}O_{56}(IO_6)]^{6-}$  is therefore very similar to that of the  $[H_4W_{19}O_{62}]^{6-}$  cluster framework.<sup>[12]</sup> The only difference is the cluster symmetry and the identity of the central atoms, which would be extraordinarily challenging to discern simply from X-ray crystallography, especially when the central atoms are located on a 3-fold axis. To rule out the possibility that compound **1** could be

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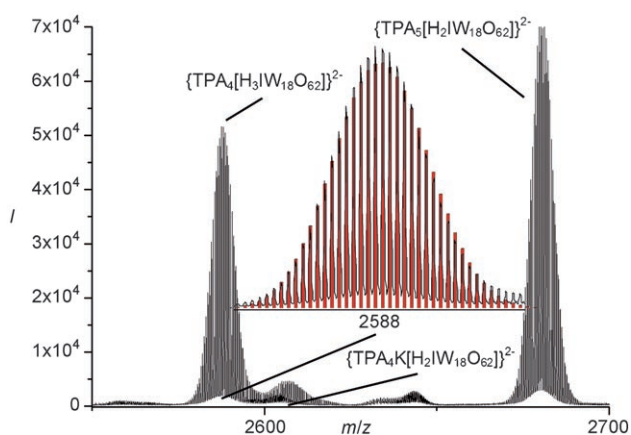
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**Figure 1.** Representation of the structure of  $\gamma^*$ -[H<sub>4</sub>W<sub>19</sub>O<sub>62</sub>]<sup>6-</sup> (left) and  $\beta^*$ -[H<sub>3</sub>W<sub>18</sub>O<sub>56</sub>(IO<sub>6</sub>)]<sup>6-</sup> (right). The {W<sub>18</sub>O<sub>54</sub>} frameworks are shown as sticks with the bottom {W<sub>3</sub>} cap on the I-centered species rotated by 60° relative to the tungsten-centered framework. The central tungsten and iodine atoms and interior oxo ligands are highlighted as large spheres (W blue, I purple, O orange).

assigned as [H<sub>4</sub>W<sub>19</sub>O<sub>62</sub>]<sup>6-</sup> or contains this cluster as an impurity in the solid state, we utilized high-resolution electrospray and cryospray mass spectrometry (MS) to identify the exact elemental constitution of the cluster anion.<sup>[15]</sup> To simplify the MS experiments, the potassium salt (**1**) was ion-exchanged with TPA<sup>+</sup> cations, yielding **2**. Figure 2



**Figure 2.** Assigned negative-mode mass spectra of (TPA)<sub>6</sub>[H<sub>3</sub>IW<sub>18</sub>O<sub>62</sub>]**2** in acetonitrile. An expansion of the peak at  $m/z = 2588$  is shown along with the calculated isotopic pattern (red columns).

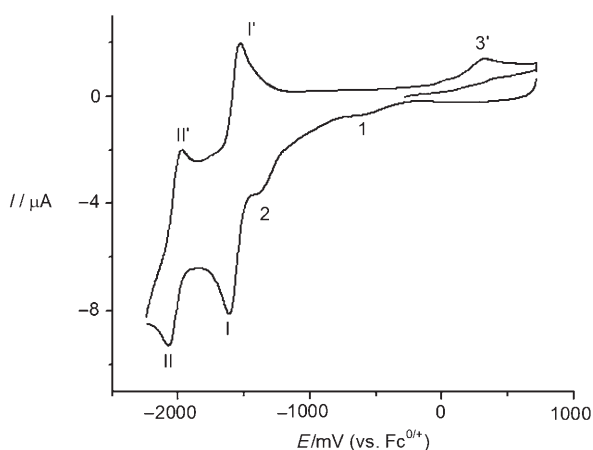
shows the mass spectra of **2** in acetonitrile in which all major peaks are related to {W<sub>18</sub>I} and can be assigned:  $m/z$  2588.1 {TPA<sub>4</sub>[H<sub>3</sub>IW<sub>18</sub>O<sub>62</sub>]}<sup>2-</sup>, 2607.1 {TPA<sub>4</sub>K[H<sub>2</sub>IW<sub>18</sub>O<sub>62</sub>]}<sup>2-</sup>, and 2680.7 {TPA<sub>5</sub>[H<sub>2</sub>IW<sub>18</sub>O<sub>62</sub>]}<sup>2-</sup>. In contrast, the TPA<sup>+</sup> salt of [H<sub>4</sub>W<sub>19</sub>O<sub>62</sub>]<sup>6-</sup><sup>[12]</sup> in acetonitrile gives a different mass spectrum in this  $m/z$  range: 1676.5 {TPA<sub>3</sub>[H<sub>2</sub>W<sub>19</sub>O<sub>61</sub>]}<sup>3-</sup>, 1682.5 {TPA<sub>3</sub>[H<sub>4</sub>W<sub>19</sub>O<sub>62</sub>]}<sup>3-</sup>, 1744.5, {TPA<sub>4</sub>[H<sub>3</sub>W<sub>19</sub>O<sub>62</sub>]}<sup>3-</sup>, 2617.4 {TPA<sub>4</sub>[H<sub>4</sub>W<sub>19</sub>O<sub>62</sub>]}<sup>2-</sup>, and 2709.9 {TPA<sub>5</sub>[H<sub>3</sub>W<sub>19</sub>O<sub>62</sub>]}<sup>2-</sup> (see the Supporting Information). Therefore, evidence from mass spectral studies, in combination with elemental analysis and crystallography, clearly show that **2** is a pure phase of

{W<sub>18</sub>I} without any contamination by other species, for example, {W<sub>19</sub>}.

The mass spectral studies show that the cluster is mainly present in solution as {(TPA)<sub>x</sub>[H<sub>n</sub>W<sub>18</sub>O<sub>56</sub>(IO<sub>6</sub>)]<sup>2-</sup>}, where  $x$  and  $n$  are either 4 and 3, or 5 and 2, respectively, with both the di- and triprotonated forms being present. However, the crystallographic data and elemental analysis demonstrate that crystalline materials presented herein contain [H<sub>3</sub>W<sub>18</sub>O<sub>56</sub>(IO<sub>6</sub>)]<sup>6-</sup> in a pure form. This observation is intriguing, as it implies that the [H<sub>3</sub>W<sub>18</sub>O<sub>56</sub>(IO<sub>6</sub>)]<sup>6-</sup> ion is probably more stable or able to pack more efficiently than the diprotonated [H<sub>2</sub>W<sub>18</sub>O<sub>56</sub>(IO<sub>6</sub>)]<sup>7-</sup> ion in the crystal lattice. Solution proton NMR spectroscopic studies were used to investigate the nature of the protonation; in these experiments **2** containing the cluster anion [H<sub>3</sub>W<sub>18</sub>O<sub>56</sub>(IO<sub>6</sub>)]<sup>6-</sup> as TBA<sup>+</sup> salts was used owing to its high solubility. It is not possible to identify the cluster protons in the room temperature NMR spectroscopy measurements, presumably because of fast solvent exchange with residual water, but three types of protons can be observed in CD<sub>3</sub>CN at -30 °C at  $\delta = 5.80$ , 5.85, and 5.90 ppm; the observation of these three resonances indicates nonequivalent chemical environments.

The synthesis of [H<sub>3</sub>W<sub>18</sub>O<sub>56</sub>(IO<sub>6</sub>)]<sup>6-</sup> also reveals an interesting fact about the role of the cations in the formation of the cluster shell: Unlike the synthesis of [H<sub>4</sub>W<sub>19</sub>O<sub>62</sub>]<sup>6-</sup>, which requires the presence of three-fold symmetrical triethanolammonium (TEAH<sup>+</sup>) cations to produce the 3-fold symmetrical [H<sub>4</sub>W<sub>19</sub>O<sub>62</sub>]<sup>6-</sup> cluster (the well-known W<sub>10</sub>O<sub>32</sub><sup>4-</sup> cluster is formed in the absence of TEAH<sup>+</sup>),<sup>[12]</sup> the formation of [H<sub>3</sub>W<sub>18</sub>O<sub>56</sub>(IO<sub>6</sub>)]<sup>6-</sup> appears, at least empirically, to be induced by the IO<sub>6</sub><sup>5-</sup> anion (which contains a three-fold symmetric axis), although the cluster is produced in a modest yield. Prompted by this observation, we undertook the synthesis of [H<sub>3</sub>W<sub>18</sub>O<sub>56</sub>(IO<sub>6</sub>)]<sup>6-</sup> in the presence of TEAH<sup>+</sup> and obtained (TEAH)<sub>6</sub>[H<sub>3</sub>W<sub>18</sub>O<sub>56</sub>(IO<sub>6</sub>)] **3** in higher yield. Once again, the combination of single-crystal structure determination,<sup>[14]</sup> elemental analysis, and mass spectrometry confirms that **3** contains the cluster anion [H<sub>3</sub>W<sub>18</sub>O<sub>56</sub>(IO<sub>6</sub>)]<sup>6-</sup>.

Synthesis of **1** represents the first time that the IO<sub>6</sub><sup>5-</sup> ion has been captured within a polyoxometalate “molecular cage”, and the first time that the nonmetal element iodine in its highest valence +7 is incorporated in a tungsten oxide cluster; the compounds reported herein serve as the first examples of crystallographically characterized tungstoperiodates, as the previously synthesized [W<sub>2</sub>I<sub>2</sub>O<sub>16</sub>]<sup>6-</sup> and [IW<sub>6</sub>O<sub>24</sub>]<sup>5-</sup> salts were reported without crystal structures.<sup>[16]</sup> This fact is significant, because although H<sub>5</sub>IO<sub>6</sub> is well known for its highly oxidative nature and tetraalkylammonium periodate salts could be explosive, in contrast, compounds **2** and **2'** are quite stable in the solid state. The integration of the IO<sub>6</sub><sup>5-</sup> ion also impacts on the physical properties of the POM. First, [H<sub>3</sub>W<sub>18</sub>O<sub>56</sub>(IO<sub>6</sub>)]<sup>6-</sup> shows very unusual electrochemical properties compared with traditional Dawson type clusters (Figure 3). The cluster is much harder to reduce in acetonitrile solution, and this is unusual, as periodate compounds are known to be highly oxidizing. The cyclic voltammetry scans only show two reversible reduction/oxidation pairs at relatively low voltages, namely -1.57 and -2.02 V vs. Fc/Fc<sup>+</sup>, which is very negative compared to [W<sub>18</sub>O<sub>54</sub>(PO<sub>4</sub>)<sub>2</sub>]<sup>6-</sup><sup>[17]</sup>



**Figure 3.** Cyclic voltammogram of 1 mM (TBA)<sub>6</sub>[H<sub>3</sub>W<sub>18</sub>O<sub>56</sub>(IO<sub>6</sub>)] **2'** in CH<sub>3</sub>CN (0.1 M THAClO<sub>4</sub>) on a glassy carbon electrode at a scan rate of 100 mVs<sup>-1</sup>. The two redox potentials associated with I/I' and II/II' are -1.57 and -2.02 V, respectively. Two small processes (1 and 2) are seen when the potential was scanned from positive to negative, but disappear after further scans. These processes are associated with protonated species derived from the POM itself or from enhanced levels of protonation associated with the presence of adventitious water in the solvent. A small oxidation process (3) was observed when switching potential after reduction process I (origin unknown).

(-0.77, -1.13 V), [W<sub>18</sub>O<sub>54</sub>(SO<sub>4</sub>)<sub>2</sub>]<sup>4-</sup> [18] (-0.24, -0.62 V), and [W<sub>18</sub>O<sub>54</sub>(SO<sub>3</sub>)<sub>2</sub>]<sup>4-</sup> [18] (-0.36, -0.76 V). Secondly, the modified redox properties also translate into a different reactivity, and the [H<sub>3</sub>W<sub>18</sub>O<sub>56</sub>(IO<sub>6</sub>)]<sup>6-</sup> anion exhibits significant catalytic activity in oxidation of benzyl alcohol.

To examine the preliminary catalytic activity of [H<sub>3</sub>W<sub>18</sub>O<sub>56</sub>(IO<sub>6</sub>)]<sup>6-</sup>, the oxidation reaction of benzyl alcohol catalyzed by **2'** in CD<sub>3</sub>CN was investigated. The catalytic experiment was performed in an NMR tube monitored by <sup>1</sup>H NMR spectroscopy. Before addition of H<sub>2</sub>O<sub>2</sub> (35%), chemical shifts for the CH<sub>2</sub> protons of benzyl alcohol were identified at δ = 4.64 ppm in a mixture of **2'** (0.43 μmol) and benzyl alcohol (0.192 mmol) in CD<sub>3</sub>CN (0.7 mL). As H<sub>2</sub>O<sub>2</sub> (35%) was gradually added and the solution was heated, benzaldehyde was produced and the aldehyde proton could be identified at δ = 10 ppm. Calculations based on the relative intensities of signals at δ = 4.64 and 10 ppm show 92% conversion after a total amount of 0.3 mmol of H<sub>2</sub>O<sub>2</sub> was added and the system was heated over 75 hrs at 60 °C. This initial result is notable, as the reaction proceeds under relatively mild conditions<sup>[19]</sup> and is selective, producing only the aldehyde. As a control, the same reaction carried out exactly as above, but with (TBA)<sub>6</sub>[W<sub>18</sub>O<sub>54</sub>(PO<sub>4</sub>)<sub>2</sub>] replacing **2'**, did not produce observable quantities of benzaldehyde or other products observable by using <sup>1</sup>H NMR spectroscopy.

The electrochemical and catalytic observations outline the potential and new features of the high-valent iodine-containing cluster. Normally, the periodate would be expected to be reduced easily, but the anion is included as IO<sub>6</sub><sup>5-</sup> within the cluster {W<sub>18</sub>O<sub>56</sub>}<sup>4-</sup> to give a highly anionic cage which is three-fold protonated as [H<sub>3</sub>W<sub>18</sub>O<sub>56</sub>(IO<sub>6</sub>)]<sup>6-</sup>. This means that superficially, the {W<sub>18</sub>} cluster cage gives a barrier to reduction, as further reduction would mean that the cluster cage has to

support an even high negative charge. This implies that the highly oxidizing guest is thereby kinetically stabilized by the overall highly anionic cluster. The fact that the cluster, with its very negative reduction potentials, is catalytically active, inspired us to examine the electronic structure using DFT calculations.<sup>[20]</sup>

DFT calculations on differently protonated varieties of the {W<sub>18</sub>O<sub>56</sub>(IO<sub>6</sub>)} system clearly identify the two μ<sub>3</sub>-oxo positions, interior to the cluster cage and interlinking the cap tungsten centers, as the most electronegative positions, thus confirming the monoprotection of these sites. Based on the calculated net charges, the third proton in [H<sub>3</sub>W<sub>18</sub>O<sub>56</sub>(IO<sub>6</sub>)]<sup>6-</sup> is bound to one of the six oxo positions of the central IO<sub>6</sub> group, which represent the second-most negative charged sites. Moreover, comparisons between [H<sub>3</sub>W<sub>18</sub>O<sub>56</sub>(IO<sub>6</sub>)]<sup>6-</sup> and a conventional Dawson polyanion (α-[W<sub>18</sub>O<sub>54</sub>(PO<sub>4</sub>)<sub>2</sub>]<sup>6-</sup>) reveal important differences in the charge distribution of the oxo positions defining the solvent-accessible surfaces of these systems. Whereas the resulting Löwdin and Mulliken point charges for terminal oxo positions of α-[W<sub>18</sub>O<sub>54</sub>(PO<sub>4</sub>)<sub>2</sub>]<sup>6-</sup> vary moderately (between -0.28 to -0.32), the corresponding values for [H<sub>3</sub>W<sub>18</sub>O<sub>56</sub>(IO<sub>6</sub>)]<sup>6-</sup> show a more modulated distribution (-0.27 to -0.35) with a maximum in electronegativity for the O<sub>term</sub> positions of the cap tungsten sites. The point charges for bridging oxo and tungsten positions, on the other hand, exhibit nearly the same distribution patterns (α-[W<sub>18</sub>O<sub>54</sub>(PO<sub>4</sub>)<sub>2</sub>]<sup>6-</sup>: -0.30 to -0.36 for μ<sub>2</sub>-O, 0.69 to 0.74 for tungsten; [H<sub>3</sub>W<sub>18</sub>O<sub>56</sub>(IO<sub>6</sub>)]<sup>6-</sup>: -0.31 to -0.36 for μ<sub>2</sub>-O, 0.69 to 0.72 for tungsten). The relatively wide spread in surface basicity, defined by the terminal oxo positions and induced by the (monoprotection) periodate guest, could account for the specific reactivity and catalytic properties of **2'**.

In summary, we have discovered a new type of tungstato periodate compound, [H<sub>3</sub>W<sub>18</sub>O<sub>56</sub>(IO<sub>6</sub>)]<sup>6-</sup>, embedded with high-valent iodine in a {W<sub>18</sub>O<sub>54</sub>} Dawson-type shell, and the first example of a β\*-Dawson isomer. We have characterized three salts of this polyanion using single-crystal structure analysis, and have confirmed the assignment of the central atom template as being iodine, as well as the degree of cluster protonation using mass spectrometry. Electrochemical, catalytic and DFT studies show significant differences compared with conventional Dawson-type polyoxotungstates. Therefore we suggest that [H<sub>n</sub>W<sub>18</sub>O<sub>56</sub>(IO<sub>6</sub>)]<sup>m-</sup> is the first in a whole new class of [H<sub>n</sub>W<sub>18</sub>O<sub>56</sub>(XO<sub>6</sub>)]<sup>m-</sup> heteropolyoxometalates (X = non-tungsten heteroatom) and that the incorporation of other XO<sub>6</sub> species will allow the development of many fascinating clusters with new physical properties. In future work we will focus on expanding this family of compounds as well as investigating the electrochemical and catalytic properties of [H<sub>n</sub>W<sub>18</sub>O<sub>56</sub>(IO<sub>6</sub>)]<sup>m-</sup> in greater detail.

### Experimental Section

**Caution!** Care should be taken when using IO<sub>6</sub><sup>5-</sup>-based materials, as there is a risk of explosion or combustion. Full analytical details are given in the Supporting Information. Synthesis of K<sub>6</sub>[H<sub>3</sub>W<sub>18</sub>O<sub>56</sub>(IO<sub>6</sub>)]·9H<sub>2</sub>O **1**: Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O (20.0 g, 60.6 mmol) was dissolved in water (50 mL) and H<sub>5</sub>IO<sub>6</sub> (1.0 g, 4.4 mmol) in water (10 mL) was

added. The pH was adjusted to 1.0 by the addition of 6 M HCl followed by heating the solution to reflux for 1 h. After the solution was cooled to around 80 °C, KCl (15 g) was added under stirring. As the solution cooled, a white powder formed and was removed by filtration, and light green crystals were isolated from the filtrate after a few hours. Collection of these crystals by soaking the solid using filtered mother liquid to remove further white powder, and recrystallization from a minimum amount of water, gave large crystals (1–2 mm in size) of **1**. Yield: 3.4 g (20.9%). **2**:  $K_6[H_3W_{18}O_{56}(IO_6)] \cdot 9H_2O$  **1** (3.0 g) was dissolved in water (50 mL). Tetrapropylammonium bromide (2.5 g) dissolved in water (10 mL) was added with stirring. The precipitate was centrifuged and washed with water and ethanol, and dried in vacuum. The compound was purified by recrystallization from acetonitrile. Yield: 2.6 g.  $(TBA)_6[H_3W_{18}O_{56}(IO_6)]$  **2'** was also obtained using the procedure as described above with TBA bromide replacing TPA. Synthesis of  $(TEAH)_6[H_3W_{18}O_{56}(IO_6)] \cdot 2H_2O$  **3**:  $Na_2WO_4 \cdot 2H_2O$  (10.0 g, 30.3 mmol) and triethanolamine hydrochloride (7.0 g, 37.7 mmol) were dissolved in water (20 mL) and  $H_3IO_6$  (0.5 g, 2.2 mmol) in water (5 mL) was added. The solution pH was adjusted to 1.3 by adding 6 M HCl dropwise, and the solution was heated to reflux and stirred for 0.5 h. After half the volume of the solvent was removed and the solution had cooled to room temperature, the light green crystalline product was then isolated after three days. The sample was then purified by recrystallisation from minimum amount of water. Yield: 5.2 g.

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- [14] Crystallographic data and structure refinements for  $K_6[H_3W_{18}O_{56}(IO_6)] \cdot 9H_2O$  **1**:  $H_{21}IK_6O_{71}W_{18}$ ,  $M_r = 4827.97$ ; block crystal:  $0.18 \times 0.14 \times 0.11 \text{ mm}^3$ ;  $T = 100(2) \text{ K}$ . Trigonal,  $R3$ ,  $a = 19.218(2)$ ,  $c = 15.668(3) \text{ \AA}$ ,  $V = 5011.7(13) \text{ \AA}^3$ ,  $Z = 3$ ,  $\rho = 4.80 \text{ g cm}^{-3}$ ,  $\mu(\text{MoK}\alpha) = 31.795 \text{ mm}^{-1}$ ,  $F(000) = 6264$ , 5435 reflections measured, 3526 unique ( $R_{\text{int}} = 0.033$ ), 277 refined parameters,  $R1 = 0.0405$ ,  $wR2 = 0.1104$ . One third of the cluster was found in the asymmetric unit with a number of disordered  $K^+$  and solvent water sites which sum to 6 and 9 per cluster, respectively.  $(TPA)_6[H_3W_{18}O_{56}(IO_6)] \cdot 2CH_3CN$  **2**:  $C_{76}H_{177}IN_8O_{62}W_{18}$ ,  $M_r = 5631.46$ ; block crystal:  $0.17 \times 0.12 \times 0.10 \text{ mm}^3$ ;  $T = 100(2) \text{ K}$ . Monoclinic,  $P2_1/n$ ,  $a = 16.8096(7)$ ,  $b = 31.8436(12)$ ,  $c = 26.2081(11) \text{ \AA}$ ,  $\beta = 90.195(2)$ ,  $V = 14028.5(10) \text{ \AA}^3$ ,  $Z = 4$ ,  $\rho = 2.666 \text{ g cm}^{-3}$ ,  $\mu(\text{MoK}\alpha) = 14.989 \text{ mm}^{-1}$ ,  $F(000) = 10280$ , 58336 reflections measured, 23569 unique ( $R_{\text{int}} = 0.038$ ), 1286 refined parameters,  $R1 = 0.0705$ ,  $wR2 = 0.1431$ . One cluster is well defined in the asymmetric unit; 6  $TPA^+$  cations and a few  $CH_3CN$  sites were refined in disorder model.  $(TEAH)_6[H_3W_{18}O_{56}(IO_6)] \cdot 2H_2O$  **3**:  $C_{36}H_{103}IN_6O_{82}W_{18}$ ,  $M_r = 5368.44$ ; block crystal:  $0.16 \times 0.12 \times 0.10 \text{ mm}^3$ ;  $T = 100(2) \text{ K}$ . Trigonal,  $R3$ ,  $a = 21.7727(5)$ ,  $c = 19.2462(11) \text{ \AA}$ ,  $V = 7901.3(5) \text{ \AA}^3$ ,  $Z = 3$ ,  $\rho = 3.385 \text{ g cm}^{-3}$ ,  $\mu(\text{MoK}\alpha) = 19.963 \text{ mm}^{-1}$ ,  $F(000) = 7206$ , 24434 reflections measured, 3021 unique ( $R_{\text{int}} = 0.088$ ), 240 refined parameters,  $R1 = 0.0332$ ,  $wR2 = 0.0784$ . One sixth of the cluster and a  $TEAH^+$  molecule were found in the asymmetric unit with a number of disordered solvent water sites which sum to 2 water molecules per cluster. Crystal data were measured on a Bruker ApexII CCD diffractometer using  $Mo K\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at  $100(2) \text{ K}$ . Further details of the crystal structure investigation (**1**) may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, [http://www.fiz-karlsruhe.de/request\\_for\\_deposited\\_data.html](http://www.fiz-karlsruhe.de/request_for_deposited_data.html)) on quoting number CSD 418917. CCDC-670205 (**2**) and CCDC-670206 (**3**) also contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).
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