

Development of a Building Block Strategy To Access Gigantic Nanoscale Heteropolyoxotungstates by Using SeO_3^{2-} as a Template Linker**

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Polyoxometalates (POMs) have potential in nanoscience due to the range of available building blocks that can allow the assembly of new nano-objects with configurable architectures.^[1–5] This, in turn, promises to lead to nanosystems with predefined functions, applications, and the discovery of new phenomena.^[6–8] Heteropolyoxometalates are an important subset of POMs. Within this class, the choice of the heteroelement not only determines certain physical properties of the cluster, but increasingly has been found to control the range and connectivity of the building blocks.^[9–12]

High nuclearity POM clusters based on Mo centers are well known; for example, $\{\text{Mo}_{132}\}$ and $\{\text{Mo}_{154}\}$ ^[13–16] clusters are synthetically accessible due to the occurrence of pentagonal and mixed-valence building blocks.^[17–19] In contrast, the exploration of high nuclearity polyoxotungstate clusters has yielded different results with somewhat lower nuclearity isopolyoxotungstates: $\{\text{W}_{34}\}$ and $\{\text{W}_{36}\}$,^[20,21] and has been more limited since tungsten-based building blocks with pentagonal geometries have only very recently been accessed.^[22–23] Instead, the use of extra linking heteroatoms are required to generate large architectures, as shown by the heteropolyoxotungstate anion $[\text{As}^{\text{III}}_6\text{W}_{65}\text{O}_{217}(\text{H}_2\text{O})_7]^{26-}$, which is the largest cluster in this class with six $\{\text{W}_9\text{As}\}$ units linked by $\{\text{WO}_6\}$ units.^[24] Further, the introduction of electrophilic linkers can result in the assembly of even bigger clusters such as the unsurpassed $[\text{As}^{\text{III}}_{12}\text{Ce}_{16}(\text{H}_2\text{O})_{36}\text{W}_{148}\text{O}_{524}]^{76-}$, and $[\text{Sn}(\text{CH}_3)_2(\text{H}_2\text{O})]_{24}[\text{Sn}(\text{CH}_3)_2]_{12}(\text{As}^{\text{V}}\text{W}_9\text{O}_{34})_{12}]^{36-}$,^[25,26] and most recently the synthesis of the spectacular $\{\text{W}_{72}\text{Fe}_{30}\}$ “Keplerate”.^[23]

Herein, we demonstrate that it is possible to generate gigantic heteropolyoxotungstates by utilizing the SeO_3^{2-} heteroanion. Furthermore, it is possible to control the size, shape, and nuclearity as a function of the ratio of W:Se employed during the synthesis. Structurally, the use of the SeO_3^{2-} heteroanion effectively prevents the ‘closure’ of the cluster assemblies to the Keggin-type cluster, and instead

gives rise to “open” lacunary $\{\text{W}_9\text{Se}\}$ units, which can be viewed as “inorganic ligands”.^[27–29] As a result, by using $\{\text{W}_9\text{Se}\}$ -based units, a series of polyoxotungstate anions have been isolated and characterized, such as $\text{K}_{22}\text{Na}_2[\text{H}_2\text{W}_{43}\text{Se}_3\text{O}_{148}]\cdot 65\text{H}_2\text{O}$ (**1**), $\text{K}_{20}\text{Na}_{24}[\text{H}_4\text{W}_{77}\text{Se}_5\text{O}_{265}]\cdot 220\text{H}_2\text{O}$ (**2**), and $\text{K}_{16}\text{Na}_{18}[\text{H}_6\text{W}_{63}\text{Se}_6\text{O}_{221}]\cdot 105\text{H}_2\text{O}$ (**3**). Not only are all these species synthesized under simple room-temperature “one-pot” conditions, these clusters also contain W-based “defect” $\{\text{W}(\text{W}_4)\}$ pentagonal units. Furthermore we present the first system that employs a lacunary building block to capture a high nuclearity tungstate fragment, leading to the assembly and isolation of the gigantic nanosized cluster $\text{K}_{52}[(\text{H}_8\text{W}_{100}\text{Se}_{16}\text{O}_{364})\text{WO}(\text{H}_2\text{O})_2]\cdot 174\text{H}_2\text{O}$ (**4**). This represents the largest ‘pure’ heteropolyoxotungstate so far characterized which does not employ heterometallic electrophilic linkers connecting the POM subunits.^[30]

Compound **1** is synthesized at pH 4.0 from the reaction of K_2WO_4 and Na_2SeO_3 (W:Se molar ratio 5:1) and structural analysis of $[\text{H}_2\text{W}_{43}\text{O}_{139}(\text{SeO}_3)_3]^{24-}$ (**1a**) shows that the cluster contains three $\{\text{W}_9\text{Se}\}$ subunits with an average Se–O bond length of 1.72 Å and a metal core assembled from 16 W centers. The $\{\text{W}_{16}\}$ “core” contains a unique $\{\text{W}_7\}$ building block comprising a pentagonal $\text{W}(\text{W}_4)$ unit plus two corner-sharing $\{\text{WO}_6\}$, as well as a $\{\text{W}_3\text{O}_{13}\}$ unit and six $\{\text{WO}_6\}$ linkers to give a core that has the three $\{\text{W}_9\text{Se}\}$ units bolted on to give the overall cluster. The average W–O bond length in the pentagonal $\{\text{WO}_7\}$ unit is 2.01 Å and it is slightly longer than that found in the $\{\text{WO}_6\}$ units. Finally, the central $\{\text{W}_3\text{O}_{13}\}$ unit (Figure 1) appears to be doubly protonated with the protons located near the central $\mu_3\text{-O}$ ligand according to the BVS calculations, and the clusters are themselves paired into a

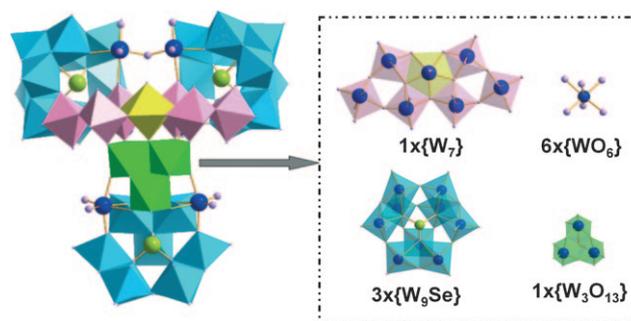


Figure 1. Representation of the structure $[\text{H}_2\text{W}_{43}\text{O}_{139}(\text{SeO}_3)_3]^{24-}$ (**1a**, left) and its building blocks (right): The $\{\text{SeW}_9\}$ units are shown in cyan, the $\{\text{W}_7\}$ units are shown in pink, and the pentagonal W center is yellow. The $\{\text{W}_3\text{O}_{13}\}$ unit is green and the $\{\text{WO}_6\}$ and Se linkers are shown in ball-and-stick mode (W: blue, O: pink, Se: green).

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supramolecular ‘bowl’, which contains 12 K^+ ions, through hydrogen-bonded interactions between the terminal oxygen atoms (see Figure S1 in the Supporting Information).

When the ionic strength of SeO_3^{2-} was increased while decreasing the W:Se molar ratio (10:1), the solution yields an even higher nuclearity anion $[H_4W_{77}O_{250}(SeO_3)_5]^{44-}$ (**2a**, see Figure 2). This cluster can be divided into three subunits that are linked by two $\{WO_6\}$ units. The first part is derived from

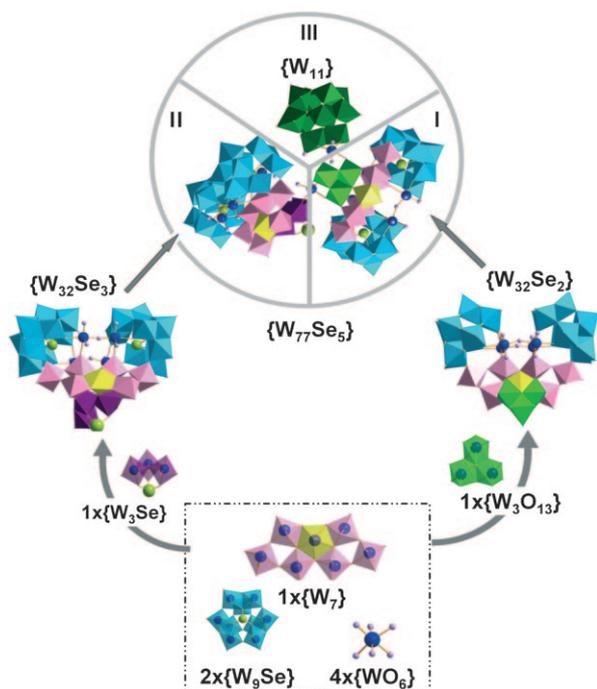


Figure 2. Representation of the structure $[H_4W_{77}O_{250}(SeO_3)_5]^{44-}$ (**2a**, top) and its building blocks (down): The $\{W_{11}\}$ unit is shown in a green polyhedral representation, the $\{W_9Se\}$ units in cyan, the $\{W_7\}$ units in pink, and the pentagonal W center is highlighted in yellow. The $\{W_3O_{13}\}$ unit is shown in light green. The $\{W_3Se\}$ unit is shown as purple polyhedra, and the $\{WO_6\}$ and Se linkers are shown in ball-and-stick mode (W: blue, O: pink, Se: green).

the parent $[H_2W_{43}O_{139}(SeO_3)_3]^{24-}$ cluster **1a**, which loses one of the terminal $\{W_9Se\}$ units thus forms a $\{W_{32}Se_2\}$ fragment plus two $\{WO_6\}$ linker ‘‘arms’’, and these two ‘‘arms’’ are linked to the other two parts separately. The second subunit can be described as a $\{W_{32}Se_3\}$ unit, which also contains two $\{W_9Se\}$ building blocks and a $\{W_7\}$ unit, which has a pentagonal $\{WO_7\}$ core similar to that found in the $\{W_{32}Se_2\}$ fragment. The only difference between these two fragments is that $\{W_{32}Se_2\}$ only contains a $\{W_3O_{13}\}$ unit, whereas the $\{W_{32}Se_3\}$ unit supports an extra SeO_3 linking to these three W centers to form a $\{W_3Se\}$ building block. The overall architecture is completed by the incorporation of a classical $\{W_{11}\}$ unit, which can be isolated as a separate cluster $[H_4W_{11}O_{38}]^{6-}$ [31], and has been observed as a building block in the isopolyoxotungstates $[H_4W_{22}O_{74}]^{12-}$ and $[H_6W_{34}O_{112}]^{22-}$ [21].

To explore the assembly of **2**, acetic acid was used as a pH buffer, but the initial SeO_3^{2-} concentration was also decreased

while increasing the W:Se molar ratio back to 5:1 and this led to the discovery of $[H_6W_{63}O_{203}(SeO_3)_6]^{34-}$ (**3a**, see Figure 3). This shows that the overall cluster is composed of two parts,

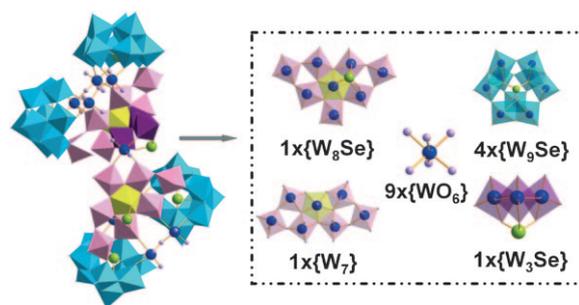


Figure 3. Representation of the structure $[H_6W_{63}O_{203}(SeO_3)_6]^{34-}$ (**3a**, left) and its building blocks (right): The $\{W_9Se\}$ units are shown in cyan, the $\{W_7\}$ units are shown in pink, and the pentagon geometric W is highlighted in yellow. The $\{W_3Se\}$ unit is shown as violet polyhedra, and the $\{WO_6\}$ and Se linker are shown in ball-and-stick mode (W: blue, O: pink, Se: green).

which are linked by one $\{WO_6\}$ unit. The top part is the same as the $\{W_{32}Se_3\}$ building block mentioned before, and the bottom part contains two $\{W_9Se\}$ and four $\{WO_6\}$ linkers plus a unique $\{W_8Se\}$ fragment. Crucially, the appearance of an additional SeO_3^{2-} bridging ligand in the $\{W_7\}$ unit changes the assembly mode of this fragment, which allows the incorporation of another $\{WO_6\}$ to the pentagonal W center, thus the $\{W_7\}$ building block found in **1a** and **2a** turns into a $\{W_8Se\}$ unit (see Figure 3). This kind of unit is unique since it can be utilized in the construction of high nuclearity clusters and these three clusters are also the first heteropolyoxotungstates isolated that are based on building blocks where molybdate cluster analogues are *not* known. Further, these clusters are isolated under ambient ‘‘one-pot’’ reaction conditions and contain pentagonal W-based building blocks.

By comparing the extended 3D structure of the three clusters and the different synthetic conditions required to isolate these systems, it is possible to propose a few basic experiential rules for the assembly of tungstoselenite polyoxometalates. First, potassium cations are crucial for the formation of the building blocks and the cluster architecture, especially since it is ligated by the cluster surface (between two $\{W_9Se\}$ units). Second, SeO_3^{2-} can act as a flexible linker. The SeO_3^{2-} in solution can not only form $\{W_9Se\}$ units, but also assemble into the new building blocks such as $\{W_3Se\}$ or $\{W_8Se\}$ as a function of concentration, thus playing the role of anion template. Interestingly, increasing the initial SeO_3^{2-} concentration appears to result in the generation of non-centrosymmetric fragments, which then assemble to give high nuclearity, low symmetry, clusters. Finally, the acid type is vital in mediating the self-assembly process from target building blocks, because the clusters always assemble gradually. For instance, the addition of acetic buffer can avoid the formation of the classical $\{W_{11}\}$ isopolyoxotungstate fragment.

The application of these rules in the synthesis, that is, by only using potassium salts (combining K_2WO_4 with excess K_2SeO_3), increasing the Se:W ratio (3:2), and employing

acetic acid, results in the discovery of the biggest heteropolyoxotungstate cluster characterized to date, namely $[(H_8W_{100}Se_{16}O_{364})]^{56-}$ (**4a**, see Figure 4 and Figure S2 in the

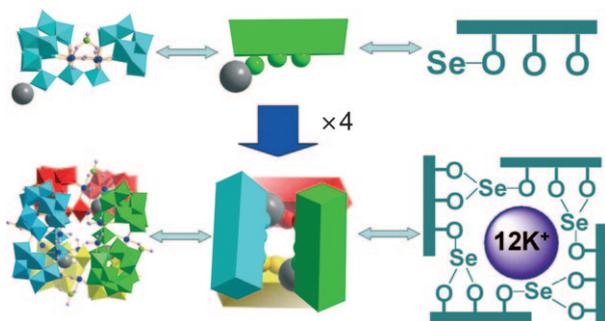


Figure 4. Representation of the assembly mode of $[(H_8W_{100}Se_{16}O_{364})]^{56-}$ (**4a**). Every $\{W_{25}Se_3\}$ branch is shown as a unique color or polyhedron. The $\{WO_6\}$ and $\{SeO_3\}$ linkers are shown ball-and-stick mode (W: blue, O: pink, Se: green) and the “head” Se are highlighted in grey space-filling mode. Of particular interest is the fact that the cavity formed by the four subunits contains 12 potassium cations.

Supporting Information). The cluster is constructed from eight Se^{IV} linkers and four equal fragments that can be assigned as $\{W_{25}Se_2\}$, which are derived from the aforementioned $\{W_{22}Se_2\}$ fragment. The half-open cavity of $\{W_{22}Se_2\}$ is occupied by three corner-shared $\{WO_6\}$ units and a K^+ ion, which results in the formation of a $\{W_{25}Se_2K\}$ subunit (see Figure 5).

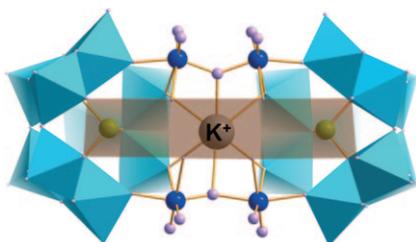


Figure 5. Representation of the structure $\{W_{25}Se_2K\}$: The $\{W_9Se\}$ are shown as cyan polyhedra. The K^+ ion is shown in space-filling mode, and the cavity is highlighted in brown. The $\{WO_6\}$ and Se linkers are shown in ball-and-stick mode (W: blue, O: pink, Se: green).

Structural and chemical analysis show that the overall cluster **4a** is charge balanced by 52 potassium cations and one disordered W center. In addition, the excess SeO_3^{2-} plays the vital role of “assistant” template and links two corner-sharing $\{WO_6\}$ linkers between two $\{W_9Se\}$ units on one side in the $\{W_{22}Se_2\}$ unit and thus forms a new type of building block: $\{W_{25}Se_3\}$. To assemble the overall $\{W_{100}Se_{16}\}$ cluster, the four $\{W_{25}Se_3\}$ subunits are linked by another four SeO_3^{2-} groups in a “head-to-tail” mode. In the assembly process, the “head” linker SeO_3^{2-} is always connected to the $\{WO_6\}$ “tail” from another building unit. The W centers are fixed by the Se-O-W interaction, thereby preventing any K/W disorder in the core

of the cluster because of this kind of unique interaction and this coordination mode also results in a new nanosized cavity with a “kite-shaped” cavity that is occupied by 12 K^+ ions.

In summary, by utilizing a “one-pot” synthetic strategy employing SeO_3^{2-} as both a heterotemplate, and linker, a group of new high nuclearity polyoxotungstates have been discovered. Also, not only are these clusters **1a** $\{W_{43}Se_3\}$, **2a** $\{W_{77}Se_3\}$, **3a** $\{W_{63}Se_6\}$ “pure” heteropolytungstate cluster anions, but they also incorporate common building units with pentagonal geometry and thus possess great potential for the development of spherical and toroidal clusters based purely on tungstate, perhaps even in analogy to the molybdate-based systems.^[13–16] Such clusters have a great deal of potential in the construction of new nanomaterials with many applications, and the ability to engineer low symmetry systems is also of fundamental interest. Finally, the assembly of the gigantic $\{W_{100}Se_{16}\}$, **4a**, showed that the general approach used for the synthesis and discovery of these clusters has a general applicability and we expect a whole new family of Se-based polyoxotungstates to be discovered in the future.

Experimental Section

Synthesis of $K_{22}Na_2[H_2W_{43}O_{139}(SeO_3)_3] \cdot 65H_2O$ (1**):** Na_2SeO_3 (0.1 g, 0.58 mmol) and K_2WO_4 (1.0 g, 3.0 mmol) were dissolved in water (40 mL). Hydrochloric acid (37%) was added with stirring to adjust the pH to 4.0, and then the solution was filtered. Slow evaporation of the filtrate in air resulted in colorless block crystals of **1** forming in four weeks. Yield: 5.7% (0.05 g, 0.0041 mmol). IR (KBr disk): $\tilde{\nu} = 3404, 1620, 962.5, 879.6, 817.8, 704\text{ cm}^{-1}$. Elemental analysis calcd (%) (part of lattice water was lost): W 64.5, K 7.0, Na 0.38, Se 1.9; found: W 64.1, K 6.8, Na 0.3, Se 1.9.

Synthesis of $K_{20}Na_{24}[H_4W_{77}O_{250}(SeO_3)_5] \cdot 220H_2O$ (2**):** Potassium chloride (0.5 g, 7.3 mmol), Na_2SeO_3 (0.4 g, 2.3 mmol), and $Na_2WO_4 \cdot 2H_2O$ (8.1 g, 24.5 mmol) were dissolved in water (50 mL). Hydrochloric acid (37%) was added with stirring to adjust the pH to 4.0, and then the solution was filtered. Slow evaporation of the filtrate in air resulted in colorless block crystals of **2** forming in two days. Yield: 10% (0.8 g, 0.037 mmol). IR (KBr disk): $\tilde{\nu} = 3404, 1624, 964, 945, 817, 742\text{ cm}^{-1}$. Elemental analysis calcd (%) (part of lattice water was lost): W 65.1, K 3.6, Na 2.5, Se 1.8; found: W 64.8, K 3.5, Na 2.3, Se 2.0.

Synthesis of $K_{16}Na_{18}[H_6W_{63}O_{203}(SeO_3)_6] \cdot 105H_2O$ (3**):** Potassium chloride (0.8 g, 10 mmol), Na_2SeO_3 (0.4 g, 2.3 mmol), and $Na_2WO_4 \cdot 2H_2O$ (3.2 g, 10 mmol) were dissolved in water (40 mL). Acetic acid (50%) was added with stirring to adjust the pH to 4.5, and then the solution was filtered. Slow evaporation of the filtrate in air resulted in colorless block crystals of **3** forming in two weeks. Yield: 16% (0.5 g, 0.03 mmol). IR (KBr disk): $\tilde{\nu} = 3389, 1624, 1554, 1412, 964, 945, 879, 817, 732, 669\text{ cm}^{-1}$. Elemental analysis calcd (%) (part of lattice water was lost): W 64.7, K 3.5, Na 2.3, Se 2.6; found: W 64.9, K 3.8, Na 2.6, Se 2.5.

Synthesis of $K_{32}[H_8W_{101}O_{317}(SeO_3)_{16}(H_2O)_2] \cdot 174H_2O$ (4**):** K_2SeO_3 (0.5 g, 2.4 mmol) and K_2WO_4 (1.1 g, 3.4 mmol) were dissolved in water (50 mL). Acetic acid (50%) was added with stirring to adjust the pH to 4.0, and then the solution was filtered. Slow evaporation of the filtrate in air resulted in colorless block crystals of **4** forming in two weeks. Yield: 30% (0.3 g, 0.01 mmol). IR (KBr disk): $\tilde{\nu} = 3408.3, 1622.2, 962.5, 947, 877.6, 817, 754, 680, 669, 651\text{ cm}^{-1}$. Elemental analysis calcd (%) (part of lattice water was lost): W 62.7, K 6.8, Se 4.3; found: W 62.8, K 6.8, Se 4.3.

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- [30] Crystal data and structure refinement for $K_{22}Na_2[H_2W_{43}Se_3O_{148}] \cdot 65H_2O$ (**1**): $H_{132}K_{22}Na_2O_{213}Se_2W_{43}$, $M_r = 12589.7$; block crystal: $0.17 \times 0.07 \times 0.06$, $T = 150(2)$ K. triclinic, space group $P\bar{1}$, $a = 20.4549(2)$, $b = 24.4531(3)$, $c = 45.7199(4)$ Å, $\alpha = 93.526(1)$, $\beta = 98.666(1)$, $\gamma = 113.660(1)^\circ$, $V = 20518.3(4)$ Å³, $Z = 4$, $\rho = 4.076$ g cm⁻³, $\mu(Cu_{K\alpha}) = 48.958$ mm⁻¹, $F(000) = 22240$, 143393 reflections measured, of which 47218 are independent ($R_{int} = 0.0465$), 4076 refined parameters, $R_1 = 0.0591$, $wR_2 = 0.1648$.
- $K_{20}Na_{24}[H_4W_{77}Se_5O_{265}] \cdot 220H_2O$ (**2**): $H_{444}K_{20}Na_{24}O_{485}Se_5W_{77}$, $M_r = 24092.56$; block crystal: $0.11 \times 0.04 \times 0.02$, $T = 150(2)$ K. triclinic, space group $P\bar{1}$, $a = 26.8581(4)$, $b = 29.0056(5)$, $c = 33.4768(6)$ Å, $\alpha = 97.585(1)$, $\beta = 105.877(1)$, $\gamma = 101.970(1)^\circ$, $V = 24040.5(7)$ Å³, $Z = 2$, $\rho = 3.328$ g cm⁻³, $\mu(Cu_{K\alpha}) = 36.319$ mm⁻¹, $F(000) = 21672$, 156438 reflections measured, of which 50551 are independent ($R_{int} = 0.0539$), 2371 refined parameters, $R_1 = 0.0550$, $wR_2 = 0.1387$.
- $K_{16}Na_{18}[H_6W_{63}Se_6O_{221}] \cdot 105H_2O$ (**3**): $H_{216}K_{16}Na_{18}O_{326}Se_6W_{63}$, $M_r = 18529.46$; prism crystal: $0.05 \times 0.04 \times 0.03$, $T = 150(2)$ K. monoclinic, space group $C2/c$, $a = 49.1155(5)$, $b = 21.4649(3)$, $c = 62.4914(8)$ Å, $\beta = 97.969(2)$, $V = 65245.9(14)$ Å³, $Z = 8$, $\rho = 3.773$ g cm⁻³, $\mu(Cu_{K\alpha}) = 43.712$ mm⁻¹, $F(000) = 65536$, 167729 reflections measured, of which 41895 are independent ($R_{int} = 0.0846$), 3033 refined parameters, $R_1 = 0.0592$, $wR_2 = 0.1681$.
- $K_{52}[(H_8W_{100}Se_{16}O_{364})WO(H_2O)_2] \cdot 174H_2O$ (**4**): $H_{360}K_{52}O_{541}Se_{16}W_{101}$, $M_r = 30884.29$; block crystal: $0.16 \times 0.09 \times 0.07$, $T = 150(2)$ K. monoclinic, space group $C2/c$, $a = 32.9318(1)$, $b = 56.5451(2)$, $c = 30.0523(2)$ Å, $\beta = 102.617(1)$, $V = 54610.0(4)$ Å³, $Z = 4$, $\rho = 3.756$ g cm⁻³, $\mu(Cu_{K\alpha}) = 43.969$ mm⁻¹, $F(000) = 54776$, 133869 reflections measured, of which 33717 are independent ($R_{int} = 0.0354$), 2333 refined parameters, $R_1 = 0.0510$, $wR_2 = 0.1406$. Several potassium cations and a few solvent water sites were refined by using a disorder model. The BVS calculation was used to determine the protonation site of all the clusters. Crystal data were measured on an Oxford Diffraction Gemini CCD diffractometer using $Cu_{K\alpha}$ radiation ($\lambda = 1.54184$ Å) at 150(2) K. CSD 759222 (**1**), 759223 (**2**), 759224 (**3**), and 759225 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de).
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