Uranium Oxo Clusters

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Self-Assembly of Polyoxo Clusters and Extended Frameworks by Controlled Hydrolysis of Low-Valent Uranium**

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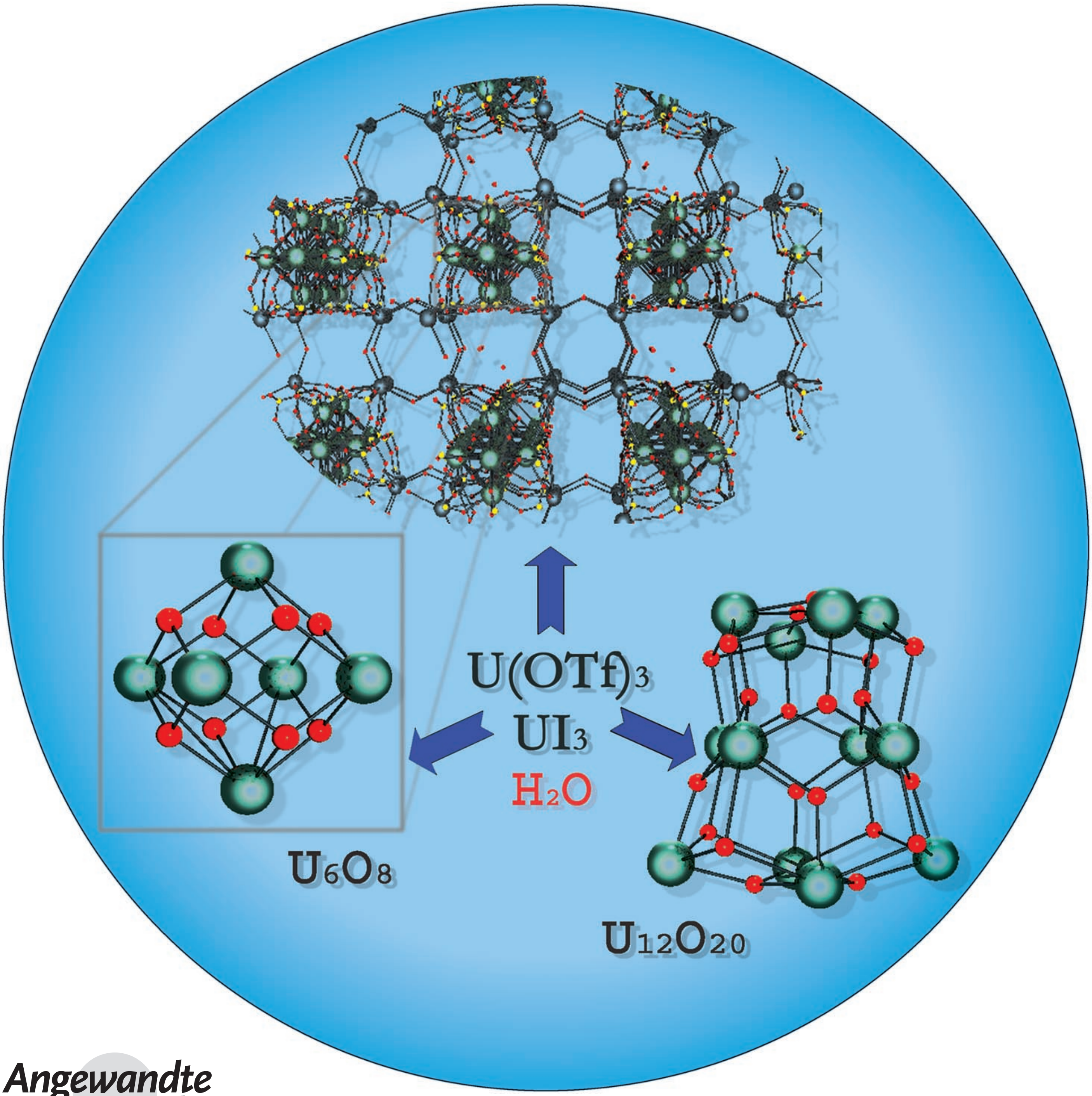

Actinide-based compounds are of great current interest not only for their relevance in the nuclear industry and the associated environmental concerns but also for their rich structural chemistry and attractive magnetic and electrochemical properties, which could lead to the development of new functional materials.[1] Of particular current interest is the self-assembly of large actinide-based clusters[2] and extended frameworks.[3–5]

Actinide-based clusters represent an attractive alternative to transition metals for the design of molecular nanomagnets.[6] Furthermore, nanoparticle formation is important in the environmental mobility of Pu^{IV}.[7,8] Similarly, molecular-scale uranium(IV) oxide clusters have been shown to form in the bacterial reduction of U^{VI}, and the solubility and reactivity of these nanoparticles are likely to strongly affect the environmental fate of uranium.[9] Despite its relevance, the cluster chemistry of actinides remains limited to a few examples,[10–15] while the very recent isolation of several astounding nanosized structures, including uranium nanotubules and nanospheres, has opened new fascinating perspectives in this area.[16,17] In particular, it is surprising that since the first report of a uranium cluster containing an isopolyoxometalate U_6O_8 core in 1952[18] only three additional examples of well-characterized uranium oxo clusters—all hexanuclear—have been described.[10–12] This contrasts dramatically with the extensive structural variety of transition-metal polyoxometalate compounds[19–21] despite the similarity of the chemical properties of uranium with respect to Mo and W.

While alkaline peroxide conditions have allowed the isolation of uranium nanoclusters containing the diamagnetic $U^{VI}O^{2+}$ group,[17] the access to clusters containing U^{IV} ($5f^2$) or U^{V} ($5f^1$), which are more attractive for the design of new magnetic materials,[21–24] requires the development of different synthetic conditions. The seminal work of Duval and coworkers[10] showed that the oxidation of an unidentified low-valent uranium species with pyridine *N*-oxide (PyNO) leads to the isolation of an organometallic U_6O_{13} cluster. This work suggests that the controlled oxidation of low-valent uranium species in non-aqueous conditions might be the key to the synthesis of uranium oxoclusters. The use of non-aqueous conditions prevents the formation of trans-dioxouranyl $U^{VI}O_2^{2+}$ compounds, which are the most stable form of uranium in aqueous media. However, previous studies of oxidation chemistry of trivalent uranium by controlled addition of water or other oxidizing agents performed in our group led only to the formation of mononuclear or trinuclear oxo complexes of U^{IV} in the presence of tetradentate amines,[25] while controlled oxidation of $[UI_3(thf)_4]$ in pyridine by PyNO or by PyNO and H_2O produces respectively the $U^{VI}O_2^{2+}$ and $U^{V}O_2^{+}$ pyridine solvates $[UO_2I_2(Py)_3]$ and $\{(UO_2Py_5)(KI_2Py_2)\}_n$.[26]

Here we show that the controlled hydrolysis of trivalent uranium in acetonitrile can indeed lead to the self-assembly of a large dodecanuclear discrete oxide cluster in a pure form or to mixtures of discrete clusters and extended networks depending on the ligand (iodide or trifluoromethanesulfonate (triflate)) and on the reaction time. A series of mixed-valence uranium oxo clusters were structurally characterized, anticipating the fascinating structural variety of this chemistry. We found four remarkably different structures (Figure 1) resulting from this process: 1) a discrete mixed-valence ($2\,U^{IV}/4\,U^{V}$) hexanuclear cluster, 2) a 2D array of mixed-valence ($4\,U^{IV}/2\,U^{V}$) hexanuclear clusters, 3) an unprecedented 3D framework with zeolite-like topology composed of U^{IV} hexanuclear clusters and potassium ions, and 4) a discrete mixed-valence ($10\,U^{IV}/2\,U^{V}$) dodecanuclear cluster with an unprecedented $U_{12}O_{20}$ core.

The reaction of $[UI_3(thf)_4]$[27] with two equivalents of H_2O in the presence of potassium triflate at room temperature in acetonitrile results in a rapid color change of the solution from dark green to brown. After 15 h, the color of the

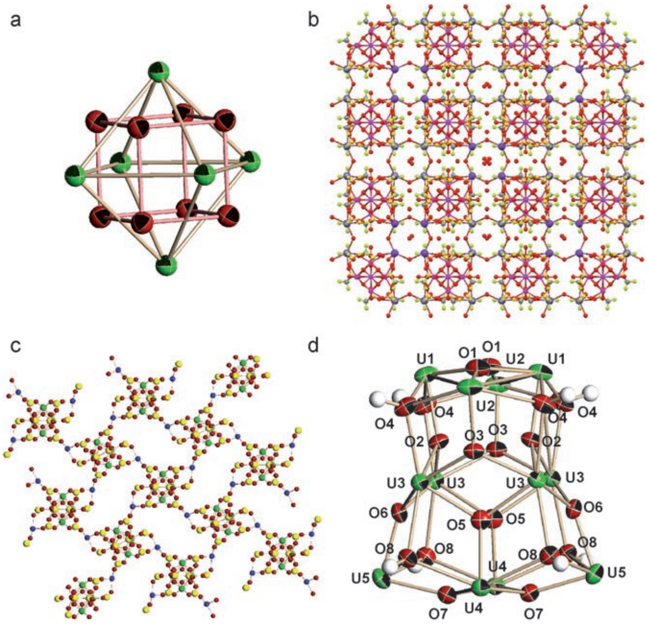

Figure 1. a) ORTEP view of the O_h-symmetric U_6O_8 core found in the clusters **2**, **3**, and **4** (thermal ellipsoids are shown at the 30% probability level; U green, O red). b) Extended 3D framework formed by complex **2** (Mercury 1.4.1; U green, K blue, O red, S yellow). c) Extended 2D framework formed by complex **3** (XSHELL version 4.02; carbon and fluorine atoms are omitted for clarity; U green, K blue, O red, S yellow). d) ORTEP view of the $U_{12}O_{20}$ cluster core in the complex **1** (thermal ellipsoids are shown at the 30% probability level).

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reaction mixture changes from brown to the final emerald green. The evolution of the UV/Vis/NIR spectra during the hydrolysis reaction (Figure S1 in the Supporting Information) shows that the reaction is complete after 15 h as indicated by the disappearance of the NIR band at 910 nm assigned to the $[U^{III}(CH_3CN)_9]^{3+}$ chromophore.[28] Addition of diisopropyl ether to the reaction mixture after 15 h allows the reproducible and quantitative isolation in pure form of the dodecanuclear cluster $[U_{12}(\mu_3\text{-}OH)_8(\mu_3\text{-}O)_{12}I_2(\mu_2\text{-}OTf)_{16}(CH_3CN)_8]\cdot 2\,CH_3CN\,2\,H_2O$ (**1**), which presents the new $U_{12}O_{20}$ core, as the final reaction product. Cluster **1** reacts rapidly with oxygen, while no further reactivity was observed by UV spectroscopy in the presence of excess water (up to 50 equiv).

The slow diffusion of diisopropyl ether into the reaction mixture immediately after mixing the reagents and before completion of the reaction leads to the isolation of a mixture of **1** and different intermediate products. X-ray analysis revealed the presence of three additional species with different structures, namely the 3D $\{[U_6(\mu_3\text{-}O)_8(\mu_2\text{-}OTf)_{12}(H_2O)_{3.5}][K_4(\mu_2\text{-}H_2O)_2(H_2O)_4]\cdot 4.5\,H_2O\}_n$ (**2**), the 2D $[U_6(\mu_3\text{-}O)_8(\mu_2\text{-}OTf)_8(\eta_2\text{-}OTf)_4]K_2$ (**3**) extended networks, and the discrete cluster $[U_6(\mu_3\text{-}O)_8(\mu_2\text{-}OTf)_{12}(H_2O)_3]\cdot 23\,H_2O$ (**4**), all of which contain the same U_6O_8 core. When the $[UI_3(thf)_4]$ starting material is replaced by $[U(OTf)_3(CH_3CN)_3]$[29] in the hydrolysis reaction, the formation of a cluster with nuclearity larger than six is not observed, and mixtures of compounds **2**, **3**, and **4** are isolated even after a month. This outlines the important role of the ligands in directing the cluster formation.

In the discrete hexametallic compound $[U_6(\mu_3\text{-}O)_8(\mu_2\text{-}OTf)_{12}(H_2O)_3]\cdot 23\,H_2O$ (**4**), the six uranium atoms are arranged in perfect O_h symmetry (U–U = 3.71 Å; Figure 1 a). Eight equivalent μ_3-O oxo groups cap each face of the octahedron to form the cluster core U_6O_8 (U–O = 2.26(1) Å). The overall charge of 28− distributed over the neutral complex **4** gives an average charge of +4.66 for uranium. The U−O bond lengths are in agreement with a formal interpretation in terms of the presence of two U^{IV} and four U^{V} ions, while the high symmetry of this mixed-valence cluster suggests that the valency is completely delocalized.

In the second type of isolated crystals, the U_6O_8 octahedrons are arranged in a 3D network with the formula $\{[U_6(\mu_3\text{-}O)_8(\mu_2\text{-}OTf)_{12}(H_2O)_{3.5}][K_4(\mu_2\text{-}H_2O)_2(H_2O)_4]\cdot 4.5\,H_2O\}_n$ (**2**), which presents a zeolite-like topology with a large nanosized cavity occupied by water molecules. The overall cluster charge is in agreement with the presence of six U^{IV} ions. On each one of the four non-adjacent faces of the octahedron, three oxygen centers from three different triflate anions bind a potassium ion. The four potassium ions form a tetrahedron (K–K = 12.36 Å) which include the uranium cluster (Figure S5 in the Supporting Information). Eight potassium tetrahedrons are connected together by bridging water molecules to form the 3D network (Figure 1 b). This framework has a zeolite-like topology with two different types of adjacent cavities. Eight U_6O_8 clusters are connected by 24 potassium ions to form a large nanosized cavity about 2.5 nm wide with a rhombihexahedron shape which is connected to six cubic cavities 5.4 Å wide formed by eight potassium ions in adjacent unit cells (Figure 2). The square cavity opening, as defined by the shortest K–K contact, is about 2.6 Å wide. Both cavities contain water molecules. The last 12 twofold rectangular faces are directly connected with the adjacent rhombihexahedron-shaped cavity. Crystals of the 2D coordination network $[U_6(\mu_3\text{-}O)_8(\mu_2\text{-}OTf)_8(\eta_2\text{-}OTf)_4]K_2$ (**3**) were also isolated. In **3**, the bridging triflate anions on two sets of adjacent faces of the D_{2d}-symmetric $U_6(\mu_3\text{-}O)_8$ core bind two potassium ions. Each potassium ion binds also two or three triflate anions from an adjacent cluster leading to the formation of the 2D network (Figure 1 c). The overall charge of 26− distributed over the dianionic cluster $[U_6(\mu_3\text{-}O)_8(\mu_2\text{-}OTf)_8(\eta_2\text{-}OTf)_4]^{2-}$ gives an average charge of +4.33 for the uranium. The U−O bond lengths are in agreement with the presence of four U^{IV} ions and two U^{V} ions.

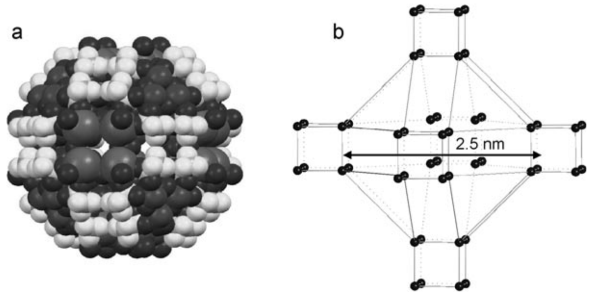

Figure 2. a) Space-fill representation of the rhombihexahedron-shaped cavity in **2** (F white; gray spheres: K large, U medium, O small). b) Polyhedral representation of the cavities formed by the potassium ions in **2**.

Finally, the X-ray crystal structure of **1** reveals the presence of a discrete dodecanuclear oxo/hydroxo complex with a $U_{12}O_{20}$ core (Figure 1 d). The geometrical arrangement of the 12 uranium atoms can be described as a double-decker square-antiprism, in which two stacked distorted square-antiprisms share the square plane formed by the four symmetry-related U3 ions with a total height of 8.3 Å (U1–U5 distance; Figure 3). Each one of the eight triangular faces of each antiprism is capped by triply bridging oxygen atoms resulting in 16 capping oxygens. From the mean U−O distances, two types of triply bridging oxygen atoms can be distinguished which alternate on the triangular faces. The four U−O distances ranging from 2.151 to 2.287 Å have been

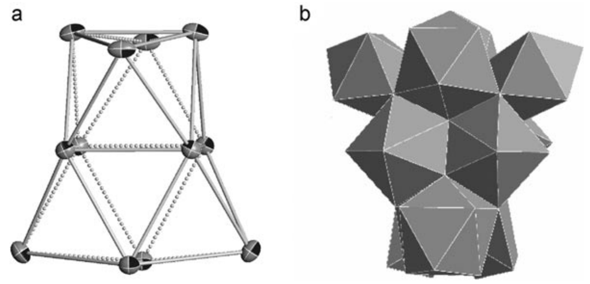

Figure 3. a) ORTEP view of the polyhedron (two adjacent square antiprisms) formed by the 12 uranium atoms in **1** (thermal ellipsoids are shown at the 30% probability level). b) Polyhedral representation of cluster **1**.

assigned to μ_3-O^{2-} groups.[11] The four longer U–O distances ranging from 2.461 to 2.580 Å are in agreement with the presence of μ_3-OH^- groups. Two additional μ_3-oxo groups cap each one of the distorted square faces.

The presence of eight hydroxo ligands, 12 oxo ligands, 16 coordinated OTf^- ions, and two iodide ions adds up to an overall charge of 50– in the neutral complex **1** which, distributed over 12 uranium centers, gives an average positive charge of +4.16. This charge can be formally interpreted in terms of the presence of a mixed-valence cluster with ten U^{IV} (f^2) and two U^V (f^1) ions. The similarity of the U-to-ligand bond lengths for the different uranium atoms is in agreement with a complete delocalization of the charge. The bond valence sum analysis (BVS),[30] a widely used procedure to assign valency in metal clusters, is in agreement with the assigned valences in the four compounds, although the obtained values are more ambiguous for compound **3** (an alternative formulation as $[U_6^{IV}(\mu_3\text{-}O)_6(\mu_3\text{-}OH)_2]$ cannot be ruled out by the BVS analysis). The solid-state magnetic susceptibility (χ_M) of the dodecanuclear cluster **1** was measured in the temperature range 6–300 K in a 500 G (0.05 T) field (the resulting effective magnetic moment (μ_{eff}) is plotted versus temperature in Figure S7 in the Supporting Information). The μ_{eff} value at 300 K is 2.79 μ_B, which is slightly lower than the $\mu_{eff} = 3.33\ \mu_B$ value expected in the presence of ten U^{IV} and two U^V ions behaving as independent paramagnets. The presence of U^{IV} was confirmed by the presence of the typical band[28] at 690 nm in the UV/Vis spectrum (Figure S3 in the Supporting Information). Work is currently in progress to further characterize the magnetic properties of this mixed-valence cluster.

Compound **1** is to our knowledge the largest reported uranium cluster which does not contain actinyl groups, and the first uranium oxo cluster in which the structure of the polyhedral cage represents one of the common coordination geometries of f elements.

The variety of structures isolated from the hydrolysis reaction of U^{III} triflate and iodide salts including a U^{IV} 3D framework with zeolite-like topology and the observed ligand dependency of the nuclearity of the cluster provides impetus for further reactivity studies aimed at isolating pure forms of differently sized uranium oxide clusters. The iodide ligands probably promote the evolution of the initial structural organization based on the hexanuclear core cluster into the assembly of the larger dodecanuclear cluster. Given the number of potential ligands and the number of possible reaction variables that could be envisioned, the scope for the synthesis of new materials is very large.

Uranium oxides have important technological applications, such as fuel for nuclear reactors or catalysis, and large uranium oxide clusters represent a good model for the study of substrate–catalyst interactions and could also provide new soluble materials with different physicochemical properties that should facilitate further applications of uranium oxides. Finally, the assembly of large uranium clusters from the hydrolysis of low-valent uranium could provide important model systems for actinide aggregates involved in the transport of actinides in the environment.

Experimental Section

The synthetic details and analytical data for complex **1** are described in the Supporting Information.

Crystal data for $[U_{12}(\mu_3\text{-}OH)_8(\mu_3\text{-}O)_{12}I_2(\mu_2\text{-}OTf)_{16}(CH_3CN)_8]\cdot 2\,CH_3CN\,2\,H_2O$ (**1**): $C_{36}H_{42}F_{48}I_2N_{10}O_{70}S_{16}U_{12}$, $M_r = 6269.92$, orthorhombic, space group *Cmcm*, $a = 24.999(4)$, $b = 21.689(3)$, $c = 25.688(4)$ Å, $V = 13\,928(3)$ Å^3, $Z = 4$, $\rho_c = 2.990\ \text{g cm}^{-3}$, $\mu = 14.731\ \text{mm}^{-1}$, $T = 193(2)$ K. Of the 34708 reflections collected, 9050 were unique ($R_{int} = 0.0317$). Refinement on all data converged at $R_1 = 0.0692$, $wR2 = 0.1337$. Max/min residual density: 3.119 and $-6.222\ \text{e Å}^{-3}$.

Crystal data for $[U_6(\mu_3\text{-}O)_8(\mu_2\text{-}OTf)_{12}(H_2O)_{3.5}][K_4(\mu_2\text{-}H_2O)_2(H_2O)_4]\cdot 4.5\,H_2O$ (**2**): $C_{12}H_{22}F_{36}K_4O_{70}S_{12}U_6$, $M_r = 3699.60$, cubic, space group $Fm\bar{3}m$, $a = 28.3054(14)$ Å, $V = 22\,678.2(19)$ Å^3, $Z = 8$, $\rho_c = 2.167\ \text{g cm}^{-3}$, $\mu = 9.037\ \text{mm}^{-1}$, $T = 193(2)$ K. Of the 28870 reflections collected, 1523 were unique ($R_{int} = 0.0422$). Refinement on all data converged at $R_1 = 0.0750$, $wR2 = 0.1545$. Max/min residual density: 1.235 and $-0.833\ \text{e Å}^{-3}$.

Crystal data for $[U_6(\mu_3\text{-}O)_8(\mu_2\text{-}OTf)_8(\eta_2\text{-}OTf)_4]K_2$ (**3**): $C_{12}H_{7.50}F_{36}K_2O_{44}S_{12}U_6$, $M_r = 3430.78$, orthorhombic, space group *Cmca*, $a = 23.433(4)$, $b = 18.803(3)$, $c = 21.242(3)$ Å, $V = 9359(3)$ Å^3, $Z = 4$, $\rho_c = 2.435\ \text{g cm}^{-3}$, $\mu = 10.843\ \text{mm}^{-1}$, $T = 193(2)$ K. Of the 29425 reflections collected, 5984 were unique ($R_{int} = 0.0281$). Refinement on all data converged at $R_1 = 0.0716$, $wR2 = 0.1726$. Max/min residual density: 4.822 and $-2.912\ \text{e Å}^{-3}$.

Crystal data for $[U_6(\mu_3\text{-}O)_8(\mu_2\text{-}OTf)_{12}(H_2O)_3]\cdot 23\,H_2O$ (**4**): $C_{12}H_{52}F_{36}O_{70}S_{12}U_6$, $M_r = 3814.44$, cubic, space group $Pm\bar{3}m$, $a = 14.1431(10)$ Å, $V = 2829.0(3)$ Å^3, $Z = 1$, $\rho_c = 2.238\ \text{g cm}^{-3}$, $\mu = 8.925\ \text{mm}^{-1}$, $T = 193(2)$ K. Of the 17997 reflections collected, 764 were unique ($R_{int} = 0.0325$). Refinement on all data converged at $R_1 = 0.0362$, $wR2 = 0.0936$. Max/min residual density: 1.088 and $-0.590\ \text{e Å}^{-3}$.

Data were collected using a Bruker SMART CCD area detector three-circle diffractometer (ω scans, $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, graphite monochromator). CCDC 648363 (**1**), 648361 (**2**), 648362 (**3**), and 648360 (**4**) 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.

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