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**Title:** Structural Snapshots of Cluster Growth from {U6} to {U38} During the Hydrolysis of UCl<sub>4</sub>

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Structural Snapshots of Cluster Growth from {U<sub>6</sub>} to {U<sub>38</sub>} During the Hydrolysis of UCl<sub>4</sub>Lucile Chatelain,<sup>a</sup> Radmila Faizova,<sup>a</sup> Farzaneh Fadaei-Tirani,<sup>a</sup> Jacques Pécaut,<sup>b</sup> and Marinella Mazzanti<sup>\*a</sup>

**Abstract:** Here we report the assembly of large uranium(IV) clusters with novel nuclearities and/or shapes from the controlled hydrolysis of UCl<sub>4</sub> in organic solution and in the presence of the benzoate ligands. {U<sub>6</sub>}, {U<sub>13</sub>}, {U<sub>16</sub>}, {U<sub>24</sub>}, {U<sub>38</sub>} oxo and oxo/hydroxo clusters were isolated and crystallographically characterized. These structural snapshots indicate that larger clusters are slowly built from the condensation of octahedral {U<sub>6</sub>} building blocks. The uranium/benzoate ligand ratio, the reaction temperature and the presence of base play an important role in determining the structure of the final assembly. Moreover, the isolation of different size cluster {U<sub>6</sub>} (few hours), {U<sub>16</sub>} (3 days), {U<sub>24</sub>} (21 days) from the same solution in a chosen set of conditions shows that the assembly of uranium oxo clusters in hydrolytic conditions is time dependent.

The chemistry of uranium clusters has received increasing attention in the last ten years<sup>[1]</sup> due to their potential application in the nuclear-fuel cycle technology, in catalysis or in the design of molecular magnets.<sup>[2]</sup> Moreover, actinide oxo/hydroxo clusters provide useful models for the nanosized species involved in spent fuel separation and in the migration behavior of actinides in the environment.<sup>[1c]</sup> [3] The chemistry of these species is also important for the understanding of geochemical reactions and for the development of new remediation strategies.<sup>[1c, 3c, 4]</sup> [5] Notably, discrete clusters have been isolated from hydrolysis and condensation reactions of low valent actinides in aqueous condition in the presence of anionic ligands such as halides or carboxylic acids.<sup>[1c, 6]</sup>

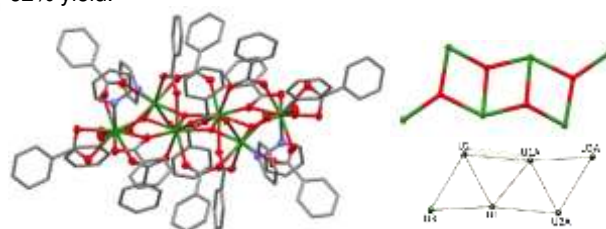
However, the chemistry of uranium oxide clusters remains underdeveloped especially compared to transition metal polyoxometalates.<sup>[1b, 1c, 7]</sup> Moreover, most of the reported uranium clusters<sup>[1b, 8]</sup> [1a] contain uranyl(VI) cations supported by peroxide ligands. A significantly lower number of clusters containing low valent uranium (U(IV) and U(V)) has been characterized.<sup>[1a, 9]</sup> By far the most common structural motif for U(IV) clusters remains the hexameric octahedron with a [U<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub>] or a [U<sub>6</sub>O<sub>8</sub>] core.<sup>[6a, 10]</sup> Low nuclearity (tetra- or penta-nuclear) U(V)/U(IV) oxo clusters have also been isolated from the disproportionation of uranyl(V) complexes of polydentate Schiff bases in non protic media.<sup>[11]</sup> Our group reported the first examples of low-valent (U(IV) and U(IV)/U(V)) high nuclearity uranium clusters that were isolated by controlling the rate of hydrolysis of a uranium(III) precursor ([U<sub>3</sub>(thf)<sub>4</sub>) in organic solution. {U<sub>10</sub>},<sup>[10g]</sup> {U<sub>12</sub>}<sup>[10b]</sup> and {U<sub>16</sub>}

clusters<sup>[10g]</sup> with [U<sub>10</sub>O<sub>8</sub>(OH)<sub>6</sub>], [U<sub>12</sub>O<sub>12</sub>(OH)<sub>8</sub>] and [U<sub>16</sub>O<sub>22</sub>(OH)<sub>2</sub>] cores respectively, were prepared, by using triflate (CF<sub>3</sub>SO<sub>3</sub>)<sup>[10b]</sup> or benzoate (PhCOO<sup>-</sup>) organic capping ligands.<sup>[10g]</sup> More recently, the use of the controlled hydrolysis strategy in the presence of the benzoate capping ligand carried out under solvothermal conditions led to the isolation of a large {U<sub>38</sub>} cluster.<sup>[12]</sup> [13] In spite of these recent reports, the cluster chemistry of low valent uranium remains practically unexplored with a limited number of structures being reported. Moreover, although several studies were directed to identify the factors controlling the formation of hexanuclear clusters in aqueous solution,<sup>[1c, 6b, 6d, 10i, 10k, 14]</sup> the parameters leading to larger U(IV) assemblies and cluster growth remain undetermined.

Here we report several uranium clusters with new shapes and sizes, including a large {U<sub>24</sub>} cluster, that were isolated from the controlled hydrolysis of UCl<sub>4</sub> in organic solution. We also show how, ligand/metal ratio, reaction time, addition of base and temperature determine the growth of different size clusters ({U<sub>6</sub>}, {U<sub>13</sub>}, {U<sub>16</sub>}, {U<sub>24</sub>}, {U<sub>38</sub>}) from the same precursor.

Controlled hydrolysis of UCl<sub>4</sub> in pyridine (or in acetonitrile followed by redissolution in pyridine) in the presence of two equivalents of potassium benzoate and two equivalents of water led to the hexameric U(IV) octahedron [U<sub>6</sub>O<sub>4</sub>(OH)<sub>4</sub>(PhCOO)<sub>12</sub>(Py)<sub>3</sub>], **1** previously obtained from the hydrolysis of UCl<sub>4</sub> in the same conditions.<sup>[10d]</sup> UV-visible studies indicate that the formation of the cluster is slower for UCl<sub>4</sub> than for UCl<sub>3</sub> (Figure S6).

In contrast when the hydrolysis reaction is carried out in the presence of larger amounts of capping ligand (three-six equivalents of potassium benzoate) in acetonitrile an insoluble green/white precipitate was obtained that was only soluble in pyridine. Slow diffusion of diisopropylether (DIPE) into the pyridine solution allowed for the crystallization of the new oxo cluster [U<sub>6</sub>O<sub>4</sub>(PhCOO)<sub>16</sub>(Py)<sub>4</sub>] **2** with a U<sub>6</sub>O<sub>4</sub> core (Figure 1) in 62% yield.



**Figure 1.** Molecular structure of **2** and U<sub>6</sub>O<sub>4</sub> core. (Ellipsoids are set at 30% probability). H atoms, disorder and solvent molecules are removed for clarity, ligands represented as pipes. U green, O red, C grey, N blue. (Atoms A are found with the inversion center). Average bond lengths [Å]: U-μ<sub>3</sub>O=2.24(8).

The structure consists of 6 uranium(IV) ions connected by four oxide and 16 benzoate ligands with 3 crystallographically independent uranium ions. The cluster size is about 26.5×17.5×17 Å<sup>3</sup>, with the largest U-U distance being 10.6 Å. The geometrical arrangement of the 6 uranium atoms can be described as four equilateral triangles (with a 3.8(2) Å long side) that share one edge with each other in the same plane (mean deviation from the plane= 0.09 Å). The increased number of benzoate ligands fits well in the planar [U<sub>6</sub>O<sub>4</sub>] core of cluster **2** while only one benzoate ligand can bridge two adjacent uranium centers in the U<sub>6</sub>O<sub>8</sub> core.

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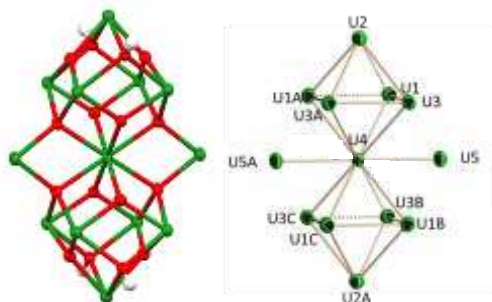
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Therefore, the structure of the hydrolysis product is determined (with all other conditions being equivalent) by the  $\text{UCl}_4$ :benzoate ratio. Clusters of larger size were not isolated from pyridine at any  $\text{UCl}_4$ :benzoate ratio.

In contrast, the hydrolysis of  $\text{UCl}_4$  with 2 equiv. of water in the presence of 2 equiv. of potassium benzoate in acetonitrile resulted in the isolation of two discrete U(IV) oxo/hydroxo clusters with novel  $[\text{U}_{13}\text{K}_x\text{O}_{16}]$  ( $x=2$  or 4) cores and the chemical formulas  $[\text{U}_{13}\text{K}_4\text{O}_{12}(\text{OH})_4(\text{PhCOO})_{12}\text{Cl}_{14}]\text{Cl}_2$  **3** and  $[\text{U}_{13}\text{K}_2\text{O}_9(\text{OH})_7(\text{PhCOO})_{12}\text{Cl}_{16}]\text{Cl}$  **4**, respectively. This result indicates that larger clusters can be obtained in acetonitrile for the  $\text{UCl}_4$ :benzoate ratio of 2. Crystals of these two species were isolated either from a concentrated acetonitrile solution or by slow diffusion of DIPE into an acetonitrile solution after 3 days. The solid state structures of **3** and **4** are presented in Figures 2 and S10 respectively. In both clusters the geometrical arrangement of the 13 uranium atoms can be described as two octahedrons sharing U4 as a common summit with U-U distances ranging from 3.7463(10) Å to 3.8639(5) Å. Two additional oxo-bridged uranium ions are located in the plane between the two octahedrons. The arrangement of the uranium and oxygen atoms is the same for both structures, leading to very small differences in the structural parameters. In both complexes the BVS (bond valence sum)<sup>[15]</sup> is in agreement with the presence of 13 U(IV) ions. However, the charge of the two clusters is different due to differing number of potassium ions and chloride ligands and to the different ratio of bridging oxide/hydroxides. In both complexes the  $\text{U}_{13}\text{O}_{16}$  cores are decorated by bridging benzoate and bridging chloride ligands. The UV-visible spectrum of the mixture of the two clusters features a characteristic band around 690nm assigned to uranium(IV) (Figure S7).<sup>[16]</sup>



**Figure 2.** ORTEP diagrams of the  $\text{U}_{13}\text{K}_4\text{O}_{16}$  core in **3** (ellipsoids are set at 30% probability). U green, O red, H white. Average bond lengths [Å]:  $\text{U}-\mu_3\text{O}=2.27(4)$ ;  $\text{U}-\mu_4\text{O}=2.38(12)$ ;  $\text{U}-\text{OH}=2.46(9)$ .

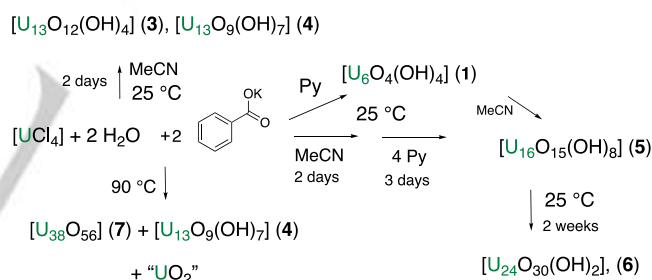
As the two clusters **3** and **4** crystallize under the same conditions, we were not able to separate them. Moreover, only a very small amount of the crystalline mixture of **3** and **4** was reproducibly isolated (15% yield). The  $^1\text{H}$  NMR spectrum in  $\text{CD}_3\text{CN}$  of the reaction mixture, obtained after hydrolysis of  $\text{UCl}_4$  with 2 equiv. of water in the presence of 2 equiv. of potassium benzoate, is broad, whereas the isolated mixture of **3** and **4** gives a well-defined (see Figure S4). Attempts to isolate larger amounts led to a green powder, which does not have the well-defined proton NMR spectrum of **3** and **4**. These observations led us to think that a larger number of species is present in the acetonitrile reaction mixture.

These results reveal that the nature of the precursor has a significant effect on the structure and nuclearity of the final cluster obtained from controlled hydrolysis in acetonitrile in presence of the same capping ligand. Notably, from the hydrolysis of  $\text{U}_3$ , performed in the same conditions as for  $\text{UCl}_4$ , only a mixture of discrete oxo/hydroxo clusters with a  $[\text{U}_{10}\text{O}_{14}]$  core

( $[\text{U}_{10}\text{O}_6(\text{OH})_6(\text{PhCOO})_{12.8}\text{I}_{3.2}(\text{H}_2\text{O})_4(\text{MeCN})_3\text{I}_2]$ )<sup>[109]</sup> was isolated. A similar result was obtained for  $\text{U}_4$  (see supporting information). The two products of hydrolysis ( $[\text{U}_{13}\text{O}_{16}]$  and  $[\text{U}_{10}\text{O}_{14}]$ ) display important structural differences. In particular, beside the difference in nuclearity, the ratio between Cl/benzoate or I/benzoate is 1.17 (14/12) in **3** and **4**, and 0.25 (3.2/12.8) in the  $[\text{U}_{10}\text{O}_{14}]$  cluster, respectively. The higher affinity of U(IV) for hard donors such as chloride and benzoate may slow down the Cl/benzoate ligand exchange and favor the formation of the larger  $[\text{U}_{13}\text{O}_{16}]$  cluster from  $\text{UCl}_4$ .

However, the  $[\text{U}_{10}\text{O}_{14}]$  is also probably present in the reaction mixture obtained after 56 hours upon controlled hydrolysis of  $\text{UCl}_4$  in acetonitrile. Notably, the addition of base (4 equiv. of pyridine) to this mixture yielded after 3 days at 25 °C the new  $\{\text{U}_{16}\}$  cluster  $[\text{U}_{16}\text{O}_{15}(\text{OH})_8(\text{PhCOO})_{26}(\text{Py})_2]$  **5** (Figure 3) with a novel  $[\text{U}_{16}\text{O}_{15}(\text{OH})_8]$  core in 54 % yield (Scheme 1). The structure of **5** is likely to assemble upon the deprotonation of the hydroxo groups of a  $[\text{U}_{10}\text{O}_{14}]$  species present in acetonitrile and further condensation with two additional  $\{\text{U}_6\}$  units. Assembling of **5** from  $[\text{U}_{13}\text{O}_{16}]$  would require a complete disruption of the cluster. After two weeks the larger cluster  $[\text{U}_{24}\text{O}_{30}(\text{OH})_2(\text{PhCOO})_{30}(\text{Py})_4\text{Cl}_4]$ , **6**, (Figure 4) with a  $[\text{U}_{24}\text{O}_{30}(\text{OH})_2]$  core was isolated. This cluster can be built either from  $[\text{U}_{16}\text{O}_{15}(\text{OH})_8]$  or directly from two  $[\text{U}_{13}\text{O}_{16}]$  clusters through further condensation with two additional  $\{\text{U}_6\}$  units promoted by further deprotonation. Compounds **5** and **6** have well identified and unique morphology and could be reliably isolated from the same mother liquor by a time-resolved crystallization process<sup>[17]</sup> where crystals of each cluster are removed from solution before crystallization of the second species.

**Scheme 1.** Synthesis of clusters **1**, **3**, **4**, **5**, **6**, and **7** from the hydrolysis of  $\text{UCl}_4$ .

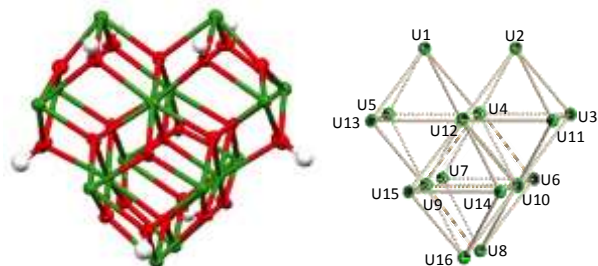


Solubility (the two complexes have both very low solubility, once formed, in acetonitrile) and concentration do not affect the process indicating that the cluster growth after pyridine addition is time-dependent. A similar time-dependency can be anticipated for the assembly of  $\{\text{U}_{13}\}$  from  $\{\text{U}_6\}$  in the absence of base. Notably, if pyridine is added to the hydrolytic acetonitrile mixture after periods of time shorter than 56 hours, only the  $[\text{U}_6\text{O}_8]$  cluster **1** is obtained suggesting that the time-dependent formation of larger clusters such as  $\{\text{U}_{13}\}$  or  $\{\text{U}_{10}\}$  is required in order for the addition of base to result in further assembly.

The X-ray crystal structure of **5** shows the presence of a discrete oxo/hydroxo cluster with a  $[\text{U}_{16}\text{O}_{23}]$  core and a 1.6:1 benzoate/uranium ratio (Figure 3). The geometrical arrangement of the uranium atoms in the  $[\text{U}_{16}\text{O}_{23}]$  core can be described as four fused octahedrons with sixteen crystallographically inequivalent uranium atoms with U-U distances ranging from 3.764(1) Å to 3.858(1) Å. Each octahedron shares three edges of three different neighboring octahedrons. The overall cluster size is approximately  $24 \times 21 \times 22$  Å<sup>3</sup> while the core structure is 7.73 Å wide (U3-U5 distance) and 8.60 Å long (U2-U8 distance). The calculated BVS for the uranium atoms is in agreement with the

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presence of 16 U ions in the +IV oxidation state. An overall positive charge of 64 for the cluster is consistent with the presence of 8 hydroxo and 15 oxo groups in the neutral complex.

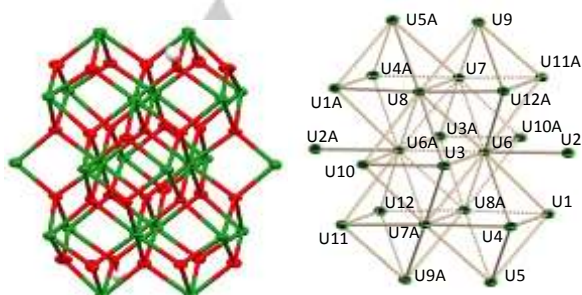


**Figure 3.** ORTEP diagram of the  $[U_{16}O_{15}(\mu_3\text{-OH})_8]$  (left) and  $U_{16}$  (right) core in **5** (ellipsoids are set at 30% probability). U green, O red, H white. Average bond lengths [Å]:  $U-\mu_3O=2.24(3)$ ,  $U-\mu_4O=2.37(8)$ ,  $U-\mu_3OH=2.43(5)$ .

The structure of **5** differs significantly from the previously reported  $\{U_{16}\}$  oxo cluster ( $\{[K(\text{MeCN})_2][U_{16}O_{22}(\text{OH})_2(\text{PhCOO})_{24}]\}$ )<sup>[109]</sup> obtained by addition of a strong base (TMEDA) to the products of controlled hydrolysis of  $U_3$ . Both clusters contain 16 uranium atoms arranged in four fused octahedra sharing common edges. However, the two cores have a different shape and the uranium ions have different oxidation states. The structural parameters and BVS indicate that the sixteen uranium atoms of **5** are in the +IV oxidation state, while the  $[U_{16}O_{22}(\text{OH})_2]$  cluster consists of twelve uranium(IV) ions and four uranium(V) ions. This difference arises from the difference in uranium oxidation state of the precursors used in these reactions. The trivalent uranium precursor is very reactive and unstable towards water. Concomitant with its hydrolysis, U(III) is oxidized to form U(IV) or U(V), while the hydrolysis of U(IV) does not result in a redox reaction.

The X-ray crystal structure of **6** reveals the presence of a novel  $[U_{24}O_{30}(\text{OH})_2]$  core (Figure 4), containing 24 uranium atoms structurally arranged as six fused octahedra. These six octahedrons can be described as three pairs of fused octahedrons, sharing one edge, and perpendicular to each other. In total, each octahedron shares three edges of three different neighboring octahedrons. Two additional uranium centers (U2 and U2A) are located on the straight line defined by the two central uranium atoms (U6 and U6A).

The overall cluster size is approximately  $21 \times 23 \times 21 \text{ \AA}^3$  and the U-U distances range from  $3.6418(7) \text{ \AA}$  to  $3.9030(6) \text{ \AA}$ . The uranium atoms are held in close proximity by 14  $\mu_3$ -oxo and two  $\mu_3$ -hydroxo ligands capping the octahedron triangular faces and 16  $\mu_4$ -oxo ligands bridging uranium from different octahedrons. Bridging benzoate and  $\mu_4$ -chloride anions decorate the cluster core. The presence of 24 U(IV) ions results in a +96 positive charge balanced by 2 hydroxo, 30 oxo, 4 chloride and 30 benzoate groups.

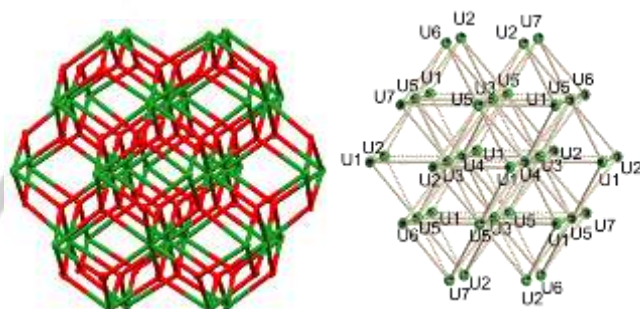


**Figure 4.** ORTEP diagrams of the  $[U_{24}O_{30}(\text{OH})_2]$  (left) and  $U_{24}$  (right) core in **6** (ellipsoids are set at 30% probability). U green, O red, H white. (atoms A are found with the inversion center). Average bond lengths [Å]:  $U-\mu_3O=2.26(5)$ ,  $U-\mu_4O=2.36(6)$ ,  $U-\mu_3OH=2.37(5)$ .

The results obtained in acetonitrile differ significantly from those obtained in pyridine where only the hexanuclear cluster is formed. They also differ from what recently obtained by Knope and coworkers from dissolution of  $UCl_4$  and hydroxybenzoic acid in water or a 50:50 mixture water/acetonitrile where only hexanuclear clusters are formed that evolve upon heating ( $75/100^\circ\text{C}$ ) to yield  $UO_2$  nanoparticles.<sup>[10K]</sup>

We also investigated the influence of the temperature on our system by refluxing, for 32 hours at  $82^\circ\text{C}$  and atmospheric pressure under argon, the mixture of  $UCl_4$  reacted with two equivalents of water and two equivalents of potassium benzoate in acetonitrile (Scheme 1). The slow diffusion of DIPE into the mother liquor yielded a few dark green X-ray quality crystals of  $[U_{38}O_{56}Cl_{18}(\text{PhCOO})_{22}(\text{CH}_3\text{CONH}_2)_{10}]$ , **7** combined to a few crystals of the  $U_{13}K_xO_{16}$  cluster and a darker solid identified as  $UO_2$  by X-ray powder crystallography (XPRD). As previously observed for the hydrolysis of  $UCl_4$  in solvothermal conditions<sup>[12]</sup> [13] larger amounts of water used in the hydrolysis (400 equiv.) result in the unique formation of  $UO_2$ .

The X-ray crystal structure of **7** reveals the presence of a discrete oxo cluster with a  $[U_{38}O_{56}]$  core, with a fluorite-type structural packing (Figure 5). The structure consists of 38 uranium atoms connected together by bridging oxides (56) forming the  $[U_{38}O_{56}]$  core, surrounded by chloride (18), benzoate (22) and acetamide (10) ligands. The cluster size is about  $26 \times 25 \times 23 \text{ \AA}^3$ , with the largest U-U distance being  $12.1 \text{ \AA}$ . The geometrical arrangement of the 38 uranium atoms in the structure can be described as thirteen fused octahedrons with U-U distances ranging from  $3.584(1) \text{ \AA}$  to  $3.8424(7) \text{ \AA}$ . Each external octahedron shares five edges of five different neighboring octahedrons. Thus, the center of the octahedrons forms a centered cuboctahedron and each external uranium ion is placed at the summit of a truncated octahedron (Figure 5).



**Figure 5.** Ortep diagram of the  $[U_{38}O_{56}]$  core in **7** and arrangement of the octahedrons (Ellipsoids are set at 30% probability). U green, O red. Average bond lengths [Å]:  $U-\mu_3O=2.24(3)$ ,  $U-\mu_4O=2.36(3)$ .

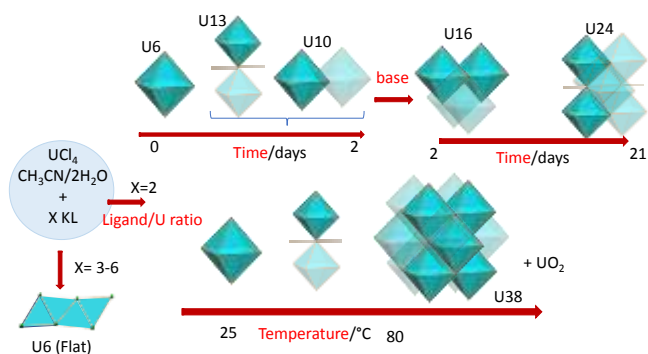
24  $\mu_3$ -O ligands cap 24 triangular faces of the octahedrons; 32  $\mu_4$ -O ligands are located in the tetrahedral cavities formed by adjacent octahedrons. The calculated bond valence sum (BVS) is in agreement with the presence of 56 oxide oxygen atoms and 38 U(IV) ions. The mean U-O distances are  $2.24(3) \text{ \AA}$  for the  $\mu_3$ -O and  $2.36(3) \text{ \AA}$  for the  $\mu_4$ -O atoms.

The acetamide ligand results from the partial hydrolysis of acetonitrile bound to the acidic metal center catalyzed by  $H^+$  released during the formation of the cluster. Nitriles are extremely resistant to hydrolysis, but Lewis acidic metal ions were shown to significantly enhance hydrolysis rates.<sup>[18]</sup>

The core of the structure of **7** is closely related to that of the  $[U_{38}O_{56}Cl_{18}(\text{PhCOO})_{24}(\text{THF})_8]$  cluster isolated from the solvothermal hydrolysis of  $UCl_4$  in THF in the presence of benzoic acid<sup>[12]</sup> and of the Pu(IV) nanoclusters  $Li_{14}(H_2O)_n[Pu_{38}O_{56}Cl_{54}(H_2O)_8]$  and  $Li_2[Pu_{38}O_{56}Cl_{42}(H_2O)_{20}]$ , which

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were isolated from colloidal solutions of plutonium.<sup>[2e, 6g]</sup> While the assignment of the composition and uranium charge remained ambiguous in the previously reported  $[U_{38}O_{56}Cl_{18}]$  cluster, the composition and the uranium oxidation state (+IV) are non-ambiguous in **7**. Due to the very low yield in **7** and to the presence of multiple products further characterization of this cluster was not possible. From a comparison of the structure of  $\{U_{24}\}$  and  $\{U_{38}\}$  it can be clearly seen that the latter builds up from the first through the deprotonation of two hydroxo ligands still present in the  $\{U_{24}\}$  cluster. Attempts to build  $\{U_{38}\}$  from  $\{U_{24}\}$  by using different bases have not been yet successful but should provide a more convenient route to  $\{U_{38}\}$ .



**Figure 6.** Assembly pathway of uranium oxo/hydroxo clusters in the controlled hydrolysis of  $UCl_4$  in presence of the benzoate ligand.

In summary (Figure 6) during the hydrolysis of  $UCl_4$  in presence of the benzoate ligand in coordinating solvents (pyridine), the formation of the hexanuclear  $[U_6O_4(OH)_4]$  cluster occurs rapidly and formation of larger assembly is not observed. In contrast the hexanuclear clusters assemble slowly in acetonitrile solution, probably via oxolation condensation reactions, leading to a mixture of  $\{U_{10}\}$  and  $\{U_{13}\}$  clusters. The addition of base to these clusters promotes further condensation affording a  $\{U_{16}\}$  cluster with a  $[U_{16}O_{15}(OH)_8]$  core. Both the  $\{U_{16}\}$  and  $\{U_{13}\}$  can further slowly assemble with additional  $\{U_{13}\}$  and/or  $\{U_6\}$  units to yield a  $\{U_{24}\}$  cluster with a  $[U_{24}O_{30}(OH)_2]$  core. When the reaction of hydrolysis is carried at higher temperature small amounts of a  $\{U_{38}\}$  cluster with a  $[U_{38}O_{56}]$  core, were isolated. The  $\{U_{38}\}$  cluster most likely is formed by the condensation of two  $\{U_{24}\}$  clusters and two additional  $\{U_6\}$  units prior to the formation of the final  $UO_2$  product. In conclusion the controlled hydrolysis of uranium(IV) complexes in organic solvents provides an attractive route to the synthesis of uranium clusters with diverse structure and nuclearity. Moreover, it provides insightful snapshots of the time-dependent assembly pathway from uranium hexamers to larger oligomeric species. These results pave the way to the further development of the cluster chemistry of low valent actinides.

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**Keywords:** cluster compounds • uranium • actinides • self-assembly • polyoxometalates

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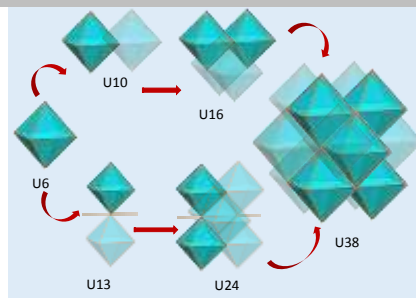
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**Growing uranium oxo clusters**

Large U(IV) cluster slowly assemble in organic solution, upon controlled hydrolysis of  $\text{UCl}_4$ , from an hexanuclear  $\{\text{U}_6\}$  cluster in a time dependent process that is affected by temperature and added base.



*Lucile Chatelain, Radmila Faizova, Farzaneh Fadaei-Tirani, Jacques Pécaut and Marinella Mazzanti\**

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**Structural Snapshots of Cluster Growth from  $\{\text{U}_6\}$  to  $\{\text{U}_{38}\}$  During the Hydrolysis of  $\text{UCl}_4$**