Uranium Cluster

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Isolation of a Star-Shaped Uranium(V/VI) Cluster from the Anaerobic Photochemical Reduction of Uranyl(VI)

*Lucile Chatelain, Sarah White, Rosario Scopelliti, and Marinella Mazzanti**

Abstract: *Actinide oxo clusters are an important class of compounds due to their impact on actinide migration in the environment. The photolytic reduction of uranyl(VI) has potential application in catalysis and spent nuclear fuel reprocessing, but the intermediate species involved in this reduction have not yet been elucidated. Here we show that the photolysis of partially hydrated uranyl(VI) in anaerobic conditions leads to the reduction of uranyl(VI), and to the incorporation of the resulting* U^V *species into the stable mixed-valent star-shaped* U^{VI}/U^V *oxo cluster* $[U(UO_2)_5(\mu_3\text{-}O)_5(PhCOO)_5(Py)_7]$ (***1***). *This cluster is only the second example of a* U^{VI}/U^V *cluster and the first one associating uranyl groups to a non-uranyl(V) center. The* U^V *center in* ***1*** *is stable, while the reaction of uranyl(V) iodide with potassium benzoate leads to immediate disproportionation and formation of the* $U_{12}^{IV}U_4^VO_{24}$ *cluster* $\{[K(Py)_2]_2[K(Py)]_2[U_{16}O_{24}(PhCOO)_{24}(Py)_2]\}$ (***5***).

Actinide oxo clusters are important because of their impact on actinide migration in the environment.[1] The photolytic reduction of uranyl(VI) has attracted large interest due to its relevance in spent nuclear fuel reprocessing[2] and storage[3] and to its potential application in catalysis.[4] Early studies reported spectroscopic evidence showing that metastable U^V species are produced by photolysis of alcoholic solutions of uranyl(VI) and can be stabilized with respect to disproportionation at high uranyl(VI) concentration by U^V/U^{VI} cluster formation.[5] However, well defined compounds that incorporate U^V have never been isolated by photolysis of uranyl(VI) solutions.

Formation of peroxide compounds from the photolysis of uranyl(VI) in the presence of water has also been reported.[3b,6] Most reports suggest that peroxide formation involves water oxidation by a light-generated excited $*UO_2^{2+}$ to yield H_2O_2 and the reduced pentavalent uranyl species UO_2^+ that is subsequently reoxidized by O_2[6] or may disproportionate to yield UO_2^{2+} and U^{IV} species. An analogous mechanism has also been proposed for the photochemical and photocatalytic oxidation of organic substrates by U^{VI} molecular compounds and materials.[7] Pentavalent uranyl species are of high interest because of their important environmental implications. Notably the UO_2^+ species has been identified as a key intermediate in the anaerobic bacterial[8] or mineral-mediated[9] reduction of highly soluble hexavalent uranyl species. This reduction may lead to precipitation of insoluble UO_2 or to the incorporation of U^V in soluble oxo clusters.[10]

Although the UO_2^+ species tend to rapidly disproportionate, several stable complexes of pentavalent uranyl[11] have been reported in the last ten years. Following the first report of a U^V hexanuclear cluster,[12] large mixed valent U^{IV}/U^V clusters have also been obtained by controlled hydrolysis of U^{III} species or from UO_2^+ disproportionation.[13] However, oxo cluster compounds have never been isolated from the photolysis of uranyl(VI).

Here we show that the photolysis of uranyl(VI) in the presence of water and of the benzoate ligand leads to the reduction of uranyl(VI), and to the incorporation of the resulting U^V into the mixed-valent U^{VI}/U^V oxo cluster $[U(UO_2)_5(\mu_3\text{-}O)_5(PhCOO)_5(Py)_7]$ (**1**) shown in Figure 1. The photolytic reduction of UO_2^{2+} results in an important rearrangement of the uranyl oxo groups. In **1** the U^V center binds five uranyl(VI) groups through five oxo bridging ligands. This cluster is only the second example of a U^{VI}/U^V cluster[11c] and the first one associating uranyl groups to a non-uranyl(V) center.

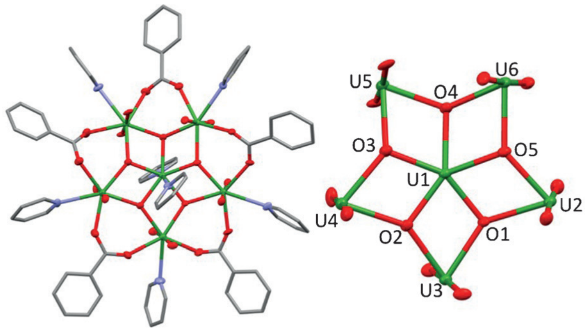

Figure 1. Molecular structure of $[U(UO_2)_5O_5(PhCOO)_5(Py)_7]$ (left) and enhanced view of the "$U(UO_2)_5O_5$"core (right) (ligands were represented in pipes, H and co-crystallized solvent molecules were omitted for clarity).

We also show that the reaction of uranyl(V) iodide with potassium benzoate leads to immediate disproportionation and formation of the $U_{12}^{IV}U_4^V$ cluster $\{[K(Py)_2]_2[K(Py)]_2[U_{16}O_{24}(PhCOO)_{24}(Py)_2]\}$ (**5**) and the polymeric uranyl(VI) complex $\{[UO_2(PhCOO)_3][K(Py)_2]\}_n$ (**6**).

The reaction of $UO_2(NO_3)_2(H_2O)_{1.5}$ with one equivalent of potassium benzoate (PhCOOK) in anhydrous pyridine

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[*] L. Chatelain, S. White, Dr. R. Scopelliti, Prof. M. Mazzanti
Institut des Sciences et Ingénierie Chimiques
Ecole Polytechnique Fédérale de Lausanne (EPFL)
CH-1015 Lausanne (Switzerland)
E-mail: marinella.mazzanti@epfl.ch

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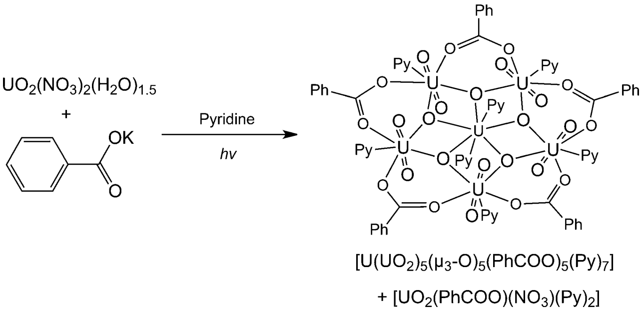
under argon led to the isolation of single crystals of the mixed-valent U^{VI}/U^{V} cluster compound $[U(UO_2)_5(\mu_3\text{-}O)_5(PhCOO)_5(Py)_7]$ (**1**) that was structurally characterized by X-ray crystallography.

The complex **1** was isolated after stirring the reaction mixture for 24 hours in the glove box under the visible light emitted by a fluorescent lamp (Scheme 1). The uranyl(VI) complex $[U^{VI}O_2(PhCOO)(NO_3)(Py)_{1.8}]$ (**2**) was also recovered from the mother liquor.



Scheme 1. Formation of $[U(UO_2)_5(\mu_3\text{-}O)_5(PhCOO)_5(Py)_7]$ (**1**) from the photolysis of uranyl(VI).

In order to confirm that the formation of complex **1** requires the presence of UV/visible light, the reaction of $UO_2(NO_3)_2(H_2O)_{1.5}$ with one equivalent of the potassium salt PhCOOK was also carried out in anhydrous pyridine under argon in the absence of light. In this case only the uranyl(VI) complex $[UO_2(PhCOO)(NO_3)(Py)_2]$ is formed and the proton NMR spectrum of the reaction mixture did not show any traces of the signals assigned to cluster **1** even after 10 days stirring.

In order to increase the yield of complex **1** different conditions were tested, but in all cases the complete conversion of **2** to cluster **1** was not observed. Increasing the water present in the media to 6 equivalents did not lead to significant changes in the composition of the reaction mixture. The effect of higher intensity UV light source was also explored using a mercury lamp. Exposure of the 1:1 reaction mixture of $UO_2(NO_3)_2(H_2O)_{1.5}$/PhCOOK in pyridine to UV light from a mercury lamp for 20 minutes affords $[U(UO_2)_5O_5(PhCOO)_5(Py)_7]$ with yields comparable to those obtained from the reaction under fluorescent light. Quantitative evaluation by ^1H NMR spectroscopy of the conversion rates after exposure to the UV light from a mercury lamp for 45 minutes, 2 h, 5 h and 24 h shows 22 %, 30 %, 38 % and 42 % yield in cluster **1**, respectively. However, after irradiation for 24 hours unidentified insoluble species, that are difficult to separate from complex **1,** also formed. These results show that lengthening the exposure to light leads to small increases in the amount of cluster **1** formed and additional decomposition products.

In order to identify the origin of the oxo groups present in complex **1**, the anhydrous precursor $[UO_2I_2(Py)_3]$ was reacted with one equivalent of potassium benzoate in pyridine under fluorescent light. Proton NMR spectroscopy indicated that this reaction does not lead to the formation of **1**.

However, the subsequent addition to the reaction mixture of 1.5 equivalents of a 0.5 M water solution in pyridine under irradiation by fluorescent light resulted in the appearance in the ^1H NMR spectrum of the signals assigned to the U^{VI}/U^{V} cluster **1**. This indicates that both the presence of water and irradiation with UV/vis light are essential for the formation of the cluster.

The solid-state structure of the cluster **1** was determined by single-crystal X-ray crystallography. The structure shows the presence of five uranyl(VI) groups arranged around a non-uranyl U^{V} center in a star-shaped cluster (Figure 1). The U^{V} center U1 is seven-coordinated, in a slightly distorted pentagonal bipyramidal geometry, by five μ_3-oxo groups and two nitrogen atoms from two pyridine molecules in *trans* to each other. Each of the five μ_3-oxo groups bridges the U^{V} center to two uranyl(VI) moieties. Each uranium atom of the uranyl(VI) units is seven-coordinated, with a slightly distorted pentagonal bipyramidal geometry, by two *trans* oxo groups, one nitrogen atom from a pyridine molecule, two oxygen atoms from two different benzoate ligands and two μ_3-O groups. Each benzoate ligand bridges two uranyl(VI) units. The uranyl(VI) moieties adopt the typical linear geometry (mean value of O-U-O angle: 175(2)°). The $U{=}O_{yl}$ bond lengths (mean value: 1.797(24) Å) and the $U{-}O_{carboxylate}$ bond lengths (ranging from 2.361(20) Å to 2.417(20) Å) are in the range of other structurally characterized uranyl(VI) carboxylate complexes.[14] The mean $U_{yl}{-}(\mu_3\text{-}O)$ distance is 2.33(4) Å while the mean $U1{-}(\mu_3\text{-}O)$ distance is 2.17(4) Å. The mean $U1{-}(\mu_3\text{-}O)$ distance is slightly longer than the $U^{V}{-}(\mu\text{-}O)$ bond distances found in dinuclear uranium(V) bis-μ-oxo complexes (2.094(12)–2.12(13) Å)[15] probably due to the triply bridging coordination mode of the oxo group. This distance remains shorter than bridging U−O distances found in dinuclear uranium(V) alkoxide complex (2.29(1) Å).[16] U−O distances ranging from 2.1 to 2.4 Å are reported for the pentagonal bipyramidal non-uranyl U^{V} cation found in the mineral wyartite of formula $CaU^{V}(U^{VI}O_2)_2(CO_3)O_4(OH)(H_2O)_7$.[17]

The X-band (9.40 GHz) EPR spectrum of **1** shows an intense signal at 10 K with fitted *g*-values of 1.78, 1.46, 0.44 confirming the presence of uranium in the oxidation state +V. Notably, U^{VI} is EPR-silent and U^{IV} is not expected to give an EPR signal in the used conditions.[18]

The five triply bridging oxo groups surrounding the central U^{V} cation in the structure of **1** are most likely derived from deprotonation of three water molecules and from the rearrangement of the two *trans* oxo groups of the UO_2^{+} moiety. A similar rearrangement upon reduction of the UO_2^{2+} moiety to U^{V} has been previously observed in the reductive silylation of a uranyl(VI) complex of a macrocyclic Schiff base.[15c]

Both complexes $[U(UO_2)_5(\mu_3\text{-}O)_5(PhCOO)_5(Py)_7]$ (**1**) and $[UO_2(PhCOO)(NO_3)(Py)_{1.8}]$ (**2**) are easily identified by ^1H NMR spectroscopy in the mixtures obtained from the reaction of $UO_2(NO_3)_2(H_2O)_{1.5}$ with one equivalent of potassium benzoate in pyridine under light irradiation.

Evidence of the retention of the hexanuclear cluster in pyridine solution was provided by pulsed-field gradient stimulated echo (PFGSTE) diffusion NMR measurements. The value of the diffusion coefficient (*D*) for the cluster

1 compared to that measured for the mononuclear complex **2** in pyridine solutions confirmed the presence of a hexanuclear cluster in solution (see the Supporting Information (SI)). The value of the spherical hydrodynamic radii (calculated using the Stokes–Einstein equation) for **1** (8.09 Å) compares well with the value estimated from the crystal structure (7.90 Å). The value of the spherical hydrodynamic radius calculated for **2** (4.23 Å) is in agreement with the value measured for analogous mononuclear uranyl(VI) complexes.[14a]

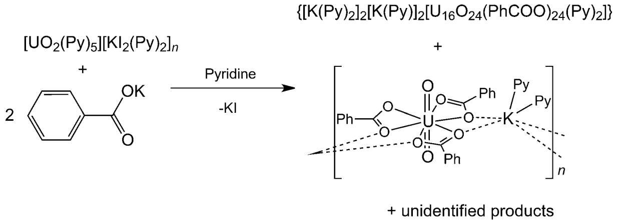
The electronic absorption spectrum of **1** reveals the presence of an intense band between 530 and 630 nm and fine features between 400 and 450 nm (see the SI). The electronic spectrum of a reaction mixture of $UO_2(NO_3)_2(H_2O)_{1.5}$ with one equivalent of the potassium salt PhCOOK in pyridine under light exposure of fluorescent lamp evolves over time. The intensity of the band around 600 nm increases over time, suggesting that this band is associated with the formation of **1**.

The formation of **1** under UV/vis light involves the reduction of a uranyl(VI) species to uranyl(V) and the concomitant formation of an oxidation product. In light of the fact that the photolysis reaction of the complexes $[UO_2(NO_3)_2(H_2O)_6]$ and $[UO_2(OAc)_2(H_2O)_2]$ in pyridine solution was found to yield peroxo complexes, the most likely oxidation product is H_2O_2. The presence of a Raman band at 862 cm^{-1} (Figure S32 in the SI) assigned to the presence of peroxo complexes[3b] was observed in the reaction mixtures after photolysis of **2** both in air and in anaerobic conditions (see the SI). When the reaction is carried out in the presence of ^{18}O-labeled H_2O, the band assigned to the symmetric stretching mode of the peroxide is shifted to 828 cm^{-1}. When the photolysis of **2** was carried out in aerobic conditions the formation of **1** was not observed as indicated by ^1H NMR and UV/vis spectroscopies (see the SI).

In order to assess the effect of the benzoate stoichiometry on the outcome of the photolysis reaction, $UO_2(NO_3)_2(H_2O)_{1.5}$ was reacted with two equivalents of potassium benzoate in anhydrous pyridine under argon. After exposure to visible light of the reaction mixture for 24 h, single crystals were obtained. X-ray crystallography showed the presence of the mixed-valent U^{VI}/U^{V} cluster compound $[U(UO_2)_5O_5(PhCOO)_5(Py)_7]$ (**1**) that cocrystallizes with the bis-benzoate uranyl(VI) complex $[UO_2(PhCOO)_2(Py)_2]$ (**3**) (Figure S1). The structural data of this compound (**1**.**3**·2 Py) are of better quality compared to those of **1** and lead to slightly different values of the bond distances in complex **1** (the mean $U_{yl}-(\mu_3\text{-}O)$ distance is 2.312(14) Å while the mean $U1-(\mu_3\text{-}O)$ distance is 2.157(21) Å). The calculated bond valence sum (BVS)[19] (see the SI) is in agreement with the presence of five U ions in the +VI oxidation state (5.80, 5.79, 5.64, 5.82, 5.81 v.u. for U2, U3, U4, U5, U6) and one U ion in the +V oxidation state (4.9 v.u. for U1), localized in the center (U1).

A few crystals of the U^{IV} hydroxo cluster $[U_6(\mu\text{-}O_4)(\mu\text{-}OH)_4(OH_2)_6(PhCOO)_6(NO_3)_6]\cdot 8\,Py$ (**4**; Figure S2) were also isolated after long irradiation (more than one week) of $UO_2(NO_3)_2(H_2O)_{1.5}$ in reaction with the potassium salt PhCOOK in pyridine, but the isolation of this compound in larger amounts was not possible. However, this result suggest that U^{IV} is also obtained in the photolysis reaction either by direct reduction or from disproportionation of the UO_2^{+} species.

In order to understand if the formation of **1** could arise from the disproportionation of the putative UO_2^{+} intermediate produced in the uranyl(VI) photochemical reduction we decided to investigate the reaction of the polymeric uranyl(V) precursor $\{[UO_2(Py)_5][KI_2(Py)_2]\}_n$ with two equivalents of potassium benzoate in pyridine. This reaction leads to a mixture of disproportionation products, the $U_{12}^{IV}U_4^{V}O_{24}$ cluster $\{[K(Py)_2]_2[K(Py)]_2[U_{16}O_{24}(PhCOO)_{24}(Py)_2]\}$ (**5**) and the polymeric uranyl(VI) complex $\{[UO_2(PhCOO)_3][K(Py)_2]\}_n$ (**6**) according to Scheme 2. Both species crystallized from pyridine by slow diffusion of hexane. A quantitative separation of these two products was prevented by their similar solubility properties in pyridine solution.



Scheme 2. Uranyl(V) disproportionation reaction in presence of potassium benzoate.

Both products were characterized by X-ray diffraction studies. The X-ray crystal structure of the polymeric $\{[UO_2(PhCOO)_3][K(Py)_2]\}_n$ (see the SI) shows the presence of uranyl(VI) cations eight-coordinate, with a hexagonal bipyramidal geometry, by two *trans* oxo groups and six oxygen atoms from three bidentate benzoate ligands. A potassium cation, bound to two pyridine molecules and four oxygen atoms of the benzoate ligands from two different $[UO_2(PhCOO)_3]^{-}$ units, bridges the uranyl(VI) complexes to afford a polymeric structure. The uranyl(VI) moieties have the typical linear geometry (179(1)°) and the U=O bond lengths (mean value 1.773(7) Å) and the $U-O_{carboxylate}$ bond distances (ranging from 2.429(4) Å to 2.525(4) Å) are in the range of other structurally characterized uranyl(VI) carboxylate complexes.[14]

The solid state structure of **5** consists of a discrete hexadecanuclear uranium oxo cluster with a $U_{16}O_{24}$ core (Figure 2) with a 1.5:1 benzoate:uranium ratio. The geometrical arrangement of the uranium and oxo bridging groups is identical to that found in the $U_{12}^{IV}U_4^{V}O_{22}(OH)_2$ oxo/hydroxo cluster $\{[K(MeCN)]_2[U_{16}O_{22}(OH)_2(PhCOO)_{24}]\}$ obtained from the controlled hydrolysis of $UI_3(THF)_4$ in the presence of a base.[13b] The structural arrangement of the 16 uranium atoms in the structure of **5** can be described as consisting of four fused octahedrons. The uranium atoms are connected by 24 oxo groups (18 μ_3-O and 6 μ_4-O) and 24 bridging benzoate ligands. The mean U−O distances is 2.29(11) Å for the μ_3-O groups and 2.38(8) Å for the μ_4-O groups, in agreement with previous U−O bond distances reported in uranium oxo clusters.[1c,13b,c] The mean value of the $U-O_{PhCOO}$ distances is 2.433(60) Å. The calculated BVS for

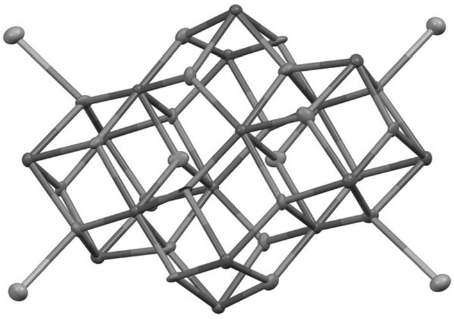


Figure 2. Molecular structure of the $U_{16}O_{24}K_4$ core of $\{[K(Py)_2]_2[K(Py)]_2\text{-}[U_{16}O_{24}(PhCOO)_{24}(Py)_2]\}$.

the uranium atoms is in agreement with the presence of 12 U ions in the +IV oxidation state and 4 U ions in the +V oxidation state (localized on U1 and U5).

^1H NMR spectroscopy of the reaction mixture revealed only the characteristic peaks of the uranyl(VI) tris-benzoate complex $\{[UO_2(PhCOO)_3][K(Py)_2]\}_n$ immediately after mixing the two reagents (see the SI). The absence of ^1H NMR signals for the oxo cluster $\{[K(Py)_2]_2[K(Py)]_2\text{-}[U_{16}O_{24}(PhCOO)_{24}(Py)_2]\}$ may due to a fluxional behavior of the benzoate ligands. The signals assigned to complex **1** were not observed. This indicates that rapid disproportionation of uranyl(V) occurs in the presence of two equivalents of potassium benzoate but does not lead to complex **1**. The previously reported disproportionation of uranyl(V) in the presence of benzoic acid did not afford **1** either but a uranium(IV) cluster $[U_6O_4(OH)_4(PhCOO)_{12}(Py)_3]$, and the uranyl(VI) complex $[UO_2(PhCOO)_2(Py)_2]$.[14a] These results suggest that the cluster **4** might be formed from the disproportionation of UO_2^+.

In conclusion, we have isolated and structurally characterized the first example of actinide oxo cluster obtained from the photoreduction of uranyl(VI). The solid-state structure shows the presence of a uranium cluster associating uranyl(VI) and non-uranyl U^V. In this cluster the UO_2^+ species formed during the UO_2^{2+} photolysis has undergone rearrangement of the uranyl oxo groups and is stabilized by unreacted uranyl(VI) benzoate. In contrast the reaction of a UO_2^+ with benzoate leads to immediate disproportionation and formation of a rare example of large U^{IV}/U^V cluster ($U_{12}^{IV}U_4^VO_{24}$). We also demonstrated that the presence of both UV/visible light and stoichiometric water are necessary to form cluster **1** by reduction of uranyl(VI) benzoate. These results provide the first example of a U^V species isolated from the photolysis of uranyl(VI). Moreover, they suggest that light-induced reduction may also play an important role in the formation of oxo cluster in environmental conditions.

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Keywords: actinides · cluster compounds · pentavalent uranyl · uranium · uranyl compounds

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