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Ligand-Supported Facile Conversion of Uranyl(VI) into Uranium(IV) in Organic and Aqueous Media

Radmila Faizova, Farzaneh Fadaei-Tirani, Rizlan Bernier-Latmani, and Marinella Mazzanti*

Abstract: Reduction of uranyl(VI) to U^V and to U^{IV} is important in uranium environmental migration and remediation processes. The anaerobic reduction of a uranyl U^{VI} complex supported by a picolinate ligand in both organic and aqueous media is presented. The $[U^{VI}O_2(dpaea)]$ complex is readily converted into the *cis*-boroxide U^{IV} species via diborane-mediated reductive functionalization in organic media. Remarkably, in aqueous media the uranyl(VI) complex is rapidly converted, by $Na_2S_2O_4$, a reductant relevant for chemical remediation processes, into the stable uranyl(V) analogue, which is then slowly reduced to yield a water-insoluble trinuclear U^{IV} oxo-hydroxo cluster. This report provides the first example of direct conversion of a uranyl(VI) compound into a well-defined molecular U^{IV} species in aqueous conditions.

Uranyl(VI) species (UO_2^{2+}) are highly stable and highly soluble in aqueous solutions which results in a problematic high mobility in a contaminated environment where they are the predominant form of uranium.^[1] Efforts to mitigate the migration of uranium in the environment have focused on the anaerobic microbially and chemically mediated reduction of UO_2^{2+} to insoluble U^{IV} phases,^[2] a process that is thought to involve a U^V intermediate.^[3] The reduction process is also affected by the presence of complexing inorganic or organic ligands such as carboxylates, resulting in the formation of unidentified soluble U^{IV} species.^[4]

The need for a better understanding of the mechanism of the environmental reduction of uranyl(VI) to uranium(IV), which is key for the development of remediation strategies, has spurred numerous studies of the reduction and functionalization of uranyl species both in the gas phase^[5] and in non-aqueous anaerobic media.^[1a,b,6] Significant progress has been made in recent years in the development of systems that allowed the reduction of uranyl(VI) to uranyl(V).^[1a] In contrast, fewer examples of controlled reduction of uranyl(VI) and uranyl(V) complexes to well-defined U^{IV} compounds have been reported and they all require the prelimi-

nary functionalization of the two uranyl oxo ligands with Lewis acids^[1a,6a,b,7] or metal cations.^[8]

However, the low stability in aqueous media of the reported uranyl(V) systems both with respect to ligand dissociation and proton induced disproportionation^[9] renders impossible their use in the study of uranyl reduction under environmentally relevant conditions, namely in aqueous media.

Recently, we reported^[10] the synthesis and the structure of the uranyl(V) complex $[K(2.2.2.cryptand)][UO_2(dpaea)]$, **2** ($dpaea^{2-}$ (bis(pyridyl-6-methyl-2-carboxylate)-ethylamine), which was isolated from pyridine. Complex **2** disproportionates in acidic water conditions to yield the U^{VI} $[UO_2(dpaea)]$, **1** and U^{IV} $[U(dpaea)_2]$ complexes, but it is stable in water at pH 7–11. The ability of the ligand $dpaea^{2-}$ to stabilize uranyl(V) in organic and aqueous solutions provides access to the study of the reactivity of this species in both media.

Herein we report that the uranyl(VI) complex $[UO_2(dpaea)]$ can be reduced in organic solution to afford a *cis*-boroxide uranium(IV) species ($[U^{IV}(dpaea)(OBpin)_2(py)]$) (**3**) via uranyl oxo functionalization. More importantly, we show, for the first time, that reduction of the uranyl(VI) (**1**) and uranyl(V) (**2**) complexes can be effected in anaerobic water, without preliminary functionalization of the oxo ligands, to give well-defined molecular U^{IV} species, namely the trinuclear U^{IV} oxo-hydroxo clusters $[Na(H_2O)_5\{U(dpaea)\}_3(\mu-O)_2(\mu-OH)(\mu_3-SO_3)]$ (**4**) and $[Na(2.2.2.crypt)][\{U(dpaea)\}_3(\mu-O)_2(\mu-OH)(\mu_3-SO_3)]$ (**5**). We also report the structure of the uranyl(V) $[\{UO_2(dpaea)(H_2O)\}_2\{\mu-Na(H_2O)_2\}_2\{H_2O\}_2]$ complex (**6**) as obtained from the reduction of U^{VI} with sodium dithionite in water, which is the first example of uranyl(V) isolated from water.

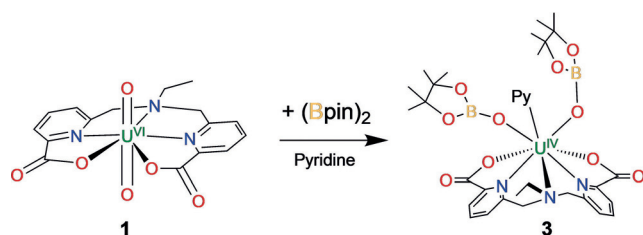
First the reduction of **1** was explored in organic solution (pyridine). Upon addition of 1 equiv of diborane pinacolate ($(Bpin)_2$ (pin = pinacolate)) to the uranyl(VI) complex **1** at room temperature, the 1H NMR spectrum of the reaction mixture revealed conversion of the insoluble diamagnetic U^{VI} species into paramagnetic U^{IV} containing species (Supporting Information, Figure S1). Green crystals of $[U^{IV}(dpaea)(OBpin)_2(py)]$ (**3**) suitable for X-ray diffraction studies were obtained in 33% yield by diffusion of heptane into the pyridine solution (Scheme 1).

The solid-state structure of the complex **3** (Figure 1) shows the presence of a octa-coordinate U^{IV} complex where the two *trans* uranyl(VI) oxo groups of **1** have been converted into two *cis*-boroxide ligands. The conversion involves diborane binding into the uranyl oxo groups and two-electron transfer through cleavage of the B–B bond. The process is accompanied by a rearrangement of the flexible $dpaea$ ligand from planar to bent, which renders possible the switch of the

[*] R. Faizova, Dr. F. Fadaei-Tirani, Prof. Dr. M. Mazzanti
Institute of Chemical Sciences and Engineering
Swiss Federal Institute of Technology Lausanne (EPFL)
1015 Lausanne (Switzerland)
E-mail: marinella.mazzanti@epfl.ch

Prof. Dr. R. Bernier-Latmani
School of Architecture, Civil and Environmental Engineering, EPFL
1015 Lausanne (Switzerland)

Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under:
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Scheme 1. Synthesis of $[\text{U}^{\text{IV}}(\text{dpaea})(\text{OBpin})_2(\text{py})]$ (**3**).

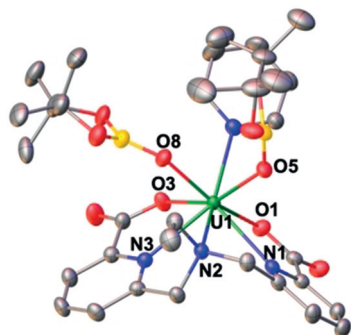
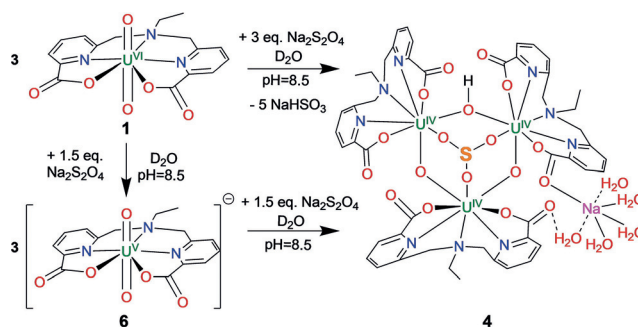


Figure 1. Molecular structure of **3**. H atoms and solvent molecules are removed for clarity. C gray, N blue, O red, B yellow, U green.^[17]

oxo groups for a *trans*- to *cis*- position. The ^1H NMR spectrum of the reaction mixture shows 50 % conversion of **1** into **3**, but also shows the presence of signals assigned to the pyridine adduct of $\text{OB}(\text{pin})_2$ ^[7b] and of additional paramagnetic signals (Supporting Information, Figure S3). The observed signals suggest that additional U^{IV} species are formed that result from reductive oxo abstraction. Oxo-bridged $[\text{O}-\text{U}-\text{O}-\text{U}-\text{O}]^{4+}$ species resulting from reductive oxo abstraction were observed as the only product of the diborane reduction of a macrocyclic uranyl(VI) complex recently reported by Love and Arnold.^[7b]

In view of the observed facile reduction of the U^{VI} complex to U^{IV} in pyridine solution and of the high stability of complexes **1** and **2** in water we investigated the reduction of uranyl(VI) in water. The reaction of **1** in aqueous media with AQDSH₂ (1,8-dihydroxy-9,10-anthraquinone-2,7-disulphonic sodium), NaBH_4 and Fe^{2+} did not result in the reduction of the uranyl(VI) complex.

In contrast, the addition of 0.5 equiv of $\text{Na}_2\text{S}_2\text{O}_4$ to a yellow suspension of $[\text{UO}_2(\text{dpaea})]$ in water at pH 8.5 resulted in immediate reaction yielding a pink solution. The ^1H NMR spectrum of the reaction mixture, when compared to the spectrum of **2** in D_2O at pH 8.5, revealed the quantitative conversion of **1** into the uranyl(V) species $[\text{UO}_2(\text{dpaea})]^-$ (Scheme 2; Supporting Information, Figure S4). Crystals of the uranyl(V) complex $[\{\text{UO}_2(\text{dpaea})(\text{H}_2\text{O})\}_2\{\mu\text{-Na}(\text{H}_2\text{O})_2\}_2\{\text{H}_2\text{O}\}_2]$ (**6**) were obtained by slow evaporation of the H_2O solution at room temperature (Figure 2; Supporting Information, Figure S21). The structure shows a dimer with two anionic $\{\text{UO}_2(\text{dpaea})(\text{H}_2\text{O})\}^-$ moieties bridged by two Na cations binding the carboxylate oxygen atoms. Additionally, two H-bonds ($\text{O}\cdots\text{H}$ 1.96(6) and 2.07(5) Å) are observed between the uranyl(V) oxo group and the water molecules present in the structure.



Scheme 2. One and two electrons reduction of **1** in water at pH 8.5 to afford **6** and **4**.

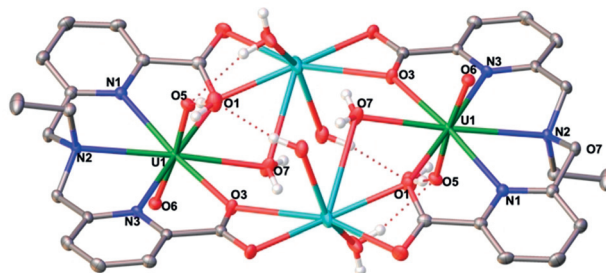


Figure 2. Molecular structure of the $[\{\text{UO}_2(\text{dpaea})(\text{H}_2\text{O})\}_2\{\mu\text{-Na}(\text{H}_2\text{O})_2\}_2\{\mu_2\text{-O}\}_2\{\mu_2\text{-OH}\}_2\{\mu_3\text{-SO}_3\}]$ complex **6** (H atoms of the ligand were removed for clarity). C gray, H white, N blue, O red, U green.^[17]

Moreover, the reduction of $[\text{UO}_2(\text{dpaea})]$ with 1–2 equiv of $\text{Na}_2\text{S}_2\text{O}_4$ in water buffered with HEPES at pH 8.5 for seven days at room temperature led to the formation of the trinuclear uranium(IV) μ -oxo/hydroxo bridged cluster $[\text{Na}(\text{H}_2\text{O})_5\{\text{U}(\text{dpaea})\}_3(\mu\text{-O})_2(\mu\text{-OH})(\mu_3\text{-SO}_3)]$ (**4**) that was isolated as a red crystalline solid in up to 68 % yield (obtained using 2 equiv $\text{Na}_2\text{S}_2\text{O}_4$). XPS analysis of the isolated solid indicated that only U^{IV} species are present (Supporting Information, Figure S18).

Complex **4** could also be isolated by reduction of the uranyl(V) complex $[\text{K}(2.2.2.\text{cryptand})][\text{UO}_2(\text{dpaea})]$ with 0.5 equiv of sodium dithionite in water at $\text{pH} \geq 8$ but with lower yield (up to 40 %), which is probably due to the presence of cryptand (Supporting Information, Figure S5).

^1H NMR studies show that the conversion of U^{VI} into U^{V} is relatively fast (less than 1 hour), but the reduction of the U^{V} species to U^{IV} is very slow and requires more than seven days to be complete for 15 mM solutions (signals of the U^{V} species are still present after seven days; Supporting Information, Figures S6 and S7).

Complex **4** is insoluble in water as well as in pyridine, DMSO, or MeCN, but can be solubilized in water at pH 8 by the addition of 1 equiv of 2.2.2.cryptand. The ^1H NMR spectrum of the resulting orange solution in D_2O (at $\text{pD} = 8$) showed signals in the broad range of chemical shifts usually observed for paramagnetic U^{IV} species (Supporting Information, Figure S9). Slow evaporation of a water solutions generated by addition of 1 equiv of 2.2.2.cryptand to **4** allowed crystals of complex $[\text{Na}(2.2.2.\text{crypt})][\{\text{U}(\text{dpaea})\}_3(\mu\text{-O})_2(\mu\text{-OH})(\mu_3\text{-SO}_3)]$ (**5**) to be isolated.

The ^1H NMR spectrum of **5** shows the presence of 19 resonances ranging from ca. +45 to –75 ppm, in agreement

with the presence of rigid C_s symmetric trinuclear solution species. A diffusion coefficient of $2.2 \cdot 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ and a hydrodynamic radius of 9 Å were calculated, close to the spherical radius estimated from the crystal structure of the complex **5** (8 Å; Supporting Information, Table S1).

The FTIR spectrum of the trinuclear complex **4** shows the disappearance of the band assigned to the asymmetric uranyl $\text{O}=\text{U}=\text{O}$ stretch ($\text{UO}_2^{2+} \approx 790 \text{ cm}^{-1}$; $\text{UO}_2^+ \approx 920 \text{ cm}^{-1}$), which is in agreement with the formation of the U^{IV} -oxo species (Supporting Information, Figure S12).

The solid-state structure of complex **4** was determined by X-ray diffraction studies (Figure 3). The molecular structure of **4** shows the presence of a trinuclear cluster with three uranium(IV) cations bridged by two oxide and one hydroxide ligand to yield a six-membered ring. A sulfite anion also bridges the three U^{IV} centers, with a mean $\text{U}-\text{O}_{\text{sulf}}$ distance of 2.35(4) Å, being located at 2.1295(12) Å above the plane of the three uranium(IV) cations. Each uranium ion is octa-coordinated by the dpaea ligand, one O_{sulf} and two bridging $\text{O}_{\text{oxo}}/\text{O}_{\text{hydr}}$ atoms. The value of the $\text{U}-\text{O}_{\text{oxo}}$ bond distances ranges from 2.0477(17) to 2.1699(17) Å and $\text{U}-\text{O}_{\text{hydroxo}}$ averages at 2.327(3) Å which are both in the range of typical for uranium(IV) oxo and U^{IV} hydroxo bond distances.^[12] The value of the $\text{U}-\text{O}-\text{U}$ angles in the trimer range from $138.20(9)^\circ$ for $\text{U}-\mu\text{-OH}-\text{U}$ to $144.39(9)^\circ$ and $148.83(8)^\circ$ ($\text{U}-\mu\text{-O}-\text{U}$) and is similar to those found for the only three other trinuclear U^{IV} clusters reported so far.^[12] A sodium counter-cation is bound to one of the carboxylate oxygens of the dpaea ligand and its coordination sphere is completed by 5 H_2O molecules.

The molecular structure of **5** (Supporting Information, Figure S20) shows the presence of a structure very similar to that of complex **4**. Removal of the bound sodium counterion does not lead to important changes of the metrical parameters (Supporting Information, Table S3).

The clusters **4** and **5** are the first examples of trinuclear oxo clusters isolated from aqueous media.^[12] The stability of

complex **5** at different pH conditions was investigated by ^1H NMR spectroscopy. The complex was shown to be stable at pH 7–9, while from more acidic solutions (pH 5) lead to extrusion of the remaining oxo ligands and formation of crystals of the previously reported mononuclear U^{IV} complex $[\text{U}^{\text{IV}}(\text{dpaea})_2]$ that has very low solubility in water (Supporting Information, Figure S10).

We also investigated how the reduction of **1** is affected by pH. The reduction of $[\text{UO}_2(\text{dpaea})]$ with $\text{Na}_2\text{S}_2\text{O}_4$ cannot be performed in acidic aqueous media (pH lower than 7) (Supporting Information, Figure S8) because the uranyl(V) $[\text{U}^{\text{V}}\text{O}_2(\text{dpaea})]^-$ complex was found to disproportionate to $[\text{U}^{\text{VI}}\text{O}_2(\text{dpaea})]$ and $[\text{U}^{\text{IV}}(\text{dpaea})_2]$ in these conditions.^[10] In contrast, no disproportionation is observed in water solutions of $[\text{NaUO}_2(\text{dpaea})]$ at pH 8 to 11, but the reduction of U^{V} to U^{IV} is increasingly slower with increasing of pH. In strongly basic conditions ($\text{pH} \geq 11$), the uranyl(V) is not reduced by $\text{Na}_2\text{S}_2\text{O}_4$ despite the fact that the reducing power^[13] of $\text{Na}_2\text{S}_2\text{O}_4$ is increased at more basic pH (Supporting Information, Figure S11). This result suggests that the redox properties of $[\text{UO}_2(\text{dpaea})]^-$ are pH-dependent, as previously reported for uranyl(VI) carbonate or phosphate.^[14]

In view of the ability of the weakly reducing agent $\text{Na}_2\text{S}_2\text{O}_4$ ($E_{\text{red}}(\text{Na}_2\text{S}_2\text{O}_4) = -0.87 \text{ V}$ (vs. Ag/AgCl pH 7) to reduce the complexes **1** and **2** to U^{IV} complexes at pH 8.5, we re-examined the previously reported^[10] interpretation of the cyclic voltammogram of **2** measured in water solution.

The voltammogram of **2** measured in 0.02 M HEPES buffered water solutions (pH 7) at a glassy carbon working electrode showed the presence of a $\text{U}^{\text{V}}/\text{U}^{\text{VI}}$ oxidation event found at $E = -0.16$ – 0.00 V vs. Ag/AgCl . A second redox event was observed at $E = (-1.56)$ – $(-1.65) \text{ V}$ vs. Ag/AgCl depending on the scan speed.

This redox event was also found in the voltammogram of the non-redox active Zn^{2+} cation $[\text{Zn}(\text{dpaea})]$ (Supporting Information, Figure S13) and was assigned to the reduction of the dpaea ligand rather than the U center. At lower scanning speeds a redox event was resolved at $E = -0.6 \text{ V}$ (vs. Ag/AgCl ; pH 7) and it was assigned to the $\text{U}^{\text{VI}}/\text{U}^{\text{V}}$ reduction. Cyclic voltammetry experiments were also carried out at pH 10 (Supporting Information, Figure S14) and resulted in a shift of the redox event associated to the $\text{U}^{\text{VI}}/\text{U}^{\text{V}}$ reduction to a more negative potential. This could explain the increased stability of the uranyl(V) species during the reduction with $\text{Na}_2\text{S}_2\text{O}_4$ at basic pH.

The observed pH dependency of the reduction of the stable uranyl(V) complex suggest that formation of complex **4** is likely to proceed via a proton-coupled electron transfer from the reducing agent $\text{Na}_2\text{S}_2\text{O}_4$. This should result in a *cis*-bis-hydroxo intermediate that is structurally analogous to the boroxide complex **3** formed in organic solution. A similar proton-coupled electron transfer mechanism was computed for the reduction of uranyl(V) carbonate to U^{IV} by Fe^{2+} in aqueous solution, but it was found to have a high thermodynamic barrier preventing $\text{U}^{\text{V}}/\text{U}^{\text{IV}}$ conversion in the presence of carbonate.^[15] Here, the putative *bis*-hydroxo U^{IV} intermediate formed from the reduction of **1** and **2** undergoes condensation due to the basicity of the hydroxo ligand to yield the trinuclear oxo-hydroxo bridged cluster **4** via exclusion of

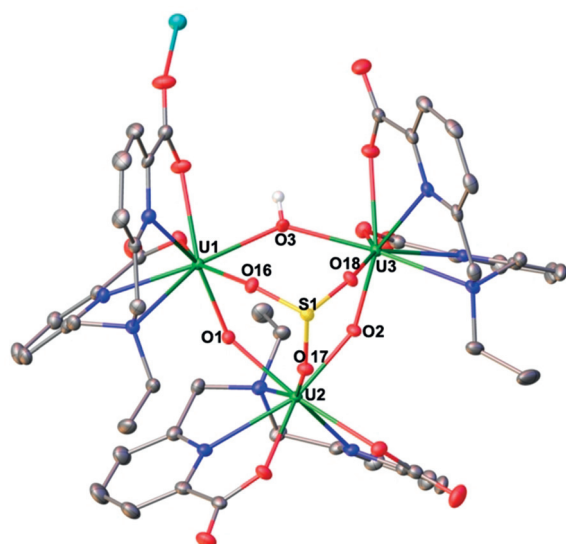


Figure 3. Molecular structure of **4** (ellipsoids are set at 50% probability). H atoms of the ligand, disorder and solvent molecules and H_2O coordinated to Na^+ are removed for clarity. C gray, H white, N blue, O red, S yellow, U green, Na light blue.^[17]

one oxo group as a water molecule. The formation of actinide oxo clusters from condensation reactions is an important process in the water chemistry of actinides that has attracted numerous studies both in organic and water solution owing to its relevance in the migration of actinides in the environment.^[2d,11,16] However, the isolation of well-defined U^{IV} oxo clusters from the direct reduction of uranyl(VI) in water is unprecedented. It is of interest to note that even in the presence of the picolinate derivative dpaea water insoluble polynuclear U^{IV} species are formed and that the solubility of such species is strongly affected by cation binding. This finding raises the question of whether clusters of this type might form during the homogeneous and heterogeneous reduction of U^{VI} by aqueous sulfide in groundwater, a key process influencing the fate of uranium in the environment.

In conclusion, we have shown that in the presence of polydentate carboxylate ligands it is possible to bring about the conversion of U^{VI} into a stable uranyl(V) complex in aqueous media. This uranyl(V) complex can be further reduced to U^{IV} using a reductant (Na₂S₂O₄) relevant to chemical remediation. The reduction to U^{IV} is slow but proceeds without the help of oxo functionalization and leads to the formation of a trinuclear oxo cluster via extrusion of one oxo ligand. These findings provide unprecedented insight into the mechanism of abiotic reduction of UO₂²⁺ to U^{IV} in aqueous media rich in organic ligands providing insight into the mechanism and the end-product of U^{VI} reduction in the environment.

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Conflict of interest

The authors declare no conflict of interest.

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- [17] CCDC 1970863, 1970860, 1970861, and 1970862 (**3**, **4**, **5**, and **6**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

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