

RESEARCH ARTICLE

"This is the accepted version of the following article: [Angew. Chem. Int. 2021, DOI: 10.1002/anie.202016123], which has been accepted for publication [Link to final article using the DOI: DOI: 10.1002/anie.202016123]. This article may be used for non-commercial purposes in accordance with Wiley Terms and Conditions for Self-Archiving."

Synthesis and Characterization of Water Stable Uranyl(V) Complexes

Radmila Faizova, Farzaneh Fadaei-Tirani, Anne-Sophie Chauvin and Marinella Mazzanti*

Institut des Sciences et Ingénierie Chimiques
Ecole Polytechnique Fédérale de Lausanne (EPFL)
CH-1015 Lausanne, Switzerland
E-mail: marinella.mazzanti@epfl.ch

Supporting information for this article is given via a link at the end of the document

Abstract: The importance of uranyl(V) (UO_2^+) species associated with environmental and geologic applications is becoming increasingly evident, but the tendency of the uranyl(V) cation to disproportionate in water has prevented the isolation of stable complexes. Here we demonstrate that in the presence of the tridentate complexing dipicolinate (dpa^{2-}), a ligand highly abundant in soil, the uranyl(V) species can be stabilized and isolated in anoxic basic water. Stable uranyl(V) dipicolinate complexes are readily formed from the reduction of the uranyl(VI) analogue both in organic solution and in basic water, and their solution and solid-state structure were determined. A bis- dpa $\text{U}^{\text{V}}\text{O}_2^+$ complex was obtained from water at pH10, while at higher pH values, a trinuclear mono- dpa cation-cation complex was isolated. These results present the second ever isolated water stable uranyl(V) complex. Moreover, we demonstrate that dipicolinate complexes of $\text{U}^{\text{VI}}\text{O}_2^{2+}$, $\text{U}^{\text{V}}\text{O}_2^+$ and U(IV) are strongly luminescent with a signature characteristic of each oxidation state. This provides unique examples of luminescent U(V) and U(IV) compounds.

Introduction

Uranyl(VI) (UO_2^{2+}) compounds are the dominant uranium species in environmental conditions, and their solubility is responsible for uranium migration.^[1] In an anoxic environment, uranium migration can be mitigated by iron containing minerals and bacteria which reduce uranyl(VI) to insoluble forms of U(IV) such as UO_2 or polymeric complexes of organic ligands.^{[2],[3]} The mechanism of the environmental reduction remains elusive but its knowledge is crucial for the development of remediation strategies at sites contaminated with uranium.^[4] The low stability of uranyl(V) (UO_2^+) in water, where it tends to disproportionate to UO_2^{2+} and to U(IV), has previously minimized its environmental relevance. More recently, the occurrence of uranyl(V) (UO_2^+) in the environment and its role as an intermediate in the mineral-mediated and microbial reduction of uranyl(VI) has been documented in an increasing number of studies.^{[4d],[5]} However, the complexity of the environmental conditions often prevents the characterization of the species involved, rendering the study of simpler chemical

models highly desirable. In recent years, an increasing number of stable mononuclear and polynuclear complexes of uranyl(V) were isolated from organic solutions and structurally characterized.^{[5b],[6]} Understanding of the parameters controlling the chemical reduction of uranyl(VI) to uranyl(V) in organic solution is also increasing.^[1a, 1b, 7] Fewer examples of direct reduction of complexes of uranyl(VI) to U(IV) species have been reported, either in the gas phase^[8] or in non-aqueous anaerobic media, where they usually involve the preliminary functionalization of the uranyl oxo groups.^[1a, 6k, 7d, 7e, 9]

Moreover, studies of the reduction of uranyl(VI) to yield stable uranyl(V) species^[5b, 10] in environmentally relevant aqueous conditions were limited, until recently, to early reports on the aqua ion at low pH (2-4)^[10-11] and to the carbonate complex $[\text{UO}_2(\text{CO}_3)_3]^{12-}$ that was produced electrochemically in basic conditions (pH=11.7-12) but was never isolated.

Recently, we reported the first example of a structurally characterized uranyl(V) complex, $[\text{UO}_2(\text{dpaea})]^-$ (left, Figure 1; H_2dpaea = bis(pyridyl-6-methyl-2-carboxylate)-ethylamine), stable in water at pH 7-11.^[13] We demonstrated that the stepwise reduction of the uranyl(VI) complex $[\text{UO}_2(\text{dpaea})]$ can be effected with stoichiometric amounts of sodium dithionite in water to yield a stable uranyl(V) analogue and a well-defined molecular U(IV) species.^[14]

The high denticity of the dpaea^{2-} ligand, which tightly occupies five coordination sites in the equatorial plane of the UO_2^+ species, is believed to be crucial in stabilizing $[\text{UO}_2(\text{dpaea})]^-$ against disproportionation. Notably, the ligand prevents the interaction between the basic uranyl(V) oxo group and the U center of another UO_2^+ species, also known as cation-cation interactions (CCI),^[15] that were identified as intermediates in uranyl(V) disproportionation.^[6n, 6p, 15] Additionally, the presence of picolinate binding groups in the dpaea^{2-} ligand is also crucial in preventing ligand dissociation in water solution.^[13, 16]

RESEARCH ARTICLE

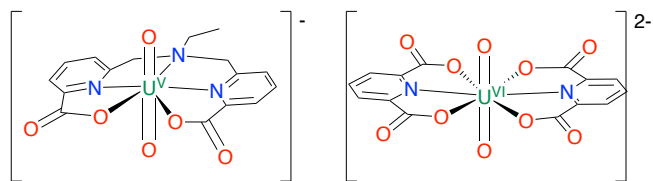


Figure 1. Structure of the uranyl(V) complex $[UO_2(dpaea)]^-$ (left) and of the uranyl(VI) dipicolinate $[UO_2(dpa)_2]^{2-}$ (right).

The structural,^[17] the thermodynamic^[18] and the kinetic^[19] properties of the uranyl(VI) (right, Figure 1) and neptunyl(V) complexes of the dipicolinate ligand (dpa^{2-} ; H_2dpa =pyridine-2,6-dicarboxylic acid), a low denticity analogue of $dpaea^{2-}$, have attracted numerous studies due to its relevance as an effective extractant of actinides for spent nuclear fuel reprocessing applications.^[20] The chemistry of the dipicolinate ligand was also studied for a broad range of heavier actinide ions.^{[21],[22]} Stability constant data previously measured in moderately acidic aqueous solutions (pH < 7) by spectrophotometry show that dpa^{2-} strongly binds both UO_2^{2+} and NpO_2^{2+} .^[18] However, the stepwise reduction of uranyl(VI) dpa complexes has never been investigated and uranyl(V) complexes of dipicolinate remain elusive.

Herein, we report the stepwise reduction of uranyl(VI)-dipicolinate complexes in both organic and aqueous solutions, resulting in the structural characterization and isolation of stable mono- and bis-dpa complexes of uranyl(V). We find that a high ligand denticity is not essential in isolating water stable complexes of uranyl(V). Instead, the tridentate ligand dpa^{2-} is able to stabilize uranyl(V) both in organic and in aqueous solution, which is of high environmental relevance. Notably, dipicolinic acid is highly abundant in soil^[23] where it composes up to 20% of the dry weight of sedimental bacterial spores.^[24]

Further, we have synthesized and characterized dipicolinate complexes of uranium in three oxidation states. We show that the UO_2^{2+} , UO_2^+ , and U(IV) all form water stable dipicolinate complexes which are strongly luminescent and which show different spectral signatures. This suggests that luminescence spectroscopy is well poised to probe the reduction of UO_2^{2+} in dipicolinate rich environments.

Results and Discussion

Synthesis, structure and stability in organic solution.

The synthesis of stable dipicolinate complexes of uranium in three oxidation states was pursued.

First, we investigated the possibility of preparing a uranyl(V) complex of the dpa^{2-} ligand in organic solution both by reduction of the uranyl(VI) analogue and by direct salt metathesis reaction with the uranyl(V) precursor $[(U^VO_2Py_5)(Kl_2Py_2)]_n$.^[6a]

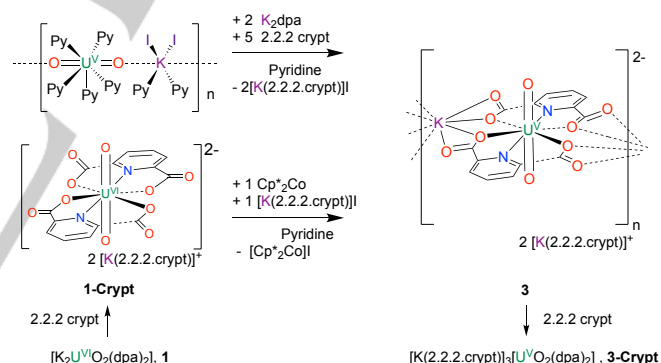
The addition of 2.2.2.cryptand (2.2.2.crypt) to the insoluble polymeric uranyl(VI) dipicolinate complex $[K_2U^VI O_2(dpa)_2]_{25}$ **1** afforded the mononuclear U(VI) complex $[K(2.2.2.crypt)]_2[U^VI O_2(dpa)_2]$, **1-Crypt** (Scheme 1)(Fig. S56).

The pyridine solutions of **1-Crypt** demonstrated to be photosensitive leading to the formation of reduced uranium species after exposure for several hours to visible light emitted by a fluorescent lamp. The irradiation of the solution of **1-Crypt** in a photoreactor at $\lambda=420$ nm resulted in the complete disappearance of the 1H NMR signals assigned to **1-Crypt** resulting in the formation of a mixture of photo-reduced U(IV) and

U(V) products (Scheme 2). One set of signals was clearly identified and assigned to the U(IV) complex $[K(2.2.2.crypt)]_2[U^{IV}(dpa)_3]$ (**2-Crypt**). Quantitative integration of the 1H NMR spectrum showed ca. 30% conversion (based on U) to the uranium(IV) complex $[U^{IV}(dpa)_3]^{2-}$ (**2-Crypt**) after 1.5 hours of irradiation at 420 nm (Fig. S2-S4). X-ray quality crystals of $[K(2.2.2.crypt)]_2[U^{IV}(dpa)_3]$ (**2-Crypt**) were isolated by slow diffusion of DIPE into a solution of **1-Crypt** in pyridine after irradiation at $\lambda=420$ nm for 1.5 hours (Fig. S57).

The U(IV) complex $[K(2.2.2.crypt)]_2[U^{IV}(dpa)_3]$, **2-Crypt**, was independently prepared from the reaction of the uranium(IV) iodide precursor $[U^{IV}(dioxane)]_{1.8}$ with 3 equiv. of K_2dpa in pyridine followed by the addition of 2.2.2.crypt (Fig. S5). The insoluble analogue of $[K_2U^{IV}(dpa)_3]$, **2**, formed in the absence of 2.2.2.crypt. Photochemical reduction of uranyl(VI)-containing complexes to U(IV) or U(V) species has been reported,^[1a] but the products of the reduction have rarely been structurally characterized.^[1a, 26]

With the uranyl(VI) dipicolinate **1-Crypt** on hand we then pursued the chemical synthesis of the uranyl(V) analogue. The uranyl(V) dipicolinate complex $[K(2.2.2.crypt)]_{2n}[(U^VO_2(dpa)_2)]_n$, **3** was prepared by the salt metathesis reaction of 1 equiv. of $[(U^VO_2Py_5)(Kl_2Py_2)]_n$ with 2 equiv. of K_2dpa in anhydrous pyridine solution in the presence of 5 equiv. of 2.2.2.cryptand (Scheme 1). Complex **3** was obtained analytically pure as a blue crystalline solid in 46% yield by slow diffusion of DIPE into a MeCN solution of the reaction mixture. The EPR measurement confirmed the presence of a U(V) species in solid state.^[6g, 13] The spectrum could be fitted with a rhombic set of g values ($g_1=2.7$; $g_2=1.28$; $g_3=1.1$) (SI Section IV, Fig. S32).

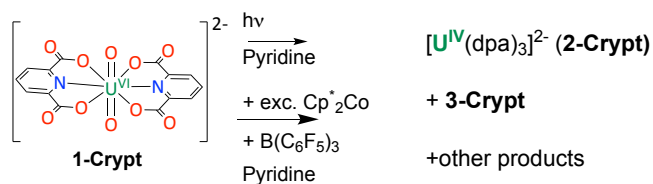


Scheme 1. Synthesis of the complexes **3** and **3-Crypt**.

The uranyl(V) complex $[U^VO_2(dpa)_2]^{3-}$, can also be prepared by the chemical reduction of the uranyl(VI) complex **1-Crypt** with 1 equiv. of Cp^*_2Co in pyridine as indicated by 1H NMR spectroscopy (Fig. S6). The addition of excess reducing agent to **1-Crypt** or to the isolated uranyl(V) complex **3** did not lead to further reduction (Fig. S6-S7). However, upon addition of pentafluorophenyl borane to the reaction mixture, further reduction of the uranyl(V) species was observed. Notably, the 1H NMR spectrum of a pyridine solution of **1-Crypt** after addition of 2 equiv. of $B(C_6F_5)_3$ and 2 equiv. of Cp^*_2Co (Scheme 2) shows the appearance of resonances assigned to the uranium(IV) complex $[U^{IV}(dpa)_3]^{2-}$ (**2-Crypt**) along with the disappearance of the peaks assigned to the uranyl(V) complex **3** (Fig. S6). This result suggests that $B(C_6F_5)_3$ binds to the uranyl(V) oxo groups resulting in a more facile reduction to the uranium(IV) species. Hayton and co-workers reported previously that binding of $B(C_6F_5)_3$ to the uranyl(V) oxo

RESEARCH ARTICLE

groups facilitate the reduction $[\text{Cp}^*\text{Co}][\text{U}^{\text{V}}\text{O}_2(\text{Ar}^i\text{acnac})_2]$ to the corresponding U(IV) species.^[7e]



Scheme 2. Chemical reduction and photoreduction of **1-Crypt** to **2-Crypt** in pyridine.

The solid-state structure of **3** was determined by X-ray diffraction studies and is presented in Figure 2.

The molecular structure of **3** shows the presence of an anionic polymeric 1-D chain built from the binding of potassium cations to four carboxylate groups between two crystallographically inequivalent $[\text{U}^{\text{V}}\text{O}_2(\text{dpa})_2]^{3-}$ moieties. In addition, two well-separated $[\text{K}(2.2.2.\text{crypt})]^+$ cations complete the crystal structure. The uranium cations in **3** are octacoordinated with a hexagonal bipyramidal geometry by two tridentate dpa^{2-} ligands in the equatorial plane and by two oxo groups in axial positions. The values of the U=O bond distances are characteristic of uranyl(V) (1.841(2) and 1.853(2) Å)^[5b, 6a, 6d, 6g, 6i] and the O=U=O arrangement is perfectly linear. The O=U=O is slightly tilted with respect to the N-U-N axis (O1-U1-N1=86.05(8)^o). Interestingly, in complex **3** no cation-cation interaction (CCI) is observed between the axial oxo groups and K^+ . The presence of CCI interactions between the electron-rich uranyl(V) oxo group and alkali ions was found in most previously reported crystal structures of anionic uranyl(V) complexes isolated from organic solutions.^[6g, 6m, 6n, 6p, 6q, 7c] The absence of such interaction in complex **3** could be explained by the strong alkali ion coordination site provided by the four carboxylate units of the dpa^{2-} ligands from two neighboring $[\text{UO}_2(\text{dpa})_2]^{3-}$ anions leading to the formation of a polymer. The uranyl oxo groups are H-bonded to the co-crystallized molecule of MeCN (mean U=O...H 2.31(5) Å).

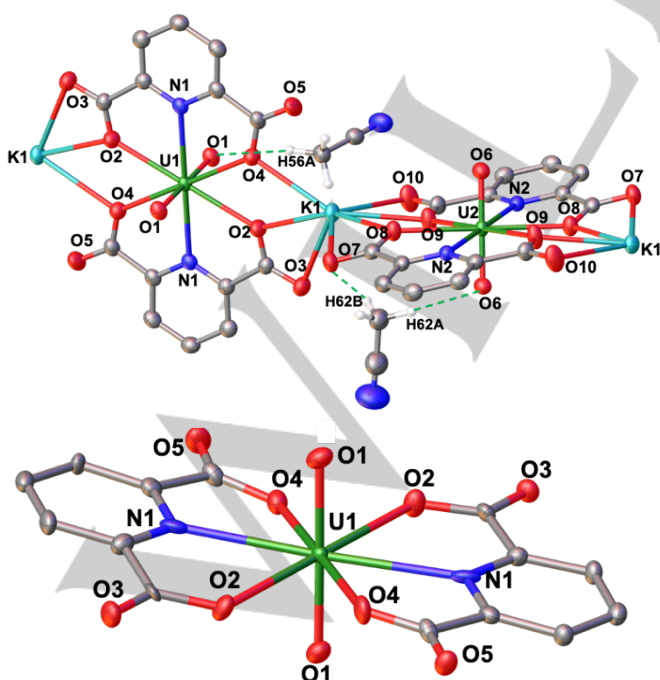


Figure 2. Ellipsoid plot at 50% probability of $[\text{K}(2.2.2.\text{crypt})]_{2n}[[\text{KU}^{\text{V}}\text{O}_2(\text{dpa})_2]]_n$ (**3**) (co-crystallized MeCN molecules, $[\text{K}(2.2.2.\text{crypt})]^+$ cations and the H of the dpa ligands were omitted for clarity. H-bonding is represented by a green dashed line (top); detail of the U(V) coordination sphere (bottom). Selected distances (Å) U(1)–O(1) 1.841(2), U(2)–O(6) 1.853(2), O(1)–H(56A) 2.278(2), O(6)–H(62A) 2.455(2), K(1)–O(8) 2.788(2), K(1)–O(7) 3.173(2), O(7)–H(62B) 3.834(3). CCDC numbers are given in Supporting Information.

Dissolution of crystals of the polymeric complex **3** in pyridine yielded a colloidal solution, but the subsequent addition of 1 equiv. of 2.2.2.crypt resulted in the complete dissolution of **3** and in the shift of the NMR signals. This is assigned to the removal of an additional binding potassium yielding the $[\text{K}(2.2.2.\text{crypt})]_3[\text{U}^{\text{V}}\text{O}_2(\text{dpa})_2]$ (**3-Crypt**) species. The higher solubility of **3-Crypt** suggests a mononuclear nature of the product, but the broad character of the ¹NMR signals indicates that some exchange occurs in solution between bound and unbound potassium which could result in the presence of oligomeric species. (Fig. S8–S9).

The ¹H NMR spectrum of **3-Crypt** in pyridine solution remains unchanged for at least one month indicating that the complex **3-Crypt** is stable in pyridine solution (Fig. S10). Complex **3-Crypt** was also demonstrated to be photostable in pyridine (Fig. S11). In contrast, the complete or partial disproportionation of complexes **3** and **3-Crypt** respectively was observed in acetonitrile after 2 days (Fig. S12).

Moreover, the addition of 1 equiv. of PyHOTf to a pyridine solution of **3-Crypt** resulted in the immediate disproportionation of the uranyl(V) to afford the U(VI) complex **1-Crypt**, the U(IV) complex **2-Crypt** and other unidentified products as indicated by proton NMR spectroscopy (Fig. S13). Proton induced disproportionation of otherwise stable uranyl(V) complexes has been observed previously both in organic and water solution.^[6p, 13, 27]

We also observed that the salt metathesis reaction between 1 equiv. of K_2dpa and 1 equiv. of the uranyl(V) iodide precursor $[(\text{U}^{\text{V}}\text{O}_2\text{Py}_5)(\text{KI}_2\text{Py}_2)]_n$ in pyridine in the presence of a stoichiometric amount of 2.2.2.cryptand results in the immediate disproportionation of a putative U(V) mono-dipicolinate intermediate to afford U(IV) and U(VI) products (Fig. S14).

These results indicate that, binding of one dipicolinate ligand to the stable pyridine adduct of uranyl(V) in pyridine, leads to a decreased stability and immediate disproportionation probably through a CCI intermediate. Alternatively, the *bis*-dipicolinate complex of uranyl(V) revealed stable in pyridine solution with respect to the disproportionation reaction. The high stability of **3-Crypt** in pyridine is probably due to the strong binding of the two tridentate ligands in the equatorial plane which prevents cation-cation interaction from occurring.

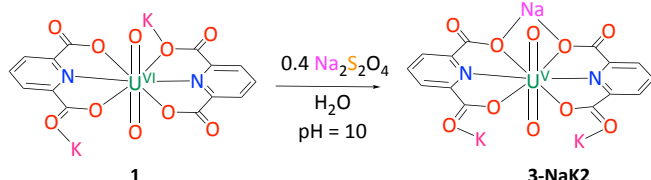
Structure and Stability in Water

The stability of the isolated uranyl(V) complex **3** in water was investigated at pH 7, 9 and 10. The proton NMR spectrum indicated that complete disproportionation of **3** occurs at pH=7 to yield $[\text{U}^{\text{IV}}(\text{dpa})_3]^{2-}$ and $[\text{U}^{\text{VI}}\text{O}_2(\text{dpa})_2]^{2-}$ (Fig. S15), partial disproportionation is observed at pH=9, while no products of the disproportionation reaction are observed on the proton NMR spectrum of the uranyl(V) complex at pH=9.5–10 or above, demonstrating its stability in basic water solution (Fig. S16–17). Additionally, the presence of U(V) in basic water solution was confirmed by the measurement of the room temperature magnetic moment $\mu_{\text{eff}} = 2.2 \mu_{\text{B}}$ by ¹H NMR spectroscopy using the Evans method.^[28] This value compares well with the value measured in

RESEARCH ARTICLE

pyridine ($\mu_{\text{eff}} = 2.1 \mu_{\text{B}}$) and is consistent with the presence of one unpaired $5f^1$ electron. (See SI section V).^[29]

The uranyl(V) dipicolinate complex can also be directly obtained in water by the reduction of the U(VI) analogue $[\text{K}_2\text{U}^{\text{VI}}\text{O}_2(\text{dpa})_2]$ (**1**) with 0.4 equiv. of $\text{Na}_2\text{S}_2\text{O}_4$ at pH=10 (Scheme 3) (Fig. S18). The addition of excess $\text{Na}_2\text{S}_2\text{O}_4$ at pH>10 does not result in further reduction of the uranyl(V) (Fig. S19), but the formation of U(IV) complex **2** is observed upon addition of sodium dithionite to the U(V) complex **3** at pH<10 (pH=9.8; Fig. S20).



Scheme 3. Chemical reduction of **1** in water at pH=10.

Red X-ray quality crystals of the uranyl(V) complex $[\text{KNa}_2\text{UO}_2(\text{dpa})_2]$ (**3-NaK2**) (Fig. S58) were obtained upon slow evaporation of the reaction mixture. X-ray diffraction data showed that the uranium center in **3-NaK2** has a very similar coordination environment to complex **3** despite the presence of two additional picolinate bound cations. However, in the solid-state structure of **3-NaK2** an extended H-bonding network is present and results in a reduced symmetry. Namely, a H-bonding interaction is present between the uranyl(V)-oxo groups and the co-crystallized water molecules ($\text{OU}=\text{O}\dots\text{H}=1.98(6)\text{\AA}$). The extended H-bonding interaction, which is not observed in the crystal packing of the uranyl(VI) complex $[\text{Na}_2\text{UO}_2(\text{dpa})_2]$, **1-Na** (See Supporting information Fig. S59), reflects the increased basicity of the axial oxo-groups of uranyl(V) in comparison to the uranyl(VI) analogue.

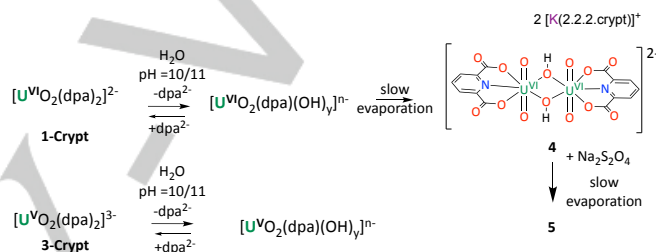
It should be noted that **1-Crypt** also undergoes photoreduction in water at pH=8-11 (2 h @ $\lambda=254$) resulting in the formation of uranyl(V) and U(IV) products (Fig. S21-S24). When irradiated with a fluorescent lamp the reduction occurs at a significantly slower rate than what observed in pyridine solution (Fig. S25; assignment was based on the ^1H NMR of independently isolated products). At high pH the formation of uranyl(V) is favored compared to U(IV).

^1H NMR studies for both the U(VI) and U(V) complexes were carried out in the dark at different pH values to further investigate the nature of the stable solution species. The ^1H NMR spectrum of **1-Crypt** measured in water at pH \leq 8 suggests that only one major species is present at this pH that was identified as $[\text{U}^{\text{VI}}\text{O}_2(\text{dpa})_2]^{2-}$ (Fig. S26). In contrast, under more basic conditions (pH=9-11) the ^1H NMR data indicate that free dpa ligand is present in solution together with two uranyl species, that were assigned as the bis-dipicolinate complex $[\text{U}^{\text{VI}}\text{O}_2(\text{dpa})_2]^{2-}$, and a mono-dipicolinate species (Scheme 4) (Fig. S27-S28). The loss of one dipicolinate ligand at high pH can only be explained by the formation of hydroxide species $[\text{U}^{\text{VI}}\text{O}_2(\text{dpa})(\text{OH})_y]^{n-}$. X-ray quality crystal of the hydroxo complex $[\text{K}(2.2.2.\text{crypt})]_2[\text{U}^{\text{VI}}\text{O}_2(\text{dpa})_2(\text{OH})_2]$ (**4**) (Fig. S60) were isolated by slow evaporation of a solution of **1-Crypt** at pH=10 confirming the presence of hydroxo species although the nuclearity of **4** and the number of bound hydroxides may vary in solution. The ^1H NMR of crystals of **4** (Fig. S29) shows a broad signal for the dpa ligand that is also found in the spectra of **1-Crypt** at pH10. The synthesis, ^1H NMR spectrum and crystal structure of the hydroxo-

bridged uranyl(VI)-dpa complex $[(\text{U}^{\text{VI}}\text{O}_2)(\text{dpa})(\text{OH})]_2^{2-}$ had been reported previously with a different counterion.^[17a]

^1H NMR studies of water solutions of **3** showed that the dissociation of one ligand occurs also for uranyl(V) above pH10 and increases with increasing the pH (Fig. S30), as observed for **1-Crypt**, probably as a result of the formation of a uranyl(V) mono-dpa hydroxo species. Notably, dissolution of complex **3** in water at pH \geq 10 results in the presence of ^1H NMR signals assigned to the bis-ligand $[\text{U}^{\text{VI}}\text{O}_2(\text{dpa})_2]^{3-}$, mono-ligand species $[\text{U}^{\text{VI}}\text{O}_2(\text{dpa})(\text{OH})_y]^{n-}$ and free dpa (Scheme 4). The stability of the putative mono-ligand $[\text{U}^{\text{VI}}\text{O}_2(\text{dpa})(\text{OH})_y]^{n-}$ species in water solution contrasts with the immediate disproportionation of the mono-dpa complex in pyridine.

These results indicate that, at high pH, the hydroxo groups are tightly bound to the uranium center and therefore are capable of saturating the uranium coordination sphere and prevent cation-cation interactions even in the absence of polydentate ligands.



Scheme 4. ^1H NMR speciation of U(VI) and U(V) in water.

We investigated the possibility of isolating this species from the reduction of *in situ* prepared uranyl(VI) mono-dpa complex $[\text{K}(2.2.2.\text{crypt})]_2[\text{U}^{\text{VI}}\text{O}_2(\text{dpa})(\text{OH})_2]$, **4** with $\text{Na}_2\text{S}_2\text{O}_4$ in basic water solution (Fig. S31). From the reaction mixture we isolated, together with crystals of the complex **3-NaK2**, a few crystals of a novel triangular CCI species with a proposed formula $[\text{K}(2.2.2.\text{crypt})]_{0.5}[\text{H}_2\text{KNa}_{1.5}\{\text{UO}_2(\text{dpa})\}_3\text{SO}_3]$ **5**, and presenting a U_3O_6 core with three uranyl groups involved in $\text{U}=\text{O}\dots\text{U}$ interaction (Figure 3). Stable uranyl(V) CCI complexes of different geometries have been isolated in organic solutions.^[6p, 6q, 30] and similar compounds have been isolated from water solution for neptunyl(V)^[31] but not for uranyl(V).

Complex **5** is a rare example of triangular-shaped cation-cation complex and the first example of uranyl(V) CCI isolated from water. A similar triangular geometry was reported for a U(VI)/U(VI)/U(VI) uranyl complex,^[32] a U(V)/U(V)/U(V) uranyl complex,^[6o] and a mixed-valence μ_3 -Cl-bridged U(V)/U(V)/U(VI) carbene complex^[30b] all isolated from organic solutions.

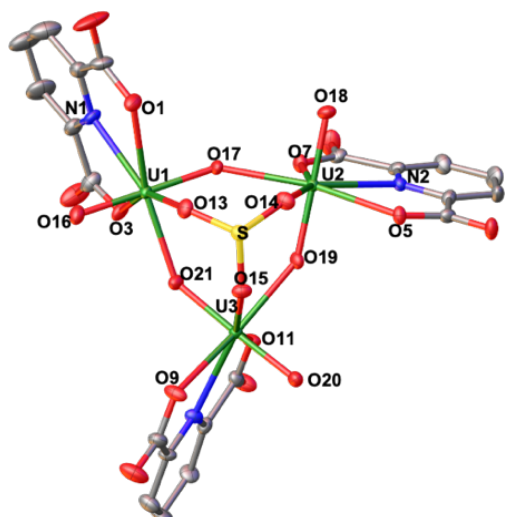


Figure 3. Ellipsoid plot at 50% probability of $[K(2.2.2.crypt)]_{0.5}[H_2KNa_{1.5}(UO_2(dpa))_3SO_3] \cdot 5$ ($[K(2.2.2.crypt)]$, K and Na counter-cations, co-crystallized H_2O and H were omitted for clarity, C are represented in grey, O in red, N in blue, S in yellow and U in green). CCDC numbers are given in Supporting Information.

Each uranyl center in **5** is coordinated by a dpa^{2-} ligand in the equatorial plane. The lengths of three terminal (U1–O16 1.858(4) Å; U2–O18 1.843(4) Å; U3–O20 1.880(4) Å), of the three bridging (U1–O17 1.907(4) Å; U2–O19 1.912(3) Å; U3–O21 1.924(4) Å) uranyl-oxo bonds and of the U=O...U CCI bonds (U1–O21 2.354(3) Å; U2–O17 2.373(4) Å; U3–O19 2.359(4) Å), are very similar to those found in the triangular CCI U(V)/U(V)/U(V) $[UO_2L]_3$ (L = 2-(4-Tolyl)-1,3-bis(quinolyl)malondiiminato) complex,^[60] (mean terminal oxo 1.84(1) Å; bridging 1.93(2) Å; CCI 2.37(1) Å). The bond distances between U-centres and O-atom of a μ_3 - SO_3 are all similar (U1–O13 2.376(4) Å; U2–O14 2.405(4) Å; U3–O15 2.384(3) Å). The values of U–O bond distances in **7** are slightly longer in comparison with mixed-valence U(V)/U(V)/U(VI) CCI trimer $[UO(\mu-O)(L)(\mu_3-Cl)\{UO(\mu-O)(L)\}_2]$.^[30b] (mean terminal 1.86(2) Å vs 1.83(5) Å; mean bridging 1.91(1) Å vs 1.89(7) Å). While it was not possible to identify the presence of 2 additional protons because they are probably delocalized over the structure, the observed bond distances point to the presence of a U(V)/U(V)/U(V). Additionally, the calculated bond valence sum (BVS)^[33] is in agreement with the presence of three U(V) centres in complex **5** (Table S3). Due to the poor yield of complex **5** and the presence of contaminating amounts of **3-NaK2**, it was not possible to perform further characterization. However, the structure of the cluster **5** confirms that stable uranyl(V) mono dpa^{2-} species are formed at basic pH.

These results clearly indicate that uranyl(V) species can be stabilized in anaerobic basic water solutions in the presence of environmentally relevant low denticity ligands such as dipicolinates.

Cyclic Voltammetry

In order to further understand the properties of the uranyl-dpa system, cyclic voltammetry (CV) studies of complexes **1-Crypt**, **3-Crypt** and **3** were performed in pyridine and water solutions. Firstly, the measurements were performed on 4 mM pyridine solutions of **1-Crypt** using $[Bu_4N][PF_6]$ as supporting electrolyte. An irreversible redox wave is observed in pyridine if alkali ions are present (Figure S40 top). The addition of 1 equiv. of

2.2.2.cryptand is necessary to observe the reversible redox couple of interest suggesting that the interaction of cations with the complex plays an important role on the electron transfer kinetics. Compound **1-Crypt** exhibits a quasi-reversible event at $E_{1/2} = -1.78$ V (Fig. S40, bottom), which corresponds to the U(VI)/U(V) couple. The same redox wave is observed for complex **3-Crypt** (Fig. S41) confirming the assignment of the redox event. The value of the measured redox potential is in the range (-0.93 V to -1.82 V) of those previously reported for uranyl(V) complexes in organic media.^[61, 13, 34]

The electrochemical properties of complexes **1-Crypt** and **3** were also investigated in 0.02 M HEPES buffered aqueous solution at different pH conditions. The voltammograms of **1-Crypt** and **3** display redox events that were assigned to uranium centered electron transfers. The observed redox events are irreversible at all investigated pH conditions and are pH dependent (Figure 4 and Fig. S42). The CV at pH=4 for **1-Crypt** shows two irreversible cathodic waves at -0.7 V and -1.6 V with no associated wave in reverse scan. In neutral (pH=7) and basic (pH=11) conditions only a single cathodic wave is observed at -0.96 V and -1.4 V respectively with associated anodic peaks at 0.3 V and 0.9 V respectively.

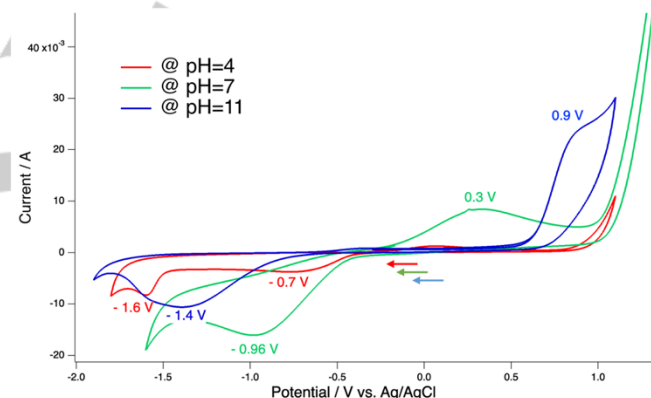


Figure 4. Cyclic voltammograms for 4 mM solutions of $[K(2.2.2.crypt)]_2[UO_2(dpa)_2]$ (**1-Crypt**) recorded in 0.02 M HEPES H_2O at pH=4; pH=7 and pH=11 solution at 100 mV/s scan rate.

The voltammetric data demonstrate that in acidic environment two different reduction events can be differentiated that were assigned to the U(VI)/U(V) redox couple and to the reduction of the dpa^{2-} ligand in the $[UO_2(dpa)_2]^{3-}$ species (the same redox event at -1.6 V was observed for $[K_2Zn(dpa)_2]$, Fig. S44). At $pH \geq 7$ only one large cathodic wave assigned to the U(VI)/U(V) redox couple can be observed which is shifted at lower potential with increasing pH. The presence of irreversible redox features in water was observed for other uranyl complexes^[14, 35] and was interpreted in terms of slow electron transfer kinetics due to structural rearrangements. The observed pH dependence suggests that such rearrangements may involve proton binding to the uranyl oxygen.

The electrochemical behavior of the studied uranyl-dpa system can be compared to that previously reported for the $[UO_2(dpa)_2]^-$ complex which shows the U(VI)/U(V) reduction at -0.6 V at $pH = 7$.^[14] Both systems show pH dependence of the observed redox events with a shift to more negative potentials of the reduction events at more basic pH conditions. Therefore, in both systems the reduction proceeds via a proton-coupled electron-transfer mechanism.

Luminescence spectroscopy

Luminescence is a highly useful spectroscopical tool to study uranium speciation both in organic and aqueous conditions and to monitor redox transformations of uranium in biological systems or inorganic media.^[4c] The photophysical properties of the dominant form of uranium, the uranyl(VI) cation $U^{VI}O_2^{2+}$, originating from partially forbidden charge transfer transitions from oxo-based molecular orbitals to non-bonding f-orbitals, have been extensively studied.^[36] In contrast, only a few studies of the luminescence of uranyl(V) and uranium(IV) compounds were reported,^[4c, 36-37] and none of these studies presents a direct comparison of the photophysical properties of uranyl(VI), uranyl(V) and U(IV) species containing the same organic ligand. A better knowledge of the photochemical properties of uranyl(V) and uranium(IV) compounds is needed and should provide a useful tool to study uranium speciation in complex systems, e.g. in microbial bio-reduction of U or nuclear waste processing.

The luminescence emission and excitation spectra were measured for the solid-state complexes **1**, **2** (see supporting information), **3** and the free ligand (H_2dpa) (Figure 5). Upon excitation at 320 nm at room temperature, $[K_2U^{VI}O_2(dpa)_2]$ **1** displays the characteristic uranyl(VI) sharp bands due to the deactivation of LMCT from uranyl-oxo molecular orbitals to unoccupied f-orbital, centered at 504 nm. The vibrational progression corresponds to the coupling of ground state Raman active vibrational mode (ν_1) with the $^3\Pi_u$ excited state. The observed bands are only slightly shifted (5 nm) compared to those reported for the analogous neutral $[U^{VI}O_2(dpaH)_2]$ complex.^[25] The emission in all complexes is essentially excitation wavelength independent as reported for other systems.^[36] The measured lifetimes decays are found to be bi-exponential with $\tau_1 = 666 \pm 1 \mu s$ and $\tau_2 = 261 \pm 9 \mu s$. The shorter lifetime can be attributed to deactivation pathways taking place within the solid phase.

The solid-state room temperature emission spectrum of the uranyl(V) complex **3** is significantly shifted to lower wavelengths compared to that of complex **1**. The emission spectrum, with two maxima at 415 and 430 nm, is slightly red shifted compared to that reported for solutions of $[U^VO_2(CO_3)_3]^{5-}$ (404 and 419 nm) at low temperature,^[37b] and blue-shifted compared to that of uranyl U(V) perchlorate aqueous solutions (440 nm) (Fig. S52).^[38] The measured radiative lifetime ($\tau = 8 \pm 0.1 \mu s$), which is probably associated to the $O'yl' \rightarrow U$ LMCT transitions is significantly shorter than that measured for **1** U(VI). A second shorter lifetime was also measured ($0.6 \pm 0.03 \mu s$) that could be possibly associated to ligand-metal LMCT. The excitation spectra present two broad bands centered at 365 nm and 271 nm and are independent of the emission wavelengths (415 and 430 nm) suggesting that they originate from the same excited level.

The emission spectrum of the uranium(IV) complex **2** upon excitation at 320 nm has similar emission profile compared to the uranyl(V) complex **3** but is red-shifted by 6 nm (436 nm) and can be deconvoluted in 3 bands (Fig. S53). Rare luminescence studies of U(IV)-doped solid-state materials^[39] and simple U(IV) compounds in water and organic solvent showed metal-centered emission into the UV and visible region arising from excitation into vibrationally coupled states of the $5f^16d^1$ configuration or from $5f^25f^2$ transitions.^[37a, 37c]

The lifetime decay is bi-exponential and the values of the emission lifetimes are $\tau_1 = 7.7 \pm 0.2 \mu s$ and $\tau_2 = 0.7 \pm 0.02 \mu s$, are

longer than those reported for the metal centered transitions in U(IV) chlorides (4 ns)^[37a] and in $[U(DO3A)]Br$ (8-12 ns).

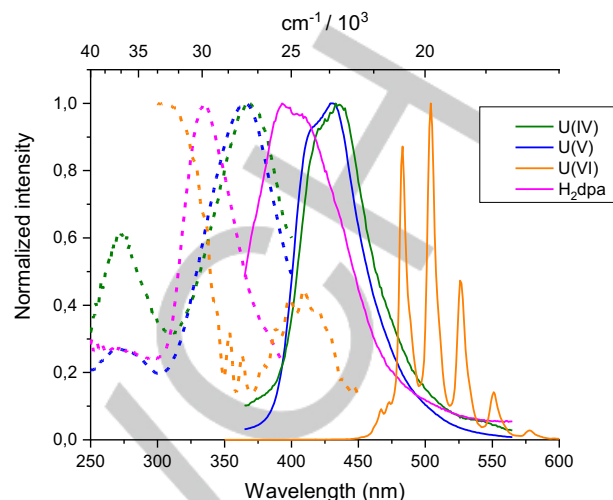


Figure 5. Normalized room-temperature luminescence emission (solid line, $\lambda_{ex}=320$ nm) and excitation (dashed line) spectra of powdered $[K_2U^{VI}O_2(dpa)_2]$ (**1**) ($\lambda_{em}=504$ nm) (orange); $[K_2U^{IV}(dpa)_3]$ (**2**) ($\lambda_{em}=436$ nm) (green); $[K(2.2.2.crypt)]_2[KU^{V}O_2(dpa)_2]$ (**3**) ($\lambda_{em}=430$ nm) (blue), and H_2dpa ($\lambda_{em}=336$ nm) (magenta).

The luminescence of the three complexes in pyridine and water solution (at room temperature and in frozen solution due to luminescence quenching occurring at r.t.) was also investigated (2.2.2.cryptand was added to increase solubility).

All 3 compounds showed luminescence emission in 5 mM pyridine solution and demonstrated very different excitation and emission profiles at room temperature (Figure 6). As found for the solid-state sample, the uranyl(VI) complex **1-Crypt** yields a vibrationally resolved excitation wavelength independent emission centered at 505 nm. In contrast, the uranyl(V) (**3-Crypt**) and uranium(IV) (**2-Crypt**) complexes demonstrate very different behavior in pyridine solution in comparison to solid-state (ss). The room temperature emission spectrum of **3-Crypt** ($\lambda_{ex} = 360$ nm) is broad with two maxima at 404 and 459 nm (415 and 430 nm in ss), while **2-Crypt** ($\lambda_{ex} = 320$ nm) shows an even broader emission with maxima at 475, 534 and 587 nm. Very different shapes of both excitation and emission spectra were observed for **3-Crypt** (U(V)) and **2-Crypt** (U(IV)) at 77 K, while only a better resolution was observed for **1-Crypt** compared to the room temperature spectrum (detailed description in SI). Lifetime decays of **3-Crypt** and **2-Crypt** were analyzed for different excitation and emission wavelengths, at room temperature and in frozen solution. They were best fitted by using a bi or tri-exponential model and values were found in the microsecond range (see Table S1). The longest one at room temperature was around 11 μs for **3-Crypt** and 8 μs for **2-Crypt**. Within experimental errors, the values were identical for the whole emission and excitation selected, which indicating that the emission occurs from a common excited state.

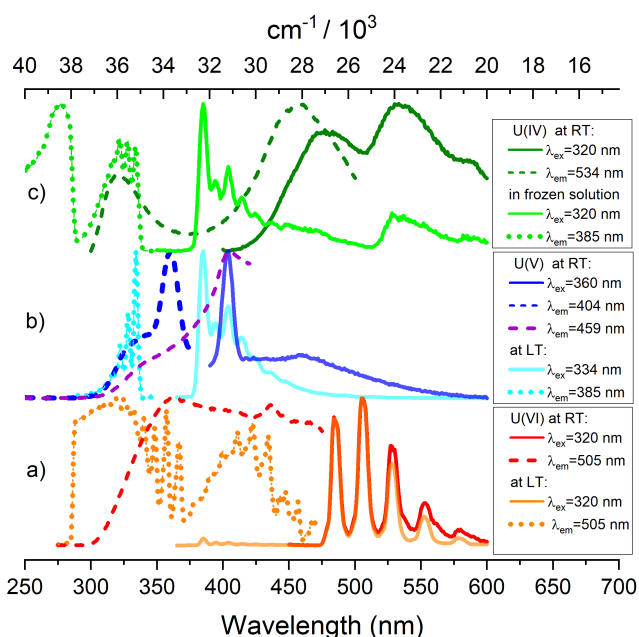


Figure 6. Normalized luminescence excitation and emission spectra of 5 mM pyridine solutions of **1-Crypt** (U(VI)), **2-Crypt** (U(IV)) and **3-Crypt** (U(V)) at room temperature and in frozen solutions.

Finally, the luminescent properties of 5 mM water solutions of all three species were investigated (Figure 7). The luminescence of complex **1-Crypt** could be observed at room temperature but it showed weak emission due to deactivation processes taking place in the presence the O-H oscillators of water molecules. When working with frozen solution (77 K), the spectra are well-resolved and the excitation spectrum is similar to that observed in solid state. The emission spectrum presents additional lines blue shifted by approx. 10 nm compared to solid state.

The uranyl(V) complex **3** showed excitation wavelength-dependent photoluminescence in 5 mM water solution (pH=10) at room temperature. Three different emission spectra with $\lambda_{\text{max}} = 408$ nm, 434 nm and 524 nm were obtained upon excitation at $\lambda_{\text{ex}} = 320$ nm, 380 nm and 445 nm respectively. In frozen solution a significant increase of the luminescence intensity and a different profile for both emission and excitation spectra were obtained. The excitation at $\lambda_{\text{ex}} = 271$ and 291 nm yields two similar emission spectra at $\lambda_{\text{max}} = 403$ nm. The values of the measured lifetimes, fitted using a bi or tri-exponential model, are similar to those found in pyridine solutions indicating similar coordination environment for the solution species in pyridine and water at pH=10.

Finally, the photoluminescence spectra of 5 mM **2** aqueous solution (pH=7) were recorded, also demonstrating wavelength dependence of the emission bands. Notably, complex **2** yields two distinct excitation spectra at $\lambda_{\text{em}} = 445$ and 525, as well as three different emission spectra ($\lambda_{\text{ex}} = 304$, 385 and 445). This differs from the excitation independent emission spectra previously reported for U(IV) chlorides or for the $[\text{U}(\text{DO}_3\text{A})]^{+}$.^[40] [37a]

Moreover, excitation at 253 nm through the dipicolinate ligand does not results in quenching of the 5f-centered emission as found in the rare examples of reported coordination complexes.^[37d] Lifetimes decays were not shortened compared to those found in pyridine, suggesting the presence of uranium solution species with similar coordination environment in both solvents. The emission spectra of **2** are a rare example of spectra

of a U(IV) complex coordinated to an organic ligand which are observable at room temperature.

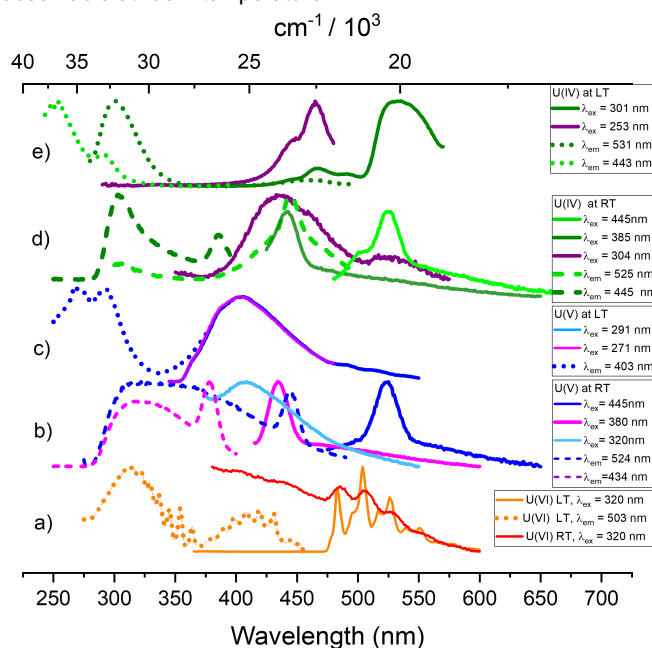


Figure 7. a) Normalized luminescence excitation and emission spectra of 5 mM water solution of **1-Crypt** at pH = 7 at room temperature (red) and at 77 K (orange). **b)** Normalized luminescence excitation and emission spectra of 5 mM water solution of **3** at pH = 10 at room temperature (bottom) and **c)** in frozen solution (top). **d)** Normalized luminescence excitation (dashed) and emission (solid) spectra of 5 mM water solution of **2** at pH = 7 at room temperature (bottom) and **e)** in frozen solution (top).

Conclusions

The low stability of uranyl(V) (UO_2^{2+}) in water, where it tends to disproportionate to UO_2^{2+} and to U(IV), has minimized its environmental relevance. Herein, we demonstrated that in the presence of the low denticity complexing ligand dpa^{2-} , the uranyl(V) species can be stabilized and isolated in basic aqueous conditions. This is particularly relevant in view of the presence of dipicolinic acid in the soil. The dipicolinate complexes of uranyl(VI) **1** and **1-Crypt** can be reduced both in organic solution and in basic anoxic water to yield stable complexes of uranyl(V) (**3**, **3-Crypt** and **3-NaK2**). Additionally, the uranyl(VI) dipicolinate **1-Crypt** also undergoes photochemical reduction both in pyridine and in basic water to yield the analogues U(V) (**3-Crypt**) and U(IV) (**2-Crypt**) species. Uranyl(V) bis-dipicolinate complexes formed at pH 10 and were isolated in the solid state as polymeric chains resulting from the alkali ion coordination. Alternatively, stable mono-dipicolinate complexes of uranyl(V) were obtained in water upon reduction of $[\text{U}^{\text{VI}}\text{O}_2(\text{dpa})(\text{OH})]_2^{2-}$ at higher pH values. Additionally, crystals of a trinuclear mono-dipicolinate uranyl(V) cation-cation complex **5** were isolated from the reaction mixture. The measured voltammetric data show pH dependence of the observed redox events suggesting that the reduction proceeds via a proton-coupled electron-transfer mechanism. Finally, the uranyl(VI), **1-Crypt**, uranyl(V), **3-Crypt** and U(IV) **2-Crypt** dipicolinate complexes display very different measurable luminescent spectra characteristic of the uranium oxidation state,

RESEARCH ARTICLE

suggesting that luminescence provides a tool to discriminate between these species in different environments.

Acknowledgements

We thank Dr. Rosario Scopelliti for his contribution to the X-ray single crystal structure data collection and analyses. We thank Dr. A. Sienkiewicz for EPR data collection. This work was supported by the Ecole Polytechnique Fédérale de Lausanne (EPFL) and by the Swiss National Science Foundation grant (number CR2312_16645).

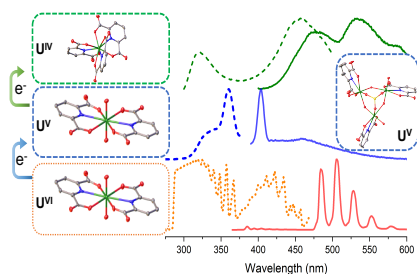
Keywords: Uranium • actinides • uranyl • redox chemistry • luminescence

- [1] a)B. E. Cowie, J. M. Purkis, J. Austin, J. B. Love, P. L. Arnold, *Chem. Rev.* **2019**, *119*, 10595-10637; b)S. Fortier, T. W. Hayton, *Coord. Chem. Rev.* **2010**, *254*, 197-214; c)S. A. Cumberland, G. Douglas, K. Grice, J. W. Moreau, *Earth-Sci. Rev.* **2016**, *159*, 160-185.
- [2] E. J. Schofield, H. Veeramani, J. O. Sharp, E. Suvorova, R. Bernier-Latmani, A. Mehta, J. Stahlman, S. M. Webb, D. L. Clark, S. D. Conradson, E. S. Ilton, J. R. Bargar, *Environ. Sci. Technol.* **2008**, *42*, 7898-7904.
- [3] S. E. Bone, J. J. Dynes, J. Cliff, J. R. Bargar, *Proc Natl Acad Sci USA* **2017**, *114*, 711-716.
- [4] a)D. R. Lovley, E. J. P. Phillips, Y. A. Gorby, E. R. Landa, *Nature* **1991**, *350*, 413-416; b)D. M. Singer, S. M. Chatman, E. S. Ilton, K. M. Rosso, J. F. Banfield, G. A. Waychunas, *Environ. Sci. Technol.* **2012**, *46*, 3821-3830; c)D. L. Jones, M. B. Andrews, A. N. Swinburne, S. W. Botchway, A. D. Ward, J. R. Lloyd, L. S. Natrajan, *Chem. Sci.* **2015**, *6*, 5133-5138; d)L. S. Natrajan, A. N. Swinburne, M. B. Andrews, S. Randall, S. L. Heath, *Coord. Chem. Rev.* **2014**, *266*, 171-193.
- [5] a)P. C. Burns, R. J. Finch, *Am. Mineral.* **1999**, *84*, 1456-1460; b)P. L. Arnold, J. B. Love, D. Patel, *Coord. Chem. Rev.* **2009**, *253*, 1973-1978; c)J. C. Renshaw, L. J. C. Butchins, F. R. Livens, I. May, J. M. Charnock, J. R. Lloyd, *Environ. Sci. Technol.* **2005**, *39*, 5657-5660; d)E. S. Ilton, A. Haiduc, C. L. Cahill, A. R. Felmy, *Inorg. Chem.* **2005**, *44*, 2986-2988; e)E. S. Ilton, J. S. L. Pacheco, J. R. Bargar, Z. Shi, J. Liu, L. Kovarik, M. H. Engelhard, A. R. Felmy, *Environ. Sci. Technol.* **2012**, *46*, 9428-9436; f)E. S. Ilton, J.-F. Boily, E. C. Buck, F. N. Skomurski, K. M. Rosso, C. L. Cahill, J. R. Bargar, A. R. Felmy, *Environ. Sci. Technol.* **2010**, *44*, 170-176; g)C. Dewey, D. Sokaras, T. Kroll, J. R. Bargar, S. Fendorf, *Environ. Sci. Technol.* **2020**, *54*, 6021-6030; h)G. F. Vettese, K. Morris, L. S. Natrajan, S. Shaw, T. Vitova, J. Galanzew, D. L. Jones, J. R. Lloyd, *Environ. Sci. Technol.* **2020**, *54*, 2268-2276.
- [6] a)L. Natrajan, F. Burdet, J. Pécaut, M. Mazzanti, *J. Am. Chem. Soc.* **2006**, *128*, 7152-7153; b)J. C. Berthet, G. Siffredi, P. Thuery, M. Ephritikhine, *Chem. Commun.* **2006**, 3184-3186; c)M. B. Jones, A. J. Gaunt, *Chem. Rev.* **2013**, *113*, 1137-1198; d)P. L. Arnold, D. Patel, C. Wilson, J. B. Love, *Nature* **2008**, *451*, 315-318; e)K. Takao, S. Tsushima, S. Takao, A. C. Scheinost, G. Bernhard, Y. Ikeda, C. Hennig, *Inorg. Chem.* **2009**, *48*, 9602-9604; f)P. Horeglad, G. Nocton, Y. Filinchuk, J. Pécaut, M. Mazzanti, *Chem. Commun.* **2009**, 1843-1845; g)G. Nocton, P. Horeglad, V. Vetere, J. Pécaut, L. Dubois, P. Maldivi, N. M. Edelstein, M. Mazzanti, *J. Am. Chem. Soc.* **2010**, *132*, 495-508; h)V. Mougél, J. Pécaut, M. Mazzanti, *Chem. Commun.* **2012**, *48*, 868-870; i)T. W. Hayton, G. Wu, *J. Am. Chem. Soc.* **2008**, *130*, 2005-2014; j)T. W. Hayton, G. Wu, *Inorg. Chem.* **2008**, *47*, 7415-7423; k)P. L. Arnold, B. E. Cowie, M. Suvova, M. Zegke, N. Magnani, E. Colineau, J. C. Griveau, R. Caciuffo, J. B. Love, *Angew. Chem. Int. Ed. Engl.* **2017**, *56*, 10775-10779; l)P. L. Arnold, E. Hollis, G. S. Nichol, J. B. Love, J. C. Griveau, R. Caciuffo, N. Magnani, L. Maron, L. Castro, A. Yahia, S. O. Odoh, G. Schreckenbach, *J. Am. Chem. Soc.* **2013**, *135*, 3841-3854; m)P. L. Arnold, A. F. Pecharman, E. Hollis, A. Yahia, L. Maron, S. Parsons, J. B. Love, *Nat. Chem.* **2010**, *2*, 1056-1061; n)V. Mougél, P. Horeglad, G. Nocton, J. Pécaut, M. Mazzanti, *Chem. Eur. J.* **2010**, *16*, 14365-14377; o)L. Chatelain, V. Mougél, J. Pécaut, M. Mazzanti, *Chem. Sci.* **2012**, *3*, 1075-1079; p)V. Mougél, P. Horeglad, G. Nocton, J. Pécaut, M. Mazzanti, *Angew. Chem. Int. Ed. Engl.* **2009**, *48*, 8477-8480; q)G. Nocton, P. Horeglad, J. Pécaut, M. Mazzanti, *J. Am. Chem. Soc.* **2008**, *130*, 16633-16645; r)F. Burdet, J. Pécaut, M. Mazzanti, *J. Am. Chem. Soc.* **2006**, *128*, 16512-16513.
- [7] a)A. Kumar, D. Lionetti, V. W. Day, J. D. Blakemore, *J. Am. Chem. Soc.* **2020**, *142*, 3032-3041; b)T. K. Ghosh, P. Mahapatra, M. G. B. Drew, A. Franconetti, A. Frontera, A. Ghosh, *Chem. Eur. J.* **2020**, *26*, 1612-1623; c)M. Zegke, X. B. Zhang, I. Pidchenko, J. A. Hlina, R. M. Lord, J. Purkis, G. S. Nichol, N. Magnani, G. Schreckenbach, T. Vitova, J. B. Love, P. L. Arnold, *Chem. Sci.* **2019**, *10*, 9740-9751; d)J. J. Kiernicki, M. Zeller, S. C. Bart, *Angew. Chem. Int. Ed. Engl.* **2017**, *56*, 1097-1100; e)D. D. Schnaars, G. Wu, T. W. Hayton, *J. Am. Chem. Soc.* **2009**, *131*, 17532-17533; f)J. J. Kiernicki, D. P. Cladis, P. E. Fanwick, M. Zeller, S. C. Bart, *J. Am. Chem. Soc.* **2015**, *137*, 11115-11125.
- [8] a)R. J. Abergel, W. A. de Jong, G. J. P. Deblonde, P. D. Dau, I. Captain, T. M. Eaton, J. W. Jian, M. J. van Stipclonk, J. Martens, G. Berden, J. Oomens, J. K. Gibson, *Inorg. Chem.* **2017**, *56*, 12930-12937; b)Y. Gong, W. A. de Jong, J. K. Gibson, *J. Am. Chem. Soc.* **2015**, *137*, 5911-5915.
- [9] a)J. L. Brown, C. C. Mokhtarzadeh, J. M. Lever, G. Wu, T. W. Hayton, *Inorg. Chem.* **2011**, *50*, 5105-5112; b)B. E. Cowie, G. S. Nichol, J. B. Love, P. L. Arnold, *Chem. Commun.* **2018**, *54*, 3839-3842; c)N. L. Bell, B. Shaw, P. L. Arnold, J. B. Love, *J. Am. Chem. Soc.* **2018**, *140*, 3378-3384; d)J. R. Pankhurst, N. L. Bell, M. Zegke, L. N. Platts, C. A. Lamfus, L. Maron, L. S. Natrajan, S. Sproules, P. L. Arnold, J. B. Love, *Chem. Sci.* **2017**, *8*, 108-116.
- [10] J. Selbin, J. D. Ortego, *Chem. Rev.* **1969**, *69*, 657-671.
- [11] a)K. A. Kraus, F. Nelson, *J. Am. Chem. Soc.* **1949**, *71*, 2517-2522; b)A. Ekstrom, *Inorg. Chem.* **1974**, *13*, 2237-2241.
- [12] a)D. Ferri, I. Grenthe, F. Salvatore, *Inorg. Chem.* **1983**, *22*, 3162-3165; b)T. I. Docrat, J. F. W. Mosselmans, J. M. Charnock, M. W. Whiteley, D. Collison, F. R. Livens, C. Jones, M. J. Edmiston, *Inorg. Chem.* **1999**, *38*, 1879-1882; c)D. W. Wester, J. C. Sullivan, *Inorg. Chem.* **1980**, *19*, 2838-2840; d)K. Mizuoka, I. Grenthe, Y. Ikeda, *Inorg. Chem.* **2005**, *44*, 4472-4474; e)A. Ikeda, C. Hennig, S. Tsushima, K. Takao, Y. Ikeda, A. C. Scheinost, G. Bernhard, *Inorg. Chem.* **2007**, *46*, 4212-4219.
- [13] R. Faizova, R. Scopelliti, A. S. Chauvin, M. Mazzanti, *J. Am. Chem. Soc.* **2018**, *140*, 13554-13557.
- [14] R. Faizova, F. Fadaei-Tirani, R. Bernier-Latmani, M. Mazzanti, *Angew. Chem. Int. Ed. Engl.* **2020**, *59*, 6756-6759.
- [15] a)M. Sundararajan, R. S. Assary, I. H. Hillier, D. J. Vaughan, *J. Chem. Soc.-Dalton Trans.* **2011**, *40*, 11156-11163; b)H. Steele, R. J. Taylor, *Inorg. Chem.* **2007**, *46*, 6311-6318.
- [16] A. Pellissier, Y. Bretonniere, N. Chatterton, J. Pécaut, P. Delangle, M. Mazzanti, *Inorg. Chem.* **2007**, *46*, 3714-3725.
- [17] a)B. Masci, P. Thuery, *Polyhedron* **2005**, *24*, 229-237; b)A. Cousson, J. Proust, E. N. Rizkalla, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1991**, *47*, 2065-2069; c)A. Immirzi, G. Bombieri, S. Degetto, G. Marangoni, *Acta Crystallogr., Sect. B: Struct. Sci.* **1975**, *31*, 1023-1028.
- [18] a)C. Xu, G. X. Tian, S. J. Teat, L. F. Rao, *Inorg. Chem.* **2013**, *52*, 2750-2756; b)G. X. Tian, L. F. Rao, S. J. Teat, *Inorg. Chem.* **2009**, *48*, 10158-10164.
- [19] J. I. Friese, K. L. Nash, M. P. Jensen, J. C. Sullivan, *Radiochim. Acta* **2001**, *89*, 35-41.
- [20] a)M. Y. Alyapyshev, V. A. Babain, L. I. Tkachenko, Eliseev, I. A. V. Didenko, M. L. Petrov, *Solvent Extr. Ion Exch.* **2011**, *29*, 619-636; b)J. L. Lapka, A. Paulenova, M. Y. Alyapyshev, V. A. Babain, R. S. Herbst, J. D. Law, *Radiochim. Acta* **2009**, *97*, 291-296.
- [21] S. K. Cary, S. S. Galley, M. L. Marsh, D. L. Hobart, R. E. Baumbach, J. N. Cross, J. T. Stritzinger, M. J. Polinski, L. Maron, T. E. Albrecht-Schmitt, *Nat. Chem.* **2017**, *9*, 856-861.
- [22] a)M. P. Kelley, J. Su, M. Urban, M. Luckey, E. R. Batista, P. Yang, J. C. Shafer, *J. Am. Chem. Soc.* **2017**, *139*, 9901-9908; b)M. A. Silver, S. K. Cary, J. A. Johnson, R. E. Baumbach, A. A. Arico, M. Luckey, M. Urban, J. C. Wang, M. J. Polinski, A. Chemey, G. Liu, K. W. Chen, S. M. Van Cleve, M. L. Marsh, T. M. Eaton, L. J. V. de Burgt, A. L. Gray, D. E. Hobart, K. Hanson, L. Maron, F. Gendron, J. Autschbach, M. Speldrich, P. Kogerler, P. Yang, J. Braley, T. E. Albrecht-Schmitt, *Science* **2016**, *353*; c)S. K. Cary, M. Vasiliu, R. E. Baumbach, J. T. Stritzinger, T. D. Green, K. Diefenbach, J. N. Cross, K. L. Knappenberger, G. Liu, M. A. Silver, A. E. DePrince, M. J. Polinski, S. M. Van Cleve, J. H. House, N. Kikugawa, A. Gallagher, A. A. Arico, D. A. Dixon, T. E. Albrecht-Schmitt, *Nat. Commun.* **2015**, *6*.
- [23] B. Setlow, S. Atluri, R. Kitchel, K. Koziol-Dube, P. Setlow, *J. Bacteriol.* **2006**, *188*, 3740-3747.
- [24] J. Fichtel, J. Koster, J. Rullkotter, H. Sass, *FEMS Microbiol. Ecol.* **2007**, *61*, 522-532.
- [25] J. M. Harrowfield, N. Lugan, G. H. Shahverdizadeh, A. A. Soudi, P. Thuery, *Eur. J. Inorg. Chem.* **2006**, 389-396.
- [26] a)L. Chatelain, S. White, R. Scopelliti, M. Mazzanti, *Angew. Chem. Int. Ed. Engl.* **2016**, *55*, 14323-14327; b)A. E. Vaughn, D. B. Bassil, C. L. Barnes, S. A. Tucker, P. B. Duval, *J. Am. Chem. Soc.* **2006**, *128*, 10656-10657; c)S. Kannan, A. E. Vaughn, E. M. Weis, C. L. Barnes, P. B. Duval, *J. Am. Chem. Soc.* **2006**, *128*, 14024-14025; d)S. Kannan, M. A. Moody, C. L. Barnes, P. B. Duval, *Inorg. Chem.* **2006**, *45*, 9206-9212.
- [27] V. Mougél, B. Biswas, J. Pécaut, M. Mazzanti, *Chem. Commun.* **2010**, *46*, 8648-8650.
- [28] D. F. Evans, *J. Chem. Soc.* **1959**, 2003-2005.
- [29] D. R. Kindra, W. J. Evans, *Chem. Rev.* **2014**, *114*, 8865-8882.
- [30] a)L. Chatelain, V. Mougél, J. Pécaut, M. Mazzanti, *Chem. Sci.* **2012**, *3*, 1075-1079; b)D. P. Mills, O. J. Cooper, F. Tuna, E. J. L. McInnes, E. S. Davies, J. McMaster, F. Moro, W. Lewis, A. J. Blake, S. T. Liddle, *J. Am. Chem. Soc.* **2012**, *134*, 10047-10054.
- [31] N. N. Krot, M. S. Grigoriev, *Russ. Chem. Rev.* **2004**, *73*, 89-100.
- [32] J. C. Taylor, A. Ekstrom, C. H. Randall, *Inorg. Chem.* **1978**, *17*, 3285-3289.

RESEARCH ARTICLE

- [33] I. D. Brown, D. Altermatt, *Acta Crystallogr. Sect. B* **1985**, *B41*, 244-247.
- [34] a)R. Faizova, S. White, R. Scopelliti, M. Mazzanti, *Chem. Sci.* **2018**, *9*, 7520-7527; b)G. Nocton, P. Horeglad, V. Vetere, J. Pecaut, L. Dubois, P. Maldivi, N. M. Edelstein, M. Mazzanti, *J. Am. Chem. Soc.* **2010**, *132*, 495-508.
- [35] D. E. Morris, *Inorg. Chem.* **2002**, *41*, 3542-3547.
- [36] L. S. Natrajan, *Coord. Chem. Rev.* **2012**, *256*, 1583-1603.
- [37] a)E. Hashem, A. N. Swinburne, C. Schulzke, R. C. Evans, J. A. Platts, A. Kerridge, L. S. Natrajan, R. J. Baker, *Rsc Advances* **2013**, *3*, 4350-4361; b)K. Grossmann, T. Arnold, A. Ikeda-Ohno, R. Steudtner, G. Geipel, G. Bernhard, *Spectrochim. Acta A Mol. Biomol. Spectrosc.* **2009**, *72*, 449-453; c)A. Kirishima, T. Kimura, O. Tochiyama, Z. Yoshida, *Chem. Commun.* **2003**, 910-911; d)D. J. Hilton, R. P. Prasankumar, E. J. Schelter, V. K. Thorsmolle, S. A. Trugman, A. P. Shreve, J. L. Kiplinger, D. E. Morris, A. J. Taylor, *J. Phys. Chem. A* **2008**, *112*, 7840-7847.
- [38] R. Steudtner, T. Arnold, K. Grossmann, G. Geipel, V. Brendler, *Inorg. Chem. Commun.* **2006**, *9*, 939-941.
- [39] B. Ordejon, L. Seijo, Z. Barandiaran, *J. Chem. Phys.* **2005**, *123*.
- [40] L. S. Natrajan, *J. Chem. Soc.-Dalton Trans.* **2012**, *41*, 13167-13172.

Entry for the Table of Contents



The tridentate dipicolinate ligand dpa^{2-} , allowed to stabilize and isolate mononuclear and trinuclear uranyl(V) species in anoxic basic water providing the second example ever isolated of a water stable uranyl(V) and further demonstrating the environmental relevance of U(V). The uranyl(VI), uranyl(V) and U(IV) dipicolinate complexes show very different measurable luminescent spectra characteristic of the uranium oxidation state.

Institute and/or researcher Twitter usernames: [@Mazzantilab](#)