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Synthesis, reactivity, and environmental relevance of uranyl(V) complexes.

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par

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### Abstract

Knowledge of fundamental chemical properties of all environmentally relevant uranium species is essential to understand environmental uranium mobility and develop novel remediation strategies. A myriad of uranium(VI) and uranium(IV) compounds has been studied for decades but the uranyl(V) analog was traditionally thought of as a highly unstable species of limited environmental importance. This understanding has changed in the last decade with studies demonstrating uranyl(V) to be a persistent species in Fe rich environments and an intermediate in the biological /abiotic transformations of soluble uranyl(VI) compounds into insoluble uranium(IV) polynuclear species. These processes are imperative for drinking water remediation but their mechanism and the role of U(V) remains unclear.

A stable uranyl(V) complex in organic media was first reported more than 10 years ago and this led to rapid development in the field. However, a stable compound in aqueous media at environmentally relevant pH could not be obtained and this was selected as the primary goal of this thesis.

Our research produced the first uranyl(V) complex that is stable in both organic and aqueous media. This was achieved using an aminopicolinate ligand, combining the pentadentate binding mode with the ability to form stable complexes with metal ions in water. This molecule has allowed us to investigate the persistence of U(V) in certain environments, its conversion to insoluble complexes, and the mechanism of bacterial reduction of uranium with collaborators in microbiology.

The effect of Fe<sup>2+</sup> on the stability of U(V) towards proton-induced disproportionation and redox reactions was investigated. Cation-cation interaction between uranyl(V) oxygen and Fe<sup>2+</sup> was shown to stabilize U(V), explaining its unusual persistence in Fe-rich environments.

Additionally, the effect of iron and the impact of a supporting ligand on the electronic structure of U(V) was investigated in collaboration by a high-resolution X-ray absorption spectroscopy and computational study.

Several rational routes for the preparation of uranium polyoxometalates (POM) were developed. The resulting clusters provide a good model of uranate species formed upon environmental reduction of uranyl(VI). An insoluble well-defined molecular trinuclear U(IV) oxo/hydroxo cluster was isolated in a good yield from the direct reduction of a uranyl(VI) complex in aqueous media. This unprecedented 2-electron reduction was accomplished by utilizing a readily available and non-toxic reductant (Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>).

Finally, controlled hydrolysis of UCl<sub>4</sub> in organic solution was explored to investigate the factors that govern the assembly of uranium POMs. The formation of discrete uranium(IV) clusters of various nuclearities (U6 – U38) was shown to be dependent on multiple factors, however, the time variable was found to be paramount.

#### **Keywords:**

Uranyl(V), cation-cation interaction, disproportionation, reduction, uranium(IV) clusters, POMs, metal oxo, iron binding.

« Nothing in life is to be feared, it is only to be understood. Now is the time to understand more, so that we may fear less. » — Marie Curie

### Résumé

La connaissance des propriétés chimiques fondamentales de toutes les espèces d'uranium naturellement présentes dans l'environnement est essentielle pour comprendre la transformation de l'uranium dans cet environnement, et développer de nouvelles stratégies en vue du traitement des sols. Une myriade de composés d'uranium (VI) et U(IV) a été étudiée pendant des décennies. En revanche, l'uranyle(V) U(V) était traditionnellement considéré comme une espèce hautement instable, et par conséquence de faible impact environnemental. Pour autant, cette hypothèse a évolué au cours de la dernière décennie et les études ont démontré que l'uranyle (V) est une espèce persistante dans des environnements riches en Fe; il agit comme intermédiaire dans les transformations biologiques / abiotiques des composés uranyle(VI) solubles en espèces polynucléaires et insolubles de l'uranium (IV). La compréhension de ces processus est impérative pour l'assainissement de l'eau potable, mais leur mécanisme et le rôle de l'U (V) restent incertains.

Un complexe uranyle (V) stable en milieu organique a été isolé pour la première fois il y a plus de 10 ans, ce qui a ouvert de nombreuses voies. Cependant, un composé stable dans un milieu aqueux à un pH respectueux de l'environnement n'avait encore jamais été obtenu. Cela a donc été l'objectif principal de cette thèse.

Nos recherches ont permis d'obtenir le premier complexe d'uranyle(V) stable dans les milieux organiques et aqueux. Ceci a été réalisé en utilisant un ligand aminopicolinate, combinant le mode de liaison pentadentate, avec la capacité de former des complexes stables dans l'eau en présence d'ions métalliques. Cette molécule nous a permis d'étudier la persistance de l'U(V) dans certains environnements, sa conversion en complexes insolubles et le mécanisme de réduction bactérienne de l'uranium grâce à une collaboration avec des microbiologistes.

L'effet du fer ferreux Fe<sup>2+</sup> sur la stabilité de cet U(V) a été étudié vis-à-vis de la disproportionation induite par les protons et des réactions redox. L'interaction cation-cation entre l'oxygène de l'uranyle (V) et le Fe<sup>2+</sup> s'est avérée comme un élément stabiliseur de l'U(V), expliquant sa persistance inhabituelle dans les environnements riches en Fe.

De plus, l'effet du fer et la stabilisation induite par le choix du ligand sur la structure électronique de l'U (V) ont été étudiés, en collaboration, par la spectroscopie d'absorption des rayons X à haute résolution et une modélisation de ce système.

Plusieurs voies rationnelles ont été développées pour la préparation des polyoxométalates d'uranium (POM). Les structures résultantes fournissent des espèces qui servent de modèle pour l'étude d'uranates formées lors de la réduction environnementale de l'uranyle (VI). Un groupe moléculaire trinucléaire U (IV) oxo / hydroxo insoluble bien défini a été isolé avec un bon rendement, à partir de la réduction directe d'un complexe uranyle (VI) en milieu aqueux. Cette réduction sans précédent de 2 électrons a été réalisée en utilisant un réducteur facilement disponible et non toxique (Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>).

Finalement, une hydrolyse contrôlée de le l'espèce UCl<sub>4</sub> en solution organique a été explorée, afin d'étudier les facteurs qui régissent l'assemblage des POM d'uranium. Il a été démontré que la formation d'amas discrets d'uranium (IV) de diverses nucléarités (U6 - U38) dépendait de plusieurs facteurs, mais la variable de temps s'est avérée primordiale.

#### Mots-clés :

Uranyle (V), interaction cation-cation, disproportionation, réduction, amas d'uranium (IV), POM, oxo métallique, liaison du fer.

« Dans la vie, rien n'est à craindre, tout est à comprendre.

C'est maintenant le moment de comprendre davantage, afin de craindre moins. » – Marie Curie

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# Abbreviations

18c6	1,4,7,10,13,16-hexaoxacyclooctadecane
AD	Anno Domini
An	actinide
СС	cation-cation
CCI	cation-cation interaction
cryptand	1,10-diaza-4,7,13,16,21,24-hexaoxabicyclo[8.8.8]hexacosane
Cp*	pentamethylcyclopentadienyl
DFT	density functional theory
DMF	dimethylformamide
DMSO	dimethyl sulfoxide
Е <sub>н</sub>	electrical potential
EPR	electron paramagnetic resonance
Et	ethyl
equiv.; eq.	equivalents
ESI-MS	electro-spray ionization mass spectrometry
Fc	ferrocene
Fe	iron
HR-TEM	high-resolution transmission electron microscopy
Hz	Herz
<sup>i</sup> Pr	isopropyl
IR	infrared
К	Kelvin
Ln	lanthanide
М	transition metal
Me	methyl
NMR	nuclear magnetic resonance
OTf	triflate: $CF_3SO_3^-$
Ph	phenyl
рН	potential of hydrogen
рК <sub>а</sub>	dissociation constant

POM	polyoxometalate
ppm	parts per million
r.t.	room temperature
t <sub>1/2</sub>	half-life
THF	tetrahydrofuran
TMS	trimethylsilyl
U	uranium
UiO-66	(Universitetet i Oslo) metal organic framework
EXAFS	extended X-ray absorption fine structure

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## Chapter 1 : Introduction

### **1.1** Introduction to uranium

Though the use of uranium as a yellow coloring agent in ceramic glazes dates back to AD 79, the identification of uranium as an element only occurred in 1789 in Berlin by the German chemist Martin Heinrich Klaproth. While working with pitchblende, which was believed to be an iron/zinc ore, Klaproth noticed that excess potash dissolved a yellow precipitate. This reaction was not characteristic of any known element, so Klaproth concluded that he had just discovered a new element, uranium.<sup>[1]</sup> In reality, Klaproth had identified uranium oxide; pure elemental uranium was isolated in 1841 by the French chemist Eugene-Melchior Peligot by heating UCl<sub>4</sub> with potassium.

In 1896, Antoine H. Becquerel noticed that uranium emitted invisible rays. This was the moment when one of the most fascinating properties of uranium was discovered – its radioactivity. But it was not until 1934 that Idda Noddack, Otto Hahn, Lise Meitner and others realized and proved the nuclear fission capacities of uranium, eventually enabling the development of nuclear energy and the creation of nuclear weapons (Figure 1).<sup>[2]</sup>



Figure 1. Representation of the fission process from <sup>235</sup>U. Adapted form [3].

Nowadays, uranium is mainly used as fuel for nuclear reactors. Nuclear reactions release much more energy than chemical reactions, e.g. the fission of 1 g of <sup>235</sup>U produces the same amount of energy as burning 1.5 tons of coal. Naturally occurring uranium has only 0.7% of the fissile isotope <sup>235</sup>U, so for use in nuclear power plants, uranium is enriched to contain about 3–5% of <sup>235</sup>U. The by-product of this enrichment process is depleted uranium (DU). Though it is approximately half as radioactive

as natural uranium, DU only has a few niche uses (ammunition, counterweights, radiography equipment), and every year 50,000 tons are added to the current stockpile of 1.6 million tons of DU.<sup>[4]</sup> Safe storage of DU is highly important to protect people and the environment. While significant effort has been directed to the development of novel storage solutions, several leakages from DU stockpiles have been reported.<sup>[5]</sup> Therefore, it is important to understand the environmental chemistry of uranium to ensure safety, as well as find some applications for the growing stocks of this element.

#### **1.2** Uranium in the environment, its mobility and health effects

Although uranium is radioactive, it is widely spread throughout the environment due to its very long half-life (e.g. for <sup>238</sup>U,  $t_{1/2}$  = 4.46 billion years). It can be found naturally in soil, rocks, sediments, water and air, though concentrations are generally very low (e.g. 0.0033 mg/kg in seawater). Humans significantly contribute to the redistribution of uranium via industrial activity, and the four principal sources are nuclear fuel cycle, military use of depleted uranium, use of coal, and agricultural use of phosphate fertilizers.

The concentration of natural uranium is controlled by factors such as pH (hydrolysis), E<sub>H</sub> (oxidation state), reactions with complexants (carbonate, phosphate, humic acids, etc.), sorption on mineral surfaces/colloids, etc. The dominant form of uranium in oxidizing environments is U(VI), while U(IV)containing colloidal fractions play an important role under anoxic reducing conditions.<sup>[6]</sup> The uranyl ion,  $UO_2^{2+}$ , is the dominant species in surface water, and it forms stable complexes with organic ligands that contribute to its migration in aquatic systems.<sup>[7]</sup> In rivers, more than 90% of uranium may be associated with the iron colloidal fraction, which governs transport mechanisms of uranium in hydro systems.<sup>[8]</sup> Retention of uranium by matter in suspensions and sediment decreases as oxidant and alkaline conditions increase.<sup>[9]</sup> Therefore, two major pathways for uranium precipitation are associated with a reducing environment and the tendency for uranium to combine with iron hydroxides. Additionally, approximately 30 strains of bacteria are known to reduce uranium and also present a pathway for precipitation of uranium.<sup>[10]</sup> It has been suggested that U(VI) reduction by metal-reducing bacteria occurs in a two-step process. The first step is a single electron transfer to U(VI), resulting in the formation of transient uranyl(V) intermediates. This is followed by the second step, where resulting uranyl(V) species disproportionate to yield insoluble U(IV) and soluble U(VI), where the latter species re-enters the reduction cycle.

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Exposure to a certain amount of uranium from food, air, soil, and water is unavoidable, as it is naturally present in all these components. However, due to very low concentrations in the natural environment, it generally does not pose any danger to human health. That being said, exposure to elevated levels of uranium can be harmful to human health, and it has been linked to kidney failure and cancer.<sup>[11]</sup> Thus, it is important to have an understanding of uranium migration and environmental chemistry to develop novel remediation pathways.

Considering the large volumes of groundwater and low concentrations of uranium, techniques relying on pump-and-treat (groundwater extraction and ex situ treatment) have been shown to be inefficient and simple ground-water flashing to lower metal concentration often takes several decades or longer.<sup>[12]</sup> Therefore, bioremediation of U(VI) by anaerobic subsurface microorganisms has recently attracted significant attention. This approach takes advantage of uranium's redox chemistry and relies on the ability of anaerobes to reduce metals that precipitate from groundwater. However, the mechanism of the biotic reduction of uranium is not fully understood and therefore requires more detailed investigation. Once the genes that are responsible for the bioremediation reactions of interest are deciphered, microorganisms with a faster rate of reduction can be designed that would significantly improve groundwater remediation technologies.

During the course of this thesis, the mechanism of bioreduction of uranium by the anaerobic bacterium *Shewanella oneidensis* was investigated in collaboration with the microbiology group of Prof. Bernier-Latmani (Chapter 3: Sub-Chapter 3b).

### **1.3** Fundamental properties of uranium

#### 1.3.1 Electronic structure of actinides

Uranium is found in the f-block of the periodic table, and more specifically in the actinide series. The chemical properties of the actinides do not exhibit uniformity across the series; the early members (Pa–Am) resemble the d-block metals, while the heavier counterparts are more similar to the lanthanides. For the early actinides, the energies of the 5f orbitals are higher than the 6d orbitals, and this is evident from the ground-state electronic configurations (Table 1). Filling of the 5f orbitals starts with protactinium, and with the exception of curium and lawrencium, the 6d orbitals are not occupied again. The wide range of oxidation states observed for the early actinides is due to the small energy gap between 5f<sup>n</sup>7s<sup>2</sup> and 5f<sup>n-1</sup>6d7s<sup>2</sup> configurations, resulting in more outer-shell electrons that can participate in bonding. However, the energies of the 5f orbitals rapidly drop with

increasing atomic number due to the poor shielding ability of 5f electrons, causing the later actinides to strongly resemble the lanthanides. It is important to note that due to the high atomic numbers of the elements in the 5f series, relativistic effects play an important role, contributing to the expansion of non-penetrating 5f orbitals, and this can be observed in the radial distribution plots of various orbitals (Figure 2).

**Table 1.** Electron configuration of the actinides for the neutral atoms and accessible oxidation

 states. The most stable oxidation states are printed in green and the rare configurations in red.

An	Electron	Ground state electronic configuration						
	Configuration	M <sup>2+</sup>	<b>M</b> 3+	$M^{4+}$	$MO_{2^{+}}$	$MO_{2^{2+}}$		$MO_{2^{3+}}$
Ac	[Rn] 6d <sup>1</sup> 7s <sup>2</sup>		[Rn]					
Th	[Rn] 6d <sup>2</sup> 7s <sup>2</sup>	[Rn] 5f <sup>1</sup> 6d <sup>1</sup>	[Rn] 5f <sup>1</sup>	[Rn]				
Ра	[Rn] 5f <sup>2</sup> 6d <sup>1</sup> 7s <sup>2</sup>			[Rn] 5f <sup>1</sup>	L	[Rn]		
U	[Rn] 5f <sup>3</sup> 6d <sup>1</sup> 7s <sup>2</sup>	[Rn] 5f <sup>4</sup>	[Rn] 5f <sup>3</sup>	[Rn] 5f <sup>2</sup>	2	[Rn] 5f <sup>1</sup>	[Rn]	
Np	[Rn] 5f <sup>4</sup> 6d <sup>1</sup> 7s <sup>2</sup>		[Rn] 5f4	[Rn] 5f <sup>a</sup>	3	[Rn] 5f <sup>2</sup>	[Rn] 5f <sup>1</sup>	[Rn]
Pu	[Rn] 5f <sup>6</sup> 7s <sup>2</sup>		[Rn] 5f⁵	[Rn] 5f	1	[Rn] 5f <sup>3</sup>	[Rn] 5f <sup>2</sup>	[Rn]
Am	[Rn] 5f <sup>7</sup> 7s <sup>2</sup>		[Rn] 5f <sup>6</sup>	[Rn] 5f <sup>s</sup>	5	[Rn] 5f <sup>4</sup>	[Rn] 5f <sup>3</sup>	[Rn]
Cm	[Rn] 5f <sup>7</sup> 6d <sup>1</sup> 7s <sup>2</sup>		[Rn] 5f <sup>7</sup>	[Rn] 5f <sup>e</sup>	5			
Bk	[Rn] 5f <sup>9</sup> 7s <sup>2</sup>		[Rn] 5f <sup>8</sup>	[Rn] 5f7	7			
Cf	[Rn] 5f <sup>10</sup> 7s <sup>2</sup>		[Rn] 5f <sup>9</sup>	[Rn] 5f <sup>ɛ</sup>	3			
Es	[Rn] 5f <sup>11</sup> 7s <sup>2</sup>		[Rn] 5f <sup>10</sup>					
Fm	[Rn] 5f <sup>12</sup> 7s <sup>2</sup>	[Rn] 5f <sup>12</sup>	[Rn] 5f <sup>11</sup>					
Md*	[Rn] 5f <sup>13</sup> 7s <sup>2</sup>	[Rn] 5f <sup>13</sup>	[Rn] 5f <sup>12</sup>					
No*	[Rn] 5f <sup>14</sup> 7s <sup>2</sup>	[Rn] 5f <sup>14</sup>	[Rn] 5f <sup>13</sup>					
Lr*	[Rn] 5f <sup>14</sup> 6d <sup>1</sup> 7s <sup>2</sup>		[Rn] 5f <sup>14</sup>					

[Rn]1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup> 3s<sup>2</sup> 3p<sup>6</sup> 3d<sup>10</sup> 4s<sup>2</sup> 4p<sup>6</sup> 4d<sup>10</sup> 4f<sup>14</sup> 5s<sup>2</sup> 5p<sup>6</sup> 5d<sup>10</sup> 6s<sup>2</sup> 6p<sup>6</sup>; \*Predicted



Figure 2. Radial distribution functions for 4f, 5s, 5p, 5d, 5f, 6s, 6p and 6d orbitals. Adapted from [13].

Nonetheless, all actinides share certain characteristics, such as a tendency for high coordination numbers (up to 12) due to their large ionic radii, and primarily ionic and largely non-directional bonding. That said, the level of localization and participation of the 5f orbitals in covalent bonding is one of the long-standing debates in actinide chemistry.

In recent years significant progress in the understanding of covalency in f-element complexes has been achieved due to the latest advances in spectroscopic methods that can experimentally probe covalency in metal–ligand bonds, such as EPR spectroscopy, photoelectron spectroscopy, and more recently X-ray absorption spectroscopy.<sup>[14]</sup> Additionally, progress in modern computational chemistry allows for precise electronic structure calculations of large An systems. The combination of these techniques has resulted in the emergence of a new understanding of the bonding in actinide complexes. A longstanding FEUDAL (f's essentially unaffected, d's accommodate ligands) bonding model is being challenged and generally, a covalent contribution is now widely accepted to play an important role in 5f-element bonding.<sup>[15]</sup> Interestingly, for the earlier actinides, the structure-directing role of the f-orbitals results in the overlap-driven covalency<sup>[16]</sup> while the late actinides participate in more covalent interactions due to energy degeneracy-driven covalency.<sup>[17]</sup>

#### **1.4** Overview of the oxidation states

Being an early actinide, uranium exhibits a wide range of accessible oxidation states, from +2 to +6, with the latter being the most common in aerobic systems. Whereas a simple  $U^{n+}$  form is encountered with complexes of uranium(II)–uranium(IV), the chemistry of uranium(VI) and uranium(V) is dominated by the bis-oxo uranyl cation,  $UO_2^{n+}$  (non-uranyl U(VI) and U(V) are also known). These two forms give rise to very different coordination environments: the presence of two *trans*-oxygen atoms in uranyl cations restricts the coordination of additional ligands exclusively to the equatorial plane, while spherical  $U^{n+}$  does not tend to demonstrate significant directional preferences in bonding.

Current work is aiming to better understand the environmental chemistry of uranium. Consequently, this introduction focuses on the three highest oxidation states of uranium (from +4 to +6), as  $U^{3+}$  and especially  $U^{2+}$  are highly reducing and are not found in the environment. Particular emphasis is given to stabilization of the uranyl(V) cation.

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#### 1.4.1 +VI oxidation state

Uranium(VI) is mainly present in the uranyl form,  $UO_2^{2+}$ , presenting the most stable species of uranium that is persistent in aqueous and aerobic environments. In contrast to transition metal dioxo complexes, which often adopt bent geometries, the uranyl ion is essentially linear. This configuration is achieved by hybridization of 5f orbitals with semi-core  $6p_z$  and 6d orbitals that results in effective overlap with oxygen 2p orbitals to produce one  $\sigma$  bond and two  $\pi$  bonds, giving a formal U=O triple bond and stabilizing the linear arrangement (Figure 3).<sup>[18]</sup> This effect is also known as "pushing-from-below", where transfer of electron density from "pseudocore" 6p orbitals to vacant 5f orbitals results in a 6p hole being directed to the *trans* position, so that *trans*-bonded ligands reinforce each other, raising the  $\sigma$ -bond energy.<sup>[13]</sup> The resulting U=O bonds are particularly thermodynamically strong and kinetically inert. More broadly (incl. non-uranyl complexes) it is referred to as the inverse trans influence (ITI), a thermodynamic ground-state phenomenon in which U–L<sub>trans</sub> bonds are stronger and shorter than U–L<sub>cis</sub> bonds for an identical anionic ligand (L).<sup>[19]</sup>



Figure 3. Qualitative MO diagram for bonding in the uranyl ion. Reproduced from reference [20].

The coordination chemistry of uranyl(VI) has been thoroughly investigated in aqueous and organic media, and a broad range of mono- and poly-nuclear complexes with a variety of ligands have been isolated and characterized. As mentioned previously, additional ligands (4–6) can coordinate in the

equatorial plane of uranyl, and the bonding is mainly ionic, though covalency in some cases can be observed both spectroscopically and computationally.<sup>[13, 14]</sup>

The uranyl(VI) cation is a hard acid effective charge +3.3)<sup>[22]</sup> that forms stronger complexes with oxygen and fluoride donors than with *N*-donor ligands. In spite of this, a variety of complexes bearing *N*-donor ligands such as pyrrole, pyridine, amido, Schiff base salicylidene-derived and other cyclic and acyclic ligands have been reported.<sup>[23,24]</sup> In addition, the lone pairs of the uranyl-oxo atoms can donate their electron density to the uranium center in neighboring uranyl cations, forming cation-cation interactions (CCIs). Due to the low basicity of oxo-groups in uranyl(VI), these interactions are rarely observed and they play a much more important role in uranyl(V) chemistry. Therefore, they are discussed in detail in the following section.

The large effective charge of the uranium center in uranyl(VI) triggers the formation of various oxo and hydroxo (Figure 4). The size of these clusters varies but can reach 120 uranium atoms. The hydrolysis of uranyl(VI) in aqueous solution as a function of pH,<sup>[25]</sup> temperature<sup>[26]</sup> and concentration<sup>[27]</sup> has been thoroughly studied. At low concentrations (< 10<sup>-4</sup> M), the first product of hydrolysis is believed to be UO<sub>2</sub>(OH)<sup>+</sup>, while at higher concentrations the formation of dimers and trimers of uranyl hydroxo species has been observed<sup>[25,28]</sup>. It is useful to think of the aqueous uranyl ion as a weak acid (pK<sub>a</sub> = *ca.* 4.2)<sup>25</sup> that dissociates according to the following equilibrium:  $[UO_2(H_2O)_4]^{2+} \Rightarrow [UO_2(H_2O)_3(OH)]^+ + H^+.$ 



Figure 4. Possible structures formed on hydrolysis of uranyl under basic conditions.<sup>[25,28]</sup>

#### 1.4.2 +V oxidation state

The environmental chemistry of uranium in the plus 5 oxidation state is also dominated by the uranyl moiety UO2+. Due to the lower effective charge on the metal center (+2.2)<sup>[29]</sup> in comparison to the uranyl(VI) analog, the stability of uranyl(V) complexes with organic ligands is lower compared to the U(VI) analogues. The addition of one electron to uranyl(VI) also causes elongation and weakening of the bonds between uranium and the "yl" oxygen atoms, resulting and results in an increase in the Lewis basicity of the oxo ligands. This leads to the formation of previously mentioned cationcation interaction (CCI) complexes. The specific interaction of AnO2+ and AnO22+ (An= actinide) that is commonly referred to as a CCI has been observed for the first time in a study of the reduction of Np(VI) by U(IV). The resulting products, namely Np(V) and U(VI), has been shown to form an unusual interaction between two cations in an acidic non-complexing medium, giving the corresponding name to the newly discovered phenomenon.<sup>[30]</sup> Later, the CCI was reported for many other actinyl(V) cations, including the CCI complexes containing actynyl with various transition metal cations.[29] The CCI is often found between two uranyl moieties or between uranyl and another metal cation that results in the formation of polynuclear species with different geometries, as demonstrated in Figure 5.



**Figure 5.** Types of cation-cation interactions typical for uranyl(V) (M represents another metal cation).

Resulting CCI complexes have relatively low stability and are thought to be a key step in the disproportionation of uranium(V). In general, the thermodynamic stability of uranyl(V) in water is very low, resulting in disproportionation to U(IV) and uranyl(VI) in most cases. In aqueous media, disproportionation occurs according to Equation 1, resulting in the formation of uranyl(VI), uranium(IV) and a molecule of water. In aprotic media, formation of oxo-bridged clusters was previously reported.<sup>[30]</sup>

#### Equation 1.

$$2 UO_2^+(aq) + 4H^+(aq) \longrightarrow UO_2^{2+}(aq) + U^{4+}(aq) + 2H_2O(I)$$

Until recently, aqueous uranyl(V) was thought to be stable over a very limited range of potentials in a small pH region, e.g. in concentrated carbonate media or at selected mineral surfaces under slightly reducing conditions. In non-aqueous and non-protic solvents in the presence of bulky ligands, the stability of uranyl(V) can be significantly increased by preventing CCIs and subsequent electron transfer. This strategy was used to achieve significant progress in uranyl(V) chemistry over the last two decades, resulting in the isolation and characterization of multiple U(V)-containing complexes, and this is quite remarkable considering that the very first crystal structure of a uranyl(V) species was serendipitously isolated in non-reproducible conditions in 2003 by Ephritikhine *et al*<sup>[33]</sup> and the very first reproducible synthesis of a uranyl(V) complex was reported in our group by Natrajan et al in 2006.<sup>[34]</sup>

#### **1.4.2.1** Mechanism of uranyl(V) disproportionation.

Pourbaix diagrams highlight the extremely low E<sub>H</sub>-pH stability range for uranyl(V) (highlighted by a yellow oval) in two different aqueous uranium systems. Despite of its low stability, uranyl(V) plays an important role as an intermediate in several reactions, such as photo-<sup>[35]</sup> and bio-reduction of uranyl(VI),<sup>[36]</sup> isotopic exchange of uranium in U(IV)/U(VI) systems,<sup>[37]</sup> and oxo-exchange between U(VI) and water<sup>[38]</sup> to name a few. Therefore, it is crucial to have an understanding of the mechanism of disproportionation and of the conditions under which uranyl(V) is stable. The maximum metastability of aqueous U(V) is achieved under mildly acidic conditions in a very narrow pH range of 2–3 and only for a short time of approximately 1 hour,<sup>[39]</sup> as shown in **Figure 6** (left)



Figure 6. Pourbaix diagram of U-H<sub>2</sub>O (left) and U-CO<sub>2</sub>-H<sub>2</sub>O (right) systems. Adapted form [40,41]

In aqueous conditions the disproportionation reaction proceed according to Equation 2. This reaction is thermodynamically favored with  $\Delta G$  of -142 kJ/mol, but it is worth noting that thermodynamics of this reaction is significantly affected by changes in pH conditions.

#### Equation 2.

$$2[U^{\vee}O_{2}(H_{2}O)_{5}]^{+} + 2H_{2}O \longrightarrow [U^{\vee}O_{2}(OH)(H_{2}O)_{4}]^{+} + [U^{\vee}(OH)(H_{2}O)_{4}]^{+}$$

Early studies on the mechanism have found that the rate of the disproportionation reaction is 1<sup>st</sup> order in H<sup>+</sup> concentration, leading researchers to believe that the first step is protonation.<sup>[42]</sup> Further investigation in deuterated solvents found that the rate of the reaction does not lower as expected for the proton transfer reaction;<sup>[43]</sup> therefore, a new mechanistic proposition was required. In the following years, evidence for the formation of CCI species and rate dependence of the disproportionation reaction on uranyl(VI) association with uranyl(V) were obtained, leading to the suggestion of an alternative mechanism. Originally proposed by Ekström, the first step of the disproportionation steps.<sup>[44]</sup> More recently, DFT was used to calculate molecular orbital occupancies to support this mechanism. In this study, Steele and Taylor demonstrated that quantum modeling results align with experimental data, suggesting that after the dimer formation two successive protonations of the axial oxygen atoms occur and the electron transfer occurs after the first protonation (**Scheme 1**).<sup>[45]</sup>



**Scheme 1.** Schematic diagram of  $[U^VO_2]^+-[U^VO_2]^+$  disproportionation reaction, reproduced from [45].

#### 1.4.2.2 Stable uranyl(V) coordination complexes

#### 1.4.2.2.1 In aqueous solution

Since as early as the 1940s, a wide range of studies has been carried out on the  $UO_2^{+}$  species in water. U(V)-containing species have been formed by the *in situ* reduction of the  $UO_2^{2+}$  cation, mainly by electrochemical methods. As stated previously, due to the inherent propensity of U(V) toward disproportionation, none of the resulting species have been fully structurally characterized. The only known example of a stable uranyl(V) species in water solution is the tris-carbonate complex  $[UO_2(CO_3)_3]^{5-}$ , which was obtained by electrolysis of  $UO_2^{2+}$  in Na<sub>2</sub>CO<sub>3</sub> solution. This compound was found to be stable for several days in water at pH >11 and was characterized by EXAFS, <sup>13</sup>C NMR spectroscopy studies, and its stability was supported by quantum chemical calculations, though it was never isolated in crystalline form. On the basis of the experimental data, the structure of this U complex was concluded to be unchanged on one-electron reduction, with only subtle conformational changes and elongation of both axial and equatorial U–O distances (Scheme 2). The unexpected stability of this complex suggested that uranyl(V) could be stabilized in aqueous media in the absence of protons and upon full saturation of the equatorial plane to prevent CCI formation.



Scheme 2. Schematic structures of the uranyl(VI) and uranyl(V) tris(carbonato) complexes.

Earlier studies of the uranyl(VI) carbonate systems pointed out that several complexes can exist in rapid equilibria, and the speciation depends on the ionic strength and pH of the solution. The composition and the molecular structures of two species: the tris(carbonato) complex  $[UO_2(CO_3)_3]^{4-}$  and trinuclear hexa(carbonato)  $[(UO_2)_3(CO_3)_6]^{6-}$  have been reported (**Figure 7**).<sup>[46]</sup> This speciation in carbonate media can affect the stability of uranyl(V) resulting from the reduction of the parent uranyl(VI) carbonate complex. Thus, the use of polydentate anionic ligands would be advantageous for the stabilization of uranyl(V) in aqueous media. This would not only prevent CCI but also impose control on the solution speciation.



**Figure 7.** Molecular structures of  $[UO_2(CO_3)_3]^{4-}$  and  $[(UO_2)_3(CO_3)_6]^{6-}$  and  ${}^{13}C$  NMR spectra of a uranyl carbonate solution (2.5 M) recorded at 0 °C as a function of pH. Reproduced from [46].

#### 1.4.2.2.2 In organic solution

In spite of the low stability of uranyl(V), the first stable complex was prepared by electrochemical reduction in anaerobic solution in 2003.<sup>[47]</sup> The authors utilized a polydentate Schiff base ligand (salophen) to stabilize U(V) and determined the potential of the redox couple to be -1.73 V vs. Fc/Fc<sup>+</sup> in dmso. Additionally, the authors obtained an IR spectrum of uranyl(V), but a solid-state structure or a reproducible synthesis could not be achieved by this method. The first reproducible synthesis of a uranyl(V) complex was developed in 2006 by our group and and briefly after the group of Ephritikhine reported the same species prepared by a different route. The uranyl(V) coordination polymer { $(UO_2Py_5)(KI_2Py_2)_n$  (**Figure 8**) was reproducibly synthesized by oxidation of  $[UI_3(THF)_4]$  by a mixture of pyridine *N*-oxide<sup>[34]</sup> and water in our group, or by the reduction of  $[UO_2I_2(THF)_3]$  with KC<sub>5</sub>R<sub>5</sub> (R = Me, H) in pyridine by Ephritikhine et al.<sup>[48]</sup>



**Figure 8.** Structural formula (left) and molecular structure (right) of  $\{(UO_2Py_5)(KI_2Py_2)\}_n$  (ellipsoid plot at 50% probability (H were omitted; C are represented in grey, O in red, K in purple, N in blue and U in green). Reproduced from [34].

The synthesis of  $\{(UO_2Py_5)(KI_2Py_2)\}_n$  allowed for the quick development of uranyl(V) coordination chemistry by our group and also during this PhD project, the  $\{(UO_2Py_5)(KI_2Py_2)\}_n$  polymer was used

as the main starting material. In our group, the reaction of this polymer with various polydentate ligands (Figure 9) in pyridine led to the isolation of stable uranyl(V) species. More specifically, 1,3-diketonate ligand (Kdbm),<sup>[49]</sup> β-diketiminate ligand<sup>[50]</sup> (potassium 2-(4-tolyl)-1,3-bis(quinolyl)malon-diiminate and Schiff base ligands (K<sub>2</sub>salan-<sup>t</sup>Bu<sub>2</sub>,<sup>[51,52]</sup> K<sub>2</sub>salen,<sup>[53]</sup> K<sub>2</sub>acacen, <sup>[53]</sup> K<sub>2</sub>salophen, <sup>[53]</sup> K<sub>2</sub>salophen, <sup>[53]</sup> K<sub>2</sub>salophen-<sup>t</sup>Bu<sub>2</sub>,<sup>[52]</sup> K<sub>2</sub>Mesaldien,<sup>[32]</sup> K<sub>2</sub>salfen-<sup>t</sup>Bu<sub>2</sub><sup>[54]</sup>) resulted in the isolation and characterization of various mononuclear and polynuclear U(V)-containing coordination complexes.



Figure 9. Examples of ligands used by Mazzanti et. al for the synthesis of uranyl(V) complexes.

As mentioned previously, uranyl(V) oxo atoms exhibit higher Lewis basicity that results in the emergence of polynuclear complexes (Figure 10). Their geometry and stability are highly dependent on various factors, such as the nature of the ligand, presence of another metal cation, or solvent, to name a few.



Figure 10. Examples of different CCI complexes of uranyl(V) by Mazzanti et.al. [49,50,55]

Data from these studies suggests that the formation of CCIs, and/or the presence of protons and/or highly charged cations increase the rate of disproportionation of uranyl(V). The use of bulky tetraand penta-dentate anionic ligands results in stronger binding in the equatorial plane of the uranyl moiety, disfavoring dimerization through cation-cation interactions, thus significantly increasing the stability of U(V) with respect to disproportionation in organic anhydrous solvents.

An alternative strategy to access uranyl(V) compounds consists in the reduction of a parent uranyl(VI) complex. This strategy was employed by several research groups, expanding the range of synthetic methods as well as our understanding of uranyl(V) chemistry.<sup>[18,56,57]</sup>

The Arnold and Love Groups employed a polypyrrolic macrocyclic "Pacman" ligand to obtain a neutral uranyl(VI) complex, [UO<sub>2</sub>(thf)(H<sub>2</sub>Pacman)], which on reaction with silylamide base gave oneelectron reduction of uranium and oxo functionalization. Specifically, the addition of K{N(SiMe<sub>3</sub>)<sub>2</sub>} and Fel<sub>2</sub> to [UO<sub>2</sub>(thf)(H<sub>2</sub>Pacman)] generated a stable uranyl(V) complex, [U<sup>V</sup>O(OSiMe<sub>3</sub>)(thf)Fe<sub>2</sub>I<sub>2</sub>(Pacman)]. Importantly, the coordination of iron in the *endo*-compartment of the ligand allowed isolation of this uranium(V) complex. Following the seminal work on the uranyl(V) Pacman complex, the researchers broadly explored the chemistry of this system, resulting in the series of stable homoand hetero-metallic uranyl(V) oxo-functionalized complexes. In summary, reductive functionalization of [UO<sub>2</sub>(thf)(H<sub>2</sub>Pacman)] by metalation using group 1, group 2, group 12, group 13, group 14, as well as lanthanides and the actinides were reported.<sup>[57]</sup> The authors also explored the ability of a redox-active dipyrrin ligand to stabilize U(V), demonstrating the importance of oxo-group activation and the role of anionic ligands on the redox properties of U(V) (**Figure 11**).



Figure 11. Examples of stable uranyl(V) complexes by Arnold, Love and coworkers.

Another interesting direction in uranium(VI) chemistry was developed by Hayton and colleagues. On treatment of the uranyl(VI) complexes containing  $\beta$ -diketonate,  $\beta$ -diketiminate or  $\beta$ -ketoiminate ligands with decamethylcobaltocene or alkali metal reducing reagents, a variety of novel uranyl(V) species were isolated. Importantly, the preference of U(V) for *N*-donor ligands<sup>[58]</sup> in comparison to U(VI) analogs was rationalized on the basis of the greater polarizability of uranium(V) cations. The effect of Lewis acids (LA), such as boranes and silane derivatives, on the accessibility and stability of the resulting U(V) species was also investigated. In line with other studies, the researchers have demonstrated that the coordination of LAs to uranyl-oxo groups results in a significant shift in the redox potentials of the species of interest, and this allowed the synthesis of uranyl(V) as well as some non-uranyl U(V) species.



Figure 12. Examples of stable uranyl(V) complexes by Hayton and colleagues.

Lastly, bulky carbene ligands were also found to stabilize uranyl(V), presenting the first example of the organometallic uranyl(V) complex. This was achieved by one-electron reduction of the uranyl(VI)-methanide [(BIPMH)UO<sub>2</sub>Cl(THF)] (BIPMH = HC(PPh<sub>2</sub>NSiMe<sub>3</sub>)<sub>2</sub>), resulting in the isolation of a rare bimetallic uranyl(VI)-uranyl(V) and a trinuclear uranyl(VI)/uranyl(V)/uranyl(V) cation-cation species.<sup>[59]</sup>



Figure 13. Synthesis of the organometallic uranyl(VI)/uranyl(V) CCI species.<sup>[59]</sup>

In summary, fine-tuning the steric and electronic properties of  $UO_2^+$  complexes can inhibit disproportionation reactions by preventing CCIs. Additionally, several DFT studies suggest that covalent contributions to the  $UO_2^+$ -ligand bond contributes to uranyl(V) stability. Thus, both electronic and steric factors need to be taken into account for the choice of the ligand for the synthesis of stable uranyl(V) compounds.

#### 1.4.3 +IV oxidation state

#### 1.4.3.1 In aqueous media

As mentioned previously, U(IV) is a very common form of uranium in the environment due to its high stability in anaerobic aqueous solutions. The high effective charge on the metal center (the highest amongst all oxidation states (Table 2)) results in extensive hydrolysis and the formation of polynuclear species that often precipitate out of solution.

#### Table 2.

Cation	U <sup>4+</sup>	UO <sub>2</sub> <sup>2+</sup>	U <sup>3+</sup>	UO₂ <sup>+</sup>
Effective charge	+4	+3.3	+3	+2.2

The hydrolysis of U(IV) generally results in oxo/hydroxo polyoxometalates, often referred to as Uclusters. These clusters are formed through two main pathways: olation and oxolation reactions, as shown in **Scheme 3**.

Hydrolysis of U(IV) ions	U <sup>4+</sup> + n H <sub>2</sub> O	<u> </u>	$[U(OH)_n]^{(4-n)+} + n H^+$
Olation reaction	$\left[ U(OH)_{n} \right]^{(4-n)+} + \left[ U(OH_{2}) \right]_{n}^{4+}$	<u> </u>	" U– <mark>O</mark> H–U " + H <sub>2</sub> O
Oxolation reaction	2 [U(OH) <sub>n</sub> ] <sup>(4-n)+</sup>	<u></u>	" U– <mark>O</mark> –U " + H <sub>2</sub> O

Scheme 3. Hydrolysis, olalation and oxolation of uranium(IV).

If U(IV)-bearing clusters are not terminated by organic ligands, O atoms tend to form bridges to other metals, favoring extended solid formation. Some of the U(IV) oxo clusters have a well-known fluorite-type structure, where each U(IV) is bound to eight oxygen atoms and each O atom is coordinated to four U(IV) cations.<sup>[60]</sup> Certain ligands, usually organic, are able to passivate the surface of an oxo/hydroxo cluster, allowing for the isolation of the species of lower nuclearities. Polynuclear complexes of uranium(IV) are discussed in more detail in section 1.6.

#### 1.4.3.2 In organic media

In anhydrous solution, the most common precursors are uranium(IV) halides that can be prepared by a various methods.<sup>[61–64]</sup> Probably the most popular method for the synthesis of UCl<sub>4</sub> is the reaction of UO<sub>3</sub> with hexachloropropene (HCP)<sup>[65]</sup> that proceeds according to Scheme 4. Though this reaction yields solvent-free emerald green powder in a high yield, it has some drawbacks such as a potentially violent exotherm on initiation, and toxicity and environmental concerns associated with HCP. Alternatively, the uranium tetraiodide complex [UI<sub>4</sub>(1,4-dioxane)<sub>n</sub>] can be prepared in nearly quantitative yield by the direct reaction of 1 equiv. of U metal with Don2 equiv. of iodine in 1,4dioxane.<sup>[61]</sup> These two uranium(IV) starting materials were prepared and used extensively throughout this PhD project.



Scheme 4. Synthesis of UCl<sub>4</sub> and Ul<sub>4</sub>.

Access to UCl<sub>4</sub> and Ul<sub>4</sub> allowed for the fast development of low oxidation state uranium chemistry, resulting in various coordination and organometallic complexes of uranium(IV).<sup>[18]</sup> Additionally, the reduction of the resulting U(IV) complexes yielded a number of uranium(III) and mixed valence compounds.<sup>[13]</sup>

### 1.5 Optical properties of uranyl(VI), uranyl(V) and uranium(IV)

The optical properties of uranium, more specifically of uranyl(VI)-containing materials, are quite remarkable and have found multiple applications. Uranium-containing glasses and ceramics were quite popular in the mid-20<sup>th</sup> century due to the bright green fluorescent emission observed under ultraviolet light (Figure 14). Additionally, the luminescent properties of uranyl(VI) have been used for uranium detection,<sup>[66,67]</sup> luminescent sensing,<sup>[68]</sup> luminescence dating<sup>[69]</sup> and the scattering power of uranium was also used in transmission electron microscopy in biological chemistry<sup>[70]</sup>.



Figure 14. Vaseline glassware under UV-light, adopted from reference. Adapted from [71].

As for chemical properties, the electronic properties of uranium fall in between those of the lanthanides and the transition metals. In general, the interpretation of the electronic and magnetic spectra of uranium is complicated and has a qualitative rather than a quantitative character. This is due to the fact that for uranium inter-electronic repulsion plays the dominant role, but both spin-orbit coupling (ca. 2000 cm<sup>-1</sup>) and crystal-field effects (ca. 1000 cm<sup>-1</sup>) are relatively large. Consequently, neither the Russell-Saunders coupling scheme nor the j-j coupling scheme particularly well describe the electronic structure of uranium. Due to the greater nephelauxetic effect resulting in some covalency in U–L bonds, variation in both position and intensity of absorption bands depending on the coordination is observed. "Forbidden" f-f transitions are allowed in the presence of an asymmetric ligand field. Additionally, parity allowed 5f–6d and metal–ligand charge-transfer transitions can also be observed. The latter often has the tail of a very intense absorption band in the visible region and is responsible for the various colors of the uranium complexes.

#### 1.5.1 Uranyl(VI)

The photophysical properties of uranyl(VI) are remarkable, and  $UO_2^{2^+}$  displays vibrationally resolved ligand-to-metal charge transfer (LMCT) emission in the solid-state, as well as in aqueous and organic solutions. This LMCT transition involves the promotion of an electron from a bonding oxygen orbital  $(\sigma_u, \sigma_g, \pi_u \text{ and } \pi_g)$  to a non-bonding  $5f_{\delta}$  or  $5f_{\phi}$  uranium orbital, with the absorption typically centered at *ca*. 420 nm. The corresponding emission that results from the deactivation of the excited triplet state is centered at *ca*. 520 nm (Figure 15). The emission correlates well with the absorption with both exhibiting vibrational fine structure.

The electronic transitions of the uranyl(VI) ion are inherently governed by the parity selection rule. Thus, a formally forbidden LMCT in a ground state of the centrosymmetric point group symmetry can be observed due to the relaxation of parity through vibrations, solid-state defects, and the

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presence of solvent. LMCT transitions from equatorial ligand donor atoms tend to occur in the far-UV part of the spectrum, and are thus often overlooked.<sup>[72]</sup> The electronically excited state of the  $UO_2^{2+}$  ion has a long lifetime in the solid-state or frozen solution (hundreds of microseconds), while in solution luminescence is often quenched and the lifetime is often shortened (from tens of microseconds to sub nanosecond).



**Figure 15.** Typical excitation and emission spectra of uranyl(VI) in solid state or frozen solution (excitation and emission spectra of [K<sub>2</sub>UO<sub>2</sub>(dpa)<sub>2</sub>]).

However, the interpretation of the resulting data is often complicated by the speciation of the uranyl(VI) in aqueous media. Additionally, a strong dependence of LMCT lifetimes was observed on slight changes of the coordination environment which led to extensive studies of emissive properties of the uranyl(VI) ion in ionic liquids.<sup>[73,74]</sup> The luminescent properties of uranyl(VI) complexes in aprotic solvents were also reported in several studies. Generally, the emission is quenched in solution at room temperature, therefore most of the spectra were reported at 77 K. Furthermore, nonradiative energy transfer<sup>[75]</sup> and the presence of various metals<sup>[76]</sup> were shown to impact or fully quench the uranyl(VI) LMCT emission.

#### **1.5.1.1** Photoreduction of uranyl

Photoluminescence and photoreduction of  $UO_2^{2+}$  are closely related, as in both cases the first step is the photoexcitation of U(VI) to a higher excited state. The excited uranyl(VI) ion  $UO_2^{2+*}$  is wellknown to be strongly oxidizing (+2.6 V vs. SHE)<sup>[77]</sup> and can be accessed using UV–vis light (300–420 nm). The highly reactive uranyl(V) oxyl ion species formed as a result of LMCT can either be quenched by a hydrogen atom abstraction (including unactivated C–H bonds), an oxygen atom transfer or an electron transfer. Several reports have shown that in the presence of water a lightgenerated  $UO_2^{2^+*}$  can yield uranyl peroxide complexes as a result of water oxidation<sup>[78,79]</sup> or reaction with molecular oxygen.<sup>[80,81]</sup> In organic media, photoexcited uranyl(VI) was reported to catalyze photooxidation of alkanes, alkenes, aldehydes, and alcohols by molecular oxygen;<sup>[82,83]</sup> perform fluorination of cycloalkanes;<sup>[84]</sup> cyanation of anilines;<sup>[85]</sup> and oxidation of borohydrides to boric acid.<sup>[35]</sup>

#### **1.5.2 Uranyl(V)**

Due to the low stability of uranyl(V), the fundamental optical and photoluminescent properties of this 5f<sup>1</sup> ion are nearly unexplored. It was previously reported that upon electrochemical reduction of a basic (pH > 11) U(VI) carbonate aqueous solution, the characteristic LMCT band of uranyl(VI) disappeared, while several absorption bands in the visible–near-infrared (NIR) region (765 nm, 990 nm, and 1120 nm) appeared.<sup>[86]</sup> To circumvent the problem of strong absorption of H<sub>2</sub>O in the lower energy region, a study in dmso was performed utilizing various polydentate ligands to stabilize electrochemically generated uranyl(V) complexes.<sup>[87]</sup> On comparison of the visible–NIR absorption bands observed are due to electronic transitions in U<sup>V</sup>O<sub>2</sub><sup>+</sup> core. As for the uranyl(VI) ion, the electronic transitions are Laporte forbidden; therefore, the low extinction coefficients ( $\epsilon$ ) are characteristic for the observed absorption bands, with higher  $\epsilon$  values observed for the complexes with lower symmetry. The origin of the bands in the NIR range of uranyl(V) compounds was assigned to f–f transitions as the LMCT bands in uranyl(V) must be found in the higher energy region of the spectrum.

To date, there have been only two uranyl(V) luminescence emission spectra reported. The first example was reported by Steudner *et al.* in 2006, where uranyl(V) was accessed by the photoreduction of an aqueous uranyl(VI)-containing perchlorate solution in the presence of 2-propanol at pH = 2.4.<sup>[88]</sup> A broad emission band centered at 440 nm was obtained upon pulsed laser excitation at 255 or 408 nm. In the second study, a uranyl(V) carbonate system was investigated, and while no emission was detected at room temperature, at 153 K a broad emission centered at 405 nm ( $\lambda_{ex}$  = 255 nm) was obtained. The lifetime of the emission was found to be 120 µs, indicating its metal character (**Figure 16**). It is important to notice that both of the samples contained some uranyl(VI) impurities; therefore, the full assignment of other observed bands could not be performed. Additionally, the optical properties of U(V) were reported in molten salts<sup>[89]</sup> and the fluorescence was demostrated in association with biofilms (resulting from the bio-reduction of  $UO_2^{2+}$ ), both confirming the luminescent properties of the uranyl(V).



**Figure 16.** Peak deconvolution (left) and florescence decay (right) of the emission spectrum of  $[U^{V}O_{2}(CO_{3})_{3}]^{5-}$ . Adapted from [90].

#### 1.5.3 Uranium(IV)

In contrast to the more straightforward assignment of the spectroscopic data of the closed shell electron configuration of U(VI) and simple 1-electron containing 5f<sup>1</sup> electron configuration of U(V), the open shell f<sup>2</sup> uranium(IV) ion presents a remarkable challenge for the assignment and prediction of spectroscopic data. The absence of uranyl–oxo bonds means that all seven 5f orbitals are in principle available for bonding in the spherical U<sup>4+</sup> ion. For the U(IV) ion, inter-electronic repulsion dominates, but spin–orbit coupling and crystal-field effects are relatively large and impact the optical spectra of this ion (**Figure 17**).<sup>[91]</sup> Therefore, on comparison with isoelectronic Pr<sup>3+</sup>,<sup>[72]</sup> which has essentially ionic bonding and negligible crystal-field effects, line-broadening supposably as a result of greater covalency and an increase in absorption intensities is often observed. Additionally, the competition between the  $5f^27s^2$  and  $5f^16d^17s^2$  electronic configurations for the lower energy configuration results in  $5f^2 \rightarrow 5f^16d^1$  transitions being observed in the UV–vis region of the spectrum, while the numerous energy sub-levels make the assignment of the absorption and emission bands challenging.



Figure 17. A qualitative energy-level diagram for U<sup>4+</sup> ion. Adapted from reference [91].

While several reports of the luminescence of solid-sate U<sup>4+</sup> materials have been published, until very recently the luminescent properties of uranium(IV) in solution were practically unexplored. In the solid state (e.g. U<sup>4+</sup> doped LiYF<sub>4</sub>,<sup>[92]</sup> Cs<sub>2</sub>UCl<sub>6</sub><sup>[93]</sup> matrix or UCl<sub>4</sub><sup>[94]</sup>), the emission bands were assigned to transitions from the lowest excited state to different sub-levels of the 5f<sup>2</sup> manifold. In 2003, Kirishima et al. reported the photoluminescent spectrum of an aqueous solution of U(IV), and they suggested that the emission bands originate from the highest Russell-Saunders coupled <sup>1</sup>S<sub>0</sub> state to the lower lying 5f<sup>2</sup> spin–orbit coupled levels. In recent years, several studies of emissive uranium(IV) compounds have been published by Natrajan et al. By the careful selection of ligands that do not mask or quench the emissions arising from the 5f<sup>2</sup> ground state, the authors were able to record luminescence spectra of various U(IV) complexes, including uranium(IV) halides (e.g. [Li(THF)<sub>4</sub>][UCl<sub>5</sub>(THF)])<sup>[95]</sup> and the U(IV) chelate complex [U(DO3A)(DMSO)<sub>2</sub>]Br<sup>[96]</sup> (DO3A = [4,7,10-tris-carboxymethyl-,1,4,7,10-tetraaza-cyclododec-1-yl]-acetic acid). The emission spectral finger-print of U(IV) is of interest for its potential application in the environmental detection of U<sup>4+</sup> ions.
# **1.6** Polynuclear Molecular Clusters of Uranium

In contrast to transition metal polyoxometalates (POMs), which have been extensively studied, actinide POMs only emerged as a research theme in the last couple of decades, as previously it was thought that f-elements were incapable of self-assembly into well-structured nanomaterials.<sup>[97]</sup> Several families of uranium clusters can be distinguished, namely: uranyl (UO<sub>2</sub><sup>n+</sup>) vs. uranium (U<sup>n+</sup>) based clusters; oxygen bridged (oxo/peroxo/hydroxo) vs. non-oxygen bridged clusters; further differentiation can be made by oxidation state and nuclarity of the clusters. For this PhD thesis, the oxo/hydroxo clusters of U<sup>4+</sup> are of particular interest due to their relevance to the environment; therefore, emphasis is given to the clusters containing that motif.

## **1.6.1** Relevance of uranium clusters in the environment

As mentioned earlier, the strong Lewis acidic character of uranium results in the pronounced oxophilicity of uranium and in the formation of very stable oxo/hydroxo/peroxo complexes under a broad range of pH conditions. The hydrolysis of uranyl(VI) is the main contributor to the formation of uranium polynuclear clusters in the environment, leading to the formation of oligomers or infinite chains or sheets. An interesting example of such formations are the minerals studtite,  $(UO_2)O_2(H_2O)_4$ , and metastudtite,  $(UO_2)O_2(H_2O)_2$ , which are the only two known peroxide-containing minerals. Interestingly, the source of peroxide ligand in these minerals is the alpha radiolysis of water.<sup>[98]</sup>



Figure 18. Photograph of studtite (left) and its crystal unit cell. Reproduced from [99].

Studies in laboratory conditions have confirmed that uranyl peroxide nanoclusters can be easily formed and they could play a significant role in the context of spent nuclear waste in long-term storage.<sup>[100]</sup>

Uranium(IV) is also known to form polynuclear clusters under almost any environmentally relevant pH conditions, as low as pH = 0.<sup>[101]</sup> This is a result of the high electric charge on U(IV) that promotes the hydrolysis reaction in aqueous media. The final products of hydrolysis are soluble or insoluble polynuclear oxo/hydroxo complexes that also form stable colloids in oversaturated solutions which contribute to the mobility of uranium in the environment.<sup>[102]</sup>

The second pathway for the formation of U(IV) polynuclear clusters in the environment is via biotic or abiotic reduction of U(VI). The abiotic pathway utilizes the reductive power of Fe(II)-bearing minerals<sup>[103–105]</sup> or clays in the presence of organic materials<sup>[106]</sup> to yield U(V)/U(IV) species that are often associated with the mineral surfaces. One of the other major contributors to the redox migration of uranium in the environment is the result of interactions with various microorganisms, i.e. the biotic pathway. The discovery that bacteria can convert soluble U(VI) to insoluble U(IV), in the uraninite form, was published nearly 30 years ago,<sup>[107]</sup> and during the last few decades attracted significant attention due to its prospects for bioremediation applications. Over the years, it has been shown that under anaerobic conditions various bacteria can utilize highly soluble uranyl(VI) as an electron acceptor, allowing for respiration in these microorganism.<sup>[108]</sup> The products of the reduction were found to be discrete, as well as aggregated particles of uraninite that can be found outside of the bacterial cells.<sup>[109]</sup> The size of the resulting U(IV) clusters, determined by HR-TEM, varied, but extended from 3 nm down to molecular-scale clusters (**Figure 19**).



**Figure 19.** TEM image of: bacteria with UO<sub>2</sub> nanoparticles (a), cell surface(b), UO<sub>2</sub> particle on the cell surface (c), single uraninite particle (e), fitted XAFS data for the sediments(d) and structural model of nanobiogenic uraninite (right). Reproduced from [109] and [110].

It is important to note that the products that are formed on the bio-reduction of uranium are highly dependent on the media. The presence of various organics was found to promote the development of anoxic conditions, increasing the reductive power of metal-reducing bacteria, which in turn favors the formation of insoluble nanoparticles and clusters.<sup>[111]</sup>

In conclusion, U(IV)-containing polynuclear species play an important role in the migration of uranium in the environment, but the processes involved in their formation are very complex and highly dependent on various factors such as Eh, pH, species of microorganisms, availability of ligands, etc. An understanding of the chemistry and complex interactions between all components would allow for the development of better technologies for the management of uranium and other actinides' environmental migration.

#### 1.6.2 Oxo/hydroxo uranium clusters

#### 1.6.2.1. Synthesis of uranium POMs in water

As seen previously, despite the high importance of U(IV) oxo/hydroxo clusters in the environment, very few polynuclear clusters had been structurally characterized until very recently. The majority of the clusters isolated from aqueous solution present a hexanuclear cluster with an octahedral  $U_6O_4(OH)_4$  core (**Figure 20**). These clusters were isolated by utilizing the bridging nature of the carboxylate or sulfonate ligands to stabilize the resulting assembly.<sup>[112,113]</sup>



**Figure 20.** Model of the crystal structure of  $[U_6O_4(OH)_4(SO_4)_6]$  (U in yellow, O in red, S in magenta). Adapted from [97].

More recently, the effect of bulkier ligands on the formation of U(IV) self-assemblies in aqueous media was examined. Several groups have reported examples of the stabilization of the  $[U_6O_4(OH)_4]$  motif by carboxylate ligands, e.g. Takao *et al.* isolated a formate-supported  $[U_6O_4(OH)_4(HCOO)_{12}(H_2O)_6]$  cluster,<sup>[112]</sup> while Knope *et al.* demonstrated that upon the addition of an excess of 4-hydroxybenzoic acid (4-HB) to UCl<sub>4</sub> in water,  $[U_6O_4(OH)_4(4-HB)_{12}(H_2O)_6]$  can be

isolated. Interestingly, even significantly larger ligands like the polyamino carboxylic acid DOTA (1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetic acid) have been shown to stabilize the hexanuclear core, resulting in the isolation of the  $[U_6O_4(OH)_4(H_2O)_8(HDOTA)_4]$  cluster under acidic aqueous conditions.<sup>[114]</sup>

On the other hand, the use of polydentate carboxylic acids (i.e. phthalate = 1,2-bdc or mellitic =mel) resulted in the isolation of 2D coordination polymers based on  $[UO(H_2O)(1,2-bdc)]_2$  or  $[U_2(OH)_2(H_2O)_2(mel)]$ , showing the directing role of the ligand in the formation of oxo/hydroxo U(IV) species (**Figure 21**).<sup>[115]</sup>



Figure 21. Crystal structures of  $[U_2(OH)_2(H_2O)_2(mel)]$  (left) and  $[UO(H_2O)(1,2-bdc)]_2$  (right). Adapted from [115].

## 1.6.2.2. Synthesis of U(IV) POMs by controlled hydrolysis of U precursors in low oxidation states.

The difficulty with the isolation of clusters from an aqueous solution resides in the extensive hydrolysis that results in a broad range of solutions species with different structural features. In order to obtain better control for the U(IV) POMs synthesis, the controlled hydrolysis in organic solution was utilized by different research groups to isolate POMs of different nuclearities and morphologies.<sup>[97]</sup> The formation of low nuclearity  $0x0^{[116]}$  or hydrox0<sup>[117]</sup> complexes from uranium in low oxidation states precursors by the reaction with a stoichiometric amount of water has been previously reported, but it was only in 2003 that Mazzanti *et al.* demonstrated that larger oxo-clusters can be formed on controlled hydrolysis of U(III) complexes supported by a TPA ((tris(2-pyridyl)methyl)amine) ligand.<sup>[118]</sup> Ephritikhine *et al.* have also demonstrated that even larger U(IV)-oxo assemblies can be isolated, including the octanuclear clusters [U<sub>8</sub>Cl<sub>24</sub>O<sub>4</sub>(cp\*py)<sub>2</sub>]<sup>[119]</sup> (cp\*py = tetramethyl-5-(2-pyridyl)cyclopentadiene) and (Hpy)<sub>2</sub>[U<sub>8</sub>L<sub>4</sub>Cl<sub>10</sub>O<sub>4</sub>]<sup>[120]</sup> (L = *N*,*N*<sup>-</sup>*bis*(3-hydroxysalicylidene)-1,2phenylenediamine); however, no rational route for the synthesis of these clusters was reported and adventitious water/O<sub>2</sub> was hypothesized to yield oxo-ligands. A more rational approach for the synthesis of the larger uranium POMs was demonstrated in our group, where the controlled hydrolysis of  $[UI_3(thf)_4]$  in the presence of triflate ligand yielded the mixed-valence dodecanuclear U(IV)/U(V) cluster  $[U_{12}(\mu_3-OH)_8(\mu_3-O)_{12}I_2(\mu-OTf)_{16}(CH_3CN)_8]$  (**U12**).<sup>[121]</sup> Interestingly, depending on the reaction time and the nature of the ligand, different products could be isolated, from a discrete hexanuclear cluster to 2D or 3D arrays of mixed-valence U<sub>6</sub>O<sub>8</sub> POMs (**Figure 22**).



**Figure 22.** Molecular structures of a)  $U_6O_8$  core found in 2D and 3D arrays; b) extended 3D array; c) extended 2D array; d)  $U_{12}O_{20}$  core found in U12. Adapted from [121].

Further, the effect of the bridging ligand on the stability of the U12 cluster was investigated. The addition of bidentate dbm ligand to the U12 cluster resulted in the cleavage of the dodecanuclear core and the formation of a monomeric uranium(IV) dbm complex.<sup>[122]</sup> This demonstrated the importance of the bridging nature of the capping ligand for the stability of the uranium in low oxidation states polyoxo-clusters.

In view of the role of the bridging ligand on the stability of the U(IV) POMs, further investigation was performed utilizing a different type of a bridging ligand, namely the benzoate ligand. The choice of this ligand was driven by the environmental relevance of this functional group as it is a common motif in soil. The addition of 2 equiv. of water to  $[UI_3(thf)_4]$  in the presence of potassium benzoate yielded clusters of different sizes. The use of a less coordinating solvent, i.e. acetonitrile, resulted in the formation of a cluster with a  $U_{10}O_{12}(OH)_2$  core, while the identical reaction in pyridine yielded smaller  $U_6O_8$  hexanuclear cluster. Moreover, the addition of a Lewis base (TMEDA) was found to promote the formation of even larger clusters, resulting in the isolation of novel  $U_{16}O_{22}(OH)_2$ -containing species (U16). While the addition of acid (PyHCl) to U16 results in protonation of the oxo groups and the formation of  $U_6O_4(OH)_4$  cluster (**Scheme 5**).<sup>[123]</sup>





Loiseau and colleagues have extended the controlled hydrolysis approach to get access to a variety of U(IV) MOFs (metal–organic framework) by utilizing a range of dicarboxylate ligands. The 3D networks present  $[U_6O_4(OH)_4(H_2O)_6]$  units linked by different ditopic linkers: 4,4'-biphenyldicarboxylate (4,4'-bpdc, **1**), 2,6-naphthalenedicarboxylate (2,6-ndc, **2**), terephthalate (1,4-bdc, **3**), and fumarate (fum, **4**). The compounds were obtained by solvothermal reactions of UCl<sub>4</sub> with 6.5 equiv. of H<sub>2</sub>O in DMF in the presence of a stoichiometric amount of a given ligand. The resulting UiO-66 type of compounds present materials with different porosities and stabilities, depending on the nature of the ligand.<sup>[124]</sup>



**Figure 23.** Evolution of the size of the octahedral cavity in the series  $[U_6O_4(OH)_4(H_2O)_6(L)_6]$ . Adapted from [124].

The biggest uranium oxo cluster isolated to date,  $[U_{38}O_{56}CI_{18}(thf)_8(PhCOO)_{24}]$ , was also originally prepared by the controlled hydrolysis of UCl<sub>4</sub> with benzoic acid under solvothermal conditions in

THF. The authors investigated the effect of different equivalents of water on the U38 cluster formation, showing that the maximum yield of 72% is achieved with the addition of 15 equiv. of H<sub>2</sub>O (per U). Interestingly, the addition of more water led to the formation of uranium oxide (UO<sub>2</sub>) as a main product.<sup>[125]</sup> A different U38 cluster, [U<sub>38</sub>O<sub>56</sub>Cl<sub>42</sub>(H<sub>2</sub>O)<sub>20</sub>], was isolated during the time frame of the PhD by Knope *et al*.<sup>[126]</sup> also utilizing controlled hydrolysis, but this time at significantly lower temperatures. This large cluster was isolated by storing a thf solution containing UCl<sub>4</sub>, 3 equiv. of water and 2 equiv. of 2-furoic acid at 50 °C for 1 week.

#### 1.6.2.3. Synthesis of uranium POMs by disproportionation of uranyl(V)

Another pathway for the formation of uranium oxo/hydroxo assemblies is based on the disproportionation of uranyl(V) complexes.<sup>[97]</sup> It is worth noting that the bacterial reduction of U(VI) to U(IV) species discussed previously is generally thought to be a result of the disproportionation of biotically generated uranyl(V) rather than a two-electron reduction of the parent uranyl(VI) species.<sup>[36]</sup>

In our group, polynuclear complexes of uranium were synthesized by proton-<sup>[53]</sup> or U(IV)<sup>[32]</sup>-induced disproportionation of otherwise stable uranyl(V) complexes in pyridine. Of particular relevance to this work is the study of the disproportionation reaction of the uranyl(V) polymer { $(UO_2Py_5)(KI_2Py_2)$ } in presence of benzoic acid in pyridine. This reaction yields a hexanuclear U(IV) cluster,  $[U_6O_4(OH)_4(PhCOO)_{12}(Py)_3]$ , along with 1 equiv. of the uranyl(VI) tris-benzoate complex and H<sub>2</sub>O (**Scheme 6** (left)). The authors demonstrated an example of a clean acid-induced disproportionation of uranyl(V) that results in the formation of a polymetallic assembly of U(IV) that is likely to be the mechanism of the U(IV) cluster formation in the environment.<sup>[127]</sup> In a follow-up study, the effect of a proton on the mechanism of this disproportionation was investigated by the reaction of the same uranyl(V) polymer with potassium benzoate in a pyridine solution. The reaction also proceeds via a disproportionation mechanism to yield multiple products, including a large mixed-valence U(V)/U(IV) cluster,  $[[K(Py)_2]_2[K(Py)]_2[U_{16}O_{24}(PhCOO)_{24}(Py)_2]\}$ .<sup>[128]</sup>



**Scheme 6.** The disproportionation reaction of uranyl(V) in the presence of benzoic acid or potassium benzoate.

#### 1.6.2.4. Alternative pathways for uranium POMs

In addition to the previously described methods for the synthesis of U POMs, less conventional pathways have been also reported over the years. Ephritikhine *et al.* reported the isolation of U(IV)-containing hexanuclear clusters resulting from comproportionation reactions. One example presents the reaction between the uranyl(VI) and uranium(III) triflate complexes to afford the oxo-cluster  $[U_6O_8(OTf)_8(Py)_8]$ .<sup>[129]</sup> The same cluster can be obtained by the comproportionation between the uranocene complex  $[U(\eta^8-C_8H_8)_2]$  with the uranyl(VI) triflate species  $[UO_2(OTf)_2]$ . Interestingly, when the uranocene was reacted with the uranyl(V) triflate complex  $[UO_2(Py)_{2.3}K(OTf)_2]$ , the reaction yielded the same product along with a neutral COT molecule.<sup>[130]</sup>

A different pathway to afford a similar hexanuclear assembly was demonstrated by Carrano *et.al* by reducing uranyl(VI) acetate with a vanadium(III) precursor in the presence of diphenylphosphate ligands. While the authors suggested the formula  $[U_6(OH)_8(Ph_2PO_2)_{12}]$  for the isolated cluster, considering the reaction conditions and the structural parameters, it is more likely to contain a more common  $[U_6O_4(OH)_4]$  core.<sup>[131]</sup>

A very different pathway for the oxo-cluster formation is the photolysis of uranyl(VI) complexes. Mazzanti *et al.* have recently shown that mixed-valence clusters can also be formed upon the photoreduction of uranyl(VI) to yield a  $[U(UO_2)_5O_5(PhCOO)_5(Py)_7]$  cluster.<sup>[128]</sup>

In conclusion, various synthetic approaches can be used to achieve the formation of polynuclear uranium oxo/hydroxo assemblies. As exemplified, the size, charge and bonding in the resulting clusters depend on many parameters, making the rational design of U POMs particularly challenging. The controlled hydrolysis of U(IV) precursors in organic solution presents the most straightforward approach for the synthesis of the U(IV) polyoxometalates, andeach parameter can be isolated, and its effect on the formation of the cluster can be examined . This approach is discussed in more detail in Chapter 6. A novel pathway for the formation of oxo/hydroxo U(IV) clusters in aqueous media is also presented in Chapter 4.

### **1.7** Purpose and objectives on the project

The development of better remediation technologies for uranium-contaminated sites is essential for human health in the post-atomic age. An understanding of the fundamental properties of uranium can improve not only the nuclear industry but also provide information about uranium reactivity, speciation, and migration in the environment. To this end, the goal of this doctorate is to develop new synthetic models of various environmentally relevant uranium species, with a particular focus on the uranyl(V) chemistry. More specifically, the project is divided into three main objectives:

1 - Synthesis and reactivity of U(V)-Fe(II) model compounds

2 - Design and synthesis of water stable uranyl(V) complexes and a study of their reactivity

3 - Development of the rational synthetic routes for uranate model compounds (*uranate refers to a relatively symmetric coordination environment that lacks the short dioxo uranyl bonds*).

The chemistry of uranyl(V) in organic solution has seen significant development in the last decade but we have lacked appropriate uranyl(V) models for comparison with environmental systems. For example, several research groups reported the presence of stable absorbed or incorporated U(V) species in Fe-rich environments,<sup>[103,132,133]</sup> but the mechanism of the stabilization remained ambiguous. This is addressed by the first objective of this doctorate; synthesize and characterize a stable Fe<sup>2+</sup>---U<sup>V</sup>O<sub>2</sub><sup>+</sup> compound that can provide a suitable model for the investigation of the U(V)-Fe(II) interaction. We aim to use a polydentate Schiff base ligand (trensal) for the complexation of the uranyl(V) species whilst preventing U<sup>V</sup>O<sub>2</sub><sup>+</sup>---U<sup>V</sup>O<sub>2</sub><sup>+</sup> interaction and following disproportionation. Additionally, the tripodal nature of the ligand will allow for the controlled formation of the heterodimetallic U(V)-Fe(II) complexes. Finally, with the aim of understanding the role of U(V)-Fe(II) CCI in the increased stability of U(V), various analogs will be synthesized and fully characterized, providing an insight into the role of iron-binding in the stabilization of uranyl(V) in the environmental mineralmediated reduction of uranium.

The second objective will focus on the synthesis of water-stable uranyl(V) complex and an evaluation of its reactivity. The utilization of multidentate ligand with a high binding affinity for U(V) in aqueous solution will allow for the isolation of the first water-stable uranyl(V) complex at

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environmentally relevant pH. The use of a high denticity ligand with carboxylate functionalities will allow for the improved stability against ligand dissociation and resulting disproportionation. Furthermore, a detailed study of reactivity and the physical properties of the novel system will be performed, which is crucial for an improved understanding of the environmental fate of uranyl(V). The development of a water-stable uranyl(V) complex will permit the investigation of the uranium reduction mechanism in aqueous media. Chemical mimicking of the environmentally relevant reduction will allow for a better understanding of the potential for either two one-electron transfer, one two-electron transfer (U(VI) to U(IV)), or one-electron transfer leading to stable U(V) intermediates. Tuning the flexibility of the ligand will enable the isolation of molecular U(IV) oxo/hydroxo clusters while preventing ligand scrambling and extended structure formation. Direct reduction of uranyl(VI), via a uranyl(V) intermediate to U(IV), will be achieved utilizing readily available reducing reagents under aqueous conditions. Fine-tuning of the reaction conditions (pH, concentration, etc) and investigation in the organic solvent will allow for the isolation of intermediate species that will provide information about the reduction mechanism.

Finally, with the objective of understanding the directing parameters for the assembly of uranium clusters and nanoparticles, the synthesis of large uranium(IV) polyoxometalates will be carried out. In particular, the controlled hydrolysis synthetic approach in the presence of environmentally relevant ligands will be explored. Specific media characteristics, such as solvent, presence of a base, stoichiometry, temperature, as well as time-dependence of the cluster formation and resulting topologies will be investigated. The formation of uranium oxo nanoparticles in the environment can occur via bacterial reduction, which has potential applications in the bio-remediation of uranium. Hence, the second approach involving the disproportionation of uranyl(V) in the presence of carboxylate ligand will be examined. Specifically, the effect of metal cations on the formation of polynuclear U(V)/U(IV) assemblies will be investigated.

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#### References

[1] Mary Elvira Weeks, *Discovery Of The Element*, Journal Of Chemical Education, **1956**.

[2] B. Goldschmidt, "Atomic Complex: A Worldwide Political History of Nuclear Energy (Hardcover) -- ANS / ANS Store / Special Publications," can be found under https://www.ans.org/store/item-690007/, **1982**.

[3] "10.6: Fission," can be found under https://phys.libretexts.org/Bookshelves/University\_Physics/Book%3A\_University\_Physics\_(OpenStax)/Map%3A\_University\_Physics\_III\_-\_Optics\_and\_Modern\_Physics\_(OpenStax)/10%3A\_\_Nuclear\_Physics/10.06%3A\_Fission, **2016**.

[4] "Uranium and Depleted Uranium - World Nuclear Association," can be found under https://www.world-nuclear.org/information-library/nuclear-fuel-cycle/uranium-resources/ura-nium-and-depleted-uranium.aspx, **n.d.** 

[5] **N.d.**, 48.

[6] L. R. Morss, N. Edelstein, J. Fuger, *The Chemistry of the Actinide and Transactinide Elements* (*3rd Ed., Volumes 1-5*), Springer Science & Business Media, **2007**.

[7] J.-C. Dran, J. Chaumont, G. Della Mea, V. Moulin, J.-C. Petit, V. Rigato, *Nucl. Instrum. Methods Phys. Res. Sect. B Beam Interact. Mater. At.* **1992**, *64*, 523–527.

[8] P. S. Andersson, D. Porcelli, G. J. Wasserburg, J. Ingri, *Geochim. Cosmochim. Acta* **1998**, *62*, 385–392.

[9] G. A. Bird, W. G. Evenden, *Water. Air. Soil Pollut.* **1996**, *86*, 251–261.

[10] L. L. Barton, R. J. C. McLean, *Environmental Microbiology and Microbial Ecology*, John Wiley & Sons, **2019**.

[11] S. Keith, O. Faroon, N. Roney, F. Scinicariello, S. Wilbur, L. Ingerman, F. Llados, D. Plewak, D. Wohlers, G. Diamond, *HEALTH EFFECTS*, Agency For Toxic Substances And Disease Registry (US), **2013**.

[12] R. T. Anderson, H. A. Vrionis, I. Ortiz-Bernad, C. T. Resch, P. E. Long, R. Dayvault, K. Karp, S. Marutzky, D. R. Metzler, A. Peacock, D. C. White, M. Lowe, D. R. Lovley, *Appl. Environ. Microbiol.*2003, *69*, 5884–5891.

[13] S. T. Liddle, Angew. Chem. Int. Ed. 2015, 54, 8604–8641.

[14] M. L. Neidig, D. L. Clark, R. L. Martin, *Coord. Chem. Rev.* **2013**, *257*, 394–406.

[15] E. Lu, S. Sajjad, V. E. J. Berryman, A. J. Wooles, N. Kaltsoyannis, S. T. Liddle, *Nat. Commun.* **2019**, *10*, DOI 10.1038/s41467-019-08553-y.

[16] T. Vitova, I. Pidchenko, D. Fellhauer, P. S. Bagus, Y. Joly, T. Pruessmann, S. Bahl, E. Gonzalez-Robles, J. Rothe, M. Altmaier, M. A. Denecke, H. Geckeis, *Nat. Commun.* **2017**, *8*, 16053.

- [17] 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.
- [18] M. B. Jones, A. J. Gaunt, Chem. Rev. 2013, 113, 1137–1198.
- [19] A. J. Lewis, K. C. Mullane, E. Nakamaru-Ogiso, P. J. Carroll, E. J. Schelter, *Inorg. Chem.* **2014**, *53*, 6944–6953.
- [20] J. A. Platts, R. J. Baker, *Dalton Trans.* **2020**, *49*, 1077–1088.
- [21] C. Fillaux, D. Guillaumont, J.-C. Berthet, R. Copping, D. K. Shuh, T. Tyliszczak, C. Den Auwer, *Phys. Chem. Chem. Phys.* **2010**, *12*, 14253–14262.
- [22] G. R. CHOPPIN, *Radiochim. Acta* **1983**, *32*, 43–54.
- [23] J. Sessler, P. Melfi, G. Pantos, *Coord. Chem. Rev.* **2006**, *250*, 816–843.
- [24] P. A. Vigato, V. Peruzzo, S. Tamburini, *Coord. Chem. Rev.* 2012, 256, 953–1114.
- [25] F. Quilès, C. Nguyen-Trung, C. Carteret, B. Humbert, *Inorg. Chem.* **2011**, *50*, 2811–2823.
- [26] P. Zanonato, P. Di Bernardo, A. Bismondo, G. Liu, X. Chen, L. Rao, *J. Am. Chem. Soc.* **2004**, *126*, 5515–5522.
- [27] J. Sutton, J. Chem. Soc. Resumed 1949, S275.
- [28] F. Quilès, A. Burneau, Vib. Spectrosc. 2000, 23, 231–241.
- [29] G. R. Choppin, J. Nucl. Radiochem. Sci. 2005, 6, 1–5.
- [30] J. C. Sullivan, J. C. Hindman, A. J. Zielen, J. Am. Chem. Soc. 1961, 83, 3373–3378.
- [31] N. N. Krot, M. S. Grigoriev, *Russ. Chem. Rev.* **2004**, *73*, 89–100.
- [32] V. Mougel, J. Pécaut, M. Mazzanti, *Chem. Commun.* **2012**, *48*, 868–870.
- [33] J.-C. Berthet, M. Nierlich, M. Ephritikhine, Angew. Chem. Int. Ed. 2003, 42, 1952–1954.
- [34] L. Natrajan, F. Burdet, J. Pecaut, M. Mazzanti, J. Am. Chem. Soc. 2006, 128, 7152–7153.
- [35] K. Takao, S. Tsushima, *Dalton Trans.* **2018**, *47*, 5149–5152.
- [36] 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.
- [37] B. J. Masters, L. L. Schwartz, J. Am. Chem. Soc. 1961, 83, 2620–2624.
- [38] W.-S. Jung, Y. Ikeda, H. Tomiyasu, H. Fukutomi, Bull. Chem. Soc. Jpn. 1984, 57, 2317–2318.
- [39] K. R. Howes, A. Bakac, J. H. Espenson, *Inorg. Chem.* **1988**, *27*, 791–794.
- [40] H.-H. Huang, *Metals* **2016**, *6*, 23.
- [41] J. Schmets, J. van Muylder, M. Pourbaix, Atlas of Electrochemical Equilibria in Aqueous Solu-
- tion, 2nd English Ed, National Association Of Corrosion Engineers, 1974.
- [42] D. M. H. Kern, E. F. Orlemann, J. Am. Chem. Soc. **1949**, 71, 2102–2106.
- [43] F. R. Duke, R. C. Pinkerton, J. Am. Chem. Soc. 1951, 73, 2361–2362.

- [44] A. Ekstrom, *Inorg. Chem.* **1974**, *13*, 2237–2241.
- [45] H. Steele, R. J. Taylor, *Inorg. Chem.* **2007**, *46*, 6311–6318.
- [46] P. G. Allen, J. J. Bucher, D. L. Clark, N. M. Edelstein, S. A. Ekberg, J. W. Gohdes, E. A. Hudson,
  N. Kaltsoyannis, W. W. Lukens, M. P. Neu, others, *Inorg. Chem.* **1995**, *34*, 4797–4807.
- [47] K. Mizuoka, Y. Ikeda, *Inorg. Chem.* **2003**, *42*, 3396–3398.
- [48] M. Ephritikhine, J.-C. Berthet, G. Siffredi, P. Thuéry, Chem. Commun. 2006, 0, 3184–3186.
- [49] G. Nocton, P. Horeglad, J. Pécaut, M. Mazzanti, J. Am. Chem. Soc. 2008, 130, 16633–16645.
- [50] L. Chatelain, V. Mougel, J. Pecaut, M. Mazzanti, *Chem. Sci.* **2012**, *3*, 1075–1079.
- [51] P. Horeglad, G. Nocton, Y. Filinchuk, J. Pécaut, M. Mazzanti, *Chem. Commun.* 2009, 0, 1843–1845.
- [52] 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.
- [53] V. Mougel, P. Horeglad, G. Nocton, J. Pécaut, M. Mazzanti, *Chem. Eur. J.* 2010, *16*, 14365–
   14377.
- [54] C. Camp, L. Chatelain, V. Mougel, J. Pécaut, M. Mazzanti, Inorg. Chem. 2015, 54, 5774–5783.
- [55] V. Mougel, L. Chatelain, J. Pécaut, R. Caciuffo, E. Colineau, J.-C. Griveau, M. Mazzanti, *Nat. Chem.* **2012**, *4*, 1011–1017.
- [56] P. L. Arnold, J. B. Love, D. Patel, *Coord. Chem. Rev.* **2009**, *253*, 1973–1978.
- [57] B. E. Cowie, J. M. Purkis, J. Austin, J. B. Love, P. L. Arnold, *Chem. Rev.* **2019**, acs.chemrev.9b00048.
- [58] M. F. Schettini, G. Wu, T. W. Hayton, *Inorg. Chem.* **2009**, *48*, 11799–11808.
- [59] 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.
- [60] Z. Zheng, Ed. , *Recent Development in Clusters of Rare Earths and Actinides: Chemistry and Materials*, Springer Berlin Heidelberg, Berlin, Heidelberg, **2017**.
- [61] J. L. Kiplinger, D. E. Morris, B. L. Scott, C. J. Burns, *Organometallics* **2002**, *21*, 5978–5982.
- [62] T. Yoshimura, C. Miyake, S. Imoto, J. Nucl. Sci. Technol. 1971, 8, 498–502.
- [63] S. S. Rudel, F. Kraus, *Dalton Trans.* **2017**, *46*, 5835–5842.
- [64] J.-C. Berthet, P. Thuéry, M. Ephritikhine, *Inorg. Chem.* **2005**, *44*, 1142–1146.
- [65] D. Patel, A. J. Wooles, E. Hashem, H. Omorodion, R. J. Baker, S. T. Liddle, *New J. Chem.* **2015**, *39*, 7559–7562.
- [66] J. Liu, A. K. Brown, X. Meng, D. M. Cropek, J. D. Istok, D. B. Watson, Y. Lu, Proc. Natl. Acad.
   Sci. 2007, 104, 2056–2061.

47

- [67] N. W. Hayes, C. J. Tremlett, P. J. Melfi, J. D. Sessler, A. M. Shaw, Analyst 2008, 133, 616–620.
- [68] C.-C. Chen, D. Pestov, J. D. Nelson, J. E. Anderson, G. Tepper, J. Fluoresc. 2011, 21, 119–124.
- [69] K. Munyikwa, Lumin. Outlook Phenom. Their Appl. 2016, DOI 10.5772/65119.

[70] V. Gopal, J. Xavier, Md. Z. Kamal, S. Govindarajan, M. Takafuji, S. Soga, T. Ueno, H. Ihara, N.M. Rao, *Bioconjug. Chem.* 2011, *22*, 2244–2254.

[71] Realfintogive, English: Various Vaseline Glasswares Glowing under a Few Large UV Black Lights., **2012**.

[72] L. S. Natrajan, *Coord. Chem. Rev.* **2012**, *256*, 1583–1603.

[73] P. Nockemann, R. Van Deun, B. Thijs, D. Huys, E. Vanecht, K. Van Hecke, L. Van Meervelt, K. Binnemans, *Inorg. Chem.* **2010**, *49*, 3351–3360.

[74] M.-O. Sornein, C. Cannes, C. Le Naour, G. Lagarde, E. Simoni, J.-C. Berthet, *Inorg. Chem.* 2006, 45, 10419–10421.

[75] T. Yayamura, S. Iwata, S. Iwamaru, H. Tomiyasu, *J. Chem. Soc. Faraday Trans.* **1994**, *90*, 3253–3259.

[76] R. Tamilarasan, T. Ramakrishan, J. F. Endicot, *Inorganica Chim. Acta* **1988**, *142*, 321–327.

[77] S. Fortier, T. W. Hayton, *Coord. Chem. Rev.* **2010**, *254*, 197–214.

[78] B. T. McGrail, L. S. Pianowski, P. C. Burns, J. Am. Chem. Soc. 2014, 136, 4797–4800.

[79] B. Masci, P. Thuéry, *Polyhedron* **2005**, *24*, 229–237.

[80] G. H. John, I. May, M. J. Sarsfield, H. M. Steele, D. Collison, M. Helliwell, J. D. McKinney, *Dalton Trans.* **2004**, *0*, 734–740.

[81] D. Rose, Y.-D. Chang, Q. Chen, J. Zubieta, Inorg. Chem. 1994, 33, 5167–5168.

[82] W.-D. Wang, A. Bakac, J. H. Espenson, *Inorg. Chem.* **1995**, *34*, 6034–6039.

[83] P. L. Arnold, J. M. Purkis, R. Rutkauskaite, D. Kovacs, J. B. Love, J. Austin, *ChemCatChem* n.d.,
 0, DOI 10.1002/cctc.201900037.

[84] J. G. West, T. A. Bedell, E. J. Sorensen, Angew. Chem. Int. Ed. 2016, 55, 8923–8927.

[85] M. Azam, S. I. Al-Resayes, A. Trzesowska-Kruszynska, R. Kruszynski, P. Kumar, S. L. Jain, *Polyhedron* **2017**, *124*, 177–183.

[86] D. Cohen, J. Inorg. Nucl. Chem. **1970**, 32, 3525–3530.

[87] K. Mizuoka, S. Tsushima, M. Hasegawa, T. Hoshi, Y. Ikeda, *Inorg. Chem.* **2005**, *44*, 6211–6218.

[88] R. Steudtner, T. Arnold, K. Großmann, G. Geipel, V. Brendler, *Inorg. Chem. Commun.* **2006**, *9*, 939–941.

[89] T. NAGAI, T. FUJII, O. SHIRAI, H. YAMANA, J. Nucl. Sci. Technol. **2004**, 41, 690–695.

48

- [90] K. Grossmann, T. Arnold, A. Ikeda-Ohno, R. Steudtner, G. Geipel, G. Bernhard, *Spectrochim. Acta. A. Mol. Biomol. Spectrosc.* **2009**, *72*, 449–453.
- [91] S. Cotton, in *Lanthan. Actin. Chem.*, John Wiley & Sons, Ltd, **2006**, pp. i–xv.
- [92] S. V. Godbole, A. G. Page, Sangeeta, S. C. Sabharwal, J. Y. Gesland, M. D. Sastry, *J. Lumin.* **2001**, *93*, 213–221.
- [93] R. A. Satten, C. L. Schreiber, E. Y. Wong, J. Chem. Phys. 1965, 42, 162–171.
- [94] C. Görller-Walrand, M. P. Gos, W. D'Olieslager, Radiochim. Acta 1993, 62, 55–60.
- [95] E. Hashem, A. N. Swinburne, C. Schulzke, R. C. Evans, J. A. Platts, A. Kerridge, L. S. Natrajan,
- R. J. Baker, RSC Adv. 2013, 3, 4350–4361.
- [96] L. S. Natrajan, *Dalton Trans.* **2012**, *41*, 13167–13172.
- [97] J. Qiu, P. C. Burns, *Chem. Rev.* **2013**, *113*, 1097–1120.
- [98] K.-A. H. Kubatko, K. B. Helean, A. Navrotsky, P. C. Burns, *Science* **2003**, *302*, 1191–1193.
- [99] P. F. Weck, E. Kim, E. C. Buck, *RSC Adv.* **2015**, *5*, 79090–79097.
- [100] L. R. Sadergaski, W. Stoxen, A. E. Hixon, *Environ. Sci. Technol.* 2018, 52, 3304–3311.
- [101] D. L. Clark, D. E. Hobart, M. P. Neu, Chem. Rev. 1995, 95, 25–48.
- [102] V. Neck, J. I. Kim, *Radiochim. Acta* **2001**, *89*, 1–16.

[103] 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.

[104] M. S. Massey, J. S. Lezama-Pacheco, M. E. Jones, E. S. Ilton, J. M. Cerrato, J. R. Bargar, S. Fendorf, *Geochim. Cosmochim. Acta* **2014**, *142*, 166–185.

[105] F. Huber, D. Schild, T. Vitova, J. Rothe, R. Kirsch, T. Schäfer, *Geochim. Cosmochim. Acta* **2012**, *96*, 154–173.

[106] D. M. Giaquinta, L. Soderholm, S. E. Yuchs, S. R. Wasserman, *Radiochim. Acta* **1997**, *76*, 113–122.

- [107] D. R. Lovley, E. J. P. Phillips, Y. A. Gorby, E. R. Landa, *Nature* **1991**, *350*, 413–416.
- [108] N. M. Koribanics, S. J. Tuorto, N. Lopez-Chiaffarelli, L. R. McGuinness, M. M. Häggblom, K. H.
- Williams, P. E. Long, L. J. Kerkhof, PLoS ONE 2015, 10, DOI 10.1371/journal.pone.0123378.
- [109] Y. Suzuki, S. D. Kelly, K. M. Kemner, J. F. Banfield, *Nature* **2002**, *419*, 134.
- [110] E. J. Schofield, H. Veeramani, J. O. Sharp, E. Suvorova, R. Bernier-Latmani, A. Mehta, J. Stahl-

man, S. M. Webb, D. L. Clark, S. D. Conradson, E. S. Ilton, J. R. Bargar, *Environ. Sci. Technol.* **2008**, *42*, 7898–7904.

[111] D. R. Lovley, *Science* **2001**, *293*, 1444–1446.

[112] S. Takao, K. Takao, W. Kraus, F. Emmerling, A. C. Scheinost, G. Bernhard, C. Hennig, *Eur. J. Inorg. Chem.* **2009**, *2009*, 4771–4775.

[113] "G. Lundgren, Arkiv. Kemi. 1952, 5, 421 – 428. - Google Scholar," can be found under https://scholar.google.com/scholar?hl=en&q=%0AG.+Lundgren%0A%2C+Arkiv.+Kemi.%0A1952%0 A%2C+5%0A%2C+421%0A%E2%80%93428%0A., n.d.

[114] C. Tamain, T. Dumas, C. Hennig, P. Guilbaud, *Chem. – Eur. J.* **2017**, *23*, 6864–6875.

[115] N. P. Martin, J. März, C. Volkringer, N. Henry, C. Hennig, A. Ikeda-Ohno, T. Loiseau, *Inorg. Chem.* **2017**, *56*, 2902–2913.

[116] W. W. Lukens, S. M. Beshouri, L. L. Blosch, R. A. Andersen, *J. Am. Chem. Soc.* **1996**, *118*, 901–902.

[117] J.-C. Berthet, M. Ephritikhine, M. Lance, M. Nierlich, J. Vigner, J. Organomet. Chem. **1993**, 460, 47–53.

[118] L. Karmazin, M. Mazzanti, J. Pécaut, Inorg. Chem. 2003, 42, 5900–5908.

[119] L. Moisan, T. Le Borgne, P. Thuéry, M. Ephritikhine, Acta Crystallogr. C 2002, 58, m98–m101.

[120] L. Salmon, P. Thuéry, M. Ephritikhine, *Polyhedron* **2004**, *23*, 623–627.

[121] G. Nocton, F. Burdet, J. Pecaut, M. Mazzanti, Angew. Chem.-Int. Ed. 2007, 46, 7574–7578.

[122] G. Nocton, J. Pecaut, Y. Filinchuk, M. Mazzanti, *Chem. Commun.* **2010**, *46*, 2757–2759.

[123] B. Biswas, V. Mougel, J. Pécaut, M. Mazzanti, Angew. Chem. Int. Ed. 2011, 50, 5745–5748.

[124] C. Falaise, C. Volkringer, J.-F. Vigier, N. Henry, A. Beaurain, T. Loiseau, *Chem. – Eur. J.* 2013, 19, 5324–5331.

[125] C. Falaise, C. Volkringer, J.-F. Vigier, A. Beaurain, P. Roussel, P. Rabu, T. Loiseau, *J. Am. Chem. Soc.* **2013**, *135*, 15678–15681.

[126] N. A. Vanagas, R. F. Higgins, J. N. Wacker, D. R. C. Asuigui, E. Warzecha, S. A. Kozimor, S. L.
 Stoll, E. J. Schelter, J. A. Bertke, K. E. Knope, *Chem. – Eur. J.* **2020**, *26*, 5872–5886.

[127] V. Mougel, B. Biswas, J. Pecaut, M. Mazzanti, *Chem. Commun.* **2010**, *46*, 8648–8650.

[128] L. Chatelain, S. White, R. Scopelliti, M. Mazzanti, *Angew. Chem.-Int. Ed.* **2016**, *55*, 14323–14327.

[129] J.-C. Berthet, P. Thuéry, M. Ephritikhine, *Chem. Commun.* **2005**, *0*, 3415–3417.

[130] J.-C. Berthet, P. Thuéry, M. Ephritikhine, Inorg. Chem. 2010, 49, 8173–8177.

[131] L. M. Mokry, N. S. Dean, C. J. Carrano, Angew. Chem. Int. Ed. Engl. 1996, 35, 1497–1498.

[132] K. Yuan, E. S. Ilton, M. R. Antonio, Z. Li, P. J. Cook, U. Becker, *Environ. Sci. Technol.* **2015**, *49*, 6206–6213.

[133] S. Tsarev, R. N. Collins, E. S. Ilton, A. Fahy, T. D. Waite, *Env. Sci Nano* **2017**, *4*, 1304–1313.

# Chapter 2: The Effect of Iron Binding on Uranyl(V) Stability

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## **2.1 Introduction**

The uranyl(V)<sup>[1-5]</sup> has been proposed as an important transient intermediate in the biological or abiotic mineral-mediated transformation of soluble uranyl(VI) compounds into the insoluble uranium(IV) dioxide (UO<sub>2</sub>). These processes provide a convenient strategy to sequester uranium in the environment and, as such, are very important for ground-water remediation. In particular, stable adsorbed or incorporated uranyl(V) species have been reported to form during the U(VI) reduction by Fe(II)-bearing minerals such as mica<sup>[5]</sup> or magnetite ([Fe<sup>2+(</sup>Fe<sup>3+</sup>)<sub>2</sub>O<sub>4</sub>]<sup>[6-9]</sup> and the presence of iron as a second nearest neighbor has been identified.<sup>[10][11]</sup> Uranyl(V) species have low stability in aqueous media and they quickly disproportionate to uranyl(VI) and U(IV),<sup>[12]</sup> but the incorporation into iron minerals may prevent disproportionation or further reduction of U(V) to U(IV) and thus lead to long-term immobilization of U(V). However, the role of iron binding to uranyl(V) species in their stabilization remains ambiguous in spite of its importance for the correct speciation of uranium in the environment.

Dinuclear or polynuclear complexes of uranyl(V) built from the interaction of a uranyl(V) oxo group with the uranium center from a UO<sub>2</sub><sup>+</sup> moiety (UO<sub>2</sub><sup>+</sup>– UO<sub>2</sub><sup>+</sup>), also known as cation-cation interaction (CCI),<sup>[13]</sup> have been proposed as intermediates in the proton promoted disproportionation of uranyl(V) to afford UO<sub>2</sub><sup>+</sup> and U(IV) species.<sup>[3][14][15]</sup> The subsequent addition of protons to these polynuclear uranyl(V) intermediates leads to complete electron transfer followed by dissociation of the resulting U(VI)–U(IV) complex. In aprotic media stable polynuclear UO<sub>2</sub><sup>+</sup>–UO<sub>2</sub><sup>+</sup> complexes have been isolated.<sup>[16-20]</sup> We showed that the addition of protons (PyHCI) to a pyridine solution of stable tetrameric UO<sub>2</sub><sup>+</sup>–UO<sub>2</sub><sup>+</sup> complexes leads to the immediate disproportionation of the uranyl(V) species affording uranyl(VI) and U(IV) complexes and water.<sup>[17]</sup> Disproportionation of polynuclear cationcation complexes was also observed in the absence of protons upon addition of strong Lewis acids (Li<sup>+</sup> or U<sup>4+</sup>)<sup>[17][21]</sup> to stable uranyl(V) Schiff base complexes and was found to lead to complex mixtures of soluble mixed-oxidation state U(IV)/U(V) uranium oxo clusters. The groups of T. Hayton and P. Arnold also showed that the binding of strong Lewis acids or Group 1 metals to the uranyl(VI) oxo group renders the reduction of U(VI) to U(V).<sup>[22-25]</sup> Moreover, it has been demonstrated that the binding of strong Lewis acids such as  $B(C_6F_5)_3$  to the uranyl(V) oxo groups renders the reduction of U(V) to U(IV).<sup>[25-29]</sup> Fewer studies have been directed to investigate the effect of the interaction of uranyl(V) with 3d transition metals on the stability and redox reactivity of uranyl(V) species. Moreover, in spite of the fact that several uranyl(V) complexes stable in organic solution have been isolated in recent years,<sup>[21][30-41]</sup> only a few examples of heter-opolymetallic complexes presenting a UO<sub>2</sub><sup>+</sup>–M interaction, where M is a 3d transition metal, have been prepared, some of them have shown interesting single-molecule magnet properties.<sup>[42-48]</sup> Arnold and Love suggested that the addition of Fel<sub>2</sub> to an unstable putative uranyl(V) dipotassium complex of a macrocyclic Schiff base Pacman ligand resulted in higher stability of the uranyl(V) Pacman species which was corroborated by the isolation of the corresponding heterobimetallic UO<sub>2</sub><sup>+</sup>–Fe<sup>2+</sup> CC complex. However, the effect of the interaction UO<sub>2</sub><sup>+</sup>–Fe<sup>2+</sup> on the stability of these uranyl(V) species was not further investigated.<sup>[44]</sup>

In this Chapter, the synthesis of uranyl(V) supported by the tripodal Schiff base ligand H<sub>3</sub>trensal (2,2',2''-tris(salicylideneimino)triethylamine) the  $UO_2^+-K^+[UO_2(trensal)K]K$ , **3**, and the heterobime-tallic  $UO_2^+-Fe^{2+}$  complex  $[UO_2(trensal)Fe(Py)_3]$ , **6** are reported. The two arms from the trensal ligand bind the uranyl cation in the equatorial plane while the third arm support the coordination of Fe<sup>2+</sup> to the oxo group The reactivity of these complexes toward protons and their redox properties were compared and these studies unambiguously show the increased stability of the iron-bound species.

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Author contributions: R.F. and S.W. carried out synthetic experiments. S.W. performed preliminary experiments on the synthesis and stability of uranyl(V) complexes with the trensal ligand and crystallized complexes **6**, **7** and **8**. R.F. has further studied the stability, reactivity and redox properties of all the complexes, crystallized complexes **2**, **4**, **5**, **9** and **10** and fully characterized all the complexes. R.S. performed the X-ray single crystal structure analyses. R.F and M.M. analyzed the data and wrote the manuscript. M.M. originated the central idea, coordinated the work and analyzed the experimental data.

## 2.2 Results and discussion

#### Uranyl(VI) and Uranyl(V) complexes of trensal<sup>3-</sup>.

We firstly started with the synthesis of uranyl(VI) complexes of the ligand trensal. The reaction of  $K_3$ trensal with the nitrate salt of uranyl (VI) leads to the isolation of the uranyl(VI) complex  $[UO_2(trensal)K]$ , **1** in 59% yield. The broad <sup>1</sup>H NMR spectrum of **1** in pyridine suggests the presence of fluxional solution species. A higher resolution of the <sup>1</sup>H NMR spectrum is observed in deuterated THF and a well resolved <sup>1</sup>H NMR spectrum could be obtained in CD<sub>3</sub>OD solution (Figure 24).



**Figure 24.** <sup>1</sup>H NMR spectrum (400 MHz, 298 K) of the complex  $[UO_2(trensal)K]$  (1) in C<sub>5</sub>D<sub>5</sub>N (bottom), 1 in C<sub>4</sub>D<sub>8</sub>O (middle) and 1 in CD<sub>3</sub>OD (top).

X-ray quality crystals of **1** could not be obtained, but the addition of one equivalent of PyHCl to a pyridine solution of **1** led to the isolation of X-ray quality crystals of the neutral complex  $[UO_2(Htrensal)]$ , **2**, in 60% yield. The proton NMR spectrum of **2** in pyridine shows the presence of 15 overlapping narrow signals in agreement with the presence of C<sub>2</sub> symmetric solution species (Figure 25).



**Figure 25.** <sup>1</sup>H NMR spectrum (400 MHz,  $C_5D_5N$ , 298 K) of the crystals of [UO<sub>2</sub>(Htrensal)] (2).

The X-ray crystal structure of this complex is presented in Figure 26 and shows that the uranium atom is heptacoordinated, with a slightly distorted pentagonal bipyramidal coordination geometry, by two uranyl oxygen atoms in axial position and five donor atoms of the trensal<sup>3-</sup> ligand in the equatorial plane. The third protonated arm of the trensal<sup>3-</sup> ligand is not coordinated to the uranyl cation and the phenol proton is hydrogen-bonded with the Schiff base nitrogen N4. The value of the U(VI)=O bond lengths lie in the range of those typically observed for uranyl(VI) complexes (U – O3 = 1.783(3) Å and U – O4 = 1.787(3) Å).<sup>[16][49][21][50][51]</sup> The average U-Ophenoxide (2.231 Å) and the average U-N<sub>imine</sub> (2.612 Å bond) lengths are also in the range of those found in other reported Schiff base complexes of uranyl(VI).<sup>[16][49][21][50][51]</sup>



**Figure 26.** Ellipsoid plot at 50% probability of **2** (co-crystallised pyridine molecule and hydrogen atoms were omitted for clarity, C are represented in grey, O in red, N in blue and U in green).

In the attempt to reduce the uranyl(VI) complex **2** we added 1 eq. of decamethyl cobaltocene  $(Cp_{2}^{*}Co)$  to pyridine solutions of **2**. The <sup>1</sup>H NMR spectrum of the resulting reaction mixture immediately after addition shows the presence of a large number of signals in the -45 – 45 ppm range suggesting that a putative uranyl(V) intermediate species undergoes rapid disproportionation (Appendix 1: Fig. S2).

In contrast, the uranyl(V) complex  $[UO_2(trensal)K]K$ , **3**, is conveniently prepared in 70 % yield from the salt metathesis reaction between K<sub>3</sub>Trensal and  $[(UO_2Py_5)(KI_2Py_2)]_n$  in pyridine (Scheme 7).



Scheme 7. Synthesis of the complexes 3 and 4.

The proton NMR spectrum of **3** in deuterated pyridine showed the presence of fluxional species with signals in the paramagnetic region characteristic of U(V). Cooling down or heating up the NMR sample did not lead to a better resolution of the spectrum.

The addition of stoichiometric amounts of 2.2.2.cryptand (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane to complex **3**, resulted in a well-resolved <sup>1</sup>H NMR spectrum (Figure 27). This suggests that fluxional potassium binding to the uranyl oxygen is the cause of the broad features in the <sup>1</sup>H NMR spectrum of **3**.



**Figure 27.** <sup>1</sup>H NMR spectrum (400 MHz, C<sub>5</sub>D<sub>5</sub>N, 298 K) of [UO<sub>2</sub>(trensal)(K(2.2.2crypt)] [K(2.2.2crypt)] (4).

The complex [UO<sub>2</sub>(trensal)(K(2.2.2crypt)][K(2.2.2crypt)], **4**, was obtained analytically pure as a green solid in 62% yield. The solid-state structure of **4** was determined by X-ray diffraction studies and is presented in Figure 28. The overall quality of the crystal structure of compound **4** is rather poor (very weakly diffracting sample) but its connectivity is well determined.



**Figure 28.** Ellipsoid plot at 50% probability of the anion  $[UO_2(trensal)(K(2.2.2crypt)]^-$  in 4 (H and  $[K(2.2.2crypt)]^+$  were omitted for clarity, C are represented in grey, O in red, N in blue, K in light blue and U in green).

The coordination environment around the uranium center is similar to that found in complex **2**. In **4** the uranium atom is heptacoordinated in a pentagonal bipyramidal coordination geometry. Five donor atoms of the trensal ligand (two oxygen and three nitrogen atoms) occupy the equatorial plane of the uranium ion, while the third arm of the trensal<sup>3-</sup> ligand does not interact with any cation and one [K(cryptand)] cation is found as an isolated ion in the unit cell of **4**. The bipyramid axial positions in **4** are occupied by two oxo ligands with U-O distances (1.824(15) and 1.865(16) Å) significantly longer than those found in the uranyl(VI) complex **2** (1.785(3) Å). These distances are in the range of those found in previously reported complexes of uranyl(V).<sup>[30][34][35]</sup>

The proton NMR spectrum of **4** in pyridine shows the presence of 12 narrow signals in agreement with the presence of  $C_2$  symmetric solution species (Figure 27).

The solid-state X-band EPR spectra measured at 298 K and 10 K revealed that the complex **3** is EPR silent.

In contrast, the solid-state X-Band (9.40 GHz) EPR spectrum of **4** shows an intense signal at 10 K with a fitted rhombic set of g-values ( $g_1$ =2.44;  $g_2$ =1.10;  $g_3$ <0.6), confirming the presence of uranium in the oxidation state +5 (Figure 29). Notably, the encapsulation of potassium enables to obtain an EPR signal from the otherwise EPR silent complex **3**.



**Figure 29.** Band (9.40 GHz) EPR spectrum of crystals of **4** in the solid state at 10 K (black lines) and simulated EPR spectrum (green lines).

Complex **4** is stable up to one month in the solid state and in pyridine and THF solutions. In order to assess the stability of these uranyl(V) complexes with respect to proton-induced disproportionation, we have investigated the reaction of **3** and **4** with protons. After the addition of 1 eq. of PyHCl to complex **3**, partial disproportionation of the uranyl(V) complex was observed by proton NMR spectroscopy. The addition of 2 eq. of PyHCl resulted in the complete disproportionation of the uranyl(V) to afford the uranyl(VI) complex **2** and new U(IV) product as indicated by proton NMR spectroscopy (Figure 30) and X-ray diffraction of the single crystal of the complex **2**. The U(IV) species formed in the disproportionation were identified as the product of the hydrolysis of the [U(trensal)]I (compound 9) as confirmed by the <sup>1</sup>H NMR spectrum of a 1:1:2 mixture of [UO<sub>2</sub>(Htrensal)], [U(trensal)]I and H<sub>2</sub>O (Appendix 1: Fig. S4).



**Figure 30.** <sup>1</sup>H NMR spectrum (400 MHz,  $C_5D_5N$ , 298 K) of [UO<sub>2</sub>(trensal)K]K (3) (bottom), of the reaction mixture of 3 + 1 eq. PyHCl (middle) and of 3 + 2 eq. PyHCl (top).

Further investigation showed that when the uranium(IV) iodide complex **9** is reacted with H<sub>2</sub>O hydrolysis of the imine bond takes place to yield an oxo-bridged U(IV)-U(IV) [U(trensal- $\mu$ O)- $\mu$ O-U(EthylamineSaldien)]I complex **10**. Complex **10** can be prepared analytically pure in 50% yield by reacting the U(IV) [U(trensal)]I complex **9** with 2 eq. of water in pyridine. X-ray quality crystals of **10** were obtained by slow diffusion of toluene in a pyridine solution of **10** (Figure 31). The structure of

**10** shows the presence of cationic dinuclear complex in which one U(IV) is coordinated by trensal<sup>3-</sup> ligand, while the second uranium center by the (ethylamine)saldien ligand that is the product of Schiff base hydrolysis. The two U(IV) ions are bridged by an oxo ligand and one phenolate arm of the trensal ligand.



**Figure 31.** Ellipsoid plot at 50% probability of  $[U(trensal)(py)]^+$  in complex **9** (left) and  $[U(trensal-<math>\mu$ O)- $\mu$ O-U(EthylamineSaldien)]<sup>+</sup> in complex **10** (right) (co-crystallised pyridine molecule, I<sup>-</sup> and most H were omitted for clarity, C are represented in grey, O in red, N in blue, and U in green).

Interestingly, no hydrolysis of the trensal Schiff base is observed on the addition of H<sub>2</sub>O to the chloride analogue of **9** [U(trensal)Cl] as indicated by proton NMR spectroscopy (Appendix 1: Fig. S19). This suggests that due to the binding of chloride in [U(trensal)Cl], water molecule cannot form a bond with a coordinatively saturated U(IV) centre and the hydrolysis of the ligand does not take place.

On the other hand, addition of PyHCl to **4** initially resulted in the formation of NMR silent species, but after 3 days the proton NMR spectrum shows the formation of the same disproportionation products as those found in the reaction of **3** with 2 eq. of PyHCl (Appendix 1: Fig. S5).

### Iron binding to uranyl(V) complexes.

In view of the potential important role of iron binding in the abiotic reduction of uranyl(VI) as well as in the stabilization of uranyl(V) at iron mineral surfaces we have investigated the reactivity of complexes **1** and **3** with iron salts.

The reaction of **1** with Fel<sub>2</sub> affords the trinuclear complex {UO<sub>2</sub>(trensal)}<sub>2</sub>Fe], **5**, in 93% yield according to the Scheme 8.



Scheme 8. Synthesis of [(UO<sub>2</sub>(trensal))<sub>2</sub>Fe(Py)<sub>2</sub>], 5.

The solid-state structure of **5** shows the presence of a neutral trimeric complex where two  $[UO_2(trensal)]$  moieties are held together by a Fe(II) cation bound by two trensal O,N donor atoms not involved in the coordination of the uranyl cation (Figure 32). Thus, the replacement of the potassium cation in **1** with a Fe(II) cation leads to formation of a trimeric structure.



**Figure 32.** Ellipsoid plot at 50% probability of 5 (co-crystallised pyridine molecule and H were omitted for clarity, C are represented in grey, O in red, N in blue, Fe in dark blue and U in green).

In order to prepare a trinuclear uranyl(V) analogue, we allowed to react **5** with  $Cp^{*}_{2}Co$ . The <sup>1</sup>H NMR spectrum after addition of 1 eq. of  $Cp^{*}_{2}Co$  to complex **5** revealed the formation of a complex reaction mixture. One of the products could be identified by X-ray diffraction studies, revealing the formation of the dinuclear heterobimetallic complex [UO<sub>2</sub>(trensal)Fe(py)<sub>3</sub>], **6**. The addition of 2.5 eq. of  $Cp^{*}_{2}Co$  to a pyridine solution of **5** led to an intractable reaction mixture from which none of the components could be identified (Appendix 1: Fig. S7c).

Complex **6** can be conveniently prepared in 81% yield from the reaction of  $Fel_2$  with complex **3** in pyridine in a 1:1 ratio (Scheme 9).



**Scheme 9.** Synthesis of  $[UO_2 (trensal)Fe(py)_3]$ , **6**.

The solid-state structure of **6**, represented in Figure 33 shows the presence of a neutral dinuclear complex where a  $[U^{V}O_{2}(\text{trensal})]$  dianion binds a Fe<sup>2+</sup> cation trough a UO<sub>2</sub><sup>+</sup>–Fe<sup>2+</sup> CCI. The Fe<sup>2+</sup> cation is hexacoordinated, with a slightly distorted octahedral geometry, by two donor atoms of the trensal<sup>3-</sup> ligand, one uranyl oxo group and three pyridine molecules. The uranium cation is heptacoordinate with a slightly distorted pentagonal bipyramid geometry, by two uranyl oxygen atoms and five donor atoms of the trensal<sup>3-</sup> ligand in the equatorial plane. The mean U-O bond lengths lie in the range of values typically observed for uranyl(V) complexes,<sup>[1][18][30][34][35][47]</sup> with the UO<sub>2</sub><sup>+</sup>–Fe<sup>2+</sup> interaction resulting in a slight lengthening of the bond (U1–O4 = 1.930 (2) Å and U1–O3 = 1.837(3) Å). The value of the Fe-O bond length (2.018(3) Å) falls in the range of those found in the only two previously reported examples of uranyl(V) complexes presenting a cation-cation interaction with a Fe<sup>2+</sup> cation (1.946(4)-2.132(4) Å).<sup>[44][47]</sup>



**Figure 33.** Ellipsoid plot at 50% probability of complex **6** (co-crystallised pyridine molecule and H were omitted for clarity, C are represented in grey, O in red, N in blue, Fe in dark blue and U in green).

The proton NMR spectrum of **6** in pyridine shows the presence of 12 signals over a broad range of chemical shifts (-30 to +51 ppm). The large shift of the proton NMR signals observed for **6** compared to complex **4** indicate that the  $UO_2^+$ –Fe<sup>2+</sup> CCI is present in pyridine solution (Figure 34). The ESI/MS spectrum ({ $UO_2$ (trensal)Fe(Py)<sup>+</sup>}: m/z = 859.83) of **6** also indicates the presence of the heterobime-tallic complex in pyridine solution (Appendix 1 : Fig. S20).



**Figure 34.** <sup>1</sup>H NMR spectrum (400 MHz,  $C_5D_5N$ , 298 K) of crystals of  $[UO_2(trensal)Fe(py)_3]$  (6).

The stability and reactivity of **6** were then investigated and compared with those found for **3** and **4** in order to elucidate the effect of the Fe<sup>2+</sup> ion. The addition of 1 eq. of PyHCl to a solution of **6** in pyridine results in the partial disproportionation of the uranyl(V) complex (Scheme 10) with a 2:1 ratio of **6** to the disproportionation product  $[UO_2(trensal)Fe(py)_3U(trensal)]Cl$ **7b** (Appendix 1 : Fig. S8). The addition of 2 equivalents of PyHCl to **6** led to the complete disappearance of the signals of complex **6** in the <sup>1</sup>H NMR spectrum. (Appendix 1 : Fig. S9) and to an increased intensity of the signals assigned to **7b**. The presence of the uranyl(VI) complex  $[UO_2(Htrensal)]$  as the second disproportionation product was also identified by <sup>1</sup>H NMR spectroscopy.

However, in both cases, the disproportionation was not complete. Notably, the trinuclear cationcation complex **7b** contains unreacted uranyl(V) (Scheme 10).



Scheme 10. Addition of PyHCl to the complex 6 and synthesis of 7.

However, the iodide analogue [UO<sub>2</sub>(trensal)Fe(py)<sub>3</sub>U(trensal)]I, **7** was prepared in 80% yield from the reaction of complex **6** with 1 eq. of the [U(trensal)]I complex in pyridine (Scheme 10). This complex is a rare example of actinide-functionalized uranyl complex and only the third example of a uranyl(V) complex presenting a CCI between the uranyl(V) oxo group and a U(IV) cation.<sup>[21][41]</sup> The structure of complex **7** (Figure 35) shows the presence of a cationic trimeric complex built *via* CCI between the U(IV) center from the [U(trensal)]<sup>+</sup> complex and the oxo group of the uranyl(V) [UO<sub>2</sub>(trensal)Fe(py)<sub>3</sub>] fragment. The three metal ions adopt a close to linear arrangement with a Fe-O-U angle of 170.3(3) ° and a U-O-U angle of 171.2(3) °. The U=O bond distance for the uranyl(V) oxo group bound to the Fe<sup>2+</sup> remains unchanged at 1.922(6) Å compared to complex **6**, but a significant lengthening of the U=O bond is observed upon binding of the U(IV) cation in **7** (1.960(6) Å). The UO<sub>2</sub><sup>+---</sup>U(IV) distance (2.317(6) Å is comparable to those found in the only two other complexes reported to have a UO<sub>2</sub><sup>+---</sup>U(IV) CCI (2.198(13) and 2.245(3) Å).<sup>[21][41]</sup> The UO<sub>2</sub><sup>+---</sup>Fe<sup>2+</sup> distance (2.144(6) Å) is slightly longer that in **6** but is in the range of those found in the two previously reported complexes presenting a UO<sub>2</sub><sup>+---</sup>Fe<sup>2+</sup> interaction (1.946(4) Å - 2.132(4) Å).<sup>[44][47]</sup>

These results indicate that the presence of  $Fe^{2+}$  increases the stability of the uranyl(V) species in **6** with respect to proton induced disproportionation. Notably the addition of 2 eq. of PyHCl led to full disproportionation of the complexes **3**, and **4** while it resulted only in the partial disproportionation of **6** and the formation of  $[UO_2(Htrensal)]$  and of the Fe-U(V)-U(IV) trimer. The addition of five equivalents of pyridinium chloride is required for the full disproportionation of complex **6** to occur. This indicates that the iron bound uranyl(V) complex **6** displays an increased stability towards the proton

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induced disproportionation compared to the potassium bound uranyl(V) complexes **3** and **4** (Figure 36).



**Figure 35**. Ellipsoid plot at 50% probability of the cation  $[UO_2(trensal)Fe(py)_3U(trensal)]^+$  in **7** (cocrystallized pyridine molecule and H were omitted for clarity, C are represented in grey, O in red, N in blue, Fe in dark blue and U in green).



**Figure 36.** <sup>1</sup>H NMR spectrum (400 MHz, C<sub>5</sub>D<sub>5</sub>N, 298 K) of the crystals of compound [UO<sub>2</sub>(trensal)Fe(py)<sub>3</sub>U(trensal)]I (**7**) (a) and of the reaction mixtures after : addition of 1 eq. of PyHCI to  $[UO_2(trensal)Fe(py)_3]$  (**6**) (b), addition of 3 eq. of PyHCI to **6** (c), addition of 5 eq. of PyHCI to **6** (d) and addition of 2 eq. of PyHCI to  $[UO_2(trensal)K]K$  (**3**) (e).

The binding of U(IV) to the uranyl(V) oxo group was previously reported to promote partial disproportionation and formation of multimetallic U(IV)–U(V) oxo-bridged complexes.<sup>[21]</sup>

In contrast, complex **7** is stable in pyridine solution over one-month period. <sup>1</sup>H NMR studies show that the addition of [U(trensal)]I to complex **3** also leads to the formation of a stable unidentified species (Appendix 1: Fig. S10). The subsequent addition of FeI<sub>2</sub> to this species led to the formation of complex **7**. These results suggest that stable U(IV)–U(V) species also form in the absence of iron bound to uranyl(V) oxo group. However, the formation of these species is not observed during the addition of PyHCI to **3**, which undergoes complete disproportionation after the addition of 2 eq. of PyHCI.

Moreover, the addition of 2 eq. of PyHCl to the U(IV)–U(V) adduct results in full disproportionation, as indicated by <sup>1</sup>H NMR spectrum, suggesting that the binding of U(IV) to the uranyl(V) oxo does not lead to increased stability (Appendix 1: Fig. S10). This further confirms the stabilizing role of Fe(II) binding with respect to proton induced disproportionation of uranyl(V).

The <sup>1</sup>H NMR spectrum of **7** in pyridine shows the presence of 45 signals over a large range of chemical shifts (-35 to +53 ppm) in agreement with the presence of the trimeric complex **7** in solution. (Fig. S11). Additionally, the ESI/MS spectrum of **7** in pyridine solution  $(UO_2(trensal)Fe_3U(trensal)^+)$ m/z = 1474.42) indicated that the complex **7** retains its trinuclear structure in the pyridine solution (Appendix 1: Fig. S21).

The addition of 1 eq. of pyridinium chloride to **7** results in partial disproportionation with a 3:1 ratio of complex **7** to the disproportionation products as shown by <sup>1</sup>H NMR spectroscopy (Appendix 1: Fig. S12). The complete disproportionation of complex **7** requires the addition of 4 eq. of PyHCI. The coordination of U(IV) does not increase the stability of the uranyl(V) species in **7** with respect to **6**. In view of the increased stability of **7** and **6** compared to **3** towards proton induced disproportionation, we set out to investigate how the coordination of a second Fe<sup>2+</sup> cation to complex **6** would affect the structure and reactivity of the U(V) centre.

The <sup>1</sup>H NMR of the reaction mixture resulting from the addition of 0.5 equivalents of iron(II) iodide to **6** in pyridine indicated the formation of a new species (Appendix 1: Fig. S13).

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Scheme 11. Synthesis of [(UO<sub>2</sub>(trensal)Fe(py)<sub>3</sub>)<sub>2</sub>Fe(py)<sub>3</sub>]I<sub>2</sub>, 8.

X-ray quality crystals of  $[(UO_2(trensal)Fe(py)_3)_2Fe(py)_3]I_2$ , **8**, were obtained in 65% yield from this reaction (Scheme 11). The solid-state structure (Figure 37) of **8** shows the presence of a pentametallic structure where a Fe(Py)\_3 moiety bridges two iron-bound uranyl (V)  $[UO_2(trensal)Fe(py)_3]$  moieties. Overall, this results in the presence of  $UO_2^+...Fe^{2+}$  CCIs for both uranyl(V) oxo-groups. The central Fe<sup>2+</sup> cation is penta- coordinated by one oxo atom from each of the two uranyl(V) groups and three pyridine molecules. The mean Fe(2)-O(oxo) bond lengths is 1.988 Å. The  $[UO_2(trensal)Fe(py)_3]$  moieties of the crystal structure possess the same geometry found in the mononuclear complex **6**, but the additional uranyl–iron interaction results in a slight lengthening of the  $UO_2^+...Fe^{2+}$  bonds compared to **6** (2.061(4) Å vs. 2.018(3) Å). The arrangement of the 5 metal ions is not linear, with a  $Fe1\overline{Fe2}Fe3$  angle of 136°.



**Figure 37.** Molecular structure of the structure of the dication  $[{UO_2(trensal)Fe(py)_3}_2Fe(py)_3]^{2+}$  in **8** (H were omitted for clarity, C are represented in grey, O in red, Fe in dark blue, N in blue, I in purple and U in green). Selected distances U1 – O2 = 1.920 (4) Å, U1 – O5= 1.935 (4) Å, U2 – O6 = 1.927 (4) Å and U2 – O9 = 1.927 (5) Å.

The ESI/MS spectrum of **8** (Appendix 1: Fig. S22) did not show the presence of a pentanuclear architecture in pyridine solution but showed only the peaks corresponding to the trinuclear {*Fe-U-Fe*} and dinuclear {*Fe-U*} species. The addition of 1 eq. of the complex  $[UO_2(trensal)Fe(py)_3]$  to a solution

of **8** in pyridine resulted only in a slight broadening of the proton NMR signals of the **8** suggesting the presence in solution of a fast exchange between the  $[UO_2(trensal)Fe(py)_3]$  moiety and **8** (Figure 38).



**Figure 38.** <sup>1</sup>H NMR spectrum (400 MHz,  $C_5D_5N$ , 298 K) of the crystals of compound [(UO<sub>2</sub>(trensal)Fe(py)<sub>3</sub>)<sub>2</sub>Fe(py)<sub>3</sub>]I<sub>2</sub> (8) (bottom), of crystals of [UO<sub>2</sub>(trensal)Fe(py)<sub>3</sub>] (6) (top) and of the reaction mixture after addition of 1 eq. of 6 to 8 (middle).

The labile binding of the central  $Fe(Py)_3^{2+}$  cation in **8**, does not lead to an increased stability of **8** towards proton induced disproportionation compared to **6**. Notably, the proton NMR indicated a 2:1 ratio between the starting complex **8** and the disproportionation products upon addition of 1 eq. of H<sup>+</sup> per uranyl(V) which is identical to the ratio observed for the complex **6**. (Appendix 1: Fig. S8)

#### Redox reactivity.

Iron binding to the uranyl(V) oxo is anticipated to have an important effect on its redox reactivity. Moreover, it has been suggested that iron binding at mica surfaces leads to the stabilization of uranyl(V) intermediates but the effect of iron binding on the redox properties of isolated uranyl(V) complexes has not been investigated.

At first, we explored the chemical oxidation of uranyl(V) by  $Fe^{3+}$ . The reaction of **3** with 1 eq.  $FeCI_3$ leads to the oxidation of the uranium center and to the formation of the uranyl(VI)-Fe(II) complex [(UO<sub>2</sub>(trensal))<sub>2</sub>Fe] as identified by X-ray diffraction crystallography and <sup>1</sup>H NMR spectroscopy. The oxidation of uranyl(V) complex to uranyl(VI) by Fe(III) is explained in terms of the respective redox potential (Fe(III)/Fe(II)= 0.0 eV;  $UO_2^{2+}/UO_2^{+}$ = -1.6 vs. eV (Fc/Fc<sup>+</sup>)) (Appendix 1: Fig. S14).

In order to probe the possibility of obtaining a uranyl(V)-Fe(III) complex we explored the reactivity of **3** and **6** with increasingly electron-rich FeLCl<sub>n</sub> complexes, (L= tpa and tdmba; tpa= (tris(pyridin-2ylmethyl)amine and H<sub>3</sub>tdmba= (tris-(2-hydroxy-3,5-dimethylbenzyl)amine). The reaction of **6** with [Fe(tpa)Cl<sub>3</sub>] led to the oxidation of uranyl(V) to uranyl(VI) with concomitant formation of [Fe(tpa)Cl<sub>2</sub>] (as shown by X-ray diffraction studies and <sup>1</sup>H NMR spectroscopy (Appendix 1: Fig. S15)). The reaction of **6** with the neutral Fe(III) complex [Fe(tdmba)] did not result in any change observable in the <sup>1</sup>H NMR spectrum of **6** (Figure 39) indicating that the Fe(III) cation in [Fe(tdmba)] does not form CCIs with the uranyl(V) oxo group but does not oxidizes the uranyl(V) either. In contrast, when complex **3** is reacted with [Fe(tdmba)], <sup>1</sup>H NMR spectroscopy indicated that a redox reaction occurs yielding uranyl(VI) and Fe(II) species (Appendix 1: Fig. S16). These results are in agreement with the reported influence of chelating agents on the reoxidation by Fe(III) of biogenic products of uranyl(VI) reduction.<sup>[52]</sup>



**Figure 39.** <sup>1</sup>H NMR spectrum (400 MHz,  $C_5D_5N$ , 298 K) of  $[UO_2(trensal)Fe(py)_3]$  (6) (bottom) of [Fe(tdmba)] (middle) and after addition of [Fe(tdmba)] to 6 in pyridine (top).
These results suggest that the presence of  $UO_2^{+}-Fe^{2+}$  CCI stabilizes the uranyl(V) oxidation state with respect to the oxidation of U(V). In order to further probe the role of iron binding on the redox properties of uranyl(V) species we performed comparative cyclic voltammetry studies of complexes **1**, **2**, **5**, **6** and **8** (Figure 40, Figure 41 and Appendix 1: Fig. SCV1-SCV3). The voltammogram of **1** in pyridine (Figure 40) shows an irreversible redox event at -1.75 V, but when the voltammogram of **1** is measured in the presence of cryptand a reversible redox event assigned to the U(VI)/U(V) couple is observed at  $E_{1/2} = -1.69$  V vs Fc/Fc<sup>+</sup> (Figure 40, green curve). The voltammogram of the protonated uranyl(VI) complex **2** also shows the presence of a reversible redox event at  $E_{1/2} = -1.66$  V vs Fc/Fc<sup>+</sup> assigned to the U(VI)/U(V) couple. These values compare well with the values previously measured in pyridine for other uranyl(V) complexes of tetradentate ( $E_{1/2} = -1.61$  V or -1.67 V vs Fc/Fc<sup>+</sup>)<sup>[50][34]</sup> and pentadentate Schiff bases ( $E_{1/2} = -1.58$  V vs Fc/Fc<sup>+</sup>).<sup>[53]</sup> A second irreversible redox event is observed at  $E_{1/2} = -2.47$  V vs Fc/Fc<sup>+</sup> for complex **2**, but not for complex **1**. This event is consistent with the reduction of the metal centre (values of redox potential ranging from -2.02 to -2.88 V vs Fc/Fc<sup>+</sup> were previously assigned to the U(V)/U(IV) couple<sup>[27]</sup>).

The possibility that this event could be related to the reduction of the Schiff base ligand is unlikely since this feature is absent from the voltammograms of the H<sub>3</sub>trensal, K<sub>3</sub>trensal ligands and of the complex **1**. Moreover, the shift of the U(V)/U(IV) couple at a more positive potential in complex **2** could be explained by the presence of a proton on the complex.



Figure 40. Room temperature cyclic voltammograms of 4 mM pyridine solutions of [UO<sub>2</sub>(trensal)K]
1 in the presence of 1 eq. of cryptand (green), of [UO<sub>2</sub>(trensal)H] 2 (red) and of [UO<sub>2</sub>(trensal)Fe(py)<sub>3</sub>]
6 (blue) recorded in 0.1 M [Bu<sub>4</sub>N][PF<sub>6</sub>] at 100 mV/s scan rate, Cp<sub>2</sub>Fe/Cp<sub>2</sub>Fe<sup>+</sup> (Fc/Fc<sup>+</sup>) corrected.

Similar redox events are observed in the voltammogram of complex **6** in addition to the quasi-reversible wave at  $E_{1/2} = 0.0 \text{ V}$  vs Fc/Fc<sup>+</sup>, assigned to the Fe(III)/Fe(II) couple. However, the U(VI)/U(V) reduction process is found at -1.03 V vs Fc/Fc<sup>+</sup> in the voltammogram of **6** and the second reduction event occurs at  $E_{1/2} = -2.7 \text{ V}$  vs Fc/Fc<sup>+</sup> demonstrating that the range of stability of the uranyl(V) species is significantly extended compared to complex **2** as a result of Fe(II) binding. Both reduction and oxidation of the uranyl(V) cation are more difficult in the presence of Fe(II). No additional redox stabilisation was observed upon addition of two or more equivalents of Fe(II) to complex **6** as indicated by the voltammogram of the complex **8** (Appendix 1: Fig. SCV2). This is probably due to the labile binding of the second Fe(II) cation to the uranyl(V) oxo group in pyridine.

Moreover, in the voltammogram of complex **5** (Figure 41) the redox event assigned to the U(VI)/U(V) couple is found at  $E_{1/2} = -1.66$  V vs Fc/Fc<sup>+</sup> as in complexes **1** and **2** in spite of the presence of a Fe(II) ion bound through the Schiff base acting as a bridging ligand. These results indicate that cation-cation interaction between the uranyl(V) oxygen and the Fe<sup>2+</sup> is essential for the stabilization of U(V) while the presence of a Fe(II) bound through the ligand has no significant effect on the redox properties of the uranyl(V).



**Figure 41.** Room temperature cyclic voltammograms for and  $[U^VO_2(\text{trensal})Fe^{II}(py)_3]$  **6** (blue) and  $[(U^{VI}O_2(\text{trensal}))_2Fe^{II}]$  **5** (mustard) recorded in 0.1 M [Bu<sub>4</sub>N][PF<sub>6</sub>] in 2 mM pyridine solution at 100 mV/s scan rate, Cp<sub>2</sub>Fe/Cp<sub>2</sub>Fe<sup>+</sup> corrected.

# **2.3 Conclusions**

In this chapter, the synthesis and characterization of uranyl(V) complexes presenting  $UO_2^+-K^+$  or UO<sub>2</sub><sup>+</sup>-Fe<sup>2+</sup> cation-cation interactions supported by tripodal heptadentate Schiff base trensal<sup>3-</sup> ligand was presented. The reported uranyl(V) complexes showed similar stability in pyridine solution, but the presence of Fe<sup>2+</sup> bound to the uranyl(V) oxygen led to increased stability with respect to proton induced disproportionation. A stable  $Fe^{2+} - UO_2^+ - U^{4+}$  intermediate (7b) containing both  $UO_2^+ - Fe^{2+}$ and UO<sub>2</sub><sup>+</sup>– U<sup>4+</sup> cation-cation interactions formed upon addition of 2 eq. of PyHCl to the iron bound uranyl(V) complex (6). In contrast, the addition of 2 eq. of PyHCl to the potassium bound uranyl(V) complexes (3 and 4) resulted in the immediate formation of U(IV) and  $UO_2^+$  species. The  $UO_2^+$ ---Fe<sup>2+</sup> (6) complex reacted with an additional  $Fe^{2+}$  cation leading to the formation of a pentameric  $Fe^{2+}$  $UO_2^+$  - Fe<sup>2+</sup> -  $UO_2^+$  - Fe<sup>2+</sup> complex (8) but the additional Fe<sup>2+</sup> -  $UO_2^+$  cation-cation interactions did not lead to increased stability. Redox reactivity and cyclic voltammetry studies also showed an increased range of stability of the uranyl(V) species in the presence of Fe<sup>2+</sup> with respect both to oxidation and reduction reactions, while the presence of a proton in the uranyl(VI) complex (2) resulted in a smaller stability range for the uranyl(V) species. Cyclic voltammetry studies also showed that the presence of a Fe<sup>2+</sup> cation bound only through one trensal<sup>3-</sup> arm in the trinuclear complex {UO<sub>2</sub>(trensal)}<sub>2</sub>Fe], **5** did not lead to increased redox stability of the uranyl(V) demonstrating the important role of UO<sub>2</sub><sup>+</sup>–Fe<sup>2+</sup> cation-cation interactions in increasing the stability of uranyl(V). These results provide important insight on the role that iron binding may play in stabilizing uranyl(V) species in the environmental mineral-mediated reduction of uranium(VI).

Future work will seek to elucidate the stabilization effect of Fe on uranyl(V) in more environmentally relevant aqueous media. For this purpose, the ligand structure would need to be modified to increase the stability and solubility of the resulting uranyl(V) species in water. For example, the use of a heptadentate tripodal ligand H<sub>3</sub>tpaa ( $\alpha, \alpha', \alpha''$ -nitrilo(6-methyl-2-pyridinecarboxylic acid) can be foreseen as this ligand will allow the stabilization of uranyl(V) in water along with the controlled binding of Fe to a uranyl-oxo group. We have demonstrated that aminocarboxylate ligand dpaea<sup>2-</sup> (H<sub>2</sub>dpaea =bis(pyridyl-6-methyl-2-carboxylate)-ethylamine) can be successfully utilized for stabilization of uranyl(V) in water solution.\* The use of H<sub>3</sub>tpaa could allow a controlled synthesis of uranyl(V)/Fe(II) hetero-bimetallic complexes where two bidentate picolinate arms of the tpaa ligand and the central

nitrogen would tightly bind the uranyl(V) in the equatorial plane, while the third arm would remain available for the binding of a ferrous cation.

\*R. Faizova, R. Scopelliti, A.-S. Chauvin, M. Mazzanti, J. Am. Chem. Soc. 2018, 140, 13554–13557

# Experimental

**General Considerations.** All manipulations were carried out under an inert argon atmosphere using Schlenk techniques and an MBraun glovebox equipped with a purifier unit. The water and oxygen level were always kept at less than 1 ppm. The solvents were purchased from Aldrich or Cortecnet (deuterated solvents) in their anhydrous form, conditioned under argon and vacuum distilled from K/benzophenone (diisopropylether, hexane, pyridine, toluene, benzene and THF) or freeze-degassed and stored over activated 3 Å molecular sieves (pyridine-d<sub>5</sub>). Depleted uranium was purchased from IBILABS, USA.

 $[(UO_2Py_5)(KI_2Py_2)]_n$  and  $UI_4$  were synthesized as previously described.<sup>[30][54]</sup>  $UO_2(NO_3)_2(H_2O)_6$  was purchased from Sigma-Aldrich : Fluka.  $UO_2(NO_3)_2$  was obtained by high vacuum drying of  $UO_2(NO_3)_2(H_2O)_6$  for 5 days at 120°C. Anhydrous FeI<sub>2</sub>, FeCI<sub>3</sub> and PyHCI were purchased from Aldrich and were used without further purification. The H<sub>3</sub>trensal<sup>[55]</sup> and H<sub>3</sub>tdmba<sup>[56]</sup> ligands were prepared according to the published procedure.

Elemental analyses were performed under argon with a Thermo Scientific Flash 2000 Organic Elemental Analyzer by the EPFL elemental analyses service. <sup>1</sup>H NMR experiments were carried out using NMR tubes adapted with J. Young valves. <sup>1</sup>H NMR spectra were recorded on Bruker 400 MHz spectrometer. NMR chemical shifts are reported in ppm with solvent as internal reference. EPR spectra were recorded with a Bruker Elexsys E500 spectrometer working at 9.4 GHz frequency with an oxford ESR900 cryostat for 4-300 K operation. Simulation was performed with the Easyspin 5.1.3 program.

**Caution:** Depleted uranium (primary isotope <sup>238</sup>U) is a weak  $\alpha$ -emitter (4.197 MeV) with a half-life of 4.47×10<sup>9</sup> years. Manipulations and reactions should be carried out in monitored fume hoods or in an inert atmosphere glovebox in a radiation laboratory equipped with  $\alpha$ - and  $\beta$ -counting equipment.

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#### Synthetic procedures

#### Synthesis of K<sub>3</sub>trensal.

Potassium hydride (50.8 mg, 1.267 mmol, 2.9 eq.) was added slowly to a stirred solution of H<sub>3</sub>trensal (200.0 mg, 0.436 mmol, 1 eq.) in THF (5 mL) and stirred overnight. After 12 hours of stirring, the resulting white solid was filtered off, washed with THF and dried under vacuum to give K<sub>3</sub>trensal.(THF)<sub>0.5</sub> (244.3 mg, 0.379 mmol, 87 % yield). The residual amount of THF present in the solid was determined at each preparation by quantitative titration using naphthalene as standard. <sup>1</sup>H NMR (400 MHz, C<sub>5</sub>D<sub>5</sub>N, 298 K):  $\delta$  = 8.18 (s, 3H), 7.27 (d, 3H), 7.04 (t, 3H), 6.61 (d, 3H), 6.44 (t, 3H), 3.42 (s, 6H), 2.42 (s, 6H) (Appendix 1: Fig. S1).

#### Synthesis of [UO<sub>2</sub>(trensal)K], 1.

A yellow solution of  $UO_2(NO_3)_2$  (30.8 mg, 0.078 mmol, 1 eq.) in pyridine (1mL) was slowly added to a stirred suspension of K<sub>3</sub>trensal(THF)<sub>0.5</sub> (50.3 mg, 0.078 mmol, 1 eq.) in pyridine (1 mL) and the mixture was stirred for 60 minutes, resulting in an orange solution. Then KNO<sub>3</sub> was removed by centrifugation and the resulting solution was layered with *n*.hexane (2 mL). Slow diffusion of hexane yielded [UO<sub>2</sub>(Ktrensal)].Py as orange solid (39.0 mg, 0.046 mmol, 59%) Anal. Calcd. for [UO<sub>2</sub>(trensal)K].Py (C<sub>32</sub>H<sub>32</sub>N<sub>5</sub>O<sub>5</sub>KU, MW=843.66) C 45.56, H 3.82 and N 8.30; found C 45.47, H 3.64 and N 8.15. The <sup>1</sup>H NMR spectrum (400 MHz, C<sub>5</sub>D<sub>5</sub>N, 298 K) was recorded but the assignment was not possible due to the fluxional behaviour of **1** in pyridine solution.

#### Synthesis of [UO<sub>2</sub>(Htrensal)], 2.

A yellow solution of UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub> (20.0 mg, 0.051 mmol, 1 eq) in pyridine (1mL) was slowly added to a stirred suspension of K<sub>3</sub>trensal(THF)<sub>0.5</sub> (32.9 mg, 0.051 mmol, 1 eq.) in pyridine (1mL) and was stirred for 60 minutes, resulting in an orange solution. Then, a solution of PyHCl (5.9 mg, 0.051 mmol, 1 eq.) in pyridine (0.5 mL) was added to the reaction mixture. The reaction mixture was stirred overnight, then KNO<sub>3</sub> was removed by centrifugation and the resulting solution was layered with *n*.hexane (2 mL). Slow diffusion of hexane yielded [UO<sub>2</sub>(Htrensal)].Py<sub>0.5</sub> as an orange microcrystalline solid (23.0 mg, 0.031 mmol, 60%) Anal. Calcd. for [UO<sub>2</sub>(Htrensal)].Py<sub>0.5</sub> (C<sub>29.5</sub>H<sub>30.5</sub>N<sub>4.5</sub>O<sub>5</sub>U, MW=766.07) C 46.25, H 4.01 and N 8.23; found C 46.58, H 3.80 and N 8.07. <sup>1</sup>H NMR (400 MHz, C<sub>5</sub>D<sub>5</sub>N, 298 K)  $\delta$  = 11.94 (s, 1H), 6.26 (m, 3H), 6.16 (dd, 2H), 6.05 (m, 4H), 5.86 (m, 2H), 5.61 (t, 1H), 5.38 (t, 2H), 3.74 (t, 2H), 3.08 (dd, 2H), 2.93 (t, 2H), 2.74 (m, 5H), 2.57 (td, 2H). Orange single crystals of **2.py** suitable for X-ray diffraction were obtained by slow diffusion (one week) of hexane into pyridine solution of **2**.

#### Synthesis of [UO<sub>2</sub>(trensal)K]K, 3.

An orange solution of  $[(UO_2Py_5)(KI_2Py_2)]_n$  (20.0 mg, 0.018 mmol, 1 eq.) in pyridine (2mL) was slowly added to a stirred suspension of K<sub>3</sub>trensal(THF)<sub>0.5</sub> (11.6 mg, 0.018 mmol, 1 eq.) in pyridine (2 mL). The reaction mixture was stirred for 2 hours, resulting in a bright blue solution and a white precipitate. The white precipitate was centrifuged out. Upon slow diffusion of n.hexane into the resulting solution, a blue solid was obtained (13.0 mg, 0.014 mmol, 70%). Anal. Calcd for  $[UO_2(trensal)K]K.KI_{0.6}$  $(C_{27}H_{27}N_4O_5I_{0.6}K_{2.6}U, MW=903.363) C 35.9, H 3.01 and N 6.20; found C 36.13, H 2.63 and N 6.43.$ Synthesis of  $[UO_2(trensal)(K(2.2.2crypt)] [K(2.2.2crypt)], 4.$ 

An orange solution of  $[(UO_2Py_5)(KI_2Py_2)]_n$  (47.6 mg, 0.040 mmol, 1 eq.) in pyridine (1.5 mL) was slowly added to a stirred suspension of K<sub>3</sub>trensal(THF)<sub>0.5</sub> (25.8 mg, 0.040 mmol, 1 eq.) in pyridine (0.5 mL) resulting in a dark blue solution. The solution was stirred for 30 minutes and then a solution of 2.2.2.cryptand (60.2 mg, 0.016 mmol, 4 eq.) in pyridine (0.5 mL) was added resulting in a colour change to bright green. The resulting solution was stirred for 30 minutes, the solvent was evaporated and the residue was dissolved in THF (2 mL). The resulting green solution was filtered to remove K(2.2.2cryptand)I and the filtrate was layered with DIPE (2 mL). Upon slow diffusion of DIPE, complex 4.THF was obtained as green crystals (40.0 mg, 0.025 mmol, 62%). Anal. Calcd. for [UO<sub>2</sub>(trensal)(K(2.2.2crypt)][K(2.2.2crypt)].THF (C<sub>67</sub>H<sub>107</sub>N<sub>8</sub>O<sub>18</sub>K<sub>2</sub>U<sub>1</sub>, MW=1628.859) C 49.40, H 6.62 and N 6.88; found C 49.43, H 6.69 and N 7.03. <sup>1</sup>H NMR (400 MHz, C<sub>5</sub>D<sub>5</sub>N, 298 K)  $\delta$  = 6.94 (m, 3H), 5.99 (s, 1H), 5.24 (s, 3H), 4.47 (s, 4H), 4.26 (s, 4H), 3.84 (s, 24H), 3.78 (s, 24H), 2.73 (s, 24H), -2.16 (s, 2H), -3.32 (s, 2H), -4.63 (s, 2H), -7.71 (s, 2H), -9.49 (s, 2H), -10.04 (s, 2H). Bright green single crystals of 4 suitable for X-ray diffraction were obtained after slow diffusion (4 weeks) of DIPE (1 mL) into a THF (1 mL) solution of 4.

# Synthesis of [(UO<sub>2</sub>(trensal))<sub>2</sub>Fe(py)<sub>2</sub>], 5.

A yellow solution of  $UO_2(NO_3)_2$  (20 mg, 0.05 mmol, 2 eq.) in pyridine (0.5 mL) was slowly added to a stirred suspension of  $K_3$ trensal(THF)<sub>0.5</sub> (32.2 mg, 0.05 mmol, 2 eq.) in pyridine (1 mL) and was stirred for 1 hour. A suspension of FeI<sub>2</sub> (7.9 mg, 0.025 mmol, 1 eq) in pyridine (0.5 mL) was added to the resulting orange solution and the reaction mixture was stirred overnight, yielding a deep purple solution. KI was removed by centrifugation and the solution was layered with hexane (1 mL). [( $UO_2$ (trensal))<sub>2</sub>Fe(py)<sub>2</sub>].py<sub>2</sub> was obtained as a dark brown solid after 6 days (43 mg, 0.024 mmol,

93%). <sup>1</sup>H NMR (400 MHz,  $C_5D_5N$ , 298 K):  $\delta = 51.62$  (s, 2H), 36.64 (s, 1H) 6.77-0.51 (br, 49H), -14.85 (s, 2H). Elemental analysis calcd (%) for [(UO<sub>2</sub>(trensal))<sub>2</sub>Fe(py)<sub>2</sub>].py<sub>2</sub> ( $C_{74}H_{74}N_{12}O_{10}FeU_2$ , MW=1823.2) C 48.75, H 4.09 and N 9.22; found C 48.36, H 3.71 and N 9.30. Dark purple single crystals of 5 suitable for X-ray diffraction were obtained by slow diffusion (two weeks) of hexane (1 mL) into a pyridine (2 mL) solution of 5.

#### Synthesis of [UO<sub>2</sub>(trensal)Fe(py)<sub>3</sub>], 6.

An orange solution of  $[(UO_2Py_5)(KI_2Py_2)]_n$  (75.4 mg, 0.068 mmol, 1 eq.) in pyridine (3 mL) was slowly added to a stirred suspension of  $K_3$  trensal(THF)<sub>0.5</sub> (43.6 mg, 0.068 mmol, 1 eq.) in pyridine (2 mL) and was stirred for 1 hour. A suspension of Fel<sub>2</sub> (21.1 mg, 0.068 mmol, 1 eq.) in pyridine (1 mL) was added to the resulting blue solution, yielding a deep purple solution. The reaction mixture was stirred overnight, KI was removed by filtration. The resulting solution was layered with hexane (3 mL) to afford, after two weeks, a dark purple microcrystalline solid that was dried under vacuum (65.0 mg, 0.055 mmol, 81%). Electrospray ionization mass spectrometry (ESI-MS): m/z = 859.89(%)  $\{UO_2(trensal)Fe(Py)^+\}.$ Elemental analysis calcd for  $[UO_2(trensal)Fe(py)_3]KI_{0.8}$ (C<sub>42</sub>H<sub>42</sub>N<sub>7</sub>O<sub>5</sub>I<sub>0.8</sub>K<sub>0.8</sub>FeU, MW=1151.5) C 43.81, H 3.68 and N 8.51; found C 43.76, H 3.53 and N 8.60. <sup>1</sup>H NMR (400 MHz, C<sub>5</sub>D<sub>5</sub>N, 298 K): δ = 51.48 (s, 3H), 38.28 (s, 3H), 2.67 (s, 3H), -2.72 (s, 2H), -4.50 (s, 2H), -5.46 (s, 2H), -7.93 (s, 2H), -10.92 (s, 2H), -12.21 (s, 3H), -14.56 (s, 2H), -27.65 (s, 1H), 31.06 (s, 1H). Dark purple single crystals of 6.py.0.5hex suitable for X-ray diffraction were obtained by slow diffusion (two weeks) of hexane (1 mL) into a pyridine (1 mL) solution of 6.

#### Synthesis of [UO₂(trensal)Fe(py)₃U(trensal)]I, 7.

A pyridine (1 mL) solution of [U(trensal)(py)]I (16.3 mg 0.020 mmol, 1 eq) prepared *in situ* (KI formed was removed by filtration) was added to a deep purple pyridine (1 mL) solution of  $[UO_2(trensal)Fe(py)_3]$  (20.2 mg, 0.020 mmol, 1 eq), prepared *in situ* (KI formed was removed by filtration). The reaction mixture was stirred overnight. A white precipitate (KI formed) was removed by filtration. The resulting solution layered with hexane (2 mL). After a week  $[UO_2(trensal)Fe(py)_3U(trensal)]I.KI$  (32 mg, 0.016 mmol, 80%) was obtained as a purple crystalline powder. Electrospray ionization mass spectrometry (ESI-MS):  ${UO_2(trensal)Fe_3U(trensal)^+} m/z = 1474.42$ ; Elemental analysis calcd (%) for  $[UO_2(trensal)Fe(py)_3U(trensal)]I.KI$  ( $C_{69}H_{69}N_{11}O_8I_2KFeU_2$ , MW=2005.2) C 41.33, H 3.47 and N 7.68; found C 41.36, H 3.38 and N 7.57. <sup>1</sup>H NMR (400 MHz, C<sub>5</sub>D<sub>5</sub>N, 298 K):  $\delta$  = 53.66 (s, 1H), 49.65 (s, 1H),

41.17 (s, 1H), 35.97 (s, 1H), 27.52 (s, 1H), 23.54 (s, 1H), 21.81 (s, 1H), 17.32 (s, 1H), 16.35 (s, 1H), 15.60 (s, 1H), 13.58 (s, 1H), 12.82 (s, 1H), 11.96 (s, 1H), 11.24 (s, 1H), 10.81 (s, 1H), 9.22 (s, 1H), 8.01 (s, 1H), 4.89 (s, 1H), 4.43 (s, 1H), 4.19 (s, 1H), 3.92 (s, 1H), 3.57 (s, 2H), 3.28 (s, 1H), 2.69 (s, 1H), 2.21 (s, 1H), 1.01 (s, 2H), -1.46 (s, 2H), -4.71 (s, 1H), -5.56 (s, 1H), -8.98 (s, 1H), -9.47 (s, 1H), -9.94 (s, 1H), -11.44 (s, 1H), -11.82 (s, 1H), -12.28 (s, 1H), -13.32 (d, 2H), -14.62 (s, 1H), -17.90 (s, 1H), 18.00 (s, 1H), -18.90 (s, 1H), -20.29 (s, 1H), -21.16 (d, 3H), -29.45 (s, 1H), -31.97 (s, 1H), -35.64 (s, 1H). Dark purple single crystals of 7 suitable for X-ray diffraction were obtained by slow diffusion (two weeks) of hexane (1 mL) into a pyridine (0.5 mL) solution of 7.

#### Synthesis of [(UO<sub>2</sub>(trensal)Fe(py)<sub>3</sub>) <sub>2</sub>Fe(py)<sub>3</sub>]I<sub>2</sub>, 8.

An orange solution of  $[(UO_2Py_5)(KI_2Py_2)]_n$  (50 mg, 0.035 mmol, 1 eq) in pyridine (0.5 mL) was slowly added to a stirred suspension of K<sub>3</sub>trensal (THF)<sub>0.5</sub> (22.6 mg, 0.035 mmol, 1 eq) in pyridine (1 mL) and was stirred for 1 hour. A suspension of FeI<sub>2</sub> (16.3 mg, 0.053 mmol, 1.5 eq) in pyridine (1 mL) was added to the resulting blue solution, yielding a deep purple solution. The reaction mixture was left stirring overnight, KI was removed by centrifugation and filtration and the resulting solution was layered with hexane (2.5 mL). After a week [(UO<sub>2</sub>(trensal)Fe(py)<sub>3</sub>)<sub>2</sub>Fe(py)<sub>3</sub>]I<sub>2</sub>].KI (63 mg, 0.023 mmol, 65%) was obtained as a purple crystalline powder. Dark purple X-ray quality crystals of **8** were obtained by slow diffusion (one week) of hexane (1 mL) into a pyridine (0.5 mL) solution **8**. Electrospray ionization mass spectrometry (ESI-MS): m/z = *859.83* {*UO<sub>2</sub>*(*trensal*)*Fe*(*Py*)<sup>+</sup>}. Elemental analysis calcd (%) for [(UO<sub>2</sub>(trensal)Fe(py)<sub>3</sub>)<sub>2</sub>Fe(py)<sub>3</sub>]I<sub>2</sub>].KI (C<sub>99</sub>H<sub>99</sub>N<sub>17</sub>O<sub>10</sub>I<sub>3</sub>K<sub>1</sub>Fe<sub>3</sub>U<sub>2</sub>, MW=2750.4) Calculated C 43.23, H 3.63 and N 8.66; found C 42.93, H 4.02 and N 8.46. <sup>1</sup>H NMR (400 MHz, Pyridine, 298 K):  $\delta$  = 53.62 (s, 3H), 40.36 (s, 3H), 5.53-0.63 (m, 29H), -3.50 (s, 2H), 13.46 (s, 3H), -17.16 (s, 2H), -20.47 (s, 2H).

#### Synthesis of [U(trensal)(py)]I, 9.

A bright orange solution of  $[UI_4(dioxane)_{1.8}]$  (30.0 mg, 0.033 mmol, 1 eq) in pyridine (1 mL) was added to a suspension of K<sub>3</sub>trensal (THF)<sub>0.5</sub> (21.3 mg, 0.033 mmol, 1 eq) in pyridine (0.5 mL) and was stirred for 2 hours. Residual solid (KI) was removed by centrifugation and resulting orange solution was layered with hexane (2 mL). Slow diffusion of hexane yielded [U(trensal)(py)]I.KI<sub>0.1</sub> as orange solid (0.02 mmol, 72%) Elemental analysis calcd (%) for [U(trensal)(py)]I.KI<sub>0.1</sub> (C<sub>32</sub>H<sub>32</sub>N<sub>5</sub>O<sub>3</sub>I<sub>1.1</sub>K<sub>0.1</sub>U, MW=916.17) Calculated C 41.95, H 3.52 and N 7.64; found C 41.85, H 3.31 and N 7.26. <sup>1</sup>H NMR (400 MHz, C<sub>5</sub>D<sub>5</sub>N, 298 K):  $\delta$  = 41.26 (s, 3H), 16.30 (s, 3H), 12.39 (s, 3H), 10.64 (s, 3H), 10.35 (s, 3H), -6.83 (s, 6H), -18.82 (s, 6H). Orange single crystals of **9.**0.5py suitable for X-ray diffraction were obtained after two weeks by slow diffusion of hexane into pyridine solution of **9**. Complex **9** was shown to undergo hydrolysis reaction on the addition of trace amounts of  $H_2O$  to a pyridine solution of **9**. Crystals of complex **10** were isolated and characterized.

Synthesis of [U(trensal- $\mu$ O)- $\mu$ O-U(EthylamineSaldien)]I 10.



A bright orange solution of [UI<sub>4</sub>(dioxane)<sub>1.8</sub>] (124.7 mg, 0.138 mmol, 1 eq) in pyridine (1 mL) was added to a suspension of K<sub>3</sub>trensal(THF)<sub>0.4</sub> (82.7 mg, 0. 138 mmol, 1 eq) in pyridine (0.5 mL) and was stirred for 30 minutes. Then 0.552 ml of 0.5 M H<sub>2</sub>0 solution in pyridine was added and reaction mixture was left stirring overnight. Residual solid (KI) was removed by centrifugation and resulting orange solution was layered with toluene (2 mL). Slow diffusion of toluene yielded [U(trensal- $\mu$ O)-( $\mu$ O)-U(ethylamineSaldien)]I as dark red crystalline solid (0.05 mmol, 50 %). Elemental analysis calcd (%) [U(trensal- $\mu$ O)- $\mu$ O-U(ethylamineSaldien)]I.Py<sub>1</sub>Tol<sub>1</sub> (C<sub>59</sub>H<sub>64</sub>N<sub>8</sub>O<sub>6</sub>I<sub>1</sub>U<sub>2</sub>, MW=1598.1) Calculated C 44.34, H 4.04 and N 7.89; found C 44.36, H 4.21 and N 7.82. <sup>1</sup>H NMR (400 MHz, C<sub>5</sub>D<sub>5</sub>N, 298 K):  $\delta$  = 87.77 (s, 1H), 85.45 (s, 1H), 56.67 (s, 1H), 52.64 (s, 1H), 51.43 (s, 1H), 48.59 (s, 1H), 47.48 (s, 1H), 45.08 (s, 1H), 34.23 (s, 1H), 31.84 (s, 1H), 28.82 (s, 1H), 27.03 (s, 1H), 26.87 (s, 1H), 25.53 (s, 1H), 25.10 (s, 1H), 21.34 (s, 1H), 18.05 (s, 1H), 13.69 (s, 1H), 9.46 (s, 1H), 7.37 (s, 2H), 1.66(s, 1H), 0.41 (s, 2H), 0.18 (s, 1H), -2.05 (s, 1H), -4.29 (s, 1H), -5.65 (s, 1H), -10.29 (s, 1H), -10.87 (s, 1H), -12.32 (s, 1H), -13.00 (s, 1H), -13.36 (s, 1H), -14.63 (s, 1H), -15.00 (s, 1H), -17.93 (s, 1H), -19.63 (s, 1H), -21.22 (s, 1H), -27.17 (s, 1H), -37.09 (s, 1H), -38.37 (s, 1H), -42.05 (s, 1H), -43.98 (s, 1H), -47.18 (s, 1H), -49.14 (s, 1H), -50.41 (s, 1H), -51.14 (s, 1H), -53.45 (s, 1H), -54.50 (s, 1H), -56.32 (s, 1H), -84.22z (s, 1H) (Fig. S18). Orange single crystals of **10** suitable for X-ray diffraction were obtained after two weeks by slow diffusion of toluene into pyridine solution of **10** (Fig. 31).

#### Reaction of 2 with Cp<sup>\*</sup><sub>2</sub>Co.

A bright orange solution of  $[UO_2(Htrensal)]$  (10.0 mg, 0.01 mmol, 1 eq) in pyridine (1 mL) was added to a pyridine solution (0.5 mL) of  $Cp_2^*Co$  (4.5 mg, 0.01 mmol, 1 eq) and stirred for 30 minutes. The <sup>1</sup>H NMR spectrum of the reaction mixture indicated partial disproportionation (Appendix 1: Fig. S2).

#### Reaction of 3 with PyHCl.

A pyridine (0.3 mL) solution of PyHCl (3.0 mg, 0.026 mmol, 1 eq.) was slowly added to a blue pyridine solution (1.5 mL) of **3** (21.3 mg, 0.026 mmol, 1 eq.) prepared *in situ* resulting in a khaki solution. The proton <sup>1</sup>H NMR spectrum of the solution indicated partial disproportionation (Fig. 7, middle). The resulting solution was stirred for 8 hours and a second equivalent of PyHCl in pyridine solution (0.3 mL) was added to the reaction mixture. The <sup>1</sup>H NMR spectrum of the resulting orange solution indicated full disproportionation (Fig. 36, top).

#### Reaction of 4 with PyHCl.

A pyridine (0.3 mL) solution of PyHCl (3.0 mg, 0.026 mmol, 1 eq.) was slowly added to a green pyridine solution (1.5 mL) of 4 (40.8 mg, 0.026 mmol, 1 eq.) prepared *in situ* resulting in a khaki solution. The <sup>1</sup>H NMR spectrum of the solution indicated the presence of <sup>1</sup>H NMR silent species (Fig. S5 middle). The solution was stirred for 8 hours and a second equivalent of PyHCl in pyridine solution (0.3 mL) was added to the reaction mixture. The <sup>1</sup>H NMR spectrum of the resulting orange solution indicated full disproportionation after 3 days (Appendix 1: Fig. S5 top).

#### Reaction of 6 with PyHCl.

A colourless pyridine (0.3 mL) solution of PyHCl (1.6 mg, 0.014 mmol, 1 eq.) was slowly added to a purple pyridine solution (1.5 mL) of **6** (14.3 mg, 0.014 mmol, 1 eq.) prepared *in situ*. The <sup>1</sup>H NMR of the resulting solution indicated partial disproportionation. The resulting solution was stirred for 2 hours and 4 additional equivalents of PyHCl in pyridine solution (0.3 mL) were added stepwise to the reaction mixture resulting. The <sup>1</sup>H NMR spectrum of the resulting orange solution indicated full disproportionation (Fig. 36 (d)).

#### Reaction of 7 with PyHCl.

A colourless pyridine (0.3 mL) solution of PyHCI (1.0 mg, 0.0082 mmol, 1 eq.) was slowly added to a purple pyridine solution (1.5 mL) of **7** (16.5 mg, 0.0082 mmol, 1 eq.) prepared *in situ*. The <sup>1</sup>H NMR of the resulting solution indicated partial disproportionation (Appendix 1: Fig. S12). The resulting solution was stirred for 2 hours and 3 additional equivalents of PyHCl in pyridine solution (0.3 mL) were added stepwise to the reaction mixture. The <sup>1</sup>H NMR spectrum of the resulting orange solution indicated full disproportionation.

#### Reaction of 8 with PyHCl.

A colourless pyridine (0.3 mL) solution of PyHCI (0.5 mg, 0.0044 mmol, 1 eq.) was slowly added to a purple pyridine solution (1.0 mL) of **8** (12.0 mg, 0.0044 mmol, 1 eq.) prepared *in situ*. The <sup>1</sup>H NMR spectrum of this solution indicated partial disproportionation (Appendix 1: Fig. S8). The resulting solution was stirred for 2 hours and 4 additional equivalents of PyHCl in pyridine solution (0.3 mL) were added stepwise to the reaction mixture. The <sup>1</sup>H NMR spectrum of the resulting orange solution indicated full disproportionation.

#### Reaction of 3 with FeCl<sub>3.</sub>

An orange pyridine (0.3 mL) solution of FeCl<sub>3</sub> (1.5 mg, 0.009 mmol, 1 eq.) was slowly added to a blue pyridine solution (0.5 mL) of 3 prepared *in situ* (7.4 mg, 0.009 mmol, 1 eq.) resulting in a dark orange solution. The <sup>1</sup>H NMR spectrum of this solution showed the formation of 5 (Appendix 1: Fig. S14). The solution was stirred for 30 minutes, filtered and layered with hexane (1 mL). A few red single crystals of 5 suitable for X-ray diffraction were obtained after three weeks.

#### Reaction of 6 with [Fe(tpa)Cl<sub>3</sub>].

A purple solution of 6 (10.0 mg, 0.008 mmol, 1 eq.) in pyridine (0.5 mL) was added to an orange solution of [Fe(tpa)Cl<sub>3</sub>] prepared *in situ* from FeCl<sub>3</sub> and tpa (3.8 mg, 0.008 mmol, 1 eq) in pyridine (0.3 mL). The reaction mixture was stirred overnight, then centrifuged to remove KCl. The <sup>1</sup>H NMR spectrum of the reaction mixture indicated that a redox reaction had occurred (Appendix 1: Fig. S15). A few orange single crystals of [Fe(tpa)Cl<sub>2</sub>] suitable for X-ray diffraction were obtained after two weeks by slow diffusion of hexane (1 mL) into the resulting pyridine solution confirming that the iron was reduced.

#### Synthesis of [Fe(tdmba)].

A pyridine (1 mL) solution of FeCl<sub>3</sub> (24.0 mg 0.146 mmol, 1 eq) was added to a stirred solution of K<sub>3</sub>tdmba (82.0 mg, 0.146 mmol, 1 eq.) in pyridine (1 mL) and was stirred for 1 hour. The resulting suspension was evaporated, the residue was dissolved in THF, KI was removed by filtration and the solution was layered with hexane (1 mL). [Fe(tdmba)].py was obtained as a dark brown solid after 6 days (66 mg, 0.121 mmol, 83%). Elemental analysis calcd (%) for [Fe(tdmba)].py ( $C_{32}H_{35}N_2O_3Fe$ , MW=551.4) C 69.71, H 6.40 and N 5.08; found C 69.96, H 6.14 and N 5.25.

#### Reaction of 6 with [Fe(tdmba)].

A purple solution of 6 (10.0 mg, 0.008 mmol, 1 eq.) in pyridine (0.5 mL) was added to a prepared *in situ* dark orange solution of [Fe(tdmba)] (3.8 mg, 0.008 mmol, 1 eq) in pyridine (0.3 mL). The reaction mixture was left stirring overnight. The <sup>1</sup>H NMR spectrum of the resulting solution indicates that no reaction occurs (Fig. 39).

#### Reaction of 3 with [Fe(tdmba)].

A blue solution of 3 (8.0 mg, 0.010 mmol, 1 eq.) in pyridine (0.5 mL) was added to a prepared *in situ* dark orange solution of [Fe(tdmba)] (4.7 mg, 0.010 mmol, 1 eq) in pyridine (0.3 mL). The reaction mixture was left stirring overnight, then centrifuged to remove KI. The <sup>1</sup>H NMR spectrum of the resulting solution shows that redox reaction has occurred between uranyl(V) and the Fe(III) complexes affording uranyl(VI) and Fe(II) complexes (Appendix 1: Fig. S16).

#### References

[1] P. L. Arnold, J. B. Love, D. Patel, *Coord. Chem. Rev.* **2009**, *253*, 1973–1978.

[2] L. S. Natrajan, A. N. Swinburne, M. B. Andrews, S. Randall, S. L. Heath, *Coordination Chemistry Reviews* **2014**, *266–267*, 171–193.

[3] H. Steele, R. J. Taylor, *Inorganic Chemistry* **2007**, *46*, 6311–6318.

[4] 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.

[5] E. S. Ilton, A. Haiduc, C. L. Cahill, A. R. Felmy, *Inorg. Chem.* **2005**, *44*, 2986–2988.

[6] K. Yuan, E. S. Ilton, M. R. Antonio, Z. Li, P. J. Cook, U. Becker, *Environmental Science & Tech*nology **2015**, *49*, 6206–6213.

[7] 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.

[8] F. N. Skomurski, E. S. Ilton, M. H. Engelhard, B. W. Arey, K. M. Rosso, *Geochimica et Cosmochimica Acta* **2011**, *75*, 7277–7290.

[9] I. Pidchenko, K. O. Kvashnina, T. Yokosawa, N. Finck, S. Bahl, D. Schild, R. Polly, E. Bohnert, A. Rossberg, J. Göttlicher, et al., *Environ. Sci. Technol.* **2017**, *51*, 2217–2225.

[10] E. S. Ilton, J. S. L. Pacheco, J. R. Bargar, Z. Shi, J. Liu, L. Kovarik, M. H. Engelhard, A. R. Felmy, *Environmental Science & Technology* **2012**, *46*, 9428–9436.

[11] H. E. Roberts, K. Morris, G. T. W. Law, J. F. W. Mosselmans, P. Bots, K. Kvashnina, S. Shaw, *Environ. Sci. Technol. Lett.* **2017**, *4*, 421–426.

[12] L. R. Morss, N. Edelstein, J. Fuger, *The Chemistry of the Actinide and Transactinide Elements* (*3rd Ed., Volumes 1-5*), Springer Science & Business Media, **2007**.

[13] N. N. Krot, M. S. Grigoriev, Russian Chemical Reviews 2004, 73, 89–100.

[14] M. Sundararajan, A. J. Campbell, I. H. Hillier, *The Journal of Physical Chemistry A* **2008**, *112*, 4451–4457.

- [15] V. Mougel, B. Biswas, J. Pecaut, M. Mazzanti, *Chem. Commun.* **2010**, *46*, 8648–8650.
- [16] M. B. Jones, A. J. Gaunt, Chem. Rev. 2013, 113, 1137–1198.
- [17] V. Mougel, P. Horeglad, G. Nocton, J. Pecaut, M. Mazzanti, *Chem.-Eur. J.* 2010, *16*, 14365–14377.
- [18] L. Chatelain, V. Mougel, J. Pecaut, M. Mazzanti, *Chem. Sci.* **2012**, *3*, 1075–1079.
- [19] G. Nocton, P. Horeglad, J. Pecaut, M. Mazzanti, J. Am. Chem. Soc. 2008, 130, 16633–16645.
- [20] F. Burdet, J. Pecaut, M. Mazzanti, J. Am. Chem. Soc. 2006, 128, 16512–16513.
- [21] V. Mougel, J. Pecaut, M. Mazzanti, *Chem. Commun.* **2012**, *48*, 868–870.
- [22] P. L. Arnold, N. A. Potter (née Jones), N. Magnani, C. Apostolidis, J.-C. Griveau, E. Colineau,

A. Morgenstern, R. Caciuffo, J. B. Love, Inorg. Chem. 2010, 49, 5341–5343.

- [23] J. L. Brown, G. Wu, T. W. Hayton, J. Am. Chem. Soc. 2010, 132, 7248-+.
- [24] D. D. Schnaars, G. Wu, T. W. Hayton, Inorg. Chem. 2011, 50, 4695–4697.
- [25] T. W. Hayton, G. Wu, Inorg. Chem. 2009, 48, 3065–3072.
- [26] D. D. Schnaars, G. Wu, T. W. Hayton, J. Am. Chem. Soc. 2009, 131, 17532–17533.

[27] J. R. Pankhurst, N. L. Bell, M. Zegke, L. N. Platts, C. A. Lamfsus, L. Maron, L. S. Natrajan, S.

- Sproules, P. L. Arnold, J. B. Love, Chem. Sci. 2017, 8, 108–116.
- [28] N. L. Bell, B. Shaw, P. L. Arnold, J. B. Love, J. Am. Chem. Soc. 2018, 140, 3378–3384.

[29] J. J. Kiernicki, M. Zeller, S. C. Bart, *Angewandte Chemie International Edition* **2017**, *56*, 1097–1100.

- [30] L. Natrajan, F. Burdet, J. Pecaut, M. Mazzanti, J. Am. Chem. Soc. 2006, 128, 7152–7153.
- [31] J.-C. Berthet, G. Siffredi, P. Thuéry, M. Ephritikhine, *Dalton Transactions* **2009**, *0*, 3478–3494.
- [32] K. Takao, S. Tsushima, S. Takao, A. C. Scheinost, G. Bernhard, Y. Ikeda, C. Hennig, *Inorg. Chem.***2009**, *48*, 9602–9604.
- [33] P. Horeglad, G. Nocton, Y. Filinchuk, J. Pécaut, M. Mazzanti, *Chemical Communications* **2009**, *0*, 1843–1845.

[34] 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] T. W. Hayton, G. Wu, J. Am. Chem. Soc. 2008, 130, 2005–2014.

[36] S. Fortier, G. Wu, T. W. Hayton, *Inorg. Chem.* **2008**, *47*, 4752–4761.

[37] P. L. Arnold, B. E. Cowie, M. Suvova, M. Zegke, N. Magnani, E. Colineau, J.-C. Griveau, R. Caciuffo, J. B. Love, *Angewandte Chemie International Edition* **2017**, *56*, 10775–10779.

[38] P. L. Arnold, E. Hollis, G. S. Nichol, J. B. Love, J.-C. Griveau, R. Caciuffo, N. Magnani, L. Maron,
L. Castro, A. Yahia, et al., *J. Am. Chem. Soc.* 2013, *135*, 3841–3854.

[39] P. L. Arnold, A.-F. Pecharman, E. Hollis, A. Yahia, L. Maron, S. Parsons, J. B. Love, *Nat. Chem.* **2010**, *2*, 1056–1061.

[40] P. L. Arnold, A.-F. Pecharman, R. M. Lord, G. M. Jones, E. Hollis, G. S. Nichol, L. Maron, J. Fang,
T. Davin, J. B. Love, *Inorg. Chem.* 2015, *54*, 3702–3710.

[41] P. L. Arnold, M. S. Dutkiewicz, M. Zegke, O. Walter, C. Apostolidis, E. Hollis, A.-F. Pécharman, N. Magnani, J.-C. Griveau, E. Colineau, et al., *Angew. Chem. Int. Ed.* **2016**, *55*, 12797–12801.

[42] V. Mougel, L. Chatelain, J. Pécaut, R. Caciuffo, E. Colineau, J.-C. Griveau, M. Mazzanti, *Nat Chem* **2012**, *4*, 1011–1017.

[43] L. Chatelain, J. P. S. Walsh, J. Pecaut, F. Tuna, M. Mazzanti, *Angew. Chem.-Int. Edit.* 2014, 53, 13434–13438.

[44] P. L. Arnold, D. Patel, C. Wilson, J. B. Love, *Nature* **2008**, *451*, 315-U3.

[45] L. Chatelain, F. Tuna, J. Pecaut, M. Mazzanti, *Dalton Trans.* **2017**, *46*, 5498–5502.

[46] L. Chatelain, F. Tuna, J. Pecaut, M. Mazzanti, *Chem. Commun.* **2015**, *51*, 11309–11312.

[47] L. Chatelain, J. Pécaut, F. Tuna, M. Mazzanti, *Chem. Eur. J.* **2015**, *21*, 18038–18042.

[48] V. Mougel, L. Chatelain, J. Hermle, R. Caciuffo, E. Colineau, F. Tuna, N. Magnani, A. de Geyer,
J. Pecaut, M. Mazzanti, *Angew. Chem.-Int. Edit.* 2014, *53*, 819–823.

[49] V. Mougel, P. Horeglad, G. Nocton, J. Pecaut, M. Mazzanti, *Angew. Chem.-Int. Edit.* 2009, *48*, 8477–8480.

[50] C. Camp, L. Chatelain, V. Mougel, J. Pécaut, M. Mazzanti, *Inorg. Chem.* **2015**, *54*, 5774–5783.

[51] A. Ikeda, C. Hennig, S. Tsushima, K. Takao, Y. Ikeda, A. C. Scheinost, G. Bernhard, *Inorg. Chem.***2007**, *46*, 4212–4219.

[52] B. D. Stewart, C. Girardot, N. Spycher, R. K. Sani, B. M. Peyton, *Environ. Sci. Technol.* 2013, 47, 364–371.

- [53] K. Takao, M. Kato, S. Takao, A. Nagasawa, G. Bernhard, C. Hennig, Y. Ikeda, *Inorganic Chemistry* **2010**, *49*, 2349–2359.
- [54] M. J. Monreal, R. K. Thomson, T. Cantat, N. E. Travia, B. L. Scott, J. L. Kiplinger, *Organometallics* **2011**, *30*, 2031–2038.
- [55] S. Mandal, D. K. Seth, P. Gupta, *Polyhedron* **2012**, *31*, 167–175.
- [56] K. Kubono, N. Hirayama, H. Kokusen, K. Yokoi, *Analytical Sciences* **2001**, *17*, 913–914.

# Chapter 3: Synthesis and Characterization of a Water Stable Uranyl(V) Complex

# Chapter 3: Synthesis and Characterization of a Water Stable Uranyl(V) Complex

# **3.1 Introduction**

In recent years an increasing number of molecular complexes containing actinides in rare and unstable oxidation states have been isolated by using appropriate supporting ligands,<sup>1</sup> but ligands capable of stabilizing U(V) in water remain an unmet target. Uranyl(V) (UO<sub>2</sub><sup>+</sup>) is reported to have a very limited range of stability in aqueous solution where it disproportionates to the more stable uranyl(VI) and uranium(IV) aqua species.<sup>2</sup> However, in the last decade the importance of uranyl(V) species in aqueous uranium chemistry associated to environmental, geologic and nuclear technology applications has become increasingly more evident.<sup>1e, 3</sup> Notably, there has been an increasing number of reports documenting the occurrence of U(V) during the mineral mediated and microbial reduction of soluble uranyl(VI) species to insoluble U(IV) ones.<sup>3c, 3d, 4</sup> Despite the importance of these processes for the removal from the groundwater of uranium, occurring from mining or disposal of radioactive waste, the role of U(V) remains unclear due the low stability of this species in aqueous media and the lack of appropriate synthetic models.

So far, studies of aqueous uranyl(V) chemistry are limited to the aqua ion at low pH (2-4) where disproportionation is slow<sup>5</sup> and to the carbonate complex  $[UO_2(CO_3)_3]^{4-6}$  produced by electrochemical reduction of the uranyl(VI) analogue in concentrated carbonate solutions that were stable in a narrow pH range (11.7-12) over a period of at least two hours, but never isolated.

The first example of a uranyl(V) complex that could be reproducibly isolated was prepared in nonaqueous media more than ten years ago.<sup>1f, 7</sup> Driven by this report, the chemistry of uranyl(V) in nonprotic media has experienced a significant expansion.<sup>1e, 3b, 8</sup> Monometallic and polymetallic complexes of uranyl(V) that are stable in organic solvents have been isolated using bulky polydentate supporting ligands. Several of these complexes have shown interesting magnetic properties and reactivity, but none of these complexes is stable in water solution.<sup>3, 9</sup> Hence, in spite of the significant development of uranyl(V) chemistry in the last decade, very little is still known about the chemistry of this species in water. The isolation of a U(V) complex that is stable in water, at environmentally relevant pH, has been a long sought-after goal because it would provide a valuable tool for the study

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of stability and reactivity of this species in environmental media, but the low charge of the uranyl(V) cation and its tendency to disproportionate renders the formation of stable complexes difficult.

Here we report the synthesis in anaerobic organic solution and the characterisation both in organic and water solution of a uranyl(V) complex that shows high stability in anaerobic water. Previous studies in organic solution indicate that pentadentate O,N donor Schiff base ligands<sup>8e</sup> prevent disproportionation of uranyl(V) in organic solution, through geometric and electronic effects, forming stable complexes, but releases the uranyl(V) cation in water solution.

The aminocarboxylate ligand dpaea<sup>2-</sup> (dpaeaH<sub>2</sub>=bis(pyridyl-6-methyl-2-carboxylate)-ethylamine) combining the pentadentate binding mode and the ability to form stable complexes with metal cations in water,<sup>10</sup> is revealed to be perfectly suited to stabilize the uranyl(V) cation in anaerobic water in the pH range 7-10.

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Author contributions: R.F. carried out all synthetic experiments. R.S. performed the X-ray single crystal structure analyses. A.-S.C. has assisted with the H<sub>2</sub>dpaea ligand synthesis. R.F and M.M. analyzed the data and wrote the manuscript. M.M. originated the central idea, coordinated the work and analyzed the experimental data

# 3.2 Results and discussion

The uranyl(VI) complex [UO<sub>2</sub>(dpaea)] (**1**) was prepared from the reaction of UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>6</sub> with H<sub>2</sub>dpaea in methanol in the presence of a base. The uranyl(V) complexes [UO<sub>2</sub>(dpaea)]X, **2**, (X= CoCp<sub>2</sub><sup>\*+</sup>) and **3**, (X= K(2.2.2.cryptand) were prepared in pyridine solution in 68-79% yield, both by reduction of the uranyl(VI) analogue **1** and by the reaction of the uranyl(V) iodide precursor  $[(U^{V}O_{2}Py_{5})(KI_{2}Py_{2})]_{n}^{1f}$  with K<sub>2</sub>dpaea (Scheme 12) under argon. Single crystals of the uranyl(VI) complexe [UO<sub>2</sub>(dpaea)(D<sub>2</sub>O)] (**4**) were obtained by exposing a solution of **3** in deuterated water to air.



Scheme 12. Synthesis of 2, 3 and 4.

Complexes **2** and **3** could not be directly synthesized in water solution due to the extreme instability of the U(V) precursor in water and to the extreme low solubility of the U(VI) complex in water. The solid-state structures of the complexes **1**, **2**, **3** and **4** were determined by X-ray diffraction studies (Figure 42 and Appendix 2: Fig. S22-S25). The molecular structure of **1** shows the presence of a ura-nium(VI) cation heptacoordinated, with a slightly distorted pentagonal bipyramid geometry, by the three nitrogen and two oxygen atoms of the dianionic pentadentate ligand dpaea<sup>2-</sup> in the equatorial plane and by two oxo groups in axial position with values of the U=O bond distances of 1.75(3) Å.



**Figure 42.** Ellipsoid plot at 50% probability of complex [UO<sub>2</sub>(dpaea)], **1**, [UO<sub>2</sub>(dpaea)(D<sub>2</sub>O)], **4** and of the anion [UO<sub>2</sub>(dpaea)]<sup>-</sup> in **3** (co-crystallised pyridine and water molecule along with hydrogen atoms were omitted for clarity, C are represented in grey, O in red, N in blue and U in green).

The arrangement of the ligand is perfectly planar for the complex **1**, while the coordination of water in **4** results in a slight deviation from planarity (mean deviation=0.0894 Å). In the structure of complex **4**, the U(VI) is eight-coordinated by the dpaea<sup>2-</sup> ligand and one water molecule in the equatorial plane and by two oxo groups in axial position with a mean value of the U=O bond distances of 1.778(2) Å similar to those found in **1**. The U-O bond distance of the bound water molecule is longer (2.572(4) Å) than what found in 7-coordinate uranyl(VI) Schiff base complexes (2.430(5) Å).<sup>11</sup> Interestingly, the O=U=O bond in **4** deviates significantly from the usually linear arrangement (O1-U1-O2=170.72(2)°) of the UO<sub>2</sub><sup>2+</sup> group probably due to steric repulsion.<sup>12</sup> This deviation is somewhat related to the water binding since a larger angle is found in **1** (O1-U1-O1\*=176.9(7)°).

The molecular structures of **2** (Appendix 2: Fig. S24) and **3** (Figure 42 and Appendix 2: Fig. S25) show the presence of ion pairs and only differ in the nature of the counterion  $([CoCp_2^*]^+$  in **2** and  $[K(2.2.2.cryptand)]^+)$  in **3**. The structure of the  $[UO_2(dpaea)]^-$  anion is very similar in **2** and **3** and shows the presence of a uranium(V) cation heptacoordinated, with a pentagonal bipyramidal geometry, by two trans oxo groups and by the five coplanar O2N3 donor atoms of the dpaea<sup>2-</sup> ligand (with a mean deviation of 0.0304 Å). Thus, the dpaea<sup>2-</sup> ligand reveals itself to be perfectly adapted to tightly bind the uranyl(V) cation and therefore to stabilize this species in protic solvents.<sup>13</sup> The O=U=O angle is 176.98° and 176.06° for **2** and **3** respectively. The U=O bond distances in **2** and **3** (1.84(1) Å) are significantly longer compared to **1** and **4**, which is in agreement with the presence of

a reduced uranium center. These values are analogous to those reported for other crystallographically characterized heptacoordinated uranyl(V) complexes.<sup>8e</sup>

The infrared spectra of **2** and **3** as KBr pellets show strong bands at 787 cm<sup>-1</sup> and 794 cm<sup>-1</sup> respectively, which were assigned to the asymmetric  $UO_2^+$  stretching mode. These values are lower compared to the uranyl(VI) [ $UO_2$ (dpaea)] species (913 cm<sup>-1</sup>) in agreement with a weaker U-O bond due to the increased electronic repulsion between the reduced uranium center and the oxygen atom (Figure 43, Appendix 2: Fig. S14-S18). A similar difference was observed between [ $(U^VO_2Py_5)(KI_2Py_2)]_n$  (797 cm<sup>-1</sup>) and [ $U^{VI}O_2I_2Py_3$ ] (927 cm<sup>-1</sup>). <sup>1f</sup>



**Figure 43.** IR Spectra in Nujol mull of the complexes [CoCp<sub>2</sub><sup>\*</sup>][UO<sub>2</sub>(dpaea)] (**2**) and [UO<sub>2</sub>(dpaea)] (**1**).

Both uranyl(V) complexes were shown, by <sup>1</sup>H NMR spectroscopy, to be stable in non-protic solvents (pyridine, acetonitrile and DMSO) up to 4 months (Appendix 2: Fig. S3 & S8). On addition of 1 eq PyHOTf to **3** in DMSO, an immediate disproportionation reaction was observed as indicated by the complete disappearance of the <sup>1</sup>H NMR signals assigned to **3** and the appearance of the signals assigned to the U(IV) complex [U(dpaea)<sub>2</sub>], **5** and H<sub>2</sub>O (Scheme 13; Figure 44).





Scheme 13. Proposed disproportionation equation for the reaction of 3 with 1 eq. of PyOHTf.

90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90

**Figure 44.** <sup>1</sup>H NMR spectrum (400 MHz,  $(CD_3)_2SO$ , 298 K) of  $[K(2.2.2.cryptand)][UO_2(dpaea)]$  (bottom), immediately after the addition of 1 eq. of PyHOTf (middle) and 3 days after the addition of 1 eq. of PyHOTf (top) (*Inset:* zoom in on the 2.1 – 4.0 ppm region of the stacked spectra, showing the appearance of the H<sub>2</sub>O peak as a product of disproportionation).

Single crystals of the poorly soluble  $[UO_2(dpaea)]$  were also isolated from the disproportionation mixture and characterised by XRD. The complex **5** was independently prepared from the reaction of  $UI_4$  and 2 equiv. of K<sub>2</sub>dpaea and crystallographically characterized (Figure 45). These results indicated that the monomeric uranyl (V) complex undergoes disproportionation upon protonation of the uranyl oxo groups as suggested by previous computational studies.<sup>14</sup>



**Figure 45.** Ellipsoid plot at 50% probability of [U(dpaea)<sub>2</sub>] complex 5 (co-crystallised pyridine molecule and H were omitted for clarity, C are represented in grey, O in red, N in blue and U in green).

However, once isolated the complexes **2** and **3** can be dissolved in water affording yellow and pink solutions, respectively, of uranyl(V) complexes. These complexes are stable, with respect to ligand dissociation and disproportionation, as indicated by <sup>1</sup>H NMR studies in D<sub>2</sub>O (Appendix 2: Fig. S4-S7). Notably, the <sup>1</sup>H NMR spectrum of **2** and **3** in 1-15 mM D<sub>2</sub>O solutions shows after dissolution the presence of only one set of 7 signals with chemical shifts similar to those found in C<sub>5</sub>D<sub>5</sub>N solution, suggesting the presence of analogous rigid C<sub>2</sub> symmetric species in both solvents. The value of the pH measured for water solutions of **3** at various concentrations (1-15 mM) ranges from 9.2 to 10. These values indicate the presence of minor amounts of protonated species, with degrees of protonation around 1-5%. <sup>1</sup>H NMR studies of 7-15 mM D<sub>2</sub>O solutions of **3** over time indicate that the complex is stable in these conditions up to two weeks. After two weeks the amount of complex in solution slowly decreased with the half-life increasing with decreasing concentration as indicated by quantitative <sup>1</sup>H NMR (Appendix 2: Fig. S9-10). After 5 weeks and up to 3 months, 50% of **2** and **3** were still present in D<sub>2</sub>O solution (Figure 46).



**Figure 46.** <sup>1</sup>H NMR spectra (400 MHz, D<sub>2</sub>O, pH = 9.8, 298 K) of 7 mM (left) and 15 mM (right) solution of [K(2.2.2.cryptand)][UO<sub>2</sub>(dpaea)] recorded at different times after dissolution in D<sub>2</sub>O indicating slow partial decomposition of the complex in D<sub>2</sub>O.

In view of the high-water stability of complex **3** at pH 10 we also explored the stability at lower pH values. The <sup>1</sup>H NMR spectrum of a 16 mM D<sub>2</sub>O solution of **3** at pH =7 (*adjusted with DCl*) also showed the presence of a fully stable uranyl(V) complex that remained unchanged at least for 3 days. Small amounts of disproportionation products ([U(dpaea)<sub>2</sub>]) start to appear after 5 days (Appendix 2: Fig. S11-S12). The <sup>1</sup>H NMR spectrum of a 20 mM D<sub>2</sub>O solution of **3** at pH=6 showed the signals assigned to the [U(dpaea)<sub>2</sub>] complex immediately after pH adjustement with DCl. Quantitative integration of the <sup>1</sup>H NMR signals of complex **3** indicated that more than 80 % of the complex **3** had undergone disproportionation at pH=6 after 2 days (Figure 47).



**Figure 47.** <sup>1</sup>H NMR spectrum (400 MHz, D<sub>2</sub>O, 20 mmol, pH=6, 298 K) [K(2.2.2.cryptand)][UO<sub>2</sub>(dpaea)] 3 before the addition of DCI (bottom), immediately after the addition of DCI to reach a pH=6 (almost 50% of the 3 disproportionated) (middle) and 2 days after the addition of DCI (almost 80% of the 3 disproportionated) (pyridine was used as an internal standard).(*Inset:* full spectrum (200 ppm) of the top spectrum, showing [U(dpaea)<sub>2</sub>] species).

These experiments indicated that acid-induced disproportionation of the uranyl(V) dpaea complex occurs rapidly in DMSO solution in the presence of stoichiometric amounts of proton. Moreover, the  $[UO_2(dpaea)]^-$  complex is stable towards disproportionation in water solution in the pH range 10-7 for several days. Furthermore, the disproportionation rates increase rapidly at lower pH values. These results demonstrate that uranyl(V) can be stabilized by aminocarboxylate ligands in environmental conditions. Moreover, the protonation studies indicate that protonation of the uranyl(V)-oxo is most likely the first step in the disproportionation mechanism of such mononuclear complexes as suggested by DFT studies.<sup>14c</sup>

The room temperature magnetic moment of **3** was determined both in pyridine and D<sub>2</sub>O solutions at pH= 10 by <sup>1</sup>H NMR spectroscopy using the Evans method.<sup>15</sup> The measured values of 2.10 & 2.15  $\mu_{eff}$  is consistent with the presence of one 5f<sup>1</sup> uranyl(V) center and is the same in both solvents confirming the stability of **3** in water solution (Figure 48; Figure 49).

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**Figure 48**. <sup>1</sup>H NMR (400 MHz, 10 mM D<sub>2</sub>O, pH = 9.9, 298 K) of complex 3 with (bottom) and without (top) solvent capillary. Inset: zoom in on the 4.9-4.5 ppm region of the both spectra (right) and bottom spectrum (left). A magnetic moment of 2.2  $\mu_B$  was determined by the Evans method.



**Figure 49.** <sup>1</sup>H NMR (400 MHz,  $C_5D_5N$ , 298 K) of complex 3 with (bottom) and without (top) solvent capillary. Inset: zoom in on the 9.0-8.5 ppm region of the both spectra (right) and bottom spectrum (left). A magnetic moment of 2.1  $\mu_B$  was determined by the Evans method.

X-Band EPR spectra of **3** were recorded both in solid state and in D<sub>2</sub>O solution (25 mM) at 10 K. In both cases the spectra could be fitted with a rhombic set of g values:  $g_1=3.04$ ;  $g_2=1.08$ ;  $g_3<0.6$  for solid state and  $g_1=2.59$ ;  $g_2=1.21$ ;  $g_3<0.6$  for the D<sub>2</sub>O solution (Figure 50). The measured EPR data confirm the presence of uranyl(V) species in water solution.



**Figure 50.** X-band EPR spectrum of **3** recorded in solid state ( $g_1$ =3.04;  $g_2$ =1.08;  $g_3$ <0.6) (left) and 25 mM D<sub>2</sub>O solution ( $g_1$ =2.59;  $g_2$ =1.21;  $g_3$ <0.6) (right) at 10 K (v = 9.403115 GHz, P = 0.6333  $\mu$ W, amplitude modulation 5 G, frequency modulation 100 kHz). Experimental data are represented by the black line; simulation is depicted by the blue line.

Cyclic voltammetry studies of complex **3** were carried out both in pyridine and H<sub>2</sub>O solutions, but studies of 1 were prevented by its low solubility. The cyclic voltammetry data measured for 3 in pyridine solution showed the presence of two reversible redox events at  $E_{1/2}$  = -1.25 V and at  $E_{1/2}$  = -2.65 V that were assigned to the U(VI)/U(V) and U(V)/U(IV) couples respectively (Figure 51). The measured redox potential for the U(VI)/U(V) couple falls in the range (-0.93V –1.82 V) of those reported for other uranyl(V) complexes in organic media.<sup>8d, 8f, 16</sup> The voltammogram measured in 0.02 M HEPES buffered water solutions (pH=7) at a glassy carbon working electrode shows a significant shift of the U(VI)/U(V) redox potentials with the U(V)/U(VI) oxidation event found at E = -0.16 - 0.00V vs Ag/AgCl, and the U(VI)/U(V) reduction at E= - 1.56 – -1.65 V vs Ag/AgCl depending on the scan speed. These values are very similar to those previously reported for the uranyl(V)-carbonato complex ( $[UO_2(CO_3)_3]^{5-}$ ) in Na<sub>2</sub>CO<sub>3</sub> at pH=12 and a glassy carbon electrode (oxidation peak at 0- 0.25 V and reduction peak at -1.5–-1.7 V).<sup>6a, 6d</sup> The U(V)/U(IV) redox event is not observable in water solution. Similar to what was reported for the uranyl(V)-carbonate complex the U(VI)/U(V) couple is electrochemically irreversible in water solution. The different electrochemical behavior of the U(VI)/U(V) couple in water compared to pyridine, suggests that its irreversibility in water could be related to water binding and/or proton exchange reactions.



**Figure 51.** Cyclic voltammetry data recorded for 4 mM solutions of  $[K(2.2.2.cryptand)][UO_2(dpaea)]$  (**3**) in 0.1 M  $[Bu_4N][PF_6]$  pyridine solution at 100-1000K mV/s scan rate  $Cp_2Fe/Cp_2Fe^+$  corrected (left) and in aqueous HEPES solutions (pH= 7) at 10-100 mV/s scan rates vs. Ag/AgCl (right).

# **3.3 Conclusions**

We have identified a polydentate ligand that allows the stabilization of uranyl(V) in water solution in the pH range 7-10 and we have isolated and fully characterized the first uranyl(V) complex that is stable in water at neutral pH. At lower pH values the complex is protonated and readily disproportionates affording U(IV) and uranyl(VI) species. These studies indicate that uranyl (V) can be stabilized in water solution in presence of polycarboxylate ligands and that its presence in the environment is not necessarily limited to concentrated carbonate solutions. The isolation of such a stable system provides a valuable tool for investigating the mechanism of biotic and abiotic reduction of uranyl species in the environmental conditions. Future work will be directed toward isolation of novel uranyl(V) species with higher stability in water solution.

# Experimantal

#### General considerations.

All manipulations were carried out under an inert argon atmosphere using Schlenk techniques and an MBraun glovebox equipped with a purifier unit. The water and oxygen level were always kept at less than 1 ppm. The solvents were purchased from Aldrich or Cortecnet (deuterated solvents) in their anhydrous form, conditioned under argon and vacuum distilled from K/benzophenone (diisopropylether, hexane, pyridine, toluene, benzene and THF) or freeze-degassed and stored over activated 3 Å molecular sieves (C<sub>5</sub>D<sub>5</sub>N and (CD<sub>3</sub>)<sub>2</sub>SO). Depleted uranium was purchased from IBILABS, USA.

 $[(UO_2Py_5)(KI_2Py_2)]_{n}$ ,<sup>[17]</sup> UCl4<sup>[18]</sup> and UI4<sup>[19]</sup> were synthesized as previously described. UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>6</sub> was purchased from Sigma-Aldrich. Anhydrous PyHOTf and TEA (triethylamine) were purchased from Aldrich and were used without further purification. H<sub>2</sub>dpaea(HCl)<sub>3</sub> ligand was prepared according to the published procedure.<sup>[3]</sup>

Elemental analyses were performed under argon with a Thermo Scientific Flash 2000 Organic Elemental Analyzer by the EPFL elemental analyses service. <sup>1</sup>H NMR experiments were carried out using NMR tubes adapted with J. Young valves. <sup>1</sup>H NMR spectra were recorded on Bruker 400 MHz spectrometer. NMR chemical shifts are reported in ppm with solvent as internal reference. EPR spectra were recorded with a Bruker Elexsys E500 spectrometer working at 9.4 GHz frequency with an oxford ESR900 cryostat for 4-300 K operation. Simulation was performed with the Easyspin 5.1.3 program.

IR spectra were recorded with a Perkin Elmer 1600 Series FTIR spectrophotometer flushed with argon.

pH measurement was done with with Thermo Scientific Orion 3 star pH meter calibrated with pH buffers before each use.

**Caution:** Depleted uranium (primary isotope <sup>238</sup>U) is a weak  $\alpha$ -emitter (4.197 MeV) with a half-life of 4.47×10<sup>9</sup> years. Manipulations and reactions should be carried out in monitored fume hoods or in an inert atmosphere glovebox in a radiation laboratory equipped with  $\alpha$ - and  $\beta$ -counting equipment.

#### Synthetic procedures

#### Synthesis of [UO<sub>2</sub>(dpaea)] (1).

A yellow solution of  $UO_2(NO_3)_2(H_2O)_6$  (500.0 mg, 0.099 mmol, 1 eq.) in methanol (10mL) was slowly added to a stirred suspension of H<sub>2</sub>dpaea·3HCl (420.8 mg 0.990 mmol, 1 eq.) in methanol (10 mL). TEA (425 µl, 2.97 mmol, 3 eq.) was then added and the resulting suspension was stirred at reflux for 24 hours. The resulting yellow precipitate was filtered, washed with diethylether and triturated with hot methanol. The yellow solid (479.3 mg, 0.820 mmol, 83%) was collected, dried on a vacuum pump for 2 days. <sup>1</sup>H NMR (400 MHz, (CD<sub>3</sub>)<sub>2</sub>SO, 298 K):  $\delta$ =8.40 (2H, t); 8.36 (2H, d); 7.92 (2H, d); 4.23 (4H, s); 2.99 (2, q) 1.49 (3H, t) (Appendix 2: Fig. S2). Elemental analysis calcd (%) for [UO<sub>2</sub>(dpaea)] (C<sub>16</sub>H<sub>15</sub>N<sub>3</sub>O<sub>6</sub>U, MW=583.34) C 32.94, H 2.59 and N 7.20; found C 32.76, H 2.53 and N 7.07. Yellow single crystals of **1** suitable for X-ray diffraction were obtained by slow diffusion (one week) of a methanol solution of **1** into a 1 M NaOH methanolic solution of the ligand.

## Synthesis of [CoCp<sub>2</sub><sup>\*</sup>][UO<sub>2</sub>(dpaea)] (2).

A brown solution of decamethylcobaltocene (81.9 mg, 0.250 mmol, 1 eq) in pyridine (5 ml) was added to a yellow suspension of [UO<sub>2</sub>(dpaea)] (145.0 mg, 0.250 mmol, 1 eq) in pyridine (15 ml). The resulting green suspension was stirred overnight to slowly afford a dark green suspension that was filtered to unreacted starting material and then evaporated. The resulting solid was washed with hexane and recrystallized from pyridine at – 40 °C. A green crystalline solid was obtained (196.0 mg, 0.200 mmol, 79%). <sup>1</sup>H NMR (400 MHz, C<sub>5</sub>D<sub>5</sub>N, 298 K):  $\delta$ = 4.59 (2H, s); 3.51 (2H, s); 1.44 (30H, s); -0.24 (2H, d); -0.70 (2H, d); -6.85 (3H, s); -10.59 (2H, s); -15.69 (2H, s) (Fig. S3); (400 MHz, D<sub>2</sub>O, 298 K):  $\delta$  = 5.85 (2H, s); 5.51 (2H, t); 1.87 (4H, dd); 1.70 (30H, s); -6.16 (2H, s), -6.40 (3H, s), -15.36 (2H, s) (Appendix 2: Fig. S4). Elemental analysis calcd (%) for [CoCp<sub>2</sub>\*][UO<sub>2</sub>(dpaea)].py (C<sub>41</sub>H<sub>50</sub>N<sub>4</sub>O<sub>6</sub> COU, MW=991.73) C 49.66, H 5.08 and N 5.65; found C 49.73, H 5.06 and N 5.65. Green single crystals of **2** suitable for X-ray diffraction were obtained by slow diffusion (one week) of DIPE into a pyridine solution of **2** (Appendix 2: Fig. S24).

Complexes **2** could not be directly synthesized in water solution due to the low solubility of the U(VI) complex in water.

# Synthesis of [K(2.2.2.cryptand)][UO<sub>2</sub>(dpaea)] (3).

2.2.2.cryptand (31.9 mg, 0.08 mmol, 1 eq ) was added to a solution of  $[(UO_2Py_5)(KI_2Py_2)]_n$  (94.0 mg, 0.080 mmol, 1 eq) in pyridine (1 mL). The resulting orange solution was added to a stirred light-yellow solution containing K<sub>2</sub>dpaea (43.0 mg, 0.080 mmol, 1 eq.) and 2.2.2.cryptand (63.4 mg, 0.168 mmol, 2 eq) in pyridine (1 ml). The solution turned slowly to brown-blue and was stirred for 6 hours and then layered with DIPE (2.5 mL). The resulting blue solid (57 mg, 0.06 mmol, 68%) was collected and washed with cold pyridine. Blue X-ray quality crystals of **3** were obtained by slow diffusion (one week) of DIPE into a pyridine solution of **3**. <sup>1</sup>H NMR (400 MHz, C<sub>5</sub>D<sub>5</sub>N, 298 K):  $\delta$  = 4.58 (2H, s); 3.50 (2H, s); 3.46 (24H, d); -0.24 (2H, s); -0.68 (2H, s); -6.84 (3H, s); -10.56 (2H, s); -15.63 (2H, s) (Fig. S8); (400 MHz, D<sub>2</sub>O, 298 K):  $\delta$  = 5.88 (2H, d); 5.52 (2H, t); 3.68 (24H, d); 2.61 (12H, s); 1.87 (4H, dd); -6.13 (2H, s), -6.38 (3H, s), -15.31 (2H, s) (Appendix 2: Fig. S6-S7). Elemental analysis calcd (%) for [K(2.2.2.cryptand)][UO<sub>2</sub>(dpaea)] (C<sub>34</sub>H<sub>51</sub>N<sub>5</sub>O<sub>12</sub>KU, MW=998.932) C 40.88, H 5.15 and N 7.01; found C 40.66, H 5.01 and N 6.97.

The <sup>1</sup>H NMR spectra of the compound **3** in  $C_5D_5N$ ,  $CD_3CN$  and  $(CD_3)_2SO$  showed no change of the integrals of the peaks corresponding to the anion of **3** w.r.t. 2.2.2.cryptand up to 12 weeks indicating the complex **3** is fully stable in pyridine, acetonitrile and DMSO solution.

<sup>1</sup>H NMR spectra of the compound **3** were measured in D<sub>2</sub>O solutions at different concentrations ranging from 1 to 16mM. The variation of concentration is accompanied by a change in pH from 9.2 at 1mM to 10 at 15 mM. These values indicate the presence of minor amounts of protonated species, with degrees of protonation around 1-5%. In all cases the <sup>1</sup>H NMR spectra showed no change of the integrals of the peaks corresponding to the anion of **3** (with respect to pyridine as reference) for at least two weeks indicating the complex **3** is fully stable in these conditions for up to two weeks (Figure 46, Appendix 2: Fig. S9-S10).

<sup>1</sup>H NMR spectra were recorded on solutions of complex **3** in water at different pH values over time. In D<sub>2</sub>O, 15 mM, pH = 10 decomposition of 3 starts after 4 weeks. In D<sub>2</sub>O, 16 mmol, pH=7, decomposition starts after 4 days, while decomposition starts immediately in 20 mM, pH =6 and only 80% of complex is left after 2 days. The decomposition is accompanied by the crystallization of poorly soluble disproportionation products ([U(dpaea)<sub>2</sub>] was identified) (Figure S6, Fig. S11-S12).

Single crystals of the uranyl(VI) complex [UO<sub>2</sub>(dpaea)(D<sub>2</sub>O)] (**4**) were obtained by exposing a solution of **3** in deuterated water to air (Figure 42 and Appendix 2: Fig. S23).

Complex **3** could not be directly synthesized in water solution due to the extreme instability of the U(V) precursor in water.

# Synthesis of [U(dpaea)<sub>2</sub>] (5).

Suspension of K<sub>2</sub>dpaea (58.0 mg, 0.150 mmol, 2 eq.) in 1 ml of pyridine was added to an orange solution of Ul<sub>4</sub>(dioxane)<sub>1.8</sub> (67.0 mg, 0.070 mmol, 1 eq.) in pyridine (1 mL). The suspension turned slowly to brown-orange and was stirred for 12 hours, filtered and then layered with DIPE (1 mL). The resulting dark orange solid (39.0 mg, 0.045 mmol, 64%) was collected and washed with cold pyridine. Dark orange X-ray quality crystals of **5** were obtained by slow diffusion (one week) of DIPE into a pyridine solution of **5**. <sup>1</sup>H NMR (400 MHz, C<sub>5</sub>D<sub>5</sub>N, 298 K):  $\delta$  = 15.50 (2H, s); 12.75 (2H, s); 11.14 (2H, s); 10.63 (2H, s); 10.09 (2H, s); 5.35 (2H, s); 3.98 (2H, s); 1.32 (2H, s); -4.07 (6H, s); -8.86 (2H, s); -12.34 (2H, s); -15.18 (2H, s); -32.45 (2H, s); -64.88 (2H, s) (Fig. S13). Elemental analysis calcd (%) for [U(dpaea)<sub>2</sub>]Kl<sub>1.1</sub> (C<sub>32</sub>H<sub>30</sub>N<sub>6</sub>O<sub>8</sub>UK<sub>1.1</sub> l<sub>1.1</sub>, MW=1047.258) C 36.70, H 2.89 and N 8.02; found C 37.10, H 2.87 and N 7.63.

## Reaction of 3 with PyHOTf.

A bright blue solution of [K(2.2.2.cryptand)][UO<sub>2</sub>(dpaea)] (8.9 mg, 0.010 mmol, 1 eq) in DMSO (0.3 mL) was added to a DMSO solution (0.2 mL) of PyHOTf (2.0 mg, 0.010 mmol, 1 eq) and stirred for 30 minutes. <sup>1</sup>H NMR indicated disproportionation reaction and crystals of [UO<sub>2</sub>(dpaea)] were isolated and characterized by XRD.

#### References

(a) J. Su, C. J. Windorff, E. R. Batista, W. J.Evans, A. J. Gaunt, M. T. Janicke, S. A. Kozimor, B. L. Scott, D. H. Woen, P. Yang, *J. Am. Chem. Soc.* 2018, *140*, 7425-7428; (b) C. J. Windorff, G. P.Chen, J. N. Cross, W. J. Evans, F.Furche, A. J. Gaunt, M. T. Janicke, S. A. Kozimor, B. L. Scott, *J. Am. Chem. Soc.* 2017, *139*, 3970-3973; (c) G. J. P.Deblonde, M. Sturzbecher-Hoehne, P. B. Rupert, D. D. An, M. C. Illy, C. Y. Ralston, J. Brabec, W. A. de Jong, R. K. Strong, R. J. Abergel, *Nat. Chem.* 2017, *9*, 843-849; (d) H. S. La Pierre, A. Scheurer, F. W. Heinemann, W. Hieringer, K. Meyer, *Angew. Chem. Int. Ed. Engl.* 2014, *53*, 7158-7162; (e) M. B. Jones, A. J. Gaunt, *Chem. Rev.* 2013, *113*, 1137-1198; (f) L. Natrajan, F. Burdet, J. Pecaut, M. Mazzanti, *J. Am. Chem. Soc.* 2006, *128*, 7152-7153.

[2] L. R. Morss, N. M. Edelstein, J. Fuger, *The Chemistry of the Actinide and Transactinide Elements*. Springer: Dordrecht, 2006.

[3] (a) L. S. Natrajan, A. N. Swinburne, M. B. Andrews, S. Randall, S. L. Heath, *Coord. Chem. Rev.* **2014**, *266*, 171-193;

(b) P. L. Arnold, J. B. Love, D. Patel, *Coord. Chem. Rev.* 2009, *253*, 1973-1978; (c) L. J. C. Renshaw, J. C. Butchins, F. R. Livens, I. May, J. M. Charnock, Lloyd, J. R., *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) K. Yuan, E. S. Ilton, M. R. Antonio, Z. Li, P. J.Cook, U. Becker, *Environ. Sci. Technol.* 2015, *49*, 6206-6213; (f) P. C. Burns, R. J.Finch, *Am. Mineral.* 1999, *84*, 1456-1460; (g) N. L. Bell, B. Shaw, P. L. Arnold, J. B. Love, *J. Am. Chem. Soc.* 2018, *140*, 3378-3384.

[4] (a) 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; (b) 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; (c) H. E. Roberts, K. Morris, G. T. W. Law, J. F. W. Mosselmans, P. Bots, K. Kvashnina, S. Shaw, *Environ. Sci. Tech. Let.* 2017, *4*, 421-426.

[5] (a) J. Selbin, J. D. Ortego, *Chem. Rev.* **1969**, *69*, 657-671; (b) K. A. Kraus, Nelson, F. G. L. Johnson, *J. Am. Chem. Soc.* **1949**, *71*, 2510-2517; (c) A. Ekstrom, *Inorg. Chem.* **1974**, *13*, 2237-2241.

[6] (a) 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; (b) D. W. Wester, J. C. Sullivan, *Inorg. Chem.* 1980, *19*, 2838-2840; (c) K. Mizuoka, I. Grenthe, Y. Ikeda, *Inorg. Chem.* 2005, *44*, 4472-4474; (d) A. Ikeda, C. Hennig, S. Tsushima, K. Takao, Y. Ikeda, A. C. Scheinost, G. Bernhard, *Inorg. Chem.* 2007, *46*, 4212-4219.

[7] J. C. Berthet, G. Siffredi, P. Thuery, M. Ephritikhine, *Chem. Commun.* **2006**, 3184-3186.

[8] (a) P. L. Arnold, D. Patel, C. Wilson, J. B. Love, *Nature* 2008, *451*, 315-318; (b) K. Takao, S. Tsushima, S. Takao, A. C. Scheinost, G. Bernhard, Y. Ikeda, C. Hennig, *Inorg. Chem.* 2009, *48*, 9602-9604; (c) P. Horeglad, G. Nocton, Y. Filinchuk, J. Pecaut, M.Mazzanti, *Chem. Commun.* 2009, 1843-1845; (d) 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; (e) V. Mougel, J. Pecaut, M. Mazzanti, *Chem. Commun.* 2012, *48*, 868-870; (f) T. W. Hayton, G. Wu, *J. Am. Chem. Soc.* 2008, *130*, 2005-2014; (g) T. W. Hayton, G. Wu, *Inorg. Chem.* 2008, *47*, 7415-7423; (h) 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; (i) 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; (j) P. L. Arnold, A. F. Pecharman, E. Hollis, A. Yahia, L. Maron, S. Parsons, J. B. Love, *Nat. Chem.* **2010**, *2*, 1056-1061; (k) V. Mougel, P. Horeglad, G. Nocton, J. Pecaut, M. Mazzanti, *Chem. Eur. J.* **2010**, *16*, 14365-14377; (l) L. Chatelain, V. Mougel, J.Pecaut, M. Mazzanti, *Chem. Sci.* **2012**, *3*, 1075-1079; (m) V. Mougel, P. Horeglad, G. Nocton, J. Pecaut, M. Mazzanti, *Chem. Int. Ed. Engl.* **2009**, *48*, 8477-8480; (n) G. Nocton, P. Horeglad, J. Pécaut, M. Mazzanti, *J. Am. Chem. Soc.* **2008**, *130*, 16633–16645; (o) F. Burdet, J. Pecaut, M. Mazzanti, *J. Am. Chem. Soc.* **2008**, *130*, 16633–16645;

[9] (a) V. Mougel, L. Chatelain, J. Pecaut, R. Caciuffo, E. Colineau, J. C. Griveau, M. Mazzanti, , *Nat. Chem.* 2012, *4*, 1011-1017; (b) L. Chatelain, F. Tuna, J. Pecaut, M. Mazzanti, *J. Chem. Soc.-Dalton Trans.* 2017, *46*, 5498-5502; (c) L. Chatelain, J. P. S. Walsh, J. Pecaut, F. Tuna, M. Mazzanti, *Angew. Chem. Int. Ed. Engl.* 2014, *53*, 13434-13438; (d) L. Chatelain, F. Tuna, J. Pecaut, M. Mazzanti, *Chem. Commun.* 2015, *51*, 11309-11312; (e) L. Chatelain, J. Pecaut, F. Tuna, Mazzanti, M., *Chem. Eur. J.* 2015, *21*, 18038-18042; (f) V. Mougel, L. Chatelain, J. Hermle, R. Caciuffo, E. Colineau, F. Tuna, N. Magnani, A. de Geyer, J. Pecaut, M. Mazzanti, *Angew. Chem. Int. Ed. Engl.* 2014, *53*, 819-823; (g) D. D. Schnaars, G. Wu, T. W. Hayton, *J. Am. Chem. Soc.* 2009, *131*, 17532-17533; (h) T. W. Hayton, G. Wu, *Inorg. Chem.* 2009, *48*, 3065-3072; (i) J. R. Pankhurst, N. L. Bell, M. Zegke, L. N. Platts, C. A. Lamfsus, L. Maron, L. S. Natrajan, S. Sproules, P. L. Arnold, J. B. Love, *Chem. Sci.* 2017, *8*, 108-116; (j) J. J. Kiernicki, M. Zeller, S. C.Bart, *Angew. Chem. Int. Ed. Engl.* 2017, *56*, 1097-1100.

[10] (a) M. Regueiro-Figueroa, G. A. Rolla, D. Esteban-Gomez, de Blas, A.; T. Rodriguez-Blas, M. Botta, C. Platas-Iglesias, *Chem. Eur. J.* **2014**, *20*, 17300-17305; (b) A. Pellissier, Y. Bretonniere, N.Chatterton, J. Pecaut, P. Delangle, M. Mazzanti, *Inorg. Chem.* **2007**, *46*, 3714-3725.

[11] C. A. Hawkins, C. G. Bustillos, R. Copping, B. L. Scott, I. May, M. Nilsson, *Chem. Commun.* **2014**, *50*, 8670-8673.

[12] T. W. Hayton, J. Chem. Soc.-Dalton Trans. **2018**, 47, 1003-1009.

[13] (a) G. Szigethy, K. N. Raymond, *J. Am. Chem. Soc.* **2011**, *133*, 7942-7956; (b) G. Szigethy, K. N. Raymond, *Inorg. Chem.* **2010**, *49*, 6755-6765.

[14] (a) M. Sundararajan, A. J. Campbell, I. H. Hillier, *J. Phys. Chem. A* 2008, *112*, 4451-4457; (b) H.
Steele, R. J. Taylor, *Inorg. Chem.* 2007, *46*, 6311-6318; (c) R. N. Collins, K. M. Rosso, *J. Phys. Chem. A* 2017, *121*, 6603-6613.

[15] D. F. Evans, J. Am. Chem. Soc. 1959, 2003-2005.

[16] S. Y. Kim, T. Asakura, Y. Morita, Y. Ikeda, J. Alloys Compd. 2006, 408, 1291-1295.

[17] L. Natrajan, F. Burdet, J. Pecaut, M. Mazzanti, J. Am. Chem. Soc. 2006, 128, 7152–7153.

[18] M. J. Monreal, R. K. Thomson, T. Cantat, N. E. Travia, B. L. Scott, J. L. Kiplinger, *Organometallics* **2011**, *30*, 2031–2038.

[19] A. Pellissier, Y. Bretonnière, N. Chatterton, J. Pécaut, P. Delangle, M. Mazzanti, *Inorg. Chem.* **2007**, *46*, 3714–3725.
# Sub-Chapter 3a: Luminescence study of uranyl(VI) and uranyl(V) complexes of dpaea ligand

# Summary of the project

Luminescence is a highly useful spectroscopic tool to study uranium speciation. The dominant form of uranium, the uranyl(VI) cation  $U^{VI}O_2^{2^+}$ , is known for its inherent photophysical properties, originating from partially forbidden charge transfer transitions from oxo-based molecular orbitals to nonbonding f-orbitals.<sup>[1]</sup> This property of the uranyl(VI) cation was extensively studied under various conditions and in the presence of different ligands. However, the luminescence of uranyl(V) compounds is significantly less explored with only a few reported luminescent spectra for uranyl(V).<sup>[2,3]</sup> Better knowledge of photochemical properties of different uranium species can lead to a more thorough understanding of the electronic structure of uranium. In addition, luminescence is a promising technique for investigation of uranium speciation in complex systems, *e.g.* in microbial bio-reduction of U or nuclear waste processing.

Here we demonstrate that the dpaea ligand is not only effective at stabilizing U(V) species in water but also in generating luminescent complexes of uranyl(VI) and uranyl(V). This allowed their direct detection with luminescence spectroscopy, and permitted us to monitor the disproportionation reaction of the uranyl(V)-dpaea complex in water solution as a function of time.

Initially, emission and excitation spectra were measured for the solid-state uranyl(VI) [UO<sub>2</sub>(dpaea)] complex **1**.The uranyl(VI) complex shows the characteristic vibrationally resolved emission and excitation spectra due to the strong coupling of the electronic energy levels with the Raman active symmetric O=U=O stretching mode. Additionally, the excitation spectra were recorded at two emission wavelengths (540 and 502 nm) and are wavelength independent (Figure 52). Due to the extremely low solubility of the uranyl(VI)-dpaea complex, no solution luminescence spectra could be obtained.

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**Figure 52.** Normalized room-temperature luminescence spectra: emission spectrum upon excitation at  $\lambda_{ex} = 320$  nm of powdered [UO<sub>2</sub>(dpaea)] (1) (orange line); excitation spectra of powdered [UO<sub>2</sub>(dpaea)] ( $\lambda_{em} = 540$  nm, yellow line) and ( $\lambda_{em} = 502$  nm, olive line).

Further, the luminescent properties of the uranyl(V)-dpaea complex [K(2.2.2.cryptand)][UO<sub>2</sub>(dpaea)] (2) were investigated. Due to its solubility and stability in both organic (pyridine) and aqueous media, luminescence measurements were performed on samples in solution and the solid-state (Figure 53). The emission spectra of U(V) are very different from those of the uranyl(VI), being significantly shifted to lower wavelengths for all measured samples of complex 2. While solvents are known to have a quenching effect on luminescence, for solutions of 2 (both in pyridine and water), it was possible to obtain the luminescent spectra at room temperature. To the best of our knowledge, there are only two reports of uranyl(V) luminescence in aqueous media. Thus, a comparison with the previously reported examples was performed. The emission spectrum of the aqueous solution of [UO<sub>2</sub>(dpaea)]<sup>-</sup> is centered at 417 nm, which is slightly red shifted to that of the reported [U<sup>V</sup>O<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub>]<sup>5-</sup> in solution (404 and 419 nm) at low temperature, by Grossmann *et al.* <sup>[2]</sup>, and blue-shifted compared to that of uranyl(V) in aqueous perchlorate solution (440 nm).<sup>[3]</sup>



**Figure 53**. Normalized room-temperature luminescence emission spectra upon excitation at  $\lambda_{ex} =$  320 nm of powdered [K(2.2.2.cryptand)][UO<sub>2</sub>(dpaea)] (**2**) (blue line), a 5 mM solution of [K(2.2.2.cryptand)][UO<sub>2</sub>(dpaea)] water (magenta) and a 5 mM solution of [K(2.2.2.cryptand)][UO<sub>2</sub>(dpaea)] in pyridine (purple).

The stability of the 5 mM solution of uranyl(V) complex **2** in anaerobic water at pH = 10 was monitored by luminescence spectroscopy (Figure 54). The measurements were performed immediately after the dissolution of complex **2**, after 24 hours, as well as after 1 and 2 weeks. From the resulting spectra, it can be seen that immediately after dissolution, the luminescence spectrum demonstrates the presence of the uranyl(V) as the only emissive species upon an excitation at 320 nm. After 24 hours in water solution, small traces of the uranyl(VI) species **1** can be detected, which increase in intensity as a function of time. The measurements performed after 1 week showed the emission spectra of both uranyl(V) and uranyl(VI) species, while the spectrum of complex **2** after 2 weeks in water solution revealed mainly the emission corresponding to the uranyl(VI) complex **1**. At first sight, this result is contrary to previously reported (Chapter 3) high stability of complex **2** under aqueous basic (pH=10) conditions. However, the reason for this discrepancy can be attributed to highly emissive nature of the uranyl(VI) in comparison to uranyl(V) cation. Therefore, even small traces of the uranyl(VI) complex **1** would give rise to a high-intensity signal, masking the emission of complex **2.** Control experiment using the addition of 2 % of complex **1** (based on U) to a freshly prepared 5 mM basic aqueous solution (pH=10) of complex **2** yielded an identical spectrum to the one recorded after 2 weeks (orange line). However, this difference in the intensities of the emission of the U(VI) and U(V) species presents a limitation for further monitoring and analyzing the disproportionation reaction.



**Figure 54.** Normalized room-temperature luminescence emission spectra upon excitation at  $\lambda_{ex}$  = 320 nm of 5 mM solution of [K(2.2.2.cryptand)][UO<sub>2</sub>(dpaea)] (**2**) immediately after dissolution (pink line); after 24 hours (magenta); after 1 week (light pink) and after 2 weeks (orange).

In conclusion, luminescent properties of the uranyl(VI) and uranyl(V) complexes of dpaea ligand were reported. The U(V) emission was detected for the solid-state as well as for 5 mM pyridine and water solution. Additionally, the disproportionation reaction of the uranyl(V) species was monitored by recording the emission spectra as a function of time. This allowed for the detection of the first traces of the disproportionation products (< 2 %) that was not possible to observe with other techniques, such as <sup>1</sup>H NMR spectroscopy.

## References

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.

[2] K. Grossmann, T. Arnold, A. Ikeda-Ohno, R. Steudtner, G. Geipel, G. Bernhard, *Spectrochim. Acta. A. Mol. Biomol. Spectrosc.* **2009**, *72*, 449–453.

[3] R. Steudtner, T. Arnold, K. Großmann, G. Geipel, V. Brendler, *Inorg. Chem. Commun.* **2006**, *9*, 939–941.

# Sub-Chapter 3b: Uranium(V) as an intermediate in the biological reduction of U(VI) to U(IV)

# Summary of the project

As mentioned in the introduction, uranium is a ubiquitous element on Earth that can be found naturally in the surface and subsurface, but generally, in relatively low concentrations. However, the contamination of soil, sediments and groundwater, as a result of mining, ore processing, nuclear fuel manufacturing as well as DU and spent fuel storage, can increase the concentration of uranium to dangerously high levels. The prevalent form of uranium under oxic conditions is U(VI), which forms soluble complexes with various ligands in the environment and is therefore, highly mobile. The reduction of U(VI) to insoluble U(IV) in anoxic environments is one promising approach for the immobilization of this toxic and radioactive metal, that was previously shown to be catalyzed by microorganisms. On the basis of multiple studies of this biotic reduction,<sup>[1–3]</sup> the reduction of U(VI) is thought to proceeds via a one-electron transfer to form a uranyl(V) intermediate, which disproportionates to yield U(VI) and U(IV). However, the absence of the well-defined uranyl(V) species that is stable at environmentally-relevant pH, has limited the possibility to confirm the mechanism of reduction as well as to explore the possibility for further reduction of U(V) to U(IV) by a second electron transfer. The isolation of the first water-stable uranyl(V) complex, presented in this chapter, allowed our collaborators to investigate the mechanism of microbial reduction of uranyl(VI) and decouple the two-step process of the U(VI) to U(IV) reduction. The significant stability and solubility of the uranyl(V)-dpaea complex in water at pH=7, allowed for the persistence of the otherwise transient species and its detection by High Resolution X-ray Absorption Near Edge Structure (HR-XANES) spectroscopy. Additionally, the fate of uranium during this biotic reduction was monitored through time by ion exchange chromatography. The combination of HR-XANES and ion exchange chromatography, permitted not only the detection of the uranyl(V) intermediate, but also further reduction of the resulting uranyl(V) complex to solid phase U(IV). The additional advantage of the novel system was the synthetic accessibility to fully characterized uranyl(VI), uranyl(V) and uranium(IV) analogs, that allowed our collaborators to perform the bio-reduction, medium stability, solubility, speciation, optical spectroscopy and control studies, as well as an access to pure and appropriate standards for the HR-XANES measurements.

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The study demonstrated a novel mechanism of uranium reduction via two successive one-electron transfers, rather than via disproportionation of the U(V)-intermediate.

It is important to mention that during the course of the review process for the article, described in this sub-chapter, the publication identifying U(V) as a key intermediate during U(VI) reduction by metal-reducing bacteria was published.<sup>[4]</sup> The authors provided multiple lines of evidence for U(V) formation and persistence in their system, while they concluded that the resulting uranyl(V) intermediate has very limited stability and thus, disproportionates to yield U(VI) and U(IV) products. This is in contrast to the results obtained by our collaborators, demonstrating the importance of the complexing ligand in the mechanism of the biotic reduction of uranium.

Portions of this chapter are adopted from the article in submission: Margaux Molinas<sup>1</sup>, Radmila Faizova<sup>2</sup>, Ashley Brown<sup>1</sup>, Jurij Galanzew<sup>3</sup>, Bianca Schacherl<sup>3</sup>, Tonya Vitova<sup>3</sup>, Marinella Mazzanti<sup>2</sup>, Rizlan Bernier-Lat-mani<sup>1</sup>\*.

Author contributions: M.Molinas carried out all bio-reduction, control and analytical experiments. R.F. synthesized U(VI), U(V) and U(IV) dpaea compounds and contributed to the data analyses. A. B. developed an experimental technique. J. G., B.S. and T.V. has assisted with the HR-XANES measurements and data analysis. M.Mazzanti contributed to the original idea of the project and data analyses. R.B.-L originated the central idea, coordinated the work and provided funding. M.Molinas and R.B.-L. analyzed the data and wrote the manuscript.

# References

[1] 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.

[2] M. Sundararajan, A. J. Campbell, I. H. Hillier, J. Phys. Chem. A **2008**, 112, 4451–4457.

[3] L. Newsome, K. Morris, J. R. Lloyd, *Chemical Geology* **2014**, *363*, 164–184..

[4] 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.

# Sub-Chapter 3c: The impact of supporting ligands and Fe(II) binding on the uranyl(V) U-oxo bonding – A high-resolution X-ray absorption spectroscopy and computational study

# Summary of the project

The chemistry research community is increasingly interested in elucidating the role played by 5f orbitals in uranium (U) metal structure, bonding, and reactivity. Aside from its high theoretical interest, a fundamental understanding of bonding can allow for better insight into the uranium stability and mobilization behavior in the environment. Additionally, revealing U–L (L = ligand) bond formation mechanisms is of particular importance to nuclear energy and novel remediation technology development. However, the electronic structure of uranium, and more broadly of the actinides, is not very well understood. The electronic structure of the uranyl(VI) cation has been the subject of multiple studies and reviews,<sup>[1–3]</sup> while a significantly fewer number of reports are available for U(V)-containing species.<sup>[4–6]</sup> The main reason for that is the low stability of uranyl(V) in aerobic aqueous conditions and the tendency of this species for disproportionation. However, as mentioned in the introduction, stable U(V) species have been identified as products of abiotic reduction of uranyl(VI) by Fe-containing minerals. U L<sub>3</sub> edge extended X-ray absorption fine structure (EXAFS) analyses reveal that U(V) in magnetite is coordinated by Fe in the second coordination sphere. However, due to the high disorder of the studied systems, it was not possible to obtain a more detailed structural description. In Chapter 2 we have demonstrated that the binding of Fe<sup>2+</sup> to the uranyl(V) oxo group leads to increased stability of the UO2<sup>+</sup> with respect to proton-induced disproportionation. Redox reactivity and cyclic voltammetry studies also showed an increased range of stability of the uranyl(V) species in the presence of Fe<sup>2+</sup> for both oxidation and reduction reactions. However, the effects of Fe<sup>2+</sup> binding on the U(V)-yl oxo bonding were never investigated in more detail. Additionally, besides the fact that the first reproducible synthesis of stable uranyl(V) complex in organic solution was reported nearly 15 years ago, the stability of U(V) in water at environmentally relevant pH remained an unmet target until very recently. In Chapter 3 we have demonstrated the synthesis and full characterization of the first molecular uranyl(V) complex that is stable in anaerobic water under neutral and basic pH conditions (pH=7-10). In order to elucidate the parameters leading to the stabilization of uranyl(V) in water, it is important to analyze the effects of the supporting ligands on the electronic structure of uranyl(V) and compare them to analogous Schiff base complexes that are lacking such stability.

Therefore, the paper summarized in this sub-chapter presents the first spectroscopic and computational study of the impact of the supporting ligand and Fe<sup>2+</sup> on the electronic and geometric structure of uranyl(V). The series for two pentadentate ligands, i.e. Mesaldien<sup>2-</sup> (H<sub>2</sub>Mesaldien=*N*,*N*'-(2aminomethyl)diethylenebis (salicyl-imine) and dpaea<sup>2-</sup> (H<sub>2</sub>dpaea =bis(pyridyl-6-methyl-2- carboxylate)-ethylamine) is explored which lead to uranyl(V) complexes stable in organic solvents (Mesaldien<sup>2-</sup>) or in water (dpaea<sup>2-</sup>). As a second step, complexes with one or two Fe atoms to the axial O atoms of [U<sup>V</sup>O<sub>2</sub>(Mesaldien)]<sup>-</sup> were investigated allowing to detect electronic and geometric structural changes induced by Fe on the bonding properties of U(V)-yl. Moreover, 2O and 3N atoms are bound to U in the equatorial plane for both systems, which makes the two systems ideal for studies of U-O<sub>ax</sub> vs. U-O<sub>eq</sub> and U-N<sub>eq</sub> bonding changes upon systematic change of the U oxidation state and insertion of Fe (Figure 55).



Figure 55. Schematic structures of complexes 1-8.

The novel U M<sub>4</sub> edge high energy resolution X-ray absorption near edge structure (HR-XANES) experimental technique was used to probe the unoccupied 5f valence states with high energy resolution that is sensitive to changes of the covalency of the actinyl bond. Additionally, CASSCF and DFT computations were carried out to investigate in detail the bonding properties of the U(VI), U(V) and U(IV) compounds.

## U M<sub>4</sub> edge HR-XANES of the actinyls

The basic principle of the U M<sub>4</sub> edge HR-XANES technique includes excitation of U  $3d_{5/2}$  electrons to unoccupied orbitals with predominant 5f character governed by the dipole selection rule ( $\Delta J = 0, \pm$ 1). It is followed by emission of characteristic fluorescence, which is detected as a function of the excitation energy. The electronic configuration of U in the three-step process can be described as ground ( $3d^{10}4f^{14}5f^N$ , N = 0, 1 or 2), intermediate ( $3d^94f^{14}5f^{N+1}$ ) and final state ( $3d^{10}4f^{13}5f^{N+1}$ ). The experimental resolution is significantly improved applying an X-ray emission spectrometer so that it is close to the 4f core-hole lifetime broadening in the final state. As a result, the spectral peaks are much more resolved providing detailed information on the electronic structure of U.

### M4,5 edge HR-XANES and computations to measure covalency of the actinyl bond

Having access to a highly sensitive high-resolution X-ray spectroscopy technique, we were able to measure the energy shifts between the delta/phi, pi\*and sigma\* orbitals in all the compounds of interest and use the resulting energy shift to evaluate the covalency of the specific bonds. DFT and CASSCF computations allowed for the precise electronic structure calculations. The optimized geometries were in good agreement with the experimental ones. Coupling of these techniques provide a detailed in-depth analysis of the U–ligand chemical bond that confirmed previously known trends as well as revealed several novel findings.

The most important and novel findings are presented below:

1) the average axial bond length relates well with the variations of electronic density on U as measured by the HR-XANES spectroscopy, i.e. the electronic density on U changes as follows 1/6 < 3/4 < 2/7 (i.e. U(VI) < U(V)-Fe < U(V))

2) The U–Oeq bond length is much more sensitive to any changes induced along the axial bond in comparison to U–N bond.

3) Larger covalency for Mesaldien–U(VI)/(V) (**1/2**) complexes in comparison to dpaea–U(VI)/(V) (**6/7**) was suggested by the CASSCF calculations. Additionally, the covalency of the U-Oax-yl bond is slightly larger for **6/7** compared to **1/2** (U(VI)/(V).

4) The calculation of the ground states and of the first excited states revealed a significant difference between the complexes 1/2 (Mesaldien–U(VI)/(V)) and 6/7 (dpaea–U(VI)/(V)). For 1/2 the ground state is a pure U(VI) and U(V) character, while for 6/7 the respective ground states are of mixed U(VI)/U(V) and U(V)/U(IV) character coming from the low-lying excited states. Thus, complexes 2 and **7** might have very different behavior in solution and/or reactivity due to these very different electronic configurations.

5) On Fe(II)-binding in **3** (U(V)-Fe) the electronic density is removed from U(V) and the average U-Oax bond covalency is reduced as proposed by HR-XANES. The coordination of iron is thus stabilizing the U(V) complex by slightly decreasing the covalency in the U-Oax (bound to Fe) in order to form a Fe-O bond and allowing better interaction with the equatorial ligand. Interestingly, the addition of the second iron(II) cation does not significantly change the electronic environment of  $\{UO_2(Mesaldien)\}^-$  in **4** in comparison to **3**.

These findings may help us to better understand the role of the 5f electrons in the covalency of the U binding and the interconnection between bond covalency, reactivity, and bond stability in ura-nyl(V) complexes.

<sup>1</sup> Portions of this chapter are adopted from the article in preparation: T. Vitova,\* R. Faizova, A. Beck, J.
I. Amaro Estrada, L. Maron,\* Fadaei-Tirani Farzaneh, M. Mazzanti\*

Author contributions: R.F. synthesized all compounds and produced X-ray structure description and the comparison. F.F.-T. performed the X-ray single crystal structure analyses. T. V. and A.B. performed HR-XANES measurements, analyzed and described the resulting data. J. I. A. E. and L.M. performed CASSCF and DFT computations, as well as analyzed and described the results. M.M. and T.V. originated the central idea. T.V. coordinated the work. T.V., R.F., A.B. J. I. A. E., L.M. and M.M analyzed the data and wrote the manuscript.

# References

[1] R. G. Denning, J. Phys. Chem. A 2007, 111, 4125–4143.

[2] R. G. Denning, J. C. Green, T. E. Hutchings, C. Dallera, A. Tagliaferri, K. Giarda, N. B. Brookes,

L. Braicovich, J. Chem. Phys. 2002, 117, 8008-8020.

[3] N. Kaltsoyannis, Chem. Soc. Rev. 2003, 32, 9–16.

[4] M. Zegke, X. 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.

P. L. Arnold, M. S. Dutkiewicz, M. Zegke, O. Walter, C. Apostolidis, E. Hollis, A.-F. Pécharman,
N. Magnani, J.-C. Griveau, E. Colineau, R. Caciuffo, X. Zhang, G. Schreckenbach, J. B. Love, *Angew. Chem. Int. Ed.* 2016, 55, 12797–12801.

[6] B. Teyar, S. Boucenina, L. Belkhiri, B. Le Guennic, A. Boucekkine, M. Mazzanti, *Inorg. Chem.***2019**, *58*, 10097–10110.

# Chapter 4: Ligand supported facile conversion of uranyl(VI) to uranium(IV) in organic and aqueous media.

# Chapter 4: Ligand supported facile conversion of uranyl(VI) to uranium(IV) in organic and aqueous media.

# 4.1 Introduction

Uranyl(VI) species (UO<sub>2</sub><sup>2+</sup>) are highly stable and highly soluble in aqueous solutions which results in a problematic high mobility in contaminated environment where they are the predominant form of uranium.<sup>[1]</sup> 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,<sup>[2]</sup> a process that is thought to involve a U(V) intermediate.<sup>[3]</sup> 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.<sup>[4]</sup>

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 gas phase<sup>[5]</sup> and in non-aqueous anaerobic media.<sup>[1a, 1b, 6]</sup> Significant progress has been made in recent years in the development of systems that allowed the reduction of uranyl(VI) to uranyl(V).<sup>[1a]</sup> 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 preliminary functionalization of the two uranyl oxo ligands with Lewis acids <sup>[1a, 6b] [6a, 7]</sup> or metal cations.<sup>[8]</sup> However, the low stability in aqueous media of the reported uranyl(V) systems both with respect to ligand dissociation and proton induced disproportionation<sup>[9]</sup> renders impossible their use in the study of uranyl reduction under environmentally relevant conditions, i. e. in aqueous media.

Recently, we reported<sup>[10]</sup> the synthesis and the structure of the uranyl(V) complex  $[K(2.2.2.cryptand)][UO_2(dpaea)]$ , **2** (dpaea<sup>2-</sup> (bis(pyridyl-6-methyl-2-carboxylate)-ethylamine) which

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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 is stable in water at pH 7-11. The ability of the ligand dpaea<sup>2-</sup> to stabilize uranyl(V) in organic and aqueous solutions provides access to the study of the reactivity of this species in both media.

Here we report that the uranyl(VI) complex [UO<sub>2</sub>(dpaea)] can be reduced in organic solution to afford a *cis*-boroxide uranium(IV) species ([U<sup>IV</sup>(dpaea)(*cis*-OBpin)<sub>2</sub>(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<sub>2</sub>O)<sub>5</sub>{U(dpaea)}<sub>3</sub>( $\mu$ -O)<sub>2</sub>( $\mu$ -OH)( $\mu$ <sub>3</sub>-SO<sub>3</sub>)], **4** and [Na(2.2.2crypt)][{U(dpaea)}<sub>3</sub>( $\mu$ -O)<sub>2</sub>( $\mu$ -OH)( $\mu$ <sub>3</sub>-SO<sub>3</sub>)], **5**. We also report the structure of the uranyl(V) [{UO<sub>2</sub>(dpaea)(H<sub>2</sub>O)}<sub>2</sub>{ $\mu$ -Na(H<sub>2</sub>O)<sub>4</sub>}]}, **6**, complex as obtained from the reduction of U(VI) with sodium dithionite in water, which is the first example of uranyl(V) isolated from water.

<sup>1</sup> Portions of this chapter have been published:

R. Faizova, F. Fadaei-Tirani, R. Bernier-Latmani, M. Mazzanti, *ACIE* **2020**, *59*, 6756–6759.<sup>[23]</sup> Author contributions: R.F performed all the experiments, analyzed the data and wrote the original draft of the manuscript, F.F.T. measured and analyzed the diffractions data. M.M. originated the central idea, coordinated the work, provided funding and analysed the experimental data. R. F. and M. M. wrote the manuscript. R. B. L. participated in the analysis of the data and contribute to experiments design.

# 4.2 Results and discussion

First, the reduction of **1** was explored in organic solution (pyridine). Upon addition of **1** equiv. of diborane pinacolate ((Bpin)<sub>2</sub> (pin = pinacolate)) to the uranyl(VI) complex 1 at room temperature, the <sup>1</sup>H NMR spectrum of the reaction mixture revealed conversion of the insoluble diamagnetic U(VI) species to paramagnetic U(IV) containing species (Scheme 14, Figure 56).





Figure 56. <sup>1</sup>H NMR spectrum (400 MHz, C<sub>5</sub>D<sub>5</sub>N, 298 K) of the reaction mixture after 18-c-6 (1 eq. for quantitative integration) addition to the reaction mixture obtained after reacting [UO<sub>2</sub>(dpaea)] (1) with 1 eq. of (Bpin)<sub>2</sub>, showing 50% conversion of 1 to [U<sup>IV</sup>(dpaea)(*cis*- $OBpin_2(py)$ ], **3**, and formation of  $O(Bpin_2)$ .

The solid-state structure of the complex **3** (Figure 57) shows the presence of an 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 to the uranyl oxo groups and two-electrons 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 oxo groups for a *trans-* to *cis-* position. The <sup>1</sup>H 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  $O(Bpin)_2^{[7b]}$ and of additional paramagnetic signals (Figure 56). The observed signals suggest that additional U(IV) species are formed that result from reductive oxo abstraction. One of these species was identified by X-ray diffraction to be a *trans*-boroxide U(IV) complex [U<sup>IV</sup>(dpaea)(*trans*-OBpin)\_2(py)] (**7**) (Figure 57). Only a few crystals of **7** have been mechanically isolateled from the fractional crystallization of the reaction mixture due to the difference in physical appearance with complex **3**.



**Figure 57.** Molecular structure of **3** (left) and **7** (right). H atoms and solvent molecules are removed for clarity. C grey, N blue, O red, B yellow and U green.

Complex **7** is thought to undergo an oxo-extrusion forming oxo-bridged species and  $OB(pin)_2$ . This reaction is likely to be slower complex **3** due to steric clash between bulky *cis*-boroxides. Similar oxo-bridged  $[O-U-O-U-O]^{4+}$  species resulting from reductive oxo abstraction were observed as the only product of the diborane reduction of a macrocylic uranyl(VI) complex recently reported by Love and Arnold.<sup>[7b]</sup>

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 AQDSH<sub>2</sub> (1,8-dihydroxy-9,10-anthraquinone-2,7-disulphonic sodium), NaBH<sub>4</sub> and Fe<sup>2+</sup> did not result in the reduction of the uranyl(VI) complex. In contrast, the addition of 0.5 equiv. of Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> to a yellow suspension of

[UO<sub>2</sub>(dpaea)] in water at pH=8.5 resulted in immediate reaction yielding a pink solution. The <sup>1</sup>H NMR spectrum of the reaction mixture, when compared to the spectrum of **2** in D<sub>2</sub>O at pH 8.5, revealed the quantitative conversion of **1** into the uranyl(V) species  $[UO_2(dpaea)]^-$  (Scheme 15; Figure 58).



Scheme 15. One- and two-electron reduction of 1 in water at pH 8.5 to afford 6 and 4.



**Figure 58.** <sup>1</sup>H NMR spectrum (400 MHz, D<sub>2</sub>O, pH=8.5, 298 K): crystals of  $[K(2.2.2.cryptand)][UO_2(dpaea)]$  synthesized in pyridine (bottom)<sup>[3]</sup>; reaction mixture after cryptand addition to the reaction mixture obtained after reacting  $[UO_2(dpaea)]$  with 0.5 eq. of Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> in 0.5 M HEPES aqueous solution at pH=8.5 for an hour (top).

Crystals of the uranyl(V) complex [ $\{UO_2(dpaea)(H_2O)\}_2\{\mu-Na(H_2O)_2\}_2\{H_2O\}_2\}$ , **6**, were obtained by slow evaporation of the H<sub>2</sub>O solution at room temperature (**Figure 59** and Appendix 3: Fig. S13). The structure shows a dimer with two anionic  $\{UO_2(dpaea)(H_2O)\}^-$  moieties bridged by two Na cations binding the carboxylate oxygens. Additionally, two H-bonds (O...H=1.96(6) and 2.07(5) Å) are observed in the solid state structure between the uranyl(V) oxo group and the water molecules present in the structure.



**Figure 59.** Molecular structure of the  $[{UO_2(dpaea)(H_2O)}_2{\mu Na(H_2O)}_2]$  complex **6** (H atoms of the ligand were removed for clarity). C grey, H white, N blue, O red and U green.

Moreover, the reduction of  $[UO_2(dpaea)]$  with 1-2 equiv. of  $Na_2S_2O_4$  in water buffered with HEPES at pH=8.5 for seven days at room temperature led to the formation of the trinuclear uranium(IV)  $\mu$ -oxo/hydroxo bridged cluster  $[Na(H_2O)_5{U(dpaea)}_3(\mu-O)_2(\mu-OH)(\mu_3-SO_3)]$  (4) that was isolated as a red crystalline solid in up to 68 % yield (obtained using 2 equiv.  $Na_2S_2O_4$ ). XPS analysis of the isolated solid indicated that only U(IV) species are present (Appendix 3: Fig. S10).

Complex **4** could also be isolated by the reduction of the uranyl(V) complex  $[K(2.2.2.cryptand)][UO_2(dpaea)]$  with 0.5 equiv. of sodium dithionite in water at pH  $\geq$  8 but with lower yield (up to 40 %) probably due to the presence of cryptand.

<sup>1</sup>H NMR studies show that the conversion of U(VI) to 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 as shown in Appendix 3: Fig. S4 and S5).

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 <sup>1</sup>H NMR spectrum of the resulting orange solution in D<sub>2</sub>O (at pD=8) showed signals in the broad range of chemical shifts usually observed for paramagnetic U(IV) species (Figure 60).



**Figure 60.** <sup>1</sup>H NMR spectrum (400 MHz, D<sub>2</sub>O, pH=8, 298 K) of a solution of  $[Na(H_2O)_5U_3(dpaea)_3O_2(OH)(SO_3)]$  (4) after the addition of 1 equiv. of 2.2.2.cryptand.

Slow evaporation of a water solutions generated by addition of 1 equiv. of 2.2.2.cryptand to 4 allowed to isolated crystals of complex [Na(2.2.2crypt)][{U(dpaea)}<sub>3</sub>( $\mu$ -O)<sub>2</sub>( $\mu$ -OH)( $\mu$ <sub>3</sub>-SO<sub>3</sub>)], 5.

The <sup>1</sup>H 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<sub>s</sub> symmetric trinuclear solution species. A diffusion coefficient of  $2.2.10^{-6}$  cm<sup>2</sup>.s<sup>-1</sup> 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) (Table 3).

Cluster	Diffusion coefficient (cm <sup>2</sup> .s <sup>-10</sup> )	Hydrodynamic radius (Å)	Radius evaluated from
			crystal structure (Å)
«U <sub>3</sub> O <sub>3</sub> » <b>5</b>	2.2 x 10 <sup>-6</sup>	9	8

Table 3. Diffusion coefficient value of 5 and estimated spherical radii.

The FTIR spectrum of the trinuclear complex **4** shows the disappearance of the band assigned to the asymmetric uranyl O=U=O stretch  $(UO_2^{2+}\approx790 \text{ cm}^1; UO_2^{+}\approx920 \text{ cm}^{-1})$  in agreement with the formation of the U(IV)-oxo species (Figure 61).



**Figure 61.** IR Spectrum in Nujol mull of the complex  $[Na(H_2O)_5U_3(dpaea)_3O_2(OH)(SO_3)]$  (4).

The solid-state structure of complex **4** was determined by X-ray diffraction studies (Figure 62). 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 sulphite anion also bridges the three U(IV) centres, with a mean U-O<sub>sulp</sub> 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 octacoordinated by the dpaea ligand, one O<sub>sulp</sub> and two bridging O<sub>oxo</sub>/O<sub>hydr</sub> atoms. The value of the U-O<sub>oxo</sub> bond distances ranges from 2.0477(17) to 2.1699(17) Å and U-O<sub>hydroxo</sub> averages at 2.327(3) Å which are both in the range of typical for uranium(IV) oxo and U(IV) hydroxo bond distances.<sup>[12]</sup> The value of the U-O-U angles in the trimer range from 138.20(9)° for U- $\mu$ -OH-U to 144.39(9)° and 148.83(8)° (U- $\mu$ -O-U) and is similar to those found for the only three other trinuclear U(IV) clusters reported so far.<sup>[12]</sup> 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** is presented in Appendix 3: Fig. S12 and 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 (Appendix 3: Table S2). The clusters **4** and **5** are the first examples of trinuclear oxo clusters isolated from aqueous media.<sup>[12]</sup>



**Figure 62.** 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<sup>+</sup> are removed for clarity. C grey, H white, N blue, O red, S yellow, U green and Na in light blue.

The stability of complex **5** at different pH conditions was investigated by <sup>1</sup>H 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 [U<sup>IV</sup>(dpaea)<sub>2</sub>] that has very low solubility in water (Figure 63).



**Figure 63.** <sup>1</sup>H NMR spectrum (400 MHz, D<sub>2</sub>O, 298 K): of the solution of  $[Na(2.2.2crypt)][U_3(dpaea)_3O_2(OH)(SO_3)]$  at pH=8.5 (bottom); pH=11 (middle) and pH=5 (top). Indicating decomposition of complex 5 at acidic and basic pH.

We also investigated how the reduction of **1** is affected by pH. The reduction of  $[UO_2(dpaea)]$  with Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> cannot be performed in acidic aqueous media (pH lower than 7) (Appendix 3: Fig. S6) because the uranyl(V)  $[U^VO_2(dpaea)]^-$  complex was found to disproportionate to  $[U^{VI}O_2(dpaea)]$  and  $[U^{IV}(dpaea)_2]$  in these conditions.<sup>[10]</sup> In contrast, no disproportionation is observed in water solutions of  $[NaUO_2(dpaea)]$  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 (pH  $\ge$  11) the uranyl(V) is not reduced by Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> in spite of the fact that the reducing power<sup>[13]</sup> of Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> is increased at more basic pH (Figure 64). This result suggests that the redox properties of  $[UO_2(dpaea)]^-$  are pH dependent as previously reported for uranyl(VI) carbonate or phosphate.<sup>[14]</sup>



**Figure 64**. <sup>1</sup>H NMR spectrum (400 MHz, D<sub>2</sub>O, pH=11, 298 K): of the reaction of  $[UO_2(dpaea)]$  with 2 eq. of Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> after 30 minutes (bottom); after 1 week (2<sup>nd</sup> from the bottom); after 3 weeks (2<sup>nd</sup> from the top) and after 2 months (top). Showing increased redox stability of ura-nyl(V) complex 2 at basic pH.

In view of the ability of the weakly reducing agent  $Na_2S_2O_4$  ( $E_{red}(Na_2S_2O_4)$ = - 0.87 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<sup>[10]</sup> 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 U(V)/U(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 V vs Ag/AgCl depending on the scan speed.



**Figure 65.** Cyclic voltammetry data recorded for 4 mM solutions of [K(2.2.2.cryptand)][UO2(dpaea)] in 0.05 M aqueous HEPES solutions (pH= 7 & pH= 10) at 5 mV/s scan rate vs. Ag/AgCI.

This redox event was also found in the voltammogram of the non-redox active  $Zn^{2+}$  cation [Zn(dpaea)] (Appendix 3: Fig. S7) 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 V (vs. Ag/AgCl) (pH=7) and it was assigned to the U(VI)/U(V) reduction. The low intensity of the signal could be due to the extremely low solubility of [U<sup>VI</sup>O<sub>2</sub>(dpaea)] and hence its extremely low aqueous concentration. The U(V)/U(IV) redox event is not observable in water solution probably due to the slow kinetics of electron transfer and to the important structural rearrangement associated to this redox event resulting in the formation of complex **4**. Cyclic voltammetry experiments were also carried out at pH=10 (

Figure **65**) and resulted in a shift of the redox event associated to the U(VI)/U(V) reduction to a more negative potential. This could explain the increased stability of the uranyl(V) species during the reduction with Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> at basic pH.

Cyclic voltammetry measurements carried out on complex **5** at pH 7 showed the presence of two irreversible redox events at -1.46 V (vs. Ag/AgCl) and at 0.63 V (vs. Ag/AgCl) assigned to the ligand reduction event and U(IV)/U(V) oxidation respectively (Figure 66).



**Figure 66.** Cyclic voltammetry data recorded for 4 mM solutions of  $[Na(2.2.2crypt)][U_3(dpaea)_3O_2(OH)(SO_3)]$  (5) in 0.05 M aqueous HEPES solutions (pH= 7) at 100 mV/s scan rate vs. Ag/AgCl.

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 Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>. This should result in a *cis*-bis-hydroxo intermediate that is structurally analogue 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<sup>2+</sup> in aqueous solution, but it was found to have a high thermodynamic barrier preventing U(V)/U(IV) conversion in the presence of carbonate.<sup>[15]</sup> 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 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 due to its relevance in the migration of actinides in the environment.<sup>[2d, 11, 16]</sup> 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.

# **4.3 Conclusions**

In conclusion, we have shown that in the presence of polydentate carboxylate ligands it is possible to perform the conversion of U(VI) to a stable uranyl(V) complex in aqueous media. This uranyl(V) complex can be further reduced to U(IV) using a reductant (Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>) 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 UO<sub>2</sub><sup>2+</sup> 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.

# Experimantal

#### General considerations.

All manipulations were carried out under an inert argon atmosphere using Schlenk techniques and an MBraun glovebox equipped with a purifier unit. The oxygen level was always kept at less than 0.1 ppm. The solvents were purchased from Aldrich or Cortecnet (deuterated solvents) in their anhydrous form, or freeze-degassed. Depleted uranium was purchased from IBILABS, USA.

 $[(UO_2Py_5)(KI_2Py_2)]_{n_r}^{[21]}$  was synthesized as previously described.  $UO_2(NO_3)_2(H_2O)_6$  was purchased from Sigma-Aldrich. Bis-diborane pinacolate (Bpin)<sub>2</sub>, 2.2.2.cryptand (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane, 18crown6 (1,4,7,10,13,16-hexaoxacyclooctadecane) were purchased from Aldrich and sublimated prior to use.  $Na_2S_2O_4$ ,  $Na_2SO_3$  and HEPES were purchased from Aldrich and were used without further purification.  $H_2$ dpaea(HCl)<sub>3</sub> ligand was prepared according to the published procedure.<sup>[22]</sup>

Elemental analyses were performed under argon with a Thermo Scientific Flash 2000 Organic Elemental Analyzer by the EPFL elemental analyses service. <sup>1</sup>H NMR experiments were carried out using NMR tubes adapted with J. Young valves. <sup>1</sup>H NMR spectra were recorded on Bruker 400 MHz spectrometer. NMR chemical shifts are reported in ppm with solvent as internal reference.

X-Ray Photoelectron Spectroscopy (XPS) measurements were carried out using a PHI VersaProbe II scanning XPS microprobe (Physical Instruments AG, Germany).

IR spectra were recorded with a Perkin Elmer 1600 Series FTIR spectrophotometer flushed with argon.

pH measurements were done with Thermo Scientific Orion 3 star pH meter calibrated with pH buffers before each use.

Caution: Depleted uranium (primary isotope <sup>238</sup>U) is a weak  $\alpha$ -emitter (4.197 MeV) with a halflife of 4.47×10<sup>9</sup> years. Manipulations and reactions should be carried out in monitored fume hoods or in an inert atmosphere glovebox in a radiation laboratory equipped with  $\alpha$ - and  $\beta$ counting equipment.

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#### Synthetic Procedures.

## Synthesis of [U(dpaea)(cis-OBpin)<sub>2</sub>(py)] (3).

A colorless solution of bis(pinacolato)diboron (14.5 mg,0.057 mmol, 1 eq) in pyridine (1 ml) was added to a yellow suspension of  $[UO_2(dpaea)]$  (34.0 mg, 0.057 mmol, 1 eq) in pyridine (2 ml). The resulting suspension was stirred overnight to afford a green-yellow suspension that was filtered and the resulting green-yellow solution was layered with heptane. Green crystals (17 mg, 0.02 mmol, 33%) were collected after 1 week. Elemental analysis calcd (%) for [U(dpaea)( *cis*-OBpin)<sub>2</sub>(py)<sub>0.9</sub>] (C<sub>28</sub>H<sub>38</sub>N<sub>3</sub>O<sub>10</sub>U<sub>1</sub>.(Py)<sub>0.9</sub>, 3 MW=907.372) C 43.02, H 4.72 and N 6.02; found C 42.85, H 4.65 and N 6.10. <sup>1</sup>H NMR (400 MHz, C<sub>5</sub>D<sub>5</sub>N, 298 K):  $\delta$ : = 17.31 (2H, s); 11.11 (2H, s); 6.80 (24H, s); -2.66 (2H, s); -5.05 (3H, s); -9.99 (2H, s); -30.88 (2H, s); -44.86 (2H, s) (Fig. S1). <sup>11</sup>B NMR spectrum (128 MHz, C<sub>5</sub>D<sub>5</sub>N, 298 K):  $\delta$ : 153.02 (s) (Appendix3: Fig. S2). <sup>1</sup>H NMR spectroscopy of the reaction mixture after (Bpin)<sub>2</sub> addition to  $[UO_2(dpaea)]$  showed 50% conversion of  $[UO_2(dpaea)]$  to complex 3 as well as O(Bpin)<sub>2</sub> formation (Figure 56).

#### Reduction of $[U^{VI}O_2(dpaea)]$ to $[NaU^VO_2(dpaea)]$ in water.

A colorless solution of sodium dithionite (2.4 mg, 0.0135 mmol, 0.5 eq) in 0.5 M aqueous HEPES (pH=8.5; 1 ml) was added to a yellow suspension of  $[UO_2(dpaea)]$  (20.1 mg, 0.034 mmol, 1 eq) in D<sub>2</sub>O (1 ml). The resulting suspension was stirred for 1 hour to afford a red solution. 2.2.2.cryptand (12.8 mg, 0.034 mmol, 1 eq) was added for quantitative integration. The <sup>1</sup>H NMR spectrum of the solution shows the signals assigned to the uranyl(V) complex and integration of the signals showed quantitative conversion of  $[UO_2(dpaea)]$  to the previously reported uranyl(V) complex  $[UO_2(dpaea)]^-$  (Figure 58).<sup>[3]</sup> The reported uranyl(V) complex is fully stable in aqueous solution at pH above 7 for 2 weeks but disproportionates at pH 6 with only 80% of the complex remaining after 2 days. Crystals of the uranyl(V) complex the  $[{UO_2(dpaea)(H_2O)}_2{_2{H_2O}}_2]$  (Figure 59 and Appendix 3: Fig. S13) were obtained by slow evaporation of water solution of **6**.

#### Reduction attempts with various reducing reagents.

To a yellow suspension of  $[UO_2(dpaea)]$  (10-30 mg, 0.02-0.05 mmol) in  $D_2O$  (1 ml) 1 equiv. of AQDSH<sub>2</sub> (1,8-dihydroxy-9,10-anthraquinone-2,7-disulphonic sodium) in 1 ml of  $D_2O$ ; exc. Zn (solid); 3 equiv. of NaBH<sub>4</sub>; 1 equiv. of Fe<sup>II</sup>(dpaea) in 1 ml of  $D_2O$  were added. Reaction mixtures

were stirred for 2 days. The <sup>1</sup>H NMR spectra of the reaction mixtures indicated that no reaction has occurred for all the reduction attempts.

# Synthesis of $[Na(H_2O)_5U_3(dpaea)_3O_2(OH)(SO_3)]$ (4).

A colorless solution of sodium dithionite (11.8 mg, 0.068 mmol, 2 eq) in 0.5 M aqueous HEPES (pH=8.5; 1 ml) was added to a yellow suspension of  $[UO_2(dpaea)]$  (20.2 mg, 0.034 mmol, 1 eq) in D<sub>2</sub>O (1 ml). The resulting suspension was stirred for 1 hour to afford a red solution. The <sup>1</sup>H NMR spectrum of the solution immediately after addition of sodium dithionite shows the signals assigned to the uranyl(V) complex Na[UO<sub>2</sub>(dpaea)]. The reaction mixture was left reacting at room temperature for a week to yield [Na(H<sub>2</sub>O)<sub>2</sub>U<sub>3</sub>(dpaea)<sub>3</sub>O<sub>2</sub>(OH)(SO<sub>3</sub>)], 4 as red single crystals suitable for X-ray diffraction (14.0 mg, 0.0078 mmol, 68%). Elemental analysis calcd (%) for [Na(H<sub>2</sub>O)<sub>2</sub>U<sub>3</sub>(dpaea)<sub>3</sub>O<sub>2</sub>(OH)(SO<sub>3</sub>)] (C<sub>48</sub>H<sub>50</sub>N<sub>9</sub>O<sub>20</sub>S<sub>1</sub>NaU<sub>3</sub>, MW=1842.11) C 31.30, H 2.74 and N 6.84; found C 31.43, H 3.02 and N 6.51.

XPS analysis of the bulk isolated solid showed only the presence of U(IV) species in agreement with the single crystal X-ray data (Appendix 3: Fig. S10).

The <sup>1</sup>H NMR spectrum of the reaction mixture recorded after one week still shows small amounts of unreacted uranyl(V) complex (Appendix 3: Fig. S4-S5).

Complex 4 was also obtained analytically pure by performing the reduction in a water solution (adjusted with NaOH at pH=8.5 during the course of the reaction), but the best yield is obtained from buffered solutions (0.5 M HEPES).

The reduction of [UO<sub>2</sub>(dpaea)] to complex 4 is also observed by <sup>1</sup>H NMR spectroscopy upon addition of 1 equivalent of sodium dithionite at pH 8.5, but the best isolated yield was obtained upon addition of 2 equiv. of sodium dithionite (Appendix 3: Fig. S4-S5). Higher stoichiometries (5-10 equivalents of sodium dithionite) do not lead to increased yield but lead to the formation of additional unidentified products.

The reduction of  $[UO_2(dpaea)]$  to complex 4 is also observed at lower concentration (10-15 mM).

The complex 4 is insoluble in water at pH=8 but can be solubilized by addition of 1 eq. of 2.2.2.cryptand affording an orange solution. <sup>1</sup>H NMR spectrum of the solution (400 MHz, D<sub>2</sub>O, 298 K):  $\delta$ : = 44.09 (2H, s); 35.96 (2H, s); 31.31 (2H, s); 23.70 (2H, s); 19.53 (2H, s); 14.68 (2H, s); 13.22 (4H, s); 3.69 (24H, s); 3.06 (5H, s); 2.65 (7H, d); 0.53 (2H, s); -2.95 (2H, s); -3.50 (2H, s); -

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s); -4.30 (2H, s); -15.38 (8H, s); -18.40 (2H, s); -21.83 (3H, s); -33.39 (2H, s); -43.93 (2H, s); -53.61 (2H, s); -74.41(2H, s) (Figure 60).

Orange single crystals of  $[Na(2.2.2crypt)][U_3(dpaea)_3O_2(OH)(SO_3)]$  5 suitable for X-ray diffraction were obtained from a 1:1 2.2.2.cryptand: 4 water solution at room temperature.

Complex 4 was also obtained analytically pure by performing the reduction of the uranyl(V) complex [K(2.2.2.cryptand)][UO<sub>2</sub>(dpaea)] with 0.5 equiv. for one week in water solution at pH =8.5 (Appendix 3: Fig. S3), however with max 40% isolated yield, probably due to the presence of cryptand.

## Stability studies of $[Na(2.2.2crypt)][U_3(dpaea)_3O_2(OH)(SO_3)]$ (5).

The stability of complex 5 in function of pH was investigated, using <sup>1</sup>H NMR spectroscopy, by addition of DCl and NaOD to an orange solution of complex 5 (10 mM) in D<sub>2</sub>O. Complex 5 was shown to be stable at pH 7-9, while outside of this pH range all the proton NMR signals disappear. From solutions of 5 at pH=5 crystals of the  $[U^{IV}(dpaea)_2]$  were isolated and characterized by XRD. The formation of the  $[U^{IV}(dpaea)_2]$  indicates that the uranyl oxo groups are extrudes as H<sub>2</sub>O at low pH. At basic pH (pH=11) formation of insoluble precipitate was observed (Figure 63).

#### References

a) B. E. Cowie, J. M. Purkis, J. Austin, J. B. Love, P. L. Arnold, *Chem. Rev.* 2019, *119*, 10595-10637; b) D. Ribera, F. Labrot, G. Tisnerat, J. F. Narbonne, in *Reviews of Environmental Contamination and Toxicology, Vol 146, Vol. 146* (Ed.: G. W. Ware), **1996**, pp. 53-89; c) S. A. Cumberland, G. Douglas, K. Grice, J. W. Moreau, *Earth-Science Reviews* 2016, *159*, 160-185; d) S. Fortier, T. W. Hayton, *Coord. Chem. Rev.* 2010, *254*, 197-214.

[2] a) D. R. Lovley, E. J. P. Phillips, Y. A. Gorby, E. R. Landa, *Nature* 1991, *350*, 413-416; b) R. Bernier-Latmani, H. Veeramani, E. D. Vecchia, P. Junier, J. S. Lezama-Pacheco, E. I. Suvorova, J. O. Sharp, N. S. Wigginton, J. R. Bargar, *Environ. Sci. Technol.* 2010, *44*, 9456-9462; c) 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; d) 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; e) S. D. Taylor, M. C. Marcano, K. M. Rosso, U. Becker, *Geochim. Cosmochim. Acta* 2015, *156*, 154-172; f) L. S. Natrajan, A. N. Swinburne, M. B. Andrews, S. Randall, S. L. Heath, *Coord. Chem. Rev.* 2014, *266*, 171-193.

[3] 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.

[4] a) M. I. Boyanov, K. E. Fletcher, M. J. Kwon, X. Rui, E. J. O'Loughlin, F. E. Loffler, K. M. Kemner, *Environ. Sci. Technol.* 2011, 45, 8336-8344; b) A. J. Francis, C. J. Dodge, *Environ. Sci. Technol.* 2008, 42, 8277-8282.

[5] J. J. Kiernicki, M. Zeller, S. C. Bart, Angew. Chem. Int. Ed. Engl. 2017, 56, 1097-1100.

[6] a) N. L. Bell, B. Shaw, P. L. Arnold, J. B. Love, *J. Am. Chem. Soc.* 2018, 140, 3378-3384; b) J. R.
Pankhurst, N. L. Bell, M. Zegke, L. N. Platts, C. A. Lamfsus, L. Maron, L. S. Natrajan, S. Sproules, P. L.
Arnold, J. B. Love, *Chem. Sci.* 2017, *8*, 108-116; c) M. B. Jones, A. J. Gaunt, *Chem. Rev.* 2013, 113, 1137-1198.

[7] a) P. L. Arnold, D. Patel, C. Wilson, J. B. Love, *Nature* 2008, *451*, 315-318; b) P. Horeglad, G. Nocton, Y. Filinchuk, J. Pecaut, M. Mazzanti, *Chem. Commun.* 2009, 1843-1845; c) P. L. Arnold, G. M. Jones, S. O. Odoh, G. Schreckenbach, N. Magnani, J. B. Love, *Nat. Chem.* 2012, *4*, 221-227; d) 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.

[8] D. D. Schnaars, G. Wu, T. W. Hayton, J. Am. Chem. Soc. 2009, 131, 17532-17533.

141

[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.
[10] 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.

[11] D. E. Morris, *Inorg. Chem.* **2002**, *41*, 3542-3547.

[12] V. Mougel, B. Biswas, J. Pecaut, M. Mazzanti, Chem. Commun. 2010, 46, 8648-8650.

[13] V. Mougel, P. Horeglad, G. Nocton, J. Pécaut, M. Mazzanti, *Chem. Eur. J.* 2010, *16*, 14365-14377.

[14] K. E. Knope, L. Soderholm, *Chem. Rev.* **2013**, *113*, 944-994.

[15] a) C. T. Palumbo, L. Barluzzi, R. Scopelliti, I. Zivkovic, A. Fabrizio, C. Corminboeuf, M. Mazzanti, *Chem. Sci.* 2019, *10*, 8840-8849; b) L. Karmazin, M. Mazzanti, J. Pecaut, *Inorg. Chem.* 2003, *42*, 5900-5908; c) J.-C. Berthet, M. Ephritikhine, M. Lance, M. Nierlich, J. Vigner, *J. Organomet. Chem.* 1993, *460*, 47-53.

[16] R. Faizova, R. Scopelliti, A. S. Chauvin, M. Mazzanti, *J. Am. Chem. Soc.* **2018**, *140*, 13554-13557.

[17] S. G. Mayhew, *Eur. J. Biochem.* **1978**, *85*, 535-547.

[18] K. Mizuguchi, Y. Y. Park, H. Tomiyasu, Y. Ikeda, J. Nucl. Sci. Technol. **1993**, 30, 542-548.

[19] M. C. F. Wander, S. Kerisit, K. M. Rosso, M. A. A. Schoonen, J. Phys. Chem. A 2006, 110, 96919701.

[20] a) L. Chatelain, R. Faizova, F. Fadaei-Tirani, J. Pecaut, M. Mazzanti, *Angew. Chem. Int. Ed. Engl.* **2019**, *58*, 3021-3026; b) L. Soderholm, P. M. Almond, S. Skanthakumar, R. E. Wilson, P. C. Burns, Angew. Chem. Int. Ed. Engl. **2008**, *47*, 298-302.

[21] L. Natrajan, F. Burdet, J. Pecaut, M. Mazzanti, J. Am. Chem. Soc. 2006, 128, 7152–7153.

[22] A. Pellissier, Y. Bretonnière, N. Chatterton, J. Pécaut, P. Delangle, M. Mazzanti, *Inorg. Chem.***2007**, *46*, 3714–3725.

[23] R. Faizova, F. Fadaei-Tirani, R. Bernier-Latmani, M. Mazzanti, Angew. Chem. Int. Ed. n.d., n/a,
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# Chapter 5: Disproportionation of uranyl(V) promoted by the benzoate ligand

# Chapter 5: Disproportionation of uranyl(V) promoted by the benzoate ligand

#### **5.1 Introduction**

As mentioned previously, the tendency of uranyl(V) towards disproportionation is well known, and and a large number of studies in aqueous and organic media have been published over the years.<sup>[1]</sup> This process is driven by the low effective charge on U(V) metal centers, resulting in weak electrostatic interactions with external ligands. Due to the high electron density on the axial oxygen ligands in uranyl(V), the direct linkage of two or more uranyl(V) units can be formed leading to the formation of various di- and poly-nuclear assemblies with different geometries (Figure 67).



**Figure 67.** Types of cation-cation interactions (CCIs) encountered with uranyl(V). M represents any other metal cation.

The stability of uranyl(V) CC (cation–cation) complexes is relatively low, as the formation of a CCI between two uranyl(V) moieties enables electron transfer, resulting in the formation of uranyl(VI) and various U(IV) products. However, the stability of these CC complexes is significantly increased in organic media.

Seminal work on the CC complexes of uranyl(V) in organic media was conducted in our group, and this was enabled by the development of the first uranyl(V) starting material  $[(UO_2Py_5)(KI_2Py_2)]_n^{[2]}$ 

and careful choice of supporting ligands. Notably, the use of bulky polydentate ligands was shown to lead to an increase in stability of the UO<sub>2</sub><sup>+</sup> moiety, while the addition of protons accelerates the rate of disproportionation. Interestingly, in the presence of other metal cations, CC complexes with different geometries were obtained, and they varied in stability with respect to disproportionation. The first example of a uranyl(V)-containing CC complex {[UO<sub>2</sub>(dbm)<sub>2</sub>]<sub>4</sub>[K<sub>6</sub>(Py)<sub>10</sub>]}l<sub>2</sub>Py<sub>2</sub>}, reported by the Mazzanti Group, demonstrated that the bidentate dibenzoylmethanate (dbm<sup>-</sup>) ligand can stabilize uranyl(V) and form T-shaped CCIs in the presence of K<sup>+</sup> ions, while on the addition of 18crown6 the CCI species rearranged to afford the dinuclear diamond-shaped CCI complex [UO<sub>2</sub>(dbm)<sub>2</sub>K(18C6)]<sub>2</sub> (Scheme 16).<sup>[3]</sup>



Scheme 16. Synthesis of {[µ<sub>8</sub>-K(Py)]<sub>2</sub>[µ-K(Py)<sub>2</sub>]<sub>2</sub>[UO<sub>2</sub>(dbm)<sub>2</sub>]<sub>2</sub>}<sub>2</sub>I<sub>2</sub> and [UO<sub>2</sub>(dbm)<sub>2</sub>K(18C6)]<sub>2</sub>.

The formation of various uranyl(V) CCI complexes was also observed with different Schiff base ligands (salen<sup>2-</sup> = N,N'-ethylene-bis(salicylideneimine) and acacen<sup>2-</sup> = N,N'-ethylene-bis(acetylacetoneimine)), but in contrast to the dbm CC assembly, the presence of 18crown6 resulted in the tetrameric T-shaped CC complexes. However, when an aromatic analogue of the salen ligand, i.e. salophen, was used, the reaction with the U(V) polymer yielded immediate disproportionation. Although, the encapsulation of K<sup>+</sup> with 18crown6 and 2.2.2.cryptand prevents disproportionation and a structure similar to those obtained with dbm, salen and acacen U(V) CCIs was obtained (Scheme 17). Additionally, the authors investigated the effect of the cation by studying the reactivity of the uranyl(V) complex [Cp\*<sub>2</sub>Co][U<sup>V</sup>O<sub>2</sub>(salen)(py)] with different alkali metal cations. It was shown that upon the addition of potassium and rubidium salts to the stable mononuclear uranyl(V) complex in pyridine solution, the formation of stable tetranuclear assemblies was observed, whereas the presence of lithium cations led to a disproportionation reaction resulting in a formation of a mixture of products. These studies highlight the strong influence of the ligand and cation on the stability and geometry of the uranyl(V) complexes.



Stable U(V) tetramer

**Scheme 17.** The reaction of U(V) polymer with various Schiff bases in the presence and absence of 18c6 and 2.2.2.cryptand.

Additionally, the role of benzoate supporting ligands for the stabilization of uranyl(V) was investigated. Carboxylates are of particular interest as they are common functional groups in the natural environment and tris-carboxylate uranyl(V) species could possess high stability with respect to disproportionation, in analogy to a previoulsy reported stable tris-carbonate U(V) complex,  $[UO_2(CO_3)_3]^{5-[4]}$  (Scheme 18).



Scheme 18. Structure of [UO<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub>]<sup>5-</sup> and an expected structure of [UO<sub>2</sub>(PhCOO)<sub>3</sub>]<sup>2-</sup>.

In a previously published study, our group showed that the reaction of the  $[(UO_2Py_5)(KI_2Py_2)]_n$  precursor with two equiv. of PhCOOK resulted in immediate disproportionation of the uranyl(V), yielding a  $U_{12}^{IV}U_4^{V}O_{24}$  cluster,  $\{[K(Py)_2]_2[K(Py)]_2[U_{16}O_{24}(PhCOO)_{24}(Py)_2]\}$ , and a polymeric uranyl(VI) complex  $\{[UO_2(PhCOO)_3][K(Py)_2]\}_{n,}\}$  (Scheme 19).<sup>[5]</sup> Further investigation has demonstrated that the use of 3 equiv. of PhCOOK under the same reaction conditions leads to the same disproportionation products.



**Scheme 19.** Uranyl(V) disproportionation reaction in presence of potassium benzoate.

These results indicated the possibility of obtaining nanosized clusters from the disproportionation of uranyl(V). However, the intermediates of disproportionation, namely uranyl(V)-containing CCI species have not been isolated for this system.

In this chapter, we investigate the role that K cations play in the disproportionation of the uranyl(V) benzoate system and the possibility of trapping the U(V)–CCI intermediate. Here we show that the encapsulation of potassium with 2.2.2.cryptand did not lead to significant stabilization of uranyl(V), but it did enable the trapping of the U(V)–U(V) benzoate bridging dimer intermediate  $[K(2.2.2.crypt)]_2[UO_2(PhCOO)_2]_2$  (1). Ultimately, this reaction leads to disproportionation yielding a uranyl(VI) complex  $[K(2.2.2.crypt)][(U^{VI}O_2(PhCOO)_3)]$  and a mixed-valence U(IV)/U(V) hexadecanuclear  $U_{16}$  oxo cluster.

#### 5.2 Results and discussion

To investigate the role of K cations in the disproportionation of uranyl(V), the reaction of  $[(UO_2Py_5)(KI_2Py_2)]_n$  with 2 equiv. of PhCOOK was carried out in the presence of a stoichiometric amount of 2.2.2.cryptand (Scheme 20). This reaction led to disproportionation of uranyl(V), indicating that the removal of potassium does not result in higher stability of a putative  $UO_2^+$ -benzoate complex.



**Scheme 20.** The reaction of  $\{[UO_2(Py)_5][KI_2(Py)_2]\}_n$  with 2 equiv. of PhCOOK and 4 equiv. of 2.2.2-cryptand in pyridine.

Two products were isolated in crystalline form, one being the mononuclear uranyl(VI) complex  $[[K(2.2.2.crypt)][(U^{VI}O_2(PhCOO)_3)]$  (2), and the second, the U<sub>16</sub> cluster  $[K(2.2.2.crypt)]_4[U_{16}O_{24}(PhCOO)_{22}]$  (3). Both species strongly resemble the disproportionation products of the reaction of the U(V) precursor with two equiv. of PhCOOK (Scheme 19). The only noticeable difference is in the nature of the counter-cations for both products, being an outer-sphere  $[K(2.2.2.crypt)]^+$  in place of bound K<sup>+</sup> in the previously reported system.

The new large mixed-valence uranium oxo cluster  $[K(2.2.2.crypt)]_4[U_{16}O_{24}(PhCOO)_{22}]$  has a similar topology to that found in previously synthesized  $U_{16}$  clusters:  $[U_{16}O_{24}(PhCOO)_{24}K_4(py)_{10}]^{[5]}$  (obtained from U(V) disproportionation) and  $\{[K(MeCN)]_2[U_{16}O_{22}(OH)_2(PhCOO)_{24}]\}$ ·4MeCN<sup>[6]</sup> (obtained from hydrolysis of U(III) (Figure 68).

It is important to note that the overall quality of the crystal data of the novel  $U_{16}$  cluster is poor but the connectivity was well determined. Both  $[U_{16}O_{24}]$  structures obtained from the disproportionation of uranyl(V) are hexadecanuclear uranium oxo clusters, but the average oxidation state of the uranium in the two clusters differ, being 4.25 for the previously reported cluster<sup>[3]</sup> and 4.625 for **3**  (not reliable). The geometry of the core consists of four fused octahedrons with six uranium ions that are each arranged at the corners of an octahedron. Each one of the eight triangular faces are capped by a triply bridging, or occasionally quadruply bridging, oxygen. The cluster is built from four of these octahedrons. The structure also contains four 2.2.2.cryptand-encapsulated potassium cations per  $U_{16}$  cluster.



**Figure 68.** Molecular structure of the clusters  $[K(2.2.2.cryptand)]_4[U_{16}O_{24}(PhCOO)_{22}]$  (top left) with a  $U_{16}O_{24}$  core (bottom left), and  $[U_{16}O_{24}(PhCOO)_{24}K_4(py)_{10}]$  (top right) with a  $U_{16}O_{24}K_4$  core (bottom right); [K(2.2.2.cryptand)] and H were omitted for clarity; C are represented in grey, O in red, K in purple, N in blue and U in green).

Further, an attempt to synthesize a previously mentioned tris-benzoate uranyl(V) species was pursued. Firstly, a <sup>1</sup>H NMR titration study was performed to identify the reaction products at different stoichiometries in the presence of a stoichiometric amount of 2.2.2.cryptand. On addition of two equivalents of [K(cryptand)][PhCOO], the <sup>1</sup>H NMR signals associated with complex [U<sup>VI</sup>O<sub>2</sub>(PhCOO)<sub>3</sub>]<sup>-</sup> can be identified, indicating immediate disproportionation of the uranyl(V) starting material. Further addition of 1 equiv. of [K(cryptand)][PhCOO] results in the appearance of the peaks of free benzoate ligand in the <sup>1</sup>H NMR spectrum (Figure 69).



**Figure 69.** <sup>1</sup>H NMR spectra (400 MHz,  $C_5D_5N$ , 298 K) of the reaction mixtures from reactions of: 1 equiv. PhCOOK with 1 equiv. of 2.2.2.cryptand (a); 1 equiv. of  $UO_2(NO_3)_2$  with 3 equiv. of PhCOOK and 3 equiv. of 2.2.2.cryptand (b); 1 equiv. of  $[(UO_2Py_5)(KI_2Py_2)]_n$  with 1 equiv. of PhCOOK and 2 equiv. of 2.2.2.cryptand (c); 1 equiv. of  $[(UO_2Py_5)(KI_2Py_2)]_n$  with 2 equiv. of PhCOOK and 3 equiv. of 2.2.2.cryptand (d); 1 equiv. of  $[(UO_2Py_5)(KI_2Py_2)]_n$  with 3 equiv. of PhCOOK and 4 equiv. of 2.2.2.cryptand (d); 1 equiv. of  $[(UO_2Py_5)(KI_2Py_2)]_n$  with 3 equiv. of PhCOOK and 4 equiv. of 2.2.2.cryptand (e).

Upon simultaneous addition of three equivalents of [K(cryptand)][PhCOO] to a solution of  $[(UO_2Py_5)(KI_2Py_2)]_n$  in pyridine with a stoichiometric amount of 2.2.2.cryptand, the same outcome of the reaction was confirmed by <sup>1</sup>H NMR spectroscopy (Figure 70).



10.0 99 9.8 9.7 9.6 9.5 9.4 9.3 9.2 9.1 9.0 8.9 8.8 8.7 8.6 8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7

**Figure 70.** <sup>1</sup>H NMR spectra (400 MHz,  $C_5D_5N$ , 298 K) of the reaction mixtures from reactions of: 1 equiv. PhCOOK with 1 equiv. of 2.2.2.cryptand (bottom); 1 equiv. of  $UO_2(NO_3)_2$  with 3 equiv. of PhCOOK and 3 equiv. of 2.2.2.cryptand (middle); 1 equiv. of  $[(UO_2Py_5)(KI_2Py_2)]_n$  with 3 equiv. of PhCOOK and a stoichiometric amount 2.2.2.cryptand (top).

These results are in agreement with the immediate disproportionation reaction of uranyl(V), yielding a U<sub>16</sub> cluster and a U(VI)-tris-benzoate complex. Another interesting observation from the <sup>1</sup>H NMR study is apparent when comparing the spectrum of the reaction mixture of the  $[(UO_2Py_5)(KI_2Py_2)]_n$  precursor with 1 equiv. of PhCOOK in the presence of 2.2.2.cryptand of previously reported for the reaction of  $[UO_2(NO_3)_2(H_2O)_{0.01}]$  with 1 equv. of PhCOOK after irradiation with a fluorescent lamp for 24 hours. Both spectra show the signals of the mixed-valence U(V)/U(VI) cluster  $[U(UO_2)_5O_5(PhCOO)_5(Py)_7]$  (Figure 71).<sup>[5]</sup>



**Figure 71.** <sup>1</sup>H NMR spectra (400 MHz,  $C_5D_5N$ , 298 K) of reaction mixtures resulting from reactions of: 1 equiv. PhCOOK with 1 equiv. of 2.2.2.cryptand (bottom); 1 equiv. of  $UO_2(NO_3)_2$  with 3 equiv. of PhCOOK and 3 equiv. of 2.2.2.cryptand (middle); 1 equiv. of  $[(UO_2Py_5)(KI_2Py_2)]_n$  with 3 equiv. of PhCOOK and a stoichiometric amount of 2.2.2.cryptand (top).

Crystallization of the reaction mixture of the  $[(UO_2Py_5)(KI_2Py_2)]_n$  precursor with 3 equiv. of PhCOOK in the presence of stoichiometric amount of 2.2.2.cryptand was attempted to gain further insight into the various products of disproportionation and possible intermediates species. When attempting to isolate the products in a crystalline form, several problems were encountered, such as oiling out of the reaction mixture and powder formation. Despite these difficulties, several crystals of the unusual uranyl(V)–uranyl(V) dimer [K(2.2.2.crypt)]<sub>2</sub>[UO<sub>2</sub>(PhCOO)<sub>2</sub>]<sub>2</sub> (**1**) were isolated. Interestingly, similar CCI species were previously reported for neptunyl and plutonyl (Figure 72), <sup>[7]</sup> but not for uranyl(V) cations.



**Figure 72.** Molecular structures of [K(2.2.2.cryptand)]<sub>2</sub>[UO<sub>2</sub>(PhCOO)<sub>2</sub>]<sub>2</sub>, [NpO<sub>2</sub>(PhCOO)(bipy)]<sub>2</sub> and [PuO<sub>2</sub>(PhCOO)(bipy)]<sub>2</sub>; ([K(2.2.2crypt)] and H atoms are omitted for clarity; C are represented in grey, O in red, N in light blue, U in dark green, Np in light green and Pu in blue.

In this complex, the two uranyl(V) moieties are connected by a diamond-shaped CCI and are bridged by two carboxylate groups of two benzoate ligands. The coordination sphere of each uranyl is completed by one carboxylate groups from another benzoate ligand coordinated in a bidentate fashion. The charge of the assembly is balanced by the presence of two [K(2.2.2.crypt)] counterions per dimer. The most striking structural feature of this complex is the short distance between neighboring U atoms (3.3942(4) Å), among the shortest described in the literature. Comparison of the interactinide distances (Np 3.4281(2) Å and Pu 3.4089(13) Å) in the Np and Pu dimers, while taking into account the actinide contraction effect, indicates that the strength of the CCI decreases in the order  $UO_2^+ > NpO_2^+ > PuO_2^+$  as previously reported.<sup>[8]</sup>

Only a few crystals of the uranyl(V) dimer were isolated, precluding further characterization of this compound.

Due to the difficulties in the synthesis of uranyl(V)-benzoate species via a salt metathesis route, an attempt to prepare it by the reduction of the corresponding uranyl(VI)-tris-benzoate complex was performed. On addition of 1 equiv. of  $CoCp^{*}_{2}$  to  $[K(2.2.2.crypt)][U^{VI}O_{2}(PhCOO)_{3}]$  or  $[KU^{VI}O_{2}(PhCOO)_{3}]$  in pyridine, <sup>1</sup>H NMR spectroscopy (Figure 73) indicated the presence of  $[U^{VI}O_{2}(PhCOO)_{3}]^{-}$  peaks and a resonance assigned to Cp\* that corresponds to a Co<sup>III</sup> species. Further addition of the reducing reagent did not result in further reduction as indicated by the shift of the Cp\*-assigned resonance.



**Figure 73.** <sup>1</sup>H NMR spectraum (400 MHz,  $C_5D_5N$ , 298 K) of the reaction mixtures resulting from reactions of: 1 equiv. of  $[KU^{VI}O_2(PhCOO)_3]$  with 1 equiv. of  $CoCp^*_2$  (bottom); 1 equiv. of  $[KU^{VI}O_2(PhCOO)_3]$  with 2 equiv. of  $CoCp^*_2$  (middle); and 1 equiv.  $[K(2.2.2.crypt)][U^{VI}O_2(PhCOO)_3]$  with 1 equiv. of  $CoCp^*_2$  (top), showing only the peaks of the uranyl(VI) complex  $[K(2.2.2.crypt)][U^{VI}O_2(PhCOO)_3]$ .

#### 5.3 Conclusions

Herein, we have described a study of the effect of potassium cations on the outcome of disproportionation reactions of a uranyl(V)-benzoate system. We hypothesize that the U(V)–U(V) dimer  $[K(2.2.2.cryptand)]_2[UO_2(PhCOO)_2]_2$ , which is a likely intermediate in the disproportionation of the uranyl(V)-benzoate complex, eventually results in the formation of the uranyl(VI) complex  $[[K(2.2.2.crypt)][(U^{VI}O_2(PhCOO)_3)]$  (**2**) and the U<sub>16</sub> cluster  $[K(2.2.2.crypt)]_4[U_{16}O_{24}(PhCOO)_{22}]$  (**3**). (Scheme 23).



unidentified disproportionation products

**Scheme 21.** Proposed reaction pathway of uranyl(V) with 2 and 3 equiv. of PhCOOK in the presence of 2.2.2cryptand.

The rare uranyl(V) diamond CCI complex **1** indicates that disproportionation can be promoted by the bridging benzoate ligands, bringing two metal centers in close proximity, potentially enabling electron transfer. The strong basicity of uranyl(V) oxo groups might result in competition with the benzoate ligand for coordination to U-metal centre, potentially preventing the formation of uranyl(V) tris-benzoate species.

#### 5.4 Experimental

#### **General Considerations.**

All manipulations were carried out under an inert argon atmosphere using Schlenk techniques and an MBraun glovebox equipped with a purifier unit. The water and oxygen levels were always kept at less than 1 ppm. The solvents were purchased from Aldrich or Cortecnet (deuterated solvents) in their anhydrous form, conditioned under argon and vacuum distilled from K/benzophenone (diisopropylether, hexane, pyridine, toluene, benzene and THF) or freeze-degassed and stored over activated 3 Å molecular sieves (pyridine-d<sub>5</sub>). Depleted uranium was purchased from IBILABS, USA.

 $[(UO_2Py_5)(KI_2Py_2)]_n$  was synthesized as previously described.<sup>[2]</sup>  $[UO_2(NO_3)_2(H_2O)_6]$  was purchased from Sigma-Aldrich : Fluka.  $[UO_2(NO_3)_2]$  was obtained by high vacuum drying of  $[UO_2(NO_3)_2(H_2O)_6]$ for 5 days at 120°C. Benzoic acid, 2.2.2.cryptand and decamethylcobaltocene were purchased from Aldrich. 2.2.2.cryptand and decamethylcobaltocene were dried under high vacuum and used without further purification. PhCOOH was purified by sublimation. Potassium benzoate was isolated from the reaction of benzoic acid with potassium hydride in THF.

<sup>1</sup>H NMR experiments were carried out using NMR tubes adapted with J. Young valves. <sup>1</sup>H NMR spectra were recorded on Bruker 400 MHz spectrometer. NMR chemical shifts are reported in ppm with solvent as internal reference.

**Caution:** Depleted uranium (primary isotope <sup>238</sup>U) is a weak  $\alpha$ -emitter (4.197 MeV) with a halflife of 4.47×10<sup>9</sup> years. Manipulations and reactions should be carried out in monitored fume hoods or in an inert atmosphere glovebox in a radiation laboratory equipped with  $\alpha$ - and  $\beta$ counting equipment.

#### Synthetic procedures

#### Isolation of [K(2.2.2.cryptand)]<sub>2</sub>[UO<sub>2</sub>(PhCOO)<sub>2</sub>]<sub>2</sub> (1).

2.2.2.cryptand (11.4 mg, 0.03 mmol, 1 eq.) was added to a suspension of [(UO<sub>2</sub>Py<sub>5</sub>)(KI<sub>2</sub>Py<sub>2</sub>)] (33.8 mg, 0.03 mmol, 1 eq.) in pyridine (2.0 mL). The resulting orange solution was added to a stirred colorless solution containing potassium benzoate (14.4 mg, 0.09 mmol, 3 eq.) and 2.2.2.cryptand (33.9 mg, 0.09 mmol, 3 eq.) in pyridine (2.0 mL). The resulting light brown solution was stirred for 12 hours. Slow diffusion of hexane into the resulting brown solution afforded light orange X-ray quality crystals of [K(2.2.2.cryptand)]<sub>2</sub>[UO<sub>2</sub>(PhCOO)<sub>2</sub>]<sub>2</sub> (**1**). Only a few crystals of complex **1** were isolated, and thus no elemental analysis or yield are reported for this compound.

#### Isolation of [K(2.2.2.crypt)][(U<sup>VI</sup>O<sub>2</sub>(PhCOO)<sub>3</sub>)] (2) and [K(2.2.2.crypt)]<sub>4</sub>[U<sub>16</sub>O<sub>24</sub>(PhCOO)<sub>22</sub>] (3)

2.2.2.cryptand (11.4 mg, 0.03 mmol, 1 eq) was added to a suspension of  $[(UO_2Py_5)(KI_2Py_2)]$  33.8 mg, 0.03 mmol, 1 eq.) in pyridine (2.0 mL). The resulting orange solution was added to a stirred colorless solution containing potassium benzoate (9.6 mg, 0.06 mmol, 2 eq.) and 2.2.2.cryptand (22.6 mg, 0.06 mmol, 2 eq.) in pyridine (2.0 mL). The resulting light brown solution was stirred for 12 hours, then taken to dryness. The resulting solid was dissolved in THF and slow diffusion of DIPE into the resulting brown solution afforded yellow X-ray quality crystals of [K(2.2.2.crypt)][(U<sup>VI</sup>O<sub>2</sub>(PhCOO)<sub>3</sub>)] (**2**) and brown X-ray quality crystals of [K(2.2.2.crypt)]4[U<sub>16</sub>O<sub>24</sub>(PhCOO)<sub>22</sub>] (**3**). No elemental analysis or yield are reported for these two products, as they could not be separated.

#### Reduction of $[KU^{VI}O_2(PhCOO)_3]$ with $Cp^*_2Co$ .

A suspension of potassium benzoate (12.2 mg, 0.076 mmol, 3 eq.) in 1 mL of pyridine was added to a yellow suspension of  $[UO_2(NO_3)_2]$  (10 mg, 0.025 mmol, 1 eq.) in 1 mL of pyridine. A brown solution of decamethylcobaltocene (8.2 mg, 0.025 mmol, 1 eq.) in pyridine (1.0 mL) was added to the resulting yellow suspension. <sup>1</sup>H NMR spectroscopy indicated the presence of the resonances assigned to the uranyl(VI)-trisbenzoate species. Further addition of 1 equiv. of Cp\*<sub>2</sub>Co did not result in reduction, as indicated by <sup>1</sup>H NMR spectroscopy (Figure 73).

#### Reduction of $[K(2.2.2.crypt)][U^{VI}O_2(PhCOO)_3]$ with $Cp^*_2Co$ .

2.2.2.cryptand (28.6 mg, 0.076 mmol, 3 eq.) was added to a suspension of a suspension of potassium benzoate (12.2 mg, 0.076 mmol, 3 eq.) in 2 mL of pyridine. The resulting colorless solution was added to a yellow suspension of  $[UO_2(NO_3)_2]$  (10 mg, 0.025 mmol, 1 eq.) in 1 mL of pyridine. A brown solution of decamethylcobaltocene (8.2 mg, 0.025 mmol, 1 eq.) in pyridine (1.0 mL) was added to the resulting yellow suspension. <sup>1</sup>H NMR spectroscopy indicated the presence of the result not result in reduction, as indicated by <sup>1</sup>H NMR spectroscopy (Figure 73).

#### References

[1] L. J. Heidt, K. A. Moon, J. Am. Chem. Soc. **1953**, 75, 5803–5809.

[2] L. Natrajan, F. Burdet, J. Pecaut, M. Mazzanti, J. Am. Chem. Soc. 2006, 128, 7152–7153.

[3] G. Nocton, P. Horeglad, J. Pecaut, M. Mazzanti, J. Am. Chem. Soc. 2008, 130, 16633–16645.

[4] 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.

[5] L. Chatelain, S. White, R. Scopelliti, M. Mazzanti, *Angew. Chem.-Int. Edit.* **2016**, *55*, 14323–14327.

[6] B. Biswas, V. Mougel, J. Pécaut, M. Mazzanti, Angew. Chem.-Int. Edit. 2011, 50, 5745–5748.

[7] I. A. Charushnikova, N. N. Krot, Z. A. Starikova, *Radiochimica Acta* **2007**, *95*, 495–499.

[8] N. N. Krot, M. S. Grigoriev, *Russian Chemical Reviews* 2004, 73, 89–100.

Chapter 6: Structural Snapshots of Cluster Growth from  $\{U_6\}$  to  $\{U_{38}\}$  During the Hydrolysis of UCl<sub>4</sub>

# Chapter 6: Structural Snapshots of Cluster Growth from $\{U_6\}$ to $\{U_{38}\}$ During the Hydrolysis of UCl<sub>4</sub>

# 6.1 Introduction

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

However, the chemistry of uranium oxide clusters remains underdeveloped especially compared to transition metal polyoxometalates.<sup>[1b, 1c, 7]</sup> Moreover, most of the reported uranium clusters <sup>[1b, 8]</sup> <sup>[1a]</sup> contain uranyl(VI) cations supported by peroxide ligands. A significantly lower number of clusters containing uranium in lower oxidation states (U(IV) and U(V)) has been characterized.<sup>[1a, 9]</sup> By far the most common structural motif for U(IV) clusters remains the hexameric octahedron with a  $[U_6O_4(OH)_4]$  or a  $[U_6O_8]$  core.<sup>[6a, 10]</sup> Low nuclearity (tetra- or penta-nuclear) U(V)/U(IV) oxo clusters have also been isolated from the disproportionation of uranyl(V) complexes of polydentate Schiff bases in non protic media.<sup>[11]</sup>

Our group reported the first examples of high nuclearity uranium clusters (U(IV) and U(IV)/U(V)) that were isolated by controlling the rate of hydrolysis of a uranium(III) precursor ([UI<sub>3</sub>(thf)<sub>4</sub>]) in organic solution.  $\{U_{10}\}$ , [10g]  $\{U_{12}\}^{[10b]}$  and  $\{U_{16}\}$ 

clusters<sup>[10g]</sup> with  $[U_{10}O_8(OH)_6]$ ,  $[U_{12}O_{12}(OH)_8]$  and  $[U_{16}O_{22}(OH)_2]$  cores respectively, were prepared, by using triflate (CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>) <sup>[10b]</sup> or benzoate (PhCOO<sup>-</sup>) organic capping ligands.<sup>[10g]</sup> More recently, the use of the controlled hydrolysis strategy in the presence of the benzoate capping ligand carried out under solvothermal conditions led to the isolation of a large {U<sub>38</sub>} cluster. <sup>[12]</sup> <sup>[13]</sup>

In spite of these recent reports, the cluster chemistry of uranium in low oxidation states remains practically unexplored with a limited number of structures being reported. Moreover, although several studies were directed to identify the factors controlling the formation of hexanuclear clusters in aqueous solution,<sup>[1c, 6b, 6d, 10i, 10k, 14]</sup> the parameters leading to larger U(IV) assemblies and cluster growth remain undetermined.

Here we report several uranium clusters with new shapes and sizes, including a large  $\{U_{24}\}$  cluster, that were isolated from the controlled hydrolysis of UCl<sub>4</sub> in organic solution. We also show how, ligand/metal ratio, reaction time, addition of base and temperature determine the growth of different size clusters ( $\{U_6\}, \{U_{13}\}, \{U_{16}\}, \{U_{24}\}, \{U_{38}\}$ ) from the same precursor.

<sup>1</sup> Portions of this chapter have been published:

L. Chatelain, R. Faizova, F. Fadaei-Tirani, J. Pécaut, M. Mazzanti, *ACIE* **2019**, *58*, 3021–3026.<sup>[21]</sup> Author contributions: L.C. has isolated clusters 2, 3, 4, 5 and 7 and fully characterized cluster 2, 3 and 4. R.F. has isolated cluster 6 and characterized clusters 5 and 6. L.C. and R.F. performed NMR and UV-Vis experiments, analyzed the data and wrote the original draft of the manuscript. F.F.T. and J.P. measured and analyzed the diffractions data. M.M. originated the central idea, coordinated the work, provided funding and analysed the experimental data. L.C., R. F. and M. M. wrote the manuscript.

## 6.2 Results and discussion

Controlled hydrolysis of UCl<sub>4</sub> in pyridine (or in acetonitrile followed by redissolution in pyridine) in the presence of two equivalents of potassium benzoate and two equivalents of water led to the hexameric U(IV) octahedron  $[U_6O_4(OH)_4(PhCOO)_{12}(Py)_3]$ , **1** previously obtained from the hydrolysis of Ul<sub>4</sub> or Ul<sub>3</sub> in similar reaction conditions (Scheme 22).<sup>[10d]</sup>



**Scheme 22**. Synthesis of clusters **1** in pyridine from U(IV) chloride and from uranium(III) or uranium(IV) iodide precursors in pyridine or MeCN with trace amount of pyridine.

The UV/Vis spectra of the reaction mixtures are all consistent with uranium(IV), with broad absorptions in the range of  $\lambda$ =600 to 700 nm assigned to H<sub>4</sub> $\rightarrow$ <sup>3</sup>P<sub>0</sub>, <sup>3</sup>H<sub>4</sub> $\rightarrow$ <sup>1</sup>G<sub>4</sub>, and <sup>3</sup>H<sub>4</sub> $\rightarrow$ <sup>1</sup>D<sub>2</sub> transitions. UV-visible studies indicate that the formation of the cluster is slower for UCl<sub>4</sub> than for UI<sub>4</sub> (Figure 74).



**Figure 74.** UV-visible spectra of  $[UI_4(OEt_2)_2]$  (c = 1.14.10<sup>-3</sup> M) (left) and  $[UCI_4]$  (c = 2.94.10<sup>-3</sup> M) (right) in pyridine and the evolution over time of the reaction mixtures from the hydrolysis of  $[UI_4(OEt_2)_2]$  and  $[UCI_4]$  in pyridine in the presence of potassium benzoate.

In contrast when the hydrolysis reaction is carried out in the presence of larger amounts of capping ligand (three-six equivalents of potassium benzoate) in acetonitrile an insoluble green/white precipitate was obtained that was only soluble in pyridine. Slow diffusion of diisopropylether (DIPE) into the pyridine solution allowed for the crystallization of the new oxo cluster  $[U_6O_4(PhCOO)_{16}(Py)_4]$  **2** with a  $U_6O_4$  core (Figure 75) in 62% yield.



**Figure 75.** Molecular structure of **2** and  $U_6O_4$  core. (Ellipsoids are set at 30% probability). H atoms, disorder and solvent molecules are removed for clarity, ligands represented as pipes. U green, O red, C grey, N blue. (Atoms A are found with the inversion center). Average bond lengths [Å]: U- $\mu_3O=2.24(8)$ .

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

Proton NMR studies of **2**  $[U_6O_4(PhCOO)_{16}(Py)_4]$  revealed a well-defined spectrum (Figure 76) and showed that cluster  $[U_6O_4(PhCOO)_{16}(Py)_4]$  **2** is stable in pyridine solution for more than one month and it retains its hexanuclear structure according to Pulsed-Field Gradient Stimulated Echo (PFGSTE) diffusion NMR experiments (Appendix 4: Table S1).



Figure 76. <sup>1</sup>H NMR spectrum (200 MHz, CD<sub>3</sub>CN, 298 K) of crystals of 2.

Therefore, the structure of the hydrolysis product is determined (with all other conditions being equivalent) by the UCl<sub>4</sub>:benzoate ratio. Clusters of larger size were not isolated from pyridine at any UCl<sub>4</sub>:benzoate ratio.

In contrast, the hydrolysis of UCl<sub>4</sub> with 2 equiv. of water in the presence of 2 equiv. of potassium benzoate in acetonitrile resulted in the isolation of two discrete U(IV) oxo/hydroxo clusters with novel [U<sub>13</sub>K<sub>x</sub>O<sub>16</sub>] (x=2 or 4) cores and the chemical formulas [U<sub>13</sub>K<sub>4</sub>O<sub>12</sub>(OH)<sub>4</sub>(PhCOO)<sub>12</sub>Cl<sub>14</sub>]Cl<sub>2</sub> **3** and [U<sub>13</sub>K<sub>2</sub>O<sub>9</sub>(OH)<sub>7</sub>(PhCOO)<sub>12</sub>Cl<sub>16</sub>]Cl **4**, respectively. This result indicates that larger clusters can be obtained in acetonitrile for the UCl<sub>4</sub>:benzoate ratio of 2. Crystals of these two species were isolated either from a concentrated acetonitrile solution or by slow diffusion of DIPE into an acetonitrile solution after 3 days. The solid-state structures of **3** and of **4** are presented in Figure 77 and Appendix4: Fig. S6. In both clusters the geometrical arrangement of the 13 uranium atoms but the charge of the two clusters is different due to differing number of potassium ions and chloride ligands and to the different ratio of bridging oxide/hydroxides.



**Figure 77.**  $[U_{13}K_4O_{12}(OH)_4]$  core in the molecular structure of  $[U_{13}K_4O_{12}(OH)_4(PhCOO)_{12}Cl_{14}]Cl_2$  (**3**) (left) and  $[U_{13}K_2O_9(OH)_7]$  core in the molecular structure of of  $[U_{13}K_2O_9(OH)_7(PhCOO)_{12}Cl_{16}]Cl$ , 4 (right) (ellipsoids are set at 30% probability). U green, O red, C grey, N blue, Cl light green, K purple, H white.

The structure of [U<sub>13</sub>K<sub>4</sub>O<sub>12</sub>(OH)<sub>4</sub>(PhCOO)<sub>12</sub>Cl<sub>14</sub>]Cl<sub>2</sub> **3** consists of 13 uranium atoms connected together by bridging oxide (12), hydroxide (4), chloride (14) and benzoate ligands (12) (Figure 77; Appendix 4: Fig. S6). The cluster size is about 21×20×9 Å<sup>3</sup>, with the largest U-U distance being 11.1401(16) Å. The geometrical arrangement of the 13 uranium atoms can be described as two octahedrons sharing U4 as a common summit (inversion center located on U4 at the intersection between a mirror and a 2-fold axis). Two additional uranium ions U5 are located in the plane between the two octahedrons, with a U5-U4-U5 angle of 180.0°. Four potassium ions are also present in this plane. The calculated BVS is in agreement with the presence of 13 U(IV) ions. Four triply bridging oxides and two triply bridging hydroxides alternatively cap eight triangular faces defined by the U1, U2, U3 atoms and their symmetry equivalents. The position of the hydroxo ligands in the crystal structure has been assigned on the basis of geometrical parameters. The mean U-O distances are 2.268(65)Å for the  $\mu_3$ -O groups and 2.455(98) Å for the  $\mu_3$ -OH groups. Four  $\mu_4$ -oxides cap four faces of the two octahedrons and they bridge three uranium atoms of the octahedrons (mean U- $\mu_4$ O distance of 2.36(13) Å). Eight benzoate ligands bridge eight external edges of each octahedron while four additional benzoates bridge the U1, U5 and K2 atoms connecting one octahedron to the middle plane. Eight bridging chloride  $\mu_2$ -Cl<sup>-</sup> connect U1, U3 and their 6 equivalent positions to the closest potassium atom among K2 atom. Two chloride ligands bridge two potassium ions. Then four μ<sub>3</sub>-Cl<sup>-</sup>

connect U3, K2 and U5 ions and their equivalent positions. The presence of 12 oxo ligands, 4 hydroxo ligands, 12 benzoates, 14 coordinated chlorides and two free chloride anions adds up to an overall charge of -56 for complex **3**, which is distributed over the 13 uranium(IV) centers. One acetonitrile molecule is also found in the coordination sphere of U2 in axial position.

The second type of crystals from the controlled hydrolysis of [UCl<sub>4</sub>] in the presence of potassium benzoate shows the presence of the oxo/hydroxo cluster  $[U_{13}K_2O_9(OH)_7(PhCOO)_{12}Cl_{16}]Cl 4$  with a  $U_{13}K_2O_{16}$  core. The structure of the  $U_{13}O_{16}$  core in **4** is similar to the one in **3**, consisting of 13 uranium atoms arranged as two octahedrons sharing U4 as a common summit and two other uranium U3 ions present in the middle plane between the two octahedrons. However, only two potassium ions are present in this plane, and they are perpendicular to the line U3-U4-U3 (U3-U4-U3 angle 180.0°, U3-U4-K1 angle 90.0°). The uranium and potassium ions are connected by  $\mu_3$ - and  $\mu_4$ -oxide,  $\mu_3$ -hydroxide, chloride and benzoate ligands. Only the position of four hydroxo ligands in the crystal structure has been assigned on the basis of geometrical parameters. The mean U-O distances are 2.27(4) Å for the μ<sub>3</sub>-O groups and 2.46(9)Å for the μ<sub>3</sub>-OH groups. Four μ<sub>4</sub>-oxides cap the faces of four octahedrons and they bridge three uranium atoms of the octahedrons (mean  $U-\mu_4O$  distance of 2.38(12)Å) and one potassium ion (K-O: 3.026(9)Å). Four other  $\mu_4$ -oxo groups bridge the U3 atom to three uranium atoms of the octahedron (mean U-O distance of 2.38(12) Å). Eight benzoate ligands bridge eight external edges of each octahedron while four additional benzoates bridge the U3 and U5 atoms connecting one octahedron to the middle plane. Twelve bridging chloride ligands  $\mu_2$ -Cl<sup>-</sup> connect U2/U3, U2/K1 and U5/K1 and their equivalents. Then four μ<sub>3</sub>-Cl<sup>-</sup> ligands connect U2, U3 and K1 ions and their crystallographically equivalent U ions. The three extra negative charges found in this cluster may be compensated by the presence of three delocalized hydroxides ligands consistent with the presence of the neutral uranium(IV) compound  $[U_{13}K_2O_9(OH)_7(PhCOO)_{12}Cl_{16}]Cl$ . An alternative interpretation of the cluster formula would involve a mixed-oxidation states U(IV)/U(V) complex containing 10 U(IV) and 3 U(V). However, the bond valence sum calculation is in agreement with the presence of 13 U(IV). Moreover, the formation of U(V) species from the hydrolysis of U(IV) is improbable while delocalization of hydroxides ligand over different cluster positions has already been reported. As the two clusters **3** and **4** crystallize under the same conditions, we were not able to separate them. Moreover, only a very small amount of the crystalline mixture of **3** and **4** was reproducibly isolated (15% yield).

The UV-visible spectrum of the mixture of the two clusters features a characteristic band around 690 nm assigned to uranium(IV) (Figure 78).<sup>[16]</sup>



**Figure 78.** Absorption spectra of the crystals of **3** and **4** ( $c = 4,3.10^{-3}$  M) in acetonitrile.

The <sup>1</sup>H NMR spectrum in CD<sub>3</sub>CN of the reaction mixture, obtained after hydrolysis of UCl<sub>4</sub> with 2 equiv. of water in the presence of 2 equiv. of potassium benzoate, is broad, whereas the isolated mixture of **3** and **4** gives a well-defined <sup>1</sup>H NMR spectrum (Figure 79).



**Figure 79.** <sup>1</sup>H NMR spectrum (200 MHz, 298 K) of the reaction mixture after reacting UCl<sub>4</sub> with 2 equiv. of H<sub>2</sub>O in the presence of PhCOOK in CD<sub>3</sub>CN (A); of a mixture of isolated crystals of **3** and **4** in CD<sub>3</sub>CN (B); of a mixture of isolated crystals of **3** and **4** in C<sub>5</sub>D<sub>5</sub>N (C); and in [CD<sub>3</sub>CN after <sup>1</sup>H NMR spectrum recorded in C<sub>5</sub>D<sub>5</sub>N (D).

Attempts to isolate larger amounts led to a green powder, which does not have the well-defined proton NMR spectrum of **3** and **4**. These observations led us to think that a larger number of species is present in the acetonitrile reaction mixture.

These results reveal that the nature of the precursor has a significant effect on the structure and nuclearity of the final cluster obtained from controlled hydrolysis in acetonitrile in presence of the same capping ligand. Notably, from the hydrolysis of UI<sub>3</sub>, performed in the same conditions as for UCl₄. mixture of discrete oxo/hydroxo clusters with а onlv а  $[U_{10}O_{14}]$ core (([U<sub>10</sub>O<sub>8</sub>(OH)<sub>6</sub>(PhCOO)<sub>12.8</sub>I<sub>3.2</sub>(H<sub>2</sub>O)<sub>4</sub>(MeCN)<sub>3</sub>]I<sub>2</sub>)<sup>[10g]</sup> was isolated. A similar result was obtained for hydrolysis of [UI<sub>4</sub>(OEt<sub>2</sub>)<sub>2</sub>] in the presence of potassium benzoate in acetonitrile (see experimental section). The two products of hydrolysis ([U<sub>13</sub>O<sub>16</sub>] and [U<sub>10</sub>O<sub>14</sub>]) display important structural differences (Figure 80). In particular, beside the difference in nuclearity, the ratio between Cl/benzoate or I/benzoate is 1.17 (14/12) in **3** and **4**, and 0.25 (3.2/12.8) in the [U<sub>10</sub>O<sub>14</sub>] cluster, respectively. The higher affinity of U(IV) for hard donors such as chloride and benzoate may slow down the Cl/benzoate ligand exchange and favor the formation of the larger [U<sub>13</sub>O<sub>16</sub>] cluster from UCl<sub>4</sub>.



**Figure 80.** ORTEP diagram of the  $U_{13}O_{16}$  core of cluster **4** (left) and  $U_{10}O_{14}$  core of the previously reported cluster  $[U_{10}O_8(OH)_6(PhCOO)_{12.8}I_{3.2}(H_2O)_4(MeCN)_3]I_2.5MeCN$  (ellipsoids are set at 30% probability). U green, O red, C gray, H white and K purple.

However, the  $[U_{10}O_{14}]$  is also probably present in the reaction mixture obtained after 56 hours upon controlled hydrolysis of UCl<sub>4</sub> in acetonitrile. Notably, the addition of base (4 equiv. of pyridine) to this mixture yielded after 3 days at 25 °C the new {U<sub>16</sub>} cluster [U<sub>16</sub>O<sub>15</sub>(OH)<sub>8</sub>(PhCOO)<sub>26</sub>(Py)<sub>2</sub>] **5** (with a novel [U<sub>16</sub>O<sub>15</sub>(OH)<sub>8</sub>] core in 54 % yield (Figure 81).



**Figure 81.** ORTEP diagram of the  $[U_{16}O_{15}(\mu_3-OH)_8]$  (left) and U16 (right) core in **5** (ellipsoids are set at 30% probability). U green, O red, H white. Average bond lengths [Å]: U- $\mu_3$ O=2.24(3), U- $\mu_4$ O=2.37(8), U- $\mu_3$ OH=2.43(5).

The structure of **5** is likely to assemble upon the deprotonation of the hydroxo groups of an  $[U_{10}O_{14}]$  species present in acetonitrile and further condensation with two additional {U<sub>6</sub>} units. Assembling of **5** from  $[U_{13}O_{16}]$  would require a complete disruption of the cluster. The X-ray crystal structure of **5** shows the presence of a discrete oxo/hydroxo cluster with a  $[U_{16}O_{23}]$  core and a 1.6:1 benzoate/uranium ratio. The geometrical arrangement of the uranium atoms in the  $[U_{16}O_{23}]$  core can be described as four fused octahedrons with sixteen crystallographically inequivalent uranium atoms with U-U distances ranging from 3.764(1) Å to 3.858(1) Å. Each octahedron shares three edges of three different neighboring octahedrons. The overall cluster size is approximately 24×21×22 Å<sup>3</sup> while the core structure is 7.73 Å wide (U3-U5 distance) and 8.60 Å long (U2-U8 distance). The calculated BVS for the uranium atoms is in agreement with the presence of 16 U ions in the +IV oxidation state. An overall positive charge of 64 for the cluster is consistent with the presence of 8 hydroxo and 15 oxo groups in the neutral complex.

The structure of **5** differs significantly from the previously reported {U<sub>16</sub>} oxo cluster  $(\{[K(MeCN)]_2[U_{16}O_{22}(OH)_2(PhCOO)_{24}]\})^{[10g]}$  obtained by addition of a strong base (TMEDA) to the products of controlled hydrolysis of Ul<sub>3</sub> (Figure 82). Both clusters contain 16 uranium atoms arranged in four fused octahedra sharing common edges. However, the two cores have a different shape and the uranium ions have different oxidation states. The structural parameters and BVS indicate that the sixteen uranium atoms of **5** are in the +IV oxidation state, while the [U<sub>16</sub>O<sub>22</sub>(OH)<sub>2</sub>] cluster consists of twelve uranium(IV) ions and four uranium(V) ions. This difference arises from the difference in uranium oxidation state of the precursors used in these reactions. The uranium(III)

precursor is very reactive and unstable towards water. Concomitant with its hydrolysis, U(III) is oxidized to form U(IV) or U(V), while the hydrolysis of U(IV) does not result in a redox reaction.



**Figure 82.** Arrangement of the octahedrons in  $[U_{16}O_{15}(OH)_8(PhCOO)_{26}(Py)_2]$ , **5** (left) and in the previously reported { $[K(MeCN)]_2[U_{16}O_{22}(OH)_2(PhCOO)_{24}]$ } (right).

After two weeks the larger cluster  $[U_{24}O_{30}(OH)_2(PhCOO)_{30}(Py)_4Cl_4]$ , **6**, with a  $[U_{24}O_{30}(OH)_2]$  core was isolated. This cluster can be built either from  $[U_{16}O_{15}(OH)_8]$  or directly from two  $[U_{13}O_{16}]$  clusters through further condensation with two additional  $\{U_6\}$  units promoted by further deprotonation. Compounds **5** and **6** have well identified and unique morphology and could be reliably isolated from the same mother liquor by a time-resolved crystallization process<sup>[17]</sup> where crystals of each cluster are removed from solution before crystallization of the second species.

Solubility (the two complexes have both very low solubility, once formed, in acetonitrile) and concentration do not affect the process indicating that the cluster growth after pyridine addition is time-dependent. A similar time-dependency can be anticipated for the assembly of  $\{U_{13}\}$  from  $\{U_6\}$ in the absence of base. Notably, if pyridine is added to the hydrolytic acetonitrile mixture after periods of time shorter than 56 hours, only the  $[U_6O_8]$  cluster **1** is obtained suggesting that the timedependent formation of larger clusters such as  $\{U_{13}\}$  or  $\{U_{10}\}$  is required in order for the addition of base to result in further assembly.

The X-ray crystal structure of **6** reveals the presence of a novel  $[U_{24}O_{30}(OH)_2]$  core (Figure 83) (containing 24 uranium atoms structurally arranged as six fused octahedra. These six octahedrons can be described as three pairs of fused octahedrons, sharing one edge, and perpendicular to each other. In total, each octahedron shares three edges of three different neighboring octahedrons. Two additional uranium centers (U2 and U2A) are located on the straight line defined by the two central uranium atoms (U6 and U6A).



**Figure 83.** ORTEP diagrams of the  $[U_{24}O_{30}(OH)_2]$  (left) and  $U_{24}$  (right) core in **6** (ellipsoids are set at 30% probability). U green, O red, H white. (atoms A are found with the inversion center). Average bond lengths [Å]: U- $\mu_3$ O=2.26(5), U- $\mu_4$ O=2.36(6), U- $\mu_3$ OH=2.37(5).

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

The results obtained in acetonitrile differ significantly from those obtained in pyridine where only the hexanuclear cluster is formed. They also differ from what recently obtained by Knope and coworkers from dissolution of UCl<sub>4</sub> and hydroxybenzoic acid in water or a 50:50 mixture water/acetonitrile where only hexanuclear clusters are formed that evolve upon heating (75/100°C) to yield UO<sub>2</sub> nanoparticles.<sup>[10k]</sup>

We also investigated the influence of the temperature on our system by refluxing, for 32 hours at 82°C and atmospheric pressure under argon, the mixture of UCl<sub>4</sub> reacted with two equivalents of water and two equivalents of potassium benzoate in acetonitrile. The slow diffusion of DIPE into the mother liquor yielded a few dark green X-ray quality crystals of [U<sub>38</sub>O<sub>56</sub>Cl<sub>18</sub>(PhCOO)<sub>22</sub>(CH<sub>3</sub>CONH<sub>2</sub>)<sub>10</sub>], **7** combined to a few crystals of the U<sub>13</sub>K<sub>x</sub>O<sub>16</sub> cluster and a darker solid identified as UO<sub>2</sub> by X-ray powder crystallography (XPRD). As previously observed for the hydrolysis of UCl<sub>4</sub> in solvothermal conditions<sup>[12] [13]</sup> larger amounts of water used in the hydrolysis (400 equiv.) result in the unique formation of UO<sub>2</sub>.



Scheme 23. Synthesis of clusters 1, 3, 4, 5, 6, and 7 from the hydrolysis of UCl<sub>4</sub>.

The X-ray crystal structure of **7** reveals the presence of a discrete oxo cluster with a [U<sub>38</sub>O<sub>56</sub>] core, with a fluorite-type structural packing (Figure 84). The structure consists of 38 uranium atoms connected together by bridging oxides (56) forming the [U<sub>38</sub>O<sub>56</sub>] core, surrounded by chloride (18), benzoate (22) and acetamide (10) ligands. The cluster size is about 26×25×23 Å<sup>3</sup>, with the largest U-U distance being 12.1 Å. The geometrical arrangement of the 38 uranium atoms in the structure can be described as thirteen fused octahedrons with U-U distances ranging from 3.584(1) Å to 3.8424(7) Å. Each external octahedron shares five edges of five different neighboring octahedrons. Thus, the center of the octahedrons forms a centered cuboctahedron and each external uranium ion is placed at the summit of a truncated octahedron.



**Figure 84.** Ortep diagram of the  $[U_{38}O_{56}]$  core in **7** and arrangement of the octahedrons (Ellipsoids are set at 30% probability). U green, O red. Average bond lengths [Å]: U- $\mu_3$ O=2.24(3), U- $\mu_4$ O=2.36(3).

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

The acetamide ligand results from the partial hydrolysis of acetonitrile bound to the acidic metal center catalyzed by H<sup>+</sup> released during the formation of the cluster. Nitriles are extremely resistant to hydrolysis, but Lewis acidic metal ions were shown to significantly enhance hydrolysis rates.<sup>[18]</sup> The core of the structure of **7** is closely related to that of the  $[U_{38}O_{56}Cl_{18}(PhCOO)_{24}(THF)_8]$  cluster isolated from the solvothermal hydrolysis of UCl<sub>4</sub> in THF in the presence of benzoic acid <sup>[12]</sup> and of the Pu(IV) nanoclusters Li<sub>14</sub>(H<sub>2</sub>O)<sub>n</sub>[Pu<sub>38</sub>O<sub>56</sub>Cl<sub>54</sub>(H<sub>2</sub>O)<sub>8</sub>] and Li<sub>2</sub>[Pu<sub>38</sub>O<sub>56</sub>Cl<sub>42</sub>(H<sub>2</sub>O)<sub>20</sub>], which were isolated from colloidal solutions of plutonium.<sup>[2e, 6g]</sup> While the assignment of the composition and uranium charge remained ambiguous in the previously reported [U<sub>38</sub>O<sub>56</sub>Cl<sub>18</sub>] cluster, the composition and the uranium oxidation state (+IV) are non-ambiguous in **7**.Due to the very low yield in **7** and to the presence of multiple products further characterization of this cluster was not possible. From a comparison of the structure of {U<sub>24</sub>} and {U<sub>38</sub>} it can be clearly seen that the latter builds up from the first through the deprotonation of two hydroxoligands still present in the {U<sub>24</sub>} cluster. Attempts to build {U<sub>38</sub>} from {U<sub>24</sub>} by using different bases have not been yet successful but should provide a more convenient route to {U<sub>38</sub>}.

# 6.3 Conclusions

In summary (Figure 6) during the hydrolysis of UCl<sub>4</sub> in presence of the benzoate ligand in coordinating solvents (pyridine), the formation of the hexanuclear  $[U_6O_4(OH)_4]$  cluster occurs rapidly and formation of larger assembly is not observed. In contrast the hexanuclear clusters assemble slowly in acetonitrile solution, probably via oxolation condensation reactions, leading to a mixture of  $\{U_{10}\}$ and  $\{U_{13}\}$  clusters. The addition of base to these clusters promotes further condensation affording a  $\{U_{16}\}$  cluster with a  $[U_{16}O_{15}(OH)_8]$  core. Both the  $\{U_{16}\}$  and  $\{U_{13}\}$  can further slowly assemble with additional  $\{U_{13}\}$  and/or  $\{U_6\}$  units to yield a  $\{U_{24}\}$  cluster with a  $[U_{24}O_{30}(OH)_2]$  core. When the reaction of hydrolysis is carried at higher temperature small amounts of a  $\{U_{38}\}$  cluster with a  $[U_{38}O_{56}]$  core, were isolated. The  $\{U_{38}\}$  cluster most likely is formed by the condensation of two  $\{U_{24}\}$  clusters and two additional  $\{U_6\}$  units prior to the formation of the final UO<sub>2</sub> product. In conclusion the controlled hydrolysis of uranium(IV) complexes in organic solvents provides an attractive route to the synthesis of uranium clusters with diverse structure and nuclearity. Moreover, it provides insightful snapshots of the time-dependent assembly pathway from uranium hexamers to larger oligomeric species. These results pave the way to the further development of the cluster chemistry of actinides in low oxidation states.



**Figure 85.** Assembly pathway of uranium oxo/hydroxo clusters in the controlled hydrolysis of UCl₄ in presence of the benzoate ligand.

# Experimantal

## General considerations.

Unless otherwise noted, all manipulations were carried out under an inert argon atmosphere using Schlenk techniques and an MBraun glovebox equipped with a purifier unit. The water and oxygen level were always kept at less than 0.1 ppm. The solvents were purchased from Aldrich in their anhydrous form conditioned under argon and were vacuum distilled from K/benzophenone (acetonitrile, diisopropyl ether, pyridine). Depleted uranium turnings were purchased from the Ibilabs Florida, USA.

Glassware was dried overnight at 130°C before use. <sup>1</sup>H NMR experiments were carried out using NMR tubes adapted with J. Young valves. <sup>1</sup>H NMR spectra were recorded on Bruker 200 and 400 MHz spectrometers. NMR chemical shifts are reported in ppm with solvent as internal reference. Elemental analyses were performed under argon by Analytische Laboratorien GMBH at Lindlar, Germany and using a Thermo Scientific Flash 2000 Organic Elemental Analyzer at the Institute of Chemistry and Chemical Engineering at EPFL.

 $\mathsf{UCl}_4^{[19]}$  and  $[\mathsf{UI}_4(\mathsf{OEt}_2)_2]^{[20]}$  were prepared according to the published procedures.

**Caution:** Depleted uranium (primary isotope <sup>238</sup>U) is a weak  $\alpha$ -emitter (4.197 MeV) with a half-life of 4.47×10<sup>9</sup> years. Manipulations and reactions should be carried out in monitored fume hoods or in an inert atmosphere glovebox in a radiation laboratory equipped with  $\alpha$ - and  $\beta$ -counting equipment.
#### Synthetic Procedures.

#### Synthesis of $[U_6O_4(OH)_4(PhCOO)_{12}Py_4]$ (1).

421 μL of a 0.5 M solution of water (0.211 mmol, 2 equiv.) in pyridine were added dropwise under vigorous stirring to a blue solution of [UCl<sub>4</sub>] (40.0 mg, 0.105 mmol, 1 equiv.) in pyridine (2 mL), resulting in a color change to green after 5 minutes stirring. A suspension of potassium benzoate (33.7 mg, 0.211 mmol, 2 equiv.) in pyridine (1.5 mL) was then added to the solution. The green resulting solution was stirred at room temperature over 48 h and then filtered to remove potassium chloride. The green solution was layered with diisopropylether yielding X-ray quality crystals of **1** over 2 weeks in 65 % yield (40 mg, 0.012 mmol). X-ray diffraction confirmed the presence of the previously reported cluster **1**.<sup>[10d] 1</sup>H NMR (200 MHz, Py-d<sub>5</sub>, 298 K):  $\delta$ = 17.76 (s, 2H), 9.96 (t, 2H), 9.69 (t, 1H). Synthesis of [U<sub>6</sub>O<sub>4</sub>(PhCOO)<sub>16</sub>(Py)<sub>4</sub>], (2).

526 μL of a 0.5 M solution of water (0.263 mmol, 2 equiv.) in acetonitrile were added dropwise under vigorous stirring to a green suspension of [UCl<sub>4</sub>] (50.0 mg, 0.132 mmol, 1 equiv.) in 0.5 mL of acetonitrile. A suspension of potassium benzoate (62,5 mg, 0.390 mmol, 3 equiv.) in acetonitrile (1.5 mL) was then added to the solution resulting to resulting a light green solution and the formation of white-green powder. After 1 day stirring at room temperature the precipitate was filtered. This solid was partially solubilized in pyridine resulting to a green solution and a white solid removed by filtration. The green solution was layered with diisopropylether and after a week, the  $[U_6O_4(PhCOO)_{16}(Py)_4]$ .1.8Pyridine compound was recovered (53.8 mg, 62 %). Elemental analysis calcd (%) for  $[U_6O_4(PhCOO)_{16}(Py)_4]$ .1.8 Pyridine  $(C_{141}H_{109}N_{5.8}O_{36}U_6 MW = 3888.62) C 43.55$ , H 2.83, N 2.09; found C 43.50, H 2.98, N 2.16. <sup>1</sup>H NMR (200 MHz, Py-d<sub>5</sub>, 298 K):  $\delta$ = 17.78 (s, 2H), 9.97 (t, 2H), 9.71 (t, 1H). X-ray quality crystals of **2**.3Pyridine.DIPE were obtained by slow diffusion of diisopropylether into the pyridine solution containing the cluster.

# Isolation of $[U_{13}K_4O_{12}(OH)_4(PhCOO)_{12}Cl_{14}]Cl_2.6MeCN$ (3).6MeCN and $[U_{13}K_2O_9(OH)_7(PhCOO)_{12}Cl_{16}]Cl$ (4).

1.05 mL of a 0.5 M solution of water (0.527 mmol, 2 equiv.) in acetonitrile were added dropwise under vigorous stirring to a green suspension of [UCl<sub>4</sub>] (100.0 mg, 0.263 mmol, 1 equiv.) in 0.5 mL of acetonitrile. A suspension of potassium benzoate (169.2 mg, 0.527 mmol, 2 equiv.) in acetonitrile (2.0 mL) was then added to the solution. The green resulting solution was stirred at room temperature over 48 h and then filtered to remove potassium chloride. The green solution was layered with diisopropylether yielding 17 mg (15%) of a mixture of **3** and **4**. X-ray quality crystals of both **3**.6MeCN and **4** compounds were obtained independently by slow diffusion of diisopropylether into the acetonitrile solution or in concentrated acetonitrile solution. <sup>1</sup>H NMR (200 MHz, CD<sub>3</sub>CN, 298 K):  $\delta$ = 28.33 (s, 1H), 25.72(s, 1H), 18.90(s, 1H), 15.72(s, 1.5H), 12.06(s, 1.5H), 12.05(s, 1.5H), 11.79(s, 1H), 11.19(s, 3.5H), 10.30(s, 1.5H), 10.04(s, 3.5H), 9.03(s, 2H), 8.52(s, 2H), 7.91(s, 2H), 7.19 (s, 2.5H).

The <sup>1</sup>H NMR spectrum of the reaction mixture of a stoichiometric amount of water with [UCl<sub>4</sub>] in the presence of potassium benzoate in acetonitrile is broad, whereas the isolated mixture of **3** and **4** gives a well-defined <sup>1</sup>H NMR spectrum in acetonitrile. Similar spectra have been obtained from different mixtures of **3** and **4** from different syntheses, however the integration ratios are slightly different, suggesting that the ratio between **3** and **4** is not always the same. After measurement of the diffusion coefficient with PFGSTE studies, no difference was observed between the different peaks. A diffusion coefficient of 9.04.10<sup>-10</sup> m<sup>2</sup>.s<sup>-1</sup> and a hydrodynamic radii of 7.1 Å were calculated, close to the spherical radii estimated from the crystal structures (8.3 Å) (Table 4)

Cluster	Diffusion coefficient (m².s <sup>-10</sup> )	Hydrodynamic radii (Å)	Evaluated radii (Å)
U <sub>6</sub> O <sub>8</sub> <b>1</b>	3.29 10 <sup>-10</sup>	7.5	8.5
U <sub>6</sub> O <sub>4</sub> <b>2</b>	3.09 10 <sup>-10</sup>	8.0	9.2
U <sub>13</sub> O <sub>16</sub> K <sub>x</sub> <b>3-4</b>	9.04.10 <sup>-10</sup>	7.1	8.3

Table 4. Diffusion coefficient values of 1, 2, 3 and 4 and estimated spherical radii.

The proton NMR spectrum of mixtures of **3** and **4** in pyridine does not have well-defined peaks suggesting that the cluster may be disrupted, however, the <sup>1</sup>H NMR spectrum in acetonitrile of a residue obtained after evaporation of the pyridine shows the characteristic peaks of **3** and **4**, suggesting that the formation/disruption of the clusters is reversible.

#### Isolation of $[U_{10}O_8(OH)_6(PhCOO)_{12.8}I_{3.2}(H_2O)_4(MeCN)_3]I_2$ .

158  $\mu$ L of a 0.5 M solution of water (0.078 mmol, 2 equiv.) in acetonitrile were added to a vigorously stirred dark red solution of [UI<sub>4</sub>(OEt<sub>2</sub>)<sub>4</sub>] (14.8 mg, 0.039 mmol, 1 equiv.) in MeCN (3 mL). A suspension of potassium benzoate (12.5 mg, 0.078 mmol, 2 equiv.) in MeCN (1 mL) was then added to the resulting solution. The light green resulting solution was stirred over 48 hours and then filtered to remove potassium iodide. Slow evaporation of the resulting solution lead to the formation of green X-ray quality crystals of **5** after 1 week.

#### Synthesis of [U<sub>16</sub>O<sub>15</sub>(OH)<sub>8</sub>(PhCOO)<sub>26</sub>(Py)<sub>2</sub>] (5) and isolation of [U<sub>24</sub>O<sub>30</sub>(OH)<sub>2</sub>(PhCOO)<sub>30</sub>Cl<sub>4</sub>(Py)<sub>4</sub>] (6)

536 µL of a 0.5 M solution of water (0.268 mmol, 1.7 equiv.) in acetonitrile were added dropwise under vigorous stirring to a green suspension of [UCl<sub>4</sub>] (60.0 mg, 0.160 mmol, 1 equiv.) in acetonitrile (1 mL). A suspension of potassium benzoate (43.0 mg, 0.268 mmol, 1.7 equiv.) in acetonitrile (0.5 mL) was then added to the solution. The resulting dark green solution was stirred at room temperature for more than 60 hours and then filtered to remove potassium chloride. 50 µL of pyridine were added (0.630 mmol, 4 equiv.) resulting in a darker green solution. X-ray quality crystals of **5** start to form after 2 days. After 10 days, 40 mg (0.085 mmol, 54 %) of **5** were recovered. Elemental analysis calcd (%) for  $[U_{16}O_{15}(OH)_8(PhCOO)_{26}(Py)_2]$  (C<sub>192</sub>H<sub>148</sub>N<sub>2</sub>O<sub>75</sub>U<sub>16</sub> MW = 7491.70) C 30.78, H 1.99 and N 0.37; found C 30.56, H 1.96 and N 0.37.

After filtration of the crystals of **5**, the mother liquor was left standing at room temperature. Amber cubic crystals of  $[U_{24}O_{32}(PhCOO)_{30}Cl_4(Py)_4]$  (**6**) (9.0 mg 0.0009 mmol, 13%) were isolated after 11 days. Elemental analysis calcd (%) for  $[U_{24}O_{30}(OH)_2(PhCOO)_{30}Cl(Py)_4]$ .Py  $(C_{235}H_{177}N_5O_{92}Cl_4U_{24} MW = 10397.4)$  C 27.15, H 1.72 and N 0.67; found C 26.87, H 1.70 and N 1.00.

Both complexes show extremely low solubility in acetonitrile once isolated.

# Effect of dilution on the formation of 5 and 6 by pyridine addition to the acetonitrile reaction mixture.

536  $\mu$ L of a 0.5 M solution of water (0.268 mmol, 1.7 equiv.) in acetonitrile were added dropwise under vigorous stirring to a green suspension of [UCl<sub>4</sub>] (60.0 mg, 0.160 mmol, 1 equiv.) in acetonitrile (2 mL). A suspension of potassium benzoate (43.0 mg, 0.268 mmol, 1.7 equiv.) in acetonitrile (1 mL) was then added to the solution. The green resulting solution was stirred at room temperature for 72 hours and a solution of 50  $\mu$ L of pyridine in 5 ml of MeCN was added (0.630 mmol, 4 equiv.) resulting in a dark green suspension, which was filtered and let stand at room temperature. X-ray quality crystals of **5** (17 mg, 0.002 mmol, 23-27%) were collected after 5-10 days. The resulting solution was further diluted (2 ml of MeCN were added) and left standing at room temperature. After 20 days 9 mg (0.0009 mmol, 13 %) of **6** were recovered.

#### Dependency of the cluster assembly on the time of controlled hydrolysis in acatonitrile.

536  $\mu$ L of a 0.5 M solution of water (0.268 mmol, 1.7 equiv.) in acetonitrile were added dropwise under vigorous stirring to a green suspension of [UCl<sub>4</sub>] (60.0 mg, 0.160 mmol, 1 equiv.) in acetonitrile (1 mL). A suspension of potassium benzoate (43.0 mg, 0.268 mmol, 1.7 equiv.) in acetonitrile (0.5 mL) was then added to the solution. The resulting green solution was stirred at room temperature overnight and then filtered to remove potassium chloride. 50  $\mu$ L of pyridine were added (0.630 mmol, 4 equiv.) and the resulting suspension was filtered and let stand at room temperature. X-ray quality crystals of crystals of cluster **1** (25 mg, 0.085 mmol, 28 %) were recovered after 24 hours. Thus, if the controlled hydrolysis process in acetonitrile is stopped after 12 hours, subsequent addition of pyridine only leads to the formation of **1**. Addition of pyridine after times longer than 60 hours leads to formation of **5** and **6** (see above).

#### Effect of temperature on the synthesis of 5.

536  $\mu$ L of a 0.5 M solution of water (0.268 mmol, 1.7 equiv.) in acetonitrile were added dropwise under vigorous stirring to a green suspension of [UCl<sub>4</sub>] (60.0 mg, 0.160 mmol, 1 equiv.) in acetonitrile (2 mL). A suspension of potassium benzoate (43.0 mg, 0.268 mmol, 1.7 equiv.) in acetonitrile (1.5 mL) was then added to the solution. The green resulting solution was stirred at room temperature for 1 hour, then 50  $\mu$ L of pyridine were added (0.630 mmol, 4 equiv.). Reaction mixture was filtered and resulting solution was left at reflux without stirring for 36 h. X-ray quality crystals of **5** start to form after a night. After 36 hours of reflux 40 mg (0.085 mmol, 54 %) of **5** were recovered.

### Reaction at high temperature: Isolation of [U<sub>38</sub>O<sub>56</sub>Cl<sub>18</sub>(PhCOO)<sub>22</sub>(CH<sub>3</sub>CONH<sub>2</sub>)<sub>10</sub>], (7)

A Schlenk round bottom flask was charged with [UCl<sub>4</sub>] (100.0 mg, 0.263 mmol, 1 equiv.) in 10 mL of acetonitrile and 1.05 mL of a 0.5 M water solution in acetonitrile (0.523 mmol, 2 equiv.). A white suspension of potassium benzoate (84.3 mg, 0.523 mmol, 2 equiv.) was then added. The light green mixture was refluxed for 32 hours under argon outside of the glove box and overtime the color became darker. A brownish-green solid was removed by centrifugation from the dark green solution which was layered with DIPE. X-ray quality crystals of [U<sub>38</sub>O<sub>56</sub>Cl<sub>18</sub>(PhCOO)<sub>22</sub>(CH<sub>3</sub>CONH<sub>2</sub>)<sub>10</sub>] **7** and of cluster **4** were obtained by slow diffusion of diisopropylether into the acetonitrile solution concomitant to the formation of a green precipitate.

When the same reaction is carried out with excess water (400 eq.) and refluxed for 32 hours only  $UO_2$  is formed as characterized by PXRD.

#### References

- a) S. Hickam, P. C. Burns, in *Recent Development in Clusters of Rare Earths and Actinides: Chemistry and Materials, Vol. 173* (Ed.: Z. Zheng), **2017**, pp. 121-153; b) J. Qiu, P. C. Burns, *Chem. Rev.* **2013**, *113*, 1097-1120; c) K. E. Knope, L. Soderholm, *Chem. Rev.* **2013**, *113*, 944-994.
- [2] a) J. D. Rinehart, T. D. Harris, S. A. Kozimor, B. M. Bartlett, J. R. Long, *Inorg. Chem.* 2009, *48*, 3382-3395; b) S. T. Liddle, J. van Slageren, *Chem. Soc. Rev.* 2015, *44*, 6655-6669; c) D. P. Mills, F. Moro, J. McMaster, J. van Slageren, W. Lewis, A. J. Blake, S. T. Liddle, *Nat. Chem.* 2011, *3*, 454-460; d) V. Mougel, L. Chatelain, J. Pecaut, R. Caciuffo, E. Colineau, J. C. Griveau, M. Mazzanti, *Nat. Chem.* 2012, *4*, 1011-1017; e) R. E. Wilson, S. Skanthakumar, L. Soderholm, *Angew. Chem. Int. Ed. Engl.* 2011, *50*, 11234-11237; f) T. E. Albrecht-Schmitt, *Angew. Chem. Int. Ed. Engl.* 2015, *44*, 4836-4838; g) J. D. Rinehart, S. A. Kozimor, J. R. Long, *Angew. Chem. Int. Ed. Engl.* 2010, *49*, 2560-2564; h) W. J. Evans, S. A. Kozimor, J. W. Ziller, *Science* 2005, *309*, 1835-1838; i) G. Nocton, J. Pecaut, M. Mazzanti, *Angew. Chem. Int. Ed. Engl.* 2008, *47*, 3040-3042.
- [3] a) A. B. Kersting, D. W. Efurd, D. L. Finnegan, D. J. Rokop, D. K. Smith, J. L. Thompson, *Nature* 1999, *397*, 56-59; b) A. P. Novikov, S. N. Kalmykov, S. Utsunomiya, R. C. Ewing, F. Horreard, A. Merkulov, S. B. Clark, V. V. Tkachev, B. F. Myasoedov, *Science* 2006, *314*, 638-641; c) Y. Suzuki, S. D. Kelly, K. M. Kemner, J. F. Banfield, *Nature* 2002, *419*, 134-134; d) L. R. Morss, N. M. Edelstein, J. Fuger, *The Chemistry of the Actinide and Transactinide Elements*, Springer, Dordrecht, 2006; e) P. Crancon, E. Pili, L. Charlet, *Sci. Total Environ.*, *408*, 2118-2128; f) G. J. Vazquez, C. J. Dodge, A. J. Francis, *Inorg. Chem.* 2009, *48*, 9485-9490.
- [4] a) D. E. Latta, C. A. Gorski, M. I. Boyanov, E. J. O'Loughlin, K. M. Kemner, M. M. Scherer, *Environ. Sci. Technol.* 2012, *46*, 778-786; b) M. Stylo, N. Neubert, Y. H. Wang, N. Monga, S. J. Romaniello, S. Weyer, R. Bernier-Latmani, *Proc Natl Acad Sci USA* 2015, *112*, 5619-5624.
- K. P. Carter, J. W. Jian, M. M. Pyrch, T. Z. Forbes, T. M. Eaton, R. J. Abergel, W. A. de Jong, J.
   K. Gibson, *Chem. Commun.* **2018**, *54*, 10698-10701.
- [6] a) S. Takao, K. Takao, W. Kraus, F. Ernmerling, A. C. Scheinost, G. Bernhard, C. Hennig, *Eur. J. Inorg. Chem.* 2009, 4771-4775; b) C. Hennig, S. Takao, K. Takao, S. Weiss, W. Kraus, F. Emmerling, A. C. Scheinost, *J. Chem. Soc.-Dalton Trans.* 2012, *41*, 12818-12823; c) L. S. Natrajan, A.

N. Swinburne, M. B. Andrews, S. Randall, S. L. Heath, *Coord. Chem. Rev.* 2014, *266*, 171-193;
d) K. Takao, S. Takao, A. C. Scheinost, G. Bernhard, C. Hennig, *Inorg. Chem.* 2012, *51*, 1336-1344; e) K. E. Knope, R. E. Wilson, M. Vasiliu, D. A. Dixon, L. Soderholm, *Inorg. Chem.* 2011, *50*, 9696-9704; f) K. E. Knope, M. Vasiliu, D. A. Dixon, L. Soderholm, *Inorg. Chem.* 2012, *51*, 4239-4249; g) L. Soderholm, P. M. Almond, S. Skanthakumar, R. E. Wilson, P. C. Burns, *Angew. Chem. Int. Ed. Engl.* 2008, *47*, 298-302.

- [7] a) A. Kondinski, T. N. Parac-Vogt, Front. Chem. 2018, 6; b) A. Muller, P. Gouzerh, Chem. Soc.
   Rev. 2012, 41, 7431-7463; c) A. Dolbecq, E. Dumas, C. R. Mayer, P. Mialane, Chem. Rev. 2010, 110, 6009-6048; d) D. L. Long, R. Tsunashima, L. Cronin, Angew. Chem. Int. Ed. Engl. 2010, 49, 1736-1758.
- [8] P. C. Burns, K. A. Kubatko, G. Sigmon, B. J. Fryer, J. E. Gagnon, M. R. Antonio, L. Soderholm, Angew. Chem. Int. Ed. Engl. 2005, 44, 2135-2139.
- P. B. Duval, C. J. Burns, D. L. Clark, D. E. Morris, B. L. Scott, J. D. Thompson, E. L. Werkema, L. Jia, R. A. Andersen, *Angew. Chem. Int. Ed. Engl.* 2001, 40, 3357-3361.
- [10] a) L. M. Mokry, N. S. Dean, C. J. Carrano, *Angew. Chem. Int. Ed. Engl.* 1996, *35*, 1497-1498;
  b) G. Nocton, F. Burdet, J. Pecaut, M. Mazzanti, *Angew. Chem. Int. Ed. Engl.* 2007, *46*, 7574-7578; c) G. Nocton, J. Pecaut, Y. Filinchuk, M. Mazzanti, *Chem. Commun.* 2010, *46*, 2757-2759; d) V. Mougel, B. Biswas, J. Pecaut, M. Mazzanti, *Chem. Commun.* 2010, *46*, 8648-8650;
  e) J. C. Berthet, P. Thuery, M. Ephritikhine, *Chem. Commun.* 2005, 3415-3417; f) J. C. Berthet,
  P. Thuery, M. Ephritikhine, *Inorg. Chem.* 2010, *49*, 8173-8177; g) B. Biswas, V. Mougel, J. Pecaut, M. Mazzanti, *Angew. Chem. Int. Ed. Engl.* 2011, *50*, 5744-5747; h) C. Tamain, T. Dumas, C. Hennig, P. Guilbaud, *Chem. Eur. J.* 2017, *23*, 6864-6875; i) C. Falaise, H. A. Neal, M. Nyman, *Inorg. Chem.* 2017, *56*, 6591-6598; j) J. Diwu, S. Wang, T. E. Albrecht-Schmitt, *Inorg. Chem.* 2012, *51*, 4088-4093; k) N. A. Vanagas, J. N. Wacker, C. L. Rom, E. N. Glass, I. Colliard, Y. S. Qiao, J. A. Bertke, E. Van Keuren, E. J. Schelter, M. Nyman, K. E. Knope, *Inorg. Chem.* 2018, *57*, 7259-7269.
- [11] a) V. Mougel, P. Horeglad, G. Nocton, J. Pecaut, M. Mazzanti, *Chem. Eur. J.* 2010, *16*, 14365-14377; b) V. Mougel, J. Pecaut, M. Mazzanti, *Chem. Commun.* 2012, *48*, 868-870.
- [12] C. Falaise, C. Volkringer, J.-F. Vigier, A. Beaurain, P. Roussel, P. Rabu, T. Loiseau, J. Am. Chem. Soc. 2013, 135, 15678-15681.

- [13] N. P. Martin, C. Volkringer, N. Henry, X. Trivelli, G. Stoclet, A. Ikeda-Ohno, T. Loiseau, Chem. Sci. 2018, 9, 5021-5032.
- [14] Y. J. Hu, K. E. Knope, S. Skanthakumar, L. Soderholm, *Eur. J. Inorg. Chem.* 2013, 2013, 4159-4163.
- [15] al. D. Brown, D. Altermatt, , Acta cryst. Section B 1985, B41, 244-247; b) P. C. Burns, R. C.
   Ewing, F. C. Hawthorne, Can. Mineral. 1997, 35, 1551-1570.
- [16] A. E. Enriquez, B. L. Scott, M. P. Neu, Inorg. Chem. 2005, 44, 7403-7413.
- [17] C. H. Zhan, J. M. Cameron, J. Gao, J. W. Purcell, D. L. Long, L. Cronin, *Angew. Chem. Int. Ed. Engl.* 2014, 53, 10362-10366.
- [18] a) R. D. Swartz, M. K. Coggins, W. Kaminsky, J. A. Kovacs, J. Am. Chem. Soc. 2011, 133, 3954-3963; b) J. H. Kim, J. Britten, J. Chin, J. Am. Chem. Soc. 1993, 115, 3618-3622; c) R. Cini, F. P. Fanizzi, F. P. Intini, L. Maresca, G. Natile, J. Am. Chem. Soc. 1993, 115, 5123-5131.
- [19] a) J. A. Hermann, J. F. Suttle, *Inorg. Synth.* 1957, *5*, 143-145; b) J. L. Kiplinger, D. E. Morris, B.
   L. Scott, C. J. Burns, *Organometallics* 2002, *21*, 5978-5982.
- [20] C. D. Carmichael, N. A. Jones, P. L. Arnold, *Inorg. Chem.* **2008**, *47*, 8577-8579.
- [21] L. Chatelain, R. Faizova, F. Fadaei-Tirani, J. Pécaut, M. Mazzanti, ACIE 2019, 58, 3021–3026.

# General conclusion

The global objective of this PhD thesis work was the development of rational methods for the synthesis of various environmentally relevant uranium species, with a particular focus on the uranyl(V) chemistry and formation of discrete polynuclear uranium assemblies. The access to well-defined uranium POMs and particularly to water-stable uranyl(V) species is crucial for a better understanding of uranium migration and transformations in the environment and relevant to nuclear fuel processing concerns. This work has brought some important novel information both on the chemistry of uranyl(V) and on the key role played by uranyl(V) species in environmental settings, on the importance of iron in uranyl(V) stabilization as well as afforded original polynuclear uranium assemblies obtained by employing different synthetic strategies.

The first part of this project was dedicated to the investigation of the effect of iron on the stability of uranyl(V). The tripodal Schiff base trensal ligand allowed the synthesis and characterization of a series of homometallic, as well as iron-containing uranyl(VI) and uranyl(V) complexes. This system was used to evaluate the relative stability and reactivity of uranyl(V) upon binding of iron and establish the importance of cation-cation interaction between the uranyl(V) oxo and Fe<sup>2+</sup>. Complexes with Fe<sup>2+</sup> bound UO<sub>2</sub><sup>+</sup> demonstrated increased stability with respect to proton-induced disproportionation and yielded a stable Fe<sup>2+</sup>-UO<sub>2</sub><sup>+</sup>-U<sup>4+</sup> intermediate. Additionally, iron-binding increased the range of redox stability of the uranyl(V) as demonstrated by reactivity and cyclic voltammetry studies. These findings suggest that uranyl(V) may be significantly stabilized upon iron-binding during the mineral-mediated uranyl(VI) reduction in the environment.

The second and the most challenging aim of this work was the design and synthesis of the waterstable uranyl(V) complex that would have significant stability at environmentally relevant pH. The isolation of a stable mononuclear U(V) complex with a pentadentate dpaea ligand has been achieved by two different synthetic routes, namely by the reduction of the uranyl(VI) analog or by a direct salt metathesis reaction. The resulting uranyl(V) species [UO<sub>2</sub>(dpaea)]<sup>-</sup> was fully characterized and has shown stability in aqueous solution in the pH range 7-10. Besides being of fundamental interest, the isolation of this complex provided a valuable and previously missing tool for investigating the mechanism of biotic and abiotic reduction of uranyl species under the environmental conditions. As a result of this finding, our collaborators have not only demonstarted that uranyl(V) is the key intermediate in biotic reduction of uranium, but also achieved an unprecedented further reduction of the resulting uranyl(V) complex to solid phase U(IV).

The results of the second collaborative project have demonstrated that a combination of synthetic inorganic chemistry, HR-XANES spectroscopy and advanced computations can advance the understanding of the role of the 5f electrons in the covalency of the U binding and the interconnection between bond covalency, reactivity, and bond stability in uranyl(V) complexes.

Further, with the goal of chemically mimicking the environmental reduction of uranyl(VI) to uranium(IV), the investigation of the reactivity of the novel system was carried out. The reduction studies were performed in both organic and aqueous solutions and resulted in the isolation of different reduction products. It was demonstrated for the first time that in anaerobic water the reduction of uranyl(VI) and uranyl(V) can be performed without prior functionalization of the oxo groups yielding a molecular trinuclear U(IV) oxo/hydroxo cluster. Notably, the variation of the reduction conditions led to the isolation of the first uranyl(V) X-ray solid-state structure obtained from water. Additionally, the *cis*-boroxide U(IV) species accessed from the reduction in organic media shed some light on the potential reduction mechanism in aqueous media.

Finally, the development of new synthetic methodologies for the synthesis of molecular oxo/hydroxo uranium clusters was pursued. The first approach consisted of the controlled hydrolysis of uranium(IV) precursor in organic media in the presence of a benzoate ligand. The study focused on understanding the directing parameters, such as the nature of the precursor, solvent, stoichiometry of the ligand, temperature, media basicity, and the duration of the experiment, on the formation of high nuclearity clusters. The variation of the reaction conditions during the hydrolysis led to the isolation of clusters containing 6, 10, 13, 16, 24, and 38 uranium atoms in the core.

Using the same ligand, the formation of mixed-valence oxo-clusters has been examined by an alternative pathway, namely the disproportionation of uranyl(V) precursor. It was demonstrated that the disproportionation of uranyl(V) can be utilized for the formation of large (U16) uranium POMs even in the absence of a cation, which was previously thought to promote this disproportionation

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reaction. Additionally, a novel U(V)-U(V) diamond-shaped intermediate was isolated, which may suggest that the bridging nature of the benzoate ligand plays a significant role in promoting the formation of uranyl(VI) and U(IV) from otherwise stable uranyl(V) precursor.

In conclusion, the results reported in this doctorate granted a better understanding of fundamental chemistry and reactivity of uranyl(V) that have strong implications in elucidating the environmental fate of uranium. The development of novel methodologies for the synthesis of distinct polynuclear assemblies opens up new horizon in discovering not only the fundamental properties and environmental behavior, but also potential applications for uranium-based materials.

"Never confuse education with intelligence, you can have a PhD and still be an idiot." — Richard P. Feynman

# Appendix

## **APPENDIX 1: Supporting information for Chapter 2**

#### NMR Spectroscopic data



**Figure S1.** <sup>1</sup>H NMR spectrum (400 MHz, C<sub>5</sub>D<sub>5</sub>N, 298 K) of the K<sub>3</sub>trensal ligand.



**Figure S2.** <sup>1</sup>H NMR spectrum (400 MHz,  $C_5D_5N$ , 298 K) of the reaction mixture immediately after the addition of Cp\*<sub>2</sub>Co to [UO<sub>2</sub>(Htrensal)] (**2**) showing that the reduction of the protonated uranyl(VI) leads to disproportionation.



Figure S3. <sup>1</sup>H NMR spectrum (400 MHz,  $C_5D_5N$ , 298 K) of  $[UO_2(trensal)K]K$  (3).



**Figure S4.** <sup>1</sup>H NMR spectrum (400 MHz,  $C_5D_5N$ , 298 K) of the reaction mixture of  $[UO_2(trensal)K]K$  (**3**) + 2 eq. PyHCl (top) and of  $[UO_2(Htrensal)]$  (**2**) + [U(trensal)I] (**9**) + 2 H<sub>2</sub>O (bottom).



**Figure S5**. <sup>1</sup>H NMR spectrum (400 MHz,  $C_5D_5N$ , 298 K) of a solution of  $[UO_2(trensal)(K(2.2.2crypt)][K(2.2.2crypt)]$ , **4** (bottom) and immediately after the addition of 1 eq. PyHCl to **4** (middle), and 3 days after the addition of 2 eq. PyHCl to **4** (top).



**Figure S6.** <sup>1</sup>H NMR spectrum (400 MHz,  $C_5D_5N$ , 298 K) of crystals of [(UO<sub>2</sub>(trensal))<sub>2</sub>Fe(py)<sub>2</sub>] (5).



**Figure S7.** <sup>1</sup>H NMR spectrum (400 MHz,  $C_5D_5N$ , 298 K) of crystals of  $[(UO_2(trensal))_2Fe(py)_2]$  (5) (a), of the solution after addition of 1 eq.  $Cp_2*Co$  to 5 (b), addition of 2.5 eq.  $Cp_2*Co$  to 5 (c) and crystals of compound  $[UO_2(trensal)Fe(py)_3]$  (6) (d).



**Figure S8.** <sup>1</sup>H NMR spectrum (400 MHz,  $C_5D_5N$ , 298 K) of crystals of  $[(UO_2(trensal)Fe(py)_3)_2Fe(py)_3]I_2$ (8) (bottom), of the reaction mixture after addition of 2 eq. of PyHCl to 8 (middle), of the reaction mixture after addition of 1 eq. of PyHCl to  $[UO_2(trensal)Fe(py)_3]$  (6) (top) *Inset:* zoom in on the 33.6 – 36.6 ppm region showing the 2:1 ratio of 8 to disproportionation product that is the same as that found for the reaction of 2 eq. of PyHCl with complex **6**.



Figure S9. <sup>1</sup>H NMR spectrum (400 MHz, C<sub>5</sub>D<sub>5</sub>N, 298 K) of crystals of [UO<sub>2</sub>(trensal)Fe(py)<sub>3</sub>U(trensal)]I
(7) (bottom) and of the reaction mixture after the addition of 2 eq. of PyHCl to [UO<sub>2</sub>(trensal)Fe(py)<sub>3</sub>]
(6) (top)(*Inset:* Zoom of the diamagnetic region (0-6 ppm) of the spectra).



**Figure S10.** <sup>1</sup>H NMR spectrum (400 MHz,  $C_5D_5N$ , 298 K) of the addition of [U(trensal)]I (**9**) to complex UO<sub>2</sub>(trensal)K]K (**3**) (bottom) and addition of 2 eq. PyHCl to the 1:1 mixture of [U(trensal)]I, **9** and complex **3**.



**Figure S11**. <sup>1</sup>H NMR spectrum (400 MHz, C<sub>5</sub>D<sub>5</sub>N, 298 K) of crystals of [UO<sub>2</sub>(trensal)Fe(py)<sub>3</sub>U(trensal)]I (7).



**Figure S12**. <sup>1</sup>H NMR spectrum (400 MHz, C<sub>5</sub>D<sub>5</sub>N, 298 K) of the crystals of compound [UO<sub>2</sub>(trensal)Fe(py)<sub>3</sub>U(trensal)]I (**7**) (top) and of the reaction mixture after addition of 1 eq. of PyHCl to **7** (bottom) (*Inset:* zoom in on the 33.6 – 36.6 ppm region of the bottom spectrum, showing a 3:1 ratio of **7** to decomposition products).



Figure S13. <sup>1</sup>H NMR spectrum (400 MHz,  $C_5D_5N$ , 298 K) of the crystals of [(UO<sub>2</sub>(trensal)Fe(py)<sub>3</sub>)<sub>2</sub>Fe(py)<sub>3</sub>]I<sub>2</sub> (8).



**Figure S14**. <sup>1</sup>H NMR spectrum (400 MHz,  $C_5D_5N$ , 298 K) of the crystals of compound [(UO<sub>2</sub>(trensal))<sub>2</sub>Fe(py)<sub>2</sub>] **5** (bottom) and of the reaction mixture after the reaction of [UO<sub>2</sub>(trensal)K]K (**3**) with FeCl<sub>3</sub> (top).



**Figure S15**. <sup>1</sup>H NMR spectrum (400 MHz,  $C_5D_5N$ , 298 K) of the crystals of compound [(UO<sub>2</sub>(trensal))<sub>2</sub>Fe(py)<sub>2</sub>] (**6**) (top) and of the reaction mixture after the reaction of **6** with [Fe(tpa)Cl<sub>3</sub>] (bottom).



**Figure S16.** <sup>1</sup>H NMR spectrum (400 MHz,  $C_5D_5N$ , 298 K) of the reaction mixture after addition of [Fe(tdmba)] to [UO<sub>2</sub>(trensal)K]K (**3**) in pyridine (bottom) and of the complex [Fe(tdmba)]K (top).



**Figure S17**. <sup>1</sup>H NMR spectrum (400 MHz, C<sub>5</sub>D<sub>5</sub>N, 298 K) of the crystals of compound [U(trensal)(py)]I (9).



**Figure S18.** <sup>1</sup>H NMR spectrum (400 MHz, C<sub>5</sub>D<sub>5</sub>N, 298 K) of the crystals of compound **10**.



**Figure S19.** <sup>1</sup>H NMR spectrum (400 MHz,  $C_5D_5N$ , 298 K) of the reaction mixture immediately after addition of 2 eq. of H<sub>2</sub>O to 1 eq. of [U(trensal)Cl] (bottom), after 12 hours (middle) and after 24 hours (top).

### **Mass Spectroscopy**



**Figure S20:** ESI/MS spectra of **6**-[UO<sub>2</sub>(trensal)Fe(Py)<sub>3</sub>], in pyridine (top) and zoom on the molecular peak (centre) compared with the theoretical isotopic (bottom) profile calculated for  $\{UO_2(trensal)Fe(Py)^+\}$  m/z = 859.83



**Figure S21:** ESI/MS spectra of **8** [UO<sub>2</sub>(trensal)Fe(py)<sub>3</sub>U(trensal)][I], in pyridine (top) and zoom on the molecular peak (centre left) compared with the theoretical isotopic profile calculated for { $UO_2(trensal)Fe_3U(trensal)(Py)^+$ } m/z = 1552.00; zoom on the molecular peak (centre right) compared with the theoretical isotopic profile calculated for { $UO_2(trensal)Fe_3U(trensal)^+$ } m/z= 1474.42; zoom on the molecular peak (bottom) compared with the theoretical isotopic profile calculated for { $U(trensal)^+$ } m/z = 693.50



**Figure S22:** ESI/MS spectra of **7**-[(UO<sub>2</sub>(trensal)Fe(Py)<sub>3</sub>)<sub>2</sub>Fe(Py)<sub>3</sub>]I<sub>2</sub>] in pyridine (top) and zoom on the molecular peak (bottom) compared with the theoretical isotopic profile calculated for calculated for  $\{UO_2(trensal)Fe(Py)^+\} m/z = 859.83.$ 

### Electrochemistry



**Figure SCV1.** Room temperature cyclic voltammograms for  $[U^{VI}O_2(Htrensal)]$  **2** (red) and  $[U^{VI}O_2(trensal)K]$ , **1** (green) recorded in 0.1 M  $[Bu_4N][PF_6]$  in 2 mM pyridine solution at 100 mV/s scan rate, Cp<sub>2</sub>Fe/Cp<sub>2</sub>Fe<sup>+</sup> corrected.



**Figure SCV2.** Room temperature cyclic voltammograms for  $[U^VO_2(\text{trensal})Fe^{II}(py)_3]$  **6** (blue) and  $[(U^{VI}O_2(\text{trensal})Fe^{II}(py)_3)_2Fe(py)_3]I_2$  **8** (purple) recorded in 0.1 M [Bu<sub>4</sub>N][PF<sub>6</sub>] in 2 mM pyridine solution at 100 mV/s scan rate, Cp<sub>2</sub>Fe/Cp<sub>2</sub>Fe<sup>+</sup> corrected.



**Figure SCV3**. Room temperature cyclic voltammograms for  $[U^{VI}O_2(Htrensal)]$  **2** (red) and K<sub>3</sub>trensal (yellow) recorded in 0.1 M  $[Bu_4N][PF_6]$  in 2 mM pyridine solution at 100 mV/s scan rate, Cp<sub>2</sub>Fe/Cp<sub>2</sub>Fe<sup>+</sup> corrected.

Complex	E <sub>1/2</sub> U(VI)/U(V)	E U(V)/U(IV)
[UO <sub>2</sub> (trensal)K], <b>1+</b> cryptand	-1.69 V	-
[UO <sub>2</sub> (trensal)H], <b>2</b>	- 1.66 V	-2.47 V
[(UO <sub>2</sub> (trensal)) <sub>2</sub> Fe], s	- 1.66 V	-2.70 V
[UO <sub>2</sub> (trensal)Fe(py) <sub>3</sub> ], 6	-1.03 V	-2.70 V
[(UO <sub>2</sub> (trensal)Fe(py) <sub>3</sub> ) <sub>2</sub> Fe(py) <sub>3</sub> ]I <sub>2</sub> , 8	-1.03 V	-2.70 V

**Table S1.** Redox potential of  $[UO_2(trensal)K]$  after addition of cryptand to increase solubility(1),  $[UO_2(trensal)H]$  (2),  $[(UO_2(trensal))_2Fe]$  (5),  $[UO_2(trensal)Fe(py)_3]$  (6) and  $[(UO_2(trensal)Fe(py)_3)_2Fe(py)_3]I_2$  (8) complexes.

#### **X-ray Crystal Structure Determination Details**

The diffraction data of **4**, **7**, **9** and **10** were measured at low temperature using Mo radiation on a Bruker APEX II CCD diffractometer equipped with a kappa geometry goniometer. Both datasets were reduced by *EvalCCD*<sup>[1]</sup> and then corrected for absorption.<sup>[2]</sup> The data collection of compounds **2**, **5**, **6** and **8** were measured at low temperature using Cu radiation on an Agilent Technologies SuperNova dual system in combination with an Atlas CCD detector (type 1 or 2). The data reduction was carried out by Crysalis<sup>Pro</sup>.<sup>[3]</sup> The solutions and refinements were performed by *SHELX*.<sup>[4]</sup> The crystal structures were refined using full-matrix least-squares based on *F*<sup>2</sup> with all non hydrogen atoms anisotropically defined. All hydrogen atoms (including the H forming the intramolecular bond in **2**) were placed in calculated positions by means of the "riding" model.

In the case of the crystal structure of **4**, the refinement of light atoms was difficult because crystal was very weak, being 0.953 Å the highest resolution, and rigid bond restraints (RIGU card) were used in the last stages of least-squares, in combination with *SQUEEZ*<sup>[4]</sup> to remove the electron density due to the disordered solvent. However, the connectivity is well established by the structural data. The same rigid bond restraints were employed for the crystal structure or compound **7**, whereas in the case of **8** all the pyridine solvent molecules displayed rotational disorder and were removed by the *SQUEEZE*<sup>[5]</sup> algorithm in *OLEX2*.<sup>[6]</sup>

CCDC Numbers for the crystal structures deposited at the Cambridge Crystallographic Data Center: Complex 2: CCDC 1842376 - Complex 4: CCDC 1842377- Complex 5: CCDC 1842378- Complex 6: CCDC 1842379- Complex 7: CCDC 1842380- Complex 8: CCDC 1842381- Complex 9: CCDC 1842382.

	<u>2.py</u>	<u>4</u>	<u>5</u>
Formula	$C_{32}H_{233}N_5O_5U$	$C_{63}H_{99}K_2N_8O_{17}U$	$C_{64}H_{64}FeN_{10}O_{10}U_2$
Crystal size (mm <sup>3</sup> )	0.319 x 0.170 x 0.12	0.336 x 0.156 x 0.111	0.135 x 0.087 x 0.025
cryst syst	Triclinic	Triclinic	Monoclinic
space group	P1	P1	C2/c
volume (ų)	1500.76(7)	3997(6)	8465(4)
a (Å)	10.3182(3)	12.542(6)	46.746(5)
b (Å)	12.47104(19)	13.779(10)	13.2744(3)
c (Å)	12.8143(3)	23.86(3)	24.296(3)
α (deg)	82.2874(17)	81.55(6)	90
β (deg)	68.197(3)	78.59(5)	145.84(3)
γ (deg)	79.3609(17)	86.58(4)	90
Z	2	2	4
formula weight (g/mol)	805.66	1551.69	1665.16
density (g cm <sup>-3</sup> )	1.783	1.289	1.307
absorption coefficient (mm <sup>-1</sup> )	15.630	2.196	11.557
F(000)	784	1588	3232
temp (K)	100.01(10)	120(2)	100.01(10)
total no. reflections	10197	37059	30689
unique reflections [R(int)]	6064 [ 0.0183]	9507 [ 0.1127]	8737 [ 0.0238]
Final R indices	$R_1 = 0.0256,$	$R_1 = 0.1093,$	$R_1 = 0.0182,$
[I > 2σ(I)]	$wR_2 = 0.0673$	<i>wR</i> <sub>2</sub> = 0.2765	$wR_2 = 0.0480$
Largest diff. peak and hole (e.A <sup>-3</sup> )	1.890 and -2.137	2.393 and -2.380	1.461 and -0.845
GOOF	1.148	1.110	1.069

 Table S2. Crystallographic parameters for complexes 2, 4-10.

	<u>6.py.0.5hex</u>	<u>7</u>	<u>8</u>
Formula	$C_{50}H_{54}FeN_8O_5U$	$C_{69}H_{69}FeIN_{11}O_8U_2$	$C_{99}H_{99}Fe_3I_2N_{17}O_{10}U_2$
Crystal size (mm <sup>3</sup> )	0.276 x 0.196 x 0.116	0.329 x 0.312 x 0.196	0.350 x 0.241 x 0.087
cryst syst	Monoclinic	Monoclinic	Triclinic
space group	P21/c	P21/n	<i>P</i> -1
volume (ų)	4717.8(3)	7359.3(14)	6888.8(2)
a (Å)	19.5691(7)	15.964(2)	13.7743(3)
b (Å)	13.9341(3)	23.884(3)	21.1783(4)
c (Å)	19.6431(6)	20.0642(9)	24.4520(5)
α (deg)	90	90	99.7615(17)
β (deg)	118.260(4)	105.849(6)	95.7326(16)
γ (deg)	90	90	98.8026(16)
Z	4	4	2
formula weight (g/mol)	1140.89	1839.16	2584.36
density (g cm <sup>-3</sup> )	1.606	1.660	1.246
absorption coeffi- cient (mm <sup>-1</sup> )	12.500	5.062	12.901
F(000)	2272	3548	2520
temp (K)	139.99(13)	120(2)	140.00(10)
total no. reflec- tions	34891	94039	53233
unique reflec- tions [R(int)]	9657 [ 0.0454]	16710 [ 0.0700]	27994 [ 0.0443]

Final R indices [I > 2σ(I)]	$R_1 = 0.0326,$ $wR_2 = 0.0858$	$R_1 = 0.0584,$ $wR_2 = 0.1091$	$R_1 = 0.0558,$ $wR_2 = 0.1438$
Largest diff. peak and hole (e.A <sup>-3</sup> )	2.267 and -1.771	1.896 and -3.104	5.508 and -2.564
GOOF	1.032	1.130	1.036

	<u>9.0.5py</u>	<u>10</u>
Formula	$C_{32}H_{32}IN_5O_3U$	$C_{67}H_{71}IN_{12}O_6U_2$
Crystal size (mm <sup>3</sup> )	0.198 x 0.140 x 0.064	0.35×0.26×0.24
cryst syst	Monoclinic	triclinic
space group	P21/n	<i>P</i> -1
volume (ų)	3416.2(3)	3409.49(16)
a (Å)	14.3842(6)	11.2845(2)
b (Å)	14.1543(8)	13.0010(4)
c (Å)	16.8027(7)	24.8385(7)
α (deg)	90	101.796(2)
β (deg)	93.045(4)	101.652(2)
γ (deg)	90	99.660(2)
Z	2	2
formula weight (g/mol)	939.11	1743.31
density (g cm <sup>-3</sup> )	1.826	1.698
absorption coefficient (mm <sup>-1</sup> )	5.697	5.254
F(000)	1796	1684.0
temp (K)	100.01(10)	140.00(10)
total no. reflections	29812	38751
unique reflections [R(int)]	8463 [ 0.0473]	20805
Final R indices	$R_1 = 0.0447,$	<i>R</i> <sup>1</sup> (all data) 0.0541
[I > 2σ(I)]	<i>wR</i> <sub>2</sub> = 0.0900	<i>wR</i> <sub>2</sub> (all data) 0.0753
Largest diff. peak and hole (e.A <sup>-3</sup> )	2.413 and -1.076	2.679 and -3.059
GOOF	1.079	1.050

#### References

A. J. M. Duisenberg, L. M. J. Kroon-Batenburg, A. M. M. Schreurs, *J Appl Cryst* 2003, *36*, 220–229.

[2] R. H. Blessing, Acta Cryst A **1995**, *51*, 33–38.

[3] *Crysalis PRO*, Agilent Technologies, release 1.171.38.46, **2015**.

[4] *SHELXT* - *Integrated space-group and crystal-structure determination*, G. M. Sheldrick, *Acta Crystallogr.*, *Sect. A* **2015**, *71*, 3-8. *Crystal structure refinement with SHELXL*. G. M. Sheldrick, *Acta Crystallogr.*, *Sect. C* **2015**, *71*, 3-8.

[5] SQUEEZE: a tool for the calculation of the disordered solvent contribution to the calculated structure factors, A. L. Spek, Acta Crystallogr., Sect. C 2015, 71, 9-18.
[6] OLEX2: a complete structure solution, refinement and analysis program. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann. J. Appl. Cryst. 2009. 42, 339-341.
# **APPENDIX 2: Supporting information for Chapter 3**

## NMR Spectroscopic data



**Figure S1.** <sup>1</sup>H NMR spectrum (400 MHz, CD<sub>3</sub>OD, 298 K) of H<sub>2</sub>dpaea.



Figure S2.<sup>1</sup>H NMR spectrum (400 MHz, (CD<sub>3</sub>)<sub>2</sub>SO, 298 K) of [UO<sub>2</sub>(dpaea)]



**Figure S3**. <sup>1</sup>H NMR spectrum (400 MHz, 8 mM, C<sub>5</sub>D<sub>5</sub>N, 298 K) of [CoCp<sub>2</sub><sup>\*</sup>][UO<sub>2</sub>(dpaea)].



**Figure S4**. <sup>1</sup>H NMR spectrum (400 MHz, 10 mM, D<sub>2</sub>O, 298 K) of [CoCp<sub>2</sub><sup>\*</sup>][UO<sub>2</sub>(dpaea)].



**Figure S5.** <sup>1</sup>H NMR spectrum (400 MHz, 2 mM, D<sub>2</sub>O, 298 K) of [CoCp<sub>2</sub><sup>\*</sup>][UO<sub>2</sub>(dpaea)].



**Figure S6.** <sup>1</sup>H NMR spectrum (400 MHz, 9 mmol, D<sub>2</sub>O, 298 K) of [K(2.2.2.cryptand)][UO<sub>2</sub>(dpaea)].



Figure S7. <sup>1</sup>H NMR spectrum (400 MHz, 1 mmol, D<sub>2</sub>O, 298 K) of [K(2.2.2.cryptand)][UO<sub>2</sub>(dpaea)].



Figure S8. 2D COSY NMR spectrum (400 MHz, 8 mM,  $C_5D_5N$ , 298 K) of [K(2.2.2.cryptand)][UO<sub>2</sub>(dpaea)].



**Figure S9.** <sup>1</sup>H NMR spectra (400 MHz,  $D_2O$ , 15 mM, pH=10, 298 K) of [K(2.2.2.cryptand)][UO<sub>2</sub>(dpaea)] recorded at different times after dissolution in  $D_2O$ . A signal of the complex was integrated against the pyridine peak as a reference.



**Figure S10.** <sup>1</sup>H NMR spectra (400 MHz,  $D_2O$ , 2 mM, pH = 9.3, 298 K) of [K(2.2.2.cryptand)][UO<sub>2</sub>(dpaea)] recorded at different times after dissolution in  $D_2O$  indicating slow partial decomposition of the complex in  $D_2O$ .



**Figure S11.** <sup>1</sup>H NMR spectrum (400 MHz,  $D_2O$ , 16 mmol, 298 K) of [K(2.2.2.cryptand)][UO<sub>2</sub>(dpaea)] before the addition of DCI (a), immediately after addition (b), 3 days (c) and 6 days (d) after the adjustement of pH at 7 with DCI (pyridine was added as an internal standard).



**Figure S12.** <sup>1</sup>H NMR spectrum (400 MHz,  $D_2O$ , 16 mmol, pH=7, 298 K) of [K(2.2.2.cryptand)][UO<sub>2</sub>(dpaea)] 6 days after dissolution enlarged to show the presence of [U(dpaea)<sub>2</sub>] species.



Figure S13. <sup>1</sup>H NMR spectrum (400 MHz, C<sub>5</sub>D<sub>5</sub>N, 298 K) of [U(dpaea)<sub>2</sub>] (5).

# IR spectra



Figure S14. IR Spectrum in Nujol mull of the complex [UO<sub>2</sub>(dpaea)].



**Figure S15.** IR Spectrum in Nujol mull of the complex [CoCp<sub>2</sub><sup>\*</sup>][UO<sub>2</sub>(dpaea)].



Figure S16. IR Spectrum in Nujol mull of the complex [K(2.2.2.cryptand)][UO<sub>2</sub>(dpaea)].



**Figure S17.** IR Spectra in Nujol mull of the complexes [K(2.2.2.cryptand)][UO<sub>2</sub>(dpaea)] (3) and oxidised 3 in air.



**Figure S18.** IR Spectra in Nujol mull of the complexes  $[CoCp_2^*][UO_2(dpaea)]$  and  $[K(2.2.2.cryptand)][UO_2(dpaea)]$ .

#### Magnetic Moment Determination in Solution.

The magnetic moment of complex **3** was determined for pyridine and  $D_2O$  solution using the Evans method<sup>[1]</sup>.

The magnetic moment was calculated from the equation:

$$\mu_{eff} = 2.84 \sqrt{\chi_P T}$$
 , where  $\chi_P = \chi_{meas} - \chi_D$ 

and T is the temperature (298 K) of the measurement.

1) For the D<sub>2</sub>O solution:

$$\chi_{meas} = -\frac{3}{4\pi} \frac{\Delta f}{f m} = 1.58 * 10^{-3}$$

2) For the  $C_5D_5N$  solution:

$$\chi_{meas} = -\frac{3}{4\pi} \frac{\Delta f}{f m} = 1.43 * 10^{-3}$$

where  $\Delta f$  is the paramagnetic shift of the solvent in Hz (24 Hz (for pyridine) and 26.4 Hz (for D<sub>2</sub>O), f is the frequency of the NMR instrument in Hz (400 MHz) and m (0.01 g/cm<sup>3</sup>) is the molality of the complex. The  $\chi_D$  was calculated to be - 0.44 \* 10<sup>-3</sup> for the compound **3**.<sup>[2]</sup> Hence, for the D<sub>2</sub>O solution  $\mu_{eff} = 2.2 \ \mu_B$  and for the C<sub>5</sub>D<sub>5</sub>N solution  $\mu_{eff} = 2.1 \ \mu_B$ .

## Electrochemistry data.



**Figure S19.** Cyclic voltammograms for 4 mM solutions of  $[CoCp_2^*][UO_2(dpaea)]$  (2) recorded in 0.1 M  $[Bu_4N][PF_6]$  pyridine solution at 100-1000K mV/s scan rate  $Cp_2Fe/Cp_2Fe^+$  corrected.



**Figure S20.** Cyclic voltammograms for 4 mM solutions of [K(2.2.2.cryptand)][UO<sub>2</sub>(dpaea)] (3) recorded in 0.1 M [Bu<sub>4</sub>N][PF<sub>6</sub>] pyridine solution at 100-1000K mV/s scan rate Cp<sub>2</sub>Fe/Cp<sub>2</sub>Fe<sup>+</sup> corrected.



**Figure S21.** Cyclic voltammograms for 4 mM solutions of  $[K(2.2.2.cryptand)]_2$ dpaea recorded in 0.1 M  $[Bu_4N][PF_6]$  pyridine solution at 100K mV/s scan rate  $Cp_2Fe/Cp_2Fe^+$  corrected.

## Table S1. Voltammetric data for complexes 2 and 3.

Complex	Electrolyte solution	E <sub>1/2</sub> U(VI)/U(V)	E <sub>1/2</sub> U(V)/U(IV)
$\frac{[CoCp_2^*][UO_2(dpaea)]}{(2)}$	0.1M [Bu <sub>4</sub> N][PF <sub>6</sub> ] in pyridine	-1.23 V	-2.63 V
[K(2.2.2.cryptand)][UO <sub>2</sub> (dpaea)] ( <b>3</b> )	0.1M [Bu <sub>4</sub> N][PF <sub>6</sub> ] in pyridine	- 1.25 V	-2.65 V

Complex	Electrolyte	Scan	Epc	Epa
	solution	Speed		
K(2.2.2.cryptand)][UO <sub>2</sub> (dpaea)]	0.02M HEPES	10 mV/s	-1.56 V	-0.16 V
(3)	in water (pH=7)			
K(2.2.2.cryptand)][UO <sub>2</sub> (dpaea)]	0.02M HEPES	25 mV/s	-1.62 V	-0.14
(3)	in water (pH=7)			
K(2.2.2.cryptand)][UO <sub>2</sub> (dpaea)]	0.02M HEPES	50 mV/s	-1.65 V	-0.03 V
(3)	in water (pH=7)			
K(2.2.2.cryptand)][UO <sub>2</sub> (dpaea)]	0.02M HEPES	75 mV/s	-1.65 V	0.0 V
(3)	in water (pH=7)			
K(2.2.2.cryptand)][UO <sub>2</sub> (dpaea)]	0.02M HEPES	100 mV/s	-1.65 V	0.0 V
(3)	in water (pH=7)			

## **Crystallographic data**

#### X-ray Experimental Part:

The diffraction data (except compound **4**) were measured at low temperature using Cu  $K_{\alpha}$  radiation on a Rigaku SuperNova dual system in combination with Atlas type CCD detector. The data reduction was carried out by *CrysAlis<sup>Pro</sup>*.<sup>[3]</sup> The data for crystal structure **4** was collected at 120 K using Mo  $K_{\alpha}$ radiation on a Bruker APEX II CCD diffractometer equipped with a kappa geometry goniometer. The datasets were reduced by *EvalCCD*<sup>[4]</sup> and then corrected for absorption.<sup>[5]</sup>

The solutions and refinements were performed by *SHELXT*<sup>[6]</sup> and *SHELXL*<sup>[7]</sup>, respectively. The crystal structures were refined using full-matrix least-squares based on *F*<sup>2</sup> with all non hydrogen atoms anisotropically defined. Hydrogen atoms were placed in calculated positions by means of the "rid-ing" model. Additional electron density found in the difference Fourier map of compound **3** and **5** was treated by the *SQUEEZE* algorithm of *PLATON*.<sup>[8]</sup> Pseudo merohedral twinning was found for compound **2** and treated directly by *CrysAlis*<sup>Pro 1</sup> obtaining a BASF factor of 0.216(2). Similarity and rigid bond restraints (SIMU and RIGU cards) were employed during the last stages of refinement of **1** and **2**, because of the disorder displayed by the two structures.

The checkcif for the structure of **1** present several alerts A due to the poor quality of the sample. However, the connectivity is clearly established.

The checkcif of complex **4** present one A alert: Short Inter D-H..H-D D11B ..D11B 1.27 Ang.

The alert is related to wrongly located deuterium atoms but they have been obtained directly from difference Fourier map and then their geometry slightly modified in order to obtain acceptable D...O bonds and D-O-D angles.

The alert is probably due to the fact that the heavy water molecules display different orientations (which we were not able to determine) to create slightly different H-bond networks.



**Figure S22.** Ellipsoid plot at 50% probability of  $[UO_2(dpaea)]$  complex 1 (co-crystallised methanol molecule and H were omitted for clarity, C are represented in grey, O in red, N in blue and U in green); Selected distances (Å) U(1)–O(1) 1.75(3), U(1)–O(2) 1.310(13), U(1)–N(1) 2.46(2), U(1)–N(2) 2.64(2).



**Figure S23.** Ellipsoid plot at 50% probability of  $[UO_2(dpaea)(D_2O)]$  complex 4 (co-crystallised water molecule and H were omitted for clarity, C are represented in grey, O in red, N in blue and U in green). Selected distances (Å) U(1)–O(1) 1.780(4), U(1)–O(2) 1.777(4), U(1)–O(3) 2.443(4), U(1)–O(5) 2.434(3), U(1)–N(1) 2.623(4), U(1)–N(2) 2.694(5), U(1)-N(3) 2.615(4), U(1)–O(7) 2.572(4).



**Figure S24.** Ellipsoid plot at 50% probability of  $[CoCp_2^*][UO_2(dpaea)]$  complex 2 (co-crystallised pyridine molecule and H were omitted for clarity, C are represented in grey, O in red, N in blue, Co in dark blue and U in green). Selected distances (Å) U(1)–O(1) 1.833(11), U(1)–O(2) 1.842(11), U(1)–O(3) 2.409(12), U(1)–N(1) 2.526(9), U(1)–N(2) 2.706(18).



**Figure S25.** Ellipsoid plot at 50% probability of [K(2.2.2.cryptand)][UO<sub>2</sub>(dpaea)] complex 3 (co-crystallised pyridine molecule and H were omitted for clarity, C are represented in grey, O in red, N in blue, K in light blue and U in green). Selected distances (Å) U(1)–O(1) 1.8471(17), U(1)–O(2) 1.8373(18), U(1)–O(3) 2.4589(18), U(1)–O(5) 2.4533(18), U(1)–N(1) 2.575(2), U(1)–N(2) 2.6962(19), U(1)–N(3) 2.574(2).

	1	<u>2.3ру</u>	<u>3</u>
Formula	$C_{16}H_{15}N_{3}O_{6}U$	C56H65C0N7O6U	C34H51KN5O12U
Crystal size (mm <sup>3</sup> )	0.659 x 0.295 x 0.106	0.472 x 0.129 x 0.111	0.325 x 0.150 x 0.129
cryst syst	Orthorhombic	Orthorhombic	Monoclinic
space group	Pmmn	Pnma	$P2_{1}/c$
volume (Å <sup>3</sup> )	836.16(13)	5362.3(3)	4382.75(16)
a (Å)	6.9848(8)	14.3320(5)	12.6577(3)
b (Å)	14.4980(10)	20.4637(7)	23.5758(4)
c (Å)	8.2571(7)	18.2836(5)	15.4346(3)
a (deg)	90	90	90
β (deg)	90	90	107.908(2)
γ (deg)	90	90	90
Z	2	4	4
formula weight (g/mol)	583.34	1229.11	998.92
density (g cm <sup>-3</sup> )	2.317	1.522	1.514
absorption coefficient (mm <sup>-1</sup> )	27.696	11.302	3.857
F(000)	544	2468	1988
temp (K)	100.00(10)	140.00(10)	140.00(10)
total no. reflections	5394	9930	54935
unique reflections [R(int)]	981 [ 0.1667]	9930 [ <i>R</i> <sub>int</sub> = ?]	15207 [ $R_{int} = 0.0357$ ]
Final R indices	$R_1 = 0.1015,$	$R_1 = 0.0856,$	$R_1 = 0.0319,$
$[I > 2\sigma(I)]$	$wR_2 = 0.2511$	$wR_2 = 0.2190$	$wR_2 = 0.0594$
Largest diff. peak and hole (e.A-3)	10.008 and -4.061 e.Å <sup>-3</sup>	7.794 and -3.065	1.808 and -1.361
GOOF	1.170	1.055	1.018

## Table S2. Crystallographic data of 1, 2.3Py, 3, 4 and 5.

	4	<u>5</u>
Formula	$C_{16}H_{15}D_{10}N_3O_{11}U$	C <sub>32</sub> H <sub>30</sub> N <sub>6</sub> O <sub>8</sub> U
Crystal size (mm <sup>3</sup> )	0.221 x 0.212 x 0.195	0.693 x 0.407 x 0.278
cryst syst	Triclinic	Triclinic
space group	<i>P</i> -1	<i>P</i> -1
volume (Å <sup>3</sup> )	1034.2(2)	3897.26(18)
a (Å)	6.8944(8)	10.3525(3)
b (Å)	11.1491(12)	19.8443(5)
c (Å)	14.7213(15)	19.8538(5)
a (deg)	67.959(7)	84.793(2)
$\beta$ (deg)	81.512(10)	78.643(2)
γ (deg)	82.702(10)	77.371(2)
Z	2	4
formula weight (g/mol)	683.48	864.65
density (g cm <sup>-3</sup> )	2.195	1.474
absorption coeffi- cient (mm <sup>-1</sup> )	7.912	12.149
F(000)	644	1680
temp (K)	120(2)	140.00(10)
total no. reflections	17879	28537
unique reflections [R(int)]	$6005 [R_{int} = 0.0523]$	$15609 [R_{int} = 0.0491]$
Final R indices	$R_1 = 0.0372,$	$R_1 = 0.0623,$
$[I > 2\sigma(I)]$	$wR_2 = 0.0801$	$wR_2 = 0.1638$
Largest diff. peak and hole $(e.A^{-3})$	.955 and -2.430	4.201 and -5.287
GOOF	1.077	1.042

	1. [UO <sub>2</sub> (dpaea)]	<b>4.</b> [UO <sub>2</sub> (dpaea)(D <sub>2</sub> O)]	<b>2.</b> [CoCp <sub>2</sub> *] [UO <sub>2</sub> (dpaea)]	<b>3.</b> [K(2.2.2.cryptand)] [UO <sub>2</sub> (dpaea)]	<b>5.</b> [U(dpaea) <sub>2</sub> ]
U(1)–O(1)	1.75(3) Å	1.780(4) Å	1.833(11) Å	1.8471(17) Å	2.281(5) Å
U(1)–O(2)	1.310(13) Å	1.777(4) Å	1.842(11) Å	1.8373(18) Å	
U(1)–O(3)		2.443(4) Å	2.409(12) Å	2.4589(18) Å	2.344(5) Å
U(1)–O(5)		2.434(3) Å		2.4533(18) Å	2.263(5) Å
U(1)–O(7)		2.572(4) Å			2.348(5) Å
U(1)–N(1)	2.46(2) Å	2.623(4) Å	2.526(9) Å	2.575(2) Å	2.643(7) Å
U(1)–N(2)	2.64(2) Å	2.694(5) Å	2.706(18) Å	2.6962(19) Å	2.986(6) Å
U(1)-N(3)				2.574(2) Å	2.648(6) Å
U(1)–N(4)					2.625(6) Å
U(1)–N(5)					2.952(6) Å
U(1)–N(6)					2.624(6) Å

#### Table S3. Selected bond distances data for 1, 2.3Py, 3, 4 and 5.

- [1] E. M. Schubert, J. Chem. Educ. **1992**, 69, 62.
- [2] G. A. Bain, J. F. Berry, J. Chem. Educ. 2008, 85, 532.
- [3] CrysAlis<sup>Pro</sup>, Rigaku Oxford Diffraction, release 1.171.39.46, **2018.**
- [4] A. J. M. Duisenberg, L. M. J. Kroon-Batenburg, A. M. M. Schreurs, *J Appl Cryst* 2003, *36*, 220–229.
- [5] R. H. Blessing, Acta Cryst A **1995**, *51*, 33–38.
- [6] G. M. Sheldrick, Acta Cryst A **2015**, 71, 3–8.
- [7] G. M. Sheldrick, *Acta Cryst C* **2015**, *71*, 3–8.
- [8] A. L. Spek, Acta Crystallogr. 2009, Sect. D, 148–155.

# **APPENDIX 3: Supporting information for Chapter 4**

## NMR Spectroscopic data



**Figure S1.** <sup>1</sup>H NMR spectrum (400 MHz,  $C_5D_5N$ , 298 K) of crystals of  $[U^{IV}(dpaea)(OBpin)_2(py)]$ , 3. 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.

-153.77



Figure S2. <sup>11</sup>B NMR spectrum (128 MHz, C<sub>5</sub>D<sub>5</sub>N, 298 K) of crystals of [U<sup>IV</sup>(dpaea)(OBpin)<sub>2</sub>(py)], 3.



**Figure S3.** <sup>1</sup>H NMR spectrum (400 MHz, D<sub>2</sub>O, pH=8.5, 298 K): of the reaction of  $[K(2.2.2.cryptand)][UO_2(dpaea)]$  with 0.5 eq. of Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>: after 12 hours (bottom) after 2 days (middle) and after 1 week (top). Indicating reduction of uranyl(V) complex 2 to complex 5. Up to 12 hours only the signals of  $[K(2.2.2.cryptand)][UO_2(dpaea)]$  are observed.



**Figure S4.** <sup>1</sup>H NMR spectrum (400 MHz, D<sub>2</sub>O, pH=8.5, 298 K): of the reaction mixture of  $[UO_2(dpaea)]$  with 1 eq. Of Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> after 3 days (bottom); 4 days; 5 days (middle); 6 days; 7 days (top). This shows that reduction of the in situ generated U(V) to complex **4** starts after 3 days and is not complete after seven days. Signals of complex **4** are only observed after 3 days because after that it precipitates.



**Figure S5.** <sup>1</sup>H NMR spectrum (400 MHz, D<sub>2</sub>O, pH=8.5, 298 K): of the reaction mixture of  $[UO_2(dpaea)]$  with 2 eq. Of Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> after 1 day (bottom); 2 days (2<sup>nd</sup> from the bottom); 4 days (2<sup>nd</sup> form the top); 7 days (top). Peak of  $[UO_2(dpaea)]^-$  was integrated with respect to the solvent peak.



**Figure S6.** <sup>1</sup>H NMR spectrum (400 MHz, D<sub>2</sub>O, pH=5, 298 K): of the reaction mixture of [UO<sub>2</sub>(dpaea)] with 2 eq. of Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>.

#### **Diffusion coefficients measurements**

The diffusion NMR experiments were performed using a Pulsed-Field Gradient STimulated Echo (PFG-STE) sequence, using bipolar Gradients, at 298 K and no spinning was applied to the NMR tube.<sup>[1]</sup>

The spherical hydrodynamic radius (called Stokes radius) of the molecule was calculated from the Stokes-Einstein equation and compared to the value obtained from the solid-state structure and with a similar reference compound in the same solvent:

$$r_{sph} = \frac{k_B T}{6\pi n D}$$
 where

- *D* Diffusion coefficient ( $m^2.s^{-1}$ )
- $k_B$  Boltzmann constant (m<sup>2</sup>.kg.s<sup>-2</sup>.K<sup>-1</sup>)
- T Temperature (K),
- *n* dynamic viscosity (Pa.s<sup>-1</sup>)
- $\pi$  pi
- r radius of the spherical particle (Å)

#### Electrochemistry data.

The U(V)/U(IV) redox event is not observable in water solution probably due to the slow kinetics of electron transfer and to the important structural rearrangement associated to this redox event resulting in the formation of complex 4.



**Figure S7.** Cyclic voltammetry data recorded for 4 mM solutions of [Zn(dpaea)] in 0.05 M in aqueous HEPES solutions (pH= 7) at 100 mV/s scan rates vs. Ag/AgCl.

Cyclic voltammetry measurements for complexes **3** and **5** were also performed in organic solution (pyridine). Both U(IV)-containing compounds demonstrated redox events occurring at similar potentials. Two irreversible oxidations are observed at  $E_{pa1}$ = 0.08 eV;  $E_{pa2}$ = 0.3 eV (complex **3**) and  $E_{pa1}$ = -0.04 eV;  $E_{pa2}$ = 0.17 eV (complex **5**) most likely corresponding to U(IV)/U(V) and U(V)/(VI) events (Fig S14-15).



**Figure S8.** Cyclic voltammetry data recorded for 4 mM solutions of  $[Na(2.2.2crypt)][U_3(dpaea)_3O_2(OH)(SO_3)]$  (5) in 0.1 M aqueous  $[Bu_4N][PF_6]$  pyridine solution at 100 mV/s scan rate vs. Cp<sub>2</sub>Fe/Cp<sub>2</sub>Fe<sup>+</sup>.



**Figure S9.** Cyclic voltammetry data recorded for 4 mM solutions of  $[U(dpaea)(OBpin)_2(py)]$  (3) in 0.1 M aqueous  $[Bu_4N][PF_6]$  pyridine solution at 100 mV/s scan rate vs.  $Cp_2Fe/Cp_2Fe^+$ .

#### **XPS** data

Curve fitting was performed using the PHI Multipak software. The oxidation state of uranium was assigned based on the satellite energies (s) relative to the primary peak U4f<sub>7/2</sub> ( $\Delta E_{s-p}$ ). In both spectra  $\Delta E_{s-p}$  are around 6 eV (5.9 and 6.1 eV), consistent with a pure U(IV)-containing compound.



Figure S10. XPS narrow scans of U4f: Crystals of complex 4 [Na(H<sub>2</sub>O)<sub>5</sub>U<sub>3</sub>(dpaea)<sub>3</sub>O<sub>2</sub>(OH)(SO<sub>3</sub>)] (top);

solid isolated from the reduction of  $[UO_2(dpaea)]$  with 2 eq.  $Na_2S_2O_4$  in 0.5 M HEPES  $D_2O$  solution (pH= 8.5) (bottom) (s = satellite peak).

#### **Crystallographic data**

Bragg-intensities of **3**, **4**, **5** and **6** were collected at 140 K using Cu or Mo  $K\alpha$  radiation (See Table S2). A Rigaku SuperNova dual system diffractometer with an Atlas S2 CCD detector was used for compounds **3**, **4** and **6**, and one equipped with an Atlas CCD detector for compound **5**. The datasets were reduced and corrected for absorption, with the help of a set of faces enclosing the crystals as snugly as possible, with *CrysAlis<sup>Pro</sup>*.<sup>[2]</sup>

The solutions and refinements of the structures were performed by the latest available version of *ShelXT* <sup>[3]</sup>and *ShelXL*<sup>[4]</sup>. All non-hydrogen atoms were refined anisotropically using full-matrix least-squares based on  $|F|^2$ . The hydrogen atoms were placed at calculated positions by means of the "riding" model where each H-atom was assigned a fixed isotropic displacement parameter with a value equal to 1.2  $U_{eq}$  of its parent C-atom (1.5  $U_{eq}$  for the methyl groups), but in the structures **4** and **6**, hydrogen atom positions bound to water molecules were found in a difference map and refined freely. Crystallographic and refinement data are summarized in Table S2. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre and correspond to the following codes: **3** (1970863), **4** (1970860), **5** (1970861) and **6** (1970862). These data can be obtained free of charge via www.ccdc.cam.ac.uk/data\_request/cif, or by emailing data\_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

In the structure **3**, two boroxide ligands are disordered over two positions found in a difference map and which were refined anisotropically imposing distance and similarity restraints (SADI and SIMU) for the least-squares refinement, yielding site occupancies of 0.512(5)/0.488(5) and 0.742(3)/0.258(3), respectively.

In the structure **4**, additional electron density found in the difference Fourier map (due to highly disordered solvent molecules of water) was removed by help of the solvent-masking program in *OLEX2*.<sup>[5]</sup>

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**Figure S11.** Ellipsoid plot at 50% probability of  $[Na(H_2O)_5U_3(dpaea)_3O_2(OH)(SO_3)]$  complex **4** (cocrystallized water molecules and most H atoms were omitted for clarity, C are represented in grey, H in white O in red, N in blue, S in yellow, Na light blue and U in green.



**Figure S12.** Ellipsoid plot at 50% probability of  $[Na(2.2.2crypt)][U_3(dpaea)_3O_2(OH)(SO_3)]$  complex **5** (co-crystallized water molecules and H atoms of the ligand were omitted for clarity, C are represented in grey, H in white, O in red, N in blue, S in yellow and U in green.



**Figure S13.** Ellipsoid plot at 50% probability of molecular structure of the  $[{UO_2(dpaea)(H_2O)}H_2O]^-$  anion of the complex **6** (H atoms of the ligand are removed for clarity) H white, C grey, N blue, O red and U green.

#### Structural details of 6

The O=U=O angle (174.03(9)°) and U=Oyl bond distances (1.861(2) and 1.855(2) Å) are similar to those found in the monomeric complex **2** isolated from pyridine solution with the main difference between the two complexes being the presence of one water molecule bound in the equatorial plane and resulting in a hexagonal bipyramidal geometry of the U(V) center

# Table S1. X-ray crystallographic data for 3, 4, 5 and 6.

Compound	3	4	5	6
Formula	$C_{33}H_{44}B_2N_4O_{10}U$	$C_{48}H_{56}N_9NaO_{23}SU_3$	$C_{66}H_{82}N_{11}NaO_{24}SU_3$	$C_{32}H_{46}N_6Na_2O_{20}U_2\\$
$D_{calc.}$ / g cm <sup>-3</sup>	1.572	1.687	1.962	2.155
μ/mm <sup>-1</sup>	12.271	6.592	19.341	22.600
Formula Weight	916.37	1896.15	2182.56	1356.79
Colour	clear intense green	clear dark orange	clear intense orange	clear intense red
Shape	prism	prism	irregular	needle
Size/mm <sup>3</sup>	0.17×0.08×0.07	0.28×0.19×0.05	0.11×0.07×0.04	0.65×0.08×0.06
<i>T</i> /K	140.00(10)	139.99(10)	140.00(10)	140.00(10)
Crystal System	orthorhombic	triclinic	triclinic	monoclinic
Space Group	Pbca	$P\overline{1}$	PĪ	$P2_{1}/c$
a/Å	15.50019(6)	13.25028(19)	13.0844(14)	9.37479(6)
b/Å	21.09635(7)	15.3491(2)	15.742(2)	13.52608(9)
$c/\text{\AA}$	23.68744(9)	18.9837(3)	20.4534(16)	16.49213(11)
$\alpha/^{\circ}$	90	103.5118(14)	105.334(9)	90
β/°	90	95.7198(13)	102.401(8)	90.3798(6)
γ/°	90	90.3357(12)	106.666(11)	90
$V/Å^3$	7745.73(5)	3733.67(10)	3694.8(7)	2091.23(2)
Ζ	8	2	2	2
Ζ'	1	1	1	0.5
Wavelength/Å	1.54184	0.71073	1.54184	1.54184
Radiation type	Cu Ka	Μο Κα	Cu Kα	Cu Ka
$\Theta_{min}/^{\circ}$	3.732	2.695	3.715	3.267
$\Theta_{max}/^{\circ}$	76.163	32.933	74.763	72.710
Measured Refl's.	81625	47007	25879	16662
Ind't Refl's	8083	24649	14508	4120
Refl's with $I > 2(I)$	7935	21217	7632	4090
R <sub>int</sub>	0.0178	0.0266	0.1116	0.0294
Parameters	597	802	958	314
Restraints	466	45	1275	3
Largest Peak/e Å <sup>-3</sup>	0.614	1.738	4.896	1.540
Deepest Hole/e Å <sup>-3</sup>	-0.697	-1.313	-2.218	-1.476
GooF	1.117	1.019	0.979	1.156
$wR_2$ (all data)	0.0450	0.0569	0.2268	0.0491
$wR_2$	0.0448	0.0550	0.1709	0.0490
$R_1$ (all data)	0.0187	0.0340	0.1536	0.0189
$R_I$	0.0184	0.0266	0.0747	0.0188
CCDC code	1970863	1970860	1970861	1970862

Crystals structure and selected distances of the cores of trinuclear clusters	2.3291(18) A 03 04 05 05 05 05 05 05 05 05 05 05	2.315(tal) A 2.322(13) A 2.035(tal) A 2.322(13) A 2.039(13) A 2.322(13) A 2.322(13) A 2.039(13) A 2.322(13) A 2.32
Formula	[Na(H <sub>2</sub> O) <sub>5</sub> U <sub>3</sub> (dpaea) <sub>3</sub> O <sub>2</sub> (OH)(SO <sub>3</sub> )] ( <b>4</b> )	[Na(2.2.2crypt)][U <sub>3</sub> (dpaea) <sub>3</sub> O <sub>2</sub> (OH)(SO <sub>3</sub> )] ( <b>5)</b>
Angle U1-O3-U3 ( <b>4</b> ) U3-O2-U2 ( <b>5</b> )	138.20(9)°	139.4(8)
Angle U3-O2-U2 ( <b>4</b> ) U2-O1-U1 ( <b>5</b> )	144.39(9)°	143.2(9)
Angle U2-O1-U1 ( <b>4</b> ) U1-O3-U3 ( <b>5</b> )	148.83(8)°	150.1(8)

## Table S2. Selected distances and angles for complexes 4 and 5

#### References

- [1] D. H. Wu, A. D. Chen, C. S. Johnson, *J. Magn. Reson. A* **1995**, *115*, 260–264.
- [2] CrysAlis<sup>Pro</sup> Software System, Rigaku Oxford Diffraction, **2019**.
- [3] Sheldrick, G.M., Acta Cryst., **2015**, A71, 3-8.
- [4] Sheldrick, G.M., *Acta Cryst.*, **2015**, C71, 3-8.
- [5] O.V. Dolomanov, L.J. Bourhis, R.J. Gildea, J.A.K. Howard, H. Puschmann, *J. Appl. Cryst.*, 2009, 42, 339-341.

# **APPENDIX 4: Supporting information for Chapter 6**

#### NMR Spectroscopic data



**Figure S1.** <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN, 298 K) spectrum of the reaction mixture between 2 equivalents of potassium benzoate, 2 equivalents of water and 1 equivalent of UCl<sub>4</sub>.



**Figure S2.** <sup>1</sup>H NMR (200 MHz,  $CD_3CN$ , 298 K) of the crystals of **1** from the reaction between 2 equivalents of potassium benzoate, 2 equivalents of water and 1 equivalent of  $UCl_4$ .

## **Diffusion coefficients measurements**

The diffusion NMR experiments were performed using a Pulsed-Field Gradient STimulated Echo (PFG-STE) sequence, using bipolar Gradients, at 298 K and no spinning was applied to the NMR tube.<sup>[1]</sup>

The spherical hydrodynamic radius (called Stokes radius) of the molecule was calculated from the Stokes-Einstein equation and compared to the value obtained from the solid-state structure and with a similar reference compound in the same solvent:

$$D \quad \text{Diffusion coefficient } (\text{m}^2.\text{s}^{-1})$$

$$k_B \quad \text{Boltzmann constant } (\text{m}^2.\text{kg.s}^{-2}.\text{K}^{-1})$$

$$T \quad \text{Temperature } (\text{K}),$$

$$n \quad \text{dynamic viscosity } (\text{Pa.s}^{-1})$$

$$\pi \quad \text{pi}$$

$$r \quad \text{radius of the spherical particle } (\text{Å})$$

Table S1. Diffusion coefficient values of 1, 2, 3 and 4 and estimated spherical radii.

Cluster	Diffusion coefficient (m².s <sup>-10</sup> )	Hydrodynamic radii (Å)	Evaluated radii (Å)
U <sub>6</sub> O <sub>8</sub> <b>1</b>	3.29 10 <sup>-10</sup>	7.5	8.5
U <sub>6</sub> O <sub>4</sub> <b>2</b>	3.09 10 <sup>-10</sup>	8.0	9.2
U <sub>13</sub> O <sub>16</sub> K <sub>x</sub> <b>3-4</b>	9.04.10 <sup>-10</sup>	7.1	8.3

## **UV-Vis Absorption spectra**



**Figure S3.** Absorption spectra of the crystals of **1** in Pyridine ( $c = 1.47.10^{-3}$  M).



**Figure S4.** UV-visible spectra of  $[UCl_4]$  (c = 4.5.10<sup>-3</sup> M) in MeCN and the evolution over time of the reaction mixtures in the presence of 2 equiv. of potassium benzoate and H<sub>2</sub>O.

#### **Crystallographic data**

Diffraction data were taken using an Oxford-Diffraction XCallibur S kappa geometry diffractometer (Mo-K $\alpha$  radiation, graphite monochromator,  $\lambda = 0.71073$  Å). To prevent evaporation of co-crystallized solvent molecules the crystals were coated with light hydrocarbon oil and the data were collected at 150 K. The cell parameters were obtained with intensities detected on three batches of 5 frames. The crystal-detector distance was 4.5 cm. The number of settings and frames has been established taking in consideration the Laue symmetry of the cell by CrysAlisPro Oxford-diffraction software.[2] 501 for **2**, 107 and 333 for **3**, 128 and 139 for **7** narrow data were collected for 1° increments in ω with a 2 s exposure time for 2, 60s and 300s respectively exposure time for 3, 60s for 4, 60 s and 300s respectively for 7. Unique intensities detected on all frames using the Oxford-diffraction Red program were used to refine the values of the cell parameters. The substantial redundancy in data allows empirical absorption corrections to be applied using with the ABSPACK Oxford-diffraction program[2] for 2, 3, and 7. Space groups were determined from systematic absences, and they were confirmed by the successful solution of the structure. The structures were solved by direct methods using the SHELX[3] or by charge flipping method using superflip[2a] in Olex2[2a, [4]] software environment. All non-hydrogen atoms were found by difference Fourier syntheses and refined on F2 using ShelXL[5]. For 2, 3, and 7 hydrogen atoms were fixed in ideal position. Full crystallographic details are given in Table S2.

Data diffraction were measured at low temperature using Cu K $\alpha$  and Mo K $\alpha$  radiation for **5** and **6**, respectively on a Rigaku SuperNova dual system diffractometer equipped with an Atlas S2 type CCD detector for **5** and with an Atlas type CCD detector for **6**. The datasets were reduced and then corrected for absorption by means of CrysAlisPro,<sup>[2]</sup> with the help of a set of faces enclosing the crystals as snugly as possible. The solutions and refinements for the structures were performed by SHELXT<sup>[3]</sup> and SHELXL-2018 (release 3)<sup>[5]</sup> respectively. All non-hydrogen atoms were refined anisotropically using full-matrix least squares based on  $|F|^2$ . All hydrogen atoms were placed in geometrically calculated positions and refined by using a riding model where each H-atom was assigned a fixed isotropic displacement parameter with a value equal to 1.2  $U_{eq}$  of its parent C-atom.

In the structure of **5**, SIMU restraints were applied on the displacement parameters of the light atoms. Phenyl rings were constrained to regular hexagons using AFIX 66 commands. EADP

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constraints were applied to some oxygen atoms of the ligands. Seven disordered acetonitrile solvent molecules were removed with the help of the solvent-masking program in Olex2.<sup>[4]</sup>

In the case of **6**, SIMU restraints were also applied on the displacement parameters of the light atoms and Phenyl rings were also constrained to regular hexagons using AFIX 66 commands. Some C-O bond lengths were restrained using SADI commands. Additional solvent molecules, too disordered to be located in the electron density map, were taken into account using the solvent-masking program in OLEX2.<sup>[4]</sup> CCDC numbers 1875247-1875252 for compounds **2** (1875251), **3**, (1875249), **4** (1875247), **5**, (1875252), **6** (1875250), and **7** (1875248), contain the supplementary crystallographic data for this paper. These data can be obtained, free of charge, from The Cambridge Crystallographic Data Centre via <u>www.ccdc.cam.ac.uk/structures</u>.

# Table S2. X-ray crystallographic data.

Compound	[2]3Py.1DIPE	[3].6MeCN	[4]	
Formula	$C_{153}H_{129}N_7O_{37}U_6$	$C_{96}H_{82}CI_{16}K_4N_6O_{40}U_{13}$	$C_{84}H_{67}CI_{17}K_2O_{40}U_{13}$	
Crystal size [mm]	0.58x0.47x 0.41	0.20 x 0.14 x 0.05	0.23x 0.11 x 0.08	
Crystal system	Triclinic	Monoclinic	Monoclinic	
Space group	Р	l 2/m	I2/m	
V [ų]	3596.1(2)	7843.1(5)	7764(3)	
a [Å]	14.7314(6)	15.1988(5)	15.2373(17)	
b [Å]	15.4129(5)	20.6495(8)	20.511(4)	
c [Å]	17.1466(6)	25.1583(12)	25.029(9)	
α [°]	70.709(3)	90	90	
β [°]	79.131(3)	96.627(4)	96.99(2)	
γ [°]	81.968(3)	90	90	
Z	1	2	2	
Abs. coef. [mm <sup>-1</sup> ]	6.812	13.809	13.905	
F (000)	1944	5128	4828	
Т [К]	150(2)	293(2)	150.0(10)	
Total no. reflexions	32879	29333	44710	
Unique reflexions	14701 [R(int) =	9884 [R/int) - 0 0971]	12412 [B 0.0490]	
[R(int)]	0.0465]	9884 [N(int) = 0.0971]	12412 [Rint - 0.0490]	
Final R indice [1>20(1)]	R1 = 0.0381, wR2 =	R1 = 0.0582, wR2 =	R <sub>1</sub> = 0.0738, wR <sub>2</sub> =	
	0.0786	0.1058	0.1931	
Largest diff. peak and hole [eA <sup>-3</sup> ]	3.30 and -1.64	2.27 and -1.68	4.35 and-1.71	
GOOF	1.039	0.988	0.866	
[5]	[6]	[7]		
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$C_{192}H_{148}N_2O_{75}U_{16}$	$C_{230}H_{172}CI_4N_4O_{92}U$	$C_{174}H_{160}CI_{18}N_{10}O_{11}$		
	24	<sub>0</sub> U <sub>38</sub>		
0.07x0.05x 0.02	0.32 x 0.22 x0.12	0.06x0.04 x 0.03		
Monoclinic	Monoclinic	Tetragonal		
P2 <sub>1</sub> /n	P2 <sub>1</sub> /n	I 4/m		
22912.2(7)	13301.1(7)	14039.3(12)		
20.7682(3)	20.9570(4)	21.7282(8)		
32.8915(7)	29.9330(6)	21.7282(8)		
33.6517(5)	21.5136(10)	29.7370(14)		
90	90	90		
94.6354(14)	99.738(3)	90		
90	90	90		
4	2	2		
31.992	14.671	22.073		
13544	9184	11912		
139.99(10)	100.00(10)	150(2)		
96045	174026	35509		
46291 [ <i>R</i> <sub>int</sub> =	45199 [ <i>R</i> <sub>int</sub> =	10896 [R <sub>int</sub> =		
0.0625]	0.1043]	0.1206]		
$R_1 = 0.0889, wR_2$	$R_1 = 0.0674, wR_2$	R1 = 0.0675, wR2		
= 0.2240	= 0.1563	= 0.0724		
7.281 and -7.654	7.937 and -2.944	2.73 and -2.25		
1.026	1.023	0.955		

Structural comparison. A summary of structural parameters is reported in Table S2 for the complexes obtained from the controlled hydrolysis of [UCl<sub>4</sub>] in the presence of potassium benzoate. The hydroxo groups of 3, 4, 5 and 6 were assigned thanks to longer U-µ<sub>3</sub>OH bond lengths (mean value 2.43(4) Å) compared to the mean U-O distances for the U-μ<sub>3</sub>O groups (mean value 2.25(1) Å). These distances are in the range of previous  $U-\mu_3OH$  and  $U-\mu_3O$  distances reported for oxo/hydroxo clusters. <sup>[6-8]</sup> The clusters **3**, **4**, **5**, **6** and **7** containing μ<sub>4</sub>-oxo ligands, have U-μ<sub>4</sub>O bond lengths (2.367(9) Å) that are 0.12 Å longer than the U- $\mu_3$ O bonds. The U- $\mu_4$ O distances found in these clusters are similar in length to the U-O bonds found in UO<sub>2</sub> nanoparticles (mean value of 2.346(6) Å). <sup>[9]</sup> The U-U distances in the discrete synthesized clusters lie in the same range as those in the UO<sub>2</sub> nanoparticle (synthetic UO<sub>2</sub>: 3.867(4) Å and biogenic UO<sub>2</sub>: 3.842(5) Å ).<sup>[9]</sup> The average diameter of UO<sub>2</sub> uraninite nanoparticles formed from the reduction of uranyl(VI) is 1.2 nm while the overall particle size is approximately 2.5 nm.<sup>[9-10]</sup> These structural parameters are really close to the cluster **7** that has a volume of 26×25×23 Å<sup>3</sup> (size with ligands around the core) with the largest U-U distance in the core of 12.077(1) Å. The mean U- $\mu_4$ O distance is in the same range than in the UO<sub>2</sub> nanoparticle, whereas the U-U is shorter of 0.05 Å for 7. This can be due to the distortion induced by the chloride and benzoate ligands surrounding the cluster core. These parameters show that 7 can be used as a good synthetic model of the environmental relevant uraninite nanoparticle

Compound	U(1)	U(2)	U(3)	U(4)	U(5)	U(6)	U(7)	U(8)
2	4.15	4.16	4.10	-	-	-	-	-
3	4.00	4.04	4.07	3.56	3.	-	-	-
4	3.87	4.31	4.15	3.85	4.30	-	-	-
5	3.97	3.93	4.09	4.12	4.17	4.27	4.12	4.28
6	3.99	3.88	4.24	4.44	4.36	4.43	4.10	4.10
7	3.94	4.28	4.19	4.23	4.24	4.03	3.92	-

Table S3. Bond valence sum for compounds 2, 3, 4, 5, 6 and 7.

Compound	U(9)	U(10)	U(11)	U(12)	U(13)	U(14)	U(15)	U(16)
5	3.99	4.00	4.34	4.12	4.34	4.34	4.34	4.12
6	4.36	4.30	4.34	4.28	-	-	-	-

Com-	1	2	3	4	5	6	7
pound							
U-µ₃OH	2.439(4)	-	2.45(9)	2.46(9)	2.43(5)	2.37(5)	-
U-μ₃Ο	2.251(4)	2.24(8)	2.24(2)	2.27(4)	2.24(3)	2.26(5)	2.24(3)
U-µ₄O	-	-	2.36(13)	2.38(12)	2.37(8)	2.36(6)	2.36(3)

**Table S4.** Average core bond lengths (in Å) found in clusters 1 (from ref.<sup>[11]</sup>), 2, 3, 4, 5, 6 and 7.

## Detailed description of the structure of cluster 5 and structural comparison with the previously reported U16 cluster {[K(MeCN)]<sub>2</sub>[U<sub>16</sub>O<sub>22</sub>(OH)<sub>2</sub>(PhCOO)<sub>24</sub>]}<sup>[12]</sup>

The U1, U2, U3, U5, U11 and U13 atoms in cluster **5** (Figure S5 left) are eight- coordinate with a cubic geometry for U1, U2, U3 and U5, and a bicapped trigonal prismatic geometry for U11 and U13. The remaining uranium atoms are nine coordinates with a tricapped trigonal prismatic coordination geometry for U4, U7, U8 and U12, while U6, U9, U10, U14, U15 and U16 feature a capped square antiprismatic coordination geometry. The uranium atoms are connected by 15 oxo, 8 hydroxo and 26 benzoate ligands. 8  $\mu_3$ -O ligands and 8  $\mu_3$ -OH ligands cap 16 triangular faces of the octahedrons; and 7  $\mu_4$ -O ligands are located in the tetrahedral cavity formed by two or four adjacent octahedrons. The position of the hydroxo ligands in the crystal structure has been assigned on the basis of geometrical parameters. The mean U-O distance of the  $\mu_3$ -O groups (2.238(26) Å) is significantly shorter than for the  $\mu_3$ -OH groups (2.425(51) Å). The mean U-O distance is 2.371(84) Å for the  $\mu_4$ -O groups. Fourteen benzoate ligands bridge two adjacent uranium(IV) centers of a same octahedron. Ten additional bidentate bridging benzoate ligands are each monodentate but the non-coordinated oxygen is engaged in hydrogen bonding with a  $\mu_3$ -hydroxo group. One pyridine molecule is found in the coordination spheres of U3 and U5, respectively.

In the core of the previously reported  $\{[K(MeCN)]_2[U_{16}O_{22}(OH)_2(PhCOO)_{24}]\}, [12]$  (Figure S5 right) the two external octahedrons share one edge with each one of the two adjacent octahedrons. Overall, each octahedron shares one edge with all of the neighboring octahedrons. In **5**, each octahedron shares three edges of three different neighboring octahedrons, forming a compact tetrahedron. The asymmetric unit of  $\{[K(MeCN)]_2[U_{16}O_{22}(OH)_2(PhCOO)_{24}]\}$  consists of eight crystallographically inequivalent uranium atoms related to their symmetry equivalents by an inversion center (located in

the middle of the U1-U1A and U3-U3A edges) while sixteen crystallographically inequivalent uranium atoms are present in **5**.



**Figure S5.** Arrangement of the octahedrons in  $[U_{16}O_{15}(OH)_8(PhCOO)_{26}(Py)_2]$ , 5 (left) and in the previously reported { $[K(MeCN)]_2[U_{16}O_{22}(OH)_2(PhCOO)_{24}]$ } (right).



**Figure S6.** Molecular structure of **3**  $[U_{13}K_4O_{12}(OH)_4(PhCOO)_{12}Cl_{14}]Cl_2$ . (Ellipsoids are set at 30% probability). Most H atoms, disorder and solvent molecules are removed for clarity. U green, Cl in light green, O red, C grey, N blue, K in light blue and H in white.

## References

[1] D. H. Wu, A. D. Chen, C. S. Johnson, *Journal of Magnetic Resonance, Series A* **1995**, *115*, 260–264.

[2] a) CrysAlisPRO, **2015**; b) L. C. SUPERFLIP program (Palatinus, G. J. Appl. Cryst., 2007, 40, 786-790), **2007**.

[3] G. M. Sheldrick, Acta Crystallogr., Sect. A 2015, 71, 3-8.

[4] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. a. K. Howard, H. Puschmann, *J Appl Cryst* **2009**, *42*, 339–341.

- [5] G. M. Sheldrick, Acta Cryst C 2015, 71, 3–8.
- [6] V. Mougel, B. Biswas, J. Pecaut, M. Mazzanti, Chem. Commun. 2010, 46, 8648-8650.
- [7] B. Biswas, V. Mougel, J. Pecaut, M. Mazzanti, Angew. Chem. Int. Ed. Engl. 2011, 50, 5744-5747.
- [8] G. Nocton, F. Burdet, J. Pecaut, M. Mazzanti, Angew. Chem. Int. Ed. Engl. 2007, 46, 7574-7578.
- [9] 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.
- [10] J. R. Bargar, R. Bernier-Latmani, D. E. Giammar, B. M. Tebo, *Elements* 2008, 4, 407-412.
- [11] V. Mougel, B. Biswas, J. Pecaut, M. Mazzanti, Chem. Commun. 2010, 46, 8648-8650.
- [12] B. Biswas, V. Mougel, J. Pecaut, M. Mazzanti, *Angew. Chem. Int. Ed. Engl.* **2011**, *50*, 5744-5747.

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Strengths	<ul> <li>Organic &amp; Inorganic synthesis</li> <li>Analytical chemistry</li> <li>Air &amp; moisture sensitive techniques</li> <li>Experience with radioactive sources</li> <li>Scientific communication</li> <li>Working in interdisciplinary teams</li> <li>Data analysis</li> </ul>					
Education Present- 2016	<ul> <li>PhD (Inorganic/Coordination Chemistry)</li> <li>EPFL, Lausanne (Prof. Mazzanti's group)</li> <li>Title: Synthesis and reactivity of environmentally relevant uranium species.</li> <li>Main goals: Stabilization of uranyl(V) in water, investigation of the stability, reactivity and electronic structure of uranium species under environmentally relevant conditions. Collaborative development of the bacterial reduction mechanism of uranium.</li> </ul>					
2015- 2011	MSci Chemistry with a Year in Industry University of Nottingham, UK, 1st Class Degree Title: Development of a novel catalyst-free trifluoroethylation reaction Main achievement: Nature Communications article published (ref. 6).					
2011 1999	Maardu Gymnasium, Estonia Graduate with Honors					
Professional Experience Present- 2016	<ul> <li>EPFL– Lausanne, Switzerland</li> <li>Graduate Student in Coordination Chemistry group</li> <li>Project: Development of environmentally relevant chemistry of uranium.</li> <li>Acquired skills: air/moisture sensitive and a wide range of analytical techniques, maintenance of advanced laboratory equipment, C lab experience, scientific writing, student supervision, independent and efficient project execution.</li> </ul>					
2016- 2015	Novartis Pharma – Basel, Switzerland Postgraduate internship in Chemical & Pharma Development group Project: Scale-up flow crystallization development Acquired skills: large scale crystallization, FBRM, PSD, statistical data analysis (Minitab), work in interdisciplinary team.					
2014- 2013	Actelion Pharmaceuticals Ltd – Allschwil, Switzerland Internship in High Throughput and Medicinal Chemistry group Project: Anticancer drug development Acquired skills: medicinal and parallel synthesis, LC/MS, HPLC & MS and their basic maintenance					

Professional Skills Synthetic	Organic, coordination and inorganic synthesis, han compounds	dling air and moisture sensitive		
Analytical	Multi-nuclear NMR, IR spectroscopy, UV-Vis-NIR spectroscopy, fluorescence spectroscopy, X-ray crystallography, X-ray spectroscopy (XANES, XPS), mass spectrometry, GC-MS, LC/MS, HPLC, EPR spectroscopy, cyclic voltammetry, microanalysis, FBIR.			
Laboratory	Maintenance of the glove boxes and advanced analytical equipment, autoclave and centrifuge use, general responsibility for the safety and functional workspace in the laboratory and Master's students supervision.			
IT Additional	Microsoft Office, Igor Pro, Origin, MestreNova, O Draw, Perkin-Elmer UV & IR, Chemical & Crysta Adobe Illustrator, Python (beginner)	lex, Mercury, EC-lab, Chem- llographic databases,		
Experiences Teaching	General and organic chemistry laboratory I Advanced general chemistry Chemistry analytic laboratory II	Mathematics 1A General chemistry I Risk management		
Student Supervision	Supervision of two Master's students during my doctoral thesis. Specifically, scientif- ic education on the topic, development of the project to produce novel outcomes and training in laboratory techniques such as the use of Schlenk lines and glove boxes.			
Trainings	Radiation protection, Project management and Per-	sonal efficiency		
Publications				
2020	1) Faizova, R.; Fadaei-Tirani F.; Bernier-Latmani F facile conversion of uranyl(VI) to uranium(IV) in c 2020, 59, 6756–6759.	R., Mazzanti, M. Ligand supported organic and aqueous media, <i>ACIE</i> ,		
	2) Molinas M., <u>Faizova R.</u> , Brown A., Galanzew zanti M., Bernier-Latmani R., Pentavalent uranium cal reduction of U(VI) to U(IV), in submission.	J., Schacherl B., Vitova T., Maz- as an intermediate in the biologi-		
2019	3) Chatelain L., <u>Faizova R.</u> , Fadaei-Tirani F., Pécaut J., Mazzanti M., Structural Snapshots of Cluster Growth from $\{U6\}$ to $\{U38\}$ During the Hydrolysis of UCl <sub>4</sub> , <i>ACIE</i> 2019 58 (10) 3021–3026			
2018	4) <u>Faizova, R.</u> ; Scopelliti, R.; Chauvin, AS.; Mazi ization of a Water Stable Uranyl(V) Complex. <i>JAC</i>	zanti, M. Synthesis and Character- CS, 2018, 140 (42), 13554–13557.		
	5) <u>Faizova, R.</u> ; White, S.; Scopelliti, R.; Mazzanti, Uranyl(V) Stability. <i>Chemical Science</i> , 2018, 9 (38	M. The Effect of Iron Binding on 3), 7520–7527.		
2017	<ul> <li>6) Andrews, K. G.; Faizova, R.; Denton, R. M.</li> <li>A Practical and Catalyst-Free Trifluoroethylation Reaction of Amines Using Trifluoroacetic Acid. <i>Nature Communication</i>, 2017, 8, 15913.</li> </ul>			

## **Conferences**

	Driving lice	nce: Yes			
Details	Permit: Valid B permit	<b>Age:</b> 28			
Personal	Nationality: Estonian (EU)	Civil Status: Single			
Other Interests	Sharing my passion for science thoug I also enjoy spending time in the more and latin dance.	gh different education outreach efforts. untains, as well as practicing and teaching yoga			
Languages	English – fluent (C2); Russian – nativ Estonian – intermediate (B1); Spanis	ve speaker; French – intermediate (B2); h – beginner (A2)			
2013- 2012	Nottingham Advantage Award President of Nottingham Russian Spe International Students Representative	eaking Society e in the School of Chemistry			
2015	Bravo Award (Novartis) - Personal co CHAD Award 2015 (Novartis) - Dev Crystallization	ontribution during the internship elopment of Next Generation			
2019	National Security Education Center a SCNAT Chemistry Travel Award My Thesis in 180 seconds competitio	on (2nd place at EPFL)			
Awards	Best Poster Presentation Award (Run	ner-un) SCS 2019			
2017	Swiss Chemical Society Fall meeting - Poster Presentation				
2018	Swiss Chemical Society Fall meeting International Conference on f-Block	g - Poster Presentation Elements (ICFE10) - Oral Presentation			
Attended 2019	ACS National Meeting & Expo - Ora Swiss Chemical Society Fall meeting TEDxLausanne 2019 - Invited Oral	al Presentation g - Poster Presentation Presentation			
Organization	Organization committee member of (ICFE10 Lausanne-2018)	10th International Conference on f-elements			

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