Uranium Clusters

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Stable Pentavalent Uranyl Species and Selective Assembly of a Polymetallic Mixed-Valent Uranyl Complex by Cation–Cation Interactions**

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Cation–cation interactions are a key feature of actinide chemistry. These interactions can be used in two areas that currently attract great interest, namely the expansion of f-element supramolecular chemistry and the enhancement of magnetic interactions in actinide compounds.[1–12] Moreover, oligomeric cation–cation species that present mutually coordinated actinyl ions are likely to play a crucial role in nuclear waste reprocessing and in the migration of radioactive actinides in the environment.[1]

Cation–cation interactions are known to be important in neptunyl(V) structural chemistry,[13] but are more rarely found in uranyl(VI) compounds because of the lower basicity of the UO_2^{2+} oxygen atoms. Dimeric compounds formed through the mutual binding of pentavalent uranyl(V) ions have been proposed as intermediates in the disproportionation of pentavalent uranyl ions to UO_2^{2+} and U^{IV} species.[14] As a result, bulky ligands have been used in the past few years to disfavor cation–cation interactions and allow the synthesis of rare UO_2^+ complexes,[15–21] which have been the subject of two recent reviews.[21] In some of the reported UO_2^+ systems, the ligand bulk does not prevent cation–cation interactions and results in decomposition. However, only two examples of $UO_2^+\cdots UO_2^+$ intermediate complexes have been reported to date: the tetrameric $[UO_2(dbm)_2]_4[K_4(CH_3CN)_4]$ (**1**) and the dimeric $[\{UO_2(dbm)_2K(18C6)\}_2]$ (dbm^- = dibenzoylmethanate, 18C6 = [18]crown-6) complexes.[8] The presence of antiferromagnetic coupling between the oxo-bridged uranium centers was unambiguously demonstrated for the dimetallic complex but is less evident for the tetrametallic complex.[8] The decomposition of these polymetallic complexes of pentavalent uranyl ions to UO_2^{2+} and U^{IV} species starts rapidly after dissolution in organic solvents and is accelerated by traces of water. From these reactivity studies, it occurred to us that the stability of these polymeric systems could possibly be modulated by fine-tuning the electronic and steric properties of the ligand and coordinating cation. Herein, we report the first example of a $UO_2^+\cdots UO_2^+$ complex that is highly stable in organic solvents and, significantly, is stable toward hydrolysis. We also describe the selective synthesis and the structure of the first mixed-valent $UO_2^+\cdots UO_2^{2+}$ molecular complex, which provides a rare example of functionalization of the $U^{VI}{=}O$ group.[20,22] By breaking away from the current trend of using steric bulk to prevent dimer formation and the associated disproportionation of UO_2^+ complexes, we show that the non-bulky Schiff base ligand $salen^{2-}$ (*N*,*N'*-bis(salicylidene)ethylenediamine) can stabilize pentavalent uranyl ions through the formation of a highly stable cation–cation complex. Moreover, we demonstrate that the resulting tetrameric uranyl(V) complex exhibits unambiguous antiferromagnetic coupling between the uranium centers.

The reaction of the recently reported UO_2^+ complex $[(UO_2Py_5)(KI_2Py_2)]_n$ (**2**; Py = pyridine)[23] with $salenK_2$ in pyridine led to the formation of the complex of pentavalent uranyl **3** as a violet powder that was insoluble in pyridine. The elemental analysis of **3** indicates the presence of a complex of general formula $[(UO_2)(salen)K(Py)]\cdot 1.4\,KI$, which most likely has a solid-state polymeric structure. Compound **3** can be dissolved in pyridine by the addition of [18]crown-6, or in DMSO. The addition of *n*-hexane to the resulting pyridine solution yielded blue crystals of the tetrameric pentavalent uranyl complex $[\{UO_2(salen)\}_4(\mu_8\text{-}K)_2][\{K(18C6)Py\}_2]$ (**4**) in which four uranyl(V) units are assembled by a T-shaped cation–cation interaction with two linear UO_2^+ groups arranged perpendicularly to each other (Scheme 1). Complex **4** can be reproducibly obtained in 55 % overall yield.

The crystal structure of **4** was determined by single-crystal X-ray diffraction. The structure of the $[\{UO_2(salen)\}_2(\mu_8\text{-}K)_2]^{2-}$ ion in **4** is presented in Figure 1 a. The anion consists of a centrosymmetric tetramer of mutually coordinated UO_2^+ units that form a square plane, which contains two crystallographically inequivalent uranyl groups. Two potassium ions that are located above and below the plane of the UO_2^+ tetramer (at 2.14 Å) interact with four different uranyl oxygen atoms and four different salen oxygen atoms. Two isolated $K(18C6)^+$ ions are also found in the unit cell. The two crystallographically independent U atoms in **4** are seven-coordinated, with a slightly distorted pentagonal bipyramidal geometry, by two *trans* oxo groups, two nitrogen atoms, two oxygen atoms from the $salen^{2-}$ ligand, and one bridging oxygen atom from the adjacent uranyl complex. Similar to the dbm tetramer **1**, the $UO_2^+\cdots UO_2^+$ interaction results in a significant lengthening of the U=O bonds (average U=O = 1.933(5) Å) with respect to the unbound oxygen atoms

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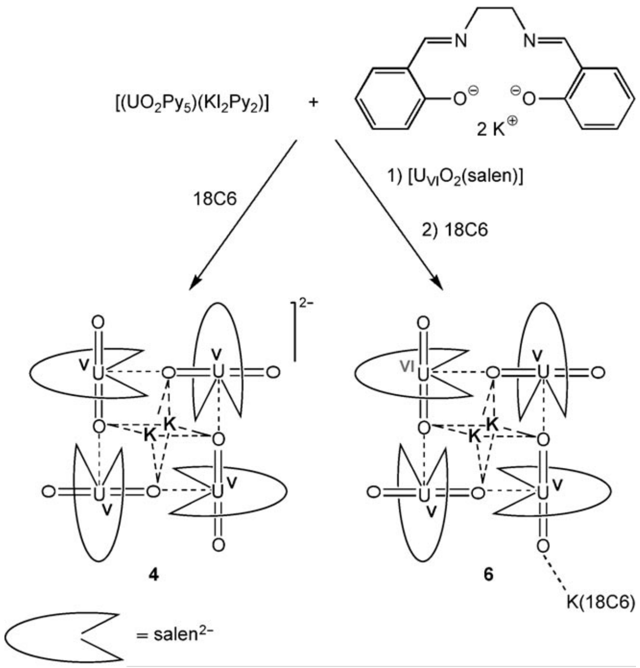

Scheme 1. Synthesis of the tetranuclear salen complex of pentavalent uranyl and of the analogous mixed-valent $3UO_2^{+}/UO_2^{2+}$ species.

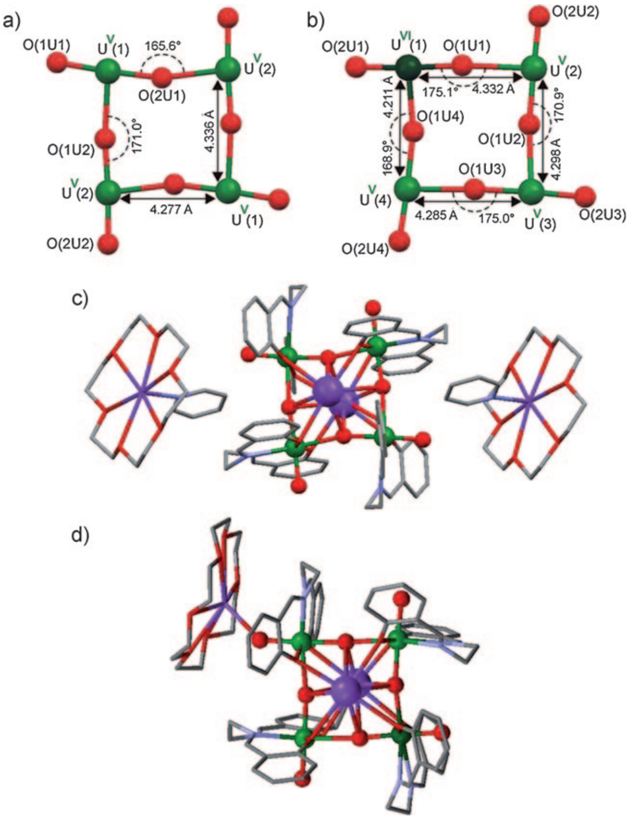

Figure 1. Detail of the tetrameric cores in **4** (a) and in **6** (b), and structures of **4** (c) and **6** (d) generated using Mercury. Hydrogen atoms, counterions for **4**, and solvent molecules were omitted for clarity. Selected bond lengths [Å] and angles [°] for **4**: U(1)–O(1U1) 1.841(5), U(1)–O(2U1) 1.936(5), U(1)–O(1U2) 2.421(5), U(2)–O(1U2) 1.929(5), U(2)–O(2U2) 1.840(5), U(2)–O(2U1) 2.374(5), O(1U1)-U(1)-O(2U1) 176.9(2), O(1U2)-U(2)-O(2U2) 176.2(2); for **6** U(1)–O(1U1) 1.862(14), U(1)–O(2U1) 1.804(12), U(1)–O(1U4) 2.208(11), U(2)–O(1U2) 1.941(12), U(2)–O(2U2) 1.797(14), U(2)–O(1U1) 2.474(14), U(3)–O(1U3) 1.964(12), U(3)–O(2U3) 1.863(13), U(3)–O(1U2) 2.369(12), U(4)–O(1U4) 2.022(11), U(4)–O(2U4) 1.833(11), U(4)–O(1U3) 2.324(12).

(average U=O = 1.840(7) Å) with a similar mean difference between the two U=O bonds of 0.1 Å. The overall metric parameters of the square core are also very similar in the complexes **1** and **4** (mean U–U distance = 4.315(5) Å in **1** and 4.31(3) in **4**; mean U–O–U angle = 172.2(7)° in **1** and 168.3(7)° in **4**).

^{1}H NMR studies of **4** show that the complex is stable in pyridine solution for up to one month. PFGSTE diffusion NMR and ESI/MS (*m*/*z* 1111.4, corresponding to $[\{UO_2(salen)\}_2\{\mu_8\text{-}K\}_2]^{2-}$) of solutions of **4** in pyridine indicate that complex **4** retains its tetrameric form in pyridine and acetonitrile solutions. The polymetallic structure is also retained in DMSO solution, contrary to that observed for the dbm complex **1**, which is immediately disrupted in DMSO to form a stable monomeric complex. This observation suggests that the mutual coordination of the uranyl groups in complex **4** is stronger than in **1** and that DMSO cannot effectively compete for the coordination of the UO_2^{+} ion.

Complex **4** can also be obtained by a different route. Notably, the reduction of the uranyl(VI) complex $[UO_2(salen)(Py)]$ (**5**) with Cp^{*}_2Co (Cp = cyclopentadiene) in pyridine solution led to a highly soluble UO_2^{+} species that yielded the tetrameric complex **4** after addition of K(18C6)I. The same result was observed when [2.2.2]cryptand was used. This behavior underlines the fact that the uranyl(V) groups can compete with 18C6 and [2.2.2]cryptand for potassium binding, probably because of the high stability of the resulting tetrameric complex **4**. The seminal work of Ikeda and coworkers suggested that stable Schiff base complexes of pentavalent uranyl could be produced by electrochemical reduction of the hexavalent analogue in DMSO, although these complexes were never isolated.[24] However, the reaction of $[(UO_2Py_5)(KI_2Py_2)]_n$ with salophenK$_2$ (salophenH$_2$ = *N*,*N'*-bis(salicylidene)-1,2-phenylenediamine) resulted in the immediate disproportionation of the resulting pentavalent complex with a probable cation–cation intermediate.[8] In contrast, use of the salen ligand resulted in a cation–cation complex of pentavalent uranyl that shows a remarkable stability in organic solvents. The different behavior of the two systems is likely to arise from small differences in the stability of the resulting polymetallic pentavalent uranyl complexes. The lack of unfavorable steric interactions in the final tetrameric assembly that is supported by the more flexible salen ligand (compared to the salophen ligand) probably plays an important role in the overall stability of the final complex. This result highlights the fact that small electronic or steric effects can play an important role on the stability of pentavalent uranyl cation–cation species. Moreover, complex **4** shows a remarkable stability even when precise amounts of water (5–25 equivalents) were added to the solution. Conversely, we found that the addition of water significantly accelerates the decomposition of the tetramer **1**.

Cyclic voltammetry studies of complex **4**, in which two consecutive redox process could be identified, were per-

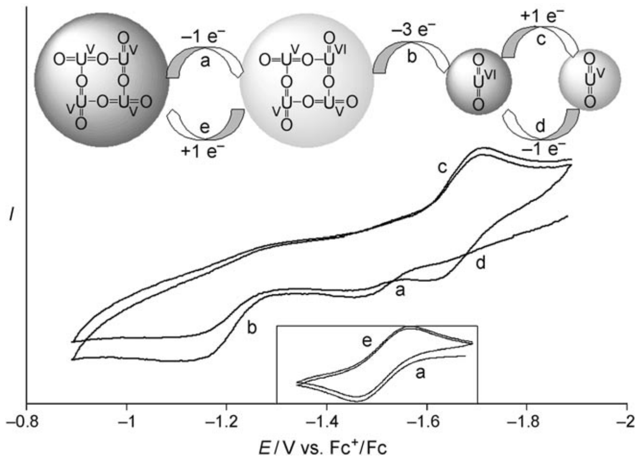

Figure 2. Room-temperature cyclic voltammogram at 100 mV s^{-1} for **4** in pyridine (vs. ferrocenium/ferrocene (Fc$^+$/Fc), 0.1 M NBu$_4$PF$_6$ as supporting electrolyte). The inset shows the cyclic voltammogram at 100 mV s^{-1} centered at −1.51 V vs. Fc$^+$/Fc.

formed in pyridine (Figure 2). Firstly, complex **4** undergoes a reversible (Figure 2, inset) one-electron oxidation at $E_{1/2} = -1.51$ V (vs. the Fc$^+$/Fc couple), which does not involve a rearrangement of the tetrameric structure. At higher potential, the irreversible three-electron oxidation of the monooxidized tetramer occurs to produce the monomeric uranyl(VI) complex **5**, which can be reversibly reduced to the monomeric pentavalent form ($E_{1/2} = -1.68$ V vs. Fc$^+$/Fc, wave d in Figure 2). These results encouraged us to find synthetic methods to selectively produce the corresponding mixed-valent complex.

Accordingly, the reaction of 0.75 equivalents of **3** with one equivalent of [U^{VI}O$_2$(salen)(Py)] (**5**) allows the selective synthesis of the first uranyl(VI)/uranyl(V) mixed-valent cation–cation complex, [{UO$_2$(salen)μ-K(18C6)}{UO$_2$(salen)}$_3$(μ$_8$-K)$_2$] (**6**). The crystal structure of **6** was determined by single-crystal X-ray diffraction. A view of **6** is presented in Figure 1b. Similar to the structure of **4**, the crystal structure of **6** presents a tetrameric unit that consists of uranyl moieties coordinated to each other to form a square plane capped by two bridging potassium ions.

However, in this case, the four uranyl complexes are crystallographically inequivalent as a result of the presence of a K(18C6) cation bound to the uranyl oxygen atom of one of the four uranyl complexes. Moreover, as clearly shown in Figure 1b, the smaller values of the U=O distances (1.804(12) and 1.862(14) Å) found for U1 with respect to the distances of the other uranyl groups (1.833(12)–2.022(11) Å, 1.797(14)–1.941(12) Å, and 1.863(13)–1.964(12) Å for U4, U2, and U3 respectively) suggest that the valence is localized, with U1 identified as a U^{VI} ion. Very similar values of the U^{VI}=O distances were found in extended frameworks that contain UO$_2^{2+}$···UO$_2^{2+}$ cation–cation interactions.[25,26] The replacement of one UO$_2^+$ ion by a UO$_2^{2+}$ ion results in significant differences in the metric parameters of the tetranuclear core, which is less distorted in **6** than in **4**. The bond valence sum analysis, performed using the empirical expression and constants proposed by Brown and Altermatt,[27] is in agreement with the presence of three pentavalent uranium ions and one localized hexavalent uranium ion in **6** (see the Supporting Information).

The mixed-valent tetrameric compound **6** was obtained as a pure crystalline solid. However, when **6** is dissolved in pyridine, it quickly undergoes a rearrangement to yield a mixture of complexes **6**, **5**, and **4**. Complex **6** can also be obtained by chemical oxidation of **4** with CuI. In turn, the reduction of **6** with one equivalent of Cp*$_2$Co yields **4**, thus indicating that the oxidation process is reversible. Complex **6** was the only mixed-valent complex isolated or identified in the electrochemical or chemical oxidation processes. Similarly, **6** is the only mixed-valent species obtained from the reaction of **4** with **5**, regardless of the stoichiometric ratio used, thus confirming that three U^V species and one U^{VI} species self-assemble selectively. The presence of mixed-valent U^V/U^{VI} systems has been reported in few naturally occurring oxide minerals[28] and in rare examples of oxide compounds obtained under hydrothermal conditions.[29–31] The first example of mixed-valent Np^V/Np^{VI} cation–cation complex was isolated only very recently.[5]

Temperature-dependent magnetic data were collected in the temperature range 2–300 K. At 300 K, **4** displays an effective magnetic moment of 1.96 μ$_B$ per uranium ion, which is lower that the theoretical value calculated for the free f^1 ion in the L–S coupling scheme ($\mu_{\mathrm{eff}} = 2.54$ μ$_B$), but within the range of values reported for U^V compounds.[32,33] The plot of χ versus T (Figure 3) clearly indicates the presence of an unambiguous antiferromagnetic coupling[6] between the f^1 ions, with a maximum at 6 K. Unambiguous evidence of magnetic communication between uranium centers is limited to three examples of dimeric complexes, which include the [{UO$_2$(dbm)$_2$K(18C6)}$_2$] dimer.[6,8,34] This is the first example of tetranuclear complex that shows unambiguous magnetic coupling, although the presence of magnetic coupling at temperature lower than 2 K had been suspected for **1**. The observation of a stronger coupling in the salen tetramer **4** compared to **1** could be the result of small differences in the structural parameters associated with the presence of a stronger UO$_2^+$···UO$_2^+$ interaction and anticipates the possibility of establishing the first magnetostructural correlation in actinides. Further work, including detailed EPR and DFT

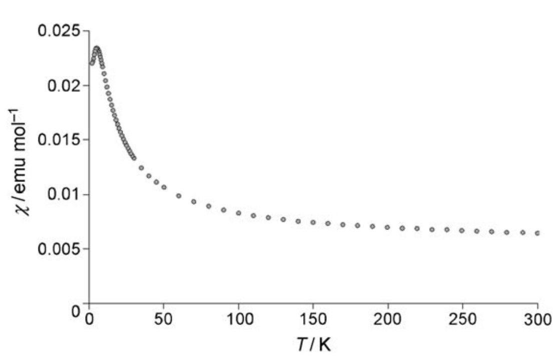

Figure 3. Temperature-dependent magnetic susceptibility data for **4** in the range 2–300 K. A μ_{eff} of 1.96 μ$_B$ per uranium ion at 300 K was calculated for **4** ($\chi_{\mathrm{dia}} = -1.61 \times 10^{-3}$ emu mol^{-1}, $m = 22.7$ mg, $M_r = 3667.66$ g mol^{-1}).

studies, will address the magnetic coupling in these and analogous systems.

In conclusion, we have shown that the cation–cation interaction, previously suggested as a reaction pathway that promotes decomposition, can lead to stable pentavalent uranyl species even in the absence of bulky ligands. This is a major breakthrough in uranium(V) chemistry and provides a new approach to the expansion of the chemistry of pentavalent uranyl ions. Moreover, the isolation of a $U^{V}O_2^{+}/U^{VI}O_2^{2+}$ compound demonstrates that the cation–cation interaction can provide a route to the functionalization of hexavalent uranyl ions and to the rational synthesis of mixed-valent polymetallic actinide complexes. The extension of this work to 5f–5f hetero-polymetallic systems such as U–Np systems is in progress.

Experimental Section

Complex **3**: Compound **2** (150 mg, 0.134 mmol) was added to a suspension of salenK$_2$ (47.3 mg, 0.134 mmol, 1 equiv) in pyridine (2 mL) to afford a dark blue solution. After stirring for 4 h at room temperature, a violet powder formed, which was filtered, washed 3 times with pyridine (3 mL), and dried under vacuum to yield 70 mg (0.077 mmol, 58 %) of a light-purple powder. Elemental analysis calcd (%) for [UO$_2$(salen)K(Py)]·1.4 KI ($C_{21}H_{19}I_{1.4}K_{2.4}N_3O_4U$, $M_r = 886.83$) C 28.44, H 2.16, N 4.74; found C 28.42, H 2.55, N 4.92.

Complex **4**: To a suspension of **3** (39.0 mg, 0.0439 mmol) in pyridine (1.5 mL), 18C6 (17 mg, 0.065 mmol, 1.5 equiv) were added. After stirring for 3 h at room temperature, the violet suspension turned into a clear dark blue solution. The slow diffusion of hexane into this solution yielded 37.9 mg of **4** (0.0103 mmol, 94 %) as deep-blue crystals suitable for X-ray diffraction. ESI/MS: *m*/*z*: 1111.4 $[[\{UO_2(salen)\}_2(\mu_8\text{-}K)_2]^{2-}]$; elemental analysis calcd (%) for $[\{UO_2(salen)\}_4(\mu_8\text{-}K)_2][\{K(18C6)(Py)\}_2]\cdot(18C6)KI\cdot1.5\,KI$ ($C_{110}H_{138}I_{2.5}K_{6.5}N_{10}O_{34}U_4$, $M_r = 3667.66$) C 36.02, H 3.79, N 3.82; found C 36.09, H 4.04, N 3.89.

Complex **6**: A solution of **4** (11.5 mg, 0.018 mmol, 1 equiv) in pyridine (1 mL) was added to a suspension of **3** (49.0 mg, 0.055 mmol, 3 equiv) in pyridine (2 mL). After stirring for 1 h, a solution of 18C6 (42.8 mg, 0.162 mmol, 9 equiv) in pyridine (0.5 mL) was added to this mixture. The clear brown solution obtained after stirring for 18 h was evaporated under vacuum to a quarter of the initial volume. Slow diffusion of *n*-hexane into the resulting solution afforded complex **6** as deep brown crystals (21 mg, 0.0083 mmol, 46 %). ESI/MS: *m*/*z*: 2222.8, $[[\{UO_2(salen)\}_2(\mu_8\text{-}K)]_2^{-}]$; Elemental analysis (%) calcd for $[\{UO_2(salen)\mu\text{-}K(18C6)\}\{UO_2(salen)\}_3(\mu_8\text{-}K)_2]$ ($C_{76}H_{80}K_3N_8O_{22}U_4$, $M_r = 2525.63$) C 36.12, H 3.19, N 4.43; found C 36.31, H 3.41, N 4.62.

CCDC 737627 (**4**), 737628 (**5**), and 737629 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Graphics were generated using MERCURY 2.2 supplied with the Cambridge Structural Database, CCDC, Cambridge 2004–2009.

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