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Isolation of a Tetrameric Cation−Cation Complex of Pentavalent Uranyl

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The chemistry of actinyl species (AnO_2^+ and AnO_2^{2+}) is highly relevant for the development of novel nuclear waste reprocessing technologies and for the speciation of radioactive metals in the environment.[1,2]

While other actinides (Np, Pu, Am) form stable AnO_2^+ species isolable in crystalline compounds, UO_2^+ is known to readily disproportionate in water to form U(IV) and UO_2^{2+}.[1] Due to its low stability, the knowledge of the chemistry of the pentavalent uranyl is very limited[3,4] in spite of its importance for the understanding of the properties of highly radioactive AnO_2^+ species and of the interesting chemical reactivity that can be anticipated. In contrast to d-block transition metal oxo complexes which are involved in a variety of catalytic and stoichiometric transformations, the oxo groups in hexavalent uranyl are generally thermodynamically and kinetically inert.[3] The reactivity of hexavalent oxo groups or their coordination to a Lewis acid has only been rarely observed in the presence of particular coordination environments enhancing the Lewis basic nature of the U═O oxygens.[5] Conversely the Lewis base interaction of the oxo groups of pentavalent actinyl with metal cations has allowed the structural characterization of several Np(V) cation−cation complexes.[6] However, unambiguous evidence of the presence of such interactions in solutions is still lacking. The higher Lewis basicity of the U═O oxygens in pentavalent uranyl is expected to favor the interaction with metal cations leading to the formation of cation−cation complexes. Such species are probably implicated in the mechanism of U(V) disproportionation, and therefore their isolation has been reputed barely possible although it could bring insights into the actinide speciation. In the past the mechanism of U(V) disproportionation has been the subject of several spectroscopic and kinetic studies which suggest the implication of dimeric intermediates that, however, have not been isolated.[3,7]

Recent studies suggested that it might be possible to prepare stable pentavalent uranium compounds by a careful choice of ligands and media.[8] Very recently we reported the synthesis and the characterization of the first isolated stable pentavalent uranyl iodide which crystallizes as a coordination polymer $\{[UO_2Py_5][KI_2Py_2]\}_n$, (**1**) as a result of cation−cation interactions between UO_2^+ and potassium.[9] Here we investigate the reaction of **1** with dibenzoylmethanate (dbm^-). Ikeda and co-workers recently reported that $[U^VO_2(dbm)_2(DMSO)]^-$ (**2**) can be produced by electrochemical reduction of the U(VI) complex $[UO_2(dbm)_2(DMSO)]$, but the UO_2^+ species was never isolated in the solid state.[10]

The reaction of **1** with two equivalents of Kdbm in pyridine allows the isolation, after diffusion of diisopropylether, of blue crystals of the tetrameric pentavalent uranyl complex $\{[UO_2(dbm)_2]_4[K_6Py_{10}]\}\cdot I_2\cdot Py_2$ (**3**) in which four $[UO_2(dbm)_2]$ complexes are assembled by cation−cation interactions between the UO_2^+ groups. The complex formula is in agreement with the presence of four pentavalent uranyl complexes. The structure of **3** was analyzed by single-crystal X-ray diffraction; ORTEP views of the cation $\{[UO_2(dbm)_2]_4[K_6Py_{10}]\}^{2+}$ are shown in Figure 1.

The structure of the cation consists of a centrosymmetric tetramer of UO_2^+'s coordinated to each other in a monodentate fashion to form a square plane with two crystallographically inequivalent uranyl complexes. Each UO_2^+ coordinates two adjacent uranyl groups and is involved in two T-shaped cation−cation interactions (two linear UO_2^+ groups arranged perpendicular to each other). This pattern of cation−cation interactions has been observed in polymeric and trimeric solid-state structures of neptunyl complexes.[6] Each UO_2^+ is also involved in a cation−cation interaction with a potassium ion. Four potassium ions form a square plane with two crystallographically inequivalent potassiums which includes the plane formed by the uranium ions. Two additional potassium ions are coordinated to the dbm oxygens in apical positions with respect to the plane of the uranium atoms, resulting in an overall octahedral arrangement. The potassium ions in the plane are pentacoordinated by two bridging dbm oxygens from one $[UO_2(dbm)_2]$ complex, one uranyl oxo group from the adjacent $[UO_2(dbm)_2]$ complex and two pyridine nitrogens. The two potassium ions in apical positions are pentacoordinated by four bridging dbm oxygens from four different uranyl complexes and by one pyridine nitrogen. The two crystallographically independent U atoms in **3** are seven-coordinated by two trans oxo groups, four oxygen atoms of two bidentate dbm ligands and one bridging oxygen from the adjacent uranyl complex with a pentagonal bypiramidal geometry. The identity of the UO_2^+ groups is not lost in the formation of the cation−cation complex; the corresponding U−O distances remain much shorter than the distance between U and the bridging oxygen (2.346(8) and 2.373(10) Å) which is similar to the mean U−O distance found for the dbm oxygens (2.44(2)Å). The interaction results nevertheless in a significant lengthening of the involved U═O bonds (1.923(10) and 1.934(8) Å). The value of the U−O distances (1.828(10) and 1.811(9) Å) for the oxo groups coordinating the potassium ions are very similar to those found in the uranyl iodide complex **1**, indicating that the uranium remains in the pentavalent oxidation state. This desymmetrization of the uranyl cation is the consequence of the strong electrostatic interaction between the two UO_2^+ cations. The mean difference between the two U═O bonds is significantly larger (0.11 Å) than the largest difference observed in cation−cation complexes of pentavalent neptunium (0.07 Å),[6] suggesting a stronger interaction in the uranium species.

The $\nu_{\text{asymm.}}$ (U═O) in the IR spectrum of **3** is shifted (782 cm^{-1}) to lower frequencies compared to the value found for the $\nu_{\text{asymm.}}$ (U═O) of complex **1** (797 cm^{-1}) in agreement with the longer U═O distances. The position of the $\nu_{\text{asymm.}}$ (U═O) peak remains unchanged in pyridine solution in agreement with the presence of UO_2^+/UO_2^+ complexes in solution. The presence of the polymetallic assembly in solution was confirmed by both 1D and diffusion NMR experiments. The proton NMR spectrum of pyridine solutions of **3**

10.1021/ja067445t CCC: $33.50 © 2006 American Chemical Society

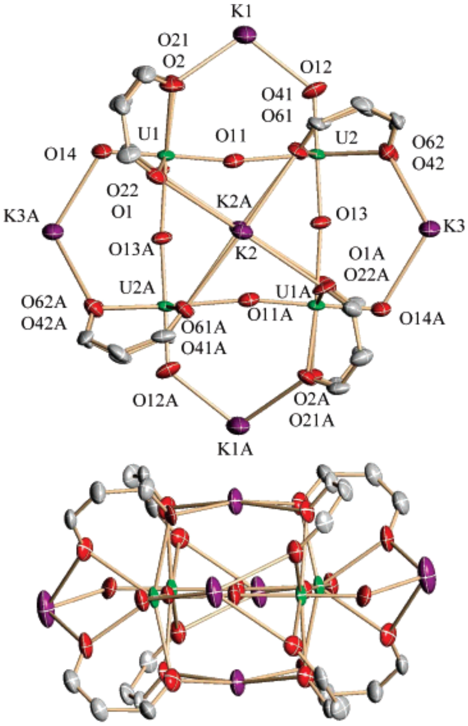

Figure 1. Top and side view of $\{[UO_2(dbm)_2]_4[K_6py_{10}]\}\cdot I_2\cdot Py_2$ (**3**) (the pyridine and the dbm phenyl groups are omitted for clarity) with thermal ellipsoids at the 30% probability level. Selected distance (Å) and angles (deg): U(1)−O(14), 1.828(10); U(1)−O(11), 1.923(10); U(1)−O(13)#, 2.346(8); U(2)−O(12), 1.811(9); U(2)−O(13), 1.934(8);); U(2)−O(11), 2.373(10); O(14)−U(1)−O(11), 179.0(4); O(12)−U(2)−O(13), 178.9(4); O(14)−U(1)−O(13)#, 90.6(4); O(11)−U(1)−O(13)#, 88.4(3). (Symmetry transformations used to generate equivalent atoms #: $-x + 1, -y + 2, -z + 1$.)

shows the presence of a major rigid C_{4h} symmetric solution species in agreement with the retention of the T-shaped tetrameric structure in solution. In contrast the dissolution of **3** in DMSO yields a simpler (C_{2v}) NMR spectrum in agreement with the disruption of the cation−cation interactions and the formation of monomeric species. Significant differences are also observed in the visible−NIR spectra (with a shift of the absorption maximum from 877 nm in DMSO to 620 nm in pyridine). The Stokes−Einstein equation allows to relate auto-diffusion coefficients (D) of molecules to their molecular weight.[11] The diffusion coefficients of **3** were measured by NMR[12] relative to a reference complex in pyridine ($D_{Py} = 2.1 \times 10^{-10}$ m^2 s^{-1}) and in DMSO ($D_{DMSO} = 1.6 \times 10^{-10}$ m^2 s^{-1}). The measured values are in agreement with the presence of a tetrameric complex in pyridine solution and of a monomeric species in DMSO solution. The calculated value of the spherical hydrodynamic radius (11.3 Å) compares very well with the value estimated from the crystal structure (10.8 Å).

Complex **3** is rapidly oxidized in the presence of trace oxygen and decomposes in pyridine solution. ^{1}H NMR and IR spectroscopy show rapid evolution (within a few hours) of pyridine solutions of **3** to produce new unidentified U(VI) and U(IV) species with complete transformation observed after three weeks. Work in progress is directed to further characterize the degradation products. The stability of complex **3** is much higher in DMSO solution, although the formation of traces of the hexavalent species can be detected after several days by ^{1}H NMR. These results support the hypothesis that the formation of inner-sphere cation−cation (UO_2^+/UO_2^+) complexes is involved in the dispropotionation of pentavalent uranyl. Furthermore this work shows that media which do not favor the formation of cation−cation complexes in solution can slow down the decomposition of pentavalent uranyl. Highly reactive UO_2^+ species can therefore be prepared in such conditions which are suitable for further functionalization of the uranyl moiety.

In conclusion, in this study we have reported the first example of UO_2^+/UO_2^+ interaction and unambiguous evidence of the presence of the resulting tetrameric cation−cation complex in pyridine solution. These results expand the possibilities for the preparation of polymetallic assemblies involving f-elements,[13] and a rich chemistry can be anticipated from the reaction of pentavalent uranyl with different metal cations including 3d metals and other actinyls.

Acknowledgment. This work was supported by the Commissariat à l'Energie Atomique, Direction de l'Energie Nucléaire. We thank Pierre Alain Bayle for his great help with the NMR experiments.

Supporting Information Available: Crystallographic files for compound **3** (CIF), visible, NMR and IR spectra, synthetic details, description of the pulse sequence, the equations, and of the experimental conditions used for the determination of the diffusion coefficients. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA067445T