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Synthesis and Structure of a Stable Pentavalent-Uranyl Coordination Polymer

Louise Natrajan,[†] Fabien Burdet,[†] Jacques Pécaut,[‡] and Marinella Mazzanti*,[†]

Laboratoire de Reconnaissance Ionique and Laboratoire de Coordination et Nanochimie, SCIB,
(UMR-E 3 CEA-UJF), Département de Recherche Fondamentale sur la Matière Condensée, CEA-Grenoble,
17 rue des Martyrs, 38054 Grenoble, Cedex 09, France

Received February 10, 2006; E-mail: marinella.mazzanti@cea.fr

The isolation of stable UO_2^+ species is extremely challenging due to the high tendency of pentavalent uranium to undergo the disproportionation reaction yielding U(IV) and UO_2^{2+}.[1] Apart from its fundamental interest,[2] this elusive species, which has the simplest electronic configuration of the AnO_2^{n+} series, has important environmental implications.[3] The highly soluble, and therefore mobile, and biologically available AnO_2^+ species are key players in the long-term environmental risks associated with the disposal of radioactive waste.[4] To date, knowledge of the spectroscopic and coordination properties of the UO_2^+ cation are extremely limited due to the lack of reliable synthetic routes to these species.[4,5] Pure uranyl complexes for spectroscopic studies have been produced by electrochemical reduction of U(VI) species but not isolated.[6] These reports suggest that appropriate organic ligands can stabilize UO_2^+ in solution. Crystals of the complex $[UO_2(OPPh_3)_4](OTf)]$ were serendipitously obtained during the synthesis of its hexavalent analogue.[7] The crystals proved kinetically stable toward disproportionation. However, attempts to provide a synthetic method by reduction of the hexavalent derivative for this species were inconclusive. Very recently the first pentavalent-uranium silicate has been prepared by reduction of UO_3 in the presence of KOH and excess KF under hydrothermal conditions, with water acting most likely as a reducing agent.[8]

Here we describe the first reproducible synthetic route to a UO_2^+ coordination complex via a two-electron oxidation of U(III) and the first structurally characterized dioxouranium(V) halide which is found to form a 1D coordination polymer in the presence of potassium iodide. Uranyl(VI) halides have been extensively studied, due to their fundamental importance, and the corresponding solvates have provided very useful starting materials for the synthesis of U(VI) coordination compounds. Recently the last member of this family has been unambiguously characterized.[9,10]

Very slow diffusion of air into a pyridine solution of $UI_3\cdot thf_4$[11] in the presence of potassium iodide led to the reproducible isolation of orange crystals of the pentavalent uranyl coordination polymer $\{[UO_2Py_5][KI_2Py_2]\}_n$, (**1**) with 28% yield. To reproduce the synthesis of **1** the diffusion rate of air into the starting reaction mixture is found to be crucial. Fast diffusion of air or dry oxygen yields only the previously described U(VI) adduct $[UO_2I_2(Py)_3]$.[10] However **1** is stable in a pyridine solution over long periods of time in the absence of oxygen suggesting that the pyridine stabilizes the UO_2^+ species against the disproportionation reaction. Minor unidentified products are formed during the oxidation reaction rendering it difficult to obtain **1** in analytically pure form. We have therefore investigated the possibility of using as an oxidizing agent, the oxygen atom transfer reagent pyridine-*N*-oxide (PyNO), that has been previously employed to produce U(V) mono-oxo complexes from U(III) organometallic compounds.[12] The reaction of $UI_3\cdot thf_4$ with 1 or 2 equiv of PyNO yields the U(VI) species as the only identifiable product even in the presence of KI. Indeed when 2 equiv of PyNO are employed, analytically pure $[UO_2I_2(Py)_3]$ is isolated from a pyridine solution in 40% yield after addition of *n*-hexane, providing an alternative and convenient synthetic route to this complex.

The target uranyl(V) iodide complex **1** was finally obtained by using a mixture of PyNO and water.

$$UI_3\cdot thf_4 + PyNO + H_2O \rightarrow \text{“}[UO_2Py_x]I\text{”} + 2PyHI \xrightarrow{KI} \mathbf{1} \qquad (1)$$

Reaction 1 provides a more controlled way to synthesize **1** than the slow air diffusion route. The “$[UO_2Py_x]I$” species is very soluble in organic solvents, but the presence of potassium iodide favors the crystallization of the uranyl(V) complex **1** in 54% yield. Work in progress is directed in gaining more insight into the mechanism of reaction 1 that could involve the formation of U(V) oxohydroxo intermediates.

The molecular structure of **1** was elucidated by X-ray diffraction which confirmed the presence of the UO_2^+ cation; an ortep view of **1** is presented in Figure 1. The uranium atom is seven-coordinated by two trans oxo ligands and five coplanar pyridine nitrogens (with a mean deviation of 0.05°) yielding a pentagonal bipyramidal coordination geometry. The angle between the pentagonal plane and the plane passing through the UO_2 moiety is 88.92°. Both oxo groups are coordinated to a potassium ion resulting in the construction of a 1-D chain (along the a+c diagonal of the unit cell) with a mean K−O distance of 2.84(7) Å; the separation between neighboring U(V) ions is 9.35 Å.

The molecular structure of **1** provides some insight into the electronic structure of the pentavalent uranyl species. The polymeric arrangement is the result of the ability of UO_2^+ to form cation−cation complexes[13] which can be explained in terms of the large negative charge on the UO_2^+ oxygens. Moreover, in the pentavalent uranyl complex **1** the iodide ion is not coordinated to the metal ion, while both iodides remain coordinated to the metal center in the hexavalent uranyl iodide $[UO_2I_2(Py)_3]$. The easier dissociation of the U−I bond in the pentavalent uranyl iodide can be explained by the lower positive charge and the higher electron density on U(V). These results can be compared with the Mulliken atomic charges calculated for penta-aqua uranyl species.[14] The displacement of coordinated iodide by neutral N-donor ligands[15] or by a polar solvent has been observed for UI_3 and UI_4.[16] Accordingly, the value of the mean U−N bond distance is shorter in the UO_2^{2+} complex (2.54(3) Å) than in the U(V) complex (2.605(5) Å). The values of the U═O bond distances (1.834(2) and 1.836(2) Å) are similar to those predicted for the pentavalent aqua-complex $[UO_2(H_2O)_5]^+$ (1.810 Å).[17] They are slightly longer than those found in the corresponding U(V) triflate $[UO_2(OPPh_3)_4]OTf$ (1.817(6) and 1.821(6) Å) probably due to potassium coordination to the oxygen

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[†] Laboratoire de Reconnaissance Ionique.
[‡] Laboratoire de Coordination et Nanochimie.

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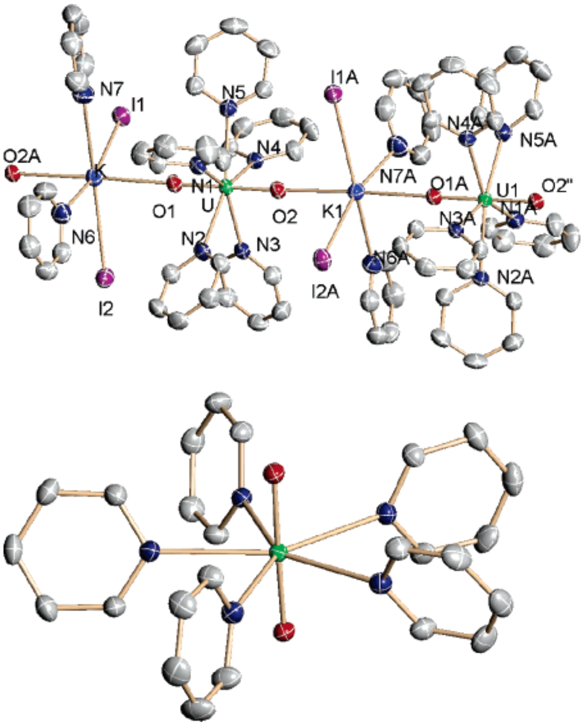

Figure 1. Ortep views (top) of $\{[UO_2Py_5][KI_2Py_2]\}_n$, (**1**) and (bottom) of the uranium coordination environment with thermal ellipsoids at the 30% probability level. Selected distance (Å) and angles (deg): U−O(2), 1.834(2); U−O(1), 1.836(2); U−N(1), 2.601(2); U−N(2), 2.602(2); U−N(4), 2.603(2); U−N(3), 2.610(2); U−N(5), 2.612(2); O(2)−U−O(1), 178.88(7); O(2)−U−N(1), 90.68(7); N(1)−U−N(2), 71.50(7); N(1)−U−N(4), 143.87(6).

atoms. Comparison with the $U{=}O$ bond lengths found in the U(VI) complex $[UO_2I_2(Py)_3]$ (1.757(6) and 1.754(6) Å) reveals a lengthening of 0.08 Å. This value can be compared to the decrease of 0.1 Å observed by EXAFS spectroscopy upon one-electron reduction of the U(VI) tricarbonate complex $[UO_2(CO_3)_3]$,[4−6c] and to the decrease of 0.06 Å found in the $[UO_2(OPPh_3)_4]OTf_n$ ($n = 1$ and 2) complexes.[7]

A significant difference is expected between the UO_2 infrared stretching frequency of the UO_2^+ and UO_2^{2+} complexes.

The infrared spectrum of **1** as KBr pellets shows a strong band at 797 cm^{-1} that was assigned to the asymmetric UO_2^+ stretching mode. The spectrum of the pentavalent uranyl compound before addition of KI shows the same band at 800 cm^{-1} suggesting a similar coordination environment of the U(V). The UO_2 stretching frequency is shifted to a lower value compared to the hexavalent $[UO_2I_2(Py)_3]$ species (927 cm^{-1}) in agreement with the greater electron density on the U(V) center which results in a weaker $U{=}O$ bond due to the increased electronic repulsion between the uranium atom and the oxygen atom. A similar difference in the stretching frequencies was observed for dmso solutions of salophen (salophenH_2 = *N*,*N*′-Bis(salicylidene)-1,2-phenylenediamine) complexes of UO_2^+ (770 cm^{-1}) with respect to UO_2^{2+} (895 cm^{-1})[18] and is consistent with the observed decrease in the $U{=}O$ bond length found in complex **1** with respect to its hexavalent counterpart.

Reaction 1 provides a unique and facile synthetic method to produce a pure pentavalent uranyl complex under mild conditions. Complex **1** which has an original polymeric structure is the first isolated and structurally characterized iodide uranyl(V) compound. It represents a potential precursor for the synthesis of new UO_2^+ complexes and should promote the development of the coordination chemistry of UO_2^+ in anhydrous media.

Preliminary work shows that complex **1**, although sparingly soluble, can successfully be reacted in pyridine or acetonitrile with organic ligands such as neutral PPh_3O or anionic salophen leading to complete dissolution of the starting compound. The characteristic visible−NIR bands at 635, 738, and 877 nm and the infrared UO_2 asymmetric stretching frequency (band at 757 cm^{-1})[18] of the resultant green pyridine solution of the salophen complex are in agreement with the presence of a pentavalent uranyl species confirming the versatility of the reported compound as a reagent for the preparation of new uranyl(V) complexes.

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Supporting Information Available: Crystallographic files for compound **1** (CIF), visible and IR spectra, and synthetic details (Word). This material is available free of charge via the Internet at http://pubs.acs.org.

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