Synthesis and Structure of UO₂I₂(OH₂)₂·4Et₂O: First Structurally Characterized U(VI)−I Bond and Lightest Missing Member of the UO₂X₂ (X = Halide) Series

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The dioxouranium dihalides (UO₂X₂) are extremely important in the chemistry of U(VI). Not only do they serve as useful starting materials (as various adducts) for the preparation of other dioxouranium(VI) compounds, but they are also of importance due to their conceptually simple nature. Whereas the UO₂F₂, UO₂Cl₂, and UO₂Br₂ entities have been extensively investigated and structurally characterized with various coordinating ligands,[1] only sparse reports exist in the literature of the heavier analogue UO₂I₂,[2] and hitherto no structural data have been reported.[3] In the series UO₂X₂ (X = F, Cl, Br), a distinct trend of decreasing thermal stability has been observed, with UO₂I₂ never having been unambiguously isolated in the solid state either as free UO₂I₂ or with solvent molecules coordinated. Moreover, it has only been described in solution as a very thermally unstable species, with no convincing characterization having been reported.[3] This is in stark contrast to the situation for the lighter halogen homologues.

If one compares the U−X bond strengths in U(III)X₃ species,[4] the U−I bond energy is clearly much weaker than its lighter halogen counterparts (BE for UF₃ = 619, for UCl₃ = 495.4, for UBr₃ = 424.3, and for UI₃ = 343 kJ mol⁻¹).[5] Uranium−iodine bonds are of particular interest to us for precisely this reason. Weak U(VI)−I bonds could provide a useful new starting material in the chemistry of U(VI). A very good example of utilizing the weaker U−I bond in the synthesis of new uranium compounds is UI₃·4thf,[6] which has been shown to be one of the most useful precursors for the synthesis of new organoactinide species.[7] Moreover, it is worthwhile to note that, while all UX₄ and UX₃ (X = F, Cl, Br, I) species are known and have been structurally characterized,[8] for the higher (V and VI) oxidation states of uranium, neither UI₅ nor UI₆ has been structurally characterized, in contrast to UCl₅, UBr₅, and UCl₆ which have all been structurally characterized.[9] Preliminary results from our laboratory showed that, on reaction of UO₂(NO₃)₂·6H₂O with BaI₂·2H₂O in diethyl ether solution, large, bright orange crystals formed on cooling, which were observed to melt at temperatures marginally above −28 °C and to decompose within minutes at room temperature. However, surprisingly, the crystals were not found to be the expected UO₂I₂(OH₂)₂ product, but rather an X-ray diffraction investigation elucidated that the crystal contained a mixture of products; two probable component compounds are both separately depicted in Figure 1. In the case of the mixed compound formed in reaction 1, it is very difficult to assert the precise nature of the mixture. In both cases, the U atom occupies a center of symmetry, and a 69%:31% iodine:nitrate occupancy of the sites has been determined. A comparison of the U=O, U−OH₂, and U−ONO₂ bond lengths in **1** with those observed in UO₂(NO₃)₂·6H₂O shows

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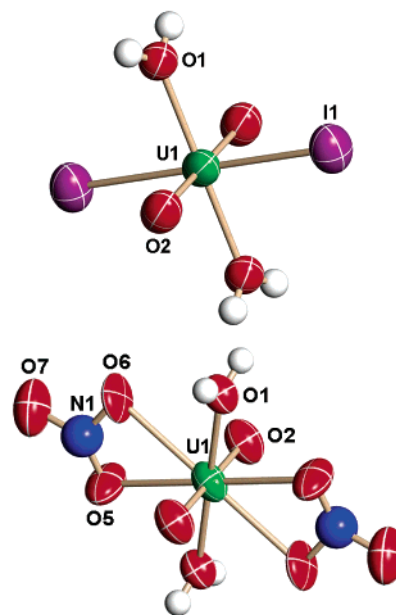
Figure 1. Two probable component compounds for the mixed UO₂I₁.₃₈(NO₃)₀.₆₂ compound (**1**) (see text for NO₃ occupancies) with thermal ellipsoids at the 50% probability level. Selected distances (Å) and angles (deg): U(1)−O(2), 1.758(6); U(1)−O(1), 2.321(7); U(1)−I(1), 2.939(3); U(1)−O(5), 2.65(2); U(1)−O(6), 2.68(2); O(5)−N(1), 1.29(2); O(7)−N(1), 1.34(5) N(1)−O(6), 1.30(2); O(2)−U(1)−(O2), 180; I(1)−U(1)−I(1), 180; O(1)−U(1)−O(1), 180; O(1)−U(1)−I(1), 90.20(15); O(5)−N(1)−O(7), 119(3).

very nice agreement.[10] The reason for the formation of this mixed species is still unclear, and work is ongoing in our laboratory to establish this.

$$UO_2(NO_3)_2 \cdot 6H_2O + BaI_2 \cdot 2H_2O \rightarrow \mathbf{1} + Ba(NO_3)_2 \quad (1)$$
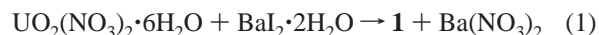
We therefore considered a different synthetic strategy in order to prepare the novel UO₂I₂(OH₂)₂ (Figure 2) which avoided the use of UO₂(NO₃)₂·6H₂O as a starting material. The reaction of UO₂Cl₂·xH₂O (x > 1) with NaI in diethyl ether at room temperature, followed by subsequent cooling of the dark orange/red solution, was found to result in the formation of bright orange crystals of UO₂I₂(OH₂)₂·4Et₂O (**2**). This reaction had been very briefly mentioned in the literature;[2h] however, no identification of the reaction products was undertaken, and therefore the formation of UO₂I₂ was speculative. The desired product, UO₂I₂(OH₂)₂·4Et₂O, slowly decomposes over several hours at −28 °C, but it decomposes within minutes at 4 °C when not covered by solvent. When the product is covered by a layer of diethyl ether, the decomposition of the crystals is markedly slower.
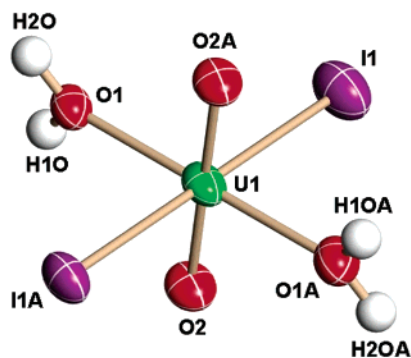
Figure 2. Structural drawing of $UO_2I_2(OH_2)_2$ unit in **2** with thermal ellipsoids at the 50% probability level. Selected distances (Å) and angles (deg): U(1)−O(2), 1.773(3); U(1)−O(1), 2.318(4); U(1)−I(1), 3.0267(6); O(2)−U(1)−(O2A), 180; I(1)−U(1)−I(1A), 180; O(1)−U−O(1A), 180; O(1)−U−I(1), 90.27(10); O(2)−U−I(1), 89.0 (1).

$$UO_2Cl_2 \cdot xH_2O + 2NaI \rightarrow UO_2I_2(OH_2)_2 + 2NaCl \quad (2)$$

The U=O bond length of 1.773(3) Å in $UO_2I_2(OH_2)_2 \cdot 4Et_2O$ (**2**) is in good agreement with the analogous U=O bonds in $UO_2Cl_2 \cdot$ 3thf (1.765, 1.766 Å)[1c] and $UO_2Br_2 \cdot$3thf (1.747, 1.767 Å).[1d] As in all UO_2X_2 (X = halide)-containing species, the O=U=O unit is linear (180°). The halide ligands are trans with respect to one another, and the compound adopts a slightly distorted D_{2h} structure. A comparison of the U−I bond lengths in various species shows the U(VI)−I bond length in **2** (d(U−I) = 3.0267(6) Å) to be in very nice agreement with the U(IV) species $UI_4 \cdot (O=C(NMe_2)_2)_2$ (d(U−I) = 3.027, 2.997 Å)[11] and $(Ph_4P)_2UI_6$ (d(U−I) = 2.986, 3.001 (equitorial); 3.005 (axial) Å),[12] although slightly shorter than the U−I bond lengths in the uranium(III) species $UI_3 \cdot$4thf (d(U−I) = 3.119, 3.166, 3.103 Å).[5] As this is, to our knowledge, the only experimentally determined U(VI)−I bond length, comparison with similar systems is not possible. The weak nature of the U(VI)−I bond in both **1** and **2** has been shown by the rapid decomposition of both compounds at 0 °C and room temperature, yielding decomposition products including I_2, and **1** and **2** appear to be considerably less thermally stable in comparison to the related U(III) and U(IV) compounds discussed above. However, **2** is not air sensitive, in contrast to both $UI_3 \cdot$4thf and $UI_4 \cdot (O=C(NMe_2)_2)_2$.[6,11]

A low-temperature Raman spectrum (−110 °C) recorded for **2**[13] shows several distinct peaks which correspond to diethyl ether and one very intense peak at 846 cm^{-1} which corresponds to the ν(O−U). A further peak at 171 cm^{-1} may be tentatively assigned to the ν(U−I); however, this requires further investigation.[14,15] In **1** and **2** we were able to establish the existence of U(VI)−I bonds without requiring the use of bulky stabilizing ligands, and we are now further investigating the structure and reactivity of such species both theoretically and experimentally. A further aim is to prepare related compounds, which are thermally much more stable, in order that U(VI)−I-containing compounds do not remain only chemical curiosities.

Supporting Information Available: Crystallographic files for compounds **1** and **2** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Zachariasen, W. H. *Acta Crystallogr.* **1948**, *1*, 277. (b) Debets, P. C. *Acta Crystallogr.* **1973**, *B29*, 1073. (c) Taylor, J. C.; Wilson, P. W. *Acta Crystallogr.* **1974**, *B30*, 169. (d) Debets, P. C. *Acta Crystallogr.* **1968**, *24*, 400. (e) Rebizant, J.; Van der Bossche, G.; Spirlet, M. R.; Goffart, J. *Acta Crystallogr.* **1987**, *43C*, 1298. (f) Wilkerson, M. P.; Burns, C. J.; Paine, R. T.; Scott, B. L. *Inorg. Chem.* **1999**, *38*, 4156.

(2) (a) Lynds, L. *J. Inorg. Nucl. Chem.* **1962**, *24*, 1007. (b) Kumar, N.; Tuck, D. G. *Inorg. Chim. Acta* **1984**, *95*, 211. (c) Truttwin, H. German Patent D.R.P. No. 420,391; Brauer, A.; D'Ans, J. *Fortsch Anorg.-Chem. Ind. 1924−1927*, *III*, 1327. (d) Aloy, J. *Ann. Chim. Phys.* **1901**, *24*, 412. (e) du Preetz, J. G. H.; Zeelie, B. *Inorg. Chim. Acta* **1989**, *161*, 187. (f) Cernjaev, I. I. *Complex Compounds of Uranium*; Israel Program for Scientific Transl.: Jerusalem, 1966; p 227. (g) Bagnall, K. W. *Coord. Chem. Rev.* **1967**, *2*, 145. (h) Lamisse, M. M.; Rohmer, R. *Bull. Soc. Chim. Fr.* **1963**, 24. (i) Day, J. P.; Venanzi, L. M. *J. Chem. Soc. A* **1966**, 1363.

(3) (a) Katz, J. J.; Morss, L. R.; Seaborg, G. T. *The Chemistry of the Actinide Elements*; Chapman and Hall: New York, 1986; Vols. 1 and 2. (b) Keller, C. In *Gmelin Handbuch der Anorganischen Chemie Uranium Supplement Volume C9*; Springer-Verlag: Berlin, 1979; p 178.

(4) The bond energies of UX_n (X = F, Cl, Br, I) are considered where uranium is in the coordination state +III instead of uranium in the oxidation state +VI because, hitherto, neither UBr_6, UI_5, UI_6, nor UO_2I_2 has been unequivocally experimentally established.

(5) Huheey, J. E. *Inorganic Chemistry*, 3rd ed.; Harper International: Cambridge, 1983; p A34.

(6) (a) Clark, D. N.; Sattelberger, A. P.; Bott, S. G.; Vrtis, R. N. *Inorg. Chem.* **1989**, *28*, 1771. (b) Avens, L. R.; Bott, S. G.; Clark, D. L.; Sattelberger, A. P.; Watkin, J. G.; Zwick, B. D. *Inorg. Chem.* **1994**, *33*, 2248. (c) Clark, D. L.; Sattelberger, A. P. *Inorg. Synth.* **1997**, *31*, 307.

(7) (a) Odom, A. L.; Arnold, P. L.; Cummins, C. C. *J. Am. Chem. Soc.* **1998**, *120*, 5836. (b) Diaconescu, P. L.; Odom, A. L.; Agapie, T.; Cummins, C. C. *Organometallics* **2001**, *20*, 4993.

(8) (a) Schleid, T.; Meyer, G.; Morss, L. R. *J. Less Common Met.* **1987**, *132*, 69. (b) Bros, J. P.; Gaune-Escard, M.; Szczepaniak, W.; Boacz, A.; Hewat, A. W. *Acta Crystallogr.* **1987**, *C43*, 113. (c) Levy, J. H.; Taylor, J. C.; Wilson, P. W. *J. Less Common Met.* **1975**, *39*, 265. (d) Taylor, J. C.; Wilson, P. W. *Acta Crystallogr.* **1974**, *B30*, 2664. (e) Murasik, A.; Fischer, P.; Szczepaniak, W. *J. Phys. Chem.* **1981**, *14*, 1847. (f) Levy, J. H.; Taylor, J. C.; Waugh, A. B. *Inorg. Chem.* **1980**, *19*, 672.

(9) (a) Smith, G. S.; Johnson, Q.; Elson, R. E. *Acta Crystallogr.* **1967**, *22*, 300. (b) Taylor, J. C.; Wilson, P. W. *Acta Crystallogr.* **1974**, *B30*, 1481. (c) Levy, J. H.; Taylor, J. C.; Wilson, P. W. *J. Inorg. Nucl. Chem.* **1978**, *40*, 1055.

(10) Hall, D.; Rae, A. D.; Water, T. N. *Acta Crystallogr.* **1965**, *19*, 389.

(11) du Preetz, J. G. H.; Zeelie, B.; Casellato, U.; Graziani, R. *Inorg. Chim. Acta* **1987**, *129*, 289.

(12) Casellato, U.; Graziani, R. *Z. Kristallogr.* **1998**, *123*, 361.

(13) A low-temperature Raman spectrum (−110 °C) was recorded of crystals of **2** which were removed from the reaction mixture and, therefore, were still wet with diethyl ether. Leaving the crystals to become dry on the surface through evaporation of the diethyl ether either at room temperature or 4 °C resulted in decomposition on the surface of the crystals, yielding elemental iodine (Raman: 181 (100), 191 (10)).

(14) It is noteworthy that even when the sample was cooled to −110 °C, a laser power of 200 mW caused significant decomposition of the sample within minutes, as evidenced by the similtaneous decrease in intensity of the ν(O−U) peak at 846 cm^{-1} and increase in intensity of the 181 cm^{-1} peak which is due to the formation of iodine. Therefore, low laser power is required in order to prevent decomposition of the sample. The precise nature of the other decomposition products formed is still unknown.

(15) Raman spectrum of **2** (Nd:YAG laser, 1067 nm, −110 °C, 50 mW): 2976 (27), 2935 (28), 2874 (23), 2817 (7), 1456 (20), 1274 (5), 1154 (7), 1147 (7), 1084 (6) Et$_2$O; 847 (100) ν(O−U); 423 (10) Et$_2$O; 191 (5), 180 (15), I$_2$; 171 (17) ν(U−I).

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