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Synthesis, Structural and Computational Investigations of $UO_2I_4^{2-}$: A Structurally Characterized U(VI)-I Anion

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The synthesis and characterization of $(Ph_4P)_2UO_2I_4\cdot 2NCCH_3$ is reported. The $UO_2I_4^{2-}$ anion is not only the first unambiguously characterized anion containing a uranium^{VI}–iodine bond, but is also the last member of the $UO_2X_4^{2-}$ ($X = Cl$, Br, I) series to be unambiguously identified and structurally characterized, in contrast to salts of the $UO_2Cl_4^{2-}$ and $UO_2Br_4^{2-}$ anions, which have all been thoroughly investigated and structurally characterized. $(Ph_4P)_2UO_2I_4\cdot 2NCCH_3$ was characterized using IR, Raman, ^1H, ^{13}C, and ^{31}P NMR spectroscopy as well as X-ray diffraction. In addition, a computational investigation of the $UO_2I_4^{2-}$ anion was undertaken and compared with the experimentally observed structure.

The uranyl halides have been extensively investigated as they are fundamentally important compounds in the chemistry of uranium in its highest (+VI) oxidation state,[1] and serve as highly useful starting materials for the synthesis of a wide range of compounds, including $[UO_2Cl_2(thf)_2]_2$, which is an excellent anhydrous uranyl dichloride starting material.[2]

In addition to the well-investigated neutral UO_2X_2 hydrates and coordination compounds, the $UO_2X_4^{2-}$ ($X = F$, Cl, Br) anions have also been thoroughly investigated and structurally characterized. Whereas $Cs_2UO_2F_4\cdot H_2O$ is a dimer,[3a] the $UO_2Cl_4^{2-}$ and $UO_2Br_4^{2-}$ dianions are monomeric.[1,3] In particular, numerous crystal structures for the $UO_2Cl_4^{2-}$ anion have been reported.[3b−g] However, for the $UO_2Br_4^{2-}$ anion the number of structurally characterized compounds is far fewer,[3f−m] and for $UO_2I_4^{2-}$, no structure has been reported. The structurally characterized $UO_2X_4^{2-}$ ($X = Cl$, Br) have been shown to possess approximate octahedral symmetry, with a linear, *trans*-uranyl (OUO) unit with the four halogen atoms in the equatorial plane.[1,3]

We have recently published a report describing the uranyl diiodide dihydrate, $UO_2I_2\cdot 2H_2O$ which contained the first structurally characterized $U^{VI}{-}I$ bond and was the first structurally characterized compound containing the uranyl diiododide moiety.[4] Three further neutral uranyl diiodide compounds have since been reported which are room-temperature stable,[5] however, no anionic $U^{VI}{-}I$ containing compound has been unequivocally established, and the $UO_2I_4^{2-}$ dianion remains only partially characterized in the literature.[6]

Recently, Schreckenbach et al.[7] have investigated computationally the $UO_2F_4^{2-}$, $UO_2Cl_4^{2-}$, and $UO_2(OH)_4^{2-}$ dianions and have found that the energy difference between the cis isomer with a bent uranyl group and the trans uranyl isomer with a linear uranyl group is relatively small.[8] In

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† Crystal structure determination.

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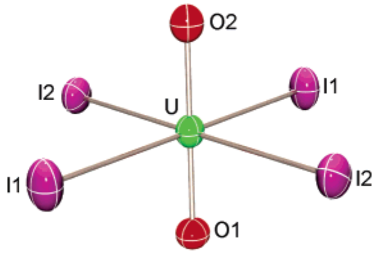

Figure 1. Molecular structure of the $UO_2I_4^{2-}$ anion in **1** with thermal ellipsoids at the 50% probability level. Selected bond lengths (Å) and angles (deg): U1−O1 1.771(5), U1−O2 1.755(5), U1−I1 3.0665(4), U1−I2 3.0397(4), O1−U1−O2 180.0, I2−U1−I2i 179.87(2), I1−U1−O1 90.04(1).

addition, it was found that the calculated structures of the trans isomers reproduced the experimentally determined structures relatively well. However, to the best of our knowledge, no theoretical study of U^{VI}−I containing compounds has been reported.

The $UO_2I_4^{2-}$ dianion is of further interest as the binary uranium^{VI} iodide, UI_6 remains an elusive species.[1] In addition, the number of iodine atoms that can be coordinated to the U^{VI} center is of interest, as, until now, only two iodine atoms have been coordinated to a uranium^{VI} center. It is worthwhile to mention that the $UO_2I_4^{2-}$ dianion is valence isoelectronic with the neutral and elusive UI_6. It is also interesting to note that for uranium in its lower (+IV) oxidation state, both UI_4L_4 (L = neutral coordinating ligand) and the UI_6^{2-} dianion have been synthesized and structurally characterized.[8]

The $UO_2I_4^{2-}$ anion could be prepared in the form of its *bis*(tetraphenylphosphonium) salt by the method briefly described previously.[6a,9] On slow addition of a dilute $Ph_4PI/CH_3CH_2CN/CH_3CN$ solution to the UO_2I_2/CH_3CH_2CN reaction mixture, dark red needle-type crystals precipitated from the clear red solution (eq. 1). The crystalline precipitate was filtered off and left in air to dry (Figure 1). The red crystals were soluble in MeCN, but decomposed quickly in solvents such as methanol or thf.

$$UO_2I_2{\cdot}xH_2O + 2Ph_4PI \rightarrow (Ph_4P)_2UO_2I_4 + xH_2O \qquad (1)$$

A Raman spectrum recorded of the crystals[10] showed that the ν_s(OUO) had shifted considerably from 878 cm^{-1} in the $UO_2Cl_2{\cdot}xH_2O$ ($2 \le x \le 3$) starting material (847 cm^{-1} in $UO_2I_2{\cdot}2H_2O$)[5a] to 832 cm^{-1} in compound **1**. The ν_s(OUO) observed for compound **1** compares well with those observed for $UO_2I_2(OP(NMe_2)_3)_2$ (837 cm^{-1}) and $UO_2I_2(OPPh_3)_2$ (837 cm^{-1}),[5a] where both compounds also have four ligands in the equatorial plane. If a comparison is made within the $UO_2X_4^{2-}$ series, then it can be observed that the ν_s(OUO) in $UO_2I_4^{2-}$ is in good agreement with ν_s(OUO) observed for [K(18-crown-6)]$_2UO_2Cl_4$ (ν_s(OUO) = 826 cm^{-1}) and [K(18-crown-6)]$_2UO_2Br_4$ (ν_s(OUO) = 831 cm^{-1}) and are more similar than within the neutral $UO_2X_2{\cdot}xH_2O$ (X = Cl, Br, I) hydrate series (ν_s(OUO) in $UO_2Cl_2{\cdot}xH_2O$ ($2 \le x \le 3$) = 878 cm^{-1}; ν_s(OUO) in $UO_2Br_2{\cdot}3H_2O$ = 871 cm^{-1}; ν_s(OUO) in $UO_2I_2{\cdot}2H_2O$ = 847 cm^{-1}).[5a] The IR spectrum of compound **1**[11] shows the ν_{as}(OUO) stretch at 915 cm^{-1}, which is not significantly shifted from that observed for the $UO_2Cl_2{\cdot}xH_2O$ ($2 \le x \le 3$) starting material, and is again very similar to the neutral six-coordinate uranyldiiodide complexes $UO_2I_2(OP(NMe_2)_3)_2$ (ν_{as}(OUO) = 917 cm^{-1}) and $UO_2I_2(OPPh_3)_2$ (ν_{as}(OUO) = 920 cm^{-1}).[5a] The presence of the Ph_4P^+ cation was established from multinuclear NMR spectroscopy (^{1}H, ^{13}C, and ^{31}P) as well as from IR and Raman spectroscopy which showed the characteristic peaks for the Ph_4P^+ cation.[10]

In addition, the solid-state structure of compound **1** was determined using X-ray diffraction.[11] The $UO_2I_4^{2-}$ dianion possesses a structure similar to that of the lighter $UO_2X_4^{2-}$ analogues $UO_2Cl_4^{2-}$,[1,3] and $UO_2Br_4^{2-}$.[1,3] The uranyl unit in $UO_2I_4^{2-}$ is in a linear, trans arrangement with four iodine atoms in the equatorial plane. The average U−I bond length of 3.0531 Å is similar to those observed for the neutral uranium^{VI}−iodides $UO_2I_2{\cdot}2H_2O$ (d(U−I) = 3.0476(1) Å),[4] $UO_2I_2(OP(NMe_2)_3)_2$ (d(U−I)$_{average}$ = 2.985 Å) and $UO_2I_2(OPPh_3)_2$ (d(U−I) = 3.0476(1) Å),[5a] and is considerably shorter than the uranium^{VI}−iodine bond lengths reported for $UO_2I_2(py)_3$ (d(U−I) = 3.1089(8), 3.1254(8) Å),[5b] and also for the related uranium(III) compound $UI_3{\cdot}4THF$ (d(U−I) = 3.103(2), 3.119(2) Å).[12]

The U−X (X = Cl, Br) bond lengths of the neutral $UO_2X_2(OP(NMe_2)_3)_2$ (X = Cl, Br) compounds can be compared with those of the corresponding $UO_2X_4^{2-}$ (X = Cl, Br) anions, as both are U^{VI}−X compounds with a trans X−U−X moiety (X = Cl, Br), and four ligands in the equatorial plane perpendicular to the linear uranyl unit. For X = Cl, the average U−Cl bond length in the neutral *trans*-UO_2Cl_2(OP-

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(9) Synthesis of $(Ph_4P)_2UO_2I_4{\cdot}2NCCH_3$. **(1)**: 0.116 g of $UO_2Cl_2{\cdot}xH_2O$ ($2 \le x \le 3$; 0.3 mmol based on $x = 2.5$) and a magnetic stirrer bar were placed into a 10-mL beaker. The yellow solid was then dissolved in 5 mL of CH_3CH_2CN, followed by the addition of 0.124 g (0.6 mmol) of $AgClO_4$. A white precipitate immediately began to form, and the reaction mixture was left stirring for 30 min, after which time a clear yellow solution over white insoluble solid was observed. The yellow solution was filtered off, and 0.09 g (0.6 mmol) of NaI was added. The solution turned from yellow to dark red and was left stirring for 1 h, after which time a solution of 0.28 g (0.6 mmol) of Ph_4PI in 20 mL of CH_3CN/CH_3CH_2CN was added on stirring. After stirring for 15 min the reaction mixture was allowed to settle, and a fine precipitate began to form in the shape of very fine dark red needles. After 30 min the precipitate was filtered off and isolated as a dark red solid.

(10) Raman spectrum of compound **1** (4-mm glass sample tube, RT, 1064 nm, res. = 4 cm^{-1}, ν/cm^{-1}): 3170 (1), 3142 (1), 3065 (6), 2928 (3), 2248 (1), 1586 (5), 1578 (3), 1440 (1), 1372 (1), 1342 (1), 1312 (1), 1185 (3), 1163 (3), 1109(3), 1098 (4), 1028 (4), 1001 (6), 931 (1), 832 (10), 723 (1), 679 (1), 617 (1), 287 (1), 254 (3), 199(3), 177 (2), 118 (1). IR spectrum for **1** (RT, KBr plates, res. = 4 cm^{-1}): 2925 w, 2853 w, 2246 vw, 1583 w, 1480 m, 1435 s, 1384 w, 1182 w, 1162 w, 1107 s, 1026 w, 996 m, 915 s, 757 m, 720 s, 687 s, 530 s, 521 s. NMR data (RT, CD_3CN, δ in ppm) of **1**: ^{1}H (399.78 MHz, TMS) 7.91 (m, *p*-H, 1H), 7.76 (m, *o*-H, 2H), 7.62 (m, *m*-H, 2H). $^{13}C\{^1H\}$ (100.52 MHz, TMS): 135.3 (d, $J_{(PC)}$ = 3.0 Hz), 134.6 (d, $J_{(PC)}$ = 9.9 Hz), 130.2 (d, $J_{(PC)}$ = 12.1 Hz), 117.7 (d, $J_{(PC)}$ = 90.2 Hz). $^{31}P\{^1H\}$ (161.84 MHz, 85% H_3PO_4) 24.9. Elemental analysis for **1**. Calcd: C, 40.59%; H, 3.01%; N, 1.82%. Found: C, 41.13%; H, 2.72%; N, 1.70%.

(11) Crystallographic data collection for **1**. $C_{56}H_{52}I_4N_2O_2P_2U_1$; F wt = 1538.53; crystal size, 0.04 × 0.06 × 0.26 mm; monoclinic ($C2/c$), a = 25.4148(5) Å, b = 7.9560(2) Å, c = 28.5906(6) Å, β = 114.266(1)°, V = 5270.3(2) Å^3, Z = 4, T = 200 K, $R1[I > 2\sigma(I)]$ = 0.353, Final wR2 = 0.0821.

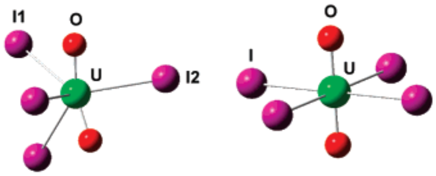

Figure 2. Calculated cis and trans isomers of the $UO_2I_4^{2-}$ dianion at B3LYP level of theory. Selected bond lengths (Å) and angles (deg): *cis*-$UO_2I_4^{2-}$ optimized in C_{2v}; U−O 1.736, U−I1 3.409, U−I2 3.226, OUO 154.2; *trans*-$UO_2I_4^{2-}$ optimized in D_{4h}; U−O 1.743, U−I 3.206, OUO 180.0.

$(NMe_2)_3)_2$ (d(U−Cl)$_{average}$ = 2.667 Å)[13] was only slightly shorter than that observed in the $UO_2Cl_4^{2-}$ anion in $(Ph_4P)_2$-$UO_2Cl_4{\cdot}CH_2Cl_2$ (d(U−Cl) = 2.675 Å).[3e] The average U−Br bond length in *trans*-$UO_2Br_2(OP(NMe_2)_3)_2$ (d(U−Br)$_{average}$ = 2.807 Å)[5a] was significantly shorter than the corresponding U−Br bond length in $(Ph_4P)_2UO_2Br_4{\cdot}CH_2Cl_2$ (d(U−Br) = 2.836 Å).[3k]

As this compound is the first U^{VI}−I anion to be structurally characterized, it is difficult to find suitable species for comparison. Therefore, a computational investigation of the $UO_2I_4^{2-}$ was undertaken to compare the experimentally observed structure (solid state) with the calculated structure (gas phase) (Figure 2).[14] As has been previously shown by Schreckenbach et al., the linear *trans*-OUO arrangement is energetically favored over the *cis*-OUO arrangement for $UO_2X_4^{2-}$ species (X = F, Cl, OH).[8] However, the difference in energy between the two isomers is relatively small at the B3LYP level of theory.

From our investigations, we have calculated the *trans*-$UO_2I_4^{2-}$ isomer also to be lower in energy than the cis isomer as would be expected, with an energy difference $\Delta E_{cis-trans}$ of 29.0 kcal mol^{-1}.[14] The calculated uranyl bond length of 1.743 Å in the trans isomer is slightly shorter than the average experimentally observed uranyl bond length in the solid state (1.763 Å). The calculated U−I bond lengths in the trans isomer (3.206 Å) were, however, substantially longer than those experimentally observed (3.0531 Å), in agreement with the theoretical results reported for the $UO_2Cl_4^{2-}$ dianion.[7] In addition, the calculated OUO angle in the cis isomer of the $UO_2I_4^{2-}$ anion (∠(OUO) = 154.2°) is slightly larger than those calculated for the $UO_2F_4^{2-}$ (∠(OUO) = 99.2°) and $UO_2Cl_4^{2-}$ (∠(OUO) = 121.8°) anions. The overall experimentally observed structure was, however, reproduced by the calculations. It is interesting to note that, whereas $UO_2I_2{\cdot}2H_2O$ is thermally unstable in the solid state at room temperature, the neutral $UO_2I_2(OP(NMe_2)_3)_2$, $UO_2I_2(OPPh_3)_2$, and $UO_2I_2(py)_3$[5] as well as $(Ph_4P)_2UO_2I_4{\cdot}2NCCH_3$, are all stable in the solid state at room temperature. In addition, it is worthwhile to compare the stability of the $UO_2Br_4^{2-}$ anion with UBr_6. The $M_2UO_2Br_4$ salts have been isolated and are stable at room temperature, however to the best of our knowledge the UBr_6 molecule has not been isolated at room temperature. We have been able to show that $(Ph_4P)_2UO_2I_4$ is also stable at room temperature, whereas UI_6 has also not been isolated, although $UO_2I_4^{2-}$ and UI_6 are valence isoelectronic species.

The dioxotetraiodouranate dianion, $UO_2I_4^{2-}$, which is the last member of the $UO_2X_4^{2-}$ (X = F, Cl, Br, I) series to be structurally characterized, has been synthesized and its structure was investigated using computational studies and X-ray diffraction. In addition, this compound is of interest as it is the first anion to be structurally characterized containing a U^{VI}−I bond.

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Supporting Information Available: Crystallographic files in CIF format for compound **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) cis- and trans-$UO_2I_4^{2-}$ were calculated at the B3LYP level of theory using the ECP78MWB (U) and ECP46MWB (I) pseudopotentials with (8s8p6d5f2g)/[5s5p4d3f2g] and (5s5p4d/[3s3p1d] basis sets for the valence electrons of U and I, respectively, for O a cc−pVDZ basis set was applied using the Gaussian G98 program.[15]

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