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Article

Synthesis and Characterization of Heavier Dioxouranium(VI) Dihalides[†]

**Margaret-Jane Crawford,*,[‡] Arkady Ellern,[§,||] Konstantin Karaghiosoff,[‡] Peter Mayer,[‡,||]
Heinrich Nöth,[‡,||] and Max Suter[‡,||]**

*Department of Chemistry and Biochemistry, Ludwig-Maximilians University,
Butenandtstrasse 5-13 (Haus D), D-81377, Munich, Germany, and Department of Chemistry,
Iowa State University, 1711 Gilman Hall, Ames, Iowa 50011*

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The synthesis and characterization of the dioxouranium(VI) dibromide and iodide hydrates, $UO_2Br_2{\cdot}3H_2O$ **(1),** $[UO_2Br_2(OH_2)_2]_2$ **(2),** and $UO_2I_2{\cdot}2H_2O{\cdot}4Et_2O$ **(3),** are reported. Moreover, adducts of UO_2I_2 and UO_2Br_2 with large, bulky $OP(NMe_2)_3$ and $OPPh_3$ ligands such as $UO_2I_2(OP(NMe_2)_3)_2$ **(4)**, $UO_2Br_2(OP(NMe_2)_3)_2$ **(5),** and $UO_2I_2(OPPh_3)_2$ **(6)** are discussed. The structures of the following compounds were determined using single-crystal X-ray diffraction techniques: (**1**) monoclinic, $P2_1/c$, $a = 9.7376(8)$ Å, $b = 6.5471(5)$ Å, $c = 12.817(1)$ Å, $\beta = 94.104(1)°$, $V = 815.0(1)$ Å^3, $Z = 4$; (**2**) monoclinic, $P2_1/c$, $a = 6.0568(7)$ Å, $b = 10.5117(9)$ Å, $c = 10.362(1)$ Å, $\beta = 99.62(1)°$, $V = 650.5(1)$ Å^3, $Z = 2$; (**4**) tetragonal, $P4_12_12$, $a = 10.6519(3)$ Å, $b = 10.6519(3)$ Å, $c = 24.0758(6)$ Å, $V = 2731.7(1)$ Å^3, $Z = 4$; (**5**) tetragonal, $P4_12_12$, $a = 10.4645(1)$ Å, $b = 10.4645(1)$ Å, $c = 23.7805(3)$ Å, $V = 2604.10(5)$ Å^3, $Z = 4$, and (**6**) monoclinic, $P2_1/c$, $a = 9.6543(1)$ Å, $b = 18.8968(3)$ Å, $c = 10.9042(2)$ Å, $\beta = 115.2134(5)°$, $V = 1783.01(5)$ Å^3, $Z = 2$. Whereas **1** and **2** are the first UO_2Br_2 hydrates and the last missing members of the UO_2X_2 hydrate ($X = Cl \rightarrow I$) series to be structurally characterized, **4** and **6** contain room-temperature stable U^{VI}–I bonds with **4** being the first structurally characterized room temperature stable U^{VI}–I compound which can be conveniently prepared on a gram scale in quantitative yield. The synthesis and characterization of **5** using an analogous halogen exchange reaction to that used for the preparation of **4** is also reported.

Introduction

The synthesis and characterization of the dioxouranium dihalides has been one of the most extensively investigated areas of uranium chemistry.[1] In particular, the dioxouranium(VI) dihalide hydrates have received much attention due to their straightforward syntheses and usefulness as precursors for a wide range of dioxouranium(VI)-containing compounds.[1] Moreover, $UO_2Cl_2{\cdot}3THF$ (THF = tetrahydrofuran) and $[UO_2Cl_2(THF)_2]_2$ syntheses have recently been reported, both of which are excellent anhydrous sources of the UO_2Cl_2 moiety, clearly useful starting materials, and interesting compounds.[2] In particular, $UO_2Cl_2{\cdot}3THF$ and $[UO_2Cl_2(THF)_2]_2$ are extremely helpful in contrast to $UO_2Cl_2{\cdot}xH_2O$ for syntheses where the presence of water has to be avoided and therefore provide anhydrous and easily accessible sources of dioxouranium compounds. The use of $UO_2Cl_2{\cdot}3THF$ and $[UO_2Cl_2(THF)_2]_2$ as excellent anhydrous starting materials has been demonstrated in the synthesis of, for example, $[Na(THF)_2][UO_2\{N(SiMe_3)_2\}_3]$[3] and $[UO_2Cl_2(IMes)_2]$ (IMes = 1,3-dimesitylimidazol-2-ylidene).[4] Despite many investigations and extensive structural characterization of complexes of the lighter dioxouranium dihalide, $UO_2Cl_2{\cdot}xL$ (L = neutral coordinating ligand),[5] the heavier analogues have been much less investigated.[1] For example, the structure of a dioxouranium dibromide hydrate has not been reported although the structure of the anhydrous $UO_2Br_2{\cdot}3THF$ is known.[6] Moreover, the first structurally characterized compound

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* To whom correspondence should be addressed. E-mail: mjc@cup.uni-muenchen.de. Phone: +49 89 2180 77503. Fax: +49 89 2180 77492.

[†] Dedicated to Professor Dr. Ingo-Peter Lorenz on the occasion of his 60th birthday.

[‡] Department of Chemistry and Biochemistry, Ludwig-Maximilians University.

[§] Department of Chemistry, Iowa State University.

[||] X-ray structure determination.

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containing a $U^{VI}-I$ bond and the dioxouranium diiodide moiety has only very recently been described.[7] Furthermore, despite a significant number of reports on $UO_2Br_2 \cdot xL$ [8] and $UO_2I_2 \cdot xL$ compounds,[9] only very few of these compounds, for example $UO_2Br_2(OAsPh_3)_2$, have been structurally characterized.[8] It is interesting to note, that whereas $UO_2Cl_2 \cdot 3H_2O$ is stable at room temperature, $UO_2I_2 \cdot 2H_2O$ decomposes at temperatures well below 0 °C.[7] As has been shown for the binary uranium(III) halides, the U−X (X = halide) bond strength decreases substantially down the group whereby U−F (UF_3) = 619 kJ mol^{-1}, U−Cl (UCl_3) = 495.4 kJ mol^{-1}, U−Br (UBr_3) = 424.3 kJ mol^{-1}, and U−I (UI_3) = 343 kJ mol^{-1}.[10] Moreover, it is worthwhile to note that the structures of the halides of higher oxidation states for uranium(V,VI), UF_5, UF_6, UCl_6, and UBr_5, have all been determined,[11] whereas UBr_6, UI_5, and UI_6 have not been structurally characterized.[1] From the expected weak $U^{VI}-I$ bonds, we considered room temperature stable derivatives of $[UO_2Br_2(OH_2)_2]_2$ **(2)** likely to be highly useful as new starting materials for the synthesis of new dioxouranium(VI) compounds through metathesis reactions involving the $U^{VI}-I$ bonds. However, until now only $UO_2I_2 \cdot 2H_2O \cdot 4Et_2O$ (**3**) has been prepared and structurally characterized,[7] but due to its thermal instability it is not an ideal precursor for further reactions. We therefore wanted not only to establish the existence and first structural characterization of a room temperature stable $U^{VI}-I$ bond but also to develop a larger scale synthesis for an anhydrous compound of this type which may be useful as a precursor for the synthesis of new dioxouranium(VI) compounds. Preliminary reports of parts of this work have been presented[12] including the crystal structure of $UO_2I_2(OP(NMe_2)_3)_2$ (**4**),[12b] prior to which various UO_2I_2 containing compounds had been reported,[9] for example $UO_2I_2(tmu)_2$ (tmu = *N*,*N*,*N*′,*N*′-tetramethylurea). However, only incomplete and inconclusive characterization was reported, and therefore, the existence of room temperature stable $U^{VI}-I$ containing compounds remained uncertain. During the review process of this paper, an interesting publication on the synthesis and crystal structure of the $U^{VI}-I$ compound $UO_2I_2(py)_3$ (py = pyridine) appeared which was synthesized via a different route using anhydrous conditions and the uranyl triflate starting material $UO_2(OTf)_2$ and was also found to be stable under ambient conditions.[13]

Experimental Section

General Information. $UO_2(NO_3)_2 \cdot 6H_2O$ and $UO_2I_2 \cdot 2H_2O \cdot 4Et_2O$ **(3)** were prepared according to the literature procedures.[7,14] $UO_2Br_2 \cdot 3H_2O$ **(1)** and $UO_2Cl_2 \cdot xH_2O$ ($2 < x < 3$) were synthesized according to the literature from $UO_2(OOCCH_3)_2 \cdot 2H_2O$ with HX (X = Cl, Br) and by evaporating off the solvent under vacuum.[15] NaI (Merck), NaBr (Merck), $OP(NMe_2)_3$ (Fluka), $OPPh_3$ (Aldrich), HBr (Acros Organics), H_3COH, Et_2O, and $BaI_2 \cdot 2H_2O$ (Aldrich) were used as supplied without further purification. Standard procedures for the handling and disposal of uranium containing compounds were employed at all times. IR spectra were recorded as solids between KBr plates using a Perkin-Elmer Spectrum One FT-IR spectrometer. Raman spectra were recorded using a Perkin-Elmer FT-IR R2000 spectrometer fitted with a Nd:YAG laser (1064 nm). Multinuclear NMR spectra were recorded using a JEOL EX 400 FT-NMR spectrometer, operating at 399.78 MHz (^1H), 100.52 MHz (^{13}C), 28.89 MHz (^{14}N), and 161.84 MHz (^{31}P). Chemical shifts are given with respect to tetramethylsilane (for ^1H, ^{13}C), $MeNO_2$ (for ^{14}N), and 85% H_3PO_4 (for ^{31}P) as external standards. The C/H/N analyses were performed by the analytical service of the chemistry department of Ludwig-Maximilians University. The X-ray diffraction studies were carried out for **1** using a Siemens P4 instrument equipped with a CCD area detector, for **2** using a STOE IPDS area detector device diffractometer, and for **4**, **5**, and **6** using a Nonius Kappa CCD diffractometer. Compounds **1**, **2,** and **6** were solved by direct methods using SHELXS-97, and compounds **4** and **5** were solved using SiR97 and refined by means of full-matrix least-squares procedures using SHELXL-97.[16,17]

Recrystallization of $UO_2Br_2 \cdot 3H_2O$ (1). $UO_2Br_2 \cdot 3H_2O$ was prepared according to the literature.[15] Yellow crystals suitable for X-ray diffraction were grown by placing a concentrated solution of the reaction mixture over P_4O_{10} in a desiccator for several days. The yellow crystals formed were highly hygroscopic.

Raman (4 mm sample tube, 1064 nm, room temperature, 200 mW, ν/cm^{-1}): 1591(0.5), 871(10) (ν_s(OUO)), 197(1).

Synthesis of $[UO_2Br_2 \cdot 2H_2O]_2$ (2). A concentrated aqueous solution of $UO_2Br_2 \cdot xH_2O$ was prepared according to the literature.[15]

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Yellow crystals suitable for X-ray diffraction were grown by placing a highly concentrated solution of the reaction mixture over P_4O_{10} in a desiccator for several days. The yellow crystals formed were highly hygroscopic.

Raman (4 mm sample tube, 1064 nm, room temperature, 200 mW, ν/cm^{-1}): 1592(0.5), 867(10) (ν_s(OUO)), 204(1), 189(2), 183(2), 163(1).

Synthesis of $UO_2I_2(OP(NMe_2)_3)_2$ (4). A 0.386 g amount of $UO_2Cl_2 \cdot xH_2O$ (1.0 mmol based on $UO_2Cl_2 \cdot 2.5H_2O$ ($UO_2Cl_2 \cdot xH_2O$, ($2 < x < 3$)[15]) was suspended in 10 mL of Et_2O. While the mixture was stirred vigorously, an excess (1.5 g, 10.0 mmol) of NaI was added to the beaker and a color change from yellow to orange was observed. The reaction mixture was allowed to stir for 12 h, after which time the stirring was stopped and the solid was allowed to settle. The dark orange solution was then separated from the NaCl byproduct and unreacted NaI, and 0.35 mL (2.0 mmol) of $OP(NMe_2)_3$ was then added under constant stirring, whereby a bright yellow solid precipitated immediately. The reaction mixture was stirred for 10 min, and the solid was filtered off and dried under vacuum, leaving only a yellow solid product. A small portion of the solid product was redissolved in acetone and resulted in a clear, yellow-orange solution. The acetone solution was left at 3 °C for several hours to evaporate and resulted in yellow-orange crystals suitable for X-ray diffraction. Yield = 0.571 g, 65% (based on $UO_2Cl_2 \cdot 2.5H_2O$).[15]

IR (KBr plates, room temperature, ν/cm^{-1}): 2923wv, 1384s, 1302m, 1271m, 1187w, 1074m, 992m, 926m, 917m, 763w,sh, 756m, 667w, 475m. Raman (4 mm sample tube, 1064 nm, room temperature, 200 mW, ν/cm^{-1}): 3002(1), 2941(3), 2903(2), 2858(2), 2811(2), 1487(2), 1444(2), 1417(1), 1113(2), 1063(1), 1005(1), 837(10), 758(1), 654(4), 513(2), 478(1), 348(1), 171(2). Anal. Calcd for $C_{12}H_{36}I_2N_6O_4P_2U_1$ (882.24): H, 4.11; C, 16.34; N, 9.53. Found: H, 4.29; C, 16.88; N, 9.73.

^1H NMR (d_6-acetone): $\delta = 2.93$ (d, $^3J_{PH} = 9.9$ Hz). $^{13}C\{^1H\}$ NMR (d_6-acetone): $\delta = 36.8$ (d, $^2J_{PC} = 4.4$ Hz). ^{14}N NMR (d_6-acetone): $\delta = -355$ (s, $\nu_{1/2} = 663$ Hz). $^{31}P\{^1H\}$ NMR (d_6-acetone): $\delta = 35.6$ (s).

Synthesis of $UO_2Br_2(OP(NMe_2)_3)_2$ (5). A 0.193 g amount (0.5 mmol based on $UO_2Cl_2 \cdot 2.5H_2O$ ($UO_2Cl_2 \cdot xH_2O$, ($2 < x < 3$)[15])) of $UO_2Cl_2 \cdot xH_2O$ was suspended in 10 mL of Et_2O. While the mixture was stirred vigorously, an excess (1.5 g, 14.6 mmol) of NaBr was added to the beaker, and slowly, a clear yellow solution was observed over white solid. The reaction mixture was allowed to stir for 12 h, after which time the stirring was stopped and the reaction mixture was allowed to settle. The clear yellow solution was then separated from the NaCl byproduct and unreacted NaBr. A 0.18 mL (1.0 mmol) aliquot of $OP(NMe_2)_3$ was added to the solution under constant stirring, whereby a pale yellow solid precipitated immediately. The solid was filtered off and dried under vacuum leaving a yellow solid product. A small portion of the solid product which was redissolved in acetone and left at 3 °C for several hours to evaporate yielded yellow crystals suitable for X-ray diffraction. Yield = 0.231 g, 62% (based on $UO_2Cl_2 \cdot 2.5H_2O$[15]).

IR (KBr plates, room temperature, ν/cm^{-1}): 2994vw, 2926wv, 2900w, 2856w, 2813w, 1484m, 1462m, 1451m, 1384m, 1303s, 1188s, 1177sh, 1084vs, 1071 sh, 989vs, 919vs, 761s, 755s, 651ww. Raman (4 mm sample tube, 1064 nm, room temperature, 200 mW, ν/cm^{-1}): 2998(2), 2942(4), 2908(3), 2860(3), 2814(3), 1486(1), 1445(2), 1417(1), 1303(1), 1191(1), 1124(2), 1072(1), 996(1), 833(10), 758(1), 654(4), 634(1), 509(1), 478(1), 348(1), 188(2), 155(2). Anal. Calcd for $C_{12}H_{36}Br_2N_6O_4P_2U_1$ (788.24): H, 4.60; C, 18.28; N, 10.66. Found: H, 4.79; C, 18.85; N, 10.83. ^1H NMR (d_6-acetone): $\delta = 2.78$ (d, $^3J_{PH} = 9.2$ Hz). $^{13}C\{^1H\}$ NMR (d_6-acetone): $\delta = 35.9$ (d, $^2J_{PC} = 4.6$ Hz). ^{14}N NMR (d_6-acetone): $\delta = -358$ (s, $\nu_{1/2} = 500$ Hz). $^{31}P\{^1H\}$ NMR: (d_6-acetone) $\delta = 35.1$(s).

Synthesis of $UO_2I_2(OPPh_3)_2$ (6). A 0.386 g (1.0 mmol based on $UO_2Cl_2 \cdot 2.5H_2O$ ($UO_2Cl_2 \cdot xH_2O$, ($2 < x < 3$)[15])) portion of $UO_2Cl_2 \cdot xH_2O$ was suspended in 10 mL of Et_2O. While the mixture was stirred vigorously, an excess (1.5 g, 10.0 mmol) of NaI was added to the beaker and slowly, a clear orange solution was observed over white solid. The reaction mixture was allowed to stir for 12 h, after which time the stirring was stopped and the reaction mixture was allowed to settle. The clear yellow solution was then separated from the NaCl byproduct and unreacted NaI, and 0.557 g (2.0 mmol) of $OPPh_3$ in 2 mL of MeOH was then added under constant stirring, whereby a bright orange solid precipitated. The reaction mixture was stirred for 10 min, and the orange precipitate was filtered off and dried under vacuum. A small portion of the solid product was redissolved in methanol and left at room temperature for several hours to evaporate yielded orange crystals suitable for X-ray diffraction. Yield = 0.817 g, 76% (based on $UO_2Cl_2 \cdot 2.5H_2O$[15]).

IR (KBr plates, room temperature, ν/cm^{-1}): 3076vw, 3056vw, 1589w, 1485w, 1437m, 1122s, 1060s, 1025m, 997m, 931m, 920s, 749m, 690s, 536s. Raman (4 mm sample tube, 1064 nm, room temperature, 200 mW, ν/cm^{-1}): 3179(1), 3147(1), 3056(6), 2959(1), 1590(5), 1575(2), 1486(1), 1439(1), 1186(2), 1160(3), 1131(3), 1080(2), 1029(4), 998(10), 930(1), 837(10), 728(1), 686(3), 617(3), 469(1), 297(1), 257(3), 210(1), 195(2), 177(2), 149(1), 131(1). Anal. Calcd for $C_{36}H_{30}I_2O_4P_2U_1$ (1080.41): H, 2.80; C, 40.02. Found: H, 2.88; C, 40.70. ^1H NMR (CD_3OD): $\delta = 7.55-7.69$ (m, arom-H). $^{13}C\{^1H\}$ NMR (CD_3OD): $\delta = 132.0$ (d, $^2J_{PC} = 10.4$ Hz, (-o)), 128.8 (d, $^3J_{PC} = 12.5$ Hz, (-m)), 132.8 (d, $^4J_{PC} = 1.7$ Hz, (-p)), 130.1 (br) (-i). $^{31}P\{^1H\}$ NMR (CD_3OD): $\delta = 35.8$ (s, $OPPh_3$).

Results and Discussion

In our previous communication on the synthesis and characterization of $UO_2I_2 \cdot 2H_2O \cdot 4Et_2O$ **(3)**, we were able to unequivocally establish for the first time the existence of a $U^{VI}-I$ bond.[7] We have now been able to prepare compounds **4** and **6** and to determine the structures of anhydrous and room temperature stable $U^{VI}-I$ containing species.[12] In a previous communication on parts of this work,[7] we have already described the reaction of uranylnitrate hexahydrate with barium diiodide dihydrate which yielded crystals containing a mixture of products and not the expected $UO_2I_2 \cdot 2H_2O$, even when an excess of $BaI_2 \cdot 2H_2O$ was employed. Further reaction of the orange solution obtained from this reaction with Ph_3PO resulted in the synthesis of a room temperature stable product which was not homogeneous, and the stoichiometry of which was unable to be ascertained in the bulk material.[18] As the reaction of $UO_2(NO_3)_2 \cdot 6H_2O$ and $BaI_2 \cdot 2H_2O$ did not yield a pure product, the reaction of $UO_2Cl_2 \cdot xH_2O$ with NaI was utilized to synthesize a stable derivative of the convenient to prepare but thermally labile **3** (eq 1).

$$UO_2Cl_2 \cdot xH_2O + 2NaI \rightarrow \underset{\mathbf{3}}{UO_2I_2 \cdot 2H_2O} + 2NaCl + (x-2)H_2O \quad (1)$$

Compound **3** could be successfully converted into the room temperature stable **4** and **6** by replacing the water ligands with the bulky, strong Lewis base $OP(NMe_2)_3$ or $OPPh_3$ ligands. Although **3** is unstable in the solid state at ambient temperature, in diethyl ether solution **3** is stable for at least several hours. The reaction of $UO_2Cl_2{\cdot}xH_2O$ with NaI in diethyl ether is a convenient synthetic route for the formation of $UO_2I_2{\cdot}2H_2O$, and this allowed the preparation of several grams of **4** (eq 2) and smaller quantities of **6** (eq 3).

$$UO_2I_2{\cdot}2H_2O + 2OP(NMe_2)_3 \rightarrow \underset{\mathbf{4}}{UO_2I_2(OP(NMe_2)_3)_2} + 2H_2O \quad (2)$$

$$UO_2I_2{\cdot}2H_2O + 2OPPh_3 \rightarrow \underset{\mathbf{6}}{UO_2I_2(OPPh_3)_2} + 2H_2O \quad (3)$$

In contrast to the synthesis utilizing $BaI_2{\cdot}2H_2O$, it was found that the reaction of $UO_2Cl_2{\cdot}xH_2O$ with NaI followed by the addition of $OPPh_3$ yielded the desired $UO_2I_2(OPPh_3)_2$ **(6)** and not the heterogeneous mixture obtained via the other method. Compound **4** is a room-temperature and air-stable yellow solid which is soluble in organic solvents such as acetone, CH_3CN, or THF. Compound **6** is also air-stable and stable in the solid state at room temperature but does, however, slowly decompose in acetone at room temperature. The Raman spectra of **4** and **6** show the strong ν_s(OUO) vibration at 837 cm^{-1} which is shifted significantly from that of **3** (847 cm^{-1}). It is well-known from Badger's rules[19] that a correlation exists between bond lengths, ν_s(OUO), and force constants for the uranyl moiety. However, for compounds **3**, **4,** and **6**, a comparison of the bond lengths and vibrational data was not possible as the experimentally determined bond lengths do not vary significantly within 3σ. However, when the strong donor ligands $OP(NMe_2)_3$ or $OPPh_3$ are used to replace the H_2O ligands in $UO_2I_2(OH_2)_2$ in the plane perpendicular to the OUO moiety, the ν_s(OUO) was observed to shift approximately 10 cm^{-1} to lower wavenumber. It is interesing to note that recently it has been discussed for $UO_2X_4^{2-}$ (X = Cl, Br) complexes,[20] if electron-donating substituents are present in the plane perpendicular to the OUO axis, longer uranyl bonds are expected. Compounds **3**, **4,** and **6** are useful to compare, because both compounds are neutral $UO_2I_2L_2$ (L = H_2O (**3**), $OP(NMe_2)_3$ (**4**), OPh_3 (**6**)) complexes and both possess a hexacoordinated central uranium atom. If the ν_s(OUO) of **3**, **4,** and **6** are compared, the Raman spectra suggest a weakening of the uranyl bonds in **4** and in **6** (ν_s(OUO) = 837 cm^{-1}), both of which have stronger equatorial donor ligands with respect to **3** (ν_s(OUO) = 847 cm^{-1}). Moreover, it is interesting to note that on coordinating the strong donor ligand $OP(NMe_2)_3$ to the hydrate $UO_2Br_2{\cdot}3H_2O$ a similar trend is observed as that observed for the iodide complexes, whereby ν_s(OUO) shifts from 871 cm^{-1} in **1** to 833 cm^{-1} in **5**. To compare the ν_s(OUO) in the $UO_2X_2(OP(NMe_2)_3)_2$ (X = Cl, Br, I) series, we synthesized $UO_2Cl_2(OP(NMe_2)_3)_2$ and measured the Raman spectrum of this compound. In $UO_2Cl_2(OP(NMe_2)_3)_2$, the ν_s(OUO) was observed at 831 cm^{-1}, similar to $UO_2I_2(OP(NMe_2)_3)_2$ (837 cm^{-1}) and $UO_2Br_2(OP(NMe_2)_3)_2$ (833 cm^{-1}). The ν_{as}(OUO) observed in the IR spectra appear to remain relatively unchanged within the $UO_2X_2(OP(NMe_2)_3)_2$ series (X = Cl, Br, I), (ν_{as}(OUO) = 917 cm^{-1} in $UO_2Cl_2(OP(NMe_2)_3)_2$, 917 cm^{-1} in **4** and 919 cm^{-1} in **5**). In addition, a trend in the ν_s(OUO) can be ascertained in the members of the uranyldihalide hydrate series (ν_s(OUO) = 878 cm^{-1} in $UO_2Cl_2{\cdot}6H_2O$, 871 cm^{-1} in $UO_2Br_2{\cdot}3H_2O$, and 847 cm^{-1} in $UO_2I_2{\cdot}2H_2O$) whereby the ν_s(OUO) decreases in wavenumber through the series Cl to I. This trend may again suggest a weakening of the uranyl U=O bonds in compounds **1** and **3** with respect to $UO_2Cl_2{\cdot}xH_2O$.

The ^{14}N and ^{31}P NMR spectra of **4** clearly show the presence of the $OP(NMe_2)_3$ ligands and no other side products, whereby the peak at −355 ppm in the ^{14}N NMR spectrum is typical for the $OP(NMe_2)_3$ ligand. In the ^{31}P NMR spectrum of **6**, the presence of the $OPPh_3$ ligand can be deduced from the peak at 35.8 ppm. From the X-ray diffraction studies and the analytical data of **3**, **4**, and **6** it was concluded that metathesis of $UO_2Cl_2{\cdot}xH_2O$ with NaI in Et_2O is a convenient method for the preparation of uranyliodide compounds. For comparison, we also wanted to investigate whether this route was also applicable for the synthesis of uranyl bromide complexes. The synthesis of $UO_2Br_2{\cdot}xH_2O$ reported in the literature requires the reaction of uranyl acetate dihydrate with concentrated aqueous (48%) HBr in methanol solution, followed by the removal of all solvents under vacuum. However, uranyl dibromide hydrates have been reported to slowly decompose at room temperature under the evolution of bromine.[1] Therefore, the reaction of $UO_2Cl_2{\cdot}xH_2O$ with NaBr in Et_2O was undertaken in analogy to that described for the synthesis of $UO_2I_2{\cdot}2H_2O$, and after stirring for several hours, a clear yellow solution as well as insoluble white solid was observed. Addition of 2 equiv of $OP(NMe_2)_3$ to the solution resulted in the precipitation of a pale yellow solid in good yield. The solid obtained has been shown by vibrational (IR, Raman) and multinuclear NMR (^1H, ^{13}C, ^{14}N, ^{31}P) spectroscopy as well as elemental analysis and single-crystal X-ray diffraction to be **5**, $UO_2Br_2(OP(NMe_2)_3)_2$. As was discussed at length above, the Raman spectrum of **5** was extremely similar to that of **4** which enabled trends in the vibrational spectra for the uranyl dihalide hydrates and complexes with strong equatorial donor ligands to be discussed. The solid obtained was redissolved in methanol or acetonitrile and leaving the solvent to slowly evaporate resulted in yellow crystals of **5** which were suitable for X-ray diffraction.

The solid-state structures of both **4** and **5** show the typical trans OUO moiety with *d*(U=O) bond lengths of 1.758(8) (**4**) and 1.766(5) Å (**5**) which are in agreement with those

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(18) An ^{14}N NMR spectrum obtained of the bulk material clearly showed the presence of the nitrate group with a peak at −5 ppm relative to $MeNO_2$. In the ^{13}C NMR spectrum, four resonances were observed indicating the presence of Ph_3PO (133 → 128), and in the ^{31}P NMR spectrum, one resonance indicating the presence of the Ph_3PO moiety was observed at 34.7 ppm. In the Raman and the IR spectra, the presence of the uranyl group is clearly observed at 919 cm^{-1} (IR) and 837 cm^{-1} (Raman). A single crystal isolated from the bulk material gave the following stoichiometry: $UO_2I_{(1.01)}(NO_3)_{(0.99)}(OPPh_3)_2$. However this stoichiometry was not reflected in the analysis of the bulk product; therefore, the stoichiometry of the product of this reaction cannot be reliably assigned.

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Table 1. Crystallographic Data for $UO_2Br_2{\cdot}3H_2O$ **(1)**, $[UO_2Br_2{\cdot}2H_2O]_2$ **(2)**, $UO_2I_2{\cdot}2H_2O{\cdot}4Et_2O$ **(3)**, $UO_2I_2(OP(NMe_2)_3)_2$ **(4)**, $UO_2Br_2(OP(NMe_2)_3)_2$ **(5),** and $UO_2I_2(OPPh_3)_2$ **(6)**

formula	$UO_2Br_2{\cdot}3H_2O$	$[UO_2Br_2{\cdot}2H_2O]_2$	$UO_2I_2{\cdot}2H_2O{\cdot}$ $4Et_2O$	$UO_2I_2\,(OP(NMe_2)_3)_2$	$UO_2Br_2\,(OP(NMe_2)_3)_2$	$UO_2I_2(OPPh_3)_2$
formula mass (amu)	477.85	931.73	854.33	882.24	788.24	1080.41
crystal system	monoclinic	monoclinic	triclinic	tetragonal	tetragonal	monoclinic
space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P4_12_12$	$P4_12_12$	$P2_1/c$
a (Å)	9.7376(8)	6.0568(7)	8.771(2)	10.6519(3)	10.4645(1)	9.5643(1)
b (Å)	6.5471(5)	10.5117(9)	9.295(2)	10.6519(3)	10.4645(1)	18.8968(3)
c (Å)	12.817(1)	10.362(1)	10.859(3)	24.0758(6)	23.7805(3)	10.9042(2)
α (deg)	90	90	67.686(4)	90	90	90
β (deg)	94.104(1)	99.62(1)	66.975(5)	90	90	115.2134(5)
γ (deg)	90	90	74.360(5)	90	90	90
V (Å^3)	815.0(1)	650.5(1)	746.1(3)	2731.7 (1)	2604.10(5)	1783.01(5)
Z	4	2	1	4	4	2
T (K)	193	200	173	200	200	200
crystal size (mm)	0.05 × 0.10 × 0.10	0.04 × 0.11 × 0.14	0.1 × 0.1 × 0.1	0.03 × 0.16 × 0.30	0.07 × 0.09 × 0.24	0.05 × 0.10 × 0.16
ρ_{calcd} (g cm^{-3})	3.894	4.757	1.901	2.145	2.011	2.012
μ(Mo Kα) (mm^{-1})	29.672	37.162	7.537	8.345	9.451	6.410
$R(F)$ for $F_o^2 > 2\sigma(F_o^2)^a$	0.0447	0.0265	0.0380	0.0464	0.0392	0.0366
$R_w(F_o^2)^b$	0.1206	0.0551	0.0693	0.1405	0.0986	0.0903

$^a\ R(F) = \{\sum||F_o| - |F_c||\}/\{\sum|F_o|\}$. $^b\ R_w(F_o^2) = [\{\sum|w(F_o^2 - F_c^2)^2]\}/\{\sum wF_o^4\}]^{1/2}$.

Table 2. Selected Structural Parameters for $UO_2Br_2{\cdot}3H_2O$ **(1)**, $[UO_2Br_2{\cdot}2H_2O]_2$ **(2)**, $UO_2I_2{\cdot}2H_2O{\cdot}4Et_2O$ **(3)**, $UO_2I_2(OP(NMe_2)_3)_2$ (**4**), $UO_2Br_2(OP(NMe_2)_3)_2$ (**5**), and $UO_2I_2(OPPh_3)_2$ (**6**)

Parameter (d/Å, $\angle$/deg)	$UO_2Br_2{\cdot}3H_2O$	$[UO_2Br_2{\cdot}2H_2O]_2$	$UO_2I_2{\cdot}2H_2O{\cdot}4Et_2O$	$UO_2I_2\,(OP(NMe_2)_3)_2$	$UO_2Br_2\,(OP(NMe_2)_3)_2$	$UO_2I_2(OPPh_3)_2$
d(U−X1)	2.904(2)	2.8441(9)	3.0267(6)	2.920(2)	2.784(1)	3.0476(1)
d(U−X2)	2.897(2)	2.9456(8)	3.0267(6)	3.050(1)	2.830(1)	
d(U−O1)	1.74 (1)	1.763(6)	1.773(3)	1.758(8)	1.766(5)	1.760(4)
d(U−O2)	1.72 (1)	1.762(5)	1.773(3)	1.758(8)	1.766(5)	
d(U−O3)	2.40 (1)	2.452(6)	2.318(4)	2.266(9)	2.278(6)	2.298(4)
d(U−O4)	2.47(1)	2.421(6)	2.318(4)	2.266(9)	2.278(6)	
d(U−O5)	2.44 (1)					
$\angle$(X1−U−X2)	79.56(6)	148.00(2)	180	180.00(3)	180.00(3)	180.0
$\angle$(O1−U−O2)	178.4(6)	178.3(3)	180	179.8(7)	179.8(4)	180.0
$\angle$(X1−U−O1)	88.5(4)	94.4(2)	89.0(1)	90.1(3)	90.1(2)	90.8(1)
$\angle$(X1−U−O3)	152.9(3)	71.9(1)	90.3(1)	90.3(2)	88.7(1)	89.5(1)
$\angle$(O1−U−O3)	87.1(5)	88.1(2)	90.0 (2)	89.5(4)	89.8(2)	90.2(1)

observed in the related $UO_2Cl_2(OP(NMe_2)_3)_2$ and *trans-cis*-$[UO_2Br_2(OAsPh_3)_2]$ species[5,8] (d(U=O) in $UO_2Cl_2(OP(NMe_2)_3)_2$ = 1.76(1) Å,[5] d(U=O) in *trans-cis*-$[UO_2Br_2(OAsPh_3)_2]$ = 1.765(3) Å) (Tables 1, 2 and Figures 1, 2).[8] In both compounds **4** and **5**, as well as in the previously determined crystal structure of $UO_2Cl_2(OP(NMe_2)_3)_2$, the coordination number at the central uranium atom remains six. The U−I bond lengths in **4** and **6** are difficult to compare with other compounds, because the only other structurally determined U^{VI}−I bonds reported are those in $UO_2I_2{\cdot}2H_2O{\cdot}4Et_2O$ (**3**) and in the very recently reported and thermally stable $UO_2I_2(py)_3$. However, the bond lengths determined for **4** (d(U−I) = 2.920(2), 3.050(1) Å) and **6** (d(U−I) = 3.0476(4) Å) are in agreement with those previously reported for **3** (d(U−I) = 3.0267(6) Å) (Tables 1 and 2)[7] but are however, shorter than those recently reported for $UO_2I_2(py)_3$ (d(U−I) = 3.1089(8), 3.1254(8) Å).[13] The linear, trans I−U−I arrangement observed for both **4** and **6** is also in agreement with the above-mentioned and related compounds $UO_2Cl_2(OP(NMe_2)_3)_2$ [5] and $UO_2Br_2(OP(NMe_2)_3)_2$. The U−I bond lengths in **4** of 2.920(2) and 3.050(1) Å and in **6** of 3.0476(1) Å can also be compared with those observed for U−I containing systems with lower oxidation states. For example for uranium in oxidation state +III, the U−I bond lengths in $UI_3(THF)_4$ are 3.119, 3.166, and 3.103 Å[21] which are slightly longer than those observed for **3** and **4**, where uranium is in the +VI oxidation state. For uranium in the +IV oxidation state, both neutral compounds (e.g., UI_4(OC-

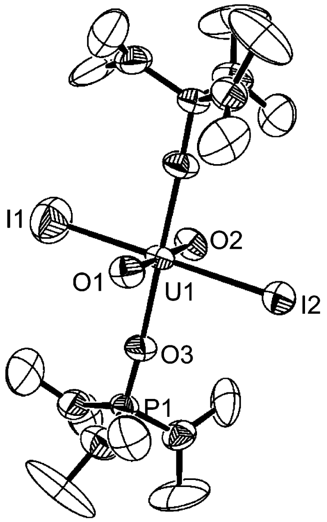

Figure 1. Molecular structure of the centrosymmetric $UO_2I_2(OP(NMe_2)_3)_2$ **(4)** in the crystalline state. ORTEP representation shows thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity.

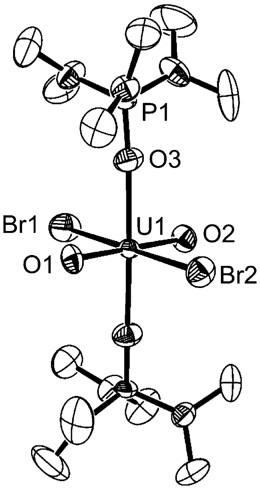

Figure 2. Molecular structure of the centrosymmetric $UO_2Br_2(OP(NMe_2)_3)_2$ **(5)** in the crystalline state. ORTEP representation shows thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity.

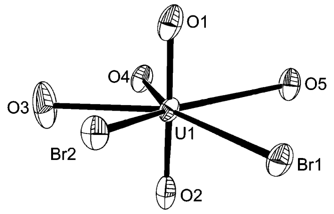

Figure 3. Molecular structure of $UO_2Br_2{\cdot}3H_2O$ **(1)** in the crystalline state. ORTEP representation shows thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity.

$(NMe_2)_2)_4)$[22] and anionic species (e.g., $(Ph_4P)_2UI_6$)[23] have been reported. The bond lengths reported for $UI_4(OC(NMe_2)_2)_4$ (d(U−I) = 3.027 and 2.997 Å)[22] and $(Ph_4P)_2UI_6$ (d(U−I) = 2.986, 3.001, and 3.005 Å)[23] (where uranium is in the +IV oxidation state) compare well with those of **3**, **4,** and **6**, where uranium is in the +VI oxidation state (d(U−I) = 3.0267(6) Å in $UO_2I_2{\cdot}2H_2O{\cdot}4Et_2O$ **(3)**,[5] d(U−I) = 2.920(2), 3.050(1) in **4,** and d(U−I) = 3.0476(1) in **6**). Moreover, the bond lengths observed in **4** fit nicely into the $UO_2X_2(OP(NMe_2)_3)_2$ series, whereby the U−Cl bond lengths and U−Br bond lengths are both shorter than those observed for **4** (d(U−Br) = 2.784(1), 2.830(1) Å in **5**; d(U−Cl) in $UO_2Cl_2(OP(NMe_2)_3)_2$ = 2.661(5) , 2.672(5) Å).[5] If a similar comparison is undertaken for the bromide complexes as that described above for the iodide complexes, for example between the bromide **5** and the U^{IV} compounds $UBr_4((OP(NMe_2)_3)_4$ [24] and $(Ph_4P)_2UBr_6{\cdot}4CH_3CN$,[25] again the U−Br bond lengths in compound **5** (d(U−Br) = 2.784(1), 2.830(1)) agree with those of the uranium(IV) compounds $UBr_4((OP(NMe_2)_3)_4$ (d(U−Br) = 2.778, 2.783 Å)[23] and $(Ph_4P)_2UBr_6{\cdot}4CH_3CN$ (d(U−Br) = 2.768, 2.754, 2.777 Å).[24] The $U{-}OP(NMe_2)_3$ distances in **4** and **5** (d(U−O = 2.266(9) Å in **4**; d(U−O = 2.278(6) Å in **5**) and the $U{-}OPPh_3$ distances in **6** (d(U−O = 2.298(4) Å) are shorter than the corresponding $U{-}OH_2$ bond lengths in **3** (d(U−O) = 2.318(4) Å) but are in agreement with the $U{-}OP(NMe_2)_3$ reported for the related chlorine compound $UO_2Cl_2(OP(NMe_2)_3)_2$ (d(U−O) = 2.30(1) Å).[5d] The use of $OP(NMe_2)_3$ as a coordinating ligand has resulted in the high yield, gram-scale synthesis of a non-air-sensitive U^{VI}−I compound which is soluble in various organic solvents, may be a useful new starting material, and does not require the use of difficult to prepare or air-sensitive starting materials, or even anhydrous conditions. Moreover, **4** is the first structurally characterized room temperature stable U^{VI}−I containing compound. In addition, the synthesis and structure determination of a further U^{VI}−I containing compound which is stable in the solid state at room temperature, $UO_2I_2(OPPh_3)_2$ **(6),** has also been achieved (Figure 5) and can be compared to the all-*trans*-$[UO_2Br_2(OAsPh_3)_2]$ which has been recently reported and also to $UO_2I_2(py)_3$ which has provided further evidence for the existence and stability of U^{VI}−I compounds.

To place $UO_2I_2{\cdot}2H_2O$ **(3)** in context, the uranyl dibromide hydrates, $UO_2Br_2{\cdot}xH_2O$ **(1)** and $[UO_2Br_2(OH_2)_2]_2$ **(2)**, were also investigated. Despite the considerable number of reports regarding the structure and reactivity of the uranyl dichloride hydrates,[1,26] only few reports exist in the literature regarding the heavier uranyl dihalide hydrates. Although spectroscopic data has been reported for dioxouranium dibromide hydrates and their existence is firmly established through these spectroscopic investigations,[1] to our knowledge, no report exists in the literature regarding the structure of a dioxouranium dibromide hydrate although the structures of dioxouranium dichloride hydrates have been reported.[25]

Crystallization of **1** and **2** were achieved by leaving two highly concentrated samples of separate reaction mixtures over P_4O_{10} in desiccators. Crystals of **1** and **2** were obtained from separate recrystallization attempts both compounds being highly hygroscopic (eqs 4 and 5).

$$UO_2(OOCCH_3)_2{\cdot}2H_2O + 2HBr + H_2O \rightarrow \underset{\mathbf{1}}{UO_2Br_2{\cdot}3H_2O} + 2CH_3COOH \quad (4)$$

$$2UO_2(OOCCH_3)_2{\cdot}2H_2O + 4HBr \rightarrow \underset{\mathbf{2}}{[UO_2Br_2(OH_2)_2]_2} + 4CH_3COOH \quad (5)$$

The solid-state structures of **1** and **2** show the trans, linear OUO unit which, as expected, has U═O bond lengths (d(U−O) = 1.72(1) and 1.74(1) Å for **1** and d(U−O) = 1.763(6) and 1.762(5) Å for **2**) similar to those observed in the related dioxouranium dichloride monohydrate (d(U−O) = 1.70(3), 1.74(3) Å in $UO_2Cl_2{\cdot}H_2O$[25]) and $UO_2Br_2{\cdot}3THF$ (d(U−O) = 1.75(1), 1.77(1) Å)[6] (Tables 1, 2 and Figures 3, 4). The

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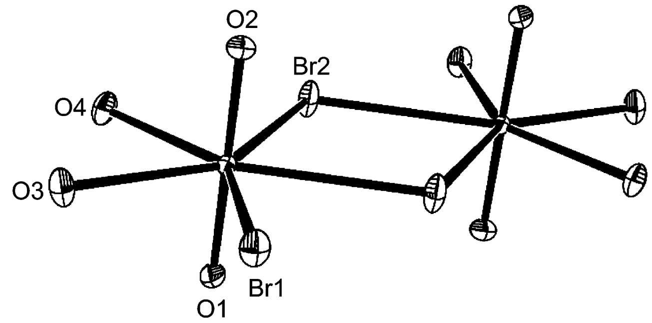

Figure 4. Molecular structure of the centrosymmetric $[UO_2Br_2{\cdot}2H_2O]_2$ **(2)** in the crystalline state. ORTEP representation showing thermal ellipsoids at the 50% probability level, hydrogen atoms omitted for clarity.

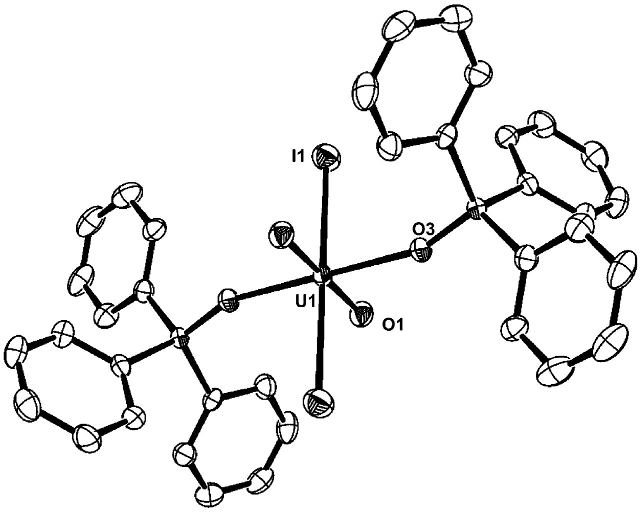

Figure 5. Molecular structure of $UO_2I_2(OPPh_3)_2$ **(6)** in the crystalline state. ORTEP representation shows thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity.

U−Br bond lengths of 2.904(2) and 2.897(2) Å in **1** are slightly longer than those reported in *trans-cis*-$[UO_2Br_2(OAsPh_3)_2]$ (d(U−Br) = 2.828(1) Å)[8] and in $UO_2Br_2{\cdot}3THF$ (d(U−Br) = 2.845(3), 2.856(3) Å).[8a] In contrast, **2** has both terminal and bridging U−Br bonds with the bridging U−Br bonds (d(U−Br) = 2.9456(8) Å) being significantly longer than the U−Br terminal bonds in both **2** (d(U−Br) = 2.8441(9) Å) and in **1** (d(U−Br) = 2.897(2), 2.904(2) Å) as would be expected. The U−OH_2 bond lengths in **1** (d(U−OH_2) = 2.40(1), 2.47(1), and 2.44(1) Å) are slightly longer than those observed for **3** (d(U−OH_2) = 2.318(4) Å) but are still within reasonable values. In **1**, **2,** and **3**, the U−OH_2 bond lengths are considerably longer than the U═O bond lengths, as would be expected (in **1**, d(U═O) = 1.74(1), 1.72(1) Å; d(U−OH_2) = 2.40(1), 2.47(1), 2.44(1) Å; in **2**, d(U═O) = 1.763(6) and 1.762(5) Å; d(U−OH_2) = 2.452(6), 2.421(6) Å; in **3,** d(U═O) = 1.773(3) Å; d(U−OH_2) = 2.318(4) Å). In $UO_2Br_2{\cdot}3THF$, $UO_2Br_2{\cdot}3H_2O$ **(1)**, and $[UO_2Br_2(OH_2)_2]_2$ **(2)**, the uranium atom has a pentagonal bipyramidal environment of ligands with an essentially linear OUO unit as would be expected. Whereas in **1** the two Br atoms are neighbors, in $UO_2Br_2{\cdot}3THF$ this is not the case.[6] In the related compound $UO_2Br_2(OAsPh_3)_2$, the solid-state structures of both the all-*trans*-$[UO_2Br_2(OAsPh_3)_2]$ and *trans-cis*-$[UO_2Br_2(OAsPh_3)_2]$ isomers have been determined using X-ray diffraction.[8] Establishing the geometry of a dioxouranium dibromide hydrate in the solid state is important, as the dioxouranium dihalide hydrates are small, conceptually simple compounds. It is interesting to note that under slightly different reaction conditions, **2** was obtained and not the expected trihydrate **(1)**. Crystals of **2** showed this species to be dimeric with bromine bridges linking the two monomeric units, each of which has only two water molecules coordinated. The crystal structures of **1** and **2** complete the structural characterization of the UO_2X_2 hydrates (X = Cl → I) in the solid state; however, the heaviest member of this series, $UO_2At_2{\cdot}xH_2O$, still remains unknown. It can also be noted that the stability of the most stable dioxouranium dihalide hydrate appears to decrease with increasing mass of halide present.

Conclusion

From this synthetic and structural study, the following conclusions can be drawn. Following the first report on a structurally characterized U^{VI}−I bond in the thermally labile $UO_2I_2{\cdot}2H_2O{\cdot}4Et_2O$ **(3)**, we now present room temperature stable dioxouranium(VI) diiodides containing large coordinating ligands, namely, $UO_2I_2{\cdot}L_2$ (L = $OP(NMe_2)_3$ (**4**) and $OPPh_3$ (**6**)). In addition, for the first time, the structures of the dioxouranium(VI) dibromide hydrates, $UO_2Br_2{\cdot}3H_2O$ **(1)** and $[UO_2Br_2{\cdot}2H_2O]_2$ (**2**), have been determined. The above-mentioned compounds have been fully characterized and are of importance in developing a more comprehensive understanding of simple dioxouranium containing species. It is hoped that future investigations will show **4** which is the first thermally stable and structurally characterized U^{VI}−I compound to have synthetic potential for the preparation of new U^{VI} compounds due to the weaker nature of U^{VI}−I bonds.

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Supporting Information Available: X-ray crystallographic files for $UO_2Br_2{\cdot}3H_2O$ **(1)**, $[UO_2Br_2{\cdot}2H_2O]_2$ **(2)**, $UO_2I_2(OP(NMe_2)_3)_2$ (**4**), $UO_2Br_2(OP(NMe_2)_3)_2$ **(5)**, and $UO_2Br_2(OP(NMe_2)_3)_2$ (**6**) are available in CIF format. The synthesis and characterization details for the impure product from the reaction discussed in ref 17 are also included. This material is available free of charge via the Internet at http://pubs.acs.org.

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