Synthesis of the stable UO$_2$I$_2$, the last of the uranyl dihalides. X-Ray crystal structure of [UO$_2$I$_2$(py)$_3$]†

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Treatment of UO$_2$(OTf)$_2$ with pure Me$_3$SiI led to the quantitative formation of UO$_2$I$_2$ (1). This compound dissolved in pyridine and thf to give the red adducts [UO$_2$I$_2$L$_3$] {L = py (2) or thf (3)}, which were also obtained from the metathetical reaction of UO$_2$(OTf)$_2$ and KI. The crystal structure of 2 has been determined. The uranyl diiodide complexes 1–3 are thermally quite stable, providing that strictly anhydrous conditions are employed.

The recent Communication by Crawford *et al.*[1] on the synthesis and structure of [UO$_2$I$_2$(OH$_2$)$_2$]·4Et$_2$O prompts us to present the results of our current studies on UO$_2$I$_2$. At the beginning of the 20th century, the earliest attempts at the preparation of this compound by reaction of I$_2$ or HI vapors with a mixture of UO$_2$ and carbon were unsuccessful.[2] Solutions of UO$_2$I$_2$ in water or organic solvents have since been prepared, but their evaporation failed to yield the solvent-free product because of extensive decomposition with liberation of iodine.[2–4] Thus, UO$_2$I$_2$ remains the last dioxouranium dihalide not to have been isolated, and its reputed great thermal instability is attributed to the weak nature of the U(VI)–I bond.[2] In addition to being a challenging synthetic goal, convenient access to UO$_2$I$_2$ would represent a new entry into uranium chemistry precisely because of the weakness and chemical reactivity of the U–I bond.[5] It can be anticipated that UO$_2$I$_2$ or its solvated forms, if stable, would be valuable starting materials for the synthesis of U(VI) compounds, just as [UI$_3$(thf)$_4$] has proven to be the most useful precursor to trivalent uranium complexes.[6] Whereas substitution of the iodide ligand would give new U(VI) derivatives, its reductive elimination might afford uranium species in lower oxidation states.[7] Crawford *et al.* succeeded, with the aquo adduct [UO$_2$I$_2$(OH$_2$)$_2$], in determining the first crystal structure of an uranyl diiodide derivative. This result, all the more remarkable as the compound rapidly decomposes at 0 °C, led the authors to conclude that preparation of thermally much more stable UO$_2$I$_2$ complexes is highly desirable "…in order that U(VI)–I compounds do not remain only chemical curiosities". Here, we present the synthesis of UO$_2$I$_2$ (1) and its Lewis base adducts [UO$_2$I$_2$L$_3$] {L = pyridine (2), thf (3)}, along with the X-ray crystal structure of 2; all these complexes were easily isolated under strictly anhydrous conditions and are thermally quite stable.

Compound 1 was prepared in almost quantitative yield by treating the uranyl triflate UO$_2$(OTf)$_2$[8] with pure iodotrimethylsilane (eqn. 1). After 48 h at 20 °C, pentane was added to the suspension and the beige powder of 1 was filtered off and dried under vacuum.†

$$UO_2(OTf)_2 + 2\ Me_3SiI \rightarrow UO_2I_2 + 2\ Me_3SiOTf \quad (1)$$

Insoluble in toluene, compound 1 dissolves sparingly in Et$_2$O and readily in thf or pyridine to give orange to red colored solutions. Addition of a mixture of diethyl ether and pentane to a pyridine solution of 1 led to a red precipitate of [UO$_2$I$_2$(py)$_3$] (2; 95% yield); red crystals of 2 suitable for X-ray diffraction analysis were obtained by carefully layering diethyl ether onto a solution of 1 in pyridine.‡ A view of 2 is presented in Fig. 1, together with selected bond distances and angles. The uranium atom is found in the

classical pentagonal bipyramidal configuration, with the linear UO$_2$ fragment perpendicular to the equatorial plane defined by the three nitrogen atoms of the pyridine ligands and two non-adjacent iodide groups. This structure is familiar in numerous UO$_2$X$_2$ adducts, while the [UO$_2$I$_2$(OH$_2$)$_2$] derivative, which is unexpectedly sterically unsaturated, adopts an octahedral configuration.[1] The average U=O bond distance of 1.755(2) Å is identical to that measured in the analogous seven-coordinate halide complexes [UO$_2$Cl$_2$(THF)$_3$] {1.765(1) Å},[9] [UO$_2$Br$_2$(THF)$_3$] {1.76(1) Å}[10] or [UO$_2$(OTf)$_2$(py)$_3$] {1.745(2) Å}.[8] The U–I distances of 3.1089(8) and 3.1254(8) Å are longer by *ca.* 0.18 Å than that found in the hexacoordinate [UO$_2$I$_2$(OH$_2$)$_2$] compound {2.939(3) Å}. The U–N bond lengths in 2 average 2.54(3) Å; this distance is close to that found in [UO$_2$(OTf)$_2$(py)$_3$] {2.53(2) Å}[8] or [UO$_2$(η^2-NO$_3$)$_2$(py)$_2$] {2.543(15) Å},[11] but is slightly shorter than the U–N distances in the acetylacetonate compounds [UO$_2${RC(O)CHC(O)R'}$_2$(py)] {R = R' = Ph: 2.569(6) Å; R = ^{t}Bu, R' = Me: 2.595(24) Å}.[12]

In order to avoid the use of Me$_3$SiI, a relatively expensive reagent, another synthetic route was envisaged for the preparation of the Lewis base adducts [UO$_2$I$_2$L$_n$]. Substitution reactions of hydrated UO$_2$X$_2$ species (X = SO$_4$, NO$_3$, ClO$_4$, Cl) with NaI or BaI$_2$ at room temperature in organic solvents led invariably to orange–red solutions that failed to yield the anhydrous compound by evaporation.[1,2,13] In particular, thermally unstable crystals of the aforementioned aquo adduct [UO$_2$I$_2$(H$_2$O)$_2$]·4Et$_2$O were prepared from UO$_2$Cl$_2$·xH$_2$O and NaI in diethyl ether. However, we found that this method is straightforward for the formation of stable UO$_2$I$_2$ adducts, providing that strictly anhydrous conditions are employed (eqn. 2 and 3). Thus, treatment of UO$_2$(OTf)$_2$ with excess KI in diethyl ether gave, after 48 h at room temperature, an orange solution which, upon addition of a small quantity of freshly distilled pyridine, deposited a red powder of 2 in 91% yield.
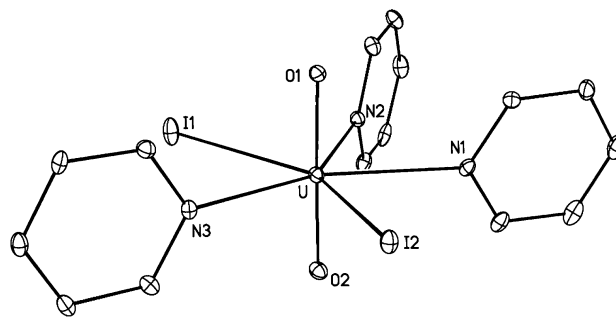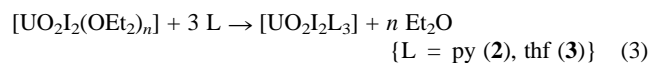
$$UO_2(OTf)_2 + 2\ KI \xrightarrow{Et_2O} [UO_2I_2(OEt_2)_n] + 2\ KOTf \quad (2)$$

$$[UO_2I_2(OEt_2)_n] + 3\ L \rightarrow [UO_2I_2L_3] + n\ Et_2O$$
$$\{L = py\ (2),\ thf\ (3)\} \quad (3)$$

Fig. 1 View of [UO$_2$I$_2$(py)$_3$] with displacement ellipsoids at the 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): U–O(1) 1.757(6), U–O(2) 1.754(6), U–I(1) 3.1089(8), U–I(2) 3.1254(8), U–N(1) 2.564(7), U–N(2) 2.548(7), U–N(3) 2.517(6); O(1)–U–O(2) 178.1(3), I(1)–U–I(2) 144.65(2), I(1)–U–N(2) 72.3(2), I(1)–U–N(3) 71.8(2), I(2)–U–N(1) 76.7(2), I(2)–U–N(3) 73.0(2), I(1)–U–O(1) 88.6(2), I(1)–U–O(2) 92.2(2), I(2)–U–O(1) 87.5(2), I(2)–U–O(2) 92.8(2).

The same reaction in thf afforded $[UO_2I_2(thf)_3]$ (**3**), which was isolated as a red powder in 80% yield after extraction in toluene. In contrast to $[UO_2Cl_2(thf)_3]$, which readily loses one thf molecule to give the chloro-bridged dimer $[UO_2Cl_2(thf)_2]_2$,[9] compound **3**, as with its triflate analogue, is stable under vacuum. Complexes **1**–**3** gave satisfactory elemental analyses.†

The IR spectrum of **1** as a Nujol mull exhibits a strong band with two major peaks at 988 and 982 cm^{-1} assigned to the asymmetric UO_2 stretching mode. Identical $\nu_{asym}(UO)$ frequencies are observed for $UO_2(OTf)_2$, whereas the corresponding band is described at 1000 cm^{-1} for UO_2F_2.[14] The splitting of the band can be ascribed to interactions between the UO_2^{2+} groups *via* the oxygen atoms, similarly to the assignment in UO_2Cl_2 (958 and 946 cm^{-1}) from the crystal structure.[15] In accordance with the greater electron richness of the adducts, the $\nu_{asym}(UO)$ frequencies of **2** and **3** are shifted to the lower values of 927 and 928 cm^{-1} respectively; these can be compared with those of $[UO_2Cl_2(py)_3]$ (925 cm^{-1}), $[UO_2(OTf)_2(py)_3]$ (943 cm^{-1}) or $[UO_2Cl_2(thf)_2]_2$ (921 cm^{-1}).[9,16]

Complexes **1**–**3** were found to be stable for several days under argon at room temperature, both in solution and the solid state. This stability is comparable to that of the few adducts of UO_2I_2 which are stabilized with bulky and strongly coordinating ligands.[17] Compound **1** decomposes with liberation of iodine above 150 °C; melting of **2** and **3**, at 165 and 115 °C, respectively, is presumably related to the dissociation of pyridine or thf ligands, as formation of I_2 was not detected at these temperatures.§ That traces of water are detrimental to the stability of the UO_2I_2 complexes was confirmed by carrying out reaction 2 with hydrated $UO_2(OTf)_2$ or by adding H_2O to a solution of **1** in diethyl ether. In these experiments, after 48 h at room temperature, evaporation of the solvent afforded a brown–black residue with concomitant release of iodine. This material, presumably some uranium oxide, was insoluble in diethyl ether. These observations are in agreement with previous reports on the formation of brown–black decomposition products upon concentration and drying of aqueous solutions of UO_2I_2.[2,4]

The convenient synthesis of **1** which, contrary to previous assumptions, exhibits good thermal stability, provides a further demonstration that uranyl chemistry will witness important progress with the use of anhydrous experimental conditions. While studies of the UO_2X_2 species (X = halide, NO_3, ClO_4, …) in aqueous solutions have so far afforded limited information on the chemical reactivity of the uranyl ion, spectacular developments have been recently observed by using $[UO_2Cl_2(thf)_2]_2$ and $UO_2(OTf)_2$ as starting materials in anhydrous organic media. Formation of highly reactive uranyl complexes,[16,18] the discovery of a novel coordination geometry for the UO_2^{2+} ion,[19] the first crystallographic characterization of a pentavalent UO_2^+ ion,[20] and transformation of UO_2^{2+} into new U(VI) or lower valent species[21] have considerably enlarged the area of uranyl chemistry. In view of the specific features of the U–I bond, UO_2I_2 and its adducts **2** and **3** are potentially useful precursors for the synthesis of new uranium compounds.

Notes and references

‡ *Crystal data* for **2**: $C_{15}H_{15}I_2N_3O_2U$, M = 761.13, orthorhombic, a = 14.968(3), b = 15.662(3), c = 17.193(3) Å, V = 4030.5(14) Å^3, space group *Pbca*, Z = 8, D_c = 2.509 g cm^{-3}, μ(Mo-Kα) = 11.128 mm^{-1}, T = 123(2) K, 25 092 measured reflections, 3364 independent, 2616 [$I > 2\sigma(I)$], 208 parameters, R_1 = 0.0339, wR_2 = 0.0676, GOF = 0.884; the data were collected on a Nonius Kappa CCD diffractometer with Mo-Kα radiation (λ = 0.71073 Å), absorption effects were empirically corrected. CCDC 226281. See http://www.rsc.org/suppdata/cc/b4/b400717d/ for crystallographic data in CIF or other electronic format.

§ The melting points of **2** and **3** were measured with an electrothermal melting point apparatus from samples placed in glass capillaries under argon. The thermal decomposition range of **1** was estimated by observing the release of iodine.

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