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Low-Valent Uranium Iodides: Straightforward Solution Syntheses of UI_3 and UI_4 Etherates

Christopher D. Carmichael, Natalie A. Jones, and Polly L. Arnold*

School of Chemistry, University of Edinburgh, West Mains Road, Edinburgh, Scotland EH9 3JJ

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Uranium turnings react with elemental iodine in diethyl ether at room temperature, with sonication and/or stirring, over a period of days to afford UI_3, $UI_4(OEt_2)_2$, or $UI_4(OBu^n{}_2)$ depending on the stoichiometry or ether solvent. This is the first room temperature, and thus safe and convenient, synthesis of UI_3.

An understanding of the subtle differences in bonding between actinide(III) and lanthanide(III) complexes is key to their effective separation in nuclear waste, and low-oxidation-state uranium chemistry provides important model systems for this. The idea of exploiting covalency differences between the 5f and 4f metals in actinide(III)/lanthanide(III) separation has been explored both theoretically[1] and synthetically[2] and has been discussed in a recent review.[3] Fundamental to the continuing synthetic exploration of this chemistry is the availability of appropriate low-valent uranium compounds.

Low-valent uranium(III) chemistry is typically accessed via the metal or the tetrahydrofuran (THF) adduct of the uranium iodide, $UI_3(THF)_4$.[4,5] The synthetic utility of the solvated iodide has been considerably greater than that of the chloride $UCl_3(THF)_x$, which is made in situ and is a poorly understood material.[6] Readily synthesized from a THF solution of amalgamated uranium turnings and iodine, $UI_3(THF)_4$ and related solvent adducts are at the center of an ever-expanding literature of low-valent uranium chemistry.[3,7] However, while the THF imparts solubility to the metal center, the presence of THF can restrict chemistry. For example, uranium(III) is known to ring open THF,[8] and the synthesis of $UI_3(THF)_4$ is performed below 10 °C to minimize the formation of ring-opened products.[5] The use of unsolvated UI_3 has permitted the synthesis of complexes unobtainable in the presence of strong donor solvents. For example, Cloke and co-workers have utilized UI_3 in the synthesis of an unsolvated pentalene complex that activates dinitrogen[9] and a trimetallic system that activates diethyl ether.[10] The Evans group has used UI_3 in developing new syntheses for various tetramethylcyclopentadienyluranium halides.[11]

This is in contrast to the coordination chemistry of uranium(IV), where the solvent-free chloride, UCl_4, is a commonly used starting material. The tetravalent iodide, UI_4, is rarely utilized; its synthesis is laborious, and it is unstable at room temperature, decomposing to UI_3 and I_2.[12] Recently, however, synthetically useful preparations of UI_4 supported by nitrile ligands have been developed, including the complexes $UI_4(NCMe)_4$ and $UI_4(NCPh)_4$.[13] Trivalent plutonium is more stable than trivalent uranium, and a solution synthesis of $PuI_3(OEt_2)_x$, formed as a pale-blue powder from an excess of plutonium metal and I_2 in diethyl ether, was recently reported and used in the synthesis of $Pu[N(SiMe_3)_2]_3$.[14]

Historically, UI_3 has been synthesized by the reduction of UI_4 with zinc metal in sealed silica vessels at about 600 °C.[15,16] Recently, Cloke optimized Corbett's solid-state metal iodide synthesis,[17] demonstrating that UI_3 can be synthesized from

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* To whom correspondence should be addressed. E-mail: polly.arnold@ed.ac.uk.

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uranium and HgI_2 at 320 °C in a sealed glass ampule.[9] Evans and co-workers have demonstrated a mercury-free synthesis by controlled reaction of the elements at elevated temperature.[11] Although these reactions produce UI_3 in excellent yields, they involve the heating of uranium turnings to red heat[11] or utilize mercury[9] and are thus potentially dangerous or have undesirable environmental implications, respectively. We report herein simple, direct solution syntheses of the unsolvated uranium(III) iodide, UI_3, and the new solvates $UI_4(OEt_2)_2$ and $UI_4(OBu^n{}_2)$ by reaction of the elements at room temperature mediated by diethyl ether or dibutyl ether.

$$\mathrm{U} + 1.5\mathrm{I}_2 \xrightarrow{\mathrm{Et_2O}} \underset{\mathbf{1}}{\mathrm{UI}_3} \tag{1}$$

Adduct-free UI_3 is synthesized according to eq 1. The addition of diethyl ether to an ampule containing cleaned uranium turnings, less than 1.5 equiv of iodine, and a large ovoid stirbar produced an immediate brown color of dissolved iodine. The heterogeneous mixture was vigorously stirred, with occasional sonication (but see below), over 48 h, during which time the solution became dark red and the majority of the uranium reacted. Occasional sonication, coupled with vigorous stirring, was continued for 5 days, and a finely divided, purple-black solid was deposited. The precipitation of the solid was accompanied by fading of the red solution to a pale purple and consumption of the remaining uranium. The mixture was filtered, and the residue was washed several times with diethyl ether and then dried under vacuum to yield the product, UI_3 (**1**), as a dark-purple-black solid in essentially quantitative yield (96%). An electronic absorption spectrum of the 800−1400 nm region, obtained by dissolving **1** in THF, is in excellent agreement with previously obtained spectra of $UI_3(THF)_4$ (Figure 1 in the Supporting Information).[5]

The material as isolated contains small quantities of impurities that, like the UI_3, are almost completely insoluble in noncoordinating solvents, but its purity is sufficient to allow its use in further synthetic chemistry. Analytical values for uranium and iodine were approximately 3% below calculated values,[11,15] and a CHN analysis indicates that a small amount of carbon and hydrogen is present. Exhaustive extraction of **1** with the coordinating solvents THF, pyridine, and 1,2-dimethoxyethane (DME) produces the solvated complexes $UI_3(THF)_4$, $UI_3(py)_4$, and $UI_3(DME)_2$ in excellent yields, leaving an insoluble black solid residue (1−2% by weight). The identity of this material remains unknown, however, given recent work on reductive cleavage of ether by uranium(III);[10] the material is assumed to be carbon-rich products arising from a small amount of diethyl ether decomposition and possibly residual metallic impurities from the surface of the turnings.

$$\mathrm{U} + 2\mathrm{I}_2 \xrightarrow{\mathrm{Et_2O}} \underset{\mathbf{2}}{\mathrm{UI}_4(\mathrm{Et_2O})_2} \tag{2}$$

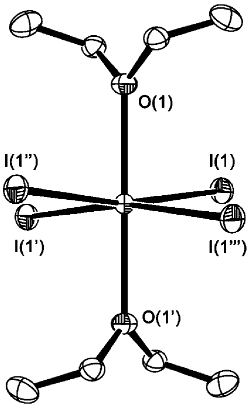

Figure 1. Displacement ellipsoid drawing of **2**. Ellipsoids are drawn at 50% probability. Hydrogen atoms are omitted for clarity. Selected distances (Å) and angles (deg): U−O, 2.366(8); U−I, 2.9614(6); O(1)−U−I(1), 84.68(1); O(1)−U−I(1′), 95.32(1); I(1)−U−I(1′), 89.36(3); I(1)−U−I(1″), 169.36(2); I(1)−U−I(1‴), 91.63(3).

We postulated that the red solution observed during the reaction to form **1** is a soluble uranium tetraiodide, which subsequently reacted with more uranium turnings to form insoluble UI_3. An independent reaction of uranium turnings with 2 equiv of I_2 in diethyl ether, encouraged by vigorous stirring and occasional sonication, affords a bright-red solution containing a red solid after 48 h (eq 2). Concentration of the solution to approximately 5 mL volume, filtration, and drying of the solid under vacuum yield the solvate $UI_4(OEt_2)_2$ (**2**) as a microcrystalline red solid in 77% yield. Uranium and iodine analyses are in agreement with the expected values. Complex **2** is sensitive to loss of diethyl ether if heated above ambient temperature, turning from red to black. In solution, **2** displays two broad and paramagnetically shifted singlets at −10.45 and −22.54 ppm in the ^1H NMR spectrum, attributable to the methyl and methylene protons of diethyl ether, respectively. The electronic absorption spectrum obtained in diethyl ether shows several weak and broad absorptions typical of six-coordinate uranium(IV) species (Figure 1 in the Supporting Information).[18] Evans' method yields a value of 2.15 μ_B. This value is significantly lower than that calculated for a $^3H_4$ ground state of free U^{4+} (3.58 μ_B), but the magnetic moments reported for normal uranium(IV) coordination complexes are invariably lower and usually in the range 2.5−2.8 μ_B.[19]

Concentration of a diethyl ether solution of **2** yields dark-red, octahedral crystals of X-ray quality. The structure of **2** is a distorted octahedron (Figure 1), with trans-bound diethyl ether molecules. Complex **2** crystallizes in the high-symmetry tetragonal space group $I4_1/acd$, resulting in crystallographically equivalent U−I and U−O bond distances. The U−I bond distance [2.9614(6) Å] is at the short end of the range found in similar uranium(IV) iodide complexes $UI_4(py)_3$ [2.9558(4)−3.0438(4) Å],[13a] $UI_4(NCPh)_4$ [3.027(1) Å],[13b] and $UI_4[O{=}C(NMe_2)_2]_2$ [2.9986(3)−3.027(3) Å][18] presumably because of the weaker donor strength of diethyl ether. Coordination of diethyl ether to uranium complexes is rare, with only two structurally characterized examples reported in the literature, the borohydride complex $U(BH_4)_4(OEt_2)$[20] and the oxygen-bridged dimer $U_2Cl_2O_2(Cp^*py)_2(OEt_2)_2$[21] [Cp*py = 1,2,3,4-tetramethyl-5-(2-pyridyl)cyclopentadienide]; the U−O bond distance of **2** falls in between the reported distances. A distortion

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of the iodide ligands from the equatorial plane by approximately 5° is also observed. A similar distortion has been noted in the dimethylurea complex mentioned above.[18]

To confirm that **2** can be an intermediate in the synthesis of **1**, uranium turnings were treated with **2**, according to eq 3. After stirring for only a few hours, a small amount of dark precipitate was noted. The reaction was stirred with occasional sonication for 5 days, during which time the red color of the solution faded, and a dark solid was deposited. After 5 days, **1** was isolated, as described above, in 93% yield. Uranium and iodine analyses were in agreement with those obtained for the samples above.

$$\underset{\mathbf{2}}{3UI_4(Et_2O)_2} + U \xrightarrow{Et_2O} \underset{\mathbf{1}}{4UI_3} \qquad (3)$$

This result suggests that, during the synthesis of **1**, iodine quickly oxidizes the uranium metal to uranium(IV), which is then followed by a slower reduction to uranium(III) by the remaining uranium metal. The intermediate nature of **2** can be further reinforced by stopping a reaction prior to completion, when the solution remains dark red. For example, a reaction filtered after 48 h yielded a small amount of **1** (25% by U), while a significant amount of **2** was isolated from the filtrate (50% by U).

It must be noted that the reactions to synthesize **1** and **2** are very dependent on the efficacy of agitation. Reactions that utilize either vigorous stirring or periodic sonication, but not both, can take up to 20 days to reach completion. It is thought that a combination of sonication and stirring helps to maintain a clean reaction surface better than either alone. Elevation of the reaction temperature was also investigated as a means to reduce reaction times. Reactions performed in refluxing diethyl ether rapidly form **2**, in the form of a dark-red solution; however, no further reaction was observed with the remaining uranium turnings, even upon extended heating (10 days at 40 °C). Once cooled to ambient temperature, however, the formation of **1** was complete within 5 days. It is not known why a heated solution of **2** does not react with uranium; perhaps the elevated temperature hinders the presentation of a clean metal surface for reaction.

Reactions performed at room temperature in dibutyl ether produce an insoluble green solid after several days that has been formulated as $UI_4(OBu^n{}_2)$ (**3**) based on elemental analyses. ^1H NMR experiments using a known internal standard (1,3,5-tri-*tert*-butylbenzene) confirm the presence of one dibutyl ether per uranium center. However, because of its insolubility in noncoordinating solvents, we were unable to grow single crystals suitable to determine the solid-state structure. No further reactivity of **3** with uranium was observed in dibutyl ether, even with prolonged sonication, presumably because of its insolubility.

Samarium and ytterbium diiodides can be prepared by the reaction of the metal with THF solutions of 1,2-diiodoethane,[22] and similar reactions with plutonium and neptunium form the solvated triiodides.[23] However, uranium and thorium were found to be unreactive under similar conditions.[23] The reaction of uranium turnings with a diethyl ether solution of 1,2-diiodoethane did not produce any evidence of reaction, even under prolonged heating to 40 °C and sonication of the reaction mixture.

The preparation of the uranium turnings is important to the synthesis of **1**, with the highest yields achieved utilizing uranium turnings cleaned according to standard procedures[5] but not amalgamated with mercury. Reactions using amalgamated turnings, or reactions carried out with the addition of a small amount (1−2 mg) of HgI_2 to cleaned turnings, lead to significantly lower isolated yields of **1**, with correspondingly larger amounts of **2** remaining in the filtrate. The reason for this exaggerated effect is not known, although it is possible that an amalgamated surface retards the reduction of uranium(IV) to uranium(III). The direct synthesis of **2** appears to be uninfluenced by the presence of mercury.

In order to demonstrate the utility of these solution-based syntheses, **1** and **2** have been used to prepare other uranium(III) and uranium(IV) starting materials. For example, the uranium tris(silylamide), $U[N(SiMe_3)_2]_3$, can be efficiently synthesized from $UI_3(THF)_4$ and $Na[N(SiMe)_3]$ in THF in 82% yield (on a 19 g scale).[5] The addition of toluene to a mixture of **1** and $K[N(SiMe_3)_2]$ on a small scale afforded a dark-red-purple solution from which $U[N(SiMe_3)_2]_3$ was isolated in 63% yield, lower mainly because of the small scale of the reaction. Likewise, $U(Cp)_3I$[24] can be made in 71% yield from **2** and NaCp.

In conclusion, we have developed the first room-temperature procedure to synthesize the important uranium(III) precursor UI_3, using simple solution techniques, and demonstrated its utility in the synthesis of other uranium(III) starting materials. Using the same procedure, we have also synthesized the uranium(IV) solvate $UI_4(OEt_2)_2$ and, in dibutyl ether, $UI_4(OBu^n{}_2)$. This demonstrates that thermally stable tetravalent uranium iodides are also readily accessible in the presence of bases with protons of very low acidity and should prove to be valuable reagents in low-oxidation-state uranium chemistry.

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Supporting Information Available: Experimental details for complexes **1**−**3** and crystallographic data for **2** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org. The atomic coordinates for this structure have been deposited with the Cambridge Crystallographic Data Centre as CCDC 691375. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.

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