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A Convenient Entry into Trivalent Actinide Chemistry: Synthesis and Characterization of $AnI_3(THF)_4$ and $An[N(SiMe_3)_2]_3$ (An = U, Np, Pu)

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The reaction of excess, oxide-free amalgamated uranium metal turnings with elemental iodine or bromine in coordinating solvents at 0 °C provides dark purple $UI_3(THF)_4$ (**1**), royal blue $UBr_3(THF)_4$ (**2**), purple $UI_3(dme)_2$ (**3**), or jet black $UI_3(py)_4$ (**4**) in 65–80% isolated yield (THF = tetrahydrofuran, dme = 1,2-dimethoxyethane, py = pyridine). Neptunium and plutonium metal also react cleanly with elemental iodine in aprotic coordinating solvents to give yellow-orange $NpI_3(THF)_4$ (**5**), off-white $PuI_3(THF)_4$ (**6**), and gray $PuI_3(py)_4$ (**7**) in 80–90% isolated yields. These organic-solvent-soluble Lewis base adducts of early actinide trihalides are precursors to a variety of inorganic and organometallic actinide complexes. Reaction of $AnI_3(THF)_4$ complexes (U, Np, Pu) **1**, **5**, and **6** in THF solution with 3 equiv of sodium bis(trimethylsilyl)amide provides the volatile, solvent-free tris(silylamide) complexes $An[N(SiMe_3)_2]_3$ [An = U (**8**), Np (**9**), Pu (**10**)] in 80–90% yields. The neptunium and plutonium silylamides are the first examples of homoleptic amido complexes of the transuranic elements. Compounds **1**–**10** have been fully characterized by variable-temperature proton NMR, IR, UV/vis/near-IR, thermal gravimetric, and elemental analyses. Single-crystal X-ray diffraction data for **1** revealed a pentagonal bipyramidal coordination geometry about the central uranium atom with two axial iodide ligands (U–I = 3.111(2) Å (average)) and one equatorial iodide ligand (U–I = 3.167(2) Å). All four THF ligands lie in the equatorial plane with an average U–O distance of 2.52(1) Å. Crystal data for **1** (at 23 °C): monoclinic space group $P2_1/c$, with $a = 8.750(3)$ Å, $b = 16.706(16)$ Å, $c = 17.697(7)$ Å, $\beta = 93.64(3)°$, $V = 2582$ Å^3, $d_{calc} = 2.33$ g cm^{-3}, $Z = 4$.

Introduction

The trihalides of the actinide elements are an important class of actinide materials which are typically prepared *via* high-temperature synthetic techniques.[2] The anhydrous AnX_3 compounds prepared in this fashion are polymeric solids,[2-4] insoluble in aprotic organic solvents and quite unreactive.[5] Accordingly, binary actinide(III) halides are not useful starting materials for the nonaqueous preparations of other inorganic and organometallic complexes. A decade ago, Marks and co-workers argued that further developments in nonaqueous uranium(III) chemistry were hindered by the paucity of suitable uranium(III) starting materials,[6] and although Ephritikhine and co-workers have had limited success using $(\eta\text{-}C_6Me_6)U(BH_4)_3$,[7,8] we are still lacking a readily available uranium(III) starting material. Uranium tetrachloride, UCl_4, dissolved in tetrahydrofuran (THF) can be reduced (e.g., with NaH, $NaC_{10}H_8$, or Na/Hg) to give a sparingly soluble purple solid formulated as $UCl_3(THF)_x$.[9] The exact identity of the latter material is unknown, and its utility as a precursor to uranium(III) compounds is apparently limited.[9-14] We have encountered some difficulties using "$UCl_3(THF)_x$" as a starting material. For example, the synthesis of $U[N(SiMe_3)_2]_3$ from $UCl_3(THF)_x$ (generated *in situ*) and sodium bis(trimethylsilyl)amide in THF (eq 1),[14] often yields a mixture containing the uranium(IV) metallacycle $\{[(Me_3Si)_2N]_2\overline{U(CH_2SiMe_2NSiMe_3)}\}$,[15] a material that is difficult to separate from the desired uranium(III) product.

$$UCl_3(THF)_x + 3NaN(SiMe_3)_2 \xrightarrow[25\ °C]{THF} U[N(SiMe_3)_2]_3 + 3NaCl \quad (1)$$

The thermodynamic stability of the binary early actinide(IV) halides decreases in the order F > Cl > Br > I.[2,16,17] Uranium tetraiodide, UI_4, is actually unstable at room temperature and slowly decomposes to uranium triiodide and iodine.[17-19] The fact that the trivalent oxidation state is *favored* by iodide ligands prompted a search for soluble forms of actinide triiodides, AnI_3L_x, with the anticipation that such complexes would provide useful trivalent starting materials.

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A number of synthetic pathways for the preparation of organic-solvent-soluble f-element halides have appeared in the literature, the most useful of which are outlined in eqs 2–6. The smooth

$$\mathrm{Sm} + \mathrm{ICH_2CH_2I} \xrightarrow{\mathrm{THF}} \mathrm{SmI_2(THF)}_x + \mathrm{C_2H_4} \qquad (2)$$

$$2\mathrm{La} + 6\mathrm{CH_3CH_2I} \xrightarrow{\mathrm{THF}} 2\mathrm{LaI_3(THF)}_x + 3\mathrm{C_2H_4} + 3\mathrm{C_2H_6} \qquad (3)$$

$$\mathrm{Th} + 2\mathrm{Br_2} \xrightarrow[\text{anode}]{\mathrm{MeCN}} \mathrm{ThBr_4(NCMe)_4} \qquad (4)$$

$$\mathrm{U} + 2\mathrm{HgCl_2} \xrightarrow{\mathrm{THF}} \mathrm{UCl_4(THF)_3} + 2\mathrm{Hg}^\circ \qquad (5)$$

$$\mathrm{Th} + 2\mathrm{Br_2} \xrightarrow{\mathrm{THF}} \mathrm{ThBr_4(THF)_4} \qquad (6)$$

reaction between alkyl iodides and lanthanide metals (eqs 2 and 3) has become one of the most widely used preparative routes for di- and trivalent lanthanide iodides.[20–23] Karraker has briefly described an extension of this approach to neptunium and plutonium.[24] He noted that Np and Pu react with 1,2-diiodoethane in THF to give the solvated triiodide complexes $\mathrm{AnI_3(THF)}_x$ (An = Np, Pu) and suggested that, despite the difficulty of their preparation, these complexes would be more useful than the anhydrous iodides[25,26] as precursors to organometallic complexes. Karraker also noted that uranium metal was unreactive toward 1,2-diiodoethane.[24]

Direct electrochemical oxidation of thorium metal disks into solutions of chlorine or bromine in acetonitrile has been reported to give $\mathrm{ThX_4(NCMe)_4}$ compounds (X = Cl, Br) as shown in eq 4.[27] However, 6 h of electrolysis (8 V, 50 mA) into a solution of bromine resulted in the dissolution of only 0.60 g of metal. Redox transmetalation (eq 5) between lanthanide[28,29] and actinide[30] metals and mercuric halides provides solvated f-metal halide complexes, but the actinide reaction is unsatisfactory because large quantities of actinide/mercury amalgam are produced as a byproduct. Concomitantly and perhaps more importantly, the actinide amalgam produced by this technique is not compatible with our efforts to substantially minimize the generation of mixed waste (i.e., hazardous waste with a radioactive component). The straightforward combination of actinide metal and elemental halogen in THF solution (eq 6) is clearly the best approach for large-scale preparations of solvated metal halides.[31]

Deacon and co-workers reported that redox transmetalation between mercuric iodide and uranium metal in THF solution produced a green-black solid of composition $\mathrm{UI_3(THF)_4}$ based on elemental analysis and IR data.[30] In our hands, this synthesis gives a mixture of purple $\mathrm{UI_3(THF)_4}$ (53% yield) and an oily green material of unknown identity when oxide-free uranium is employed. When partially oxidized uranium metal (i.e., metal coated with black oxide) is allowed to react with mercuric iodide in THF solution, only the oily green substance is isolated.

We sought a simplified preparation of solvated actinide triiodides which (1) would give high yields on a synthetically useful scale and (2) did not generate large volumes of organic, radioactive, and/or mixed waste. We report here a series of organic-solvent-soluble Lewis base adducts of actinide triiodides that are easy to prepare and serve as precursors to a variety of new and known trivalent actinide compounds. Preliminary accounts of this work have appeared.[32]

Results and Discussion

Synthesis and Reactivity. (a) Uranium. A slight excess of clean, amalgamated uranium metal turnings (*vide infra*) reacts with elemental iodine or bromine in THF solution at 0 °C to yield microcrystalline, dark purple $\mathrm{UI_3(THF)_4}$ (**1**) or royal blue $\mathrm{UBr_3(THF)_4}$ (**2**) in *ca.* 60–70% isolated yield after 24 h (eq 7). It is

$$\mathrm{U} + 1.5\mathrm{X_2} \xrightarrow[0\,^\circ\mathrm{C}]{\mathrm{THF}} \mathrm{UX_3(THF)_4} \qquad (7)$$

$$\mathrm{X} = \mathrm{Br, I}$$

essential that a slight excess (*ca.* 10%) of uranium metal be used in order to ensure that all the iodine or bromine is consumed and the oxidation state of uranium be maintained at +3. Compounds **1** and **2** are easily prepared on a 50–100-g scale. This is a synthetically useful quantity, and the gentle solution reaction is a significant advance over the high-temperature tube-furnace techniques which yield polymeric $\mathrm{UI_3}$.[17]

Uranium triiodide tetrakis(tetrahydrofuran) (**1**) is an air-sensitive, dark purple, crystalline solid. We have stored **1** in glass scintillation vials at −40 °C in our inert-atmosphere (helium) glovebox freezers for months and in sealed glass ampules at room temperature for as long as 2 years without noticeable signs of decomposition. Compound **1** is appreciably soluble in THF: *ca.* 3 g/100 mL of THF at 10 °C. The compound is soluble in toluene but loses THF and precipitates from solution over a period of hours as a dark green solid analyzing as $\mathrm{UI_3(THF)_{3.5}}$. Toluene solutions spiked with *ca.* 5% THF by volume are stable for long periods.

The dissolution of uranium metal turnings is accompanied by the slow discharge of color due to iodine or bromine and the appearance of a dark purple or blue solid (respectively) and solution. Care must be taken to maintain the reaction temperature at or below *ca.* 10 °C. At higher temperatures we have experienced considerable acceleration of this exothermic reaction, decreased product yield, and large amounts of an oily green product. We believe that this oily residue arises from ring opening of THF to form a 4-iodobutoxide ligand bound to uranium(IV).[33] Uranium metal turnings work best, and the halogenation reactions proceed at a convenient rate. Fine powders (difficult to control) and bulk metal (too slow) should be avoided. In addition, we have found that the black, surface-bound $\mathrm{UO_2}$ typically found on uranium metal turnings significantly reduces the yields of the desired trivalent uranium products. We scrupulously clean oxide-coated uranium turnings and coat them with a thin layer of mercury amalgam (Experimental Section) generated by reaction with small quantities of $\mathrm{HgI_2}$. The latter step renders the turnings less sensitive to oxidation and facilitates their manipulation in the glovebox. However, even in the best of glovebox atmospheres, the initial mirror finish on the turnings turns brown after 24 h.

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The solution reaction of freshly prepared uranium turnings with iodine is not specific to THF solvent alone. A slight excess of uranium turnings reacts with iodine at 0 °C in 1,2-dimethoxyethane (dme) solution to give $UI_3(dme)_2$ (**3**) as a purple microcrystalline solid in 80% yield (eq 8). The reaction is, however,

$$U + 1.5I_2 \xrightarrow[0\ °C]{L} UI_3(L)_4 \qquad (8)$$

$$L = {}^1/_2\ dme\ (\mathbf{3}),\ py\ (\mathbf{4})$$

somewhat slower than the one employing THF and requires 3 days to reach completion. In a similar fashion, with pyridine as solvent, we obtain black, microcrystalline $UI_3(py)_4$ (**4**) in 80% yield (eq 8) after 2 days of stirring.

The appreciable solubility of the solvated triiodides in organic solvents gives them a distinct advantage over the unsolvated oligomeric anhydrous halides in preparative applications. Also, the solvated triiodides exhibit greater resistance to disproportionation reactions during halide metathesis reactions. Compounds **1**–**4** are all air-sensitive and soluble in THF. Dissolution in THF is accompanied by THF ligand exchange as judged by ^1H NMR spectroscopy. Adducts **1**–**4** react quickly with halogenated solvents such as CH_2Cl_2 or CCl_4 to form U(IV) complexes.[34] As noted above, benzene and toluene solutions of **1** are unstable and slowly precipitate a dark green solid upon standing. The reaction is reversible as evidenced by the regeneration of the royal blue $UI_3(THF)_4$ solution upon addition of THF to the suspension. ^1H NMR spectroscopy of **1** in either benzene-d_6 or toluene-d_8 solvent demonstrates that the appearance of free THF is associated with formation of the green solid formulated as $UI_3(THF)_x$, possibly analogous to $UCl_3(THF)_x$.[9] It is not known whether the green solid is oligomeric. Elemental analysis corresponds to a composition of $UI_3(THF)_{3.5}$.

(b) Neptunium and Plutonium. In direct analogy with the uranium chemistry, the stoichiometric addition of iodine readily oxidizes neptunium and plutonium metals in aprotic, coordinating solvents such as THF and pyridine to give soluble Lewis base adducts $NpI_3(THF)_4$ (**5**), $PuI_3(THF)_4$ (**6**), and $PuI_3(py)_4$ (**7**) in high yields (eq 9). In contrast to the uranium procedures, it is

$$An + 1.5I_2 \xrightarrow[20\ °C]{L} AnI_3(L)_4 \qquad (9)$$

$$An = Np;\ L = THF\ (\mathbf{5})$$

$$An = Pu;\ L = THF\ (\mathbf{6})\ py\ (\mathbf{7})$$

not necessary to rigorously clean the Np and Pu surfaces immediately prior to use. Reaction progress is readily monitored by observing the consumption of metal turnings, which is generally complete within 24–48 h. The reactions of neptunium and plutonium metal with elemental iodine are not as vigorous as that for uranium and are safely performed at room temperature, providing the rate of addition of elemental iodine is controlled. Like the uranium dissolution, the rate of reaction between neptunium or plutonium and iodine is directly proportional to the metal surface area. Finely divided plutonium reacts rapidly and exothermically to the extent that THF and pyridine will boil if the rate of iodine addition is too rapid.

Adducts **5** and **6** are less soluble in the parent solvent than $UI_3(THF)_4$ (U ≫ Np > Pu) and precipitate from THF solution during preparation. Conversely, pyridine adduct **7** is quite soluble and remains in solution throughout the course of the reaction. $NpI_3(THF)_4$ (**5**) is a bright yellow-orange, microcrystalline solid; $PuI_3(THF)_4$ (**6**), similar in morphology, is off-white. The gray pyridine complex $PuI_3(py)_4$ (**7**) is obtained as a spectroscopically pure powder (as assayed by ^1H NMR and infrared spectroscopy) after reaction workup.

In contrast to the $UI_3(L)_4$ complexes, the transuranic triiodide complexes are only moderately air-sensitive, decomposing over several days' exposure to oxygen and atmospheric moisture to form intractable residues. $PuI_3(THF)_4$ is less sensitive to air than $NpI_3(THF)_4$, which, in turn, is significantly less air-sensitive than $UI_3(THF)_4$. This trend is in accord with the known stability of the trivalent oxidation states of these elements.[2] We also find that transuranic complexes **5**–**7** do not react rapidly with halogenated solvents such as $CHCl_3$ or CH_2Cl_2.

Reactivity of $AnI_3(L)_4$ Complexes. The actinide triiodide Lewis base adducts are useful precursors to a host of new and known trivalent actinide complexes. THF solutions of $AnI_3(THF)_4$ react cleanly at, or below, room temperature with alkali metal salts to give, after appropriate workup, high yields of spectroscopically pure trivalent actinide products with concomitant loss of the alkali metal iodide salt. For example, $UI_3(THF)_4$ reacts readily with 1 equiv of KC_5Me_5 (KCp*) to give $Cp^*UI_2(THF)_3$,[35] which reacts further with $K_2C_8H_8$ to give $(C_8H_8)UCp^*(THF)$ in high yield.[36] In an analogous fashion, $PuI_3(THF)_4$ reacts quickly with 3 equiv of LiC_5H_5 to give Cp_3Pu.[35] As a further demonstration of the synthetic utility of the triiodide THF adducts, we report here their use in preparation of actinide tris(silylamide) complexes.

The reaction of 3 equiv of $NaN(SiMe_3)_2$ with solutions or slurries of $AnI_3(THF)_4$ in THF at room temperature gave, after workup, air-sensitive, red-purple $U[N(SiMe_3)_2]_3$ (**8**), blue-black $Np[N(SiMe_3)_2]_3$ (**9**), and yellow-orange $Pu[N(SiMe_3)_2]_3$ (**10**) in 93–95% crude yields (eq 10). Initial removal of volatiles from

$$AnI_3(THF)_4 + 3NaN(SiMe_3)_2 \xrightarrow[25\ °C]{THF} An[N(SiMe_3)_2]_3 + 3NaI \qquad (10)$$

$$An = U\ (\mathbf{8}),\ Np\ (\mathbf{9}),\ Pu\ (\mathbf{10})$$

the hexane extract of crude $Np[N(SiMe_3)_2]_3$ (**9**) gave an oily orange solid which was spectroscopically similar (as assayed by IR) to the blue-black product obtained after further vacuum drying or sublimation.

Tris(silylamide) complexes **9** and **10**, like the previously reported **8**,[14] are hydrocarbon soluble and volatile, readily subliming at 10^{-4}–10^{-5} Torr and 60 °C. Some thermal decomposition occurs upon heating; sublimation yields range from 67% to 81%. We were unable to obtain meaningful spectroscopic data on the sublimation residues; hence the mechanism of decomposition is unknown. However, the infrared spectrum obtained after an attempt to condense the plutonium silylamide complex into an argon matrix (10^{-5} Torr, 40–60 °C) showed only hexamethyldisilazane, $HN(SiMe_3)_2$.

Solid-State and Molecular Structure. Attempts to obtain single-crystal X-ray structural data on $NpI_3(THF)_4$ and $PuI_3(THF)_4$ were unsuccessful and complicated by local regulations that require Np and Pu samples to be doubly contained. However, a single-crystal X-ray diffraction study was performed on the uranium analogue, $UI_3(THF)_4$ (**1**). A summary of data collection and crystallographic parameters is given in Table 1. Atomic positional parameters are given in Table 2, and selected bond distances and angles are given in Table 3.

$UI_3(THF)_4$. Single crystals of $UI_3(THF)_4$ were grown from a concentrated THF solution at −40 °C, and the structure was determined from X-ray diffraction data collected at 25 °C. In the solid state, $UI_3(THF)_4$ is mononuclear with a pentagonal

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Table 1. Summary of Crystallographic Data

compound	**1**
empirical formula	$UI_3O_4C_{16}H_{32}$
color and habit	purple crystal in quartz capillary
crystal dimens, mm	0.08 × 0.11 × 0.18
space group	$P2_1/c$ (No. 14)
a, Å	8.750(3)
b, Å	16.706(16)
c, Å	17.697(7)
β, deg	93.64(3)
V, Å^3	2582
Z, molecules/cell	4
fw	907.17
D_{calc}, g cm^{-3}	2.33
abs coeff, cm^{-1}	95.11
F(000)	1644
λ(Mo Kα), Å	0.710 69
temp, °C	25
2θ range, deg	2.0–45.0
no. of measd reflns	3576
no. of unique intensities	3301
no. of obsd reflns	1816 ($F > 6.0\sigma(F)$)
$R(F)^a$	0.043
$R_w(F)^b$	0.047

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

Table 2. Positional Parameters and Equivalent Isotropic Thermal Parameters for $UI_3(THF)_4$ (**1**)

atom	x	y	z	B_{eq}, Å^2
U	0.15165(9)	0.19284(4)	0.21084(5)	3.41(4)
I(1)	−0.0751(2)	0.1719(1)	0.3446(1)	6.1(1)
I(2)	0.1630(2)	0.0192(1)	0.1656(1)	7.5(1)
I(3)	0.3871(2)	0.2385(1)	0.0869(1)	7.0(1)
O(1)	−0.068(1)	0.1706(7)	0.119(8)	4.3(7)
O(2)	0.362(2)	0.1406(8)	0.3044(8)	5.3(8)
O(3)	0.275(2)	0.2988(7)	0.2946(8)	4.8(7)
O(4)	0.017(2)	0.31272(8)	0.171(1)	6.1(9)
C(1)	−0.202(3)	0.122(1)	0.119(1)	5(1)
C(2)	−0.254(3)	0.098(1)	0.040(2)	6(1)
C(3)	−0.203(3)	0.159(1)	−0.012(1)	7(1)
C(4)	−0.050(3)	0.180(1)	0.027(1)	7(1)
C(5)	0.499(3)	0.100(2)	0.282(1)	7(2)
C(6)	0.540(3)	0.049(2)	0.348(2)	9(2)
C(7)	0.485(4)	0.087(2)	0.420(2)	12(3)
C(8)	0.357(4)	0.131(2)	0.392(2)	9(2)
C(9)	0.199(3)	0.345(1)	0.352(1)	7(1)
C(10)	0.302(4)	0.408(1)	0.374(2)	10(2)
C(11)	0.443(4)	0.384(2)	0.349(2)	12(3)
C(12)	0.434(3)	0.319(2)	0.300(2)	10(2)
C(13)	−0.145(3)	0.333(1)	0.174(2)	7(2)
C(14)	−0.180(4)	0.391(2)	0.112(2)	11(2)
C(15)	−0.028(5)	0.423(1)	0.095(2)	11(2)
C(16)	0.084(4)	0.384(2)	0.143(2)	12(2)

Table 3. Selected Bond Lengths (Å) and Angles (deg) for the Coordination Sphere of $UI_3(THF)_4$ (**1**)

U–I(1)	3.103(2)	U–I(2)	3.167(2)
U–I(3)	3.119(2)	U–O(1)	2.48(1)
U–O(2)	2.51(1)	U–O(3)	2.54(1)
U–O(4)	2.56(1)		
I(1)–U–I(2)	95.90(5)	I(1)–U–I(3)	171.3(5)
I(1)–U–O(1)	87.6(3)	I(1)–U–O(2)	89.1(3)
I(1)–U–(3)	87.7(3)	I(1)–U–O(4)	89.3(4)
I(2)–U–I(3)	93.5(5)	I(2)–U–O(I)	73.9(3)
I(2)–U–O(2)	76.1(3)	I(2)–U–O(3)	146.1(3)
I(2)–U–O(4)	142.3(3)	I(3)–U–O(1)	96.6(3)
I(3)–U–O(2)	91.1(3)	I(3)–U–O(3)	84.2(3)
I(3)–U–O(4)	85.1(4)	O(1)–U–O(3)	140.1(4)
O(1)–U–O(2)	149.3(4)	O(2)–U–O(3)	70.2(4)
O(1)–U–O(4)	68.9(4)	O(3)–U–O(4)	71.4(5)
O(2)–U–O(4)	141.6(5)		

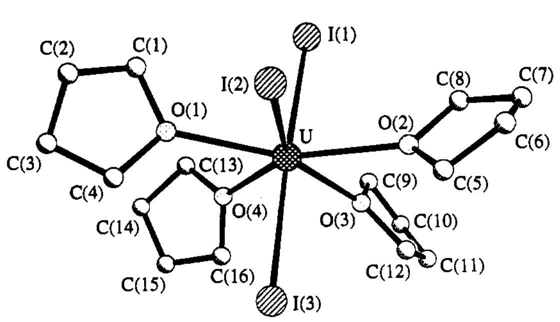

Figure 1. Ball and stick drawing of the $UI_3(THF)_4$ molecule (**1**) emphasizing the pentagonal bipyramidal coordination geometry and giving the atom-numbering scheme used in the tables.

bipyramidal coordination geometry about the central uranium atom, as shown in Figure 1. Two iodide ligands occupy axial coordination sites with an average U–I distance of 3.111(2) Å, while the third iodide ligand lies in the equatorial plane with U–I = 3.167(2) Å. These bond lengths may be compared to the U–I distances of 3.165(12), 3.244(8), and 3.456(11) Å found in polymeric UI_3, where uranium is located in a bicapped trigonal prismatic environment of iodide ligands.[5] All four THF ligands in **1** lie in the equatorial plane with an average U–O distance of 2.52(1) Å. The sum of the five angles within the equatorial plane is 360.5°, and the mean deviation is only ±0.08 Å from the plane. The I–U–I angles between equatorial and axial iodide ligands average 94.25(5)°, forcing the axial iodide ligands to bend away from the equatorial iodide. The resulting I_{ax}–U–I_{ax} angle is 171.30(5)°. Note that there are two types of THF ligands in the equatorial plane—those proximal to the unique, equatorial iodide ligand and those distal. The molecular structure bears a strong resemblance to the pentagonal bipyramidal units observed in the solid-state structures of $NdCl_3(THF)_4$[37] and $EuCl_3(THF)_4$.[38]

Spectroscopic Characterization. The primary aim of our spectroscopic studies was to determine the amount of coordinated ligand in bulk samples of AnX_3L_x formed by halogen-induced oxidative dissolution of actinide metal turnings. On the basis of elemental and thermal gravimetric analysis (TGA), ^1H NMR integration versus internal standards, and infrared spectroscopy, the stoichiometry has been established as AnX_3L_4 (An = U, Np, Pu) for bulk powdered samples where L is a monodentate Lewis base, or AnX_3L_2 for the one case where a bidentate ligand was employed (dme).

Thermal Gravimetric Analysis. The thermal stability of the THF adducts is supported by TGA studies on both single crystals and powdered samples of $UI_3(THF)_4$ that reveal no loss of THF until temperatures exceed 75 °C. Thermal gravimetric analysis of a freshly prepared single crystal of $UI_3(THF)_4$ establishes that 1 equiv of THF is removed (loss of 7.95%) at 104 °C, 2 equiv of THF is expelled between 104 and 140 °C (loss of 15.9%), and a final 1 equiv of THF is lost between 140 and 162 °C to produce anhydrous UI_3 (68.2% of original mass). Powdered samples of $UI_3(THF)_4$ show similar behavior. Thermal gravimetric analyses of powdered samples of $NpI_3(THF)_4$ and $PuI_3(THF)_4$ show similar decomposition stages and establish that 4 equiv of THF is expelled between 56 and 180 °C to produce anhydrous NpI_3 (65.5% of original mass) and PuI_3 (68.6% of original mass). Similar decomposition stages have been observed during thermal gravimetric analysis of oxygen-donor adducts of thorium tetrahalides.[31,39,40] In addition, metal analyses for triiodide complexes **5**–**7** support their formulation as tetrasolvates.

Vibrational Spectra. Infrared spectra in the region between 4000 and 400 cm^{-1} show only absorption bands characteristic of the coordinated ligands. Upon complex formation, pyridine vibrations in the high-frequency region are not appreciably shifted, whereas the in-plane ring deformation mode is generally shifted

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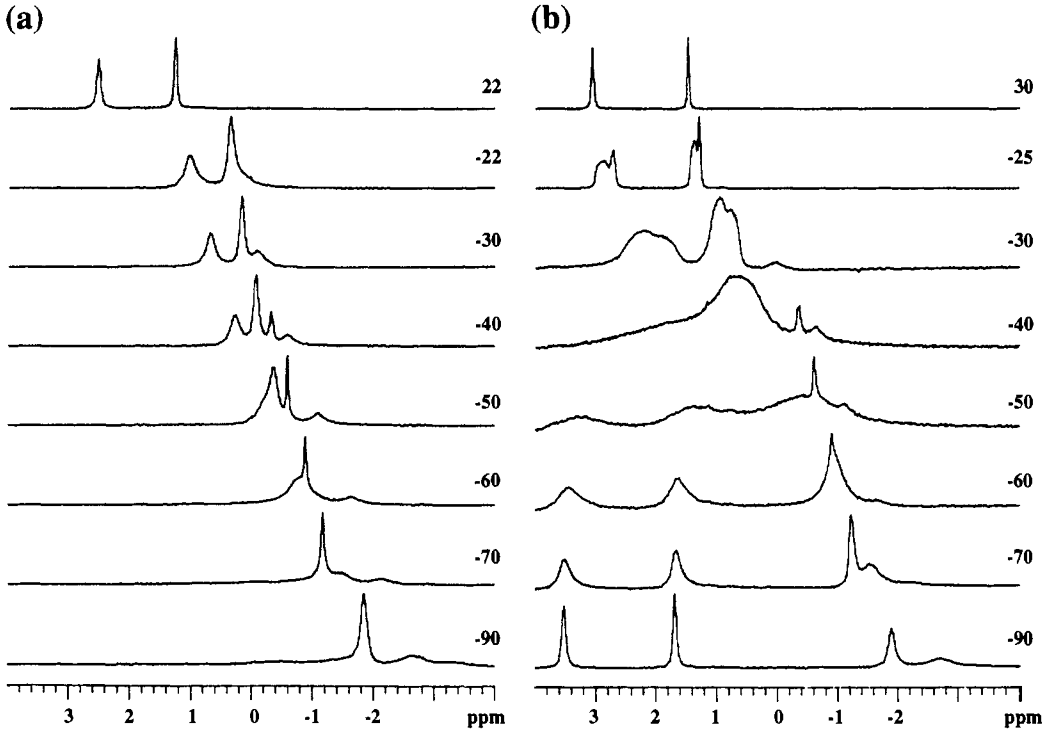


Figure 2. (a) Variable-temperature 300-MHz ^{1}H NMR behavior of $PuI_3(THF)_4$ in CD_2Cl_2 solution. (b) Variable-temperature 300-MHz ^{1}H NMR behavior of $PuI_3(THF)_4$ in CD_2Cl_2 solution in the presence of added THF.

from 604 cm^{-1} to higher energy.[41] The observed shift of this vibrational mode to 621 cm^{-1} in $UI_3(py)_4$ and to 624 cm^{-1} in $PuI_3(py)_4$, is consistent with coordinated pyridine.[41] In a similar fashion, IR absorption bands at 1011, 853, and 833 cm^{-1} for $UI_3(THF)_4$, 1009, 854, and 834 cm^{-1} for $NpI_3(THF)_4$, and 1002, 847, and 831 cm^{-1} for $PuI_3(THF)_4$ are indicative of coordinated THF ligands.[42,43]

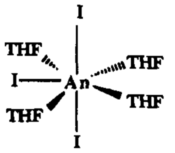
The infrared spectra of the silylamide complexes display absorption features for the asymmetric $\nu(MNSi_2)$ stretches at 988 cm^{-1} for $Np[N(SiMe_3)_2]_3$ (**9**) and at 986 cm^{-1} for the $Pu[N(SiMe_3)_2]_3$ analogue (**10**); absorptions for the symmetric $\nu(MNSi_2)$ stretches are found at 813 and 767 cm^{-1} for **9** and at 813 and 767 cm^{-1} for **10**. These compare favorably to absorptions at 990, 812, and 765 cm^{-1} reported by Andersen for $U[N(SiMe_3)_2]_3$ (**8**). The uranium silylamide complex has a pyramidal coordination geometry on the basis of comparison of the infrared spectral data to those for structurally characterized transition metal and lanthanide amide complexes.[14,44]

^{1}H NMR Spectra. Freshly prepared NMR samples of $UI_3(THF)_4$ show two broad ^{1}H NMR resonances (250 MHz, toluene-d_8, 23 °C) at δ 9.5 and 5.4 corresponding to the α and β protons of THF coordinated to the paramagnetic uranium(III) center. The room-temperature ^{1}H NMR spectrum of $NpI_3(THF)_4$ in CD_2Cl_2 exhibits a single, very broad resonance centered at δ 0.7. A spectrum obtained after warming the sample to 40 °C shows two broad resonances of equal intensity at δ 1.3 ($\Delta\nu_{1/2}$ = 97 Hz) and 2.2 ($\Delta\nu_{1/2}$ = 240 Hz). The room-temperature ^{1}H NMR spectrum of $PuI_3(THF)_4$ in $CDCl_3$ displays two resonances of equal intensity; these, however, are not nearly as broad as those seen for the U and Np congeners: δ 1.37 ($\Delta\nu_{1/2}$ = 11.4 Hz) and 2.68 ($\Delta\nu_{1/2}$ = 11.4 Hz). Thus all the $AnI_3(THF)_4$ complexes exhibit similar NMR behaviors at or near room temperature.

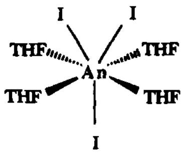
Dynamic behavior was observed for all $AnI_3(THF)_4$ complexes in variable-temperature ^{1}H NMR experiments. Since the line widths of $PuI_3(THF)_4$ samples are relatively sharp, this complex was chosen for more detailed variable-temperature studies. ^{1}H NMR data were obtained from a CD_2Cl_2 solution of **6** at temperatures between +30 and −90 °C (Figure 2a). These data clearly show a dynamic process in which the two initial resonances decoalesced into four resonances which then continued to broaden as if further decoalescence was about to occur as the low-temperature solvent limit was approached. Similar data were obtained from toluene-d_8 solutions of uranium complex **1** and CD_2Cl_2 solutions of neptunium complex **5**.

Addition of THF to a CD_2Cl_2 solution of $PuI_3(THF)_4$ shifts the two resonances observed in the room-temperature spectrum toward the frequencies for free THF at δ 1.7 and 3.5, indicative of THF ligand exchange (Figure 2b). At temperatures lower than *ca.* −50 °C, uncoordinated THF is observed along with resonances similar to and, at the lowest temperatures, identical to those observed in the first experiment.

If the THF adducts all adopt the pentagonal bipyramidal geometry found for uranium complex **1** in which the four THF molecules are in the equatorial plane as shown in I, two types of THF ligand (distal and proximal to the equatorial iodide) should be observed in the ^{1}H NMR spectra. The observation of a single THF ligand environment at room temperature is consistent with the solid-state structure, *provided* there is a rapid interconversion of seven-coordinate structures [e.g., pentagonal bipyramid (**I**) ↔ capped trigonal prism (**II**)] on the NMR time scale.[45]



I



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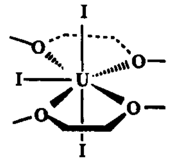

III

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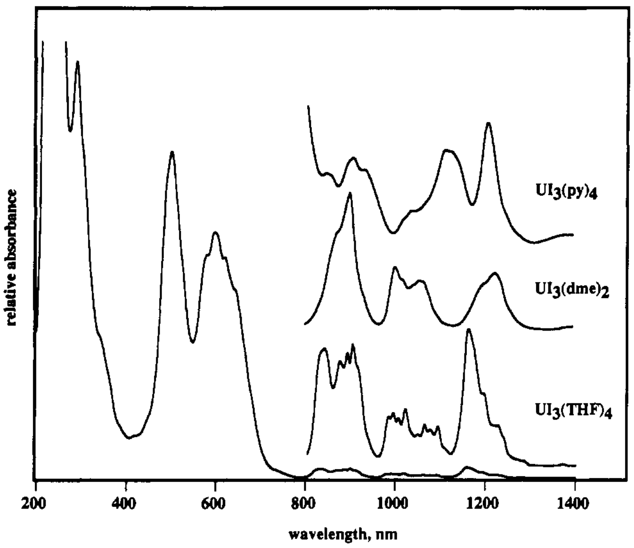

Figure 3. UV-vis-near-IR spectrum of $UI_3(THF)_4$ recorded in THF solution at 25 °C. Inserts show the intensity-expanded "fingerprint" region of Laporte-forbidden internal f → f bands for trivalent uranium compounds **1**, **3**, and **4** recorded in THF, dme, and py solvents, respectively.

The ^1H NMR spectra of the uranium (**4**) and plutonium (**7**) pyridine adducts were similar to those of other tetrasolvates in that only one type of coordinated ligand was observed at room temperature. Freshly prepared samples of $UI_3(py)_4$ show three broad ^1H NMR resonances in benzene-d_6 at δ 17.8, 15.4, and 12.0 in a 2:1:2 ratio corresponding to the α, γ, and β protons of pyridine coordinated to the paramagnetic uranium(III) center. The observed resonances for coordinated pyridine in $PuI_3(py)_4$ in the room-temperature NMR spectrum (C_6D_6, 300 MHz) at δ 6.10 (β), 6.64 (γ), and 9.07 (α) were shifted slightly from those of free pyridine [pyridine in C_6D_6: δ 6.68 (β), 7.01 (γ), 8.52 (α)]. Room-temperature ^1H NMR spectra for $UI_3(dme)_2$ reveal two methyl (δ 3.42 and 3.27) and two methylene (δ −84.54 and −84.69 ppm) resonances, consistent with maintenance of a pentagonal bipyramidal coordination environment in solution, as indicated in **III**. This geometry is similar to those of the structures observed in the solid state for $GdCl_3(dme)_2$[46] and $YCl_3(dme)_2$.[47]

Room-temperature ^1H NMR spectra of the three actinide silylamide complexes show single resonances at δ −11.0, +3.0, and +0.7 for U (**8**), Np (**9**), and Pu (**10**), respectively.

Electronic Absorption Spectra. The room-temperature electronic absorption spectrum of $UI_3(THF)_4$ recorded in THF solution from 1400 to 200 nm is shown in Figure 3. The absorption spectrum shows a manifold of weak (ϵ = 15–60 M^{-1} cm^{-1}) absorption bands in the near-IR region (1350–800 nm), two intense (ϵ = 1500–2000 M^{-1} cm^{-1}) absorption bands in the visible region, and a shoulder at 288 nm (ϵ = 2500 M^{-1} cm^{-1}) in the UV region. The band positions and weak intensity of the absorption features between 1350 and 800 nm are consistent with Laporte-forbidden f → f transitions of the uranium(III) center; these are shown for compounds **1**, **3**, and **4** in the intensity-expanded spectra shown in the insert to Figure 3. These band maxima show a striking similarity to absorption spectra for other U(III) inorganic[48] $\{[K(THF)_2]_2[U(NHAr)_5]\}\cdot$THF and organometallic[49] $[Cp_3U(OEt_2)]$ complexes and the U(III) aquo ion stabilized in perchloric acid.[50] Thus the internal f → f bands in the uranium triiodide spectra serve as a convenient electronic "fingerprint" for trivalent uranium. Through comparison with the spectrum of the uranium(III) aquo ion, it can be seen that f → f bands of the uranium(III) chromophore ride on the intense band near 600 nm. The intensities of the band maxima at 600 nm (ϵ = 1500 M^{-1} cm^{-1}) and 500 nm (ϵ = 2000 M^{-1} cm^{-1}) are too intense to be due to internal f → f transitions and are tentatively assigned as Laporte-allowed f → d transitions, which are typically low enough in energy in uranium compounds to be observed.[51] In a similar fashion, the absorption spectra of transuranic $AnI_3(THF)_4$ complexes recorded between 1200 and 600 nm show a striking similarity to those of the corresponding trivalent aquo ions. Figure 4 shows a comparison of the electronic absorption spectra of $NpI_3(THF)_4$ and $PuI_3(THF)_4$ and the $Np(H_2O)_n^{3+}$ (stabilized with ZnHg) and $Pu(H_2O)_n^{3+}$ aquo ions in perchloric acid.

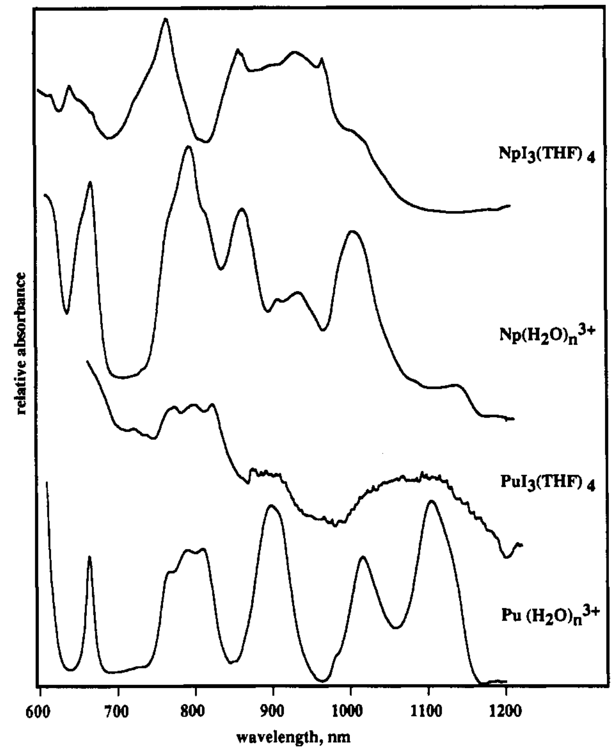

Figure 4. Near-IR "fingerprint" spectra of aquo Pu^{3+} and Np^{3+} (stabilized with ZnHg) recorded in 1 M perchloric acid compared to those of $AnI_3(THF)_4$ compounds **5** and **6** recorded in THF solution at 25 °C.

Concluding Remarks

We have shown that the gentle dissolution of light actinide (U, Np, Pu) metal turnings with elemental iodine or bromine in donor solvents represents a convenient, facile, and high-yield preparative route to synthetically useful quantities of trivalent AnX_3L_4 complexes (X = Br, I). In the case of uranium metal dissolution, preamalgamation and maintenance of the reaction temperature near 0 °C are crucial for obtaining the desired UI_3L_4 products in the stated yields. The elegance of the direct halogen dissolution procedure reported here is in its simplicity; no special equipment is required.

The $AnX_3(THF)_4$ complexes are synthetic precursors to a range of inorganic and organometallic complexes, due in part to their favorable solubility in toluene and THF. Reaction of $AnX_3(THF)_4$ with alkali metal salts of the appropriate carbocycle, aryloxide, amide, etc. provide high-yield routes to both new and known trivalent actinide complexes. For trivalent uranium chemistry, the large-scale preparation of $UI_3(THF)_4$ has allowed

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for the scale-up of several literature reactions. For example, the preparation of $U[N(SiMe_3)_2]_3$ is routinely performed in our laboratory on a 20-g scale (eq 11). It is anticipated that the use of $UI_3(THF)_4$ will provide a convenient entry into the chemistry of many other trivalent uranium compounds. The same can be said for the transuranic analogues. We already know that the plutonium triiodide complexes are more convenient to prepare and use than the more common $PuCl_3$ and M'_2PuCl_6 ($M' = Cs$, NH_4, etc.) The homoleptic hexamethyldisilylamide complexes are the first well-characterized examples of Np and Pu amide compounds and rare examples of readily volatile compounds of these two metals. Additional features of the chemistry of U(III), Np(III), and Pu(III) are under investigation.

Experimental Section

General Procedures. All manipulations were carried out under an inert argon or helium atmosphere using Schlenk techniques or gloveboxes equipped with Vacuum Atmospheres Dri-Trains. Tetrahydrofuran (J. T. Baker), diethyl ether (Mallinckrodt), hexane (E. M. Science), and dme (Aldrich) were degassed and distilled from Na–K alloy under argon and deoxygenated using freeze–pump–thaw (three times) cycles or by purging with argon for 1 h prior to use. Pyridine (E. M. Science) was predried by stirring (48 h) over KOH, distilled from CaH_2 under argon, and then degassed by bubbling with argon for 1 h. Solvents were taken into a Vacuum Atmospheres Drilab, and small amounts were tested with a solution of sodium benzophenone ketyl in THF. Solvents that failed to maintain a purple coloration from this test were recycled through the purification process. NMR solvents, dichloromethane-d_2, chloroform-d, benzene-d_6, tetrahydrofuran-d_8, and toluene-d_8 (all from Aldrich) were vacuum-distilled from an appropriate desiccant.[52]

Concentrated nitric acid (J. T. Baker) was used as received. Hexamethyldisilazane (Aldrich) was distilled and stored under argon prior to use. Sodium hydride was purchased as a 60% dispersion in mineral oil (Aldrich), washed with hexane, and dried *in vauo* to yield a white, pyrophoric powder. (N.B. The hexane filtrate contained some reactive NaH, which was destroyed outside the glovebox by careful addition of 2-propanol with stirring). Sodium bis(trimethylsilyl)amide was purchased from Aldrich and sublimed or prepared using a modification of a previous synthesis.[53] Elemental iodine (Aldrich), bromine (Aldrich), and mercuric iodide (Aldrich) were used as received. Actinide metals were obtained from Los Alamos National Laboratory (^{238}U, ^{237}Np, ^{239}Pu) or Cerac (^{238}U). Uranium turnings were cleaned of oxide and treated with mercuric iodide to form an amalgam as described below; neptunium and plutonium metal were used as received.

^1H NMR spectra were recorded on an IBM AF-250 or Varian Instruments Unity 300 spectrometer and referenced internally to the residual ^1H impurity in benzene-d_6, toluene-d_8, or dichloromethane-d_2 set at δ 7.15, 2.09, or 5.32, respectively. NMR samples containing Np and Pu were doubly contained in heat-sealed Teflon–FEP inserts (Wilmad) in 5-mm screw-top NMR tubes. Data were obtained at room temperature (17–20 °C) and are reported in ppm unless otherwise noted. NMR spectra of paramagnetic actinide species are highly temperature dependent; thus it is important to note that the temperatures quoted represent average room temperatures and are approximate values. A minimum of 10 min was allowed for sample equilibration at each temperature in variable-temperature NMR experiments; temperatures were calibrated against methanol or ethylene glycol as appropriate.

Infrared spectra were recorded on an IBM 32 spectrometer, on a Perkin-Elmer 1500 spectrophotometer interfaced with a 1502 Central Processor, or on a Digilab FTS-40 spectrophotometer as Nujol mulls between KBr salt plates. UV/vis/near-IR spectra were recorded on a Perkin-Elmer Lambda-9 spectrophotometer using matched 1-cm quartz cells; all spectra were obtained using a solvent reference blank. Thermal gravimetric analyses were recorded on a Perkin-Elmer TGA 7 thermal gravimetric analyzer. Elemental analyses for uranium compounds were performed on a Perkin-Elmer 2400 CHN analyzer; Np and Pu metal analyses were performed at Los Alamos National Laboratory by the Analytical Chemistry Group, CST-1.

Precautions for Handling Radioactive Materials. Depleted uranium (^{238}U) is a weak α emitter (4.196 MeV, half-life 4.468×10^9 years). All manipulations were carried out in a fume hood in a laboratory equipped with appropriate safeguards for manipulation of radioactive materials (monitoring devices, HEPA-filtered ventilation, etc.). Personnel wore laboratory coats and surgical gloves at all times. The significant radiological risks presented by neptunium and plutonium required their manipulation inside negative-pressure gloveboxes designed for containment of radioactive materials with personnel adhering to Los Alamos radiological protection practices and policies. IR and UV/vis/near-IR spectra of Np and Pu samples were recorded without removing the samples from glovebox containment using a spectrophotometer well fitted to the glovebox to which the appropriate optics bench was mated; TGA analyses for these samples were recorded on an instrument located in the glovebox. Generation of radioactive waste was minimized to the greatest extent possible; for this reason, Np and Pu sample sizes were kept as small as reasonably achievable. Radioactive wastes were handled in accordance with Los Alamos waste management practices and policies.

Amalgamated, "Oxide-Free" Uranium Metal Turnings. In a typical preparation, approximately 30 g of depleted ^{238}U metal turnings (nominal purity 99+%) was cut into small strips *ca.* 0.5–1.5 in. in length and transferred to a 150-mL beaker inside a well-ventilated hood. Concentrated HNO_3 (16 M) was added to the beaker to just cover the uranium turnings. The turnings were mixed and agitated in the acid by swirling. The reaction of nitric acid with uranium metal was accompanied by the evolution of heat and brown NO_2 gas as the metal turnings lost the black oxide coating to expose a shiny, metallic surface. The acid was carefully decanted away from the turnings, and fresh nitric acid was again added to just cover the metal. The turnings were agitated as before until the metal strips displayed a bright, shiny surface. The acid was decanted, and the resulting shiny turnings were washed three times with copious amounts of H_2O to remove all traces of acid, followed by three washings with acetone to remove water. (**Caution**! *Acetone waste should never be discarded in the same container as nitric acid waste.*) The shiny turnings were transferred to a paper towel, patted dry, and then placed in an oven-dried 250-mL Schlenk reaction vessel, and the vessel was evacuated/refilled three times. Under an argon purge, *ca.* 2 g of HgI_2 was added to the vessel, and the evacuate/refill cycle was repeated three times. The Schlenk reaction vessel was taken into the glovebox and 100 mL of THF added. The solution was shaken vigorously for 10 min to produce a dark blue solution of $UI_3(THF)_4$ and uranium metal turnings coated with a thin film of uranium–mercury amalgam. The amalgamated turnings were vacuum-filtered on a coarse-porosity frit, washed with THF, and dried in vacuo. This procedure yields very shiny, essentially oxide-free, amalgamated uranium turnings which are used immediately. Attempts to store the turnings invariably results in the formation of a brown-black oxide coating on the metal surface.

$NaN(SiMe_3)_2$. In the glovebox, a 250-mL Schlenk reaction vessel was charged with 4.0 g (166.7 mmol) of NaH and a Teflon-coated stir bar. A 120-mL portion of toluene was introduced; then the vessel was taken out of the drybox and connected to a Schlenk line. Under an argon purge, a slight excess (38 mL, 29.1 g, 180.1 mmol) of hexamethyldisilazane was added to the NaH suspension using a syringe. The vessel was then fitted with a reflux condenser and heated to gentle reflux under argon. After 48 h, the heat was removed and the vessel allowed to cool, resulting in some gelatinous brown precipitate and a yellow solution. The vessel was taken into a drybox, and the solution was filtered through a medium-porosity frit to give a clear yellow filtrate. The solvent was removed from the filtrate to yield an off-white powder. The powder was loaded into a Schlenk reaction vessel and pumped to dryness on a high-vacuum manifold for 8 h to ensure removal of any residual hexamethyldisilazane. Yield: 25.1 g (82% based on NaH).

$UI_3(THF)_4$ (1). Inside the glovebox, an oven-dried 250-mL Schlenk reaction vessel was charged with 23.93 g (100.5 mmol) of freshly prepared uranium turnings (*vide supra*) and a magnetic stir bar. A 200-mL portion of THF was introduced; then the vessel was taken out of the glovebox, connected to the argon manifold of a Schlenk line, and cooled to *ca.* −10 °C in an ice/NaCl bath. Under an argon purge (inverted funnel), 35.0 g (137.9 mmol, 90% of theoretical) of sublimed I_2 was weighted out, and approximately half was added to the cooled THF solution. The vessel was removed from the ice bath, shaken vigorously until it became warm to touch, and then immersed back into the ice bath to cool without shaking. The vessel should not be allowed to reach temperatures above *ca.* 30 °C, as this will decrease the yield of product through ring opening of THF by uranium(III).[33] This procedure was repeated four or five times until no more heat evolution was detected. The flask was then cooled in the ice bath and the other half of the iodine added under an argon purge. The vessel was again removed from the ice bath and the shaking/cooling

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process repeated until enough uranium metal had dissolved to allow for magnetic stirring of the resulting dark red solution. The solution was stirred for 3 h at −10 °C, after which the ice bath was removed and the solution was allowed to warm to room temperature and was stirred for 10–12 h to produce a dark blue solution with much dark blue microcrystalline precipitate and some unreacted metal turnings. The vessel was taken into the drybox, and the mixture was stirred vigorously to suspend the $UI_3(THF)_4$ precipitate in the mother liquor. The stirring was stopped and the heavy uranium metal allowed to quickly settle to the bottom of the vessel before the suspension was decanted and vacuum-filtered on a medium-porosity frit. This procedure of suspending the product, allowing the metal to settle, decanting the product onto a frit, and vacuum filtration was repeated several times. Finally, the remaining metal turnings were washed with THF and the washings decanted from the metal and onto the frit. The dark blue solid was dried *in vacuo* to yield 42.86 g of microcrystalline $UI_3(THF)_4$. The blue-green filtrate volume was reduced *in vacuo* to *ca.* 30 mL, 60 mL ether layerd on top, and the vessel cooled to −40 °C. After 12 h, an additional 10.4 g of $UI_3(THF)_4$ was collected by filtration. Combined yield: 53.16 g (63.7% based on I_2). ^{1}H NMR (250 MHz, toluene-d_8, 22 °C): δ 9.5 (s, THF), 5.4 (s, THF). Anal. Calcd for $UI_3O_4C_{16}H_{32}$: C, 21.18; H, 3.56; I, 41.97. Found: C, 20.68; H, 3.38; I, 41.20. IR (cm^{-1}; Nujol mull, KBr): 1342 (w), 1312 (w), 1292 (w), 1246 (w), 1172 (w), 1034 (w), 1011 (s), 922 (m), 853 (s), 833 (s), 721 (m), 667 (m), 574 (w). UV/vis/near-IR [THF; λ_{max}, nm (ϵ, M^{-1} cm^{-1})]: 288 (2555), 491 (1868), 502 (2021), 577 (1361), 599 (1511), 622 (1354), 635 (1200), 646 (1140), 680 (507), 825 (51), 837 (54), 861 (38), 870 (49), 878 (47), 882 (45), 888 (56), 892 (46), 894 (47), 896 (49), 901 (61), 913 (47), 938 sh (14), 980 (27), 992 (30), 1004 (26), 1021 (31), 1035 sh (19), 1047 (19), 1063 (25), 1076 (21), 1093 (22), 1111 (9), 1161 (69), 1171 (60), 1197 (37), 1217 (22), 1229 (23), 1241 (17), 1284 sh (6), 1367 (4), 1408 (3).

$UBr_3(THF)_4$ (2). A 23.7-g (99.6-mmol) sample of freshly prepared uranium metal turnings was loaded into a 500-mL Schlenk flask, which was evacuated and refilled with argon three times. Under an argon flush, 175 mL of dry THF was added to the flask as well as a Teflon-coated stir bar. The flask was immersed in an ice/water bath, and 6.9 mL (21.4 g, 133.8 mmol) of bromine (2.7 equiv) was added over a period of 0.5 h in portions of *ca.* 2 mL. The flask was regularly removed from the ice bath to allow the reaction to proceed fairly rapidly and returned to the bath if the temperature rose above *ca.* 30 °C. Once bromine addition was complete, a pale green solution was present in the flask (presumably a uranium(IV) bromide species) along with excess uranium turnings. The Schlenk flask was taken into the glovebox, and the contents were stirred at room temperature for 24 h. After this time a mass of deep blue solid was present in the flask along with a blue-purple solution. The solid was collected by filtration onto a frit, washed with a minimal volume of ether, and pumped to dryness. Yield: 25.38 g (74% based on bromine). ^{1}H NMR (250 MHz, toluene-d_8, 22 °C): δ −1.90 (br, THF β), −4.16 (br, THF α). IR (cm^{-1}; Nujol mull, KBr): 1343 (w), 1295 (w), 1244 (w), 1176 (w), 1070 (w), 1034 (m), 1010 (s), 952 (w), 918 (m), 854 (s), 726 (w), 668 (m), 612 (w).

$UI_3(dme)_2$ (3). Using a procedure analogous to that used in the preparation of **1**, 3.5 g (14.7 mmol) of freshly prepared uranium turnings in 75 mL of 1,2-dimethoxyethane (dme) was treated with 5.2 g (20.5 mmol) of sublimed I_2 at −10 °C. After 1 h of stirring at −10 °C, the dark red solution was allowed to warm to room temperature and stirred for 3 days to produce a dark purple solution. In the glovebox, unreacted uranium metal was removed by suspension and filtration as described above for $UI_3(THF)_4$. The purple solid was dried *in vacuo* to give 4.13 g of microcrystalline $UI_3(dme)_2$. The filtrate volume was reduced *in vacuo* to *ca.* 30 mL, diethyl ether layered on top, and the solution cooled to −40 °C. After 24 h, the purple microcrystalline product was collected on a medium-porosity frit and dried *in vacuo* for a combined yield of 8.23 g (76% based on I_2). ^{1}H NMR (250 MHz, benzene-d_6, 22 °C): δ 3.42 (s, CH_3), 3.27 (s, CH_3), −84.54 (s, CH_2), −84.69 (s, CH_2). Anal. Calcd for $UI_3C_8H_{20}O_4$: C, 12.03; H, 2.52; I, 47.65. Found: C, 11.91; H, 2.46; I, 47.55. IR (cm^{-1}; Nujol mull, KBr): 1458 (s), 1377 (m), 1288 (w), 1280 (w), 1247 (w), 1234 (w), 1207 (w), 1188 (w), 1153 (w), 1127 (w), 1072 (s), 1026 (s), 1006 (s), 968 (m), 845 (s), 821 (w), 806 (w), 721 (w). UV/vis/near-IR [THF; λ_{max}, nm (ϵ, M^{-1} cm^{-1})]: 751 (41), 873 (86), 895 (112), 902 (122), 1002 (56), 1020 (45), 1045 (40), 1057 (40), 1067 (43), 1202 (41), 1226 (50), 1417 (5).

$UI_3(py)_4$ (4). Using a procedure analogous to that used in the preparation of **1**, 8.1 g (34.0 mmol) of freshly prepared uranium turnings in 200 mL of pyridine was treated with 8.2 g (32.3 mmol, 90% of theoretical) of sublimed I_2 at −10 °C. (**N.B.** *This is a small-scale preparation. If a larger scale preparation is desired, the iodine should be added in aliquots to control the reaction.*) After 2 h of stirring, the ice bath was removed and the dark red solution allowed to warm to room temperature, where it was stirred for 24 h to produce a deep purple (almost black) solution. Inside the glovebox, unreacted uranium metal was removed by filtration through a coarse-porosity frit. The filtrate volume was reduced *in vacuo* to *ca.* 30 mL; then 30 mL of toluene was added and the solution stirred vigorously for 1 h to produce a black microcrystalline precipitate. The product was collected by vacuum filtration on a medium-porosity frit and dried *in vacuo* to yield 17.3 g (80% based on I_2) of analytically pure $UI_3(py)_4$. Uranium triiodide tetrakis(pyridine) is appreciably soluble in pyridine: *ca.* 17 g in 30 mL of pyridine at 10 °C. The compound is only sparingly soluble in benzene and toluene but dissolves readily in THF with ligand substitution. ^{1}H NMR (250 MHz, benzene-d_6, 22 °C): δ 17.8 (s, py), 15.4 (s, py), 12.0 (s, py). Anal. Calcd for $UI_3N_4C_{20}H_{20}$: C, 25.69; H, 2.16; N, 5.99; I, 40.70. Found: C, 25.81; H, 2.25; N, 5.89; I, 40.68. IR (cm^{-1}; Nujol mull, KBr): 1597 (m), 1304 (w), 1215 (m), 1169 (w), 1150 (m), 1061 (m), 1034 (m), 999 (m), 976 (w), 756 (s), 725 (w), 698 (s), 621 (s). UV/vis/near-IR [pyridine; λ_{max}, nm (ϵ, M^{-1} cm^{-1})]: 370 (1169), 453 (720), 563 (832), 646 (737), 678 (812), 858 (88), 910 (110), 935 (96), 1038 (46), 1115 (103), 1212 (146), 1443 (19).

$NpI_3(THF)_4$ (5). A 10-mL reaction vessel equipped with a Teflon-coated stir bar was charged with Np turnings (0.21 g, 0.88 mmol) and THF (*ca.* 5 mL). Iodine (0.33 g, 1.31 mmol, 1.5 equiv) was slowly added to the stirred Np/THF mixture, giving a deep red-purple color. The reaction vessel was stoppered and the mixture allowed to stir for 24 h, during which a finely divided yellow-orange powder precipitated from solution. The solid was collected on a medium-porosity fritted filter, washed with hexane (3 × 5 mL), and then vacuum-dried (10^{-3} Torr, 2 h) to give **5** (0.68 g, 0.75 mmol, 86%). ^{1}H NMR (300 MHz, CD_2Cl_2, 40 °C): δ 1.26 (br s, 2H), 2.20 (br s, 2H). IR (cm^{-1}; Nujol mull, KBr): 1009 (s), 854 (vs), 834 (s). UV/vis/near-IR [THF; λ_{max}, nm (ϵ, M^{-1} cm^{-1})]: 618 (19.3), 642 (20.3), 764 (28.3), 856 (24.6), 861 (24.2), 927 (24.2), 962 (23.4), 994 (15.2), 1258 (7.12), 1368 (8.80), 1400 sh (7.55). TGA anal. Calcd for $NpI_3(THF)_4$: THF, 31.8. Found: THF, 34.5 (56–180 °C). Anal. Calcd for $NpI_3(THF)_4$: Np, 26.15. Found: Np, 26.50.

$PuI_3(THF)_4$ (6). $PuI_3(THF)_4$ was prepared in a manner analogous to that for **5**, using plutonium metal (0.72 g, 3.00 mmol), I_2 (1.14 g, 4.50 mmol), and THF (*ca.* 10 mL). Workup as above gave **6** as an off-white microcrystalline powder (2.51 g, 2.75 mmol, 92%). ^{1}H NMR (300 MHz, $CDCl_3$, 20 °C): δ 1.37 (br s, 2H), 2.68 (br s, 2H). IR (cm^{-1}; Nujol mull, KBr): 1002 (vs), 847 (vs), 831 (vs). TGA anal. Calcd for $PuI_3(THF)_4$: THF, 31.7. Found: THF, 31.4 (75–180 °C). UV/vis/near-IR [THF; λ_{max}, nm (ϵ, M^{-1} cm^{-1})]: 768 (9.78), 7.90 (11.6), 8.16 (11.7), 886 (5.84), 1051 (5.62), 1216 (1.55), 1526 (2.24). Anal. Calcd for $PuI_3(THF)_4$: Pu, 26.54. Found: Pu, 26.97.

$PuI_3(py)_4$ (7). $PuI_3(py)_4$ was prepared in a manner analogous to that for **5** and **6** using Pu (0.26 g, 1.06 mmol), I_2 (0.40 g, 1.59 mmol), and pyridine (*ca.* 5 mL). After overnight stirring, no precipitate was evident. The reaction mixture was filtered, and volatiles were removed *in vacuo* from the filtrate to give a dark brown, oily residue. Vacuum-drying (10^{-5} Torr, 4 h) gave **7** as a gray powder (0.94 g, 1.00 mmol, 94%). ^{1}H NMR (300 MHz, benzene-d_6, 20 °C): δ 6.10 (br, 2H, β), 6.64 (br t, $^3J_{HH}$ = 7.3 Hz, 1H, γ), 9.07 (br, 2H, α). IR (cm^{-1}; Nujol mull, KBr): coordinated pyridine at 623 (m). TGA anal. Calcd for $PuI_3(py)_4$: py, 33.7. Found: py, 34.8 (80–240 °C). Anal. Calcd for $PuI_3(py)_4$: Pu, 25.53. Found: Pu, 25.37.

$U[N(SiMe_3)_2]_3$ (8). In the glovebox, 18.2 g (99.3 mmol) of $NaN(SiMe_3)_2$ was placed in a 250-mL Erlenmeyer flask and 100 mL of THF added. Then a 1-L Erlenmeyer flask was charged with 30.0 g (33.1 mmol) of $UI_3(THF)_4$, a 1-in. Teflon-coated stir bar, and 300 mL of THF. The sodium silylamide solution was added to the stirred uranium triiodide solution over a period of 1 h to produce a deep red-wine-colored solution. After 12 h of stirring, the solution was vacuum-filtered through Celite on a coarse filter frit, and solvent was removed *in vacuo* to provide a purple-red microcrystalline solid. The solid was extracted into 100 mL of hexane, the extract was filtered through a fine-porosity frit, and the filtrate was cooled to −40 °C to produce large purple needles, which were isolated by filtration and dried *in vacuo*. Reduction of the solvent volume and cooling to −40 °C produced another crop of purple needles. Combined yield: 19.5 g (82% based on $UI_3(THF)_4$). ^{1}H NMR (250 MHz, benzene-d_6, 22 °C): δ −11.0 (br s). IR (cm^{-1}; Nujol mull, KBr): 1248 (s), 1170 (w), 990 (s), 860 (s), 828 (s), 764 (m), 676 (m), 654 (m), 598 (s).

Np[N(SiMe$_3$)$_2$]$_3$ (9). A 10-mL reaction vessel equipped with a Teflon-coated stir bar was charged with NpI$_3$(THF)$_4$ (0.40 g, 0.44 mmol) and THF (*ca.* 7 mL). NaN(SiMe$_3$)$_2$ (0.240 g, 1.32 mmol, 3 equiv) was added to the stirred, orange slurry, giving a homogeneous orange solution after 1–2 min of stirring. The THF was removed *in vacuo* and the orange residue extracted with hexane. Filtration through a Celite plug on a medium-porosity fritted filter removed the NaI byproduct. Hexane was stripped *in vacuo* from the orange solution to give **9** as an oily, orange solid which became blue-black upon continued vacuum-drying at 10^{-3} Torr for 1 h (0.31 g, 0.42 mmol, 95%). Sublimation (0.19 g, 0.26 mmol) under dynamic vacuum at *ca.* 10^{-4} Torr and 60 °C onto an air-cooled surface gave **9** as a blue-black microcrystalline solid (0.15 g, 0.21 mmol, 81%). ^{1}H NMR (300 MHz, benzene-d_6, 20 °C): δ 3.01 (br s). IR (cm^{-1}; Nujol mull, KBr): 988 (vs), 813 (s), 767 (m). UV/vis/near-IR [hexane; λ_{max}, nm (ϵ, M^{-1} cm^{-1})]: 572 (354), 764 (70.9), 791 (55.8), 811 (45.5), 833 (40.7), 902 (42.9), 932 (33.4), 990 (23.1), 1101 (17.4), 1134 (24.5), 1374 (15.8), 1488 (11.0).

Pu[N(SiMe$_3$)$_2$]$_3$ (10). Pu[N(SiMe$_3$)$_2$]$_3$ was prepared by a procedure analogous to that for **9** using PuI$_3$(THF)$_4$ (0.81 g, 0.89 mmol) and NaN(SiMe$_3$)$_2$ (0.49 g, 2.66 mmol). Workup as above gave crude **10** as an orange powder (0.45 g, 0.82 mmol, 92%). Sublimation (0.45 g, 0.62 mmol) under dynamic vacuum at *ca.* 10^{-4} Torr and 60 °C gave **10** as an orange microcrystalline solid (0.32 g, 0.44 mmol, 71%). ^{1}H NMR (300 MHz, benzene-d_6, 20 °C): δ 0.74 (br s, $\Delta\nu_{1/2}$ = 112.0 Hz). IR (cm^{-1}; Nujol mull, KBr): 986 (vs), 813 (s), 767 (m). UV/vis/near-IR [hexane, λ_{max}, nm (ϵ, M^{-1} cm^{-1})]: 578 (45.5), 593 (38.4), 609 (36.7), 726 (16.9), 752 (16.0), 780 (15.2), 845 (17.1), 886 (14.9), 897 (13.8), 931 (9.18), 1018 (12.1), 1043 (28.8), 1062 (13.7), 1120 (39.1), 1144 (44.9), 1222 (45.9), 1314 (23.1), 1381 (12.2), 1491 (12.4), 1590 (19.7).

Crystallographic Study of UI$_3$(THF)$_4$ (1). Crystal data and data collection and processing parameters are given in Table I. A crystal measuring 0.08 × 0.11 × 0.18 mm was mounted in a Lindemann tube that was placed on the goniometer head of an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo Kα radiation. Final cell parameters were determined from the least-squares refinement of $[(\sin\theta)/\lambda]^2$ values for 24 accurately centered reflections. Data were collected by θ–2θ scans. The intensities were corrected for Lorentz and polarization effects, an 11% decay, and absorption (transmission coefficients from 0.36 to 1.00). The structure was solved by routine Patterson and Fourier methods. After location of all non-hydrogen atoms, refinement with isotropic thermal parameters converged at $R = 0.095$. After inclusion of anisotropic thermal parameters for all non-hydrogen atoms and geometrical generation of hydrogen atoms which were constrained to "ride" upon the appropriate carbon atoms with $B(\mathrm{H}) = 1.2B_{eq}(\mathrm{C})$, final refinement using 1816 unique, observed $[F > 3\sigma(F)]$ reflections converged at $R = 0.043$ and $R_w = 0.047$ [where $w = 1/\sigma(F)^2$]. All calculations were performed using the TEXRAY suite of computer programs (Molecular Structure Corp., 1987).

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Supplementary Material Available: For **1**, tables of hydrogen atom positions and isotropic thermal parameters, anisotropic thermal parameters, selected distances and angles for the ligands, and selected torsion or conformation angles (5 pages). Ordering information is given on current masthead page.