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Article

New Efficient Synthesis of [UI₄(MeCN)₄]. X-ray Crystal Structures of [UI₂(MeCN)₇][UI₆], [UI₄(py)₃], and [U(dmf)₉]I₄

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Reaction of UCl_4 and excess Me_3SiI in acetonitrile provides a convenient route to $[UI_4(MeCN)_4]$ (**1**), which was isolated in excellent yield and crystallized in acetonitrile as the ion pair complex $[UI_2(MeCN)_7][UI_6]$ (**2**). Compound **1** was transformed in pyridine (py) and dimethylformamide (dmf) into the Lewis base adducts $[UI_4(py)_3]$ (**3**) and $[UI_4(dmf)_6]$ (**4**). Crystals of **3** and $[U(dmf)_9]I_4$ (**5**) were obtained by slow diffusion of diethyl ether into pyridine or dmf solutions of **1**; compound **5** is the first tetracationic $\{U^{4+}\}$ entity to have been crystallographically characterized.

Introduction

The proper choice of halide and pseudo-halide starting materials MX_n is essential in inorganic and organometallic chemistry since the synthesis, solubility, structure, and reactivity of the complexes are strongly influenced by the nature of X. Of particular importance is the nucleophilic character of the halide group, as shown in many cases by the replacement of chloride with iodide, which permitted the obtainment of the desired compounds or avoidance of the formation of "ate complexes", a pervasive problem in f-element chemistry.[1] While the soluble Lewis bases adducts of UI_3 constitute a convenient entry into trivalent uranium chemistry,[2] in contrast to UCl_3 which is difficult to prepare and is sparingly soluble in organic solvents,[3] the reverse situation is observed for the corresponding halides of uranium(IV). By comparison with UCl_4,[4] by far the most commonly used starting material in actinide chemistry and

from which a series of other interesting UX_4 precursors can be derived (X = NR_2,[5] BH_4,[6] OSO_2CF_3),[7] UI_4 has received much less attention. This lack of consideration is largely due to the tedious synthesis of UI_4 by a high-temperature route and its ready decomposition into UI_3 and I_2 even at low temperatures.[8,9] Many efforts have been devoted to the gentle syntheses of soluble $[UI_4L_n]$ species which would be useful starting materials; most of these proved however of limited interest in not being straightforward or in generating undesirable side products.[9–18] However, Du Preez and Zeelie devised the synthesis at 20 °C of $[UI_4(MeCN)_4]$, through the

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intermediary of $[UI_4(OCPh_2)_2]$ which was itself obtained by treating uranium metal with iodine in dichloromethane in the presence of diphenyl ketone.[16] Some Lewis base adducts of general formula $[UI_4L_n]$ were prepared from UI_4 or $[UI_4-(MeCN)_4]$ by coordination of amide, phosphine oxide, sulfoxide, and lactam ligands[9–18] and only the tetramethyl-urea derivative $[UI_4\{OC(NMe_2)_2\}_2]$ has been crystallographically characterized.[17] Here, we present an efficient and practical multigrams synthesis of $[UI_4(MeCN)_4]$ and the crystal structures of $[UI_2(MeCN)_7][UI_6]$, $[UI_4(py)_3]$, and $[U(dmf)_9]I_4$.

Experimental Section

All reactions were carried out under argon (<5 ppm oxygen or water) using standard Schlenk-vessel and vacuum line techniques or in a glovebox. Solvents (pyridine and acetonitrile) were dried over NaH and distilled immediately before use. Dimethylformamide and iodotrimethylsilane (Aldrich) were stored under argon over 3 Å molecular sieves. The ^1H NMR spectra were recorded on a Bruker DPX 200 instrument and referenced internally using the residual protio solvent resonances relative to tetramethylsilane (δ 0). IR spectra were recorded on a Perkin-Elmer FT-IR 1725X spectrometer, using Nujol mulls of samples between KBr windows. Elemental analyses were performed by Analytische Laboratorien at Lindlar (Germany).

Syntheses. UCl_4 was prepared as previously described.[4]

$[UI_4(MeCN)_4]$ (1). A flask was charged with UCl_4 (1000 mg, 2.63 mmol) and acetonitrile (15 mL) was condensed in it. Addition of Me_3SiI (3 mL, 21 mmol) at 20 °C to the green suspension gave a red solution from which an orange powder was deposited in a few seconds. The suspension was then stirred for 90 min at 20 °C and further precipitation was induced by addition of diethyl ether (15 mL). The orange powder of **1** was filtered off, washed with pentane (20 mL), and dried under vacuum. Yield 92% (2390 mg). Anal. Calcd for $C_8H_{12}I_4N_4U$: C, 10.56; H, 1.33; N, 6.16; I, 55.79. Found: C, 10.30; H, 1.22; N, 6.05; I, 55.70. The ^1H NMR spectrum of **1** in pyridine-d_5 shows the signal of free acetonitrile.

Orange needles of $[UI_2(CH_3CN)_7][UI_6]$ (2), suitable for X-ray diffraction analysis, were obtained by slowly cooling to room temperature a hot saturated solution of **1** in acetonitrile.

$[UI_4(py)_3]$ (3). A flask was charged with **1** (239 mg, 0.26 mmol) and pyridine (20 mL) was condensed in it. After filtration, the volume of the solution was reduced to 10 mL and the red powder of **3** precipitated upon addition of pentane (10 mL) and diethyl ether (10 mL). The product was filtered off and dried under vacuum. Yield 91% (255 mg). Anal. Calcd for $C_{15}H_{15}I_4N_3U$: C, 18.33; H, 1.54; N, 4.27. Found: C, 18.61; H, 1.66; N, 4.45. ^1H NMR (acetonitrile-d_3, 23 °C, δ): 10.8 (s, $w_{1/2}$ = 400 Hz, 2H), 6.5 (s, $w_{1/2}$ = 90 Hz, 1 H), 5.2 (s, $w_{1/2}$ = 190 Hz, 2H).

Red crystals of **3** suitable for X-ray diffraction analysis were obtained by slow diffusion of diethyl ether into a pyridine solution.

$[UI_4(dmf)_6]$ (4). A flask was charged with **1** (100 mg, 0.11 mmol) and freshly distilled dmf (2 mL). The resulting clear yellow solution was then evaporated to dryness, affording a green sticky residue. Trituration and washing with diethyl ether (15 mL) and drying under vacuum (2 h at 60 °C and 12 h at room temperature) afforded an ochre powder which was formulated as $[UI_4(dmf)_6]$ from the elemental analyses. Yield 70% (100 mg). Anal. Calcd for $C_{18}H_{42}I_4N_6O_6U$: C, 18.26; H, 3.57; N, 7.10. Found: C, 18.20; H, 3.53; N, 7.02. ^1H NMR (acetonitrile-d_3, 23 °C, δ): 16.9 (s, $w_{1/2}$ = 250 Hz, 1H), 4.9 (s, $w_{1/2}$ = 230 Hz, 3 H), 4.51 (s, $w_{1/2}$ = 230 Hz, 3 H). IR: 1643 (vs) cm^{-1} ν(CO).

Table 1. Crystal Data and Structure Refinement Details

compound	[UI₂(MeCN)₇][UI₆] (**2**)	[UI₄(py)₃] (**3**)	[U(dmf)₉]I₄ (**5**)
chemical formula	C₁₄H₂₁I₈N₇U₂	C₁₅H₁₅I₄N₃U	C₂₇H₆₃I₄N₉O₉U
M (g mol⁻¹)	1778.64	982.93	1403.49
cryst syst	orthorhombic	monoclinic	tetragonal
space group	*Cmcm*	*P2₁/c*	*P4₁*
a (Å)	12.8779(9)	11.3294(3)	13.5474 (2)
b (Å)	11.0818(11)	13.1236(5)	13.5474 (2)
c (Å)	26.5236(15)	15.4734(6)	53.2687(14)
β (deg)	90	107.094(2)	90.0
V (Å³)	3785.2(5)	2198.99(14)	9776.5(3)
Z	4	4	8
D_{calcd} (g cm⁻³)	3.121	2.969	1.907
μ (Mo Kα) (mm⁻¹)	15.085	12.999	5.895
$F(000)$	3048	1720	5312
reflns collected	10656	14135	37438
independent reflns	1813	3741	13580
observed reflns [$I > 2\sigma(I)$]	1342	3558	11799
R_{int}	0.126	0.046	0.104
params refined	91	208	902
R1	0.050	0.026	0.069
wR2	0.119	0.060	0.180
S	1.270	1.107	1.023
$\Delta\rho_{min}$ (e Å⁻³)	−1.33	−0.92	−1.58
$\Delta\rho_{max}$ (e Å⁻³)	1.58	0.78	1.78

Cube-shaped green crystals of $[U(dmf)_9]I_4$ (**5**) suitable for X-ray diffraction analysis were grown by slow diffusion of diethyl ether into a dmf solution of **1**.

Crystallographic Data Collection and Structure Determination. The data were collected at 100(2) K on a Nonius Kappa-CCD area detector diffractometer[19] using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The crystals were placed inside glass capillaries with a protecting "Paratone-N" oil (Hampton Research) coating. The unit cell parameters were determined from 10 frames and then refined on all data. A 180° φ-range was scanned with 2° steps during data collection. The data were processed with DENZO-SMN.[20] The structures were solved by Patterson map interpretation with SHELXS-97 and subsequent Fourier-difference synthesis and refined by full-matrix least-squares on F^2 with SHELXL-97.[21] Absorption effects were corrected empirically with the program DELABS from PLATON.[22] All non-hydrogen atoms were refined with anisotropic displacement parameters, with some restraints for some badly behaving atoms (some I and C atoms in **2**, some C atoms of the dmf moieties in **5**). Restraints for three C−N bond lengths have also been applied in compound **2**. Hydrogen atoms were introduced at calculated positions and were treated as riding atoms with a displacement parameter equal to 1.2 (CH) or 1.5 (CH₃) times that of the parent atom. The molecular plots were drawn with SHELXTL.[23] The crystal data and structure refinement details are reported in Table 1.

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Results and Discussion

Treatment of UCl_4 with excess Me_3SiI in acetonitrile at 20 °C led to the formation of $[UI_4(MeCN)_4]$ (**1**), according to eq 1; the reaction mixture was stirred for 90 min and the orange powder of **1** precipitated upon addition of diethyl ether. Analytically pure complex **1** was thus reproducibly synthesized in grams quantity with yields better than 90%.

$$[UCl_4(MeCN)_4] + 4Me_3SiI \xrightarrow{MeCN} [UI_4(MeCN)_4] +$$
$$(\mathbf{1})$$
$$4Me_3SiCl \quad (1)$$
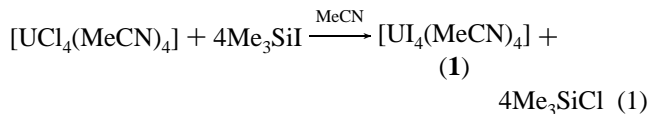
The stability of uranium tetraiodide being the lowest among the halide series,[8,12,17] the driving force of reaction 1 is certainly ensured by the large difference in bond dissociation energies between Me_3SiI and Me_3SiCl (ca. 35 kcal mol^{-1})[24,25] and the volatility of Me_3SiCl as compared with Me_3SiI.[26] Reaction 1 provides a new example of the efficiency of the iodosilane as a metathetical reagent for preparing metal iodides from the corresponding chlorides. The synthesis of **1** did not suffer from the formation of mixed halide compounds, as noted in reactions of UCl_4 and NaI.[11] Despite its numerous advantages over other substituting reagents and its chemical versatility, Me_3SiI remains poorly employed in inorganic and coordination chemistry of transition metals.[26] In the f-element series, it was used with success for the conversion of $[UO_2(OSO_2CF_3)_2]$,[27] $[Th(C_5Me_5)_2Br_2]$,[28] $[Li(thf)_4]_2[Th(C_2B_9H_{11})_2X_2]$ (X = Cl, Br),[29] $[U(\{Me_3Si\}_2C_5H_3)_2Cl_2]$,[30] and $[An(NN'_3)Cl]$ [An = Th, U; NN'_3 = $N(CH_2CH_2NSiMe_2Bu^t)_3$][31] into their iodide analogues, and for removing the coordinated thf in $[LaCp^*(CH\{SiMe_3\}_2)_2(thf)]$ by ring-opening reaction.[32]

Crystallization of **1** from acetonitrile gave crystals of $[UI_2(MeCN)_7][UI_6]$ (**2**). Such formation of ion pair compounds of the f-elements was previously illustrated by the structures of $[UCl_3(EtCONEt_2)_4][UCl_5(EtCONEt_2)]$,[33] $[UCl_2(dmso)_6][UCl_6]$,[34] and the series of lanthanide complexes $[LnX_2(thf)_5][LnX_4(thf)_2]$ (X = I, Ln = Nd, Gd, Y, Sm, Yb; X = Cl, Ln = Y, Gd, Dy, Er, Tb, Tm, Yb; X = Br, Ln = Eu).[35] The structure of **1** is quite distinct from that of the neutral acetonitrile adduct of UCl_4, $[UCl_4(MeCN)_4]$, in which the
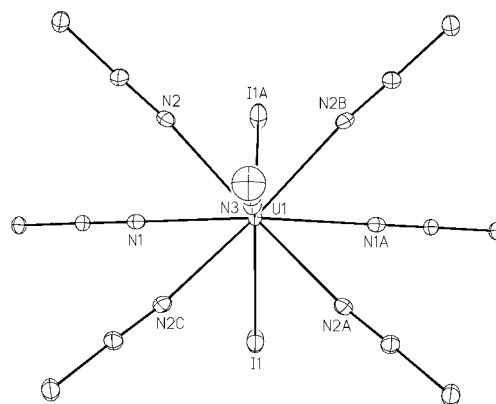
Figure 1. View of the cation $[UI_2(MeCN)_7]^{2+}$ in complex **2**. Hydrogen atoms have been omitted. Displacement ellipsoids are drawn at the 10% probability level. Selected bond lengths (Å) and angles (°): U(1)−I(1) 3.001-(2); U(1)−N(1) 2.531(17); U(1)−N(2) 2.521(14); U(1)−N(3) 2.57(3); N(1)−U(1)−N(2) 65.9(4); N(1)−U(1)−N(3) 114.8(4); N(2)−U(1)−N(3) 66.3(3); N(1)−U(1)−I(1) 73.7(3); N(2)−U(1)−I(1A) 77.3(4); N(3)−U(1)−I(1) 132.08(6). Symmetry codes: A = −x, y, 1.5 − z; B = x, y, 1.5 − z; C = −x, y, z.

uranium atom is in an almost dodecahedral arrangement.[36] The octahedral structure of the centrosymmetric $[UI_6]^{2-}$ ion in **1** is identical to that found in $[PPh_3Et]_2[UI_6]$,[37] with U(2)−I distances of 3.0117(17), 2.982(2), and 2.9331(18) Å. A view of the cation is presented in Figure 1 together with selected bond lengths and angles. In this cation, the U(1)−N(3) line is a crystallographically imposed binary axis of symmetry which is at the intersection of two mirror planes defined by the N(1), N(1A), and N(3) and I(1), I(1A), and N(3) atoms. The nine-coordinate U(1) atom is in a slightly distorted monocapped square antiprismatic configuration, the two parallel bases being defined by the N(2), N(2A), N(2B), and N(2C) atoms (coplanar by symmetry) and the I(1), I(1A), N(1), and N(1A) atoms (coplanar with a maximum deviation of 0.47 Å), and the capping position occupied by the N(3) atom. The U(1)−I(1) bond length of 3.001(2) Å is unexceptional and is similar to those measured in the cation $[UI_2\{OP(NC_4H_8)_3\}_4][BPh_4]_2$ [2.98(1) Å][38] or in UI_4 [average 3.01(1) Å],[39] $[PPh_3Et]_2[UI_6]$ [average 2.97(4) Å],[37] $[UI_4\{OC(NMe_2)_2\}_2]$ [average 3.01 Å],[17] $[UI_2(OCH_2CH_2CH_2CH_2I)_2(OPPh_3)_2]$ [3.011(1) Å],[40] and $[U(C_9H_7)_3I]$ [3.041(1) Å].[41] The U(1)−N(1) and U(1)−N(2) bond lengths of 2.531(17) and 2.521(14) Å are slightly shorter than the U(1)−N(3) distance of 2.57(3) Å corresponding to the nitrile ligand in

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the capping position. These values can be compared with the mean U—N distances found in the cationic and neutral compounds [{U(C₉H₇)Br(MeCN)₄}₂(μ-O)][UBr₆] [2.55(2) Å],[42] [U(C₉H₇)Br₂(MeCN)₄]₂[UBr₆] [2.57(3) Å],[42] [UCl₄-(MeCN)₄] [2.58(2) Å],[36] [U(C₅H₅)₃(MeCN)₂]₂[UO₂Cl₄] [2.59-(1) Å],[43] and [U(C₅H₅)₃(MeCN)₂][Th(C₅H₅)Cl₄(MeCN)] [2.54-(5) Å].[44]

Complex **1** is quite soluble in strongly coordinating solvents and was readily transformed in pyridine and dmf into the Lewis base adducts formulated as [UI₄(py)₃] (**3**) and [UI₄(dmf)₆] (**4**) from the elemental analyses; the red and ochre powders of **3** and **4** were obtained with yields of 91 and 70%, respectively. The stability of **3** and **4** is in contrast to that of [UI₄(thf)ₓ], which could not be isolated because of its rapid transformation into [UI₂(OCH₂CH₂CH₂CH₂I)₂(thf)ₓ] following ring-opening reaction of thf.[40,45] Formation of **3** can be compared with that of [ThI₄(py)₄] from [ThI₄(thf)₄];[46] the different number of coordinated pyridines in the two compounds certainly reflects the larger size of the Th⁴⁺ ion. Resonances in the ¹H NMR spectra of **3** and **4** in acetonitrile-*d₃* are broad and paramagnetically shifted, as commonly observed in the spectra of uranium(IV) complexes. In the IR spectrum of **4**, the strong band at 1643 cm⁻¹ is assigned to the ν(C=O) stretch and is decreased in energy from 1675 cm⁻¹ in the free dmf molecule; this C=O bond weakening can be compared with that observed upon coordination of *N,N*-dialkyl amides to UCl₄.[33] The synthesis of **4** is much more convenient than those reported for a dmf adduct of UI₄, either by electrochemical oxidation of uranium metal in dmf solution of iodine[15] or electrochemical reduction of UO₃ in aqueous HI solution, followed by dissolution of the resulting solid in dmf.[10] The products obtained from these experiments have not been fully characterized but their elemental analyses gave values rather close to [UI₄(dmf)₄].

Crystals of **3** were deposited upon slow diffusion of diethyl ether into a pyridine solution. A view of the molecule is presented in Figure 2 with selected bond lengths and angles. While the eight-coordinate chloride derivative [UCl₄(py)₄] adopts a square antiprismatic configuration,[47] the seven-coordinate uranium atom in **3** is in a nearly perfect pentagonal bipyramidal environment, with the I(1) and I(4) atoms in apical positions; the five N(1), N(2), N(3), I(2), and I(3) atoms define the equatorial plane and are coplanar with a maximum deviation of 0.254(3) Å. The U—I distances vary from 2.9558(4) to 3.0438(4) Å with a mean value of 3.00(3) Å, identical to that measured in **2** and other uranium-(IV) iodo complexes.[30,31,37–41,48] The U—N bond lengths, which vary from 2.586(5) to 2.634(5) Å and average 2.61-(2) Å, are in the range of the distances found in the uranium-
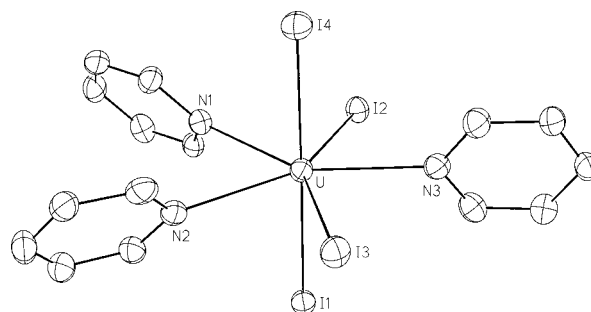
Figure 2. View of [UI₄(py)₃] (**3**). Hydrogen atoms have been omitted. Displacement ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (°): U—I(1) 2.9857(4); U—I(2) 3.0438(4); U—I(3) 3.0163(4); U—I(4) 2.9558(4); U—N(1) 2.602(5); U—N(2) 2.634-(5); U—N(3) 2.586(5); I(1)—U—I(4) 179.157(13); I(2)—U—N(1) 74.17(10); I(2)—U—N(3) 73.21(11); I(3)—U—N(2) 75.68(11); I(3)—U—N(3) 73.24-(11); N(1)—U—N(2) 65.10(15); I(1)—U—I(2) 89.170(12), I(1)—U—I(3) 88.654(12), I(1)—U—N(1) 96.12(11), I(1)—U—N(2) 83.90(11), I(1)—U—N(3) 93.92(11); I(4)—U—I(2) 91.342(12); I(4)—U—I(3) 91.293(12); I(4)—U—N(1) 83.38(11); I(4)—U—N(2) 95.27(11); I(4)—U—N(3) 86.87(11).

(IV) complexes [U(C₈H₈)Cl₂(py)₂],[49] [U(C₅H₅)₂(OSO₂CF₃)₂-(py)₂],[7] [U(NEt₂)₂(py)₅][BPh₄]₂,[50] [U(SCHMe₂)₂I₂(py)₃],[48g] and [U(C₁₈H₁₈N₂O₄)Cl₂(py)₂],[51] which display values between 2.54 and 2.70 Å.

Crystallization of **4** by slow diffusion of diethyl ether into a dmf solution afforded crystals of the ion pair compound [U(dmf)₉]I₄ (**5**). The crystal structure of **5** is quite different from that of the dmf adduct of UCl₄, which crystallizes as [UCl₃(dmf)₅]₂[UCl₆].[52] The [U(dmf)₉]⁴⁺ ion is the first tetracationic U⁴⁺ species to have been crystallographically characterized; a view of one of the two independent and quite identical cations in **5** is given in Figure 3 with U—O bond lengths. The uranium atom is surrounded by nine monodentate dmf ligands which form a slightly distorted monocapped square antiprism of oxygen atoms. The square faces are defined by the O(1)—O(4) and O(5)—O(8) atoms in the first cation and O(10)—O(13) and O(14)—O(17) atoms in the second, with atoms O(9) and O(18), respectively, in the capping position. The four atoms in each face are coplanar with a maximum deviation of 0.100(7) Å, and the two mean planes are almost parallel with dihedral angles of 3.1(8)° and 0.9(7)° in the two cations. The U(1)—O(9) and U(2)—O(18) axes are nearly perpendicular to the square faces, with angles of 2.5 and 1.7° with the normal to the plane. With

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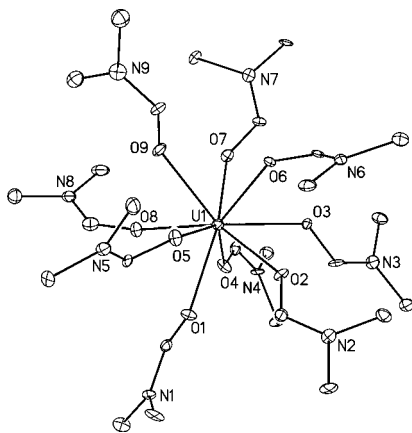
Figure 3. View of one of the two independent cations [U(dmf)$_9$]$^{4+}$ in complex **5**. Hydrogen atoms have been omitted. Displacement ellipsoids are drawn at the 10% probability level. U−O bond lengths (Å): U(1)−O(1) 2.377(13); U(1)−O(2) 2.373(11); U(1)−O(3) 2.473(12); U(1)−O(4) 2.381(14); U(1)−O(5) 2.386(14); U(1)−O(6) 2.352(12); U(1)−O(7) 2.393-(14); U(1)−O(8) 2.354(15); U(1)−O(9) 2.418(15).

the exception of the U(1)−O(3) bond length of 2.473(12) Å, the distances between the uranium and oxygen atoms defining the square antiprism, which average 2.37(1) and 2.38(2) Å in the two cations, are shorter than the U(1)−O(9) and U(2)−O(18) bond lengths of 2.418(15) and 2.486-(13) Å corresponding to the dmf ligands in capping position. These U−O distances can be compared with those in the eight-coordinate cationic complexes [UCl$_3$(dmf)$_5$]$_2$[UCl$_6$] [2.29(3)−2.45(2) Å],[52] [UCl(dmf)$_7$]$_2$[UO$_2$Cl$_4$]$_3$ [2.30(1)−2.40(1) Å],[53] and [UCl(dmf)$_7$]Cl$_3$ [2.315(2)−2.391(2) Å].[54] To the best of our knowledge, the only other tetracationic actinide complex to have been crystallographically character-ized is the homoleptic, nine-coordinate thorium compound [Th(dmso)$_9$][ClO$_4$]$_4$·4dmso, which adopts a tricapped trigonal prismatic configuration.[55]

It is interesting to compare the structures of the [U(dmf)$_9$]$^{4+}$ and [Ln(dmf)$_8$]$^{3+}$ ions (Ln = Ce, Nd, Gd, Tb)[56] and to note that the lanthanide ions accommodate only eight dmf ligands even if the ionic radii of these eight-coordinate ions are greater than that of the nine-coordinate U^{4+} ion (1.05

Å), as in the case of Ce^{3+} (1.143 Å) and Nd^{3+} (1.109 Å); the ionic radii of the eight-coordinate Gd^{3+} (1.053 Å) and nine-coordinate U^{4+} ion are quite identical, as are the average Gd−O and U−O bond lengths in the cations [U(dmf)$_9$]$^{4+}$ and [Gd(dmf)$_8$]$^{3+}$,[56a] with values of 2.39(1) and 2.39(3) Å, respectively. The distinct complexation of the U^{4+} and Ln^{3+} ions certainly reflects the greater Lewis acidity of the U^{4+} ion, due to its higher positive charge, which induces a stronger interaction with the Lewis base. It also demonstrates that the coordination sphere of the Ln^{3+} ions in the cations [Ln(dmf)$_8$]$^{3+}$ (Ln = Ce, Nd) remains unsaturated. The U−O−C angles vary from 122.3(15)° to 156.1(17)° and average 136(7)°; the latter value is larger than that of 129-(2)° in the [Gd(dmf)$_8$]$^{3+}$ ion, in line with the greater steric crowding of the uranium coordination sphere. Intramolecular O···C(carbonyl) contacts between adjacent dmf ligands shorter than ca. 3.10 Å and as low as 2.69 Å are found in **5**. These contacts may be indicative of attractive interligand interactions, as previously observed in [Al(dmf)$_6$][ClO$_4$]$_3$.[57]

Conclusion

Reaction of UCl$_4$ and Me$_3$SiI in acetonitrile constitutes a practical and efficient route to [UI$_4$(MeCN)$_4$], which should favor the use of this precursor in uranium chemistry. The more facile displacement of the iodide ligand over the chloride group is reflected in the distinct crystal structures of the corresponding Lewis base adducts of UCl$_4$ and UI$_4$, and especially in the formation of [U(dmf)$_9$]I$_4$, the first tetracationic {U^{4+}} species to have been crystallographically characterized.

Supporting Information Available: Tables of crystal data, atomic positions and displacement parameters, anisotropic displace-ment parameters, bond lengths, and bond angles in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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