

# New Efficient Synthesis of $[\text{U}_4(\text{MeCN})_4]$ . X-ray Crystal Structures of $[\text{U}_2(\text{MeCN})_7][\text{U}_6]$ , $[\text{U}_4(\text{py})_3]$ , and $[\text{U}(\text{dmf})_9]\text{I}_4$

Jean-Claude Berthet,\* Pierre Thuéry, and Michel Ephritikhine

Service de Chimie Moléculaire, DSM, DRECAM, CNRS URA 331,  
Laboratoire Claude Fréjacques, CEA/Saclay, 91191 Gif-sur-Yvette, France

Received October 7, 2004

Reaction of  $\text{UCl}_4$  and excess  $\text{Me}_3\text{SiI}$  in acetonitrile provides a convenient route to  $[\text{U}_4(\text{MeCN})_4]$  (**1**), which was isolated in excellent yield and crystallized in acetonitrile as the ion pair complex  $[\text{U}_2(\text{MeCN})_7][\text{U}_6]$  (**2**). Compound **1** was transformed in pyridine (py) and dimethylformamide (dmf) into the Lewis base adducts  $[\text{U}_4(\text{py})_3]$  (**3**) and  $[\text{U}_4(\text{dmf})_6]$  (**4**). Crystals of **3** and  $[\text{U}(\text{dmf})_9]\text{I}_4$  (**5**) were obtained by slow diffusion of diethyl ether into pyridine or dmf solutions of **1**; compound **5** is the first tetracationic  $\{\text{U}^{4+}\}$  entity to have been crystallographically characterized.

## Introduction

The proper choice of halide and pseudo-halide starting materials  $\text{MX}_n$  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.<sup>1</sup> While the soluble Lewis bases adducts of  $\text{U}^{\text{III}}$  constitute a convenient entry into trivalent uranium chemistry,<sup>2</sup> in contrast to  $\text{UCl}_3$  which is difficult to prepare and is sparingly soluble in organic solvents,<sup>3</sup> the reverse situation is observed for the corresponding halides of uranium(IV). By comparison with  $\text{UCl}_4$ ,<sup>4</sup> by far the most commonly used starting material in actinide chemistry and

from which a series of other interesting  $\text{UX}_4$  precursors can be derived ( $\text{X} = \text{NR}_2$ ,<sup>5</sup>  $\text{BH}_4$ ,<sup>6</sup>  $\text{OSO}_2\text{CF}_3$ ),<sup>7</sup>  $\text{U}^{\text{IV}}$  has received much less attention. This lack of consideration is largely due to the tedious synthesis of  $\text{U}^{\text{IV}}$  by a high-temperature route and its ready decomposition into  $\text{U}^{\text{III}}$  and  $\text{I}_2$  even at low temperatures.<sup>8,9</sup> Many efforts have been devoted to the gentle syntheses of soluble  $[\text{U}_4\text{L}_n]$  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.<sup>9–18</sup> However, Du Preez and Zeelie devised the synthesis at 20 °C of  $[\text{U}_4(\text{MeCN})_4]$ , through the

\* To whom correspondence should be addressed. E-mail: berthet@drecam.cea.fr.

- (1) (a) Schumann, H.; Meese-Marktscheffel, J. A.; Esser, L. *Chem. Rev.* **1995**, *95*, 865. (b) Edelmann, F. *Comprehensive Organometallic Chemistry*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, 1995; Vol. 4, Chapter 2, p 11. (c) Marks, T. J. *Comprehensive Organometallic Chemistry*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, 1982, Vol. 3, Chapter 21, p 173.
- (2) (a) Avens, L. R.; Bott, S. G.; Clark, D L.; Sattelberger, A. P.; Watkin, J. G.; Zwick, B. D. *Inorg. Chem.* **1994**, *33*, 2248. (b) Avens, L. R.; Burns, C. J.; Butcher, R. J.; Clark, D L.; Gordon, J. C.; Schake, A. R.; Scott, B. L.; Watkin, J. G.; Zwick, B. D. *Organometallics* **2000**, *19*, 451. (c) Kiplinger, J.; Morris, D. E.; Scott, B. L.; Burns, C. J. *Organometallics* **2002**, *21*, 5978.
- (3) Katz, J. J.; Morss, L. R.; Seaborg, G. T. *The Chemistry of the Actinide Elements*; Chapman and Hall: New York, 1986; Vols. 1 and 2, and references therein.
- (4) Hermann, J. A.; Suttle, J. F. *Inorg. Synth.* **1957**, *5*, 143.

- (5) Jones R. G.; Karmas, G.; Martin Jr., G. A., Gilman, H. *J. Am. Chem. Soc.* **1956**, *78*, 4285.
- (6) Volkov, V. V.; Myakishev, K. G. *Radiokhimiya* **1980**, *22*, 745.
- (7) Berthet, J. C.; Nierlich, M.; Ephritikhine, M. *Eur. J. Inorg. Chem.* **2002**, 850.
- (8) Katz, J. J.; Rabinowitch E. *The chemistry of uranium. The element, its binary and related compounds*; Dover: New York, 1951.
- (9) Bagnall, K. W.; Brown, D.; Jones, P. J.; Du Preez, J. G. H. *J. Chem. Soc.* **1965**, 351.
- (10) Lamiisse, M.; Heimbürger, R.; Rohmer, R. C. *R. Acad. Sci. Paris* **1964**, *258*, 2078.
- (11) Bagnall, K. W.; Brown, D.; Jones, P. J.; Du Preez, J. G. H. *J. Chem. Soc.* **1965**, 3594.
- (12) Golovnya, V. A.; Bolotova, G. T. *Russ. J. Inorg. Chem.* **1966**, *11*, 1419.
- (13) Du Preez, J. G. H.; Gibson, M. L. *J. Inorg. Nucl. Chem.* **1972**, *34*, 1771.
- (14) Du Preez, J. G. H.; Gibson, M. L.; Steenkamp, P. J. *J. Inorg. Nucl. Chem.* **1974**, *36*, 579.
- (15) Kumar, N.; Tuck, D. G. *Inorg. Chim. Acta* **1984**, *95*, 211.
- (16) Du Preez, J. G. H.; Zeelie, B. *Inorg. Chim. Acta* **1986**, *118*, L25.
- (17) Du Preez, J. G. H.; Zeelie, B.; Casellato U.; Graziani, R. *Inorg. Chim. Acta* **1987**, *129*, 289.
- (18) (a) Du Preez, J. G. H.; Zeelie, B. *Inorg. Chim. Acta* **1989**, *161*, 187. (b) Hirose, M.; Miyake, C.; Du Preez, J. G. H. *Inorg. Chim. Acta* **1990**, *178*, 17. (c) Du Preez, J. G. H.; Rohwer, H. E.; Van Brecht, B. J. A. M.; Zeelie, B.; Casellato, U.; Graziani, R. *Inorg. Chim. Acta* **1991**, *189*, 67.

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.<sup>16</sup> 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<sup>9–18</sup> and only the tetramethylurea derivative  $[UI_4\{OC(NMe_2)_2\}_2]$  has been crystallographically characterized.<sup>17</sup> 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 <sup>1</sup>H NMR spectra were recorded on a Bruker DPX 200 instrument and referenced internally using the residual protio solvent resonances relative to tetramethylsilane ( $\delta$  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.<sup>4</sup>

**$[UI_4(MeCN)_4]$  (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 <sup>1</sup>H NMR spectrum of **1** in pyridine-*d*<sub>5</sub> 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. <sup>1</sup>H NMR (acetonitrile-*d*<sub>3</sub>, 23 °C,  $\delta$ ): 10.8 (s,  $w_{1/2}$  = 400 Hz, 2H), 6.5 (s,  $w_{1/2}$  = 90 Hz, 1H), 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. <sup>1</sup>H NMR (acetonitrile-*d*<sub>3</sub>, 23 °C,  $\delta$ ): 16.9 (s,  $w_{1/2}$  = 250 Hz, 1H), 4.9 (s,  $w_{1/2}$  = 230 Hz, 3H), 4.51 (s,  $w_{1/2}$  = 230 Hz, 3H). IR: 1643 (vs)  $cm^{-1}$   $\nu(CO)$ .

**Table 1.** Crystal Data and Structure Refinement Details

compound	$[UI_2(MeCN)_7][UI_6]$ ( <b>2</b> )	$[UI_4(py)_3]$ ( <b>3</b> )	$[U(dmf)_9]I_4$ ( <b>5</b> )
chemical formula	$C_{14}H_{21}I_8N_7U_2$	$C_{15}H_{15}I_4N_3U$	$C_{27}H_{63}I_4N_9O_9U$
<i>M</i> (g mol <sup>-1</sup> )	1778.64	982.93	1403.49
cryst syst	orthorhombic	monoclinic	tetragonal
space group	<i>Cmcm</i>	<i>P2<sub>1</sub>/c</i>	<i>P4<sub>1</sub></i>
<i>a</i> (Å)	12.8779(9)	11.3294(3)	13.5474 (2)
<i>b</i> (Å)	11.0818(11)	13.1236(5)	13.5474 (2)
<i>c</i> (Å)	26.5236(15)	15.4734(6)	53.2687(14)
$\beta$ (deg)	90	107.094(2)	90.0
<i>V</i> (Å <sup>3</sup> )	3785.2(5)	2198.99(14)	9776.5(3)
<i>Z</i>	4	4	8
<i>D</i> <sub>calcd</sub> (g cm <sup>-3</sup> )	3.121	2.969	1.907
$\mu$ (Mo K $\alpha$ ) (mm <sup>-1</sup> )	15.085	12.999	5.895
<i>F</i> (000)	3048	1720	5312
reflns collected	10656	14135	37438
independent reflns	1813	3741	13580
observed reflns [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	1342	3558	11799
<i>R</i> <sub>int</sub>	0.126	0.046	0.104
params refined	91	208	902
<i>R</i> <sub>1</sub>	0.050	0.026	0.069
<i>wR</i> <sub>2</sub>	0.119	0.060	0.180
<i>S</i>	1.270	1.107	1.023
$\Delta\rho_{min}$ (e Å <sup>-3</sup> )	-1.33	-0.92	-1.58
$\Delta\rho_{max}$ (e Å <sup>-3</sup> )	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<sup>19</sup> using graphite-monochromated Mo K $\alpha$  radiation ( $\lambda$  = 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°  $\varphi$ -range was scanned with 2° steps during data collection. The data were processed with DENZO-SMN.<sup>20</sup> 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*<sup>2</sup> with SHELXL-97.<sup>21</sup> Absorption effects were corrected empirically with the program DELABS from PLATON.<sup>22</sup> 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 (CH<sub>3</sub>) times that of the parent atom. The molecular plots were drawn with SHELXTL.<sup>23</sup> The crystal data and structure refinement details are reported in Table 1.

(19) Kappa-CCD Software, Nonius BV, Delft, 1998.

(20) Otwinowski, Z.; Minor, W. *Methods Enzymol.* **1997**, 276, 307.

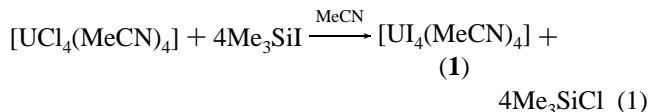
(21) Sheldrick, G. M. *SHELXS97 and SHELXL97*; University of Göttingen: Göttingen, Germany, 1997.

(22) Spek, A. L. *PLATON*; University of Utrecht: Utrecht, 2000.

(23) Sheldrick, G. M. *SHELXTL*, Version 5.1; Bruker AXS Inc.: Madison, WI, 1999.

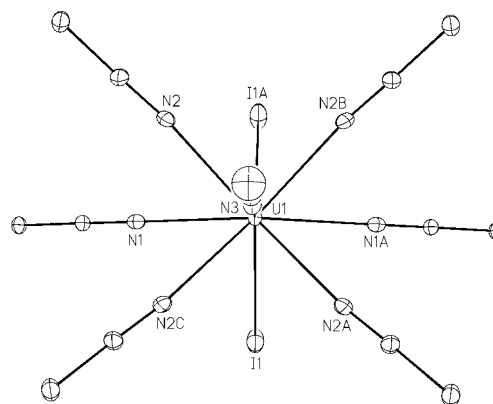
## Results and Discussion

Treatment of  $\text{UCl}_4$  with excess  $\text{Me}_3\text{SiI}$  in acetonitrile at  $20^\circ\text{C}$  led to the formation of  $[\text{U}_2(\text{MeCN})_7]^{2+}$  (**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%.



The stability of uranium tetraiodide being the lowest among the halide series,<sup>8,12,17</sup> the driving force of reaction 1 is certainly ensured by the large difference in bond dissociation energies between  $\text{Me}_3\text{SiI}$  and  $\text{Me}_3\text{SiCl}$  (ca. 35 kcal mol<sup>-1</sup>)<sup>24,25</sup> and the volatility of  $\text{Me}_3\text{SiCl}$  as compared with  $\text{Me}_3\text{SiI}$ .<sup>26</sup> Reaction 1 provides a new example of the efficiency of the iodasilane 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  $\text{UCl}_4$  and  $\text{NaI}$ .<sup>11</sup> Despite its numerous advantages over other substituting reagents and its chemical versatility,  $\text{Me}_3\text{SiI}$  remains poorly employed in inorganic and coordination chemistry of transition metals.<sup>26</sup> In the f-element series, it was used with success for the conversion of  $[\text{UO}_2(\text{OSO}_2\text{CF}_3)_2]$ ,<sup>27</sup>  $[\text{Th}(\text{C}_5\text{Me}_5)_2\text{Br}_2]$ ,<sup>28</sup>  $[\text{Li}(\text{thf})_4][\text{Th}(\text{C}_2\text{B}_9\text{H}_{11})_2\text{X}_2]$  ( $\text{X} = \text{Cl}, \text{Br}$ ),<sup>29</sup>  $[\text{U}(\{\text{Me}_3\text{Si}\}_2\text{C}_5\text{H}_3)_2\text{Cl}_2]$ ,<sup>30</sup> and  $[\text{An}(\text{NN}'_3)\text{Cl}][\text{An} = \text{Th}, \text{U}; \text{NN}'_3 = \text{N}(\text{CH}_2\text{CH}_2\text{NSiMe}_2\text{Bu}')_3]$ <sup>31</sup> into their iodide analogues, and for removing the coordinated thf in  $[\text{LaCp}^*(\text{CH}\{\text{SiMe}_3\}_2)_2(\text{thf})]$  by ring-opening reaction.<sup>32</sup>

Crystallization of **1** from acetonitrile gave crystals of  $[\text{U}_2(\text{MeCN})_7][\text{UI}_6]$  (**2**). Such formation of ion pair compounds of the f-elements was previously illustrated by the structures of  $[\text{UCl}_3(\text{EtCONEt}_2)_4][\text{UCl}_5(\text{EtCONEt}_2)]$ ,<sup>33</sup>  $[\text{UCl}_2(\text{dmsO})_6][\text{UCl}_6]$ ,<sup>34</sup> and the series of lanthanide complexes  $[\text{LnX}_2(\text{thf})_5][\text{LnX}_4(\text{thf})_2]$  ( $\text{X} = \text{I}, \text{Ln} = \text{Nd}, \text{Gd}, \text{Y}, \text{Sm}, \text{Yb}$ ;  $\text{X} = \text{Cl}, \text{Ln} = \text{Y}, \text{Gd}, \text{Dy}, \text{Er}, \text{Tb}, \text{Tm}, \text{Yb}$ ;  $\text{X} = \text{Br}, \text{Ln} = \text{Eu}$ ).<sup>35</sup> The structure of **1** is quite distinct from that of the neutral acetonitrile adduct of  $\text{UCl}_4$ ,  $[\text{UCl}_4(\text{MeCN})_4]$ , in which the



**Figure 1.** View of the cation  $[\text{U}_2(\text{MeCN})_7]^{2+}$  in complex **2**. Hydrogen atoms have been omitted. Displacement ellipsoids are drawn at the 10% probability level. Selected bond lengths (Å) and angles ( $^\circ$ ): 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.<sup>36</sup> The octahedral structure of the centrosymmetric  $[\text{UI}_6]^{2-}$  ion in **1** is identical to that found in  $[\text{PPh}_3\text{Et}]_2[\text{UI}_6]$ ,<sup>37</sup> 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  $[\text{U}_2\{\text{OP}(\text{NC}_4\text{H}_8)_3\}_4][\text{BPh}_4]_2$  [2.98(1) Å]<sup>38</sup> or in  $\text{UI}_4$  [average 3.01(1) Å],<sup>39</sup>  $[\text{PPh}_3\text{Et}]_2[\text{UI}_6]$  [average 2.97(4) Å],<sup>37</sup>  $[\text{U}_4\{\text{OC}(\text{NMe}_2)_2\}_2]$  [average 3.01 Å],<sup>17</sup>  $[\text{U}_2(\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2)_2(\text{OPPh}_3)_2]$  [3.011(1) Å],<sup>40</sup> and  $[\text{U}(\text{C}_9\text{H}_7)_3\text{I}]$  [3.041(1) Å].<sup>41</sup> 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

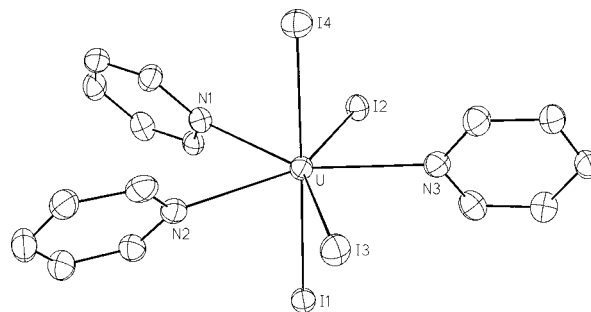
(24) Huheey, J.; Keiter, E. A.; Keiter, R. L. *Chimie Inorganique*; DeBoeck Université: Paris, 1996; Appendix A30.  
 (25) Walsh, R. *Acc. Chem. Res.* **1981**, *14*, 246.  
 (26) Leigh, G. J.; Sanders, J. R.; Hitchcock, P. B.; Fernandes, J. S.; Togrou, M. *Inorg. Chim. Acta* **2002**, *330*, 197.  
 (27) Berthet, J. C.; Nierlich, M.; Ephritikhine, M. *Chem. Commun.* **2004**, 870.  
 (28) Rabinovich, D.; Bott, S. G.; Nielsen, J. B.; Abney, K. D. *Inorg. Chim. Acta* **1998**, *274*, 232.  
 (29) Rabinovich, D.; Chamberlin, R. M.; Scott, B. L.; Nielsen, J. B.; Abney, K. D. *Inorg. Chim. Acta* **1997**, *36*, 4216.  
 (30) Lukens, W. W.; Beshouri, S. M.; Blosch, L. L.; Stuart, A. L.; Andersen, R. A. *Organometallics* **1999**, *18*, 1235.  
 (31) Roussel, P.; Alcock, N. W.; Boaretto, R.; Kingsley, A. J.; Munslow, I. J.; Sanders, C. J.; Scott, P. *Inorg. Chem.* **1999**, *38*, 3651.  
 (32) Van der Heijden, H.; Schavieren, C. J.; Orpen, A. G. *Organometallics* **1989**, *8*, 255.  
 (33) Bagnall, K. W.; Beddoes, R. L.; Mills, O. S.; Xing-fu, L. *J. Chem. Soc., Dalton Trans.* **1982**, 1361.  
 (34) Bombieri, G.; Bagnall, K. W. *J. Chem. Soc., Chem. Commun.* **1975**, 188.

(35) (a) Deacon, G. B.; Koplick, A. J. *J. Inorg. Nucl. Chem. Lett.* **1979**, *15*, 263. (b) Xie, Z.; Chiu, K.-Y.; Mak, T. C. W. *Inorg. Chem.* **1996**, *35*, 5957. (c) Niemeyer, M. *Acta Crystallogr., Sect. E* **2001**, *57*, m363. (d) Izod, K.; Liddle, S. T.; Clegg, W. *Inorg. Chem.* **2004**, *43*, 214, and references therein. (e) Petriček, S. *Polyhedron* **2004**, *23*, 2293.  
 (36) (a) Cotton, F. A.; Marler, D. O.; Schwotzer, W. *Acta Crystallogr., Sect. C* **1984**, *40*, 1186. (b) Van Den Bossche, G.; Rebizant, J.; Spirlet, M. R.; Goffart, J. *Acta Crystallogr., Sect. C* **1986**, *42*, 1478.  
 (37) Casellato, U.; Graziani, R. *Z. Kristallogr. – New Cryst. Struct.* **1998**, *213*, 361.  
 (38) Du Preez, J. G. H.; Gouws, L.; Rohwer, H.; Van Brecht, B. J. A. M.; Zeelie, B.; Casellato, U.; Graziani, R. *J. Chem. Soc., Dalton Trans.* **1991**, 2585.  
 (39) (a) Levy, J. H.; Taylor, J. C.; Waugh, A. B. *Inorg. Chem.* **1980**, *19*, 672. (b) Taylor, J. C. *Coord. Chem. Rev.* **1976**, *20*, 197.  
 (40) Avens, L. R.; Barnhart, D. M.; Burns, C. J.; McKee, S. D. *Inorg. Chem.* **1996**, *35*, 537.  
 (41) Rebizant, J.; Spirlet, M. R.; Van Den Bossche, G.; Goffart, J. *Acta Crystallogr., Sect. C* **1988**, *44*, 1710.

the capping position. These values can be compared with the mean U–N distances found in the cationic and neutral compounds  $[\{U(\text{C}_9\text{H}_7)\text{Br}(\text{MeCN})_4\}_2(\mu\text{-O})][\text{UBr}_6]$  [2.55(2) Å],<sup>42</sup>  $[\text{U}(\text{C}_9\text{H}_7)\text{Br}_2(\text{MeCN})_4]_2[\text{UBr}_6]$  [2.57(3) Å],<sup>42</sup>  $[\text{UCl}_4(\text{MeCN})_4]$  [2.58(2) Å],<sup>36</sup>  $[\text{U}(\text{C}_5\text{H}_5)_3(\text{MeCN})_2]_2[\text{UO}_2\text{Cl}_4]$  [2.59(1) Å],<sup>43</sup> and  $[\text{U}(\text{C}_5\text{H}_5)_3(\text{MeCN})_2][\text{Th}(\text{C}_5\text{H}_5)\text{Cl}_4(\text{MeCN})]$  [2.54(5) Å].<sup>44</sup>

Complex **1** is quite soluble in strongly coordinating solvents and was readily transformed in pyridine and dmf into the Lewis base adducts formulated as  $[\text{U}_4(\text{py})_3]$  (**3**) and  $[\text{U}_4(\text{dmf})_6]$  (**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  $[\text{U}_4(\text{thf})_x]$ , which could not be isolated because of its rapid transformation into  $[\text{U}_2(\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2)_2(\text{thf})_x]$  following ring-opening reaction of thf.<sup>40,45</sup> Formation of **3** can be compared with that of  $[\text{Th}_4(\text{py})_4]$  from  $[\text{Th}_4(\text{thf})_4]$ ;<sup>46</sup> the different number of coordinated pyridines in the two compounds certainly reflects the larger size of the  $\text{Th}^{4+}$  ion. Resonances in the  $^1\text{H}$  NMR spectra of **3** and **4** in acetonitrile- $d_3$  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  $1643\text{ cm}^{-1}$  is assigned to the  $\nu(\text{C}=\text{O})$  stretch and is decreased in energy from  $1675\text{ cm}^{-1}$  in the free dmf molecule; this C=O bond weakening can be compared with that observed upon coordination of  $N,N$ -dialkyl amides to  $\text{UCl}_4$ .<sup>33</sup> The synthesis of **4** is much more convenient than those reported for a dmf adduct of  $\text{U}_4$ , either by electrochemical oxidation of uranium metal in dmf solution of iodine<sup>15</sup> or electrochemical reduction of  $\text{UO}_3$  in aqueous HI solution, followed by dissolution of the resulting solid in dmf.<sup>10</sup> The products obtained from these experiments have not been fully characterized but their elemental analyses gave values rather close to  $[\text{U}_4(\text{dmf})_4]$ .

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  $[\text{UCl}_4(\text{py})_4]$  adopts a square antiprismatic configuration,<sup>47</sup> 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.<sup>30,31,37–41,48</sup> 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  $[\text{U}_4(\text{py})_3]$  (**3**). Hydrogen atoms have been omitted. Displacement ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles ( $^\circ$ ): 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  $[\text{U}(\text{C}_8\text{H}_8)\text{Cl}_2(\text{py})_2]$ ,<sup>49</sup>  $[\text{U}(\text{C}_5\text{H}_5)_2(\text{OSO}_2\text{CF}_3)_2(\text{py})_2]$ ,<sup>7</sup>  $[\text{U}(\text{N}(\text{Et})_2)_2(\text{py})_5][\text{BPh}_4]_2$ ,<sup>50</sup>  $[\text{U}(\text{SCHMe}_2)_2\text{I}_2(\text{py})_3]$ ,<sup>48g</sup> and  $[\text{U}(\text{C}_{18}\text{H}_{18}\text{N}_2\text{O}_4)\text{Cl}_2(\text{py})_2]$ ,<sup>51</sup> 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  $[\text{U}(\text{dmf})_9]_4$  (**5**). The crystal structure of **5** is quite different from that of the dmf adduct of  $\text{UCl}_4$ , which crystallizes as  $[\text{UCl}_3(\text{dmf})_5][\text{UCl}_6]$ .<sup>52</sup> The  $[\text{U}(\text{dmf})_9]^{4+}$  ion is the first tetracationic  $\text{U}^{4+}$  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  $3.1(8)^\circ$  and  $0.9(7)^\circ$  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  $1.7^\circ$  with the normal to the plane. With

(42) Beeckman, W.; Goffart, J.; Rebizant, J.; Spirlet, M. R. *J. Organomet. Chem.* **1986**, *307*, 23.

(43) Bombieri, G.; Benetollo, F.; Bagnall, K. W.; Plews, M. J.; Brown, D. *J. Chem. Soc., Dalton Trans.* **1983**, 45.

(44) Rebizant, J.; Apostolidis, C.; Spirlet, M. R.; Kanellakopoulos, B. *Inorg. Chim. Acta* **1987**, *139*, 209.

(45) Campello, M. P. C.; Domingos, A.; Santos, I. *J. Organomet. Chem.* **1994**, *484*, 37.

(46) Clark, D. L.; Franckom, T. M.; Miller, M. M.; Watkin, J. G. *Inorg. Chem.* **1992**, *31*, 1628.

(47) Berthet, J. C.; Nierlich, M.; Ephritikhine, M. Unpublished results.

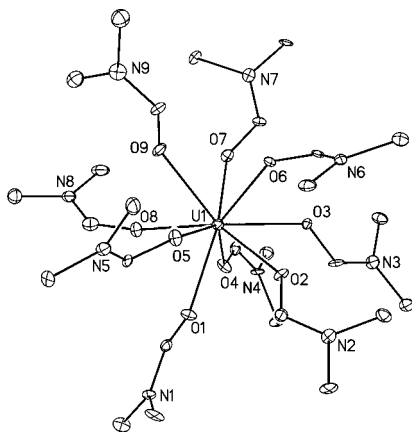
(48) (a) Rebizant, J.; Spirlet, M. R.; Apostolidis, C.; Kanellakopoulos, B. *Acta Crystallogr., Sect. C* **1991**, *47*, 854. (b) Van Der Sluys, W. G.; Huffman, J. C.; Ehler, D. S.; Sauer, N. N. *Inorg. Chem.* **1992**, *31*, 1318. (c) Campello, M. C.; Domingos, A.; Santos, I. *J. Organomet. Chem.* **1994**, *484*, 37. (d) Avens, L. R.; Barnhart, D. M.; Burns, C. J.; McKee, S. D.; Smith, W. H. *Inorg. Chem.* **1994**, *33*, 4254. (e) Clark, D. L.; Gordon, J. C.; Huffman, J. C.; Watkin, J. G.; Zwick, B. D. *New J. Chem.* **1995**, *19*, 495. (f) Blake, P. C.; Lappert, M. F.; Taylor, R. G.; Atwood, J. L.; Hunter, W. E.; Zhang, H. *J. Chem. Soc., Dalton Trans.* **1995**, 3335. (g) Leverd, P. C.; Lance, M.; Vigner, J.; Nierlich, M.; Ephritikhine, M. *J. Chem. Soc., Dalton Trans.* **1995**, 237. (h) Karmazin, L.; Mazzanti, M.; Pécault, J. *Inorg. Chem.* **2003**, *42*, 5900.

(49) Boussie, T. R.; Moore, R. M.; Streitwieser Jr., A.; Zalkin, A.; Brennan, J.; Smith, K. A. *Organometallics* **1990**, *9*, 2010.

(50) Berthet, J. C.; Boisson, C.; Lance, M.; Vigner, J.; Nierlich, M.; Ephritikhine, M. *J. Chem. Soc., Dalton Trans.* **1995**, 3019.

(51) Le Borgne, T.; Rivière, E.; Marrot, J.; Thuéry, P.; Girerd, J.-J.; Ephritikhine, M. *Chem.-Eur. J.* **2002**, *8*, 773.

(52) Charpin, P.; Lance, M.; Nierlich, M.; Vigner, D.; Marquet-Ellis, H. *Acta Crystallogr., Sect. C* **1988**, *44*, 257.



**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],<sup>52</sup>  $[UCl(dmf)_7]_2[UO_2Cl_4]_3$  [2.30(1)–2.40(1) Å],<sup>53</sup> and  $[UCl(dmf)_7]Cl_3$  [2.315(2)–2.391(2) Å].<sup>54</sup> To the best of our knowledge, the only other tetracationic actinide complex to have been crystallographically characterized is the homoleptic, nine-coordinate thorium compound  $[Th(dms)_9][ClO_4]_4 \cdot 4dms$ , which adopts a tricapped trigonal prismatic configuration.<sup>55</sup>

It is interesting to compare the structures of the  $[U(dmf)_9]^{4+}$  and  $[Ln(dmf)_8]^{3+}$  ions ( $Ln = Ce, Nd, Gd, Tb$ )<sup>56</sup> 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  $[Gd(dmf)_8]^{3+}$ ,<sup>56a</sup> 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  $[Al(dmf)_6][ClO_4]_3$ .<sup>57</sup>

## Conclusion

Reaction of  $UCl_4$  and  $Me_3SiI$  in acetonitrile constitutes a practical and efficient route to  $[U_4(MeCN)_4]$ , 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  $U_4$ , and especially in the formation of  $[U(dmf)_9]_4$ , the first tetracationic  $\{U^{4+}\}$  species to have been crystallographically characterized.

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

IC048603P

(53) Keppert, D. L.; Patrick, J. M.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1983**, 381.

(54) Oldham, W. J.; Scott, B. L.; Abney, K. D.; Smith, W. H.; Costa, D. A. *Acta Crystallogr., Sect. C* **2002**, 58, m139.

(55) Harrowfield, J. M.; Ogden, M. I.; Skelton, B. W.; White, A. H. *Inorg. Chim. Acta* **2004**, 357, 2404.

(56) (a) Harrowfield, J. M.; Skelton, B. W.; White, A. H.; Wilner, F. R. *Inorg. Chim. Acta* **2004**, 357, 2358. (b) Liu, S.; Meyers, E. A.; Shore, S. G. *Angew. Chem., Int. Ed. Engl.* **2002**, 41, 3609. (c) Jobic, S.; Poirier-Coutansais, S.; Evain, M.; Brec, R. *Mater. Res. Bull.* **2001**, 36, 2637. (d) Chen, L.; Wu, X.-T.; Gao, X.-C.; Zhang, W.-J.; Lin, P. *J. Chem. Soc., Dalton Trans.* **1999**, 4303. (e) Ishiguro, S.-I.; Umebayashi, Y.; Kato, K.; Takahashi, R.; Ozutsumi, K. *J. Chem. Soc., Faraday Trans.* **1998**, 94, 3607. (f) Huang, Q.; Wu, X.; Wang, Q.; Sheng, T.; Lu, J. *Angew. Chem., Int. Ed. Engl.* **1996**, 35, 868.

(57) Suzuki, H.; Ishiguro, S. I. *Acta Crystallogr., Sect. C* **1998**, 54, 586.