

Synthesis and Crystal Structure of $\text{UO}_2\text{Cl}_2(\text{THF})_3$: A Simple Preparation of an Anhydrous Uranyl Reagent

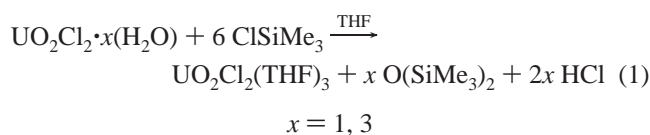
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Solid state structures of molecular uranyl compounds are commonly described in the literature.^{1,2} The vast majority of these species have been isolated from aqueous media, and the presence of water often influences the resulting structures through hydrogen bonding and/or inner-sphere water coordination. The development of nonaqueous uranyl chemistry has demonstrated the existence of novel coordination geometries in the absence of these effects.^{3–5} Further studies are required to examine the potentially unique electrochemical and spectroscopic properties of these products. Until recently, the development of nonaqueous uranyl chemistry has been inhibited by a lack of appropriate starting materials. Several thermal routes for the synthesis of anhydrous UO_2Cl_2 have been reported.⁶ However, they are generally unsuitable for the generation of reagents because of difficulties encountered separating precursors and/or side products from UO_2Cl_2 , the unavailability of a commercial source for starting materials, e.g., UCl_4 , or the limited scale of preparation.⁷ Our group has been interested in the development of nonaqueous uranyl chemistry in order to examine physical properties of uranyl species unstable to hydrolysis.^{3–5} The expansion of this chemistry has been facilitated by the development of a simple one-pot dehydration of $\text{UO}_2\text{Cl}_2 \cdot x(\text{H}_2\text{O})$ ($x = 1, 3$) for the preparation of $\text{UO}_2\text{Cl}_2(\text{THF})_3$ (**1**). The previously reported dimeric derivative, $[\text{UO}_2\text{Cl}_2(\text{THF})_2]_2$ (**2**),^{8,9} may be isolated upon desolvation of **1**. Compound **2** is an excellent starting material for the further synthesis of uranyl alkoxides and uranyl amides.

Compound **1** is obtained upon reaction of excess ClSiMe_3 with $\text{UO}_2\text{Cl}_2 \cdot x(\text{H}_2\text{O})$ in tetrahydrofuran (eq 1).¹⁰ The method



is adapted from similar dehydration reports.^{11–13} By allowing a tetrahydrofuran solution of **1** layered with hexane to cool to -30°C , shiny yellow blocks are isolated in good yield. The molecular structure of **1** was determined from single-crystal X-ray diffraction analysis,¹⁴ and it consists of a uranyl monomer. A view of the molecule is shown in Figure 1. The uranium is coordinated in a pseudopentagonal bipyramidal fashion by two apical oxo groups, and three equatorial THF ligands and two nonadjacent chlorides form the equatorial plane. The oxo groups of the uranyl moiety lie trans to one another with a bond angle of $\text{O}(1)–\text{U}–\text{O}(2) = 176.2(3)^\circ$. This angle lies within the range reported for the majority of other uranyl complexes.² The $\text{U}–\text{O}(\text{oxo})$ distances are identical at 1.766(6) and 1.765(6) Å for $\text{O}(1)$ and $\text{O}(2)$, respectively. These values are comparable to those reported for seven-coordinate uranyl complexes including $[\text{UO}_2\text{Cl}_2(\text{THF})_2]_2$ (**2**) (1.76(3) and 1.74(2) Å),⁸ $\text{UO}_2\text{Br}_2(\text{THF})_3$ (1.75(1) and 1.77(1) Å),¹⁵ and *cis*- $\text{UO}_2\text{Cl}_2(\text{Ph}_3\text{PO})_2$ (1.771(4) Å).¹⁶ The $\text{U}–\text{Cl}$ bond distances, 2.698(2) and 2.687(2) Å, are

- (10) At room temperature, an excess of ClSiMe_3 (30 mL, 0.24 mol) was added to a flask containing a slurry of $\text{UO}_2\text{Cl}_2 \cdot x(\text{H}_2\text{O})$ ($x = 1, 3$) (14 g) and tetrahydrofuran (100 mL). The solution was stirred for 1 h. The solution was concentrated to 50 mL by removal of solvent under vacuum, and hexane (50 mL) was added. After the solution had been stirred vigorously for 5 min, the liquids were decanted away. The dull yellow powder was washed with hexane (2×50 mL), and the product was dried under vacuum: yield 13.5 g (79% as **2**). IR (Nujol mull): 1347 (s), 1295 (m), 1246 (m), 1214 (w), 1172 (m), 1136 (w), 1042 (m), 1007 (s), 961 (s), 949 (s), 921 (s), 891 (w), 875 (s), 841 (s), 683 (w) cm^{-1} . Anal. Calcd for $\text{C}_8\text{H}_{16}\text{Cl}_2\text{O}_4\text{U}$: C, 19.81; H, 3.32. Found: C, 19.60; H, 3.30.
- (11) So, J.-H.; Boudjouk, P. *Inorg. Chem.* **1990**, *29*, 1592.
- (12) Samuels, J. A.; Chiang, W.-C.; Huffman, J. C.; Trojan, K. L.; Hatfield, W. E.; Baxter, D. V.; Caulton, K. G. *Inorg. Chem.* **1994**, *33*, 2167.
- (13) Cummins, C. C.; Lee, J.; Schrock, R. R.; Davis, W. D. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1501.
- (14) Crystal data for **1**: $\text{C}_{12}\text{H}_{24}\text{O}_5\text{Cl}_2\text{U}$, $M_r = 557.2$, monoclinic space group $P2_1/c$, $a = 6.8225(4)$ Å, $b = 16.791(1)$ Å, $c = 15.6088(9)$ Å, $\beta = 92.893(1)^\circ$, $V = 1785.9(2)$ Å³, $Z = 4$, $\rho_{\text{calcd}} = 2.073$ g cm^{-3} , $F(000) = 1048$, $\lambda = 0.71073$ Å, $T = -70^\circ\text{C}$, $\mu(\text{Mo K}\alpha) = 9.401$ mm^{-1} . Crystals of **1** were covered with mineral oil under an argon stream, and an irregular block of dimensions $0.17 \times 0.12 \times 0.12$ mm was mounted on a glass fiber using silicon grease. It was placed under the -70°C liquid N_2 vapor cold stream on a Siemens P4/CCD/PC diffractometer with sealed Mo $\text{K}\alpha$ X-ray source. A hemisphere of data was collected using a combination of ϕ and ω scans, with 30 s exposures and 0.3° frame widths. Data collection, indexing, and initial cell refinement were handled using SMART software.²² Frame integration and final cell refinement were carried out using SAINT software.²³ The SADABS software package was used to perform the absorption corrections.²⁴ The structure was solved using Patterson and difference Fourier techniques. The hydrogen atom positions were fixed on ideal positions. The hydrogen atoms were refined using a riding model, with isotropic temperature factors fixed to 1.2 times the equivalent isotropic U of the carbon atom to which they were bonded. The final refinements included anisotropic temperature factors on all non-hydrogen atoms. Structure solution refinement, graphics, and creation of publication materials were performed using SHELXTL 5.1 software.²⁵ For 3592 reflections, refinement by full-matrix least-squares techniques on F^2 converged with $R1 = 0.040$ and $wR2 = 0.107$, where $R1 = \sum |F_o| - |F_c| / \sum |F_o|$, $wR2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$, and $w = 1/[\sigma^2(F_o^2) + (0.10000P)^2]$. SHELXTL PC 42/360 software was used for structure solution, refinement, graphics, and publication materials. Additional details of data collection and structure refinement are given in the Supporting Information.
- (15) Rebizant, J.; van den Bossche, G.; Spirlet, M. R.; Goffart, J. *Acta Crystallogr.* **1987**, *C43*, 1298.

[†] Chemical Science and Technology Division, Los Alamos National Laboratory.

[‡] University of New Mexico.

- (1) Wells, A. F. In *Structural Inorganic Chemistry*; Clarendon Press: Oxford, 1995; Chapter 28.
- (2) Burns, J. H. In *The Chemistry of the Actinide Elements*; Katz, J. J., Seaborg, G. T., Morss, L. R., Eds.; Chapman and Hall: New York, 1986; Vol. 2.
- (3) Burns, C. J.; Sattelberger, A. P. *Inorg. Chem.* **1988**, *27*, 3692.
- (4) Burns, C. J.; Smith, D. C.; Sattelberger, A. P.; Gray, H. B. *Inorg. Chem.* **1992**, *31*, 3724.
- (5) Wilkerson, M. P.; Burns, C. J.; Morris, D. E.; Paine, R. T.; Scott, B. L. Manuscript in preparation.
- (6) Prins, G. Uranyl chloride, its hydrates, and basic salts. RCN-186; Reactor Centrum Nederlands: 1973 and references therein.
- (7) Leary, J. A.; Suttle, J. F. *Inorg. Synth.* **1957**, *5*, 148.
- (8) Charpin, P.; Lance, M.; Nierlich, M.; Vigner, D.; Baudin, C. *Acta Crystallogr.* **1987**, *C43*, 1932.
- (9) Rogers, R. D.; Green, L. M.; Benning, M. M. *Lanthanide Actinide Res.* **1986**, *1*, 185.

Scheme 1

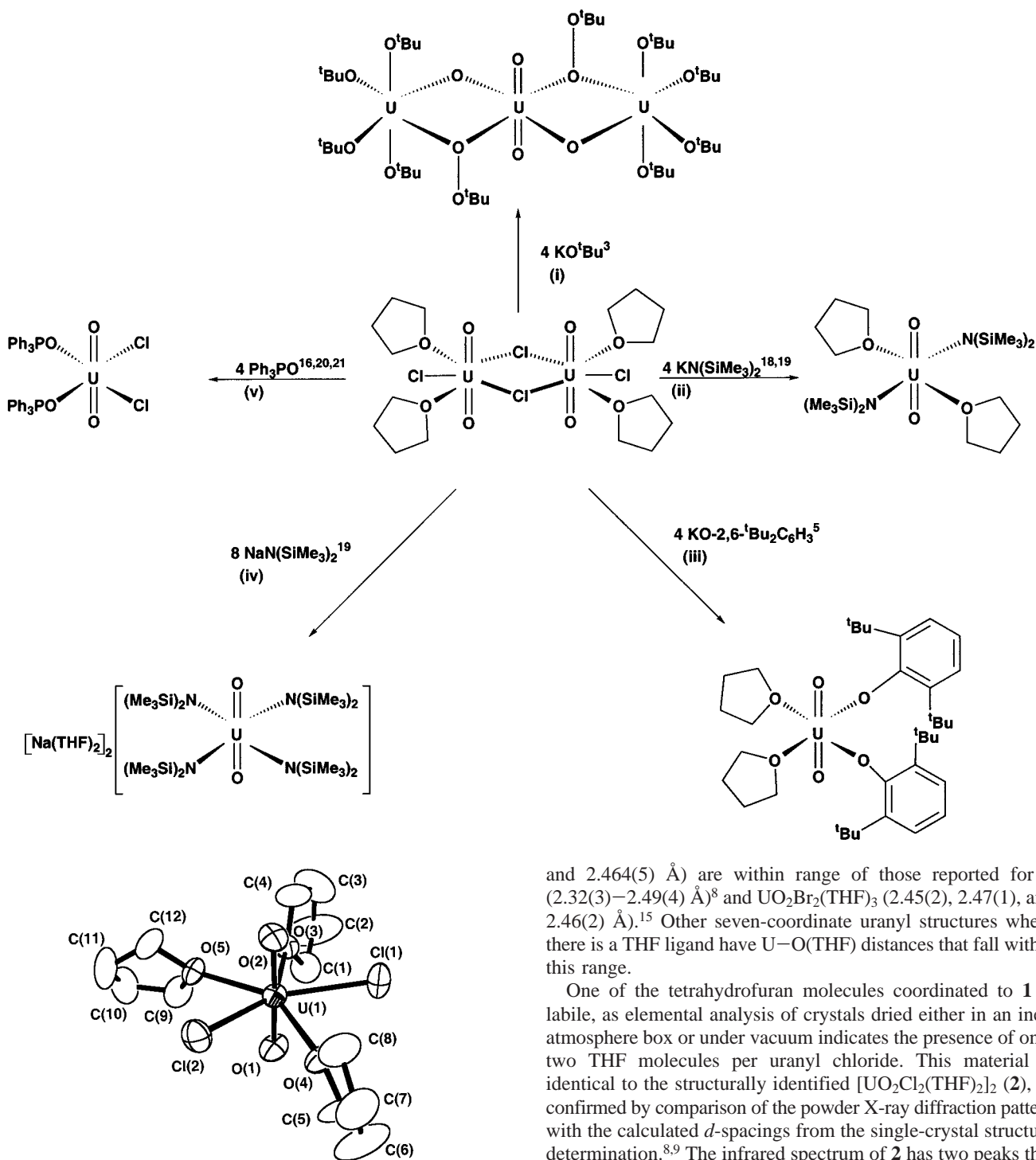


Figure 1. Molecular structure and atom-labeling scheme for $\text{UO}_2\text{Cl}_2\cdot(\text{THF})_3$, (**1**) with H atoms omitted (50% probability ellipsoids). Selected bond lengths (Å): U–O(1) 1.766(6), U–O(2) 1.765(6), U–Cl(1) 2.698(2), U–Cl(2) 2.687(2), U–O(3) 2.467(6), U–O(4) 2.443(6), U–O(5) 2.464(5). Selected bond angles (deg): O(1)–U–O(2) 176.2(3), Cl(1)–U–O(4) 72.4(2), Cl(1)–U–O(3) 73.4(2), Cl(2)–U–O(4) 73.1(2), Cl(2)–U–O(5) 75.4(2), O(3)–U–O(5) 67.8(2).

similar to the U–Cl(terminal) bond lengths for **2** (2.66(3) and 2.65(2) Å),⁸ and they lie within the range of other uranyl–Cl distances reported in the literature (2.64–2.78 Å).^{9,17} The U–O(tetrahydrofuran) bond distances in **1** (2.467(6), 2.443(6),

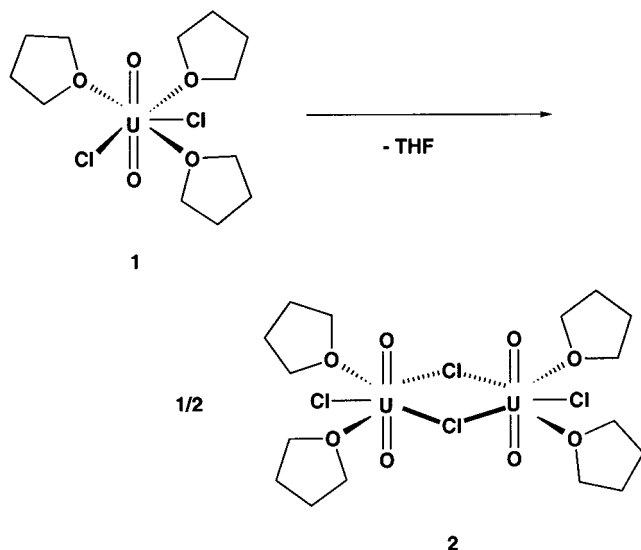
and 2.464(5) Å) are within range of those reported for **2** (2.32(3)–2.49(4) Å)⁸ and $\text{UO}_2\text{Br}_2(\text{THF})_3$ (2.45(2), 2.47(1), and 2.46(2) Å).¹⁵ Other seven-coordinate uranyl structures where there is a THF ligand have U–O(THF) distances that fall within this range.

One of the tetrahydrofuran molecules coordinated to **1** is labile, as elemental analysis of crystals dried either in an inert atmosphere box or under vacuum indicates the presence of only two THF molecules per uranyl chloride. This material is identical to the structurally identified $[\text{UO}_2\text{Cl}_2(\text{THF})_2]_2$ (**2**), as confirmed by comparison of the powder X-ray diffraction pattern with the calculated *d*-spacings from the single-crystal structure determination.^{8,9} The infrared spectrum of **2** has two peaks that lie within the expected range for the uranyl asymmetric stretch at 875 and 841 cm^{-1} .⁴ This complex has previously been isolated only as a side product obtained from the unexpected oxidation of bis(acetylacetonato)dichlorouranium(IV) in THF, or from recrystallization of contaminated UCl_4 in tetrahydrofuran. No general method of preparation or physical characterization data were referenced in either report.

Compound **2** readily redissolves in tetrahydrofuran, giving **1**. The ^1H NMR spectrum for **1** in $\text{THF-}d_8$ shows two resonances (δ 3.62 (s, α -THF) and 1.77 (s, β -THF)). These resonances are identical to those of free THF, suggesting that the labile THF

(16) Akona, S. B.; Fawcett, J.; Holloway, J. H.; Russell, D. R.; Leban, I. *Acta Crystallogr.* **1991**, *C47*, 45.

(17) Charpin, P.; Lance, M.; Nierlich, M.; Vigner, D.; Marquet-Ellis, H. *Acta Crystallogr.* **1988**, *C44*, 1489.



ligands are completely displaced by THF- d_8 in solution. Compound **2** is a useful anhydrous uranyl starting material of well-defined stoichiometry. Yellow tetrahydrofuran solutions of this compound react at room temperature with a variety of alkali metal salts to yield uranyl products of metathesis reactions (Scheme 1, i-iv).^{3,5,18,19} The coordinated THF may be readily replaced by stronger Lewis bases (Scheme 1, v).^{16,20,21} For this reason, it must be protected from atmospheric moisture because

(18) Andersen, R. A. *Inorg. Chem.* **1979**, *18*, 209.

(19) Barnhart, D. M.; Burns, C. J.; Sauer, N. N.; Watkin, J. G. *Inorg. Chem.* **1995**, *34*, 4079.

(20) Day, J. P.; Venanzi, L. M. *J. Chem. Soc. A* **1966**, 1363.

it readily exchanges coordinated tetrahydrofuran for water in air. Evaluation of the use of this material to prepare other uranyl complexes unstable in aqueous solution is in progress. For example, we have now developed synthetic routes to several uranyl alkoxide and amide compounds, including stable cluster-like aggregates.

The simple preparation of $[\text{UO}_2\text{Cl}_2(\text{THF})_2]_2$ (**2**) is allowing studies of the electronic structure of the uranyl moiety, in particular the basicity of the uranyl oxo groups in nonaqueous media.

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Supporting Information Available: An X-ray crystallographic file, in CIF format, for the structure determination of $\text{UO}_2\text{Cl}_2(\text{THF})_3$. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(21) Bombieri, G.; Forsellini, E.; Day, J. P.; Azeez, W. I. *J. Chem. Soc., Dalton Trans.* **1978**, 677.

(22) SMART Version 4.210, 1996, Bruker Analytical X-Ray Systems, 6300 Enterprise Lane, Madison, WI 53719.

(23) SAINT Version 4.05, 1996, Bruker Analytical X-Ray Systems, 6300 Enterprise Lane, Madison, WI 53719.

(24) SADABS, 1996, George Sheldrick, University of Göttingen, Germany.

(25) SHELXTL Version 5.1, 1997, Bruker Analytical X-Ray Systems, 6300 Enterprise Lane, Madison, WI 53719.