Preliminary X-ray crystallographic results establish a stoichiometry of U(BH$_4$)$_3$(18-crown-6)$_{3/4}$ for these crystals and also establish that the uranium is actually located inside the crown ether cavity for two of the three different uraniums in the unit cell. A disorder phenomenon has hindered the complete refinement of the structure, but it is hoped that a solution to this problem can be found and that precise structural data will be forthcoming.[6]

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Registry No. UCl$_3$(18-crown-6), 68212-93-1.

References and Notes

(1) This work was performed under the auspices of the U.S. Department of Energy.

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Uranyl Complexes with (Hexamethyldisilyl)amido and Nonafluoro-*tert*-butoxo Ligands

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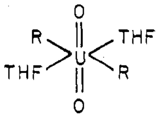
The uranyl ion UO$_2^{2+}$ is the most commonly occurring entity in uranium(VI) chemistry. A large number of complexes have been described with nitrate, sulfate, and related ligands.[1,2] In contrast only a small number of uranyl complexes have been described with alkoxide ligands, though no fluorocarbon alkoxides are known, and no amide derivatives have been prepared. Lithium methoxide and uranyl chloride yield UO$_2$(OMe)$_2$·MeOH, from which a number of substituted derivatives have been prepared by alcohol exchange with primary alcohols. The exchange reaction however takes a different course with secondary or tertiary alcohols, the disproportionation products OU(OR)$_4$·ROH (R = *i*-Pr, *s*-Bu, and *t*-Bu) being isolated. Heating these monooxo complexes results in further disproportionation affording U(OR)$_6$.[3,4]

Reaction of sodium nonafluoro-*tert*-butoxide with dinitratodioxouranium(VI)–bis(tetrahydrofuran), UO$_2$(NO$_3$)$_2$·2THF, yields the diamagnetic perfluoroalkoxide UO$_2$[OC(CF$_3$)$_3$]$_2$·2THF. This complex (I, R = (CF$_3$)$_3$CO) is readily soluble in chlorinated hydrocarbons or ethers but is insoluble in aliphatic or aromatic hydrocarbons. The complex is not volatile and decomposes when heated (130 °C) under vacuum. The asymmetric UO$_2$ stretching frequency occurs at 928 cm^{-1}, in the range for other uranyl complexes.[5] The infrared spectrum also shows absorptions associated with tetrahydrofuran and perfluoroalkoxy vibrations. The ^{1}H NMR spectrum (CDCl$_3$) consists of two equal-area multiplets centered at δ 2.22 and 4.32 due to tetrahydrofuran. The ^{19}F NMR spectrum consists of a single resonance (CDCl$_3$) at δ −80.0 (negative value being to low frequency of CFCl$_3$). These data are consistent with I, R = (CF$_3$)$_3$CO. We prefer the trans arrangement rather than that of the cis since the relatively bulky alkoxide groups doubtless prefer to be across from rather than adjacent to each other.



I

Reaction of sodium (hexamethyldisilyl)amide with uranyl chloride (UO$_2$Cl$_2$) in tetrahydrofuran yields the diamagnetic, orange-red amide UO$_2$[N(SiMe$_3$)$_2$]$_2$·2THF (I, R = (Me$_3$Si)$_2$N). The complex is soluble in pentane though it does not sublime nor yield a molecular ion in the mass spectrometer. The asymmetric UO$_2$ stretching frequency in the infrared spectrum cannot be assigned with certainty as this region contains intense absorptions due to NSi$_2$ vibrations. However, a strong shoulder at 955 cm^{-1} on the asymmetric NSi$_2$ vibration (935 cm^{-1}) can be tentatively ascribed to the UO$_2$ molecular vibration. The ^{1}H NMR spectrum is invariant to −65 °C.

Experimental Section

Microanalyses were done by Spang Microanalytical Laboratory, Eagle Harbor, MI, and the microanalytical laboratory of this department. The spectrometers used were a Varian T-60 (^{1}H) and a modified Bruker WH-180 (^{19}F) operating at 169.4 MHz and a Perkin-Elmer 597 (IR). All operations were carried out under nitrogen.

Bis(nonafluoro-*tert*-butoxo)dioxouranium(VI)–Bis(tetrahydrofuran). Sodium perfluoro-*tert*-butoxide[6] (0.73 g, 0.029 mol) dissolved in diethyl ether (25 mL) was added to a solution of dinitratodioxouranium(VI)–bis(tetrahydrofuran) (0.79 g, 0.0015 mol) in tetrahydrofuran (30 mL). The yellow suspension was stirred for 12 h. The volatile material was removed under vacuum, and diethyl ether (30 mL) was added to the residue. The solution was filtered, concentrated to ca. 10 mL, and cooled to −70 °C. The yellow *prisms* were collected, washed with diethyl ether (1 mL), and dried under vacuum; yield 0.70 g (53%). The complex decomposed when heated in a sealed capillary at ca. 230 °C. Anal. Calcd for C$_{16}$H$_{16}$F$_{18}$O$_6$U: C, 21.7; H, 1.81; F, 38.7. Found: C, 21.8; H, 1.83; F, 38.7.

Bis((hexamethyldisilyl)amido)dioxouranium(VI)–Bis(tetrahydrofuran). Sodium (hexamethyldisilyl)amide (1.1 g, 0.0058 mol) dissolved in tetrahydrofuran (20 mL) was added to dichlorodioxouranium[3] (1.0 g, 0.0029 mol) suspended in tetrahydrofuran (20 mL). The resulting red suspension was stirred for 6 h. The tetrahydrofuran was removed under vacuum, and the residue was extracted into pentane (40 mL). The solution was filtered, and the filtrate was concentrated to ca. 20 mL. Cooling to −10 °C yielded orange-red *prisms* which were collected and dried under vacuum (mp 147–148 °C dec). The yield was 1.7 g (79%). Anal. Calcd for C$_{20}$H$_{52}$N$_2$O$_4$Si$_4$U: C, 32.7; H, 7.08; N, 3.81. Found: C, 32.0; H, 6.96; N, 3.87. The ^{1}H NMR spectrum (C$_6$H$_6$) consisted of a singlet at δ 0.82 and a pair of multiplets centered at δ 1.77 and 4.50 in area ratio 36:8:8 due to (Me$_3$Si)$_2$N and tetrahydrofuran, respectively.

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