68013-54-7; salmetH$_2$, 68013-50-3; (*S*)-methionamine, 68013-51-4; (*S*)-methionamide hydrochloride, 16120-92-6; (*S*)-methionine methyl ester hydrochloride, 2491-18-1; salicylaldehyde, 90-02-8.

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The Chemistry of Trivalent Uranium. 2. Synthesis of UCl_3(18-crown-6) and $U(BH_4)_3$(18-crown-6)[1,2]

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A variety of crown ether complexes of uranium have been studied, but little evidence existed until recently to support the idea that direct coordination of uranium to the oxygens of the crown cavity had been achieved. Although a lanthanum nitrate crown ether complex had been found to possess the lanthanum coordinated in this manner,[3] only recently has a uranium(IV) complex been shown to exhibit this type of coordination.[4] The factors influencing the binding of uranium to the crown cavity still remain somewhat uncertain, however. Similarly, the extent that such coordination is oxidation state specific remains unknown. For these reasons, as well as the close similarity of La(III) and U(III) ionic radii and the limited information on chemical properties of U(III) compounds, we have undertaken the study of uranium(III)–crown ether complexes.

In this paper we wish to report the synthesis of UCl_3(18-crown-6) and its reaction with sodium borohydride yielding $U(BH_4)_3$(18-crown-6).

Experimental Section

All manipulations were performed under a dry nitrogen atmosphere by using standard Schlenk techniques or by using standard vacuum techniques. All solvents used in this study were reagent grade and were dried prior to use. UCl_4 was prepared by literature procedures.[5] 18-Crown-6 was obtained from Parish Chemical Co. and was recrystallized from acetonitrile and sublimed prior to use. NMR spectra were recorded on Varian Associates EM-360 and EM-390 spectrometers. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

$UCl_3(THF)_x$ + 18-Crown-6. As previously reported, 0.38 g (1 mmol) of UCl_4 and 0.24 g (10 mmol) of NaH were reacted in tetrahydrofuran (THF) solution to yield ~0.8 mmol of $UCl_3(THF)_x$ in 50–60 mL of THF.[2] This solution was filtered onto a stirred solution of 0.3 g (1.1 mmol) of 18-crown-6 in 30 mL of THF. An immediate reaction occurred yielding a finely divided red precipitate. The reaction was allowed to continue for 6–12 h to ensure complete reaction. The red precipitate was collected on a fine glass frit and was vacuum-dried overnight. The reaction yielded 0.45 g (0.74 mmol) of UCl_3(18-crown-6). Anal. Calcd for $C_{12}H_{24}O_6UCl_3$: C, 23.68; H, 3.97; U, 39.10; Cl, 17.47. Found: C, 22.65; H, 3.93; U, 39.11; Cl, 20.92.

Thermogravimetric analyses of UCl_3(18-crown-6) revealed no decomposition below 200 °C. Above 200 °C a weight loss of 43% was observed, which suggested loss of the crown ether (calcd 44%).

The UCl_3(18-crown-6) is insoluble in THF or acetone but reacts with water to yield a green solution. Because of this insolubility, solution NMR spectra were not obtainable. The broad-line ^1H NMR spectrum of a solid sample revealed a broad singlet which appeared to be unshifted from an external tetramethylsilane (Me_4Si) reference. However, due to the width of the peak, a shift ±10 ppm would have been undetectable.

UCl_3(18-crown-6) + $NaBH_4$. Approximately 0.45 g (0.75 mmol) of UCl_3(18-crown-6) and 0.2 g (5.3 mmol) of $NaBH_4$ were loaded into a 100-mL vessel equipped with a greaseless stopcock. The vessel was evacuated and 50 mL of THF was condensed onto the solids. After warming of the mixture to room temperature, the reaction proceeded slowly and the mixture was stirred overnight to ensure complete reaction. The orange-red slurry was filtered to remove NaCl and excess $NaBH_4$. An orange-red filtrate was obtained. The volume of this solution was reduced under vacuum to 10 mL, and 50 mL of diethyl ether was added. This precipitated an orange solid which was then filtered and dried in vacuo. The reaction yielded 0.2 g of product. The product proved to be very air sensitive so extreme caution was exercised in all manipulations. Although good analytical data were difficult to obtain due to the reactivity, elemental analyses generally support the formulation $U(BH_4)_3$(18-crown-6).

Anal. Calcd for $C_{12}H_{36}O_6B_3U$: C, 26.35; H, 6.64; B, 5.93 ($C_4H_{12}B$). Found: C, 21.68; H, 5.85; B, 4.75 ($C_4H_{13}B$). The ^1H NMR spectra in THF-d_8 also support this formulation with a broad BH_4 singlet at 103 ppm downfield from Me_4Si and a sharp singlet due to 18-crown-6 at 2.9 ppm relative to $Me_4Si = 0$ (uncomplexed 18-crown-6 is observed at 3.3 ppm). The relative intensities of these peaks are as expected 1:2.

Results and Discussion

We have found that $UCl_3(THF)_x$ readily reacts with 18-crown-6 resulting in displacement of the THF's by the crown ether and formation of UCl_3(18-crown-6). Coordination numbers greater than nine are quite common for U(III), and coordination numbers in excess of 12 have been observed. This, coupled with the extreme insolubility of UCl_3(18-crown-6), leads us to believe that a chloride-bridged structure is probably present, but a monomeric nine-coordinate structure cannot be discounted with the present data. The high thermal stability suggests that the uranium atom is actually coordinated to the oxygens of the crown cavity. If such coordination were present, one would expect a rather large paramagnetic shift of the crown ether protons in the ^1H NMR spectrum. Such shifts of 20–30 ppm have been observed for U(IV) complexes,[4] but we cannot be certain as to what magnitude of shift would be expected for similar coordination of uranium(III). The solid-state ^1H NMR spectrum of UCl_3(18-crown-6) shows little, if any, shift of the crown proton resonance from that of uncomplexed 18-crown-6. The peak is, however, very broad, and a shift of ±10 ppm could easily go undetected. More studies are currently under way in hopes of establishing the coordination about the uranium in this complex.

Although UCl_3(18-crown-6) is insoluble in THF, a slurry has been found to react with $NaBH_4$ to yield a soluble product, $U(BH_3)_3$(18-crown-6). Because of the extreme sensitivity to air and water, analytical data for this complex are consistently low in C, H, and B; however, the ratios obtained suggest that the above stoichiometry is probably correct. Similarly, the ^1H NMR spectrum supports the formulation as a 1:1 adduct with an integration of BH_4^- to crown ether protons of 1:2. The 12 BH_4^- protons are equivalent on the NMR time scale and are shifted downfield due to the paramagnetic U(III) center. The 24 crown ether protons are also equivalent yielding a single, sharp peak and are barely shifted from the position of free 18-crown-6. This small shift of the crown protons suggests either that little interaction exists between the paramagnetic U(III) center or that the crown ether is exchanging in solution.

Red crystals have been obtained from THF/diethyl ether solutions of $U(BH_4)_3$(18-crown-6), but some dissociation of the crown ether is observed during the crystallization process.

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Preliminary X-ray crystallographic results establish a stoichiometry of $U(BH_4)_3(18\text{-crown-}6)_{3/4}$ 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.

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

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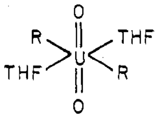
The uranyl ion UO_2^{2+} is the most commonly occurring entity in uranium(VI) chemistry. A large number of complexes have been described with nitrate, sulfate, and related ligands.[1,2] In contrast only a small number of uranyl complexes have been described with alkoxide ligands, though no fluorocarbon alkoxides are known, and no amide derivatives have been prepared. Lithium methoxide and uranyl chloride yield $UO_2(OMe)_2\cdot MeOH$, 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 $OU(OR)_4\cdot ROH$ (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), $UO_2(NO_3)_2\cdot 2THF$, yields the diamagnetic perfluoroalkoxide $UO_2[OC(CF_3)_3]_2\cdot 2THF$. This complex (I, R = $(CF_3)_3CO$) 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 ^1H 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 = $(CF_3)_3CO$. 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_2Cl_2) in tetrahydrofuran yields the diamagnetic, orange-red amide $UO_2[N(SiMe_3)_2]_2\cdot 2THF$ (I, R = $(Me_3Si)_2N$). 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 ^1H 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 (^1H) 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 $C_{16}H_{16}F_{18}O_6U$: 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 $C_{20}H_{52}N_2O_4Si_4U$: C, 32.7; H, 7.08; N, 3.81. Found: C, 32.0; H, 6.96; N, 3.87. The ^1H NMR spectrum (C_6H_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 $(Me_3Si)_2N$ and tetrahydrofuran, respectively.

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Registry No. I (R = $(CF_3)_3CO$), 68212-94-2; I (R = $(Me_3Si)_2N$), 68212-95-3; $UO_2(NO_3)_2\cdot 2THF$, 62364-66-3; UO_2Cl_2, 7791-26-6.

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