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f-Element/Crown Ether Complexes. 10.[1] Oxidation of UCl_4 to $[UO_2Cl_4]^{2-}$ in the Presence of Crown Ethers: Structural Characterization of Crown Ether Complexed Ammonium Ions $[(NH_4)(15\text{-crown-}5)_2]_2[UO_2Cl_4]\cdot 2CH_3CN$, $[(NH_4)(\text{benzo-15-crown-}5)_2]_2[UCl_6]\cdot 4CH_3CN$, and $[(NH_4)(\text{dibenzo-18-crown-}6)]_2[UO_2Cl_4]\cdot 2CH_3CN$ and Synthesis of $[Na(12\text{-crown-}4)_2]_2[UO_2Cl_4]\cdot 2OHMe$ and $[UO_2Cl_2(OH_2)_3]\cdot 18\text{-crown-}6\cdot H_2O\cdot OHMe$

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Trace amounts of H_2O and limited exposure to air of reaction mixtures of UCl_4 and 12-crown-4, 15-crown-5, benzo-15-crown-5, 18-crown-6, or dibenzo-18-crown-6 in 1:3 mixtures of CH_3OH and CH_3CN resulted in the hydrolysis and oxidation of UCl_4 to $[UO_2Cl_4]^{2-}$. In the presence of these crown ethers it has been possible to isolate intermediate products via crystallization of crown complexes of the $[UO_2Cl_4]^{2-}$ ion, the $[UCl_6]^{2-}$ ion, and $[UO_2Cl_2(OH_2)_3]$. The neutral moiety crystallizes as a hydrogen-bonded crown ether complex; however, crown ether complexation of a counterion, either an ammonium ion formed during the oxidation of U(IV) or a Na^+ ion leached from glass reaction vessels, resulted in novel crystalline complexes of the ionic species. $[(NH_4)(15\text{-crown-}5)_2]_2[UO_2Cl_4]\cdot 2CH_3CN$, $[(NH_4)(\text{benzo-15-crown-}5)_2]_2[UCl_6]\cdot 4CH_3CN$, and $[(NH_4)(\text{dibenzo-18-crown-}6)]_2[UO_2Cl_4]\cdot 2CH_3CN$ have been structurally characterized by single-crystal X-ray diffraction techniques. The 15-crown-5 complex crystallizes in the triclinic space group $P\bar{1}$ with (at 22 °C) $a = 9.343$ (1) Å, $b = 13.167$ (7) Å, $c = 15.477$ (9) Å, $\alpha = 66.45$ (5)°, $\beta = 73.08$ (4)°, $\gamma = 69.45$ (3)°, and $D_{\text{calcd}} = 1.46$ g cm^{-3} for $Z = 1$ formula unit. A final conventional R value of 0.044 was obtained by least-squares refinement of 5427 independent observed $[F_o \geq 5\sigma(F_o)]$ reflections. The benzo-15-crown-5 complex is triclinic, $P\bar{1}$, with (at −150 °C) $a = 12.561$ (4) Å, $b = 13.477$ (4) Å, $c = 13.680$ (6) Å, $\alpha = 61.73$ (4)°, $\beta = 78.01$ (3)°, $\gamma = 70.17$ (3)°, $D_{\text{calcd}} = 1.49$ g cm^{-3}, $Z = 1$, and $R = 0.062$ for 6404 observed reflections. The dibenzo-18-crown-6 complex is orthorhombic, *Fddd*, with (at −150 °C) $a = 18.232$ (6) Å, $b = 21.561$ (2) Å, $c = 27.104$ (8) Å, and $D_{\text{calcd}} = 1.56$ g cm^{-3} for $Z = 8$ formula units. The final R value for 1975 observed reflections is 0.034. The ammonium ions interact with the crown ethers via hydrogen-bonding and electrostatic interactions. 15-Crown-5 and benzo-15-crown-5 form 2:1 sandwich cations, allowing no $H_4N^+\cdots[UO_2Cl_4]^{2-}$ interaction. The dibenzo-18-crown-6 complexed ammonium ions are 1:1 and form bifurcated hydrogen bonds with the chlorine atoms in the $[UO_2Cl_4]^{2-}$ anion. The formation of $[Na(12\text{-crown-}4)_2]_2[UO_2Cl_4]\cdot 2OHMe$ and $[UO_2Cl_2(OH_2)_3]\cdot 18\text{-crown-}6\cdot H_2O\cdot OHMe$ has been confirmed by preliminary single-crystal X-ray diffraction studies.

Introduction

The oxidation of UCl_4 to $[UO_2Cl_4]^{2-}$ in the presence of trace amounts of H_2O and air has been known for some time.[2,3] In the presence of benzo-15-crown-5 the slow aerial oxidation of a solution of UCl_3 in THF and incorporation of Na^+ from the glass container resulted in the crystallization of $[Na(\text{benzo-15-crown-}5)]_2[UO_2Cl_4]$, which has been structurally characterized.[4,5] We were intrigued by these reactions and others by Charpin et al.[6] and have thus initiated the present study of UCl_4 and its oxidation products,[3] UO_2Cl_2 and $[UO_2Cl_4]^{2-}$, in the presence of crown ethers in an attempt to isolate novel crown ether complexes of these moieties and their solvates. The isolation of the title complexes also provides an excellent opportunity to use this chemistry to study crown ether complexation of the ammonium ion in the solid state, where little data exist.[7-9]

Results and Discussion

Syntheses. The oxidation of UCl_4 to $[UO_2Cl_4]^{2-}$ in CH_3CN/CH_3OH (3:1) can be qualitatively controlled by limited exposure to air and reaction with trace amounts of water in the solvent. The reactions can be monitored by color changes from forest green to bright yellow.[2,3] When crown ethers are added to the original reaction mixtures, it is possible to isolate crystalline complexes of the oxidized metal ion, solvates of the unoxidized ion, and complexes of intermediate species such as UO_2Cl_2. The control over oxidation of the U(IV) ion appears to be in the amount of time the solution is exposed to the atmosphere. Thus, reactions carried out entirely on the benchtop resulted in the complexes $[Na(12\text{-crown-}4)_2]_2[UO_2Cl_4]\cdot 2OHMe$ (U12), $[(NH_4)(15\text{-crown-}5)_2]_2[UO_2Cl_4]\cdot 2CH_3CN$ (U15), and $[(NH_4)(\text{dibenzo-18-crown-}6)]_2[UO_2Cl_4]\cdot 2CH_3CN$ (UDB18). Reaction mixtures exposed to air for short periods of time resulted in $[(NH_4)(\text{benzo-15-crown-}5)_2]_2[UCl_6]\cdot 4CH_3CN$ (UB15) and $[UO_2Cl_2(OH_2)_3]\cdot 18\text{-crown-}6\cdot H_2O\cdot OHMe$ (U18). Crystals of UB15 and U18 in the mother liquor decompose upon further exposure of the solutions to air, and thus far new complexes have not been isolated from these systems.

Despite the presence of unintended NH_4^+ or Na^+ ions, these reactions appear quite reproducible. An examination of UCl_4 and crown ether starting materials, as well as all solvents used, has not revealed an outside source for these ions. The Na^+ ion probably has been leached from the glass as seen in the formation of $[Na(\text{benzo-15-crown-}5)]_2[UO_2Cl_4]$.[4,5] (Addition of a Na^+ salt to the original reaction mixtures from which U12 was isolated resulted in additional crystallization of this complex.) One possible source of the NH_4^+ ion may be from degradation of the acetonitrile solvent during oxidation of UCl_4 to $[UO_2Cl_4]^{2-}$.

Our attempts to preclude all oxygen and water from these systems has led to the isolation of dark green crystalline complexes of UCl_4 solvates (OHMe) with hydrogen-bonded crown ethers (18-crown-6, 12-crown-4). We have been unable to completely characterize these complexes by X-ray crystallography, thus far, due to their air sensitivity and apparent twinning. Unless data are collected at low temperature, these dark green crystals will slowly oxidize, changing color and losing intensity. We are currently continuing our attempts to carry out all the reactions mentioned here under completely anhydrous conditions in order to obtain X-ray-quality crystalline samples.

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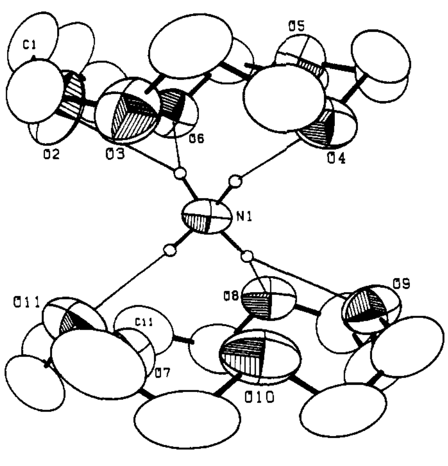

Figure 1. Sandwich cation in $[(NH_4)(15\text{-crown-}5)_2]_2[UO_2Cl_4]\cdot 2CH_3CN$. The atoms are represented by their 50% probability thermal ellipsoids.

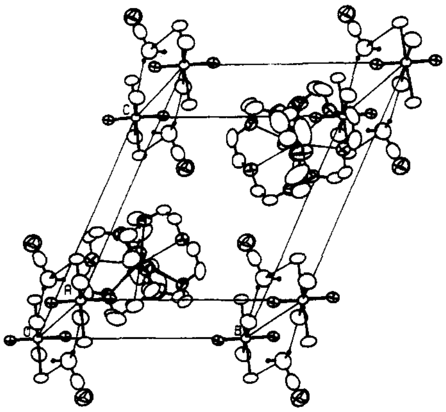

Figure 2. Cell packing diagram for U15.

Table I. Bond Distances (Å) and Angles (deg) for $[(NH_4)(15\text{-crown-}5)_2]_2[UO_2Cl_4]\cdot 2CH_3CN$

U–Cl(1)	2.645 (2)	U–Cl(2)	2.682 (2)
U–O(1)	1.763 (5)		
O–C(av)	1.42 (3)	C–C(av)	1.47 (4)
N(2)–C(21)	1.13 (1)	C(21)–C(22)	1.44 (1)
Cl(1)–U–Cl(2)	92.06 (6)	Cl(1)–U–O(1)	90.3 (2)
Cl(2)–U–O(1)	89.7 (1)	Cl(1)–U–Cl(1)^a	180.0
Cl(1)–U–Cl(2)^a	87.97 (6)	Cl(1)–U–O(1)^a	89.7 (2)
Cl(2)–U–Cl(2)^a	180.0	Cl(2)–U–O(1)^a	90.4 (1)
O(1)–U–O(1)^a	180.0		
C–O–C(av)	114 (8)	O–C–C(av)	110 (3)
N(2)–C(21)–C(22)	179 (2)		

[a] Atoms related to those in Table VIII by $-x, -y, -z$.

Overall Structures. In U15 the $[UO_2Cl_4]^{2-}$ anion resides on a center of inversion and contains two $[(NH_4)(15\text{-crown-}5)_2]^+$ sandwich cations (shown in Figure 1) and two solvent molecules per formula unit. Two of the methyl hydrogen atoms in the CH_3CN molecules participate in weak C–H···Cl hydrogen bonds with chlorine atoms from two different anions related by a unit translation along *a*, resulting in the polymeric nature of the anions and CH_3CN molecules seen in the unit cell packing diagram (Figure 2). Important average distances and angles are given in Table I.

UB15 has an overall structure very similar to that of U15. The $[UCl_6]^{2-}$ anions reside on centers of inversion in $P\bar{1}$, with two sandwich $[(NH_4)(\text{benzo-}15\text{-crown-}5)_2]^+$ cations (Figure 3) and four acetonitrile molecules completing the formula unit. The solvent methyl groups have close contacts with the chlorine atoms, indicating weak hydrogen-bonding interactions. The unit cell packing is shown in Figure 4; important average distances and angles are given in Table II. The published structure of $[Na(\text{benzo-}15\text{-crown-}5)]_2[UO_2Cl_4]$[4,5] does not contain sandwich cations, and the structural features are much more similar to those found for UDB18 discussed below.

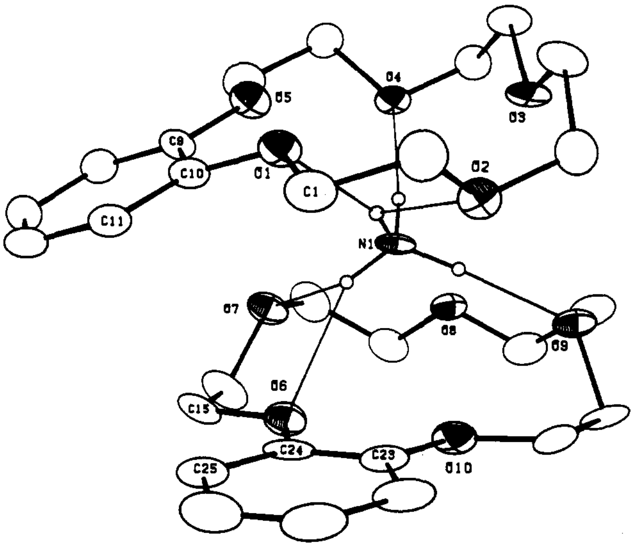

Figure 3. Sandwich cation in $[(NH_4)(\text{benzo-}15\text{-crown-}5)_2]_2[UO_2Cl_4]\cdot 4CH_3CN$.

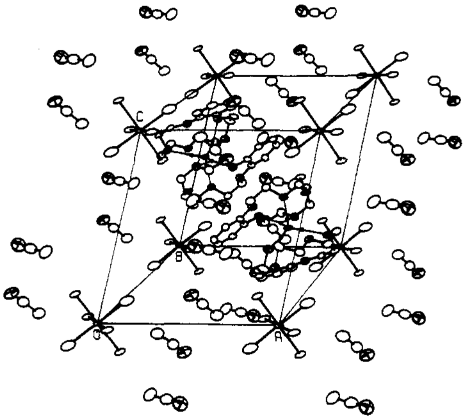

Figure 4. Cell packing diagram for UB15.

Table II. Bond Distances (Å) and Angles (deg) for $[(NH_4)(\text{benzo-}15\text{-crown-}5)_2]_2[UCl_6]\cdot 4CH_3CN$

U–Cl(1)	2.644 (2)	U–Cl(2)	2.641 (2)
U–Cl(3)	2.553 (4)		
O–C(av)	1.43 (2)	O–C(ar)	1.37 (2)
C(ar)–C(ar)^b	1.39 (2)	C–C(av)	1.50 (2)
N(2)–C(29)	1.12 (1)	N(3)–C(31)	1.19 (2)
C(29)–C(30)	1.51 (2)	C(31)–C(32)	1.45 (2)
Cl(1)–U–Cl(2)	89.50 (6)	Cl(1)–U–Cl(3)	91.73 (9)
Cl(2)–U–Cl(3)	87.94 (9)	Cl(1)–U–Cl(1)^a	180.0
Cl(1)–U–Cl(2)^a	90.50 (6)	Cl(1)–U–Cl(3)^a	88.27 (9)
Cl(2)–U–Cl(2)^a	180.0	Cl(2)–U–Cl(3)^a	92.06 (9)
Cl(3)–U–Cl(3)^a	180.0		
C(ar)–O–C(av)	118 (1)	C–O–C(av)	113 (1)
O–C–C(av)	109 (3)	C(ar)–C(ar)–C(ar)	120 (2)
O(5)–C(9)–C(10)	114 (1)	O(1)–C(10)–C(9)	114.1 (8)
O(5)–C(9)–C(14)	127.0 (7)	O(1)–C(10)–C(11)	127.2 (8)
O(10)–C(23)–C(24)	117.5 (8)	O(6)–C(24)–C(23)	113.4 (7)
O(10)–C(23)–C(28)	124 (1)	O(6)–C(24)–C(25)	123 (1)
N(2)–C(29)–C(30)	179 (1)	N(3)–C(31)–C(32)	177 (1)

[a] Atoms related to those in Table IX by $-x, -y, -z$. [b] Aryl carbon atoms are designated ar.

There is no interaction between formula units in the structure of UDB18. The uranium atom resides on a crystallographic 222 site and is surrounded by two ammonium ion complexed di-

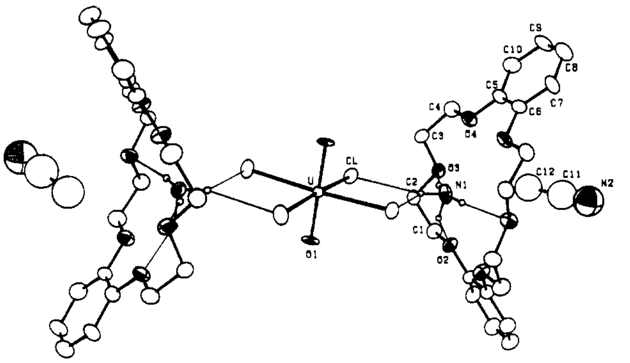

Figure 5. Formula unit for $[(NH_4)(\text{dibenzo-18-crown-6})]_2[UO_2Cl_4]\cdot 2CH_3CN$.

Table III. Bond Distances (Å) and Angles (deg) for $[(NH_4)(\text{dibenzo-18-crown-6})]_2[UO_2Cl_4]\cdot 2CH_3CN$

U-Cl	2.669 (1)	U-O(1)	1.755 (5)
O(2)-C(1)	1.446 (6)	O(2)-C(6)^a	1.376 (7)
O(3)-C(2)	1.431 (6)	O(3)-C(3)	1.434 (6)
O(4)-C(4)	1.437 (6)	O(4)-C(5)	1.381 (6)
C(1)-C(2)	1.493 (7)	C(3)-C(4)	1.508 (7)
C(5)-C(6)	1.393 (7)	C(5)-C(10)	1.393 (7)
C(6)-C(7)	1.388 (7)	C(7)-C(8)	1.402 (8)
C(8)-C(9)	1.363 (8)	C(9)-C(10)	1.389 (8)
N(2)-C(11)	1.04 (3)	C(11)-C(12)	1.41 (2)
		C(12)-C(12)	1.14 (4)
Cl-U-Cl^a	87.20 (5)	Cl-U-Cl^b	176.01 (7)
Cl-U-Cl^c	92.94 (5)	Cl-U-O(1)	88.01 (3)
Cl-U-O(1)^a	91.99 (3)	O(1)-U-O(1)^a	180.0
C(1)-O(2)-C(6)^a	115.5 (4)	C(2)-O(3)-C(3)	112.2 (4)
C(4)-O(4)-C(5)	116.3 (4)	O(2)-C(1)-C(2)	109.1 (4)
O(3)-C(2)-C(1)	107.7 (5)	O(3)-C(3)-C(4)	106.7 (5)
O(4)-C(4)-C(3)	108.0 (5)	O(4)-C(5)-C(6)	116.1 (5)
O(4)-C(5)-C(10)	124.4 (5)	C(6)-C(5)-C(10)	119.5 (6)
O(2)^a-C(6)-C(5)	115.8 (5)	O(2)^a-C(6)-C(7)	124.0 (5)
C(5)-C(6)-C(7)	120.3 (6)	C(6)-C(7)-C(8)	119.4 (5)
C(7)-C(8)-C(9)	120.3 (6)	C(8)-C(9)-C(10)	120.6 (6)
C(5)-C(10)-C(9)	119.9 (6)	N(2)-C(11)-C(12)	177 (3)

^{a} Atoms related to those in Table X by $^1/_4 - x, y, {}^1/_4 - z$. ^{b} $x, {}^1/_4 - y, {}^1/_4 - z$. ^{c} $^1/_4 - x, {}^1/_4 - y, z$.

benzo-18-crown-6 molecules (Figure 5). The ammonium ion resides on, and the crown ether around, a twofold axis that also bisects one of the Cl-U-Cl angles. The ammonium ions are disordered and form three hydrogen bonds to the crown ether and one bifurcated hydrogen bond along the twofold axis with two chlorine atoms of the anion. The solvent molecules are disordered about the twofold axis and are trapped in an envelope formed by two eclipsed dibenzo-18-crown-6 molecules with all four benzo groups bending toward the solvent molecules. The methyl groups of the CH_3CN moieties interact weakly with the crown oxygen atoms as observed in dibenzo-18-crown-6·$2CH_3CN$[11] and 18-crown-6·$2CH_3CN$.[12] A cell packing diagram is presented in Figure 6; distances and angles are given in Table III.

Both $[Na(\text{12-crown-4})_2]_2[UO_2Cl_4]\cdot 2OHMe$ and $[UO_2Cl_2(OH_2)_3]\cdot\text{18-crown-6}\cdot H_2O\cdot OHMe$ have been characterized by preliminary single-crystal X-ray diffraction studies. Their overall structures are briefly discussed in the Experimental Section.

NH_4^+ Environments. In the title complexes the NH_4^+ ions interact with the crown ether oxygen atoms via electrostatic ion···dipole and hydrogen-bonding interactions. The cations in U15 and UB15 interact exclusively with two crown ether molecules, forming a sandwich complex. The NH_4^+···O contacts range from 2.92 (1) [O(11)] to 3.096 (6) Å [O(8)] and average 3.00 (6) Å for U15 and from 2.87 (1) [O(9)] to 3.080 Å [O(1)] and average 2.96 (7) Å for UB15. The hydrogen atoms were easily located (despite the presence of uranium) but not refined. In both U15 and UB15 there is one single hydrogen bond and one bifurcated hydrogen bond to each crown ether (see Tables IV and V). In each case the shortest N···O contacts involve the crown oxygen atoms participating in the single hydrogen bond: U15, O(4) (2.923 (6) Å) and O(11) (2.92 (1) Å); UB15, O(4) (2.888 (7) Å) and O(9) (2.87 (1) Å). The bifurcated hydrogen bonds in UB15 each utilize one aryl ether oxygen atom. The less basic aryl ether oxygen atoms exhibit the longest N···O contacts in UB15: 3.04 (3) Å for O(1), O(5), O(6), and O(10) versus 2.91 (5) Å for the remaining six contacts.

In the sandwich cations, the mean planes defined by the five oxygen atoms of each crown ether are nearly parallel (∂ = 9.3°

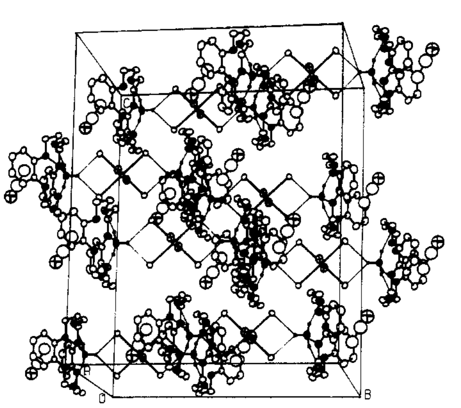

Figure 6. Cell packing diagram for UDB18.

Table IV. Hydrogen-Bonding Contact Geometries for $[(NH_4)(\text{15-crown-5})_2]_2[UO_2Cl_4]\cdot 2CH_3CN^a$

N(1)-O(2)	3.040 (8)	N(1)-O(7)	3.037 (8)
N(1)-O(3)	3.019 (7)	N(1)-O(8)	3.096 (6)
N(1)-O(4)	2.923 (6)	N(1)-O(9)	2.973 (7)
N(1)-O(5)	3.077 (9)	N(1)-O(10)	2.973 (7)
N(1)-O(6)	2.983 (6)	N(1)-O(11)	2.92 (1)
H(1)[N(1)]-O(9)	2.13	C(22)-Cl(1)^b	3.476 (9)
H(1)[N(1)]-O(8)	2.21	C(22)-Cl(1)^b	3.55 (1)
H(2)[N(1)]-O(11)	2.07	C(22)-Cl(2)	3.67 (1)
H(3)[N(1)]-O(6)	2.22		
H(3)[N(1)]-O(2)	2.30	H(1)[C(22)]-Cl(1)^b	2.63
H(4)[N(1)]-O(4)	2.12	H(2)[C(22)]-Cl(2)	2.74
N(1)-H(1)[N(1)]-O(9)	136.4	C(22)-H(1)[C(22)]-Cl(1)^b	160.1
N(1)-H(1)[N(1)]-O(8)	141.2	C(22)-H(2)[C(22)]-Cl(2)	160.5
N(1)-H(2)[N(1)]-O(11)	168.5		
N(1)-H(3)[N(1)]-O(6)	141.9		
N(1)-H(3)[N(1)]-O(2)	138.5		
N(1)-H(4)[N(1)]-O(4)	159.6		

^{a} Distances are given in angstroms and angles in degrees. ^{b} Atoms related to those in Table VIII by $1 - x, -y, -z$.

Table V. Hydrogen-Bonding Contact Geometries for $[(NH_4)(\text{benzo-15-crown-5})_2]_2[UCl_6]\cdot 4CH_3CN^a$

N(1)-O(1)	3.080 (8)	N(1)-O(6)	3.01 (1)
N(1)-O(2)	2.90 (1)	N(1)-O(7)	3.01 (1)
N(1)-O(3)	2.91 (1)	N(1)-O(8)	2.894 (8)
N(1)-O(4)	2.888 (7)	N(1)-O(9)	2.87 (1)
N(1)-O(5)	3.031 (9)	N(1)-O(10)	3.028 (8)
H(1)[N(1)]-O(9)	1.87	H(3)[N(1)]-O(1)	1.99
H(2)[N(1)]-O(6)	2.20	H(3)[N(1)]-O(2)	2.08
H(2)[N(1)]-O(7)	2.28	H(4)[N(1)]-O(4)	2.10
C(30)-Cl(1)	3.55 (1)	C(32)-Cl(2)	3.66 (1)
C(30)-Cl(2)^b	3.76 (1)		
C(30)-Cl(3)^b	3.56 (1)		
N(1)-H(1)[N(1)]-O(9)	170.8	N(1)-H(3)[N(1)]-O(1)	151.8
N(1)-H(2)[N(1)]-O(6)	144.9	N(1)-H(3)[N(1)]-O(2)	123.5
N(1)-H(2)[N(1)]-O(7)	134.6	N(1)-H(4)[N(1)]-O(4)	170.7

^{a} Distances are given in angstroms and angles in degrees. ^{b} Atoms related to those in Table IX by $-x, -y, -z$.

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Table VI. Hydrogen-Bonding Contact Geometries for $[(NH_4)(\text{dibenzo-18-crown-6})]_2[UO_2Cl_4]\cdot 2CH_3CN$[a]

N(1)–Cl	3.401 (5)	C(12)–N(1)	3.68 (2)
N(1)–O(2)	2.937 (4)	C(12)–O(2)	3.53 (2)
N(1)–O(3)	2.920 (4)	C(12)–O(3)	3.39 (2)
N(1)–O(4)	2.974 (4)	C(12)–O(4)	3.43 (2)
H(1)[N(1)]–Cl	2.65	H(2)[N(1)]–O(3)[b]	2.00
H(3)[N(1)]–O(2)	1.87		
N(1)–H(1)[N(1)]–Cl	135.9	N(1)–H(2)[N(1)]–O(3)[b]	165.6
N(1)–H(3)[N(1)]–O(2)	150.3		

[a] Distances are given in angstroms and angles in degrees. [b] Atoms related to those in Table X by $^1/_4 - x, y, ^1/_4 - z$.

(U15), 9.4° (UB15)). N(1) resides 1.85 Å from the mean plane of O(2)–O(6) and 1.81 Å from that of O(7)–O(11) in U15 and 1.82 Å (O(11)–O(15)) and 1.80 Å (O(6)–O(10)) in UB15. The benzo groups are slightly staggered and tilted toward each other in the latter complex.

The $[(NH_4)(\text{dibenzo-18-crown-6})]^+$ cations in UDB18 exhibit direct interaction (via hydrogen bonding) with the $[UO_2Cl_4]^{2-}$ anions. The ammonium ion is centered 1.14 Å above the plane of the six oxygen atoms (away from the fold of the benzo groups). The uranium atom resides on a 222 crystallographic site and therefore does not contribute to the class of reflections $h + k + l = 2n + 1$ or $4n$. As a result, it was possible to locate the disordered hydrogen atoms. N(1) resides on a twofold axis, its hydrogen atoms disordered. One hydrogen atom resides on the twofold axis and is directed between one of the Cl–U–Cl angles. This hydrogen forms bifurcated hydrogen bonds with these two chlorine positions (H···Cl = 2.65 Å, N(1)···Cl = 3.401 (5) Å; see Table VI). The remaining hydrogen atoms are disordered about the twofold axis. It is interesting to note that the closest N(1)···O contact is with the more basic alkyl ether oxygen O(3) (2.920 (4) Å). The furthest contact is N(1)···O(4) = 2.974 (4) Å. The N(1)···O(2) separation is 2.937 (4) Å.

The similarity between UDB18 and $[Na(\text{benzo-15-crown-5})]_2[UO_2Cl_4]$, as discussed in ref 5, is striking. In the latter complex, Na^+ was incorporated from the glass reaction vessel and this ion behaves in essentially the same manner as the ammonium ion in UDB18. The Na···O contacts range from 2.40 to 2.57 Å, and the Na···Cl distances are 2.82 and 2.95 Å, completely different from the sandwich ion structure we observe in UB15 for this same ether.

A few ammonium ion complexes have been structurally characterized,[7-9] although none are sandwich ions. In $[(NH_4)(\text{18-crown-6})]Br\cdot 2H_2O$,[9] there are three ammonium ion hydrogen bonds to the crown ether and the N···O contacts involving these interactions average 2.871 Å. $[(NH_4)(\text{dibenzo-18-crown-6})][\text{pic}]$[7] (pic = picrate) has two different crown ether environments. Both have two hydrogen bonds exclusively to the more basic alkyl ethers, but from the more hindered side in one (in the direction of the benzo group folding) and from the less hindered side (as in UDB18) in the other. The N···O hydrogen-bonding contacts average 3.064 Å in the former and 3.148 Å in the latter. In UDB18 the hydrogen bonding is different: there are three hydrogen bonds from the ammonium ion to the crown ether, and as a result the ammonium ion penetrates deeper into the crown cavity. The nitrogen atom resides only 1.14 Å out of the plane of the six oxygen atoms compared to 1.42 and 1.56 Å for the same values in $[(NH_4)(\text{dibenzo-18-crown-6})][\text{pic}]$. (The first value corresponds to the NH_4^+ ion on the less hindered side.) $[(NH_4)(\text{dibenzo-18-crown-6})]_2[Co(NCS)_4]\cdot 2(CH_3)_2CO$[8] has also been characterized. The ammonium ion is on the more hindered side of the crown ether and out of the six-oxygen-atom plane by 1.02 Å. Three hydrogen bonds are assumed, and the N···O contacts average 2.93 Å.

$[UO_2Cl_4]^{2-}$ and $[UCl_6]^{2-}$ Anions. The anions for all three ionic complexes are normal, the linear uranyl moiety and four chlorine atoms giving uranium an octahedral geometry in U15 and UDB18. Each chlorine atom participates in a hydrogen bond. The U=O and U–Cl separations average 1.755 (5) and 2.669 (1) Å (UDB18) and 1.763 (5) and 2.66 (3) Å (U15). These values fall within the range found for other uranyl tetrachloride compounds including the following: $[NMe_4]_2[UO_2Cl_4]$ (1.724 (7), 2.65 (1) Å),[13] [protonated 2,6-diacetylpyridine–bis(phenylhydrazine)]$_2$-$[UO_2Cl_4]\cdot CH_3CN$ (1.79 (1), 2.70 (1) Å),[14] [(protonated thiamine)]$_2[UO_2Cl_4]$ (1.78 (1), 2.67 (1) Å),[15] and $[NEt_4]_2[UO_2Cl_4]$ (1.758, 2.67 Å).[16] The three unique U–Cl separations in UB15 are 2.644 (2), 2.641 (2), and 2.553 (4) Å. Each has a solvent methyl group contact close enough for hydrogen bonding.

Crown Ether Conformation. Structurally the complexation of NH_4^+ has not had a major influence on the crown ethers. In U15 the C–O (1.42 (3) Å) and C–C (1.47 (4) Å) distances and C–O–C (114 (8)°) and C–C–O (110 (3)°) angles have large standard deviations but compare nicely with other 15-crown-5 and 18-crown-6 room-temperature structures. Similarly the bond distances and angles found for dibenzo-18-crown-6 in UDB18 at −150 °C are almost identical with those found in the literature and in dibenzo-18-crown-6·2CH$_3$CN and dibenzo-18-crown-6·2CH$_3$NO$_2$ also determined at −150 °C.[11] The average crown parameters for UB15 are given in Table V.

The torsion angles around the dibenzo-18-crown-6 ring in UDB18 are virtually identical with those found in complexes of this crown ether with complexed cations or neutral solvent molecules, again demonstrating the rigidity imposed on the molecule by the benzo substituents. The O–C–C–O angles involving the alkyl groups are denoted as "±*g*" (±60°), the C–C–O–C angles are all "*a*" (180°), and the O–C–C–O angles of the benzo carbons are "*s*" (0°). The unique angles starting with C(1)–C(2) are 63.0, 175.7, −174.6, −62.0, 178.7, −178.6, 0.8, 178.8, and 178.9°.

15-crown-5 is a more flexible molecule, and conformational changes are expected. The two unique crown ether molecules in U15 have the same conformation. The O–C–C–O torsion angles are all "±*g*". Three of the C–C–O–C angles have large deviations from the "*a*" orientation, which minimizes CH$_2$···H$_2$C repulsions. Differences found for 15-crown-5 conformations in the literature usually involve the alternation of sign for the O–C–C–O angles (±*g*) and the number and size of deviations of C–C–O–C angles from 180°. The sandwich structure of the $[(NH_4)(\text{15-crown-5})_2]^+$ cation provides oxygen contacts on one side of the crown ether only. The O–C–C–O angles do not alternate but rather have the pattern g^+, g^+, g^+, g^-, g^-, and three of the C–C–O–C angles deviate from 180°. These deviations occur between consecutive O–C–C–O angles that have the same sign, as expected. When C–C–O–C angles are forced "*g*", they usually are greater than 70° as a result of nonbonded H···H repulsion. The absolute values of the seven such angles in U15 average 87°.

The disorder of one of the 15-crown-5 molecules results in O–C–C–O angles of g^-, g^-, g^-, g^+, g^+ or g^+, g^-, g^-, g^+, g^+, essentially identical conformations. In $[Ba(\text{15-crown-5})_2]Br_2\cdot 2H_2O$,[17] a structure with a similar sandwich complex of Ba^{2+}, the two 15-crown-5 molecules adopt different conformations. One conformation is similar to that observed in U15; the other contains O–C–C–O angles of the same sign (all g^-). A more symmetric conformation is observed in the low-temperature structure of $[Y(OH_2)_8]Cl_3\cdot$15-crown-5.[18] Here the crown ether has hydrogen bonds on either side of the crown ether and its conformation resembles the D_{3d} form of 18-crown-6 ($g^+aag^-aag^+aag^-aag^+aag^-aa$).[19] The O–C–C–O angles alternate g^+, g^-, g^+, g^-, g^-, and

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Table VII. Crystal Data and Summary of Intensity Data Collection and Structure Refinement

compd	$[(NH_4)(15\text{-crown-}5)_2]_2$-$[UO_2Cl_4]\cdot 2CH_3CN$	$[(NH_4)(\text{dibenzo-}18\text{-crown-}6)]_2$-$[UO_2Cl_4]\cdot 2CH_3CN$	$[(NH_4)(\text{benzo-}15\text{-crown-}5)_2]_2$-$[UCl_6]\cdot 4CH_3CN$
color/shape	yellow/parallelepiped	green/parallelepiped	light green/parallelepiped
mol wt	1411	1251	1724
space group	$P\bar{1}$	*Fddd*	$P\bar{1}$
temp, °C	22	−150	−150
cell constants[a]			
a, Å	9.343 (1)	18.232 (6)	12.561 (4)
b, Å	13.167 (7)	21.561 (2)	13.477 (4)
c, Å	15.477 (9)	27.104 (8)	13.680 (6)
α, deg	66.45 (5)		61.73 (4)
β, deg	73.08 (4)		78.01 (3)
γ, deg	69.45 3)		70.17 (3)
cell vol, Å^3	1609	10654	1916
formula units/unit cell	1	8	1
D_{calcd}, g cm^{-3}	1.46	1.56	1.49
μ(calcd), cm^{-1}	33.3	40.0	22.65
diffractometer/scan	Enraf–Nonius CAD4/θ–2θ		
range of rel transmission factors, %	80/100	61/100	85/100
radiation (graphite monochromator)	Mo Kα (λ = 0.71073 Å)		
max cryst dimens, mm	0.42 × 0.48 × 0.62	0.28 × 0.40 × 0.40	0.32 × 0.45 × 0.60
scan width	0.80 + 0.35 tan θ	0.80 + 0.35 tan θ	0.80 + 0.35 tan θ
std reflcns	(332), (324), (213), (233)	(800), (0,12,0), (0,0,20)	(800), (0,10,0), (0,0,11)
decay of stds, %	±2	±1	−2.5
reflcns measd	5620	2650	6676
2θ range, deg	$2 \leq 2\theta \leq 50$	$2 \leq 2\theta \leq 50$	$2 \leq 2\theta \leq 50$
range of *hkl*	+11,±15,±18	+21,+25,+32	+14,±16,±16
reflcns obsd $[F_o \geq 5\sigma(F_o)]$[b]	5427	1975	6404
computer programs[c]	SHELX[27]		
structure soln	heavy-atom techniques		
no. of params varied	358	156	439
wts	$[\sigma(F_o)^2]^{-1}$		
GOF	1.3	1.9	4.2
$R = \sum\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert/\sum\lvert F_o\rvert$	0.044	0.034	0.062
R_w	0.047	0.033	0.065
largest feature in final diff map, e Å^{-1}	1.2	1.2	4.8 (<1.0 Å from U)

[a] Least-squares refinement of $((\sin\theta)/\lambda)^2$ values for 25 reflections; $\theta > 14°$ (U15), 18° (UDB18), 18° (UB15). [b] Corrections: Lorentz, polarization, and absorption (empirical, ψ scan). [c] Neutral atom scattering factors and anomalous dispersion corrections from ref 28.

only one C–C–O–C angle deviates from 180°, occurring between the two consecutive O–C–C–O angles of like sign (a result of the lower symmetry of 15-crown-5). This same crown ether conformation was observed in $CuBr_2(OH_2)_2\cdot$15-crown-5,[20] again where the crown ether is hydrogen-bonded on either side.

Interestingly, the crown ethers in UB15 adopt essentially the same conformation as in the free ether determined at −150 °C.[21] The O(5)–C(9)–C(10)–O(1) and O(10)–C(23)–C(24)–O(6) torsion angles are nearly synclinal (−0.4 and −1.9°, respectively) as expected. The remaining four C–C torsion angles starting with C(1)–C(2) and C(15)–C(16) have the sequence g^-, g^-, g^+, g^+. As a result there are two C–O–C–C angles that deviate significantly from 180°, again occurring between O–C–C–O torsion angles of like sign. The absolute values of these four angles average 81°.

Solvent Interactions. Two CH_3CN molecules per formula unit crystallize with U15 and UDB18 and four in UB15. The interactions between the solvent and the rest of the complex are quite different. In U15 and UB15, the NH_4^+ ion is sandwiched, preventing any hydrogen bonding to the chlorine atoms. Two of the C–H acidic solvent methyl protons hydrogen-bond to chlorine atoms in two different anions, resulting in a polymeric chain along *a* in U15, and all four chlorines participate such that each anion is interacting with four different solvent molecules. The third solvent hydrogen atom has no hydrogen-bonding interactions. Again in UB15 all six chlorine atoms have close contacts with solvent methyl groups indicative of hydrogen bonding.

The $[UO_2Cl_4]^{2-}$ anion in UDB18 is hydrogen-bonded to the NH_4^+ cation. The solvent molecules are disordered about a twofold axis and interact weakly with the crown ether as found for dibenzo-18-crown-6·$2CH_3CN$.[11] The acetonitrile methyl group C(12) has oxygen contacts averaging 3.45 (6) Å, and C(12) is displaced 2.48 Å from the mean plane of the crown oxygen atoms. It is possible that the disorders of the CH_3CN and NH_4^+ molecules in UDB18 are complementary, the two orientations utilizing all six crown oxygen atoms. It is worth noting that unlike the two acetonitrile complexes of 18-crown-6 and dibenzo-18-crown-6, which decompose readily when removed from solution, UDB18 is much more stable. This may be due to the envelope-like nature of the crown ethers in the title complex essentially trapping the solvent molecules and preventing their ready loss.

Conclusions

No direct complexation between the crown ether and the uranium ion has been observed in the reactions of UCl_4 and 12-crown-4, 15-crown-5, benzo-15-crown-5, 18-crown-6, or dibenzo-18-crown-6 in acetonitrile/methanol (3:1) when the reaction mixtures are exposed to air. Instead, solid solvates or hydrates of UCl_4 or UO_2Cl_2 are formed with crown ethers hydrogen-bonded in the lattice. When oxidized to $[UO_2Cl_4]^{2-}$, the crown ethers complex counterions generated in the oxidation of U(IV) to U(VI) or leached from the glass containers and crystallize as ionic solids. Structural differences in the complexed counterions and even complexation of the NH_4^+ ion versus Na^+ can be related directly to crown ether size, crown substituents, and solvent. The control of actual overall structure in the complexes discussed here appears to lie in maximization of hydrogen bonding to the crown ether and to the anion by both the ammonium ion itself and the solvent.

Experimental Section

Synthesis and Crystallization of $[(NH_4)(15\text{-crown-}5)_2]_2[UO_2Cl_4]\cdot 2CH_3CN$ (U15). Under argon, 10 mmol of 15-crown-5 in 20 mL of CH_3CN/CH_3OH (3:1) was added to a stirring solution of 10 mmol of UCl_4 in 20 mL of the same solvent. The reaction mixture was heated to 60 °C for 10 h and allowed to cool to 20 °C. The resultant solution was slowly concentrated to 10–20 mL and stored at −20 °C. After 10

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months, greenish yellow single crystals slowly crystallized out of the reaction solution. Although the reaction was initially carried out under inert conditions, subsequent exposure to air and trace amounts of H_2O present in the crown starting material and solvent mixture resulted in the hydrolysis and oxidation of UCl_4 to $[UO_2Cl_4]^{2-}$; mp 130–135 °C. Anal. Calcd for $[(NH_4)(15\text{-crown-}5)_2]_2[UO_2Cl_4]\cdot 2CH_3CN$: C, 37.45; H, 6.72; N, 3.97. Found: C, 37.24; H, 6.72; N, 3.82.

After formation of the title complex, small shifts of 5–40 cm^{-1} of the vibrational spectral bands due to the crown ether were observed in comparison to the band positions of the free crown. The O═U═O stretching frequencies were observed at 945 and 915 cm^{-1}.

When the X-ray diffraction study of U15 was complete, we reinvestigated the reactions leading to this complex. We found that it was possible to reduce the time leading to crystalline U15 by increasing the amount of exposure to air. Reaction in air allowed crystallization of the title complex in as little as 2 days. Qualitative evaluation of the reaction progress can be followed by solution color change from green to yellow. We have also found that it is possible to isolate crown ether complexes (hydrogen bonded or counterion complexed) of solvated UCl_4 and UO_2Cl_2, as well as of $[UO_2Cl_4]^{2-}$.

Synthesis and Crystallization of $[(NH_4)(\text{benzo-15-crown-5})_2]_2[UCl_6]\cdot 4CH_3CN$ (UB15). Under argon 1.3 mmol of UCl_4 in 4 mL of 3:1 CH_3CN/CH_3OH was mixed and 1.3 mmol of benzo-15-crown-5 added. The mixture was stirred at 60 °C for 1 h and centrifuged and the solution stored at 20 °C. After 2 days clear crystals of dibenzo-30-crown-10 formed. The entire solution was exposed to air during isolation of these crystals. The solution was resealed, heated to 60 °C to redissolve all solid and crystalline material (approximately 1 h), and cooled over a 24-h period to 20 °C. Very large green crystals of the title complex formed. These crystals lose CH_3CN rapidly (within 45 s) when removed from solution and quickly go to powder. An elemental analysis was carried out on the powder. Anal. Calcd for $[(NH_4)(\text{benzo-15-crown-5})_2]_2[UCl_6]$: C, 44.28; H, 5.84; N, 1.84. Found: C, 43.35; H, 5.74; N, 1.76.

Synthesis and Crystallization of $[Na(12\text{-crown-}4)_2]_2[UO_2Cl_4]\cdot 2OHMe$ (U12). To 1.3 mmol of UCl_4 in 5 mL of a 4:1 mixture of CH_3CN/CH_3OH was added 1.3 mmol of 12-crown-4. The mixture was stirred at 60 °C for 1 h and centrifuged warm and the volume reduced by one-third. A few small crystals formed after 1 week at −20 °C. Subsequently, crystals of this complex have been prepared by small additions of a Na^+ salt to the reaction mixture and crystallization at −5 °C. Anal. Calcd for $[Na(12\text{-crown-}4)_2]_2[UO_2Cl_4]\cdot 2OHMe$: C, 35.60; H, 6.33. Found: C, 33.14; H, 5.97.

This complex has been confirmed by single-crystal X-ray diffraction analysis.[22] The greenish yellow crystals are orthorhombic, *Pbca*, with a = 14.393 (4) Å, b = 23.223 (5) Å, c = 14.909 (6) Å, and D_{calcd} = 1.53 g cm^{-3} for Z = 4 formula units. The uranium lies on a center of symmetry. The two crown ethers form an approximate square antiprism around the Na^+ ion as normally observed for the $[Na(12\text{-crown-}4)_2]^+$ cation.[23-26] The methanol groups are hydrogen-bonded to the anion. The current R value is 0.030 based upon 2097 independent observed reflections.

Synthesis and Crystallization of $[UO_2Cl_2(OH_2)_3]\cdot 18\text{-crown-}6\cdot H_2O\cdot OHMe$ (U18). Under argon 1.3 mmol of 18-crown-6 was added to a solution of 1.3 mmol of UCl_4 in a 4:1 mixture of methanol and tetrahydrofuran. (The reaction mixture was briefly exposed to air after a stirring bar was added.) The reaction mixture was stirred at 60 °C for 1 h and centrifuged warm and the volume reduced by half. After 24 h at −5 °C a few yellow crystals formed along the walls of the flask. One crystal was chosen for a preliminary X-ray diffraction study; the rest were redissolved at room temperature, and we have thus far been unable to reisolate this complex. It appears that the amount of air admitted to the reaction flask is a controlling factor.

A preliminary structure was obtained from the X-ray data collected on the isolated crystal.[22] U18 is triclinic, $P\bar{1}$, with a = 9.336 (5) Å, b = 9.408 (5) Å, c = 14.746 (8) Å, α = 79.72 (4)°, β = 86.87 (4)°, γ = 74.68 (4)°, and D_{calcd} = 1.92 g cm^{-3} for Z = 2 formula units. The current R value is 0.142 for 3918 reflections.

The structure of U18 consists of polymeric chains of hydrogen-bonded crown ethers and $[UO_2Cl_2(OH_2)_3]$ pentagonal bipyramids. There are two unique crown ethers, each residing around a center of inversion. Each crown oxygen atom participates in a hydrogen bond, four to coordinated water molecules and two to the uncoordinated H_2O molecule. The uncoordinated water molecule accepts a hydrogen bond from a coordinated one, and the $[UO_2Cl_2(OH_2)_3]$ moieties themselves form hydrogen-bonded dimers via two U–O–H···Cl–U interactions. (The same two atoms participate in the symmetry-related unit.) The methanol group has extremely high thermal motion but appears to be hydrogen-bonded to the second chlorine atom. We hope to publish the details of this structure if better data are obtained.

Table VIII. Final Fractional Coordinates for $[(NH_4)(15\text{-crown-}5)_2]_2[UO_2Cl_4]\cdot 2CH_3CN$

atom	*x/a*	*y/b*	*z/c*	*U*(eqv)[a]
U	0.0000	0.0000	0.0000	0.043
Cl(1)	0.2922 (2)	−0.0731 (2)	0.0246 (2)	0.089
Cl(2)	0.0811 (2)	0.0910 (2)	−0.1901 (1)	0.071
O(1)	−0.0184 (6)	0.1319 (4)	0.0120 (3)	0.074
N(1)	−0.2457 (5)	0.7001 (4)	−0.2902 (3)	0.048
O(2)	0.0852 (7)	0.6925 (6)	−0.3969 (5)	0.104
O(3)	0.0337 (6)	0.5130 (5)	−0.2180 (4)	0.084
O(4)	−0.2451 (6)	0.4580 (4)	−0.2011 (3)	0.062
O(5)	−0.2400 (5)	0.5486 (4)	−0.4002 (3)	0.065
O(6)	−0.1478 (7)	0.7550 (4)	−0.5016 (3)	0.074
O(7)	−0.3249 (6)	0.9474 (4)	−0.2975 (4)	0.076
O(8)	−0.5245 (6)	0.8936 (4)	−0.3727 (3)	0.067
O(9)	−0.5778 (6)	0.7054 (4)	−0.2107 (3)	0.066
O(10)	−0.3704 (8)	0.6597 (5)	−0.0828 (4)	0.089
O(11)	−0.1263 (6)	0.7705 (5)	−0.1748 (4)	0.087
C(1)[b]	0.205 (2)	0.581 (1)	−0.362 (1)	0.083
C(2)[b]	0.173 (2)	0.546 (1)	−0.253 (1)	0.074
C(1)′[b]	0.179 (2)	0.641 (2)	−0.332 (2)	0.173
C(2)′[b]	0.182 (2)	0.516 (2)	−0.289 (2)	0.135
C(3)	0.030 (1)	0.3983 (7)	−0.1945 (6)	0.082
C(4)	−0.127 (1)	0.3902 (6)	−0.1439 (5)	0.079
C(5)	−0.275 (1)	0.4046 (6)	−0.2547 (6)	0.091
C(6)	−0.3501 (9)	0.4919 (7)	−0.3364 (6)	0.078
C(7)	−0.3020 (9)	0.6370 (6)	−0.4798 (5)	0.077
C(8)	−0.179 (1)	0.6895 (7)	−0.5443 (5)	0.077
C(9)	−0.005 (1)	0.7803 (9)	−0.5388 (6)	0.104
C(10)	0.116 (1)	0.7078 (9)	−0.4966 (8)	0.113
C(11)	−0.369 (1)	1.0096 (6)	−0.3896 (5)	0.081
C(12)	−0.527 (1)	1.0047 (7)	−0.3807 (5)	0.081
C(13)	−0.669 (1)	0.8692 (8)	−0.3355 (6)	0.089
C(14)	−0.6907 (9)	0.8093 (7)	−0.2294 (6)	0.087
C(15)	−0.592 (1)	0.6395 (7)	−0.1119 (6)	0.083
C(16)	−0.533 (1)	0.6764 (7)	−0.0541 (6)	0.084
C(17)	−0.314 (1)	0.706 (1)	−0.0363 (7)	0.126
C(18)	−0.152 (1)	0.7032 (9)	−0.0778 (7)	0.128
C(19)	−0.152 (1)	0.8877 (8)	−0.1914 (7)	0.111
C(20)	−0.182 (1)	0.9542 (7)	−0.2907 (7)	0.095
N(2)	0.505 (1)	0.2804 (8)	−0.3380 (6)	0.138
C(21)	0.475 (1)	0.2197 (8)	−0.2649 (8)	0.090
C(22)	0.4295 (9)	0.1412 (8)	−0.1679 (7)	0.099
H(1)[N(1)]	−0.363	0.744	−0.287	(iso)
H(2)[N(1)]	−0.218	0.730	−0.260	(iso)
H(3)[N(1)]	−0.174	0.698	−0.343	(iso)
H(4)[N(1)]	−0.235	0.630	−0.279	(iso)
H(1)[C(22)]	0.518	0.134	−0.144	(iso)
H(2)[C(22)]	0.324	0.139	−0.163	(iso)
H(3)[C(22)]	0.472	0.063	−0.173	(iso)

[a] U(eqv) is equal to $(U_{11} + U_{22} + U_{33})/3$. [b] Occupancy factors 0.5.

Synthesis and Crystallization of $[(NH_4)(\text{dibenzo-18-crown-6})]_2[UO_2Cl_4]\cdot 2CH_3CN$ (UDB18). Under argon 5 mmol of dibenzo-18-crown-6 in 30 mL of a CH_3OH/CH_3CN (1:3) mixture was added to a stirred solution of 5 mmol of UCl_4 in 30 mL of the same solvent. The reaction mixture was heated to 60 °C for 3$^1/_2$ h, and the dark green solution was allowed to cool to 20 °C. The reaction mixture was concentrated to 30–40 mL, and crystals deposited along the walls of the flask; mp 224–226 °C. Anal. Calcd for $[(NH_4)(\text{dibenzo-18-crown-6})]_2[UO_2Cl_4]\cdot 2CH_3CN$: C, 42.24; H, 5.00; N, 4.48. Found: C, 41.59; H, 4.78; N, 3.62.

After formation of the title complex, shifts of 5–25 cm^{-1} in the vibrational spectral bands due to the crown ether were observed compared to those for the free crown. The uranyl stretching frequencies were observed at 960 and 930 cm^{-1}.

X-ray Data Collection, Structure Determination, and Refinement for U15, UB15, and UDB18. Single crystals of the title complexes were

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Table IX. Final Fractional Coordinates for $[(NH_4)(\text{benzo-15-crown})_2]_2[UCl_6]\cdot 4CH_3CN$

atom	*x/a*	*y/b*	*z/c*	*U*(eqv)[a]
U	0.0000	0.0000	0.0000	0.018
Cl(1)	−0.1477 (2)	0.2101 (2)	−0.0624 (2)	0.030
Cl(2)	0.1257 (2)	0.0830 (2)	−0.1842 (2)	0.030
Cl(3)	0.1155 (3)	0.0503 (2)	0.0946 (2)	0.055
N(1)	0.1706 (6)	0.6278 (5)	0.6467 (5)	0.020
O(1)	0.4062 (5)	0.4537 (5)	0.6520 (4)	0.027
O(2)	0.2134 (5)	0.3899 (5)	0.6764 (4)	0.023
O(3)	0.1269 (5)	0.5860 (5)	0.4702 (4)	0.024
O(4)	0.1870 (5)	0.7957 (5)	0.4172 (4)	0.024
O(5)	0.3912 (5)	0.6683 (5)	0.5173 (4)	0.028
O(6)	0.2043 (5)	0.6063 (5)	0.8684 (4)	0.028
O(7)	0.2018 (5)	0.8175 (5)	0.6865 (5)	0.030
O(8)	−0.0174 (5)	0.8324 (5)	0.6252 (4)	0.026
O(9)	−0.0568 (5)	0.6074 (5)	0.6896 (4)	0.025
O(10)	0.0682 (5)	0.4989 (5)	0.8757 (4)	0.025
C(1)	0.3975 (8)	0.3372 (7)	0.7322 (7)	0.027
C(2)	0.3222 (7)	0.3104 (7)	0.6845 (7)	0.029
C(3)	0.1418 (8)	0.3914 (7)	0.6069 (7)	0.029
C(4)	0.1638 (8)	0.4681 (7)	0.4835 (7)	0.030
C(5)	0.1510 (8)	0.6667 (7)	0.3574 (6)	0.029
C(6)	0.1175 (7)	0.7878 (7)	0.3539 (7)	0.028
C(7)	0.2919 (7)	0.8160 (8)	0.3609 (7)	0.029
C(8)	0.3701 (8)	0.7920 (7)	0.4434 (7)	0.032
C(9)	0.4591 (7)	0.6238 (8)	0.6033 (7)	0.028
C(10)	0.4675 (7)	0.5018 (8)	0.6791 (7)	0.027
C(11)	0.5371 (7)	0.4466 (8)	0.7668 (7)	0.029
C(12)	0.5918 (8)	0.5082 (9)	0.7869 (7)	0.037
C(13)	0.5813 (7)	0.6275 (9)	0.7163 (7)	0.040
C(14)	0.5134 (7)	0.6831 (8)	0.6251 (7)	0.030
C(15)	0.2769 (8)	0.6720 (7)	0.8616 (7)	0.033
C(16)	0.2119 (9)	0.7976 (7)	0.7982 (7)	0.037
C(17)	0.1151 (8)	0.9207 (8)	0.6302 (8)	0.040
C(18)	−0.0017 (8)	0.9071 (8)	0.6627 (7)	0.036
C(19)	−0.1245 (8)	0.8133 (8)	0.6580 (7)	0.031
C(20)	−0.1321 (8)	0.7210 (7)	0.6280 (7)	0.029
C(21)	−0.1033 (7)	0.5420 (7)	0.8023 (6)	0.027
C(22)	−0.0076 (7)	0.4468 (8)	0.8674 (7)	0.028
C(23)	0.1621 (8)	0.4302 (8)	0.9326 (7)	0.026
C(24)	0.2368 (8)	0.4842 (8)	0.9326 (6)	0.026
C(25)	0.3347 (8)	0.4242 (8)	0.9905 (7)	0.028
C(26)	0.3565 (8)	0.3014 (8)	1.0540 (7)	0.034
C(27)	0.2841 (8)	0.2456 (8)	1.0536 (7)	0.032
C(28)	0.1859 (8)	0.3070 (8)	0.9951 (7)	0.031
N(2)	−0.4986 (9)	−0.0434 (8)	0.1653 (7)	0.055
C(29)	−0.4466 (9)	0.0120 (9)	0.0981 (9)	0.043
C(30)	−0.378 (1)	0.087 (1)	0.0074 (9)	0.067
N(3)	0.580 (1)	−0.078 (1)	−0.367 (1)	0.082
C(31)	0.482 (1)	−0.027 (1)	−0.3694 (9)	0.059
C(32)	0.362 (1)	0.037 (1)	−0.379 (1)	0.074
H(1)[N(1)]	0.088	0.629	0.656	(iso)
H(2)[N(1)]	0.195	0.647	0.694	(iso)
H(3)[N(1)]	0.243	0.542	0.654	(iso)
H(4)[N(1)]	0.175	0.668	0.581	(iso)
H(1)[C(30)]	−0.385	0.128	0.052	(iso)
H(2)[C(30)]	−0.394	0.102	−0.061	(iso)
H(3)[C(30)]	−0.303	0.030	0.006	(iso)
H(1)[C(32)]	0.333	0.060	−0.469	(iso)
H(2)[C(32)]	0.353	0.107	−0.373	(iso)
H(3)[C(32)]	0.321	−0.010	−0.320	(iso)

[a] *U*(eqv) is equal to $(U_{11} + U_{22} + U_{33})/3$.

Table X. Final Fractional Coordinates for $[(NH_4)(\text{dibenzo-18-crown-6})]_2[UO_2Cl_4]\cdot 2CH_3CN$

atom	*x/a*	*y/b*	*z/c*	*U*(eqv)[a]
U	0.1250	0.1250	0.1250	0.014
Cl	0.13009 (9)	0.21464 (6)	0.05718 (5)	0.027
O(1)	0.2213 (2)	0.1250	0.1250	0.029
N(1)	0.1250	0.3473 (3)	0.1250	0.028
O(2)	0.2579 (2)	0.4036 (2)	0.0832 (1)	0.026
O(3)	0.1325 (2)	0.3954 (2)	0.0244 (1)	0.027
O(4)	−0.0015 (2)	0.4020 (2)	0.0711 (1)	0.028
C(1)	0.2612 (3)	0.4053 (3)	0.0299 (2)	0.029
C(2)	0.1999 (3)	0.3672 (3)	0.0094 (3)	0.026
C(3)	0.0698 (3)	0.3649 (3)	0.0035 (2)	0.028
C(4)	0.0036 (3)	0.4025 (3)	0.0181 (2)	0.033
C(5)	−0.0585 (3)	0.4356 (3)	0.0915 (2)	0.025
C(6)	−0.0622 (3)	0.4360 (3)	0.1428 (2)	0.025
C(7)	−0.1179 (3)	0.4681 (2)	0.1666 (2)	0.032
C(8)	−0.1713 (3)	0.4988 (3)	0.1385 (2)	0.039
C(9)	−0.1677 (3)	0.4983 (3)	0.0883 (2)	0.038
C(10)	−0.1120 (3)	0.4664 (3)	0.0642 (2)	0.035
N(2)	0.103 (1)	0.5702 (8)	0.1824 (6)	(iso)
C(11)	0.109 (1)	0.546 (1)	0.1496 (9)	(iso)
C(12)	0.121 (2)	0.516 (1)	0.1041 (8)	(iso)
H(1)[N(1)]	0.125	0.303	0.125	(iso)
H(2)[N(1)][b]	0.123	0.356	0.159	(iso)
H(3)[N(1)][b]	0.184	0.353	0.110	(iso)

[a] *U*(eqv) is equal to $(U_{11} + U_{22} + U_{33})/3$. [b] Occupancy factors 0.75.

mounted in air on a pin and transferred to the goniometer head. UB15 and UDB18 were cooled to −150 °C by utilizing a stream of cold nitrogen gas. A summary of data collection parameters is given in Table VII.

Density calculations for U15 suggested that the uranium atom resided on a center of inversion in the space group $P\bar{1}$. A difference Fourier map phased on the uranium atom readily revealed the positions of the non-hydrogen atoms. Least-squares refinement with isotropic thermal parameters led to $R = 0.056$. An examination of the carbon atoms C(1) and C(2) of one of the 15-crown-5 ethers indicated disorder. C(1)′ and C(2)′ were located and refined (in alternate cycles) with 50% occupancy factors. Hydrogen atoms for the crown ether molecules were placed in calculated positions 0.95 Å from the bonded carbon atom and allowed to ride on that atom with *B* fixed at 5.5 Å^2. Reasonable hydrogen atom positions for the NH_4^+ molecule and the solvent methyl group were easily located from a difference Fourier map and included with fixed contributions ($B = 5.5$ Å^2). The final values of the positional parameters are given in Table VIII.

UB15 was solved and refined in an identical manner. The isotropic *R* value was 0.094. Solvent hydrogen atoms were not located. Positional parameters are given in Table IX.

The position of the uranium atom in UDB18 on a crystallographic 222 position was revealed via inspection of a Patterson map. Large thermal parameters and unrealistic C–C distances associated with the solvent molecule indicated that the CH_3CN moiety was disordered about a twofold axis. Atoms C(11), C(12), and N were refined with occupancy factors of 0.5. These atoms were treated isotropically throughout the refinement, and no attempt was made to locate the methyl hydrogen atoms. Least-squares refinement with isotropic thermal parameters led to $R = 0.065$. Hydrogen atoms associated with the crown ether were placed in calculated positions 0.95 Å from the bonded carbon atom and allowed to ride on that atom with *B* fixed at 5.5 Å^2. An examination of a difference Fourier map around N(1) revealed two possible orientations of the three hydrogen atoms. H(1)[N(1)] oriented along the C_2 axis toward the anion was full weighted (occupancy factor 0.5). H(2)[N(1)] and H(3)[N(1)] were each three-fourths weighted (occupancy factors 0.75). The final values of the positional parameters are given in Table X.

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Registry No. U15, 111267-68-6; UB15, 111267-69-7; U12, 111267-71-1; U18, 111267-72-2; UDB18, 111267-73-3; UCl_4, 10026-10-5.

Supplementary Material Available: Tables SI–SXIV, listing bond distances and angles, hydrogen atom coordinates, thermal parameters, least-squares planes results, and torsion angles (25 pages); Tables SXV–SXVII, listing observed and calculated structure factors (52 pages). Ordering information is given on any current masthead page.