Mn–O(bridging)–Mn entity is characterized by Mn–O_b = 2.053 Å, Mn–O_b–Mn = 109.4°, and Mn–Mn = 3.351 Å[36] versus Mn–O_b = 2.155 or 2.206 Å, Mn–O_b–Mn = 112.2 Å, and Mn–Mn = 3.6 Å in $Mn^{II}_3(CH_3CO_2)_6(bpy)_2$. The Mn–$O_b$–Mn system is less

"compact" in $Mn^{II}_3(CH_3CO_2)_6(bpy)_2$ than in $[L'_2Mn_2-(CH_3CO_2)_2OH]^+$.

Supplementary Material Available: Structure determination details (Table S1), H atom positions (Table S2), anisotropic thermal parameters (Table S3), distances and angles (Table S4) for non-H atoms, and distances and angles (Table S5) for H atoms (8 pages); a listing of structure factors (9 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry, Northern Illinois University, DeKalb, Illinois 60115

Synthesis and Structural Elucidation of Novel Uranyl–Crown Ether Compounds Isolated from Nitric, Hydrochloric, Sulfuric, and Acetic Acids

Robin D. Rogers,* Andrew H. Bond, William G. Hipple, Andrew N. Rollins, and Rodger F. Henry

The reactions of $UO_2SO_4 \cdot 3H_2O$ with 12-crown-4, 15-crown-5, benzo-15-crown-5, 18-crown-6, and dibenzo-18-crown-6 were investigated in nitric, acetic, hydrochloric, and sulfuric acids. Impurities in the nitric acid resulted in the isolation of the complexes $[(H_5O_2)((NO_2)_2benzo-15-crown-5)_2]_2[(UO_2(NO_3)_2)_2C_2O_4]$ (benzo-15-crown-5 was nitrated during the reaction) and $[(H_3O)(18-crown-6)]_2[(UO_2(NO_3)_2)_2C_2O_4]$, which were crystallographically characterized. $[Mg(OH_2)_6][(H_3O)(15-crown-5)]_2[(UO_2(SO_4))_2C_2O_4]_2$ was also isolated from nitric acid and partially characterized crystallographically. Reactions in acetic acid produced uranyl sulfate polymers with layers of hydrogen-bonded crown ethers in the lattice: $[UO_2(SO_4)(OH_2)_2] \cdot 0.5(12-crown-4) \cdot H_2O$, $[UO_2(SO_4)(OH_2)_2] \cdot 0.5(benzo-15-crown-5) \cdot 1.5H_2O$, and $[UO_2(SO_4)(OH_2)_3] \cdot 0.5(18-crown-6)$. Hydronium ion complexes of crown ethers stabilized by $[UO_2Cl_4]^{2-}$ anions were isolated from hydrochloric acid. The complexes $[(H_5O_2)(H_9O_4)(benzo-15-crown-5)_2][UO_2Cl_4]$ and $[(H_5O_2)_2(18-crown-6)][UO_2Cl_4]$ were isolated and crystallographically characterized. Reactions in sulfuric acid for the most part produced decomposition products. $[(H_3O)(dibenzo-18-crown-6)][HSO_4] \cdot CH_3CN$ was isolated by recrystallization of a purple precipitate from CH_3CN/CH_3OH (3:1). $[(H_5O_2)((NO_2)_2benzo-15-crown-5)_2]_2[(UO_2(NO_3)_2)_2C_2O_4]$ crystallizes in the monoclinic space group $P2_1/n$ with (at 22 °C) a = 8.995 (4) Å, b = 19.684 (5) Å, c = 24.739 (4) Å, β = 90.42 (2)°, and D_{calcd} = 1.81 g cm^{-3} for Z = 2 formula units. A final conventional R value of 0.038 was obtained by least-squares refinement with 4790 independent observed reflections $[F_o \geq 5\sigma(F_o)]$. $[(H_3O)(18-crown-6)]_2[(UO_2(NO_3)_2)_2C_2O_4]$ is monoclinic, $P2_1/n$, with (at 22 °C) a = 9.804 (1) Å, b = 21.037 (7) Å, c = 11.827 (3) Å, β = 94.70 (2)°, D_{calcd} = 1.97 g cm^{-3} for Z = 2, and R = 0.040 for 2587 observed reflections. $[UO_2(SO_4)(OH_2)_2] \cdot 0.5(12-crown-4) \cdot H_2O$ is triclinic, $P\bar{1}$, with (at 22 °C) a = 7.007 (1) Å, b = 8.0408 (6) Å, c = 10.776 (2) Å, α = 91.31 (1)°, β = 93.60 (2)°, γ = 100.18 (1)°, D_{calcd} = 2.83 g cm^{-3}, Z = 2, and R = 0.032 for 1883 observed reflections. $[UO_2(SO_4)(OH_2)_2] \cdot 0.5(benzo-15-crown-5) \cdot 1.5H_2O$ is triclinic, $P\bar{1}$ with (at 22 °C) a = 6.908 (2) Å, b = 8.717 (4) Å, c = 13.578 (2) Å, α = 79.46 (2)°, β = 75.28 (2)°, γ = 89.98 (3)°, D_{calcd} = 2.41 g cm^{-3}, Z = 2, and R = 0.056 for 2261 observed reflections. $[UO_2(SO_4)(OH_2)_3] \cdot 0.5(18-crown-6)$ is monoclinic, $P2_1/n$, with (at 20 °C) a = 9.314 (5) Å, b = 9.339 (3) Å, c = 16.734 (3) Å, β = 103.62 (3)°, D_{calcd} = 2.59 g cm^{-3} for Z = 4, and R = 0.071 for 1649 observed reflections. $[(H_5O_2)(H_9O_4)(benzo-15-crown-5)_2][UO_2Cl_4]$ is triclinic, $P\bar{1}$, with (at 20 °C) a = 8.889 (3) Å, b = 10.149 (3) Å, c = 11.626 (3) Å, α = 94.54 (2)°, β = 91.04 (2)°, γ = 104.29 (3)°, D_{calcd} = 1.74 g cm^{-3}, Z = 1, and R = 0.034 for 3455 observed reflections. $[(H_5O_2)_2(18-crown-6)][UO_2Cl_4]$ is triclinic, $P\bar{1}$, with (at −150 °C) a = 6.9265 (8) Å, b = 9.239 (1) Å, c = 10.429 (2) Å, α = 93.34 (1)°, β = 103.50 (1)°, γ = 106.15 (1)°, D_{calcd} = 2.02 g cm^{-3}, Z = 1, and R = 0.025 for 2153 observed reflections. $[(H_3O)(dibenzo-18-crown-6)][HSO_4] \cdot CH_3CN$ is triclinic, $P\bar{1}$, with (at 18 °C), a = 9.118 (2) Å, b = 9.348 (5) Å, c = 15.879 (4) Å, α = 77.60 (3)°, β = 80.99 (2)°, γ = 78.22 (3)°, D_{calcd} = 1.34 g cm^{-3}, Z = 2, and R = 0.073 for 1070 observed reflections.

Introduction

Few of the separation studies of the uranyl ion with crown ethers have actually demonstrated metal ion crown ether coordination.[1-13] The probability of the O=U=O^{2+} ion threading through a crown ether is low. Characterization of uranium complexes is usually limited to dicyclohexyl-18-crown-6 (e.g., $[UO_2(dicyclohexyl-18-crown-6)][ClO_4]_2$;[14] note the use of the poorly coordinating ClO_4^-

anion). Other crown ether complexes of uranium that have been structurally characterized include $[U(BH_4)_2(dicyclohexyl-18-crown-6)]_2[UCl_5(BH_4)]$[15] and $[UCl_3(dicyclohexyl-18-crown-6)]_2[UCl_6]$.[16] Inner-sphere complexes have also been reported for several uranium(III) chlorides and crown ethers[17] as well as $[UCl_3(18-crown-6)]$ and $[U(BH_4)_3(18-crown-6)]$.[18]

It is interesting to note the utility ascribed to dicyclohexyl-18-crown-6 and dicyclohexyl-24-crown-8 in uranyl ion extractions. Our structural results with dicyclohexyl-24-crown-8 and other reports in the literature[19-22] for dicyclohexyl-18-crown-6 and dicyclohexyl-24-crown-8 all indicate the presence of hydronium

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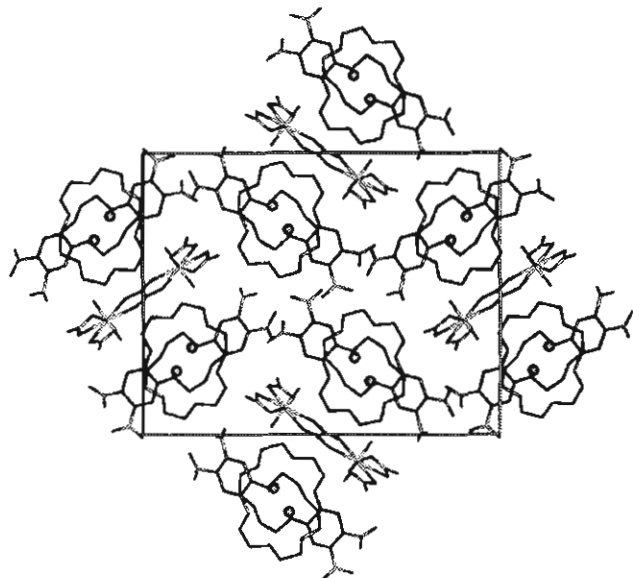(22) Wang, W.-J.; Jie, L.; Hong, S.; Peiju, Z.; Ming, W.; Boyi, W. *Radiochim. Acta* **1986**, *40*, 199.

Figure 1. SYBYL representation of a *yz* view of [(H₅O₂)((NO₂)₂benzo-15-crown-5)₂]₂[(UO₂(NO₃)₂)₂C₂O₄]. (SYBYL Molecular Modeling Software: Tripos Associates, Inc., St. Louis, MO.)

ion crown ether complexes only.

The preponderance of actinide separation processes that use or lead to high-level radioactive wastes in nitric acid and hydrochloric acid[23-26] spurred us to initiate the investigation of the reactions of the weakly associated sulfate salts of the uranyl ion with crown ethers in these acids. This report details our investigation of the crystalline products of reactions of uranyl salts and crown ethers in acidic media.

Preparation of Complexes. The reactions of $UO_2SO_4\cdot3H_2O$ with 12-crown-4, 15-crown-5, benzo-15-crown-5, 18-crown-6, and dibenzo-18-crown-6 were investigated in nitric, acetic, hydrochloric, and sulfuric acids. Products from the reactions in nitric acid were dominated by impurities in the acid. The complexes [(H₅O₂)((NO₂)₂benzo-15-crown-5)₂]₂[(UO₂(NO₃)₂)₂C₂O₄] and [(H₃O)(18-crown-6)]₂[(UO₂(NO₃)₂)₂C₂O₄] were isolated and crystallographically characterized. (Benzo-15-crown-5 was nitrated during this reaction.) [Mg(OH₂)₆][(H₃O)(15-crown-5)]₂[(UO₂(SO₄))₂C₂O₄]₂ was also isolated from nitric acid and partially characterized crystallographically.

Reactions in acetic acid produced uranyl sulfate polymers with layers of hydrogen-bonded crown ethers in the lattice. [UO₂(SO₄)(OH₂)₂]·0.5(12-crown-4)·H₂O, [UO₂(SO₄)(OH₂)₂]·0.5-(benzo-15-crown-5)·1.5H₂O, and [UO₂(SO₄)(OH₂)₃]·0.5(18-crown-6) were isolated and crystallographically characterized.

In the strong acid HCl, hydronium ion complexes of crown ethers stabilized by [UO₂Cl₄]²⁻ anions were isolated. The complexes [(H₅O₂)(H₉O₄)(benzo-15-crown-5)₂][UO₂Cl₄] and [(H₅O₂)₂(18-crown-6)][UO₂Cl₄] were isolated and crystallographically characterized.

In general, reactions in sulfuric acid produced decomposition products. When dibenzo-18-crown-6 was used in 2.25 M H_2SO_4, a purple precipitate formed immediately. Crystallization of this solid from a 3:1 CH₃CN/CH₃OH solution afforded the crystalline product [(H₃O)(dibenzo-18-crown-6)][HSO₄]·CH₃CN, which was crystallographically characterized. A similar reaction in 4.45 M H_2SO_4 produced crystalline UO₂(SO₄)·2.5H₂O as the only characterizable product.

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Figure 2. [(UO₂(NO₃)₂)₂C₂O₄]²⁻ anion in the (NO₂)₂benzo-15-crown-5 complex. Atoms are represented with their 50% probability ellipsoids for thermal motion.
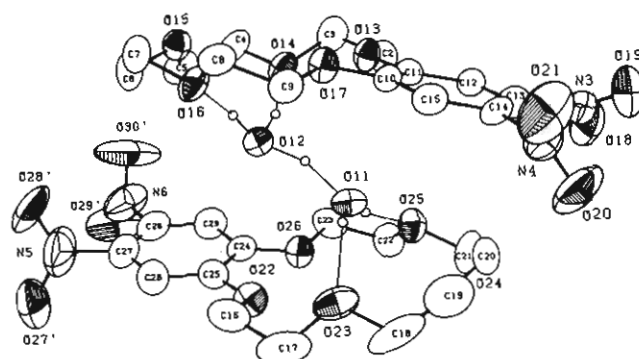

Figure 3. [(H₅O₂)((NO₂)₂benzo-15-crown-5)₂]⁺ cation.

The complexes studied in this report were obtained in low to moderate yields. Reaction conditions were purposely designed to provide diffraction-quality crystals and not to maximize yields.

Structural Results. **[(H₅O₂)((NO₂)₂benzo-15-crown-5)₂]₂-[(UO₂(NO₃)₂)₂C₂O₄].** This complex crystallizes as discrete cation, anion pairs (Figure 1). The anion consists of two UO₂(NO₃)₂ groups bridged by an oxalate ion (Figure 2), giving each uranium center a hexagonal-bipyramidal geometry. The anions are packed in columns along *a* with the anions at about 45° relative to the *a* axis. Four columns of sandwich cations surround each column of anions. These columns are also along *a*.

The anion resides on a crystallographic center of inversion (on the C(1)–C(1)′ bond axis). The coordinated nitrate ion and oxalate ion oxygens form a plane to within 0.032 Å. The average U=O, U–O(oxalate), and U–O(nitrate) distances are 1.738 (7), 2.440 (7), and 2.48 (2) Å, respectively. The oxalate ion is planar to within 0.006 Å, with the uranium atoms 0.10 Å out of this plane. This type of oxalate ion bridging has been observed previously.[27-29]

In the cation, one H₅O₂⁺ hydronium ion is sandwiched between two dinitrobenzo-15-crown-5 molecules (Figure 3). The location of the hydrogen atoms revealed hydrogen bonds to the more basic ethyl ether oxygen atoms with two such interactions to each other. Including the hydrogen atom between O(11) and O(12), each hydronium oxygen atom is pyramidal. The O···O contacts between the oxonium ion and the hydrogen-bonded etheric oxygen

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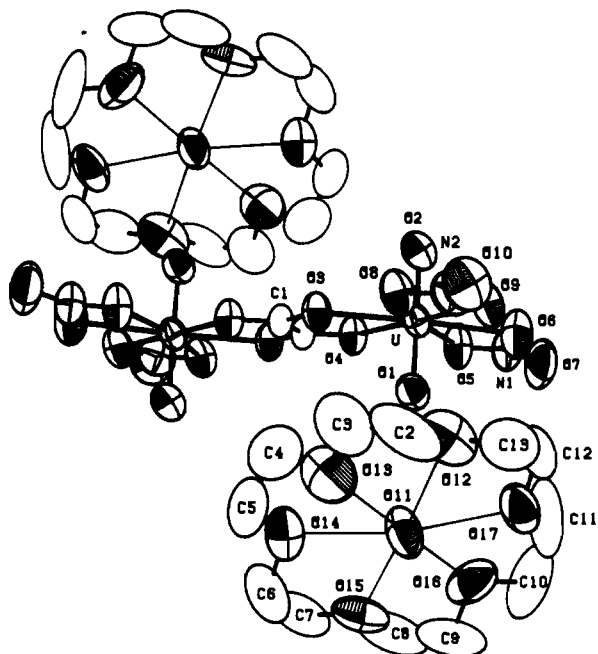
Figure 4. [(H₃O)(18-crown-6)]₂[(UO₂(NO₃)₂)₂C₂O₄] formula unit.

atoms (O(14), O(16), O(23), O(25)) range from 2.635 (8) to 2.688 (8) Å and average 2.67 (2) Å. The remaining contacts range from 2.899 (8) (O(11)–O(24)) to 3.120 (7) Å (O(12)–O(17)) and average 3.01 (8) Å. The aryl ethers exhibit the longest O···O contacts. The O(11)–O(12) separation is 2.429 (7) Å.

The observed conformation of the macrocycle positions two etheric oxygens toward the hydronium ion for hydrogen bonding. This conformation is rather symmetrical, with the O–C–C–O torsion angles alternating ±g (±60°) (except for the synclinal aryl positions of each molecule) and the C–O–C–C all anti (180°). This is the only conformation of benzo-15-crown-5 that gives good overlap angles (O···O···O) and avoids using aryl oxygen atoms in the hydrogen bonding. Within the macrocycle, the average C–C(alkyl), C–C(aryl), C–O(alkyl), and C–O(aryl) distances are 1.48 (3), 1.39 (2), 1.43 (2), and 1.356 (9) Å, respectively. The average O–C(alkyl)–C(alkyl), O–C(aryl)–C(aryl), C(alkyl)–O–C(aryl), and C(alkyl)–O–C(alkyl) angles are 109 (2), 114.8 (6), 119.8 (6), and 113 (2)°, respectively. The nitro groups (including each conformation of the disordered N(5) and N(6) groups) are twisted relative to the planes defined by the benzo substituents. Dihedral angles of 32.6 (N(3)), 46.5 (N(4)), 24.3 (N(5)), 63.2 (N(5) alternate orientation), 27.5 (N(6)), and 78.3° (N(6) alternate orientation) were observed.

The conformation observed for the crown ether is not the same as found for the free ether (NO₂)₂benzo-15-crown-5,[30] its monosubstituted analogue,[30] or the unsubstituted benzo-15-crown-5.[31] In these three compounds, the major conformation was defined by O–C–C–O torsion angles of g⁻, g⁻, g⁺, g⁺, and s with C–O–C–C angles anti except for one of each pair between C–C angles of like sign, which deviate toward gauche. The orientation of the nitro groups in the free ether are similar to that observed in this study. The observed dihedral angles between the nitro groups and phenyl ring are 47.6 and 41.3° in (NO₂)₂benzo-15-crown-5. In the monosubstituted ether the nitro group resides in the plane of the C₆ ring.

[(H₃O)(18-crown-6)]₂[(UO₂(NO₃)₂)₂C₂O₄]. This complex consists of discrete [(H₃O)(18-crown-6)]⁺ cations and [(UO₂-(NO₃)₂)₂C₂O₄]²⁻ anions (Figure 4). The anions are stacked at a 45° angle along *a*, surrounded by stacks of the cations.

The anion resides on a center of inversion and is identical with that observed in the previous compound. The average U═O,
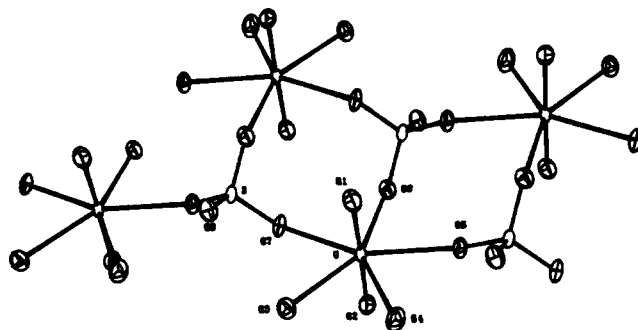

Figure 5. Polymeric nature of [UO₂(SO₄)(OH₂)₂]ₙ in [UO₂(SO₄)-(OH₂)₂]·0.5(12-crown-4)·H₂O.
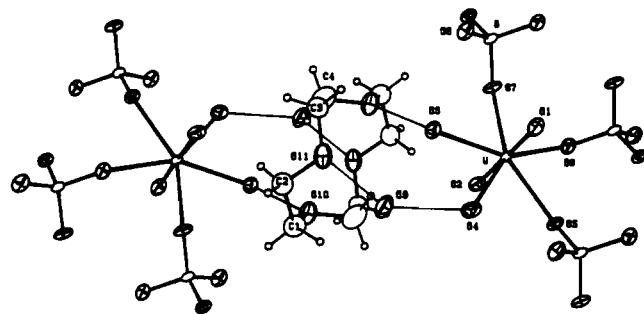
Figure 6. Detail of the hydrogen-bonding interactions separating the polymeric inorganic chains in [UO₂(SO₄)(OH₂)₂]·0.5(12-crown-4)·H₂O.

U–O(oxalate), and U–O(nitrate) distances are 1.728 (4), 2.428 (2), and 2.482 (6) Å, respectively. The 18-crown-6 molecule adopts its normal complexed D_{3d} conformation.[32,33] The average C–C and C–O distances and the C–O–C and O–C–C bond angles are 1.46 (6) Å, 1.44 (5) Å, 110 (5)°, and 106 (3)°, respectively.

The H₃O⁺ hydronium ion resides in the macrocycle cavity and is hydrogen bonded to it. The O(11)···O(13,15,17) contacts are 2.59 (2), 2.69 (2), and 2.68 (1) Å, respectively. The remaining O(11)···O contacts range from 2.78 (2) to 2.82 (2) Å. The high thermal motion of the crown ether prevented location of the hydrogen atoms and probably indicates fluxional behavior of this molecule. There are two possibilities for the hydrogen bonding. First, O(11) could be hydrogen bonded to O(13), O(15), and O(17), which exhibit the shortest O(11)···O contacts; however, O(11) is only 0.005 Å out of the plane defined by these three etheric oxygen atoms. The O(11)···O(12,14,16) contacts are longer (2.80 (2) Å, average) but still within normal O···O separations involving single hydrogen bonds, and O(11) is 0.4 Å out of the plane defined by these three atoms. This would give the hydronium ion a more pyramidal geometry.

[UO₂(SO₄)(OH₂)₂]·0.5(12-crown-4)·H₂O. In this complex, the uranium atom is coordinated to the two uranyl oxygens, two water molecules, and one oxygen atom each from three sulfate anions, giving uranium a pentagonal-bipyramidal geometry. The pentagonal plane is planar to within 0.045 Å. The sulfate anions bridge each uranium atom to two others forming polymeric double chains that propagate along the unit cell direction *a* (Figure 5). Each sulfate ion bridges three uranium centers, and the pentagonal planes of all three are coplanar. This polymeric form has been observed in the structure of α-[UO₂(SO₄)(OH₂)₂]·5H₂O.[34] As observed in our compound, the two water molecules in the primary coordination sphere are cis in the pentagonal plane. In [UO₂-(SO₄)(OH₂)₂]·0.5H₂O,[35] with similar uranyl coordination, the pentagonal coordination planes within the polymeric double chains

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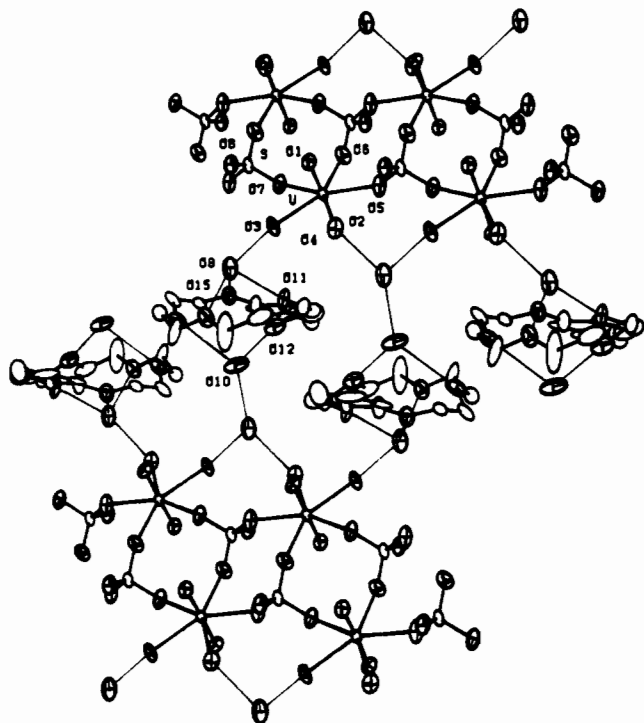(35) van der Putten, N.; Loopstra, B. O. *Cryst. Struct. Commun.* **1974**, *3*, 377.

Figure 7. Hydrogen-bonding interactions in $[UO_2(SO_4)(OH_2)_2]\cdot0.5$-(benzo-15-crown-5)$\cdot1.5H_2O$.

are perpendicular instead of parallel. The average S–O(bridging) distance is 1.483 (4) Å, while the S–O(nonbridging) distance is 1.451 (6) Å. The average U–O(sulfate), U–O(water), and U=O distances are 2.39 (3), 2.42 (2), and 1.769 (8) Å, respectively.

The crown ether and the uncoordinated water molecule form an organic layer, which separates the layers of inorganic polymeric chains. The crown ether resides around a center of inversion and accepts hydrogen bonds from the inorganic chains it separates. On one side of the inversion center the coordinated O(3) and uncoordinated O(9) donate the hydrogen bonds to the ether (Figure 6). The coordinated O(4) donates a hydrogen bond to O(9) and to the uncoordinated sulfate oxygen atom O(8). O(3) also donates one hydrogen bond to a symmetry-related O(8) position. The remaining hydrogen bond from O(9) could be either to the uranyl position O(1) or to the coordinated sulfate oxygen O(6). The distances and angles of the O···O contacts suggest O(6) as the most likely candidate, although the contact is long (3.19 (1) Å).

The crown ether adopts a C_i conformation, which easily accommodates the requirements of hydrogen bonding on both sides of the four oxygen atom plane. The average C–C and C–O distances and C–O–C and C–C–O angles are 1.50 (2) Å, 1.43 (2) Å, 114.8 (8)°, and 110 (2)°, respectively.

$[UO_2(SO_4)(OH_2)_2]\cdot0.5$(benzo-15-crown-5)$\cdot1.5H_2O$. As observed for $[UO_2(SO_4)(OH_2)_2]\cdot0.5$(12-crown-4)$\cdot H_2O$, the compound consists of $[UO_2(SO_4)(OH_2)_2]_n$ polymeric double chains that propagate along *a* and are separated by the crown ether and uncoordinated water molecules (Figure 7). The *a* dimensions of both the 12-crown-4 and benzo-15-crown-5 complexes are nearly identical. The uranium and sulfate environments and bridging modes are identical with those observed in the 12-crown-4 complex. The average bonding parameters in the inorganic layers are U=O = 1.77 (1) Å, U–O(sulfate) = 2.36 (2) Å, U–O(water) = 2.445 (5) Å, S–O(coordinated) = 1.48 (2) Å, and S–O(uncoordinated) = 1.43 (1) Å.

The crown ether and uncoordinated water molecules form an organic layer essentially in *ab* planes that separate and are hydrogen bonded to the stacks of inorganic polymers. The crown ether and water molecule O(10) are statistically disordered, as described in detail in the Experimental Section. The benzo groups are all orientated in the ±*b* direction. The conformation of the crown ether is identical with that observed in $[(H_5O_2)((NO_2)_2$-
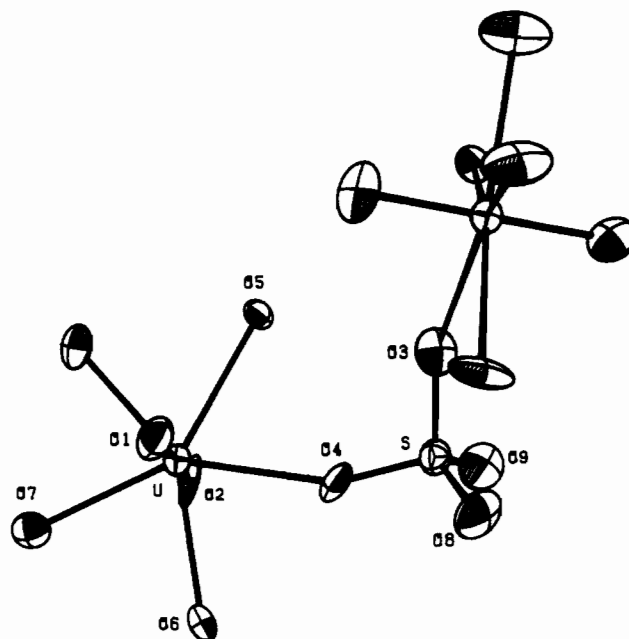
benzo-15-crown-5)$_2]_2[(UO_2(NO_3)_2)_2C_2O_4]$.

Each coordinated water molecule donates one hydrogen bond to an uncoordinated sulfate oxygen atom (O(8)) and to the ordered uncoordinated water molecule (O(9)). Each crown ether molecule and water molecule O(10) are present at 50% occupancy. Thus, O(9) has two different hydrogen-bonding patterns on each side of the disordered ethers. In one orientation, O(9) is hydrogen bonded directly to the crown ether via a single hydrogen bond to O(13) and a bifurcated hydrogen bond to O(11) and O(15). In the second orientation, O(9) is hydrogen bonded to O(10) and possibly the uranyl oxygen O(1). O(10) is hydrogen bonded to the crown ether oxygens O(12) and O(14). This hydrogen-bonding scheme allows all five crown ether oxygen atoms to participate in either orientation.

$[UO_2(SO_4)(OH_2)_3]\cdot0.5$(18-crown-6). Unlike the 12-crown-4 and benzo-15-crown-5 derivatives above, the inorganic uranyl sulfate hydrate bridging produces a single zigzag polymeric chain that propagates along *b*. There are three water molecules in the pentagonal plane of uranium, and consequently, only two sulfate oxygen atoms coordinate uranium atoms. The sulfate oxygen atoms are separated by at least one water molecule within the pentagonal coordination plane. Each sulfate ion bridges two uranium centers. Unlike the previous two compounds discussed, the pentagonal planes of the bridged uranyl moieties in this 18-crown-6 complex intersect with a dihedral angle of 80° making them almost perpendicular (Figure 8). The average bonding parameters are U=O = 1.74 (1) Å, U–O(sulfate) = 2.35 (1) Å, U–O(water) = 2.42 (2) Å, S–O(coordinated) = 1.50 (2) Å, and S–O(uncoordinated) = 1.47 (1) Å.

The 18-crown-6 molecules reside around centers of inversion and are hydrogen bonded to water molecules of two different uranyl centers (Figure 9). There are three hydrogen bonds on each side of the ether. O(7) donates two to the ether (O(11) and O(12) are the acceptors), while O(6) donates one to the etheric O(10) and one to an uncoordinated sulfate oxygen atom (O(8)). The third water molecule, O(5), is hydrogen bonded to one coordinated (O(3)) and one uncoordinated (O(8)) sulfate oxygen atom.

The 18-crown-6 molecule adopts a rather rare conformation. The O–C–C–O torsion angles have the sequence g⁻, g⁻, g⁻, g⁺, g⁺, g⁺. The four C–O–C–C angles between O–C–C–O angles that change sign are all anti. Of the remaining angles that occur between O–C–C–O angles of like sign, one of each pair is anti and one deviates significantly toward gauche (average = 79°). This conformation is the highest energy of the 14 conformations
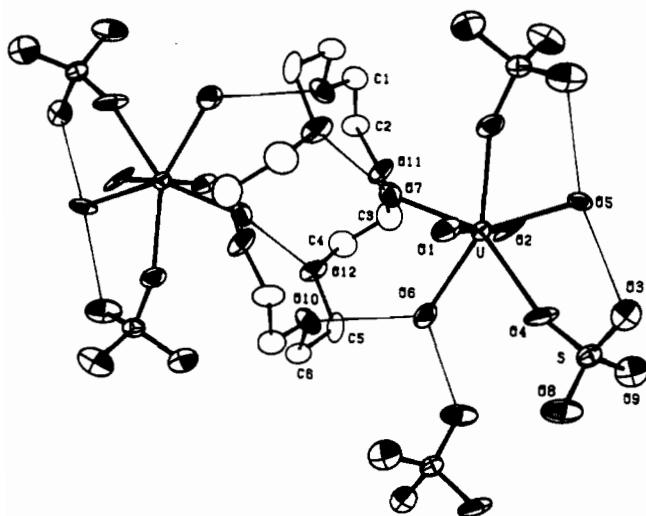

Figure 8. Polymeric nature of $[UO_2(SO_4)(OH_2)_3]_n$ in $[UO_2(SO_4)$-$(OH_2)_3]\cdot0.5(18$-crown-6).

Figure 9. Hydrogen-bonding interactions in $[UO_2(SO_4)(OH_2)_3] \cdot 0.5$-(18-crown-6).
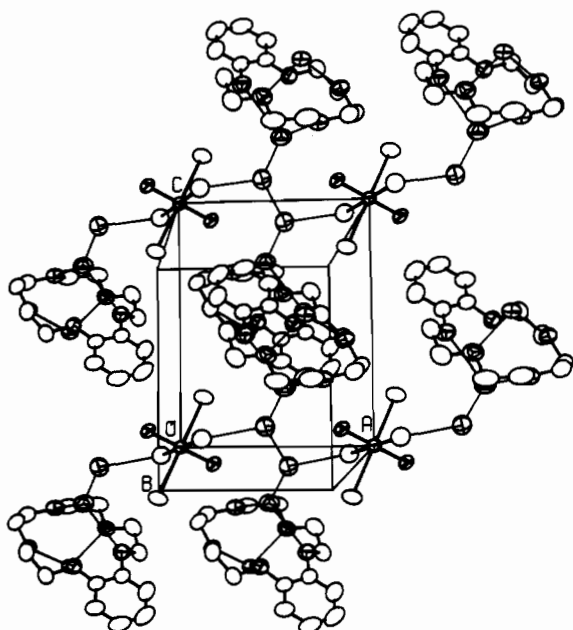
Figure 10. Cell packing in $[(H_5O_2)(H_9O_4)(benzo-15-crown-5)_2]$-$[UO_2Cl_4]$.

calculated by Uiterwijk et al.[32] to have conformational energies ≤ 21 kJ mol^{-1}. We have observed this conformation twice before in complexes with similar hydrogen-bonding interactions, $[Th(NO_3)_4(OH_2)_3] \cdot 18$-crown-6[36] and $[ThCl_2(OH_2)_7]Cl_2 \cdot 18$-crown-$6 \cdot 2H_2O$.[37] In the current study the average bonding parameters in the macroring are C–O = 1.45 (3) Å, C–C = 1.46 (2) Å, C–O–C = 113 (2)°, and O–C–C = 110 (4)°.

$[(H_5O_2)(H_9O_4)(\textbf{benzo-15-crown-5})_2][UO_2Cl_4]$. This complex consists of $[UO_2Cl_4]^{2-}$ anions hydrogen bonded polymerically to $H_9O_4^+$, cations which in turn are hydrogen bonded to the back sides of $[(H_5O_2)(benzo-15-crown-5)_2]^+$ sandwich complexes (Figure 10). The pseudooctahedral $[UO_2Cl_4]^{2-}$ anions reside on crystallographic centers of inversion and are normal with U=O = 1.747 (3) Å and U–Cl = 2.652 (1) and 2.674 (2) Å.

The benzo-15-crown-5 molecules sandwich a hydronium ion $(H_5O_2^+)$, which resides on a center of inversion. The benzo-15-crown-5 molecules have conformations identical with those observed for the similar sandwich cation in $[(H_5O_2)((NO_2)_2$-benzo-15-crown-5)_2]_2[(UO_2(NO_3)_2)_2C_2O_4]$ and for the hydro-

(36) Rogers, R. D.; Kurihara, L. K.; Benning, M. M. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1987**, *C43*, 1056.
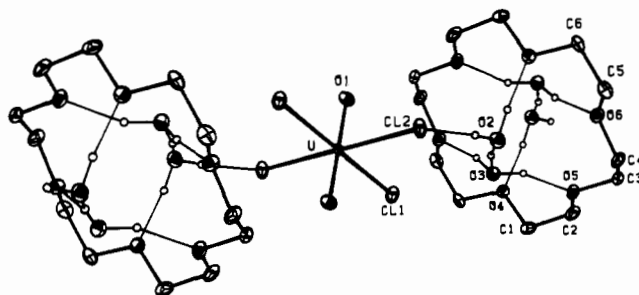(37) Rogers, R. D. *Lanth. Act. Res.* **1989**, *3*, 71.

Figure 11. Portion of the polymeric hydrogen-bonded chains in $[(H_5O_2)_2(18$-crown-6)][UO_2Cl_4]$.

gen-bonded crown ether in $[UO_2(SO_4)(OH_2)_2] \cdot 0.5$(benzo-15-crown-5)$\cdot 1.5H_2O$. The average bonding parameters include C–O(alkyl) = 1.426 (8) Å, C–O(aryl) = 1.380 (7) Å, C–C(alkyl) = 1.497 (7) Å, C–C(aryl) = 1.398 (7) Å, C(alkyl)–O–C(aryl) = 117 (1)°, C(alkyl)–O–C(alkyl) = 113 (1)°, O–C(alkyl)–C-(alkyl) = 108 (1)°, and O–C(aryl)–C(aryl) = 115.6 (5)°.

The hydrogen bonding of the $H_5O_2^+$ cation to the ethers in this complex is the same as observed for the dinitrobenzo-15-crown-5 complex discussed earlier. O(7) donates hydrogen bonds to alkyl ethers O(3) and O(5). The O(7)···O(7)^b separation is 2.427 (7) Å. On the back side of each ether, O(8) donates a single hydrogen bond to alkyl ether O(4) and possibly a bifurcated hydrogen bond to the two aryl ethers O(2) and O(6). The O(8)···O(crown) contacts are in general longer than the $H_5O_2^+$···O(crown) contacts (2.66 (4) Å average), and as expected, the O(8)···O(4) (alkyl ether) distance (2.842 (6) Å) is shorter than the average O-(8)···O(2),O(6) contact of 3.03 (7) Å.

The $H_9O_4^+$ ion is disordered, with three alternate orientations found for O(9) (each with $33^1/_3\%$ occupancy). Despite this, it is relatively easy to sort out how this ion interacts with the remaining ions in the unit cell. First the $H_9O_4^+$ ions reside on centers of inversion and connect the $[(H_5O_2)(benzo-15-crown-5)_2]^+$ sandwich cations into polymeric hydrogen-bonded chains that propagate along *c*. The ends of the $H_9O_4^+$ ions (O(8)) are hydrogen bonded to the back side of a different sandwich ion as discussed above. The two central atoms in this hydronium ion are either O(9)/O(9)^c, O(9)'/O(9)'^{c}, or O(9)''/O(9)''^{c}. One hydrogen atom resides on a center of inversion between these pairs of atoms. Each O(9) position donates one hydrogen bond to a chlorine atom in the anion and one to O(8).

In two of the alternate $H_9O_4^+$ models, O(9) and O(9)'', the donation is to Cl(2). This joins the anions into polymeric chains along *a*. The third model, O(9)', donates to Cl(1). It is noted that with $^2/_3$ of the hydrogen bonding to Cl(2) and only $^1/_3$ to Cl(1), the U–Cl(2) separation (2.674 (2) Å) is longer than observed for U–Cl(1) (2.652 (1) Å).

$[(H_5O_2)_2(\textbf{18-crown-6})][UO_2Cl_4]$. In this complex, the pseudooctahedral $[UO_2Cl_4]^{2-}$ anions are hydrogen bonded to two $H_5O_2^+$ ions via the Cl(2) positions (Figure 11). An elongation of the U–Cl(2) separation (2.706 (1) Å) is observed over the U–Cl(1) distance of 2.657 (1) Å due to this hydrogen bonding. The U=O distance is 1.763 (3) Å.

Each cation is also hydrogen bonded to an 18-crown-6 molecule, which resides around a center of inversion. Thus, the hydrogen bonding forms polymeric chains of the nature (crown ether/cation/anion/cation)$_n$. Each crown molecule accepts three hydrogen bonds each from two cations on opposite sides of the ether. This allows all six etheric oxygen atoms to participate in the hydrogen bonding. O(2), which donates one hydrogen bond to Cl(2) and one to the ether, exhibits the closest approach (O-(2)···O(4)^b = 2.604 (5) Å). O(3) has two hydrogen bonds to the macroring with contacts that average 2.72 (2) Å. The O(2)···O(3) separation is 2.418 (6) Å with one hydrogen almost exactly between the two. O(2) and O(3) are pyramidal, residing 0.31 and 0.35 Å, respectively, out of the plane defined by the three hydrogen atoms bonded to each.

The crown ether displays its common D_{3d} conformation. The average bonding parameters include C–O = 1.443 (4) Å, C–C
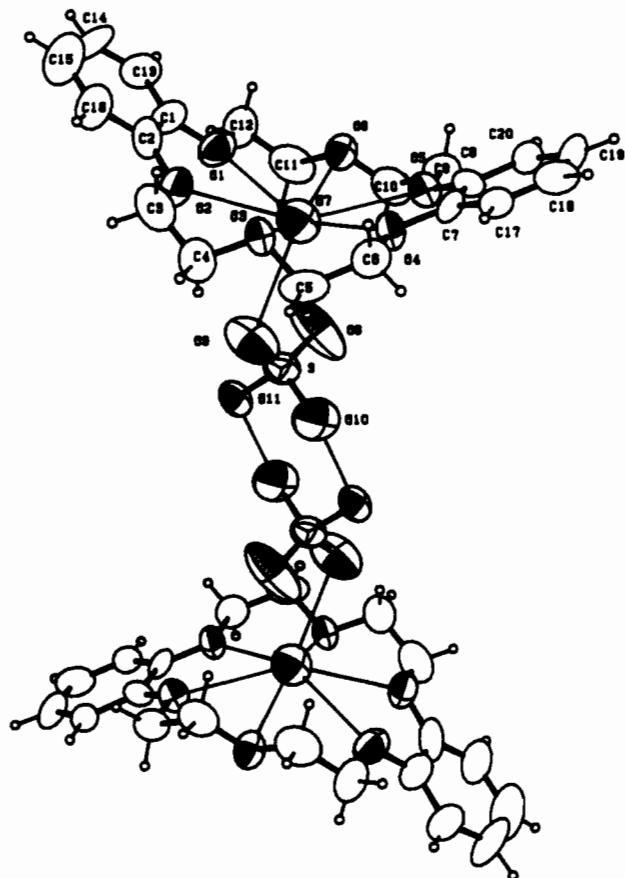
Figure 12. ORTEP illustration of the dimeric nature of [(H₃O)(dibenzo-18-crown-6)][HSO₄]·CH₃CN.

= 1.504 (5) Å, C–O–C = 111.2 (7)°, and O–C–C = 108 (1)°.

[(H₃O)(dibenzo-18-crown-6)][HSO₄]·CH₃CN. This complex crystallizes as a hydrogen-bonded dimer (Figure 12). The tedrahedral SO_4^{2-} molecules are bridged by one acidic proton from each (O(10), O(11)). The second acidic proton is associated with the hydronium ion O(7). O(7) is nearly symmetrically displaced from all six crown ether oxygen atoms. The O(7)···O distances range from 2.81 (2) (O(4)) to 2.89 (1) Å (O(3)) and average 2.85 (3) Å. The hydronium ion is also hydrogen bonded to the anion via O(9) (O(7)···O(9) = 2.83 (2) Å). The overall structure is not unlike that observed for the compound formulated as H₃PO₄·0.5(18-crown-6)·3H₂O.[38]

The two oxygen atoms participating in the strong hydrogen bonds between anions, O(10) and O(11), exhibit the largest S–O separations of 1.50 (1) and 1.51 (1) Å, respectively. The S–O(9) distance is 1.42 (1) Å, reflecting the acceptance of a hydrogen bond from O(7) and the much longer O(7)···O(9) distance. Without any hydrogen interactions the S–O(8) separation is the shortest at 1.37 (1) Å.

The crown ether displays its most commonly observed conformation. The O–C–C–O angles alternate ±g (except for the aryl carbons which are synclinal), and the C–O–C–C torsion angles are all anti. Within the macrocycle the average bonding parameters are O–C(alkyl) = 1.42 (2) Å, O–C(aryl) = 1.37 (1) Å, C–C(alkyl) = 1.49 (2) Å, C–C(aryl) = 1.40 (1) Å, C(alkyl)–O–C(alkyl) = 116 (2)°, C(alkyl)–O–C(aryl) = 113 (1)°, O–C(alkyl)–C(alkyl) = 108 (2)°, and O–C(aryl)–C(aryl) = 116 (3)°.

Discussion

Actinide separations processes must take into account the acidic matrices in which most f-element waste streams are found.[23–26] Consideration must be given not only to the possible extraction species but also to competing ions contaminating the waste stream

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and possible side reactions. The work reported here sheds some light on all of these areas with results that demonstrate ligand attack, contaminant coordination, and possible extraction complexes. In addition, it offers further evidence that actinides in high oxidation states clearly prefer anion or H₂O coordination rather than complexation to a crown ether.[39]

Reactions of UO₂(SO₄) with crown ethers in oxalate ion contaminated nitric acid produce $[(UO_2(NO_3)_2)_2C_2O_4]^{2-}$. The replacement of the weak donor SO_4^{2-} anions with the NO_3^- anions is not unexpected. The affinity for the oxalate impurities to form a binuclear complex supports the observation that oxalate impurities formed in pretreatment steps of the PUREX process may be detrimental to extraction.[40,41] The isolation of a reasonably soluble complex, however, may mean extraction is possible as the hydronium ion complexes observed here, $[(H_5O_2)((NO_2)_2\text{-}benzo\text{-}15\text{-}crown\text{-}5)_2]_2[(UO_2(NO_3)_2)_2C_2O_4]$ and $[(H_3O)(18\text{-}crown\text{-}6)]_2[(UO_2(NO_3)_2)_2C_2O_4]$. The bulky crown molecule hydronium ion complexes formed could provide enough hydrophobicity to allow for some phase transfer to occur. Certainly the formation of a crown ether sandwich around the $H_5O_2^+$ ion would facilitate cation transfer to a hydrophobic phase.

Two other processes taking place in these nitric acid solutions deserve mention. First, the presence of a benzo substituent complicates the reaction with benzo-15-crown-5. The reaction conditions provided here are similar to those observed for nitration of the free ether,[42] and the dinitrobenzo-15-crown-5 ether becomes the primary ligand present in this reaction. (We have reprepared and crystallographically characterized the free ether dinitrobenzo-15-crown-5.[30]) Reactivity of the ligand system must always be a concern in such highly acidic solutions likely to be found in actinide separation processes.

The second process to be wary of is the odd combination of cations and anions possible in these solutions. Even when uranyl sulfate is added to nitric acid, the isolation of sulfate compounds is not precluded. We have isolated the salt UO₂SO₄·2.5H₂O from the reaction of UO₂SO₄·3H₂O with dibenzo-18-crown-6 in nitric acid. In addition, the complex compound $[Mg(OH_2)_6]$- $[(H_3O)(15\text{-}crown\text{-}5)]_2[(UO_2(SO_4))_2C_2O_4]_2$ was isolated from impurities in the nitric acid in a similar reaction with 15-crown-5. This complex has not been completely crystallographically characterized. The oxalate-bridged ion and magnesium aquo ion are quite clearly defined; however, the crown ether portion of the compound is completely disordered.

The reactions of uranyl sulfate with crown ethers in the weak acetic acid produced compounds without hydronium ions or complexed ethers. The polymeric compounds $[UO_2(SO_4)\text{-}(OH_2)_2]\cdot0.5(12\text{-}crown\text{-}4)\cdot H_2O$, $[UO_2(SO_4)(OH_2)_2]\cdot0.5(benzo\text{-}15\text{-}crown\text{-}5)\cdot1.5H_2O$, and $[UO_2(SO_4)(OH_2)_3]\cdot0.5(18\text{-}crown\text{-}6)$ were produced, all of which contain polymeric uranyl sulfate and hydrogen-bonded crown ether molecules. The first two are nearly identical with linear double chains of $[UO_2(SO_4)(OH_2)_2]_n$, while the third forms a single zigzag chain with alternate pentagonal coordination planes perpendicular to one another. It does appear that the hydration of the uranyl sulfate polymer is controlled by the number of hydrogen-bonding acceptors provided by the ether. As an aside, these complexes could have interesting electronic properties such as those observed for the ferroelectric [UO₂-(SO₄)(OH₂)₂]·guanidinium·H₂O.[43]

Reactions in the strong acid HCl produced large $[UO_2Cl_4]^{2-}$ anions stabilized by bulky hydronium ion complexed crown ethers. Both $[(H_5O_2)(H_9O_4)(benzo\text{-}15\text{-}crown\text{-}5)_2][UO_2Cl_4]$ and $[(H_5O_2)_2(18\text{-}crown\text{-}6)][UO_2Cl_4]$ exhibit fairly unusual hydronium ion/crown ether complexation. When Ca²⁺ impurities are present

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in the HCl used in these reactions, it is possible to isolate crown ether complexes of the hard calcium ion. We have previously reported the isolation of $[Ca(12\text{-}crown\text{-}4)_2][UO_2Cl_4]$[44] and $[Ca(OH_2)_3(15\text{-}crown\text{-}5)][UO_2Cl_4]$[44] from the reaction of UO_2SO_4 with crown ethers in HCl.

Only one compound was isolated from H_2SO_4 reaction solutions. In all cases, reactions employing various sulfuric acid concentrations decomposed over time ranges of 24 h to several months. The only solid-state results were obtained by recrystallizing a precipitate that formed immediately upon mixing dibenzo-18-crown-6 and $UO_2SO_4\cdot3H_2O$ in 2.25 M H_2SO_4. The complex was exposed to the acid for approximately 1 h and then recrystallized from an organic mixture. Isolation of $[(H_3O)(dibenzo\text{-}18\text{-}crown\text{-}6)][HSO_4]\cdot CH_3CN$ indicates that, for short periods of time, the crown ether is stable in dilute sulfuric acid solutions. This is a particularly interesting point because, of the crown ethers that we have studied, the aromatically substituted macrocycles are the most susceptible to attack.

The isolation of these complexes has provided the opportunity to study in some detail the complexation of hydronium ions with crown ethers. We have isolated crown ether complexes of H_3O^+, $H_5O_2^+$, and $H_9O_4^+$. All three of these types are discussed in ref 45. Except for the first one, however, crown ether complexes of these ions are rare.

The H_3O^+ complex $[(H_3O)(18\text{-}crown\text{-}6)][(UO_2(NO_3)_2)_2C_2O_4]$ exhibits high thermal motion in the cations. The H_3O^+ molecule has a high vibrational ellipsoid perpendicular to the macroring making it difficult to determine how flattened it really is. It is closer to the odd-membered oxygen atoms ($O\cdots O = 2.65$ (4) Å, average) than it is to the even-numbered oxygen atoms ($O\cdots O = 2.80$ (2) Å, average); however, it is only 0.005 Å out of the plane defined by the former. This situation is similar to that found in $[(H_3O)(18\text{-}crown\text{-}6)]_2[Mo_6O_{19}]$[46] and $[(H_3O)(18\text{-}crown\text{-}6)][H_2Cl]$.[47] The range of all $H_3O^+\cdots O$ contacts in these two structures is reported to be 2.70–2.85 Å. The ion is more clearly pyramidal in $[(H_3O)(dicyclohexyl\text{-}18\text{-}crown\text{-}6)]_2[UCl_6]$,[22] $[(H_3O)(dicyclohexyl\text{-}18\text{-}crown\text{-}6)]_2[UO_2Cl_4]$,[21] $[(H_3O)(18\text{-}crown\text{-}6\text{-}tetracarboxylic acid)]$,[48] $[(H_3O)(dicyclohexyl\text{-}18\text{-}crown\text{-}6)]_2[Th(NO_3)_6]$,[49] $[(H_3O)(18\text{-}crown\text{-}6)]_2[ZnCl_4]$,[50] and $[(H_3O)(18\text{-}crown\text{-}6)]_2[MnCl_4]$.[50] The $H_3O^+\cdots O$ hydrogen-bonded contacts range from 2.51 to 2.74 Å, while the remaining contacts range from 2.76 to 2.99 Å. The contacts are much longer (2.85 (3) Å, average) in the dibenzo-18-crown-6 complex $[(H_3O)(dibenzo\text{-}18\text{-}crown\text{-}6)][HSO_4]\cdot CH_3CN$.

The $H_5O_2^+$ ion has been isolated in two interesting types of crown ether complexes, the 1:2 sandwich ions of benzo-15-crown-5 in $[(H_5O_2)((NO_2)_2benzo\text{-}15\text{-}crown\text{-}5)_2]_2[(UO_2(NO_3)_2)_2C_2O_4]$ and $[(H_5O_2)(H_9O_4)(benzo\text{-}15\text{-}crown\text{-}5)_2][UO_2Cl_4]$ and the 2:1 complex of 18-crown-6 in $[(H_5O_2)_2(18\text{-}crown\text{-}6)][UO_2Cl_4]$. The sandwich cations are nearly identical. The crown ethers have the same conformation, orientation, and hydrogen-bonding pattern. The $O\cdots O$ separations within the $H_5O_2^+$ cations are nearly identical (2.429 (7) Å, dinitrobenzo-15-crown-5 complex; 2.427 (7) Å, benzo-15-crown-5 complex). The closest approach of each cation of the ether involves a hydrogen-bonding interaction. These $O\cdots O$ contacts have a narrow range of 2.619 (5)–2.695 (4) Å for both complexes. The remaining cation crown contacts range from 2.899 (8) to 3.272 (6) Å. Among the few crystallographically examined $H_5O_2^+$/crown ether complexes are $[(H_5O_2)(dicyclo$-

hexyl-24-crown-8)$]_2[UO_2Cl_4]\cdot C_6H_6$,[20] $[(H_5O_2)(dicyclohexyl\text{-}24\text{-}crown\text{-}8)]_2[UCl_6]\cdot OHMe$,[51] and $[(H_5O_2)(dicyclohexyl\text{-}24\text{-}crown\text{-}8)]_2[UO_2Cl_4]\cdot OHMe$.[51] Due to the large cavity size of dicyclohexyl-24-crown-8, at least one $H_5O_2^+$ ion in each of these determinations is positionally disordered. The $O\cdots O$ contacts within these cations range from 2.38 to 2.54 Å.

The observed orientation of the crown ethers in the sandwich cations appears to be driven by the shape and positional orientation of the hydrogen donor positions in the cation. The benzo substituents are maximally staggered, allowing better overlap of the hydrogen bond donors with the more basic alkyl ether positions. In two crystallographically characterized benzo-15-crown-5 sandwich ions of NH_4^+, $[(NH_4)(benzo\text{-}15\text{-}crown\text{-}5)_2]_2[UCl_6]\cdot 4CH_3CN$[52] and $[(NH_4)(benzo\text{-}15\text{-}crown\text{-}5)_2]_2[Cd_2I_6]$,[53] the benzo substituents are very nearly eclipsed. The $N\cdots O$ contacts range from 2.87 to 3.23 Å for both complexes. In addition, the benzo-15-crown-5 molecules have identical conformations in the two ammonium complexes, but conformations different from those observed in the $H_5O_2^+$ complexes. In the ammonium ion complexes, the sequence of O–C–C–O torsion angles is g^-, g^-, g^+, g^+, and s, while a sequence of g^-, g^+, g^-, g^+, and s is observed in the hydronium complexes. All of the C–O–C–C angles are anti in the latter, while there are two of these angles in the former that approach gauche. (These occur between O–C–C–O angles of like sign.)

The $H_5O_2^+$ ions in $[(H_5O_2)_2(18\text{-}crown\text{-}6)][UO_2Cl_4]$ bridge (via hydrogen bonding) the anions and the crown ethers into polymeric chains. Each cation donates three hydrogen bonds to the ether and one to Cl(2) of the anion. Instead of formation of a sandwich ion, there are two cations (one on each side) per crown molecule. The $O\cdots O$ separation within the cation (2.418 (6) Å) and the range of $H_5O_2^+\cdots O$ contacts (2.604 (5)–2.741 (6) Å) are nearly identical, however, with those of the sandwich ions discussed above. The $O\cdots O$ cation contact in $[V(OH_2)_6][H_5O_2][CF_3SO_3]_4$[54] has been reported to be 2.430 (3) Å.

The $H_9O_4^+$ ion in the $[(H_5O_2)(H_9O_4)(benzo\text{-}15\text{-}crown\text{-}5)_2][UO_2Cl_4]$ complex is of the linear-chain type.[45] It functions in the unit cell to bridge (via hydrogen bonding) two $[(H_5O_2)(benzo\text{-}15\text{-}crown\text{-}5)_2]^+$ sandwich cations essentially in polymeric chains along c and two $[UO_2Cl_4]^{2-}$ anions in polymeric chains along a. The disorder of the $H_9O_4^+$ molecule arises from the several available hydrogen-bonding options with the anion. The three O(9)/O(9)^c pairs (atoms related by $\bar{x}$, $\bar{y}$, $\bar{z}$) simply give the chain a slightly different orientation. It is clear from the geometry of the four oxygen positions in each of the three orientations that a hydrogen atom must reside near the center of inversion between each O(9)/O(9)^a pair. This consideration could allow us to also consider this ion as an $H_5O_2^+$ molecule (the O(9)'s) hydrogen bonded to two terminal H_2O molecules (the O(8)'s). The terminal groups donate both of their hydrogen bonds to crown ethers. It is noted that the hydrogen-bonded O(8)$\cdots$O(crown) contacts are much longer (2.842 (6)–3.100 (5) Å) than found for the O-(7)($H_5O_2^+$)$\cdots$O(crown) hydrogen-bonded contacts of 2.619 (5) and 2.695 (4) Å.

Conclusions

While our results are not definitive, they do indicate that crown ethers are robust enough to withstand for some time the rigorous conditions found in many actinide waste streams. These studies also suggest that the dominant feature of crown ether complexation in acid solutions of the uranyl ions is the formation of hydronium ion complexes. The large actinide ions appear to be able to stabilize higher order hydronium ions. The crown ether complexed hydronium ions, especially the sandwich ions, should allow transfer of the hydronium ion from a polar to nonpolar medium. This

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feature may be the origin of the limited extraction capability crown ethers have shown for actinide ions.

Experimental Section

$UO_2SO_4 \cdot 3H_2O$ and all crown ethers were used as purchased. All solvents were of reagent quality; HCl (12.0 M), HNO_3 (15.3 M), H_2SO_4 (17.8 M), and CH_3CO_2H (17.4 M) were utilized without further purification. CH_3CN and CH_3OH were each dried over CaH_2 and distilled, and the H_2O was singly distilled.

Preparation and Crystallization of [(H5O2){(NO2)2benzo-15-crown-5}2]2[(UO2(NO3)2)2C2O4]. To $UO_2SO_4 \cdot 3H_2O$ (0.1055 g, 0.25 mmol) was added HNO_3 (5 mL) and a magnetic stir bar. The yellow solution was stirred at 60 °C for 0.33 h followed by the addition of benzo-15-crown-5 (0.1358 g, 0.51 mmol) with subsequent stirring at 60 °C for 1 h. A brown gas evolved during heating. The reaction vessel was then stored at 5 °C for 11 h and −10 °C for 18 h with no precipitate formation. The solvent volume was reduced in vacuo by 50%, and further slow evaporation afforded yellow crystals suitable for the diffraction study. The crown ether was nitrated during this reaction. Anal. Calcd: C, 29.23; H, 3.47; N, 7.05. Found: C, 28.51; H, 3.37; N, 6.69.

Preparation and Crystallization of [(H3O)(18-crown-6)]2[(UO2-(NO3)2)2C2O4]. To $UO_2SO_4 \cdot 3H_2O$ (0.1089 g, 0.26 mmol) was added HNO_3 (5 mL), 18-crown-6 (0.1349 g, 0.51 mmol), and a magnetic stir bar. The reaction solution was stirred at 60 °C for 1 h and transferred to storage at 5 °C for 11 h and −10 °C for 18 h. Alternate cycles of slow evaporation and volume reduction (in vacuo) provided yellow parallelepiped crystals. Anal. Calcd: C, 21.64; H, 3.77; N, 3.88. Found: C, 13.96; H, 3.05; N, 3.66.

Preparation and Crystallization of [UO2(SO4)(OH2)2]·0.5(12-crown-4)·H2O. CH_3CO_2H (5 mL) and $UO_2SO_4 \cdot 3H_2O$ (0.1078 g, 0.26 mmol) were magnetically stirred at 60 °C for 0.5 h. The presence of a yellow precipitate ($UO_2SO_4 \cdot 3H_2O$) indicated that the salt had not entirely solvated. H_2O (2 mL) was then added and the reaction stirred at 60 °C for another 0.5 h. 12-crown-4 (81 μL, 0.50 mmol) was then added and the resulting yellow solution stirred at 60 °C for 1 h. The reaction vessel was stored at 3 and −10 °C, for 12 and 24 h, respectively. Slow evaporation produced several yellow crystals suitable for the diffraction study. Anal. Calcd: C, 9.45; H, 2.78. Found: C, 9.50; H, 2.31.

Preparation and Crystallization of [UO2(SO4)(OH2)2]·0.5(benzo-15-crown-5)·1.5H2O. To $UO_2SO_4 \cdot 3H_2O$ (0.1079 g, 0.26 mmol) were added a magnetic stir bar, H_2O (2 mL), and CH_3CO_2H (3 mL). The yellow solution was stirred at 60 °C for 0.5 h, followed by the addition of benzo-15-crown-5 (0.1358 g, 0.51 mmol). After addition was complete the reaction solution was stirred for 1 h at 60 °C followed by storage at 5 and −10 °C for 24 h each. Slow evaporation, solvent reduction in vacuo, and further slow evaporation afforded no crystalline products. Dissolution of the precipitate with the original reaction solvent followed by heating, cooling, and slow evaporation (as above) provided gold platelike crystals. Anal. Calcd: C, 14.93; H, 3.04. Found: C, 41.07; H, 5.67. The observed elemental analysis is consistent with cocrystallization of the starting crown ether. It was not possible to completely separate the starting material from the product for a clean analysis.

Preparation and Crystallization of [UO2(SO4)(OH)3]·0.5(18-crown-6). To $UO_2SO_4 \cdot 3H_2O$ (0.1084 g, 0.26 mmol) was added CH_3CO_2H (3 mL), H_2O (2 mL), and a magnetic stir bar. The yellow solution was stirred at 60 °C for 0.5 h, 18-crown-6 (0.1314 g, 0.50 mmol) was added, and the solution was stirred again at 60 °C for 1 h. Storage for 12 h at 3 °C produced no crystals, but several hours at −10 °C afforded very small yellow crystals. Slow evaporation produced crystals of adequate size for the X-ray analysis. Anal. Calcd: C, 13.05; H, 3.28. Found: C, 13.04; H, 3.25.

Preparation and Crystallization of [(H5O2)(H9O4)(benzo-15-crown-5)2][UO2Cl4]. To $UO_2SO_4 \cdot 3H_2O$ (0.0932 g, 0.22 mmol) was added HCl (5 mL), benzo-15-crown-5 (0.1355 g, 0.51 mmol), and a magnetic stir bar. The yellow solution was stirred at 60 °C for 17.75 h, during which time a brown gas evolved. The reaction vessel was then transferred to storage at −10 °C, and within 3.5 h, yellow crystals had formed. Anal. Calcd: C, 31.77; H, 5.14. Found: C, 31.39; H, 5.41.

Preparation and Crystallization of [(H5O2)2(18-crown-6)][UO2Cl4]. 18-Crown-6 (0.1410 g, 0.53 mmol) and HCl (5 mL) were added to $UO_2SO_4 \cdot 3H_2O$ (0.0933 g, 0.22 mmol). The resulting yellow solution was magnetically stirred at 60 °C for 16 h. After 7 days in storage at −10 °C yellow platelike crystals formed. The crystalline complex was successfully reprepared and its formulation confirmed by elemental analysis and unit cell parameters. Anal. Calcd: C, 19.21; H, 4.57; Found: C, 18.51, H, 4.52.

Preparation and Crystallization of [(H3O)(dibenzo-18-crown-6)]-[HSO4]·CH3CN. A 5-mL volume of 2.25 M H_2SO_4, dibenzo-18-crown-6 (0.1866 g, 0.52 mmol), and a magnetic stir bar were added to $UO_2S-O_4 \cdot 3H_2O$ (0.1033 g, 0.25 mmol). The solution was stirred at 60 °C for

Table I. Crystal Data and Summary of Intensity Data Collection and Refinement

compd	[(H5O2){(NO2)2benzo-15-crown-5}2]2[(UO2-(NO3)2)2C2O4]	[(H3O)(18-crown-16)]2-[(UO2(NO3)2)2C2O4]	[UO2(SO4)(OH2)2]·0.5(12-crown-4)·H2O	[UO2(SO4)(OH2)2]·0.5(benzo-15-crown-5)·1.5H2O	[UO2(SO4)(OH)3]3·0.5(18-crown-6)	[(H5O2)(H9O4)(benzo-15-crown-5)2]·[UO2Cl4]	[(H5O2)2(18-crown-6)]·[UO2Cl4]	[(H3O)(dibenzo-18-crown-6)]-[HSO4]·CH3CN
fw	2383.4	1442.8	508.24	563.31	552.30	1058.6	750.24	517.55
space group	$P2_1/n$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
temp, °C	22	22	22	22	22	20	−150	18
cell consts[a]								
a, Å	8.995 (4)	9.804 (1)	7.007 (1)	6.908 (2)	9.314 (5)	8.889 (3)	6.9265 (8)	9.118 (2)
b, Å	19.684 (5)	21.037 (6)	8.0408 (6)	8.717 (4)	9.339 (3)	10.149 (3)	9.239 (1)	9.348 (5)
c, Å	24.739 (4)	11.827 (3)	10.776 (2)	13.578 (2)	16.734 (3)	11.626 (3)	10.429 (2)	15.879 (4)
α, deg			91.31 (1)	79.46 (2)		94.54 (2)	93.34 (1)	72.60 (3)
β, deg	90.42 (2)	94.70 (2)	93.60 (2)	75.28 (2)	103.62 (3)	91.04 (2)	103.50 (1)	80.99 (2)
γ, deg			100.18 (1)	89.98 (3)		104.29 (3)	106.15 (1)	78.22 (3)
V, Å³	4380	2431.1	596.0	776.5	1415	1012	617.9	1285
Z	2	2	2	2	4	1	1	2
radiation, graphite monochromator (λ, Å)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
D_{calcd}, g cm⁻³	1.81	1.97	2.83	2.41	2.59	1.74	2.02	1.34
μ_{calcd}, cm⁻¹	46.62	82.59	168.9	129.9	142.4	41.6	67.2	1.88
range of rel transm factors, %	81/100	90/100	47/100	13/100	38/100	46/100	85/100	no cor
$R = \sum \|\|F_o\| - \|F_c\|\| / \sum \|F_o\|$[b,c]	0.038	0.040	0.032	0.056	0.071	0.034	0.025	0.073
R_w	0.049	0.050	0.046	0.071	0.093	0.034	0.026	0.087

[a] Least-squares refinement of $((\sin\theta)/\lambda)^2$ value for 25 reflections $\theta > 20°$. [b] Corrections: Lorentz-polarization and absorption (empirical, ψ scan). [c] Neutral scattering factors and anomalous dispersion corrections from ref 56.

1 h, after which a purple precipitate was centrifuged and the supernatant decanted and stored at 3 °C. The supernatant afforded no crystalline results. An elemental analysis of the precipitate showed sufficient carbon percentages to accommodate complex formation. The purple solid was solvated in a 3:1 solution of CH_3CN/CH_3OH (5 mL). The solution was stirred at 60 °C for 1 h followed by storage at 3 and -10 °C for 24 h each. Slow concentration of the solution provided platelike crystals with a thin coating of the purple reaction solution. Anal. Calcd: C, 51.05; H, 6.04; N, 2.71. Found: C, 46.67; H, 6.11; N, 4.54.

Reactions in H_2SO_4. Two molar equivalents of the ligands 12-crown-4, 15-crown-5, benzo-15-crown-5, 18-crown-6, and dibenzo-18-crown-6 were individually reacted with 1 molar equiv of $UO_2SO_4·3H_2O$ in varying concentrations of H_2SO_4 solvent. The 17.8, 9.90, 4.45, and 2.25 M H_2SO_4 solutions provided no crystalline samples that could be utilized in this study. Standard Schlenk techniques, slow evaporation, shock cooling, and slow cooling of reactions at all H_2SO_4 concentrations afforded only dark oils. Precipitates were common with the reactions involving dibenzo-18-crown-6. (This can be attributed to its hydrophobicity.) The only isolable product was $[(H_3O)(dibenzo-18-crown-6)]-[HSO_4]·CH_3CN$ as discussed above.

In all reactions, over varying lengths of time, viscous brown or black oils formed. Reactions consisting solely of the acid and the ligand and the acid and $UO_2SO_4·3H_2O$ produced analogous brown oils.

X-ray Data Collection, Structure Determination, and Refinement. For each crystallographic study (except for $[(H_5O_2)_2(18-crown-6)][UO_2Cl_4]$ discussed below), a single crystal was mounted in a thin-walled glass capillary flushed with Ar and transferred to the goniometer. A summary of data collection parameters for all complexes is given in Table I. Unless otherwise indicated, the geometrically constrained hydrogen atoms 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 Å². If included, the solvent or water hydrogen atoms were located from a difference Fourier map and included with fixed contributions (B = 5.5 Å²). All non-hydrogen atoms were refined anisotropically. Structures were refined by utilizing SHELX76[55] and neutral-atom scattering factors from ref 56. Initial structure solutions were carried out with SHELXS.[57] Considerations unique to each crystallographic series are discussed below. Due to the length of the tables of fractional coordinates, these have been placed in the supplementary material.

$[(H_5O_2)((NO_2)_2benzo-15-crown-5)_2][(UO_2(NO_3)_2)_2C_2O_4]$. The space group was determined to be the centric $P2_1/n$ from the systematic absences. Orientational disorder of both nitro groups bonded to one of the crown ethers (N(5) and N(6)) was observed. The disorder was resolved into two orientations with N(5) and N(6) full weighted, O(27)–O(30) at 55% occupancy, and O(27)′–O(30)′ at 45% occupancy. The hydronium ion hydrogen atoms were located from a difference Fourier map and included with fixed contributions (B = 5.5 Å²). Refinement of non-hydrogen atoms with anisotropic temperature factors led to the final values of R = 0.038 and R_w = 0.049.

$[(H_3O)(18-crown-6)][(UO_2(NO_3)_2)_2C_2O_4]$. The space group was determined to be the centric $P2_1/n$ from the systematic absences. High thermal motion was noted for the $[(H_3O)(18-crown-6)]^+$ units. No resolvable disorder was found. The crown ether displays its normal coordinated D_{3d} conformation. It is noted that the crown ether units are not hydrogen bonded except to the hydronium ion. The resulting packing forces are not strong enough to further dampen molecular vibrations at room temperature (22 °C). The hydrogen atoms were not included in the final refinement. Refinement of non-hydrogen atoms with anisotropic temperature factors led to the final values of R = 0.040 and R_w = 0.050.

$[UO_2(SO_4)(OH_2)_2]·0.5(12-crown-4)·H_2O$. The space group was determined to be either the centric $P\bar{1}$ or acentric $P1$. The subsequent solution and successful refinement of the structure was carried out in the centric space group $P\bar{1}$. The water hydrogen atoms were not included in the final refinement. Refinement of non-hydrogen atoms with anisotropic temperature factors led to the final values of R = 0.032 and R_w = 0.046.

$[UO_2(SO_4)(OH_2)_2]·0.5(benzo-15-crown-5)·1.5(H_2O)$. The space group was determined to be either the centric $P\bar{1}$ or acentric $P1$. The subsequent solution and successful refinement of the structure was carried out

in the centric space group $P\bar{1}$ despite the presence of some disorder. The scattering is dominated by the $[UO_2(SO_4)(OH_2)_2]$ moieties, which are related by centers of inversion of $P\bar{1}$. Thus, when $P1$ is attempted, very large correlations prevent the successful refinement of the structure. It is possible to alternate refinement of these groups of atoms related by the center (in $P\bar{1}$); however, positions corresponding to the disordered crown ether are still apparent. Final refinement was carried out in $P\bar{1}$ with disorder described below.

The $[UO_2(SO_4)(OH_2)_2]_n$ polymeric chains were readily located along with one water molecule hydrogen bonded to the coordinated water molecules. The chains propagate along a and are separated by ab layers of hydrogen-bonded crown ethers. The crown molecules are disordered about centers of inversion. The crowns alternate sites on either side of the inversion points. Between two $[UO_2(SO)_4(OH_2)_2]_n$ there exist two layers of benzo-15-crown-5 molecules each containing sheets of molecules with the benzo groups of one sheet all bent down toward $-c$ and aligned along $+b$ and of the other sheet having opposite orientation. Each sheet is hydrogen bonded to a different inorganic layer. The disorder suggests equivalent orientations offset by a unit translation along a. Thus, in each layer, every other unit translation of the molecule is vacant. The two layers themselves are offset by one unit translation of a. The resulting C(2) and C(7) positions were within 1 Å of each other and were refined in alternate least-squares cycles. The entire crown molecule and the water molecule O(10) were refined at 50% occupancy. The hydrogen atoms were not included in the final refinement. Refinement of non-hydrogen atoms with anisotropic temperature factors led to the final values of R = 0.056 and R_w = 0.071.

$[UO_2(SO_4)(OH_2)_3]·0.5(18-crown-6)$. The space group was determined to be the centric $P2_1/n$ from the systematic absences. The water molecule hydrogen atoms were not included in the final refinement. Refinement of non-hydrogen atoms with anisotropic temperature factors led to the final values of R = 0.071 and R_w = 0.093.

$[(H_5O_2)(H_9O_4)(benzo-15-crown-5)_2][UO_2Cl_4]$. The space group was determined to be either the centric $P\bar{1}$ or acentric $P1$. The subsequent solution and successful refinement of the structure was carried out in the space group $P\bar{1}$. Three refinable positions were observed for O(9). These positions were refined with occupancy factors of 0.3333 each. The hydrogen atoms for the hydronium ions could not be located and were not included in the final refinement. Refinement of non-hydrogen atoms with anisotropic temperature factors led to the final values of R = 0.034 and R_w = 0.034.

$[(H_5O_2)_2(18-crown-6)][UO_2Cl_4]$. The crystal was mounted on a pin and cooled to -150 °C during data collection by using a stream of cold nitrogen gas. The space group was determined to be either the centric $P\bar{1}$ or acentric $P1$. The subsequent solution and successful refinement of the structure was carried out in the space group $P\bar{1}$. The hydrogen atoms were located from a difference Fourier map. The hydronium ion hydrogen atoms were fully refined, while the remaining hydrogen atoms were included with fixed contributions (B = 5.5 Å²). Refinement of non-hydrogen atoms with anisotropic temperature factors led to the final values of R = 0.025 and R_w = 0.026.

$[(H_3O)(dibenzo-18-crown-6)][HSO_4]·CH_3CN$. The space group was determined to be either the centric $P\bar{1}$ or acentric $P1$. The subsequent solution and successful refinement of the structure was carried out in the centric space group $P\bar{1}$. The geometrically constrained hydrogen atoms 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 Å². The acetonitrile molecule was disordered and was refined as two geometrically constrained groups with the C–C distance fixed at 1.45 Å, the C≡N separation fixed at 1.13 Å, and the overall length of the molecule at 2.58 Å. The two configurations were refined in alternate least-squares cycles. The C(21), C(22), N molecule was refined with an occupancy of 0.75, and the second orientation was refined at an occupancy of 0.25. The remaining hydrogen atoms were not included in the final refinement. Refinement of non-hydrogen atoms with anisotropic temperature factors led to the final values of R = 0.073 and R_w = 0.087.

Supplementary Material Available: Tables SI–SLVII, listing bond distances and angles, torsion angles, hydrogen-bonding contact geometries, fractional coordinates, hydrogen atom coordinates, thermal parameters, and least-squares plane results (86 pages); tables of observed and calculated structure factors (40 pages). Ordering information is given on any current masthead page. The fractional coordinates are available directly from the authors upon request.

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