Coordination Trends in Alkali Metal Crown Ether Uranyl Halide Complexes: The Series [A(Crown)]$_2$[UO$_2$X$_4$] Where A = Li, Na, K and X = Cl, Br

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UO$_2$(C$_2$H$_3$O$_2$)$_2$·2H$_2$O reacts with AX or A(C$_2$H$_3$O$_2$ or ClO$_4$) (where A = Li, Na, K; X = Cl, Br) and crown ethers in HCl or HBr aqueous solutions to give the sandwich-type compounds [K(18-crown-6)]$_2$[UO$_2$Cl$_4$] (**1**), [K(18-crown-6)]$_2$[UO$_2$Br$_4$] (**2**), [Na(15-crown-5)]$_2$[UO$_2$Cl$_4$] (**3**), [Na(15-crown-5)]$_2$[UO$_2$Br$_4$] (**4**), [Li(12-crown-4)]$_2$[UO$_2$Cl$_4$] (**5**), and [Li(12-crown-4)]$_2$[UO$_2$Br$_4$] (**6**). The compounds have been characterized by single-crystal X-ray diffraction, powder diffraction, elemental analysis, IR, and Raman spectroscopy. The [UO$_2$X$_4$]$^{2-}$ ions coordinate to two [A(crown)]$^+$ cations through the four halides only (**2**), through two halides only (**3**), through the two uranyl oxygens and two halides (**3**, **4**), or through the two uranyl oxygen atoms only (**5**, **6**). Raman spectra reveal ν_{U-O} values that correlate with expected trends. The structural trends are discussed within the context of classical principles of hard−soft acid−base theory.

Introduction

An understanding of uranium coordination chemistry is integral to the (re)processing and separation of uranium from waste streams originating from its application in civilian research, nuclear energy, and weapons industries. One essential aspect of the disposal or recycling process is the removal of actinides from waste streams. Depending on the source, actinide-containing waste streams are extremely complex and can contain a number of coordinating species, including alkali and alkaline earth metals, halides, nitrates, sulfates, phosphates, and carbonates. Separation and extraction of the actinides by complexation with crown ethers is one of the many methods proposed to remove them from waste streams.[1−3] The exceptional chelating ability of the crown ethers[4,5] along with the actinides' tendency to adopt high coordination numbers result in an abundance of possible coordination complexes. Indeed, these complexation studies led to the isolation of new uranium moieties in the solid state.[6−9] Initially, efforts were focused on the formation of inclusion complexes, where uranium(IV) or the uranyl(VI) ion (UO$_2$$^{2+}$) is threaded into the crown ether cavity facilitating phase transfer in extraction processes.[7,8,10] Limited success in this area

also led to the formation and structural characterization of many compounds with crown ethers participating in hydrogen bonding or as part of a counterion.[11−14]

[K(18-crown-6)]$_2$[UO$_2$Cl$_4$] (**1**) has been synthesized, and a brief report has been published, with details to follow.[15] In this work, we report the synthesis and X-ray structure of five alkali metal crown ether uranyl halide sandwich-type compounds, [K(18-crown-6)]$_2$ [UO$_2$Br$_4$] (**2**), [Na(15-crown-5)]$_2$[UO$_2$Cl$_4$] (**3**), [Na(15-crown-5)]$_2$[UO$_2$Br$_4$] (**4**), [Li(12-crown-4)]$_2$[UO$_2$Cl$_4$] (**5**), and [Li(12-crown-4)]$_2$[UO$_2$Br$_4$] (**6**). These anhydrous uranyl halides were isolated from aqueous or acetonitrile solutions and display interesting coordination differences from each other and from previously reported compounds. The structural trends in **1**−**6** will be discussed within the context of classical principles of hard−soft acid−base (HSAB) theory. Understanding the relationship between the structural trends and the identity of complexing agents may be helpful in developing future models and making predictions regarding complexation and migration of actinides in waste streams.

Experimental Section

General. Reagent grade chemicals were obtained commercially (uranyl acetate, Fluka; HCl (36.5%), HBr (48%), and acetonitrile, Fisher; sodium acetate, potassium bromide, 1,4,7,10,13,16-hexaoxacy-

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clooctadecane (18-crown-6), 1,4,7,10,13-pentaoxacyclopentadecane (15-crown-5), 1,4,7,10-tetraoxacyclododecane (12-crown-4), lithium chloride, and lithium perchlorate, Aldrich) and used without further purification. $UO_2(OH)_2 \cdot xH_2O$ was prepared according to previously published methods.[16] Water was purified using a Millipore Milli-Q Ultrapure water system. All reactions were carried out in glass vials either on the benchtop or in a fume hood. Crystals were isolated manually and dried in a vacuum oven at 60 °C. IR spectra were obtained from KBr pellets on a Nicolet Magna 560 FT−IR/Raman spectrometer. Raman spectra were collected on the same instrument using 20-mg crystalline samples. The IR and Raman spectra were collected with a resolution of 2.0 cm^{-1} (data spacing of 0.964 cm^{-1}). Elemental analysis was performed on a Perkin-Elmer series II 2400 CHN analyzer.

Synthesis. [K(18-crown-6)]$_2$[UO$_2$Br$_4$] 2. Uranyl acetate dihydrate (16.0 mg, 0.04 mmol), potassium bromide (9.6 mg, 0.1 mmol), 18-crown-6 (24.0 mg, 0.1 mmol), and HBr (48%, 1.5 g, excess) were combined in a vial. The yellow solution evaporated slowly at room temperature. After 2 weeks, crystals of a deep gold color precipitated from solution and were isolated manually. Yield: 37.7 mg (82.9%). IR (KBr pellet) ν_{as} (U−O) (cm^{-1}): 916 (m). Anal. Calcd for C$_{24}$H$_{48}$O$_{14}$K$_2$Br$_4$U: C, 24.09; H, 4.05. Found: C, 23.77; H, 3.94.

[Na(15-crown-5)]$_2$[UO$_2$Cl$_4$] 3. Uranyl acetate dihydrate (16.0 mg, 0.04 mmol), sodium acetate (6.5 mg, 0.1 mmol), 15-crown-5 (25.0 mg, 0.1 mmol), HCl (36.5%, 18.0 mg, 0.2 mmol), and deionized water (290 mg) were combined in a vial and briefly stirred. The resulting pale yellow solution evaporated slowly at room temperature. Within 1 week, greenish-gold crystals precipitated from solution and were isolated manually. Yield: 34.1 mg (99.9%). IR (KBr pellet) ν_{as} (U−O) (cm^{-1}): 923 (m). Anal. Calcd for C$_{20}$H$_{40}$O$_{12}$Na$_2$Cl$_4$U: C, 26.74; H, 4.50. Found: C, 26.84; H, 4.71.

[Na(15-crown-5)]$_2$[UO$_2$Br$_4$] 4. Uranyl acetate dihydrate (16.0 mg, 0.04 mmol), sodium acetate (6.8 mg, 0.1 mmol), 15-crown-5 (23.8 mg, 0.1 mmol), HBr (48%, 31.6 mg, 0.2 mmol), and deionized water (220 mg) were combined in a vial. The yellow solution evaporated slowly at room temperature. After 2 weeks, crystals of a deep gold color precipitated from solution and were isolated manually. Yield: 38.6 mg (94.4%). IR (KBr pellet) ν_{as} (U−O) (cm^{-1}): 904 (m). Anal. Calcd for C$_{20}$H$_{40}$O$_{12}$Na$_2$Br$_4$U: C, 22.32; H, 3.75. Found: C, 22.26; H, 4.16.

[Li(12-crown-4)]$_2$[UO$_2$Cl$_4$] 5. Uranyl acetate dihydrate (16.0 mg, 0.04 mmol), lithium chloride (7.2 mg, 0.1 mmol), 12-crown-4 (24.2 mg, 0.1 mmol), HCl (36.5%, 22.3 mg, 0.2 mmol), and acetonitrile (59.0 mg) were combined in a vial and briefly stirred. The resulting yellow solution evaporated slowly at room temperature. Within 2 days, pale greenish-gold crystals precipitated from solution and were isolated manually. Yield: 29.7 mg (94.3%). IR (KBr pellet) ν_{as} (U−O) (cm^{-1}): 910 (m). Anal. Calcd for C$_{16}$H$_{32}$O$_{10}$Li$_2$Cl$_4$U: C, 24.70; H, 4.14. Found: C, 25.31; H, 4.67.
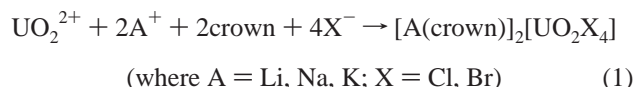
[Li(12-crown-4)]$_2$[UO$_2$Br$_4$] 6. Uranyl acetate dihydrate (16.2 mg, 0.04 mmol), lithium perchlorate (11.7 mg, 0.1 mmol), 12-crown-4 (18.4 mg, 0.1 mmol), HBr (48%, 16.6 mg, 0.1 mmol), and deionized water (378 mg) were combined in a vial. The yellow solution evaporated slowly at room temperature. Within 1 week, crystals of a deep gold color precipitated from solution and were isolated manually. Yield: 28.8 mg (79.3%). IR (KBr pellet) ν_{as} (U−O) (cm^{-1}): 913 (m). Anal. Calcd for C$_{16}$H$_{32}$O$_{10}$Li$_2$Br$_4$U: C, 20.10; H, 3.37. Found: C, 19.37; H, 3.71.

Crystallographic Studies. General Procedure. Crystals of **2**−**6** were isolated and transferred to a mineral oil matrix. In all cases, it was necessary to cut a large multifaceted crystal into smaller pieces to obtain a crystal of suitable size for X-ray diffraction analysis. Crystals of the compounds were mounted onto a thin glass fiber with silicon grease and immediately cooled to 203 K under a nitrogen coldstream. The crystallographic data were collected using a sealed, graphite monochromatized Mo Kα X-ray source ($\lambda = 0.710\ 73$ Å) on a Bruker P4/CCD/PC diffractometer. A hemisphere of data was collected using a combination of φ and ω scans, with 10- or 20-s frame exposures and 0.3° frame widths. Data collection and initial indexing and cell

refinement was handled using SMART software.[17] Frame integration and final cell parameter calculation were carried out using SAINT software. The data were corrected for absorption using the SADABS program. Decay of reflection intensity was not observed in any case. The structures were refined by full-matrix least-squares technique on F^2. The selection of the space groups $P2_1/c$ (**2** and **3**) and *Pccn* (**4**) were uniquely determined on the basis of systematic absences. The structure of **5** was initially solved in space group *I4/mmm*. However, the subsequent refinement was problematic, with high residual electron densities in chemically unreasonable positions. The refinement in *I4/mmm* converged to R1($I > 2\sigma$) = 0.0629. Solutions were also obtained in *I4/m* and *I4̄*, and the refinements converged to R1($I > 2\sigma$) = 0.0624 and 0.073, respectively. The structures in *I4̄* and *I4/m* were also refined as merohedral twins, but no improvement was observed. The chlorine atom positions were not observed in any of the *I4/m* or *I4̄* refinements. At this juncture, a solution obtained in the orthorhombic space group *Fmm2* was pursued. The orthorhombic *mmm* Laue group gave an R_{int} = 0.060, while the tetragonal 4/*mmm* and 4/*m* Laue groups gave 0.070 and 0.079, respectively. The refinement in the orthorhombic space group converged to R1($I > 2\sigma$) = 0.0624 and gave the most chemically correct structure of all the refinements. The *Fmm2* structure refined best as a merohedral twin, which is consistent with the slightly higher merging statistics for the tetragonal Laue groups over the orthorhombic Laue groups. A solution was also obtained and refined to R1($I > 2\sigma$) = 0.0525 in the space group *Fmmm*. However, the crown ether was extremely disordered, and the refinement failed to converge. The structure of **6** was solved and refined in the centric space group *Cmca*. The choice of this space group was consistent with the intensity statistics and was confirmed by the successful solution of the structure. Structure solutions and refinements were performed using SHELXTL NT[18] and SHELX-93.[19] The structures were solved by direct methods (**2**−**5**) or Patterson methods (**6**) and refined by difference Fourier techniques. In **2**−**4**, hydrogen atom positions were fixed (C−H = 0.97 Å) and refined using the riding model, with isotropic temperature factors fixed to 1.2× the equivalent isotropic U of the carbon atom to which they were bound. The final refinements included anisotropic temperature factors on all non-hydrogen atoms. In **5** and **6**, hydrogen atom positions were not fixed because of the disorder present in the crown ether molecules. In **5**, it was necessary to refine the disordered crown as a rigid body based on the atomic coordinates of a similar moeity[11] and to refine the lithium and crown ether carbon and oxygen atoms isotropically. In **6**, the DFIX command was employed to render one C−C bond distance reasonable. With the exception of O(5), the crown ether atoms were refined with the ISOR command and were all at half-occupancy. Additional details of data collection and structure refinement are listed in Table 1.

Results

Syntheses. Acidic aqueous solutions containing the uranyl ion react with alkali metal cations and crown ethers to form anhydrous uranyl tetrahalide sandwich-type compounds according to eq 1. Either uranyl acetate or uranyl hydroxide can be used in eq 1 chemistry. Different crown ethers were used with each of the alkali metals to accommodate the different sizes of the metal cations. 18-Crown-6, 15-crown-5, and 12-crown-4 were used for potassium, sodium, and lithium, respectively.

$$UO_2{}^{2+} + 2A^+ + 2\text{crown} + 4X^- \rightarrow [A(\text{crown})]_2[UO_2X_4]$$

$$(\text{where } A = \text{Li, Na, K; } X = \text{Cl, Br}) \qquad (1)$$

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Table 1. Crystallographic Data for **2**–**6**[a]

compd	2	3	4	5	6
empirical formula	$C_{24}H_{48}O_{14}K_2Br_4U$	$C_{20}H_{40}O_{12}Na_2Cl_4U$	$C_{20}H_{40}O_{12}Na_2Br_4U$	$C_{16}H_{32}O_{10}Li_2Cl_4U$	$C_{16}H_{32}O_{10}Li_2Br_4U$
fw	1196.49	898.33	1076.19	778.13	955.97
cryst syst	monoclinic	monoclinic	orthorhombic	orthorhombic	orthorhombic
space group	$P2_1/c$	$P2_1/c$	$Pccn$	$Fmm2$	$Cmca$
a, Å	10.2472(5)	14.5026(7)	15.4560(7)	13.340(1)	13.656(1)
b, Å	10.0343(5)	14.5308(7)	16.0178(7)	14.963(1)	15.039(1)
c, Å	19.7082(9)	15.4121(7)	13.6571(6)	13.151(1)	13.409(1)
β, deg	92.659(1)	92.5230(1)			
V, Å^3	2024.3(2)	3244.7(3)	3381.1(3)	2625.0(4)	2753.8(4)
Z	2	2	4	4	4
ρ (calcd), mg/m^3	1.963	1.839	2.114	1.969	2.306
abs coeff	8.216 mm^{-1}	5.411 mm^{-1}	2.401 mm^{-1}	6.635 mm^{-1}	11.741 mm^{-1}
final R indices [$I > 2\sigma(I)$]	R1[b]= 0.0249, R2$_w$[c]= 0.0670	R1[b]= 0.0287, R2$_w$[d]= 0.0700	R1[b]= 0.0297, R2$_w$[e]= 0.0755	R1[b]= 0.0403, R2$_w$[f]= 0.0918	R1[b]= 0.0506 R2$_w$[g]= 0.1261
R indices (all data)	R1 = 0.0293, R2$_w$ = 0.0686	R1 = 0.0430, R2$_w$ = 0.0745	R1 = 0.0388, R2$_w$ = 0.0791	R1 = 0.0408, R2$_w$ = 0.0921	R1 = 0.0592, R2$_w$ = 0.1272

[a] **2** = [K(18-crown-6)]$_2$[UO$_2$Br$_4$], **3** = [Na(15-crown-5)]$_2$[UO$_2$Cl$_4$], **4** = [Na(15-crown-5)]$_2$[UO$_2$Br$_4$], **5** = [Li(12-crown-4)]$_2$[UO$_2$Cl$_4$], and **6** = [Li(12-crown-4)]$_2$[UO$_2$Br$_4$]. [b] R1 = $\sigma||F_o| - |F_c||/\sigma|F_o|$ and R2$_w$ = $[\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$. [c] The parameter $w = 1/[\sigma^2(F_o^2) + (0.0381*P)^2]$. [d] The parameter $w = 1/[\sigma^2(F_o^2) + (0.031*P)^2]$. [e] The parameter $w = 1/[\sigma^2(F_o^2) + (0.046*P)^2]$. [f] The parameter $w = 1/[\sigma^2(F_o^2) + (0.0587*P)^2]$. [g] The parameter $w = 1/[\sigma^2(F_o^2) + (0.0162*P)^2]$.

Table 2. Selected Bond Distances (Å) for **1**–**6**[a]

compd	1	2	3a	3b	4	5	6
structure type	I	I	I	II	III	IV	IV
U–O$_{Ur}$	1.772(2)	1.769(2)	1.766(2)	1.764(2)	1.780(3)	1.767(9)	1.79(1)
U–X	2.681(1)[b]	2.8209(6)[b]	2.6754(9)[b]	2.6753(9)[b]	2.8141(6)[b]	2.63(2)[b]	2.793(1)
A–X	3.321(1)[b]	3.430(1)[b]	3.024(3)[b]	2.768(2)	3.306(1)		
A–O$_{Ur}$					2.456(3)	1.89(2)	1.89(3)

[a] **1** = [K(18-crown-6)]$_2$[UO$_2$Cl$_4$], **2** = [K(18-crown-6)]$_2$[UO$_2$Br$_4$], **3** = [Na(15-crown-5)]$_2$[UO$_2$Cl$_4$], **4** = [Na(15-crown-5)]$_2$[UO$_2$Br$_4$], **5** = [Li(12-crown-4)]$_2$[UO$_2$Cl$_4$], and **6** = [Li(12-crown-4)]$_2$[UO$_2$Br$_4$]. [b] Indicates average bond distances.

The reactions to produce **2**–**6** proceed in high yields (79.3–99.9%), and all of the compounds are air-stable. Crystals containing bromide are a deep gold color, and those containing chloride are pale greenish-gold. The crystallization of the gold uranyl products was accompanied by the formation of colorless [A(crown)]X salts. **1**–**6** are all water soluble with a qualitative solubility order of **1**, **2** < **3**, **4** ≪ **5**, **6**. All compounds were characterized by IR, Raman spectroscopy, elemental analysis, and single-crystal X-ray diffraction. In some cases, powder X-ray diffraction was employed to identify impurities.

I   **II**

III   **IV**
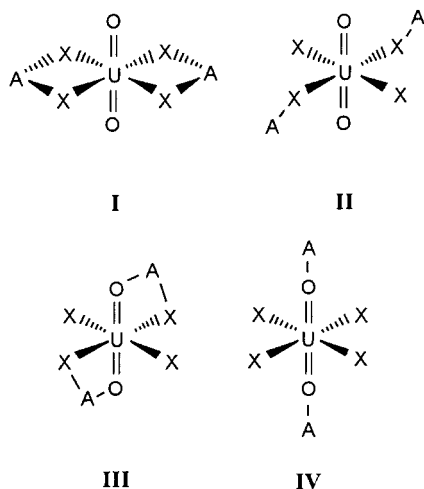
Structural Studies. General. 1–**6** are all either orthorhombic or monoclinic, but only **1** and **2** are isomorphic. A summary of crystallographic data can be found in Table 1. Selected bond distances and angles are given in Table 2. The structures of

1–**6** contain square bipyramidal [UO$_2$X$_4$]$^{2-}$ ions sandwiched between two [A(crown ether)]$^+$ ions (X = Cl, Br and A = Li, Na, K). Each uranium is bound to the two apical oxygen atoms (O$_{Ur}$) and four equatorial halide atoms. The bond distances and angles within the [UO$_2$X$_4$]$^{2-}$ units are comparable to previously reported similar compounds,[8,12,20,21] as are the A–X bond distances.[22–25] In all cases, the two U–O bond distances are equivalent, and the O–U–O bond angles are 180° as are the X(1–4)–U–X(1–4A) angles. Significant variations in the [A(crown ether)]$^+$–[UO$_2$X$_4$]$^{2-}$ interactions are found as the halide is changed from chloride to bromide and as the alkali metal is changed from potassium to sodium or lithium. The resulting four different structural types are shown, and representative ORTEP drawings are shown in Figure 1. The alkali metal cations are bound to all the crown ether oxygen atoms (O$_{Cr}$). In addition, the alkali ions are bound to either four halides (type I), two halides (II), two halides and two O$_{Ur}$ (III), or only the two uranyl oxygen atoms (IV). Structure type I is adopted by compounds **1** and **2** and by one orientation of **3**. Structure type II is adopted in the other orientation of **3**, type III is adopted by **4**, and type IV is adopted by **5** and **6**. The bond distances and angles within the [A(crown)]$^+$ ions are typical.[8,26,27] The coordination number of the alkali metal is eight in **1** and **2**,

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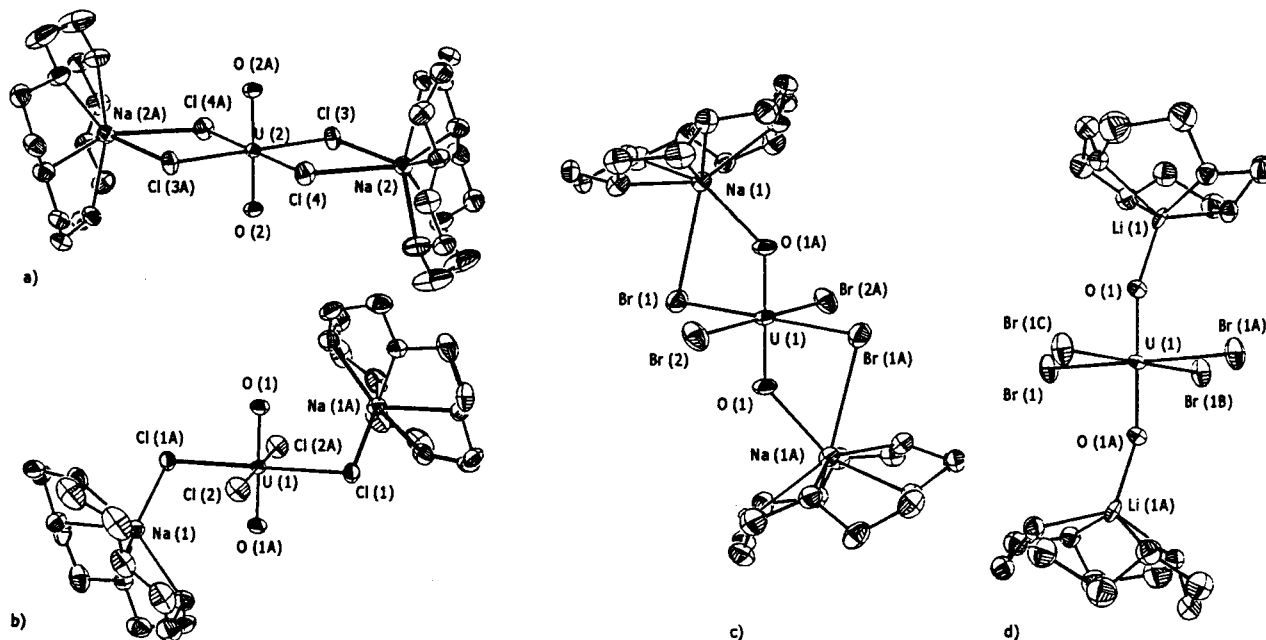
Figure 1. ORTEP views of the molecular structures of (a) **3a**, (b) **3b**, (c) **4**, and (d) **6**, representing structure types I−IV, respectively. Labels on the crown ether molecules have been omitted for clarity.

seven and six for the two different orientations of **3**, seven in **4**, and five in **5** and **6**. This change in coordination number reflects both the differing number of oxygens in the crown ethers and the variations in the [A(crown ether)]$^{+}$−[UO$_2$X$_4$]$^{2-}$ interactions.

Type I Compounds. [K(18-crown-6)]$_2$[UO$_2$Cl$_4$] 1. Two uranuim-bound chlorides of **1** coordinate in a bridging fashion to each crown-encapsulated K^{+} ion at bond distances of 3.451-(9) and 3.2974(9) Å. For reference, the K−Cl distance in KCl is 3.146(1) Å.[28,29] The six oxygen atoms of each crown ether also coordinate to the K^{+} ions with bond distances that range from 2.857(2) to 3.043(2) Å. The [UO$_2$Cl$_4$]$^{2-}$ unit is tilted with respect to the plane of the 18-crown-6 rings toward the potassium atoms (O(1)−U(1)−K(1) = 56°).

[K(18-crown-6)]$_2$[UO$_2$Br$_4$] 2. This structure also contains eight-coordinate K^{+} ions and is virtually identical to **1**. The K−Br distances are 3.3744(9) and 3.485(1) Å, which are longer than the 3.300(1) Å K−Br distances reported for the six-coordinate K^{+} in KBr.[28,29] The K−O$_{Cr}$ distances range from 2.821(3) to 2.998(3) Å. The O(1)−U(1)−K(1) angle is slightly higher than in **1** at 63°.

Type I/Type II Compound. [Na(15-crown-5)]$_2$[UO$_2$Cl$_4$] 3. In the solid-state structure of **3**, two crystallographically independent [UO$_2$Cl$_4$]$^{2-}$ units are present, with different coordination modes (types I and II). In the type I orientation, two equatorial chlorides bridge to each crown-encapsulated sodium ion (Figure 1a) with average Na−Cl contacts of 3.024(3) Å. The [UO$_2$Cl$_4$]$^{2-}$ unit is orientated with the linear UO$_2^{2+}$ approximately parallel to the planes of the crown ether rings (O(2)−U(2)−Na(2) = 87°). In the type II mode (Figure 1b), only one chloride bridges to each sodium (Na−Cl = 2.768(2) Å). Here, the [UO$_2$Cl$_4$]$^{2-}$ unit is significantly tilted (O(1)−

U(1)−Na(1A) = 31°) so that the oxygens are closer to the sodium atoms. The net effect of this rotation is to displace two of the chlorides from bonding range (Na···Cl = 3.354(2) Å) with the sodium atoms. For reference, the Na−Cl bond distance in NaCl is 2.8199(7) Å.[28] The Na−O$_{Cr}$ distances for both ions range from 2.379(3) to 2.509(3) Å.

Type III Compounds. [Na(15-crown-5)]$_2$[UO$_2$Br$_4$] 4. This compound is the only representative of structure type III and is characterized by two seven-coordinate Na^{+} ions bound by the [UO$_2$Br$_4$]$^{2-}$ ion (Figure 1c). One uranyl oxygen and one bromide ion bridge to each Na^{+} ion with Na−O$_{Ur}$ distances of 2.456(3) Å. The two Na−Br bond distances are 3.305(2) Å, which are longer than the 2.983(3) Å Na−Br distances in NaBr.[28] The linear Br(2)−U(1)−Br(2A) unit is oriented parallel to the planes of the 15-crown-5 rings (Br(2)−U(1)−Na(1) = 90°). The Na−O$_{Cr}$ distances range from 2.387(3) to 2.491(3) Å.

Type IV Compounds. [Li(12-crown-4)]$_2$[UO$_2$Cl$_4$] 5. In type IV compounds, the coordination from the [UO$_2$X$_4$]$^{2-}$ unit to the crown-encapsulated Li^{+} ions is accomplished solely through the uranyl oxygen atoms. In **5**, the Li−O$_{Ur}$ distances are 1.89-(2) Å. The uranium and four equatorial chlorides define a vertical plane separating the [Li(12-crown-4)]$^{+}$ cations, and the U(1)−O(1)−Li(1) angle is 178(3)°. The Li−O$_{Cr}$ distances range from 2.10(4) to 2.20(4) Å. The crown ether molecules in this structure are plagued by a disorder, but the [UO$_2$Cl$_4$]$^{2-}$ anionic subunit is well-behaved. Importantly, the orientation of the [UO$_2$Cl$_4$]$^{2-}$ ion relative to the [Li(12-crown-4]$^{+}$ ion, the feature of interest, is well-established.

[Li(12-crown-4)]$_2$[UO$_2$Br$_4$] 6. Compound **6** is virtually isostructural to **5** but is not isomorphic (Table 1). In **6**, the Li−O$_{Ur}$ bond distances are 1.89(3) Å, and the U(1)−O(1)−Li(1) angle of 162(1)° deviates slightly more from linear than in **5**. As in **5**, the crown ether molecules are disordered, which is not surprising since the orientation adopted by the [A(crown)]$^{+}$ ion in **5** and **6** is somewhat untethered on one side of the alkali metal (Figure 1d). Again, the [UO$_2$Br$_4$]$^{2-}$ anionic subunit is well-behaved, and the geometry in relation to the [Li(12-crown-4]$^{+}$ ion is certain. The U−Br distances are shorter (2.793(1)

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Table 3. Observed Raman and IR Bands with Corresponding Structural Data for **1**−**6**[a]

compd	Raman ν_{1U-O} frequency (cm^{-1})	IR ν_{3U-O} frequency (cm^{-1})	U−O (Å)
1	826	908	1.772(2)
2	831	916	1.769(2)
3	838, 843	923	1.766(2), 1.764(2)
4	816	904	1.780(3)
5	822	910	1.767(9)
6	824	913	1.79(1)

[a] **1** = [K(18-crown-6)]$_2$[UO$_2$Cl$_4$], **2** = [K(18-crown-6)]$_2$[UO$_2$Br$_4$], **3** = [Na(15-crown-5)]$_2$[UO$_2$Cl$_4$], **4** = [Na(15-crown-5)]$_2$[UO$_2$Br$_4$], **5** = [Li(12-crown-4)]$_2$[UO$_2$Cl$_4$], and **6** = [Li(12-crown-4)]$_2$[UO$_2$Br$_4$].

Å) than those in both **2** and **4**. The Li−O$_{Cr}$ distances range from 2.06(2) to 2.12(3) Å.

Spectroscopic Characterization. Infrared Spectroscopy. The FT−IR spectra of **1**−**6** were obtained to determine the asymmetric U−O stretching frequency, ν_3. Table 3 lists these values, along with the U−O ν_1 frequencies obtained from Raman spectra and the crystallographically determined U−O bond distances. The IR spectra were sometimes difficult to interpret because of the presence of crown ether vibrational bands in the uranyl stretching frequency region. Also, **3**, **5**, and **6** show considerable broadening of the ν_3 band as compared to **1**, **2**, and **4**. As a result, the following assignments of the asymmetric stretching frequencies are tentative. The asymmetric U−O stretch, ν_3, of **1** and **2** are at 908 and 916 cm^{-1}, respectively. An intense band that appears at 923 cm^{-1} is most likely the ν_3 frequency of **3**; however, a crown ether band is expected here also (a very weak band is present alone at 925 cm^{-1} in the spectrum of **4**). The ν_3 frequency of **4** appears as a sharp, strong band at 904 cm^{-1}, in a region where no crown bands appear, and those of **5** and **6** appear at 910 and 913 cm^{-1}, respectively.

Raman Spectroscopy. The Raman spectra of **1**−**6** are shown in Figure 2. Raman spectroscopy is especially useful in measuring the IR inactive UO$_2^{2+}$ symmetric stretching frequency, ν_1, since the resulting peak is sharp and intense. The information obtained concerning the strength of the U−O bond can provide structural details since bond strength is related to bond length.[30−32] Another advantage afforded by this technique is greater precision than can be obtained by conventional X-ray diffraction. This is especially true in the analysis of bond strength and bond length in the uranyl ion, where one constituent has much more electron density. The uranyl symmetric stretching frequencies of **1**−**6** (Table 3) were assigned through comparisons with similar compounds and through comparisons to spectra of various electrolytes in acidic crown ether solutions.

Two ν_1 frequencies are observed for **3** at 838 and 843 cm^{-1}. The two bands may result from the two crystallographically distinct [UO$_2$Cl$_4$]$^{2-}$ ions within the unit cell. However, the two sets of U−O bond distances determined by single-crystal X-ray diffraction are equivalent within experimental error. The two bands observed in the Raman spectrum indicate that the uranyl force constants are sufficiently different in the two [UO$_2$Cl$_4$]$^{2-}$ ions or that solid-state effects separate the two bands. Regardless, the two types of [UO$_2$Cl$_4$]$^{2-}$ ions can be clearly identified by Raman spectroscopy. Raman spectra with two uranyl ν_1 values have been reported for various forms of schoepite[33,34]
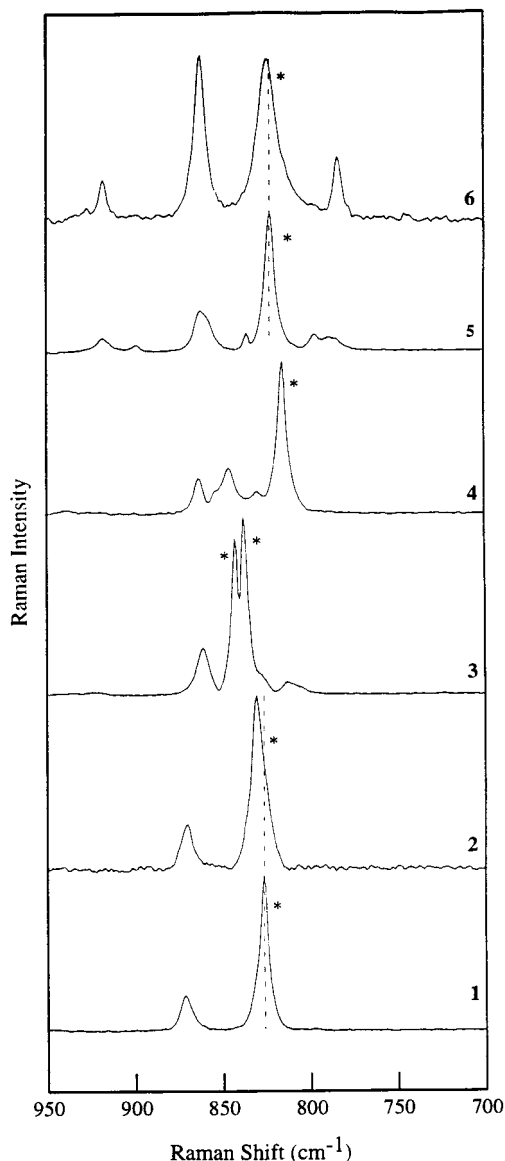
Figure 2. Raman spectra of the U−O ν_1 symmetric stretching frequencies (marked with asterisks) of **1**−**6**. The unmarked bands are due to the crown ether moieties.

and metal uranates;[35,36] however, in many cases, polycrystalline samples were analyzed raising the question of phase purity. Unlike **3**, the compounds that generally result in Raman spectra with multiple uranyl stretching frequencies feature uranyl bond lengths that are markedly different.

It is also possible that the splitting of the U−O band results from one of many solid-state effects that can occur in a crystalline solid. Fermi resonance, site symmetry related shifts, and intermolecular coupling cannot be eliminated as contributors to the band splitting.[37]

It is well-known that equatorial ligands have a direct effect on uranyl bond distances.[38−40] Electron-donating ligands in the

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equatorial plane generally result in longer U−O bond distances. Although the precision of our X-ray experiments does not allow for the comparison of U−O bond distances, the Raman data verify this trend when analogous coordination geometries are compared. For example, **1** and **2** adopt structure type I. On the basis of the aforementioned trends, it is expected that **1**, containing chlorine (higher electronegativity), would have a longer U−O bond length than the bromine-containing **2**. This is confirmed by the Raman data as ν_1 (U−O) of **1** appears at lower energy (826 cm^{-1}) than that of **2** (831 cm^{-1}). This same comparison can be applied to **5** and **6**, as both assume structure type IV. While the Raman shift difference between the two compounds is small, it indicates that **5** has a weaker, thus longer, U−O bond than does **6**. We are unable to compare **3** (types I and II) and **4** (type III) in a similar fashion, as they adopt different structure types. In **4**, the interaction of the uranyl oxygens with the Na$^+$ ions results in a lengthening of the U−O bond distance that is confirmed by the Raman data (ν_1 at 816 cm^{-1}). Importantly, the trend indicated by the Raman data is exactly mirrored by the IR data. Within analogous structure types, the U−O ν_3 frequency of chlorine-bearing compounds is lower than those of bromine-bearing compounds (see Table 3).

Discussion

Several complexes have been reported that contain [UO$_2$Cl$_4$]$^{2-}$ anionic subunits. Rogers et al. reported [(H$_5$O$_2$)$_2$(18-crown-6)]-[UO$_2$Cl$_4$] and [(H$_5$O$_2$)(H$_9$O$_4$)(benzo-15-crown-5)$_2$][UO$_2$Cl$_4$],[9] which consist of complicated polymeric networks of hydrogen bonding involving complex hydronium ions. Rogers et al. also reported a uranyl tetrachloride salt, [Na(12-crown-4)$_2$]$_2$[UO$_2$-Cl$_4$], containing [Na(12-crown-4)$_2$]$^+$ that functions as a well-separated counterion.[11] Moody and co-workers reported the sandwich-type [Na(benzo-15-crown-5)]$_2$[UO$_2$Cl$_4$],[8] which most resembles **1**, **2**, and **3a** in this paper (type I structure). For comparison, the previously reported U−O bond distances (1.74(1)[8] and 1.763(5)[11] Å) and U−Cl bond distances (2.673-(6) Å, average[8] and 2.670(2) and 2.678(2) Å[11]) compare well to those found in this work.

A number of uranyl compounds have been reported that contain the [UO$_2$Br$_4$]$^{2-}$ subunit.[21,41−43] All of these structures are ionic, differing only in the identity of the counterions, and none are sandwich-type compounds. None of the analogous chloride or bromide structures contain uranyl oxygens that participate in any type of bonding interaction other than hydrogen bonding.

It is not unexpected for a uranyl oxygen atom to interact with a cationic species. For example, uranyl oxygen atoms often participate in hydrogen bonding with lattice water molecules (H$_2$O, H$_5$O$_2^+$, H$_9$O$_4^+$, and others).[9,44] Also, some of the earliest X-ray structure determinations of uranyl compounds were carried out on alkali metal and alkaline earth metal uranates, many of which show uranyl oxygen−metal interactions within chain and layered structures.[45,46] This interaction is also represented in uranyl mineral chemistry, again in chain and layered structures.[47−49] Despite the occasional examples,[50−52] it is less common to see this type of interaction occur in a discrete molecular species.

1−6 are an ideal series with which to illustrate the principles of HSAB theory. Two separate effects influence the structural nuances of **1−6**, specifically, the hard−soft nature of the alkali metals and the hard−soft nature of the halides. While it is difficult to separate the two effects, it appears that changing the halide does not affect major structural changes. The exception is the different coordination environments of Na$^+$ in **3** and **4**. However, changing the alkali metal has a profound effect on the interactions between the [UO$_2$X$_4$]$^{2-}$ ions and the alkali metal ions. The hard Li$^+$ ion interacts exclusively with the uranyl oxygens, whereas the soft K$^+$ ion binds only to the softer halide. Na$^+$ is intermediate in hardness and binds to both oxygen and the halides in its complexes.

Conclusion

We have prepared a series of uranyl tetrahalide sandwich-type compounds of the formula [A(crown)]$_2$[UO$_2$X$_4$] where A = Li with 12-crown-4, Na with 15-crown-5, and K with 18-crown-6, and X = Cl, Br. These compounds are rare examples of anhydrous uranyl compounds isolated from aqueous solutions and are easily prepared in high yields. These features makes them ideal candidates for use as starting materials in syntheses where water must be excluded (e.g., organometallic uranyl chemistry).

The coordination trends within this comprehensive series adhere to the principles of HSAB theory and Pearson's principle "hard acids prefer to bind to hard bases and soft acids prefer to bind to soft bases".[53] When the character of the halide becomes soft (Br$^-$), the basicity of the uranyl oxygen atoms becomes a factor as it acts as a hard donor for the harder alkali metal ions (Na$^+$ and Li$^+$), thus altering the structure adopted. This may be an important factor to consider when the prediction of preferred binding is an issue, as in the case of actinide halides in a waste stream.

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