

# Macrocycle Complexation Chemistry. 37.\*

## The Isolation and Crystallographic Characterization of the $U^{4+}$ and $UO_2^{2+}$ Extraction Complexes $[(H_5O_2)(dicyclohexano-24-crown-8)]_2 [UO_2Cl_4] \cdot MeOH$ and $[(H_5O_2)(dicyclohexano-24-crown-8)]_2 [UCl_6] \cdot MeOH$

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**Abstract.** The reaction of dicyclohexano-24-crown-8 with  $UCl_4$  in 3/1 THF:MeOH under anhydrous conditions and with exposure to air, resulted in the isolation of the hydronium ion complexes,  $[(H_5O_2)(dicyclohexano-24-crown-8)]_2 [UO_2Cl_4] \cdot MeOH$  and  $[(H_5O_2)(dicyclohexano-24-crown-8)]_2 [UCl_6] \cdot MeOH$ . The  $[UO_2Cl_4]^{2-}$  complex crystallizes in the monoclinic space group,  $P2_1/n$ , with  $a = 15.200(8)$ ,  $b = 26.565(9)$ ,  $c = 16.977(8) \text{ \AA}$ ,  $\beta = 95.89(6)^\circ$  and  $D_{calc} = 1.40 \text{ g cm}^{-3}$  for  $Z = 4$  formula units. A final  $R$  value of 0.051 was obtained utilizing 5913 independent observed  $[F_o \geq 5\sigma(F_o)]$  reflections. One ether is complexed by an ordered  $H_5O_2^+$  ion, while the second crown ether is hydrogen bonded to a disordered  $H_5O_2^+$  ion. The  $[UCl_6]^{2-}$  complex is tetragonal,  $P4/n$ , with (at  $-150^\circ\text{C}$ )  $a = 16.320(4)$ ,  $c = 12.542(2) \text{ \AA}$  and  $D_{calc} = 1.47 \text{ g cm}^{-3}$  for  $Z = 2$ . A final  $R$  value of 0.038 was obtained utilizing 2466 observed reflections. The anion resides on a four-fold axis and the crown ether cation around a crystallographic two-fold axis. The  $H_5O_2^+$  ion is disordered into two orientations within the macrocycle cavity. All three crystallographically independent crown ether environments in these two structures have essentially identical conformations.

**Key words.** Dicyclohexano-24-crown-8, hydronium uranyl chloride methanol solvate complex, hydronium uranium(IV) chloride methanol solvate complex, X-ray crystal structure.

**Supplementary Data** relating to this article are deposited with the British Library as Supplementary Publication No. SUP 82114 (41 pages)

### 1. Introduction

Few of the separation studies of uranium and thorium with crown ethers have actually demonstrated metal ion crown ether coordination [2–14]. Characterization of uranium complexes is usually limited to dicyclohexano-18-crown-6 (e.g.  $[UO_2(dicyclohexano-18-crown-6)] [ClO_4]_2$  [15]: note the use of the poorly coordinating  $ClO_4^-$  anion). Other crown ether complexes of uranium that have been structurally characterized include  $[U(BH_4)_2(dicyclohexano-18-crown-6)]_2 [UCl_5(BH_4)]$  [16] and  $[UCl_3(dicyclohexano-18-crown-6)]_2 [UCl_6]$  [17]. Inner sphere complexes have also been reported for several

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$U^{3+}$  chlorides and crown ethers [18] as well as  $[UCl_3(18\text{-crown-6})]$  and  $[U(BH_4)_3(18\text{-crown-6})]$  [19].

We have studied the interactions of crown ethers with  $U^{4+}$  and  $UO_2^{2+}$  salts in polar and nonpolar solvents and acidic solutions and have yet to isolate a typical crown ether complex of the metal. We have isolated and structurally characterized several hydrogen bonded or scavenged cation complexes instead. These include  $[Na(12\text{-crown-4})_2][UO_2Cl_4] \cdot 2MeOH$  [20],  $[UO_2(SO_4)(OH_2)_2] \cdot 0.5(12\text{-crown-4}) \cdot H_2O$  [1],  $[Ca(12\text{-crown-4})_2][UO_2Cl_4]$  [21],  $[(NH_4)(15\text{-crown-5})_2][UO_2Cl_4] \cdot 2MeCN$  [22],  $[UO_2(OH_2)_5][ClO_4]_2 \cdot 3(15\text{-crown-5}) \cdot MeCN$  [23],  $[Ca(OH_2)_3(15\text{-crown-5})][UO_2Cl_4]$  [21],  $[(NH_4)(18\text{-crown-6})_2][UCl_6] \cdot 2MeCN$  [24],  $[UO_2Cl_2(OH_2)_3] \cdot 18\text{-crown-6} \cdot H_2O \cdot MeOH$  [22],  $[UO_2(OH_2)_5][ClO_4]_2 \cdot 2(18\text{-crown-6}) \cdot 2MeCN \cdot H_2O$  [23],  $[(H_5O_2)_2(18\text{-crown-6})][UO_2Cl_4]$  [1],  $[UO_2(SO_4)(OH_2)_3] \cdot 0.5(18\text{-crown-6})$  [1],  $[(H_3O)(18\text{-crown-6})_2][(UO_2(NO_3)_2)_2C_2O_4]$  [1],  $[(NH_4)(benzo-15\text{-crown-5})_2][UCl_6] \cdot 4MeCN$  [22],  $[(H_5O_2)(H_9O_4)(benzo-15\text{-crown-5})_2][UO_2Cl_4]$  [1] and  $[(NH_4)(dibenzo-18\text{-crown-6})_2][UO_2Cl_4] \cdot 2MeCN$  [1].

It is interesting to note then the utility ascribed to dicyclohexano-18-crown-6 and dicyclohexano-24-crown-8 in uranyl ion extractions. Reports in the literature [25–28] for dicyclohexano-18-crown-6 and dicyclohexano-24-crown-8 all indicate the presence of hydronium ion crown ether complexes only. The crystal structures of  $[(H_3O)(dicyclohexano-18\text{-crown-6})_2][UCl_6]$  [28],  $[(H_3O)(dicyclohexano-18\text{-crown-6})_2][UO_2Cl_4]$  [27], and  $[(H_5O_2)(dicyclohexano-24\text{-crown-8})_2][UO_2Cl_4]$  [26] have been reported.

We hope to shed some light onto the nature of the interactions responsible for the observed extraction behavior of these complexes. With this report we focus on the solid-state interactions in dicyclohexano-24-crown-8 extraction complexes of  $U^{4+}$  and  $UO_2^{2+}$ .

## 2. Experimental

### 2.1. PREPARATION AND CRYSTALLIZATION OF $[(H_5O_2)(DICYCLOHEXANO-24-CROWN-8)]_2[UO_2Cl_4] \cdot MeOH$ and $[(H_5O_2)(DICYCLOHEXANO-24-CROWN-8)]_2[UCl_6] \cdot MeOH$

Uranium(IV) chloride (0.2g, 0.54 mmole) was dissolved in 4 mL of 3:1 THF:methanol at 60°C under an Ar atmosphere. Dicyclohexano-24-crown-8 (0.22 mL) was added and the resulting mixture was stirred at 60°C for 1 hour. The mixture was centrifuged leaving a yellow-green solution and a black solid. The supernatant was stored at  $-5^\circ C$  for 1 hour and then at  $-20^\circ C$  overnight. Light green crystals formed within 24 hours. Elemental and crystallographic analysis revealed these crystals to have the formulation  $[(H_5O_2)(dicyclohexano-24\text{-crown-8})_2][UCl_6] \cdot MeOH$ . After warming to room temperature and exposure to air the green solution slowly turned yellow. A second set of yellow crystals formed from this solution. These were analysed and found to be  $[(H_5O_2)dicyclohexano-24\text{-crown-8})_2][UO_2Cl_4] \cdot MeOH$ . *Anal. Calcd.* for  $[(H_5O_2)(dicyclohexano-24\text{-crown-8})_2][UO_2Cl_4] \cdot MeOH$  C, 40.89; H, 7.14. *Found:* C, 41.74; H, 7.30. *Anal. Calcd.* for  $[(H_5O_2)(dicyclohexano-24\text{-crown-8})_2][UCl_6] \cdot MeOH$ : C, 39.82; H, 6.96. *Found:* C, 40.70; H, 7.00.

2.2. X-RAY DATA COLLECTION, STRUCTURE, DETERMINATION, AND REFINEMENT FOR  $[(H_5O_2)(DICYCLOHEXANO-24-CROWN-8)]_2[UO_2Cl_4] \cdot MeOH$ 

A yellow single crystal of the title complex was mounted on a pin and transferred to the goniometer. The space group was determined to be the centric  $P2_1/n$  from the systematic absences. A summary of data collection parameters is given in Table I.

The majority of the nonhydrogen atoms were easily located from difference Fourier maps phased on the U atom. One of the  $H_5O_2$  cations and the solvent molecule were found to be disordered. The disordered cation has two orientations within the crown cavity. Each position was refined at 50% occupancy in alternate least-squares cycles. Six atom positions were found for the disordered solvent molecule. These were refined at 0.3333 occupancy each with each site refined as 1/2 C and 1/2 O. These positions were not refined in the same least squares cycles and were refined isotropically only. The hydrogen atoms were not included. Refinement of nonhydrogen atoms (except for the solvent positions) with anisotropic temperature factors led to the final values of  $R = 0.051$  and  $R_w = 0.066$ . The final values of the positional parameters are given in Table II.

The cell parameters reported for  $[(H_5O_2)(dicyclohexano-24-crown-8)]_2[UO_2Cl_4] \cdot C_6H_6$  [26] are quite close to those we observed for this compound. The formulation of our complex as a methanol solvate arises from the resolution of the complex disorder present. We also did not have any contact between benzene and our reaction mixtures. Although certainly not the only evidence to use, we do see support for our formulation in the elemental analysis with C and H percentages within 0.85% and 0.16%, respectively for formulation as a methanol solvate versus 1.93% and 0.24%, respectively for the  $C_6H_6$  alternative. (Elemental analysis cannot rule out a THF solvate, however, the crystallographic interpretation does not fit a disordered THF molecule.) A likely explanation of the similarity in the two complexes, is that the bulky crown ethers create hydrophobic regions that can trap a variety of solvents without greatly affecting the overall structure.

2.3. X-RAY DATA COLLECTION, STRUCTURE DETERMINATION, AND REFINEMENT FOR  $[(H_5O_2)(DICYCLOHEXANO-24-CROWN-8)]_2[UCl_6] \cdot MeOH$ 

A green single crystal fragment of the title complex was mounted on a pin and transferred to the goniometer. In one of the two data sets collected with this crystal, the crystal was cooled to  $-150^\circ C$  using a stream of cold nitrogen gas. The space group was determined to be the centric  $P4/n$  from the systematic absences. A summary of data collection parameters is given in Table I.

The crystal structure at room temperature was solved first. High thermal motion was noted for the Cl(2) and Cl(3) positions on the four-fold axis, the unique cation appeared to have two orientations and a disordered solvent molecule was observed. A low temperature data set was then collected. The disorder of the cation and solvent were resolved and the thermal motion of the Cl positions was dampened but still remains high. The low temperature coordinates were subsequently used in the final refinement of the  $20^\circ C$  data. The crown hydrogen atoms were placed in calculated positions  $0.95 \text{ \AA}$  from the bonded carbon atom and allowed to ride on

Table I. Crystal data and summary of intensity data collection and structure refinement

	$[(\text{H}_5\text{O}_2)_2(\text{dicyclohexano-24-crown-8})_2][\text{UCl}_6] \cdot \text{MeOH}$	$[(\text{H}_5\text{O}_2)_2(\text{dicyclohexano-24-crown-8})_2][\text{UO}_2\text{Cl}_4] \cdot \text{MeOH}$
Cmpd		
Color/Shape	green/fragment	yellow/fragment
For. wt.	1478.1	1439.5
Space group	$P4/n$	$P2_1/n$
Temp., °C	20	20
Cell Constants <sup>a</sup>		
<i>a</i> , Å	16.462(2)	15.200(8)
<i>b</i> , Å	12.708(2)	26.565(9)
<i>c</i> , Å	3443.8	16.977(8)
$\beta$ , deg	2	95.89(6)
Cell vol., Å <sup>3</sup>	2	6819
Formula units/unit cell	2	4
$D_{\text{calc}}$ , g cm <sup>-3</sup>	1.43	1.40
$\mu_{\text{calc}}$ , cm <sup>-1</sup>	25.1	30.4
Diffractometer/Scan	Enraf-Nonius CAD-4/ $\omega$ -2 $\theta$	Enraf-Nonius CAD-4/ $\omega$ -2 $\theta$
Range of relative transm. factors, %	Enraf-Nonius CAD-4/ $\omega$ -2 $\theta$	Enraf-Nonius CAD-4/ $\omega$ -2 $\theta$
Radiation, graphite monochromator	MoK $\alpha$ ( $\lambda = 0.71073$ )	MoK $\alpha$ ( $\lambda = 0.71073$ )
Max crystal dimensions, mm	0.25 × 0.40 × 0.45	0.25 × 0.28 × 0.35
Scan width	0.80 + 0.35 tan $\theta$	0.80 + 0.35 tan $\theta$
Standard reflections	10, 0, 0; 0, 10, 0; 008	800; 0, 12, 0; 0, 0, 10
Decay of standards	± 2%	2 $\theta \leq 36^\circ$ , -2.0%;
		36° ≤ 2 $\theta \leq 50$ - 24.8%
		(corrected)
Reflections measured	3108	12631
2 $\theta$ range, deg	2 ≤ 2 $\theta \leq 50$	2 ≤ 2 $\theta \leq 50$
Range of <i>h, k, l</i>	± 19, + 19, + 14 ( $ h  <  k $ not collected)	+ 18, + 31, ± 20
Reflections observed [ $F_o \geq 5\sigma(F_o)$ ] <sup>b</sup>	2466	5913
Computer programs <sup>c</sup>	SHELX [29]	SHELX [29]
Structure solution	Coordinates from $T = 20^\circ\text{C}$	Heavy atom techniques
No. of parameters varied	181	718
Weights	$[\sigma(F_o)]^2 + 0.000004F_o^2]^{-1}$	$[\sigma(F_o)]^2 + 0.0011F_o^2]^{-1}$
GOF	1.35	0.97
$R = \Sigma \ F_o\  -  F_c  / \Sigma \ F_o\ $	0.043	0.051
$R_w$	0.043	0.066
Largest feature final diff. map	0.7e <sup>-3</sup> Å <sup>3</sup> near <i>U</i>	0.6e <sup>-3</sup> Å <sup>-3</sup>

<sup>a</sup>Least squares refinement of  $(\sin \theta / \lambda)^2$  values for 25 reflections  $\theta > 20^\circ$ .<sup>b</sup>Corrections: Lorentz-polarization and absorption (empirical, psi scan).<sup>c</sup>Neutral scattering factors and anomalous dispersion corrections from Ref. 30.

Table II. Final fractional coordinates for  $[(\text{H}_5\text{O}_2)(\text{dicyclohexano-24-crown-8})_2][\text{UO}_2\text{Cl}_4]\cdot\text{MeOH}$ 

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B</i> (eqv) <sup>a</sup>
U	0.63353(3)	0.26228(2)	0.54041(2)	2.61
Cl(1)	0.5052(2)	0.2635(1)	0.4206(1)	3.74
Cl(2)	0.7618(2)	0.2578(1)	0.6601(2)	3.85
Cl(3)	0.6343(3)	0.3626(1)	0.5437(2)	5.01
Cl(4)	0.6325(2)	0.1622(1)	0.5367(2)	4.68
O(1)	0.7148(5)	0.2632(3)	0.4716(4)	3.98
O(2)	0.5536(4)	0.2617(3)	0.6090(4)	3.61
O(3)	0.2141(5)	0.8825(3)	1.1058(4)	3.56
O(4)	0.3507(6)	0.8208(3)	1.1759(5)	4.85
O(5)	0.5094(6)	0.8092(3)	1.1015(5)	4.94
O(6)	0.5477(5)	0.8618(3)	0.9686(4)	4.22
O(7)	0.5271(5)	0.8819(3)	0.8073(4)	3.91
O(8)	0.3875(7)	0.8232(4)	0.7386(5)	5.70
O(9)	0.2267(6)	0.8123(3)	0.8086(5)	4.93
O(10)	0.1874(5)	0.8609(3)	0.9455(4)	3.98
C(1)	0.2110(9)	0.8598(5)	1.1821(7)	5.02
C(2)	0.304(1)	0.8550(5)	1.2207(7)	5.18
C(3)	0.4353(9)	0.8059(6)	1.2155(8)	5.86
C(4)	0.477(1)	0.7739(6)	1.155(1)	6.93
C(5)	0.542(1)	0.7815(5)	1.0379(9)	6.32
C(6)	0.601(1)	0.8185(5)	0.9970(8)	5.68
C(7)	0.5993(8)	0.8997(4)	0.9358(6)	3.93
C(8)	0.6132(8)	0.8877(5)	0.8517(7)	4.07
C(9)	0.5312(9)	0.8558(5)	0.7338(7)	5.13
C(10)	0.441(1)	0.8527(6)	0.6928(7)	5.24
C(11)	0.306(1)	0.8108(7)	0.6947(9)	6.77
C(12)	0.257(1)	0.7803(7)	0.748(1)	7.68
C(13)	0.189(1)	0.7846(5)	0.8712(8)	6.04
C(14)	0.1313(9)	0.8211(5)	0.9123(8)	4.77
C(15)	0.1393(7)	0.8992(4)	0.9786(7)	3.60
C(16)	0.1265(7)	0.8879(4)	1.0651(7)	3.82
C(17)	0.0766(8)	0.9313(5)	1.1022(9)	5.48
C(18)	0.126(1)	0.9835(5)	1.0919(9)	5.94
C(19)	0.1394(9)	0.9915(5)	1.0007(9)	5.48
C(20)	0.1913(8)	0.9485(4)	0.9678(7)	4.36
C(21)	0.5478(7)	0.9498(4)	0.9421(6)	3.63
C(22)	0.6068(9)	0.9919(5)	0.9149(8)	5.36
C(23)	0.6213(9)	0.9808(5)	0.8262(9)	5.52
C(24)	0.6686(8)	0.9300(5)	0.8185(8)	5.21
O(11)	0.3687(6)	0.8675(4)	1.0271(5)	6.26
O(12)	0.3663(6)	0.8704(4)	0.8852(4)	5.58
O(13)	-0.0690(6)	0.1082(5)	0.4499(6)	8.14
O(14)	-0.0280(7)	0.1667(5)	0.5840(6)	7.68
O(15)	0.0964(6)	0.1647(3)	0.7275(5)	5.21
O(16)	0.2477(5)	0.1078(3)	0.7591(4)	3.73
O(17)	0.3435(6)	0.1148(5)	0.6320(6)	9.04
O(18)	0.2932(7)	0.1789(4)	0.5043(6)	6.66
O(19)	0.1739(6)	0.1717(3)	0.3563(4)	4.61
O(20)	0.0305(5)	0.1076(3)	0.3228(4)	3.92
C(25)	-0.127(1)	0.123(1)	0.488(1)	10.67
C(26)	-0.114(1)	0.1528(6)	0.5588(9)	6.71
C(27)	-0.017(1)	0.2027(7)	0.645(1)	8.29

Table II. (continued)

Atom	$x/a$	$y/b$	$z/c$	$B(\text{eqv})^a$
C(28)	0.005(1)	0.1829(7)	0.7196(8)	7.55
C(29)	0.1153(9)	0.1384(5)	0.8015(7)	4.79
C(30)	0.213(1)	0.1363(5)	0.8201(7)	4.80
C(31)	0.3438(8)	0.1033(5)	0.7706(7)	4.53
C(32)	0.3694(9)	0.0794(7)	0.6937(9)	6.40
C(33)	0.401(1)	0.1313(8)	0.590(1)	9.40
C(34)	0.382(1)	0.1628(6)	0.5217(9)	6.19
C(35)	0.279(1)	0.2179(6)	0.4439(8)	6.11
C(36)	0.2602(9)	0.1948(5)	0.3669(7)	5.11
C(37)	0.157(1)	0.1440(5)	0.2804(7)	4.83
C(38)	0.061(1)	0.1391(5)	0.2612(7)	5.42
C(39)	-0.0647(9)	0.0975(5)	0.3091(7)	4.67
C(40)	-0.090(1)	0.0719(6)	0.3871(8)	5.88
C(41)	-0.042(1)	0.0230(6)	0.4028(8)	6.00
C(42)	-0.058(1)	-0.0151(6)	0.328(1)	7.63
C(43)	-0.037(1)	0.0127(6)	0.2501(9)	7.11
C(44)	-0.090(1)	0.0618(6)	0.2404(7)	6.28
C(45)	0.326(1)	0.0281(6)	0.6743(9)	5.93
C(46)	0.350(1)	-0.0104(6)	0.743(1)	7.00
C(47)	0.328(1)	0.0146(6)	0.821(1)	7.02
C(48)	0.372(1)	0.0659(6)	0.8377(8)	6.31
O(21)	0.1581(8)	0.1205(6)	0.5986(8)	3.66
O(22)	0.0919(9)	0.1583(5)	0.4767(7)	3.37
O(21) <sup>nb</sup>	0.111(1)	0.1180(7)	0.4823(8)	5.06
O(22)'	0.182(1)	0.1536(8)	0.6097(9)	5.96
Xs(1)	0.757(2)	0.468(1)	0.915(2)	9(1) <sup>c</sup>
Xs(2)	0.783(3)	0.538(2)	0.866(2)	11(1) <sup>c</sup>
Xs(3)	0.867(3)	0.520(2)	0.897(3)	12(1) <sup>c</sup>
Xs(4)	0.811(4)	0.514(2)	0.942(3)	16(2) <sup>c</sup>
Xs(5)	0.841(2)	0.459(1)	0.902(2)	7.5(8) <sup>c</sup>
Xs(6)	0.725(3)	0.499(2)	0.893(3)	12(1) <sup>c</sup>

$$^a B(\text{eqv}) = 4/3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos \gamma)\beta_{12} + ac(\cos \beta)\beta_{13} + bc(\cos \alpha)\beta_{23}]$$

<sup>b</sup>The primed and unprimed atoms of like number, and the solvent molecule (Xs) are disordered: See Experimental Section.

<sup>c</sup>Isotropic refinement.

that atom with B fixed at  $5.5\text{\AA}^2$ . The remaining hydrogen atoms were not included in the final refinement. Refinement of the nonhydrogen atoms with anisotropic temperature factors led to final  $R$  and  $R_w$  values given in Table I. The final values of the positional parameters are given in Table III for the low temperature data and in the supplementary material for the  $20^\circ\text{C}$  data.

### 3. Results and Discussion

The solid state structures of the title complexes provide some clues to the ability of dicyclohexano-24-crown-8 to effectively extract uranium. Each structure consists of hydronium complexed ethers surrounding the large uranium(IV) chloride or uranyl chloride anions. Inspection of the cell packing diagrams (Figures 1 and 2)

Table III. Final fractional coordinates for  $[(H_5O_2) (dicyclohexano-24-crown-8)]_2[UCl_6] \cdot MeOH$ 

Atom	$x/a$	$y/b$	$z/c$	$B(\text{eqv})^a$
U	0.7500	0.7500	0.56899(3)	1.66
Cl(1)	0.62810(9)	0.85495(9)	0.5658(1)	3.19
Cl(2)	0.7500	0.7500	0.3617(3)	4.95
Cl(3)	0.7500	0.7500	0.7766(3)	5.80
O(1) <sup>b</sup>	0.796(1)	0.204(1)	0.747(1)	4.18
O(1)'	0.6908(9)	0.281(1)	0.777(1)	3.09
O(2)	0.7042(4)	0.3071(4)	0.6804(5)	2.12
O(3)	0.6052(2)	0.4316(2)	0.8090(3)	2.39
O(4)	0.5443(2)	0.3057(2)	0.6724(3)	2.70
O(5)	0.5952(2)	0.1326(2)	0.6687(3)	2.55
O(6)	0.7260(2)	0.0698(2)	0.7835(3)	2.98
C(1)	0.7352(4)	0.4779(4)	0.8671(5)	3.03
C(2)	0.6512(3)	0.5042(4)	0.8336(5)	2.71
C(3)	0.5436(3)	0.4453(3)	0.7322(4)	2.52
C(4)	0.4940(3)	0.3691(3)	0.7182(5)	2.51
C(5)	0.4963(4)	0.2376(4)	0.6392(5)	3.49
C(6)	0.5507(4)	0.1740(4)	0.5881(5)	3.47
C(7)	0.6495(4)	0.0752(4)	0.6231(5)	3.34
C(8)	0.6852(4)	0.0213(4)	0.7060(5)	3.07
C(9)	0.7360(4)	0.4252(5)	0.9679(5)	3.89
C(10)	0.6969(5)	0.4726(5)	1.0588(5)	5.05
C(11)	0.6105(4)	0.5006(5)	1.0281(5)	4.15
C(12)	0.6117(4)	0.5510(4)	0.9260(5)	3.37
O(7)	0.687(1)	0.704(2)	0.137(2)	6.35
C(13)	0.754(8)	0.712(2)	0.083(2)	5.26

<sup>a</sup> $B(\text{eqv})$  is defined in Table II.

<sup>b</sup>O(1) and O(1)' are disordered: See Experimental Section.

reveals an interesting packing scheme for these complexes. The cation/crown ether complexes are packed around the anions in such a manner that all of the hydrophobic cyclohexyl substituents point away from the anions and toward the cyclohexyl groups of neighboring crown cations. The cyclohexyl groups are all directed essentially in the  $\pm b$  ( $[UO_2Cl_4]^{2-}$  complex) or  $\pm c$  ( $[UCl_6]^{2-}$  complex) directions. This forms layers of hydrophobic cyclohexyl groups. The anion layers are packed between the more hydrophilic 'back-side' of two crown ether layers. The overall layer-like structure thus consists of a layer of anions, two layers of crown ether complexed cations with all the cyclohexyl groups arranged toward each other, followed by another anion layer. In the  $[UCl_6]^{2-}$  complex these zones are parallel to  $ab$  (Figure 1) while they are parallel to  $ac$  in the  $[UO_2Cl_4]^{2-}$  complex (Figure 2). The solvent molecules in the  $[UO_2Cl_4]^{2-}$  complex reside between the crown ether layers, essentially bounded by four cyclohexyl substituents. This leads to the highly disordered solvent observed. As discussed in the experimental section, this region can probably support a number of different solvent molecules without greatly affecting the overall crystal structure. The methanol solvate reported here is nearly identical to the  $C_6H_6$  solvate reported in Reference 26.

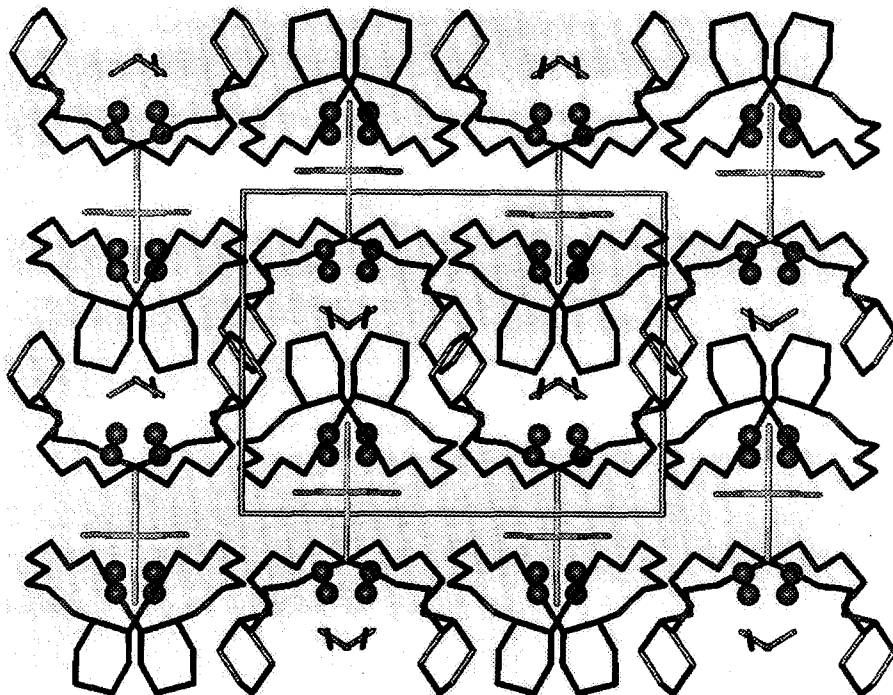


Fig. 1. Cell packing view of  $[(\text{H}_5\text{O}_2)(\text{dicyclohexano-24-crown-8})_2][\text{UCl}_6] \cdot \text{MeOH}$  ( $xz$  plane;  $-150^\circ\text{C}$  data). Representation generated using SYBYL Molecular Modeling Software: Tripos Associates, Inc. St. Louis, MO.

In the  $[\text{UCl}_6]^{2-}$  complex the solvent resides between crown ether molecules in a single layer. These solvent molecules are bounded by only two cyclohexyl groups and can thus interact via hydrogen bonding with the anions.

Although we cannot directly compare solid state results to solutions, these structures do provide some evidence that the role of the crown ether in actinide processing has very little to do with the coordination of the crown ether to the metal ion. Rather, the crown ether may be able to effect extraction of the large uranium ions by complexing the cations and surrounding the large anions creating hydrophobic environments for both. This could facilitate transfer from an acidic polar medium to an organic nonpolar extraction solvent.

The anions in both structures are unexceptional. Both are pseudooctahedral with average bonding parameters of  $[\text{UCl}_6]^{2-}$ :  $\text{U}-\text{Cl} = 2.61(1)\text{\AA}$ ;  $[\text{UO}_2\text{Cl}_4]^{2-}$ :  $\text{U}=\text{O} = 1.78(1)\text{\AA}$ ,  $\text{U}-\text{Cl} = 2.666(5)\text{\AA}$ . The  $[\text{UCl}_6]^{2-}$  anion resides on a crystallographic four-fold axis which runs along the  $\text{Cl}(2)-\text{U}-\text{Cl}(3)$  axis. The solvent in this complex has one close contact indicative of hydrogen bonding between  $\text{O}(7)$  and  $\text{Cl}(2)$ . The solvent in the  $[\text{UO}_2\text{Cl}_4]^{2-}$  complex crystallizes in lattice holes discussed above and is disordered into twelve resolvable positions.

The crown ether molecules are quite similar. Each is complexed to a  $\text{H}_5\text{O}_2^+$  cation, two of which are disordered in the rather large crown cavities. In the  $[\text{UO}_2\text{Cl}_4]^{2-}$  complex, there are two crystallographically independent crown ethers. One is complexed to an ordered  $\text{H}_5\text{O}_2^+$  ion ( $\text{O}(11)-\text{O}(12)$ ) (Figure 3), the other to



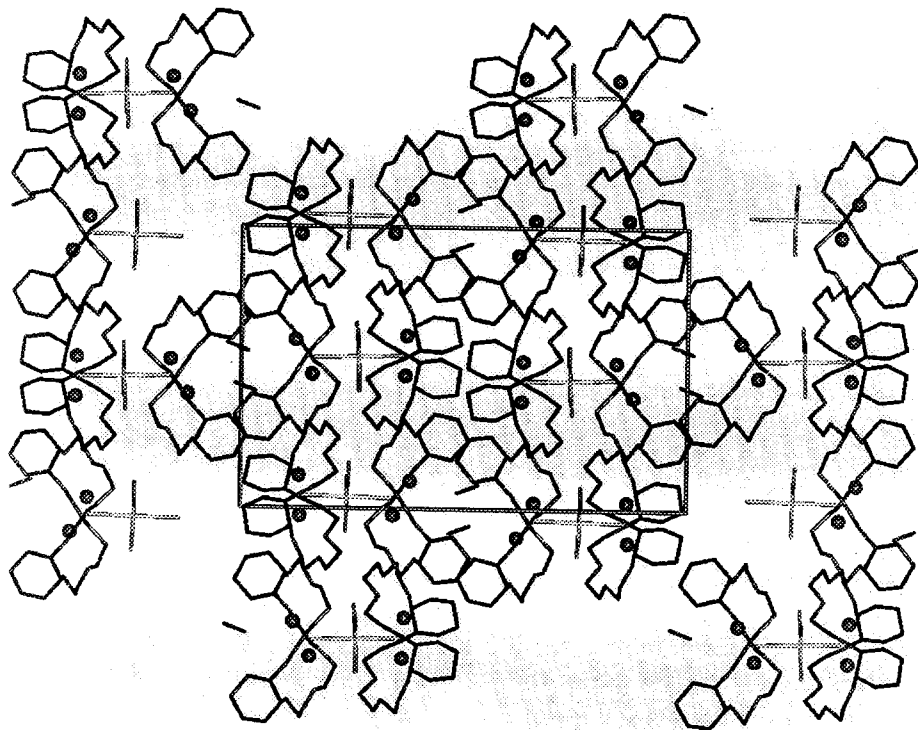


Fig. 2. Cell packing view of  $[(H_5O_2)(dicyclohexano-24-crown-8)]_2[UO_2Cl_4] \cdot MeOH$  ( $yz$  plane). Representation generated using SYBYL Molecular Modeling Software: Tripos Associates, Inc. St. Louis, MO.

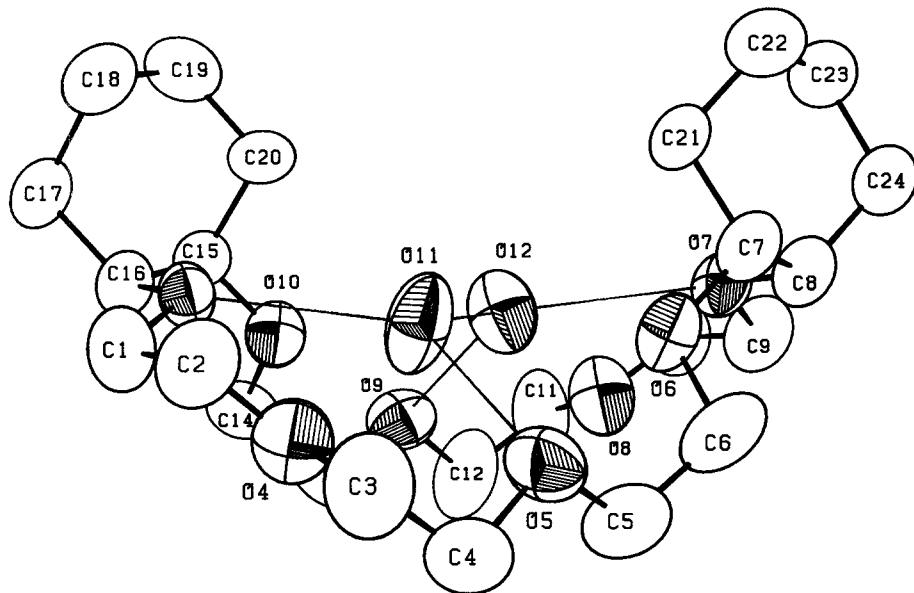


Fig. 3. The ordered  $[(H_5O_2)(dicyclohexano-24-crown-8)]^+$  ion. Atoms are represented by their 50% probability ellipsoids. Hydrogen atoms were not located.

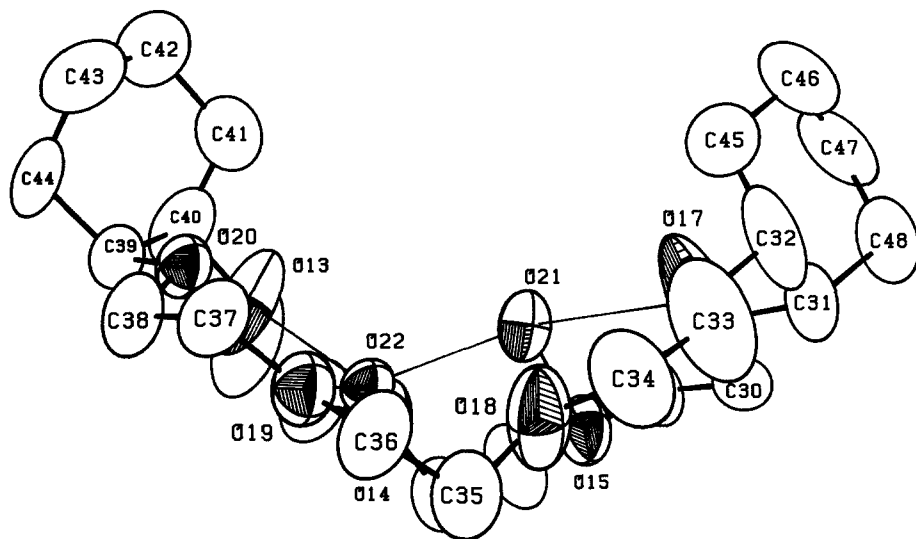


Fig. 4. One orientation of the disordered  $[(\text{H}_5\text{O}_2)(\text{dicyclohexano-24-crown-8})]^+$  cation in the  $[\text{UO}_2\text{Cl}_4]^{2-}$  complex.

a disordered  $\text{H}_5\text{O}_2^+$  molecule  $\text{O}(21)\text{—O}(22)$  (Figure 4). Each oxygen of the ordered cation has five rather long contacts with the crown ether ranging from 2.83(1) to 3.01(1) Å. The  $\text{O}(11)\text{—O}(12)$  contact is 2.41(1) Å.

The  $\text{H}_5\text{O}_2^+$  molecule in the second unique ether is disordered in a 50/50% fashion. In both orientations, the  $\text{H}_5\text{O}_2^+$  molecule is hydrogen bonded to the same four oxygen atoms ( $\text{O}(13)$ ,  $\text{O}(15)$ ,  $\text{O}(17)$  and  $\text{O}(19)$ ): Table IV). In this orientation, the cation's molecular axis is oriented along the crown cavity's largest dimension. Geometric constraints essentially force hydrogen bonding to nonconsecutive oxygens in crown ethers and thus, these five oxygen atoms are the ones the molecule would have to use to keep its molecular axis so aligned.

In addition to the molecular orientation, it is also noted that  $\text{O}(22)$  (and  $\text{O}(22)'$  in the other disordered conformation) makes a deeper penetration into the crown ether cavity.  $\text{O}(22)$  and  $\text{O}(22)'$  also make closer approaches to the oxygens of the macroring. The  $\text{O}(22)\cdots\text{O}$  and  $\text{O}(22)'\cdots\text{O}$  hydrogen bonding contacts average 2.6(1) Å versus 2.78(4) Å for  $\text{O}(21)\cdots\text{O}$  and  $\text{O}(21)'\cdots\text{O}$ . This indicates an asymmetric nature for the  $\text{H}_5\text{O}_2^+$  cation where  $\text{O}(21)$  has more  $\text{H}_3\text{O}^+$  character and  $\text{O}(22)$  more  $\text{H}_2\text{O}$  character. All four positions are pyramidal residing an average of 0.7 Å out of the plane of the hydrogen bonded oxygen atoms (versus 0.4 Å for  $\text{O}(11)$  and  $\text{O}(12)$ ). The  $\text{O}\cdots\text{O}$  contacts within the cation are 2.42(2) and 2.50(2) Å for the two orientations.

The coordination of the  $\text{H}_5\text{O}_2^+$  ion to dicyclohexano-24-crown-8 in the  $[\text{UCl}_6]^{2-}$  complex is nearly identical to the second ether above (Figure 5). The one unique ether resides around a two-fold axis. The  $\text{H}_5\text{O}_2^+$  cation is disordered into two orientations, the long axis of the molecule corresponds to the long axis of the crown cavity, only four oxygen atoms are utilized in the hydrogen bonding, and one oxygen of the cation ( $\text{O}(2)$ ) makes a deeper penetration into the cavity. The

Table IV. Hydrogen bonding contact geometries (Å, deg) for  $[(H_5O_2)(dicyclohexano-24-crown-8)]_2[UO_2Cl_4] \cdot MeOH$ 

Atoms	Distance	Atoms	Distance
O(11)—O(3)	2.83(1)	O(12)—O(7)	2.91(1)
O(11)—O(5)	2.83(1)	O(12)—O(9)	2.83(1)
O(11)—O(12)	2.41(1)		
O(21)—O(15)	2.73(2)	O(21)'—O(13)	2.75(2)
O(21)—O(17)	2.82(2)	O(21)'—O(19)	2.82(2)
O(21)—O(22)	2.42(2)	O(21)'—O(22)'	2.50(2)
O(22)—O(13)	2.78(2)	O(22)'—O(15)	2.51(2)
O(22)—O(19)	2.53(2)	O(22)'—O(17)	2.65(2)
Atoms	Angle	Atoms	Angle
O(3)—O(11)—O(5)	119.3(4)	O(7)—O(12)—O(9)	118.2(4)
O(3)—O(11)—O(12)	122.4(4)	O(7)—O(12)—O(11)	122.1(4)
O(5)—O(11)—O(12)	113.4(4)	O(8)—O(12)—O(11)	112.1(4)
O(15)—O(21)—O(17)	106.3(5)	O(13)—O(21)'—O(19)	107.7(6)
O(15)—O(21)—O(22)	111.0(6)	O(13)—O(21)'—O(22)'	122.7(8)
O(17)—O(21)—O(22)	120.8(7)	O(19)—O(21)'—O(22)'	108.4(7)
O(13)—O(22)—O(19)	115.7(5)	O(15)—O(22)'—O(17)	118.6(6)

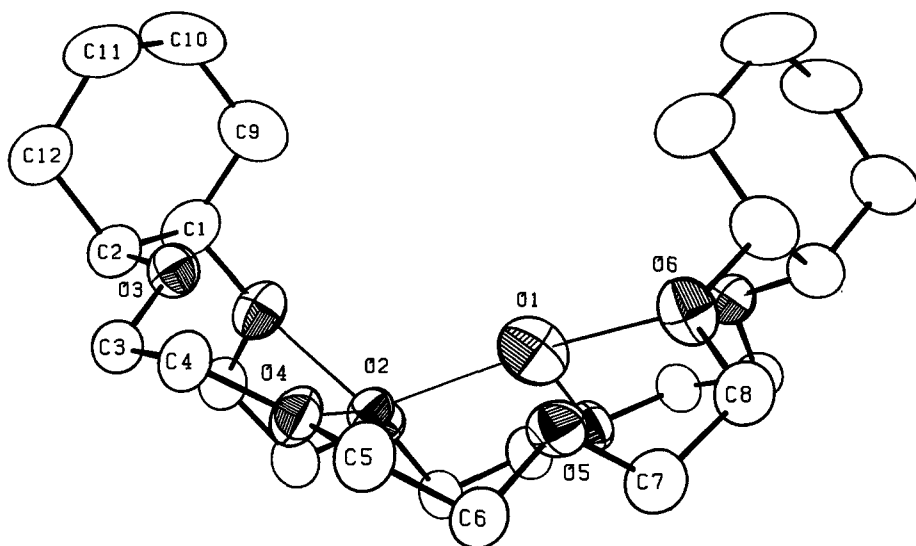
Fig. 5. One orientation of the disordered  $[(H_5O_2)(dicyclohexano-24-crown-8)]^+$  cation in the  $[UCl_6]^{2-}$  complex ( $-150^\circ C$  data). The hydrogen atoms have been omitted.

Table V. Hydrogen bonding contact geometries (Å, deg) for [(H<sub>5</sub>O<sub>2</sub>)(dicyclohexano-24-crown-8)]<sub>2</sub>[UCl<sub>6</sub>]·MeOH

Atoms	Distance	Atoms	Distance
O(1)—O(2)	2.39(2)	O(1)—O(4) <sup>a</sup>	2.78(2)
O(1)—O(6)	2.51(2)		
O(1)'—O(2) <sup>a</sup>	2.54(2)	O(1)'—O(4)	2.76(2)
O(1)'—O(6) <sup>a</sup>	2.79(2)		
O(2)—O(4)	2.611(8)	O(2)—O(6) <sup>a</sup>	2.646(8)
O(7)—Cl(2)	3.09(2)		
Atoms	Angle	Atoms	Angle
O(2)—O(1)—O(4) <sup>a</sup>	120.7(7)	O(2)—O(1)—O(6)	113.3(7)
O(4) <sup>a</sup> —O(1)—O(6)	115.8(7)		
O(2) <sup>a</sup> —O(1)'—O(4)	116.4(5)	O(2) <sup>a</sup> —O(1)'—O(6) <sup>a</sup>	100.4(5)
O(4)—O(1)'—O(6) <sup>a</sup>	107.9(5)		
O(4)—O(2)—O(6) <sup>a</sup>	117.1(3)		
O(1)—O(2)—O(4)	129.0(5)	O(1)—O(2)—O(6) <sup>a</sup>	95.4(5)
O(1)' <sup>a</sup> —O(2)—O(4)	133.4(4)	O(1)' <sup>a</sup> —O(2)—O(6) <sup>a</sup>	84.6(4)
C(13)—O(7)—Cl(2)	100(3)		

<sup>a</sup>Atoms designated 'a' are related to those in Table III by 1.5 - x, 0.5 - y, z.

O(2)···O contacts average 2.63(2)Å and the O(1)···O and O(1)'···O contacts average 2.71(6)Å (Table V). Each oxygen atom in the cation is pyramidal, an average 0.7Å out of the plane of the three hydrogen bond neighbors. The O···O contacts within the two cation orientations are 2.39(2) and 2.54(2)Å.

The three independent crown ethers in these two crystal structures have nearly identical conformations. The molecule in the [UCl<sub>6</sub>]<sup>2-</sup> compound and the complexed ether in the [UO<sub>2</sub>Cl<sub>4</sub>]<sup>2-</sup> compound with the ordered cation have O—C—C—O torsion angles which alternate ±g (ca. ±60°) around the macroring (Tables VI and VII). The C—O—C—C angles are all *anti* (ca. 180°) except for two, both of which occur leading to the cyclohexyl groups. Thus, one of the two C—O—C—C angles involving each C—C linkage in the cyclohexyl groups is forced toward *gauche*. In the [UCl<sub>6</sub>]<sup>2-</sup> complex this angle is C(8)—O(6)—C(1)<sup>a</sup>—C(2)<sup>a</sup> and its symmetry related angle. In the ordered cation in the [UO<sub>2</sub>Cl<sub>4</sub>]<sup>2-</sup> complex, these angles are C(6)—O(6)—C(7)—C(8) and C(14)—O(10)—C(15)—C(16).

The second independent ether in the [UO<sub>2</sub>Cl<sub>4</sub>]<sup>2-</sup> complex appears at first glance to have a different conformation, however, the only differences are the O(13)—C(25)—C(26)—O(14) and O(17)—C(33)—C(34)—O(18) angles which are synclinal. Further examination of the ether around these angles reveals very short O—C distances (O13)—C(25) = 1.22(2)Å, O(17)—C(33) = 1.26(2)Å). We believe that any apparent differences in conformation are a crystallographic artifact of some minor unresolved disorder in these ethylene linkages.

The average bonding parameters in the macrocycles are not unusual for crown ethers. The average parameters for the [(H<sub>5</sub>O<sub>2</sub>)(dicyclohexano-24-crown-8)]<sup>+</sup> ions ([UCl<sub>6</sub>]<sup>2-</sup> complex, [UO<sub>2</sub>Cl<sub>4</sub>]<sup>2-</sup> complex disordered cation, [UOCl<sub>4</sub>]<sup>2-</sup> complex ordered cation, respectively) are C—C (macroring) = 1.50(1), 1.47(6), 1.51(2)Å;

Table VI. Torsion angles (deg) for  $[(H_5O_2)(dicyclohexano-24-crown-8)]_2[UO_2Cl_4] \cdot MeOH$ 

Atoms	Angle
O(3)—C(1)—C(2)—O(4)	-64.9
C(1)—C(2)—O(4)—C(3)	-168.9
C(2)—O(4)—C(3)—C(4)	-175.2
O(4)—C(3)—C(4)—O(5)	77.4
C(3)—C(4)—O(5)—C(5)	-173.8
C(4)—O(5)—C(5)—C(6)	-162.3
O(5)—C(5)—C(6)—O(6)	-59.1
C(5)—C(6)—O(6)—C(7)	175.1
C(6)—O(6)—C(7)—C(8)	82.2
O(6)—C(7)—C(8)—O(7)	56.9
C(7)—C(8)—O(7)—C(9)	-162.2
C(8)—O(7)—C(9)—C(10)	-179.2
O(7)—C(9)—C(10)—O(8)	-64.0
C(9)—C(10)—O(8)—C(11)	-168.3
C(10)—O(8)—C(11)—C(12)	179.9
O(8)—C(11)—C(12)—O(9)	72.0
C(11)—C(12)—O(9)—C(13)	-171.0
C(12)—O(9)—C(13)—C(14)	-159.6
O(9)—C(13)—C(14)—O(10)	-61.2
C(13)—C(14)—O(10)—C(15)	174.5
C(14)—O(10)—C(15)—C(16)	87.7
O(10)—C(15)—C(16)—O(3)	58.0
C(15)—C(16)—O(3)—C(1)	-165.8
C(16)—O(3)—C(1)—C(2)	179.5
O(13)—C(25)—C(26)—O(14)	2.5
C(25)—C(26)—O(14)—C(27)	169.0
C(26)—O(14)—C(27)—C(28)	98.6
O(14)—C(27)—C(28)—O(15)	72.5
C(27)—C(28)—O(15)—C(29)	-172.8
C(28)—O(15)—C(29)—C(30)	-160.7
O(15)—C(29)—C(30)—O(16)	-63.0
C(29)—C(30)—O(16)—C(31)	179.6
C(30)—O(16)—C(31)—C(32)	-171.2
O(16)—C(31)—C(32)—O(17)	63.3
C(31)—C(32)—O(17)—C(33)	122.6
C(32)—O(17)—C(33)—C(34)	173.4
O(17)—C(33)—C(34)—O(18)	4.6
C(33)—C(34)—O(18)—C(35)	169.2
C(34)—O(18)—C(35)—C(36)	90.9
O(18)—C(35)—C(36)—O(19)	71.3
C(35)—C(36)—O(19)—C(37)	-174.8
C(36)—O(19)—C(37)—C(38)	-158.4
O(19)—C(37)—C(38)—O(20)	-64.9
C(37)—C(38)—O(20)—C(39)	-177.4
C(38)—O(20)—C(39)—C(40)	-170.0
O(20)—C(39)—C(40)—O(13)	60.7
C(39)—C(40)—O(13)—C(25)	120.6
C(40)—O(13)—C(25)—C(26)	169.8

Table VII. Torsion angles (deg) for  $[(H_5O_2)(dicyclohexyl-24-crown-8)]_2[UCl_6] \cdot MeOH$ 

Atoms	Angle
O(3)—C(3)—C(4)—O(4)	−66.1
C(3)—C(4)—O(4)—C(5)	−168.9
C(4)—O(4)—C(5)—C(6)	177.9
O(4)—C(5)—C(6)—O(5)	75.1
C(5)—C(6)—O(5)—C(7)	−177.4
C(6)—O(5)—C(7)—C(8)	−169.8
O(5)—C(7)—C(8)—O(6)	−57.5
C(7)—C(8)—O(6)—C(1) <sup>a</sup>	−178.7
C(8)—O(6)—C(1) <sup>a</sup> —C(2) <sup>a</sup>	85.7
O(6)—C(1) <sup>a</sup> —C(2) <sup>a</sup> —O(3) <sup>a</sup>	57.9
C(1) <sup>a</sup> —C(2) <sup>a</sup> —O(3) <sup>a</sup> —C(3) <sup>a</sup>	−151.7
C(2) <sup>a</sup> —O(3) <sup>a</sup> —C(3) <sup>a</sup> —C(4) <sup>a</sup>	−175.1

<sup>a</sup>Atoms designated 'a' are related to those in Table III by  $1.5 - x, 0.5 - y, z$ .

C—O = 1.43(1), 1.42(7), 1.44(2) Å; C—C(cyclohexyl) = 1.526(4), 1.55(3), 1.56(2) Å; C—O—C = 112(1), 115(3), 112(2)°; O—C—C(macroring) = 109.6(9), 111(6), 108(2)°, O—C—C(cyclohexyl substituents) = 109(2), 112(2), 109(3)°, C—C—C = 111(2), 111(2), 110(2)°.

There are few crystal structures for comparison with these results, however, the structure of the closely related complex,  $[(H_5O_2)(dicyclohexano-24-crown-8)]_2[UO_2Cl_4] \cdot C_6H_6$  was reported recently [26]. One cation was disordered and the second  $H_5O_2^+$  molecule was ordered exactly as observed in our  $[UO_2Cl_4]^{2-}$  complex. In the ordered cation nearly equivalent  $H_5O_2^+—O$  hydrogen bonded contacts of 2.879, 2.846, 2.845 and 2.910 Å were reported. Few other details were provided.

We have isolated the  $H_5O_2^+$  ion as a sandwich complex of benzo-15-crown-5 in  $[(H_5O_2)((NO_2)_2benzo-15-crown-5)_2]_2[(UO_2(NO_3)_2)_2C_2O_4]$  [1] and in  $[(H_5O_2)(H_9O_4)(benzo-15-crown-5)_2][UO_2Cl_4]$  [1]. The  $H_5O_2^+$  cation donates two hydrogen bonds to each crown ether. In the extraction chemistry of  $U^{6+}$ ,  $U^{4+}$ , and  $Th^{4+}$  with dicyclohexano-18-crown-6,  $H_3O^+$  complexes have been isolated including  $[(H_3O)(dicyclohexano-18-crown-6)]_2[UCl_6]$  [28],  $[(H_3O)(dicyclohexano-18-crown-6)]_2[UO_2Cl_4]$  [27] and  $[(H_3O)(dicyclohexano-18-crown-6)]_2[Th(NO_3)_6]$  [31]. It appears that the  $H_5O_2^+$  cation can only be stabilized by sandwich ion formation of smaller crown ethers or by the presence of a very large and flexible crown cavity that can accept all four hydrogen bonding interactions.

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