

# *f*-Element/Crown Ether Complexes, 11.\* Preparation and Structural Characterization of $[\text{UO}_2(\text{OH}_2)_5][\text{ClO}_4]_2 \cdot 3(15\text{-crown-5}) \cdot \text{CH}_3\text{CN}$ and $[\text{UO}_2(\text{OH}_2)_5][\text{ClO}_4]_2 \cdot 2(18\text{-crown-6}) \cdot 2\text{CH}_3\text{CN} \cdot \text{H}_2\text{O}$

ROBIN D. ROGERS\*\*, LYNN K. KURIHARA, and MATTHEW M. BENNING  
*Department of Chemistry, Northern Illinois University, DeKalb, IL 60115, U.S.A.*

(Received: 23 November 1986; in final form: 5 February 1987)

**Abstract.** The reaction of  $\text{UO}_2(\text{ClO}_4) \cdot n\text{H}_2\text{O}$  with 15-crown-5 and 18-crown-6 in acetonitrile yielded the title complexes.  $[\text{UO}_2(\text{OH}_2)_5][\text{ClO}_4]_2 \cdot 3(15\text{-crown-5}) \cdot \text{CH}_3\text{CN}$  crystallizes in the triclinic space group  $P\bar{1}$  with (at  $-150^\circ\text{C}$ )  $a = 8.288(6)$ ,  $b = 12.874(7)$ ,  $c = 24.678(7)$  Å,  $\alpha = 82.62(4)$ ,  $\beta = 76.06(5)$ ,  $\gamma = 81.06(5)^\circ$ , and  $D_{\text{calc}} = 1.67$  g cm $^{-3}$  for  $Z = 2$  formula units. Least-squares refinement using 6248 independent observed reflections [ $F_o \geq 5\sigma(F_o)$ ] led to  $R = 0.111$ .  $[\text{UO}_2(\text{OH}_2)_5][\text{ClO}_4]_2 \cdot 2(18\text{-crown-6}) \cdot 2\text{CH}_3\text{CN} \cdot \text{H}_2\text{O}$  is orthorhombic  $P2_12_12_1$  with (at  $-150^\circ\text{C}$ )  $a = 12.280(2)$ ,  $b = 17.311(7)$ ,  $c = 22.056(3)$  Å,  $D_{\text{calc}} = 1.68$  g cm $^{-3}$ ,  $Z = 4$ , and  $R = 0.032$  (3777 observed reflections). In each complex the crown ether molecules are hydrogen bonded to the water molecules of the pentagonal bipyramidal  $[\text{UO}_2(\text{OH}_2)_5]^{2+}$  ions, each crown ether having exclusive use of two hydrogen atoms from one water molecule and one hydrogen from another water molecule. In the 15-crown-5 complex the remaining hydrogen bonding interaction is between one of the water molecules and one of the perchlorate anions. The solvent molecule has a close contact between the methyl group and a perchlorate anion suggesting a weak interaction. There are a total of three  $\text{U}-\text{OH} \cdots \text{OClO}_3$  hydrogen bonds to the two perchlorate anions in  $[\text{UO}_2(\text{OH}_2)_5][\text{ClO}_4]_2 \cdot (18\text{-crown-6}) \cdot 2\text{CH}_3\text{CN} \cdot \text{H}_2\text{O}$ . The remaining coordinated water hydrogen bond is to the uncoordinated  $2\text{H}_2\text{O}$  molecule, which in turn is hydrogen bonded to a perchlorate oxygen atom and an acetonitrile nitrogen atom. One solvent methyl group interacts with an anion, the other with one of the 18-crown-6 molecules. Unlike the 15-crown-5 structure, the hydrogen bonding in this complex results in a polymeric network with formula units joined by hydrogen bonds from one of the solvent molecules and the uncoordinated water molecule.

**Key words.** 15-crown-5, 18-crown-6, hydrogen bonding, uranyl perchlorate, low temperature crystal structure.

**Supplementary data** relating to this article are deposited with the British Library as Supplementary Publication No. SUP 82051 (37 pages).

## 1. Introduction

Most *f*-element salts, even those labelled 'anhydrous', contain some water of hydration unless vigorously dried. As a result, the assignment of proper structure to their crown ether complexes in the absence of solid state data can be tricky. This is especially true when dealing with complex stoichiometry. Tomaja [2] and Seminara *et al.* [3] found only 1:1 complexes of uranyl(VI) nitrate, chloride, and perchlorate

\* For Part 10, see reference [1].

\*\* Author for correspondence.

salts with 18-crown-6, dibenzo-18-crown-6, dicyclohexano-18-crown-6, 15-crown-5, benzo-15-crown-5, and 12-crown-4 when hydrated uranyl salts were used. Under anhydrous conditions the ratio of metal to crown was found to vary with the crown ether cavity size [2] and presumably involves some sort of uranyl to crown coordination as in  $[\text{UO}_2(\text{dicyclohexano-18-crown-6})][\text{ClO}_4]_2$  [4].

In our research with hydrated lanthanide and actinide salts, the metal:crown stoichiometry has been related directly to the number of possible hydrogen bonds between the water of hydration and the crown ether. Features of these complexes of interest to us include the number of crown oxygen atoms which participate in hydrogen bonding and the extent this hydrogen bonding influences crown ether conformation and metal ion geometry. In  $[\text{M}(\text{OH}_2)_8]\text{Cl}_3 \cdot 15\text{-crown-5}$  ( $\text{M} = \text{Y}$  [5, 6],  $\text{Gd}$  [7],  $\text{Lu}$  [7]) and  $[\text{Th}(\text{NO}_3)_4(\text{OH}_2)_3] \cdot 18\text{-crown-6}$  [8] with 1:1 stoichiometry, all crown ether oxygen atoms participate in hydrogen bonds with metal coordinated water molecules forming zigzag polymer chains. In  $[\text{ThCl}_4(\text{OHC}_2\text{H}_5)_3(\text{OH}_2)] \cdot 18\text{-crown-6} \cdot \text{H}_2\text{O}$  [9], only four of six crown oxygen atoms participate in hydrogen bonding again resulting in a polymeric chain of crown/metal/crown/metal. The crown ether in the thorium nitrate complex has an unusual conformation observed only once before. The conformation of the 18-crown-6 ether in the thorium chloride complex is the commonly observed  $D_{3d}$ . In three non-1:1 complexes we have studied, we have observed nonpolymeric structures in which the crown ether has only three hydrogen bonding contacts with metal coordinated water molecules:  $[\text{Y}(\text{NO}_3)_2(\text{OH}_2)_5][\text{NO}_3] \cdot 2(15\text{-crown-5})$  [10], and the title complexes. This contribution details the synthesis and structures of  $[\text{UO}_2(\text{OH}_2)_5][\text{ClO}_4]_2 \cdot 3(15\text{-crown-5}) \cdot \text{CH}_3\text{CN}$  and  $[\text{UO}_2(\text{OH}_2)_5][\text{ClO}_4]_2 \cdot 2(18\text{-crown-6}) \cdot 2\text{CH}_3\text{CN} \cdot \text{H}_2\text{O}$ .

## 2. Experimental

### 2.1. SYNTHESIS AND CRYSTALLIZATION OF $[\text{UO}_2(\text{OH}_2)_5][\text{ClO}_4]_2 \cdot 3(15\text{-crown-5}) \cdot \text{CH}_3\text{CN}$ (U15)

1 mmol of 15-crown-5 in 5 ml of  $\text{CH}_3\text{CN}$  was added to a stirring solution of 1 mmol of  $\text{UO}_2(\text{ClO}_4)_2 \cdot n\text{H}_2\text{O}$  in 5 ml of the same solvent. The reaction mixture was heated to 60 °C for 1 h then cooled to 22 °C. The reaction mixture was stored in the dark at 5 °C for 24 h, concentrated to 2–5 ml, and placed in a brown bottle at 5 °C. Crystals deposited along the walls of the bottle after several weeks. Melting point: 185–190 °C. Anal. Calcd. for  $[\text{UO}_2(\text{OH}_2)_5][\text{ClO}_4]_2 \cdot 3(15\text{-crown-5}) \cdot \text{CH}_3\text{CN}$ : C, 30.48; H, 5.84; Found: C, 29.5; H, 5.88.

### 2.2. SYNTHESIS AND CRYSTALLIZATION OF $[\text{UO}_2(\text{OH}_2)_5][\text{ClO}_4]_2 \cdot 2(18\text{-crown-6}) \cdot 2\text{CH}_3\text{CN} \cdot \text{H}_2\text{O}$ (U18)

1 mmol of 18-crown-6 in 5 ml of  $\text{CH}_3\text{CN}$  was added to a stirring solution of 1 mmol of  $\text{UO}_2(\text{ClO}_4)_2 \cdot n\text{H}_2\text{O}$  in 5 ml of the same solvent. The reaction mixture was heated to 60 °C for 1 h and allowed to cool to 20 °C. The reaction mixture was stored in the dark at –5 °C for 24 h and then concentrated to 2–5 ml and placed in a brown bottle at –5 °C for 10 months, after which time crystals deposited along the walls of the bottle. Melting point: 56–58 °C. Anal. Calcd. for  $[\text{UO}_2(\text{OH}_2)_5][\text{ClO}_4]_2 \cdot 2(18\text{-crown-6}) \cdot 2\text{CH}_3\text{CN} \cdot \text{H}_2\text{O}$ : C, 28.31; H, 5.60; N, 2.36; Found: C, 28.55; H, 5.57; N, 3.12.

After formation of the title complex shifts of 5–45  $\text{cm}^{-1}$  of the vibrational spectral

bands due to the crown ether were observed in comparison to the free crown ether. Many of the perchlorate spectral bands were obscured by ligand absorptions, however, the asymmetric Cl—O bending mode at  $625\text{ cm}^{-1}$  indicated an ionic perchlorate.

### 2.3. X-RAY DATA COLLECTION, STRUCTURE DETERMINATION, AND REFINEMENT

A yellow single crystal of the 15-crown-5 complex and subsequently the 18-crown-6 complex were mounted in air on a pin, placed on the goniometer head, and placed on the diffractometer in a stream of cold ( $-150\text{ }^{\circ}\text{C}$ ) nitrogen gas. Final lattice parameters as determined from a least-squares refinement of  $((\sin \theta)/\lambda)^2$  values for 25 reflections ( $\theta > 15^{\circ}$  U15,  $\theta > 20^{\circ}$  U18) accurately centered on the diffractometer are given in Table I. The space group for U15 was determined to be either the centric  $P\bar{1}$  or acentric  $P1$ . Statistical tests indicated that the space group was centric and the subsequent solution and successful refinement of the structure in the space group

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

Compound	$[\text{UO}_2(\text{OH}_2)_5][\text{ClO}_4]_2 \cdot 3(15\text{-crown-5}) \cdot \text{CH}_3\text{CN}$	$[\text{UO}_2(\text{OH}_2)_5][\text{ClO}_4]_2 \cdot 2(18\text{-crown-6}) \cdot 2\text{CH}_3\text{CN} \cdot \text{H}_2\text{O}$
Color/Shape	yellow/cube	yellow/plate
Mol wt.	1260.9	1187.8
Space group	$P\bar{1}$	$P2_12_12_1$
Temp., $^{\circ}\text{C}$	-150	-150
Cell Constants		
$a$ , $\text{\AA}$	8.288(6)	12.280(2)
$b$ , $\text{\AA}$	12.874(7)	17.311(7)
$c$ , $\text{\AA}$	24.678(7)	22.056(3)
$\alpha$ , deg	82.62(4)	
$\beta$ , deg	76.06(5)	
$\gamma$ , deg	81.06(5)	
Cell vol, $\text{\AA}^3$	2513.1	4688.8
Molecules/unit cell	2	4
$\rho(\text{calc})$ , $\text{g cm}^{-3}$	1.67	1.68
$\mu(\text{calc})$ , $\text{cm}^{-1}$	41.7	44.4
Range of relative transm. factors, %	66/100	57/100
Radiation, graphite monochromator	$\text{MoK}\alpha(\lambda = 0.71073)$	$\text{MoK}\alpha(\lambda = 0.71073)$
Max crystal dimensions, mm	$0.23 \times 0.35 \times 0.40$	$0.18 \times 0.38 \times 0.48$
Scan width	$0.80 + 0.35 \tan \theta$	$0.80 + 0.35 \tan \theta$
Standard reflections	(0, 12, 0) (0, 0, 14) (200)	(600) (0, 12, 0) (0, 0, 16)
Decay of standards	-5%	$\pm 1\%$
Reflections measured	8904	4601
$2\theta$ range, deg	$2 \leq 2\theta \leq 50$	$2 \leq 2\theta \leq 50$
Range of $h, k, l$	+9, $\pm 15$ , $\pm 29$	+14, +20, +26
Reflections observed [ $F_o \geq 5\sigma(F_o)$ ]	6248	3777
No. of parameters varied	585	550
Weights	$[\sigma(F_o)^2 + 0.0002F_o^2]^{-1}$	$[\sigma(F_o)^2 + 0.00004F_o^2]^{-1}$
GOF	11.6	2.0
$R$ inverse configuration	—	0.060
$R = \sum \ F_o\  -  F_c  / \sum  F_o $	0.111	0.032
$R_w$	0.123	0.035

$P\bar{1}$  confirmed this. Systematic absences for the 18-crown-6 complex were unique to the noncentrosymmetric  $P2_12_12_1$ .

Data were collected on an Enraf-Nonius CAD-4 diffractometer by the  $\theta$ - $2\theta$  scan technique. A summary of data collection parameters is given in Table I. The intensities were corrected for Lorentz, polarization effects and for absorption.

Calculations were carried out with the SHELX system of computer programs [11]. Neutral atom scattering factors for U, Cl, O, N, C and H were taken from reference [12] and the scattering was corrected for the real and imaginary components of anomalous dispersion [12].

Both complexes were solved via heavy atom methods. Least-squares refinement of the nonhydrogen atoms with isotropic thermal parameters led to  $R = 0.130$  (U15) and  $R = 0.049$  (U18). The hydrogen atoms associated with the crown ether molecules were placed in calculated positions 0.95 Å from the bonded carbon atom and allowed to ride on that atom with B fixed at 5.5 Å<sup>2</sup>. No attempt was made to include the water molecule hydrogen atoms or those from the solvent methyl groups. Refine-

Table II. Final fractional coordinates for  $[\text{UO}_2(\text{OH}_2)_5][\text{ClO}_4]_2 \cdot 3(15\text{-crown-5}) \cdot \text{CH}_3\text{CN}$

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
U	0.3120(1)	0.25817(5)	0.24200(3)	C(1)	0.627(3)	0.294(2)	0.0338(9)
Cl(1)	-0.1153(8)	0.3127(3)	0.4613(2)	C(2)	0.481(3)	0.344(2)	0.0086(9)
Cl(2)	0.1005(8)	0.2235(3)	-0.0772(2)	C(3)	0.197(4)	0.434(2)	0.035(1)
O(1)	0.072(2)	0.2595(9)	0.2499(5)	C(4)	0.089(3)	0.353(2)	0.0544(8)
O(2)	0.543(2)	0.254(1)	0.2271(6)	C(5)	-0.091(3)	0.284(2)	0.1394(8)
O(3)	0.259(2)	0.2378(9)	0.3437(5)	C(6)	-0.081(3)	0.175(2)	0.120(1)
O(4)	0.370(2)	0.0735(8)	0.2716(5)	C(7)	0.109(3)	0.015(2)	0.1113(9)
O(5)	0.333(2)	0.1860(8)	0.1570(5)	C(8)	0.284(4)	-0.030(1)	0.1116(9)
O(6)	0.318(2)	0.4024(9)	0.1665(5)	C(9)	0.553(3)	0.015(1)	0.0702(9)
O(7)	0.296(2)	0.4235(9)	0.2760(5)	C(10)	0.644(3)	0.106(2)	0.0374(9)
O(8)	-0.195(2)	0.225(1)	0.4907(6)	C(11)	0.794(3)	0.084(1)	0.3240(8)
O(9)	-0.236(2)	0.405(1)	0.4658(7)	C(12)	0.829(3)	0.066(1)	0.2645(9)
O(10)	0.021(3)	0.332(1)	0.4834(7)	C(13)	0.756(3)	-0.103(1)	0.2591(8)
O(11)	-0.063(2)	0.297(1)	0.4030(5)	C(14)	0.617(3)	-0.158(1)	0.2555(9)
O(12)	0.245(3)	0.249(1)	-0.0631(7)	C(15)	0.339(3)	-0.178(1)	0.3045(9)
O(13)	-0.015(2)	0.317(1)	-0.0760(6)	C(16)	0.214(3)	-0.154(1)	0.3591(8)
O(14)	0.030(2)	0.143(1)	-0.0363(6)	C(17)	0.124(3)	-0.007(1)	0.4137(8)
O(15)	0.147(2)	0.187(1)	-0.1314(6)	C(18)	0.260(3)	-0.002(1)	0.4423(8)
O(16)	0.592(2)	0.195(1)	0.0674(5)	C(19)	0.508(3)	0.084(1)	0.4319(8)
O(17)	0.357(2)	0.397(1)	0.0509(6)	C(20)	0.595(3)	0.170(1)	0.3960(8)
O(18)	0.049(2)	0.340(1)	0.1135(5)	C(21)	0.208(3)	0.679(1)	0.1840(9)
O(19)	0.070(2)	0.116(1)	0.1328(6)	C(22)	0.052(4)	0.628(2)	0.209(1)
O(20)	0.381(2)	0.0379(9)	0.0728(6)	C(23)	-0.010(3)	0.646(1)	0.3068(9)
O(21)	0.648(2)	0.1527(9)	0.3375(5)	C(24)	0.033(4)	0.594(2)	0.3603(9)
O(22)	0.710(2)	0.0074(8)	0.2530(5)	C(25)	0.257(4)	0.521(2)	0.3999(9)
O(23)	0.490(2)	-0.1434(9)	0.3057(5)	C(26)	0.441(4)	0.511(2)	0.3856(9)
O(24)	0.182(2)	-0.0403(9)	0.3594(5)	C(27)	0.680(3)	0.459(2)	0.315(1)
O(25)	0.356(2)	0.0807(9)	0.4132(5)	C(28)	0.715(3)	0.457(1)	0.255(1)
O(26)	0.346(2)	0.6000(9)	0.1824(5)	C(29)	0.637(3)	0.555(2)	0.1745(8)
O(27)	0.048(2)	0.5780(9)	0.2645(5)	C(30)	0.510(3)	0.638(2)	0.1603(9)
O(28)	0.203(2)	0.5829(9)	0.3539(5)	N	0.247(3)	0.173(1)	0.5876(9)
O(29)	0.511(2)	0.455(1)	0.3404(6)	C(31)	0.299(3)	0.240(2)	0.5569(9)
O(30)	0.634(2)	0.553(1)	0.2330(6)	C(32)	0.365(3)	0.328(1)	0.5199(9)

ment of the nonhydrogen atoms with anisotropic temperature factors (except for the uranyl oxygen atoms in U15 which could not be refined anisotropically) led to final values of  $R = 0.111$ ,  $R_w = 0.123$  (U15) and  $R = 0.032$ ,  $R_w = 0.035$  (U18). A room temperature data set was collected for U15. At 22 °C the crown ether molecules displayed very high thermal motion, almost to the point of not being able to resolve the carbon atom positions. It is possible that as the crystals were cooled to -150 °C and the thermal motion dampened, that a less than perfect lattice and lattice packing were obtained. The high  $R$  value for this complex may be an indication of this. It is also possible that the high  $R$  value and inability to anisotropically refine the uranyl oxygen atoms (and consequently the deviations from normal for the O=U=O moiety) may be due to a less than perfect absorption correction (although  $\mu$  is only 41.5 for this complex). A final difference Fourier map showed large ripple peaks near the uranium atom position but no other feature greater than  $1.2e^{-}/\text{\AA}^3$  for U15 and  $0.7e^{-}/\text{\AA}^3$  for U18. No systematic variation of  $w(|F_o| - |F_c|)$  vs.  $|F_o|$  or  $(\sin \theta)/\lambda$  was noted for either complex. The final values of the positional parameters are given in Tables II and III.

Table III. Final fractional coordinates for  $[\text{UO}_2(\text{OH}_2)_5][\text{ClO}_4]_2 \cdot 2(18\text{-crown-6}) \cdot 2 \text{CH}_3\text{CN} \cdot \text{H}_2\text{O}$ 

Atom	$x/a$	$y/b$	$z/c$	Atom	$x/a$	$y/b$	$z/c$
U	0.57856(2)	0.50280(2)	0.18418(1)	N(1)	0.3015(7)	0.3985(5)	0.5014(4)
Cl(1)	0.8803(2)	0.3351(1)	0.3049(1)	N(2)	0.846(1)	0.5945(8)	0.2818(6)
Cl(2)	0.2740(2)	0.3557(1)	0.0651(1)	C(1)	0.167(1)	0.5445(7)	0.2429(6)
O(1)	0.6035(5)	0.6014(3)	0.1960(3)	C(2)	0.152(1)	0.4611(7)	0.2558(6)
O(2)	0.5486(6)	0.4042(3)	0.1714(3)	C(3)	0.245(1)	0.3421(7)	0.2594(6)
O(3)	0.4433(5)	0.5080(4)	0.2637(2)	C(4)	0.3569(8)	0.3069(6)	0.2630(5)
O(4)	0.4107(5)	0.5299(3)	0.1317(3)	C(5)	0.5079(9)	0.2957(6)	0.3284(6)
O(5)	0.6397(5)	0.5207(3)	0.0821(3)	C(6)	0.5531(9)	0.3256(6)	0.3869(5)
O(6)	0.7720(5)	0.4741(5)	0.1780(3)	C(7)	0.6391(9)	0.4335(6)	0.4333(4)
O(7)	0.6630(5)	0.4711(4)	0.2809(3)	C(8)	0.6676(8)	0.5147(7)	0.4231(5)
O(8)	0.8804(7)	0.4140(4)	0.3249(4)	C(9)	0.5979(9)	0.6335(6)	0.3860(5)
O(9)	0.8622(7)	0.3348(5)	0.2412(3)	C(10)	0.4937(9)	0.6769(6)	0.3787(5)
O(10)	0.9813(6)	0.2999(6)	0.3145(5)	C(11)	0.3300(8)	0.6861(6)	0.3251(5)
O(11)	0.7924(7)	0.2956(5)	0.3351(4)	C(12)	0.268(1)	0.6538(6)	0.2717(5)
O(12)	0.2078(6)	0.2963(4)	0.0898(4)	C(13)	0.834(1)	0.6794(7)	0.1112(5)
O(13)	0.236(1)	0.3746(6)	0.0059(5)	C(14)	0.7640(8)	0.7215(6)	0.0653(4)
O(14)	0.2666(7)	0.4228(5)	0.1049(4)	C(15)	0.6223(8)	0.7035(6)	-0.0024(5)
O(15)	0.3822(6)	0.3323(5)	0.0621(5)	C(16)	0.5216(8)	0.6568(5)	-0.0157(5)
O(16)	0.2265(6)	0.5792(4)	0.2905(3)	C(17)	0.4690(8)	0.5311(6)	-0.0431(5)
O(17)	0.2559(6)	0.4242(4)	0.2572(3)	C(18)	0.5115(8)	0.4515(6)	-0.0573(5)
O(18)	0.4028(6)	0.3299(4)	0.3195(4)	C(19)	0.6031(9)	0.3448(5)	-0.0143(4)
O(19)	0.5879(6)	0.4034(3)	0.3800(3)	C(20)	0.6714(8)	0.3202(5)	0.0368(4)
O(20)	0.5734(6)	0.5580(4)	0.4092(3)	C(21)	0.850(1)	0.3305(7)	0.0744(7)
O(21)	0.4305(6)	0.6440(3)	0.3316(3)	C(22)	0.9491(9)	0.3829(6)	0.0710(6)
O(22)	0.8865(5)	0.6169(4)	0.0818(3)	C(23)	1.0079(7)	0.5133(6)	0.0910(4)
O(23)	0.6761(5)	0.6734(4)	0.0491(3)	C(24)	0.9716(8)	0.5853(7)	0.1179(5)
O(24)	0.5557(5)	0.5804(4)	-0.0309(3)	C(25)	0.3120(8)	0.4373(5)	0.4587(4)
O(25)	0.5726(6)	0.4239(4)	-0.0058(3)	C(26)	0.3290(8)	0.4860(6)	0.4058(4)
O(26)	0.7718(6)	0.3619(4)	0.0347(3)	C(27)	0.899(1)	0.6431(8)	0.3009(6)
O(27)	0.9246(6)	0.4555(4)	0.0973(3)	C(28)	0.9671(9)	0.7048(6)	0.3227(5)
O(28)	0.2874(6)	0.6543(4)	0.1105(3)				

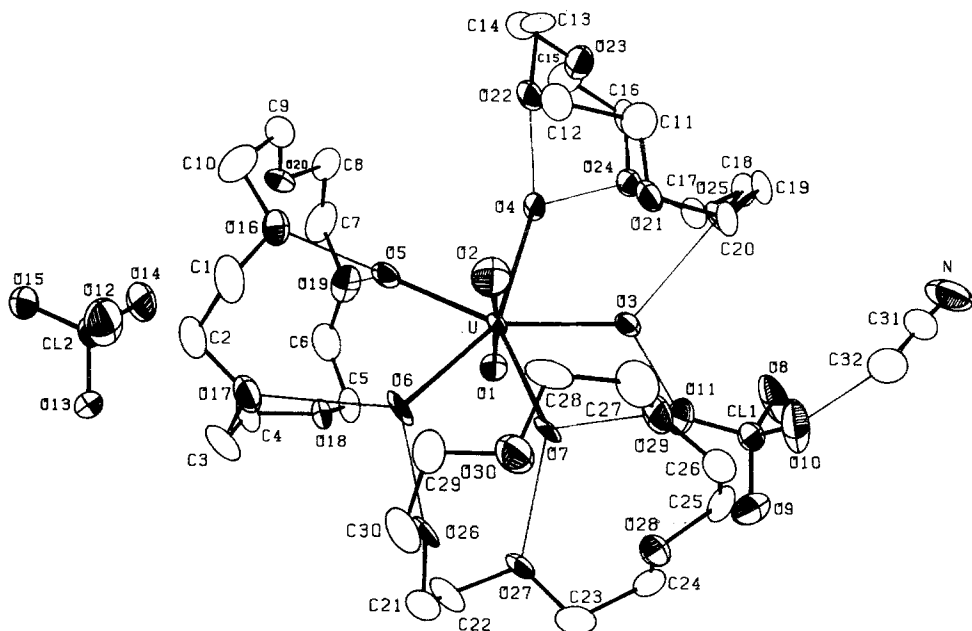


Fig. 1. Asymmetric unit and atom labelling scheme for  $[\text{UO}_2(\text{OH}_2)_5][\text{ClO}_4]_2 \cdot 3(15\text{-crown-5}) \cdot \text{CH}_3\text{CN}$ . The atoms are represented by their 50% probability ellipsoids for thermal motion. Hydrogen atoms have been omitted, probable hydrogen bonding has been indicated with a line between hydrogen donor and acceptor atoms. There are no contact distances between N and a hydrogen bond donor less than 4.0 Å.

### 3. Results and Discussion

In contrast to the results obtained for complexation of hydrated uranyl (VI) nitrate, chloride, and perchlorate salts with dibenzo-18-crown-6, dicyclohexano-18-crown-6, 18-crown-6, benzo-15-crown-5, 15-crown-5, and 12-crown-4, where only 1:1 stoichiometries were obtained [2, 3], the title complexes exhibit stoichiometries which appear to be dependent on the overall size of the crown ether molecule and the maximization of hydrogen bonding interactions.  $[\text{UO}_2(\text{OH}_2)_5][\text{ClO}_4]_2 \cdot 3(15\text{-crown-5}) \cdot \text{CH}_3\text{CN}$  (U15), shown in Figure 1, has three crown ethers hydrogen bonded to the water molecules in the equatorial plane of the cation. Each crown ether has three such interactions. The remaining water hydrogen atom and the solvent are hydrogen bonded to one of the perchlorate anions. Presumably the larger size of the 18-membered ring in 18-crown-6 prevents a similar stoichiometry for  $[\text{UO}_2(\text{OH}_2)_5][\text{ClO}_4]_2 \cdot 2(18\text{-crown-6}) \cdot 2\text{CH}_3\text{CN} \cdot \text{H}_2\text{O}$  (U18, Figure 2). In this complex only two crown molecules are hydrogen bonded to water molecules in the equatorial plane of the cation. There are, however, still only three hydrogen bonds from water molecules to each crown. The remaining four water molecule hydrogen atoms are interacting with two oxygens of one anion, one of the other anion, and the uncoordinated water molecule. One solvent molecule is hydrogen bonded to an anion and one interacts weakly with the back side of one of the crown ethers.

In many of the 1:1 hydrogen bonded crown ether complexes of *f*-elements which have been structurally characterized, a polymeric chain of metal-water/crown/

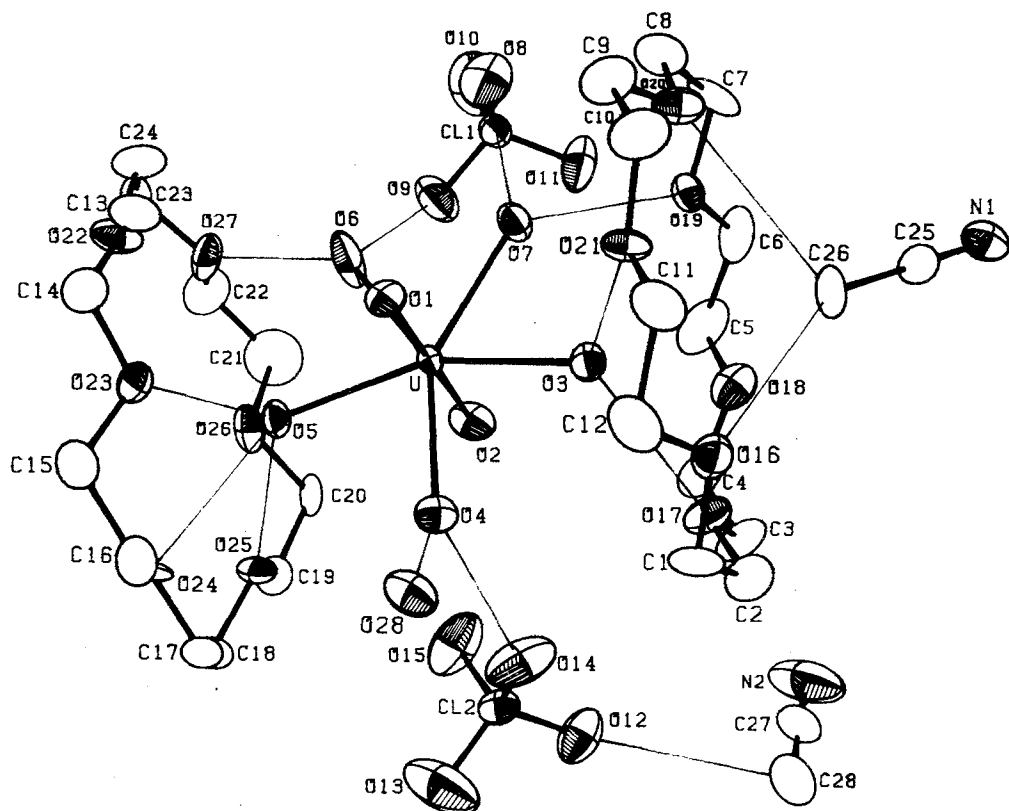


Fig. 2.  $[\text{UO}_2(\text{OH}_2)_5][\text{ClO}_4]_2 \cdot 2(18\text{-crown-6}) \cdot 2\text{CH}_3\text{CN} \cdot \text{H}_2\text{O}$ . O(28) is also hydrogen bonded to O(11) in a symmetry related formula unit and N(1) in a second one. C(26) has a close contact with O(13) as does C(28) with O(9) and O(10). The N(2)—C(27)—C(28) molecule depicted is related to the coordinates in Table III by  $(1-x, y-\frac{1}{2}, \frac{1}{2}-z)$ .

water-metal exists, as in  $[\text{M}(\text{OH}_2)_8]\text{Cl}_3 \cdot 15\text{-crown-5}$  ( $\text{M} = \text{Y}$  [5, 6],  $\text{Gd}$  [7],  $\text{Lu}$  [7]),  $[\text{Th}(\text{NO}_3)_4(\text{OH}_2)_3] \cdot 18\text{-crown-6}$  [8],  $[\text{ThCl}_4(\text{OHC}_2\text{H}_5)_3(\text{OH}_2)] \cdot 18\text{-crown-6} \cdot \text{H}_2\text{O}$  [9], and  $[\text{Dy}(\text{OH}_2)_8]\text{Cl}_3 \cdot 18\text{-crown-6} \cdot 4 \text{H}_2\text{O}$  [13]. In the title complexes the arrangement of the water molecules in an equatorial plane, the bulk of the crown molecules, and the availability of anions capable of hydrogen bonding, prevent this type of polymerization through the crown moiety and complexes of different stoichiometries result. This was also found for  $[\text{Y}(\text{NO}_3)_2(\text{OH}_2)_5][\text{NO}_3] \cdot 2(15\text{-crown-5})$  [10] where the five water molecules are also in an approximate equatorial plane. While the formula units in U15 are not joined by any hydrogen bonding interactions, U18 is polymeric via hydrogen bonding of O(6), O(7), and the uncoordinated water molecule (O(28)) to symmetry related perchlorate anions, and C(28) which is hydrogen bonded to both perchlorate molecules.

Details of the structures will be discussed below. Selected bond distances and angles are given in Tables IV (U15) and V (U18). The geometries of the hydrogen bonding interactions have been deposited in Supplementary Material. Views of the unit cell contents are given in Figures 3 (U15) and 4 (U18).

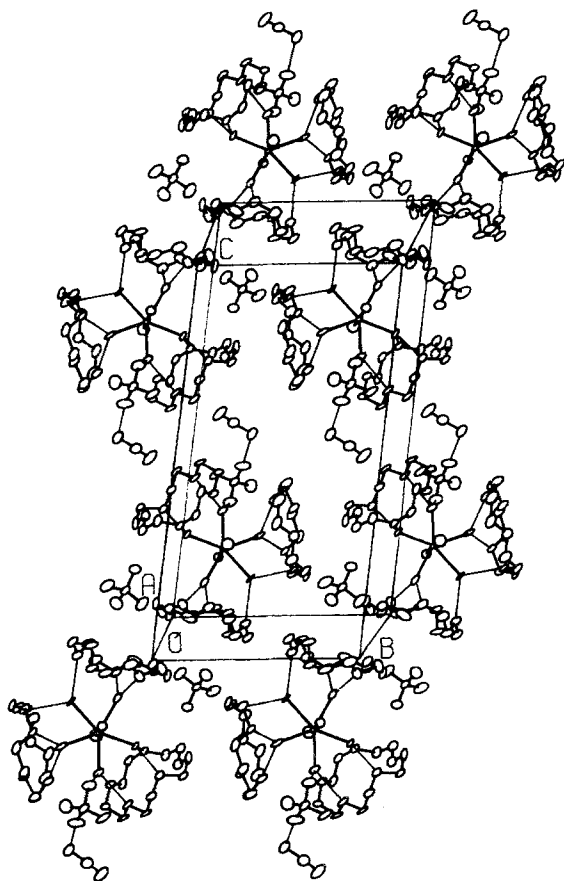


Fig. 3. Unit cell contents for  $[\text{UO}_2(\text{OH}_2)_5][\text{ClO}_4]_2 \cdot 3(15\text{-crown-5}) \cdot \text{CH}_3\text{CN}$ .

### 3.1. $[\text{UO}_2(\text{OH}_2)_5]^{2+}$ CATIONS

The cations in U15 and U18 are pentagonal bipyramidal. In U18 the uranyl moiety is normal with an average U—O distance of 1.76(1) Å and an O(1)—U—O(2) angle of 177.9(3)°. Similar values have been found for other uranyl complexes with this geometry although the range is quite large [4, 14–17]. Distortions found in the  $[\text{UO}_2(\text{OH}_2)_5]^{2+}$  cation in U15 are probably due to the crystallographic difficulties discussed in the experimental section.

An interesting variation occurs in the U—OH<sub>2</sub> separations. The average distances for each complex, 2.40(4) Å (U15) and 2.42(2) Å (U18) are normal. The water molecules which are exclusively hydrogen bonded to a single crown ether, however, exhibit shorter U—O separations than those which are hydrogen bonded to two different crown ethers (U15) or one crown ether and one anion (U18). In U15 the U—O(3), O(6) distances average 2.44(1) Å, the remaining U—O separations 2.37(2) Å. A similar but less significant trend in U18 finds U—O(6), O(7) average 2.432(2) Å, U—O(3), O(4), O(5) = 2.41(1) Å average.



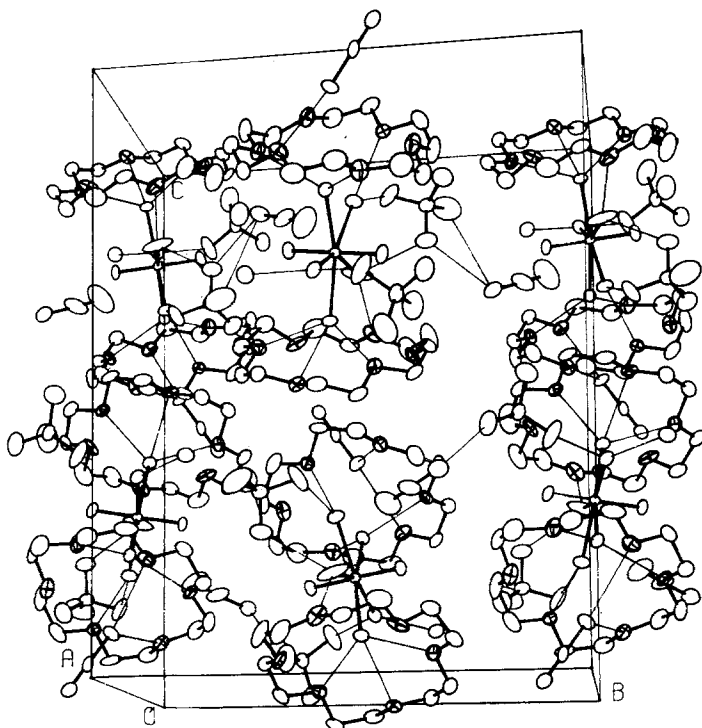


Fig. 4. Unit cell contents for  $[\text{UO}_2(\text{OH}_2)_5][\text{ClO}_4]_2 \cdot 2(18\text{-crown-6}) \cdot 2 \text{CH}_3\text{CN} \cdot \text{H}_2\text{O}$ . The hydrogen bonding to N(1) is from a symmetry related formula unit not indicated in this plot. The crown ether oxygen atoms have been shaded.

### 3.2. $\text{ClO}_4^-$ ANIONS

The bonding in the perchlorate anions are similar in both compounds and normal: U15,  $\text{Cl}-\text{O} = 1.43(1)\text{\AA}$  average,  $\text{O}-\text{Cl}-\text{O} = 110(2)^\circ$ ; U18,  $\text{Cl}-\text{O} = 1.42(2)\text{\AA}$ ,  $\text{O}-\text{Cl}-\text{O} = 109(2)^\circ$ . In the absence of hydrogen atom positions hydrogen bonding has been inferred from the  $\text{O}\cdots\text{O}$ ,  $\text{O}\cdots\text{N}$ , and  $\text{C}\cdots\text{O}$  contact geometries. Each compound has one anion which is hydrogen bonded to a coordinated water molecule and one solvent molecule (C1(1) in U15, C1(2) in U18). The second anion in U15 has no hydrogen bonding contacts. In U18 the second anion participates in four or possibly five hydrogen bonds, two with metal coordinated water molecules, one with the uncoordinated water molecule in a symmetry related unit, and one or possibly two with a solvent methyl group in a third symmetry related asymmetric unit.

### 3.3. SOLVENT INTERACTIONS

The structural parameters of the acetonitrile molecules are normal. The solvent molecule in U15 and one of the two unique solvent molecules in U18 interact with perchlorate anions. The  $\text{H}_3\text{C}\cdots\text{O}$  contacts range from  $3.18(4)\text{\AA}$  for the only contact in U15, to  $3.29(1)\text{-}3.50(1)\text{\AA}$  for the contacts in U18. In U18 C(28) interacts with both anions. There are no hydrogen bond atom contacts to N(2) in U18  $< 3.10\text{\AA}$ . This may contribute to the higher thermal motion observed for this atom.

Table IV. Bond distances (Å) and angles (deg) for  $[\text{UO}_2(\text{OH}_2)_3][\text{ClO}_4]_2 \cdot 3(15\text{-crown-5}) \cdot \text{CH}_3\text{CN}$ 

Atoms	Distance	Atoms	Distance
U—O(1)	1.95(1)	U—O(2)	1.85(2)
U—O(3)	2.43(1)	U—O(4)	2.40(1)
U—O(5)	2.36(1)	U—O(6)	2.45(1)
U—O(7)	2.36(1)		
Cl—O av	1.43(1)		
O—C av	1.42(3)	C—C av	1.48(3)
N—C(31)	1.14(3)	C(31)—C(32)	1.45(3)
Atoms	Angle	Atoms	Angle
O(1)—U—O(2)	174.2(6)	O(1)—U—O(3)	87.5(5)
O(2)—U—O(3)	98.0(6)	O(1)—U—O(4)	96.1(5)
O(2)—U—O(4)	84.1(6)	O(3)—U—O(4)	72.0(4)
O(1)—U—O(5)	83.6(5)	O(2)—U—O(5)	90.7(6)
O(3)—U—O(5)	149.6(4)	O(4)—U—O(5)	80.2(4)
O(1)—U—O(6)	90.8(6)	O(2)—U—O(6)	86.2(6)
O(3)—U—O(6)	138.0(4)	O(4)—U—O(6)	149.7(4)
O(5)—U—O(6)	71.3(4)	O(1)—U—O(7)	96.8(5)
O(2)—U—O(7)	86.7(5)	O(3)—U—O(7)	70.0(4)
O(4)—U—O(7)	139.1(4)	O(5)—U—O(7)	139.8(4)
O(6)—U—O(7)	68.5(4)		
O—Cl—O av	110(2)		
C—O—C av	114(1)	O—C—C av	109(3)
N—C(31)—C(32)	177(3)		

The second acetonitrile molecule in U18 interacts weakly with the back side of one of the crown ethers, O(13) of an anion, and is a hydrogen bond acceptor (O(28)⋯N(1) = 2.80(1) Å). From the geometry of the contacts the most likely interactions are C(26)⋯O(16) (3.26(1) Å), C(26)⋯O(20) (3.25(1) Å), and C(26)⋯O(13) (3.36(1) Å). This type of interaction has been observed before in {trans-[Ir(CO)(CH<sub>3</sub>CN)(PPh<sub>3</sub>)<sub>2</sub>]<sub>2</sub> · 18-crown-6} [PF<sub>6</sub>]<sub>2</sub> · 2 CH<sub>2</sub>Cl<sub>2</sub> [18], [(COCPh<sub>3</sub>)<sub>2</sub>-18-crown-6] · 2 CH<sub>3</sub>CN [19] and dibenzo-18-crown-6 · 2 CH<sub>3</sub>CN [20]. In the last complex the H<sub>3</sub>C⋯O contacts averaged 3.30(1) Å.

#### 3.4. CROWN ETHER CONFORMATION

The average bond distances and angles around the crown rings given in Tables IV and V for both U15 and U18 are consistent with each other and with the literature [21]. Of perhaps greater interest are conformational changes in the flexible unsubstituted crown ethers as dictated by their environment. The torsion angles around the crown ether rings for both complexes are presented in Tables VI (U15) and VII (U18).

Both 18-crown-6 molecules in U18 possess the  $D_{3d}$  conformation most commonly

Table V. Bond distances (Å) and angles (deg) for  $[\text{UO}_2(\text{OH}_2)_5] [\text{ClO}_4]_2 \cdot 2(18\text{-crown-6}) \cdot 2 \text{CH}_3\text{CN} \cdot \text{H}_2\text{O}$ 

Atoms	Distance	Atoms	Distance
U—O(1)	1.754(6)	U—O(2)	1.768(6)
U—O(3)	2.417(5)	U—O(4)	2.410(6)
U—O(5)	2.394(6)	U—O(6)	2.431(7)
U—O(7)	2.434(6)		
Cl—O av	1.42(2)		
O—C av	1.42(1)	C—C av	1.49(2)
N(1)—C(25)	1.16(1)	N(2)—C(27)	1.14(2)
C(25)—C(26)	1.45(1)	C(27)—C(28)	1.44(2)
Atoms	Angle	Atoms	Angle
O(1)—U—O(2)	177.9(3)	O(1)—U—O(3)	88.6(3)
O(2)—U—O(3)	90.5(3)	O(1)—U—O(4)	91.8(2)
O(2)—U—O(4)	86.2(3)	O(3)—U—O(4)	75.8(2)
O(1)—U—O(5)	87.6(3)	O(2)—U—O(5)	92.3(3)
O(3)—U—O(5)	153.3(2)	O(4)—U—O(5)	77.9(2)
O(1)—U—O(6)	92.1(3)	O(2)—U—O(6)	89.8(3)
O(3)—U—O(6)	136.0(2)	O(4)—U—O(6)	148.0(2)
O(5)—U—O(6)	70.5(2)	O(1)—U—O(7)	90.9(3)
O(2)—U—O(7)	90.6(3)	O(3)—U—O(7)	70.4(2)
O(4)—U—O(7)	146.0(2)	O(5)—U—O(7)	136.0(2)
O(6)—U—O(7)	65.6(2)		
O—Cl—O av	109(2)		
C—O—C av	112(2)	O—C—C av	109(1)
N(1)—C(25)—C(26)	178(1)	N(2)—C(27)—C(28)	178(1)

observed in complexes of this molecule with cations or neutral NH, CH, or OH acidic guests [22, 23]. In this conformation the crown cavity is more symmetric than in free 18-crown-6 and the oxygen atoms alternate  $\pm 0.23 \text{ \AA}$  from the mean plane of all six. The three oxygen atoms in each crown ether which are hydrogen bonded to coordinated water molecules all deviate from these planes in the direction of the cation.

Unlike the more symmetric 18-crown-6 molecule, the 15-crown-5 ether is less likely to adopt a single conformation in its complexes. Three different conformations are observed in U15. For the purposes of this discussion, we will focus on the sequence of five O—C—C—O torsion angles around the ring. Due to nonbonded repulsions these angles will all be  $\pm 60^\circ$  ( $\pm g$ ). In the  $D_{3d}$  conformation of 18-crown-6 the O—C—C—O angles alternate  $\pm g$  and the C—C—O—C angles are all  $\pm 180^\circ$  ( $a$ ). The lower symmetry of the 15-crown-5 molecule cannot support this conformation since at some point at least two consecutive O—C—C—O torsion angles must have the same sign. At least one of the torsion angles around a C—O linkage between these two is forced *syn*, although these angles are usually  $> 70^\circ$  to avoid CH...HC repulsions. One of the 15-crown-5 molecules (O(26)—O(30)) has this conformation (O—C—C—O =  $g^+$ ,  $g^+$ ,  $g^-$ ,  $g^+$ ,  $g^-$ ). A similar conformation has been observed in

Table VI. Torsion angles for  $[\text{UO}_2(\text{OH}_2)_5][\text{ClO}_4]_2 \cdot 3(15\text{-crown-5}) \cdot \text{CH}_3\text{CN}$ 

Atoms	Angle
O(16)—C(1)—C(2)—O(17)	79.5
C(1)—C(2)—O(17)—C(3)	-170.5
C(2)—O(17)—C(3)—C(4)	93.1
O(17)—C(3)—C(4)—O(18)	65.3
C(3)—C(4)—O(18)—C(5)	163.9
C(4)—O(18)—C(5)—C(6)	54.7
O(18)—C(5)—C(6)—O(19)	58.6
C(5)—C(6)—O(19)—C(7)	-172.9
C(6)—O(19)—C(7)—C(8)	164.9
O(19)—C(7)—C(8)—O(20)	-66.0
C(7)—C(8)—O(20)—C(9)	174.6
C(8)—O(20)—C(9)—C(10)	-167.3
O(20)—C(9)—C(10)—O(16)	65.5
C(9)—C(10)—O(16)—C(1)	-162.2
C(10)—O(16)—C(1)—C(2)	91.5
O(21)—C(11)—C(12)—O(22)	-69.4
C(11)—C(12)—O(22)—C(13)	-88.7
C(12)—O(22)—C(13)—C(14)	171.0
O(22)—C(13)—C(14)—O(23)	-71.0
C(13)—C(14)—O(23)—C(15)	170.7
C(14)—O(23)—C(15)—C(16)	-177.7
O(23)—C(15)—C(16)—O(24)	65.1
C(15)—C(16)—O(24)—C(17)	-156.6
C(16)—O(24)—C(17)—C(18)	83.7
O(24)—C(17)—C(18)—O(25)	67.0
C(17)—C(18)—O(25)—C(19)	-171.5
C(18)—O(25)—C(19)—C(20)	177.0
O(25)—C(19)—C(20)—O(21)	-62.7
C(19)—C(20)—O(21)—C(11)	-79.2
C(20)—O(21)—C(11)—C(12)	175.8
O(26)—C(21)—C(22)—O(27)	60.0
C(21)—C(22)—O(27)—C(23)	83.1
C(22)—O(27)—C(23)—C(24)	-165.1
O(27)—C(23)—C(24)—O(28)	68.3
C(23)—C(24)—O(28)—C(25)	-172.0
C(24)—O(28)—C(25)—C(26)	176.8
O(28)—C(25)—C(26)—O(29)	-65.6
C(25)—C(26)—O(29)—C(27)	166.6
C(26)—O(29)—C(27)—C(28)	-143.8
O(29)—C(27)—C(28)—O(30)	67.3
C(27)—C(28)—O(30)—C(29)	-171.2
C(28)—O(30)—C(29)—C(30)	162.0
O(30)—C(29)—C(30)—O(26)	-75.9
C(29)—C(30)—O(26)—C(21)	165.6
C(30)—O(26)—C(21)—C(22)	-178.6

Table VII. Torsion angles for  $[\text{UO}_2(\text{OH}_2)_5][\text{ClO}_4]_2 \cdot 2(18\text{-crown-6}) \cdot 2 \text{CH}_3\text{CN} \cdot \text{H}_2\text{O}$ 

Atoms	Angle
O(16)—C(1)—C(2)—O(17)	-63.1
C(1)—C(2)—O(17)—C(3)	-170.3
C(2)—O(17)—C(3)—C(4)	-178.1
O(17)—C(3)—C(4)—O(18)	65.3
C(3)—C(4)—O(18)—C(5)	177.0
C(4)—O(18)—C(5)—C(6)	177.2
O(18)—C(5)—C(6)—O(19)	-74.3
C(5)—C(6)—O(19)—C(7)	-175.8
C(6)—O(19)—C(7)—C(8)	-177.4
O(19)—C(7)—C(8)—O(20)	58.8
C(7)—C(8)—O(20)—C(9)	-167.4
C(8)—O(20)—C(9)—C(10)	-174.4
O(20)—C(9)—C(10)—O(21)	-68.3
C(9)—C(10)—O(21)—C(11)	179.8
C(10)—O(21)—C(11)—C(12)	175.7
O(21)—C(11)—C(12)—O(16)	72.9
C(11)—C(12)—O(16)—C(1)	179.8
C(12)—O(16)—C(1)—C(2)	163.8
O(22)—C(13)—C(14)—O(23)	68.8
C(13)—C(14)—O(23)—C(15)	-167.7
C(14)—O(23)—C(15)—C(16)	-174.0
O(23)—C(15)—C(16)—O(24)	-63.9
C(15)—C(16)—O(24)—C(17)	178.9
C(16)—O(24)—C(17)—C(18)	-178.7
O(24)—C(17)—C(18)—O(25)	59.3
C(17)—C(18)—O(25)—C(19)	172.8
C(18)—O(25)—C(19)—C(20)	176.0
O(25)—C(19)—C(20)—O(26)	-66.4
C(19)—C(20)—O(26)—C(21)	-167.8
C(20)—O(26)—C(21)—C(22)	-176.2
O(26)—C(21)—C(22)—O(27)	68.5
C(21)—C(22)—O(27)—C(23)	-173.5
C(22)—O(27)—C(23)—C(24)	178.2
O(27)—C(23)—C(24)—O(22)	-69.4
C(23)—C(24)—O(22)—C(13)	169.3
C(24)—O(22)—C(13)—C(14)	167.0

$[\text{M}(\text{OH}_2)_8]\text{Cl}_3 \cdot 15\text{-crown-5}$  [7],  $\text{CuBr}_2(\text{OH}_2)_2 \cdot 15\text{-crown-5}$  [24], and for the metal coordinated crown ether in  $[\text{M}(\text{OH}_2)_4(15\text{-crown-5})][\text{ClO}_4]_3 \cdot 15\text{-crown-5} \cdot \text{H}_2\text{O}$  (M = Sm, La) [25, 26].

The crown ether O(21)—O(25) in U15 exhibits a different conformation. The sequence of torsion angles about the C—C bonds is  $g^-$ ,  $g^-$ ,  $g^+$ ,  $g^+$ ,  $g^-$ . As a result

of three sets of consecutive angles with the same sign there are three C—C—O—C angles which deviate from  $\pm 180^\circ$ . This conformation has been observed for the hydrogen bonded crown ether in  $[M(OH_2)_4(15\text{-crown-5})][ClO_4]_3 \cdot 15\text{-crown-5} \cdot H_2O$ , for one of the two unique crown molecules in the sandwich complex,  $[Ba(15\text{-crown-5})_2]Br_2 \cdot 2 H_2O$  [27], and for both crown ethers in  $[(NH_4)(15\text{-crown-5})_2]_2[UO_2Cl_4] \cdot 2 CH_3CN$  [1].

The third crown ether in U15 exhibits a conformation for which we have thus far been unable to find reference to in the literature. All but one of the O—C—C—O torsion angles are  $g^+$  and there are three corresponding C—C—O—C angles which approach  $60^\circ$ . There are two other conformations observed in the literature for 15-crown-5. One of the two unique crown ethers in  $[Ba(15\text{-crown-5})_2]Br_2 \cdot 2 H_2O$  has a conformation in which all five of the O—C—C—O angles are  $g^-$ . In two other complexes containing direct metal-crown coordination,  $Eu(NO_3)_3(15\text{-crown-5})$  [28] and  $[F_2(CF_3CO_2)_3(OH)(15\text{-crown-5})_2][Pr_2(CF_3CO_2)_8]$  [29], and  $ZnCl_2(OH_2)_2 \cdot 15\text{-crown-5}$  [30] where the crown is hydrogen bonded to metal coordinated water molecules, one of the O—C—C—O torsion angles approaches a *syn*-periplanar value.

## Acknowledgements

We wish to thank the donors of the Petroleum Research Fund administered by the American Chemical Society for support of this work and the NSF Chemical Instrumentation Program for funds used to purchase the diffractometer.

## References

1. R. D. Rogers, L. K. Kurihara, and M. M. Benning: *Inorg. Chem.*, submitted (1987).
2. D. L. Tomaja: *Inorg. Chim. Acta* **21**, L31 (1977).
3. A. Seminara, G. Siracusa, and A. Cassol: *Inorg. Chim. Acta* **20**, 105 (1976).
4. A. Navaza, F. Villain, and P. Charpin: *Polyhedron* **3**, 143 (1984).
5. R. D. Rogers and L. K. Kurihara: *Inorg. Chim. Acta* **116**, 171 (1986).
6. R. D. Rogers and L. K. Kurihara: *Inorg. Chim. Acta*, in press (1987a).
7. R. D. Rogers and L. K. Kurihara: *Inorg. Chim. Acta*, in press (1987b).
8. R. D. Rogers, L. K. Kurihara, and M. M. Benning: *Acta Crystallogr. C*, in press (1987).
9. R. D. Rogers, L. K. Kurihara, and M. M. Benning: *J. Chem. Soc., Dalton Trans.*, in press (1986).
10. R. D. Rogers and L. K. Kurihara: *J. Less-Comm. Metals*, **127**, 199 (1987).
11. G. M. Sheldrick, SHELX, a system of computer programs for X-ray structure determination as locally modified (1976).
12. *International Tables for X-ray Crystallography*, Vol. IV, Kynoch Press, Birmingham, England, 1974, pp. 72, 99, 149 (Distr. D. Reidel, Dordrecht and Boston).
13. R. D. Rogers, *Inorg. Chim. Acta*, in press (1987).
14. T. C. W. Mak and W.-H. Yip: *Inorg. Chim. Acta* **109**, 131 (1985).
15. N. C. Jayadevan and D. M. Chackraburty: *Acta Crystallogr. B* **B28**, 3178 (1972).
16. G. Bandoli and D. A. Clemente: *J. Chem. Soc., Dalton Trans.* 612 (1975).
17. G. J. Honan, D. L. Kepert, S. F. Lincoln, J. M. Patrick, and A. H. White: *Aust. J. Chem.* **33**, 69 (1980).
18. H. M. Colquhoun, J. F. Stoddart, and D. J. Williams: *J. Am. Chem. Soc.* **104**, 1426 (1982).
19. B. L. Allwood, S. E. Fuller, P. C. Y. K. Ning, A. M. Z. Slawin, J. F. Stoddart, and D. J. Williams: *J. Chem. Soc., Chem. Commun.* 1356 (1984).
20. R. D. Rogers, L. K. Kurihara, and P. D. Richards: *J. Chem. Soc., Chem. Commun.* **604** (1987).
21. F. Vögtle and E. Weber, eds.: *Host Guest Complex Chemistry Macrocycles Synthesis, Structures, Applications*, Springer-Verlag: Berlin, 1985.

22. J. W. H. M. Uiterwijk, S. Harkema, B. W. van de Waal, F. Gobel, and H. T. M. Nibbeling: *J. Chem. Soc., Perkin Trans. 2*, 1843 (1983).
23. M. J. Bovill, D. J. Chadwick, I. O. Sutherland, and D. Watkin: *J. Chem. Soc., Perkin Trans. 2*, 1529 (1980).
24. E. Arte, J. Feneau-Dupont, J. P. Declercq, G. Germain, and M. Van Meerssche: *Acta Crystallogr. B* **B35**, 1215 (1979).
25. T. J. Lee, H.-S. Sheu, T. I. Chiu, and C. T. Chang: *Acta Crystallogr. C* **C39**, 1357 (1983).
26. T. J. Lee, H.-S. Sheu, T. I. Chiu, and C. T. Chang: *Inorg. Chim. Acta* **94**, 43 (1984).
27. J. Feneau-Dupont, E. Arte, J. P. Declercq, G. Germain, and M. Van Meerssche: *Acta Crystallogr. B* **B35**, 1217 (1979).
28. J.-C. G. Bunzli, B. Klein, G. Chapuis, and K. J. Schenk: *Inorg. Chem.* **21**, 808 (1982).
29. D. Harrison, A. Giorgetti, and J.-C. G. Bunzli: *J. Chem. Soc., Dalton Trans.* 885 (1985).
30. F. Dejehet, R. Debuyst, and J.-P. Declercq: *J. Chim. Phys.* **83**, 85 (1986).