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## Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713455674>

### Synthesis and Structural Characterization of the Monodentate 12-Crown-4 And Hexaethylene Glycol Complexes of Uranium(VI): [UO<sub>2</sub>Cl<sub>2</sub>(OH)<sub>2</sub>](12-CROWN-4)].12-Crown-4 And UO<sub>2</sub>Cl<sub>2</sub>(OH)<sub>2</sub>(Hexaethylene Glycol)

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**To cite this Article** Rogers, Robin D. , Benning, Matthew M. , Etzenhouser, Russell D. and Rollins, Andrew N.(1992) 'Synthesis and Structural Characterization of the Monodentate 12-Crown-4 And Hexaethylene Glycol Complexes of Uranium(VI): [UO<sub>2</sub>Cl<sub>2</sub>(OH)<sub>2</sub>](12-CROWN-4)].12-Crown-4 And UO<sub>2</sub>Cl<sub>2</sub>(OH)<sub>2</sub>(Hexaethylene Glycol)', *Journal of Coordination Chemistry*, 26: 4, 299 – 311

**To link to this Article:** DOI: 10.1080/00958979209407932

**URL:** <http://dx.doi.org/10.1080/00958979209407932>

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# SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF THE MONODENTATE 12-CROWN-4 AND HEXAETHYLENE GLYCOL COMPLEXES OF URANIUM(VI): [UO<sub>2</sub>Cl<sub>2</sub>(OH<sub>2</sub>)<sub>2</sub>(12-CROWN-4)]. 12-CROWN-4 AND UO<sub>2</sub>Cl<sub>2</sub>(OH<sub>2</sub>)<sub>2</sub>(HEXAETHYLENE GLYCOL)

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*(Received 16 December 1991)*

The reaction of anhydrous UO<sub>2</sub>Cl<sub>2</sub> with 12-crown-4 or hexaethylene glycol (EO6) in THF with low water content resulted in the crystallization of [UO<sub>2</sub>Cl<sub>2</sub>(OH<sub>2</sub>)<sub>2</sub>(12-crown-4)]. 12-crown-4 and UO<sub>2</sub>Cl<sub>2</sub>(OH<sub>2</sub>)<sub>2</sub>(EO6). The crystal structures of both complexes were determined. Each complex consists of a uranyl ion coordinated to two chloride anions, two water molecules, and one oxygen of the polyether. Most of the uncoordinated ether oxygen atoms participate in hydrogen bonding. The hydrogen bonding in the 12-crown-4 complex produces a dimer, while the hydrogen bonding in the EO6 complex is polymeric. The etheric U-O separation of 2.546(4) Å in the 12-crown-4 complex is the longest U-O contact in either complex, while the alcoholic U-O distance in the EO6 complex is a much shorter 2.433(5) Å.

**Keywords:** Uranyl chloride, 12-crown-4, hexaethylene glycol, X-ray crystal structure

## INTRODUCTION

We have had success in preparing several directly coordinated lanthanide(III) crown ether<sup>1,2</sup> and polyethylene glycol<sup>2,3</sup> complexes. Similar attempts to prepare polyether complexes of U<sup>4+</sup> or UO<sub>2</sub><sup>2+</sup>, however, have resulted only in the isolation of complexes with hydrogen bonded ethers,<sup>4-6</sup> or complexes in which the ether is coordinated to NH<sub>4</sub><sup>+</sup>,<sup>7,8</sup> H<sub>3</sub>O<sup>+</sup>,<sup>5</sup> H<sub>5</sub>O<sub>2</sub><sup>+</sup>,<sup>5,9</sup> or cationic impurities.<sup>5,7,10,11</sup> Structural confirmation of classic crown ether coordination to uranium is still limited to [U(BH<sub>4</sub>)<sub>2</sub>(dicyclohexyl-18-crown-6)]<sub>2</sub>[UCl<sub>5</sub>(BH<sub>4</sub>)],<sup>12</sup> [UO<sub>2</sub>(dicyclohexyl-18-crown-6)][ClO<sub>4</sub>]<sub>2</sub>,<sup>13</sup> and [UCl<sub>3</sub>(dicyclohexyl-18-crown-6)]<sub>2</sub>[UCl<sub>6</sub>].<sup>14</sup> By reducing the amount of water available to interfere with polyether coordination, we were able to isolate and structurally characterize the title complexes which we reported in a previous communication.<sup>15</sup> In this contribution we discuss the unique structural features of these monodentate polyether complexes.

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## EXPERIMENTAL

*Preparation and crystallization of  $[UO_2Cl_2(OH_2)_2(12\text{-crown-4})] \cdot (12\text{-crown-4})$* 

A 1.5 mmol sample of 12-crown-4 was added to a stirred solution of 1.5 mmol of anhydrous  $UO_2Cl_2$  in  $5\text{ cm}^3$  of THF. The reaction mixture was heated to  $60^\circ\text{C}$  for 1 hour. After the solution had cooled to room temperature, the volume was reduced by  $1/3$  and the solution was stored at  $-20^\circ\text{C}$ . The product seemed unwilling to crystallize at low temperature and so the solvent was allowed to slowly evaporate at room temperature. Within 24 hours, yellow crystals had formed on the sides of the reaction tube. Anal.; Calcd. for  $[UO_2Cl_2(OH_2)_2(12\text{-crown-4})] \cdot (12\text{-crown-4})$ : C, 26.35; H, 4.97%. Found: C, 25.87; H, 4.87%.

*Preparation and crystallization of  $UO_2Cl_2(OH_2)_2(EO6)$* 

A 1.5 mmol sample of EO6 was added to a stirred solution of 1.5 mmol of anhydrous  $UO_2Cl_2$  in  $5\text{ cm}^3$  of THF. The reaction was heated to  $60^\circ\text{C}$  for 1 hour and allowed to cool to room temperature. The yellow solution was then concentrated to  $1/2$  of its original volume and slowly cooled ( $0.1^\circ\text{C}/\text{min}$ ) to  $-20^\circ\text{C}$ . We were unable to promote crystallization at low temperature, so an equal volume of  $CH_3Cl$  was added to reduce the solubility of the complex in the solvent. After two days, crystals formed at room temperature. Anal.; Calcd. for  $UO_2Cl_2(OH_2)_2(EO6)$ : C, 21.86; H, 4.59%. Found: C, 21.92; H, 4.55%.

*X-ray Data Collection, Structure Determination and Refinement*

Yellow single crystals of the title complexes were mounted in thin-walled glass capillaries flushed with Ar and transferred to the goniometer. The crystal of the 12-crown-4 complex was cooled to  $-150^\circ\text{C}$  during data collection by using a stream of cold nitrogen gas. Each space group was uniquely determined by systematic absences. A summary of data collection parameters is given in Table I.

The geometrically constrained hydrogen atoms were placed in calculated positions  $0.95\text{ \AA}$  from the bonded carbon atom and allowed to ride on that atom with B fixed at  $5.5\text{ \AA}$ . The aquo hydrogen atoms were not included in the final refinement. Refinement of nonhydrogen atoms with anisotropic temperature factors led to the final values of  $R$  and  $R_w$  given in Table I. The final values of the positional parameters are given in Table II for the 12-crown-4 complex and in Table III for the EO6 complex.

## RESULTS

$[UO_2Cl_2(OH_2)_2(12\text{-crown-4})] \cdot 12\text{-crown-4}$  is depicted in Figure 1, bond distances and angles are given in Table IV. The uranium(VI) ion is pentagonal bipyramidal with two axial uranyl oxygen atoms, two equatorial chloride ions, two equatorial water molecules, and one equatorial monodentate 12-crown-4 molecule. The uranyl group is normal<sup>7</sup> with  $U=O=1.758(5)\text{ \AA}$  average and  $O=U=O=178.1(2)^\circ$ .

The 12-crown-4 molecule is coordinated to uranium through O(5) at  $2.546(4)\text{ \AA}$ . This long contact may be the origin of the asymmetry in the U-Cl and U-OH<sub>2</sub> separations. The shortest U-Cl distance (Cl(2),  $2.675(1)\text{ \AA}$ ) and U-OH<sub>2</sub> distance (O(4),

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

Cmpd	[UO <sub>2</sub> Cl <sub>2</sub> (OH <sub>2</sub> ) <sub>2</sub> (12-crown-4)].12-crown-4	UO <sub>2</sub> Cl <sub>2</sub> (OH <sub>2</sub> ) <sub>2</sub> (EO6)
Colour/shape	yellow/parallelepiped	yellow/parallelepiped
For. wt.	729.39	659.30
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>
Temp., °C	-150	20°
Cell constants <sup>a</sup>		
<i>a</i> , Å	17.512(8)	16.761(8)
<i>b</i> , Å	9.413(4)	7.897(5)
<i>c</i> , Å	16.723(9)	16.975(6)
β, deg	115.25(6)	107.85(4)
Cell vol., Å <sup>3</sup>	2493	2139
Formula units/unit cell	4	4
<i>D</i> <sub>calc.</sub> , g cm <sup>-3</sup>	1.94	2.05
<i>μ</i> <sub>calc.</sub> , cm <sup>-1</sup>	64.6	75.2
Diffractometer/scan		Enraf-Nonius CAD-4/ω-2θ
Range of relative transm. factors, %	30/100	56/100
Radiation, graphite monochromator		MoKα(λ=0.71073)
Max. crystal dimensions, mm	0.10 × 0.25 × 0.45	0.13 × 0.20 × 0.50
Scan width	0.80 + 0.35 tan θ	0.80 + 0.35 tan θ
Standard reflections	17,0,0; 080; 0,0,16	12,0,0; 060; 0,0,10
Decay of standards	±2.5%	-5.7%
Reflections measured	4810	4173
2θ range, deg	2 ≤ 2θ ≤ 50	2 ≤ 2θ ≤ 50
Range of <i>h, k, l</i>	±21; +12; +20	+19; +9; ±20
Reflections observed [ <i>F</i> <sub>o</sub> ≥ 5σ( <i>F</i> <sub>o</sub> )] <sup>b</sup>	3680	2708
Computer programs <sup>c</sup>	SHELX <sup>16</sup>	SHELX
Structure solution	Heavy atom techniques	Heavy atom techniques
No. of parameters varied	280	235
Weights	[σ( <i>F</i> <sub>o</sub> ) <sup>2</sup> + 0.00005 <i>F</i> <sub>o</sub> <sup>2</sup> ] <sup>-1</sup>	[σ( <i>F</i> <sub>o</sub> ) <sup>2</sup> + 0.00004 <i>F</i> <sub>o</sub> <sup>2</sup> ] <sup>-1</sup>
GOF	1.07	0.95
<i>R</i> = Σ   <i>F</i> <sub>o</sub>   -   <i>F</i> <sub>c</sub>   /Σ  <i>F</i> <sub>o</sub>	0.028	0.032
<i>R</i> <sub>w</sub>	0.029	0.032
Largest feature final diff. map	1.0 e <sup>-</sup> Å <sup>-3</sup>	1.0 e <sup>-</sup> Å <sup>-3</sup>

<sup>a</sup> Least-squares refinement of ((sin θ)/λ)<sup>2</sup> values for 25 reflections θ > 20°.

<sup>b</sup> Corrections: Lorentz-polarization and absorption (empirical, psi scan).

<sup>c</sup> Neutral scattering factors and anomalous dispersion corrections from ref 17.

2.410(3) Å) are approximately *trans* to O(5). The longer U-Cl(1)=2.711(1) Å and U-O(3)=2.443(4) Å separations are *cis* to O(5).

Both O(3) and O(4) participate in hydrogen bonds producing a hydrogen bonded dimer which resides around a crystallographic centre of inversion. O(4) donates two hydrogen bonds in a terminal fashion to the uncoordinated crown ether with one short (O(4)...O(9)=2.669(5) Å) and one long (O(4)...O(11)=2.855(8) Å) contact. This crown molecule exhibits a nearly *C*<sub>i</sub> conformation<sup>18</sup> observed when 12-crown-4 has only two contacts on one side of the molecule.

TABLE II  
Final fractional coordinates for [UO<sub>2</sub>Cl<sub>2</sub>(12-crown-4)].(12-crown-4).

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B</i> (eqv) <sup>a</sup>
U	0.20924(1)	0.47896(2)	0.38342(1)	0.69
Cl(1)	0.30896(9)	0.2898(1)	0.35039(9)	1.22
Cl(2)	0.1553(1)	0.7476(1)	0.3706(1)	1.56
O(1)	0.1277(2)	0.4351(4)	0.2802(2)	1.01
O(2)	0.2914(2)	0.5168(4)	0.4875(2)	1.11
O(3)	0.1043(3)	0.4765(4)	0.4436(2)	1.32
O(4)	0.2820(2)	0.6105(4)	0.3132(2)	1.21
O(5)	0.1994(3)	0.2434(4)	0.4533(2)	1.19
O(6)	0.1660(3)	0.3300(4)	0.5960(2)	1.17
O(7)	-0.0174(3)	0.3076(4)	0.5318(2)	1.21
O(8)	0.0326(3)	0.1393(4)	0.4218(2)	1.46
O(9)	0.3865(3)	0.7947(4)	0.4302(3)	1.46
O(10)	0.3733(3)	0.8417(4)	0.2581(3)	1.62
O(11)	0.3526(3)	0.5558(5)	0.1907(3)	2.11
O(12)	0.4653(3)	0.5757(4)	0.3731(3)	1.80
C(1)	0.2551(4)	0.2129(6)	0.5443(4)	1.45
C(2)	0.2061(4)	0.1967(6)	0.5985(4)	1.39
C(3)	0.1194(4)	0.3330(6)	0.6500(4)	1.22
C(4)	0.0410(4)	0.2454(6)	0.6138(4)	1.20
C(5)	-0.0721(4)	0.2074(6)	0.4683(4)	1.45
C(6)	-0.0498(4)	0.1977(7)	0.3908(4)	1.47
C(7)	0.0634(4)	0.1391(6)	0.3561(4)	1.66
C(8)	0.1570(4)	0.1186(6)	0.4004(4)	1.65
C(9)	0.3953(4)	0.9318(6)	0.3980(4)	1.80
C(10)	0.3395(5)	0.9370(6)	0.3002(4)	2.01
C(11)	0.3137(4)	0.8036(7)	0.1717(4)	1.88
C(12)	0.3492(5)	0.6805(7)	0.1400(4)	2.45
C(13)	0.4310(5)	0.4847(8)	0.2310(5)	3.13
C(14)	0.4967(5)	0.5580(9)	0.3076(5)	3.14
C(15)	0.5143(4)	0.6755(7)	0.4375(4)	1.90
C(16)	0.4638(4)	0.7253(7)	0.4862(4)	1.78

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

O(3) donates one hydrogen bond to two different coordinated crown molecules. O(3) is hydrogen bonded to O(6) (O(3)...O(6) = 2.685(5) Å) in the crown molecule coordinated to the same uranium centre as O(3), and is hydrogen bonded to O(7)<sup>a</sup> (O(3)...O(7)<sup>a</sup> = 2.674(6) Å) of an ether coordinated to a second uranium. Three of the four oxygen atoms of this crown ether have some interaction, all on the same side of the ether. Only O(8) does not participate in any bonding. When 12-crown-4 molecules have four interactions all on the same side, typically a C<sub>4</sub> conformation is adopted.<sup>18</sup> In the title complex the ether nearly adopts a C<sub>4</sub> conformation except that O(8) is turned out. The sequence of torsion angles starting with O(5)-C(1)-C(2)-O(6) is g<sup>-</sup>ag<sup>-</sup>g<sup>-</sup>ag<sup>-</sup>g<sup>+</sup>aag<sup>-</sup>ag<sup>-</sup>. The four italicized angles involve O(8). In a typical C<sub>4</sub> conformation these angles would be g<sup>-</sup>ag<sup>-</sup>g<sup>-</sup>.

TABLE III  
Final fractional coordinates for  $\text{UO}_2\text{Cl}_2(\text{OH})_2(\text{EO6})$ .

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B</i> (eqv) <sup>a</sup>
U	0.50479(2)	0.76156(3)	0.76218(2)	1.88
Cl(1)	0.3689(1)	0.7491(3)	0.6282(1)	2.95
Cl(2)	0.6327(1)	0.5931(3)	0.8735(1)	3.27
O(1)	0.4451(3)	0.7275(6)	0.8294(3)	2.50
O(2)	0.5669(3)	0.8010(7)	0.6983(3)	3.06
O(3)	0.4432(4)	1.0500(6)	0.7423(3)	3.12
O(4)	0.4878(4)	0.4614(7)	0.7210(3)	3.60
O(5)	0.5883(3)	0.9737(6)	0.8555(3)	2.40
O(6)	0.4772(3)	1.1785(6)	0.9091(3)	2.32
O(7)	0.3452(3)	1.3400(7)	0.7862(3)	2.76
O(8)	0.3224(3)	1.2351(7)	0.6266(3)	3.01
O(9)	0.4597(4)	1.2940(7)	0.5620(3)	3.15
O(10)	0.6318(4)	1.3529(7)	0.6660(3)	3.18
O(11)	0.6791(5)	1.2233(8)	0.8335(4)	5.15
C(1)	0.5950(5)	0.995(1)	0.9417(4)	2.73
C(2)	0.5625(5)	1.164(1)	0.9568(4)	2.61
C(3)	0.4420(5)	1.337(1)	0.9200(5)	2.64
C(4)	0.3521(5)	1.337(1)	0.8714(4)	2.86
C(5)	0.2649(5)	1.290(1)	0.7363(5)	3.14
C(6)	0.2585(5)	1.325(1)	0.6471(5)	2.98
C(7)	0.3136(5)	1.252(1)	0.5409(4)	3.53
C(8)	0.3903(6)	1.186(1)	0.5255(5)	3.52
C(9)	0.5315(6)	1.249(1)	0.5408(5)	4.08
C(10)	0.6011(6)	1.363(1)	0.5782(5)	4.20
C(11)	0.6797(7)	1.205(1)	0.6941(6)	4.55
C(12)	0.7288(6)	1.221(1)	0.7831(6)	4.06

<sup>a</sup>See Table II.

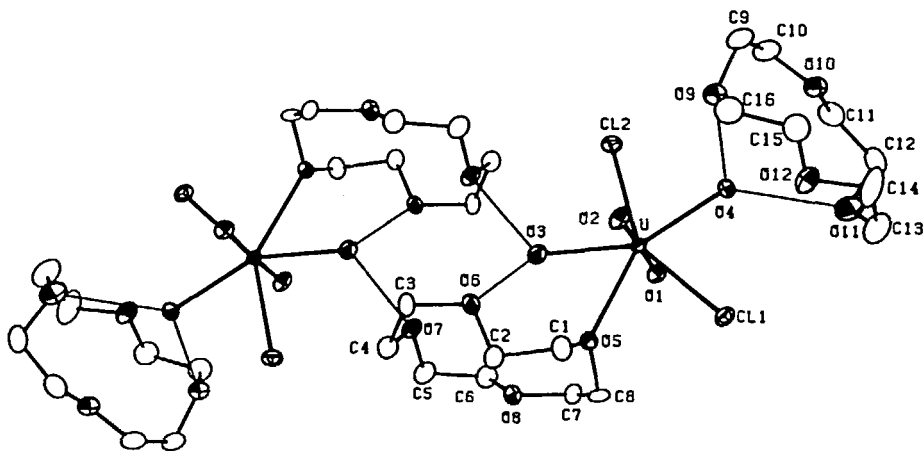


FIGURE 1 The hydrogen bonded dimer in  $[\text{UO}_2\text{Cl}_2(\text{OH})_2(12\text{-crown-4})]_2$ . The atoms are represented with 50% probability ellipsoids. Hydrogen atoms have been omitted.

TABLE IV  
Bond distances (Å) and angles (deg) for [UO<sub>2</sub>Cl<sub>2</sub>(12-crown-4)].(12-crown-4).

Atoms	Distance	Atoms	Distance
U-Cl(1)	2.711(1)	U-Cl(2)	2.675(1)
U-O(1)	1.757(4)	U-O(2)	1.758(4)
U-O(3)	2.443(4)	U-O(4)	2.410(3)
U-O(5)	2.546(4)	O(5)-C(1)	1.444(6)
O(5)-C(8)	1.467(6)	O(6)-C(2)	1.430(6)
O(6)-C(3)	1.452(6)	O(7)-C(4)	1.439(6)
O(7)-C(5)	1.437(7)	O(8)-C(6)	1.419(7)
O(8)-C(7)	1.416(6)	O(9)-C(9)	1.432(7)
O(9)-C(16)	1.434(7)	O(10)-C(10)	1.416(7)
O(10)-C(11)	1.420(7)	O(11)-C(12)	1.435(7)
O(11)-C(13)	1.413(8)	O(12)-C(14)	1.430(7)
O(12)-C(15)	1.411(7)	C(1)-C(2)	1.499(7)
C(3)-C(4)	1.491(8)	C(5)-C(6)	1.507(7)
C(7)-C(8)	1.496(8)	C(9)-C(10)	1.507(8)
C(11)-C(12)	1.513(9)	C(13)-C(14)	1.48(1)
C(15)-C(16)	1.509(8)		
Atoms	Angle	Atoms	Angle
Cl(1)-U-Cl(2)	147.19(4)	Cl(1)-U-O(1)	88.3(1)
Cl(2)-U-O(1)	91.8(1)	Cl(1)-U-O(2)	90.5(1)
Cl(2)-U-O(2)	90.0(1)	O(1)-U-O(2)	178.1(2)
Cl(1)-U-O(3)	137.80(9)	Cl(2)-U-O(3)	74.95(9)
O(1)-U-O(3)	87.9(1)	O(2)-U-O(3)	92.0(1)
Cl(1)-U-O(4)	73.60(9)	Cl(2)-U-O(4)	73.59(9)
O(1)-U-O(4)	91.1(1)	O(2)-U-O(4)	89.9(2)
O(3)-U-O(4)	148.5(1)	Cl(1)-U-O(5)	72.37(9)
Cl(2)-U-O(5)	140.27(9)	O(1)-U-O(5)	93.5(1)
O(2)-U-O(5)	84.8(1)	O(3)-U-O(5)	66.0(1)
O(4)-U-O(5)	145.5(1)	U-O(5)-C(1)	120.6(3)
U-O(5)-C(8)	122.5(3)	C(1)-O(5)-C(8)	114.6(4)
C(2)-O(6)-C(3)	113.4(4)	C(4)-O(7)-C(5)	114.5(4)
C(6)-O(8)-C(7)	112.4(4)	C(9)-O(9)-C(16)	115.6(5)
C(10)-O(10)-C(11)	112.6(5)	C(12)-O(11)-C(13)	117.1(6)
C(14)-O(12)-C(15)	110.8(5)	O(5)-C(1)-C(2)	110.8(5)
O(6)-C(2)-C(1)	107.1(4)	O(6)-C(3)-C(4)	113.6(4)
O(7)-C(4)-C(3)	108.7(4)	O(7)-C(5)-C(6)	109.9(5)
O(8)-C(6)-C(5)	107.7(5)	O(8)-C(7)-C(8)	108.4(5)
O(5)-C(8)-C(7)	111.1(5)	O(9)-C(9)-C(10)	108.2(5)
O(10)-C(10)-C(9)	107.7(5)	O(10)-C(11)-C(12)	108.4(5)
O(11)-C(12)-C(11)	109.8(5)	O(11)-C(13)-C(14)	115.6(6)
O(12)-C(14)-C(13)	107.8(6)	O(12)-C(15)-C(16)	108.3(5)
O(9)-C(16)-C(15)	113.4(5)		

An  $xz$  slice of a  $2 \times 2 \times 2$  unit cell diagram is presented in Figure 2. As is evident in the plot, the dimers stack such that there are double layers of the terminal 12-crown-4 molecules.

$\text{UO}_2\text{Cl}_2(\text{OH}_2)_2(\text{EO6})$  is presented in Figure 3 with bond distances and angles in Table V. The uranium(VI) coordination geometry is again a pentagonal bipyramid with two axial uranyl oxygen atoms ( $\text{U}=\text{O}=1.750(4)\text{ \AA}$  average,  $\text{O}=\text{U}=\text{O}=177.6(2)^\circ$ ), two equatorial chlorine atoms, two equatorial water molecules, and one equatorial alcoholic terminus of a monodentate EO6 molecule. The polyether coordination through alcohol O(5) at  $2.433(5)\text{ \AA}$  is much shorter than the U-O(etheric) separation in the 12-crown-4 complex. The two U-OH<sub>2</sub> contacts ( $2.482(5)\text{ \AA}$ , O(3);  $2.462(5)\text{ \AA}$ , O(4)) are longer than either such distance in the 12-crown-4 complex.

The U-Cl distances are asymmetric, however, this may be due to hydrogen bonding to Cl(2) from O(11). Cl(2) exhibits the longest U-Cl separation ( $2.731(2)\text{ \AA}$ ) found in either title complex.

Both water molecules (O(3) and O(4)) donate two hydrogen bonds to etheric oxygen atoms in symmetry related EO6 ligands producing linear hydrogen bonded polymers (Figure 4). The O...O contacts are long ranging from  $2.767(7)$  to  $3.079(9)\text{ \AA}$ .

The EO6 ligand itself cyclizes (Figure 5) *via* a hydrogen bond donated by O(5) to O(11) ( $\text{O}(5)\dots\text{O}(11)=2.587(9)\text{ \AA}$ ). The uncoordinated alcoholic terminus O(11) donates a hydrogen bond to the coordinated Cl(2).

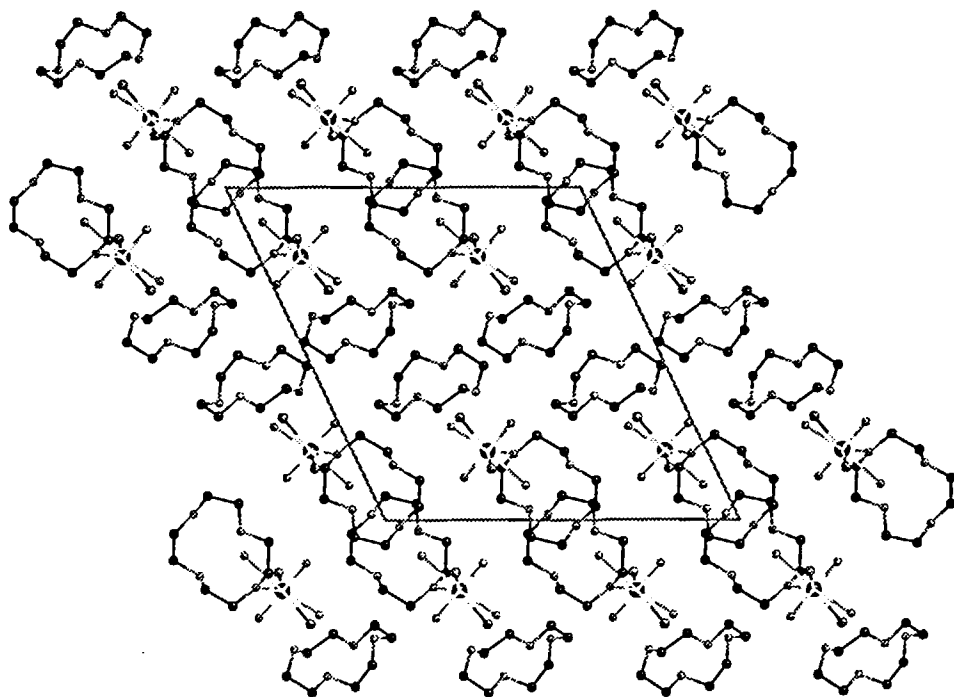


FIGURE 2 A  $2 \times 2$  unit cell representation of the  $xz$  plane in  $[\text{UO}_2\text{Cl}_2(\text{OH}_2)_2(12\text{-crown-4})]$ . 12-crown-4. (SYBYL, Tripos Assoc., St. Louis, MO, U.S.A.).



TABLE V  
Bond distances (Å) and angles (deg) for  $\text{UO}_2\text{Cl}_2(\text{OH}_2)_2(\text{EO6})$ .

Atoms	Distance	Atoms	Distance
U-Cl(1)	2.683(2)	U-Cl(2)	2.731(2)
U-O(1)	1.753(4)	U-O(2)	1.746(5)
U-O(3)	2.482(5)	U-O(4)	2.462(5)
U-O(5)	2.433(5)	O(5)-C(1)	1.442(8)
O(6)-C(2)	1.416(8)	O(6)-C(3)	1.425(8)
O(7)-C(4)	1.414(8)	O(7)-C(5)	1.408(9)
O(8)-C(6)	1.413(9)	O(8)-C(7)	1.423(8)
O(9)-C(8)	1.42(1)	O(9)-C(9)	1.404(9)
O(10)-C(10)	1.421(9)	O(10)-C(11)	1.42(1)
O(11)-C(12)	1.365(9)	C(1)-C(2)	1.49(1)
C(3)-C(4)	1.48(1)	C(5)-C(6)	1.51(1)
C(7)-C(8)	1.48(1)	C(9)-C(10)	1.46(1)
C(11)-C(12)	1.49(1)		

Atoms	Angle	Atoms	Angle
Cl(1)-U-Cl(2)	148.38(6)	Cl(1)-U-O(1)	92.4(2)
Cl(2)-U-O(1)	87.6(2)	Cl(1)-U-O(2)	89.6(2)
Cl(2)-U-O(2)	91.5(2)	O(1)-U-O(2)	177.6(2)
Cl(1)-U-O(3)	73.1(1)	Cl(2)-U-O(3)	138.3(1)
O(1)-U-O(3)	86.2(2)	O(2)-U-O(3)	93.1(2)
Cl(1)-U-O(4)	74.3(1)	Cl(2)-U-O(4)	74.1(1)
O(1)-U-O(4)	89.9(2)	O(2)-U-O(4)	92.0(2)
O(3)-U-O(4)	147.0(2)	Cl(1)-U-O(5)	138.3(1)
Cl(2)-U-O(5)	73.2(1)	O(1)-U-O(5)	90.6(2)
O(2)-U-O(5)	87.0(2)	O(3)-U-O(5)	65.7(2)
O(4)-U-O(5)	147.3(2)	U-O(5)-C(1)	126.2(4)
C(2)-O(6)-C(3)	112.6(6)	C(4)-O(7)-C(5)	112.1(6)
C(6)-O(8)-C(7)	111.0(6)	C(8)-O(9)-C(9)	112.7(6)
C(10)-O(10)-C(11)	112.6(7)	O(5)-C(1)-C(2)	110.9(6)
O(6)-C(2)-C(1)	109.4(6)	O(6)-C(3)-C(4)	108.6(6)
O(7)-C(4)-C(3)	108.6(6)	O(7)-C(5)-C(6)	108.5(6)
O(8)-C(6)-C(5)	109.4(6)	O(8)-C(7)-C(8)	109.0(7)
O(9)-C(8)-C(7)	110.6(7)	O(9)-C(9)-C(10)	111.3(7)
O(10)-C(10)-C(9)	114.0(8)	O(10)-C(11)-C(12)	110.3(8)
O(11)-C(12)-C(11)	112.5(8)		

Only the etheric O(10) does not participate in any hydrogen bonding. This is evident in the torsion angles observed for the EO6 molecule. Starting with O(5)-C(1)-C(2)-O(6) the sequence of angles is  $g^+aag^-aag^+aag^-aag^+g^+ag^+$ . (The last four involve O(10).) Note that the common  $D_{3d}$  sequence of angles found for 18-crown-6 (O-C-C-O alternate  $\pm g$ , all C-O-C-C angles *anti*) holds for the EO6 molecule except near O(10).

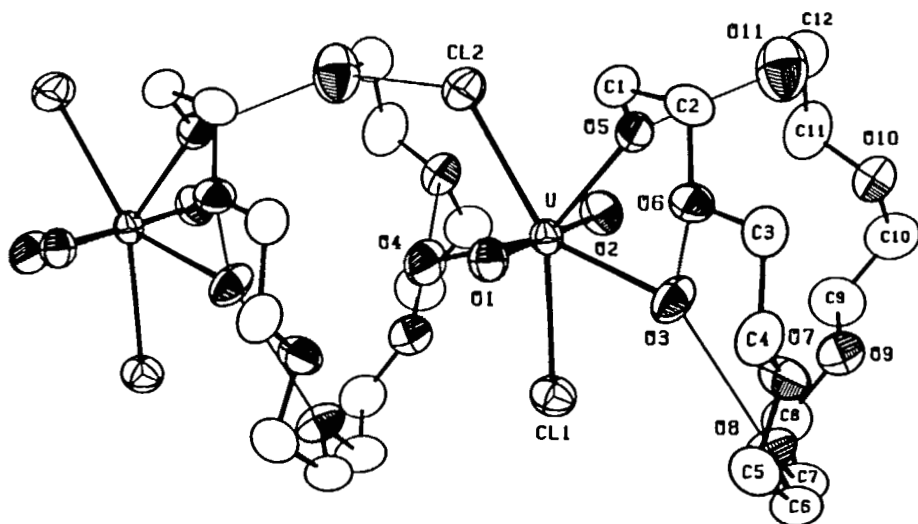


FIGURE 3 A portion of the hydrogen bonded polymeric chain in  $\text{UO}_2\text{Cl}_2(\text{OH}_2)_2(\text{EO6})$ .

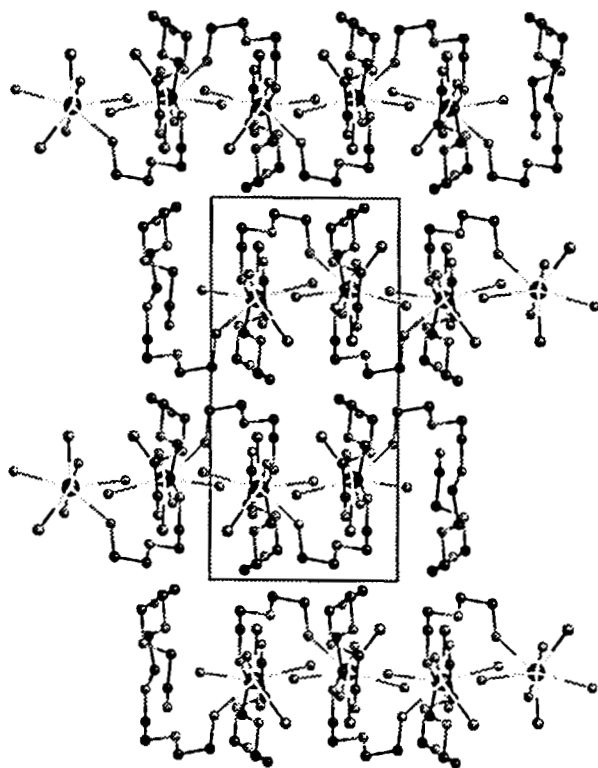


FIGURE 4 A  $2 \times 2$  unit cell representation of the  $yz$  plane in  $\text{UO}_2\text{Cl}_2(\text{OH}_2)_2(\text{EO6})$ .

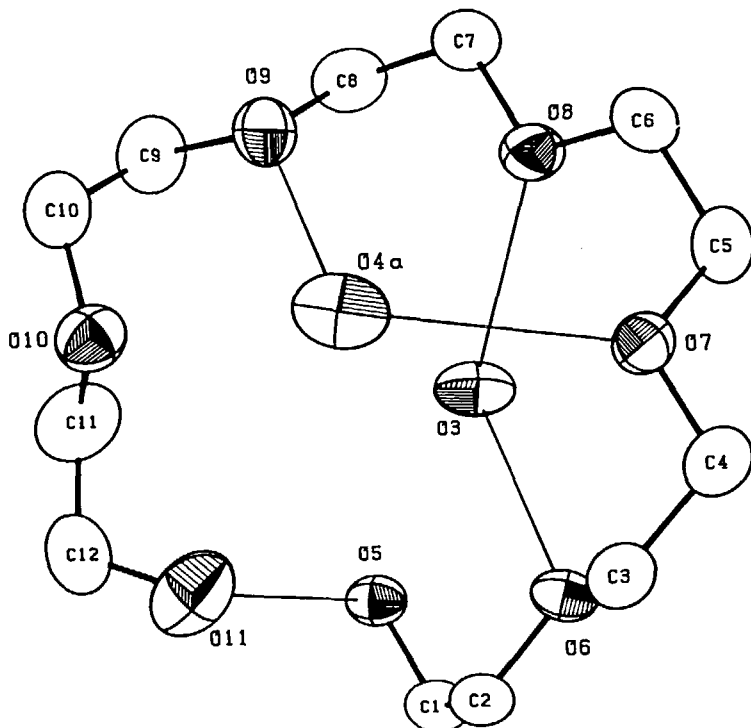


FIGURE 5 The hydrogen bonding environment of the EO6 ligand. In addition O(11) donates a hydrogen bond to C(2).

## DISCUSSION

The three structurally characterized crown ether complexes of uranium,  $[\text{U}(\text{BH}_4)_2(\text{dicyclohexyl-18-crown-6})_2][\text{UCl}_5(\text{BH}_4)]$ ,<sup>12</sup>  $[\text{UO}_2(\text{dicyclohexyl-18-crown-6})][\text{ClO}_4]_2$ ,<sup>13</sup> and  $[\text{UCl}_3(\text{dicyclohexyl-18-crown-6})]_2[\text{UCl}_6]$ <sup>14</sup> are all anhydrous. When water is available, either from the solvent, using a hydrated starting material, or by adding a weak acid, hydrated uranyl species with hydrogen bonded crown ethers are isolated such as  $[\text{UO}_2(\text{SO}_4)(\text{OH}_2)_2] \cdot 0.5(12\text{-crown-4}) \cdot \text{H}_2\text{O}$ ,<sup>5</sup>  $[\text{UO}_2(\text{SO}_4)(\text{OH}_2)_2] \cdot 0.5(\text{benzo-15-crown-5}) \cdot 1.5\text{H}_2\text{O}$ ,<sup>5</sup>  $[\text{UO}_2(\text{SO}_4)(\text{OH}_2)_3] \cdot 0.5(18\text{-crown-6})$ ,<sup>5</sup>  $[\text{UO}_2\text{Cl}_2(\text{OH}_2)_3] \cdot 18\text{-crown-6} \cdot \text{H}_2\text{O} \cdot \text{OHMe}$ ,<sup>7</sup>  $[\text{UO}_2(\text{OH}_2)_5][\text{ClO}_4]_2 \cdot 3(15\text{-crown-5}) \cdot \text{CH}_3\text{CN}$ ,<sup>4</sup>  $[\text{UO}_2(\text{OH}_2)_5][\text{ClO}_4]_2 \cdot 2(18\text{-crown-6}) \cdot 2\text{CH}_3\text{CN} \cdot \text{H}_2\text{O}$ ,<sup>4</sup>  $[\text{UO}_2(\text{OH}_2)_3(\text{OH})_2][\text{ClO}_4]_2 \cdot 3(\text{dicyclohexyl-18-crown-6}) \cdot \text{CH}_3\text{CN}$ ,<sup>13</sup>  $[\text{UO}_2(\text{NO}_3)_2(\text{OH}_2)_2] \cdot 18\text{-crown-6} \cdot 2\text{H}_2\text{O}$ ,<sup>19,20</sup>  $[\text{UO}_2(\text{NO}_3)_2(\text{OH}_2)_2] \cdot 18\text{-crown-6}$ ,<sup>21</sup>  $[\text{UO}_2(\text{NO}_3)_2(\text{OH}_2)_2] \cdot 12\text{-crown-4}$ ,<sup>22</sup>  $[\text{UO}_2(\text{NO}_3)_2(\text{OH}_2)_2] \cdot 1.5(15\text{-crown-5})$ ,<sup>23</sup>  $[\text{UO}_2(\text{NO}_3)_2(\text{OH}_2)_2] \cdot \text{benzo-15-crown-5}$ ,<sup>24</sup>  $[\text{UO}_2(\text{NO}_3)_2(\text{OH}_2)_2] \cdot 2(\text{benzo-15-crown-5})$ ,<sup>6</sup>  $[\text{UO}_2(\text{NO}_3)_2(\text{OH}_2)_2] \cdot 2(\text{dibenzo-18-crown-6})$ ,<sup>25</sup> and  $[\text{U}(\text{SCN})_4(\text{OH}_2)_4] \cdot 1.5(18\text{-crown-6}) \cdot 3\text{H}_2\text{O} \cdot \text{C}_6\text{H}_{12}\text{O}$ .<sup>26</sup> The presence of cationic impurities or hydronium ions formed by the addition of a strong acid results in crown ether complexes of the cations with large uranium complex anions

such as  $[\text{Na}(\text{benzo-15-crown-5})]_2[\text{UO}_2\text{Cl}_4]$ ,<sup>27</sup>  $[\text{Ca}(12\text{-crown-4})_2][\text{UO}_2\text{Cl}_4]$ ,<sup>11</sup>  $[\text{Ca}(\text{OH}_2)_3(15\text{-crown-5})][\text{UO}_2\text{Cl}_4]$ ,<sup>11</sup>  $[\text{Na}(12\text{-crown-4})_2]_2[\text{UO}_2\text{Cl}_4] \cdot 2\text{OHMe}$ ,<sup>10</sup>  $[\text{Mg}(\text{OH}_2)_6][(\text{H}_3\text{O})(15\text{-crown-5})]_2[(\text{UO}_2(\text{SO}_4))_2\text{C}_2\text{O}_4]_2$ ,<sup>5</sup>  $[(\text{H}_3\text{O})(18\text{-crown-6})]_2[(\text{UO}_2(\text{NO}_3)_2)_2\text{C}_2\text{O}_4]$ ,<sup>5</sup>  $[(\text{H}_5\text{O}_2)(\text{H}_9\text{O}_4)(\text{benzo-15-crown-5})]_2[\text{UO}_2\text{Cl}_4]$ ,<sup>5</sup>  $[(\text{H}_5\text{O}_2)_2(18\text{-crown-6})][\text{UO}_2\text{Cl}_4]$ ,<sup>5</sup>  $[(\text{H}_5\text{O}_2)(\text{NO}_2)_2\text{benzo-15-crown-5}]_2[(\text{UO}_2(\text{NO}_3)_2)_2\text{C}_2\text{O}_4]$ ,<sup>5</sup>  $[(\text{H}_5\text{O}_2)(\text{dicyclohexyl-24-crown-8})]_2[\text{UO}_2\text{Cl}_4] \cdot \text{OHMe}$ ,<sup>9</sup>  $[(\text{H}_5\text{O}_2)(\text{dicyclohexyl-24-crown-8})]_2[\text{UO}_2\text{Cl}_4]$ ,<sup>9</sup>  $[(\text{H}_5\text{O}_2)(\text{dicyclohexyl-18-crown-6})]_2[\text{UO}_2\text{Cl}_4]$ ,<sup>28</sup>  $[(\text{H}_3\text{O})(\text{dicyclohexyl-18-crown-6})]_2[\text{UO}_2\text{Cl}_4]$ ,<sup>29</sup>  $[(\text{H}_3\text{O})(\text{dicyclohexyl-18-crown-6})]_3[\text{UO}_2\text{Cl}_4]$ ,<sup>30</sup>  $[(\text{NH}_4)(18\text{-crown-6})]_2[\text{UCl}_6] \cdot 2\text{CH}_3\text{CN}$ ,<sup>8</sup>  $[(\text{NH}_4)(15\text{-crown-5})]_2[\text{UO}_2\text{Cl}_4] \cdot 2\text{CH}_3\text{CN}$ ,<sup>7</sup>  $[(\text{NH}_4)(\text{dibenzo-18-crown-6})]_2[\text{UO}_2\text{Cl}_4] \cdot 2\text{CH}_3\text{CN}$ ,<sup>7</sup>  $[(\text{NH}_4)(\text{benzo-15-crown-5})]_2[\text{UCl}_6] \cdot 4\text{CH}_3\text{CN}$ ,<sup>7</sup> and  $[(\text{NH}_4)(18\text{-crown-6})]_2[\text{UO}_2(\text{SCN})_4(\text{OH}_2)]$ .<sup>31</sup>

The title complexes were crystallized by limiting the water in the reaction but not by totally excluding it. We have been unable to crystallize totally anhydrous complexes, perhaps due to the stabilizing effects of the hydrogen bonding. The competition between the water molecules and the polyether results in the rather unusual monodentate complexes, despite the macrocyclic or chelate effect operating in favour of the polyethers.

There are complexes of crown ethers of variable denticity in the literature, although they are limited in number. Except in those instances where a Group 1 or 2 metal ion is too small to coordinate all of a crown ether oxygen donor atoms,<sup>32-35</sup> variably dentate crown ethers are restricted to Group 13-15 metals and the transition series. Terdentate coordination of a crown ether has been observed in  $[\text{BiCl}_3(\text{OHMe})(18\text{-crown-6})]$ ,<sup>36</sup>  $[\text{BiCl}_3(\text{OH}_2)(18\text{-crown-6})][\text{BiCl}_3(18\text{-crown-6})]$ ,<sup>37</sup> and  $[\text{AlMe}_2(18\text{-crown-6})][\text{AlCl}_2\text{Me}_2]$ .<sup>38</sup> Bidentate coordination was found in  $[\text{MCl}_3(\text{OH}_2)(18\text{-crown-6})]$  ( $\text{M} = \text{V}$ ,<sup>39</sup>  $\text{Cr}$ <sup>40</sup>),  $[\text{TiCl}_3(\text{OH}_2)(18\text{-crown-6})] \cdot \text{CH}_2\text{Cl}_2$ ,<sup>41</sup>  $[(\text{VCl}_3)_2(18\text{-crown-6})][\text{PPh}_4] \cdot 4\text{CH}_2\text{Cl}_2$ ,<sup>39</sup>  $[\text{FeCl}(18\text{-crown-6})]_2[\text{FeCl}_4]_2$ ,<sup>42</sup>  $[\text{MCl}_4(18\text{-crown-6})]$  ( $\text{M} = \text{Ti}$ ,  $\text{Sn}$ ),<sup>43</sup> and  $[\text{Eu}(\text{NO}_3)_3(\text{OH}_2)_2(15\text{-crown-5})] \cdot 0.5(15\text{-crown-5})$ .<sup>44</sup> Monodentate coordination to crown ethers is typical for trimethyl aluminum<sup>45-47</sup> and has also been observed in  $[\text{ZnCl}_2(\text{OH}_2)(18\text{-crown-6})]$ .<sup>48</sup> The later complex has a coordinated water molecule donating two hydrogen bonds to the unidentate 18-crown-6 molecule similar to the coordination we observe in the title complexes. This type of hydrogen bonding was also observed in  $[\text{TiCl}_3(\text{OH}_2)(18\text{-crown-6})] \cdot \text{CH}_2\text{Cl}_2$  and  $[\text{MCl}_3(\text{OH}_2)(18\text{-crown-6})]$  ( $\text{M} = \text{V}$ ,  $\text{Cr}$ ).

Despite being monodentate, the U-O(polyether) separations are not unduly long. Both the U-O(12-crown-4) = 2.546(4) Å and U-O(EO6) = 2.433(5) Å values are within the range of U-O(dicyclohexyl-18-crown-6) distances in  $[\text{UO}_2(\text{dicyclohexyl-18-crown-6})][\text{ClO}_4]_2$  (U-O = 2.43(4) - 2.68(4) Å),  $[\text{U}(\text{BH}_4)_2(\text{dicyclohexyl-18-crown-6})]_2[\text{UCl}_5(\text{BH}_4)]$  (U-O = 2.48(8) - 3.05(9) Å), and  $[\text{UCl}_3(\text{dicyclohexyl-18-crown-6})]_2[\text{UCl}_6]$  (U-O = 2.40 - 2.68 Å).

#### ACKNOWLEDGEMENTS

The diffractometer was purchased with funds provided by the U.S. National Science Foundation Chemical Instrumentation Program.

#### SUPPLEMENTARY MATERIAL

Tables of fractional coordinates for H atoms, thermal parameters, and observed and calculated structure factors are available from R.D.R. upon request.

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