f-Element–Crown Ether Complexes. Part 9.[1] The Role of Solvent Hydrogen Bonding: Synthesis and Crystal Structure† of Aquatetrachlorotris-(ethanol)thorium(IV)–1,4,7,10,13,16-Hexaoxacyclo-octadecane–Water (1/1/1)

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The interaction of $ThCl_4 \cdot nH_2O$ with 1,4,7,10,13,16-hexaoxacyclo-octadecane (18-crown-6) in ethanol yields crystalline $[ThCl_4(OHEt)_3(OH_2)] \cdot (18\text{-crown-}6) \cdot H_2O$. The crystal structure of this complex has been determined from three-dimensional *X*-ray diffraction data collected by counter methods. It crystallizes in the triclinic space group $P\bar{1}$, with (at −150 °C) a = 10.486(3), b = 10.859(5), c = 16.092(6) Å, α = 75.45(4), β = 72.41(4), γ = 60.58(4)°, and D_c = 1.79 g cm^{-3} for Z = 2. The final R value was 0.059 for 4 759 independent observed $[F_o \geqslant 5\sigma(F_o)]$ reflections. The thorium atom is eight-co-ordinate with square antiprismatic geometry. The four chlorines occupy *trans* positions in opposite square planes, with co-ordination completed by one water molecule and three ethanol groups. Two ethanolic hydrogen atoms participate in inter- and intra-molecular bifurcated hydrogen bonds to two of the chlorine atoms. The co-ordinated water molecule is hydrogen-bonded to the crown ether and the second water molecule. The third ethanol group is hydrogen-bonded to the other side of a symmetry related crown ether. The resulting 'supermolecule' consists of infinite zigzag chains (crown–metal–crown–metal) with the chains linked *via* the intermolecular ethanolic hydrogen to chlorine hydrogen bonds. The crown ether has the symmetric D_{3d} conformation. The Th–Cl separations average 2.790(4) Å (hydrogen-bonded chlorines) and 2.694(3) Å.

In the literature there are two major types of *f*-element crown ether complexes, those with direct metal–crown interactions and those with the crown ether hydrogen-bonded to metal-co-ordinated water molecules. Examples of the former include $[M(NO_3)_3(18\text{-crown-}6)]$ (M = La[2] or Nd[3]), $[MCl(OH_2)_2(18\text{-crown-}6)]Cl_2 \cdot 2H_2O$ (M = Sm, Gd, or Tb),[4] $[M(OH_2)_7(OHMe)][MCl(OH_2)_2(18\text{-crown-}6)]_2Cl_7 \cdot 2H_2O$ (M = Y or Dy),[4] $[M(NO_3)_3(15\text{-crown-}5)]$ (M = La, Ce, Pr, Nd, or Eu),[5–7] $[M(OH_2)_4(15\text{-crown-}5)][ClO_4]_3 \cdot (15\text{-crown-}5) \cdot H_2O$ (M = La[8] or Sm[9]), and $[M(NO_3)_3(12\text{-crown-}4)]$ (M = Eu[10] or Y[11]).‡ A growing number of structures containing metal–water–crown ether interactions have been determined, including $[Gd(NO_3)_3(OH_2)_3] \cdot (18\text{-crown-}6)$,[2] $[M(OH_2)_8]Cl_3 \cdot (15\text{-crown-}5)$ (M = Y,[12,13] Gd,[13] or Lu[13]), $[Y(NO_3)_2(OH_2)_5][NO_3] \cdot 2(15\text{-crown-}5)$,[14] $[UO_2(OH_2)_5][ClO_4]_2 \cdot 2(18\text{-crown-}6) \cdot H_2O \cdot 2MeCN$,[15] $[UO_2(OH_2)_5][ClO_4]_2 \cdot 3(15\text{-crown-}5) \cdot MeCN$,[15] and $[Th(NO_3)_4(OH_2)_3] \cdot (18\text{-crown-}6)$.[1]

The solid-state structures with no metal–crown complexation usually form 'supermolecules' containing complex hydrogen-bonding networks. These supermolecules usually have a specific energy, geometry, stability, and reactivity. The variety in these structures, including various numbers of co-ordinating anions and water and solvent molecules, raises questions about 'how' and 'why' water and solvent molecules and anions are excluded from the co-ordination sphere of the metal atom prior to crown complexation. The extractability of a metal ion may depend on the ability of a crown ether to displace metal-co-ordinated water and solvent molecules and thus enhance solubility in non-polar organic solvents.[16] We have undertaken a series of investigations in *f*-element–crown ether complexes with the hope of finding clues to the effects of metal size, crown ether cavity size, crown ether conformation, anion, solvent, conditions of complexation, and method of crystallization on these types of complexes. This contribution takes a look at the inclusion of anions in the primary co-ordination sphere of the metal as related to co-ordinating solvent.

Results and Discussion

The structure of $[ThCl_4(OHEt)_3(OH_2)] \cdot (18\text{-crown-}6) \cdot H_2O$ is depicted in Figure 1. Bond distances and angles are given in Table 1. The thorium ion is eight-co-ordinated, by four chlorine atoms, three ethanol molecules, and one water molecule. The 18-crown-6 and second water molecule are hydrogen-bonded in the lattice (Table 2). The result of the hydrogen bonding is the polymeric network shown in Figure 2. Ethanolic hydrogen atoms H(1)O2 and H(1)O3 each form a bifurcated intramolecular and intermolecular hydrogen bond, with Cl(1) and Cl(3) respectively, resulting in zigzag chains of thorium co-ordination polyhedra. (The H–Cl–H angles average 82.8°.) The co-ordinated water molecule is hydrogen-bonded to the 18-crown-6 moiety and to the unco-ordinated H_2O (which in turn is also hydrogen-bonded to the same crown ether). The remaining ethanolic hydrogen atom H(1)O4 is hydrogen-bonded to a symmetry related 18-crown-6 such that the crown ethers bridge every other thorium polyhedra in the polymeric chain.

The thorium co-ordination polyhedron can best be described as a square antiprism. Using the terminology from refs. 17 and 18, the ratio of edges l/s is 1.058 (l = average distance between atoms in opposite square faces, s = the average length of the two square faces), the dihedral angle between the square planes is 0.85°, and the average of the dihedral angles between the triangular faces is 51°. These values are all close to the ideal: 1.057, 0.0°, and 52.5° respectively.[17,18]

There are two *trans* chlorine atoms in each square base. The chlorines participating in hydrogen bonds and the hydrogen-

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

‡ Abbreviations: 18-crown-6 = 1,4,7,10,13,16-hexaoxacyclo-octadecane, 15-crown-5 = 1,4,7,10,13-pentaoxacyclopentadecane, and 12-crown-4 = 1,4,7,10-tetraoxacyclodecane.

Table 1. Bond distances (Å) and angles (°) for $[ThCl_4(OHEt)_3(OH_2)]\cdot(18\text{-crown-6})\cdot H_2O$

Th–Cl(1)	2.793(3)	Th–Cl(2)	2.692(3)	O(7)–C(11)	1.41(1)	O(8)–C(12)	1.42(1)
Th–Cl(3)	2.788(3)	Th–Cl(4)	2.696(3)	O(8)–C(13)	1.45(1)	O(9)–C(14)	1.43(2)
Th–O(1)	2.453(7)	Th–O(2)	2.513(8)	O(9)–C(15)	1.40(1)	O(10)–C(16)	1.44(1)
Th–O(3)	2.539(7)	Th–O(4)	2.498(8)	O(10)–C(17)	1.41(2)	C(1)–C(2)	1.51(2)
O(2)–C(1)	1.46(1)	O(3)–C(3)	1.45(1)	C(3)–C(4)	1.51(2)	C(5)–C(6)	1.43(2)
O(4)–C(5)	1.48(2)	O(5)–C(7)	1.45(1)	C(7)–C(8)	1.50(1)	C(9)–C(10)	1.48(2)
O(5)–C(18)	1.44(2)	O(6)–C(8)	1.43(1)	C(11)–C(12)	1.52(2)	C(13)–C(14)	1.49(2)
O(6)–C(9)	1.42(1)	O(7)–C(10)	1.43(1)	C(15)–C(16)	1.52(2)	C(17)–C(18)	1.51(2)
Cl(1)–Th–Cl(2)	87.23(8)	Cl(1)–Th–Cl(3)	107.18(8)	O(2)–Th–O(4)	137.1(2)	O(3)–Th–O(4)	75.4(2)
Cl(2)–Th–Cl(3)	137.37(8)	Cl(1)–Th–Cl(4)	139.29(8)	Th–O(2)–C(1)	131.1(6)	Th–O(3)C(3)	129.9(6)
Cl(2)–Th–Cl(4)	107.6(1)	Cl(3)–Th–Cl(4)	87.46(8)	Th–O(4)–C(5)	128.2(7)	C(7)–O(5)–C(18)	109.5(8)
Cl(1)–Th–O(1)	72.4(2)	Cl(2)–Th–O(1)	77.9(2)	C(8)–O(6)–C(9)	113.0(8)	C(10)–O(7)–C(11)	111.6(9)
Cl(3)–Th–O(1)	144.5(2)	Cl(4)–Th–O(1)	74.1(2)	C(12)–O(8)–C(13)	110(1)	C(14)–O(9)–C(15)	111.7(9)
Cl(1)–Th–O(2)	69.4(2)	Cl(2)–Th–O(2)	148.2(2)	C(16)–O(10)–C(17)	111.3(9)	O(2)–C(1)–C(2)	109.4(9)
Cl(3)–Th–O(2)	72.3(2)	Cl(4)–Th–O(2)	80.0(2)	O(3)–C(3)–C(4)	111.1(9)	O(4)–C(5)–C(6)	109(1)
O(1)–Th–O(2)	74.8(2)	Cl(1)–Th–O(3)	72.8(2)	O(5)–C(7)–C(8)	109(1)	O(6)–C(8)–C(7)	109.4(9)
Cl(2)–Th–O(3)	78.8(2)	Cl(3)–Th–O(3)	68.3(2)	O(6)–C(9)–C(10)	109.4(9)	O(7)–C(10)–C(9)	107.4(9)
Cl(4)–Th–O(3)	146.2(2)	O(1)–Th–O(3)	138.7(2)	O(7)–C(11)–C(12)	108(1)	O(8)–C(12)–C(11)	108(1)
O(2)–Th–O(3)	112.3(3)	Cl(1)–Th–O(4)	145.5(2)	O(8)–C(13)–C(14)	108(1)	O(9)–C(14)–C(13)	110(1)
Cl(2)–Th–O(4)	73.7(2)	Cl(3)–Th–O(4)	72.3(2)	O(9)–C(15)–C(16)	109(1)	O(10)–C(16)–C(15)	108(1)
Cl(4)–Th–O(4)	74.9(2)	O(1)–Th–O(4)	128.5(3)	O(10)–C(17)–C(18)	108(1)	O(5)–C(18)–C(17)	108(1)

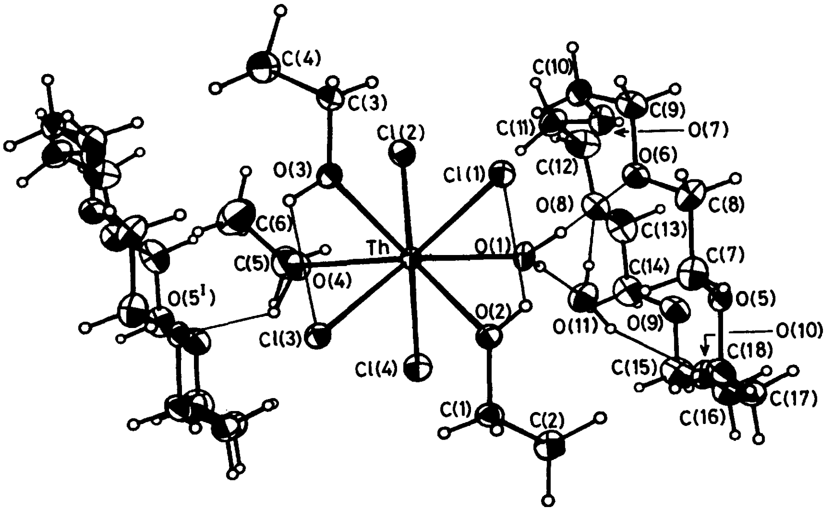

Figure 1. A portion of the polymeric network in $[ThCl_4(OHEt)_3(OH_2)]\cdot(18\text{-crown-6})\cdot H_2O$. The atoms are represented by 50% probability ellipsoids for thermal motion. The hydrogen atomic radii have been arbitrarily reduced

donating molecules are all in the same square plane. The second square plane contains the remaining chlorine atoms and the molecules participating in hydrogen bonds with the crown ether. There is a significant difference in the Th–Cl separations. Cl(1) and Cl(3) which participate in two hydrogen bonds are an average 2.790(4) Å from Th. The remaining Th–Cl distances average 2.694(3) Å. In the course of our other studies we have noted two types of behaviour for chloride anions: the anion forms a tight ion pair with the metal ion as for one of the chlorines in $[MCl(OH_2)_2(18\text{-crown-6})]Cl_2\cdot 2H_2O$ (M = Sm, Gd, or Tb),[4] or the chloride ions are hydrogen-bonded to metal-co-ordinated water molecules as in $[M(OH_2)_8]Cl_3\cdot(15\text{-crown-5})$ (M = Y,[12,13] Gd,[13] or Lu[13]). The title complex appears to be intermediate between these two extremes and we plan to study solvent effects such as this further.

The average of all four Th–Cl contacts [2.74(6) Å] falls in the range observed for other eight-co-ordinate Th^{IV} structures: 2.725(8)—2.763(7) Å in tetrachlorobis(octamethylpyrophosphoramide)thorium(IV)[19] and 2.759 and 2.757 Å in $[ThCl_4(OSPh_2)]$.[20] The Th–OH_2 distance, 2.453(7) Å, is shorter than found in eight-co-ordinate tetra-aqua(pyridine-2,6-dicarboxylato)thorium(IV)[21] [2.54(4) Å] but similar to that found [2.463(3) Å] for $[Th(NO_3)_4(OH_2)_3]\cdot(18\text{-crown-6})$.[1] The Th–OHEt separations average 2.52(2) Å.

Of major interest to us is the effect of hydrogen bonding on the crown ether conformation. In the title complex the crown ether participates in four hydrogen bonds. The torsion angles [starting with O(5)–C(7)–C(8)–O(6), of 72, −179, 179, −67, 168, 174, 72, 180, −173, −70, 174, −174, 68, 179, −180, −69, −178, −179°] are indicative of the symmetric D_{3d} conformation ($g^+aag^-aa\cdots$; g = *gauche*, ±60°; a = anti, 180°) observed in the majority of 18-crown-6 complexes.[22,23] In this conformation each oxygen alternates ±0.24 Å from the mean plane of all six. The three [O(6), O(8), O(10)] which deviate toward O(11) and the side of the metal polyhedron containing O(1) participate in hydrogen bonds to the water molecules. Of the three remaining oxygen atoms (which deviate toward the side of the metal polyhedron containing ethanol groups) only one [O(5)] participates in a hydrogen bond, that to H(1)*O*4. The average bond distances and angles around the crown are normal: C–O 1.43(2), C–C 1.50(2) Å, C–O–C 111(1), C–C–O 109(1)°. It is interesting to note that in $[Th(NO_3)_4(OH_2)_3]\cdot$(18-crown-6),[1] which also has a polymeric nature, the 18-crown-6 molecule participates in a total of six $Th–OH_2 \cdots O$(crown) hydrogen bonds and adopts an unusual conformation defined by a torsion angle sequence of $ggagaag^{-}ag^{-}g^{-}g^{-}ag^{-}aagag$.

Table 2. Distances (Å) and angles (°) for hydrogen bonds in $[ThCl_4(OHEt)_3(OH_2)]\cdot$(18-crown-6)$\cdot H_2O$

H(1)O1–O(1)	1.06	H(1)O11–O(11)	0.95
H(1)O1–O(6)	1.84	H(1)O11–O(8)	1.95
H(2)O1–O(1)	1.00	H(2)O11–O(11)	0.87
H(2)O1–O(11)	1.70	H(2)O11–O(10)	2.13
H(1)O2–O(2)	0.88	H(1)O3–O(3)	0.93
H(1)O2–Cl(1)	2.50	H(1)O3–Cl(3^{III})	2.45
H(1)O2–Cl(1^{II})	2.88	H(1)O3–Cl(3)	2.55
H(1)O4–O(4)	1.14		
H(1)O4–O(5^{I})	1.89		
O(1)–O(6)	2.71(1)	O(11)–O(8)	2.90(1)
O(1)–O(11)	2.66(1)	O(11)–O(10)	2.95(2)
O(2)–Cl(1)	3.030(7)	O(3)–Cl(3^{III})	3.183(8)
O(2)–Cl(1^{II})	3.250(9)	O(3)–Cl(3)	2.998(7)
O(4)–O(5^{I})	2.73(1)		
O(1)–H(1)O1–O(6)	137.0	O(11)–H(1)O11–O(8)	176.7
O(1)–H(2)O1–O(11)	160.7	O(11)–H(2)O11–O(10)	156.6
O(2)–H(1)O2–Cl(1)	119.3	O(3)–H(1)O3–Cl(3^{III})	135.6
O(2)–H(1)O2–Cl(1^{II})	106.8	O(3)–H(1)O3–Cl(3)	110.0
O(4)–H(1)O4–O(5^{I})	126.7		

Atoms related to those in Table 3 by the symmetry operations: I $1 + x, y, z$; II $-x, 2 - y, -z$; III $1 - x, 2 - y, -z$.

Several aspects of this structure deserve further investigation. These include the control of crown ether conformation *via* hydrogen bonding, the preference for Th–OHEt *versus* $Th–OH_2$ co-ordination, and the possible ability of the solvent to keep anions out of the Th co-ordination sphere in the solid state. In addition we plan to continue our study of how the maximization of hydrogen-bonding overlap contributes to the overall observed structure of these complexes.

Experimental

Synthesis and Crystallization of $[ThCl_4(OHEt)_3(OH_2)]\cdot$(18-crown-6)$\cdot H_2O$.—Under argon, 18-crown-6 (10 mmol) in EtOH (25 cm^3) was added to a stirring solution of $ThCl_4\cdot nH_2O$ (10 mmol) in the same solvent (25 cm^3). The reaction mixture was heated to 60 °C for 24 h, cooled to 22 °C, and concentrated to 20—30 cm^3. Crystals suitable for *X*-ray diffraction study crystallized after 1 week at 5 °C. Crystals of this complex are extremely deliquescent, dissolving within 1 min of removal from the solvent in air. No analytical data were obtained. When placed in capillaries under argon, a decomposition temperature of 290—292 °C was observed.

X-*Ray Data Collection, Structure Determination, and Refinement for* $[ThCl_4(OHEt)_3(OH_2)]\cdot$(18-crown-6)$\cdot H_2O$.—*Crystal data.* $C_{18}H_{46}Cl_4O_{11}Th$, $M = 812.4$, triclinic, $T = -150$ °C, $a = 10.486(3)$, $b = 10.859(5)$, $c = 16.092(6)$ Å, $\alpha = 75.45(4)$, $\beta = 72.41(4)$, $\gamma = 60.58(4)°$, $U = 1\,509.6$ Å^3, $Z = 2$, $D_c = 1.79$ g cm^{-3}, μ(Mo-K_α) = 50.87 cm^{-1}, $F(000) = 800$, λ(Mo-K_α) = 0.710 73 Å, space group $P\bar{1}$.

A clear single crystal (0.25 × 0.40 × 0.40 mm) of the complex was mounted on a pin and transferred to the goniometer. The crystal was cooled to −150 °C during data collection using a stream of cold nitrogen gas. The final lattice parameters were

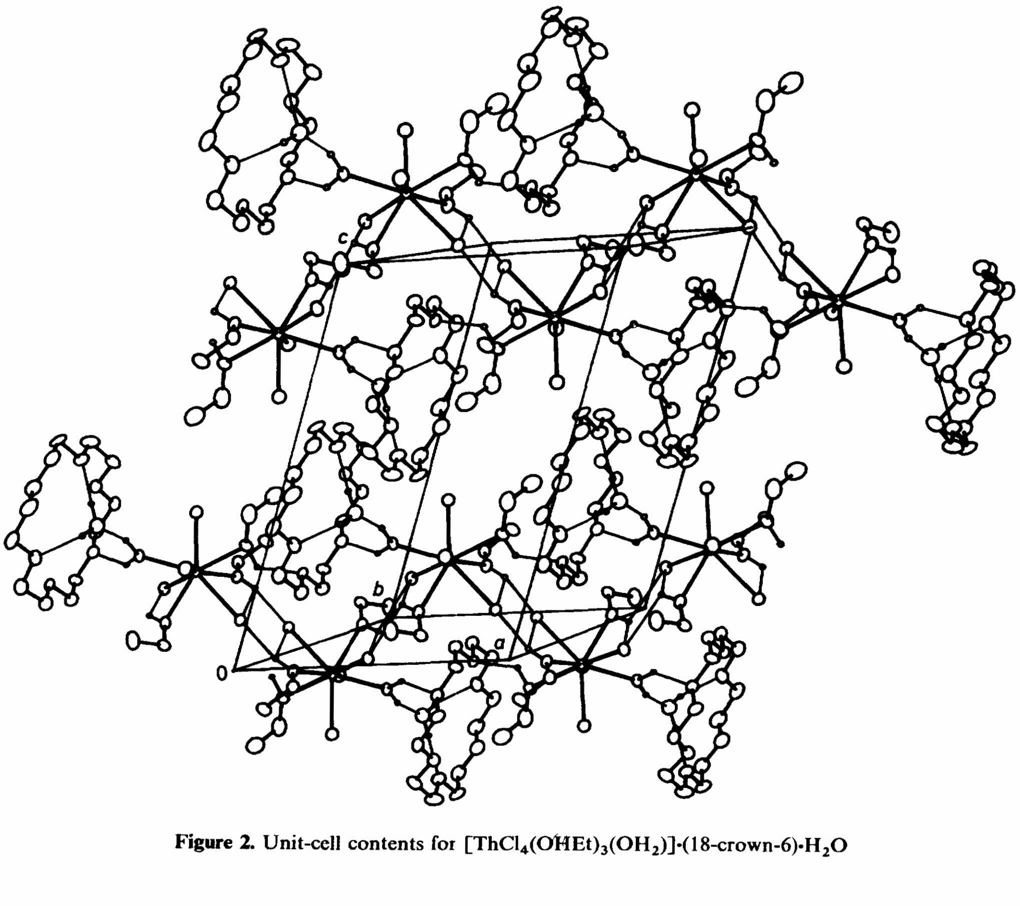

Figure 2. Unit-cell contents for $[ThCl_4(OHEt)_3(OH_2)]\cdot$(18-crown-6)$\cdot H_2O$

Table 3. Final fractional atomic co-ordinates for $[ThCl_4(OHEt)_3(OH_2)]\cdot(18\text{-crown-}6)\cdot H_2O$

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Th	0.246 97(4)	0.858 71(4)	0.166 71(3)	C(2)	0.246(1)	0.564(1)	0.018(1)
Cl(1)	0.001 3(3)	1.078 5(3)	0.100 7(2)	C(3)	0.193(1)	1.221(1)	0.151 9(8)
Cl(2)	0.118 1(3)	0.973 8(3)	0.318 6(2)	C(4)	0.265(1)	1.257(1)	0.203 4(9)
Cl(3)	0.501 4(3)	0.820 6(3)	0.033 8(2)	C(5)	0.474(2)	0.732(1)	0.328(1)
Cl(4)	0.371 6(3)	0.573 1(3)	0.206 9(2)	C(6)	0.506(2)	0.815(2)	0.366(1)
O(1)	0.037 5(8)	0.797 7(7)	0.224 4(5)	C(7)	−0.213(1)	0.836(1)	0.107 1(9)
O(2)	0.217 2(8)	0.790 2(7)	0.038 2(5)	C(8)	−0.308(1)	0.972(1)	0.147 3(8)
O(3)	0.289 4(8)	1.079 3(7)	0.125 8(5)	C(9)	−0.344(1)	1.085(1)	0.266 7(8)
O(4)	0.455 8(8)	0.798 5(8)	0.237 3(5)	C(10)	−0.286(1)	1.066(1)	0.344 4(9)
O(5)	−0.249 5(8)	0.725 6(7)	0.163 7(5)	C(11)	−0.235(1)	0.909(1)	0.473 9(9)
O(6)	−0.257 7(8)	0.962 3(7)	0.223 2(6)	C(12)	−0.283(2)	0.804(1)	0.539 9(9)
O(7)	−0.313 3(9)	0.956 5(8)	0.405 6(6)	C(13)	−0.260(1)	0.572(1)	0.563 6(9)
O(8)	−0.217 7(9)	0.676 1(8)	0.502 2(6)	C(14)	−0.175(1)	0.435(1)	0.526 0(9)
O(9)	−0.229 2(9)	0.445 7(8)	0.451 6(6)	C(15)	−0.142(1)	0.324(1)	0.409(1)
O(10)	−0.157 5(9)	0.454 2(8)	0.265 6(6)	C(16)	−0.195(1)	0.348(1)	0.325 3(9)
O(11)	−0.038 9(9)	0.601 8(8)	0.329 0(6)	C(17)	−0.202(1)	0.482(1)	0.185 5(9)
C(1)	0.312(1)	0.667(1)	−0.009 7(8)	C(18)	−0.157(1)	0.593(1)	0.126 8(9)

determined from a least-squares refinement of $[(\sin\theta)/\lambda]^2$ values for 25 reflections ($\theta > 21°$) accurately centred on the diffractometer. The space group 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 $P\bar{1}$ confirmed this.

Data were collected on an Enraf-Nonius CAD-4 diffractometer with graphite-crystal-monochromated Mo-K_α radiation by the θ–2θ scan technique. 5 434 Reflections in one independent hemisphere out to $2\theta \leqslant 50°$ were measured; 4 759 were considered observed $[F_o \geqslant 5\sigma(F_o)]$. The intensities were corrected for Lorentz and polarization effects, and for absorption.

Calculations were carried out with the (locally modified) SHELX system of computer programs.[24] The function $w(|F_o| - |F_c|)^2$ was minimized. No corrections were made for extinction. Neutral atom scattering factors for Th, Cl, O, C, and H were taken from ref. 25 and the scattering was corrected for the real and imaginary components of anomalous dispersion.[25]

The position of the thorium atom was found from a Patterson map. A difference-Fourier map phased on the thorium atom readily revealed the positions of the non-hydrogen atoms. Least-squares refinement with isotropic thermal parameters led to $R = \Sigma\,||F_o| - |F_c||/\Sigma\,|F_o| = 0.074$. The hydrogen atoms in the crown ether and ethanolic CH_2 groups 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 $Å^2$. The methyl and water hydrogen atoms were located from a difference-Fourier map and included with fixed contributions ($B = 5.5$ $Å^2$). Refinement of the non-hydrogen atoms with anisotropic thermal parameters led to final values of $R = 0.059$ and $R' = 0.062$ (goodness of fit, 4.1). A final difference-Fourier map showed ripple peaks within 1 Å of the Th position but no other feature greater than 1.2 e $Å^{-3}$. The weighting scheme was based on $[1/\sigma(F_o)^2 + (1/pF_o^2)]$ where $p = 0.000\,04$; no systematic variation of $w(|F_o| - |F_c|)$ *vs.* $|F_o|$ or $(\sin\theta)/\lambda$ was noted. The final atomic co-ordinates are given in Table 3.

Acknowledgements

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