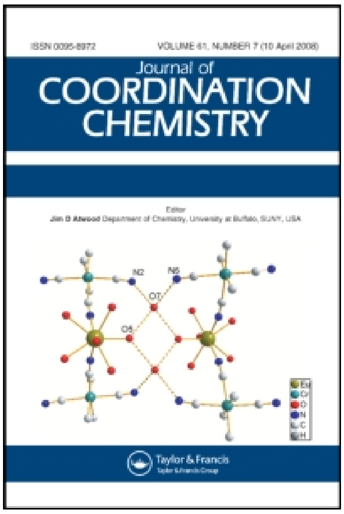

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f-ELEMENT/CROWN ETHER COMPLEXES 15. SYNTHESIS AND CRYSTAL STRUCTURE OF ($[Lu(OH_2)_8]Cl_3 \cdot 1.5(12\text{-CROWN-}4) \cdot 2H_2O$

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f-ELEMENT/CROWN ETHER COMPLEXES 15.† SYNTHESIS AND CRYSTAL STRUCTURE OF ($[Lu(OH_2)_8]Cl_3 \cdot 1.5$(12–CROWN–4)$\cdot 2H_2O$

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The title complex was crystallized at 5°C from a reaction mixture of hydrated $LuCl_3$ and 12-crown-4 in a solution of $CH_3OH:CH_3CN$ (1:3) after layering in pentane. The crystal and molecular structure of $[Lu(OH_2)_8]Cl_3 \cdot 1.5$(12-crown-4)$\cdot 2H_2O$ has been determined by single crystal X-ray diffraction. It crystallizes in the monoclinic space group $P2_1/c$ with $a = 8.816(3)$, $b = 23.387(4)$, $c = 13.544(2)$Å, $\beta = 95.14(2)°$, and $D_{calc} = 1.73$ g cm^{-3} for $Z = 4$. Least-squares refinement using 3819 independent observed $[F_o \geqslant 5\sigma(F_o)]$ reflections led to the final conventional R value of 0.041. The Lu(III) cation is coordinated to eight water molecules (Lu—O average 2.33(3)Å) in an approximate bicapped trigonal prismatic geometry. The crown ether molecules, chloride ions, and uncoordinated water molecules participate in hydrogen bonds to the cation. The hydrogen bonding of the $[Lu(OH_2)_8]^{3+}$ cations to the crown ether molecules results in zigzag chains along c. The chains are further connected by hydrogen bonding to the chloride ions and uncoordinated water molecules. One crown ether resides around a crystallographic centre of inversion and has a C_i conformation. The second crown has the C_4 conformation normally observed in metal complexes with this ligand.

Keywords: lutetium, crown ether, structure, x-ray, hydrogen bonding

INTRODUCTION

We have begun[1–13] systematic investigations into the structural chemistry of f-element/crown ether complexes in an attempt to study the conditions (e.g., metal size, crown ether cavity size, anion, solvent, conditions of crystallization, *etc.*) under which a crown ether may exclude water molecules from an f-element ion's coordination sphere and coordinate directly to the metal. We have thus far concentrated on hydrated chloride salts of the mid to later (smaller) Ln^{3+} ions (and Y^{3+}, the ionic radius of which falls between Dy^{3+} and Ho^{3+}),[14] where water molecules are strongly retained in the primary coordination sphere.

The choice of anion in studies such as these can be structurally decisive, and hard anions such as the chloride ion have been stabilized by hydrogen bonding from protic solvents or other proton donors in successful syntheses of crown ether complexes.[15] We have observed a predominance of octaaquated $[Ln(OH_2)_8]^{3+}$ ions, with chloride ions and crown ether molecules hydrogen bonded to the cation coordinated water molecules as in $[M(OH_2)_8]Cl_3 \cdot$ 15-crown-5 (M = Y,[4,5] Gd,[6] Lu[6]) and $[Dy(OH_2)_8]Cl_3 \cdot$ 18-crown-6$\cdot 4H_2O$.[12] Similar ions have been observed in two complexes that also contain a metal-complexed crown ether $[Lu(OH_2)_8][Na(12\text{-crown-}4)_2]Cl_4 \cdot 2H_2O$[1] and $[M(OH_2)_7(OHMe)][MCl(OH_2)_2(18\text{-crown-}6)]_2Cl_7 \cdot 2H_2O$(M = Dy, Y).[8] Even when the crown ether complexes the lanthanide ions in our studies, some water molecules are retained in the coordination sphere of the metal as found for $[MCl(OH_2)_2$ (18-crown-6)$]Cl_2 \cdot 2H_2O$ (M = Sm, Gd, Tb)[7] and [Tb$(OH_2)_5$(12-crown-

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‡ For Part 14 see reference 1.

4)]$Cl_3 \cdot 2H_2O$.[2] The present paper discusses how the $[M(OH_2)_8]^{3+}$ ion adapts to the hydrogen bonding requirements found in $[Lu(OH_2)_8]Cl_3 \cdot 1.5$(12-crown-4)$\cdot 2H_2O$.

EXPERIMENTAL

Synthesis and Crystallization of $[Lu(OH_2)_8]Cl_3 \cdot 1.5$*(12-crown-4)*$\cdot 2H_2O$

1 mmol of 12-crown-4 in 5 cm^3 of a 1 : 3 mixture of CH_3OH and CH_3CN was added to a stirring solution of 1 mmol of $LuCl_3 \cdot 6H_2O$ in 5 cm^3 of the same solvent mixture. The reaction mixture was heated to 60°C for 1 h then cooled to ambient temperature (22°C). The reaction mixture was allowed to slowly evaporate to 1/2 its original volume and stored at 5°C. The solution was later (2 weeks) transferred to a test tube and pentane was layered over the original liquid which had a yellowish tint. After a period of several weeks at 5°C small transparent crystals of the title complex formed. The crystals were stable to the moisture in air when removed from the solvent long enough to carry out melting point and elemental analysis determinations. However, after data collection at −150°C the crystal used rapidly melted, perhaps due to the melting of a small amount of ice which formed around the crystal during data collection. The crystals yellow and sweat at 250°C, turn dark yellow at 275°C and appear dry at 290°C. Anal; Calcd. for $[Lu(OH_2)_8]Cl_3 \cdot 1.5$(12-crown-4)$\cdot 2H_2O$: C, 19.86·, H, 6.10%. Found: C, 20.35·, H, 6.32%.

X-ray Data Collection, Structure Determination, and Refinement for $[Lu(OH_2)_8]Cl_3 \cdot$ *1.5(12-crown-4)*$\cdot 2H_2O$

A transparent single crystal fragment of the title 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. Final lattice parameters as determined from a least-squares refinement of $((\sin\theta)/\lambda)^2$ values for 25 reflections ($\theta > 22°$) accurately centred on the diffractometer are given in Table I. The space group was determined to be $P2_1/c$ from systematic absences.

Data were collected on an Enraf-Nonius CAD-4 diffractometer by the θ–2θ 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.[16] Neutral atom scattering factors for Lu, Cl, O, C and H were taken from reference 17 and the scattering was corrected for the real and imaginary components of anomalous dispersion[17]

The lutetium atom position was determined via inspection of a Patterson function map. A difference Fourier map phased on the lutetium atom readily revealed the positions of the non-hydrogen atoms. Least-squares refinement with isotropic thermal parameters led to $R = \Sigma \| F_o | - | F_c \| / \Sigma | F_o | = 0.065$. The crown hydrogen atoms were placed in calculated positions 0.95Å from the bonded carbon atom and allowed to ride on that atom with B fixed at 5.5Å^2. The water hydrogen atoms were not included in the final refinement. Refinement of the non-hydrogen atoms with anisotropic temperature factors led to final values of $R = 0.041$ and $R_w = 0.047$. A final difference Fourier showed no feature greater than 1.3 e$^-$/Å^3. The weighting scheme was based on $[\sigma(F_o)^2]^{-1}$·, no systematic variation of $w(|F_o| - |F_c|)$ *vs* $|F_o|$ or $(\sin\theta)/\lambda$ was noted. The final values of the positional parameters are given in Table II.

TABLE I
Crystal Data and Summary of Intensity Data Collection and Structure Refinement.

Cmpd	$[Lu(OH_2)_8]Cl_3 \cdot 1.5(12\text{-crown-}4) \cdot 2H_2O$
Colour/Shape	transparent/fragment
Mol wt.	725.8
Space group	$P2_1/c$
Temp., °C	−150
Cell Constants	
a, Å	8.816(3)
b, Å	23.387(4)
c, Å	13.544(2)
β, deg	95.14(2)
Cell vol, $Å^3$	2781.2
Formula units/unit cell	4
D_{calc}, g cm^{-3}	1.73
μ(calc), cm^{-1}	40.7
Range of relative transm. factors, %	80/100
Radiation, graphite monochromator	Mo$K\alpha$ ($\lambda = 0.71073$)
Max crystal dimensions, mm	0.08 × 0.13 × 0.23
Scan width	$0.80 + 0.35\tan\theta$
Standard reflections	600; 0 16 0; 00 10
Decay of standards	−0.5%
Reflections measured	5330
2θ range, deg	$2 < 2\theta < 50°$
Range of h, k, l	+10, +27, ±16
Reflections observed $[F_o \geqslant 5\sigma(F_o)]$	3819
No. of parameters varied	289
Weights	$[\sigma(F_o)^2]^{-1}$
GOF	1.45
R	0.041
R_w	0.047

RESULTS AND DISCUSSION

In our research into the interaction of crown ethers with hydrated lanthanide and actinide salts, the metal:crown stoichiometry, overall complex structure, and crown ether conformation have been related directly to the number of possible hydrogen bonds between coordinated water molecules and the crown ether. Unlike anhydrous 1:1 (metal:crown) analogs such as $Y(NO_3)_3(12\text{-crown-}4)$[10] or $Eu(NO_3)_3(15\text{-crown-}5)$,[18] where little or no interaction occurs between complexed metal groups, the hydrogen bonded complexes $[M(OH_2)_8]Cl_3 \cdot 15\text{-crown-}5$ ($M = Y$,[4,6] Gd,[5] Lu[5]) and $[Dy(OH_2)_8]Cl_3 \cdot 18\text{-crown-}6 \cdot 4H_2O$[12] are polymeric with hydrogen bonds to the crown ether bridging $[M(OH_2)_8]^{3+}$ cations. Thus, even though Bunzli has isolated 1:1 complexes of anhydrous $PrCl_3$ and $EuCl_3$ with 12-crown-4,[19–21] the hydrogen bonding resulting from the coordinated water molecules in the title complex dictates a 2:3 stoichiometry and the crystallization of $[Lu(OH_2)_8]Cl_3 \cdot 1.5(12\text{-crown-}4) \cdot 2H_2O$ results.

The polymeric nature of the formula unit in the title complex is shown in Figure 1. Each $[Lu(OH_2)_8]^{3+}$ cation is hydrogen bonded to three different crown molecules forming a zigzag chain along c. Further hydrogen bonding of the cation to the chloride anions and uncoordinated water molecules connects the chains in the a and b directions. One of the crown molecules (O(15)–O(16)) resides around a crystallographic centre of inversion.

TABLE II
Final Fractional Coordinates for $[Lu(OH_2)_8]Cl_3 \cdot 1.5(12\text{-crown-}4) \cdot 2H_2O$.

Atom	*x/a*	*y/b*	*z/c*
Lu	0.19363(4)	0.45129(2)	0.29306(3)
Cl(1)	0.6934(3)	0.5064(3)	0.3487(2)
Cl(2)	0.3770(3)	0.2556(1)	0.4182(2)
Cl(3)	−0.1441(3)	0.3107(1)	0.2087(2)
O(1)	0.4384(7)	0.4172(3)	0.2976(5)
O(2)	0.1753(7)	0.3511(3)	0.3193(4)
O(3)	0.1551(8)	0.4416(3)	0.4577(4)
O(4)	0.3502(7)	0.5180(3)	0.3856(4)
O(5)	0.1613(8)	0.4063(3)	0.1402(4)
O(6)	−0.0608(7)	0.4280(3)	0.2755(5)
O(7)	0.0532(7)	0.5344(3)	0.3153(4)
O(8)	0.2607(8)	0.5172(3)	0.1743(4)
O(9)	0.5169(8)	0.3134(3)	0.2464(5)
O(10)	0.2613(8)	0.3001(3)	0.1099(5)
O(11)	−0.0246(7)	0.6368(3)	0.4335(4)
O(12)	0.2988(8)	0.6298(3)	0.4204(5)
O(13)	0.2865(8)	0.6285(3)	0.2095(5)
O(14)	−0.0345(8)	0.6319(3)	0.2195(5)
O(15)	0.7273(8)	0.5480(3)	0.0218(4)
O(16)	0.3887(8)	0.5609(3)	0.0086(4)
C(1)	0.077(1)	0.6793(4)	0.4797(7)
C(2)	0.229(1)	0.6511(4)	0.5061(7)
C(3)	0.370(1)	0.6758(4)	0.3689(7)
C(4)	0.415(1)	0.6490(4)	0.2724(7)
C(5)	0.196(1)	0.6719(4)	0.1555(7)
C(6)	0.038(1)	0.6483(5)	0.1307(7)
C(7)	−0.095(1)	0.6814(4)	0.2700(7)
C(8)	−0.147(1)	0.6599(4)	0.3676(7)
C(9)	0.640(1)	0.5886(4)	0.0748(7)
C(10)	0.499(1)	0.6056(4)	0.0094(7)
C(11)	0.331(1)	0.5445(4)	−0.0901(7)
C(12)	0.211(1)	0.4992(4)	−0.0804(7)

$[Lu(OH_2)_8]^{3+}$ Cation

The $[Lu(OH_2)_8]^{3+}$ cation coordination polyhedron can best be described as a distorted bicapped trigonal prism. The shape determining dihedral angles at the v_1 (O(1)–O(3)) and h_1 (O(1)–O(8), O(6)–O(3)) edges, and at the square face diagonal (O(6)–O(8)) are 23.7, 45.9, and 4.69°, respectively. These values are close to the ideal parameters cited by Drew for the bicapped trigonal prism (21.8, 48.2, 0.0°).[22] The capping atoms O(2) and O(4) are the furthest from the Lu(III) cation averaging 2.372(6)Å (Table III). The six remaining Lu–O separations average 2.32(2)Å.

The geometry observed here is on the reaction pathway between an ideal square antiprism and an ideal bicapped trigonal prism. One square face is planar (O(5)–O(8) planar to within 0.04Å) and the other (O(1)–O(4)) is puckered resulting in the observed geometry. This is interesting when the geometries of the two other crystallographically characterized $[Lu(OH_2)_8]^{3+}$ ions are considered. In $[Lu(OH_2)_8][Na(12\text{-crown-}4)_2]Cl_4 \cdot 2H_2O$,[1] the Lu(III) cation has square antiprismatic geometry and average Lu–O separations of 2.34(2)Å. The cation in $[Lu(OH_2)_8]Cl_3 \cdot 15\text{-crown-}5$ is closer to dodecahedral symmetry[5] and the two different polyhedron sites show average values

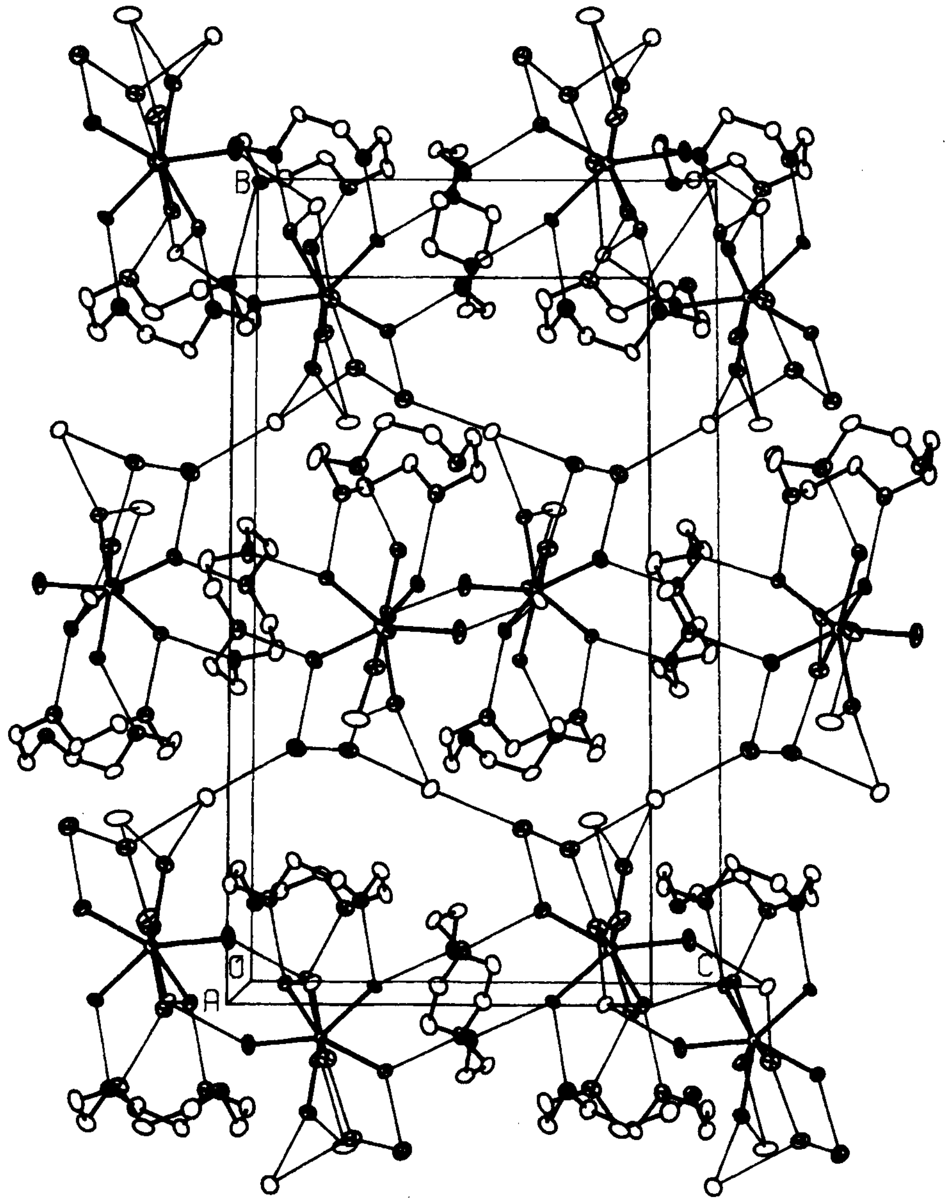

FIGURE 1 Cell packing diagram for $[Lu(OH_2)_8]Cl_3 \cdot 1.5(12\text{-crown-4}) \cdot 2H_2O$. The atoms are represented by their 50% probability ellipsoids for thermal motion. The polymeric zigzag chains propogate along *c*.

of $Lu–O_A = 2.38(4)Å$, $Lu–O_B = 2.32(2)Å$. Apparently distortions and changes in the coordination geometry of the $[Lu(OH_2)_8]^{3+}$ cations are quite easily accomplished by the different hydrogen bonding and packing requirements in these three structures.

Crown Ether Conformation

Even the relatively weak forces involved in hydrogen bonding to crown ether oxygen atoms are known to influence crown ether conformation.[23,24] The hydrogen bonding

TABLE III

Bond Distances (Å) and Angles (deg) for $[Lu(OH_2)_8]Cl_3 \cdot 1.5(12\text{-crown-}4) \cdot 2H_2O$.

Atoms	Distance	Atoms	Distance
Lu --O(1)	2.297(6)	Lu --O(2)	2.377(6)
Lu --O(3)	2.297(6)	Lu --O(4)	2.367(6)
Lu --O(5)	2.318(6)	Lu --O(6)	2.300(7)
Lu --O(7)	2.339(6)	Lu --O(8)	2.341(6)
O(11) --C(1)	1.44(1)	O(11) --C(8)	1.44(1)
O(12) --C(2)	1.45(1)	O(12) --C(3)	1.45(1)
O(13) --C(4)	1.44(1)	O(13) --C(5)	1.45(1)
O(14) --C(6)	1.46(1)	O(14) --C(7)	1.47(1)
O(15) --C(9)	1.45(1)	O(15) --C(12)[a]	1.43(1)
O(16) --C(10)	1.43(1)	O(16) --C(11)	1.44(1)
C(1) --C(2)	1.51(1)	C(3) --C(4)	1.53(1)
C(5) --C(6)	1.51(1)	C(7) --C(8)	1.52(1)
C(9) --C(10)	1.51(1)	C(11) --C(12)	1.51(1)

Atoms	Angle	Atoms	Angle
O(1) --Lu --O(2)	74.3(2)	O(1) --Lu --O(3)	99.2(2)
O(2) --Lu --O(3)	74.9(2)	O(1) --Lu --O(4)	73.3(2)
O(2) --Lu --O(4)	127.9(2)	O(3) --Lu --O(4)	71.4(2)
O(1) --Lu --O(5)	84.6(2)	O(2) --Lu --O(5)	71.4(2)
O(3) --Lu --O(5)	143.7(2)	O(4) --Lu --O(5)	142.4(2)
O(1) --Lu --O(6)	145.7(2)	O(2) --Lu --O(6)	72.8(2)
O(3) --Lu --O(6)	81.3(2)	O(4) --Lu --O(6)	136.7(2)
O(5) --Lu --O(6)	76.1(2)	O(1) --Lu --O(7)	142.4(2)
O(2) --Lu --O(7)	139.1(2)	O(3) --Lu --O(7)	80.3(2)
O(4) --Lu --O(7)	71.0(2)	O(5) --Lu --O(7)	117.9(2)
O(6) --Lu --O(7)	71.8(2)	O(1) --Lu --O(8)	87.3(2)
O(2) --Lu --O(8)	140.9(2)	O(3) --Lu --O(8)	143.1(2)
O(4) --Lu --O(8)	76.0(2)	O(5) --Lu --O(8)	72.8(2)
O(6) --Lu --O(8)	112.9(2)	O(7) --Lu --O(8)	73.2(2)
C(1) --O(11) --C(8)	114.2(7)	C(2) --O(12) --C(3)	111.3(7)
C(4) --O(13) --C(5)	115.8(7)	C(6) --O(14) --C(7)	112.4(7)
C(9) --O(15) --C(12)[a]	114.8(7)	C(10) --O(16) --C(11)	112.7(7)
O(11) --C(1) --C(2)	107.8(8)	O(12) --C(2) --C(1)	113.1(8)
O(12) --C(3) --C(4)	105.3(8)	O(13) --C(4) --C(3)	112.8(8)
O(13) --C(5) --C(6)	108.1(8)	O(14) --C(6) --C(5)	112.1(8)
O(14) --C(7) --C(8)	107.0(8)	O(11) --C(8) --C(7)	113.5(8)
O(15) --C(9) --C(10)	109.1(7)	O(16) --C(10) --C(9)	109.5(8)
O(16) --C(11) --C(12)	107.3(7)	O(15)[a] --C(12) --C(11)	111.0(8)

[a] Atoms are related to those in Table II by $1-x$, $1-y$, $-z$.

in the title complex has resulted in two very different conformations of the 12-crown-4 molecules as shown in Table IV. The first crown ether (depicted in Figure 2) has the normal C_4 conformation normally observed in metal complexes of this ligand as in $[Na(12\text{-crown-}4)_2][ClO_4]$,[23] $[Na(12\text{-crown-}4)_2]Cl \cdot 5H_2O$,[24] $[Na(12\text{-crown-}4)_2][OH] \cdot 8H_2O$,[25] $[Lu(OH_2)_8][Na(12\text{-crown-}4)_2]Cl_4 \cdot 2H_2O$,[1] $[Ca(OH_2)_4(12\text{-crown-}4)]Cl_2 \cdot 4H_2O$,[26] and $Co(NO_3)_2(12\text{-crown-}4)$.[27] A distorted form of this conformation can also be found in $M(NO_3)_3(12\text{-crown-}4)$ (M = Y,[10] Eu[18]). This conformation directs all four oxygen atoms to the same side of the crown molecule in good position for metal complexation. In the title complex all four hydrogen bonds are on this side.

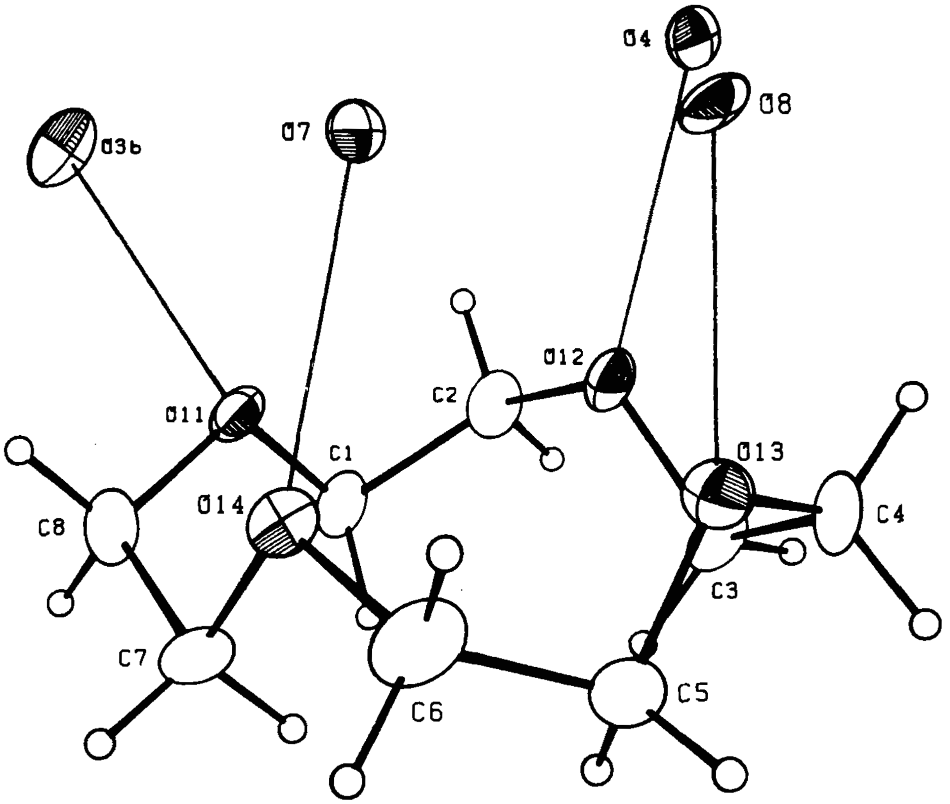

FIGURE 2 C_4 crown ether.

The oxygen atoms are planar to within 0.02Å and the average internal ring parameters are C–O = 1.45(1)Å, C–C = 1.52(1)Å, C–O–C = 113(2)°, $O–C_\alpha–C_\beta$ = 107(1)°, and $O–C_\beta–C_\alpha$ = 112.9(9)°.

The second unique crown molecule in the title complex has C_i symmetry and resides around a crystallographic centre of inversion as found for the free crown ether.[28] This conformation directs two oxygen atoms to opposite sides of the crown ether and is ideally suited to accepting two hydrogen bonds on each side as found in the title complex (Figure 3), $[Mg(OH_2)_6]Cl_2$·12-crown-4,[29] and $UO_2(NO_3)_2(OH_2)_2$·12-crown-4.[30] The oxygen atoms are planar by symmetry and the bonding parameters are consistent with the literature: C–O = 1.44(1)Å average, C–C = 1.51(1)Å, C–O–C = 114(1)°, and O–C–C = 109(1)°.

Hydrogen Bonding

No hydrogen atoms were located for the water molecules, but the hydrogen bonding is evident from the contact geometries presented in Table V. Each crown oxygen atom accepts one hydrogen bond, Cl(1) has five close contacts, Cl(2) and Cl(3) three each, O(9) donates two and accepts two, and O(10) donates two and accepts one. Of the coordinated water molecules, O(2) and O(6) donate exclusively to chloride anions, O(5) and O(8) exclusively to oxygen atoms. The O(8) ·· O(16) contact (2.794(9)Å) is the longest of any of the $Lu–OH_2 \cdots$ O(crown) separations (2.70(4)Å average), and

TABLE IV
Torsion Angles for $[Lu(OH_2)_8]Cl_3 \cdot 1.5(12\text{-crown-4}) \cdot 2H_2O$.

Atoms	Angle (deg)
O(11) --C(1) --C(2) --O(12)	61.9
C(1) --C(2) --O(12) --C(3)	78.9
C(2) --O(12) --C(3) --C(4)	−171.2
O(12) --C(3) --C(4) --O(13)	62.1
C(3) --C(4) --O(13) --C(5)	76.2
C(4) --O(13) --C(5) --C(6)	−156.1
O(13) --C(5) --C(6) --O(14)	58.9
C(5) --C(6) --O(14) --C(7)	78.8
C(6) --O(14) --C(7) --C(8)	−172.2
O(14) --C(7) --C(8) --O(11)	62.4
C(7) --C(8) --O(11) --C(1)	73.6
C(8) --O(11) --C(1) --C(2)	−154.6
O(15) --C(9) --C(10) --O(16)	77.1
C(9) --C(10) --O(16) --C(11)	−129.2
C(10) --O(16) --C(11) --C(12)	−177.7
O(16) --C(11) --C(12) --O(15)[a]	−55.9
C(11) --C(12) --O(15)[a] --C(9)[a]	−80.5
C(12) --O(15)[a] --C(9)[a] --C(10)[a]	138.1
O(15)[a] --C(9)[a] --C(10)[a] --O(16)[a]	−77.1
C(9)[a] --C(10)[a] --O(16)[a] --C(11)[a]	129.2
C(10)[a] --O(16)[a] --C(11)[a] --C(12)[a]	177.7
O(16)[a] --C(11)[a] --C(12)[a] --O(15)	55.9
C(11)[a] --C(12)[a] --O(15) --C(9)	80.5
C(12)[a] --O(15) --C(9) --C(10)	−138.1

[a] Atoms are related to those in Table II by $1-x$, $1-y$, $-z$.

TABLE V
Hydrogen Bonding Contact Geometries for $[Lu(OH_2)_8]Cl_3 \cdot 1.5(12\text{-crown-4}) \cdot 2H_2O$.

Atoms	Distance	Atoms	Distance
O(1) --Cl(1)	3.100(7)	O(1) --O(9)	2.633(9)
O(2) --Cl(2)	3.086(6)	O(2) --Cl(3)	3.212(7)
O(3) --Cl(1)[b]	3.084(6)	O(3) --O(11)[c]	2.676(9)
O(4) --Cl(1)	3.123(7)	O(4) --O(12)	2.702(9)
O(5) --O(10)	2.680(9)	O(5) --O(15)[a]	2.704(9)
O(6) --Cl(1)[d]	3.070(7)	O(6) --Cl(3)	2.961(7)
O(7) --Cl(1)[d]	3.310(9)	O(7) --O(14)	2.701(9)
O(8) --O(13)	2.653(9)	O(8) --O(16)	2.794(9)
O(9) --Cl(2)	3.046(7)	O(9) --Cl(3)[e]	3.077(8)
O(10) --Cl(2)[f]	3.154(7)	O(10) --O(9)	2.801(9)

Atoms	Angle	Atoms	Angle
Cl(1) --O(1) -- O(9)	118.5(3)	Cl(2) --O(2) --Cl(3)	115.9(2)
Cl(1)[b] --O(3) -- O(11)[c]	88.7(2)	Cl(1) --O(4) --O(12)	107.0(3)
O(10) --O(5) -- O(15)[a]	95.4(3)	Cl(1)[d] --O(6) --Cl(3)	119.3(2)
Cl(1)[d] --O(7) -- O(14)	89.8(2)	O(13) --O(8) --O(16)	75.6(3)
Cl(2) --O(9) -- Cl(3)[e]	125.7(2)	Cl(2)[f] --O(10) --O(9)	106.8(3)

[a] Atoms are related to those in Table II by $1-x$, $1-y$, $-z$, [b] $1-x$, $1-y$, $1-z$. [c] $-x$, $1-y$, $1-z$. [d] $x-1$, y, z. [e] $1+x$, y, z. [f] x, $0.5-y$, $z-0.5$.

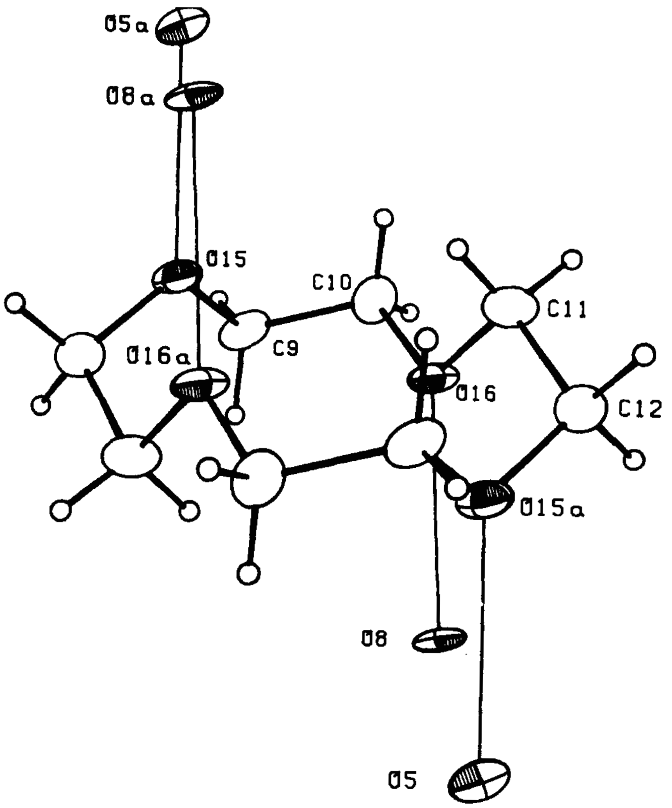

FIGURE 3 C_i crown ether.

may reflect the inability of the two crown ethers hydrogen bonded by O(8) to pack closely enough for better overlap. Every other coordinated water molecule hydrogen bonded to a crown ether has only one such interaction.

The Lu–$OH_2 \cdots OH_2$ contacts average 2.66(2)Å and the $OH_2 \cdots Cl^-$ contacts 3.11(9)Å. Of the latter the longest contact distance is between O(7) and Cl(1) (3.310(9)Å). Again, packing effects (there are a total of five close contacts to Cl(1)) may be responsible for this observation. The longest contact distance between oxygen atoms hydrogen bonded to each other involves the two uncoordinated water molecules, O(10) donating to O(9) (2.801(9)Å).

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SUPPLEMENTARY MATERIAL

Tables of fractional coordinates for calculated hydrogen atoms, thermal parameters, least-squares planes results, and observed and calculated structure factors are available from the Editor upon request.

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