f-Element/Crown Ether Complexes.
6.* Interaction of Hydrated Lanthanide Chlorides with 15-Crown-5: Crystallization and Structures of $[M(OH_2)_8]Cl_3\cdot(15\text{-crown-}5)$ (M = Gd, Lu)

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Abstract

The interaction of hydrated chloride salts of Gd^{3+} and Lu^{3+} with 15-crown-5 in a 1:3 mixture of $CH_3OH{:}CH_3CN$ produces crystalline $[M(OH_2)_8]Cl_3\cdot(15\text{-crown-}5)$ (M = Gd, Lu). The crystal and molecular structures of both complexes have been determined by single crystal X-ray diffraction. Both are isostructural with the previously determined Y analog and crystallize in the monoclinic space group $P2_1/n$ with $Z = 4$. Lattice parameters are $a = 9.247(4)$, $b = 17.312(5)$, $c = 15.191(6)$ Å, $\beta = 92.19(3)°$, $D_{calc} = 1.72$ g cm^{-3} for M = Gd and $a = 9.150(1)$, $b = 17.171(1)$, $c = 15.217(1)$ Å, $\beta = 92.64(1)°$, $D_{calc} = 1.80$ g cm^{-3} for M = Lu. Each complex was refined by least-squares to final conventional R values of 0.052 (M = Gd, 2932 observed $[F_o \geqslant 5\sigma(F_o)]$ reflections) and 0.036 (M = Lu, 3313 observed reflections). The octaaquo M(III) ions exist as a distorted dodecahedron with average $M-OH_2$ separations of 2.41(4) Å (M = Gd) and 2.35(4) Å (M = Lu). The crown ether molecule is hydrogen bonded to metal coordinated water molecules to form polymeric chains along b. The remaining water molecule hydrogen atoms participate in hydrogen bonds with the chloride ions essentially in the ac plane. Two resolvable disordered crown ether conformations are observed with occupancies of 60%/40% (M = Gd) and 75%/25% (M = Lu).

Introduction

As part of our overall synthetic and crystallographic investigation of f-element/crown ether complexation, we have recently concentrated on mid to late lanthanide (and Y which is similar in size to Dy and Ho) hydrated salt interactions with 12-crown-4 [1], 15-crown-5 [2, 3], and 18-crown-6 [4]. We are attempting to learn more about the conditions under which a crown ether can exclude water from a metal ion's coordination sphere and interact directly with the metal. In addition, we hope to be able to characterize structural changes that may occur in the lanthanide series/crown ether complexes as one proceeds across the period and the ionic size decreases. There are several good reviews which provide insight into crown ether complexes of the lighter lanthanides [5–8].

In-cavity M(III) coordination is observed for the anhydrous 18-crown-6 complexes $M(NO_3)_3(18\text{-crown-}6)$ (M = La [9], Nd [10]) and we have observed a similar coordination in the hydrated $[MCl(OH_2)_2(18\text{-crown-}6)]Cl_2\cdot 2(H_2O)$ (M = Sm, Gd, Tb) [4]. After Tb, however, we observe a structural change in the $LnCl_3\cdot 6H_2O/18\text{-crown-}6$ products which appear to be intermediate between hydrogen bonded crown interaction as in $[Y(OH_2)_8]Cl_3\cdot(15\text{-crown-}5)$ and direct metal/crown complexation as in $[MCl(OH_2)_2(18\text{-crown-}6)]Cl_2\cdot 2(H_2O)$. Two structure determinations have been carried out, $[M(OH_2)_7(OHMe)][MCl(OH_2)_2(18\text{-crown-}6)]_2Cl_7\cdot 2(H_2O)$ (M = Dy, Y) [4], which reveal considerably more strain in the 18-crown-6 moiety.

Bunzli and Wessner [8, 11] have reported the 1:1 complexes of lanthanide(III) nitrates and 12-crown-4 to be isomorphous (from X-ray powder data) despite the steady decrease in Ln^{3+} ionic radius with atomic number. The crystal structure of $Eu(NO_3)_3(12\text{-crown-}4)$ [12] revealed the actual coordination: the three nitrate ligands are bidentate on one side of the Eu^{3+} ion and the 12-crown-4 is coordinated on the other side. We isolated the isostructural Y analog in the solid state even though we used hydrated $Y(NO_3)_3$ as our starting material [1]. Similar metal–crown coordination in the structures of 15-crown-5 complexes have been observed for the larger ions Ln^{3+}, La^{3+} through Eu^{3+}, using the NO_3^- (La–Nd, Eu [6, 8, 13]) and ClO_4^- (La, [14], Sm [15]) anions. The latter two structures also contained coordinated water molecules and a second uncoordinated, hydrogen bonded crown ether. We attempted to isolate a 15-crown-5 complex of this type with

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Y(III), but obtained instead a second sphere crown coordination complex, $[Y(OH_2)_8]Cl_3$·(15-crown-5) [2]. In order to more fully investigate these types of complexes we have successfully synthesized and structurally characterized mid (Gd) and late (Lu) lanthanide analogs, $[M(OH_2)_8]Cl_3$·(15-crown-5), that also show no direct metal crown interaction.

Experimental

All reactions were carried out in an oxygen-free Ar atmosphere. All solvents were purified by standard methods. Carbon, hydrogen and nitrogen analyses were performed using a Perkin-Elmer model 240 elemental analyzer. IR absorption spectra were obtained from a Mattson Cygnus 25 FTIR spectrophotometer from KBr pellets. Melting points were obtained by use of an Electrothermal IA6304 capillary melting point apparatus and are uncorrected.

Preparation of [Gd(OH$_2$)$_8$]Cl$_3$·(15-crown-5)

A solution of 10 mmol of 15-crown-5 in 20 ml of a CH_3OH:CH_3CN (1:3) solution was added dropwise to a solution of 10 mmol of $GdCl_3$·$6H_2O$ in 20 ml of the corresponding solvent. The mixture was stirred at 60 °C for 24 h, cooled to 22 °C and concentrated to 10–20 ml. Carbon tetrachloride was used as a crystallizating agent. Melting point (m.p.) 68–72 °C. *Anal.* Calc. for $[Gd(OH_2)_8]Cl_3$·(15-crown-5): C, 19.1; H, 5.78. Found: C, 20.1; H, 5.8%.

After formation of the Gd complex, small shifts of 5–40 cm^{-1} in the vibrational spectra bands due to the crown ether were observed compared to those for the free crown. ν(C–O–C) (at 1100 cm^{-1} in the free crown) was observed to be shifted by −30 cm^{-1} and ν(C–C–O) (950 cm^{-1}) is shifted by −10 cm^{-1}.

Preparation of [Lu(OH$_2$)$_8$]Cl$_3$·(15-crown-5)

A solution of 10 mmol of 15-crown-5 in 20 ml of a CH_3OH:CH_3CN (1:3) solution was added dropwise to a solution of 10 mmol of $LuCl_3$·$6H_2O$ in 20 ml of the corresponding solvent. The mixture was stirred at 60 °C for 24 h, cooled to 22 °C and concentrated to 10–20 ml. Crystallization occurred after 3 days at 5 °C. m.p. 86–92 °C. *Anal.* Calc. for $[Lu(OH_2)_8]Cl_3$·(15-crown-5): C, 18.6; H, 5.62. Found: C, 20.8; H, 5.7%. Small shifts in the vibrational spectra bands due to the crown ether compared to those for free 15-crown-5 were also observed for this complex.

TABLE I. Crystal Data and Summary of Intensity Data Collection and Structure Refinement for $[M(OH_2)_8]Cl_3$·(15-crown-5)

Compound	M = Y [2]	M = Gd	M = Lu
Color/shape		clear/plate	clear/plate
Molecular weight	559.7	628.0	645.7
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
Temperature (°C)	22 °C	22 °C	22 °C
Cell constants			
a (Å)	9.202(2)	9.247(4)	9.150(1)
b (Å)	17.247(3)	17.312(5)	17.171(1)
c (Å)	15.208(3)	15.191(6)	15.217(1)
β (deg)	92.39(2)	92.19(3)	92.64(1)
Cell volume ($Å^3$)	2411.5	2430.0	2388.5
Molecules/unit cell	4	4	4
ρ(calc) (g cm^{-3})	1.54	1.72	1.80
μ(calc) (cm^{-1})		29.46	43.04
Radiation, graphite monochromator		Mo Kα (λ = 0.71069)	Mo Kα (λ = 0.71069)
Max crystal dimensions (mm)		0.20 × 0.33 × 0.33	0.10 × 0.23 × 0.35
Scan width		0.80 + 0.35 tan θ	0.80 + 0.35 tan θ
Standard reflections		400, 006, 080	600, 080, 006
Decay of standards		±1%	−0.3%
Reflections measured		4546	4706
2θ range (deg)		$2 < 2\theta < 50°$	$2 < 2\theta < 50°$
Range of h, k, l		+11, +20, ±18	+10, +20, ±18
Reflections observed [$F_o \geqslant 5\sigma(F_o)$]		2932	3313
No. parameters varied		260	260
Weights		$[\sigma(F_o)^2]^{-1}$	$[\sigma(F_o)^2]^{-1}$
GOF[a]		1.17	1.20
R		0.052	0.036
R_w		0.060	0.036

[a] GOF, goodness of fit.

X-ray Data Collection, Structure Determination and Refinement for [$M(OH_2)_8$]Cl_3·(15-crown-5) (M = Gd, Lu)

Clear single crystals of the title compounds were mounted in air on a pin placed on the goniometer head. Final lattice parameters as determined from a least-squares refinement of $((\sin\theta)/\lambda)^2$ values for 25 reflections ($\theta > 14°$) accurately centered on the diffractometer are given in Table I. The space group was determined to be the centric $P2_1/n$ from the 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, Gd, Cl, O, and C were taken from ref. 17 and the scattering was corrected for the real and imaginary components of anomalous dispersion [17].

The final fractional coordinates for the isostructural Y analog [2] were used as a starting point in the refinement of the Gd complex. Least-squares refinement with isotropic thermal parameters led to $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.085$. As observed for the yttrium analog high thermal motion was observed for the crown ether atoms but not for the remaining atoms. Careful examination of the crown ether moiety revealed a second resolvable conformation which could not be refined for M = Y. Carbon atoms C(2), C(4), C(6), C(8), and C(10) are common to both conformations. Disordered positions for oxygen atoms 9–13 and C(1), C(3), C(5), C(7), and C(9) make up the remainder of the second conformation. This disorder appears to be static in nature and occupancy factors for the two conformations (designated with primes in Tables II and III) refined to 60%/40%. Due to the disorder the hydrogen atoms were not located. No attempt was made to refine the atoms of the minor conformation anisotropically. Refinement of the remaining nonhydrogen atoms with anisotropic temperature factors led to final values of $R = 0.052$ and $R_w = 0.060$. A final difference Fourier showed no feature greater than 1.1 $e^-/Å^3$. The weighting scheme was based on $[(1/\sigma(F_o)^2)]$; 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.

[$Lu(OH_2)_8$]Cl_3·(15-crown-5) was treated similarly in the solution and refinement of the structure. The isotropic R value with no disorder was 0.057. The disorder of the crown ether was found to be similar in nature to the Gd analog and was treated accordingly. Final occupancies for the two conformations refined to 75%/25%. No hydrogen atoms were located. Refinement of the cation, anions and the major crown conformation with anisotropic thermal parameters and of the minor crown conformation with isotropic thermal parameters led to the final R values of $R = 0.036$ and $R_w = 0.036$. Other pertinent crystal data and structure refinement parameters are given in Table I. The final values of the positional parameters are given in Table III.

TABLE II. Final Fractional Coordinates for [$Gd(OH_2)_8$]Cl_3·(15-crown-5)

Atom	*x/a*	*y/b*	*z/c*
Gd	0.85601(6)	0.18129(3)	0.22231(4)
Cl(1)	0.6633(4)	0.1705(2)	0.4976(2)
Cl(2)	0.1474(4)	0.6579(2)	0.3271(3)
Cl(3)	0.6925(4)	0.2431(2)	0.9382(2)
O(1)	0.915(1)	0.1735(5)	0.3744(6)
O(2)	0.802(1)	0.3149(4)	0.2380(6)
O(3)	0.6241(9)	0.1921(5)	0.2972(5)
O(4)	0.782(1)	0.0498(5)	0.2456(7)
O(5)	0.664(1)	0.1629(5)	0.1150(6)
O(6)	1.092(1)	0.2439(5)	0.2455(6)
O(7)	1.046(1)	0.0900(5)	0.1874(7)
O(8)	0.9292(9)	0.2311(5)	0.0833(5)
O(9)	0.907(2)	0.4616(9)	0.366(1)
O(10)	0.942(2)	0.4391(7)	0.189(1)
O(11)	0.669(2)	0.460(1)	0.109(1)
O(12)	0.450(2)	0.4431(9)	0.241(1)
O(13)	0.652(2)	0.3891(9)	0.366(1)
C(1)	1.046(3)	0.448(1)	0.336(2)
C(2)	1.051(2)	0.469(1)	0.235(2)
C(3)	0.924(3)	0.468(2)	0.102(2)
C(4)	0.787(2)	0.4392(9)	0.058(1)
C(5)	0.543(4)	0.409(2)	0.092(2)
C(6)	0.420(2)	0.439(1)	0.142(2)
C(7)	0.435(3)	0.373(2)	0.279(2)
C(8)	0.496(2)	0.381(1)	0.373(1)
C(9)	0.704(4)	0.417(2)	0.448(2)
C(10)	0.870(3)	0.419(1)	0.438(1)
O(9)′ [a]	0.972(4)	0.469(2)	0.288(3)
O(10)′	0.863(3)	0.434(1)	0.135(2)
O(11)′	0.579(4)	0.469(2)	0.109(2)
O(12)′	0.502(6)	0.420(3)	0.305(4)
O(13)′	0.749(5)	0.408(2)	0.399(3)
C(2)′	0.987(5)	0.474(2)	0.142(3)
C(4)′	0.628(6)	0.417(3)	0.064(3)
C(6)′	0.434(6)	0.387(3)	0.214(4)
C(8)′	0.591(6)	0.435(3)	0.416(4)
C(10)′	0.991(6)	0.439(3)	0.385(4)

[a] Primed atoms are disordered. The occupancy factors refined to 0.60 for the unprimed atoms and 0.40 for the primed atoms.

Results and Discussion

The title complexes are isostructural with the previously determined Y analog, [$Y(OH_2)_8$]Cl_3·

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*Locally modified.

TABLE III. Final Fractional Coordinates for $[Lu(OH_2)_8]Cl_3\cdot(15\text{-crown-}5)$

Atom	*x/a*	*y/b*	*z/c*
Lu	0.85662(3)	0.18208(2)	0.22198(2)
Cl(1)	0.6629(3)	0.1724(1)	0.4936(1)
Cl(2)	0.1493(2)	0.6613(2)	0.3314(2)
Cl(3)	0.6915(3)	0.2434(1)	0.9395(1)
O(1)	0.9137(6)	0.1702(3)	0.3703(3)
O(2)	0.8056(6)	0.3124(3)	0.2383(4)
O(3)	0.6280(6)	0.1959(3)	0.2937(3)
O(4)	0.7781(6)	0.0546(3)	0.2469(4)
O(5)	0.6717(6)	0.1595(3)	0.1157(3)
O(6)	1.0887(6)	0.2451(3)	0.2457(3)
O(7)	1.0376(7)	0.0922(3)	0.1847(4)
O(8)	0.9338(6)	0.2310(4)	0.0874(3)
O(9)	0.9055(8)	0.4670(4)	0.3659(5)
O(10)	0.9476(9)	0.4386(4)	0.1880(4)
O(11)	0.6653(9)	0.4629(5)	0.1068(5)
O(12)	0.4442(9)	0.4462(5)	0.2343(6)
O(13)	0.648(1)	0.3887(5)	0.3647(5)
C(1)	1.051(1)	0.4481(7)	0.3359(8)
C(2)	1.056(1)	0.4785(6)	0.2393(6)
C(3)	0.930(1)	0.4732(7)	0.1001(7)
C(4)	0.790(1)	0.4380(6)	0.0570(6)
C(5)	0.539(2)	0.4118(8)	0.0875(9)
C(6)	0.418(1)	0.4426(9)	0.1404(8)
C(7)	0.425(2)	0.3728(8)	0.269(1)
C(8)	0.497(1)	0.3832(6)	0.3749(8)
C(9)	0.710(3)	0.410(1)	0.440(1)
C(10)	0.871(2)	0.4166(8)	0.4363(7)
O(9)′ [a]	1.007(5)	0.467(3)	0.301(3)
O(10)′	0.882(5)	0.438(2)	0.119(2)
O(11)′	0.557(4)	0.464(2)	0.108(2)
O(12)′	0.449(5)	0.395(2)	0.309(3)
O(13)′	0.708(4)	0.456(2)	0.457(2)
C(2)′	0.993(6)	0.474(3)	0.140(3)
C(4)′	0.633(6)	0.423(3)	0.066(3)
C(6)′	0.519(4)	0.380(2)	0.232(2)
C(8)′	0.588(4)	0.455(2)	0.403(2)
C(10)′	0.967(6)	0.440(3)	0.376(4)

[a] Primed atoms are disordered. The occupancy factors refined to 0.75 for the unprimed atoms and 0.25 for the primed atoms.

(15-crown-5) [2]. A view of the asymmetric unit and atom labelling scheme are presented in Fig. 1 for M = Gd. Bond distances and angles for both compounds are given in Table IV. The overall structure consists of eight-coordinate $[M(OH_2)_8]^{3+}$ cations hydrogen bonded to two oxygen atoms of one 15-crown-5 molecule and to three oxygen atoms of a second 15-crown-5 related to the first by $1.5 - x$, $y - 1.5$, $0.5 - z$. The resulting polymeric chain lies along the *b* axis of the unit cell as depicted in Fig. 2. The remaining eleven water molecule hydrogen atoms are hydrogen bonded to chloride ions connecting the polymeric chains along the *a* and *c* axes as well.

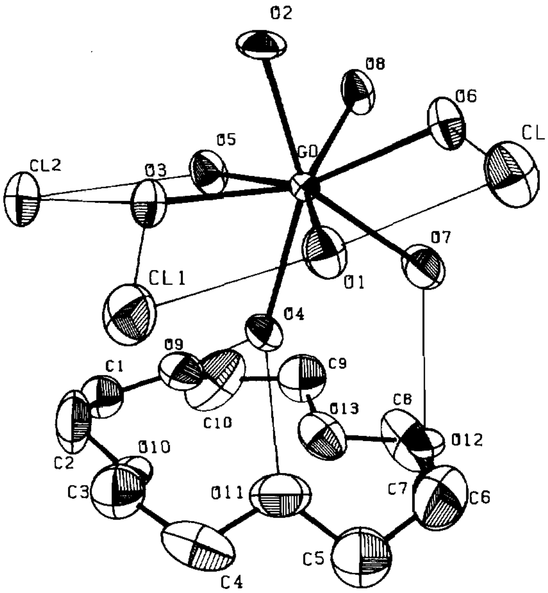

Fig. 1. Asymmetric unit and atom labelling scheme for $[M(OH_2)_8]Cl_3\cdot(15\text{-crown-}5)$ (M = Gd shown). The atoms are represented by their 50% probability ellipsoids for thermal motion. The crown ether shown is related to the coordinates in Tables II and III by $x, y - 1.0, z$.

TABLE IV. Bond Distances (Å) and Angles (deg) for $[M(OH_2)_8]Cl_3\cdot(15\text{-crown-}5)$ [a]

Atoms	M = Gd	M = Lu
Distances		
M–O(1)	2.357(9)	2.302(5)
M–O(2)	2.379(7)	2.301(5)
M–O(3)	2.473(8)	2.416(6)
M–O(4)	2.408(8)	2.340(5)
M–O(5)	2.385(9)	2.319(5)
M–O(6)	2.458(9)	2.397(5)
M–O(7)	2.44(1)	2.352(6)
M–O(8)	2.403(8)	2.351(5)
O(9)–C(10)	1.37(3)	1.43(1)
O(9)–C(1)	1.40(3)	1.47(1)
O(10)–C(3)	1.42(3)	1.47(1)
O(10)–C(2)	1.31(3)	1.41(1)
O(11)–C(4)	1.41(3)	1.46(1)
O(11)–C(5)	1.48(4)	1.47(2)
O(12)–C(6)	1.51(3)	1.44(2)
O(12)–C(7)	1.35(3)	1.38(2)
O(13)–C(8)	1.45(3)	1.40(2)
O(13)–C(9)	1.39(4)	1.31(2)
C(1)–C(2)	1.58(4)	1.56(2)
C(3)–C(4)	1.49(4)	1.54(2)
C(5)–C(6)	1.49(4)	1.49(2)
C(7)–C(8)	1.51(4)	1.72(2)
C(9)–C(10)	1.55(4)	1.48(3)

(continued)

TABLE IV. *(continued)*

Atoms	M = Gd	M = Lu
Angles		
O(1)–M–O(2)	89.9(3)	91.1(2)
O(1)–M–O(3)	74.1(3)	74.2(2)
O(2)–M–O(3)	72.0(3)	70.8(2)
O(1)–M–O(4)	81.9(3)	79.4(2)
O(2)–M–O(4)	147.3(3)	145.7(2)
O(3)–M–O(4)	75.3(3)	74.9(2)
O(1)–M–O(5)	143.2(3)	142.6(2)
O(2)–M–O(5)	92.6(3)	95.3(2)
O(3)–M–O(5)	71.9(3)	73.3(2)
O(4)–M–O(5)	76.4(3)	74.8(2)
O(1)–M–O(6)	73.3(3)	74.5(2)
O(2)–M–O(6)	75.3(3)	74.2(2)
O(3)–M–O(6)	133.2(3)	131.9(2)
O(4)–M–O(6)	130.9(3)	132.4(2)
O(5)–M–O(6)	142.4(3)	142.5(2)
O(1)–M–O(7)	92.0(3)	92.7(2)
O(2)–M–O(7)	143.8(3)	144.4(2)
O(3)–M–O(7)	142.6(3)	143.8(2)
O(4)–M–O(7)	68.4(3)	69.5(2)
O(5)–M–O(7)	106.8(3)	102.8(2)
O(6)–M–O(7)	70.8(3)	72.8(2)
O(1)–M–O(8)	145.1(3)	145.2(2)
O(2)–M–O(8)	78.9(3)	79.5(2)
O(3)–M–O(8)	131.0(3)	131.3(2)
O(4)–M–O(8)	124.1(3)	125.6(2)
O(5)–M–O(8)	71.0(3)	72.0(2)
O(6)–M–O(8)	71.8(3)	70.7(2)
O(7)–M–O(8)	79.1(3)	77.4(2)
C(10)–O(9)–C(1)	116(2)	109.7(9)
C(2)–O(10)–C(3)	115(2)	110.7(8)
C(4)–O(11)–C(5)	112(2)	110.4(8)
C(6)–O(12)–C(7)	112(2)	109(1)
C(8)–O(13)–C(9)	106(2)	108(1)
C(2)–C(1)–O(9)	110(2)	106.4(9)
O(10)–C(2)–C(1)	112(2)	108.2(8)
C(4)–C(3)–O(10)	112(2)	106.6(9)
O(11)–C(4)–C(3)	109(2)	108.6(8)
C(6)–C(5)–O(11)	108(2)	106(1)
O(12)–C(6)–C(5)	114(2)	117(1)
C(8)–C(7)–O(12)	107(2)	102(1)
O(13)–C(8)–C(7)	106(2)	104(1)
C(10)–C(9)–O(13)	104(2)	112(2)
O(9)–C(10)–C(9)	111(2)	110(1)

[a] Distances and angles are given for the major crown conformation only.

The $[M(OH_2)_8]^{3+}$ cations are distorted dodecahedrons as determined by the methods of Hoard and Silverton [18] and Porai–Koshits and Aslanov [19]. A detailed depiction of the cation can be found for M = Y in ref. 2. Table V compares the eight-coordinate M(III)–OH_2 separations. The expected decrease in M–O distance with decreasing ionic size is observed.

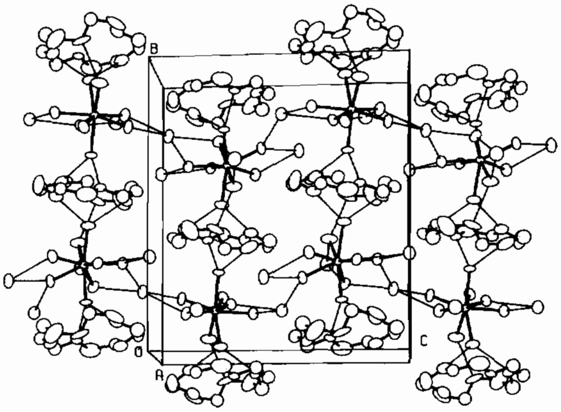

Fig. 2. Cell packing for $[M(OH_2)_8]Cl_3\cdot$(15-crown-5) (M = Gd shown) depicting the polymeric nature resulting from the hydrogen bonding.

High thermal motion was noted in the structure of $[Y(OH_2)_8]Cl_3\cdot$(15-crown-5) but refinement of resolvable disordered conformations of the crown ether was not possible. For both of the title complexes two conformations of the crown ether, a major form (60% M = Gd, 75% M = Lu, Fig. 3) and a minor form (40% M = Gd, 25% M = Lu, Fig. 4) were resolvable. Carbon atoms C(2), C(4), C(6), C(8) and C(10) are common to both conformations and were full weighted. The torsion angles for the two conformations for both complexes are given in Table VI.

Due to the proximity of the atoms defining the two crown ether conformations, the refinement of the minor conformation was not good in either complex. Important features such as C–C and C–O distances and C–C–O and C–O–C angles are thus somewhat obscured. There are, however, some very interesting features of the crown ether hydrogen bonding which can be observed (Table VII) and deserve some discussion. First, from Table V we see that the five $H_2O\cdots O$(crown) separations for the major form and the eleven $H_2O\cdots Cl$ contacts are consistent throughout the series. We notice, however, that the minor crown ether conformation has fewer (4) and longer $H_2O\cdots O$ contacts. The implication of this is that the minor form, which is in a poorer position for maximum hydrogen bonding, is necessary to stabilize the overall packing of the molecules and ions in the unit cell. If this were true one might expect a difference between the structure containing the larger Gd^{3+} ion and the smaller Lu^{3+} ion. In fact we find only a 25% contribution from the minor crown form for M = Lu and a 40% contribution for M = Gd.

The control of overall structure via hydrogen bonding, packing effects, solvent, metal size, etc., in f-element complexes of crown ethers deserves further study. In this regard we are continuing our studies in this area. We have recently isolated new crystals from

TABLE V. Comparative Aspects of the Series $[M(OH_2)_8]Cl_3\cdot(15\text{-crown-}5)$ (M = Y, Gd, Lu)

Complex	M^{3+} ionic radius[a]	M–O average (Å)	$M-O_A$ average (Å)[b]	$M-O_B$ average (Å)	$H_2O\cdots O$(crown) average (Å)[c]	$H_2O\cdots Cl$ average (Å)	Reference
$[Gd(OH_2)_8]Cl_3\cdot(15\text{-crown-}5)$	1.053	2.41(4)	2.44(4)	2.39(4)	2.74(8) (2.8(1))	3.07(3)	this study
$[Gd(OH_2)_8]Cl_3\cdot 2(C_{10}H_8N_2)$	1.053	2.40(7)	2.45(1)	2.35(1)		3.09(5)	22
$[Y(OH_2)_8]Cl_3\cdot(15\text{-crown-}5)$	1.019	2.37(4)	2.40(3)	2.35(3)	2.76(7)	3.08(4)	2
$[Y(OH_2)_8]Cl_3\cdot 2(C_{10}H_8N_2)$	1.019	2.38(6)	2.425(6)	2.327(6)		3.110(5)	23
$[Lu(OH_2)_8]Cl_3\cdot(15\text{-crown-}5)$	0.977	2.35(4)	2.38(4)	2.32(2)	2.75(6) (3.1(2))	3.08(3)	this study

[a] Ionic radii for CN = 8 from ref. 21. [b] Terms A and B for a dodecahedron defined in refs. 18, 19. [c] Minor form of the crown ether in parentheses.

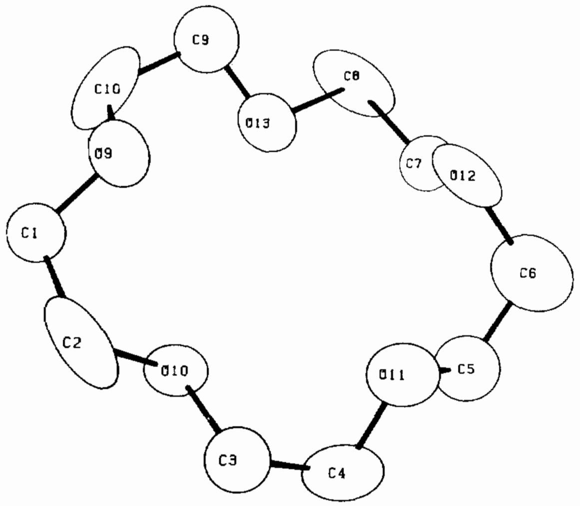

Fig. 3. Major form of the disordered crown ether (M = Gd 60% shown, M = Lu 75%).

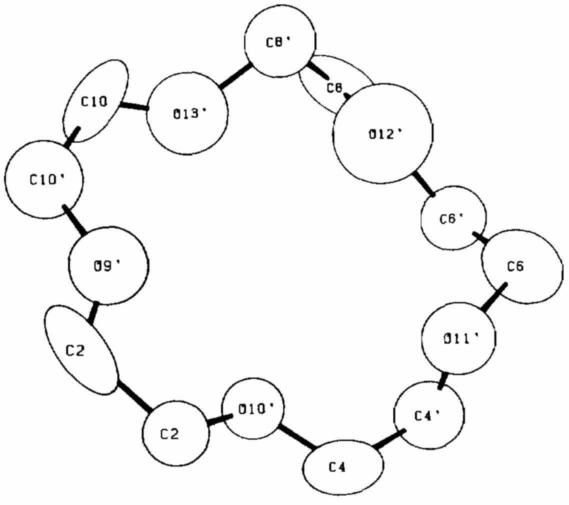

Fig. 4. Minor form of the disordered crown ether (M = Gd 40% shown, M = Lu 25%). C(2), C(4), C(6), C(8) and C(10) are common to both and are full weighted.

TABLE VI. Torsion Angles for $[M(OH_2)_8]Cl_3\cdot(15\text{-crown-}5)$

Atoms	M = Gd	M = Lu
O(9)–C(1)–C(2)–O(10)	−48.0	−61.7
C(1)–C(2)–O(10)–C(3)	168.3	170.8
C(2)–O(10)–C(3)–C(4)	−172.4	−168.1
O(10)–C(3)–C(4)–O(11)	56.7	64.6
C(3)–C(4)–O(11)–C(5)	−155.7	−161.4
C(4)–O(11)–C(5)–C(6)	−175.0	−179.2
O(11)–C(5)–C(6)–O(12)	−60.2	−58.7
C(5)–C(6)–O(12)–C(7)	−79.5	−79.6
C(6)–O(12)–C(7)–C(8)	169.0	167.8
O(12)–C(7)–C(8)–O(13)	−70.0	−71.6
C(7)–C(8)–O(13)–C(9)	164.1	169.6
C(8)–O(13)–C(9)–C(10)	176.6	179.7
O(13)–C(9)–C(10)–O(9)	54.8	53.6
C(9)–C(10)–O(9)–C(1)	−160.6	−154.6
C(10)–O(9)–C(1)–C(2)	155.1	156.9
O(9)'–C(2)–C(2)'–O(10)'	−35.8	−18.0
C(2)–C(2)'–O(10)'–C(4)	174.4	159.4
C(2)'–O(10)'–C(4)–C(4)'	−160.8	−144.6
O(10)'–C(4)–C(4)'–O(11)'	67.4	61.8
C(4)–C(4)'–O(11)'–C(6)	−165.2	−161.2
C(4)'–O(11)'–C(6)–C(6)'	78.9	76.0
O(11)'–C(6)–C(6)'–O(12)'	65.2	136.5
C(6)–C(6)'–O(12)'–C(8)	169.1	−161.7
C(6)'–O(12)'–C(8)–C(8)'	170.6	87.5
O(12)'–C(8)–C(8)'–O(13)'	−87.3	−150.5
C(8)–C(8)'–O(13)'–C(10)	−156.4	66.5
C(8)'–O(13)'–C(10)–C(10)'	−135.6	68.9
O(13)'–C(10)–C(10)'–O(9)'	17.1	−38.4
C(10)–C(10)'–O(9)'–C(2)	−159.4	−131.1
C(10)'–O(9)'–C(2)–C(2)'	157.9	111.4

the reaction of YCl_3 and 15-crown-5 which analyze as $YCl_3O_{13}C_{10}H_{36}$, but which melt below room temperature. Preliminary X-ray diffraction results [20] indicate that it is isostructural with $[Y(OH_2)_8]Cl_3\cdot$(15-crown-5) (melting point 104–108 °C). We intend to determine the structure at low temperature in

TABLE VII. Hydrogen Bonding Contact Geometries for $[M(OH_2)_8]Cl_3\cdot(15\text{-crown-}5)$

Atoms	M = Gd	M = Lu
Distances (Å)		
O(1)–Cl(1)	3.04(1)	3.030(6)
O(1)–Cl(3)[a]	3.07(1)	3.086(6)
O(2)–O(10)	2.63(2)	2.657(9)
O(2)–O(10)'	2.67(3)	2.93(4)
O(2)–O(13)	2.75(2)	2.78(1)
O(3)–Cl(1)	3.075(9)	3.069(6)
O(3)–Cl(2)[b]	3.140(9)	3.158(6)
O(4)–O(11)[c]	2.73(2)	2.757(9)
O(4)–O(11)'[c]	2.88(3)	3.04(4)
O(4)–O(9)[c]	2.84(2)	2.787(9)
O(4)–O(9)'[c]	2.76(4)	3.07(5)
O(5)–Cl(2)[b]	3.04(1)	3.082(6)
O(5)–Cl(3)[d]	3.04(1)	3.056(6)
O(6)–Cl(2)[c]	3.07(1)	3.074(6)
O(6)–Cl(3)[a]	3.043(9)	3.060(5)
O(7)–Cl(2)[c]	3.08(1)	3.121(6)
O(7)–O(12)[c]	2.77(2)	2.79(1)
O(7)–O(12)'[c]	2.98(5)	3.38(4)
O(8)–Cl(1)[a]	3.08(1)	3.076(6)
O(8)–Cl(3)[d]	3.053(9)	3.093(6)
Angles (°)		
Cl(1)–O(1)–Cl(3)[a]	117.6(3)	114.7(2)
O(10)–O(2)–O(13)	94.9(5)	95.2(3)
Cl(1)–O(3)–Cl(2)[a]	129.3(3)	128.1(2)
O(11)[c]–O(4)–O(9)[c]	105.1(6)	105.9(3)
O(11)'[c]–O(4)–O(9)'[c]	104(1)	108(1)
Cl(2)[b]–O(5)–Cl(3)[d]	112.5(3)	108.7(2)
Cl(2)[c]–O(6)–Cl(3)[d]	99.8(3)	100.8(2)
O(12)[c]–O(7)–Cl(2)[c]	112.5(5)	109.8(3)
O(12)'[c]–O(7)–Cl(2)[c]	121(1)	110.4(8)
Cl(3)[d]–O(8)–Cl(1)[a]	98.8(3)	96.1(2)

[a]Atoms are related to those in Tables II and III by 0.5 + *x*, 0.5 − *y*, *z* − 0.5. [b]0.5 − *x*, *y* − 0.5, 0.5 − *z*. [c]1.5 − *x*, *y* − 0.5, 0.5 − *z*. [d]*x*, *y*, *z* − 1.

order to find out if the minor form of the crown ether is present and to accurately locate the hydrogen atom positions.

Supplementary Material

Tables of thermal parameters, and observed and calculated structure factors for both compounds are available from the authors on request (20 pages).

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