

Structural Investigation into the Steric Control of Polyether Complexation in the Lanthanide Series: Macrocyclic 18-Crown-6 versus Acyclic Pentaethylene Glycol

Robin D. Rogers,* Andrew N. Rollins, Russell D. Etzenhouser, Eric J. Voss, and Cary B. Bauer

Department of Chemistry, Northern Illinois University, DeKalb, Illinois 60115

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The complexation reactions of $MCl_3 \cdot nH_2O$ ($M = Y, La\text{--}Pr, Sm\text{--}Lu$) with pentaethylene glycol (EO5) and $MCl_3 \cdot nH_2O$ ($M = La, Ce, Pr, Eu, Gd$) with 18-crown-6 in 1:1 molar ratios in 3:1 $CH_3CN:CH_3OH$ were investigated. X-ray structural analyses of 21 crystalline complexes were carried out. EO5 forms two different complexes with the lanthanides, a dihydrate of the form $[MCl_2(OH_2)(EO5)]Cl \cdot H_2O$ for $M = La\text{--}Pr$ and a tetrahydrate of the form $[M(OH_2)_3(EO5)]Cl_3 \cdot H_2O$ for $M = Y$ and $Sm\text{--}Lu$. Cell data are as follows. $[MCl_2(OH_2)(EO5)]Cl \cdot H_2O$ ($P2_1/c$): $M = La$ (20 °C), $a = 13.508(9)$ Å, $b = 9.825(3)$ Å, $c = 14.518(4)$ Å, $\beta = 102.97(4)^\circ$, and $D_{calc} = 1.84$ g cm^{-3} for $Z = 4$; $M = Ce$ (20 °C), $a = 13.489(2)$ Å, $b = 9.820(1)$ Å, $c = 14.514(5)$ Å, $\beta = 102.86(2)^\circ$, and $D_{calc} = 1.85$ g cm^{-3} for $Z = 4$; $M = Pr$ (20 °C), $a = 13.439(7)$ Å, $b = 9.797(5)$ Å, $c = 14.479(2)$ Å, $\beta = 102.69(3)^\circ$, and $D_{calc} = 1.86$ g cm^{-3} for $Z = 4$. $[M(OH_2)_3(EO5)]Cl_3 \cdot H_2O$ ($P2_1/c$): $M = Sm$ (20 °C), $a = 7.501(4)$ Å, $b = 32.665(9)$ Å, $c = 9.112(4)$ Å, $\beta = 109.71(7)^\circ$, and $D_{calc} = 1.79$ g cm^{-3} for $Z = 4$; $M = Eu$ (20 °C), $a = 7.497(2)$ Å, $b = 32.630(8)$ Å, $c = 9.097(3)$ Å, $\beta = 109.67(2)^\circ$, and $D_{calc} = 1.80$ g cm^{-3} for $Z = 4$; $M = Gd$ (18 °C), $a = 7.493(2)$ Å, $b = 32.595(9)$ Å, $c = 9.083(4)$ Å, $\beta = 109.68(4)^\circ$, and $D_{calc} = 1.82$ g cm^{-3} for $Z = 4$; $M = Tb$ (18 °C), $a = 7.487(4)$ Å, $b = 32.554(9)$ Å, $c = 9.066(8)$ Å, $\beta = 109.73(7)^\circ$, and $D_{calc} = 1.84$ g cm^{-3} for $Z = 4$; $M = Dy$ (22 °C), $a = 7.4744(7)$ Å, $b = 32.512(4)$ Å, $c = 9.060(2)$ Å, $\beta = 109.70(1)^\circ$, and $D_{calc} = 1.86$ g cm^{-3} for $Z = 4$; $M = Y$ (20 °C), $a = 7.477(2)$ Å, $b = 32.435(9)$ Å, $c = 9.040(2)$ Å, $\beta = 109.64(4)^\circ$, and $D_{calc} = 1.63$ g cm^{-3} for $Z = 4$; $M = Ho$ (18 °C), $a = 7.469(2)$ Å, $b = 32.470(9)$ Å, $c = 9.041(4)$ Å, $\beta = 109.67(2)^\circ$, and $D_{calc} = 1.87$ g cm^{-3} for $Z = 4$; $M = Er$ (20 °C), $a = 7.454(6)$ Å, $b = 32.379(6)$ Å, $c = 9.015(3)$ Å, $\beta = 109.68(5)^\circ$, and $D_{calc} = 1.92$ g cm^{-3} for $Z = 4$; $M = Tm$ (18 °C), $a = 7.455(1)$ Å, $b = 32.413(9)$ Å, $c = 9.017(3)$ Å, $\beta = 109.66(4)^\circ$, and $D_{calc} = 1.90$ g cm^{-3} for $Z = 4$; $M = Yb$ (20 °C), $a = 7.458(3)$ Å, $b = 32.350(9)$ Å, $c = 9.005(7)$ Å, $\beta = 109.71(6)^\circ$, and $D_{calc} = 1.92$ g cm^{-3} for $Z = 4$; $M = Lu$ (20 °C), $a = 7.452(1)$ Å, $b = 32.355(9)$ Å, $c = 9.010(3)$ Å, $\beta = 109.64(3)^\circ$, and $D_{calc} = 1.92$ g cm^{-3} for $Z = 4$. 18-Crown-6 also directly complexes the early- to mid-lanthanide chlorides. Three crystalline forms with various degrees of hydration were isolated for $M = La$. The anhydrous $[LaCl_3(18\text{-crown-6})]$ crystallizes at 70 °C in the centric space group $P2_1/c$ with cell constants (20 °C) $a = 7.540(4)$ Å, $b = 13.725(4)$ Å, $c = 18.451(7)$ Å, $\beta = 91.38(4)^\circ$, and $D_{calc} = 1.77$ g cm^{-3} for $Z = 4$. In addition, two hydrated forms, $[LaCl_2(OH_2)(18\text{-crown-6})]Cl$ and $[LaCl_2(Y)(18\text{-crown-6})]Cl \cdot 1.5H_2O$ ($Y = OH_2, OHMe$), can be crystallized from these reaction mixtures by slow evaporation at room temperature. The former crystallizes in the acentric space group $Fdd2$ with (20 °C) $a = 36.979(9)$ Å, $b = 28.418(9)$ Å, $c = 7.484(1)$ Å, and $D_{calc} = 1.78$ g cm^{-3} for $Z = 16$. The latter is disordered with either a water molecule or methanol group occupying one primary coordination site. It crystallizes in $P2_1/c$ with (20 °C) $a = 8.391(2)$ Å, $b = 7.554(2)$ Å, $c = 33.988(9)$ Å, $\beta = 97.51(3)^\circ$, and $D_{calc} = 1.75$ for $Z = 4$. Except for the disorder, it is isostructural with the cerium trihydrate complex. $[CeCl_2(OH_2)(18\text{-crown-6})]Cl \cdot 2H_2O$ crystallizes in the centric space group $P2_1/c$ with cell constants (20 °C) $a = 8.440(3)$ Å, $b = 7.469(4)$ Å, $c = 34.204(9)$ Å, $\beta = 97.76(4)^\circ$, and $D_{calc} = 1.76$ g cm^{-3} for $Z = 4$. Tetrahydrate complexes of the form $[MCl(OH_2)_2(18\text{-crown-6})]Cl_2 \cdot 2H_2O$ are isolated for $M = Pr\text{--}Tb$, which crystallize in the acentric space group $P2_12_12_1$. The two new complexes reported here are $M = Pr$ (18 °C), $a = 7.470(2)$ Å, $b = 16.063(6)$ Å, $c = 19.022(8)$ Å, and $D_{calc} = 1.70$ g cm^{-3} for $Z = 4$, and $M = Eu$ (20 °C), $a = 7.406(6)$ Å, $b = 15.906(5)$ Å, $c = 18.891(9)$ Å, and $D_{calc} = 1.78$ g cm^{-3} for $Z = 4$. The EO5 complexes and the 18-crown-6 complexes are all 9-coordinate tricapped trigonal prismatic, with alternating oxygen donors as capping atoms. The addition of LiCl as a salting out agent to the reaction of $GdCl_3 \cdot 6H_2O$ with 18-crown-6 resulted in the isolation of $[GdCl_6][GdCl_x(OH_2)_y(18\text{-crown-6})]_2 \cdot 2OHMe$ ($x = 1, y = 2; x = 2, y = 1$). This complex crystallizes in the centric space group $P\bar{1}$, with (−150 °C) $a = 9.016(2)$ Å, $b = 9.034(3)$ Å, $c = 14.812(5)$ Å, $\alpha = 76.81(3)^\circ$, $\beta = 83.43(3)^\circ$, $\gamma = 83.15(3)^\circ$, and $D_{calc} = 2.06$ g cm^{-3} for $Z = 1$. The $[GdCl_x(OH_2)_y(18\text{-crown-6})]^{n+}$ cations are also 9-coordinate tricapped trigonal prismatic. Comparison of all the crystalline complexes studied reveals that polyethylene glycols exhibit a helical wrapping pattern around the lanthanide ions, while the crown ethers attempt to fold around these cations. This feature of polyether complexation of the lanthanide(III) chlorides may be responsible for the ready isolation of EO5 complexes for all lanthanides and the lack of direct coordination of 18-crown-6 past $M = Tb$ in normal 1:1 complexation reactions.

Introduction

Cation size/cavity size arguments are often used in crown ether chemistry to explain selectivity in the extraction of group 1 or 2 metal ions.¹ These arguments are also utilized to explain the crown ether extraction of lanthanide ions or even actinides.² Our structural research has shown, however, that crown ethers do not

always interact with the lanthanides in a fashion similar to other hard ions such as the alkali metals and alkaline earths. Structures of 18-crown-6 complexes of Nd ,³ Sm ,⁴ Gd ,⁴ Tb ,⁴ Dy ,⁵ and Y ⁵

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reveal a folding of 18-crown-6 to occupy as much of the primary coordination sphere as possible rather than the normal D_{3d} crown conformation observed in the majority of 18-crown-6 complexes.

Earlier results from our laboratories have shown the smaller crown ethers 12-crown-4⁶ and 15-crown-5^{3,7} to coordinate to lanthanides in an out-of-cavity fashion similar to that found for group 1 and 2 cations.⁸⁻¹¹ (We have investigated chloride salts to reduce the effects of donor anions on the primary coordination sphere.) By removing the condition of being cyclic (i.e., utilizing polyethylene glycols (PEGs)), we have observed helical wrapping of the lanthanides in most instances for triethylene glycol (EO3)¹² and tetraethylene glycol (EO4).¹³ The PEG complexes reveal total steric control of the primary coordination sphere.

We decided to reevaluate the 18-crown-6 lanthanide interaction by filling the holes with complexes not previously studied, trying to force inner-sphere coordination of 18-crown-6 with the smallest lanthanide possible, and determining the crystal structures of the entire series of the six donor pentaethylene glycol (EO5) lanthanide complexes. The results, reported here, reveal remarkable similarities in EO5 vs 18-crown-6 complexation not observed in EO3 vs 12-crown-4 or EO4 vs 15-crown-5 comparisons. The similarities are related to the larger, more flexible cavity in 18-crown-6 vs 12-crown-4 or 15-crown-5, while the differences are a direct result of the cyclic and thus less flexible nature of 18-crown-6 vs EO5.

Results

$[MCl_2(OH_2)(EO5)]Cl \cdot H_2O$ ($M = La-Pr$). The larger, lighter lanthanides and La crystallize as dihydrates with one water molecule and two chloride ions within the 9-coordinate metal coordination sphere and one chloride ion and one water molecule per formula unit in the hydrogen-bonded secondary coordination sphere. The $M = La$ complex is presented in Figure 1, and average bonding parameters are given in Table I. The crystal structure of the isostructural $M = Nd$ complex has been previously reported.³

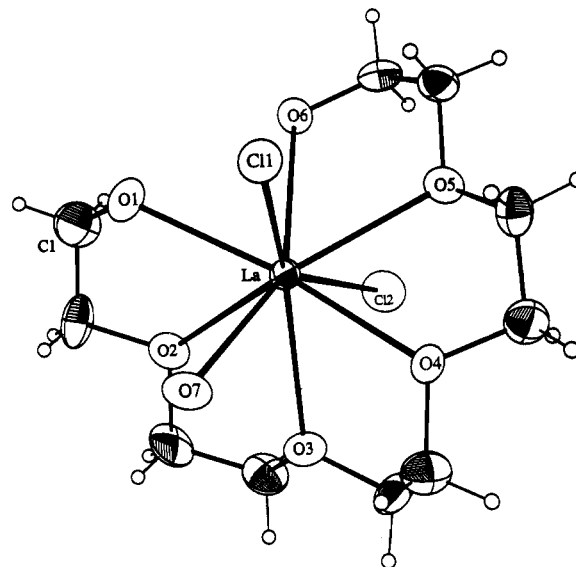


Figure 1. ORTEP illustration of the cation in $[LaCl_2(OH_2)(EO5)]Cl \cdot H_2O$ with 50% probability ellipsoids. Hydrogen atoms have been arbitrarily reduced.

As we have observed in the majority of our crystallographic studies of lanthanide chloride polyethylene glycol complexes, these lanthanide ions are 9-coordinate, tricapped trigonal prismatic with the PEG ligand wrapping the metal in a helical fashion and alternating between capping and prismatic sites. (The alcoholic O(1) and etheric O(3) and O(5) are in the capping positions.) The overall coordination environment of each lanthanide ion is similar to that found for the 18-crown-6 complexes of the early lanthanide chlorides previously reported³⁻⁵ and discussed below.

In 18-crown-6 complexes with the normal D_{3d} conformation, the O-C-C-O torsion angles alternate $\pm 60^\circ$ (\pm gauche) and all of the C-O-C-C torsion angles are 180° (anti). The EO5 conformation we observe in this series of complexes is similar except between O(3) and O(5). The O-C-C-O torsion angles are $g^- g^+ g^- g^- g^+$ (Table II). Between the O(3)-C(5)-C(6)-O(4) torsion angle (g^-) and the O(4)-C(7)-C(8)-O(5) torsion angle (g^-) we find one non-anti angle (C(5)-C(6)-O(4)-C(7)) which approaches a gauche conformation (-106° , $M = La$). The observation of C-O-C-C angles forced toward a gauche conformation between O-C-C-O angles of like sign is common in complexes of the flexible PEGs.^{3,12,13}

The hydrogen bonding environment is typically important for structures of PEG complexes. In this series a three-dimensional polymeric network of hydrogen bonding is formed. The alcoholic O(1) donates a hydrogen bond to the uncoordinated water molecule (O(8)), which in turn donates two hydrogen bonds to the uncoordinated Cl(3) and to the coordinated Cl(2) in a symmetry-related site. The other alcoholic site (O(6)) also donates one hydrogen bond to Cl(3). The coordinated water molecule O(7) donates one hydrogen bond to a symmetry-related Cl(3) (giving Cl(3) a total of three acceptor interactions) and one hydrogen bond to a second symmetry-related Cl(2) site. The two hydrogen bonds accepted by Cl(2) result in a significant lengthening of the M-Cl(2) separation versus M-Cl(1).

$[M(OH_2)_3(EO5)]Cl_3 \cdot H_2O$ ($M = Y, Sm-Lu$). The mid- to late-lanthanide chloride complexes crystallize as tetrahydrates with three water molecules and no chloride ions in the primary coordination sphere. The samarium complex is presented in Figure 2. The 9-coordinate geometries are again tricapped trigonal prismatic, and the EO5 ligand wraps in a similar fashion alternating between capping (O(1), O(3), O(5)) and prismatic sites. While this is the same general structure and helical wrapping observed in the early-lanthanide series, the PEG conformation is different. There are two sets of consecutive O-C-C-O torsion angles of like sign (the sequence is $g^- g^- g^+ g^+ g^-$), and

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Table I. Comparison of Bonding Parameters

M	CN	IR, ^a Å	G ^b	M-Cl(av), Å		M-O(av, alcoholic), Å		M-O(av, etheric), Å		M-OH ₂ (av), Å	ref
				prismatic	M-ONO ₂ (av), Å	capping	prismatic	capping	prismatic		
[MCl ₂ (OH ₂)(EO5)]Cl·H ₂ O											
La	9	1.216	tctp	2.789(2) 2.893(2) ^c		2.563(6)	2.572(6)	2.604(1)	2.61(2)	2.598(5)	<i>d</i>
Ce	9	1.196	tctp	2.7763(9) 2.871(1) ^c		2.549(3)	2.539(2)	2.588(1)	2.60(3)	2.557(3)	<i>d</i>
Pr	9	1.179	tctp	2.761(1) 2.853(1) ^c		2.535(4)	2.529(4)	2.571(6)	2.58(3)	2.548(4)	<i>d</i>
Nd	9	1.163	tctp	2.749(2) 2.841(2) ^c		2.516(5)	2.504(5)	2.556(4)	2.57(3)	2.528(5)	3
[M(OH ₂) ₃ (EO5)]Cl ₃ ·H ₂ O											
Sm	9	1.132	tctp			2.44(1)	2.46(1)	2.50(1)	2.51(2)	2.43(2)	<i>d</i>
Eu	9	1.120	tctp			2.447(6)	2.421(6)	2.486(2)	2.52(2)	2.43(1)	<i>d</i>
Gd	9	1.107	tctp			2.45(1)	2.39(1)	2.47(1)	2.48(2)	2.43(2)	<i>d</i>
Tb	9	1.095	tctp			2.421(6)	2.405(6)	2.480(9)	2.48(2)	2.40(2)	<i>d</i>
Dy	9	1.083	tctp			2.414(5)	2.385(5)	2.47(1)	2.47(2)	2.38(1)	<i>d</i>
Y	9	1.075	tctp			2.409(5)	2.381(5)	2.453(1)	2.46(1)	2.38(2)	<i>d</i>
Ho	9	1.072	tctp			2.407(4)	2.383(4)	2.460(2)	2.45(2)	2.37(2)	<i>d</i>
Er	9	1.062	tctp			2.386(6)	2.357(6)	2.432(8)	2.44(1)	2.35(2)	<i>d</i>
Tm	9	1.052	tctp			2.375(8)	2.365(8)	2.447(6)	2.436(1)	2.34(2)	<i>d</i>
Yb	9	1.042	tctp			2.381(5)	2.347(6)	2.440(1)	2.44(2)	2.34(1)	<i>d</i>
Lu	9	1.032	tctp			2.38(1)	2.32(1)	2.442(2)	2.43(1)	2.34(2)	<i>d</i>
[LaCl ₃ (18-crown-6)]											
La	9	1.216	tctp	2.822(7)				2.667(7)	2.65(3)		<i>d</i>
[LaCl ₂ (OH ₂)(18-crown-6)]Cl											
La	9	1.216	tctp	2.80(2)				2.66(4)	2.65(6)	2.51(1)	<i>d</i>
[LaCl ₂ (Y)(18-crown-6)]Cl·1.5H ₂ O (Y = OH ₂ , OHMe)											
La	9	1.216	tctp	2.817(2)				2.63(4)	2.635(4)	2.52(1)	<i>d</i>
[CeCl ₂ (OH ₂)(18-crown-6)]Cl·2H ₂ O											
Ce	9	1.196	tctp	2.789(2)				2.60(3)	2.62(2)	2.482(5)	<i>d</i>
[MCl(OH ₂) ₂ (18-crown-6)]Cl ₂ ·2H ₂ O											
Pr	9	1.179	tctp	2.722(5)				2.600(8)	2.59(3)	2.50(1)	<i>d</i>
Nd	9	1.163	tctp	2.706(4)				2.58(1)	2.58(2)	2.48(2)	3
Sm	9	1.132	tctp	2.678(3)				2.549(7)	2.54(3)	2.45(2)	4
Eu	9	1.120	tctp	2.673(4)				2.56(2)	2.53(4)	2.43(2)	<i>d</i>
Gd	9	1.107	tctp	2.663(3)				2.535(8)	2.52(4)	2.41(2)	4
Tb	9	1.095	tctp	2.69(1)				2.53(4)	2.53(5)	2.36(2)	4
[GdCl ₆][GdCl _x (OH ₂) _y (18-crown-6)] ₂ ·2OHMe (x = 1, y = 2; x = 2, y = 1)											
Gd ^e	9	1.107		2.700(4) ^f 2.753(9) ^{f,h}				2.53(1)	2.57(2)	2.38(1) ^a 2.18(2) ^h	<i>d</i>
[M(OH ₂) ₇ (OHMe)][MCl(OH ₂) ₂ (18-crown-6)] ₂ Cl ₇ ·2H ₂ O											
Dy ^e	9	1.083	tctp	2.654(2)				2.477(5)	2.44(6)	2.39(3)	5
Y ^e	9	1.075	tctp	2.647(2)				2.46(1)	2.42(6)	2.36(2)	5
[GdCl ₂ (OHEt)(18-crown-6)]Cl											
Gd	9	1.107	tctp	2.695(3) (capping) 2.734(3)				2.51(2)	2.56(4)	2.414(6) (OHEt)	15
[LaCl ₂ (NO ₃)(18-crown-6)]											
La	10	1.27		2.866(5) 2.788(5)	2.60(3) ⁱ			2.68(4) ⁱ			16
[Nd(NO ₃) ₂ (EO5)][NO ₃]											
Nd	10	1.22 ^j			2.52(3) ⁱ		2.485(5) ⁱ	2.59(3) ⁱ			17
[Nd(NO ₃) ₂ (EG5)] ₃ [Nd(NO ₃) ₆] ^{k,i}											
Nd	10	1.22 ^j			2.53(7) ^{i,m}			2.6(1) ⁱ (C ₂) 2.6(2) ⁱ (C ₁)			18
[M(NO ₃) ₃ (18-crown-6)]											
La	12	1.36			2.66(1) ⁱ			2.72(6) ⁱ			19
Ce	12	1.34			2.64(2) ⁱ			2.72(6) ⁱ			20
Pr	12				2.62(2) ⁱ			2.71(6) ⁱ			16
Nd	12	1.27			2.59(1) ⁱ 2.60(1) ⁱ			2.68(7) ⁱ 2.70(7) ⁱ			21 22
[M(NO ₃) ₂ (18-crown-6)] ₃ [M(NO ₃) ₆] ^k											
Nd	10	1.22 ^j			2.42(2) ^{i,m} (C _{2h}) 2.53(3) ^{i,m} (C ₁)			2.58(2) ⁱ (C _{2h}) 2.62(6) ⁱ (C ₁)			23
Gd	10	1.16 ^j			2.45(1) ^{i,m} (C _{2h}) 2.47(2) ^{i,m} (C ₁)			2.61(2) ⁱ (C _{2h}) 2.49(2) ⁱ (C ₁)			24
[Ca(SCN) ₂ (EG5)]											
Ca	8	1.12 ⁿ						2.534(3) ⁱ	2.48(2) ⁱ		25

Table I (Continued)

M	CN	IR, ^a Å	G ^b	M-Cl(av), Å		M-O(av, alcoholic), Å		M-O(av, etheric), Å		M-OH ₂ (av), Å	ref
				prismatic	M-ONO ₂ (av), Å	capping	prismatic	capping	prismatic		
[M(SCN) ₂ (OH) ₂ (EG5)]											
Sr	9	1.31 ^a				2.68(2) ⁱ		2.76(4) ⁱ		2.614(7) ⁱ	25
Ba	9	1.47 ^a				2.85(5) ⁱ		2.85(1) ⁱ		2.785(5) ⁱ	25
[ThCl ₃ (EO5)]Cl·CH ₃ CN											
Th	9	1.09 ^a	tctp	2.73(2)		2.51(1)	2.476(9)	2.55(3)	2.60(3)		26

^a Ionic radius for Ln³⁺ and coordination number shown from ref 14. ^b Geometry: tctp = tricapped trigonal prismatic. ^c The Cl(2) position accepts two hydrogen bonds. ^d This study. ^e Structural study carried out at -150 °C. ^f Does not include distances in [GdCl₆]³⁻. ^g O(7) is capping. ^h O(8) is disordered with Cl(2). ⁱ The averages of all M-O(alcoholic), M-O(etheric), or M-ONO₂ distances are given without subdivision by geometric site. ^j Extrapolated from data in ref 14. ^k This structure contains one severely disordered cation. ^l EG5 = pentaglyme. ^m This does not include M-O(nitrate) distances in the [M(NO₃)₆]³⁻ anion. ⁿ M²⁺. ^o Th⁴⁺.

Table II. Torsion Angle Values for EO5 and 18-Crown-6 Complexes

torsion angle label	[MCl ₂ (OH) ₂ -(EO5)]Cl·H ₂ O (M = La) C ₂ (A) ^{a,b}	[M(OH) ₂ -(EO5)]Cl ₃ ·H ₂ O (M = Sm) C ₂ ^{a,c}	[LaCl ₃ -(18-crown-6)] C ₂ (A) ^a	[MCl ₂ (OH) ₂ -(18-crown-6)]-Cl·2H ₂ O (M = Ce) C ₂ (A) ^{a,d}	[MCl(OH) ₂ -(18-crown-6)]Cl ₂ ·2H ₂ O (M = Pr) C ₂ (A) ^{a,e}	C ₂ ^{a,f}	[M(OH) ₂ -(OHMe)]-[MCl(OH) ₂ -(18-crown-6)] ₂ Cl ₇ ·2H ₂ O (M = Dy) C ₂ ^a	[GdCl ₆]-[GdCl _x (OH) ₂ -(18-crown-6)] _y ·2OHMe (x = 1, y = 1) C ₂ (A) ^a
	O(1)-C(1)-C(2)-O(2)	-53.8	-54.5	58.3 ^g	-57.5	34.0	22.2	51.0
C(1)-C(2)-O(2)-C(3)	179.5	-172.7	171.1	-169.1	153.4	-166.0	104.6	166.1
C(2)-O(2)-C(3)-C(4)	-175.9	-105.7	-177.4	158.7	110.7	-169.9	178.5	-145.6
O(2)-C(3)-C(4)-O(3)	55.7	-53.2	-57.5	56.3	57.6	-36.1	55.0	-55.4
C(3)-C(4)-O(3)-C(5)	164.8	-161.7	-163.4	-179.7	165.2	-163.4	169.3	-179.2
C(4)-O(3)-C(5)-C(6)	-171.1	169.7	170.7	-168.1	-166.3	-149.6	-178.7	176.1
O(3)-C(5)-C(6)-O(4)	-56.7	51.4	57.3	-59.4	-44.1	-37.1	-50.8	56.6
C(5)-C(6)-O(4)-C(7)	-106.0	170.7	94.5	-178.0	-175.8	-179.4	-141.7	176.2
C(6)-O(4)-C(7)-C(8)	-176.3	95.6	174.6	-94.2	-110.7	-92.5	143.3	86.7
O(4)-C(7)-C(8)-O(5)	-54.6	53.7	57.2	-56.9	-56.1	-56.1	53.5	53.9
C(7)-C(8)-O(5)-C(9)	-170.7	168.6	169.9	-166.9	-177.4	-177.4	178.8	169.9
C(8)-O(5)-C(9)-C(10)	172.8	-176.9	-175.2	163.3	163.9	163.9	-171.3	-154.4
O(5)-C(9)-C(10)-O(6)	58.3	-52.1	-58.1	54.6	51.8	51.8	-53.8	-53.4
C(9)-C(10)-O(6)-C(11)			-160.2	-179.1	170.7	170.7	-176.9	-177.2
C(10)-O(6)-C(11)-C(12)			168.7	-170.5	140.6	140.6	-111.6	174.3
O(6)-C(11)-C(12)-O(1)			58.5	-54.5	48.8	48.8	-50.4	58.1
C(11)-C(12)-O(1)-C(1)			91.0	-178.3	112.0	86.2	-97.5	176.0
C(12)-O(1)-C(1)-C(2)			177.5	-96.3	179.4	-173.0	99.2	80.7

^a Conformation of EO5 or 18-crown-6. ^b Although EO5 is acyclic, the torsion angles listed match those observed for 18-crown-6 in C₂(A) conformations, such as in [CeCl₂(OH)₂(18-crown-6)]Cl·2H₂O. ^c The torsion angles listed match those observed for 18-crown-6 in other pseudo C₂ conformations, such as in [MCl(OH)₂(18-crown-6)]Cl₂·2H₂O (M = Pr-Tb). The torsion angle values differ in sign, but this conformation is related by a center of symmetry to that observed in [PrCl(OH)₂(18-crown-6)]Cl₂·2H₂O. ^d The torsion angle values differ in sign from [LaCl₃(18-crown-6)], but this conformation is related by a center of symmetry. ^e Pseudo C₂(A) conformation. ^f Pseudo C₂ conformation. The values in this column reflect the torsion angles associated with C(1)', C(2)', C(3)', C(4)', C(5)', and C(6)'. ^g To match the torsion angle sequence given for [CeCl₂(OH)₂(18-crown-6)]Cl·2H₂O, these values are given starting with O(6)-C(11)-C(12)-O(1) and ending with C(10)-O(6)-C(11)-C(12).

consequently two C-O-C-C torsion angles are forced toward gauche. One of these is found between each set of consecutive O-C-C-O torsion angles of like sign (C(2)-O(2)-C(3)-C(4) = -105.7°, M = Sm; C(6)-O(4)-C(7)-C(8) = 95.6°, M = Sm).

The hydrogen bonding environment of these complexes is much more extensive than in the early-lanthanide complexes and again results in a three-dimensional network of interactions. The two alcoholic oxygen atoms and two of the water molecules donate exclusively to chloride anions. One water molecule donates a hydrogen bond to a chloride anion and one to the uncoordinated water molecule O(10). O(10) donates to chloride anions. Each chloride anion accepts three hydrogen bonds.

[LaCl₂(Y)(18-crown-6)]Cl·1.5H₂O (Y = OH₂, OHMe) and [CeCl₂(OH)₂(18-crown-6)]Cl·2H₂O. The cerium and lanthanum complexes are virtually isostructural with the exception of the half-weighted solvent methyl group and consequently half-weighted water molecule in the secondary coordination sphere found for the La complex. In fact the coordinates for the Ce complex were used as a starting point in the refinement of the La analog. It is important to note that the volume for the La complex is smaller than found for Ce despite lanthanum's larger size. This is further evidence of the lower hydration of the La complex.

An ORTEP illustration of the [CeCl₂(OH)₂(18-crown-6)]⁺ cation is given in Figure 3. The six crown ether oxygen atoms, two chloride anions, and one water molecule form a tricapped trigonal prismatic geometry, with alternating oxygen atoms O(1), O(3), and O(5), in capping positions. Cl(1) is coordinated to Ce on one side of the crown ether, while Cl(2) and O(7) are coordinated on the other side. This cation is nearly identical to the [MCl(OH)₂(18-crown-6)]²⁺ cation found for M = Pr-Dy and Y. Apparently the larger sizes of La³⁺ and Ce³⁺ permit the inclusion of a second larger chloride anion in the primary coordination sphere.

The crown adopts a C₂ conformation which is characterized by O-C-C-O torsion angles, having values of g- g+ g- g+ g-. As observed in the PEG complexes, one of the C-O-C-C torsion angles between two consecutive O-C-C-O torsion angles of like sign is forced gauche. These two torsion angles (C(6)-O(4)-C(7)-C(8), C(12)-O(1)-C(1)-C(2)) average -95° for M = Ce.

The crown ether wraps toward Cl(1) (the side with only one additional coordination site) for steric reasons, leaving the other side of the macrocycle open to accommodate coordination of Cl(2) and O(7) directly to La or Ce. Following the conventions defined by Fyles and Gandour,²⁷ the conformation of the crown

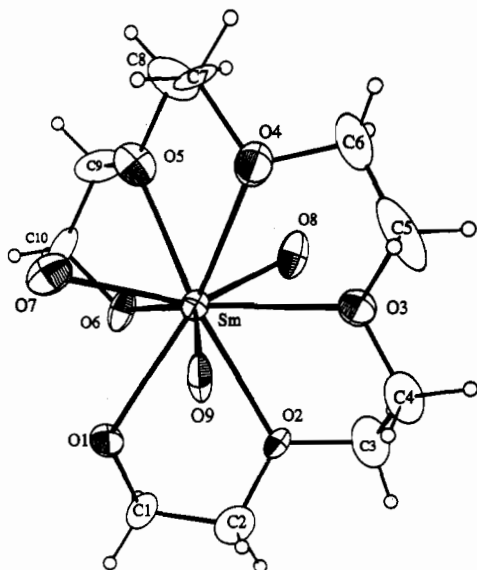


Figure 2. Cation in $[\text{Sm}(\text{OH}_2)_3(\text{EO}_5)]\text{Cl}_3 \cdot \text{H}_2\text{O}$.

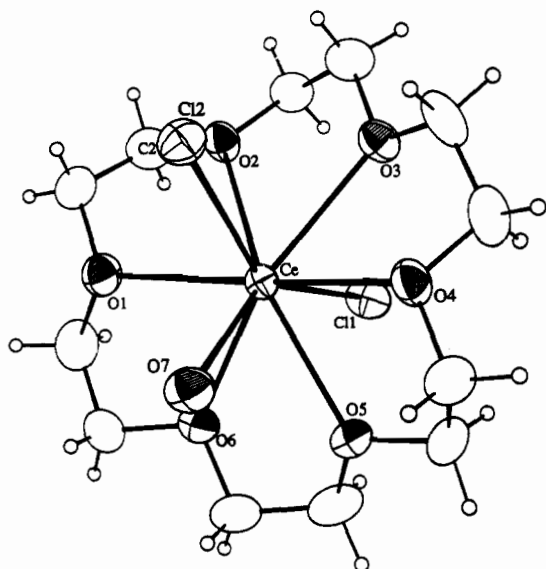


Figure 3. Cation in $[\text{CeCl}_2(\text{OH}_2)(18\text{-crown-6})]\text{Cl} \cdot 2\text{H}_2\text{O}$.

ether is $C_2(A)$, indicating the point group of the crown ether and the axial location of the C_2 rotation axis. Since the space group is centrosymmetric, both conformations of the crown ether complex exist simultaneously due to the center of symmetry in the crystal lattice. We are therefore reporting the conformation of the macrocycle in terms of its point group and rotation axis location, ignoring the sign of the $\text{O}-\text{C}-\text{C}-\text{O}$ torsion angles in this case and all similar cases to follow.

In the Ce complex, the coordinated water molecule O(7) participates in hydrogen bonding with Cl(3), O(8), and O(9). O(7) donates one hydrogen bond to the uncoordinated chloride anion (Cl(3)) and one to the uncoordinated water molecule O(9). O(9) donates to a symmetry-related Cl(3) site and to water molecule O(8). O(8) donates exclusively to Cl(3) anions. Thus, Cl(3) accepts four hydrogen bonds, while O(8) and O(9) each donate two and accept one. The hydrogen bonding forms parallel offset chains of hydrogen-bonded pairs, parallel to a .

In the La complex, the hydrogen bonding is essentially the same except that the methyl group (C(13)) is oriented in the direction of O(9). Thus, in those cations containing OHMe, O(9) is not hydrogen bonded to the cation and is absent from that

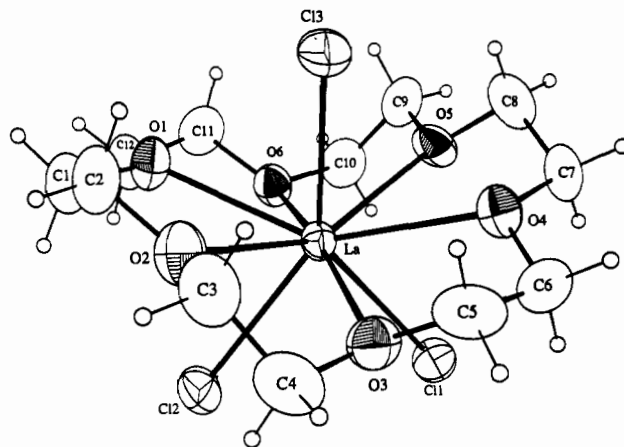


Figure 4. $[\text{LaCl}_3(18\text{-crown-6})]$.

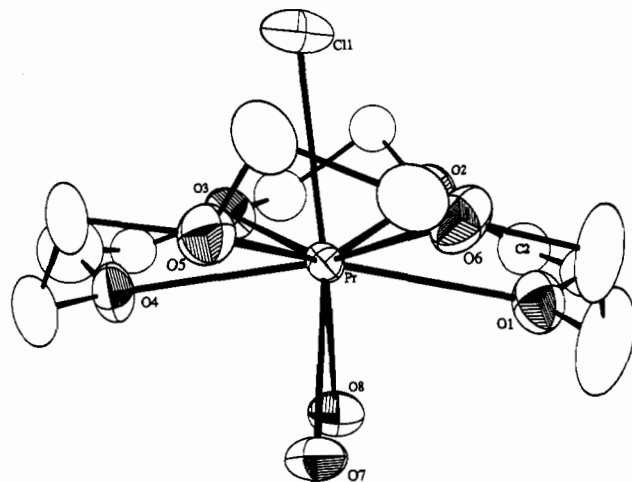


Figure 5. Cation in $[\text{PrCl}(\text{OH}_2)_2(18\text{-crown-6})]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ with the crown conformation containing C(1)–C(6).

crystallographic position. In those cations where O(7) is a water molecule, O(9) is present to accept a hydrogen bond from it.

$[\text{LaCl}_2(\text{OH}_2)(18\text{-crown-6})]\text{Cl}$. This monohydrate crystallizes without the outer-sphere H_2O molecules but with essentially the same $[\text{MCl}_2(\text{OH}_2)(18\text{-crown-6})]^+$ cation found in $[\text{CeCl}_2(\text{OH}_2)(18\text{-crown-6})]\text{Cl} \cdot 2\text{H}_2\text{O}$. Lanthanum is 9-coordinate tricapped trigonal prismatic with three crown ether oxygen atoms in capping positions (O(2), O(4), O(6)).

As observed for the Ce complex, the crown ether adopts a $C_2(A)$ conformation. Both hydrogen bonds are to symmetry-related uncoordinated chloride anions (Cl(3)), resulting in hydrogen-bonded dimers of the formula unit.

$[\text{LaCl}_3(18\text{-crown-6})]$. This completely anhydrous complex was isolated by crystallization at 70°C . An ORTEP illustration of the neutral complex (Figure 4) reveals the same 9-coordinate geometry and general structural features as observed for all of the lanthanide 18-crown-6 complexes. The crown ether folds around the La^{3+} ion occupying three capping sites (O(2), O(4), O(6)) in the tricapped trigonal prismatic geometry and leaving three open coordination sites all occupied by chloride anions. The crown ether adopts the $C_2(A)$ conformation.

$[\text{MCl}(\text{OH}_2)_2(18\text{-crown-6})]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ ($\text{M} = \text{Pr}, \text{Eu}$). These complexes are isostructural with the previously published $\text{M} = \text{Nd},^3 \text{Sm},^4 \text{Gd},^4$ and Tb^4 complexes. An ORTEP illustration of the $[\text{PrCl}(\text{OH}_2)_2(18\text{-crown-6})]^{2+}$ cation is given in Figure 5. The metal center is directly coordinated by the six crown ether oxygens, two water molecules, and only one chloride ion, resulting in a tricapped trigonal prismatic geometry. Cl(1) is coordinated to the metal center on one side of the crown ether, while O(7) and O(8) are coordinated on the other side. The decreasing size of

(27) Fyles, T. M.; Gandour, R. D. *J. Inclusion Phenom. Mol. Recognit. Chem.* 1992, 12, 313.

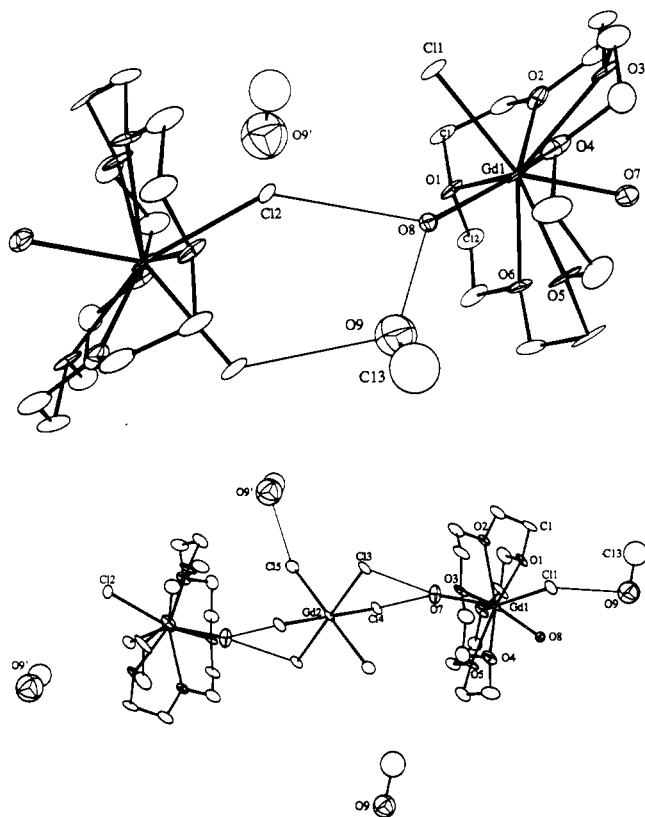


Figure 6. $[\text{GdCl}_6][\text{GdCl}_2(\text{OH}_2)(18\text{-crown-6})][\text{GdCl}(\text{OH}_2)_2(18\text{-crown-6})]\cdot 2\text{OHMe}$. (A) Top: Disordered cations hydrogen bonded across a center of inversion. (B) Bottom: Hydrogen bonding environment of the anion.

the metal centers (from Ce to Pr) results in the replacement of one of the chloride anions in the primary coordination sphere by a water molecule. As in the Ce/18-crown-6 complex, alternating oxygen donors (O(1), O(3), O(5)) are capping atoms.

The crown ether must distort further in order to coordinate to the metal center for these smaller lanthanides. Additionally, three of the ethylene units are disordered (\pm gauche). In one orientation, the macrocycle adopts a pseudo- C_3 conformation, with the pseudo-mirror plane parallel to the plane defined by O(1), O(4), and the metal center. In the other disorder model, the macrocycle adopts a pseudo- $C_2(A)$ conformation.

The hydrogen bonding forms sheets parallel to *ac*. O(7) and O(8) form hydrogen bonds with Cl(2), Cl(3), and O(9). Cl(3) and O(9) in turn form hydrogen bonds with each other and O(10). Cl(2) accepts two hydrogen bonds, Cl(3) accepts four, and O(9) and O(10) each accept one and donate two.

$[\text{GdCl}_6][\text{GdCl}_x(\text{OH}_2)_y(18\text{-crown-6})]_2\cdot 2\text{OHMe}$ ($x = 2, y = 1; x = 1, y = 2$). Additional chloride anions can be forced into the primary coordination sphere by the addition of LiCl as a salting out agent.^{3,13} A 2-fold molar excess of LiCl added to the reaction of $\text{GdCl}_3\cdot 6\text{H}_2\text{O}$ with 18-crown-6 produced very deliquescent crystals of a new Gd complex.

An ORTEP illustration of this complex is given in Figure 6. It crystallizes with a $[\text{GdCl}_6]^{3-}$ anion and two 18-crown-6 complexed cations, a dichloride monocation similar to the La and Ce complexes, and a monochloride dication similar to the Pr–Eu complexes. The chloride ions form a distorted octahedron around Gd(2) in the $[\text{GdCl}_6]^{3-}$ anion. The anion resides on an inversion center, with three unique chloride positions. Cl(3) and Cl(4) accept hydrogen bonds from the full occupancy water molecule (O(7)) coordinated to Gd(1) in the cations, while Cl(5) accepts a hydrogen bond from only one orientation of the disordered methanol molecule in the crystal lattice. The chloride anions which accept a full occupancy hydrogen bond exhibit M–Cl distances which average 2.682(2) Å. The M–Cl distance for the

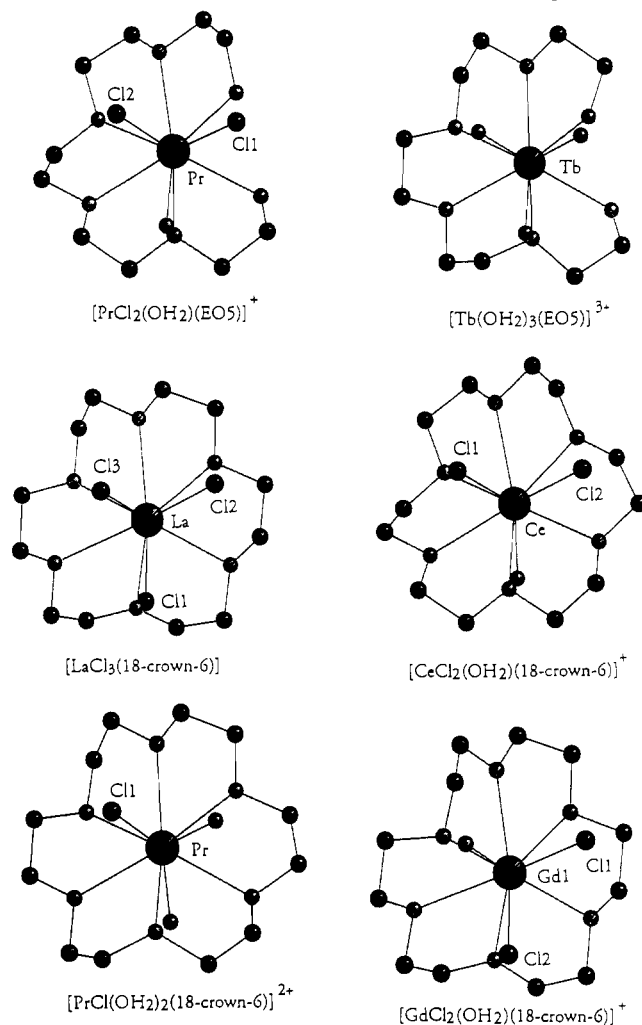


Figure 7. Ball and stick diagrams of representative members from each structurally characterized series.

chloride anion which accepts a hydrogen bond in only one of the methanol disorder models (Cl(5)) is shorter at 2.666(4) Å. This results in a slight expansion of the center of the octahedron around the Gd center.

The two Gd/crown ether cations differ in a disordered coordination site containing either a chloride ion (Cl(2)) or a water molecule (O(8)). Gd(1) is thus coordinated by the six crown ether oxygen atoms in both cases, by two chloride ions and a water molecule in one model and by a chloride and two water molecules in the second model. In both models, one water molecule (O(7)) coordinates to the Gd center on one side of the crown ether, while either the two chlorides or one chloride and one water molecule coordinate to the Gd center on the other side of the crown ether. Gd(1) in each cation is tricapped trigonal prismatic with only two crown ether oxygens (O(1) and O(4)) and one coordinated water molecule (O(7)) occupying the capping sites. The placement of O(7) in a capping position may be due to the relative bulk of the $[\text{GdCl}_6]^{3-}$ anion to which it is hydrogen bonded. In all of the other complexes the water molecules occupy prismatic sites but were hydrogen bonded to relatively small chloride anions or water molecules. (It should be noted that it is possible to describe a slightly more distorted tricapped trigonal prismatic geometry for this complex with etheric oxygen atoms O(1), O(3), and O(5) in the capping positions. This description would then be similar to those for the other structural studies of this type.)

The crown ether molecule again folds around the metal center in this complex. The O–C–O torsion angles are $g+g-g+g+g-g+g+$. As in other crown ether complexes, when two consecutive O–C–O torsion angles are of like sign, one of the C–O–C–

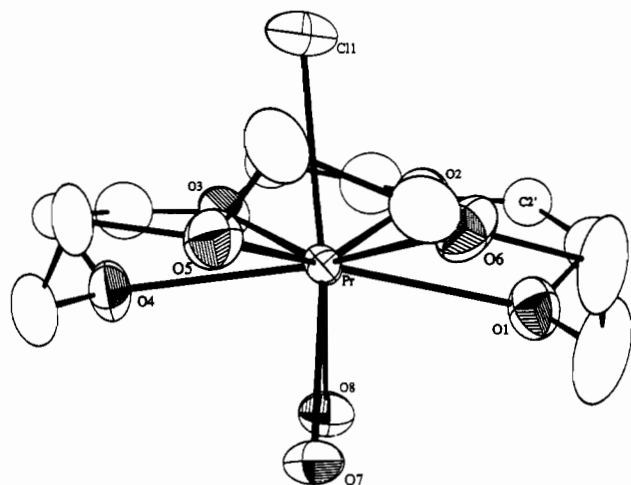


Figure 8. Cation in $[\text{PrCl}(\text{OH}_2)_2(18\text{-crown-6})]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ with the crown conformation containing $\text{C}(1)'\text{-C}(6)'$.

torsion angles between them is forced gauche, in this case these two torsion angles ($\text{C}(6)\text{-O}(4)\text{-C}(7)\text{-C}(8)$, $\text{C}(12)\text{-O}(1)\text{-C}(1)\text{-C}(2)$) average 84° . The crown conformation is $\text{C}_2(\text{A})$ as observed for $[\text{LaCl}_2(\text{Y})(18\text{-crown-6})]\text{Cl} \cdot 1.5\text{H}_2\text{O}$ ($\text{Y} = \text{OH}_2, \text{OHMe}$), $[\text{LaCl}_2(\text{OH}_2)(18\text{-crown-6})]\text{Cl}$, $[\text{LaCl}_3(18\text{-crown-6})]$, and $[\text{CeCl}_2(\text{OH}_2)(18\text{-crown-6})]\text{Cl} \cdot 2\text{H}_2\text{O}$ rather than the conformation found for $[\text{GdCl}(\text{OH}_2)_2(18\text{-crown-6})]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$.

Hydrogen bonding plays an important role in the crystallization of this complex as in the other complexes. The complex forms offset hydrogen-bonded chains throughout the crystal lattice parallel to the bc plane, where the complex ions crystallize in the following relative order: $[\text{GdCl}_2(\text{OH}_2)(18\text{-crown-6})]^+$, $[\text{GdCl}_6]^{3-}$, $[\text{GdCl}(\text{OH}_2)_2(18\text{-crown-6})]^{2+}$. The cationic crown ether complexes are oriented so that O(7) is directly toward a $[\text{GdCl}_6]^{3-}$ anion, allowing Cl(3) and Cl(4) in $[\text{GdCl}_6]^{3-}$ to accept hydrogen bonds from O(7) in the nearest $[\text{GdCl}_x(\text{OH}_2)_y(18\text{-crown-6})]^{n+}$ cation (Figure 6B). Cl(2) in the $[\text{GdCl}_2(\text{OH}_2)(18\text{-crown-6})]^+$ cation accepts a hydrogen bond from O(8) in the next $[\text{GdCl}(\text{OH}_2)_2(18\text{-crown-6})]^{2+}$ cation (Figure 6A). The disordered methanol molecule forms hydrogen bonds with Cl(1), Cl(5), and O(8). In the first disorder model the methanol molecule accepts a hydrogen bond from O(8) on one $[\text{GdCl}(\text{OH}_2)_2(18\text{-crown-6})]^{2+}$ cation and donates a hydrogen bond to Cl(1) on a $[\text{GdCl}_2(\text{OH}_2)(18\text{-crown-6})]^+$ cation related by a center of symmetry. In the second model, where it resides near the $[\text{GdCl}_6]^{3-}$ anion, the methanol molecule donates a hydrogen bond to Cl(5).

Discussion

There is a remarkable similarity in overall structure for the complexes of both EO5 and 18-crown-6 with early- to mid-lanthanide chlorides. Every complex prepared by simple complexation of the ligand and $\text{MCl}_3 \cdot n\text{H}_2\text{O}$ in a 1:1 ratio produces a 9-coordinate complex in which alternating oxygen donor atoms of the ligand occupy the capping positions (Figure 7). In the EO5 complexes of La–Nd, two of the 18-crown-6 complexes of La, and the Ce/18-crown-6 complex, the three remaining sites are occupied by two chloride anions and one water molecule. Even the relative positions of the coordination sites for these three moieties are the same.

The larger size of La^{3+} allows three chloride ions in the primary coordination sphere with 18-crown-6 as observed in $[\text{LaCl}_3(18\text{-crown-6})]$. This appears, however, to be at the limit of acceptability, and competition in solution results in the isolation of two additional forms of the La complex. Both of these latter species have only two chloride ions and one water or solvent molecule completing the primary coordination sphere.

The steric crowding produced as the size of the lanthanide decreases is manifested by the 18-crown-6 complexes at $\text{M} = \text{Pr}$

in which a chloride anion is replaced by a water molecule. This general cation $[\text{MCl}(\text{OH}_2)_2(18\text{-crown-6})]^{2+}$ is then observed from Pr to Tb. We were only partially successful in trying to force the smaller lanthanide, Gd^{3+} , to accommodate two chloride ions in the inner coordination sphere by adding a large excess of LiCl.

Past Tb it is difficult to prepare complexes containing directly coordinated 18-crown-6. In previously published work we were able to isolate $[\text{M}(\text{OH}_2)_7(\text{OHMe})][\text{MCl}(\text{OH}_2)_2(18\text{-crown-6})_2\text{Cl}_7 \cdot 2\text{H}_2\text{O}$ ($\text{M} = \text{Y}, \text{Dy}$)⁵ by crystallization at low temperature, and preliminary results suggest that high concentrations of LiCl in the reaction mixture can lead to isolation of directly coordinated compounds;¹⁶ however, it appears from our results and the thermodynamic data published by Izatt²⁸ that direct coordination of 18-crown-6 to lanthanide chlorides does not occur past Tb when 1:1 stoichiometries of metal and ligand are utilized. By contrast, the EO5 complexes of lanthanide chlorides are easily obtained through $\text{M} = \text{Lu}$. The first manifestation of steric congestion occurs at $\text{M} = \text{Sm}$, where only water molecules occupy the three additional coordination sites. There are no other changes in the overall formula through the end of the lanthanide series.

The differences between EO5 and 18-crown-6 complexation most likely reflect the more flexible nature of EO5 compared to the macrocycle. As we have shown in earlier studies, PEGs most often wrap a Ln^{3+} ion in a helical fashion when chloride anions are utilized. 18-crown-6 on the other hand must fold around the metal ion placing greater steric demands on the coordination sphere and producing torsion angle strain on the crown ether. As shown in Table I, in general the $\text{M}\text{-Cl}$ and $\text{M}\text{-OH}_2$ separations are shorter, and the $\text{M}\text{-O}$ (etheric) distances are longer in the 18-crown-6 complexes than in the EO5 compounds. This also reflects the difficulty 18-crown-6 has in folding around Ln^{3+} versus the relative ease EO5 has in flexing into Ln^{3+} coordination sites. Apparently the folding strain past $\text{M} = \text{Tb}$ is too much and instead hydrogen-bonded complexes such as $[\text{Dy}(\text{OH}_2)_8]\text{Cl}_3 \cdot 18\text{-crown-6} \cdot 4\text{H}_2\text{O}$ ²⁹ are isolated.

We note even for lanthanide nitrate salts it is difficult to isolate 18-crown-6 complexes of the mid- to late-lanthanides. The hydrogen-bonded complexes $[\text{M}(\text{NO}_3)_3(\text{OH}_2)_3] \cdot 18\text{-crown-6}$ are isolated for $\text{M} = \text{Eu}\text{-Lu}$.^{16,19}

The strain on the crown ether can also be followed by examining its conformation as the size of the lanthanide cations decrease. In complexes of the alkali metals and heavy main group metals such as Pb^{2+} ,^{30,31} Hg^{2+} ,³² etc., and in hydrogen-bonded complexes such as $[\text{Gd}(\text{NO}_3)_3(\text{OH}_2)_3] \cdot 18\text{-crown-6}$,¹⁹ the 18-crown-6 normally adopts a D_{3d} conformation. However, in complexes with the lanthanides, this macrocycle adopts successively less symmetrical conformations as the size of the cations decreases.³³ 18-Crown-6 adopts a $\text{C}_2(\text{A})$ conformation in $[\text{LaCl}_2(\text{Y})(18\text{-crown-6})]\text{Cl} \cdot 1.5\text{H}_2\text{O}$ ($\text{Y} = \text{OH}_2, \text{OHMe}$), $[\text{LaCl}_2(\text{OH}_2)(18\text{-crown-6})]\text{Cl}$, $[\text{LaCl}_3(18\text{-crown-6})]$, and $[\text{CeCl}_2(\text{OH}_2)(18\text{-crown-6})]\text{Cl} \cdot 2\text{H}_2\text{O}$, with a C_2 rotation axis perpendicular to the 18-crown-6 molecule. In $[\text{MCl}(\text{OH}_2)_2(18\text{-crown-6})]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ ($\text{M} = \text{Pr}\text{-Tb}$), the crown ether adopts a conformation that is a mixture of pseudo- $\text{C}_2(\text{A})$ and pseudo- C_i . (The crown ether molecules are disordered). The values of the torsion angles from $\text{C}(1)\text{-C}(2)\text{-O}(2)\text{-C}(3)$ to $\text{C}(9)\text{-C}(10)\text{-O}(6)\text{-C}(11)$ correspond to the values for the same angles found in $[\text{CeCl}_2(\text{OH}_2)(18\text{-crown-6})]\text{Cl} \cdot 2\text{H}_2\text{O}$. However, $\text{O}(1)\text{-C}(1)\text{-C}(2)\text{-O}(2)$ and $\text{O}(6)\text{-C}(11)\text{-C}(12)\text{-O}(1)$ are of opposite sign to their La and Ce counterparts, breaking the $\text{C}_2(\text{A})$ symmetry in the first disorder model (Figure 5). In the other disorder model, a pseudo-mirror plane is parallel to the plane defined by O(1), O(4), and the metal center (Figure 8),

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Table III. Crystal Data and Summary of Intensity Data Collection and Structure Refinement

	compound				
	[LaCl ₂ (OH ₂)(EO5)]- Cl·H ₂ O	[CeCl ₂ (OH ₂)(EO5)]- Cl·H ₂ O	[PrCl ₂ (OH ₂)(EO5)]- Cl·H ₂ O	[Sm(OH ₂) ₃ (EO5)]- Cl ₃ ·H ₂ O	[Eu(OH ₂) ₃ (EO5)]- Cl ₃ ·H ₂ O
fw	519.58	520.79	521.58	567.06	568.66
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
temp, °C	20	20	20	20	20
cell constants ^a					
<i>a</i> , Å	13.508(9)	13.489(2)	13.439(7)	7.501(4)	7.497(2)
<i>b</i> , Å	9.825(3)	9.820(1)	9.797(5)	32.665(9)	32.630(8)
<i>c</i> , Å	14.518(4)	14.514(5)	14.479(2)	9.112(4)	9.097(3)
β, deg	102.97(4)	102.86(2)	102.69(3)	109.71(7)	109.67(2)
cell vol, Å ³	1878	1874	1860	2102	2096
formula units/unit cell	4	4	4	4	4
<i>D</i> _{calc} , g cm ⁻³	1.84	1.85	1.86	1.79	1.80
μ _{calc} , cm ⁻¹	25.5	29.1	30.8	32.6	34.4
range of rel transm factors, %	85/100	62/100	79/100	80/100	92/100
radiation, graphite monochrom (λ, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
<i>R</i> = Σ <i>F</i> _o - <i>F</i> _c /Σ <i>F</i> _o	0.038	0.026	0.029	0.052	0.037
<i>R</i> _w = [Σw(<i>F</i> _o - <i>F</i> _c) ² /Σw(<i>F</i> _o) ²] ^{1/2}	0.039	0.039	0.029	0.062	0.042

	compound				
	[Gd(OH ₂) ₃ (EO5)]- Cl ₃ ·H ₂ O	[Tb(OH ₂) ₃ (EO5)]- Cl ₃ ·H ₂ O	[Dy(OH ₂) ₃ (EO5)]- Cl ₃ ·H ₂ O	[Y(OH ₂) ₃ (EO5)]- Cl ₃ ·H ₂ O	[Ho(OH ₂) ₃ (EO5)]- Cl ₃ ·H ₂ O
fw	573.95	575.63	579.20	505.61	581.63
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
temp, °C	18	18	22	20	18
cell constants ^a					
<i>a</i> , Å	7.493(2)	7.487(4)	7.4744(7)	7.477(2)	7.469(2)
<i>b</i> , Å	32.595(9)	32.554(9)	32.512(4)	32.435(9)	32.470(9)
<i>c</i> , Å	9.083(4)	9.066(8)	9.060(2)	9.040(2)	9.041(4)
β, deg	109.68(4)	109.73(7)	109.70(1)	109.64(4)	109.67(2)
cell vol, Å ³	2089	2080	2073	2065	2065
formula units/unit cell	4	4	4	4	4
<i>D</i> _{calc} , g cm ⁻³	1.82	1.84	1.86	1.63	1.87
μ _{calc} , cm ⁻¹	40.0	39.1	41.7	33.5	44.1
range of rel transm factors, %	73/100	85/100	76/100	81/100	85/100
radiation, graphite monochrom (λ, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
<i>R</i>	0.067	0.040	0.036	0.048	0.029
<i>R</i> _w	0.067	0.041	0.053	0.054	0.037

	compound			
	[Er(OH ₂) ₃ (EO5)]- Cl ₃ ·H ₂ O	[Tm(OH ₂) ₃ (EO5)]- Cl ₃ ·H ₂ O	[Yb(OH ₂) ₃ (EO5)]- Cl ₃ ·H ₂ O	[Lu(OH ₂) ₃ (EO5)]- Cl ₃ ·H ₂ O
fw	583.96	585.64	589.74	591.67
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
temp, °C	20	18	20	20
cell constants ^a				
<i>a</i> , Å	7.454(6)	7.455(1)	7.458(3)	7.452(1)
<i>b</i> , Å	32.379(6)	32.413(9)	32.350(9)	32.355(9)
<i>c</i> , Å	9.015(3)	9.017(3)	9.005(7)	9.010(3)
β, deg	109.68(5)	109.66(4)	109.71(6)	109.64(3)
cell vol, Å ³	2020	2052	2045	2046
formula units/unit cell	4	4	4	4
<i>D</i> _{calc} , g cm ⁻³	1.92	1.90	1.92	1.92
μ _{calc} , cm ⁻¹	43.6	49.1	52.5	55.0
range of rel transm factors, %	80/100	71/100	93/100	70/100
radiation, graphite monochrom (λ, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
<i>R</i>	0.038	0.040	0.042	0.056
<i>R</i> _w	0.040	0.048	0.063	0.074

	compound		
	[LaCl ₂ (Y)(18-crown-6)]Cl· 1.5H ₂ O (Y = OH ₂ , OHMe)	[LaCl ₂ (OH ₂)(18-crown-6)]Cl	[LaCl ₃ (18-crown-6)]
fw	561.64	527.60	509.59
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>F</i> dd2	<i>P</i> 2 ₁ / <i>c</i>
temp, °C	20	20	20
cell constants ^a			
<i>a</i> , Å	8.391(2)	36.979(9)	7.540(4)
<i>b</i> , Å	7.554(2)	28.418(9)	13.725(4)
<i>c</i> , Å	33.988(9)	7.484(1)	18.451(7)
β, deg	97.51(3)		91.38(4)
cell vol, Å ³	2136	7865	1909
formula units/unit cell	4	16	4
<i>D</i> _{calc} , g cm ⁻³	1.75	1.78	1.77

Table III (Continued)

	compound		
	[LaCl ₂ (Y)(18-crown-6)]Cl·1.5H ₂ O (Y = OH ₂ , OHMe)	[LaCl ₂ (OH ₂)(18-crown-6)]Cl	[LaCl ₃ (18-crown-6)]
μ_{calc} , cm ⁻¹	24.4	26.4	27.1
range of rel transm factors, %	71/100	93/100	95/100
radiation, graphite monochrom (λ, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
R	0.072	0.044	0.039
R _w	0.100	0.054	0.042

	compound			
	[CeCl ₂ (OH ₂)-(18-crown-6)]Cl·2H ₂ O	[PrCl(OH ₂) ₂ -(18-crown-6)]Cl ₂ ·2H ₂ O	[EuCl(OH ₂) ₂ -(18-crown-6)]Cl ₂ ·2H ₂ O	[GdCl ₆][GdCl _x (OH ₂) _y -(18-crown-6)] ₂ ·2OHMe (x = 1, y = 2; x = 2, y = 1)
fw	564.85	583.65	594.70	1437.6
space group	P2 ₁ /c	P2 ₁ 2 ₁ 2 ₁	P2 ₁ 2 ₁ 2 ₁	P1
temp, °C	20	18	20	-150
cell constants ^a				
a, Å	8.440(3)	7.470(2)	7.406(6)	9.016(2)
b, Å	7.469(4)	16.063(6)	15.906(5)	9.034(3)
c, Å	34.204(9)	19.022(8)	18.891(9)	14.812(5)
α, deg				76.81(3)
β, deg	97.76(4)			83.43(3)
γ, deg				83.15(3)
cell vol, Å ³	2137	2283	2225	1162
formula units/unit cell	4	4	4	1
D _{calc} , g cm ⁻³	1.76	1.70	1.78	2.06
μ_{calc} , cm ⁻¹	25.7	25.2	32.4	45.7
range of rel transm factors, %	84/100	87/100	88/100	56/100
radiation, graphite monochrom (λ, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
R	0.033	0.046	0.036	0.060
R _w	0.042	0.050	0.040	0.078

^a Least-squares refinement of $((\sin \theta)/\lambda)^2$ values for 25 reflections $\theta > 17^\circ$. ^b Corrections: Lorentz-polarization and absorption (empirical, ψ scan). ^c Neutral scattering factors and anomalous dispersion corrections from ref 38.

resulting in the pseudo-*C*₂ conformation. The mirror symmetry is broken by the torsion angles associated with C(1)'-C(2)', C(5)'-C(6)', C(7)-C(8), and C(11)-C(12).

As the size of the lanthanides continues to decrease, the symmetry of the crown ether reduces further, resulting in a *C*₂ conformation for [M(OH₂)₇(OHMe)][MCl(OH₂)₂(18-crown-6)]₂Cl₂·2H₂O (M = Y, Dy). (This is the same conformation referred to as the *S*₂ conformation by Fyles and Gandour.²⁷) As in the [MCl(OH₂)₂(18-crown-6)]Cl₂·2H₂O complexes, O(1), O(4), and the metal center lie on the pseudo-mirror plane.

Two exceptions to this trend occur for the Gd complexes [GdCl₆][GdCl_x(OH₂)_y(18-crown-6)]₂·2OHMe (x = 2, y = 1; x = 1, y = 2) and [GdCl₂(OH₂)₂(18-crown-6)]Cl.¹⁵ In these two complexes the macrocycle adopts a *C*₂(A) conformation. Two chloride anions are coordinated to the Gd center in both complexes, allowing the macrocycle to relax and adopt the more symmetrical *C*₂(A) conformation. The M-O(etheric, prismatic) distances are ca. 0.04 Å longer in [GdCl₆][GdCl_x(OH₂)_y(18-crown-6)]₂·2OHMe (x = 2, y = 1; x = 1, y = 2) and [GdCl₂(OH₂)₂(18-crown-6)]Cl versus [GdCl(OH₂)₂(18-crown-6)]Cl₂·2H₂O, while the M-O(etheric, capping) distances are essentially the same.

The conformation adopted by the polyether in the EO5 complexes is similar to the conformation observed for the corresponding crown ether complexes. For [MCl₂(OH₂)(EO5)]Cl·H₂O (M = La-Nd), the polyether adopts a "*C*₂(A)" conformation, where the conformation of the EO5 ligand is the same as O(1)-C(1)-C(2)-O(2) through O(5)-C(9)-C(10)-O(6) in the 18-crown-6 ligand in [CeCl₂(OH₂)(18-crown-6)]Cl₂·2H₂O. This conformation is indicated by the values of the O-C-C-O angles which are g-, g+, g-, g-, g+. The EO5 O-C-C-O torsion angles in [M(OH₂)₃(EO5)]Cl₃·H₂O (M = Y, Sm-Lu) have the pattern g-, g-, g+, g+, g-, where the torsion angles of the EO5 ligand are nearly identical to those values observed for O(1)-C(1)-C(2)-O(2) through O(5)-C(9)-C(10)-O(6) in [MCl(OH₂)₂(18-crown-6)]Cl₂·2H₂O (M = Pr-Tb). This allows EO5 to adopt a "*C*₂" conformation. Since EO5 is acyclic and therefore

more flexible than 18-crown-6, we do not observe conformational stress within the lanthanide series.

Although we have studied the crystal structures of MCl₃·*n*H₂O complexes of EO3,¹² EO4,¹³ EO5, 12-crown-4,⁶ 15-crown-5, and 18-crown-6,^{4,5} only the largest crown ether, 18-crown-6, is flexible enough to result in isolation of complexes so closely mimicking the open chain glycols. Both 12-crown-4 and 15-crown-5 are too small to incorporate the Ln³⁺ cations into the macrocycle cavity and thus coordinate on one side of the cation, allowing water molecules and chloride ions to occupy the open side of the coordination sphere. Complexes such as [M(OH₂)₅(12-crown-4)]Cl₃·2H₂O (M = Ce-Er, Y),⁶ [MCl₂(OH₂)₂(12-crown-4)]Cl (M = Ho-Lu),⁶ and [MCl₃(15-crown-5)] (M = La,¹⁶ Ce,¹⁶ Pr,⁷ Nd³) have been characterized. The smaller glycols EO3 and EO4 wrap the cations in a helical fashion typically giving rise to 9-coordinate species in which the oxygen atoms alternate between capping and prismatic sites. Complexes such as [M(OH₂)₅(EO3)]Cl₃ (M = Nd-Dy, Y),¹² [LaCl₃(EO4)]₂,¹³ [MCl(OH₂)₃(EO4)]Cl₂·H₂O (M = Ce-Gd),¹³ and [M(OH₂)₄(EO4)]Cl₃ (M = Tb-Yb, Y)¹³ have been isolated. This behavior is totally opposite from that we observe for the softer Bi³⁺, which as the chloride salt has the ability to organize PEGs into out-of-cavity crown ether-like structures.³⁴

A few complexes with the smaller glycols and smaller lanthanides have been isolated in which the PEGs adopt an equatorial girdle and actually mimic classic crown ether coordination. These include [MCl₃(EO3)]·CH₃CN (M = Ho-Lu),¹² [MCl₃(EO3)]·CH₃OH (M = Eu-Lu),¹² [LuCl₃(EO3)],¹² and [LuCl₂(EO4)]Cl·H₂O.¹³ A recent paper³⁵ detailing the structure of [ScCl₂(18-crown-6)][SbCl₆] reveals a pentadentate 18-crown-6 molecule with all five Sc-O donors in a pentagonal equatorial

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Table IV. Final Fractional Coordinates and $B(\text{eqv})$ Values (\AA^2) for $[\text{Sm}(\text{OH}_2)_3(\text{EO}_5)]\text{Cl}_3\cdot\text{H}_2\text{O}$

atom	x/a	y/b	z/c	$B(\text{eqv})^a$
Sm	0.2251(1)	0.38852(3)	0.1218(1)	1.18
Cl(1)	-0.2429(7)	0.4149(2)	-0.3488(5)	2.19
Cl(2)	0.2364(7)	0.5112(2)	-0.1760(6)	2.54
Cl(3)	-0.2147(8)	0.2732(2)	-0.1804(6)	2.66
O(1)	0.266(2)	0.4207(4)	-0.107(2)	1.92
O(2)	0.472(2)	0.3562(4)	0.027(2)	1.90
O(3)	0.264(2)	0.3129(4)	0.163(1)	1.80
O(4)	0.018(2)	0.3538(4)	0.247(2)	2.29
O(5)	0.152(2)	0.4300(4)	0.325(2)	2.15
O(6)	0.419(2)	0.4504(4)	0.211(2)	1.91
O(7)	-0.039(2)	0.4330(4)	0.003(2)	2.41
O(8)	0.470(2)	0.3708(4)	0.369(2)	2.04
O(9)	0.020(2)	0.3539(4)	-0.110(2)	1.90
O(10)	0.602(3)	0.2951(5)	0.469(2)	4.57
C(1)	0.437(3)	0.4130(6)	-0.139(3)	2.09
C(2)	0.473(3)	0.3676(7)	-0.123(3)	2.86
C(3)	0.526(3)	0.3149(6)	0.076(3)	2.77
C(4)	0.359(3)	0.2898(6)	0.071(2)	2.52
C(5)	0.134(3)	0.2889(7)	0.214(3)	3.32
C(6)	0.078(4)	0.3151(6)	0.330(3)	3.75
C(7)	-0.074(3)	0.3819(6)	0.331(3)	2.65
C(8)	0.067(3)	0.4106(7)	0.427(2)	2.60
C(9)	0.266(3)	0.4645(6)	0.393(3)	2.72
C(10)	0.335(3)	0.4826(6)	0.271(3)	2.62

$$^a B(\text{eqv}) = \frac{1}{3}[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos \gamma)\beta_{12} + ac(\cos \beta)\beta_{13} + bc(\cos \alpha)\beta_{23}]$$

plane. This unusual structure is almost certainly a result of the small size of Sc^{3+} and most likely would not be observed for the lanthanides.

In comparing the M–O distances in the EO3, EO4, and EO5 complexes of lanthanide chlorides, we find very few real differences. The differences which do exist appear to be related to either geometric site or the number of tight ion pairs in the primary coordination sphere. The same is in general true when comparing the 18-crown-6 complexes to the 12-crown-4 and 15-crown-5 complexes.

Conclusions

The structural data suggest that it is the flexibility of PEGs and the inability of crown ethers to fold around Ln^{3+} ions that are responsible for the ready isolation of PEG complexes of $\text{MCl}_3\cdot n\text{H}_2\text{O}$ ($\text{M} = \text{La}–\text{Lu}$, Y) and the lack of directly coordinated 18-crown-6 complexes past $\text{M} = \text{Tb}$. In the series of complexes presented here the Ln^{3+} ions once again demonstrate the complete control the steric environment has on the primary coordination sphere in the absence of strong donor anions. The results also suggest that increasing the PEG length to at least EO6 should easily yield a comparable series of $\text{MCl}_3\cdot n\text{H}_2\text{O}$ complexes for the entire lanthanide series. (This research is currently in progress in our laboratories.) The results do not suggest, however, that increasing the crown ether cavity size will allow isolation of late-lanthanide chloride complexes. In fact it appears that designing a reasonable cyclic polyether for late-lanthanide ions will require modification of the length of the ethylene bridges instead.

Experimental Section

Synthesis of Complexes. $[\text{MCl}_2(\text{OH}_2)(\text{EO}_5)]\text{Cl}\cdot\text{H}_2\text{O}$ ($\text{M} = \text{La}–\text{Pr}$). A 1.5-mmol quantity of pentaethylene glycol was added to a stirred solution of 1.5 mmol of $\text{MCl}_3\cdot n\text{H}_2\text{O}$ in 5 mL of $\text{CH}_3\text{CN}:\text{CH}_3\text{OH}$ (3:1). The reaction mixture was heated to 60 °C for 1 h. For $\text{M} = \text{Ce}$, a small amount of white precipitate formed. For $\text{M} = \text{Pr}$, a small amount of green precipitate formed. The precipitates were centrifuged, and the supernatants were decanted. The solutions were then allowed to slowly cool to room temperature.

In general, as solvent was removed, a more viscous layer became visible in the bottom of each reaction vessel. In each case, the solvent volume was reduced by ~50% under vacuum. Slow evaporation of the remaining solutions afforded suitable crystals in each case.

Table V. Final Fractional Coordinates and $B(\text{eqv})$ Values (\AA^2) for $[\text{LaCl}_3(18\text{-crown-6})]$

atom	x/a	y/b	z/c	$B(\text{eqv})^a$
La	0.01582(7)	0.26205(3)	0.37301(3)	1.70
Cl(1)	-0.2103(4)	0.0991(2)	0.3811(1)	2.59
Cl(2)	-0.1548(3)	0.2647(2)	0.2346(1)	2.96
Cl(3)	0.2583(4)	0.3681(2)	0.4605(1)	3.17
O(1)	0.256(1)	0.3379(5)	0.2845(4)	2.96
O(2)	-0.017(1)	0.4468(4)	0.3319(4)	3.14
O(3)	-0.2554(9)	0.3592(5)	0.4191(4)	2.90
O(4)	-0.0713(9)	0.2429(5)	0.5118(3)	2.68
O(5)	0.1787(9)	0.1282(5)	0.4546(3)	2.64
O(6)	0.2483(9)	0.1441(4)	0.3101(4)	2.50
C(1)	0.216(2)	0.4317(7)	0.2516(6)	3.36
C(2)	0.137(2)	0.4955(7)	0.3063(6)	3.62
C(3)	-0.139(2)	0.5070(7)	0.3697(6)	3.69
C(4)	-0.302(2)	0.4466(8)	0.3804(6)	3.95
C(5)	-0.278(1)	0.3688(8)	0.4956(6)	3.57
C(6)	-0.244(1)	0.2736(8)	0.5293(5)	3.34
C(7)	-0.006(2)	0.1586(7)	0.5508(5)	3.15
C(8)	0.181(2)	0.1410(8)	0.5310(5)	3.40
C(9)	0.333(1)	0.0789(8)	0.4288(6)	3.72
C(10)	0.289(2)	0.0544(7)	0.3508(6)	3.44
C(11)	0.399(1)	0.1869(8)	0.2775(6)	3.52
C(12)	0.340(1)	0.2717(8)	0.2365(5)	3.53

^a See footnote a of Table IV.

Anal. Calcd for $\text{M} = \text{La}$: C, 23.12; H, 5.04. Found: C, 22.51; H, 4.81. Calcd for $\text{M} = \text{Ce}$: C, 23.06; H, 5.03. Found: C, 23.13; H, 5.24. Calcd for $\text{M} = \text{Pr}$: C, 23.03; H, 5.02. Found: C, 22.86; H, 5.10.

$[\text{M}(\text{OH}_2)_3(\text{EO}_5)]\text{Cl}_3\cdot\text{H}_2\text{O}$ ($\text{M} = \text{Sm}–\text{Lu}$, Y). A 1.5-mmol amount (1.0 mmol for Sm–Eu, Ho–Tm) of pentaethylene glycol was added to a stirred solution of 1.5 mmol (1.0 mmol for Sm–Eu, Ho–Tm) of $\text{MCl}_3\cdot 6\text{H}_2\text{O}$ in 5 mL of $\text{CH}_3\text{CN}:\text{CH}_3\text{OH}$ (3:1), (8 mL for $\text{M} = \text{Gd}$, Lu). The reaction mixture was heated to 60 °C for 1 h. For $\text{M} = \text{Sm}$, a pale yellow precipitate formed. For $\text{M} = \text{Lu}$, a small amount of white precipitate formed. The precipitates were centrifuged, and the supernatants were decanted. The solutions were allowed to cool to room temperature slowly.

For $\text{M} = \text{Sm}–\text{Eu}$, the solutions were stored at –12 °C for 1 week. Slow evaporation of the solutions resulted in the formation of two-layer systems. Small crystals formed from the lower layer of each reaction vessel.

For $\text{M} = \text{Gd}$, the reaction mixture was stored at –12 °C producing colorless crystals. For $\text{M} = \text{Tb}–\text{Dy}$, the solvent volume was reduced by ~50% under vacuum at which point a two-layer system formed. Slow evaporation of the remaining solutions afforded crystals for each reaction.

For $\text{M} = \text{Ho}–\text{Tm}$, the reaction mixtures were slowly evaporated. For $\text{M} = \text{Ho}$, small peach colored crystals formed from the lower layer of a two-layer system. For $\text{M} = \text{Er}$, pink crystals formed in the same manner. For $\text{M} = \text{Tm}$, very small, thin rod-shaped crystals were observed.

For $\text{M} = \text{Yb}–\text{Lu}$ and Y, the solvent was reduced by ~50% under vacuum. Slow evaporation of the remaining solutions yielded suitable crystals of each.

Anal. Calcd for $\text{M} = \text{Sm}$: C, 21.88; H, 5.14. Found: C, 22.07; H, 5.49. Calcd for $\text{M} = \text{Gd}$: C, 21.61; H, 5.08. Found: C, 20.52; H, 5.35. Calcd for $\text{M} = \text{Tb}$: C, 21.54; H, 5.06. Found: C, 19.44; H, 5.39. Calcd for $\text{M} = \text{Dy}$: C, 21.40; H, 5.03. Found: C, 18.99; H, 5.37. Calcd for $\text{M} = \text{Tm}$: C, 21.16; H, 4.97. Found: C, 21.28; H, 5.39. Calcd for $\text{M} = \text{Yb}$: C, 21.01; H, 4.94. Found: C, 19.42; H, 5.23. Calcd for $\text{M} = \text{Y}$: C, 24.63; H, 5.79. Found: C, 23.75; H, 6.13.

$[\text{LaCl}_3(18\text{-crown-6})]$ and $[\text{LaCl}_2(\text{OH}_2)(18\text{-crown-6})]\text{Cl}$. A 1.0-mmol amount of $\text{LaCl}_3\cdot 7\text{H}_2\text{O}$ was placed in a reaction tube, to which was added 4 mL of a 3:1 $\text{CH}_3\text{CN}:\text{CH}_3\text{OH}$ mixture. The solution was shaken until all of the La salt dissolved. A 1.0-mmol amount of 18-crown-6 was then added to the solution, and the resulting mixture was shaken until all of the ligand was dissolved. The solution was heated to 54 °C with stirring for 1.5 h and then slowly evaporated at room temperature for 6 days to a final volume of 1.5 mL, at which point crystals of $[\text{LaCl}_2(\text{OH}_2)(18\text{-crown-6})]\text{Cl}$ formed. In order to recrystallize the complex, the remaining solution was heated to 70 °C for 2 h, at which time crystals of the anhydrous complex $[\text{LaCl}_3(18\text{-crown-6})]$ were isolated from the same solution. Since a precipitate of $[\text{LaCl}_2(\text{OH}_2)(18\text{-crown-6})]\text{Cl}$ would form as the solution was cooled to 20 °C, crystals of the anhydrous complex were removed from the hot solution and mounted immediately for X-ray analysis. Anal. Calcd for $[\text{LaCl}_3(18\text{-crown-6})]$: C, 28.28; H, 4.75. Found: C, 28.17; H, 4.78. Calcd for $[\text{LaCl}_2(\text{OH}_2)(18\text{-crown-6})]\text{Cl}$: C, 27.32; H, 4.97. Found: C, 26.75; H, 4.75.

Table VI. Final Fractional Coordinates and $B(\text{eqv})$ Values (\AA^2) for $[\text{LaCl}_2(\text{OH}_2)(18\text{-crown-6})]\text{Cl}$

atom	x/a	y/b	z/c	$B(\text{eqv})^a$
La	0.06076(3)	0.36953(3)	0.5000	1.99
Cl(1)	0.0400(2)	0.2901(2)	0.7005(9)	3.62
Cl(2)	0.1164(1)	0.4141(2)	0.3158(9)	3.22
Cl(3)	0.0462(1)	0.5420(2)	0.237(1)	4.22
O(1)	0.0386(4)	0.3295(4)	0.212(2)	3.00
O(2)	0.0970(4)	0.2973(5)	0.378(2)	3.64
O(3)	0.1207(4)	0.3432(5)	0.667(3)	4.06
O(4)	0.0879(3)	0.4237(4)	0.767(2)	2.75
O(5)	0.0160(3)	0.4051(4)	0.754(2)	3.05
O(6)	-0.0101(3)	0.3607(4)	0.464(2)	3.21
O(7)	0.0316(4)	0.4413(4)	0.366(2)	2.84
C(1)	0.0492(7)	0.2828(8)	0.176(4)	5.03
C(2)	0.0876(9)	0.2810(8)	0.207(5)	6.40
C(3)	0.1341(7)	0.2894(9)	0.445(5)	5.24
C(4)	0.1341(7)	0.2973(8)	0.630(4)	3.99
C(5)	0.1323(7)	0.3665(9)	0.825(5)	5.84
C(6)	0.1249(5)	0.4137(9)	0.822(5)	4.87
C(7)	0.0651(4)	0.4340(7)	0.920(3)	2.74
C(8)	0.0291(5)	0.4447(7)	0.850(3)	2.71
C(9)	-0.0217(5)	0.4073(8)	0.711(4)	4.01
C(10)	-0.0326(5)	0.3631(8)	0.617(3)	3.57
C(11)	-0.0224(5)	0.3280(8)	0.327(4)	3.83
C(12)	0.0016(6)	0.3340(8)	0.167(3)	3.24

^a See footnote a of Table IV.

$[\text{LaCl}_2(\text{Y})(18\text{-crown-6})]\text{Cl}\cdot 1.5\text{H}_2\text{O}$ ($\text{Y} = \text{OH}_2, \text{OHMe}$). A 1.0-mmol amount of $\text{LaCl}_3\cdot 7\text{H}_2\text{O}$ was placed in a reaction tube, to which was added 5 mL of a 3:1 $\text{CH}_3\text{CN}:\text{CH}_3\text{OH}$ mixture. The solution was shaken until the salt dissolved. A 1.0-mmol amount of 18-crown-6 was then added to the solution, and the resulting mixture was shaken until all the ligand dissolved. The solution was heated to 56 °C with stirring for 1.5 h and then stored at 20 °C for 4 days, 5 °C for 4 days, and -10 °C for 44 days at which point crystals of $[\text{LaCl}_2(\text{Y})(18\text{-crown-6})]\text{Cl}\cdot 1.5\text{H}_2\text{O}$ ($\text{Y} = \text{OH}_2, \text{OHMe}$) formed. Anal. Calcd: C, 26.73; H, 5.38. Found: C, 26.62; H, 5.18.

$[\text{CeCl}_2(\text{OH}_2)(18\text{-crown-6})]\text{Cl}\cdot 2\text{H}_2\text{O}$. A 1.0-mmol amount of $\text{CeCl}_3\cdot 7\text{H}_2\text{O}$ was placed in a reaction tube, to which was added 4 mL of a 3:1 $\text{CH}_3\text{CN}:\text{CH}_3\text{OH}$ mixture. The solution was shaken until all the salt dissolved. A 1.0-mmol amount of 18-crown-6 was then added to the solution, and the resulting mixture was shaken until all of the ligand dissolved. The solution was heated to 61 °C with stirring for 1 h and then stored at room temperature for 2 days and at 5 °C for 18 days, at which point several large deliquescent crystals formed. The dissolved crystals were then stored at -5 °C for 21 days, when small needlelike crystals formed. The solution was allowed to warm to room temperature and stored for 73 days. Slow evaporation of the solution was carried out for 4 days, at which point crystals suitable for X-ray crystallographic analysis formed. Anal. Calcd: C, 25.52; H, 5.35. Found: C, 25.44; H, 5.25.

$[\text{MCl}(\text{OH}_2)_2(18\text{-crown-6})]\text{Cl}_2\cdot 2\text{H}_2\text{O}$ ($\text{M} = \text{Pr}, \text{Eu}$). A 1.0-mmol amount of $\text{MCl}_3\cdot 6\text{H}_2\text{O}$ ($\text{M} = \text{Pr}, \text{Eu}$) was placed into a reaction tube, to which was added 4.0 mL of a 3:1 $\text{CH}_3\text{CN}:\text{CH}_3\text{OH}$ mixture. The resulting mixture was shaken until all the salt dissolved. A 1.0-mmol amount of 18-crown-6 was then added to the solution, and the resulting mixture was shaken until all the ligand dissolved. A small magnetic stirring bar was then added to the solution, and the solution was heated to 57 °C with stirring for 2.25 h. The solution was removed from the heating bath and the stirring bar removed from the solution. The solution was stored at room temperature for 64 days and at 5 °C for 1 day. The solution was then slowly evaporated for 1 day, at which time crystals suitable for X-ray crystallographic analysis were obtained. Anal. Calcd for $\text{M} = \text{Pr}$: C, 24.70; H, 5.53. Found: C, 24.07; H, 5.55. Calcd for $\text{M} = \text{Eu}$: C, 24.24; H, 5.42. Found: C, 24.39; H, 5.40.

$[\text{GdCl}_2(\text{OH}_2)_2(18\text{-crown-6})]\text{Cl}_2\cdot 2\text{OHMe}$ ($x = 2, y = 1; x = 1, y = 2$). A 10.0-mmol amount (3.72 g) of $\text{GdCl}_3\cdot 6\text{H}_2\text{O}$, 10.0 mmol (2.64 g) of 18-crown-6, and 23.6 mmol (1.0 g) of LiCl were combined in 30 mL of a 3:1 $\text{CH}_3\text{CN}:\text{CH}_3\text{OH}$ solvent mixture in a 50-mL Erlenmeyer flask and heated to 50 °C with stirring in an oil bath. The mixture was allowed to stir for 2.5 h at 60–65 °C, after which time there was still a white precipitate. The solution was decanted into another 50-mL flask and covered with a rubber septum. The solution was replaced in the oil bath and allowed to slowly cool with the bath. The precipitate was kept in its original 50-mL Erlenmeyer flask and was also capped with a rubber septum. Some white precipitate formed from the solution after the

Table VII. Final Fractional Coordinates and $B(\text{eqv})$ Values (\AA^2) for $[\text{CeCl}_2(\text{OH}_2)(18\text{-crown-6})]\text{Cl}\cdot 2\text{H}_2\text{O}$

atom	x/a	y/b	z/c	$B(\text{eqv})^a$
Ce	0.29795(4)	0.50945(5)	0.60828(1)	1.45
Cl(1)	0.0394(2)	0.7252(2)	0.57863(5)	2.48
Cl(2)	0.5449(2)	0.3011(2)	0.58613(5)	2.31
Cl(3)	0.2133(2)	0.1872(3)	0.73782(6)	3.18
O(1)	0.5266(5)	0.7388(6)	0.6271(1)	2.40
O(2)	0.4080(5)	0.6841(6)	0.5505(1)	2.05
O(3)	0.1971(5)	0.4220(6)	0.5343(1)	2.10
O(4)	0.1333(5)	0.2153(6)	0.5958(1)	2.19
O(5)	0.0782(5)	0.4516(6)	0.6522(1)	2.11
O(6)	0.2749(5)	0.7333(6)	0.6667(1)	2.25
O(7)	0.3965(5)	0.3467(6)	0.6701(1)	2.40
O(8)	0.1324(7)	0.5220(8)	0.7881(2)	3.86
O(9)	0.6781(8)	0.339(1)	0.7081(2)	5.62
C(1)	0.6155(8)	0.792(1)	0.5954(2)	2.75
C(2)	0.5040(9)	0.839(1)	0.5597(2)	2.80
C(3)	0.3117(9)	0.6871(9)	0.5134(2)	2.34
C(4)	0.2719(9)	0.496(1)	0.5028(2)	2.51
C(5)	0.1539(9)	0.2370(9)	0.5274(2)	2.63
C(6)	0.0470(9)	0.188(1)	0.5575(2)	2.73
C(7)	0.0404(9)	0.165(1)	0.6262(2)	2.92
C(8)	-0.0439(8)	0.325(1)	0.6397(2)	2.88
C(9)	0.0247(9)	0.601(1)	0.6746(2)	2.97
C(10)	0.1720(9)	0.687(1)	0.6952(2)	2.86
C(11)	0.4187(9)	0.814(1)	0.6857(2)	2.92
C(12)	0.5048(9)	0.885(1)	0.6547(2)	3.35

^a See footnote a of Table IV.

overnight cooling, but the solution and precipitate were stored at 5 °C for 51 days until crystallization occurred. The precipitate was composed of hygroscopic microcrystals of the complex. Due to the deliquescent nature of the crystals, a satisfactory elemental analysis was not obtained.

X-ray Data Collection, Structure Determination, and Refinement. For each crystallographic study, a single crystal was mounted in a thin-walled glass capillary flushed with Ar and transferred to the goniometer. A summary of data collection parameters for all complexes is given in Table III. All space groups were uniquely determined by systematic absences except that for $[\text{GdCl}_2(\text{OH}_2)_2(18\text{-crown-6})]\text{Cl}_2\cdot 2\text{OHMe}$ ($x = 1, y = 2; x = 2, y = 1$) as discussed below. Except where noted, geometrically constrained hydrogen atoms 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 Å². The alcoholic and aquo hydrogen atoms were not included in any of the refinements. All non-hydrogen atoms were refined anisotropically except as noted for disordered structures. Structures were refined by utilizing SHELX76³⁷ and neutral-atom scattering factors from ref 38. Initial structure solutions in a series were carried out utilizing heavy-atom techniques. Subsequent members of an isostructural series were refined by starting with the non-hydrogen coordinates of the nearest previously determined member of the series. Considerations unique to each crystallographic series are discussed below.

$[\text{MCl}_2(\text{OH}_2)(\text{EO}5)]\text{Cl}\cdot \text{H}_2\text{O}$ ($\text{M} = \text{La}-\text{Pr}$). Fractional coordinates for these complexes have been deposited in the supplementary material. The coordinates for the isostructural Nd complex appear in ref 3.

$[\text{M}(\text{OH}_2)_3(\text{EO}5)]\text{Cl}_3\cdot \text{H}_2\text{O}$ ($\text{M} = \text{Sm}-\text{Lu}, \text{Y}$). Fractional coordinates for the first member of this series ($\text{M} = \text{Sm}$) appear in Table IV. The remaining tables of fractional coordinates have been deposited as supplementary material.

$[\text{LaCl}_3(18\text{-crown-6})]$. Fractional coordinates are given in Table V.

$[\text{LaCl}_2(\text{Y})(18\text{-crown-6})]\text{Cl}\cdot 1.5\text{H}_2\text{O}$ ($\text{Y} = \text{OH}_2, \text{OHMe}$). Fractional coordinates for $[\text{CeCl}_2(\text{OH}_2)(18\text{-crown-6})]\text{Cl}\cdot 2\text{H}_2\text{O}$ were used as a starting point in the refinement of this compound after an initial assumption that the two complexes were identical. During the initial isotropic refinement, O(9) exhibited very high thermal motion and a new peak 1.4 from the coordinated O(7) was evident. The disorder model developed requires a 50/50 mixture of $[\text{LaCl}_2(\text{OH}_2)(18\text{-crown-6})]^+$ and $[\text{LaCl}_2(\text{OHMe})(18\text{-crown-6})]^+$ cations. O(9) is present at 50% occupancy and resides at a hydrogen-bonded distance from O(7) only near those cations

(37) Sheldrick, G. M. SHELX76, a system of computer programs for X-ray structure determination as locally modified. University of Cambridge, England, 1976.

(38) *International Tables for X-ray Crystallography*; Kynoch Press, Birmingham, England, 1974; Vol. IV, pp 72, 99, 149 (present distributor: Kluwer Academic Publishers, Dordrecht, The Netherlands).

containing H₂O. In the other cations the methyl group extends in the direction of O(9)'s vacant sites.

The difference in formulation results in a smaller volume for this complex compared to the Ce compound below. The final fractional coordinates have been deposited as supplementary material because of their similarity with the Ce complex.

[LaCl₂(OH₂)₂(18-crown-6)]Cl. Fractional coordinates are given in Table VI.

[CeCl₂(OH₂)₂(18-crown-6)]Cl·2H₂O. The coordinates are given in Table VII.

[MCl(OH₂)₂(18-crown-6)]Cl₂·2H₂O (M = Pr, Eu). These two complexes exhibit the same disorder in the C(1)–C(6) ethylene linkages as observed for the M = Nd complex described in ref 3. C(1)–C(6) and C(1)′–C(6)′ were isotropically refined at half-occupancy in alternating least-squares cycles. No hydrogen atoms were included in these refinements. All non-hydrogen atoms except the disordered linkages were anisotropically refined. Absolute configuration was investigated. Fractional coordinates have been deposited as supplementary material. Those for the isostructural M = Nd complex appear in ref 3.

[GdCl₂][GdCl₂(OH₂)₂(18-crown-6)]₂·2OHMe (x = 1, y = 2; y = 2, x = 1). The crystal was cooled to –150 °C during data collection using a stream of cold nitrogen gas. The space group was determined to be either the centric *P* $\bar{1}$ or acentric *P*1. The subsequent solution and successful refinement of the structure was carried out in the centric *P* $\bar{1}$. During structure solution it became obvious that one coordination site to Gd(1) was disordered. In order to have balanced charge and to fit the observed peaks near this position a 50%/50% disorder of one chlorine (C1(2)) and one oxygen (O(8), water) was assumed. These peaks were then resolved and refined in alternate cycles of least-squares refinement. In addition two positions for the unique solvent oxygen atom (O(9) and O(9)′) were resolved. This disorder model, discussed in the Results section, fits the hydrogen-bonding scheme proposed from donor/acceptor contacts. Refinement in the acentric *P*1 resulted in high correlations between atoms related by the center of symmetry, a higher *R* value, and the continued presence of disorder. Final fractional coordinates for this complex are given in Table VIII.

Geometry Determinations. In determining the geometry around the metal center in these complexes, we employed a method outlined by Drew³⁶ for 9-coordinate complexes. In this case, only the atoms directly coordinated to the metal center are taken into account. The bond distances to these atoms are normalized to 1.0 Å, and the distance of each coordinated atom to its nearest neighbors is calculated, based on the approximate geometry that best fits the metal center. These calculated distances are then compared to ideal distances. The geometry with the closest fit to the ideal case is the true geometry. This analysis, by normalizing the bond distances to the metal center to 1.0 Å, takes only bond angles into account and ignores bond distances. In a review of Table I, it is clear that the average M–O(capping) distances are not always longer than the

Table VIII. Final Fractional Coordinates and *B*(eqv) Values (Å³) for [GdCl₂][GdCl₂(OH₂)₂(18-crown-6)][GdCl(OH₂)₂(18-crown-6)]·2OHMe

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B</i> (eqv) ^a
Gd(1)	0.06156(8)	0.31972(9)	0.28084(5)	0.80
Gd(2)	0.5000	0.0000	0.0000	0.71
Cl(1)	–0.2047(4)	0.2925(4)	0.3840(3)	1.16
Cl(2)	0.0928(8)	0.4792(9)	0.4142(5)	1.17
Cl(3)	0.1991(4)	0.0255(4)	0.0166(3)	1.06
Cl(4)	0.4895(4)	0.2933(4)	0.0107(3)	1.03
Cl(5)	0.5024(4)	0.0835(5)	–0.1848(3)	1.34
O(1)	–0.051(1)	0.585(1)	0.2094(7)	1.07
O(2)	–0.128(1)	0.343(1)	0.1622(7)	1.25
O(3)	–0.022(1)	0.071(1)	0.2518(7)	1.14
O(4)	0.130(1)	0.076(1)	0.3983(8)	1.29
O(5)	0.337(1)	0.261(1)	0.3193(8)	1.23
O(6)	0.246(1)	0.515(1)	0.2040(8)	1.13
O(7)	0.193(1)	0.251(1)	0.1450(8)	1.70
O(8)	0.086(2)	0.426(2)	0.396(1)	1.0(3) ^b
C(1)	–0.200(2)	0.592(2)	0.179(1)	1.22
C(2)	–0.197(2)	0.486(2)	0.116(1)	1.32
C(3)	–0.144(2)	0.212(2)	0.123(1)	1.61
C(4)	–0.154(2)	0.082(2)	0.202(1)	1.43
C(5)	–0.024(2)	–0.058(2)	0.330(1)	1.49
C(6)	0.119(2)	–0.069(2)	0.374(1)	1.59
C(7)	0.259(2)	0.078(2)	0.447(1)	1.67
C(8)	0.393(2)	0.120(2)	0.377(1)	1.60
C(9)	0.453(2)	0.336(2)	0.258(1)	1.60
C(10)	0.395(2)	0.503(2)	0.237(1)	1.48
C(11)	0.189(2)	0.671(2)	0.179(1)	1.64
C(12)	0.043(2)	0.679(2)	0.137(1)	1.62
O(9)	–0.306(4)	0.549(4)	0.497(2)	4.9(7) ^b
O(9)′	–0.375(5)	0.795(5)	0.383(3)	8(1) ^b
C(13)	–0.414(3)	0.656(3)	0.435(2)	6.2(7) ^b

^a See footnote *a* of Table IV. ^b Isotropic refinement.

average M–O(prismatic) distances. For polyether complexes this is probably due to other factors such as conformational strain which affect the M–O separations.

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Supplementary Material Available: Tables giving crystal data and details of the structure determination, atom coordinates, bond lengths, bond angles, anisotropic thermal parameters, and hydrogen atom locations (155 pages). Ordering information is given on any current masthead page.