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Macrocycle Complexation Chemistry. 35.[1] Survey of the Complexation of the Open Chain 15-Crown-5 Analogue Tetraethylene Glycol with the Lanthanide Chlorides

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The reaction of a 1:1 molar ratio of tetraethylene glycol (EO4) with a series of lanthanide chloride hydrates and the corresponding La^{3+} and Y^{3+} salts in 3:1 acetonitrile/methanol solutions produces four types of coordination complexes: $[LaCl_3(EO4)]_2$, $[MCl(OH_2)_3(EO4)]Cl_2 \cdot H_2O$ (M = Ce–Nd, Sm–Gd), $[M(OH_2)_4(EO4)]Cl_3$ (M = Tb–Yb, Y), and $[LuCl_2(EO4)]Cl \cdot H_2O$. The reaction involving Tm produced two additional crystalline complexes, $[Tm(OH_2)_{4-x}(OHMe)_x(EO4)]Cl_3 \cdot (1 - x)(H_2O)$ (x = 0.60) and $[TmCl_2(OH_2)(EO4)]Cl$. Modification of the metal ion's primary coordination sphere was possible for the middle lanthanides by the addition of excess LiCl. A 4:1:1 molar excess resulted in the formation of $[MCl_2(OH_2)(EO4)]Cl$ (M = Sm–Tb). When a 6:1:1 molar excess was used, the anhydrous $[EuCl_3(EO4)]$ was isolated. All of these complexes were crystallographically characterized. The 9-coordinate dimer $[LaCl_3(EO4)]_2$ is triclinic, $P\bar{1}$, with $a = 8.586$ (2) Å, $b = 9.489$ (3) Å, $c = 9.593$ (3) Å, $\alpha = 86.16$ (3)°, $\beta = 72.34$ (3)°, $\gamma = 78.10$ (2)°, and $D_{calc} = 2.00$ g cm^{-3} for $Z = 1$. The early and middle lanthanides form 9-coordinate tetrahydrates with one chloride ion in the primary coordination sphere. The complexes $[MCl(OH_2)_3(EO4)]Cl_2 \cdot H_2O$ are monoclinic, $P2_1/n$, with $Z = 4$ and cell data as follows: M = Ce, $a = 9.765$ (3) Å, $b = 10.597$ (4) Å, $c = 18.427$ (9) Å, $\beta = 102.20$ (4)°, and $D_{calc} = 1.83$ g cm^{-3}; M = Pr, $a = 9.743$ (4) Å, $b = 10.585$ (3) Å, $c = 18.407$ (9) Å, $\beta = 102.33$ (6)°, $D_{calc} = 1.84$ g cm^{-3}; M = Nd, $a = 9.725$ (2) Å, $b = 10.567$ (3) Å, $c = 18.389$ (8) Å, $\beta = 102.40$ (3)°, $D_{calc} = 1.86$ g cm^{-3}; M = Sm, $a = 9.688$ (6) Å, $b = 10.539$ (8) Å, $c = 18.350$ (9) Å, $\beta = 102.53$ (5)°, $D_{calc} = 1.90$ g cm^{-3}; M = Eu, $a = 9.653$ (4) Å, $b = 10.501$ (4) Å, $c = 18.303$ (6) Å, $\beta = 102.00$ (3)°, $D_{calc} = 1.92$ g cm^{-3}; M = Gd, $a = 9.660$ (5) Å, $b = 10.516$ (3) Å, $c = 18.317$ (8) Å, $\beta = 102.63$ (4)°, $D_{calc} = 1.94$ g cm^{-3}. The late lanthanide tetrahydrates are also 9-coordinate but have all four water molecules in the primary coordination sphere. These complexes of formula $[M(OH_2)_4(EO4)]Cl_3$, are triclinic, $P\bar{1}$, with $Z = 2$ and cell data as follows: M = Tb, $a = 8.234$ (7) Å, $b = 8.417$ (3) Å, $c = 13.725$ (2) Å, $\alpha = 82.36$ (2)°, $\beta = 89.20$ (4)°, $\gamma = 71.65$ (6)°, $D_{calc} = 1.97$ g cm^{-3}; M = Dy, $a = 8.234$ (5) Å, $b = 8.398$ (4) Å, $c = 13.691$ (7) Å, $\alpha = 82.41$ (4)°, $\beta = 89.36$ (5)°, $\gamma = 71.63$ (5)°, $D_{calc} = 1.97$ g cm^{-3}; M = Y, $a = 8.215$ (6) Å, $b = 8.390$ (5) Å, $c = 13.697$ (6) Å, $\alpha = 82.46$ (4)°, $\beta = 89.30$ (5)°, $\gamma = 71.58$ (5)°, $D_{calc} = 1.73$ g cm^{-3}; M = Ho, $a = 8.217$ (5) Å, $b = 8.389$ (4) Å, $c = 13.701$ (9) Å, $\alpha = 82.46$ (5)°, $\beta = 89.32$ (6)°, $\gamma = 71.60$ (4)°, $D_{calc} = 2.01$ g cm^{-3}; M = Er, $a = 8.206$ (1) Å, $b = 8.378$ (3) Å, $c = 13.676$ (6) Å, $\alpha = 82.44$ (3)°, $\beta = 89.34$ (2)°, $\gamma = 71.57$ (2)°, $D_{calc} = 2.03$ g cm^{-3}; M = Tm, $a = 8.206$ (4) Å, $b = 8.364$ (3) Å, $c = 13.666$ (9) Å, $\alpha = 82.43$ (4)°, $\beta = 89.38$ (6)°, $\gamma = 71.61$ (4)°, $D_{calc} = 2.04$ g cm^{-3}; M = Yb, $a = 8.201$ (3) Å, $b = 8.367$ (3) Å, $c = 13.664$ (5) Å, $\alpha = 82.42$ (3)°, $\beta = 89.41$ (3)°, $\gamma = 71.59$ (4)°, $D_{calc} = 2.06$ g cm^{-3}. The smallest lanthanide, Lu^{3+}, crystallizes as the 7-coordinate complex $[LuCl_2(EO4)]Cl \cdot H_2O$ in the monoclinic space group $P2_1/c$ with $a = 7.602$ (3) Å, $b = 20.958$ (9) Å, $c = 10.041$ (6) Å, $\beta = 103.80$ (4)°, and $D_{calc} = 2.11$ g cm^{-3} for $Z = 4$. The reaction of the Tm^{+3} salt produced two other crystallographic forms. The 9-coordinate complex $[Tm(OH_2)_{4-x}(OHMe)_x(EO4)]Cl_3 \cdot (1 - x)(H_2O)$ (x = 0.60) has one coordination site disordered between a water molecule and a methanol solvent molecule. This complex is monoclinic, $P2_1/c$, with $a = 10.051$ (1) Å, $b = 11.764$ (1) Å, $c = 16.390$ (3) Å, $\beta = 98.75$ (1)°, and $D_{calc} = 1.56$ g cm^{-3} for $Z = 4$. The second additional form is the same as that obtained for M = Sm–Tb when a 4:1:1 molar excess of LiCl was added to the reaction, the 8-coordinate $[MCl_2(OH_2)(EO4)]Cl$. These complexes crystallize in the monoclinic space group Cc with $Z = 4$ and cell parameters as follows: M = Sm, $a = 12.952$ (5) Å, $b = 9.348$ (4) Å, $c = 13.764$ (6) Å, $\beta = 110.91$ (4)°, $D_{calc} = 2.00$ g cm^{-3}; M = Eu, $a = 12.932$ (4) Å, $b = 9.336$ (4) Å, $c = 13.733$ (2) Å, $\beta = 110.90$ (2)°, $D_{calc} = 2.02$ g cm^{-3}; M = Gd, a 12.925 (4) Å, $b = 9.332$ (1) Å, $c = 13.724$ (2) Å, $\beta = 110.96$ (2)°, $D_{calc} = 2.04$ g cm^{-3}; M = Tb, $a = 12.880$ (4) Å, $b = 9.318$ (8) Å, $c = 13.696$ (8) Å, $\beta = 110.90$ (4)°; $D_{calc} = 2.06$ g cm^{-3}; M = Tm, $a = 12.822$ (2) Å, $b = 9.277$ (1) Å, $c = 13.608$ (1) Å, $\beta = 110.94$ (1)°, $D_{calc} = 2.14$ g cm^{-3}. The anhydrous, 8-coordinate $[EuCl_3(EO4)]$, produced from a 6:1:1 molar excess of LiCl, is triclinic, $P\bar{1}$, with $a = 7.590$ (4) Å, $b = 8.895$ (2) Å, $c = 11.672$ (4) Å, $\alpha = 91.09$ (2)°, $\beta = 102.04$ (3)°, $\gamma = 109.48$ (3)°, and $D_{calc} = 2.08$ g cm^{-3} for $Z = 2$.

Introduction

We are investigating the structural chemistry of macrocyclic and polyfunctional acyclic chelating agent complexes of the lanthanides. Crystallographic study of the solid state gives vital information on the effect of complexation on the steric environment of the metal coordination sphere and other fundamental parameters governing coordination. We have thus far spent a good deal of time investigating[1] the simplest examples of these ligands, crown ethers and polyethylene glycols[2] (PEG's).

Isolation of directly coordinated lanthanide chloride crown ether complexes has been less than straightforward. While reactions of the early to middle lanthanide chlorides with 18-crown-6[3,4] and all of the lanthanide chlorides with 12-crown-4[5] (two macrocycles which are of sizes that bracket the cavity found for 15-crown-5) produce direct coordination, under similar conditions we have only been able to isolate second-sphere, hydrogen-bonded complexes of 15-crown-5 with hydrated lanthanide chloride salts.[6–9] Other

reports of 15-crown-5 lanthanide complexes have appeared with crystallographic characterization of a few early lanthanide nitrates[10–17] and $[YbCl_2(15\text{-crown-}5)][AlCl_2Me_2]$.[18]

PEG's do not have a specific cavity size to vary as crown ethers do; however, they have certain properties that could make them useful complexing agents. (1) PEG's are inexpensive and commercially available, whereas crown ethers are often hard to synthesize and expensive. (2) PEG's are nontoxic. (3) Crown ethers are not ionizable unless modified, while PEG's are ionizable. (4) PEG's have greater solubility in aqueous and organic media, and complexation in the presence of acid is more easily achieved. (5) The PEG's wrap the metal ion, presenting a hydrophobic exterior coordination sphere, while crown ethers often leave coordination

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sites open that are occupied by H_2O molecules.

Hirashima[19-25] has published several accounts of PEG derivatives of hydrated lanthanide nitrates and one account of hydrated lanthanide chlorides. These papers suggest that fractional crystallization using PEG's could result in reasonable separations of the lanthanides. Myasoedov has investigated the extraction of actinides in two-phase H_2O/PEG/salt systems in both the presence and absence of ionic extractants.[26,27] Only a few structures of these glycols complexed with the lanthanides have been reported ([M(NO$_3$)$_3$(EO3)] (M = Nd,[23] Eu[28]), [M-(NO$_3$)$_3$(EO4)] (M = La,[29] Nd[21]), and [Nd(NO$_3$)$_2$(EO5)]-[NO$_3$][22]). Our previous contribution to this area surveyed the coordination of triethylene glycol (EO3) with the hydrated lanthanide chlorides.[30] In the current work with EO4, we have focused on finding the structural transition points and on modification of metal ion coordination sphere.

Synthetic Results

The reaction of hydrated lanthanide chloride salts with tetraethylene glycol in a 1:1 molar ratio in a 1:3 mixture of methanol and acetonitrile has produced 1:1 tetraethylene complexes of all of the lanthanides and prelanthanides (Pm was not investigated). Analytical and structural data have confirmed the formation of four major structural types of coordination complexes. Lanthanum forms a 9-coordinate anhydrous dimer, [LaCl$_3$(EO4)]$_2$. The lanthanides Ce–Yb form 9-coordinate tetrahydrates upon crystallization: [MCl(OH$_2$)$_3$(EO4)]Cl$_2$·H$_2$O for M = Ce–Nd and Sm–Gd and [M(OH$_2$)$_4$(EO4)]Cl$_3$ for M = Tb–Yb and Y. These compounds, which have identical composition, differ in their primary coordination sphere. The larger, earlier lanthanides are able to accommodate a chloride ion in the primary sphere; as the lanthanides decrease in size, the sterically more bulky chloride ion is forced out of the primary coordination sphere and is replaced by a water molecule. The smallest ion studied, Lu^{3+}, forms the 7-coordinate species [LuCl$_2$(EO4)]Cl·H$_2$O.

The effect of the decreasing size of the lanthanide ions is demonstrated by the change of coordination number from 9 to 7 across the series. As the ions become smaller they are less able to support the higher coordination numbers or the more bulky chloride ions. Toward the end of the series we have observed the thulium reaction to produce three crystalline forms, the 9-coordinate complex mentioned above, a second 9-coordinate compound in which a methanol molecule occupies one of the inner-sphere sites instead of a water molecule on 60% of the metal ions in the crystalline lattice, [Tm(OH$_2$)$_{4-x}$(OHMe)$_x$(EO4)]Cl$_3$·(1 − x)(H$_2$O) (x = 0.60), and an eight-coordinate complex, [TmCl$_2$(OH$_2$)-(EO4)]Cl. All three complexes were obtained from the same reaction vessel. Elemental analysis of thulium complexes of EO4 were not completely consistent with any one of these forms. It appears that Tm and Yb are transition points between 9-, 8-, and 7-coordinate complexes. As a result of the competition in solution, crystallization of any complex was much more difficult with thulium and ytterbium than any of the other lanthanides. Both exhibited a tendency toward oil formation upon concentration.
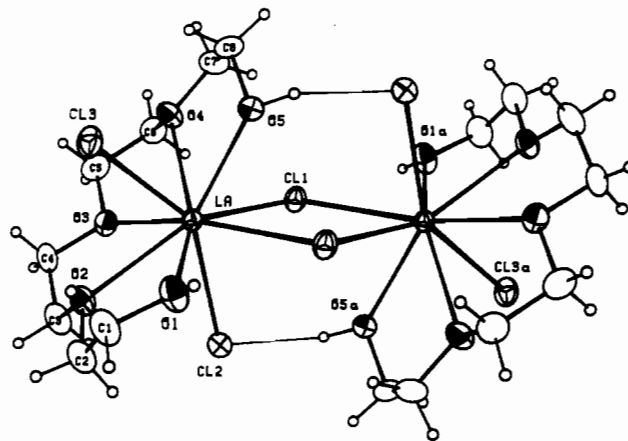
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Figure 1. ORTEP illustration of [LaCl$_3$(EO4)]$_2$. The non-hydrogen atoms are represented by their 50% probability ellipsoids for thermal motion. The hydrogen atoms have been arbitrarily reduced. The halves of the dimer are related by −x, 1 − y, 1 − z.

This was not observed in any other of the EO4 complexes studied.

The La^{3+} complex is difficult to isolate in crystalline form. After several months of very slow evaporation in one reaction tube, very small crystals of the complex were isolated around the cap of the tube. Similar difficulty in obtaining quality crystals of the EO3 complexes of La^{3+}–Pr^{3+} were noted in our previous study.[30] As found in that work, the only crystalline complex isolated for La^{3+} was a dimer.

Complexes of the lanthanides and polyethylene glycols have the greatest tendency to form precipitates with the early lanthanides. This was observed in the present work, and our previous investigations with EO3[30] and was also noted by Hirashima.[19-25] Lanthanum and cerium formed large amounts of a flocculent precipitate. Neodymium and samarium formed much smaller amounts of precipitates, which were purple and pale yellow, respectively. Analyses of the precipitates matched the composition of the crystalline forms.

Modification of the metal ion's coordination sphere was accomplished with a salting out agent, LiCl. Lithium chloride was utilized because (1) lithium is unlikely to compete with the lanthanides in glycol complexation, (2) its high hydration energy can help to dehydrate the metal ion, and (3) it increases the anion concentration in solution.

Lanthanide EO4 complexes prepared with lithium chloride show a decrease in the number of water molecules in the complex as well as a decrease in coordination number. The latter may be a consequence of forcing more chloride ions into the metal's primary coordination sphere.

Complexes of Sm–Tb were prepared by using a 4:1:1 molar ratio of LiCl/lanthanide chloride hydrate salt/tetraethylene glycol. The 8-coordinate complexes [MCl$_2$(OH$_2$)(EO4)]Cl were formed. (These are isostructural with the 8-coordinate thulium complex discussed earlier.) A europium complex was prepared by using a 6:1:1 molar ratio of LiCl/EuCl$_3$·nH$_2$O/EO4, resulting in the anhydrous 8-coordinate complex, [EuCl$_3$(EO4)]. Utilizing a 4:1:1 mixture of LiCl–salt–EO4 with NdCl$_3$·nH$_2$O yielded the same 9-coordinate complex obtained without LiCl.

In every case thus far investigated, crystallization has occurred in a similar fashion. After the removal of any precipitate and the reduction of solvent volume, either under vacuum or by slow evaporation, a system of two immiscible liquids formed. During solvent reduction, a layer of more viscous material would form in the bottom of the reaction vessel. In the case of colored solutions, the lower layer retains the color. The existence of two-layer PEG/salt systems with salt rich lower layers has been observed by Albertsson.[31] Crystals were always obtained from the bottom layer fairly easily by the programmed cooling of these "two-layer"

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Figure 2. Primary coordination sphere of [CeCl(OH$_2$)$_3$(EO4)]Cl$_2$·H$_2$O.

Figure 3. Primary coordination sphere of [Tb(OH$_2$)$_4$(EO4)]Cl$_3$. H(1)[O(5)] is obscured in this view.

systems. Crystals first occur at the liquid/liquid interface, after which any disturbance or bumping of the reaction vessel resulted in immediate crystallization of the remaining material and disappearance of the two-layer system.

Structural Results

[LaCl$_3$(EO4)]$_2$. An ORTEP illustration of this 9-coordinate dimer is presented in Figure 1; important distances and angles are averaged in Table I. The complex is bridged by two symmetry-related chloride ions. The halves of the dimer are related by a center of inversion. Each lanthanum has five coordination sites occupied by the glycol and four sites occupied by chloride ions. The geometry is that of a distorted tricapped trigonal prism. The alcoholic oxygen atoms O(1) and O(5), the etheric oxygen atom O(3), and the chloride ions Cl(1), Cl(2), and Cl(3), form a trigonal prism with the etheric oxygen atoms O(2) and O(4) and the chloride ion Cl(1)^a capping the three quadrilateral faces. The glycol oxygen atoms alternate along the acyclic chain from prismatic to capping sites. The O–C–C–O torsion angles alternate ±g(60°) (Table II), and the C–O–C–C torsion angles are all anti (180°). This symmetric conformation of the glycol chain is similar to the D_{3d} conformation commonly observed for 18-crown-6.

The halves of the dimer are hydrogen bonded between the glycol oxygens O(5) and O(5)^a and the chloride ions Cl(2) and Cl(2)^a. The two remaining alcoholic oxygen atoms (O(1), O(1)^a) hydrogen bond to symmetry-related Cl(3) positions in two different dimers, resulting in a polymeric hydrogen bonded chain of dimers along *b*.

[MCl(OH$_2$)$_3$(EO4)]Cl$_2$·H$_2$O (M = Ce–Nd, Sm–Gd). An ORTEP illustration of the structure for M = Ce is presented in Figure 2 with average bonding parameters given in Table I. Each metal ion is 9-coordinate, three coordination sites being occupied by water molecules, five sites by the EO4 ligand and one site by a chloride ion. The geometry is that of a distorted tricapped trigonal prism. The alcoholic oxygen atoms O(1) and O(5), the etheric O(3), two water molecules, O(6) and O(7), and the chloride ion, Cl(1), form the trigonal prism. The water molecule O(8) and etheric oxygen atoms O(2) and O(4) cap the three quadrilateral faces. The glycol oxygen atoms alternate along the acyclic chain from prismatic to capping sites. The O–C–C–O torsion angles are g$^+$(C(1)–C(2)), g$^-$, g$^-$, g$^+$. The C–O–C–C angles are all anti except for C(4)–O(3)–C(5)–C(6), which occurs between C–C torsion angles of like sign and deviates toward g$^-$ (101.8° for M = Ce, Table II).

The glycol and water molecule hydrogen atoms interact with the chloride ions in a polymeric network of hydrogen bonding. There are 10 possible hydrogen atoms that can participate in
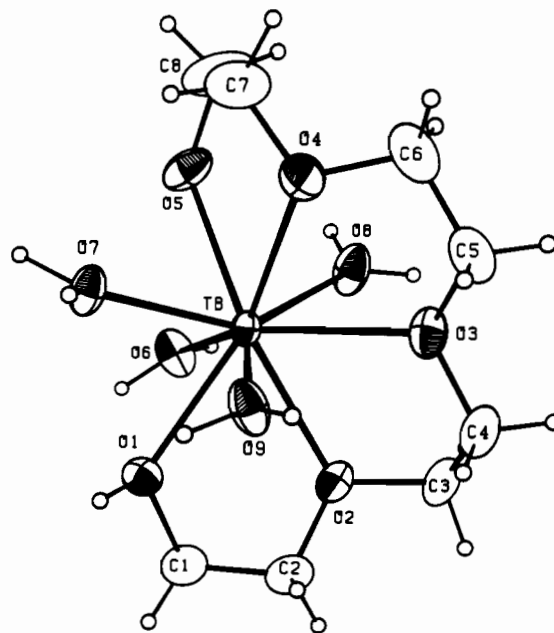
hydrogen bonding and each one does so. There are nine O–H⋯Cl$^-$ hydrogen bonds. Cl(1) accepts two hydrogen bonds, Cl(2) three, and Cl(3) accepts four. The uncoordinated water molecule (O(9)) accepts one hydrogen bond and donates two hydrogen bonds.

[M(OH$_2$)$_4$(EO4)]Cl$_3$ (M = Tb–Yb, Y). Figure 3 illustrates the coordination environment for M = Tb; Table I gives important average distances and angles. These 9-coordinate complexes are also tricapped trigonal prismatic. Four coordination sites are occupied by water molecules, and five, by the EO4 ligand. There are no tight ion pairs in these complexes. The four water molecules, O(6–9), and two etheric glycol oxygen atoms (O(2) and O(4)) form a trigonal prism with the alcoholic glycol oxygen atoms (O(1) and O(5)) and the etheric glycol oxygen atom (O(3)) capping the quadrilateral faces. The glycol oxygen atoms alternate along the acyclic chain from capping to prismatic sites. Unlike the previous series, however, the alcoholic oxygen atoms are capping and the resulting conformation of the glycol is different. The O–C–C–O torsion angles are g$^-$(C(1)–C(2)), g$^-$, g$^+$, g$^+$. The C–O–C–C angles are all anti except for C(2)–O(2)–C(3)–C(4) and C(6)–O(4)–C(7)–C(8), which occur between C–C torsion angles of like sign and deviate toward g$^-$ (–98.9° for M = Tb, Table II) and g$^+$(95.6° for M = Tb), respectively.

As observed for the previous series, an intricate polymeric network of hydrogen bonding exists. All 10 of the available hydrogen atoms participate in single hydrogen bonds. Cl(2) accepts four hydrogen bonds; Cl(1) and Cl(3) each accept three.

[Tm(OH$_2$)$_{4-x}$(OHMe)$_x$(EO4)]Cl$_3$·(1 – x)(H$_2$O) (x = 0.60). The 9-coordinate tricapped-trigonal-prismatic geometry of this complex is similar to that observed for [M(OH$_2$)$_4$(EO4)]Cl$_3$ and is depicted in Figure 4. In 60% of the coordination sites O(9) is part of a methanol molecule (with C(9), which has 0.60 occupancy) and is hydrogen bonded to Cl(2). In 40% of the coordination sites O(9) is a water molecule hydrogen bonded to both Cl(2) and uncoordinated water molecule O(10). O(10) is only present near those coordination sites where O(9) is a water molecule and thus has 0.40 occupancy. The remaining hydrogen bonding from O(1), O(5), O(6–8), and O(10) (when it is present) are all to chloride ions: three to Cl(1) and 3.4 each to Cl(2) and Cl(3).

The glycol coordination and coordination geometry are similar to those of the series [MCl(OH$_2$)$_3$(EO4)]Cl$_2$·H$_2$O (M = Ce–Nd, Sm–Gd) rather than to those of the more closely related [M-(OH$_2$)$_4$(EO4)]Cl$_3$ (M = Tb–Yb). The glycol starts with the alcoholic ends in prismatic sites with disordered O(9), the water molecules O(7) and O(8), and the etheric O(3). The etheric O(2) and O(4) along with the O(6) water molecule cap the quadrilateral
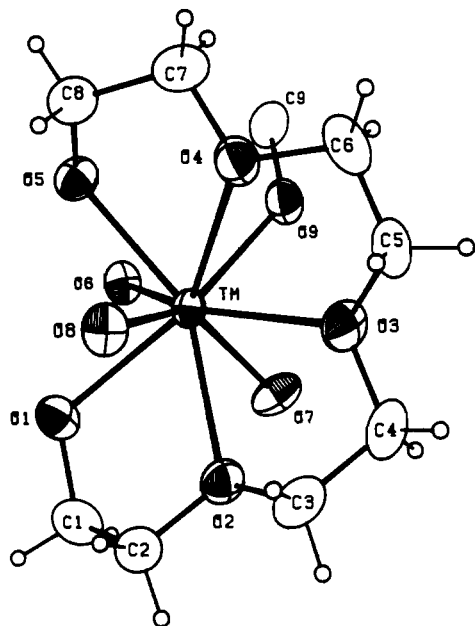
Figure 4. Metal coordination of the major form in [Tm(OH$_2$)$_{4-x}$-(OHMe)$_x$(EO4)]Cl$_3$·(1 - x)(H$_2$O) (x = 0.60). In the 40% form, O(9) is a water molecule and C(9) is not present.
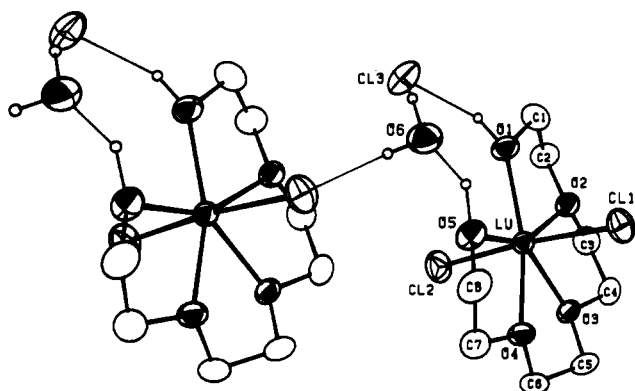
Figure 5. Portion of the polymeric hydrogen-bonded chains in [LuCl$_2$-(EO4)]Cl·H$_2$O. The atoms in the chain are related by x - 1, y, z.

faces of the trigonal prism. The O–C–C–O torsion angles are sequenced g⁻, g⁺ g⁺, g⁻, with the corner and only C–O–C–C torsion angle to deviate from anti (C(3)–C(4)–O(3)–C(5) = 116.6°, Table II) containing the prismatic O(3).

[LuCl$_2$(EO4)]Cl$_2$·H$_2$O. As shown in Figure 5, the Lu³⁺ ion is 7-coordinate, five coordination sites being occupied by the EO4 ligand and the remaining two being occupied by chloride ions. The complex forms a distorted-pentagonal-bipyramidal geometry with the five glycol oxygen atoms in the equatorial sites and the chloride ions in axial sites. The five glycol oxygen atoms are planar to within 0.097 Å, with Lu 0.049 Å out of this plane. The distortion occurs with the axial chloride ions. Each is distorted away from the noncoordinated chloride ion Cl(3) toward O(3). The Cl(1)–Lu–Cl(2) angle is 174.51 (7)°. Seven-coordinate complexes of lanthanide chlorides and EO3 were observed for Dy–Lu with all three chloride ions coordinated to the metal.[30] The lack of three bulky chloride positions may be the reason this coordination number is only observed for the small Lu³⁺ ion in this study.

The torsion angles around the ligand are as follows (starting with O(1)–C(1)–C(2)–O(2)): g⁻, a, a, g⁺, a, a, g⁻, a, a, g⁺. This sequence, with the O–C–C–O torsion angles alternating g± and all C–O–C–C angles anti, is similar to that found for the full-symmetry D$_{3d}$ conformation of 18-crown-6, and the same conformation we observed for the La/EO4 complex.

The glycol hydrogen atoms and water hydrogen atoms participate in hydrogen bonds with one of the axial chloride ions (Cl(1)) and the noncoordinated chloride ion. Hydrogen bonding
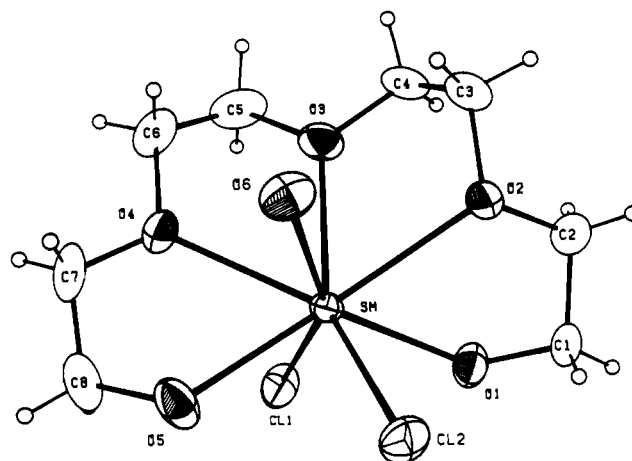

Figure 6. Primary coordination sphere of [SmCl$_2$(OH$_2$)(EO4)]Cl.

to Cl(1) results in a lengthening of the Lu–Cl(1) distance (2.562 (2) Å) compared to the Lu–Cl(2) separation of 2.530 (2) Å. Cl(1) accepts one hydrogen bond from the noncoordinated water molecule O(6). Cl(3) accepts two hydrogen bonds, and O(6) accepts one hydrogen bond and donates two. The interactions to and from Cl(1) and O(6) create hydrogen-bonded polymeric chains propagating along a.

[MCl$_2$(OH$_2$)(EO4)]Cl (M = Sm–Tb, Tm). Each metal ion is 8-coordinate, five coordination sites being occupied by the EO4 ligand, two being occupied by chloride ions and one being occupied by a water molecule. The very distorted bicapped-trigonal-prismatic geometry is shown in Figure 6 (M = Sm). The alcoholic oxygen atoms O(1) and O(5), the etheric oxygen atom O(3), the chloride ions Cl(1) and Cl(2), and the water molecule O(6) form a trigonal prism with the etheric oxygen atoms O(2) and O(4) capping two of the quadrilateral faces. The glycol oxygen atoms alternate along the acyclic chain from prismatic to capping sites. The O–C–C–O torsion angles are g⁺(C(1)–C(2)), g⁺, g⁻, g⁺. The C–O–C–C angles are all anti except for C(2)–O(2)–C(3)–C(4), which occurs between C–C torsion angles of like sign and deviates toward g⁺ (92.3° for M = Sm, Table II). The EO4 ligands in the tetrahydrates also have at least one g, g, a, g segment; however, they occur in the portion of each chain containing an etheric oxygen atom in a prismatic site in those complexes.

The four glycol and water molecule hydrogen atoms interact with the chloride ions in a polymeric network of hydrogen bonding. Coordinated Cl(1) accepts one hydrogen bond, and the noncoordinated Cl(3) accepts three. There is an elongation of the M–Cl(1) separations compared to M–Cl(2) in each complex as a result of the hydrogen bonding to Cl(1).

[EuCl$_3$(EO4)]. This anhydrous unsolvated complex is depicted in Figure 7. The metal ion is 8-coordinate with five coordination sites occupied by the EO4 ligand and three by the chloride ions. The geometry is dodecahedral. The alcoholic oxygen atoms O(1) and O(5) and the etheric oxygen atoms O(2) and O(4) occupy the A sites. The etheric oxygen atom O(3) and the chloride ions occupy the B sites. The C(7)–C(8) ethylene linkage is disordered. In one conformation, the O–C–C–O torsion angles are g⁻(C-(1)–C(2)), g⁺, g⁻, g⁻. The C–O–C–C angles are all anti except for C(5)–C(6)–O(4)–C(7), which occurs between C–C angles of like sign and deviates toward g⁻ (-97.5°, Table II). In the disordered conformation the C(7)'–C(8)' torsion angle is g⁺; however the disorder makes it difficult to ascertain whether the distorted C–C–O–C angles in this region are significant or a crystallographic artifact of the proximity of the disordered positions.

Discussion

Table I summarizes the structural features observed for the EO4 complexes and several comparative examples. The expected trends corresponding to the decreasing ionic radius across the series are realized. The range in ionic radii in [MCl(OH$_2$)$_3$(EO4)]-Cl$_2$·H$_2$O complexes (M = Ce–Gd) is 0.089 Å[35] and the observed ranges in the parameters tabulated in Table I average 0.075 Å.

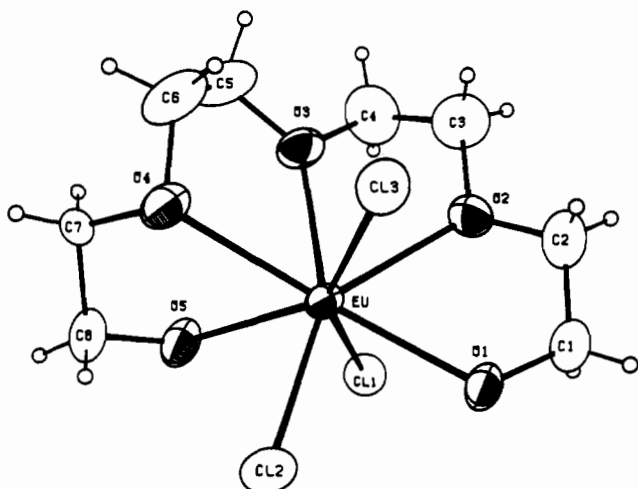**Table I. Comparison of Bonding Parameters in Lanthanide Tetraethylene Glycol Complexes**

complex	CN	IR,[a] Å	G[b]	M–Cl(av), Å prismatic	M–Cl(av), Å other	M–OH₂(av), Å capping	M–OH₂(av), Å prismatic	M–OH₂(av), Å capping	M–EO4(av), Å alcoholic prismatic	M–EO4(av), Å alcoholic other	M–EO4(av), Å etheric capping	M–EO4(av), Å etheric prismatic	M–EO4(av), Å etheric other	ref
[LaCl₃(EO4)]₂	9	1.216	tctp	3.013 (2) (br)[d]; 2.85 (1) (term)	2.932 (2) (br, cap)				2.57 (1)		2.68 (2)	2.690 (5)		f
[MCl(OH₂)₃(EO4)]Cl₂·H₂O														
M = Ce	9	1.196	tctp	2.843 (1)		2.543 (3)	2.50 (2)		2.48 (1)		2.61 (2)	2.572 (3)		f
M = Pr	9	1.179	tctp	2.8226 (9)		2.543 (2)	2.48 (3)		2.47 (1)		2.59 (2)	2.565 (2)		f
M = Nd	9	1.163	tctp	2.813 (1)		2.529 (3)	2.46 (3)		2.45 (2)		2.58 (2)	2.541 (3)		f
M = Sm	9	1.132	tctp	2.786 (1)		2.503 (4)	2.43 (3)		2.41 (2)		2.56 (1)	2.526 (4)		f
M = Eu	9	1.120	tctp	2.770 (2)		2.488 (6)	2.41 (3)		2.42 (1)		2.55 (1)	2.501 (6)		f
M = Gd	9	1.107	tctp	2.770 (1)		2.495 (4)	2.41 (3)		2.39 (1)		2.54 (1)	2.502 (4)		f
[M(OH₂)₄(EO4)]Cl₃														
M = Tb	9	1.095	tctp				2.388 (8)	2.45 (2)			2.489 (3)	2.466 (8)		f
M = Dy	9	1.083	tctp				2.38 (1)	2.44 (2)			2.474 (3)	2.457 (8)		f
M = Y	9	1.075	tctp				2.36 (1)	2.43 (2)			2.470 (3)	2.44 (1)		f
M = Ho	9	1.072	tctp				2.36 (1)	2.43 (2)			2.461 (3)	2.451 (8)		f
M = Er	9	1.062	tctp				2.36 (1)	2.42 (2)			2.461 (4)	2.431 (4)		f
M = Tm	9	1.052	tctp				2.34 (1)	2.42 (2)			2.445 (3)	2.43 (2)		f
M = Yb	9	1.052	tctp				2.34 (1)	2.41 (3)			2.452 (6)	2.43 (1)		f
[Tm(OH₂)₄₋ₓ(OHMe)ₓ(EO4)]Cl₁·(1 − x)(H₂O) (x = 0.60)	9	1.052	tctp			2.411 (5)	2.350 (1)	2.36 (2)			2.400 (5)	2.51 (5)		f
[LuCl₂(EO4)]ClH₂O	7	0.919[c]	pbp		2.55 (2) (ax)					2.24 (1) (eq)			2.31 (1) (eq)	f
[MCl₂(OH₂)(EO4)]Cl														
M = Sm	8	1.079	bctp	2.68 (3)			2.428 (5)		2.440 (8)		2.557 (4)	2.492 (5)		f
M = Eu	8	1.066	bctp	2.67 (3)			2.413 (6)		2.43 (1)		2.555 (4)	2.484 (7)		f
M = Gd	8	1.053	bctp	2.66 (3)			2.41 (1)		2.42 (1)		2.55 (1)	2.45 (1)		f
M = Tb	8	1.040	bctp	2.65 (3)			2.379 (6)		2.418 (2)		2.540 (3)	2.479 (7)		f
M = Tm	8	0.994	bctp	2.61 (2)			2.331 (7)		2.362 (2)		2.51 (1)	2.419 (8)		f
[EuCl₃(EO4)]	8	1.066	dod		2.70 (6) (B-site)					2.450 (2) (A-site)			2.526 (5) (A-site) 2.473 (6) (B-site)	f
[LaCl₂(OH₂)₂(EO3)]₂Cl₂	9	1.216	tctp	2.872 (2) (br) 2.862 (2) (term)	2.959 (2) (br, cap)		2.57 (1)	2.656 (6)	2.556 (5)		2.596 (6)	2.621 (6)		32
[Nd(OH₂)₃(EO3)]Cl₃	9	1.163	tctp			2.506 (7)	2.500 (8)	2.480 (7)	2.469 (7)		2.596 (7)	2.500 (8)		30
[Gd(OH₂)₃(EO3)]Cl₃	9	1.107	tctp			2.455 (6)	2.451 (7)	2.440 (5)	2.408 (5)		2.564 (6)	2.466 (7)		30
[LuCl₃(EO3)]	7	0.919[c]	pbp		2.584 (2) (ax) 2.547 (2) (eq)					2.279 (5) (eq)			2.351 (5) (eq)	30
[CeCl(OH₂)₃(EG4)]Cl₂·H₂O	9	1.196	tctp	2.786 (3)			2.50 (2)				2.63 (3)	2.62 (3)		32
[Nd(NO₃)₃(EO4)]	11	1.23[c]	mcpap											21
[La(NO₃)₃(15-crown-5)]	11	1.32[c]	mcpap									2.68 (3)		13
[Eu(NO₃)₃(15-crown-5)]	11	...	mcpap							2.51 (3)		2.63 (6)	2.65 (4)	10, 34
[NdCl₃(15-crown-5)]	8	1.109	bctp	2.70 (1)							2.630 (9)	2.55 (4)		32
[BiCl₃(15-crown-5)]	8	1.17	bctp	2.530 (7)	2.549 (5) (cap)						2.88 (1)	2.83 (5)		32
[BiCl₃(EO4)]	8	1.17	bctp	2.54 (2)	2.58 (2) (cap)				2.72 (8)		2.78 (5)	2.83 (4)		32

[a]Ionic radius for M³⁺ and CN shown from ref 35. [b]Coordination geometries: tctp = tricapped trigonal prism; pbp = pentagonal bipyramid; bctp = bicapped trigonal prism; dod = dodecahedron; mcpap = monocapped pentagonal antiprism. [c]Extrapolated from data in ref 35. [d]br = bridging, term = terminal, cap = capping, ax = axial, and eq = equatorial. [e]EG4 = tetraglyme. [f]This study.

Table II. Representative Torsion Angles (deg) for the Series of Tetraethylene Glycol Complexes

angles	$[LaCl_3(EO4)]_2$	$[CeCl(OH_2)_3$ $(EO4)]Cl_2\cdot$ H_2O	$[Tb(OH_2)_4\cdot$ $(EO4)]Cl_3$	$[Tm(OH_2)_{4-x}\cdot$ $(OHMe)_x(EO4)]Cl_3\cdot$ $(1-x)(H_2O)$ $(x=0.60)$	$[LuCl_2(EO4)]Cl\cdot$ H_2O	$[SmCl_2(OH_2)$ $(EO4)]Cl$	$[EuCl_3(EO4)]$
O(1)–C(1)–C(2)–O(2)	−55.8	50.9	−50.7	−53.5	−49.4	52.3	−46.0
C(1)–C(2)–O(2)–C(3)	−174.7	177.4	−173.7	−176.3	−169.8	−167.6	−170.9
C(2)–O(2)–C(3)–C(4)	165.1	−169.2	−98.9	174.7	179.6	92.3	175.5
O(2)–C(3)–C(4)–O(3)	57.8	−57.1	−51.8	52.5	50.2	52.6	51.2
C(3)–C(4)–O(3)–C(5)	179.6	−176.5	−167.9	116.6	179.3	150.1	121.9
C(4)–O(3)–C(5)–C(6)	174.1	−101.8	177.2	175.9	−177.5	−143.5	−147.5
O(3)–C(5)–C(6)–O(4)	−57.3	−59.0	47.7	50.3	−55.0	−50.4	−42.6
C(5)–C(6)–O(4)–C(7)	−161.9	−172.6	174.7	170.6	−171.7	−169.9	−85.0
C(6)–O(4)–C(7)–C(8)	178.9	178.7	95.6	175.2	171.4	174.7	160.0
O(4)–C(7)–C(8)–O(5)	53.5	53.1	49.0	−52.8	51.7	48.9	−55.9
C(5)–C(6)–O(4)–C(7)′							−97.5
C(6)–O(4)–C(7)′–C(8)′							99.2
O(4)–C(7)′–C(8)′–O(5)							40.9

Figure 7. ORTEP illustration of $[EuCl_3(EO4)]$. The ethylene group C(7)–C(8) is disordered into two conformations.

In the $[M(OH_2)_4(EO4)]Cl_3$ (M = Tb–Yb, Y) and the $[MCl_2\text{-}(OH_2)(EO4)]Cl$ (M = Sm–Tb, Tm) complexes, the ranges in ionic radii and average parameter ranges are 0.053 and 0.042 Å for M = Tb–Yb and Y and 0.085 and 0.073 Å for M = Sm–Tb and Tm. These values are certainly within a 3σ confidence level of being a result of the decreasing ionic radii.

No obvious relationships are found when the lanthanide chloride triethylene glycol results are compared with those for EO4. The Lu–Cl and Lu–O distances are consistently shorter in $[LuCl_2\text{-}(EO4)]Cl\cdot H_2O$ than in $[LuCl_3(EO3)]$;[30] however the average difference of 0.038 Å is at the edge of statistical significance. No obvious trend like this is observed when the 9-coordinate lanthanide chloride complexes of EO3 and EO4 are compared.

We have isolated and structurally characterized one tetraglyme (EG4) complex of $CeCl_3\cdot nH_2O$. While this complex, $[CeCl\text{-}(OH_2)_3(EG4)]Cl_2\cdot H_2O$,[32] has the same formulation, metal ion geometry, and inner-sphere ligands as the EO4 complex, the glyme chain starts in a capping position such that the two ends, O(1) and O(5), and the central oxygen, O(3), occupy the three capping positions. In the EO4 complex of Ce³⁺, the chain starts in a prismatic position. The resulting sequence of torsion angles in the glyme chain is different, with O–C–C–O angles sequenced g^+, g^+, g^-, g^+. This conformation is identical with that observed in the $[MCl_2(OH_2)(EO4)]Cl$ series of complexes. These latter complexes, although 8-coordinate, also had the terminal oxygen atoms in the capping positions of a distorted-bicapped-trigonal-prismatic geometry.

The Ce–O distances in each category for the EO4 and EG4 complex are identical at 3σ. The shorter Ce–Cl separation of 2.786 (3) Å in the glyme complex versus 2.843 (1) Å in the glycol

complex is probably a result of one less hydrogen bond to this chlorine position in the former.

Although limited by the scarcity of structurally characterized lanthanide 15-crown-5 complexes, a few comparisons are made in Table I. After correction is made for differences in ionic radii, the 15-crown-5 complexes of nitrate salts exhibit shorter Ln–O-(etheric) distances and the chloride salts longer separations than their EO4 analogues. A similar comparison with $[La(NO_3)_3\text{-}(EO4)]$[29] and $[Nd(NO_3)_3(EO4)]$[21] reveals that the Ln–O(glycol) distances are in general shorter in the tetraethylene glycol complexes of nitrate salts than observed for chloride salts.

The competition between chloride ions and H_2O molecules in the primary coordination sphere is dictated by ion size. The largest ion, La³⁺, is 9-coordinate with four chloride ions in the coordination sphere, in addition to the glycol. One choride ion and three H_2O molecules complete the coordination to M = Ce–Gd, while there are no tight ion pairs for M = Tb–Yb. Only by reduction of the coordination number can more chloride ions reside in the primary coordination spheres, as observed for $[MCl_2(OH_2)(EO4)]Cl$ (M = Sm–Tb, Tm), $[EuCl_3(EO4)]$, and $[LuCl_2(EO4)]Cl\cdot H_2O$.

A major feature of structural interest is the conformation of the glycol ligand. In $[LaCl_3(EO4)]_2$ and $[LuCl_2(EO4)]Cl\cdot H_2O$ the glycol adopts a symmetrical conformation very similar to the D_{3d} form of 18-crown-6. This same conformation was observed in $[M(NO_3)_3(EO4)]$ (M = La²⁹, Nd²¹). The tetrahydrate complexes reveal similar but different conformations. The lighter lanthanides have glycol coordination alternating from prismatic to capping sites, while the heavier tetrahydrates have glycol co-ordination from capping to prismatic sites. Corners occur when an etheric oxygen atom resides in a prismatic site. Thus, the sequence of O–C–C–O torsion angles for M = Ce–Gd and $[Tm\text{-}(OH_2)_{4-x}(OHMe)_x(EO4)]Cl_3\cdot(1-x)(H_2O)$ $(x = 0.60)$ is g^+, g^-, g^-, g^+, with the prismatic O(3) between C–C torsion angles of like sign. For the M = Tb–Yb tetrahydrates this same sequence is g^-, g^-, g^+, g^+ where O(2) and O(4) are prismatic and are between C–C torsion angles of like sign. In the 8-coordinate monohydrates and anhydrous Eu³⁺ complex, yet another glycol conformation is observed where all of the O–C–C–O torsion angles are g and all but one have the same relative sign.

It is interesting to compare the results obtained here with the ionic lanthanide ions to a softer metal ion such as Bi³⁺. Whereas coordination of the lanthanides is most greatly affected by the ionic radius, 15-crown-5 and EO4 complexes of $BiCl_3$ reveal that the covalent Bi–Cl bonds are the most important feature in these coordination complexes. In $[BiCl_3(15\text{-crown-}5)]$[32] and $[BiCl_3\text{-}(EO4)]$,[32] the Bi³⁺ ions have identical coordination spheres and the 15-crown-5 and EO4 ligands have identical conformations.

Isolation of complexes of EO4 with lanthanide chlorides is relatively easy, contrasted to the formation of second-sphere hydrogen-bonded complexes of 15-crown-5. Reactions identical with those reported here, but with 15-crown-5 substituted for EO4, produced $[M(OH_2)_8]Cl_3\cdot15\text{-crown-}5$,[6-8] $[Nd(OH_2)_9]Cl_3\cdot15\text{-crown-}5\cdot H_2O$,[9] and $[NdCl_2(OH_2)_6]Cl\cdot15\text{-crown-}5$.[9] Only under the stringent conditions of electrocrystallization have we been able to isolate a directly coordinated 15-crown-5 to a lanthanide

(32) Rogers, R. D.; Nunez, L.; Rollins, A. N.; Bond, A. H.; Henry, R. F. Unpublished results, 1990.

chloride, [MCl$_3$(15-crown-5)] (M = Pr, Nd).[32] Formation of a 15-crown-5 complex with early lanthanide nitrates is somewhat easier and [M(NO$_3$)$_3$(15-crown-5)] (M = La,[13] Eu[10]) have been isolated and structurally characterized. Second-sphere complexes such as [Y(NO$_3$)$_2$(OH$_2$)$_5$][NO$_3$]·2(15-crown-5)[33] are also known, however.

The lower cost and increased coordinative ability of glycols could bode well for their use in lanthanide separations if the size selectivity is great enough. Some of the necessary complexation features are there, having been observed in our studies and those of Hirashima:[19–25] yields decrease with increasing atomic number, precipitation markedly decreases across the series, and the heavier lanthanides crystallize much more slowly.[25] All complexation is affected by stoichiometry and the amount of H$_2$O present in the solution. Fractional quantitative crystallization or precipitation has been proposed as a technique for lanthanide separations.[19] We would like to add that the ready formation of a two-layer system in solutions of these complexes could form the basis for a separation process and is being actively investigated by us.

The structural transitions points occur at La/Ce, Gd/Tb, Er/Tm, and Yb/Lu. The most dramatic changes occur at Er/Tm and Yb/Lu where the coordination number drops from 9 to 8 and from 8 to 7, respectively. The difficulty others have had in isolating and crystallizing stable glycol complexes of the later lanthanides may be due to solution dynamics where several competing forms are present. The three complex forms isolated for M = Tm, for example, reveal a very close competition between solvent, H$_2$O molecules, and chloride ions, the balance resulting in either 9-coordinate or 8-coordinate complexes.

In the EO3 series,[30] transition points between CN = 10 and CN = 9 occurred at Ce/Nd and between CN = 9 and CN = 7 at Tb/Dy. Notably, two forms were isolated for Dy–Er with the 7-coordinate form increasing from a very minor product with M = Dy to the major form with M = Er.

One of the more interesting properties of the work reported here is the ability to control the metal ion's primary coordination sphere. Utilizing LiCl as a salting out agent in a 4:1:1 ratio with the lanthanide and glycol results in the formation of an additional tight ion pair and a reduction in coordination number. If a 6:1:1 ratio is used, all H$_2$O is eliminated and all three chloride ions are forced into the primary coordination sphere. Unfortunately, we have thus far been unsuccessful in applying this technique to any lanthanide prior to Nd where the tetrahydrates are isolated even with the addition of a salting out agent.

In all of the 9-coordinate complexes, the EO4 ligand wraps the metal ion in what appears to be the beginning of a helical pattern. As we increase the glycol chain length, we present an increasingly hydrophobic exterior. From the EO3 complexes we have reported earlier and the EO4 complexes reported here to the EO5, EO6, and EO7 complexes currently under investigation, we are effectively dehydrating the metal ion, one coordination site at a time. These ligands are exhibiting structural features simply impossible for crown ethers to emulate. A crown ether will always leave at least one side of the metal ion's coordination sphere open to solvent or H$_2$O molecules, which must be removed prior to extraction.

Conclusions

Polyethylene glycols offer many advantages over the use of crown ethers in lanthanide complexation chemistry. They are less expensive, more flexible, and offer the double action of coordination and hydrogen bonding. The structural results have shown that as they wrap around a metal ion they can produce a more hydrophobic environment than their crown ether analogues. This work has also shown the relative ease with which the primary coordination sphere can be modified while keeping the glycol interaction intact.

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Experimental Section

Synthesis and Crystallization of [LaCl$_3$(EO4)]$_2$. A 2.0 mmol quantity of tetraethylene glycol was added to a stirred solution of 2.0 mmol of LaCl$_3$·nH$_2$O in 5 mL of CH$_3$OH/CH$_3$CN (1:3). The reaction mixture was heated to 60 °C for 1 h and centrifuged while hot and the supernatant decanted and cooled to 20 °C. A large quantity of white precipitate formed. The solvent was allowed to reduce by slow evaporation. After a month, small colorless deliquescent crystals had formed. Anal. Calcd: C, 21.86; H, 4.13. Found: C, 21.67; H, 4.14.

Synthesis and Crystallization of [MCl(OH$_2$)$_3$(EO4)]Cl$_2$·H$_2$O (M = Ce–Nd, Sm–Gd). A 2.0 mmol quantity of tetraethylene glycol was added to a stirred solution of 2.0 mmol of MCl$_3$·nH$_2$O in 8 mL of CH$_3$OH/CH$_3$CN (1:3). The reaction mixture was heated to 60 °C for 1 h. For M = Ce, a white powder formed; for M = Nd, a small amount of purple powder formed; for M = Sm a pale yellow powder formed. The precipitates were centrifuged and the supernatants were decanted. The solutions were allowed to cool to 22 °C.

In general, as the solvent was removed, a more viscous layer became evident in the bottom of the reaction tubes. In those solutions involving colored ions, the lower more viscous layer was always more strongly colored than the upper layer. For M = Ce, the solvent volume was allowed to reduce by slow evaporation, and small thin colorless crystals were observed after 2 weeks. No solid formed in the M = Pr reaction after cooling to –12 °C. The volume was reduced by 10% under vacuum and the solution was placed in a computer-controlled low-temperature bath and cooled slowly to –25 °C over a period of 36 h. Large green crystals (ca. 3 mm on edge) formed from a two-layer system.

Large violet crystals formed after allowing the supernatant to cool to 22 °C for M = Nd. The solvent volume was reduced by 50% at –10 °C under vacuum for M = Sm after which the two-layer system observed for the other metal ions formed. Large crystals, ca. 2 mm on edge, formed after the mixture was stored overnight.

For M = Eu the solvent volume was reduced by 25% at –10 °C under vacuum. Suitable crystals formed after the solution was allowed to stand at 22 °C overnight. The M = Gd solution remained clear after cooling to –12 °C. The solvent volume was reduced by 50% at –10 °C under vacuum. The solution formed crystals after being stored at –12 °C for 5 days. The small cube-shaped crystals were deliquescent.

Anal. Calcd for M = Ce: C, 19.74; H, 5.77. Found: C, 21.51; H, 4.56. Calcd for M = Pr: C, 18.71; H, 5.10. Found: C, 18.08; H, 5.02. Calcd for M = Nd: C, 18.59; H, 5.07. Found: C, 18.64; H, 5.16. Calcd for M = Sm: C, 18.37; H, 5.01. Found: C, 18.58; H, 5.21. Calcd for M = Eu: C, 18.32; H, 5.00. Found: C, 18.13; H, 4.89. Calcd for M = Gd: C, 18.13; H, 4.95. Found: C, 17.58; H, 4.87.

Synthesis and Crystallization of [M(OH$_2$)$_4$(EO4)]Cl$_3$ (M = Tb–Yb, Y). A 2 mmol quantity of tetraethylene glucol (1.15 mmol for M = Tm) was added to a stirred solution of 2 mmol of MCl$_3$·nH$_2$O (M = Tm, 1.15 mmol) in 5 mL of CH$_3$OH/CH$_3$CN (1:3). The reaction mixture was heated to 60 °C for 1 h and slowly cooled to 22 °C.

For M = Tb, Dy, Y, Er, and Tm the solvent volume was reduced under vacuum at –10 °C by 50% (M = Ho, 10%; M = Yb, 20%). After each solution was stored at –12 °C for a few days, suitable crystals were obtained for M = Dy, Er. Suitable single crystals for M = Tb, Y, and Tm were obtained by program cooling 0.1 °C/min to –20 °C. For M = Ho, suitable crystals were obtained after the solution was stored at –12 °C for 2 days.

For M = Tm and Yb, oils were formed initially. In each case the oils were redissolved in 1–2 mL of CH$_3$OH/CH$_3$CN (1:3). Crystallization of any complex of ytterbium proved most difficult. Suitable crystals were obtained in the threads of the reaction vessel cap after the solvent was allowed to evaporate very slowly over 14 months. The Tm complex was only one of three crystalline forms isolated from this reaction.

All solutions formed a two-layer system with crystals appearing in the lower, more viscous layer. The crystals obtained for M = Tb and Ho were most stable to moisture in the air. The remaining crystals, M = Dy, Y, Er, Tm, and Yb, were all slightly deliquescent.

Anal. Calcd for M = Tb: C, 18.08; H, 4.93. Found: C, 17.15; H, 4.75. Calcd for M = Dy: C, 17.96; H, 4.90. Found: C, 17.88; H, 4.99. Calcd for M = Y: C, 20.82; H, 5.68. Found: C, 20.22; H, 5.91. Calcd for M = Ho: C, 17.87; H, 4.87. Found: C, 17.59; H, 5.08. Calcd for M = Er: C, 17.80; H, 4.85. Found: C, 17.16; H, 4.99; Calcd for M = Yb: C, 17.61; H, 4.80. Found: C, 17.44; H, 5.08.

Synthesis and Crystallization of [Tm(OH$_2$)$_{4-x}$(OHMe)$_x$(EO4)]Cl$_3$·(1 − x)(H$_2$O) (x = 0.60) and [TmCl$_2$(OH$_2$)(EO4)]Cl. The reaction of TmCl$_3$·nH$_2$O and tetraethylene glycol reported above yielded two additional deliquescent crystalline compounds from the same flask. Anal. Calcd for [Tm(OH$_2$)$_4$(EO4)]Cl$_3$: C, 17.74; H, 4.84. Calcd for [Tm(OH$_2$)$_{4-x}$(OHMe)$_x$(EO4)]Cl$_3$·(1 − x)(H$_2$O) (x = 0.60): C, 18.54; H, 5.06. Calcd for [TmCl$_2$(OH$_2$)(EO4)]Cl: C, 19.71; H, 4.13. Found: C, 18.29; H, 5.12.

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

compd	$[LaCl_3(EO4)]_2$	cell consts (θ_{min},[a] deg)	(12)	cell vol, Å^3	728.7	μ_{calc}, cm^{-1}	35.25
fw	878.98	a, Å	8.586 (2)	Z	1	range of rel transm factors,[b] %	84–100
space group	$P\bar{1}$	b, Å	9.489 (3)	radiation, graphite	Mo Kα (λ =	$R = \sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\|$	0.036
temp., °C	22	c, Å	9.593 (3)	monochrm	0.71073 Å)	R_w	0.044
		α, deg	86.16 (3)	D_{calc}, g cm^{-3}	2.00		
		β, deg	72.34 (3)				
		γ, deg	78.10 (2)				

	[MCl(OH$_2$)$_3$(EO4)]Cl$_2$·H$_2$O					
	M = Ce	M = Pr	M = Nd	M = Sm	M = Eu	M = Gd
fw	512.77	513.56	516.89	523.01	524.61	529.90
space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$
temp, °C	20	22	20	20	20	20
cell consts (θ_{min},[a] deg)	(24)	(23)	(23)	(23)	(20)	(23)
a, Å	9.765 (3)	9.743 (4)	9.725 (2)	9.688 (6)	9.653 (4)	9.660 (5)
b, Å	10.597 (4)	10.585 (3)	10.567 (3)	10.539 (8)	10.501 (4)	10.516 (3)
c, Å	18.427 (9)	18.407 (9)	18.389 (8)	18.350 (9)	18.303 (6)	18.317 (8)
β, deg	102.20 (4)	102.33 (6)	102.40 (3)	102.53 (5)	102.00 (3)	102.63 (4)
cell vol, Å^3	1864	1855	1846	1829	1815	1816
Z	4	4	4	4	4	4
radiation, graphite monochrm	Mo Kα (λ = 0.71073 Å)	Mo Kα (λ = 0.71073 Å)	Mo Kα (λ = 0.71073 Å)	Mo Kα (λ = 0.71073 Å)	Mo Kα (λ = 0.71073 Å)	Mo Kα (λ = 0.71073 Å)
D_{calc}, g cm^{-3}	1.83	1.84	1.86	1.90	1.92	1.94
μ_{calc}, cm^{-1}	27.2	30.8	32.9	34.8	39.6	39.2
range of rel transm factors,[b] %	61–100	78–100	66–100	97–100	56–100	81–100
$R = \sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\|$	0.026	0.024	0.023	0.027	0.034	0.025
R_w	0.032	0.038	0.026	0.028	0.041	0.027

	[M(OH$_2$)$_4$(EO4)]Cl$_3$					
	M = Tb	M = Dy	M = Y	M = Ho	M = Er	M = Tm	M = Yb
fw	531.57	535.15	461.55	537.58	539.91	541.58	545.69
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
temp, °C	20	20	22	20	20	22	22
cell consts (θ_{min},[a] deg)	(23)	(20)	(20)	(20)	(20)	(20)	(20)
a, Å	8.234 (7)	8.234 (5)	8.215 (6)	8.217 (5)	8.206 (1)	8.206 (4)	8.201 (3)
b, Å	8.417 (4)	8.398 (4)	8.390 (5)	8.389 (4)	8.378 (3)	8.364 (3)	8.367 (3)
c, Å	13.725 (2)	13.691 (7)	13.697 (6)	13.701 (9)	13.676 (6)	13.666 (9)	13.664 (5)
α, deg	82.36 (2)	82.41 (4)	82.46 (4)	82.46 (5)	82.44 (3)	82.43 (4)	82.42 (3)
β, deg	89.20 (4)	89.36 (5)	89.30 (5)	89.32 (6)	89.34 (2)	89.38 (6)	89.41 (3)
γ, deg	71.65 (6)	71.63 (5)	71.58 (5)	71.60 (4)	71.57 (2)	71.61 (4)	71.59 (4)
cell vol, Å^3	894.4	890.1	887.5	888.0	883.8	881.8	881.3
Z	2	2	2	2	2	2	2
radiation, graphite monochrm	Mo Kα (λ = 0.71073 Å)	Mo Kα (λ = 0.71073 Å)	Mo Kα (λ = 0.71073 Å)	Mo Kα (λ = 0.71073 Å)	Mo Kα (λ = 0.71073 Å)	Mo Kα (λ = 0.71073 Å)	Mo Kα (λ = 0.71073 Å)
D_{calc}, g cm^{-3}	1.97	1.97	1.73	2.01	2.03	2.04	2.06
μ_{calc}, cm^{-1}	42.0	44.5	38.8	47.0	49.8	57.0	60.8
range of rel transm factors,[b] %	64–100	56–100	65–100	63–100	92–100	67–100	40–100
$R = \sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\|$	0.021	0.028	0.038	0.023	0.029	0.030	0.040
R_w	0.023	0.030	0.050	0.025	0.029	0.050	0.050

	[MCl$_2$(OH$_2$)(EO4)]Cl				
	M = Sm	M = Eu	M = Gd	M = Tb	M = Tm
fw	468.96	470.56	475.85	477.53	487.53
space group	Cc	Cc	Cc	Cc	Cc
temp, °C	20	23	22	20	20
cell consts (θ_{min},[a] deg)	(19)	(21)	(20)	(20)	(23)
a, Å	12.952 (5)	12.932 (4)	12.925 (4)	12.880 (4)	12.822 (2)
b, Å	9.348 (4)	9.336 (4)	9.332 (1)	9.318 (8)	9.277 (1)
c, Å	13.764 (6)	13.733 (2)	13.724 (2)	13.696 (8)	13.608 (1)
β, deg	110.91 (4)	110.90 (2)	110.96 (2)	110.90 (4)	110.94 (1)
cell vol, Å^3	1557	1549	1546	1536	1512
Z	4	4	4	4	4
radiation, graphite monochrm	Mo Kα (λ = 0.71073 Å)	Mo Kα (λ = 0.71073 Å)	Mo Kα (λ = 0.71073 Å)	Mo Kα (λ = 0.71073 Å)	Mo Kα (λ = 0.71073 Å)
D_{calc}, g cm^{-3}	2.00	2.02	2.04	2.06	2.14
μ_{calc}, cm^{-1}	43.6	46.3	49.4	52.3	66.1
range of rel transm factors,[b] %	80–100	56–100	81–100	82–100	53–100
$R = \sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\|$	0.024	0.022	0.035	0.030	0.028
R_w	0.033	0.029	0.039	0.040	0.037

Table III (Continued)

	[EuCl$_3$(EO4)]	[Tm(OH$_2$)$_{4-x}$(OHMe)$_x$(EO4)]Cl$_3$· (1 − x)(H$_2$O) (x = 0.60)	[LuCl$_2$(EO4)]Cl·H$_2$O
fw	452.55	450.85	493.57
space group	P$\bar{1}$	P2$_1$/c	P2$_1$/c
temp, °C	20	20	20
cell consts (θ_{min},^{a} deg)	(20)	(20)	(21)
a, Å	7.590 (4)	10.051 (1)	7.602 (3)
b, Å	8.895 (2)	11.764 (1)	20.958 (9)
c, Å	11.672 (4)	16.390 (3)	10.041 (6)
α, deg	91.09 (2)		
β, deg	102.04 (3)	98.75 (1)	103.80 (4)
γ, deg	109.48 (3)		
cell vol, Å^3	723.2	1915.4	1554
Z	2	4	4
radiation, graphite monochrm	Mo Kα (λ = 0.710 73 Å)	Mo Kα (λ = 0.710 73 Å)	Mo Kα (λ = 0.710 73 Å)
D_{calc}, g cm^{-3}	2.08	1.56	2.11
μ_{calc}, cm^{-1}	46.3	48.2	65.7
range of rel transm factors,^{b} %	67–100	82–100	85–100
R = $\sum \|\|F_o\| - \|F_c\|\|/\sum\|F_o\|$	0.038	0.033	0.030
R_w	0.042	0.048	0.031

^{a} Least-squares refinement for $((\sin\theta)/\lambda)^2$ values for 25 reflections (θ_{min} as indicated). ^{b} Corrections: Lorentz–polarization and absorption (empirical, ψ scan).

Synthesis and Crystallization of [LuCl$_2$(EO4)]Cl·H$_2$O.

A 2 mmol quantity of tetraethylene glycol was pipetted into a stirred solution of 2 mmol of LuCl$_3$·nH$_2$O in 5 mL of CH$_3$OH/CH$_3$CN (1:3). The mixture was heated to 60 °C for 1 h and cooled slowly to 20 °C. The solvent volume was reduced by 20% under vacuum at −10 °C. A two-layer system was observed. The mixture was program cooled 0.1 °C/min to −20 °C, and suitable crystals formed, which were found to be deliquescent. Anal. Calcd for [LuCl$_2$(EO4)]Cl·H$_2$O: C, 19.47; H, 4.08. Found: C, 19.52; H, 4.34.

Synthesis and Crystallization of [MCl$_2$(OH$_2$)(EO4)]Cl (M = Sm–Tb).

A 1.2 mmol quantity of tetraethylene glycol was added to a stirred solution of 1.2 mmol of MCl$_3$·nH$_2$O and 4.8 mmol of LiCl in 5 mL of CH$_3$OH/CH$_3$CN (1:3). The reaction mixture was heated at 60 °C for 1 h, the precipitates were centrifuged hot, and the supernatants were decanted. The M = Sm reaction formed the most precipitate, a small amount of a white precipitate formed for M = Gd, and the solution remained clear and colorless for M = Tb. A similar reaction with NdCl$_3$·nH$_2$O was carried out. After addition of LiCl, the solution turned blue; however, the tetrahydrate was the only complex crystallized from this solution. Suitable crystals for M = Gd–Tb were obtained by allowing the clear solutions to cool to 20 °C. For M = Sm suitable crystals were obtained by cooling to 5 °C. The crystals were stable to the moisture in air during periods of low humidity.

Anal. Calcd for M = Sm: C, 20.49; H, 4.29. Found: C, 19.99; H, 4.77. Calcd for M = Eu: C, 20.42; H, 4.28. Found: C, 19.95; H, 4.13. Calcd for M = Gd: C, 20.19; H, 4.24. Found: C, 18.15; H, 5.32. Calcd for M = Tb: C, 20.12; H, 4.24. Found: C, 19.66; H, 4.43.

Synthesis and Crystallization of [EuCl$_3$(EO4)].

A 2.0 mmol quantity of tetraethylene glycol was added to a stirred solution of 2.0 mmol of EuCl$_3$·nH$_2$O and 12.0 mmol of LiCl in 8 mL of CH$_3$OH/CH$_3$CN (1:3). The reaction mixture was heated at 60 °C for 1 h, after which time the solution remained clear and colorless. The mixture was cooled to room temperature, and the solvent volume was reduced under vacuum at −10 °C by 25%. Deliquescent crystals formed overnight. Anal. Calcd: C, 21.23; H, 4.01. Found: C, 21.20; H, 4.00.

X-ray Data Collection, Structure Determination, and Refinement. For each crystallographic study, a transparent 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. The 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 Å^2. The alcoholic and water hydrogen atoms were located from a difference Fourier map and included with fixed contributions (B = 5.5 Å^2). All nonhydrogen atoms were refined anisotropically. Structures were refined by utilizing SHELX76[36] and neutral atom scattering factors from ref 37. Initial

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

(37) *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).

Table IV. Final Fractional Coordinates for [LaCl$_3$(EO4)]$_2$

atom	x/a	y/b	z/c	B(eqv),^{a} Å^2
La	0.00643 (5)	0.29754 (4)	0.66448 (4)	1.06
Cl(1)	0.0659 (2)	0.6011 (2)	0.6090 (2)	1.55
Cl(2)	−0.3078 (2)	0.4822 (2)	0.7894 (2)	1.74
Cl(3)	0.1883 (2)	0.0124 (2)	0.6689 (2)	1.83
O(1)	−0.1735 (7)	0.1433 (6)	0.5958 (6)	2.09
O(2)	−0.1859 (6)	0.1516 (6)	0.8763 (5)	1.69
O(3)	0.0140 (6)	0.3054 (5)	0.9421 (5)	1.66
O(4)	0.2878 (6)	0.3179 (6)	0.7161 (5)	1.77
O(5)	0.2688 (6)	0.2805 (5)	0.4454 (5)	1.58
C(1)	−0.246 (1)	0.0373 (9)	0.6949 (9)	2.49
C(2)	−0.317 (1)	0.1029 (9)	0.8415 (9)	2.30
C(3)	−0.231 (1)	0.2073 (9)	1.0227 (8)	1.94
C(4)	−0.074 (1)	0.2148 (8)	1.0524 (8)	1.80
C(5)	0.168 (1)	0.3146 (9)	0.9702 (9)	2.12
C(6)	0.266 (1)	0.3960 (8)	0.8456 (9)	1.89
C(7)	0.4190 (9)	0.3526 (9)	0.5939 (9)	2.21
C(8)	0.4300 (9)	0.261 (1)	0.4679 (9)	2.24

$^a B(eqv) = {}^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

Table V. Final Fractional Coordinates for [CeCl(OH$_2$)$_3$(EO4)]Cl$_2$·H$_2$O

atom	x/a	y/b	z/c	B(eqv),^{a} Å^2
Ce	0.42393 (2)	0.25441 (2)	1.13303 (1)	1.38
Cl(1)	0.4137 (1)	0.3372 (1)	0.98523 (6)	2.14
Cl(2)	0.2264 (2)	0.6879 (1)	1.12356 (7)	3.08
Cl(3)	0.5624 (1)	0.5709 (1)	1.31689 (8)	3.20
O(1)	0.2304 (3)	0.4066 (3)	1.1271 (2)	2.32
O(2)	0.1800 (3)	0.1873 (3)	1.0573 (1)	1.93
O(3)	0.4002 (4)	0.0349 (2)	1.0721 (2)	2.52
O(4)	0.5559 (3)	0.0687 (3)	1.2126 (2)	2.25
O(5)	0.5350 (4)	0.2997 (3)	1.2652 (2)	2.79
O(6)	0.2655 (3)	0.1581 (3)	1.2095 (2)	2.43
O(7)	0.6683 (3)	0.2328 (3)	1.1179 (2)	3.00
O(8)	0.5182 (3)	0.4787 (3)	1.1470 (2)	2.39
O(9)	0.7673 (3)	0.4080 (3)	1.0371 (2)	2.55
C(1)	0.0874 (4)	0.3735 (4)	1.0975 (3)	2.61
C(2)	0.0811 (5)	0.2865 (5)	1.0325 (3)	2.70
C(3)	0.1799 (5)	0.0938 (4)	1.0012 (3)	2.51
C(4)	0.2645 (6)	−0.0129 (4)	1.0387 (3)	3.07
C(5)	0.4976 (6)	−0.0609 (4)	1.1073 (3)	3.34
C(6)	0.5086 (6)	−0.0558 (4)	1.1888 (3)	3.14
C(7)	0.5886 (6)	0.0841 (5)	1.2906 (3)	3.24
C(8)	0.6390 (6)	0.2160 (5)	1.3068 (3)	3.54

^{a} See footnote a in Table IV.

structure solutions were carried out with SHELXS.[38] Considerations unique to each crystallographic series are discussed below.

Table VI. Final Fractional Coordinates for $[Tb(OH_2)_4(EO4)]Cl_3$

atom	x/a	y/b	z/c	$B(eqv),^a$ Å^2
Tb	0.22263 (2)	0.21805 (2)	0.23297 (1)	1.14
Cl(1)	0.8509 (1)	−0.1809 (1)	0.26836 (8)	2.16
Cl(2)	0.7217 (1)	0.3523 (1)	0.05513 (9)	2.45
Cl(3)	0.6439 (1)	0.3882 (1)	0.35829 (9)	2.45
O(1)	0.0910 (3)	0.3361 (3)	0.0715 (2)	1.71
O(2)	0.3376 (4)	0.0384 (3)	0.1031 (2)	1.99
O(3)	0.3142 (4)	−0.0913 (3)	0.2899 (2)	2.11
O(4)	0.1570 (4)	0.1339 (4)	0.4036 (2)	2.52
O(5)	0.2744 (4)	0.3968 (4)	0.3500 (2)	2.36
O(6)	0.3599 (3)	0.4041 (3)	0.1466 (2)	2.17
O(7)	−0.0359 (3)	0.4379 (3)	0.2502 (2)	1.81
O(8)	0.5189 (3)	0.1171 (3)	0.2835 (2)	2.36
O(9)	−0.0126 (3)	0.1152 (3)	0.2124 (2)	2.04
C(1)	0.1609 (6)	0.2543 (5)	−0.0126 (3)	2.38
C(2)	0.2277 (6)	0.0675 (5)	0.0174 (3)	2.41
C(3)	0.4276 (6)	−0.1391 (5)	0.1351 (3)	2.50
C(4)	0.3382 (6)	−0.2046 (5)	0.2176 (3)	2.45
C(5)	0.2612 (7)	−0.1536 (6)	0.3828 (3)	2.85
C(6)	0.2496 (7)	−0.0295 (6)	0.4516 (4)	3.47
C(7)	0.1233 (8)	0.2643 (7)	0.4653 (4)	3.93
C(8)	0.2511 (7)	0.3493 (8)	0.4541 (4)	3.98

^{a} See footnote a in Table IV.

Table VII. Final Fractional Coordinates for $[SmCl_2(OH_2)(EO4)]Cl$

atom	x/a	y/b	z/c	$B(eqv),^a$ Å^2
Sm	0.0000	0.79621 (2)	0.7500	1.20
Cl(1)	−0.1993 (1)	0.8519 (2)	0.6020 (1)	2.27
Cl(2)	0.0312 (2)	0.5323 (2)	0.8253 (1)	2.39
Cl(3)	0.3176 (1)	1.0745 (2)	0.9919 (1)	2.21
O(1)	−0.0124 (4)	0.6600 (7)	0.5943 (4)	2.15
O(2)	0.1779 (5)	0.7654 (7)	0.7122 (5)	2.19
O(3)	0.0854 (5)	1.0201 (6)	0.7153 (5)	2.42
O(4)	−0.0548 (5)	1.0327 (6)	0.8120 (4)	2.13
O(5)	−0.1135 (7)	0.7818 (6)	0.8575 (7)	2.94
O(6)	0.1451 (4)	0.8396 (7)	0.9169 (4)	2.16
C(1)	0.0837 (6)	0.5793 (8)	0.5969 (6)	2.15
C(2)	0.1753 (9)	0.6872 (9)	0.6195 (8)	2.47
C(3)	0.2466 (6)	0.8928 (8)	0.7291 (6)	2.40
C(4)	0.1778 (6)	1.0147 (9)	0.6789 (6)	2.50
C(5)	0.039 (1)	1.162 (1)	0.7206 (9)	3.46
C(6)	0.0086 (8)	1.155 (1)	0.8144 (7)	2.71
C(7)	−0.1041 (7)	1.028 (1)	0.8896 (7)	2.90
C(8)	−0.1751 (9)	0.902 (1)	0.8709 (9)	3.52

^{a} See footnote a in Table IV.

[LaCl$_3$(EO4)]$_2$. The space group was determined to be the centric $P\bar{1}$ or acentric $P1$. The subsequent solution and successful refinement of the structure was carried out in the centric $P\bar{1}$. The fractional coordinates for this complex are given in Table IV.

[MCl(OH$_2$)$_3$(EO4)]Cl$_2$·H$_2$O (M = Ce–Nd, Sm–Gd). The space group for this series was determined to be the centric $P2_1/n$ from the systematic absences. The Nd complex was solved by using Patterson techniques. Subsequent members of this series used the coordinates from the nearest completed member of the series as a starting point. The final values of the positional parameters for the Ce complex are given in Table V. The remaining tables of fractional coordinates have been deposited.

[M(OH$_2$)$_4$(EO4)]Cl$_3$ (M = Tb–Yb, Y). The space group was determined to be either the centric $P\bar{1}$ or acentric $P1$. Subsequent solution and successful refinement of the structure was carried out in the centric space group $P\bar{1}$. The first member of this series studied (M = Er) was solved by utilizing heavy-atom techniques. The fractional coordinates of the nearest solved member of this series were utilized in subsequent determinations. The final values of the positional parameters are given in Table VI for M = Tb.

[MCl$_2$(OH$_2$)(EO4)]Cl (M = Sm–Tb, Tm). The space group was determined to be either the centric $C2/c$ or acentric Cc from the systematic absences. Subsequent solution and successful refinement of the structure was carried out in the acentric space group Cc. Structure solution was carried out as above. The absolute configuration of each isolated complex was tested by inversion of the coordinates and recal-

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Table VIII. Final Fractional Coordinates for $[EuCl_3(EO4)]$

atom	x/a	y/b	z/c	$B(eqv),^a$ Å^2
Eu	0.16372 (7)	0.34461 (6)	0.26550 (4)	1.62
Cl(1)	0.1428 (4)	0.3550 (3)	0.5003 (2)	2.62
Cl(2)	0.3702 (4)	0.6457 (3)	0.2475 (2)	2.95
Cl(3)	0.2680 (4)	0.2292 (3)	0.0875 (2)	2.94
O(1)	0.4901 (9)	0.3688 (8)	0.3679 (6)	2.46
O(2)	0.205 (1)	0.0915 (8)	0.3396 (6)	2.51
O(3)	−0.126 (1)	0.1010 (8)	0.2250 (6)	2.65
O(4)	−0.094 (1)	0.3404 (9)	0.0872 (6)	2.58
O(5)	−0.065 (1)	0.4748 (9)	0.2922 (6)	2.78
C(1)	0.529 (2)	0.237 (1)	0.422 (1)	3.71
C(2)	0.395 (2)	0.086 (1)	0.360 (1)	4.29
C(3)	0.058 (2)	−0.057 (1)	0.296 (1)	4.07
C(4)	−0.127 (2)	−0.035 (1)	0.289 (1)	4.61
C(5)	−0.276 (2)	0.076 (2)	0.119 (1)	3.90
C(6)	−0.207 (2)	0.183 (2)	0.031 (1)	3.88
C(7)	−0.235 (3)	0.412 (2)	0.092 (2)	2.30
C(8)	−0.131 (3)	0.549 (3)	0.187 (2)	2.78
C(7)'	−0.165 (3)	0.481 (2)	0.094 (2)	3.13
C(8)'	−0.211 (3)	0.500 (3)	0.204 (2)	3.65

^{a} See footnote a in Table IV.

Table IX. Final Fractional Coordinates for $[Tm(OH_2)_{4-x}(OHMe)_x(EO4)]Cl_3 \cdot (1 - x)(H_2O)$ $(x = 0.60)$

atom	x/a	y/b	z/c	$B(eqv),^a$ Å^2
Tm	0.75303 (3)	0.31011 (2)	0.85932 (2)	1.41
Cl(1)	0.7322 (2)	0.4300 (2)	0.5958 (1)	2.54
Cl(2)	0.8421 (2)	0.0455 (2)	0.6454 (1)	2.29
Cl(3)	0.6757 (2)	0.7057 (2)	0.8431 (1)	2.83
O(1)	0.6295 (5)	0.4679 (4)	0.8995 (3)	2.15
O(2)	0.5198 (5)	0.2636 (4)	0.8763 (3)	2.13
O(3)	0.7015 (6)	0.1109 (4)	0.8514 (3)	2.40
O(4)	0.9340 (6)	0.1731 (4)	0.9276 (3)	2.31
O(5)	0.9519 (5)	0.3982 (4)	0.9224 (3)	2.00
O(6)	0.8028 (5)	0.4761 (4)	0.7832 (3)	2.09
O(7)	0.6087 (5)	0.3033 (4)	0.7323 (3)	2.39
O(8)	0.7444 (5)	0.2908 (4)	1.0009 (3)	2.16
O(9)	0.8831 (5)	0.2529 (4)	0.7583 (3)	2.21
O(10)	1.118 (3)	0.316 (2)	0.754 (2)	6.38
C(1)	0.4830 (8)	0.4601 (7)	0.8877 (5)	2.83
C(2)	0.4486 (8)	0.3439 (7)	0.9185 (5)	2.49
C(3)	0.4903 (9)	0.1492 (6)	0.8954 (6)	2.74
C(4)	0.5621 (9)	0.0759 (7)	0.8405 (6)	2.93
C(5)	0.7933 (8)	0.0212 (6)	0.8862 (5)	2.50
C(6)	0.9329 (9)	0.0646 (6)	0.8885 (5)	2.67
C(7)	1.0658 (8)	0.2213 (7)	0.9477 (5)	2.61
C(8)	1.0477 (8)	0.3381 (7)	0.9811 (5)	2.28
C(9)	1.002 (1)	0.291 (1)	0.7291 (8)	2.32

^{a} See footnote a in Table IV.

Table X. Final Fractional Coordinates for $[LuCl_2(EO4)]Cl \cdot H_2O$

atom	x/a	y/b	z/c	$B(eqv),^a$ Å^2
Lu	0.15801 (4)	0.12422 (2)	0.78010 (3)	1.49
Cl(1)	0.3265 (3)	0.22988 (9)	0.7770 (2)	2.76
Cl(2)	0.0163 (3)	0.0167 (1)	0.8020 (2)	3.03
Cl(3)	−0.3494 (3)	0.1198 (1)	0.4102 (2)	3.29
O(1)	0.0256 (7)	0.1295 (3)	0.5568 (5)	2.33
O(2)	0.3455 (7)	0.0831 (2)	0.6520 (5)	1.89
O(3)	0.4222 (7)	0.0822 (2)	0.9201 (5)	1.82
O(4)	0.1782 (7)	0.1471 (2)	1.0072 (5)	1.94
O(5)	−0.0898 (7)	0.1779 (3)	0.8026 (5)	2.28
O(6)	−0.3516 (8)	0.2251 (3)	0.6235 (6)	2.98
C(1)	0.130 (1)	0.1139 (4)	0.4582 (8)	2.67
C(2)	0.259 (1)	0.0619 (4)	0.5174 (7)	2.46
C(3)	0.498 (1)	0.0449 (4)	0.7181 (8)	2.50
C(4)	0.574 (1)	0.0741 (4)	0.8585 (8)	2.23
C(5)	0.475 (1)	0.1093 (4)	1.0570 (7)	2.31
C(6)	0.304 (1)	0.1119 (4)	1.1095 (7)	2.32
C(7)	0.011 (1)	0.1638 (4)	1.0439 (8)	2.46
C(8)	−0.083 (1)	0.2081 (4)	0.9332 (8)	2.71

^{a} See footnote a in Table IV.

culation of the R factors. A sufficient number of reflections equivalent in $C2/c$ but not in Cc were used to make this determination. The alco-

holic and water hydrogen atoms were not included in the final refinement. The final values of the positional parameters for M = Sm are given in Table VII.

[EuCl₃(EO4)]. The space group was determined to be either the centric *P*1̄ or acentric *P*1. Subsequent solution and successful refinement of the structure was carried out in the centric space group *P*1̄. Least-squares refinement with isotropic thermal parameters led to $R = 0.062$. The ethylene group containing C(7) and C(8) was found to be disordered. Two orientations were resolved for this group and refined with 50% occupancy in alternate least-squares cycles of refinement. The alcoholic hydrogen atoms were not included in the final refinement. The final values of the positional parameters are given in Table VIII.

[Tm(OH₂)₄₋ₓ(OHMe)ₓ(EO4)]Cl₃·(1 − x)(H₂O) (x = 0.60). The space group was determined to be the centric $P2_1/c$ from the systematic absences. An interesting disorder was observed during the initial stages of refinement involving O(9) and the uncoordinated O(10). It was determined that O(9) was a water molecule in some of the Tm coordination spheres and a methanol group in others. Refinement of the occupancy factors resulted in 60% occupancy for the methanol group and 40% occupancy for the water molecule. The different hydrogen-bonding capabilities of these molecules resulted in further disorder in the unit cell. O(10), an uncoordinated water molecule has 40% occupancy, corresponding to the occupancy of O(9) as a water molecule to which it is

hydrogen bonded. The methyl hydrogen atoms were included as a rigid group with rotational freedom at the bonded carbon atom (C–H = 0.95 Å, $B = 5.5$ Å²). The disordered methyl C(9) and O(9) water molecule hydrogen atoms were not included in the final refinement. The final values of the positional parameters are given in Table IX.

[LuCl₂(EO4)]Cl·H₂O. The space group was determined to be the centric $P2_1/c$ from the systematic absences. Least-squares refinement with isotropic thermal parameters led to $R = 0.049$. The final values of the positional parameters are given in Table X.

Supplementary Material Available: Tables SI–SCXXV, listing bond distances and angles, hydrogen-bonding contact geometries, fractional coordinates not listed in the text, hydrogen atom coordinates, thermal parameters, and least-squares planes results (173 pages); tables of observed and calculated structure factors or amplitudes (197 pages). Ordering information is given on any current masthead page.

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Synthesis, X-ray Structure Determination, and Spectroscopy of the Silver(I) Polyselenides [(Ph₄P)Ag(Se₄)]ₙ, [(Me₄N)Ag(Se₅)]ₙ, [(Et₄N)Ag(Se₄)]₄, and (Pr₄N)₂[Ag₄(Se₄)₃]. Extreme Structure Dependence on Counterion Size

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The reaction of sodium pentaselenide with silver nitrate in dimethylformamide (DMF) was investigated. The addition of various counterions, Ph₄P⁺, Me₄N⁺, Et₄N⁺, and Pr₄N⁺, to this common reaction solution resulted in the isolation of four new soluble silver(I) polyselenide complexes, [(Ph₄P)Ag(Se₄)]ₙ (I), [(Me₄N)Ag(Se₅)]ₙ (II), [(Et₄N)Ag(Se₄)]₄ (III), and (Pr₄N)₂[Ag₄(Se₄)₃] (IV), in high yield. Compound I (85% in yield) crystallizes in the monoclinic space group $P2_1/c$ with unit cell dimensions $a = 14.145$ (3) Å, $b = 7.076$ (2) Å, $c = 24.939$ (5) Å, $\beta = 105.23$ (2)°, and $V = 2408$ Å³. Compound II (93% in yield) crystallizes in the monoclinic space group *Cc* with unit cell dimensions $a = 11.350$ (2) Å, $b = 18.764$ (3) Å, $c = 7.434$ (1) Å, $\beta = 124.59$ (1)°, and $V = 1303$ Å³. Compounds III and IV (96% and 76% in yield, respectively) belong to the monoclinic space group $P2_1/n$ with unit cell dimensions $a = 16.229$ (3) Å, $b = 11.480$ (5) Å, $c = 17.171$ (3) Å, $\beta = 106.06$ (1)°, and $V = 3074$ Å³ and $a = 10.493$ (2) Å, $b = 24.573$ (3) Å, $c = 17.499$ (1) Å, $\beta = 93.84$ (1)°, and $V = 4502$ Å³, respectively. All structures were solved and refined by direct methods and Fourier techniques. All non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were calculated and included but not refined. Refinement by full-matrix least-squares methods on these structures gave final R values of 7.5% for I, 5.2% for II, 2.8% for III, and 3.3% for IV. The four compounds are divided into two different structural categories: one-dimensional chains, [(Ph₄P)Ag(Se₄)]ₙ and [(Me₄N)Ag(Se₅)]ₙ, and discrete molecular clusters, [(Et₄N)Ag(Se₄)]₄ and (Pr₄N)₂[Ag₄(Se₄)₃]. The structures of these four silver(I) polyselenide compounds feature two types of coordination spheres for the Ag atoms, trigonal planar and tetrahedral. Compound I consists of infinite macroanionic chains separated by the cation Ph₄P⁺, forming a unique one-dimensional structure containing five-membered AgSe₄ rings. These rings are generated from each other by a 2-fold screw axis operation. Each [Ag(Se₄)]ₙⁿ⁻ chain contains trigonal-planar Ag⁺ atoms. Similarly, compound II is a one-dimensional polymer consisting of AgSe₅ as repeat units in which AgSe₄ forms a five-membered ring. The [Ag(Se₅)]ₙⁿ⁻ chain can be generated by a 2-fold screw axis along the chain direction. The Ag⁺ atoms in this structure adopt a tetrahedral coordination geometry. Compound III is molecular. The anion [Ag(Se₄)]₄⁴⁻ possesses a crystallographic inversion center. Four silver atoms are symmetrically disposed around the inversion center, forming a planar rhombus. The structure features two different kinds of Ag coordination, Ag(1) and Ag'(1) are tetrahedrally coordinated, while the other two Ag(2) and Ag'(2) possess a trigonal-planar coordination. The [Ag₄(Se₄)₃]²⁻ anion features a tetrahedral array of Ag atoms "glued" together by three Se₄²⁻ ligands, forming a Ag₄Se₆ central adamantane-like core in which all Ag⁺ ions assume a trigonal-planar coordination. We found a correlation of counterion size and Ag coordination number in these compounds. The smaller the counterions, the higher the silver coordination number. Variable-temperature ⁷⁷Se NMR spectra of I–IV are reported. The IR spectra of the compounds exhibit two absorptions at ∼265 and ∼195 cm⁻¹. The former is assigned tentatively to the ν_{Se-Se} vibration. I–III have similar UV/vis spectra in DMF with two absorptions at ∼450 and ∼630 nm, while IV has a featureless spectrum. Thermal gravimetric analysis data are reported.

1. Introduction

Not only is the coordination chemistry of metal polyselenides or polytellurides less well developed when compared to that of polysulfides[1] but, most interestingly, it does not exactly parallel

that of metal polysulfides.[2] It is quite common that a given metal polysulfide compound does not possess a corresponding polyselenide or polytelluride analogue. Plausible reasons are (a) the propensity for catenation of chalcogen atoms decreases from S to Te, which greatly affects Q_x^{2-} ligand sizes, (b) the reduction potentials required to split the Q–Q bonds vary with the nature

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