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f-Element/Crown Ether Complexes. 22.[1] Preparation and Structural Characterization of Lanthanide Chloride Complexes of 12-Crown-4

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The interaction of the macrocyclic polyether 12-crown-4 with hydrated lanthanide chlorides, $MCl_3 \cdot nH_2O$ (M = Ce–Nd, Sm–Lu, Y, La), was investigated via reactions in 1:1 molar ratios in acetonitrile/methanol mixtures (3:1). Upon initial mixing at 25 °C precipitates of formulation $MCl_3 \cdot 12\text{-crown-}4 \cdot 1.5H_2O$ were observed for M = La, Ce, Pr, Nd and of formulation $MCl_3 \cdot 12\text{-crown-}4 \cdot 2.5H_2O$ for M = Sm–Lu, Y. Heating of the solutions to 60 °C for 1.5 h, followed by centrifugation and very slow evaporation (1–2 weeks) of the supernatant, resulted in the crystallization of $[M(OH_2)_5(12\text{-crown-}4)]Cl_3 \cdot 2H_2O$ (M = Ce, Nd, Sm–Er, Y) and $[MCl_2(OH_2)_2(12\text{-crown-}4)]Cl$ (M = Dy–Lu). All of these, except for $[DyCl_2(OH_2)_2(12\text{-crown-}4)]Cl$ (for which this form is a very minor product and suitable crystals were unavailable), were studied via single-crystal X-ray diffraction techniques. When the M = Y reaction was investigated, deliquescent crystals were observed to form around the top of the reaction vessel during heating. Crystallographic characterization of these revealed the monohydrate, solvate form $[YCl_2(OH_2)(OHMe)(12\text{-crown-}4)]Cl$. The nine-coordinate complexes crystallize in the acentric space group $Pna2_1$. Cell data for these complexes are as follows. $[M(OH_2)_5(12\text{-crown-}4)]Cl_3 \cdot 2H_2O$: M = Ce (20 °C), a = 18.969 (6) Å, b = 10.156 (3) Å, c = 10.307 (4) Å, and D_{calc} = 1.84 g cm^{-3} for Z = 4; M = Nd (20 °C), a = 18.893 (5) Å, b = 10.130 (3) Å, c = 10.279 (3) Å, and D_{calc} = 1.87 g cm^{-3} for Z = 4; M = Sm (20 °C), a = 18.808 (6) Å, b = 10.101 (3) Å, c = 10.263 (4) Å, and D_{calc} = 1.90 g cm^{-3} for Z = 4; M = Eu (20 °C), a = 18.780 (4) Å, b = 10.089 (2) Å, c = 10.243 (2) Å, and D_{calc} = 1.92 g cm^{-3} for Z = 4; M = Gd (20 °C), a = 18.773 (4) Å, b = 10.082 (3) Å, c = 10.236 (3) Å, and D_{calc} = 1.94 g cm^{-3} for Z = 4; M = Dy (20 °C), a = 18.717 (4) Å, b = 10.056 (5) Å, c = 10.216 (3) Å, and D_{calc} = 1.97 g cm^{-3} for Z = 4; M = Y (20 °C), a = 18.679 (5) Å, b = 10.051 (4) Å, c = 10.213 (4) Å, and D_{calc} = 1.72 g cm^{-3} for Z = 4; M = Ho (20 °C), a = 18.688 (5) Å, b = 10.048 (2) Å, c = 10.203 (3) Å, and D_{calc} = 1.99 g cm^{-3} for Z = 4; M = Er (20 °C), a = 18.695 (1) Å, b = 10.048 (1) Å, c = 10.210 (1) Å, and D_{calc} = 1.99 g cm^{-3} for Z = 4. The crown ether and five of the water molecules are coordinated to the metal ions in a slightly distorted capped-square-antiprismatic geometry. The crown ether is C_4, and all four oxygen atoms are planar. A complex network of hydrogen bonding results from the 14 water-donated hydrogen bonds. The deliquescent $[YCl_2(OH_2)(OHMe)(12\text{-crown-}4)]Cl$ is triclinic, $P\bar{1}$, with (at −150 °C) a = 7.301 (4) Å, b = 8.148 (2) Å, c = 14.032 (3) Å, α = 89.66 (2)°, β = 81.75 (3)°, γ = 74.36 (4)°, and D_{calc} = 1.76 g cm^{-3} for Z = 2. The crown ether has a C_4 conformation, and the metal ion geometry is square-antiprismatic with the two coordinated chloride ions cis in one square face. Dimers of the formula unit exist around centers of inversion with metal polyhedra bridged by hydrogen bonds from the coordinated water molecules to the noncoordinated chloride anions. The series of eight-coordinate complexes $[MCl_2(OH_2)_2(12\text{-crown-}4)]Cl$ starts with M = Dy, but only those complexes with M = Ho, Er, Tm, Yb, Lu were structurally characterized. These complexes are monoclinic, $P2_1/m$, with cell data as follows: M = Ho (20 °C), a = 7.401 (4) Å, b = 8.708 (2) Å, c = 11.798 (4) Å, β = 95.51 (5)°, and D_{calc} = 2.12 g cm^{-3} for Z = 2; M = Er (20 °C), a = 7.377 (4) Å, b = 8.690 (2) Å, c = 11.794 (4) Å, β = 95.44 (5)°, and D_{calc} = 2.14 g cm^{-3} for Z = 2; M = Tm (20 °C), a = 7.356 (5) Å, b = 8.674 (2) Å, c = 11.809 (4) Å, β = 95.46 (5)°, and D_{calc} = 2.16 g cm^{-3} for Z = 2; M = Yb (20 °C), a = 7.334 (3) Å, b = 8.662 (2) Å, c = 11.843 (4) Å, β = 95.65 (3)°, and D_{calc} = 2.18 g cm^{-3} for Z = 2; M = Lu (20 °C), a = 7.323 (4) Å, b = 8.653 (4) Å, c = 11.844 (4) Å, β = 95.42 (5)°, and D_{calc} = 2.19 g cm^{-3} for Z = 2. The metal ion and chloride ions reside on crystallographic mirror planes, one of which bisects the crown ether. The carbon atoms are disordered, resulting in two C_4 conformations of the ether, mirror images of each other. The coordination geometry is bicapped-trigonal-prismatic with the chloride ions in prismatic sites and the water molecules in capping sites. The hydrogen bonds are to the noncoordinated and one of the coordinated chloride anions, producing pairs of staggered hydrogen-bonded chains along b.

Introduction

Complexation reactions of crown ethers with 4f-element salts under anhydrous conditions promote interaction of the metal ion with the crown ether in solution; however, these complexes are often very difficult to crystallize, as evidenced by the relatively few crystal structure determinations in this area.[2-4] We have investigated reactions of this type utilizing hydrated lanthanide and prelanthanide salt starting materials in anhydrous solvents and successfully crystallized and structurally characterized a variety of complexes. In many cases, the crown ether acts merely as a hydrogen bond acceptor from metal-coordinated water molecules; often, however, f-element/crown ether complexation can still be realized, despite competition with the water molecules. The reactions of $MCl_3 \cdot nH_2O$ with 15-crown-5 and 18-crown-6 illustrate this point. Using 15-crown-5, we have isolated only hydrogen-bonded complexes—$[M(OH_2)_8]Cl_3 \cdot 15\text{-crown-}5$ (M = Gd,[5] Y,[6] Yb,[8] Lu[5]), $[Nd(OH_2)_9]Cl_3 \cdot 15\text{-crown-}5 \cdot H_2O$,[7] and $[NdCl_2(OH_2)_6]Cl \cdot 15\text{-crown-}5$.[7] We have observed three types of coordination complexes with the larger 18-crown-6 across the lanthanide series: $[CeCl_2(OH_2)(18\text{-crown-}6)]Cl \cdot 2H_2O$,[8] $[MCl(OH_2)_2(18\text{-crown-}6)]Cl_2 \cdot 2H_2O$ (M = Nd,[8] Sm,[9] Eu,[8] Gd,[9] Tb[9]), and $[M(OH_2)_7(OHMe)][MCl(OH_2)_2(18\text{-crown-}6)]_2Cl_7 \cdot 2H_2O$ (M = Dy,[10] Y[10]).

Despite the lack of success with the smaller 15-crown-5, we began investigating the even smaller 12-crown-4 with somewhat mixed results. Initially, one complex with a coordinated ether, $[Tb(OH_2)_5(12\text{-crown-}4)]Cl_3 \cdot 2H_2O$,[11] and one hydrogen-bonded complex, $[Lu(OH_2)_8]Cl_3 \cdot 1.5(12\text{-crown-}4) \cdot 2H_2O$,[12] were isolated and structurally characterized. Due to the success in complexing 12-crown-4 to Tb^{3+}, and to the general lack of structural data on 12-crown-4 complexes of the lanthanides (in addition to the Tb complex above, $[M(NO_3)_3(12\text{-crown-}4)]$ complexes (M = Eu,[13] Y[14]) are known), we continued to pursue the complexation of 12-crown-4 to hydrated lanthanide chloride salts. This report details the chemistry of these reactions and the crystallographic characterization of two hydrated forms of these complexes: [M-

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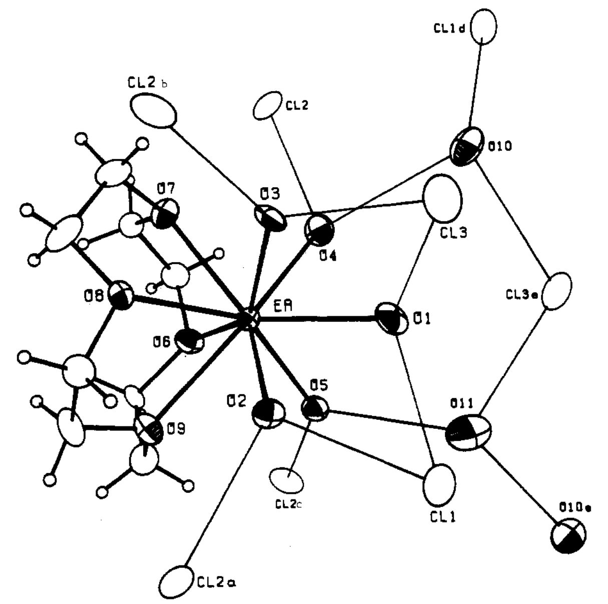

Figure 1. ORTEP illustration of the metal ion's primary coordination sphere and all hydrogen-bonding contacts donated by water molecules in the asymmetric unit of $[M(OH_2)_5(12\text{-crown-4})]Cl_3\cdot 2H_2O$ (M = Er shown). The letter designations atoms refer to different symmetry-related asymmetric units. Hydrogen atoms have been arbitrarily reduced; 50% probability ellipsoids for thermal motion are shown.

$(OH_2)_5(12\text{-crown-4})]Cl_3\cdot 2H_2O$ (M = Ce, Nd, Sm, Eu, Gd, Tb, Dy, Y, Ho, Er) and $[MCl_2(OH_2)_2(12\text{-crown-4})]Cl$ (M = Dy (cell only), Ho, Er, Tm, Yb, Lu). In addition the characterization of $[YCl_2(OH_2)(OHMe)(12\text{-crown-4})]Cl$ is reported.

Synthetic Results

The reactions of hydrated lanthanide chloride salts with 12-crown-4 in 1:1 molar ratios in 3:1 mixtures of acetonitrile and methanol produce 1:1 complexes of the metal and the macrocyclic polyether for all metals studied (M = La, Ce–Nd, Sm–Lu, Y). Initially a precipitate of formulation $MCl_3\cdot 12\text{-crown-4}\cdot 1.5H_2O$ forms for M = La, Ce, Pr, Nd and $MCl_3\cdot 12\text{-crown-4}\cdot 2.5H_2O$ for M = Sm–Lu, Y. The amount of precipitate decreases from copious amounts for M = La, Ce, Pr, Nd to steadily smaller amounts for M = Sm–Lu. Two other hydrated forms can be crystallized from the remaining solutions, heptahydrates for the early- and mid-series lanthanides M = Ce, Nd, Sm–Er, Y, and dihydrates of the late-series lanthanides M = Dy–Lu. The change in complex type appears to occur at M = Dy, with both forms isolated for M = Dy, Ho, Er. An increase in the formation of the dihydrate is observed from M = Dy to M = Er.

In each case the crystallization process follows a set pattern. After removal of the precipitate and initiation of the slow evaporation process, a viscous immiscible layer slowly forms at the bottom of the reaction flask. For colored solutions, as this layer grows it drains all color from the top layer. Crystallization of the complexes occurs from this bottom layer. Separation of the hepta- and dihydrate forms for M = Dy–Er was accomplished by utilizing differences in crystal morphology. In every case if evaporation of the solutions is carried out too rapidly, crystals of the starting hydrated chloride salt are obtained without the formation of a second layer.

Structural Results

$[M(OH_2)_5(12\text{-crown-4})]Cl_3\cdot 2H_2O$ (M = Ce, Nd, Sm, Eu, Gd, Tb,[11] Dy, Y, Ho, Er). An ORTEP illustration of the metal ion coordination environment is given in Figure 1 (M = Er); bond distances and angles for the series are presented in Table I. The domination of the scattering in these complexes by the metal and chloride anions, which approximate a centric space group, results in certain correlations between parameters when the complexes are refined in an acentric space group, in these structures $Pna2_1$. As a result, the standard deviations are higher than normal in the values derived from these parameters (e.g., bond lengths, angles, etc.). The space group ambiguity is described in the Experimental Section.

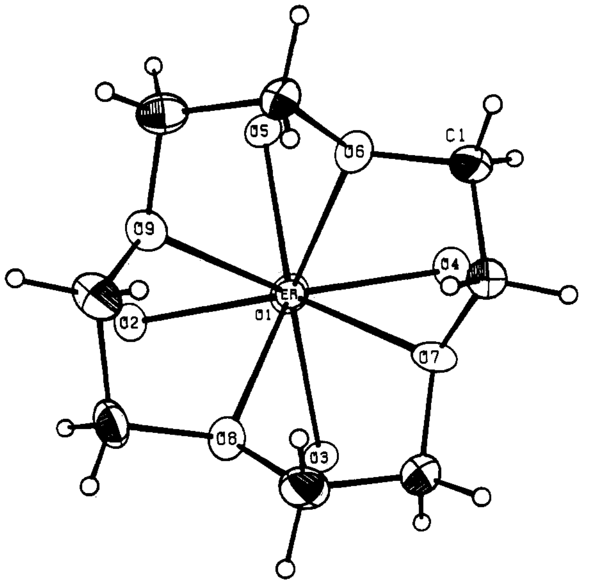

Figure 2. Metal ion coordination geometry in $[M(OH_2)_5(12\text{-crown-4})]Cl_3\cdot 2H_2O$ (M = Er shown).

The four oxygen atoms of the ether and five coordinated water molecules form a distorted capped square antiprism around the metal ion. The M–OH$_2$(capping), M–OH$_2$(plane), and M–O(crown) average distances range from 2.570 (6), 2.49 (2), and 2.61 (2) Å for M = Ce to 2.481 (5), 2.34 (2), and 2.50 (2) Å for M = Er. The major distortion in coordination geometry is a slight twist of the two square planes away from a perfectly staggered arrangement as seen in Figure 2 for M = Er. This results in two sets of O···O between-plane contacts, the averages of which range from 2.89 (3) and 3.34 (5) Å for M = Ce to 2.74 (2) and 3.14 (5) Å for M = Er.

The 12-crown-4 molecule adopts a C_4 conformation which directs all four oxygen atoms toward one side of the ring, a conformation normally found for metal complexes of this polyether. This conformation is characterized by gauche (60°) O–C–C–O torsion angles of the same sign and C–O–C–C torsion angles that alternate between gauche (of the same sign as the C–C angles) and anti (180°). As expected when C–O–C–C angles are forced gauche, these angles are all $>70°$.[15] In this conformation of 12-crown-4 there are two unique symmetry sites for the carbon atoms. Each set of four forms a plane, the four α-C atoms, C(1), C(3), C(5), and C(7), closer to the metal ion than the four β-C atoms, C(2), C(4), C(6), and C(8). The distance of the metal to the centroid of these planes varies from 2.25 (α) and 2.80 (β) Å for M = Ce to 2.14 (α) and 2.68 (β) Å for M = Er.

The five coordinated water molecules, three chloride ions, and two noncoordinated water molecules participate in a complex hydrogen-bonded network. There are 11 O–H···Cl$^-$ hydrogen bonds (Cl(1) accepts only three such interactions), while O(10) accepts two and donates two hydrogen bonds and O(11) accepts one and donates two. Despite the presence of all of the coordinated hydrogen bond donors on one side of the metal ion coordination sphere, there do not appear to be distinct organic and inorganic zones in the unit cell. Instead, the hydrogen-bonding network isolates each individual crown unit. (A view of the unit cell contents can be found in ref 11.)

$[MCl_2(OH_2)_2(12\text{-crown-4})]Cl$ (M = Ho, Er, Tm, Yb, Lu). The eight-coordinate bicapped-trigonal-prismatic coordination geometry of these complexes is depicted in Figure 3 (M = Ho); bond distances and angles are given in Table II. The metal ion and all three chlorine atoms reside on crystallographic mirror planes. Two of the chloride ions are in the primary coordination sphere

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Table I. Bond Distances (Å) and Angles (deg) for $[M(OH_2)_5(12\text{-crown-}4)]Cl_3\cdot 2H_2O$

atoms	M = Ce	M = Nd	M = Sm	atoms	M = Ce	M = Nd	M = Sm
Distances							
M–O(1)	2.570 (6)	2.548 (7)	2.527 (8)	M–O(6)	2.598 (8)	2.580 (9)	2.53 (1)
M–O(2)	2.450 (7)	2.438 (7)	2.390 (9)	M–O(7)	2.618 (8)	2.578 (9)	2.56 (1)
M–O(3)	2.49 (1)	2.42 (1)	2.41 (1)	M–O(8)	2.584 (8)	2.558 (9)	2.54 (1)
M–O(4)	2.520 (7)	2.492 (8)	2.44 (1)	M–O(9)	2.631 (8)	2.615 (9)	2.58 (1)
M–O(5)	2.49 (1)	2.47 (1)	2.41 (1)				
O–C (av)	1.44 (2)	1.44 (3)	1.45 (3)	C–C (av)	1.51 (2)	1.51 (6)	1.50 (4)
Angles							
O(1)–M–O(2)	70.0 (2)	69.7 (3)	70.4 (3)	O(2)–M–O(8)	81.4 (2)	81.5 (3)	80.1 (3)
O(1)–M–O(3)	70.7 (5)	71.4 (6)	71.6 (6)	O(3)–M–O(8)	69.4 (3)	68.6 (3)	68.4 (4)
O(2)–M–O(3)	84.0 (3)	84.6 (3)	83.8 (4)	O(4)–M–O(8)	126.7 (3)	126.9 (4)	127.6 (3)
O(1)–M–O(4)	70.0 (2)	69.2 (2)	69.4 (3)	O(5)–M–O(8)	144.4 (3)	145.1 (3)	145.5 (4)
O(2)–M–O(4)	140.0 (2)	138.9 (2)	139.7 (3)	O(6)–M–O(8)	94.5 (2)	95.4 (3)	95.9 (3)
O(3)–M–O(4)	81.7 (3)	81.0 (4)	81.9 (3)	O(7)–M–O(8)	62.5 (2)	63.5 (3)	63.7 (3)
O(1)–M–O(5)	70.1 (5)	69.5 (6)	69.1 (6)	O(1)–M–O(9)	132.0 (3)	131.9 (3)	131.6 (4)
O(2)–M–O(5)	84.1 (3)	83.8 (3)	85.1 (4)	O(2)–M–O(9)	68.8 (2)	69.2 (3)	68.9 (3)
O(3)–M–O(5)	140.8 (2)	140.9 (2)	140.6 (3)	O(3)–M–O(9)	127.0 (3)	127.4 (3)	127.2 (4)
O(4)–M–O(5)	84.0 (3)	83.6 (4)	82.6 (4)	O(4)–M–O(9)	145.9 (3)	146.3 (4)	145.9 (3)
O(1)–M–O(6)	132.9 (5)	132.3 (5)	132.0 (6)	O(5)–M–O(9)	82.0 (3)	82.1 (3)	82.6 (4)
O(2)–M–O(6)	126.6 (2)	126.9 (3)	128.0 (3)	O(6)–M–O(9)	62.6 (2)	62.7 (3)	63.6 (3)
O(3)–M–O(6)	144.0 (3)	143.3 (3)	142.8 (4)	O(7)–M–O(9)	94.5 (2)	95.7 (2)	96.4 (3)
O(4)–M–O(6)	83.4 (3)	83.8 (3)	82.4 (3)	O(8)–M–O(9)	62.4 (2)	63.1 (3)	63.0 (3)
O(5)–M–O(6)	69.0 (3)	69.0 (3)	69.4 (4)	M–O(6)–C(1)	114.0 (7)	111.7 (8)	114.1 (9)
O(1)–M–O(7)	133.5 (3)	132.4 (3)	131.9 (4)	M–O(6)–C(8)	119.5 (8)	121.4 (9)	123 (1)
O(2)–M–O(7)	143.8 (3)	144.8 (3)	143.5 (3)	M–O(7)–C(2)	120 (1)	119 (1)	119 (1)
O(3)–M–O(7)	81.4 (3)	80.0 (3)	79.4 (4)	M–O(7)–C(3)	113.7 (7)	114.1 (9)	113.1 (9)
O(4)–M–O(7)	69.7 (3)	69.3 (3)	69.2 (3)	M–O(8)–C(4)	122.3 (8)	120.7 (9)	120 (1)
O(5)–M–O(7)	126.6 (3)	126.8 (3)	127.3 (4)	M–O(8)–C(5)	114.6 (7)	114.5 (8)	114 (1)
O(6)–M–O(7)	62.7 (2)	63.4 (3)	63.6 (3)	M–O(9)–C(6)	121 (1)	123 (1)	123 (1)
O(1)–M–O(8)	132.6 (5)	132.2 (5)	132.2 (6)	M–O(9)–C(7)	112.3 (8)	112.4 (8)	112.6 (9)
C–O–C (av)	114 (1)	113 (2)	113 (2)	O–C_β–C_α (av)	107 (1)	106 (1)	106 (2)
O–C_α–C_β (av)	109.5 (9)	110 (2)	109 (2)				
atoms	**M = Eu**	**M = Gd**	**M = Dy**	**atoms**	**M = Eu**	**M = Gd**	**M = Dy**
Distances							
M–O(1)	2.511 (7)	2.500 (5)	2.488 (7)	M–O(6)	2.551 (9)	2.502 (6)	2.490 (9)
M–O(2)	2.404 (7)	2.371 (5)	2.347 (8)	M–O(7)	2.537 (8)	2.543 (6)	2.518 (9)
M–O(3)	2.42 (1)	2.440 (7)	2.38 (1)	M–O(8)	2.523 (9)	2.546 (6)	2.498 (9)
M–O(4)	2.440 (8)	2.428 (5)	2.380 (8)	M–O(9)	2.568 (9)	2.534 (5)	2.543 (9)
M–O(5)	2.38 (1)	2.346 (7)	2.38 (1)				
O–C (av)	1.44 (2)	1.45 (3)	1.45 (3)	C–C (av)	1.50 (4)	1.52 (6)	1.48 (4)
Angles							
O(1)–M–O(2)	69.9 (2)	69.6 (2)	70.7 (3)	O(2)–M–O(8)	80.4 (3)	79.5 (2)	80.1 (3)
O(1)–M–O(3)	70.9 (5)	69.0 (4)	72.4 (6)	O(3)–M–O(8)	68.7 (3)	67.9 (2)	68.3 (3)
O(2)–M–O(3)	84.0 (3)	82.9 (2)	84.3 (3)	O(4)–M–O(8)	127.7 (3)	127.0 (2)	128.2 (3)
O(1)–M–O(4)	69.3 (2)	69.5 (2)	68.5 (3)	O(5)–M–O(8)	144.3 (3)	145.5 (2)	145.0 (3)
O(2)–M–O(4)	139.2 (2)	139.1 (2)	139.2 (3)	O(6)–M–O(8)	96.3 (2)	96.7 (2)	97.3 (3)
O(3)–M–O(4)	81.5 (3)	80.9 (2)	81.8 (3)	O(7)–M–O(8)	64.1 (3)	63.8 (2)	63.9 (3)
O(1)–M–O(5)	70.0 (5)	71.3 (4)	68.7 (6)	O(1)–M–O(9)	131.4 (3)	132.4 (2)	130.6 (3)
O(2)–M–O(5)	83.8 (3)	84.9 (2)	84.4 (3)	O(2)–M–O(9)	68.8 (3)	69.1 (2)	68.4 (3)
O(3)–M–O(5)	140.9 (2)	140.3 (2)	141.0 (2)	O(3)–M–O(9)	127.6 (3)	126.9 (2)	128.1 (3)
O(4)–M–O(5)	83.9 (3)	84.1 (2)	82.9 (3)	O(4)–M–O(9)	146.2 (3)	147.1 (2)	145.9 (3)
O(1)–M–O(6)	132.1 (5)	134.1 (3)	130.0 (6)	O(5)–M–O(9)	81.2 (3)	82.4 (2)	80.8 (3)
O(2)–M–O(6)	127.6 (3)	128.9 (2)	127.8 (3)	O(6)–M–O(9)	63.5 (3)	64.1 (2)	64.1 (3)
O(3)–M–O(6)	143.5 (3)	143.0 (2)	143.3 (3)	O(7)–M–O(9)	96.8 (2)	96.9 (2)	97.5 (3)
O(4)–M–O(6)	82.8 (3)	83.0 (2)	82.1 (3)	O(8)–M–O(9)	63.4 (3)	63.3 (2)	64.3 (3)
O(5)–M–O(6)	68.9 (3)	69.9 (2)	68.3 (3)	M–O(6)–C(1)	113.1 (7)	114.9 (5)	114.3 (8)
O(1)–M–O(7)	131.8 (3)	130.5 (2)	131.9 (3)	M–O(6)–C(8)	121 (1)	122.4 (6)	123.3 (8)
O(2)–M–O(7)	144.3 (3)	142.9 (2)	143.8 (3)	M–O(7)–C(2)	119.0 (8)	117.6 (5)	119 (1)
O(3)–M–O(7)	79.7 (3)	79.0 (2)	79.1 (3)	M–O(7)–C(3)	114.3 (7)	114.5 (5)	113.9 (8)
O(4)–M–O(7)	69.1 (3)	69.0 (2)	69.7 (3)	M–O(8)–C(4)	119.7 (9)	121.2 (6)	120 (1)
O(5)–M–O(7)	127.6 (3)	128.6 (2)	127.6 (3)	M–O(8)–C(5)	114.4 (8)	113.3 (5)	114.6 (8)
O(6)–M–O(7)	63.9 (3)	64.1 (2)	64.4 (3)	M–O(9)–C(6)	122 (1)	126.5 (7)	120 (1)
O(1)–M–O(8)	131.6 (5)	129.2 (3)	132.7 (5)	M–O(9)–C(7)	113.5 (8)	113.8 (5)	113.4 (8)
C–O–C (av)	114 (2)	111 (3)	113 (2)	O–C_β–C_α (av)	108 (1)	106 (3)	107 (1)
O–C_α–C_β (av)	109 (1)	109.3 (8)	109.5 (9)				
atoms	**M = Y**	**M = Ho**	**M = Er**	**atoms**	**M = Y**	**M = Ho**	**M = Er**
Distances							
M–O(1)	2.494 (9)	2.491 (8)	2.481 (5)	M–O(6)	2.56 (1)	2.50 (1)	2.488 (7)
M–O(2)	2.329 (9)	2.35 (1)	2.310 (6)	M–O(7)	2.445 (9)	2.50 (1)	2.495 (7)
M–O(3)	2.23 (1)	2.39 (1)	2.31 (8)	M–O(8)	2.42 (1)	2.52 (1)	2.497 (7)
M–O(4)	2.389 (9)	2.38 (1)	2.376 (6)	M–O(9)	2.59 (1)	2.53 (1)	2.528 (7)
M–O(5)	2.47 (1)	2.33 (1)	2.342 (8)				
O–C (av)	1.46 (2)	1.43 (5)	1.45 (2)	C–C (av)	1.48 (2)	1.52 (9)	1.50 (6)

Table I (Continued)

atoms	M = Y	M = Ho	M = Er	atoms	M = Y	M = Ho	M = Er
			Angles				
O(1)-M-O(2)	70.9 (3)	70.6 (3)	70.2 (2)	O(2)-M-O(8)	81.7 (3)	78.6 (4)	79.7 (2)
O(1)-M-O(3)	74.1 (5)	69.0 (7)	70.0 (4)	O(3)-M-O(8)	70.4 (4)	68.5 (4)	69.0 (2)
O(2)-M-O(3)	86.4 (4)	83.6 (4)	83.9 (2)	O(4)-M-O(8)	131.5 (3)	128.1 (3)	128.5 (2)
O(1)-M-O(4)	67.7 (3)	68.8 (3)	68.5 (2)	O(5)-M-O(8)	143.5 (4)	145.1 (4)	144.5 (2)
O(2)-M-O(4)	138.6 (3)	139.4 (3)	138.6 (2)	O(6)-M-O(8)	97.6 (3)	97.7 (3)	97.7 (2)
O(3)-M-O(4)	84.3 (4)	80.9 (4)	81.0 (2)	O(7)-M-O(8)	65.7 (3)	64.8 (4)	64.9 (2)
O(1)-M-O(5)	66.1 (5)	71.7 (7)	70.3 (4)	O(1)-M-O(9)	128.8 (4)	132.0 (4)	131.3 (3)
O(2)-M-O(5)	81.8 (4)	85.7 (4)	84.0 (2)	O(2)-M-O(9)	67.6 (3)	68.0 (3)	68.6 (2)
O(3)-M-O(5)	140.2 (3)	140.6 (3)	140.2 (2)	O(3)-M-O(9)	130.0 (4)	127.6 (4)	128.5 (2)
O(4)-M-O(5)	80.1 (4)	83.1 (4)	83.5 (2)	O(4)-M-O(9)	142.8 (3)	147.1 (3)	146.4 (2)
O(1)-M-O(6)	126.2 (5)	132.9 (7)	131.4 (4)	O(5)-M-O(9)	79.3 (3)	81.8 (4)	80.7 (2)
O(2)-M-O(6)	124.8 (3)	128.6 (4)	128.2 (2)	O(6)-M-O(9)	63.1 (3)	65.0 (3)	64.3 (2)
O(3)-M-O(6)	145.5 (3)	143.1 (4)	143.8 (2)	O(7)-M-O(9)	97.7 (3)	98.0 (3)	97.8 (2)
O(4)-M-O(6)	80.3 (3)	82.3 (3)	82.4 (2)	O(8)-M-O(9)	64.3 (3)	63.4 (4)	63.9 (2)
O(5)-M-O(6)	66.6 (3)	68.4 (4)	68.4 (3)	M-O(6)-C(1)	112.5 (9)	112 (1)	114.4 (6)
O(1)-M-O(7)	133.0 (4)	130.0 (4)	130.9 (2)	M-O(6)-C(8)	120.4 (9)	122 (1)	121.9 (7)
O(2)-M-O(7)	147.4 (4)	143.1 (4)	144.4 (2)	M-O(7)-C(2)	124 (1)	119 (1)	120.1 (6)
O(3)-M-O(7)	81.7 (3)	78.9 (4)	79.8 (2)	M-O(7)-C(3)	113.7 (9)	117 (1)	114.1 (6)
O(4)-M-O(7)	70.3 (3)	69.0 (4)	69.3 (2)	M-O(8)-C(4)	121.1 (8)	118 (1)	119.7 (7)
O(5)-M-O(7)	125.4 (3)	127.4 (4)	127.5 (2)	M-O(8)-C(5)	116.0 (8)	115 (1)	114.1 (6)
O(6)-M-O(7)	64.1 (3)	64.4 (3)	64.2 (2)	M-O(9)-C(6)	118 (1)	125 (1)	124.6 (8)
O(1)-M-O(8)	136.1 (5)	129.4 (7)	130.9 (4)	M-O(9)-C(7)	114.3 (8)	114 (1)	113.8 (6)
C-O-C (av)	113 (1)	112 (2)	112 (2)	O-C_β-C_α (av)	107 (1)	107 (2)	107 (2)
O-C_α-C_β (av)	109 (2)	108 (2)	109.1 (5)				

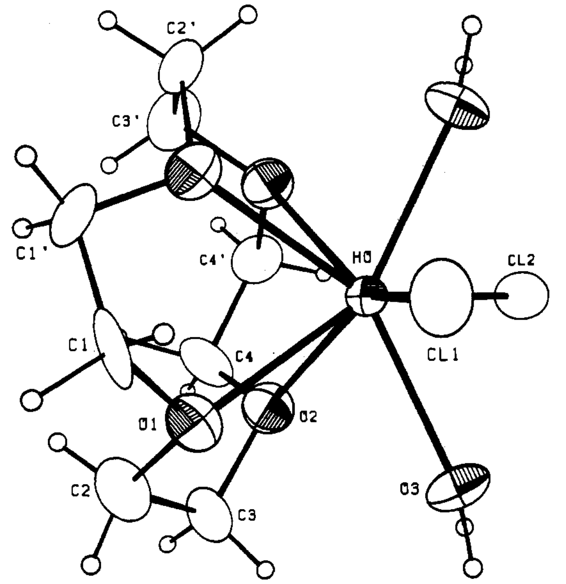

Figure 3. Coordination geometry of $[MCl_2(OH_2)_2(12\text{-crown-}4)]Cl$ (M = Ho shown). Primed and unprimed carbon atoms are disordered.

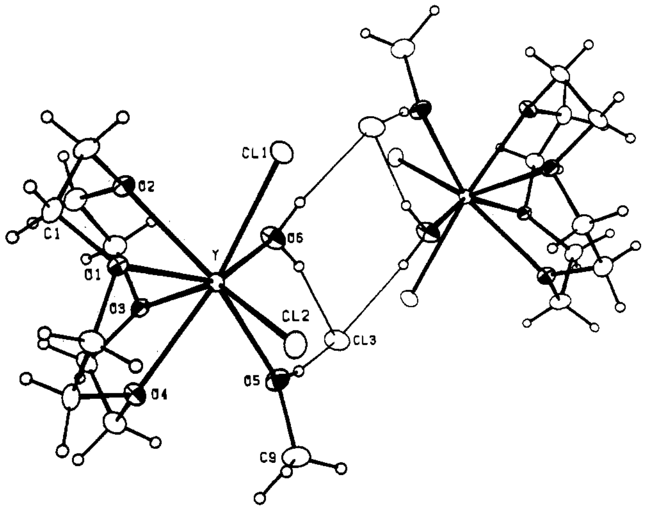

Figure 4. Dimers of the formula unit bridged by hydrogen bonds to Cl(3) in $[YCl_2(OH_2)(OHMe)(12\text{-crown-}4)]Cl$. The two Cl(3) ions are related by $1 - x, -y, 1 - z$. The O···Cl(3) contacts are O(5)···Cl(3) = 3.025 (3) Å, O(6)···Cl(3) = 3.028 (3) Å, and O(6)···Cl(3)^a = 3.112 (3) Å. All hydrogen atoms were located.

of the metal ion in prismatic coordination sites, as are all four of the crown ether oxygen atoms. The two water molecules, O(3) and O(3)a, are in capping positions slightly distorted toward forming a square face with Cl(1) and Cl(2).

The carbon atoms of the 12-crown-4 ring are disordered into two orientations, which are mirror images of each other. Although the disorder leads to high standard deviations, the average crown ether parameters are not unusual. The crown ring adopts the C_4 conformation as observed for the complexes above. The distances the metal ions reside from the planes of the four α (C(1), C(2)', C(4)', C(3)) and four β (C(1)', C(2), C(4), C(3)') carbon atoms range from 2.04 (α) and 2.59 (β) Å for M = Ho to 2.01 (α) and 2.50 (β) Å for M = Lu.

The hydrogen atoms associated with the unique water molecule, O(3), were located in difference Fourier maps for the five determinations in this series. Since there are only two unique hydrogen bonds, the overall hydrogen-bonding patterns are much less complex and much more regular than observed in the heptahydrates. Formula units related by a unit translation along *b* are bridged by O(3) hydrogen bonding to Cl(3) (the noncoordinated chloride ion) and Cl(2). These interactions result in parallel offset chains hydrogen bonded in pairs. The two hydrogen bonds to Cl(2) have a dramatic effect on the M-Cl(2) separation compared to Cl(1), which has no hydrogen-bonding interactions. The M-Cl(1) and M-Cl(2) distances range from 2.598 (2) and 2.684 (2) Å (M = Ho) to 2.575 (3) and 2.656 (3) Å (M = Lu).

$[YCl_2(OH_2)(OHMe)(12\text{-crown-}4)]Cl$. Despite the similarity in formula with the other eight-coordinate 12-crown-4 complexes isolated, this complex is quite different structurally. An ORTEP diagram is presented in Figure 4; bond distances and angles are given in Table III. Unlike the structures observed for $[MCl_2(OH_2)_2(12\text{-crown-}4)]Cl$, this complex is square-antiprismatic with the chloride ions in cis positions in one square face. In addition, the hydrogen bonding is not polymeric; instead, dimers form of two formula units, with the water molecule O(6) and methanol group O(5) donating one hydrogen bond each to the noncoordinated chloride ion (Cl(3)) in one asymmetric unit and O(6) donating another hydrogen bond to Cl(3) related through a center of inversion ($1 - x, -y, 1 - z$). The hydrogen bonding is confined to a narrow region, almost a single layer of the unit cell.

The 12-crown-4 molecule again exhibits a C_4 conformation. This complex was studied at −150 °C and does not exhibit disorder

Table II. Bond Distances (Å) and Angles (deg) for $[MCl_2(OH_2)_2(12\text{-crown-4})]Cl^a$

atoms	M = Ho	M = Er	M = Tm	atoms	M = Ho	M = Er	M = Tm
			Distances				
M–Cl(1)	2.598 (2)	2.590 (3)	2.585 (4)	M–O(2)	2.471 (4)	2.457 (5)	2.446 (6)
M–Cl(2)	2.684 (2)	2.674 (3)	2.666 (4)	M–O(3)	2.326 (4)	2.311 (5)	2.296 (6)
M–O(1)	2.434 (4)	2.429 (5)	2.407 (6)				
O–C (av)	1.45 (9)	1.45 (9)	1.43 (8)	C–C (av)	1.50 (2)	1.49 (4)	1.54 (4)
			Angles				
Cl(1)–M–Cl(2)	118.90 (7)	118.8 (1)	118.3 (1)	O(1)–M–O(3)a	142.8 (1)	143.0 (2)	142.8 (2)
Cl(1)–M–O(1)	82.2 (1)	82.0 (1)	82.3 (2)	O(2)–M–O(2)a	65.9 (2)	65.6 (2)	65.7 (3)
Cl(2)–M–O(1)	142.22 (9)	142.3 (1)	142.3 (1)	O(2)–M–O(3)a	137.6 (1)	137.4 (2)	137.2 (2)
Cl(1)–M–O(2)	142.51 (9)	142.8 (1)	143.0 (1)	O(3)–M–O(3)a	128.0 (2)	127.7 (3)	128.4 (3)
Cl(2)–M–O(2)	81.7 (1)	81.5 (1)	81.3 (2)	M–O(1)–C(1)	108.2 (5)	110.4 (7)	108.5 (9)
O(1)–M–O(2)	65.5 (1)	65.9 (2)	66.2 (2)	M–O(1)–C(2)	127.6 (5)	126.1 (7)	126.3 (8)
Cl(1)–M–O(3)	79.78 (9)	79.7 (1)	79.8 (1)	M–O(1)a–C(1)′	126.5 (5)	124.3 (6)	125.9 (7)
Cl(2)–M–O(3)	74.63 (9)	74.5 (1)	74.6 (1)	M–O(1)a–C(2)′	108.6 (4)	108.9 (6)	111.3 (7)
O(1)–M–O(3)	79.6 (1)	79.6 (2)	79.2 (2)	M–O(2)–C(3)	108.9 (4)	111.7 (7)	110.8 (8)
O(2)–M–O(3)	76.2 (1)	76.4 (2)	75.9 (2)	M–O(2)–C(4)	124.2 (5)	123.9 (7)	126.8 (8)
O(1)–M–O(1)a	65.9 (2)	66.2 (2)	66.2 (3)	M–O(2)a–C(3)′	125.1 (5)	122.9 (7)	123.1 (8)
O(1)–M–O(2)a	100.1 (1)	100.6 (2)	100.9 (2)	M–O(2)a–C(4)′	108.9 (4)	110.0 (5)	109.5 (6)
C–O–C (av)	111 (1)	111 (2)	112 (2)	O–C_β–C_α (av)	102 (2)	105 (2)	103 (3)
O–C_α–C_β (av)	111 (1)	110 (3)	110 (3)				

atoms	M = Yb	M = Lu	atoms	M = Yb	M = Lu
		Distances			
M–Cl(1)	2.576 (2)	2.575 (3)	M–O(2)	2.439 (4)	2.429 (5)
M–Cl(2)	2.661 (2)	2.656 (3)	M–O(3)	2.283 (3)	2.276 (4)
M–O(1)	2.397 (4)	2.395 (5)			
O–C (av)	1.42 (9)	1.44 (9)	C–C (av)	1.50 (1)	1.51 (3)
		Angles			
Cl(1)–M–Cl(2)	118.41 (7)	118.64 (9)	O(1)–M–O(3)a	143.1 (1)	142.9 (2)
Cl(1)–M–O(1)	82.1 (1)	81.7 (1)	O(2)–M–O(2)a	66.1 (2)	65.9 (2)
Cl(2)–M–O(1)	142.24 (9)	142.2 (1)	O(2)–M–O(3)a	137.6 (1)	137.7 (2)
Cl(1)–M–O(2)	142.99 (9)	143.0 (1)	O(3)–M–O(3)a	127.4 (2)	127.4 (2)
Cl(2)–M–O(2)	81.0 (1)	80.9 (1)	M–O(1)–C(1)	110.0 (5)	111.2 (5)
O(1)–M–O(2)	66.4 (1)	66.7 (2)	M–O(1)–C(2)	125.0 (5)	125.1 (6)
Cl(1)–M–O(3)	79.44 (9)	79.2 (1)	M–O(1)a–C(1)′	123.8 (4)	124.8 (6)
Cl(2)–M–O(3)	74.47 (9)	74.7 (1)	M–O(1)a–C(2)′	109.0 (4)	109.0 (6)
O(1)–M–O(3)	79.4 (1)	79.1 (2)	M–O(2)–C(3)	110.5 (4)	111.5 (6)
O(2)–M–O(3)	76.1 (1)	76.3 (2)	M–O(2)–C(4)	124.4 (5)	122.5 (6)
O(1)–M–O(1)a	66.6 (2)	66.8 (2)	M–O(2)a–C(3)′	123.4 (5)	123.0 (7)
O(1)–M–O(2)a	101.5 (1)	101.8 (2)	M–O(2)a–C(4)′	109.9 (4)	111.3 (5)
C–O–C (av)	111 (3)	114 (4)	O–C_β–C_α (av)	105 (1)	106 (1)
O–C_α–C_β (av)	110 (1)	104 (6)			

[a] Primed atoms refer to the disordered carbon atom positions; atoms designated with the letter "a" refer to atoms related by the crystallographic mirror planes.

or pseudosymmetry. As a result, the average crown ether parameters can be used to illustrate the differences in the α (C(2), C(4), C(6), C(8)) and β (C(1), C(3), C(5), C(7)) carbon positions. The α-carbon atoms reside in a plane closer to the metal ion (2.05 Å) than the plane of the β-carbon atoms (2.61 Å). In addition, the C_β–C_α–O bond angles (109.0 (2)° average) are wider than the C_α–C_β–O angles (106.2 (6)°). The C_β–C_α–O–C_β torsion angles are the ones that are forced gauche in the C_4 conformation of 12-crown-4. These angles average 88° in $[YCl_2(OH_2)(OHMe)(12\text{-crown-4})]Cl$. The C–O and C–C bond distances and C–O–C bond angles average 1.450 (6) Å, 1.498 (5) Å, and 112.4 (7)°, respectively.

Discussion

Izatt[16,17] studied the reactions of 18-crown-6 with hydrated lanthanide chlorides in aqueous methanol and found little evidence for complexation past M = Gd. This was attributed to lower solvation of the late-series lanthanide(III) ions (because of their size) and a consequently lower entropy contribution from the loss of solvent or water molecules upon complexation of the crown ether. While we have prepared complexes of this ether with Ln(III) ions as small as Y^{3+} (chloride salt)[10] by modifying the solvent system, differences in solvation of the lanthanide series ions continue to play a major role in their complexation chemistry.

Studies of reactions of 18-crown-6 with $LaCl_3{\cdot}nH_2O$ by us and others reveal no reaction past M = Y as indicated above. Structural studies on those complexes that do form reveal a competition in the late-series lanthanides between complexation and the formation of hydrogen-bonded aquated complexes ($[M(OH_2)_7(OHMe)][MCl(OH_2)_2(18\text{-crown-6})]_2Cl_7{\cdot}2H_2O$ (M = Dy, Y)[10] and $[Dy(OH_2)_8]Cl_3{\cdot}18\text{-crown-6}{\cdot}4H_2O$[18] have been characterized). Only aquated ions with hydrogen-bonded ethers and chloride anions have been isolated for 15-crown-5 (although Atwood has prepared and structurally characterized a complex containing $[YbCl_2(15\text{-crown-5})]^+$ under anhydrous conditions[19]). In the investigation of the acyclic four-oxygen donor triethylene glycol (EO3), solvation was also found to interfere with the formation of complexes of the heavier lanthanides; however, it was still possible to isolate and characterize EO3 complexes of all of the lanthanide ions, hydrates of the early- and mid-series lanthanides ($[LaCl_2(OH_2)_2(EO3)]_2Cl_2$[8] and $[M(OH_2)_5(EO3)]Cl_3$ (M = Nd, Sm–Gd, Dy, Y)[20]) and anhydrous solvates of the

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Table III. Bond Distances (Å) and Angles (deg) for $[YCl_2(OH_2)(OHMe)(12\text{-crown-4})]Cl$

	Distances		
Y–Cl(1)	2.647 (1)	Y–Cl(2)	2.625 (1)
Y–O(1)	2.430 (3)	Y–O(2)	2.466 (3)
Y–O(3)	2.472 (3)	Y–O(4)	2.458 (3)
Y–O(5)	2.364 (3)	Y–O(6)	2.325 (3)
O(1)–C(1)	1.461 (5)	O(1)–C(8)	1.442 (5)
O(2)–C(2)	1.445 (5)	O(2)–C(3)	1.452 (5)
O(3)–C(4)	1.451 (5)	O(3)–C(5)	1.446 (5)
O(4)–C(6)	1.448 (5)	O(4)–C(7)	1.453 (5)
O(5)–C(9)	1.469 (5)	C(1)–C(2)	1.493 (6)
C(3)–C(4)	1.501 (6)	C(5)–C(6)	1.499 (6)
C(7)–C(8)	1.501 (6)		
	Angles		
Cl(1)–Y–Cl(2)	82.63 (4)	Cl(1)–Y–O(1)	88.42 (7)
Cl(2)–Y–O(1)	80.08 (7)	Cl(1)–Y–O(2)	76.31 (7)
Cl(2)–Y–O(2)	140.06 (7)	O(1)–Y–O(2)	65.96 (9)
Cl(1)–Y–O(3)	131.90 (7)	Cl(2)–Y–O(3)	145.36 (7)
O(1)–Y–O(3)	100.64 (9)	O(2)–Y–O(3)	65.3 (1)
Cl(1)–Y–O(4)	152.99 (7)	Cl(2)–Y–O(4)	83.45 (7)
O(1)–Y–O(4)	66.41 (9)	O(2)–Y–O(4)	100.5 (1)
O(3)–Y–O(4)	65.92 (9)	Cl(1)–Y–O(5)	124.76 (8)
Cl(2)–Y–O(5)	78.30 (8)	O(1)–Y–O(5)	136.9 (1)
O(2)–Y–O(5)	141.3 (1)	O(3)–Y–O(5)	78.2 (1)
O(4)–Y–O(5)	74.4 (1)	Cl(1)–Y–O(6)	75.19 (8)
Cl(2)–Y–O(6)	121.81 (8)	O(1)–Y–O(6)	149.6 (1)
O(2)–Y–O(6)	85.1 (1)	O(3)–Y–O(6)	73.7 (1)
O(4)–Y–O(6)	131.7 (1)	O(5)–Y–O(6)	72.3 (1)
Y–O(1)–C(1)	120.7 (2)	Y–O(1)–C(8)	113.3 (2)
C(1)–O(1)–C(8)	113.2 (3)	Y–O(2)–C(2)	113.1 (2)
Y–O(2)–C(3)	120.9 (2)	C(2)–O(2)–C(3)	112.5 (3)
Y–O(3)–C(4)	113.4 (2)	Y–O(3)–C(5)	119.4 (2)
C(4)–O(3)–C(5)	111.2 (3)	Y–O(4)–C(6)	114.1 (2)
Y–O(4)–C(7)	119.4 (2)	C(6)–O(4)–C(7)	112.8 (3)
Y–O(5)–C(9)	133.8 (3)	O(1)–C(1)–C(2)	106.0 (3)
O(2)–C(2)–C(1)	108.9 (4)	O(2)–C(3)–C(4)	105.7 (3)
O(3)–C(4)–C(3)	108.8 (3)	O(3)–C(5)–C(6)	105.8 (3)
O(4)–C(6)–C(5)	109.2 (4)	O(4)–C(7)–C(8)	107.1 (3)
O(1)–C(8)–C(7)	109.3 (3)		

late-series lanthanides ($[MCl_3(EO3)]\cdot CH_3CN$ (M = Ho, Lu),[20] $[MCl_3(EO3)]\cdot OHMe$ (M = Er, Yb, Lu),[20]and $[LuCl_3(EO3)]$[20]). The latter complexes appeared only after slowly concentrating the solutions. The early-series lanthanides formed a two-layer system as observed in our 12-crown-4 reactions.

Other researchers in this field[2,3] have tended to study 12-crown-4 complexation under anhydrous conditions, with 1:1 complexes of $Ln(NO_3)_3$ compounds,[13,21,22] 2:1 complexes with the poorer donor perchlorate salts,[21,22] and a variety of stoichiometries with the trifluoroacetate anion[23] observed. The few studies utilizing chloride salts have given rise to 1:1 complexes of $PrCl_3$ and $EuCl_3$, a monohydrate complex of $PrCl_3$ and 12-crown-4,[21,24] and the hydrated complex $[Lu(OH_2)_8]Cl_3\cdot 1.5(12\text{-crown-4})\cdot 2H_2O$.[12]

The previous work in this area and our observations of the title reactions suggest to us that these reactions follow set patterns. Where complexation is favored by entropic solvent loss and where the Ln^{III}/OH_2 interactions are the weakest (both apply to the early-series lanthanides), we observe immediate precipitation of a 1:1 complex. (Copious quantities of $MCl_3\cdot 12\text{-crown-4}\cdot 1.5H_2O$ form for M = La, Ce–Nd; smaller decreasing amounts of $MCl_3\cdot 12\text{-crown-4}\cdot 2.5H_2O$ are observed for M = Sm–Lu, including Y.) Clues to the structures of these complexes may be found in two recently determined crystal structures from our group: $[PrCl_3(OHMe)(12\text{-crown-4})]$[8] and $[PrCl_3(OH_2)(12\text{-crown-4})]\cdot 12\text{-crown-4}$.[8] The former was obtained by passing a low-level electric current through the supernatant solution prior to the formation of the second layer and the latter by increasing the crown to metal salt stoichiometry to 10:1. Both prove that eight-coordination with 12-crown-4, all three chloride anions, and one solvent or water molecule in the metal ion's primary coordination sphere is a viable alternative for even the larger lanthanide ions, and both indicate to us that well-ordered hydrogen bonding increases the likelihood of obtaining good single crystals.

We assume that the solutions remaining contain predominantly aquo ions and hydrogen-bonded crown ethers. We note that if these solutions are evaporated quickly, the starting salt, $LnCl_3\cdot nH_2O$, is crystallized. If, however, the solutions are very slowly concentrated, via evaporation, the 12-crown-4 ethers displace some of the solvation molecules, complex the metal ions, and form the viscous bottom layer observed in each reaction. For colored solutions this process can be followed by the slow draining of all color from the top layer until it is colorless, at which time the bottom, highly colored, layer stops growing. We believe that once this layer is formed, crystallization of the two forms is dictated by size considerations. The early- and mid-series lanthanides, which can easily support nine-coordination, crystallize as $[M(OH_2)_5(12\text{-crown-4})]Cl_3\cdot 2H_2O$; the later-series lanthanides form the eight-coordinate complexes $[MCl_2(OH_2)_2(12\text{-crown-4})]Cl$. Most likely the chloride ions in the latter enter the metal's primary coordination sphere upon crystallization.

While the Ln^{III}/12-crown-4 interactions may seem to be less favorable than complexation by 18-crown-6, where the ether can encircle the cation, or by 15-crown-5, with its larger cavity size, we have been able to easily isolate these 12-crown-4 complexes of $LnCl_3\cdot nH_2O$ salts. The same cannot be said of the larger ethers. As indicated above, we have been unable to complex 18-crown-6 to a chloride salt past M = Y and even those that do form with M = Dy, Y are very unstable. We have not yet been able to isolate a 15-crown-5 complex of any $LnCl_3\cdot nH_2O$ salt, obtaining instead aquated ions hydrogen-bonded to the ether in the solid state. We were thus curious to know if perhaps the conformation and size of the 12-crown-4 ether were of an ideal geometry to result in Ln(III) complexation. Toward investigation of that point we carried out the crystallographic examinations of as many of these complexes as we could obtain suitable single crystals for.

The 12-crown-4 molecule dominates the adoption of a preferred geometry in the complexes isolated: capped square antiprismatic for $[M(OH_2)_5(12\text{-crown-4})]Cl_3\cdot 2H_2O$ (M = Ce, Nd, Sm, Eu, Gd, Tb,[11] Dy, Y, Ho, Er), bicapped trigonal prismatic in $[MCl_2(OH_2)_2(12\text{-crown-4})]Cl$ (M = Ho, Er, Tm, Yb, Lu), and square antiprismatic in $[YCl_2(OH_2)(OHMe)(12\text{-crown-4})]Cl$. In each case the four ether oxygen atoms can be coplanar and the macrocyclic ring can adopt the favorable C_4 conformation. This was not the case in the two other structurally characterized lanthanide/12-crown-4 complexes, $[M(NO_3)_3(12\text{-crown-4})]$ (M = Eu,[13] Y[14]). In the latter 10-coordinate complexes, the crown ether was severely distorted to fit the observed 4A,6B-expanded dodecahedral geometry.

The nine-coordinate heptahydrates do not exhibit the normally observed geometry for complexes with unidentate or small-bite chelating ligands, that of a tricapped trigonal prism.[25] (In the nine-coordinate pentahydrates of $[M(OH_2)_5(EO3)]Cl_3$, the acyclic polyether has enough flexibility to allow the metal ion to adopt a tricapped-trigonal-prismatic geometry.[20]) The geometry observed for the title complexes not only allows the coplanarity of the crown ether donor atoms but also directs the hydrogen-bonding water molecules to one side of the coordination geometry. The $M\text{–}OH_2$(capping) and $M\text{–}OH_2$(square) separations follow the trends in ionic radii,[26] decreasing from M = Ce (2.570 (6), 2.49 (2) Å; Table IV) to M = Er (2.481 (5), 2.34 (2) Å).

The same trend is true for the M–O(crown) distances, and it is interesting to note how as the metal ion size is decreased, it is drawn closer to the crown ether cavity. The distance of the metal to the centroid of the plane defined by the crown oxygen atoms decreases from 1.77 Å (M = Ce) to 1.65 Å for M = Er. (This

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Table IV. Comparison of Bonding Parameters in Lanthanide 12-Crown-4 Complexes

complex	CN	G[a]	IR[b]	M–OH_2 (av), Å capping	M–OH_2 (av), Å other	M–O-(crown) (av), Å	M–cent-(OH_2),[c] Å	M–cent-(crown), Å	cent–M–cent, deg	M–Cl(1), Å	M–Cl(2), Å	ref[d]
$[M(OH_2)_5(12\text{-crown-}4)]Cl_3\cdot 2H_2O$												
M = Ce	9	csap	1.196	2.570 (6)	2.49 (2)	2.61 (2)	0.84	1.77	179			11
M = Nd	9	csap	1.163	2.548 (7)	2.46 (3)	2.58 (2)	0.84	1.74	178			
M = Sm	9	csap	1.132	2.527 (8)	2.41 (2)	2.55 (2)	0.82	1.71	177			
M = Eu	9	csap	1.120	2.511 (7)	2.41 (2)	2.54 (2)	0.82	1.69	178			
M = Gd	9	csap	1.107	2.500 (5)	2.40 (4)	2.53 (2)	0.82	1.68	175			
M = Tb	9	csap	1.095	2.504 (7)	2.38 (2)	2.52 (1)	0.82	1.67	178			
M = Dy	9	csap	1.083	2.488 (7)	2.37 (1)	2.51 (2)	0.81	1.66	179			
M = Y	9	csap	1.075	2.494 (9)	2.35 (8)	2.50 (7)	0.81	1.64	169			
M = Ho	9	csap	1.072	2.491 (8)	2.36 (2)	2.51 (1)	0.81	1.65	176			
M = Er	9	csap	1.062	2.481 (5)	2.34 (2)	2.50 (2)	0.81	1.65	178			
$[MCl_2(OH_2)_2(12\text{-crown-}4)]Cl$												
M = Ho	8	bctp	1.015	2.326 (4)		2.45 (2)		1.57		2.598 (2)	2.684 (2)	
M = Er	8	bctp	1.004	2.311 (5)		2.44 (1)		1.56		2.590 (3)	2.674 (3)	
M = Tm	8	bctp	0.994	2.296 (6)		2.43 (2)		1.55		2.585 (4)	2.666 (4)	
M = Yb	8	bctp	0.985	2.283 (3)		2.42 (2)		1.53		2.576 (2)	2.661 (2)	
M = Lu	8	bctp	0.977	2.276 (4)		2.41 (2)		1.52		2.575 (3)	2.656 (3)	
$[YCl_2(OH_2)(OHMe)(12\text{-crown-}4)]Cl$[e]												
	8	sap	1.019		2.325 (3) 2.364 (3) (OHMe)	2.46 (2)		1.57		2.647 (1)	2.625 (1)	
$[La(NO_3)(OH_2)_4(12\text{-crown-}4)]Cl_2\cdot CH_3CN$												
	10	edod	1.27			2.66 (4)		1.84				8
$[LaCl_2(NO_3)(12\text{-crown-}4)]_2$												
	9	csap	1.216			2.62 (2)		1.79				8
$[PrCl_3(OHMe)(12\text{-crown-}4)]$												
	8	bctp	1.126			2.59 (2)		1.75				8
$[M(NO_3)_3(12\text{-crown-}4)]$												
M = Eu	10	edod				2.49 (5)						13
M = Y	10	edod				2.46 (4)						14

[a] Coordination geometry: sap = square antiprism, bctp = bicapped trigonal prism, csap = capped square antiprism, edod = 4A,6B-expanded dodecahedron. [b] Ionic radius for M^{3+} with CN shown from ref 26. [c] cent(OH_2) and cent(crown) refer to the centroids of the planes defined by the four prismatic coordinated water molecules in the heptahydrates and by the four coordinated ether atoms in all complexes, respectively. [d] All from this study unless otherwise indicated. [e] Crystal structure determined at −150 °C.

trend continues smoothly to M = Lu, where the M–centroid separation is 1.58 Å when corrected for the difference in ionic radii of eight-coordinate Lu^{3+} versus nine-coordinate Lu^{3+}.) It is apparent both from the average crown ether bonding parameters in Tables I–III and from the O(crown)···O(crown) contacts on the four sides of the square planes that the closer metal approach does not have much of an effect on the crown ether. The averages of the latter values range from 2.708 (9) Å (M = Ce) to 2.648 (7) Å (M = Lu), a difference of only 0.06 Å. In contrast, the distances of the metals to the centroids of the planes of the unidentate water molecules in the squares range only from 0.84 Å (M = Ce) to 0.81 Å (M = Er), and as a result a much greater change is noted in the $OH_2\cdots OH_2$ contacts around the square plane: 3.31 (3) Å for M = Ce to 3.11 (3) Å for M = Er, a difference of 0.20 Å.

The eight-coordinate complexes exhibit similar trends in coordination distances with decreasing ionic size. The two types of molecules do have, however, interesting differences in coordination geometry. The $[MCl_2(OH_2)_2(12\text{-crown-}4)]Cl$ complexes are bicapped-trigonal-prismatic distorted toward a square-antiprismatic geometry in which the coordinated chloride ions would be trans in one square face. The yttrium complex $[YCl_2(OH_2)(OHMe)(12\text{-crown-}4)]Cl$ is square-antiprismatic, and the two coordinated chloride ions are cis in one square face. The differences appear to be controlled by the hydrogen bonding in the lattice. Hydrogen bonding occurs to the noncoordinated and one coordinated chloride ion in the former, producing pairs of staggered hydrogen-bonded chains along *b*. In the latter, dimers of the formula units occur in the unit cell with all hydrogen bonds accepted by the noncoordinated chloride ions. In neither case are the coordination geometries even close to the commonly observed dodecahedral geometry,[25] which would have required large distortions away from planarity for the four crown oxygen atoms. We have previously observed a similar influence of coordination geometry by hydrogen-bonding patterns in these types of complexes. The metal ion is dodecahedral in $[M(OH_2)_8]Cl_3\cdot 2C_{10}H_8H_2$ (M = Gd,[27] Y,[28]), dodecahedral with distortions toward bicapped trigonal prismatic in $[M(OH_2)_8]Cl_3\cdot 15\text{-crown-}5$ (M = Gd,[5] Y,[6] Yb,[8] Lu[5]), bicapped trigonal prismatic distorted toward dodecahedral geometry in $[Dy(OH_2)_8]Cl_3\cdot 18\text{-crown-}6\cdot 4H_2O$,[18] bicapped trigonal prismatic distorted toward square antiprismatic in $[Lu(OH_2)_8]Cl_3\cdot 1.5(12\text{-crown-}4)\cdot 2H_2O$,[12] and square antiprismatic (both Na^+ and Lu^{3+}) in $[Lu(OH_2)_8][Na(12\text{-crown-}4)_2]Cl_4\cdot 2H_2O$.[29]

A final feature of crystallographic interest involves a comparison of the M–O distances in the 12-crown-4 complexes to those we have thus far obtained for several 18-crown-6 complexes of hydrated lanthanide chlorides. These 18-crown-6 complexes are nine-coordinate tricapped trigonal prismatic with the crown ether folded around the metal ion, yet despite the differences, the average M–O(18-crown-6) separations are virtually identical with those found in this study: $[CeCl_2(OH_2)(18\text{-crown-}6]Cl\cdot 2H_2O$,[8] 2.61 (2) Å; $[MCl(OH_2)_2(18\text{-crown-}6)]Cl_2\cdot 2H_2O$, 2.58 (2) Å (M = Nd[8]), 2.55 (2) Å (M = Sm[9]), 2.55 (4) Å (M = Eu[8]), 2.52 (3) Å (M = Gd[9]), 2.53 (5) Å (M = Tb[9]). The values observed for

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the low-temperature structure determinations of $[M(OH_2)_7(OHMe)][MCl(OH_2)_2(18\text{-crown-}6)]_2Cl_7{\cdot}2H_2O$[10] (M = Dy, 2.46 (5) Å; M = Y, 2.44 (5) Å) exhibit shorter averages when taken at face value than those for the 12-crown-4 complexes with the corresponding metal ion, but these differences are probably not too significant due to the relatively large esd's. For comparison, when the differences in eight- and nine-coordinate M^{3+} ionic radii are added to the M–O separations in the eight-coordinate complexes, values of 2.52 (Y), 2.51 (Ho), 2.50 (Er), 2.49 (Tm), 2.48 (Yb), and 2.46 (Lu) Å are obtained for $[YCl_2(OH_2)(OHMe)(12\text{-crown-}4)]Cl$ and $[MCl_2(OH_2)_2(12\text{-crown-}4)]Cl$, respectively. The values obtained for the two determinations of M = Ho and M = Er are identical when compared in this manner.

Conclusions

Small amounts of H_2O play a vital role in the formation of Ln(III) complexes with the weaker donating crown ethers and polyethylene glycols and in the crystallization of well-ordered complexes. We see the need for further study of all 4f-metal/crown ether reactions under these conditions as well as detailed correlations of observed crystal structures with crystallization conditions. We hope that the latter will include crystallographic investigation of series of lanthanide(III)/crown ether complexes that will allow us to correlate subtle structural features with the observed differences in complexation chemistry other than metal ion size alone.

Several areas are currently under investigation in our laboratories that add some promise in the crystallization of new 12-crown-4 complexes of the rare earths. In one we are attempting to modify the anion environment by providing a mixture of "reasonably good" and "poor" donating anions. We have successfully crystallized both anhydrous and hydrated La^{III}/12-crown-4 complexes from the same reaction mixtures and recently structurally characterized $[La(NO_3)(OH_2)_4(12\text{-crown-}4)]Cl_2{\cdot}CH_3CN$ and $[LaCl_2(NO_3)(12\text{-crown-}4)]_2$. Another avenue we are pursuing involves the passage of low-level electric currents through the solutions containing $LnCl_3{\cdot}H_2O$ and 12-crown-4 prior to the formation of the viscous second layer. This has led to the crystallization and characterization of the anhydrous $[PrCl_3(OHMe)(12\text{-crown-}4)]$. A similar complex has been prepared by increasing the initial crown to metal ratio to 10:1, $[PrCl_3(OH_2)(12\text{-crown-}4)]{\cdot}12\text{-crown-}4$. These results are exciting to us because of the relative ease with which crystalline anhydrous complexes apparently can be obtained from hydrated starting materials and the ease with which the primary coordination sphere can be modified and still retain the 12-crown-4 linkage. Further reports from our group will focus on the structural and complexation chemistry of 12-crown-4 and the hydrated lanthanide chlorides modified in these ways.

Experimental Section

General Preparation of Complexes. A 1.236-mmol amount of hydrated lanthanide chloride salt (M = La, Ce–Nd, Sm–Lu, Y) was dissolved in 5 mL of a 3:1 mixture of acetonitrile/methanol. A 1.236-mmol (0.2-mL) amount of 12-crown-4 was pipetted into the solution. Immediate precipitation occurred, ranging from copious amounts for M = La, Ce–Nd to small amounts for M = Lu. Elemental analyses of the precipitates (given below) revealed the general formulation $MCl_3{\cdot}12\text{-crown-}4{\cdot}1.5H_2O$ for M = La, Ce, Pr, Nd and $MCl_3{\cdot}12\text{-crown-}4{\cdot}2.5H_2O$ for M = Sm–Lu, Y. The solutions containing the precipitates were heated with stirring for 1.5 h at 60 °C. The supernatants were then separated from the precipitates by centrifugation and cooled to room temperature. Refrigeration at 5 °C for 10 days produced no changes in these solutions.

A technique of very slow evaporation of the supernatant solutions was employed to obtain single crystals suitable for the crystallographic studies. It was observed that quick evaporation of the solutions (1–3 days) resulted in the crystallization of the chloride salt starting material, $MCl_3{\cdot}nH_2O$. When the evaporation rate was modified, crystallization of 12-crown-4 complexes was accomplished in 2–4 weeks. In all cases the crystallization processes followed a set pattern. First, a small drop of an immiscible viscous liquid or oil would begin forming at the bottom of the reaction flask. In the colored solutions this layer was highly colored and continued to form until all of the color had been drained from the top layer. Continued slow evaporation resulted in the crystallization of the 12-crown-4 complexes from this bottom viscous layer. Two hydrated forms were obtained for M = Dy–Er. The crystals had to be separated by hand. The heptahydrates formed very flat plates and the dihydrates elongated parallelepipeds. The formation of the dihydrate increased from Dy to Er and was the only form obtained for M = Tm–Lu. Very few crystals of the M = Dy dihydrate were obtained, and none of these were suitable for a detailed crystallographic study; however, preliminary cell data were obtained, confirming the formation of this complex. Suitable samples for M = La and M = Pr could not be obtained for the crystallographic study.

Elemental analyses on the precipitates obtained immediately upon addition of 12-crown-4 to the hydrated chloride salt are as follows. For M = La, Ce, Pr, and Nd, the formula was determined to be $MCl_3{\cdot}12\text{-crown-}4{\cdot}1.5H_2O$. Anal. Calcd for M = La: C, 21.42; H, 4.27. Found: C, 21.18; H, 4.48. Calcd for M = Ce: C, 21.37; H, 4.26. Found: C, 21.06; H, 4.20. Calcd for M = Pr: C, 21.33; H, 4.25. Found: C, 21.47; H, 4.37. Calcd for M = Nd: C, 21.17; H, 4.22. Found: C, 21.56; H, 4.34. For M = Sm–Lu, Y, the formula was determined to be $MCl_3{\cdot}12\text{-crown-}4{\cdot}2.5H_2O$. Anal. Calcd for M = Sm: C, 20.10; H, 4.43. Found: C, 19.99; H, 4.36. Calcd for M = Eu: C, 20.04; H, 4.41. Found: C, 20.12; H, 4.46. Calcd for M = Gd: C, 19.82; H, 4.37. Found: C, 20.34; H, 4.32. Calcd for M = Tb: C, 19.75; H, 4.35. Found: C, 19.81; H, 4.20. Calcd for M = Dy: C, 19.61; H, 4.32. Found: C, 19.80; H, 4.46. Calcd for M = Ho: C, 19.51; H, 4.30. Found: C, 19.49; H, 4.41. Calcd for M = Er: C, 19.42; H, 4.28. Found: C, 19.14; H, 4.15. Calcd for M = Tm: C, 19.35; H, 4.26. Found: C, 19.54; H, 4.11. Calcd for M = Yb: C, 19.19; H, 4.23. Found: C, 19.24; H, 4.26. Calcd for M = Lu: C, 19.12; H, 4.21. Found: C, 18.89; H, 4.30. Calcd for M = Y: C, 23.07; H, 5.08. Found: C, 23.23; H, 5.58.

Preparation and Crystallization of $[M(OH_2)_5(12\text{-crown-}4)]Cl_3{\cdot}2H_2O$ (M = Ce, Nd, Sm–Er, Y). These complexes were prepared as indicated above. Large platelike crystals grew from the bottom layer in each reaction flask as each solution was slowly evaporated. The crystals of these complexes do not appear to be hygroscopic, although they were studied in a period of low humidity. These complexes dehydrate at approximately 68–75 °C and decompose before melting. Analytical data on these samples confirm the formulation found in the crystallographic work. Anal. Calcd for M = Ce: C, 17.51; H, 5.51. Found: C, 17.70; M, 5.76. Calcd for M = Nd: C, 17.38; H, 5.47. Found: C, 17.26; H, 5.66. Calcd for M = Sm: C, 17.19; H, 5.41. Found: C, 17.42; H, 5.33. Calcd for M = Eu: C, 17.14; H, 5.39. Found: C, 16.30; H, 5.40. Calcd for M = Gd: C, 16.98; H, 5.34. Found: C, 16.09; H, 5.30. Calcd for M = Tb: C, 16.93; H, 5.34. Found: C, 17.39; H, 5.49. Calcd for M = Dy: C, 16.82; H, 5.29. Found: C, 16.85; H, 4.38. Calcd for M = Ho: C, 16.75; H, 5.27. Found: C, 16.25; H, 5.23. Calcd for M = Er: C, 16.69; H, 5.25. Found: C, 16.99; H, 5.42. Calcd for M = Y: C, 19.31; H, 6.08. Found: C, 20.31; H, 6.07.

Preparation and Crystallization of $[MCl_2(OH_2)_2(12\text{-crown-}4)]Cl$ (M = Dy–Lu). These complexes were prepared as indicated above. Crystallization of these was also observed to occur from the viscous bottom layer. For M = Dy, Ho, and Er these crystals had to be separated from the heptahydrate form on the basis of shape. A maximum of three or four crystals of this form were observed for M = Dy with increasing amounts for M = Ho and Er. This was the only form observed for M = Tm–Lu. These crystals are elongated parallelepipeds. Each dehydrates at approximately 145–155 °C and decomposes before melting. Enough crystals of M = Dy were not available for elemental analysis, and confirmation of the formation of this complex is limited to preliminary unit cell data. Elemental analyses of the remaining complexes confirmed the formulation obtained via the crystallographic work. Anal. Calcd for M = Ho: C, 19.87; H, 4.17. Found: C, 17.60; H, 5.42. Calcd for M = Er: C, 19.78; H, 4.15. Found: C, 19.64; H, 4.05. Calcd for M = Tm: C, 19.71; H, 4.14. Found: C, 19.90; H, 4.68. Calcd for M = Yb: C, 19.55; H, 4.10. Found: C, 18.75; H, 4.44. Calcd for M = Lu: C, 19.47; H, 4.08. Found: C, 19.55; H, 4.20.

Preparation and Crystallization of $[YCl_2(OH_2)(OHMe)(12\text{-crown-}4)]Cl$. This complex was prepared as above. During the heating step, crystals were observed to have formed around the top of the reaction flask. The crystals of this complex are extremely deliquescent, and no elemental or melting point data could be obtained. The formation of this complex was determined by single-crystal X-ray analysis at −150 °C.

X-ray Data Collection, Structure Determination, and Refinement for $[M(OH_2)_5(12\text{-crown-}4)]Cl_3{\cdot}2H_2O$ (M = Ce, Nd, Sm, Eu, Gd, Dy, Y, Ho, Er). Single crystals of these complexes were mounted on pins and transferred to the goniometer. The space groups were determined to be either the centric *Pnam* or acentric *Pna*2_1 from the systematic absences. These structures are isostructural with the previously determined Tb[11] analogue, which was determined to be noncentrosymmetric. The coordinates from M = Tb were used as a starting point in the refinement for the Er complex, and for the other complexes the coordinates of the

Table V. Crystallographic Data[a]

	$[M(OH_2)_5(12\text{-crown-4})]Cl_3 \cdot 2H_2O$					
	M = Ce	M = Nd	M = Sm	M = Eu	M = Gd	M = Dy
a, Å	18.969 (6)	18.893 (5)	18.808 (6)	18.780 (4)	18.773 (4)	18.717 (4)
b, Å	10.156 (3)	10.130 (3)	10.101 (3)	10.089 (2)	10.082 (3)	10.056 (5)
c, Å	10.307 (4)	10.279 (3)	10.263 (4)	10.243 (2)	10.236 (3)	10.216 (3)
α, deg						
β, deg						
γ, deg						
V, $Å^3$	1985.6	1967.3	1949.8	1940.8	1937.4	1922.8
Z	4	4	4	4	4	4
fw	548.8	552.9	559.1	560.6	565.9	571.2
space group	$Pna2_1$ (No. 33)	$Pna2_1$	$Pna2_1$	$Pna2_1$	$Pna2_1$	$Pna2_1$
T, °C	20	20	20	20	20	20
ρ_{calc}, g cm^{-3}	1.84	1.87	1.90	1.92	1.94	1.97
μ_{calc}, cm^{-1}	25.7	29.1	32.8	34.8	36.8	41.3
range of rel transmissn factors, %	64–100	61–100	64–100	77–100	55–100	62–100
$R(F_o)^{c,d}$	0.032	0.034	0.034	0.031	0.023	0.032
$R_w(F_o)$	0.033	0.036	0.043	0.032	0.026	0.033

	$[M(OH_2)_5(12\text{-crown-4})]Cl_3 \cdot 2H_2O$			$[YCl_2(OH_2)(OHMe)\text{-}(12\text{-crown-4})]Cl$	$[MCl_2(OH_2)_2(12\text{-crown-4})]Cl$	
	M = Y	M = Ho	M = Er		M = Ho	M = Er
a, Å	18.679 (5)	18.688 (5)	18.695 (1)	7.301 (4)	7.401 (4)	7.377 (4)
b, Å	10.051 (4)	10.048 (2)	10.048 (1)	8.148 (2)	8.708 (2)	8.690 (2)
c, Å	10.213 (4)	10.203 (3)	10.210 (1)	14.032 (3)	11.798 (4)	11.794 (4)
α, deg				89.66 (2)		
β, deg				81.75 (3)	95.51 (5)	95.44 (5)
γ, deg				74.36 (4)		
V, $Å^3$	1917.4	1915.9	1918.0	795.1	756.8	752.7
Z	4	4	4	2	2	2
fw	497.6	573.6	575.9	421.5	483.5	485.9
space group	$Pna2_1$	$Pna2_1$	$Pna2_1$	$P\bar{1}$ (No. 2)	$P2_1/m$ (No. 11)	$P2_1/m$
T, °C	20	20	20	−150	20	20
ρ_{calc}, g cm^{-3}	1.72	1.99	1.99	1.76	2.12	2.14
μ_{calc}, cm^{-1}	34.2	43.7	46.0	40.9	55.0	58.3
range of rel transmissn factors, %	58–100	95–100	87–100	57–100	85–100	70–100
$R(F_o)^{c,d}$	0.049	0.035	0.025	0.036	0.025	0.030
$R_w(F_o)$	0.055	0.036	0.027	0.038	0.027	0.035

	$[MCl_2(OH_2)_2(12\text{-crown-4})]Cl$		
	M = Tm	M = Yb	M = Lu
a, Å	7.356 (5)	7.334 (3)	7.323 (4)
b, Å	8.674 (2)	8.662 (2)	8.653 (4)
c, Å	11.809 (4)	11.843 (4)	11.844 (4)
α, deg			
β, deg	95.46 (5)	95.65 (3)	95.42 (5)
γ, deg			
V, $Å^3$	750.1	748.6	747.2
Z	2	2	2
fw	487.5	491.6	493.6
space group	$P2_1/m$	$P2_1/m$	$P2_1/m$
T, °C	20	20	20
ρ_{calc}, g cm^{-3}	2.16	2.18	2.19
μ_{calc}, cm^{-1}	61.6	64.9	68.3
range of rel transmissn factors, %	61–100	68–100	65–100
$R(F_o)^{b,c}$	0.034	0.024	0.029
$R_w(F_o)$	0.045	0.026	0.031

[a] Enraf-Nonius CAD-4 diffractometer, θ–2θ scan technique, Mo Kα radiation (λ = 0.71073 Å, graphite monochromated), SHELX computer programs.[30] [b] Corrections: Lorentz–polarization and absorption (empirical, ψ scan). [c] Neutral scattering factors and anomalous dispersion corrections from ref 31.

member of the series indicated in Table V were used. A reinvestigation of the space group ambiguity again revealed $Pna2_1$ to be the correct choice. Were the space group to be centric, one chlorine, the carbon atoms, and a few of the oxygen atoms would be disordered. Refinement in the centric *Pnam* (a nonstandard setting of *Pnma*) produced the disorder and elongated ellipsoids even for those atoms on the mirror. Refinement was, therefore, carried out in the noncentrosymmetric $Pna2_1$. As a consequence of the pseudo mirror symmetry, correlations between parameters were noted in the 0.55–0.68 range. Standard deviations for bond lengths and angles involving these atoms are, therefore, a bit high.

A summary of data collection parameters is given in Table V. The crown 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 remaining hydrogen atoms were not included in the final refinement. Refinement of the non-hydrogen atoms with anisotropic temperature factors led to the final values of *R* given in Table V. The final values of the positional parameters are given in Table VI for M = Ce. The fractional coordinates for the remaining complexes have been deposited in the supplementary material.

X-ray Data Collection, Structure Determination, and Refinement for $[YCl_2(OH_2)(OHMe)(12\text{-crown-4})]Cl$. A transparent single crystal of the title complex was mounted on a pin and transferred to the goniometer. The crystal was cooled to −150 °C during data collection by using a stream of cold nitrogen gas. The space group was determined to be either the centric $P\bar{1}$ or acentric $P1$. Statistical tests indicated that the space group was centric, and the subsequent solution and successful refinement of the structure in the space group $P\bar{1}$ confirmed this. A summary of data collection parameters is given in Table V.

Least-squares refinement with isotropic thermal parameters led to *R* = 0.054. The crown 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 solvent and water hydrogen atoms were located from a difference Fourier map and included with fixed contributions (*B* = 5.5 $Å^2$). Refinement of the non-hydrogen atoms with

Table VI. Final Fractional Coordinates for $[Ce(OH_2)_5(12\text{-crown-4})]Cl_3{\cdot}2H_2O$

atom	*x/a*	*y/b*	*z/c*	*B*(eqv),[a] Å^2
Ce	−0.72554 (2)	−0.61266 (5)	0.0000	1.06
Cl(1)	−0.5383 (1)	−0.9403 (3)	0.0032 (8)	2.90
Cl(2)	−0.7525 (1)	−0.1157 (2)	0.0002 (8)	1.87
Cl(3)	−0.5290 (3)	−0.6118 (5)	−0.2803 (6)	3.47
O(1)	−0.5901 (3)	−0.6208 (7)	−0.001 (2)	2.11
O(2)	−0.6854 (3)	−0.8399 (7)	−0.0302 (8)	1.93
O(3)	−0.6820 (5)	−0.5823 (8)	−0.226 (1)	1.59
O(4)	−0.6761 (3)	−0.3836 (7)	0.025 (1)	1.73
O(5)	−0.6811 (6)	−0.6430 (9)	0.225 (1)	2.06
O(6)	−0.8171 (4)	−0.5304 (8)	0.1690 (8)	1.70
O(7)	−0.8177 (4)	−0.4379 (8)	−0.0779 (8)	1.57
O(8)	−0.8194 (4)	−0.6884 (8)	−0.1657 (8)	1.73
O(9)	−0.8211 (4)	−0.7819 (8)	0.0798 (8)	1.67
O(10)	−0.5418 (4)	−0.2571 (8)	−0.018 (1)	2.50
O(11)	−0.5415 (7)	−0.660 (1)	0.270 (2)	4.81
C(1)	−0.8403 (6)	−0.397 (1)	0.148 (1)	1.88
C(2)	−0.8696 (5)	−0.386 (1)	0.014 (3)	1.54
C(3)	−0.8444 (7)	−0.462 (1)	−0.206 (1)	2.14
C(4)	−0.8733 (9)	−0.599 (1)	−0.217 (2)	1.74
C(5)	−0.8462 (6)	−0.818 (1)	−0.144 (1)	1.78
C(6)	−0.8772 (5)	−0.826 (1)	−0.007 (3)	2.03
C(7)	−0.8447 (7)	−0.755 (1)	0.206 (1)	1.81
C(8)	−0.873 (1)	−0.618 (1)	0.212 (2)	2.15

[a] $B(\text{eqv}) = {}^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^3\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

Table VII. Final Fractional Coordinates for $[YCl_2(OH_2)(OHMe)(12\text{-crown-4})]Cl$

atom	*x/a*	*y/b*	*z/c*	*B*(eqv),[a] Å^2
Y	0.89397 (6)	−0.16633 (5)	0.23216 (3)	0.54
Cl(1)	0.6565 (2)	0.1194 (1)	0.18463 (7)	0.88
Cl(2)	0.7267 (2)	−0.3041 (1)	0.11311 (8)	1.04
Cl(3)	0.6131 (2)	−0.2659 (1)	0.53220 (7)	1.15
O(1)	1.1038 (4)	−0.1583 (4)	0.0822 (2)	0.69
O(2)	1.0795 (4)	0.0452 (4)	0.2342 (2)	0.78
O(3)	1.1290 (4)	−0.2229 (4)	0.3470 (2)	0.81
O(4)	1.1560 (4)	−0.4291 (4)	0.1943 (2)	0.77
O(5)	0.7988 (4)	−0.3776 (4)	0.3276 (2)	1.05
O(6)	0.7286 (4)	−0.0361 (4)	0.3782 (2)	1.05
C(1)	1.2323 (6)	−0.0474 (6)	0.0739 (3)	0.96
C(2)	1.1331 (7)	0.1037 (6)	0.1395 (3)	0.98
C(3)	1.2305 (7)	0.0236 (6)	0.2939 (3)	1.09
C(4)	1.1703 (7)	−0.0701 (6)	0.3800 (3)	1.05
C(5)	1.3025 (6)	−0.3613 (6)	0.3262 (3)	0.91
C(6)	1.2467 (6)	−0.4989 (6)	0.2764 (3)	0.96
C(7)	1.2928 (6)	−0.4417 (6)	0.1067 (3)	0.89
C(8)	1.1917 (6)	−0.3243 (6)	0.0363 (3)	0.90
C(9)	0.7925 (7)	−0.5524 (6)	0.3074 (4)	1.52

[a] See footnote *a* of Table VI.

anisotropic temperature factors led to final values of $R = 0.036$ and $R_w = 0.038$. The final values of the positional parameters are given in Table VII.

X-ray Data Collection, Structure Determination, and Refinement for $[MCl_2(OH_2)_2(12\text{-crown-4})]Cl$ (M = Ho, Er, Tm, Yb, Lu). The space group was determined to be either the centric $P2_1/m$ or acentric $P2_1$ from the systematic absences. Statistical tests indicated that the space group was centric, and the subsequent solution and successful refinement of the structure in the space group $P2_1/m$ confirmed this despite the presence of disorder discussed below. A summary of data collection parameters is given in Table V.

Table VIII. Final Fractional Coordinates for $[HoCl_2(OH_2)_2(12\text{-crown-4})]Cl$

atom	*x/a*	*y/b*	*z/c*	*B*(eqv),[a] Å^2
Ho	−0.00005 (5)	0.2500	0.21495 (3)	1.39
Cl(1)	0.2835 (3)	0.2500	0.3629 (2)	2.63
Cl(2)	0.0480 (3)	0.2500	−0.0076 (2)	2.45
Cl(3)	0.3361 (3)	0.7500	0.2901 (2)	2.29
O(1)	−0.1269 (5)	0.0980 (4)	0.3613 (3)	2.29
O(2)	−0.2686 (5)	0.0958 (4)	0.1461 (3)	2.26
O(3)	0.1202 (5)	0.0099 (4)	0.1795 (3)	2.35
C(1)	−0.114 (2)	0.192 (1)	0.4708 (9)	3.40
C(2)	−0.276 (2)	0.009 (1)	0.3496 (9)	2.47
C(3)	−0.283 (2)	−0.041 (1)	0.2254 (8)	2.22
C(4)	−0.434 (2)	0.155 (1)	0.117 (1)	2.68
C(1)′[b]	−0.211 (2)	0.346 (1)	0.4534 (9)	2.91
C(2)′	−0.229 (2)	0.542 (1)	0.3035 (9)	2.55
C(3)′	−0.369 (2)	0.489 (1)	0.213 (1)	2.79
C(4)′	−0.398 (1)	0.303 (1)	0.0617 (8)	2.21

[a] See footnote *a* of Table VI. [b] Primed and unprimed carbon atoms are disordered with occupancy factors of 50% each.

$P2_1/m$ was initially chosen as the space group, and the metal position (M = Ho was solved first) on a crystallographic mirror plane was determined via inspection of a Patterson map. The three chlorine atoms, also on mirror planes, and the three unique oxygen atoms were easily located in a difference Fourier map. It was then obvious that either the space group choice was incorrect or there were two possible orientations of the carbon atoms, mirror images of each other, resulting in disorder. An attempt was made to refine in the acentric space group $P2_1$. Only the oxygen atoms would be affected by this change, and they showed high correlations (0.85–0.99); the resulting M–O distances had very large esd's. It was possible to refine to a rather low R value in $P2_1$; however, it was felt that the large variances in M–O separations and high correlations between oxygen atoms were more indicative of refining a centrosymmetric structure in a noncentrosymmetric space group. A disorder model was thus developed in $P2_1/m$, and the two carbon atom orientations (C(1)–C(4) and C(1)′–C(4)′) were refined with 50% occupancy in alternate least-squares cycles. As further evidence of the correctness of this choice it was possible to locate the water hydrogen atoms related by the mirror plane and all thermal parameters for the metal, chlorine, and oxygen atoms exhibited no unusual elongation or other distortions. The crown 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 (occupancy 50%). The water hydrogen atoms were located from a difference Fourier map and included with fixed contributions ($B = 5.5$ Å^2). Refinement of the non-hydrogen atoms with anisotropic temperature factors led to the final values of R given in Table V. The final values of the positional parameters are given in Table VIII for M = Ho. The fractional coordinates for the other members of this series have been deposited in the supplementary material.

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Supplementary Material Available: Tables SI–SLXXXVI, listing full crystallographic details, thermal parameters and hydrogen atom positions for all complexes, fractional coordinates for those complexes not in the text, hydrogen bond contact geometries, all bond distances and angles, and representative torsion angles, and cell packing diagrams for the three unique structural types (62 pages); tables of calculated and observed structure factors or structure factor amplitudes for all complexes (89 pages). Ordering information is given on any current masthead page.