Triethylene glycol complexes of the early lanthanide(III) chlorides

Robin D. Rogers*, Russell D. Etzenhouser and James S. Murdoch
Department of Chemistry, Northern Illinois University, DeKalb, IL 60115 (USA)

(Received December 16, 1991; revised March 10, 1992)

Abstract

The complexation of triethylene glycol (EO3) with the earlier lanthanide(III) chlorides has been investigated in 1/1 and 10/1 stoichiometries and with the addition of LiCl. Two well resolved crystalline forms of La^{3+} and Ce^{3+} have been isolated and structurally characterized: $[MCl(OH_2)(EO3)_2]Cl_2$ and $[MCl_2(OH_2)_2(EO3)]_2Cl_2$ (M = La, Ce). The former are ten-coordinate bicapped square antiprismatic while the latter are dimers of nine-coordinate tricapped trigonal prisms. A third disordered crystalline form has been isolated containing the same dimeric cation above and a disordered aquo/chloro metal anion. To round out our structural characterization of the series of lanthanide(III) chloride EO3 complexes, the crystal structures of $[M(OH_2)_5(EO3)]Cl_3$ (M = Sm, Tb), $[DyCl_3(EO3)]\cdot CH_3CN$, and $[TmCl_3(EO3)]\cdot CH_3OH$ are also presented.

Introduction

We recently published [1–3] the preparation and crystal structure of several triethylene glycol (EO3) complexes of the lanthanide(III) chlorides including $[M(OH_2)_5(EO3)]Cl_3$ (M = Nd, Eu, Gd, Dy, Y), $[MCl_3(EO3)]\cdot$18-crown-6 (M = Dy, Y), $[MCl_3(EO3)]\cdot CH_3CN$ (M = Ho, Lu), $[MCl_3(EO3)]\cdot CH_3OH$ (M = Er, Yb, Lu) and $[LuCl_3(EO3)]$. A size effect was clearly observed with the mid lanthanides exhibiting a nine-coordinate structure, while a seven-coordinate structure was found for the late lanthanides. At the time we had difficulty obtaining good crystals of any EO3 complex of the largest early lanthanides. In order to investigate whether our difficulty in crystallizing early lanthanide complexes was related to their size, we continued our attempts to crystallize these complexes. It now appears that this difficulty is related to a competition between possible crystalline forms as discussed in this paper. During this investigation, we also further studied the points of structural discontinuity in the series of EO3/$LnCl_3$ complexes.

In this contribution we report on our efforts to modify the crystallization conditions which resulted in the isolation of two new forms of EO3 complexes of La and Ce. We also discuss the new structural results in relation to those already published and include several previously unpublished structures which fill in holes in the series of mid to late lanthanide(III) chloride EO3 complexes. The new structures reported here include $[MCl(OH_2)(EO3)_2]Cl_2$ (M = La, Ce), $[MCl_2(OH_2)_2(EO3)]_2Cl_2$ (M = La, Ce), $[M(OH_2)_5(EO3)]Cl_3$ (M = Sm, Tb), $[DyCl_3(EO3)]\cdot CH_3CN$ and $[TmCl_3(EO3)]\cdot CH_3OH$.

Experimental

Synthesis and crystallization of complexes

$[LaCl_2(OH_2)_2(EO3)]_2Cl_2$

1.5 mmol of $LaCl_3\cdot 7H_2O$ were added to a stirred solution of 1.5 mmol of EO3 in 5ml of 3:1 CH_3CN:CH_3OH. The reaction mixture was heated at 60 °C for 1 h. Crystals were grown by slow evaporation.

$[CeCl_2(OH_2)_2(EO3)]_2Cl_2$

1.5 mmol of $CeCl_3\cdot 6H_2O$ were added to a stirred solution of 1.5 mmol of EO3 in 5ml of 3:1 CH_3CN:CH_3OH. An eight-fold molar excess of LiCl (12 mmol) was added and the solution was then heated with stirring to 60 °C for 1 h. Crystals were grown by slow evaporation.

$[MCl(OH_2)(EO3)_2]Cl_2$ (M = La, Ce)

1.5 mmol of the hydrated lanthanide salt were added to a stirred solution containing a ten-fold molar excess of EO3 (15 mmol) in 2.5 ml of 3:1 CH_3CN:CH_3OH. The reaction mixture was heated with stirring for 1 h. Slow evaporation produced the diffraction quality crystals.

---

*Author to whom correspondence should be addressed.

0020-1693/92/$5.00

TABLE 1. Crystal data and summary of intensity data collection and structure refinement

	$[LaCl(OH_2)(EO3)_2]Cl_2$	$[CeCl(OH_2)(EO3)_2]Cl_2$	$[LaCl_2(OH_2)_2(EO3)]_2Cl_2$
Color/shape	colorless/parallelepiped	colorless/parallelepiped	colorless/fragment
Formula weight	563.63	564.84	862.94
Space group	$C2/c$	$C2/c$	$P2_1/n$
Temperature (°C)	22	20	20
Cell constants[a]			
a (Å)	11.915(2)	11.916(2)	8.801(5)
b (Å)	14.951(2)	14.946(5)	9.678(9)
c (Å)	24.415(4)	24.411(4)	16.648(9)
β (°)	98.34(2)	98.32(2)	93.06(6)
Cell volume (Å^3)	4303.3	4301.8	1416
Formula units/unit cell	8	8	2
D_{calc} (g cm^{-3})	1.74	1.74	2.02
μ_{calc} (cm^{-1})	24.3	25.4	33.6
Diffractometer/scan		Enraf-Nonius CAD-4/ω–2θ	
Range of relative transmission factors (%)	75/100	83/100	81/100
Radiation, graphite monochromator		Mo Kα ($\lambda = 0.71073$)	
Max. crystal dimensions (mm)	0.18×0.33×0.65	0.30×0.33×0.45	0.13×0.20×0.30
Scan width		$0.80 + 0.35\tan\theta$	
Standard reflections	10,0,0; 0,12,0; 0,0,22	10,0,0; 0,12,0; 0,0,14	800; 080; 0,0,10
Decay of standards (%)	±3	±2	±3
Reflections measured	4130	4118	2816
2θ range (°)	$2 \leq 2\theta \leq 50$	$2 \leq 2\theta \leq 50$	$2 \leq 2\theta \leq 50$
Range of h, k, l	$+14, +11, \pm 29$ ($h+k=2n$ only)	$+14, +17, \pm 29$ ($h+k=2n$ only)	$+10, +11, \pm 19$
Reflections observed ($F_o \geq 5\sigma(F_o)$)[b]	3181	3191	2207
Computer programs[c]		SHELX [4]	
Structure solution	SHELXS [5]	coordinates from M=La	SHELXS
No. parameters varied	227	227	153
Weights	$[\sigma(F_o)^2 + 0.0005F_o^2]^{-1}$	$[\sigma(F_o)^2 + 0.0007F_o^2]^{-1}$	$[\sigma(F_o)^2]^{-1}$
GOF	0.74	0.82	2.2
$R = \Sigma \lvert \lvert F_o \rvert - \lvert F_c \rvert \rvert / \Sigma \lvert F_o \rvert$	0.026	0.030	0.038
R_w	0.036	0.043	0.041
R inverse configuration			
Largest feature final difference map (e$^-$Å^{-3})	0.4	0.7	0.9

[a] Least-squares refinement of $((\sin\theta)/\lambda)^2$ values for 25 reflections $\theta > 19°$. [b] Corrections: Lorentz-polarization and absorption (empirical, psi scan). [c] Neutral scattering factors and anomalous dispersion corrections from ref. 6.

$[M(OH_2)_5(EO3)]Cl_3$ (M=Sm, Tb), $[DyCl_3(EO3)]\cdot CH_3CN$ and $[TmCl_3(EO3)]\cdot CH_3OH$

These complexes were prepared as described in ref. 1 for their isostructural analogs.

X-ray data collection, structure determination and refinement

A summary of data collection parameters is presented in Table 1. The coordinates of one member of the isostructural series [1] were used as a starting point in the refinements of $[M(OH_2)_5(EO3)]Cl_3$ (M=Sm, Tb), $[DyCl_3(EO3)]\cdot CH_3CN$ and $[TmCl_3(EO3)]\cdot CH_3OH$. The La derivatives in both $[MCl(OH_2)(EO3)_2]Cl_2$ and $[MCl_2(OH_2)_2(EO3)]_2Cl_2$ were solved first using SHELXS [5] and these coordinates were then used as a starting point for the refinement of the Ce analogs. The final fractional coordinates for $[LaCl(OH_2)(EO3)_2]Cl_2$ and $[LaCl_2(OH_2)_2(EO3)]_2Cl_2$ are given in Tables 2 and 3, respectively. (See also 'Supplementary Material'.) The coordinates of at least one member of each isostructural series can be found in ref. 1. All 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. Other details unique to each structure are detailed below.

$[MCl(OH_2)(EO3)_2]Cl_2$ (M=La, Ce)

Of the two possible space groups ($C2/c$ or Cc), the centric $C2/c$ provided successful refinement. The alcoholic and aquo hydrogen atoms were located from a difference Fourier and included with fixed contributions ($B = 5.5$ Å^2).

$[MCl_2(OH_2)_2(EO3)]_2Cl_2$ (M=La, Ce)

High thermal motion for atoms C(5) and C(6) indicated possible disorder. A disorder model was de-

$[CeCl_2(OH_2)_2(EO3)]_2Cl_2$	$[Sm(OH_2)_5(EO3)]Cl_3$	$[Tb(OH_2)_5(EO3)]Cl_3$	$[DyCl_3(EO3)]\cdot CH_3CN$	$[TmCl_3(EO3)]\cdot CH_3OH$
colorless/parallelepiped	colorless/parallelepiped	colorless/fragment	colorless/fragment	colorless/parallelepiped
865.37	496.97	505.54	460.09	457.51
$P2_1/n$	$Pna2_1$	$Pna2_1$	$P2_1/c$	$P2_1/c$
22	18	20	22	20
8.783(2)	14.374(5)	14.286(3)	9.020(3)	7.454(1)
9.685(2)	9.724(4)	9.684(2)	10.839(8)	14.380(3)
16.571(5)	12.186(9)	12.121(6)	16.393(8)	14.223(5)
93.42(2)			103.78(3)	102.00(3)
1407	1703	1677	1557	1491
2	4	4	4	4
2.04	1.94	2.00	1.96	2.04
38.2	40.0	44.8	54.6	67.0
Enraf-Nonius CAD-4/ω–2θ				
86/100	72/100	96/100	23/100	57/100
Mo Kα ($\lambda = 0.71073$)				
0.20×0.25×0.45	0.20×0.20×0.40	0.20×0.28×0.30	0.50×0.50×0.60	0.30×0.35×0.35
$0.80+0.35\tan\theta$				
800; 080; 0,0,12	800; 060; 0,0,10	14,0,0; 080; 0,0,10	500; 060; 0,0,14	$\bar{4}00$; 0, $\overline{12}$,0; $00\bar{8}$
±1	±2	−1.8	±3.5	±3.5
2810	1744	1715	3070	2940
$2 \leqslant 2\theta \leqslant 50$	$2 \leqslant 2\theta \leqslant 50$	$2 \leqslant 2\theta \leqslant 50$	$2 \leqslant 2\theta \leqslant 50$	$2 \leqslant 2\theta \leqslant 50$
+10, +11, ±19	+17, +11, +14	+17, +11, +14	+10, +12, ±19	+8, +16, ±17
2160	1293	1455	2093	2159
SHELX [4]				
coordinates from M = La	coordinates from M = Gd [1]	coordinates from M = Gd [1]	coordinates from M = Ho [1]	coordinates from M = Yb [1]
163	171	171	157	145
$[\sigma(F_o)^2+0.00059F_o^2]^{-1}$	$[\sigma(F_o)^2+0.0034F_o^2]^{-1}$	$[\sigma(F_o)^2]^{-1}$	$[\sigma(F_o)^2+0.00058F_o^2]^{-1}$	$[\sigma(F_o)^2+0.002F_o^2]^{-1}$
0.81	0.77	3.8	1.38	0.92
0.026	0.045	0.023	0.048	0.039
0.039	0.061	0.026	0.061	0.055
	0.048	0.028		
0.8	1.0	0.5	1.5	0.9

veloped with C(5) and C(6) at 2/3 occupancy and a minor conformation of these atoms, C(5)′ and C(6)′, at 1/3 occupancy. C(5)′ and C(6)′ were refined isotropically only. The alcoholic and aquo hydrogen atoms were not included in the final refinement.

$[M(OH_2)_5(EO3)]Cl_3$ (M = Sm, Tb)

The alcoholic and aquo hydrogen atoms were not included in the final refinement. Tests were made for absolute configuration.

$[DyCl_3(EO3)]\cdot CH_3CN$

The alcoholic hydrogen atoms were located from a difference Fourier map and included with fixed contributions. The methyl hydrogen atoms were included as a rigid group with rotational freedom at the bonded carbon atom (C–H = 0.95 Å, $B = 5.5$ Å^2).

$[TmCl_3(EO3)]\cdot CH_3OH$

Two orientations with 50% occupancy each were resolved for the methanol oxygen atom O(5). Each position was refined in alternate least-squares cycles. The alcoholic and solvent hydrogen atoms were not included in the final refinement.

Results

Crystal structures of $[MCl(OH_2)(EO3)_2]Cl_2$ (M = La, Ce)

An ORTEP illustration of the M = La complex is presented in Fig. 1. Each metal ion is ten-coordinate in a distorted bicapped square antiprismatic geometry with the etheric oxygen atoms O(3) and O(6) in capping positions. The square planes are planar to within 0.13 Å and have a dihedral angle of 9.5°. This is the same

TABLE 2. Final fractional coordinates for $[LaCl(OH_2)(EO3)_2]Cl_2$

Atom	x/a	y/b	z/c	B_{eq}[a]
La	0.68958(2)	0.45016(1)	0.117498(8)	1.47
Cl(1)	0.5694(1)	0.37063(7)	0.01964(4)	2.71
Cl(2)	1.0000	0.30066(9)	0.2500	2.38
Cl(3)	1.0000	0.5906(1)	0.2500	2.60
Cl(4)	0.28752(9)	0.43846(8)	0.09453(4)	2.98
O(1)	0.9009(2)	0.4998(2)	0.1411(1)	2.51
O(2)	0.8486(2)	0.3556(2)	0.0773(1)	2.92
O(3)	0.6911(2)	0.2673(2)	0.1270(1)	2.54
O(4)	0.5195(2)	0.3727(2)	0.1525(1)	2.44
O(5)	0.7379(3)	0.5409(2)	0.0344(1)	2.68
O(6)	0.7266(3)	0.6318(2)	0.1282(1)	2.59
O(7)	0.6439(3)	0.5370(2)	0.2084(1)	2.70
O(8)	0.7714(2)	0.3894(2)	0.2142(1)	2.41
O(9)	0.5107(2)	0.5426(2)	0.0926(1)	2.35
C(1)	0.9934(4)	0.4491(3)	0.1249(2)	3.11
C(2)	0.9500(4)	0.4049(4)	0.0718(2)	3.46
C(3)	0.8673(4)	0.2645(3)	0.0953(2)	3.10
C(4)	0.7560(4)	0.2189(3)	0.0922(2)	3.25
C(5)	0.5840(4)	0.2261(3)	0.1305(2)	3.48
C(6)	0.5256(4)	0.2800(3)	0.1688(2)	3.43
C(7)	0.7855(5)	0.6295(3)	0.0410(2)	3.44
C(8)	0.7253(4)	0.6810(3)	0.0781(2)	3.25
C(9)	0.6720(4)	0.6775(3)	0.1685(2)	3.17
C(10)	0.6868(5)	0.6269(3)	0.2195(2)	3.56
C(11)	0.6560(5)	0.4824(4)	0.2573(2)	3.97
C(12)	0.7597(4)	0.4326(3)	0.2650(2)	3.37

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

TABLE 3. Final fractional coordinates for $[LaCl_2(OH_2)_2(EO3)]_2Cl_2$

Atom	x/a	y/b	z/c	B_{eq}
La	0.37242(5)	0.36429(5)	0.40328(3)	1.51
Cl(1)	0.6458(2)	0.3745(2)	0.5053(1)	2.13
Cl(2)	0.4861(3)	0.5706(2)	0.2989(1)	2.54
Cl(3)	0.0277(3)	0.2382(2)	0.6384(1)	2.80
O(1)	0.1082(6)	0.4717(6)	0.3810(4)	2.98
O(2)	0.1336(6)	0.2070(6)	0.4046(3)	2.67
O(3)	0.4160(7)	0.0973(6)	0.4172(4)	3.28
O(4)	0.5941(6)	0.2536(6)	0.3222(3)	2.37
O(5)	0.2740(6)	0.2824(6)	0.2623(3)	2.39
O(6)	0.3150(6)	0.3029(6)	0.5480(3)	2.48
C(1)	−0.025(1)	0.387(1)	0.3640(6)	3.63
C(2)	−0.015(1)	0.264(1)	0.4105(6)	3.54
C(3)	0.154(1)	0.0691(9)	0.4322(6)	3.34
C(4)	0.293(1)	0.0095(9)	0.3983(6)	4.93
C(5)[a]	0.576(2)	0.052(1)	0.3995(8)	2.99
C(6)[a]	0.604(2)	0.107(2)	0.3114(8)	3.83
C(5)′ [a]	0.499(3)	0.033(3)	0.343(2)	4.5(6)[b]
C(6)′ [a]	0.628(2)	0.115(2)	0.339(1)	2.0(4)[b]

[a] Primed and unprimed atoms are disordered at 2/3 (C(5), C(6)) and 1/3 (C(5)′,C(6)′) occupancy. [b] Isotropic refinement.

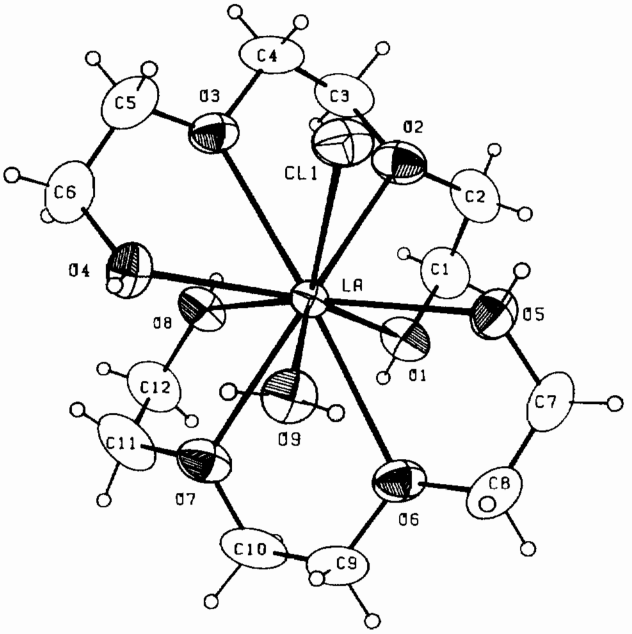

Fig. 1. ORTEP illustration of the cation in $[LaCl(OH_2)(EO3)_2]Cl_2$ represented with 50% probability ellipsoids for thermal motion. Hydrogen atoms have been arbitrarily reduced.

geometry observed in the 2/1 EO4/Nd^{3+} cation in $[Nd(EO4)_2]_4[NdCl_6]Cl_4$ [7]. The only other 2/1 PEG/metal complex that has been crystallographically characterized is the eight-coordinate dodecahedral $[Ca(EO3)_2]Cl_2 \cdot 4H_2O$ [8].

The cations are connected via hydrogen bonds to the anions in polymeric chains along the long unit cell axis *c*. The coordinated chloride ion accepts a hydrogen bond from a coordinated H_2O molecule in a symmetry related cation. The remaining chloride anions accept two (Cl(3), Cl(2)) or three (Cl(4)) hydrogen bonds.

The two glycol molecules adopt the same conformation observed for the $[M(OH_2)_5(EO3)]Cl_3$ complexes. The torsion angles starting with O(1)–C(1)–C(2)–O(2) have the sequence $g^-g^-ag^-aag^+$. One C–O–C–C torsion angle between O–C–C–O angles of like sign is forced *gaùche* (M = La: C(1)–C(2)–O(2)–C(3) = −89.6°).

Crystal structures of $[MCl_2(OH_2)_2(EO3)]_2Cl_2$ (M = La, Ce)

An ORTEP illustration of the M = La complex is presented in Fig. 2. These complexes contain dimeric cations residing around crystallographic centers of inversion. Each metal ion is nine-coordinate tricapped trigonal prismatic with the bridging $Cl(1)^a$, the alcoholic O(4) and the etheric O(2) in capping positions.

The terminal chloride anion (Cl(2)) accepts two hydrogen bonds, one from O(6) coordinated to La^a in the same dimer and one from O(5) on a symmetry related dimer. The uncoordinated anion, Cl(3), accepts the four remaining hydrogen bonds producing a polymeric network throughout the unit cell.

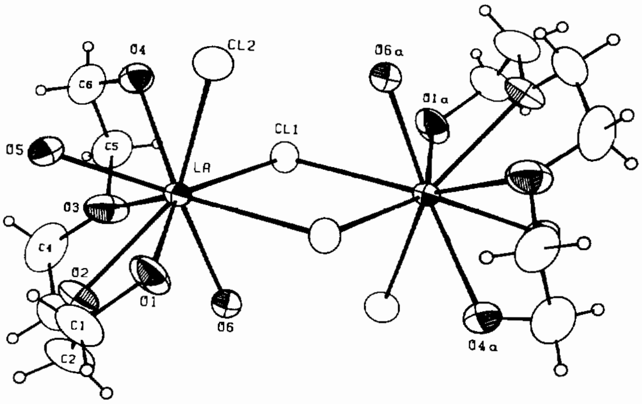

Fig. 2. The dimeric cation in $[LaCl_2(OH_2)_2(EO3)]_2Cl_2$.

The EO3 molecules are disordered with the C(5)–C(6) ethylene linkage resolved into two orientations. In one orientation (C(5)–C(6)) the glycol chain has the same conformation described above. In the second conformation the three O–C–C–O torsion angles alternate g^-, g^+, g^- and the C–O–C–C angles are all *anti*. This latter conformation is the one found for all of the seven-coordinate late lanthanide EO3 complexes.

Crystal structures of $[M(OH_2)_5(EO3)]Cl_3$ (M = Sm, Tb), $[DyCl_3(EO3)]\cdot CH_3CN$ and $[TmCl_3(EO3)]\cdot CH_3OH$

The nine-coordinate tricapped trigonal prismatic complexes $[M(OH_2)_5(EO3)]Cl_3$ (M = Sm, Tb) are isostructural with their M = Nd, Eu, Gd, Dy and Y analogs reported in ref. 1. Both $[DyCl_3(EO3)]\cdot CH_3CN$ and $[TmCl_3(EO3)]\cdot CH_3OH$ are seven-coordinate pentagonal bipyramidal. The Dy complex is isostructural with its M = Ho and Lu analogs [1], while the Tm complex is isostructural with its M = Er [1], Yb [1] and Lu [2] analogs. Full descriptions of the structures can be found in refs. 1 and 2. The average bonding parameters have been included in Table 4.

Discussion

The difficulty in isolating crystalline complexes of EO3 and the early lanthanides appears to be related to the number of solution species present. (A similar difficulty was observed isolating early Ln^{3+} complexes of EO4 [9].) One to one reaction of $LaCl_3\cdot 6H_2O$ with EO3 in 3/1 CH_3CN:CH_3OH leads to the nine-coordinate $[LaCl_2(OH_2)_2(EO3)]_2Cl_2$. This same reaction for M = Nd, Sm–Dy leads to $[M(OH_2)_5(EO3)]Cl_3$. Cesium gives a disordered crystalline complex which seems to be intermediate between the two containing clearly resolved $[CeCl_2(OH_2)_2(EO3)]_2^{2+}$ dimeric cations and disordered $CeCl_x(OH_2)_y$ anions. Cesium can be forced to adopt the ordered crystalline form observed for La by the addition of an eight-fold excess of LiCl. (The use of LiCl to modify the metal ion's primary coordination sphere in these types of complexes is discussed in ref. 9.) These same conditions for the slightly smaller Pr^{3+} and Nd^{3+}, lead instead to the disordered structure containing a dimeric EO3 complexed cation and disordered chloro/aquo anions.

The coordination number of the early lanthanide complexes can be forced upto 10 by utilizing a 2/1 excess of EO3 resulting in the complexes $[MCl(OH_2)(EO3)_2]Cl_2$ (M = La, Ce). It has not thus far been possible to isolate similar complexes of Pr^{3+} and beyond.

The average bonding parameters of all crystallographically characterized Ln^{3+}/EO3 complexes are presented in Table 4. By virtue of their larger size and in the case of the 2/1 complexes their higher coordination number, the bonding parameters for the La and Ce complexes are at the high end of the ranges of M–Cl and M–O separations. The long M–Cl(terminal) separations are also a consequence of hydrogen bonding to these coordinated anions. The chloro bridges in the dimeric complexes are asymmetric with the longer of each pair corresponding to a bridging chloride ion in a capping position in the M^{3+} coordination geometry.

The differences in the M–OH_2 contacts are statistically insignificant in the four La^{3+} and Ce^{3+} complexes, although they are much longer than observed for the pentahydrates (M = Nd–Y). The M–O(etheric, capping) distances of 2.750(8) (M = La^{3+}) and 2.740(4) (M = Ce^{3+}) Å in the ten-coordinate 2/1 complexes represent the longest M–O separations of any type in all structurally characterized lanthanide/EO3 complexes. There is a significant but certainly much smaller difference between the M–O(EO3, prismatic) distances in the ten-coordinate versus nine-coordinate M = La and Ce complexes.

There is a rather large decrease in average M–O(EO3) coordination distance between the La and Ce complexes and the remaining lanthanide complexes that is greater than the differences in effective ionic radii. For the ten-coordinate complexes much of this difference may be due to the higher coordination number, but some must also be due to the presence of a tight ion pair—one coordinated chloride ion. For the dimeric complexes, the difference is most likely the result of three tight ion pairs resulting in a lengthening of the M–O separations versus the pentahydrate structures which do not have any tight ion pairs.

Supplementary material

Tables listing fractional coordinates, thermal parameters, torsion angles, bond distance and angles, and

TABLE 4. Comparison of bonding parameters in lanthanide triethylene glycol complexes

Complex	*CN*	IR[a]	G	M–Cl(av.) (Å)		M–OH$_2$(av.) (Å)		M–EO3(av.) (Å)[c]				Reference
				Axial	Others	Capping	Others	Capping		Others		
								a	e	a	e	
[MCl(OH$_2$)(EO3)$_2$]Cl$_2$												
M=La	10	1.27	bcsap		2.860(1)		2.539(3)		2.750(8)	2.59(1)	2.68(2)	this study
M=Ce	10	1.25	bcsap		2.859(1)		2.548(3)		2.740(4)	2.59(1)	2.67(1)	this study
[MCl$_2$(OH$_2$)$_2$(EO3)]$_2$Cl$_2$												
M=La	9	1.216	tctp		2.862(2) (term) 2.872(2) (br) 2.959(2) (br,cap)		2.57(1)	2.656(6)	2.596(6)	2.556(5)	2.621(6)	this study
M=Ce	9	1.196	tctp		2.831(1) (term) 2.852(1)(br) 2.952(1) (br, cap)		2.55(1)	2.633(4)	2.575(4)	2.536(4)	2.612(4)	this study
[M(OH$_2$)$_5$(EO3)]Cl$_3$												
M=Nd	9	1.163	tctp			2.506(7)	2.500(8)	2.480(7)	2.596(7)	2.469(7)	2.500(8)	1
M=Sm	9	1.132	tctp			2.47(1)	2.46(2)	2.436(9)	2.59(1)	2.42(1)	2.48(1)	this study
M=Eu[d]	9	1.120	tctp			2.483(8)	2.452(3)	2.457(7)	2.577(7)	2.426(7)	2.471(9)	1
M=Gd	9	1.107	tctp			2.455(6)	2.451(7)	2.440(5)	2.564(6)	2.408(5)	2.466(7)	1
M=Tb	9	1.095	tctp			2.440(6)	2.425(8)	2.426(6)	2.552(6)	2.392(6)	2.453(7)	this study
M=Dy	9	1.083	tctp			2.428(6)	2.41(1)	2.416(6)	2.539(6)	2.373(6)	2.445(7)	1
M=Y	9	1.075	tctp			2.437(6)	2.409(7)	2.420(5)	2.544(6)	2.376(6)	2.439(6)	1
[MCl$_3$(EO3)]·18-crown-6												
M=Dy[d]	7	0.97	pbp	2.626(2)	2.605(2)					2.331(4)	2.442(5)	1
M=Dy[d,e]	7	0.97	pbp	2.607(1)	2.621(2)					2.316(4)	2.455(4)	3
M=Y	7	0.96	pbp	2.611(2)	2.588(3)					2.326(5)	2.431(5)	1
M=Y[d]	7	0.96	pbp	2.622(2)	2.595(3)					2.306(5)	2.435(5)	1
[MCl$_3$(EO3)]·CH$_3$CN												
M=Dy	7	0.97	pbp	2.586(8)	2.550(3)					2.290(6)	2.372(6)	this study
M=Ho	7	0.96[f]	pbp	2.616(1)	2.571(1)					2.330(1)	2.398(6)	1
M=Lu	7	0.92[f]	pbp	2.568(5)	2.537(2)					2.278(8)	2.350(2)	1
[MCl$_3$(EO3)]·CH$_3$OH												
M=Er	7	0.945	pbp	2.60(1)	2.565(2)					2.323(5)	2.40(2)	1
M=Tm	7	0.94[f]	pbp	2.59(1)	2.556(2)					2.310(5)	2.38(2)	this study
M=Yb	7	0.925	pbp	2.58(1)	2.546(3)					2.31(1)	2.38(2)	1
M=Lu	7	0.92[f]	pbp	2.56(1)	2.536(3)					2.296(7)	2.357(7)	2
[LuCl$_3$(EO3)][d]	7	0.92[f]	pbp	2.584(2)	2.547(2)					2.279(5)	2.351(5)	1
[M(NO$_3$)$_3$(EO3)]												
M=Nd	10	1.22[f]								2.50(1)	2.52(2)	10
M=Eu	10	1.17[f]								2.45(2)	2.502(7)	11

[a] Ionic radius for M^{3+} and *CN* shown from ref. 12. [b] Coordination geometries: tctp = tricapped trigonal prism, pbp = pentagonal bipyramid, bcsap = bicapped square antiprism. [c] Symbols a and e refer to alcoholic and etheric oxygen atoms, respectively. [d] Crystal structure determination at −150 °C. [e] Second crystallographic form. [f] Extrapolated from data in ref. 12.

observed and calculated structure factors or amplitudes (90 pages) are available from the authors on request.

Acknowledgement

The US National Science Foundation's Chemical Instrumentation Program provided funds used to purchase the diffractometer.

References

1 R. D. Rogers, E. J. Voss and R. D. Etzenhouser, *Inorg. Chem., 27* (1988) 533.

2 R. D. Rogers and R. D. Etzenhouser, *Acta Crystallogr., Sect. C, 44* (1988) 1400.

3 R. D. Rogers and R. D. Etzenhouser, *Acta Crystallogr., Sect. C, 44* (1988) 1533.

4 G. M. Sheldrick, *SHELX76,* a system of computer programs for X-ray structure determination as locally modified, University of Cambridge, UK, 1976.

5 G. M. Sheldrick, SHELXS, in G. M. Sheldrick, C. Krüger and R. Goddard (eds.), *Crystallographic Computing 3*, Oxford University Press, London, 1985, pp. 175–189.

6 *International Tables for X-ray Crystallography*. Vol. IV, Kynoch Press, Birmingham, UK, 1974, pp. 72, 99, 149. (Present distributor: Kluwer Academic Publishers, Dordrecht, Netherlands.)

7 R. D. Rogers, A. N. Rollins, R. F. Henry, J. S. Murdoch, R. D. Etzenhouser, S. E. Huggins, and L. Nuñez, *Inorg. Chem., 30* (1991) 4946.

8 R. D. Rogers and A. H. Bond, *Acta Crystallogr., Sect. C,* (1992) in press.

9 R. D. Rogers, R. D. Etzenhouser, J. S. Murdoch and E. Reyes, *Inorg. Chem., 30* (1991) 1445.

10 Y. Hirashima, T. Tsutsui, and J. Shiokawa, *J. Chem. Lett.,* (1982) 1405.

11 E. Forsellini, U. Casellato, G. Tomat, R. Graziani and P. Di Bernardo, *Acta Crystallogr., Sect. C, 40* (1984) 795.

12 R. D. Shannon, *Acta Crystallogr., Sect. A, 32* (1976) 751.