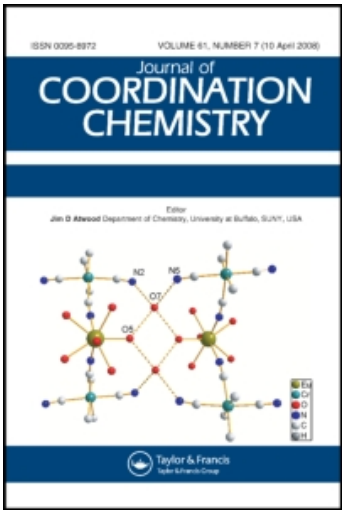

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PREPARATION AND CRYSTAL STRUCTURES OF $LaCl_3$(15-crown-5) AND $[LaCl_2(phen)(H_2O)_2(\mu\text{-}Cl)]_2 \cdot$ (15-crown-5) $\cdot$ MeCN

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NOTE

PREPARATION AND CRYSTAL STRUCTURES OF $LaCl_3$(15-crown-5) AND $[LaCl_2(phen)(H_2O)_2(\mu\text{-}Cl)]_2 \cdot$ (15-crown-5)·MeCN

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$LaCl_3$(15-crown-5), **I** was prepared by the reaction of $LaCl_3 \cdot nH_2O$ with 15-crown-5 and bipy (2,2'-bipyridyl). $[LaCl_2(phen)(H_2O)_2(\mu\text{-}Cl)]_2 \cdot$(15-crown-5)·MeCN, **II**, was crystallized from a mixture of $LaCl_3 \cdot nH_2O$, phen (1,10-phenanthroline) and 15-crown-5 in MeOH/MeCN, Crystal structures of these two complexes have been determined by X-ray methods. The La(III) ion in **I** is coordinated by three Cl anions and five oxygen atoms of a crown ether. The two metal ions in **II** are bridged by two Cl anions and the crown ligand is hydrogen-bonded to the coordinated water molecules to form polymeric... crown/cation/cation/crown... chains.

KEYWORDS: lanthanum chloride, crown ether, crystal structure

INTRODUCTION

Rare earth, crown ether, mixed-ligand complexes are of special interest because of their unusual structures. Reaction of $RECl_3 \cdot nH_2O$ with 18-crown-6 and triethyleneglycol (EO3) gives $[RECl_3(EO3)] \cdot$(18-crown-6) (RE = Dy,Y),[1] in which the crown ligand contacts with the RE(III) ions only by hydrogen bonds. The crown ether molecule in $[La(NO_3)_3(bipy)(H_2O)_2] \cdot$(benzo-15-crown-5) is also in the second coordination sphere.[2] However, it bonds directly to the cation in the complex $La(NO_3)_3$(benzo-15-crown-5).[3]

In our exploration of the interaction between lanthanide crown ether binary complexes with a second ligand such as bipy or phen, we have synthesized single crystals of $LaCl_3$(15-crown-5) by reaction of $LaCl_3 \cdot nH_2O$ with 15-crown-5 and bipy in methanol. $LaCl_3 \cdot nH_2O$, reacting with phen and 15-crown-5 in MeOH/MeCN, produces the complex $[LaCl_2(phen)(H_2O)_2(\mu\text{-}Cl)]_2 \cdot$(15-crown-5)·MeCN. We have determined their crystal structures and present our results herein.

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EXPERIMENTAL

Carbon hydrogen, nitrogen and chlorine analyses were carried out on a 1106 elemental analyzer. The lanthanum element was determined by titration. Infrared spectra were recorded on a Perkim Elmer 580 FT-IR in the range 4000-400 cm^{-1}.

Syntheses

Before use, $LaCl_3 \cdot nH_2O$ was dissolved in MeOH and, the resultant solution refluxed over 4Å molecular sieves for 24 hours to eliminate a part of the contained water molecules.

$LaCl_3$(15-crown-5), **I**

A methanol solution of lanthanide chloride (0.5 mmol) was mixed with 0.6 mmol of 15-crown-5 in MeCN and stirred for 20 minutes to ensure the formation of lanthanum 15-crown-5 complex. Bipy (0.5 mmol) was then added to the mixture with stirring. Crystals of the complex I (0.12 g) were obtained by slow evaporation. Anal 'for $C_{10}H_{20}O_5LaCl_3$' calculated: C, 25.77; H, 4.30; Cl, 22.87; La, 29.68%. Found: C, 25.23; H, 4.07; Cl, 22.36; La, 29.68%. IR spectrum indicates that ν(COC) in the crown ether shifts to lower frequency by 43 cm^{-1}.

$[LaCl_2(phen)(H_2O)_2(\mu\text{-}Cl)]_2 \cdot$(15-crown-5)$\cdot$MeCN, **II**

The method for the preparation of **II** were similar to that of **I**, with yield of 41%. Anal 'for $C_{36}H_{47}O_9N_5La_2Cl_6$; calculated: C, 36.47; H, 3.97; N, 5,91; Cl, 17.98; La, 23.46%. Found: C, 37.74; H 3.61; N 5.56; Cl 17.65; La, 23.30%, The IR spectrum shows ν(COC) shifted to lower frequency by 15 cm^{-1}, ν(O-H) at 3324 cm^{-1}, δ(O-H) at 1621 cm^{-1}, and ν(C = N) at 2248 cm^{-1}.

X-ray data collection, structure determination and refinement

Determinations of unit cells and data collection were preformed with MoKα radiation (λ -0.71069Å) on an R3m/E four circle diffractometer equipped with a graphite crystal monochromator. Correction for LP factors and empirical absorption, based on a ψ scan technique, were applied.

The space group for complex **II** was either $P\bar{1}$ or $P1$. Statistical tests indicated that the space group was more likely to be acentric. When $P\bar{1}$ was selected as the space group it was easy to locate the $LaCl_3(phen)(H_2O)_2$ part of the structure, indicating the La_2 dimer has an approximate symmetry of $\bar{1}$. However, it was impossible to locate the crown ether molecule which does not have a molecular symmetry of $\bar{1}$. Thus we chose acentric $P1$ as the space group and determined the structure successfully. The crystal structures were solved by either direct or heavy-atom methods. Positions of remaining non-hydrogen atoms were determined from successive difference Fourier syntheses. All non-hydrogen atoms were refined by block-matrix least-squares method, with positional and anisotropic thermal factors, except non-hydrogen atoms of the crown ligand and C(4) C(5) C(6) C(7) C(15) C(16) C(23) atoms of the phen molecule in complex **II**, which were refined with isotropic thermal parameters. The coordinates of hydrogen atoms were fixed

by theoretical models and only isotropic thermal factors were refined. All calculations were performed on an eclipse S/140 computer using the SHELXTL program package. Lists of crystal data, and a summary of data collections and structure refinements are given in Table 1.

RESULTS AND DISCUSSION

Coordinates and thermal parameters as well as significant bond lengths for the title complexes are given in Tables 2, 3 and 4, respectively. Molecular structures are shown in Figures 1 and 2, respectively.

Structure of $LaCl_3$(15-crown-5)

The complex is isostructural with $LnCl_3$(15-crown-5) (Ln-Pr–Sm).[4,5] In this complex, three Cl anions and five oxygen atoms of the crown ligand bond with the La(III) ion; the Cl anions and the crown molecule occupy the opposite sides of the cation respectively (Figure 1). The average La-Cl and La-O (crown) separations are 2.762(2) and 2.645(5)Å (Table 4), being the longest of its anologues. Due to the lanthanide contraction, the Ln-Cl and Ln-O(crown) distances decrease from La to Sm. The coordination geometry of the La(III) ion most closely resembles a bicapped trigonal prism[6] with O(1) and O(4) atoms in the capping positions (Table 5). Three

Table 1 Crystal data and summary of intensity data collection and structure refinement for **I** and **II**.

Complex	I	II
Formula	$C_{10}H_{20}O_5LaCl_3$	$C_{36}H_{47}O_9N_5La_2\ Cl_6$
Mr. Weight	465.6	1184.4
Cryst. System	monoclinic	triclinic
Space Group	$P2_1/c$	$P\ 1$
a (Å)	8.222(2)	11.321(3)
b (Å)	14.302(4)	12.916(3)
c (Å)	14.336(4)	9.265(2)
α (°)	90	104.86(2)
β (°)	104.91(2)	108.99(2)
γ (°)	90	72.24(2)
V (Å^3)	1629.1(8)	1201.3(4)
Dc (g.cm^{-3})	1.90	1.64
μ (cm^{-1})	31.6	21.7
F (000)	912	586
Z	4	1
Size (mm)	0.44 × 0.26 × 0.76	0.46 × 0.48 × 0.32
Scan mode	$\omega/2\theta$	$\omega/2\theta$
Scan range (°)	$3<2\theta<52$	$3<2\theta<50$
Range of relate transmission factors	92–71%	94–79%
Range of h, k, l	$11, 18, \pm 18$	$14, \pm 16, \pm 12$
Reflections measured	3229	4271
Reflections with $I > 3\sigma$ (I)	2560	3785
Structure solution methods	direct	heavy atom
No. parameters varied	172	439
GOF	1.197	1.345
R	0.041	0.035
R_w	0.047	0.039

Table 2 Atomic coordinates and equivalent isotropic parameters ($Å^2$) for $LaCl_3$ (15-crown-5).

Atom	*X/a*	*Y/b*	*Z/c*	*Ueq**
La	0.1602(1)	0.2402(1)	0.0071(1)	0.025(1)
Cl(1)	0.3425(2)	0.1127(1)	-0.0709(1)	0.043(1)
Cl(2)	0.3415(2)	0.3823(1)	-0.0477(1)	0.039(1)
Cl(3)	-0.0563(3)	0.2353(2)	-0.1754(2)	0.092(1)
0(1)	0.4220(5)	0.1879(3)	0.1511(3)	0.039(1)
0(2)	0.1289(5)	0.0896(3)	0.1140(3)	0.041(2)
0(3)	-0.1289(6)	0.2005(3)	0.0371(4)	0.054(2)
0(4)	-0.0433(5)	0.3789(3)	0.0297(3)	0.037(1)
0(5)	0.2492(5)	0.3456(3)	0.1602(3)	0.034(1)
C(1)	0.4257(8)	0.0901(5)	0.1729(5)	0.049(2)
C(2)	0.2653(8)	0.0605(5)	0.1932(5)	0.052(3)
C(3)	-0.031(1)	0.0708(6)	0.1338(7)	0.067(4)
C(4)	-0.1608(8)	0.1060(5)	0.0550(7)	0.066(4)
C(5)	-0.255(1)	0.2657(5)	0.0426(6)	0.049(3)
C(6)	-0.2190(8)	0.3544(5)	-0.0019(5)	0.044(2)
C(7)	-0.0040(8)	0.4282(5)	0.1218(5)	0.042(2)
C(8)	0.1802(8)	0.4376(4)	0.1551(5)	0.045(3)
C(9)	0.4269(7)	0.3430(5)	0.2082(4)	0.039(2)
C(10)	0.4675(9)	0.2453(4)	0.2364(5)	0.043(3)

* Equivalent isotropic *U* defined as one third of the trace of the orthogonalised *Uij* tensor.

chloride anions and O(2) O(3) O(5) atoms form the trigonal prism with O(1) capping the face formed by Cl(1), Cl(2), O(2), O(5) and O(4) capping the plane formed by Cl(2), Cl(3), O(3) and O(5). The La-O(1) and La-O(4) distances average 2.673(4)Å *vs* 2.628(4)Å for the remaining La-O separations.

The crown molecule itself is normal. O-C-C-O torsion angles starting with C(1)-C(2) have the pattern g^+ *(+60°)*, g^-, g^-, g^-, g^+. One C-C-O-C angle between consecutive O-C-C-O angle of like sign deviates toward gauche (the three such angles average 96.6°), and the remainder are *anti* (180°; Table 3). This conformation is also found in $NdCl_3$(15-crown-5) and $La(NO_3)_3$(monoazo-15-crown-5).[7]

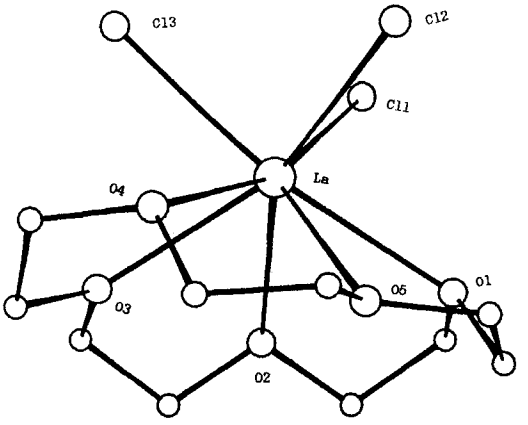

Figure 1 Molecular structure of $LaCl_3$ (15-crown-5).

Table 3 Atomic coordinates and isotropic thermal parameters (Å × 10^3) for $[LaCl_2(phen)(H_2O)_2(\mu\text{-}Cl)]_2 \cdot (15\text{-crown-}5) \cdot MeCN$.

Atom	*X/a*	*Y/b*	*Z/c*	*Ueq**
La(1)	0.0765	0.2632	0.4495	27(1)
La(2)	-0.0017(1)	0.0072(1)	-0.0067(1)	28(1)
Cl(1)	-0.1247(2)	0.1618(2)	0.2204(3)	37(1)
Cl(2)	0.2044(2)	0.1082(2)	0.2186(3)	32(1)
Cl(3)	-0.0888(3)	0.2970(2)	0.6335(3)	44(1)
Cl(4)	0.0937(3)	-0.1237(2)	0.2294(3)	56(1)
Cl(5)	0.1691(3)	-0.0309(2)	-0.1907(3)	47(1)
Cl(6)	-0.0118(3)	0.3929(2)	0.2185(3)	44(1)
N(1)	0.3026(7)	0.3185(6)	0.4771(8)	24(3)
N(2)	0.264(2)	0.255(1)	0.723(2)	39(6)
N(3)	-0.1885(7)	0.0268(5)	-0.2689(8)	24(3)
N(4)	-0.222(1)	-0.0415(8)	-0.0428(9)	50(4)
N(5)	-0.351(2)	0.599(1)	0.082(2)	104(8)
Ow(1)	0.0716(8)	0.458(1)	0.5943(6)	49(3)
Ow(2)	0.1264(7)	0.0636(6)	0.5060(8)	41(3)
Ow(3)	-0.0583(7)	0.1976(5)	-0.0671(7)	38(3)
Ow(4)	0.0190(7)	-0.1903(5)	-0.1566(8)	44(3)
O(1)	0.060(2)	0.716(2)	0.547(2)	162(7)
O(2)	0.250(2)	0.601(2)	0.719(2)	203(9)
O(3)	0.152(2)	0.555(2)	0.938(2)	166(7)
O(4)	-0.113(2)	0.638(2)	0.848(2)	189(8)
O(5)	-0.161(2)	0.655(2)	0.539(2)	160(7)
C(1)	0.316(1)	0.3592(9)	0.382(1)	45(5)
C(2)	0.428(1)	0.384(1)	0.379(2)	72(7)
C(3)	0.531(2)	0.362(2)	0.521(2)	35(6)
C(4)	0.517(1)	0.3310(8)	0.626(1)	34(2)
C(5)	0.6179(8)	0.3092(7)	0.7644(9)	22(2)
C(6)	0.602(1)	0.2688(8)	0.882(1)	36(2)
C(7)	0.488(1)	0.2511(8)	0.877(1)	37(4)
C(8)	0.481(2)	0.213(2)	0.988(2)	44(6)
C(9)	0.360(2)	0.2045(8)	0.976(2)	33(4)
C(10)	0.2477(8)	0.2237(7)	0.8306(9)	27(3)
C(11)	0.3884(7)	0.2658(6)	0.7417(8)	13(1)
C(12)	0.4035(9)	0.3051(7)	0.605(2)	27(3)
C(13)	-0.174(1)	0.0633(9)	-0.396(1)	49(5)
C(14)	-0.259(2)	0.0793(9)	-0.524(3)	45(5)
C(15)	-0.375(2)	0.049(1)	-0.550(2)	30(4)
C(16)	-0.407(1)	0.0183(8)	-0.420(1)	40(2)
C(17)	-0.533(1)	-0.009(1)	-0.438(2)	63(6)
C(18)	-0.553(1)	-0.039(2)	-0.320(3)	95(9)
C(19)	-0.442(1)	-0.0521(9)	-0.187(1)	47(5)
C(20)	-0.454(2)	-0.096(2)	-0.044(2)	53(8)
C(21)	-0.357(1)	-0.1020(9)	0.067(1)	45(5)
C(22)	-0.239(1)	-0.0734(8)	0.086(1)	39(4)
C(23)	-0.3209(9)	-0.0313(7)	-0.172(1)	32(2)
C(24)	-0.297(1)	0.0020(9)	-0.282(1)	53(5)
C(31)	0.161(2)	0.683(2)	0.499(2)	92(5)
C(32)	0.268(2)	0.665(2)	0.632(2)	132(8)
C(33)	0.329(2)	0.575(2)	0.861(2)	104(6)
C(34)	0.269(3)	0.592(3)	0.991(3)	250(18)
C(35)	0.046(2)	0.583(2)	1.009(2)	123(7)
C(36)	-0.057(2)	0.528(3)	0.900(5)	344(29)
C(37)	-0.237(2)	0.630(2)	0.746(3)	160(10)
C(38)	-0.259(2)	0.645(3)	0.597(3)	198(14)
C(39)	-0.177(2)	0.738(1)	0.468(2)	99(6)
C(40)	-0.061(1)	0.715(2)	0.412(2)	102(6)
C(51)	-0.330(2)	0.470(1)	0.247(2)	72(7)
C(52)	-0.337(1)	0.537(1)	0.154(2)	63(6)

* Equivalent isotropic *U* defined as one third of the trace of the orthogonalised *Uij* tensor.

Table 4 Selected bond lengths (Å).

$LaCl_3$(15–Crown–5)					
La-Cl(1)	2.772(2)	La-Cl(2)	2.753(2)	La-Cl(3)	2.761(2)
La-O(1)	2.677(4)	La-O(2)	2.693(5)	La-O(3)	2.584(5)
La-O(4)	2.669(4)	La-O(5)	2.607(4)	O(1)-C(1)	1.431(8)
O(1)-C(10)	1.440(8)	O(2)-C(2)	1.437(7)	O(2)-C(3)	1.44(1)
O(3)-C(4)	1.414(9)	O(3)-C(5)	1.408(9)	O(4)-C(6)	1.441(7)
O(4)-C(7)	1.457(8)	O(5)-C(8)	1.427(1)	O(5)-C(9)	1.447(7)
$[LaCl_2(phen)(H_2O)_2(\mu\text{-}Cl)]_2\cdot$(15-crown-5)·MeCN					
La(1)-Cl(1)	2.942(2)	La(1)-Cl(2)	2.955(2)	La(1)-Cl(3)	2.792(3)
La(1)-Cl(6)	2.795(3)	La(1)-N(1)	2.779(8)	La(1)-N(2)	2.73(2)
La(2)-Ow(1)	2.524(7)	La(1)-Ow(2)	2.617(8)	La(2)-Cl(1)	2.900(2)
La(2)-Cl(2)	2.966(2)	La(2)-Cl(4)	2.838(3)	La(2)-Cl(5)	2.833(4)
La(2)-N(3)	2.661(6)	La(2)-N(4)	2.65(1)	La(2)-Ow(3)	2.507(9)
La(2)-Ow(4)	2.553(6)				

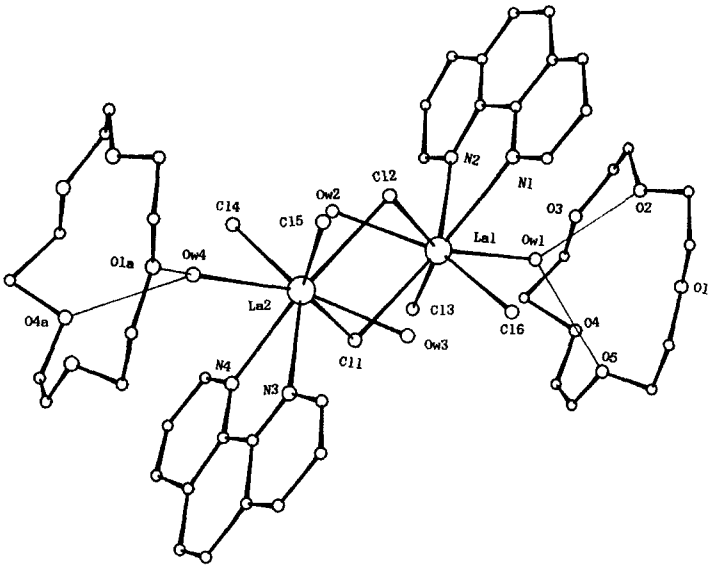

Figure 2 Molecular structure of $[LaCl_2(phen)H_2O)_2(\mu\text{-}Cl)]_2\cdot$(15-crown-5)·MeCn.

Table 5 Selected bond angles (°) for complex **I**.

Cl(1)-La-Cl(2)	88.9(1)	Cl(1)-La-Cl(3)	83.4(1)	Cl(2)-La-Cl(3)	90.7(1)
Cl(1)-La-O(1)	73.5(1)	Cl(2)-La-O(1)	92.3(1)	Cl(3)-La-O(1)	156.7(1)
Cl(1)-La-O(2)	81.1(1)	Cl(2)-La-O(2)	153.0(1)	Cl(3)-La-O(2)	112.8(1)
O(1)-La-O(2)	60.9(1)	Cl(1)-La-O(3)	122.6(1)	Cl(2)-La-O(3)	143.0(1)
Cl(3)-La-O(3)	75.9(1)	O(1)-La-O(3)	113.7(2)	O(2)-La-O(3)	60.2(1)
Cl(1)-La-O(4)	163.5(1)	Cl(2)-La-O(4)	83.6(1)	Cl(3)-La-O(4)	82.1(1)
O(1)-La-O(4)	121.3(1)	O(2)-La-O(4)	111.8(1)	O(3)-La-O(4)	60.7(1)
Cl(1)-La-O(5)	131.0(1)	Cl(2)-La-O(5)	76.0(1)	Cl(3)-La-O(5)	141.7(1)
O(1)-La-O(5)	61.1(1)	O(2)-La-O(5)	91.8(1)	O(3)-La-O(5)	93.3(2)
O(4)-La-O(5)	61.1(1)				

Table 6 Selected torsion angles (°).

$LaCl_3$(15-crown-5)			
O(1)-C(1)-C(2)-O(2)	53.0	C(6)-O(4)-C(7)-C(8)	171.6
C(1)-C(2)-O(2)-C(3)	-174.4	O(4)-C(7)-C(8)-O(5)	-56.9
C(2)-O(2)-C(3)-C(4)	176.9	C(7)-C(8)-O(5)-C(9)	-169.6
O(2)-C(3)-C(4)-O(3)	-52.5	C(8)-O(5)-C(9)-C(10)	161.8
C(3)-C(4)-O(3)-C(5)	-121.8	O(5)-C(9)-C(10)-O(1)	57.3
C(4)-O(3)-C(5)-C(6)	-165.8	C(9)-C(10)-O(1)-C(1)	-168.5
O(3)-C(5)-C(6)-O(4)	-44.9	C(10)-O(1)-C(1)-C(2)	84.0
C(5)-C(6)-O(4)-C(7)	-84.0		
$[LaCl_2(phen)(H_2O)_2(\mu\text{-}Cl)]_2\cdot$(15-crown-5)·MeCN			
O(1)-C(31)-C(32)-O(2)	49.2	C(36)-O(4)-C(37)-C(38)	-121.5
C(31)-C(32)-O(2)-C(33)	-174.7	O(4)-C(37)-C(38)-O(5)	7.7
C(32)-O(2)-C(33)-C(34)	130.1	C(37)-C(38)-O(5)-C(39)	-128.6
O(2)-C(33)-C(34)-O(3)	42.8	C(38)-O(5)-C(39)-C(40)	-175.1
C(33)-C(34)-O(3)-C(35)	-160.4	O(5)-C(39)-C(40)-O(1)	-64.6
C(34)-O(3)-C(35)-C(36)	176.2	C(39)-C(40)-O(1)-C(31)	172.5
O(3)-C(35)-C(36)-O(4)	-95.8	C(40)-O(1)-C(31)-C(32)	-167.7
C(35)-C(36)-O(4)-C(37)	171.6		

Structure of $[LaCl_2(Phen)(H_2O)_2(\mu\text{-}Cl)]_2\cdot$(15-crown-5)·MeCN

The two eight-coordinated La(III) ions are bridged through two Cl^- ions (Figure 2). The La-Cl separations of these two bridging anions average 2.941(2)Å, being significantly larger than the remaining La-Cl distances (2.814(7)Å, average). The mean La-N(phen) and La-O(water) bond lengths are 2.70(1) and 2.55(1)Å, respectively.

The crown ligands are in the second coordination sphere by forming hydrogen bonds with Ow(1) and Ow(4). The Ow(1)...O(2) and Ow(1)...O(5) separations are 2.910 and 3.064Å, respectively, being a little longer than Ow(4)...O(1a) and Ow(4)...O(4a) (2.827 and 3.048Å, respectively; crown atoms related by symmetry code: x, $1+y$, $1+z$). This makes the La(2)–Ow(4) distance slightly longer than La(1)–Ow(1). These hydrogen bonds result in polymeric, zig-zig...crown/cation/cation/crown... chains along b. This kind of chain structure has not yet been reported. The average C-O-C bond angle of 119(2)° is much larger than that in **I** (113.0(5)°).

Reaction of phen with lanthanum-15-crown-5 also induces a conformational change in the crown ligand. When 15-crown-5 accepts hydrogen bonds on both sides it can adopt a conformation very similar to the D_{3d} form of 18-crown-6 (where all C-O-C-C torsion angles are *anti* and the O-C-C-O angles alternate from $g+$ to $g-$). In this complex the O-C-C-C angles alternate from $g+$ to $g-$ except at one point two consecutive O-C-C-O angles must have the same sign due to the lower symmetry of 15-crown-5 (Table 3).[3] The O(3)-C(35)-C(36)-O(4) angle is unusually large (-95.8°) and the O(4)-C(37)-C(38)-O(5) angle is only +7.7°; this phenomenon is also observed in $[Gd(H_2O)_8]Cl_3$(15-crown-5).[9]

Reaction of $LaCl_3 nH_2O$ with 15-crown-5 and bipy gives $LaCl_3$(15-crown-5), perhaps due to the strong La/15-crown-5 interaction;[10] replacement of 15-crown-5 by bipy needs activation and coordination of bipy and crown to La(III) concurrently would induce strong steric hindrance. However, the La-15-crown-5-phen ternary complex does form and is stable in air, probably because of the stronger

coordination of phen compared to bipy (as demonstrated for aqueous solution by stability constant values)[11] and the stabilizing effects of hydrogen bonding chains.

SUPPLEMENTARY MATERIAL

Tables listing fractional coordinates, thermal parameters, bond distances and angles, and observed and calculated structure factors are available from the authors on request.

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