Macrocycle Complexation Chemistry

32*. Modification of the Lanthanide Ion Coordination Sphere via Electrocrystallization of Hydrated Lanthanide Chloride Complexes of 12-Crown-4

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Abstract

Electrochemical techniques have been utilized to modify the crystallization of 12-crown-4 complexes of $PrCl_3 \cdot nH_2O$ from $CH_3CN{:}CH_3OH$ (3:1) solutions. $[PrCl_3(OH_2)(12\text{-}crown\text{-}4)] \cdot 12\text{-}crown\text{-}4$ crystallized from a 10:1 (12-crown-4:Pr) solution in the centric space group *Pnma*, with $a = 23.338(7)$, $b = 13.103(5)$, $c = 7.713(4)$ Å and $D_{calc} = 1.74$ g cm^{-3} for $Z = 4$. $[PrCl_3(OHMe)(12\text{-}crown\text{-}4)]$ crystallized in the centric $P\bar{1}$, with $a = 7.486(3)$, $b = 9.365(4)$, $c = 11.268(4)$ Å, $\alpha = 91.92(3)$, $\beta = 93.87(3)$, $\gamma = 102.00(3)°$ and $D_{calc} = 1.96$ g cm^{-3} for $Z = 2$. Both complexes differ markedly from the series of 12-crown-4 early lanthanide chloride complexes that were obtained by slow evaporation ($[M(OH_2)_5(12\text{-}crown\text{-}4)]Cl_3 \cdot 2H_2O$). Utilization of an electrochemical cell produces complexes in which all three chloride anions are in the metal's primary coordination sphere, the coordination number is reduced, and most of the water or solvent molecules are eliminated.

Introduction

In our research on the complexation chemistry of crown ethers with lanthanide salts [1], we have attempted to promote crystallization of these complexes in order to study their detailed solid state structure. We have observed that small amounts of H_2O promote crystallization by adding the stabilizing effects of hydrogen bonding networks, while too much H_2O can preclude metal to crown ether coordination. Previously, we have reacted 12-crown-4, 15-crown-5 and 18-crown-6 with the entire series (except Pm^{3+}) of lanthanide chloride hydrates in

anhydrous solutions of acetonitrile and methanol (3:1).

Bünzli and Pilloud [2] have measured the stability constants for the lanthanide ions and several common crown ethers. They observed maximum stability with 18-crown-6 for the early lanthanides and with 15-crown-5 for the later lanthanides. The formation of 1:1 and 1:2 complexes of 15-crown-5 and 12-crown-4 has also been reported [2–4].

The results of our investigations have been mixed. With 15-crown-5 we have thus far isolated only second sphere hydrogen bonded complexes such as $[M(OH_2)_8]Cl_3 \cdot 15\text{-}crown\text{-}5$ (M = Gd, Y, Yb, Lu) [5–7], $[Nd(OH_2)_9]Cl_3 \cdot 15\text{-}crown\text{-}5 \cdot H_2O$ [8] and $[NdCl_2(OH_2)_6]Cl \cdot 15\text{-}crown\text{-}5$ [8]. Early to middle lanthanides and 18-crown-6 form three types of coordination complexes $[CeCl_2(OH_2)(18\text{-}crown\text{-}6)]Cl \cdot 2H_2O$ [7], $[MCl(OH_2)_2(18\text{-}crown\text{-}6)]Cl_2 \cdot 2H_2O$ (M = Nd–Tb) [7, 9]) and $[M(OH_2)_7(OHMe)][MCl(OH_2)_2(18\text{-}crown\text{-}6)]_2Cl_7 \cdot 2H_2O$ (M = Dy, Y) [10]. Near the end of the series only hydrogen bonded complexes such as $[Dy(OH_2)_8]Cl_3 \cdot 18\text{-}crown\text{-}6 \cdot 4H_2O$ [11] have been isolated.

Of the crown ethers we have investigated, 12-crown-4 has produced the most crystalline complexes of the lanthanide chlorides; 12-crown-4 complexes all of the lanthanides, Ce–Lu, under our conditions [12]. We have isolated two major structural types. For Ce–Er, nine-coordinate complexes $[M(OH_2)_5(12\text{-}crown\text{-}4)]Cl_3 \cdot 2H_2O$ form, while eight-coordinate species $[MCl_2(OH_2)_2(12\text{-}crown\text{-}4)]Cl$ form for Dy–Lu. Both types are observed for Dy–Er.

Since the Ln/12-crown-4 linkage appeared so robust under our reaction conditions, we set out to modify the cation environment and structurally probe the effects of any observed changes. Electrocrystallization is a technique used in preparing complexes of various types including organic superconductors [13] and cation radical salts of arenes [14]. Our utilization of these techniques for our reactions of 12-crown-4 and $PrCl_3 \cdot nH_2O$ is the subject of this report.

Experimental

Preparation of [PrCl₃(OH₂)(12-crown-4)]·12-crown-4

A solution of 1.23 mmol of 12-crown-4 in 10 ml of a 3:1 $CH_3CN:CH_3OH$ solution was added to one compartment of an H cell (40 ml capacity). The other compartment contained a solution of 1 mmol of $PrCl_3 \cdot 6H_2O$ in 10 ml of 3:1 $CH_3CN:CH_3OH$ solution. The two compartments were separated by fine porosity glass frits. Inserted in each compartment was a platinum wire electrode (0.1–0.4 cm^2) that was connected to a power supply consisting of a variable d.c. constant current source with range from 0.1–600 μA. A current of 10 $\mu A/cm^2$ was passed through the cell. After a week green crystals were observed in the cell. Crystallographic examination revealed the crystals to be [PrCl₃(OH₂)(12-crown-4)]·12-crown-4.

In a second experiment, a solution of 10 mmol of 12-crown-4 in 20 ml of 3:1 $CH_3CN:CH_3OH$ solution was added dropwise to a 1 mmol solution of $PrCl_3 \cdot 6H_2O$ in 20 ml of the same solvent. The mixture was stirred at 60 °C for 24 h, cooled to 22 °C and concentrated to 10–15 ml. The remaining mixture was then allowed to slowly evaporate over a period of several weeks. Small green crystals were observed on the bottom of the storage vessel. Crystallographic examination again revealed [PrCl₃(OH₂)(12-crown-4)]·12-crown-4. The crystals are thermally stable. *Anal.* Calc. for [PrCl₃(OH₂)(12-crown-4)]·12-crown-4: C, 31.11; H, 5.55. Found: C, 31.72; H, 5.98%.

Preparation of [PrCl₃(OHMe)(12-crown-4)]

A solution of 12.3 mmol 12-crown-4 in 10 ml of 3:1 $CH_3CN:CH_3OH$ solution was added to one compartment of an H cell. The other compartment contained a 1 mmol solution of $PrCl_3 \cdot 6H_2O$ in 10 ml of $CH_3CN:CH_3OH$. A current of 10 $\mu A/cm^2$ was passed through the cell and after a few weeks green crystals were observed on the cell wall. The crystals are thermally stable (melting point 325 °C). *Anal.* Calc. for [PrCl₃(OHMe)(12-crown-4)]: C, 23.73; H, 4.43. Found: C, 23.23; H, 4.36%.

X-ray Data Collection, Structure Determination and Refinement for [PrCl₃(OHMe)(12-crown-4)]

A transparent green single crystal of the title complex was mounted on a pin and transferred to the goniometer. The space group was determined to be either the centric $P\bar{1}$ or acentric $P1$. Successful refinement of the structure was carried out in the space group $P\bar{1}$. A summary of data collection parameters is given in Table 1.

Least-squares refinement with isotropic thermal parameters led to $R = 0.078$. 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 methyl and alcoholic 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 final values of $R = 0.030$ and $R_w = 0.031$. The final values of the positional parameters are given in Table 2.

X-ray Data Collection, Structure Determination and Refinement for [PrCl₃(OH₂)(12-crown-4)]·12-crown-4

The space group was determined to be either the centric *Pnma* or acentric *Pn2₁a* from the systematic absences. The subsequent solution and successful refinement of the structure was carried out in the space group *Pnma* despite the presence of disorder. A summary of data collection parameters is given in Table 1.

Location of the metal atom, water molecule, one chlorine atom and two oxygen atoms of the hydrogen bonded crown ether on a mirror plane, and of the two unique oxygen atoms of the coordinated ether, the remaining unique hydrogen bonded ether oxygen atom and chlorine atom off the mirror was easily accomplished. The carbon atoms of the coordinated ether were found to be disordered, resulting in two mirror related C_4 conformations of this crown. The disordered atoms C(1)–C(4) and C(1)′–C(4)′ together make up one conformation and each was thus refined at 50% occupancy. High thermal motion was also noted for the hydrogen bonded crown ether, however, a disorder model could not be developed for this ether. Due to the space group ambiguity and the presence of disorder an attempt was made to utilize the non-centrosymmetric space group, *Pn2₁a* (a non-standard setting of *Pna2₁*). A higher R value, high correlations between atoms related by the mirror in *Pnma* and the continued presence of disorder in the coordinated ether, ruled out the choice of this space group. The disorder thus appears to represent a static distribution of the carbon atoms where each carbon position is α 50% of the time and β 50% of the time.

Least-squares refinement with isotropic thermal parameters and the disorder model led to $R = 0.071$. Due to the disorder, the hydrogen atoms were not included in the final refinement. Refinement of the non-hydrogen atoms with anisotropic temperature factors led to final values of $R = 0.042$ and $R_w = 0.047$. The final values of the positional parameters are given in Table 3.

Structural Results

[PrCl₃(OHMe)(12-crown-4)]

An ORTEP illustration of the metal ion coordination sphere is given in Fig. 1; bond distances and

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

Compound	[PrCl₃(OHMe)(12-crown-4)]	[PrCl₃(OH₂)(12-crown-4)]·12-crown-4
Color/shape	green/fragment	green/fragment
Formula weight	455.52	617.71
Space group	$P\bar{1}$	$Pnma$
Temperature (°C)	20	20
Cell constants[a]		
a (Å)	7.486(3)	23.338(7)
b (Å)	9.365(4)	13.103(5)
c (Å)	11.268(4)	7.713(4)
α (°)	91.92(3)	
β (°)	93.87(3)	
γ (°)	102.00(3)	
Cell volume, (Å³)	770.0	2359
Formula units/unit cell	2	4
D_{calc} (g cm⁻³)	1.96	1.74
μ_{calc} (cm⁻¹)	34.9	23.0
Diffractometer/scan	Enraf-Nonius CAD-4/ω−2θ	Enraf-Nonius CAD-4/ω−2θ
Range relative transmission factors (%)	78/100	92/100
Radiation, graphite monochromator	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)
Max. crystal dimensions (mm)	0.08 × 0.15 × 0.20	0.08 × 0.13 × 0.28
Scan width	0.80 + 0.35 tan θ	0.80 + 0.35 tan θ
Standard reflections	500; 040; 009	600; 0,10,0; 0,0,12
Decay of standards (%)	±1	−4.8
Reflections measured	2681	2391
2θ range (°)	2 ⩽ 2θ ⩽ 50	2 ⩽ 2θ ⩽ 50
Range of h, k, l	+8, ±11, ±13	+27, +15, +9
Reflections observed [$F_o \geqslant 5\sigma(F_o)$][b]	2422	1682
Computer programs[c]	SHELX [15]	SHELX [15]
Structure solution	heavy atom techniques	heavy atom techniques
No. parameters varied	163	175
Weights	$[\sigma(F_o)^2]^{-1}$	$[\sigma(F_o)^2]^{-1}$
GOF	1.21	1.02
$R = \Sigma\|F_o\| - \|F_c\|/\Sigma\|F_o\|$	0.030	0.042
R_w	0.031	0.047
Largest feature final difference map (e Å⁻³)	1.1	1.0

[a]Least-squares refinement of $((\sin\theta)/\lambda)^2$ values for 21 reflections $\theta > 19°$. [b]Corrections: Lorentz−polarization and absorption (empirical, psi scan). [c]Neutral scattering factors and anomalous dispersion corrections from ref. 16.

angles are presented in Table 4. The four oxygen atoms of the crown ether, the three chloride anions and the methanol molecule form a distorted square antiprism around the metal ion. The Pr−O(crown) distances range from 2.563(4)−2.618(4) Å, (2.59(2) Å, average), the Pr−Cl separations from 2.708(2)− 2.773(1) Å (2.73(3) Å, average) and the Pr−O-(methanol) distance is 2.507(4) Å. The major distortion in coordination geometry involves the Cl(1), Cl(2), Cl(3), O(5) square which is distorted towards a bicapped trigonal prismatic geometry where O(5) and Cl(2) would be the capping atoms. O(1)−O(4) are planar to within 0.01 Å and Pr is 1.75 Å from this plane.

The 12-crown-4 molecule adopts a C_4 conformation (Table 5) which directs all four oxygen atoms toward one side of the ring. This is a typical 12-crown-4 conformation for metal complexation [17]. The conformation is characterized by gauche (60°) O−C−C−O torsion angles of the same sign and
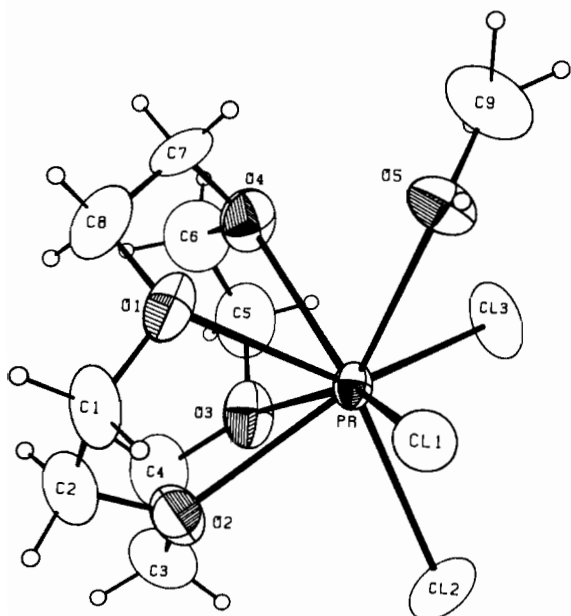
C−O−C−C torsion angles that alternate between gauche and anti (180°). (When C−O−C−C are forced gauche, these angles are typically greater than 70° [17].) In this conformation of 12-crown-4 there are two unique symmetry sites for the carbon atoms. Each set of four carbons form a plane; the four α-carbons C(1), C(3), C(5), C(7) closer to the Pr atom than the four β-carbons C(2), C(4), C(6), C(8). The distances from the centroid of these planes to Pr are 2.24 (α) and 2.77 (β) Å. The average crown ether bonding parameters are C−C = 1.47(2), C(α)−O = 1.48(1), C(β)−O = 1.398(7) Å, C−O−C = 112.6(6), O−C(α)−C(β) = 110.6(4), O−C(β)−C(α) = 106.4(5)°.

The single hydrogen bond present is between H(1)[O(5)] and Cl(1) and forms a dimer of formula units (Fig. 2). The hydrogen bond to Cl(1) considerably lengthens the Pr−Cl(1) distance (2.773(1) Å) compared to the remaining Pr−Cl separations (2.709-(1) Å, average).

TABLE 2. Final fractional coordinates for [PrCl₃(OHMe)-(12-crown-4)]

Atom	x/a	y/b	z/c	B_{eq} [a]
Pr	0.68605(4)	0.24894(3)	0.76955(2)	1.55
Cl(1)	0.8734(2)	0.2891(2)	0.9930(1)	2.28
Cl(2)	0.8106(2)	−0.0028(2)	0.7620(2)	3.52
Cl(3)	0.8642(2)	0.3021(2)	0.5691(2)	3.73
O(1)	0.4596(6)	0.3536(5)	0.8961(4)	2.91
O(2)	0.4187(6)	0.0651(5)	0.8479(4)	3.14
O(3)	0.4342(6)	0.1171(5)	0.6147(4)	3.19
O(4)	0.4810(6)	0.4077(5)	0.6620(4)	3.29
O(5)	0.8551(6)	0.5094(4)	0.8037(3)	2.63
C(1)	0.3805(9)	0.2466(8)	0.9815(6)	3.29
C(2)	0.288(1)	0.1065(8)	0.9183(7)	3.97
C(3)	0.336(1)	−0.0482(7)	0.7547(7)	4.09
C(4)	0.279(1)	0.0214(8)	0.6458(7)	4.27
C(5)	0.395(1)	0.2186(9)	0.5210(6)	4.09
C(6)	0.344(1)	0.346(1)	0.5740(7)	4.88
C(7)	0.418(1)	0.5073(7)	0.7463(7)	4.11
C(8)	0.331(1)	0.4272(8)	0.8447(7)	4.16
C(9)	0.912(1)	0.6282(8)	0.7215(7)	4.43

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

TABLE 3. Final fractional coordinates for [PrCl₃(OH₂)(12-crown-4)]·12-crown-4

Atom	x/a	y/b	z/c	B_{eq} [a]
Pr	0.83164(2)	0.2500	0.32663(7)	1.66
Cl(1)	0.7494(1)	0.2500	0.0702(4)	3.16
Cl(2)	0.86725(9)	0.4273(2)	0.1746(3)	2.75
O(1)	0.8558(2)	0.1466(4)	0.6093(7)	2.54
O(2)	0.7488(2)	0.1464(5)	0.4720(7)	3.12
O(3)	0.9375(3)	0.2500	0.355(1)	2.41
O(4)	1.0561(4)	0.2500	0.096(1)	4.72
O(5)	1.0212(3)	0.1005(5)	0.3372(9)	4.09
O(6)	1.0561(5)	0.2500	0.580(1)	5.23
C(1)	0.8936(7)	0.212(1)	0.730(2)	2.95
C(2)	0.8183(7)	0.085(2)	0.700(2)	3.95
C(3)	0.7754(8)	0.048(1)	0.562(2)	2.87
C(4)	0.7012(8)	0.186(2)	0.564(3)	4.99
C(1)'[b]	0.8721(8)	0.313(1)	0.769(2)	3.22
C(2)'	0.8118(7)	0.441(1)	0.630(3)	4.26
C(3)'	0.7562(7)	0.410(1)	0.627(2)	3.35
C(4)'	0.6969(6)	0.291(1)	0.479(2)	3.84
C(5)	1.0287(5)	0.1582(9)	0.046(1)	4.59
C(6)	1.0485(5)	0.0802(8)	0.173(2)	5.31
C(7)	1.0531(5)	0.0838(9)	0.494(2)	6.20
C(8)	1.0905(5)	0.1605(9)	0.545(2)	5.55

[a]$B_{eq} = \frac{4}{3}[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos \gamma)\beta_{12} + ac(\cos \beta)\beta_{13} + bc(\cos \alpha)\beta_{23}]$. [b]Primed atoms are disordered and were refined with 50% occupancy.

Fig. 1. ORTEP illustration of [PrCl₃(OHMe)(12-crown-4)].

Fig. 2. Cell packing diagram of [PrCl₃(OHMe)(12-crown-4)].
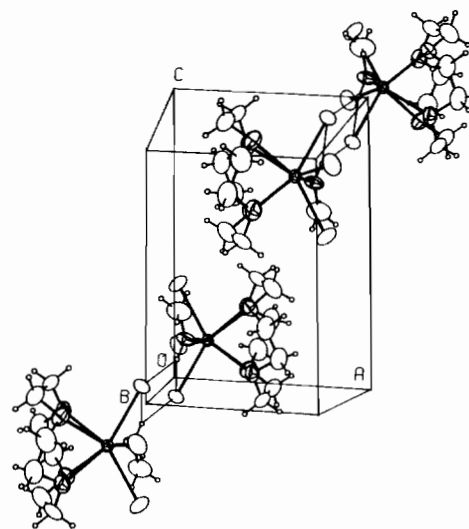
[PrCl₃(OH₂)(12-crown-4)]·12-crown-4

An ORTEP illustration of the metal ion coordination geometry is depicted in Fig. 3. Table 6 contains the bond distances and angles for this complex. There are two unique 12-crown-4 molecules. The macrocycle directly coordinated to the metal is disordered into two C_4 conformations related by the mirror plane. The second ether is hydrogen bonded to the metal coordinated water molecule

and exhibits a C_s conformation (Table 7) [18]. This conformation is characterized by *gauche* O–C–C–O torsion angles, two consecutively of the same sign, the next two of opposite sign. All but two of the C–O–C–C tortion angles are *anti*, the two *gauche* angles occurring between O–C–C–O angles of the same sign. The two unique C–C bond distances in the C_s macrocycle are 1.39(2) and 1.49(2) Å; the

TABLE 4. Bond distances (Å) and angles (°) for [PrCl₃(OHMe)(12-crown-4)]

Atoms	Distance	Atoms	Distance
Pr–Cl(1)	2.773(1)	Pr–Cl(2)	2.710(2)
Pr–Cl(3)	2.708(2)	Pr–O(1)	2.606(4)
Pr–O(2)	2.580(4)	Pr–O(3)	2.563(4)
Pr–O(4)	2.618(4)	Pr–O(5)	2.507(4)
O(1)–C(1)	1.476(7)	O(1)–C(8)	1.404(8)
O(2)–C(2)	1.405(8)	O(2)–C(3)	1.476(8)
O(3)–C(4)	1.387(8)	O(3)–C(5)	1.498(8)
O(4)–C(6)	1.397(8)	O(4)–C(7)	1.476(8)
O(5)–C(9)	1.484(8)	C(1)–C(2)	1.484(9)
C(3)–C(4)	1.49(1)	C(5)–C(6)	1.45(1)
C(7)–C(8)	1.473(9)		

Atoms	Angle	Atoms	Angle
Cl(1)–Pr–Cl(2)	83.35(5)	Cl(1)–Pr–Cl(3)	121.34(5)
Cl(2)–Pr–Cl(3)	83.82(6)	Cl(1)–Pr–O(1)	78.2(1)
Cl(2)–Pr–O(1)	135.3(1)	Cl(3)–Pr–O(1)	140.2(1)
Cl(1)–Pr–O(2)	91.5(1)	Cl(2)–Pr–O(2)	77.9(1)
Cl(3)–Pr–O(2)	140.2(1)	O(1)–Pr–O(2)	62.4(1)
Cl(1)–Pr–O(3)	153.9(1)	Cl(2)–Pr–O(3)	85.3(1)
Cl(3)–Pr–O(3)	80.4(1)	O(1)–Pr–O(3)	93.9(1)
O(2)–Pr–O(3)	63.2(1)	Cl(1)–Pr–O(4)	130.3(1)
Cl(2)–Pr–O(4)	146.2(1)	Cl(3)–Pr–O(4)	80.4(1)
O(1)–Pr–O(4)	62.5(1)	O(2)–Pr–O(4)	95.7(1)
O(3)–Pr–O(4)	62.8(1)	Cl(1)–Pr–O(5)	69.90(9)
Cl(2)–Pr–O(5)	130.7(1)	Cl(3)–Pr–O(5)	76.7(1)
O(1)–Pr–O(5)	79.5(1)	O(2)–Pr–O(5)	140.6(1)
O(3)–Pr–O(5)	133.6(1)	O(4)–Pr–O(5)	73.8(1)
Pr–O(1)–C(1)	110.5(4)	Pr–O(1)–C(8)	122.0(4)
C(1)–O(1)–C(8)	112.5(5)	Pr–O(2)–C(2)	123.4(4)
Pr–O(2)–C(3)	110.7(4)	C(2)–O(2)–C(3)	112.7(5)
Pr–O(3)–C(4)	122.4(4)	Pr–O(3)–C(5)	110.7(4)
C(4)–O(3)–C(5)	113.5(5)	Pr–O(4)–C(6)	121.3(5)
Pr–O(4)–C(7)	112.1(4)	C(6)–O(4)–C(7)	111.8(6)
Pr–O(5)–C(9)	132.6(4)	O(1)–C(1)–C(2)	110.5(5)
O(2)–C(2)–C(1)	106.1(5)	O(2)–C(3)–C(4)	110.0(6)
O(3)–C(4)–C(3)	106.0(6)	O(3)–C(5)–C(6)	110.9(6)
O(4)–C(6)–C(5)	107.3(6)	O(4)–C(7)–C(8)	111.1(5)
O(1)–C(8)–C(7)	106.2(6)		

TABLE 5. Torsion angles (°) for [PrCl₃(OHMe)(12-crown-4)]

Atoms	Angle
O(1)–C(1)–C(2)–O(2)	53.5
C(1)–C(2)–O(2)–C(3)	–163.8
C(2)–O(2)–C(3)–C(4)	87.5
O(2)–C(3)–C(4)–O(3)	55.9
C(3)–C(4)–O(3)–C(5)	–168.7
C(4)–O(3)–C(5)–C(6)	85.0
O(3)–C(5)–C(6)–O(4)	53.5
C(5)–C(6)–O(4)–C(7)	–161.9
C(6)–O(4)–C(7)–C(8)	87.8
O(4)–C(7)–C(8)–O(1)	55.5
C(7)–C(8)–O(1)–C(1)	–169.3
C(8)–O(1)–C(1)–C(2)	83.4

C–O distances range from 1.42(1)–1.45(1) Å. The average bonding parameters in the coordinated ether are C–C = 1.47(7), O–C(α) = 1.54(4), O–C(β) = 1.40(1) Å, C–O–C = 112(1), C(β)–C(α)–O = 114(4), C(α)–C(β)–O = 104(3)°. A similar conformation of 12-crown-4 was observed in [CuCl₂(12-crown-4)] [18].

The four crown oxygen atoms, three chloride anions and the water molecule also form a capped squared antiprism strongly distorted toward a bicapped trigonal prismatic geometry around the metal ion. The water molecule and Cl(1) occupy capping positions in the bctp description. The Pr–O-(crown) distances average 2.621(7) Å, the Pr–O-(water) distance is 2.481(7) Å and the average Pr–Cl distance is 2.74(1) Å. In the absence of hydrogen

TABLE 6. Bond distances (A) and angles (°) for $[PrCl_3(OH_2)(12\text{-crown-4})]\cdot12\text{-crown-4}$

Atoms	Distance	Atoms	Distance
Pr−Cl(1)	2.756(3)	Pr−Cl(2)	2.731(2)
Pr−O(1)	2.628(5)	Pr−O(2)	2.614(5)
Pr−O(3)	2.481(7)	O(1)−C(1)	1.54(2)
O(1)−C(2)	1.38(2)	O(1)[a]−C(1)'	1.40(2)
O(1)[a]−C(2)'	1.54(2)	O(2)−C(3)	1.59(2)
O(2)−C(4)	1.42(2)	O(2)[a]−C(3)'	1.41(2)
O(2)[a]−C(4)'	1.47(2)	O(4)−C(5)	1.42(1)
O(5)−C(6)	1.44(1)	O(5)−C(7)	1.44(2)
O(6)−C(8)	1.45(1)	C(1)−C(1)'	1.44(2)
C(2)−C(3)	1.54(2)	C(4)−C(4)'	1.53(3)
C(2)'−C(3)'	1.36(2)	C(5)−C(6)	1.49(2)
C(7)−C(8)	1.39(2)		

Atoms	Angle	Atoms	Angle
Cl(1)−Pr−Cl(2)	84.49(5)	Cl(1)−Pr−O(1)	138.1(1)
Cl(2)−Pr−O(1)	136.8(1)	Cl(1)−Pr−O(2)	78.0(1)
Cl(2)−Pr−O(2)	148.3(1)	O(1)−Pr−O(2)	62.3(2)
Cl(1)−Pr−O(3)	139.3(2)	Cl(2)−Pr−O(3)	74.6(1)
O(1)−Pr−O(3)	73.3(2)	O(2)−Pr−O(3)	134.3(2)
Cl(2)−Pr−Cl(2)[a]	116.51(9)	O(1)−Pr−O(1)[a]	62.1(2)
O(2)−Pr−O(2)[a]	62.6(3)	Cl(2)−Pr−O(1)[a]	81.5(1)
Cl(2)−Pr−O(2)[a]	88.1(1)	O(1)−Pr−O(2)[a]	94.0(2)
Pr−O(1)−C(1)	109.6(6)	Pr−O(1)−C(2)	125.9(8)
C(1)−O(1)−C(2)	112(1)	Pr−O(1)[a]−C(1)'	126.5(7)
Pr−O(1)[a]−C(2)'	108.8(8)	C(1)'−O(1)[a]−C(2)'	112(1)
Pr−O(2)−C(3)	108.7(7)	Pr−O(2)−C(4)	127.3(9)
C(3)−O(2)−C(4)	112(1)	Pr−O(2)[a]−C(3)'	122.9(7)
Pr−O(2)[a]−C(4)'	109.6(7)	C(3)'−O(2)[a]−C(4)'	111(1)
C(5)−O(4)−C(5)[a]	116(1)	C(6)−O(5)−C(7)	119.0(8)
C(8)−O(6)−C(8)[a]	108(1)	O(1)−C(1)−C(1)'	116(1)
O(1)−C(2)−C(3)	104(1)	O(2)−C(3)−C(2)	108(1)
O(2)−C(4)−C(4)'	99(1)	O(1)[a]−C(1)'−C(1)	105(1)
O(1)[a]−C(2)'−C(3)'	115(1)	O(2)[a]−C(3)'−C(2)'	107(1)
O(2)[a]−C(4)'−C(4)	118(1)	O(4)−C(5)−C(6)	105.0(9)
O(5)−C(6)−C(5)	108.4(9)	O(5)−C(7)−C(8)	117(1)
O(6)−C(8)−C(7)	107(1)		

[a]Atoms related by a crystallographic mirror plane.

TABLE 7. Torsion angles (°) for $[PrCl_3(OH_2)(12\text{-crown-4})]\cdot$ 12-crown-4

Atoms	Angle
O(4)−C(5)−C(6)−O(5)	72.4
C(5)−C(6)−O(5)−C(7)	−143.6
C(6)−O(5)−C(7)−C(8)	81.4
O(5)−C(7)−C(8)−O(6)	63.6
C(7)−C(8)−O(6)−C(8)[a]	−150.7
C(8)−O(6)−C(8)[a]−C(7)[a]	150.7
O(6)−C(8)−C(7)[a]−O(5)[a]	−63.6
C(8)[a]−C(7)[a]−O(5)[a]−C(6)[a]	−81.4
C(7)[a]−O(5)[a]−C(6)[a]−C(5)[a]	143.6
O(5)[a]−C(6)[a]−C(5)[a]−O(4)	−72.4
C(6)[a]−C(5)[a]−O(4)−C(5)	155.2
C(5)[a]−O(4)−C(5)−C(6)	−155.2

[a]Atoms related by a crystallographic mirror plane.

bonding to the chlorine atoms the Pr−Cl separations are more nearly equivalent.

The only hydrogen bonds involve O(3) to the C_s ether. The $O(3)\cdots O(5)$ separation and $O(5)\cdots O(3)\cdots O(5)^a$ angle are 2.772(8) Å and 89.9(3)°, respectively. The cell packing is illustrated in Fig.4.

Discussion

The lanthanides from La to Er all crystallize as 1:1 heptahydrates when their hydrated chloride salts are reacted with 12-crown-4 in a 1:1 stoichiometry in 3:1 acetonitrile:methanol. The resulting nine-coordinate complexes, $[M(OH_2)_5(12\text{-crown-4})]\cdot$ $Cl_3\cdot2H_2O$ contain no tight ion pairs [12]. Modification of this metal ion environment has been possible

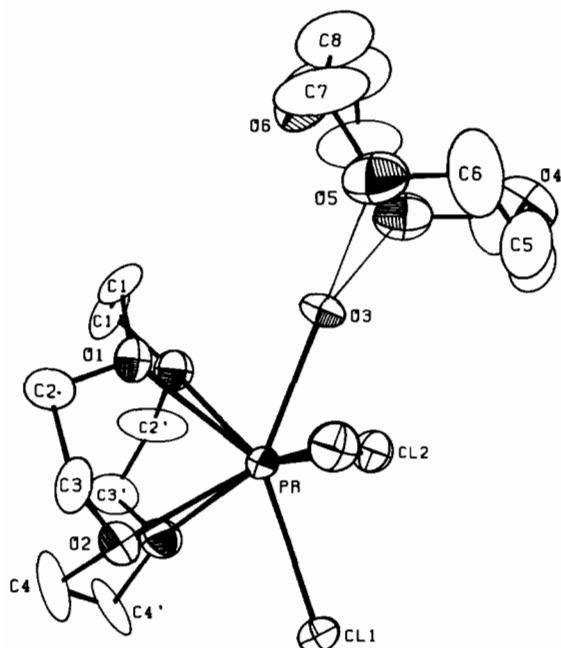Fig. 3. The formula unit of [PrCl₃(OH₂)(12-crown-4)]·12-crown-4.
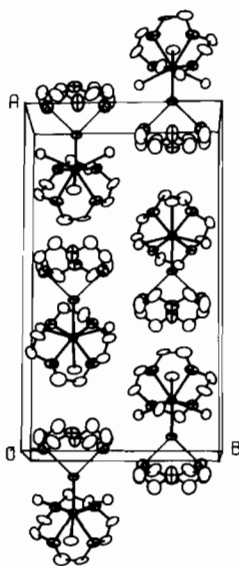
Fig. 4. Cell packing diagram of [PrCl₃(OH₂)(12-crown-4)]·12-crown-4.

by electrocrystallization. Electrocrystallization from solutions of 1:1 stoichiometry produced [PrCl₃(OH₂)(12-crown-4)]·12-crown-4. When 10:1 (crown: Pr) solutions were utilized all H₂O was eliminated and one solvent molecule was incorporated into [PrCl₃(OHMe)(12-crown-4)]. It has also been possible to isolate [PrCl₃(OH₂)(12-crown-4)]·12-crown-4 without electrocrystallization by utilizing a 10:1 stoichiometry and slow evaporation.

The title complexes with their eight-coordinate geometries are similar to the complexes isolated from reactions of hydrated chloride salts of the late lanthanides (Dy–Lu) with 12-crown-4 in 1:1 stoichiometries. Apparently, the late lanthanides are too small to support three chloride ions in the primary coordination sphere. By reducing the available H₂O molecules for a larger lanthanide such as Pr³⁺, the formation of three tight ion pairs was accomplished. It is interesting to note that we have yet to observe the formation of sandwich complexes in the solid state despite the 10:1 stoichiometries utilized.

The Pr–O(12-crown-4) distances appear to be significantly longer in the title complexes than comparable distances in the previously characterized series. Taking into account the differences in ionic radii [19] between eight-coordinate Pr³⁺ and nine-coordinate Ce³⁺ (−0.07 Å), nine-coordinate Nd³⁺ (−0.037 Å) and eight-coordinate Ho³⁺ (+0.111 Å), the 2.621(7) Å average in [PrCl₃(OH₂)(12-crown-4)]·12-crown-4 is 0.06 to 0.08 Å longer than expected from the previous results and the 2.59(2) Å average in [PrCl₃(OHMe)(12-crown-4)] is 0.03 to 0.05 Å longer. The average M–O(crown) separations observed for [Ce(OH₂)₅(12-crown-4)]Cl₃·2H₂O, [Nd(OH₂)₅(12-crown-4)]Cl₃·2H₂O and [HoCl₂(OH₂)₂(12-crown-4)]Cl, are 2.61(2), 2.58(2) and 2.45(2) Å, respectively.

This study has shown that electrocrystallization is an effective method of modifying the lanthanide ion environment in macrocycle complexation reactions. Its future utility may well lie in the ability to precisely control the metal ion environment. Toward that end we are continuing the study of this technique and the accompanying effects of concentration and diffusion rates.

Supplementary Material

Tables of thermal parameters, hydrogen atom coordinates, least-squares planes and observed and calculated structure factors are available from the authors on request (17 pages).

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