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f-Element/Crown Ether Complexes.
26.* Crystallization of Two Hydrated Forms of Hydrogen Bonded Complexes of $NdCl_3 \cdot nH_2O$ and 15-Crown-5. Crystal Structures of $[Nd(OH_2)_9]Cl_3 \cdot$15-crown-5$\cdot H_2O$ and $[NdCl_2(OH_2)_6]Cl \cdot$15-crown-5

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Abstract

When slowly evaporated, the reaction of $NdCl_3 \cdot nH_2O$ with 15-crown-5 in a 3:1 mixture of acetonitrile:methanol produces two crystalline hydrates. The decahydrate, $[Nd(OH_2)_9]Cl_3 \cdot$15-crown-5$\cdot H_2O$, is orthorhombic, $P2_12_12_1$, with (at −150 °C) $a = 10.571(4)$, $b = 15.220(7)$, $c = 15.686(7)$ Å, and $D_{calc} = 1.71$ g cm^{-3} for $Z = 4$. These crystals are stable to the moisture in air. Each Nd is nine-coordinate with tricapped trigonal prismatic geometry. The nine coordinated water molecules are hydrogen bonded to two symmetry related crown ethers, all three chloride ions, and the tenth water molecule. The crown ether has a total of six hydrogen bonds, four on one side (two to a single oxygen atom) and two on the other. This ether exhibits conformational disorder. The hexahydrate, $[NdCl_2(OH_2)_6]Cl \cdot$15-crown-5 is deliquescent, dissolving in air and recrystallizing as $[NdCl_2(OH_2)_6]Cl$. Crystals of this complex are monoclinic, $P2_1/n$, with (at 20 °C) $a = 9.821(3)$, $b = 16.978(9)$, $c = 12.849(8)$ Å, $\beta = 94.06(5)°$, and $D_{calc} = 1.80$ g cm^{-3} for $Z = 4$. The Nd atom exists in a distorted dodecahedral geometry with one chlorine in an A site and one in a B site. The coordinated chlorine atoms accept hydrogen bonds producing polymeric zigzag hydrogen bonded chains along *c*. The third noncoordinated chloride ion accepts four hydrogen bonds, three from one formula unit and one from a second formula unit related by a unit translation along *a*. The crown ethers accept five hydrogen bonds, two on one side, and three on the other, thus separating the zigzag chains along *b*.

Introduction

We have successfully crystallized and structurally characterized metal/crown ether complexes of 18-crown-6 and 12-crown-4 with hydrated lanthanide chloride salts including: $[CeCl_2(OH_2)(\text{18-crown-6})]Cl \cdot 2H_2O$ [2], $[MCl(OH_2)_2(\text{18-crown-6})]Cl_2 \cdot 2H_2O$ (M = Nd, Sm, Eu, Gd, Tb) [2, 3], $[M(OH_2)_7(OHMe)][MCl(OH_2)_2(\text{18-crown-6})]_2Cl_7 \cdot 2H_2O$ (M = Dy, Y) [4], $[M(OH_2)_5(\text{12-crown-4})]Cl_3 \cdot 2H_2O$ (M = Ce, Nd, Sm, Eu, Gd, Tb, Dy, Y, Ho, Er) [5], $[YCl_2(OH_2)(OHMe)(\text{12-crown-4})]Cl$ [5] and $[MCl_2(OH_2)_2(\text{12-crown-4})]Cl$ (M = Ho, Er, Tm, Yb, Lu) [5]. The larger 18-crown-6 wraps the 4f ions, allowing essentially 'in-cavity' complexation for the early and middle lanthanides. Complexation of the smaller late lanthanides has thus far been impossible and even complexes like $[Dy(OH_2)_7(OHMe)][DyCl(OH_2)_2(\text{18-crown-6})]_2Cl_7 \cdot 2H_2O$ are relatively unstable and can undergo rearrangement to form hydrogen bond complexes such as $[Dy(OH_2)_8]Cl_3 \cdot$18-crown-6$\cdot 4H_2O$ [6]. The smaller 12-crown-4 adopts a C_4 conformation and the metal ions sit on top of the crown cavity for M = Ce to Lu. The differences in the structures of the complexes mentioned above relate only to how many other coordinating groups will fit around the metal ion.

Despite the success with 18-crown-6 and 12-crown-4, two macrocycles which are of sizes that bracket the cavity found for 15-crown-5, we have only been able to isolate second-sphere, hydrogen bonded complexes of 15-crown-5 with hydrated lanthanide salts. This in spite of the formation and structural characterization of similar 15-crown-5 complexes under anhydrous conditions ($[Eu(NO_3)_3(\text{15-crown-5})]$ [7] and $[YbCl_2(\text{15-crown-5})][AlCl_2Me_2]$ [8]) which show that lanthanide ions may complex 15-crown-5 either in the crown cavity for the late lanthanides or on top of the cavity for the larger 4f-elements. Two studies of 15-crown-5 and hydrated lanthanide perchlorates have resulted in both complexed and hydrogen bonded ethers in the same structures: $[M(OH_2)_4(\text{15-crown-5})][ClO_4]_3 \cdot$15-crown-5$\cdot H_2O$ (M = La [9], Sm [10]). The interaction of 15-crown-5 with hydrated lanthanide chlorides in our laboratories has produced

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*For Part 25 see ref. 1.

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only $[M(OH_2)_8]Cl_3\cdot$15-crown-5 (M = Gd [11], Y [12, 13], Lu [11]), $[Y(NO_3)_2(OH_2)_5][NO_3]\cdot2$(15-crown-5) [14] and $[Y(NO_3)_3(OH_2)_3]\cdot1.5$(15-crown-5)$\cdot Me_2CO$ [15].

We realized that the early lanthanides were less likely to adopt the 8-coordination found for the $[M(OH_2)_8]^{3+}$ ions mentioned above [16] and decided to further investigate the interaction of 15-crown-5 with earlier lanthanide chloride salts. We have not succeeded in isolating lanthanide/15-crown-5 complexes, however, we have crystallized and characterized two new forms of second sphere hydrogen bonded complexes. We now report the crystal structures of $[Nd(OH_2)_9]Cl_3\cdot$15-crown-5$\cdot H_2O$ and $[NdCl_2(OH_2)_6]Cl\cdot$15-crown-5.

Experimental

Preparation of $[Nd(OH_2)_9]Cl_3\cdot$15-crown-5$\cdot H_2O$ and $[NdCl_2(OH_2)_6]Cl\cdot$15-crown-5

A solution of 10 mmol of 15-crown-5 in 20 ml of a 3:1 CH_3CN:CH_3OH solution was added dropwise to a solution of 10 mmol of $NdCl_3\cdot nH_2O$ in 20 ml of the same solvent mixture. 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 almost to dryness over a period of several weeks. Small pink parallelepipeds were observed to form at the bottom of the storage vessel. A crystallographic examination of several of these revealed the presence of two different crystal forms: the decahydrate-$[Nd(OH_2)_9]Cl_3\cdot$15-crown-5$\cdot H_2O$ and the hexahydrate-$[NdCl_2(OH_2)_6]Cl\cdot$15-crown-5.

X-ray Data Collection, Structure Determination and Refinement

Transparent, pink single crystals of the title complexes were mounted on pins and transferred to the goniometer. The decahydrate was cooled to −150 °C during data collection using a stream of cold nitrogen gas. The space groups were uniquely determined from the systematic absences. A summary of data collection parameters is given in Table I.

Least-squares refinement of $[Nd(OH_2)_9]Cl_3\cdot$15-crown-5$\cdot H_2O$ with isotropic thermal parameters led to $R = 0.058$. At this point in the refinement secondary positions were located for O(14) and O(15) and large thermal motion was noted for several of the carbon atoms in this portion of the crown ring. The disorder model developed has O(14) and O(15) with 60% occupancy and a minor orientation (O(14)′ and O(15)′) with 40% occupancy. Due to the close proximity of the disordered carbon

TABLE I. Crystal Data and Summary of Intensity Data Collection and Structure Refinement

Compound	$[Nd(OH_2)_9]Cl_3\cdot$15-crown-5$\cdot H_2O$	$[NdCl_2(OH_2)_6]Cl\cdot$15-crown-5
Color/Shape	pink/parallelepiped	pink/parallelepiped
Formula weight	651.0	579.0
Space Group	$P2_12_12_1$	$P2_1/n$
Temperature (°C)	−150	20
Cell Constants		
a (Å)	10.571(4)[a]	9.821(3)[b]
b (Å)	15.220(7)	16.978(9)
c (Å)	15.686(7)	12.849(8)
β (deg)		94.06(5)
Cell volume (Å^3)	2523.7	2137
Formula units/unit cell	4	4
D_{calc} (g cm^{-3})	1.71	1.80
μ_{calc} (cm^{-1})	22.8	26.8
Diffractometer/scan	Enraf-Nonius CAD-4/θ–2θ	Enraf-Nonius CAD-4/θ–2θ
Range of relative transmission factors (%)	72/100	94/100
Radiation, graphite monochromator	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)
Maximum crystal dimensions (mm)	0.25 × 0.40 × 0.50	0.25 × 0.40 × 0.50
Scan width	0.80 + 0.35tan θ	0.80 + 0.35tan θ
Standard reflections	800; 0,16,0; 0,0,18	400; 0,0,12; 006
Decay of standards	±2%	−19% (linear decay correction applied)
Reflections measured	2538	1691
2θ range (deg)	$2 \leq 2\theta \leq 50$	$2 \leq 2\theta \leq 36$
Range of h,k,l	+12, +18, +18	+8, +14, ±11
Reflections observed [$F_o \geq 5\sigma(F_o)$][c]	2441	1113
Computer programs[d]	SHELX [17]	SHELX [17]
Structure solution	heavy atom techniques	heavy atom techniques
No. of parameters varied	275	121

(continued)

TABLE I. *(continued)*

Weights	$[\sigma(F_o)^2]^{-1}$	$[\sigma(F_o)^2]^{-1}$
GOF	8.63	8.87
$R = \Sigma \lVert F_o \rvert - \lvert F_c \rVert / \Sigma \lvert F_o \rvert$	0.031	0.109
R_w	0.036	0.128
R inverse configuration	0.041	
Largest feature final diff. map	1.2 e$^-$ Å^{-3} near Nd	1.3 e$^-$ Å^{-3} near Nd

[a] Least-squares refinement of $((\sin\theta)/\lambda)^2$ values for 25 reflections $\theta > 20°$. [b] 15 reflections $\theta > 15°$. [c] Corrections: Lorentz-polarization and absorption (empirical, psi scan). [d] Neutral scattering factors and anomalous dispersion corrections from ref. 18.

atoms it was impossible to refine distinct carbon positions. The atom most affected by this is C(6) and this atom was refined isotropically. A further description of the disorder of the crown ether ring is presented in the 'Results and Discussion' section. Due to the disorder, hydrogen atom positions were not included in the refinement. Refinement of the nonhydrogen atoms (except C(6)) with anisotropic temperature factors led to final values of $R = 0.031$ and $R_w = 0.036$. The final values of the positional parameters are given in Table II.

TABLE II. Final Fractional Coordinates for $[Nd(OH_2)_9]Cl_3 \cdot 15\text{-crown-5} \cdot H_2O$

Atom	*x/a*	*y/b*	*z/c*
Nd	0.02447(3)	0.00222(3)	0.02574(2)
Cl(1)	−0.2486(2)	0.0054(2)	0.2623(1)
Cl(2)	0.1458(2)	0.2948(1)	−0.0424(1)
Cl(3)	−0.2831(2)	−0.2080(1)	0.0068(1)
O(1)	0.1042(5)	0.0005(4)	0.1762(3)
O(2)	0.1374(5)	0.0065(5)	−0.1127(3)
O(3)	−0.1053(6)	−0.0958(4)	0.1232(4)
O(4)	−0.1168(6)	0.1000(4)	0.1101(3)
O(5)	0.0013(5)	−0.1550(3)	−0.0371(3)
O(6)	−0.0347(6)	0.1346(3)	−0.0597(3)
O(7)	−0.1827(5)	−0.0199(3)	−0.0479(3)
O(8)	0.1868(6)	0.1198(3)	0.0508(3)
O(9)	0.2243(5)	−0.0854(3)	0.0352(4)
O(10)	−0.2532(6)	0.1688(4)	−0.1339(4)
O(11)	0.3126(7)	0.1180(4)	0.2102(4)
O(12)	0.1538(6)	0.0881(5)	0.3511(4)
O(13)	0.0621(7)	−0.0832(5)	0.3270(5)
O(14)[a]	0.246(2)	−0.171(1)	0.1923(9)
O(15)	0.403(1)	−0.0489(7)	0.1432(7)
O(14)′	0.285(1)	−0.1483(7)	0.2758(7)
O(15)′	0.423(1)	−0.038(1)	0.2156(8)
C(1)	0.295(1)	0.1826(7)	0.2713(7)
C(2)	0.158(1)	0.1713(6)	0.3034(6)
C(3)	0.031(1)	0.064(1)	0.3773(7)
C(4)	0.041(1)	−0.033(1)	0.4025(6)
C(5)	0.105(1)	−0.1719(8)	0.344(1)
C(6)	0.159(2)	−0.207(1)	0.257(1)
C(7)	0.3695(9)	−0.1867(6)	0.2171(6)
C(8)	0.465(1)	−0.1195(6)	0.1889(6)
C(9)	0.471(1)	0.0301(6)	0.1408(8)
C(10)	0.448(1)	0.1005(9)	0.2020(7)

[a] Primed and unprimed atoms of like number are disordered (50% occupancy each).

Crystals of $[NdCl_2(OH_2)_6]Cl \cdot 15\text{-crown-5}$ decompose over a period of several days in air by the absorption of water vapor, whereupon they dissolve and recrystallize as the chloride salt, $[NdCl_2(OH_2)_6]Cl$. A corresponding 19% decay in the standards was observed and a linear decay correction applied. Only a very limited data set ($\theta \leqslant 18°$) could be collected. The crown ether 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. With the limited data available only the Nd and three Cl atoms were refined anisotropically, leading to rather high final *R* values of $R = 0.109$ and $R_w = 0.128$. The final values of the positional parameters for this complex are given in Table III.

TABLE III. Final Fractional Coordinates for $[NdCl_2(OH_2)_6]Cl \cdot 15\text{-crown-5}$

Atom	*x/a*	*y/b*	*z/c*
Nd	0.3951(3)	0.4206(2)	0.2568(2)
Cl(1)	0.350(1)	0.4160(7)	0.0420(9)
Cl(2)	0.291(2)	0.4285(8)	0.447(1)
Cl(3)	0.847(1)	0.4163(8)	0.266(1)
O(1)	0.145(3)	0.414(2)	0.218(2)
O(2)	0.578(3)	0.500(2)	0.170(2)
O(3)	0.582(3)	0.324(2)	0.237(2)
O(4)	0.328(3)	0.558(2)	0.262(2)
O(5)	0.592(3)	0.456(2)	0.383(2)
O(6)	0.320(3)	0.283(2)	0.265(2)
O(7)	0.115(3)	0.170(2)	0.370(2)
O(8)	0.080(3)	0.227(2)	0.172(2)
O(9)	0.299(4)	0.147(2)	0.096(2)
O(10)	0.545(4)	0.169(2)	0.227(3)
O(11)	0.404(4)	0.160(2)	0.399(3)
C(1)	0.014(7)	0.221(4)	0.341(5)
C(2)	−0.037(6)	0.209(4)	0.229(4)
C(3)	0.078(5)	0.196(3)	0.068(3)
C(4)	0.217(5)	0.195(3)	0.034(4)
C(5)	0.437(5)	0.145(3)	0.063(4)
C(6)	0.524(5)	0.107(3)	0.146(3)

(continued)

TABLE III. *(continued)*

Atom	x/a	y/b	z/c
C(7)	0.608(6)	0.128(4)	0.322(4)
C(8)	0.494(5)	0.099(3)	0.387(4)
C(9)	0.307(6)	0.131(3)	0.475(4)
C(10)	0.173(6)	0.183(3)	0.465(4)

Results and Discussion

Crystallographic difficulties were encountered with the structure determinations of both the title complexes. In $[Nd(OH_2)_9]Cl_3 \cdot 15\text{-crown-}5 \cdot H_2O$ the crown ether ligand is disordered, and this disorder could not be fully resolved. A very limited data set was available for $[NdCl_2(OH_2)_6]Cl \cdot 15\text{-crown-}5$. As a result, neither determination is suitable for detailed comparison of specific distances and angles. Fortunately, it is the overall structure of these complexes we want to compare with the literature, and these determinations are suitable for this purpose.

Neodymiun has a 3+ ionic radius [19] which is too large to easily support a coordination number of eight for unidentate ligands. Expected coordination numbers for the Ln(III) ions are nine or above, even for the smaller late lanthanide ions, although 8- or even 7-coordination for the latter are possible. It was, therefore, not expected that complexes prepared of $NdCl_3 \cdot nH_2O$ and 15-crown-5 would contain the $[M(OH_2)_8]^{3+}$ ion as observed for $[M(OH_2)_8]Cl_3 \cdot 15\text{-crown-}5$ (M = Gd, Y, Lu: [11–13]). It was, however, surprising to us that two such different metal environments as found in the title complexes could be isolated from the same reaction. Nevertheless, both ions have been observed before (e.g., $[Nd(OH_2)_9]^{3+}$ in $[Nd(OH_2)_9][C_2H_5SO_4]_3$ [20] and $[NdCl_2(OH_2)_6]^+$ in $[NdCl_2(OH_2)_6]Cl$ [21]).

The metal cation and its hydrogen bonds to the crown ether in $[Nd(OH_2)_9]Cl_3 \cdot 15\text{-crown-}5 \cdot H_2O$ are presented in Fig. 1. Bond distances and angles are given in Table IV and hydrogen bonding contacts in Table V. The overall structure (depicted in the cell packing diagram, Fig. 2) is similar to that observed in $[M(OH_2)_8]Cl_3 \cdot 15\text{-crown-}5$ and in $[NdCl_2(OH_2)_6]Cl \cdot 15\text{-crown-}5$. The nine metal coordinated water molecules hydrogen bond the tenth water molecule and the chloride ions in a polymeric network. Two crown ethers are hydrogen bonded to the cation. Cl(1) and Cl(2) have a total of four hydrogen bonding interactions each, Cl(3) has five. The O···Cl contacts range from 3.069(6) to 3.214(6) Å and average 3.12(5) Å. The crown ether accepts a total of six hydrogen bonds, four on one side (including two to O(11)) and two on the other. The O···O contacts range from 2.60(1) to 2.89(1) Å and average 2.78(9) Å. Hydrogen atoms were not located.

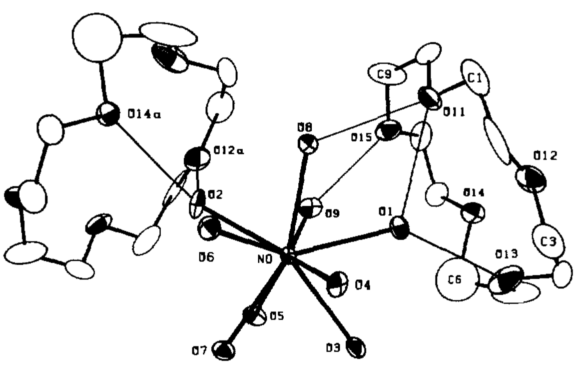

Fig. 1. Metal cation and crown ether hydrogen bonds in $[Nd(OH_2)_9]Cl_3 \cdot 15\text{-crown-}5 \cdot H_2O$. 50% probability ellipsoids for thermal motion; H atoms not located.

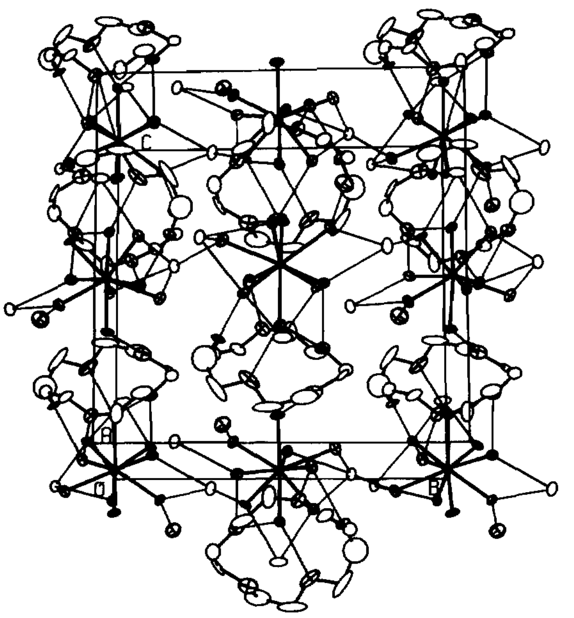

Fig. 2. Cell packing diagram for $[Nd(OH_2)_9]Cl_3 \cdot 15\text{-crown-}5 \cdot H_2O$.

The crown ether molecule is disordered. Two alternate positions for O(14) and O(15) were located and included at 40% occupancy. Thus, O(9) donates to either O(15) or O(14)′ and O(2) to either O(14)a or O(15)′a. The disorder appears to be caused by the low symmetry of the 15-crown-5 molecule. 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 (180°) and the O–C–C–O torsion angles alternate $\pm g$ ($\pm 60°$)). In this complex the O–C–C–O torsion angles alternate $\pm g$ except at one point two consecutive C–C angles must have the same sign due to the lower symmetry of

TABLE IV. Bond Distances (Å) and Angles (deg) for $[Nd(OH_2)_9]Cl_3 \cdot 15\text{-crown-5} \cdot H_2O$

Bond distances			
Nd–O(1)	2.506(4)	Nd–O(2)	2.479(5)
Nd–O(3)	2.538(6)	Nd–O(4)	2.489(6)
Nd–O(5)	2.600(5)	Nd–O(6)	2.499(5)
Nd–O(7)	2.498(5)	Nd–O(8)	2.510(6)
Nd–O(9)	2.502(6)	O(11)–C(1)	1.39(1)
O(11)–C(10)	1.46(1)	O(12)–C(2)	1.47(1)
O(12)–C(3)	1.41(1)	O(13)–C(4)	1.43(1)
O(13)–C(5)	1.45(1)	O(14)–C(6)	1.48(2)
O(14)–C(7)	1.38(2)	O(15)–C(8)	1.44(1)
O(15)–C(9)	1.40(1)	O(14)'–C(6)	1.63(2)
O(14)'–C(7)	1.41(1)	O(15)'–C(8)	1.38(2)
O(15)'–C(9)	1.65(2)	C(1)–C(2)	1.54(2)
C(3)–C(4)	1.54(2)	C(5)–C(6)	1.57(2)
C(7)–C(8)	1.50(1)	C(9)–C(10)	1.46(2)
Bond angles			
O(1)–Nd–O(2)	131.6(2)	O(1)–Nd–O(3)	67.0(2)
O(2)–Nd–O(3)	143.4(2)	O(1)–Nd–O(4)	73.0(2)
O(2)–Nd–O(4)	137.6(2)	O(3)–Nd–O(4)	73.0(2)
O(1)–Nd–O(5)	112.3(2)	O(2)–Nd–O(5)	74.8(2)
O(3)–Nd–O(5)	68.7(2)	O(4)–Nd–O(5)	134.1(2)
O(1)–Nd–O(6)	126.7(2)	O(2)–Nd–O(6)	68.3(2)
O(3)–Nd–O(6)	131.4(2)	O(4)–Nd–O(6)	69.7(2)
O(5)–Nd–O(6)	121.0(2)	O(1)–Nd–O(7)	136.8(2)
O(2)–Nd–O(7)	91.2(2)	O(3)–Nd–O(7)	74.1(2)
O(4)–Nd–O(7)	78.5(2)	O(5)–Nd–O(7)	67.5(2)
O(6)–Nd–O(7)	69.0(2)	O(1)–Nd–O(8)	68.3(2)
O(2)–Nd–O(8)	77.9(2)	O(3)–Nd–O(8)	133.9(2)
O(4)–Nd–O(8)	84.3(2)	O(5)–Nd–O(8)	141.3(2)
O(6)–Nd–O(8)	71.4(2)	O(7)–Nd–O(8)	140.1(2)
O(1)–Nd–O(9)	69.8(2)	O(2)–Nd–O(9)	70.1(2)
O(3)–Nd–O(9)	96.2(2)	O(4)–Nd–O(9)	142.5(2)
O(5)–Nd–O(9)	67.1(2)	O(6)–Nd–O(9)	132.3(2)
O(7)–Nd–O(9)	134.1(2)	O(8)–Nd–O(9)	78.1(2)
C(1)–O(11)–C(10)	108.7(9)	C(2)–O(12)–C(3)	113.4(9)
C(4)–O(13)–C(5)	113(1)	C(6)–O(14)–C(7)	109(1)
C(8)–O(15)–C(9)	115(1)	C(6)–O(14)'–C(7)	100(1)
C(8)–O(15)'–C(9)	104(1)	O(11)–C(1)–C(2)	105.8(9)
O(12)–C(2)–C(1)	106.8(8)	O(12)–C(3)–C(4)	105(1)
O(13)–C(4)–C(3)	108.2(9)	O(13)–C(5)–C(6)	105(1)
O(14)–C(6)–C(5)	135(1)	O(14)'–C(6)–C(5)	88(1)
O(14)–C(7)–C(8)	115.4(9)	O(14)'–C(7)–C(8)	109.4(8)
O(15)–C(8)–C(7)	110.7(9)	O(15)'–C(8)–C(7)	108(1)
O(15)–C(9)–C(10)	122(1)	O(15)'–C(9)–C(10)	86.7(9)
O(11)–C(10)–C(9)	111(1)		

TABLE V. Hydrogen Bonding Contact Geometries (Å, deg) for $[Nd(OH_2)_9]Cl_3 \cdot 15\text{-crown-5} \cdot H_2O$

Bond distances			
O(1)–O(11)	2.887(9)	O(1)–O(13)	2.724(9)
O(2)–O(12)[a]	2.696(9)	O(2)–O(14)[a]	2.89(1)
O(2)–O(15)'[a]	2.81(1)		
O(3)–Cl(1)	3.071(6)	O(3)–Cl(3)	3.128(6)
O(4)–Cl(1)	3.117(6)	O(4)–Cl(2)[b]	3.161(6)
O(5)–Cl(3)	3.126(6)	O(5)–Cl(3)[c]	3.188(6)
O(6)–Cl(2)	3.108(6)	O(6)–O(10)	2.638(9)
O(7)–Cl(1)[d]	3.073(5)	O(7)–Cl(3)	3.171(5)

(continued)

TABLE V. *(continued)*

Bond distances			
O(8)–Cl(2)	3.069(6)	O(8)–O(11)	2.832(8)
O(9)–Cl(3)^c	3.214(6)	O(9)–O(14)′	2.80(1)
O(9)–O(15)	2.60(1)		
O(10)–Cl(1)^d	3.110(7)	O(10)–Cl(2)^b	3.016(7)
Bond angles			
O(11)–O(1)–O(13)	104.7(2)		
O(12)^a–O(2)–O(14)^a	92.3(3)	O(12)^a–O(2)–O(15)′^{a}	94.3(4)
Cl(1)–O(3)–Cl(3)	113.1(2)	Cl(1)–O(4)–Cl(2)^b	97.9(2)
Cl(3)–O(5)–Cl(3)^c	119.1(2)	Cl(2)–O(6)–O(10)	114.9(2)
Cl(1)^d–O(7)–Cl(3)	104.3(2)	Cl(2)–O(8)–O(11)	119.7(2)
Cl(3)^c–O(9)–O(14)′	74.2(3)	Cl(3)^c–O(9)–O(15)	111.1(3)
Cl(1)^d–O(10)–Cl(2)^b	129.7(2)		

[a] Atoms are related to those in Table II by $0.5 - x, -y, z - 0.5$. [b] $x - 0.5, 0.5 - y, -z$. [c] $0.5 + x, -y - 0.5, -z$. [d] $-x - 0.5, -y, z - 0.5$.

15-crown-5. Where this occurs, normally, one of the two C–O–C–C angles between these two will be forced *g*. O(14)–C(7)–C(8)–O(15) and O(15)–C(9)–C(10)–O(11) are both *g*– (−64.1, −47.7°) as is C(8)–O(15)–C(9)–C(10) (−95.3°). In the minor conformation C(8)–O(15)′–C(9)–C(10) is anti (−163.4°) and the two consecutive gauche angles are O(13)–C(5)–C(6)–O(14)′ (47.6°) and O(14)′–C(7)–C(8)–O(15)′ (54.0°). The O–C angle found gauche is C(5)–C(6)–O(14)′–C(7) (83.7°). The crown ether has undergone no major conformational changes to get O(11) in a position to accept two hydrogen bonds on the same side of the ether. A major conformational change was observed for 18-crown-6 in a similar situation in $[Dy(OH_2)_8]Cl_3 \cdot$18-crown-6$\cdot 4H_2O$ [6].

As observed for all other $[M(OH_2)_9]^{3+}$ (M = Ln(III) [16]) ions, the $[Nd(OH_2)_9]^{3+}$ cation has a tricapped trigonal prismatic geometry. The capping atoms, O(1), O(5), and O(6), are an average of 2.54(5) Å from Nd. The remaining Nd–O separations average 2.50(2) Å.

Bond distances and angles for $[NdCl_2(OH_2)_6]Cl \cdot$15-crown-5 are given in Table VI, hydrogen bond contact geometries in Table VII. The cation and its crown ether interactions are depicted in Fig. 3, a cell packing diagram in Fig. 4. The metal coordinated water molecules, O(2) and O(5), donate hydrogen bonds to coordinated chlorine atoms Cl(1) and Cl(2) in different formula units forming zigzag polymeric chains propagating along *c*. The third chloride ion, Cl(3), separates the cations in the *a* direction. O(2), O(3), and O(5) donate one hydrogen bond each to the same Cl$^-$ anion on one side and O(1) from a different formula unit (related by $1 + x, y, z$) donates a fourth hydrogen bond to this anion. The O···Cl contacts range from 3.03(3) to 3.20(3) Å and average 3.11(7) Å.

The crown ether molecules separate the cations in the *b* direction, accepting a total of five hydrogen bonds, three from one cation on one side, two

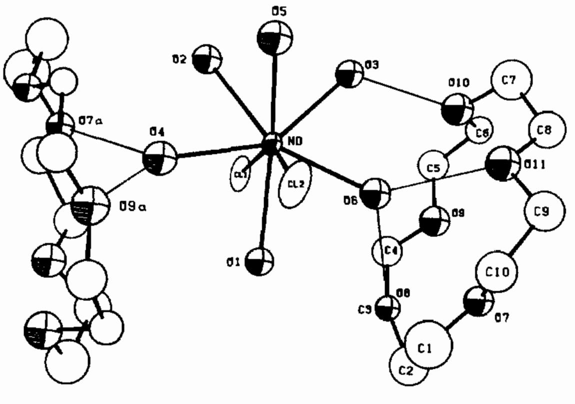

Fig. 3. Metal cation and crown ether hydrogen bonds in $[NdCl_2(OH_2)_6]Cl \cdot$15-crown-5.

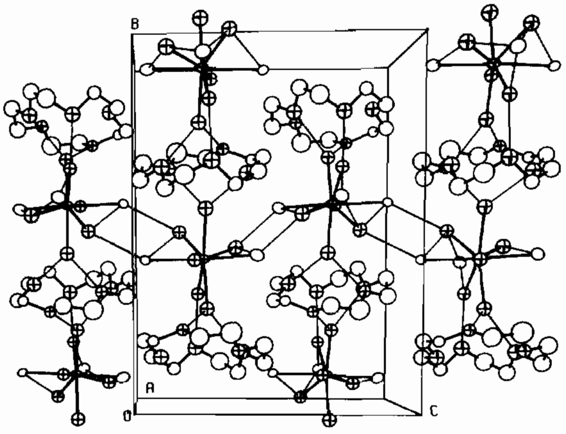

Fig. 4. Cell packing diagram for $[NdCl_2(OH_2)_6]Cl \cdot$15-crown-5.

TABLE VI. Bond Distances (Å) and Angles (deg) for $[NdCl_2(OH_2)_6]Cl \cdot 15\text{-crown-}5$

Bond distances			
Nd–Cl(1)	2.76(1)	Nd–Cl(2)	2.72(1)
Nd–O(1)	2.47(3)	Nd–O(2)	2.56(3)
Nd–O(3)	2.49(3)	Nd–O(4)	2.42(3)
Nd–O(5)	2.50(3)	Nd–O(6)	2.46(3)
O(7)–C(1)	1.36(6)	O(7)–C(10)	1.33(5)
O(8)–C(2)	1.44(6)	O(8)–C(3)	1.44(5)
O(9)–C(4)	1.36(5)	O(9)–C(5)	1.45(5)
O(10)–C(6)	1.48(5)	O(10)–C(7)	1.50(6)
O(11)–C(8)	1.38(5)	O(11)–C(9)	1.49(5)
C(1)–C(2)	1.51(7)	C(3)–C(4)	1.46(6)
C(5)–C(6)	1.46(6)	C(7)–C(8)	1.52(7)
C(9)–C(10)	1.58(7)		
Bond angles			
Cl(1)–Nd–Cl(2)	148.8(4)	Cl(1)–Nd–O(1)	73.3(7)
Cl(2)–Nd–O(1)	75.6(7)	Cl(1)–Nd–O(2)	69.5(7)
Cl(2)–Nd–O(2)	133.1(7)	O(1)–Nd–O(2)	131(1)
Cl(1)–Nd–O(3)	86.9(7)	Cl(2)–Nd–O(3)	116.9(7)
O(1)–Nd–O(3)	133(1)	O(2)–Nd–O(3)	76(1)
Cl(1)–Nd–O(4)	91.9(8)	Cl(2)–Nd–O(4)	78.8(8)
O(1)–Nd–O(4)	78(1)	O(2)–Nd–O(4)	73(1)
O(3)–Nd–O(4)	147(1)	Cl(1)–Nd–O(5)	135.5(8)
Cl(2)–Nd–O(5)	74.3(8)	O(1)–Nd–O(5)	148(1)
O(2)–Nd–O(5)	68(1)	O(3)–Nd–O(5)	71(1)
O(4)–Nd–O(5)	87(1)	Cl(1)–Nd–O(6)	89.4(8)
Cl(2)–Nd–O(6)	82.8(8)	O(1)–Nd–O(6)	71(1)
O(2)–Nd–O(6)	138(1)	O(3)–Nd–O(6)	67(1)
O(4)–Nd–O(6)	146(1)	O(5)–Nd–O(6)	115(1)
C(1)–O(7)–C(10)	114(4)	C(2)–O(8)–C(3)	116(4)
C(4)–O(9)–C(5)	112(4)	C(6)–O(10)–C(7)	107(4)
C(8)–O(11)–C(9)	106(4)	O(7)–C(1)–C(2)	112(5)
O(8)–C(2)–C(1)	103(5)	O(8)–C(3)–C(4)	109(4)
O(9)–C(4)–C(3)	112(4)	O(9)–C(5)–C(6)	108(4)
O(10)–C(6)–C(5)	105(4)	O(10)–C(7)–C(8)	109(5)
O(11)–C(8)–C(7)	108(4)	O(11)–C(9)–C(10)	109(4)
O(7)–C(10)–C(9)	106(4)		

TABLE VII. Hydrogen Bonding Contact Geometries (Å, deg) for $[NdCl_2(OH_2)_6]Cl \cdot 15\text{-crown-}5$

Bond distances			
O(1)–Cl(1)	3.14(3)	O(1)–Cl(2)	3.19(3)
O(1)–Cl(3)[b]	3.03(3)		
O(2)–Cl(1)	3.04(3)	O(2)–Cl(1)[c]	3.20(3)
O(2)–Cl(3)	3.17(3)		
O(3)–Cl(3)	3.04(3)	O(3)–O(10)	2.67(4)
O(4)–O(7)[a]	2.64(4)	O(4)–O(9)[a]	2.75(4)
O(5)–Cl(2)	3.10(4)	O(5)–Cl(2)[d]	3.16(4)
O(5)–Cl(3)	3.08(4)		
O(6)–O(8)	2.73(4)	O(6)–O(11)	2.79(5)
Bond angles			
Cl(1)–O(1)–Cl(2)	113(1)	Cl(1)–O(1)–Cl(3)[b]	146(1)
Cl(2)–O(1)–Cl(3)	100.8(9)		
Cl(1)–O(2)–Cl(1)[c]	86.8(8)	Cl(1)–O(2)–Cl(3)	124(1)
Cl(1)[c]–O(2)–Cl(3)	108(1)		
Cl(3)–O(3)–O(10)	129(1)	O(7)[a]–O(4)–O(8)[a]	99(1)

(continued)

TABLE VII. *(continued)*

Bond angles			
Cl(2)–O(5)–Cl(2)[d]	102(1)	Cl(2)–O(5)–Cl(3)	102(1)
Cl(2)[d]–O(5)–Cl(3)	154(1)		
O(8)–O(6)–O(11)	102(1)		

[a] Atoms related to those in Table III by 0.5 − x, 0.5 + y, 0.5 − z. [b] x − 1, y, z. [c] 1 − x, 1 − y, −z. [d] 1 − x, 1 − y, 1 − z.

from a symmetry related cation on the other side. The O···O contacts range from 2.64(4) to 2.79(5) Å and average 2.72(5) Å. The crown ether conformation is the same as that observed for the decahydrate. The two O–C–C–O torsion angles of like sign are O(9)–C(5)–C(6)–O(10) (−76.1°) and O(10)–C(7)–C(8)–O(11) (−49.3°). The C(6)–O(10)–C(7)–C(8) angle is −89.3°.

Although the $[NdCl_2(OH_2)_6]^+$ cation has been structurally characterized in the chloride salt, $[NdCl_2(OH_2)_6]Cl$ [21], the actual metal ion geometry is different. In the chloride salt the geometry is a distorted square antiprism, while in the title complex, the geometry is much closer to dodecahedral with 'A' sites occupied by Cl(2), O(1), O(2), and O(3) and 'B' sites by Cl(1), O(4), O(5), and O(6). The two Nd–Cl distances are also shorter in this complex (2.76(1), 2.72(1) Å) than observed in the chloride salt (2.815(2) Å). This is probably due to the fact that each coordinated chlorine in the salt accepts three hydrogen bonds, while only one or possibly two are accepted by Cl(1) and Cl(2) in the title complex. The six Nd–O separations average 2.48(4) Å in the title complex and 2.461(1) Å in the chloride salt.

Supplementary Material

Tables of thermal parameters, torsion angles, least-squares planes results, and observed and calculated structure factors or amplitudes for both complexes and hydrogen atom positions for the hexahydrate are available from the author on request.

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