Inorganica Chimica Acta, *116* (1986) 171–177

f-Element/Crown Ether Complexes. 1. Synthesis and Structure of $[Y(OH_2)_8]Cl_3 \cdot$(15-crown-5)

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(Received December 2, 1985)

Abstract

The crystal and molecular structure of $[Y(OH_2)_8]Cl_3 \cdot$(15-crown-5) has been determined by single-crystal X-ray diffraction. The complex crystallizes in the monoclinic space group $P2_1/n$ with $Z = 4$. Lattice parameters are $a = 9.202(2)$, $b = 17.247(3)$, $c = 15.208(3)$ Å, and $\beta = 92.39(2)°$. The structure was solved by Patterson and Fourier techniques and refined by least-squares to a final conventional R value of 0.081. The Y(III) ion is eight coordinate, bonded to the oxygen atoms of the eight water molecules. Three of the water molecules are hydrogen bonded to crown ether molecules. The three chloride ions participate in hydrogen bonds with the remaining five water molecules. The Y–O(water) distances range from 2.322(6) to 2.432(7) Å and average 2.37(4) Å. The average O(water)···Cl and O(water)···O(crown) hydrogen bonded separations are 3.08(4) and 2.76(7) Å, respectively.

Introduction

Rare earth–crown ether chemistry has attracted considerable interest [1, 2], but the crystallographic investigations have lagged behind the synthetic advances. As an example of this, several complexes of lanthanoid salts and the macrocyclic ligand 15-crown-5 (IUPAC name: 1,4,7,10,13-pentaoxacyclopentadecane) have been reported [3–10], however structural studies have been carried out on only a few of these [7, 9, 10]. Part of the reason for this may lie in the fact that these complexes often trap solvent molecules in the crystal lattice which are lost when the crystals are removed from the mother liquor and as a result the lattice collapses. We are beginning the investigation of such compounds and hope to prevent solvent loss by carrying out the X-ray data collection at low (−120 °C) temperatures. In those instances where there is no solvent loss the structural studies can normally be carried out at room temperature and we have recently completed studies of $[Y(NO_3)_2(OH_2)_5][NO_3] \cdot 2$(15-crown-5) [11], $Y(NO_3)_3 \cdot$(12-crown-4) [11] and the title compound.

In addition to the obvious benefits of the synthetic and crystallographic investigations we envisage, we hope to study the elimination of water and the formation of direct metal–crown ether interactions. It has been suggested that this may be an important factor in the separations chemistry of crown ether macrocyclic ligands. This paper opens our investigations in this area and we report here the synthesis and crystal structure of a hydrogen bonded 15-crown-5 complex of yttrium(III) chloride octahydrate.

Experimental

All reactions were carried out under anhydrous conditions in an oxygen-free Ar atmosphere. All solvents were purified by standard methods. Carbon, hydrogen and nitrogen analyses were performed using a Perkin–Elmer model 240 elemental analyzer. IR absorption spectra were obtained from a Mattson Cygnus 25 FTIR spectrophotometer from KBr pellets. ^1H NMR spectra were recorded with an IBM WP-200SY (200 MHz) NMR spectrometer by using DMSO-d6 with tetramethylsilane (TMS) as an internal standard. Melting points were obtained by use of an Electrothermal IA6304 capillary melting point apparatus and are uncorrected.

Preparation of $[Y(OH_2)_8]Cl_3 \cdot$*(15-crown-5)*

A solution of 10 mmol of 15-crown-5 (1,4,7,10,13-pentaoxacyclopentadecane) in 30 ml of a CH_3OH:CH_3CN (1:3) solution was added dropwise to a solution of 10 mmol of $YCl_3 \cdot nH_2O$ in 30 ml of the corresponding solvent. The mixture was stirred at 60 °C for 20 h; cooled to 20 °C and concentrated to 15–30 ml. Crystals deposited along the walls of the flask after four days at −20 °C. Melting point: 104–108 °C. *Anal.* Calc. for $[Y(OH_2)_8]Cl_3 \cdot$(15-crown-5): C, 21.46; H, 6.48. Found: C, 21.41; H, 6.75%.

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0020-1693/86/$3.50

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

Compound formula	$[Y(OH_2)_8]Cl_3 \cdot (C_{10}H_{20}O_5)$
Molecular weight	559.7
Space group	$P2_1/n$
Cell constants	
a (Å)	9.202(2)
b (Å)	17.247(3)
c (Å)	15.208(3)
β (deg)	92.39(2)
Cell volume (Å^3)	2411.5
Molecules/unit cell	4
ρ(calc) (g cm^{-3})	1.54
μ(calc) (cm^{-1})	28.79
Radiation	Mo Kα
Maximum crystal dimensions (mm)	0.25 × 0.58 × 0.58
Scan width	0.80 + 0.20 tan θ
Standard reflections	(6,0,0)(0,14,0)(0,0,8)
Decay of standards	±1.5%
Reflections measured	3500
2θ range	50°
Reflections collected	2847
Number of parameters varied	244
Weighting scheme	$[(1/\sigma F_o^2) - (1/0.001F_o^2]$
Goodness of fit	1.54
R	0.081
R_w	0.085

After formation of the title compound small shifts of 5–35 cm^{-1} in the vibrational spectra bands due to the crown ether were observed compared to those for the free crown, ν(C–O–C) at ~1100 cm^{-1} in the free ligand were observed to be shifted by −10 cm^{-1}. Other crown vibrations at 940–990 cm^{-1} and ~860 cm^{-1} are shifted by −5 cm^{-1} and −35 cm^{-1}, respectively in the spectrum of the title compound.

X-ray Data Collection, Structure Determination, and Refinement for $[Y(OH_2)_8]Cl_3 \cdot$(15-crown-5)

Clear single crystals of the title compound were sealed under Ar in thin-walled glass capillaries. Final lattice parameters as determined from a least-squares refinement of $((\sin\theta)/\lambda)^2$ values for 25 reflections ($\theta > 16°$) accurately centered on the diffractometer are given in Table I. The space group was determined to be the centric $P2_1/n$ from the systematic absences.

Data were collected on an Enraf-Nonius CAD-4 diffractometer by the θ–2θ scan technique. A summary of data collection parameters is given in Table I. The intensities were corrected for Lorentz, polarization effects, and for absorption.

Calculations were carried out with the SHELX system of computer programs [12]. Neutral atom scattering factors for Y, Cl, O, C and H were taken from ref. 13 and the scattering was corrected for the real and imaginary components of anomalous dispersion [13].

The position of the yttrium atom was revealed via inspection of a Patterson map. Difference Fourier maps phased on the yttrium atom readily revealed the positions of the non-hydrogen atoms. Least-squares refinement with isotropic thermal parameters led to $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.110$. The hydrogen atoms bonded to the crown ether were placed in calculated positions 0.95 Å from the bonded carbon atom and allowed to ride (with B fixed at 5.5 Å^2) on this atom. All hydrogen atoms associated with the water molecules could not be located and these atoms were, therefore, not included in the final refinement. Refinement of the non-hydrogen atoms with anisotropic temperature factors led to final values of $R = 0.081$ and $R_w = 0.085$. A final difference Fourier showed no feature greater than 1.2 e$^-$/Å^3. The weighting scheme was based on $[(1/\sigma F_o^2) + (1/pF_o^2)]$ where $p = 0.001$; no systematic variation of $w(|F_o| - |F_c|)$ *versus* $|F_o|$ or $(\sin\theta)/\lambda$ was noted. The final values of the positional parameters are given in Table II*.

*See also 'Supplementary Material'.

TABLE II. Final Fractional Coordinates for $[Y(OH_2)_8]Cl_3 \cdot$(15-crown-5)

Atom	x/a	y/b	z/c
Y	0.8563(1)	0.18187(5)	0.22234(6)
Cl(1)	0.6629(3)	0.1716(2)	0.4958(2)
Cl(2)	0.1484(3)	0.6595(2)	0.3287(2)
Cl(3)	0.6914(3)	0.2430(2)	0.9391(2)
O(1)	0.9129(8)	0.1721(4)	0.3732(4)
O(2)	0.8049(8)	0.3128(3)	0.2380(5)
O(3)	0.6278(7)	0.1949(4)	0.2958(4)
O(4)	0.7804(7)	0.0532(3)	0.2469(5)
O(5)	0.6680(7)	0.1615(4)	0.1145(5)
O(6)	1.0891(7)	0.2445(4)	0.2449(4)
O(7)	1.0405(8)	0.0913(4)	0.1863(6)
O(8)	0.9317(7)	0.2318(4)	0.0860(4)
O(9)	0.591(1)	0.9643(6)	0.138(1)
O(10)	0.560(2)	0.9390(5)	0.3157(9)
O(11)	0.849(2)	0.9628(6)	0.3908(7)
O(12)	1.052(1)	0.9434(7)	0.255(1)
O(13)	0.842(2)	0.8909(7)	0.1291(9)
C(1)	0.461(2)	0.9475(9)	0.164(2)
C(2)	0.459(2)	0.9779(9)	0.257(1)
C(3)	0.571(2)	0.9703(9)	0.392(1)
C(4)	0.717(2)	0.9384(8)	0.4413(9)
C(5)	0.946(2)	0.914(1)	0.415(1)
C(6)	1.079(2)	0.940(1)	0.358(1)
C(7)	1.058(2)	0.876(1)	0.231(2)
C(8)	1.009(2)	0.883(1)	0.128(1)
C(9)	0.818(3)	0.924(1)	0.057(1)
C(10)	0.640(2)	0.921(1)	0.066(1)
H(1)[C(1)]	0.388(2)	0.9710(9)	0.127(2)
H(2)[C(1)]	0.447(2)	0.8929(9)	0.164(2)

(continued)

TABLE II *(continued)*

Atom	*x/a*	*y/b*	*z/c*
H(3)[C(2)]	0.364(2)	0.9707(9)	0.278(1)
H(4)[C(2)]	0.481(2)	1.0316(9)	0.255(1)
H(5)[C(3)]	0.579(2)	1.0250(9)	0.387(1)
H(6)[C(3)]	0.489(2)	0.9578(9)	0.425(1)
H(7)[C(4)]	0.712(2)	0.8834(8)	0.4437(9)
H(8)[C(4)]	0.726(2)	0.9586(8)	0.4993(9)
H(9)[C(5)]	0.968(2)	0.916(1)	0.476(1)
H(10)[C(5)]	0.918(2)	0.862(1)	0.399(1)
H(11)[C(6)]	1.160(2)	0.908(1)	0.372(1)
H(12)[C(6)]	1.101(2)	0.992(1)	0.376(1)
H(13)[C(7)]	1.155(2)	0.857(1)	0.238(2)
H(14)[C(7)]	0.995(2)	0.843(1)	0.261(2)
H(15)[C(8)]	1.035(2)	0.839(1)	0.095(1)
H(16)[C(8)]	1.051(2)	0.929(1)	0.104(1)
H(17)[C(9)]	0.852(3)	0.976(1)	0.052(1)
H(18)[C(9)]	0.847(3)	0.894(1)	0.008(1)
H(19)[C(10)]	0.614(2)	0.868(1)	0.074(1)
H(20)[C(10)]	0.592(2)	0.940(1)	0.014(1)

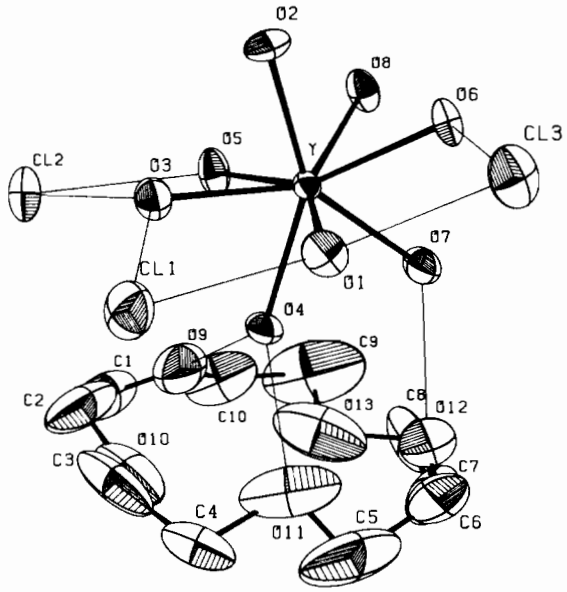

Fig. 1. Asymmetric unit and atom labelling scheme for $[Y(OH_2)_8]Cl_3 \cdot$(15-crown-5). The atoms are represented by their 50% probability ellipsoids for thermal motion. Hydrogen atoms have been omitted. The crown ether portrayed is related to the coordinates in Table II by $x, y - 1.0, z$.

Results and Discussion

A view of the asymmetric unit and the atom labelling scheme are presented in Fig. 1. A stereoscopic view of the unit cell contents can be found in Fig. 2. Bond distances and angles are given in Table III. The yttrium atom coordination consists of eight water molecules and the coordination polyhedron is best described as a distorted dodecahedron (Fig. 3).

The two different types of Y–O separations average: $Y-O_A$, 2.40(3) Å (O(3), O(4), O(6), O(8)) and $Y-O_B$ 2.35(3) Å (O(1), O(2), O(5), O(7)). In a related compound, $[Y(OH_2)_8]Cl_3 \cdot 2(C_{10}H_8N_2)$ [14] a similar yttrium geometry was observed with average Y–O distances of $Y-O_A = 2.425(8)$ Å and $Y-O_B = 2.327(9)$ Å.

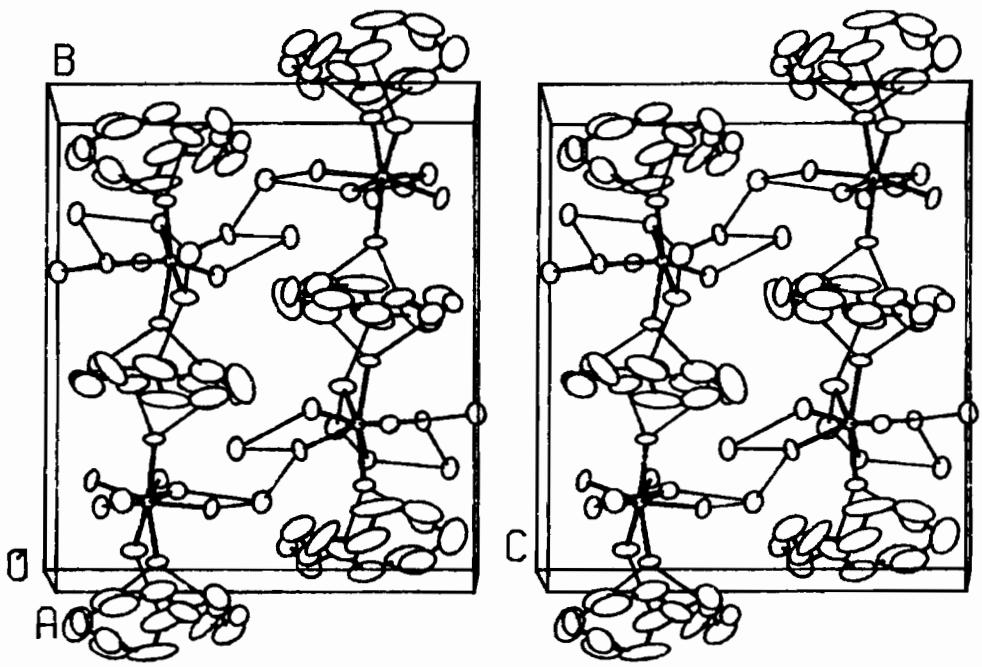

Fig. 2. Stereoscopic view of the unit cell contents.

TABLE III. Bond Distances (Å) and Angles (°) for $[Y(OH_2)_8]Cl_3 \cdot$(15-crown-5)

Atoms	Distance	Atoms	Distance
Y–O(1)	2.338(6)	Y–O(2)	2.322(6)
Y–O(3)	2.432(7)	Y–O(4)	2.360(6)
Y–O(5)	2.362(7)	Y–O(6)	2.412(6)
Y–O(7)	2.385(7)	Y–O(8)	2.376(6)
O(9)–C(1)	1.32(2)	O(9)–C(10)	1.42(2)
O(10)–C(2)	1.43(2)	O(10)–C(3)	1.28(2)
O(11)–C(4)	1.53(2)	O(11)–C(5)	1.27(2)
O(12)–C(6)	1.57(2)	O(12)–C(7)	1.22(2)
O(13)–C(8)	1.54(2)	O(13)–C(9)	1.25(2)
C(1)–C(2)	1.50(2)	C(3)–C(4)	1.60(2)
C(5)–C(6)	1.59(2)	C(7)–C(8)	1.62(3)
C(9)–C(10)	1.65(3)		
Atoms	**Angle**	**Atoms**	**Angle**
O(1)–Y–O(2)	90.4(2)	O(1)–Y–O(3)	73.6(2)
O(2)–Y–O(3)	71.3(2)	O(1)–Y–O(4)	80.3(2)
O(2)–Y–O(4)	146.6(2)	O(3)–Y–O(4)	75.3(2)
O(1)–Y–O(5)	142.9(3)	O(2)–Y–O(5)	94.0(2)
O(3)–Y–O(5)	73.1(2)	O(4)–Y–O(5)	75.9(2)
O(1)–Y–O(6)	74.4(2)	O(2)–Y–O(6)	74.5(2)
O(3)–Y–O(6)	132.3(2)	O(4)–Y–O(6)	131.7(2)
O(5)–Y–O(6)	141.9(2)	O(1)–Y–O(7)	92.7(3)
O(2)–Y–O(7)	144.1(2)	O(3)–Y–O(7)	143.3(2)
O(4)–Y–O(7)	68.8(2)	O(5)–Y–O(7)	104.5(3)
O(6)–Y–O(7)	72.0(2)	O(1)–Y–O(8)	145.2(2)
O(2)–Y–O(8)	78.8(3)	O(3)–Y–O(8)	131.1(2)
O(4)–Y–O(8)	125.3(2)	O(5)–Y–O(8)	71.4(2)
O(6)–Y–O(8)	70.9(2)	O(7)–Y–O(8)	78.5(3)
C(1)–O(9)–C(10)	116(2)	C(2)–O(10)–C(3)	114(1)
C(4)–O(11)–C(5)	104(1)	C(6)–O(12)–C(7)	105(2)
C(8)–O(13)–C(9)	100(2)	O(9)–C(1)–C(2)	105(1)
O(10)–C(2)–C(1)	113(1)	O(10)–C(3)–C(4)	108(2)
O(11)–C(4)–C(3)	110(1)	O(11)–C(5)–C(6)	102(2)
O(12)–C(6)–C(5)	117(1)	O(12)–C(7)–C(8)	102(2)
O(13)–C(8)–C(7)	104(1)	O(13)–C(9)–C(10)	93(2)
O(9)–C(10)–C(9)	113(2)		

A more elegant determination of the coordination polyhedron can be found from the data in Table IV. The notation of the edges (a, m, g, b) and angles (θ_A, θ_B) follows that used by Hoard and Silverton [15]. The shape determining angles, δ and ω, were calculated by the method used by Porai–Koshits and Aslanov [16] and Muetterties and Guggenberger [17]. As Table IV shows the shape determining angles, δ, are near the ideal value for a dodecahedron of 29.5° [17]. The angle, ω, between the mean square planes of the two trapezoids, 89.6°, is also near the idealized value of 90° [16].

Since it was not possible to locate the coordinated water hydrogen atoms, the presence of hydrogen bonding must be inferred from close O···O or O···Cl nonbonded contacts. These are listed in Table V. It appears that each coordinated water participates in two hydrogen bonding interactions. For O(1), O(3), O(5), O(6) and O(8) these are exclusively with chloride ions. O(2) and O(3) form two hydrogen bonds to four crown ether oxygen atoms and O(7) forms one such interaction with Cl(2) and another with a fifth crown oxygen. There are eleven total Cl···H–O(water) interactions with an average Cl···O separation of 3.08(4) Å (Cl(1) only has three). In $[M(OH_2)_8]Cl_3 \cdot 2(C_{10}H_8N_2)$ (M = Y [14] and Gd [18]) both of which have similar structures, each chloride ion participated in four hydrogen bonding interactions with the metal coordinated water molecules with average Cl···O distances of 3.11(1) Å (Y) and 3.10(3) Å (Gd).

The five O(water)···O(crown ether) contacts suggesting hydrogen bonds range from 2.65(1) to 2.82(2) Å and average 2.76(7) Å. This type of hydro-

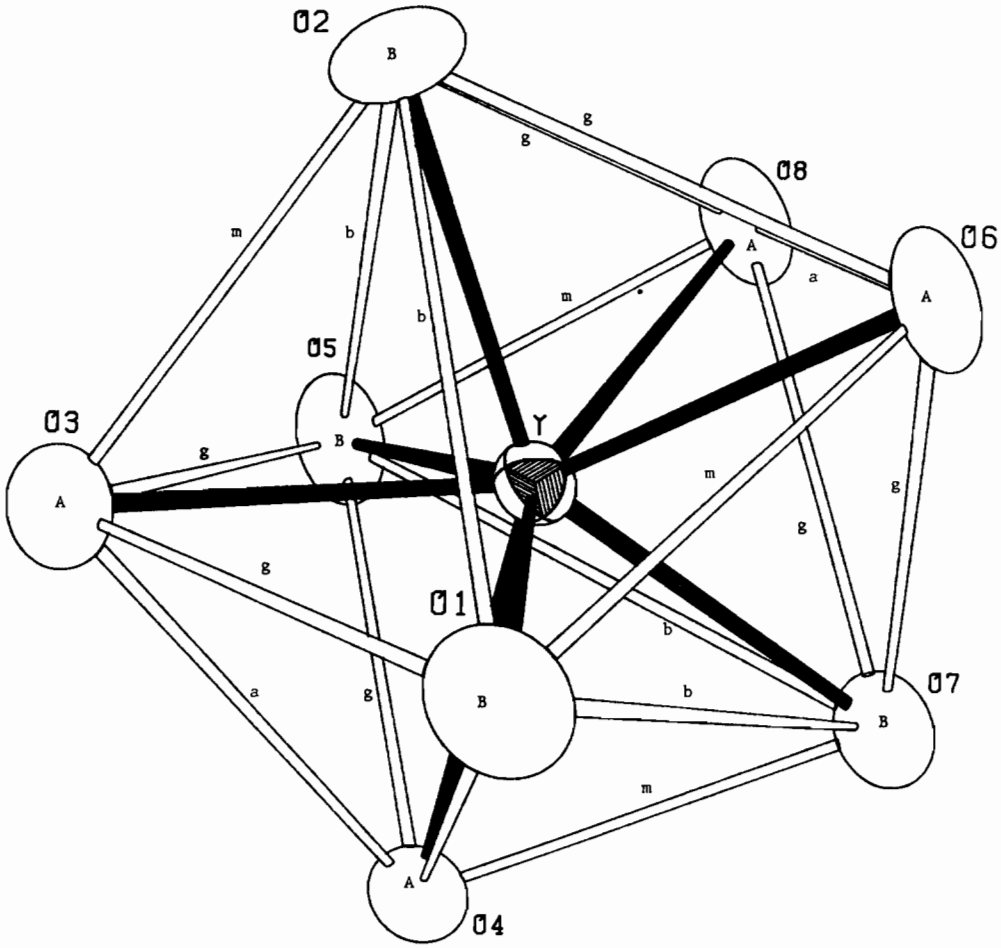

Fig. 3. $[Y(OH_2)_8]^{3+}$ coordination polyhedron.

TABLE IV. Mean Dimensions of the Dodecahedron Formed by the Eight Coordinated Oxygen Atoms in $[Y(OH_2)_8]Cl_3 \cdot$ (15-crown-5)[a]

Edge (Å)	Mean (Å)	Range (Å)
a	2.8(1)	2.775(9)–2.929(9)
m	2.77(8)	2.68(1)–2.874(9)
g	2.92(8)	2.818(9)–3.031(9)
b	3.5(1)	3.307(9)–3.75(1)

Metal–oxygen distances (Å)		Range (Å)
M–A	2.40(3)	2.360(6)–2.432(9)
M–B	2.35(3)	2.322(6)–2.385(7)

Dihedral angles δ at type b edges (°)

34.5 33.3 30.9 19.7 Ideal = 29.5° [18]

Dihedral angles δ' at remaining edges (°)

68.2 63.6 64.1 54.9 58.4 63.6 60.6

Angle ω between the mean square planes of trapezoids (°)

89.6 Ideal = 90° [17]

[a]Terms defined as in references [16, 17, 18].

TABLE V. Short Intermolecular Contacts Indicative of Hydrogen Bonding

Atoms	Distance (Å)	Atoms	Distance (Å)
Cl(1)···O(1)	3.021(8)	Cl(2)···O(3)[b]	3.164(7)
Cl(1)···O(8)[a]	3.069(7)	Cl(3)···O(1)[a]	3.082(8)
Cl(1)···O(3)	3.071(7)	Cl(3)···O(5)[d]	3.031(8)
Cl(2)···O(5)[b]	3.072(8)	Cl(3)···O(6)[a]	3.069(7)
Cl(2)···O(6)[c]	3.075(7)	Cl(3)···O(8)[d]	3.083(7)
Cl(2)···O(7)[c]	3.112(8)		
O(2)···O(10)[e]	2.65(1)	O(4)···O(11)[f]	2.74(1)
O(2)···O(13)[e]	2.82(2)	O(7)···O(12)[f]	2.76(2)
O(4)···O(9)[f]	2.81(1)		

[a]Atoms related to those in Table II by $x - 0.5$, $0.5 - y$, $0.5 + z$. [b]$0.5 - x$, $0.5 + y$, $0.5 - z$. [c]$1.5 - x$, $0.5 + y$, $0.5 - z$. [d]$x, y, 1.0 + z$. [e]$1.5 - x$, $y - 0.5$, $0.5 - z$. [f]$x, y - 1.0, z$.

gen bonding is not unknown for 15-crown-5 and has, for example, been observed in the structure of $[Sm(15\text{-crown-5})(OH_2)_4][ClO_4]_3 \cdot (15\text{-crown-5}) \cdot H_2O$

TABLE VI. Torsion Angles (°) for the 15-Crown-5 Ether

O(9)–C(1)–C(2)–O(10)	–64.7
C(1)–C(2)–O(10)–C(3)	172.3
C(2)–O(10)–C(3)–C(4)	–163.6
O(10)–C(3)–C(4)–O(11)	62.9
C(3)–C(4)–O(11)–C(5)	–157.4
C(4)–O(11)–C(5)–C(6)	178.2
O(11)–C(5)–C(6)–O(12)	–56.8
C(5)–C(6)–O(12)–C(7)	–77.8
C(6)–O(12)–C(7)–C(8)	172.8
O(12)–C(7)–C(8)–O(13)	–78.9
C(7)–C(8)–O(13)–C(9)	156.6
C(8)–O(13)–C(9)–C(10)	175.7
O(13)–C(9)–C(10)–O(9)	63.6
C(9)–C(10)–O(9)–C(1)	–161.3
C(10)–O(9)–C(1)–C(2)	159.6

[10] where one crown is coordinated to the metal and the other is hydrogen bonded to the coordinated water molecules. The four relevant O(water)···O-(crown) contacts in the samarium compound average 2.74(1) Å. We have also found this type of interaction in the structure of $[Y(NO_3)_2(OH_2)_5][NO_3]\cdot 2$(15-crown-5) [11].

The overall view of the hydrogen bonding in this compound reveals an interesting polymeric structure. The hydrogen bonding of O(4) and O(7) to one molecule of 15-crown-5 'below' the yttrium cation and to O(2) to another 15-crown-5 molecule 'above' related by $1.5-x$, $y-1.5$, $0.5-z$ results in polymeric zigzag chains along b. The chloride ions appear to reside in layers in the ac plane and the hydrogen bonding to these atoms results in a 2-dimensional polymeric network. The overall structure gives the appearance of layers of crown ether molecules separating individual cations.

The crown ether itself is normal for uncoordinated 15-crown-5. The mean C–O and C–C distances and the mean C–C–O and C–O–C angles are 1.4(1) Å, 1.59(6) Å, 107(7)°, and 108(7)°, respectively. Although the standard deviations are high these values are similar to those reported for the hydrogen bonded 15-crown-5 molecule in $[Sm(15\text{-crown-5})(OH_2)_4][ClO_4]_3\cdot(15\text{-crown-5})\cdot H_2O$ [10] (1.44(9) Å, 1.47(5) Å, 106(8)°, 110(8)°). The O–C–C–O torsional angles are nearly synclinal and are in good agreement with other reported structures [8, 19] (Table VI).

Conclusions

The recently published structure of [Gd(18-crown-6)Cl_2(EtOH)]Cl [20] contains Gd(III) coordinated in the crown cavity, to two chlorines and to the ethanolic oxygen with the third chlorine not coordinated. Lanthanide nitrate complexes $[La(NO_3)_3$(18-crown-6)] and $[Gd(NO_3)_3(OH_2)_3]\cdot$(18-crown-6) have also been published [21]. Since most even 'anhydrous' lanthanide salts contain some water unless vigorously purified, the assignment of proper structure in the absence of solid state data can be tricky and the need to explore how and why water is excluded under certain conditions becomes evident. Our investigations into this will continue and our next publications will detail the synthesis and structures of $[Y(NO_3)_3$(12-crown-4)] and $[Y(NO_3)_2(OH_2)_5][NO_3]\cdot 2$(15-crown-5).

Supplementary Material

Tables of thermal parameters, and observed and calculated structure factors are available from the authors on request (8 pages).

Acknowledgements

We would like to thank the donors to the Petroleum Research Fund Administered by the American Chemical Society, NIU's Graduate School Fund and Research Corporation for support of this work. The diffractometer was purchased with funds from NSF's Chemical Instrumentation Program.

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