# f-Element/Crown Ether Complexes.
# 13.* Direct Coordination of 12-Crown-4 to Hydrated Terbium Chloride. Synthesis and Crystal Structure of $[Tb(OH_2)_5(12\text{-crown-}4)]Cl_3\cdot 2H_2O$

ROBIN D. ROGERS

*Department of Chemistry, Northern Illinois University, DeKalb, Ill. 60015, U.S.A.*

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## Abstract

The interaction of hydrated $TbCl_3$ with 12-crown-4 in a 1:3 mixture of $CH_3OH{:}CH_3CN$ produces crystalline $[Tb(OH_2)_5(12\text{-crown-}4)]Cl_3\cdot 2H_2O$. The crystal and molecular structure of this complex has been determined by single crystal X-ray diffraction techniques. It crystallizes in the orthorhombic space group $Pna2_1$ with $a = 18.758(3)$, $b = 10.080(2)$, $c = 10.242(2)$ Å, and $D_{calc} = 1.95$ g cm$^{-3}$ for $Z = 4$. Least-squares refinement using 1698 independent observed $[F_o \geqslant 5\sigma(F_o)]$ reflections led to the final conventional $R$ value of 0.033. The Tb(III) cation is coordinated to the four crown ether oxygen atoms (Tb–O average 2.52(1) Å) and five water molecules in a capped square antiprismatic geometry. The capping water molecule is 2.504(7) Å from Tb, the remaining $Tb{-}OH_2$ separations average 2.38(2) Å. A complex network of hydrogen bonding connects the coordinated water molecules, the noncoordinated water molecules, and the chloride anions.

## Introduction

Continuing our systematic investigation of the structural chemistry of f-element/crown ether complexes, we are investigating under what conditions (e.g., metal size, crown ether cavity size, anion, solvent, etc.) a crown ether may exclude water molecules from a lanthanide ion's coordination sphere and coordinate directly to the metal. Thus far we have concentrated on the later (smaller) $Ln^{3+}$ ions (and $Y^{3+}$ whose ionic radius falls between $Dy^{3+}$ and $Ho^{3+}$ [2]) where water molecules are strongly retained in the metal's primary coordination sphere. Our results to date have not as yet shown us the consistent trends we had originally expected, and our investigations of various crown ethers with hydrated lanthanide chlorides are indicative of this.

Reaction of 12-crown-4 with $LuCl_3\cdot 6H_2O$ yields $[Lu(OH_2)_8]Cl_3\cdot 1.5(12\text{-crown-}4)\cdot 2H_2O$ [3], or after the addition of NaCl, $[Lu(OH_2)_8][Na(12\text{-crown-}4)_2]Cl_4\cdot 2H_2O$ [4] (both of which have been structurally characterized), while 1:1 stoichiometries were obtained for $PrCl_3$ and $EuCl_3$ under anhydrous conditions by Bunzli [5, 6]. Similar reactions of the hydrated chloride salts with 15-crown-5 also yield octaaquated M(III) cations and no crown/metal interaction as in the isostructural $[M(OH_2)_8]Cl_3\cdot$ 15-crown-5 (M = Y [7, 8], Gd [9], Lu [9]). In contrast to these results, 18-crown-6, the cavity size of which may be more well suited to some of the $Ln^{3+}$ ions, directly complexes the metal ions in $[MCl(OH_2)_2(18\text{-crown-}6)]Cl_2\cdot 2H_2O$ (M = Sm, Gd, Tb) [10]. The structures of the cations in these complexes are similar to that observed in $[GdCl_2(OHEt)(18\text{-crown-}6)]Cl$ [11] although one less metal chloride ion pair is present in the former. Later lanthanides, $Dy^{3+}$ and $Y^{3+}$, crystallize at 5 °C in a complex that can best be described as intermediate between direct coordination of the crown and the octahydrates mentioned above: $[M(OH_2)_7(OHMe)][MCl(OH_2)_2(18\text{-crown-}6)]_2Cl_7\cdot 2H_2O$ (M = Dy, Y) [12]. Indeed when allowed to warm up and slowly evaporate the Dy reaction produces crystalline $[Dy(OH_2)_8]Cl_3\cdot 18\text{-crown-}6\cdot 4H_2O$ [13].

We have continued our investigations with 12-crown-4 and have been successful in preparing a direct metal/crown complex with $TbCl_3$ starting from the hydrated salt. Unlike the results for 18-crown-6, where at least one tight ion pair is maintained, the remainder of Tb's coordination sphere is comprised of water molecules. We now report the preparation and structural determination of $[Tb(OH_2)_5(12\text{-crown-}4)]Cl_3\cdot 2H_2O$.

## Experimental

### *Synthesis and Crystallization of* $[Tb(OH_2)_5(12\text{-crown-}4)]Cl_3\cdot 2H_2O$

1 mmol of 12-crown-4 in 5 ml of a 1:3 mixture of $CH_3OH$ and $CH_3CN$ was added to a stirring solution of 1 mmol of $TbCl_3\cdot 6H_2O$ in 5 ml of the same solvent mixture. The reaction mixture was heated

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*For Part 12 see ref. 1.

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

| | |
|---|---|
| Compound | $[Tb(OH_2)_5(12\text{-crown-4})]Cl_3 \cdot 2H_2O$ |
| Color/Shape | Clear/Plate |
| Molecular wt. | 567.6 |
| Space group | $Pna2_1$ |
| Temperature (°C) | 20 |
| Cell constants | |
| $a$ (Å) | 18.758(3) |
| $b$ (Å) | 10.080(2) |
| $c$ (Å) | 10.242(2) |
| Cell volume (Å$^3$) | 1936.5 |
| Molecules/unit cell | 4 |
| $\rho$(calc) (g cm$^{-3}$) | 1.95 |
| $\mu$(calc) (cm$^{-1}$) | 38.9 |
| Range of relative transmission factors | 62%/100% |
| Radiation, graphite monochromator | Mo K$\alpha$ ($\lambda$ = 0.71073) |
| Max crystal dimensions (mm) | 0.18 × 0.35 × 0.53 |
| Scan width | $0.80 + 0.35 \tan \theta$ |
| Standard reflections | 10, 0, 0; 0, 12, 0; 0, 0, 22 |
| Decay of standards | ±0.6% |
| Reflections measured | 1969 |
| $2\theta$ range, deg | $2 < 2\theta < 50°$ |
| Range of $h, k, l$ | +22, +12, +12 |
| Reflections observed $[F_o \geqslant 5\sigma(F_o)]$ | 1698 |
| No. of parameters varied | 207 |
| Weights | unit |
| *GOF*[a] | 3.22 |
| $R$ | 0.033 |
| $R_w$ | 0.041 |

[a] Goodness of fit.

to 60 °C for 1 h then cooled to 22 °C. The reaction mixture was transferred to a storage vessel and kept at 5 °C. Crystals deposited along the bottom of the vessel after several months. The yield was very low, however, a crystal suitable for the X-ray diffraction study was obtained. The crystal was not hygroscopic and did not decompose in air during data collection. A sufficient sample of the crystalline material was not available for elemental analysis. Thus far no other crystalline product has been forthcoming.

### *X-ray Data Collection, Structure Determination and Refinement for $[Tb(OH_2)_5(12\text{-crown-4})]Cl_3 \cdot 2H_2O$*

A clear plate-like crystal of the title complex was mounted on a pin and transferred to the goniometer. Final lattice parameters as determined from a least-squares refinement of $((\sin\theta)/\lambda)^2$ values for 25 reflections ($\theta > 23°$) accurately centered on the diffractometer are given in Table I. The space group was determined to be either the centric *Pnma* or acentric $Pn2_1a$ from the systematic absences. Statistical tests indicated that the space group was centric, but as discussed below the correct choice was the acentric $Pn2_1a$. The data and cell were transformed to the standard setting $Pna2_1$.

Data were collected on an Enraf-Nonius CAD-4 diffractometer by the $\theta$–$2\theta$ 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 [14]. Neutral atom scattering factors for Tb, Cl, O, C and H were taken from reference [15] and the scattering was corrected for the real and imaginary components of anomalous dispersion [15].

The position of the terbium atom was determined via inspection of a Patterson function map. The terbium atom was initially assumed to reside on a crystallographic mirror plane in *Pnma*. A difference Fourier map phased on the terbium atom in *Pnma* revealed disorder of the crown ether and one of the chloride anions. A quick investigation of the acentric space group revealed the nonhydrogen atoms and no evidence of disorder. Least-squares refinement with isotropic thermal parameters led to $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.063$. 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 remaining hydrogen atoms were not located. Refinement of the nonhydrogen atoms with anisotropic temperature factors led to final values of $R = 0.033$ and $R_w = 0.041$. (The $R$ value for the inverse configuration was 0.037). A final difference Fourier showed no feature greater than 1.3 e$^-$/Å$^3$. 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.

## Results and Discussion

The reaction of 12-crown-4 with hydrated $TbCl_3$ in a 3:1 mixture of acetonitrile:methanol results in a complex with both the crown ether and five water molecules in the Tb(III) ion's coordination sphere. The resulting structure exhibits complete charge separation with the chloride anions and two additional uncoordinated water molecules forming an extensive three dimensional network of hydrogen bonds in which the coordinated water molecules also participate. An ORTEP of the cation environment is presented in Fig. 1 representing all hydrogen bonds of the water molecules in the formula unit.

As a result of the tetradentate nature of the 12-crown-4 ligand, the $[Tb(OH_2)_5(12\text{-crown-4})]^{3+}$ cation adopts a capped square antiprismatic geometry rather than the tricapped trigonal prism normally found for nine-coordinate complexes with unidentate

TABLE II. Final Fractional Coordinates for $[Tb(OH_2)_5(12\text{-crown-}4)]Cl_3 \cdot 2H_2O$

| Atom | *x/a* | *y/b* | *z/c* |
|---|---|---|---|
| Tb | 0.72960(2) | 0.61684(4) | 0.0000 |
| Cl(1) | 0.5405(2) | 0.9372(3) | −0.0055(8) |
| Cl(2) | 0.7520(2) | 0.1173(3) | −0.001(1) |
| Cl(3) | 0.5323(3) | 0.6099(5) | 0.2794(6) |
| O(1) | 0.5961(4) | 0.6215(8) | 0.000(3) |
| O(2) | 0.6898(4) | 0.8365(8) | 0.0342(9) |
| O(3) | 0.6886(5) | 0.581(1) | 0.217(1) |
| O(4) | 0.6809(5) | 0.3972(9) | −0.028(1) |
| O(5) | 0.6851(6) | 0.648(1) | −0.215(1) |
| O(6) | 0.8169(5) | 0.5353(9) | −0.168(1) |
| O(7) | 0.8163(5) | 0.4445(9) | 0.076(1) |
| O(8) | 0.8202(5) | 0.6947(9) | 0.166(1) |
| O(9) | 0.8208(5) | 0.7848(9) | −0.0791(9) |
| O(10) | 0.5440(5) | 0.261(1) | 0.023(2) |
| O(11) | 0.5443(9) | 0.663(2) | −0.267(2) |
| C(1) | 0.8418(8) | 0.403(1) | −0.148(2) |
| C(2) | 0.8695(6) | 0.389(1) | −0.012(4) |
| C(3) | 0.8448(8) | 0.466(1) | 0.208(2) |
| C(4) | 0.876(1) | 0.605(2) | 0.212(2) |
| C(5) | 0.8483(8) | 0.825(1) | 0.143(2) |
| C(6) | 0.8777(6) | 0.832(1) | 0.007(3) |
| C(7) | 0.8466(8) | 0.760(1) | −0.213(1) |
| C(8) | 0.874(1) | 0.619(2) | −0.224(3) |

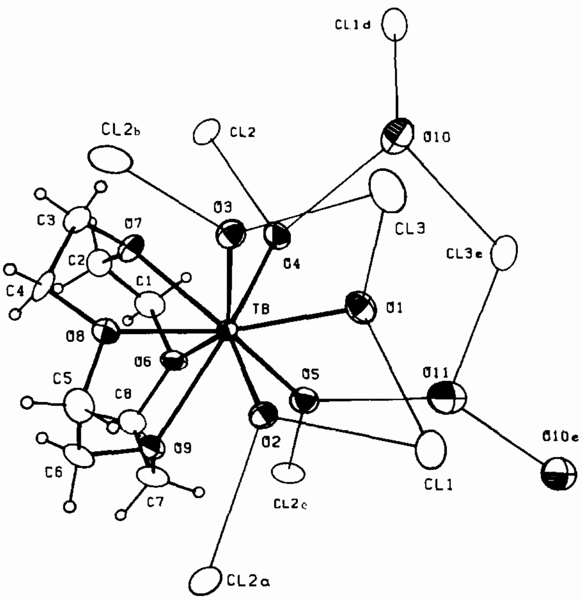

Fig. 1. The structure of $[Tb(OH_2)_5(12\text{-crown-}4)]Cl_3 \cdot 2H_2O$ depicting the hydrogen bonding contacts of the water molecules. Hydrogen atoms have been omitted, the atoms are represented by their 50% probability ellipsoids for thermal motion. The symmetry is defined in Table IV.

or small bite ($NO_3^-$) chelating ligands [16]. The geometry can be clearly seen in Fig. 2. O(1) caps the square face comprised of the four remaining coordinated water molecules, residing 1.69 Å from this plane. The capping ligand spreads out this face and the O···O contacts average 3.17(2) Å for the four sides. The Tb atom is only 0.82 Å out of this plane. A slight contraction of the other square face comprised of the ether oxygen atoms is also observed as expected (O···O = 2.68(1) Å) and Tb is 1.67 Å above this plane. The two square faces are planar to within 0.02 Å and have a dihedral angle of only 0.93°.

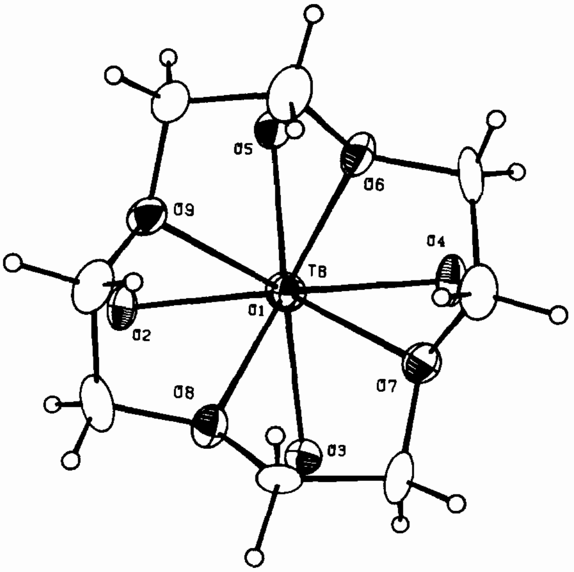

Fig. 2. View of the cation showing the nature of the capped square antiprism coordination polyhedron.

The Tb–O(ether) distances average 2.52(1) Å (Table III) compared to the 2.53(5) Å observed for the Tb–O(18-crown-6) separations in the nine-coordinate $[TbCl(OH_2)_2(18\text{-crown-}6)]Cl_2 \cdot 2H_2O$ [10]. When corrected for differences in the nine-coordinate ionic radii of Tb(III) and Gd(III) or Sm(III) [2], this value is very close to the observed M–O(crown) distances in $[Sm(OH_2)_4(15\text{-crown-}5)][ClO_4]_3 \cdot 15\text{-crown-}5 \cdot H_2O$ (2.51(1) Å) [17] and $[MCl(OH_2)_2(18\text{-crown-}6)]Cl_2 \cdot 2H_2O$ (M = Sm, 2.55(2) Å; M = Gd, 2.52(3) Å) [10]. The conformation and internal parameters of the crown ether will be discussed below.

The capping Tb–O(1) distance is longer (2.504(7) Å) than the average of the remaining four Tb–$OH_2$ distances (2.38(2) Å). These values are consistent with other Ln(III)–$OH_2$ separations observed in nine-coordinate structures: $[Tb(OH_2)_9][BrO_3]_3$ (tricapped trigonal prism), Tb–O(capping) = 2.47 Å, Tb–O(prismatic) = 2.40 Å [18]; $[TbCl(OH_2)_2(18\text{-crown-}6)]Cl_2 \cdot 2H_2O$, Tb–$OH_2$ = 2.36(4) Å [10]; $[Y(NO_3)_2(OH_2)_5][NO_3] \cdot 2(15\text{-crown-}5)$, Y–$OH_2$ = 2.36(3) Å [19]; $[Sm(OH_2)_4(15\text{-crown-}5)][ClO_4]_3 \cdot 15\text{-crown-}5 \cdot H_2O$, Sm–$OH_2$ = 2.43(2) Å [17].

TABLE III. Bond Distances (Å) and Angles (deg) for [Tb$(OH_2)_5$(12-crown-4)]$Cl_3 \cdot 2H_2O$

| | | | |
|---|---|---|---|
| Distances | | | |
| Tb–O(1) | 2.504(7) | Tb–O(2) | 2.363(8) |
| Tb–O(3) | 2.38(1) | Tb–O(4) | 2.412(9) |
| Tb–O(5) | 2.38(1) | Tb–O(6) | 2.51(1) |
| Tb–O(7) | 2.502(9) | Tb–O(8) | 2.53(1) |
| Tb–O(9) | 2.539(9) | O(6)–C(1) | 1.43(2) |
| O(6)–C(8) | 1.48(2) | O(7)–C(2) | 1.45(3) |
| O(7)–C(3) | 1.47(2) | O(8)–C(4) | 1.46(2) |
| O(8)–C(5) | 1.43(2) | O(9)–C(6) | 1.47(2) |
| O(9)–C(7) | 1.47(2) | C(1)–C(2) | 1.49(4) |
| C(3)–C(4) | 1.52(2) | C(5)–C(6) | 1.50(4) |
| C(7)–C(8) | 1.52(2) | | |
| Angles | | | |
| O(1)–Tb–O(2) | 70.5(3) | O(1)–Tb–O(3) | 71.4(7) |
| O(2)–Tb–O(3) | 84.3(3) | O(1)–Tb–O(4) | 68.8(3) |
| O(2)–Tb–O(4) | 139.3(3) | O(3)–Tb–O(4) | 81.5(4) |
| O(1)–Tb–O(5) | 69.3(7) | O(2)–Tb–O(5) | 84.4(3) |
| O(3)–Tb–O(5) | 140.6(3) | O(4)–Tb–O(5) | 82.9(4) |
| O(1)–Tb–O(6) | 131.0(6) | O(2)–Tb–O(6) | 127.9(3) |
| O(3)–Tb–O(6) | 143.2(3) | O(4)–Tb–O(6) | 82.2(3) |
| O(5)–Tb–O(6) | 68.7(4) | O(1)–Tb–O(7) | 131.5(4) |
| O(2)–Tb–O(7) | 144.1(3) | O(3)–Tb–O(7) | 79.4(3) |
| O(4)–Tb–O(7) | 69.3(3) | O(5)–Tb–O(7) | 127.4(3) |
| O(6)–Tb–O(7) | 64.0(3) | O(1)–Tb–O(8) | 131.8(6) |
| O(2)–Tb–O(8) | 79.7(3) | O(3)–Tb–O(8) | 68.7(3) |
| O(4)–Tb–O(8) | 128.4(3) | O(5)–Tb–O(8) | 144.8(3) |
| O(6)–Tb–O(8) | 97.1(3) | O(7)–Tb–O(8) | 64.6(3) |
| O(1)–Tb–O(9) | 131.4(4) | O(2)–Tb–O(9) | 68.6(3) |
| O(3)–Tb–O(9) | 128.0(3) | O(4)–Tb–O(9) | 145.9(3) |
| O(5)–Tb–O(9) | 81.5(3) | O(6)–Tb–O(9) | 63.9(3) |
| O(7)–Tb–O(9) | 97.1(3) | O(8)–Tb–O(9) | 63.5(3) |
| Tb–O(6)–C(1) | 114.7(9) | Tb–O(6)–C(8) | 123(1) |
| C(1)–O(6)–C(8) | 111(1) | Tb–O(7)–C(2) | 121(1) |
| Tb–O(7)–C(3) | 114.9(8) | C(2)–O(7)–C(3) | 112(1) |
| Tb–O(8)–C(4) | 120.4(9) | Tb–O(8)–C(5) | 115.0(9) |
| C(4)–O(8)–C(5) | 111(1) | Tb–O(9)–C(6) | 121(1) |
| Tb–O(9)–C(7) | 113.9(8) | C(6)–O(9)–C(7) | 112(1) |
| O(6)–C(1)–C(2) | 109(1) | O(7)–C(2)–C(1) | 108(1) |
| O(7)–C(3)–C(4) | 108(1) | O(8)–C(4)–C(3) | 107(1) |
| O(8)–C(5)–C(6) | 109(1) | O(9)–C(6)–C(5) | 106(1) |
| O(9)–C(7)–C(8) | 110(1) | O(6)–C(8)–C(7) | 105(2) |

Table IV presents the O···O and O···Cl contacts which are indicative of hydrogen bonding (no hydrogen atom positions were located). There are fourteen hydrogen atoms capable of hydrogen bonding and all fourteen are utilized with four hydrogen bonds to Cl(2) and Cl(3), two (in addition to the two donated) to O(10), only three to Cl(1) and only one to O(11). O(4) and O(5), comprising one side of a square face in the Tb coordination polyhedron, are the only coordinated water molecules to hydrogen bond with O(10) or O(11), each has one such interaction. The O(4)···O(10) separation is very long at 2.96(1) Å. The eleven O···$Cl^-$ contacts average 3.14(9) Å. A portion of the hydrogen bonding network is depicted in the cell packing diagram (Fig. 3).

The torsion angles given in Table V show the 12-crown-4 ether adopts an approximate $C_4$ conformation which directs all of the oxygen atoms to the same side of the ligand and all of the hydrogen atoms out [20, 21]. The O–C–C–O angles are all +g (60°). The C–C–O–C angles alternate between +g and a (180°). It should be noted that when a conformation results in C–C–O–C angles which are gauche, these angles are almost always >70° to avoid CH···HC overlap. This conformation is very good for metal coordination and has been observed in [Na(12-crown-4$)_2$][$ClO_4$] [22], [Lu$(OH_2)_8$][Na(12-crown-4$)_2$]$Cl_4 \cdot 2H_2O$ [4], [Ca$(OH_2)_4$(12-crown-4)]-$Cl_2 \cdot 4H_2O$ [23], Co$(NO_3)_2$(12-crown-4) [24], [Na(12-crown-4$)_2$]Cl·$5H_2O$ [25], and [Na(12-crown-4$)_2$][OH]·$8H_2O$ [26]. Two other 12-crown-4 conformations have been observed in the literature. The $C_i$ conformation, observed in the free crown ether [27], $UO_2(NO_3)_2(OH_2)_2$·12-crown-4 [28], [Mg$(OH_2)_6$]$Cl_2$·12-crown-4 [29], and for one of the crowns in [Lu$(OH_2)_8$]$Cl_3$·1.5(12-crown-4)·$2H_2O$ [3], presents two oxygen atoms on each side and is suited to accepting two hydrogen bonds on each side of the crown ether as observed in the last three of the above structures. A $C_s$ conformation which di-

TABLE IV. Distances (Å) and Angles (deg) for H-bonding Contacts in [Tb$(OH_2)_5$(12-crown-4)]$Cl_3 \cdot 2H_2O$

| | | | |
|---|---|---|---|
| Distance | | | |
| O(1)–Cl(1) | 3.349(9) | O(1)–Cl(3) | 3.11(2) |
| O(2)–Cl(1) | 3.007(9) | O(2)–Cl(2)$^a$ | 3.083(8) |
| O(3)–Cl(2)$^b$ | 3.12(1) | O(3)–Cl(3) | 3.02(1) |
| O(4)–Cl(2) | 3.133(9) | O(4)–O(10) | 2.96(1) |
| O(5)–Cl(2)$^c$ | 3.17(2) | O(5)–O(11) | 2.70(2) |
| O(10)–Cl(1)$^d$ | 3.28(1) | O(10)–Cl(3)$^e$ | 3.15(2) |
| O(11)–Cl(3)$^e$ | 3.14(2) | O(11)–O(10)$^e$ | 2.82(2) |
| Angle | | | |
| Cl(1)–O(1)–Cl(3) | 86.0(5) | Cl(1)–O(2)–Cl(2)$^a$ | 91.5(2) |
| Cl(2)$^b$–O(3)–Cl(3) | 98.0(3) | Cl(2)–O(4)–O(10) | 86.3(3) |
| Cl(2)$^c$–O(5)–O(11) | 100.9(6) | Cl(1)$^d$–O(10)–Cl(3)$^e$ | 109.4(4) |
| Cl(3)$^e$–O(11)–O(10)$^e$ | 94.8(5) | | |

[a] Atoms related to those in Table II by $x, 1+y, z$. [b] $1.5-x, 0.5+y, 0.5+z$. [c] $1.5-x, 0.5+y, z-0.5$. [d] $x, y-1, z$. [e] $1-x, 1-y, z-0.5$.

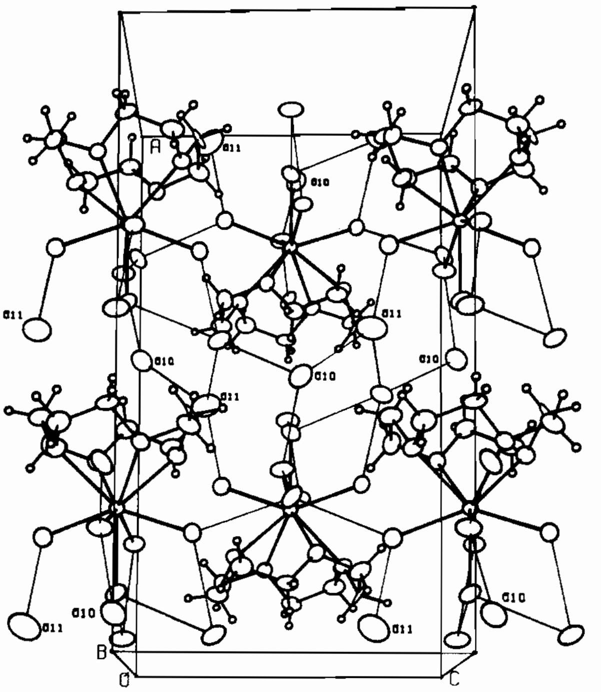

Fig. 3. Cell packing.

TABLE V. Torsion Angles (deg) for $[Tb(OH_2)_5(12\text{-crown-}4)]Cl_3 \cdot 2H_2O$

| | |
|---|---|
| O(6)–C(1)–C(2)–O(7) | 48.9 |
| C(1)–C(2)–O(7)–C(3) | –166.4 |
| C(2)–O(7)–C(3)–C(4) | 89.9 |
| O(7)–C(3)–C(4)–O(8) | 52.3 |
| C(3)–C(4)–O(8)–C(5) | –169.0 |
| C(4)–O(8)–C(5)–C(6) | 86.9 |
| O(8)–C(5)–C(6)–O(9) | 52.1 |
| C(5)–C(6)–O(9)–C(7) | –168.3 |
| C(6)–O(9)–C(7)–C(8) | 88.5 |
| O(9)–C(7)–C(8)–O(6) | 49.1 |
| C(7)–C(8)–O(6)–C(1) | –167.1 |
| C(8)–O(6)–C(1)–C(2) | 92.9 |

rects all four oxygens to the same side of the crown has been observed in $Cu(12\text{-crown-}4)Cl_2$ [30]. In $M(NO_3)_3(12\text{-crown-}4)$ (M = Eu [31], Y [32]) the coordination geometry dictates a less planar arrangement of the oxygen atoms and a distorted conformation based on the $C_4$ mentioned above results.

The 12-crown-4 ring parameters are normal. The C–O and C–C bonds average 1.46(2) and 1.51(1) Å, respectively, the C–O–C angles 112(1)°. Perhaps due to the standard deviations the differences in the two types of O–C–C angles are barely significant at the $3\sigma$ level: 109(1)° for C(1), C(3), C(5), and C(7) *versus* 106(1)° for C(2), C(4), C(6), and C(8). In $[Na(12\text{-crown-}4)_2][OH] \cdot 8H_2O$ [26] the two types of O–C–C angles averaged 112.9($\beta$) and 107.9°($\alpha$).

## Conclusions

Displacement of water from late lanthanide ions (with known affinity for water) and coordination of a crown ether is of interest if future separation studies of $Ln^{3+}$ ions are to be realized. Thus far 18-crown-6 and 12-crown-4 have been shown to be partially successful in this respect, reactions with hydrated chloride salts resulting in $[MCl(OH_2)_2(18\text{-crown-}6)]Cl_2 \cdot 2H_2O$ (M = Sm, Gd, Tb), $[M(OH_2)_7(OHMe)][MCl(OH_2)_2(18\text{-crown-}6)]_2Cl_7 \cdot 2H_2O$ (M = Y, Dy), and now the title complex, $[Tb(OH_2)_5(12\text{-crown-}4)]Cl_3 \cdot 2H_2O$. In each case some water molecules remain in the metal ion's primary coordination sphere. It is interesting that when the smaller Lu(III) ion is utilized no direct metal/crown coordination is observed ($[Lu(OH_2)_8]Cl_3 \cdot 1.5(12\text{-crown-}4) \cdot 2H_2O$) and that neither Tb(III) nor Lu(III) exhibit the sandwich structure found in $[Na(12\text{-crown-}4)_2][OH] \cdot 8H_2O$, $[Na(12\text{-crown-}4)_2]Cl \cdot 5H_2O$, or $[Lu(OH_2)_8][Na(12\text{-crown-}4)_2]Cl_4 \cdot 2H_2O$. The title complex is more like the structurally characterized $[Ca(OH_2)_4(12\text{-crown-}4)]Cl_2 \cdot 4H_2O$.

During the preparation of this manuscript, a Ho analog of the title complex was isolated. Preliminary cell parameters indicate that the crystals are of formulation $[Ho(OH_2)_5(12\text{-crown-}4)]Cl_3 \cdot 2H_2O$ and are isostructural with the Tb complex. A complete structural analysis is currently underway.

## Supplementary Material

Tables of calculated hydrogen atom positions, thermal parameters, least-squares planes, and observed and calculated structure factor amplitudes are available from the authors on request (11 pages).

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