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f-Element/Crown Ether Complexes.
16*. Synthesis, Crystallization and Crystal Structure of $[Dy(OH_2)_8]Cl_3 \cdot 18\text{-crown-6} \cdot 4H_2O$

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Abstract

When crystals of $[Dy(OH_2)_7(OHMe)][DyCl(OH_2)_2(18\text{-crown-6})]_2Cl_7 \cdot 2H_2O$ [1] are allowed to warm from 5 °C to ambient temperature (22 °C) under the original solvent mixture (1:3 CH_3OH:CH_3CN), they redissolve and the title complex can be isolated by slow evaporation of the resulting solution. The crystal structure of this complex, $[Dy(OH_2)_8]Cl_3 \cdot 18\text{-crown-6} \cdot 4H_2O$, has been determined. It crystallizes in the monoclinic space group, $P2_1/c$, with $a = 10.395(1)$, $b = 18.684(1)$, $c = 16.259(3)$ Å, $\beta = 102.56(1)°$, and $D_{calc} = 1.61$ g cm^{-3} for $Z = 4$. A final conventional R value of 0.041 was obtained by least-squares refinement using 3453 independent observed $[F_o \geqslant 5\sigma(F_o)]$ reflections. The $[Dy(OH_2)_8]^{3+}$ cations and crown ether molecules are hydrogen bonded in a polymeric chain with the crown molecules separating the cations and a total of seven $Dy–OH_2 \cdots O$(crown ether) hydrogen bonds. The chains are connected by a hydrogen bonding network consisting of the cations, chloride ions, and uncoordinated water molecules. The geometry of the cation is best described as a bicapped trigonal prism with distortions on the reaction pathway toward dodecahedral symmetry. The two capping atoms average 2.41(1) Å from Dy, the remaining Dy–O distances average 2.38(2) Å. The 18-crown-6 molecule has the D_{3d} conformation normally observed except for a distortion of one O–C–C–O unit containing the oxygen atom accepting two hydrogen bonds.

Introduction

Izatt *et al.* [2] investigated the complexation of hydrated lanthanide chlorides with 18-crown-6 in methanolic solution and found no reaction with a lanthanide ion heavier than Gd^{3+}. Utilizing a 3:1 mixture of CH_3CN and CH_3OH we extended the list of $LnCl_3 \cdot nH_2O$ salts that would complex 18-crown-6 to Tb with the synthesis and structural characterization of $[MCl(OH_2)_2(18\text{-crown-6})]Cl_2 \cdot 2H_2O$ (M = Sm, Gd, Tb) [3]. In our attempts to expand this list further we carried out similar reactions with $DyCl_3 \cdot 6H_2O$ and $YCl_3 \cdot 6H_2O$. Both crystallized at 5 °C as $[M(OH_2)_7(OHMe)][MCl(OH_2)_2(18\text{-crown-6})]_2Cl_7 \cdot 2H_2O$ (M = Dy, Y) [1], structures that appear to be intermediate between the Sm, Gd, and Tb complexes mentioned above and hydrogen bonded complexes such as $[M(OH_2)_8]Cl_3 \cdot 15\text{-crown-5}$ (M = Y [4, 5], Gd [6], Lu [6]) and $[Lu(OH_2)_8]Cl_3 \cdot 1.5(12\text{-crown-4}) \cdot 2H_2O$ [7]. Upon warming a portion of the Dy reaction mixture containing crystalline product and the solvent to room temperature, the crystals redissolved and a viscous liquid immiscible with the solvent formed, possibly indicating a change in metal:ligand stoichiometry. Bunzli has observed a similar effect in reference [8].

The crystallization of $[Dy(OH_2)_8]Cl_3 \cdot 18\text{-crown-6} \cdot 4H_2O$ from the above solution gives us this opportunity to compare the $[M(OH_2)_8]^{3+}$ ion in the structures of the title complex, $[M(OH_2)_8]Cl_3 \cdot 15\text{-crown-5}$ (M = Y, Gd, Lu), and $[Lu(OH_2)_8]Cl_3 \cdot 1.5(12\text{-crown-4}) \cdot 2H_2O$, all of which contain uncoordinated water molecules and a crown ether hydrogen bonded in the lattice. This report is a continuation of our investigations into how the possible hydrogen bonding patterns in these complexes influence overall structure, crown conformation, and metal ion geometry.

Experimental

Synthesis and Crystallization of $[Dy(OH_2)_8]Cl_3 \cdot 18\text{-crown-6} \cdot 4H_2O$

The synthesis of $[Dy(OH_2)_7(OHMe)][DyCl(OH_2)_2(18\text{-crown-6})]_2Cl_7 \cdot 2H_2O$ has been reported in ref. 1. This complex is thermally unstable and when the crystalline substance under the original reaction mixture (1:3 CH_3OH:CH_3CN) is allowed to warm to room temperature a viscous liquid forms at the bottom of the flask. When the solution is allowed to slowly evaporate clear rod-like crystals form and a gummy yellowish precipitate appears. The crystals

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[*] For Part 15 see ref. 7.

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

Compound	$[Dy(OH_2)_8]Cl_3 \cdot 18\text{-crown-}6 \cdot 4H_2O$
Color/Shape	transparent/plate
Molecular weight	749.4
Space group	$P2_1/c$
Temperature (°C)	20
Cell constants	
a (Å)	10.395(1)
b (Å)	18.684(1)
c (Å)	16.259(3)
β (deg)	102.56(1)
Cell volume (Å^3)	3082.4
Formula units/unit cell	4
D_{calc} (g cm^{-3})	1.61
μ(calc) (cm^{-1})	26.0
Range of relative transmission factors	64%/100%
Radiation, graphite monochromator	Mo Kα ($\lambda = 0.71073$)
Maximum crystal dimensions (mm)	0.10 × 0.25 × 0.35
Scan width	$0.80 + 0.35 \tan\theta$
Standard reflections	600; 0, 14, 0; 0, 0, 14
Decay of standards	−5%
Reflections measured	5901
2θ range (deg)	$2 < 2\theta < 50$
Range of h, k, l	+12, +22, ±19
Reflections observed $[F_o \geqslant 5\sigma(F_o)]$	3453
No. of parameters varied	307
Weights	$[\sigma(F_o)^2]^{-1}$
GOF	1.97
R	0.041
R_w	0.045

are thermally stable (melting point 59–61 °C) and are not hygroscopic. *Anal.* Calc. for $[Dy(OH_2)_8]Cl_3 \cdot$ 18-crown-6•$4H_2O$: C, 19.23; H, 6.46. Found: C, 19.02; H, 6.69%.

X-ray Data Collection, Structure Determination and Refinement for $[Dy(OH_2)_8]Cl_3 \cdot 18$-crown-6• $4H_2O$

A transparent single 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 ($\theta > 20°$) accurately centered on the diffractometer are given in Table I. The space group was determined to be the centric $P2_1/c$ from the systematic absences.

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 [9]. Neutral atom scattering factors for Dy, Cl, O, C and H were taken from ref. 10 and the scattering was corrected for the real and imaginary components of anomalous dispersion [10].

The dysprosium atom position was determined via inspection of a Patterson function map. A difference Fourier map phased on the Dy atom readily revealed the positions of the nonhydrogen atoms. Least-squares refinement with isotropic thermal parameters led to $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.065$. Higher than normal thermal motion was noted for the crown carbon atoms, but no disorder was resolvable. Perhaps a consequence of the high thermal motion and possible disorder, one of the C–C bond lengths is quite long, C(9)–C(10) = 1.56(1) Å. The hydrogen atom contributions were not included in the final refinement. Refinement of the nonhydrogen atoms with anisotropic temperature factors led to final values of $R = 0.041$ and $R_w = 0.045$. A final

TABLE II. Final Fractional Coordinates for $[Dy(OH_2)_8]$-$Cl_3 \cdot 18$-crown-6•$4H_2O$

Atom	x/a	y/b	z/c	U_{eq}
Dy	0.68082(4)	0.75206(2)	0.11274(2)	0.024
Cl(1)	0.3017(3)	0.6110(1)	0.0476(2)	0.051
Cl(2)	0.3022(3)	0.8936(1)	0.0373(2)	0.052
Cl(3)	1.0039(3)	0.9703(2)	0.2516(2)	0.067
O(1)	0.8669(6)	0.7827(3)	0.0600(3)	0.041
O(2)	0.6211(7)	0.7487(3)	−0.0384(3)	0.039
O(3)	0.6058(7)	0.6326(3)	0.0812(4)	0.038
O(4)	0.8493(6)	0.6705(3)	0.1789(4)	0.041
O(5)	0.6386(6)	0.7324(3)	0.2495(4)	0.038
O(6)	0.4460(6)	0.7536(3)	0.0949(4)	0.043
O(7)	0.6053(7)	0.8696(3)	0.0765(4)	0.044
O(8)	0.8175(7)	0.8313(3)	0.2134(4)	0.041
O(9)	0.7594(9)	0.9859(4)	0.1008(5)	0.079
O(10)	0.7407(8)	0.5060(3)	0.1020(5)	0.057
O(11)	1.0879(8)	0.8491(5)	0.1353(5)	0.088
O(12)	1.077(1)	0.6129(5)	0.1581(6)	0.095
O(13)	0.4043(7)	0.7449(4)	−0.2006(4)	0.057
O(14)	0.5204(9)	0.8728(4)	−0.1360(5)	0.066
O(15)	0.7751(9)	0.8931(4)	−0.1787(4)	0.063
O(16)	0.9340(8)	0.7823(5)	−0.0925(4)	0.066
O(17)	0.8406(9)	0.6459(4)	−0.1191(5)	0.067
O(18)	0.562(1)	0.6264(4)	−0.1422(5)	0.073
C(1)	0.324(1)	0.8038(9)	−0.1860(9)	0.083
C(2)	0.396(1)	0.8713(8)	−0.1994(8)	0.077
C(3)	0.586(2)	0.9411(6)	−0.1288(8)	0.081
C(4)	0.669(1)	0.9471(5)	−0.1921(8)	0.077
C(5)	0.881(2)	0.9068(7)	−0.1076(8)	0.087
C(6)	0.987(1)	0.8528(9)	−0.1089(8)	0.090
C(7)	1.025(1)	0.726(1)	−0.1000(8)	0.090
C(8)	0.971(2)	0.6588(9)	−0.0703(9)	0.085
C(9)	0.785(2)	0.5821(8)	−0.093(1)	0.112
C(10)	0.648(2)	0.5700(6)	−0.154(1)	0.109
C(11)	0.435(2)	0.6193(8)	−0.1998(8)	0.080
C(12)	0.349(1)	0.6787(8)	−0.1815(8)	0.074

U_{eq} is equal to $(U_{11} + U_{22} + U_{33})/3$.

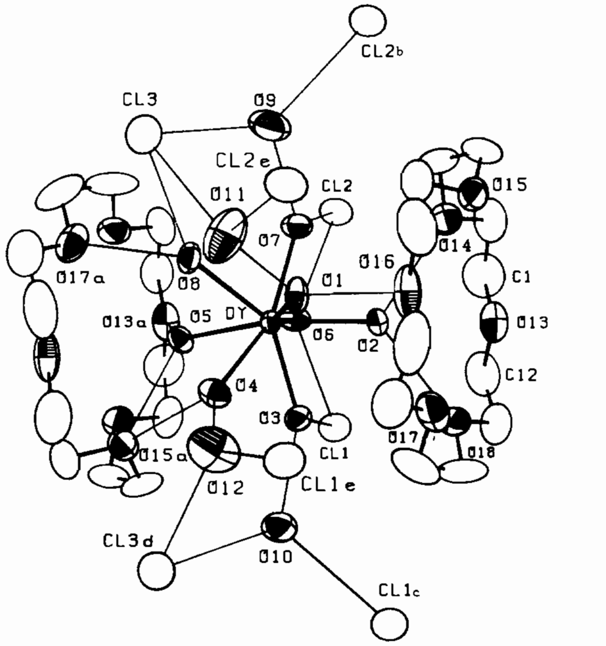

Fig. 1. A portion of the polymeric hydrogen bonded chain in $[Dy(OH_2)_8]Cl_3 \cdot 18$-crown-6$\cdot 4H_2O$. The atoms are represented by their 50% probability ellipsoids for thermal motion. The symmetry is defined in Table V.

difference Fourier showed no feature greater than 1.0 $e^-/Å^3$. The weighting scheme was based on $[\sigma(F_o)^2]^{-1}$, 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

The hydrogen bonding contacts of the water molecules in $[Dy(OH_2)_8]Cl_3 \cdot 18$-crown-6$\cdot 4H_2O$ and the atom labelling scheme of the formula unit are depicted in Fig. 1. Each cation is hydrogen bonded to two crown ether molecules forming a hydrogen bonded polymeric chain of cation/crown/cation/crown···. There are seven hydrogen bonds to the crown ether, three on one side by water molecules coordinated to one Dy^{3+} ion and four on the other side donated by a symmetry related $[Dy(OH_2)_8]^{3+}$ cation. The chains are connected by a polymeric network of hydrogen bonds between the coordinated and uncoordinated water molecules and the chloride anions. The bond distances and angles are presented in Table III and a cell packing diagram is shown in Fig. 2.

TABLE III. Bond Distances (Å) and Angles (deg) for $[Dy(OH_2)_8]Cl_3 \cdot 18$-crown-6$\cdot 4H_2O$

Distances			
Dy–O(1)	2.350(6)	Dy–O(2)	2.400(5)
Dy–O(3)	2.383(6)	Dy–O(4)	2.394(6)
Dy–O(5)	2.387(5)	Dy–O(6)	2.395(6)
Dy–O(7)	2.363(6)	Dy–O(8)	2.424(6)
O(13)–C(1)	1.43(1)	O(13)–C(12)	1.43(1)
O(14)–C(2)	1.47(2)	O(14)–C(3)	1.44(1)
O(15)–C(4)	1.47(1)	O(15)–C(5)	1.43(1)
O(16)–C(6)	1.48(1)	O(16)–C(7)	1.44(1)
O(17)–C(8)	1.44(2)	O(17)–C(9)	1.43(2)
O(18)–C(10)	1.42(2)	O(18)–C(11)	1.44(2)
C(1)–C(2)	1.51(2)	C(3)–C(4)	1.49(2)
C(5)–C(6)	1.50(2)	C(7)–C(8)	1.50(2)
C(9)–C(10)	1.56(2)	C(11)–C(12)	1.50(2)
Angles			
O(1)–Dy–O(2)	71.5(2)	O(1)–Dy–O(3)	114.0(2)
O(2)–Dy–O(3)	75.9(2)	O(1)–Dy–O(4)	74.9(2)
O(2)–Dy–O(4)	116.4(2)	O(3)–Dy–O(4)	70.9(2)
O(1)–Dy–O(5)	135.2(2)	O(2)–Dy–O(5)	152.9(2)
O(3)–Dy–O(5)	86.5(2)	O(4)–Dy–O(5)	75.4(2)
O(1)–Dy–O(6)	148.3(2)	O(2)–Dy–O(6)	81.2(2)
O(3)–Dy–O(6)	73.0(2)	O(4)–Dy–O(6)	133.6(2)
O(5)–Dy–O(6)	74.1(2)	O(1)–Dy–O(7)	86.4(2)
O(2)–Dy–O(7)	76.8(2)	O(3)–Dy–O(7)	137.8(2)
O(4)–Dy–O(7)	151.0(2)	O(5)–Dy–O(7)	104.9(2)
O(6)–Dy–O(7)	71.6(2)	O(1)–Dy–O(8)	71.9(2)
O(2)–Dy–O(8)	133.6(2)	O(3)–Dy–O(8)	146.5(2)
O(4)–Dy–O(8)	79.7(2)	O(5)–Dy–O(8)	70.4(2)
O(6)–Dy–O(8)	120.4(2)	O(7)–Dy–O(8)	73.4(2)

(continued)

TABLE III. *(continued)*

C(1)–O(13)–C(12)	111(1)	C(2)–O(14)–C(3)	114(1)
C(4)–O(15)–C(5)	114(1)	C(6)–O(16)–C(7)	111(1)
C(8)–O(17)–C(9)	112(1)	C(10)–O(18)–C(11)	111(1)
O(13)–C(1)–C(2)	107(1)	O(14)–C(2)–C(1)	108(1)
O(14)–C(3)–C(4)	110.3(9)	O(15)–C(4)–C(3)	112.0(9)
O(15)–C(5)–C(6)	108(1)	O(16)–C(6)–C(5)	107(1)
O(16)–C(7)–C(8)	107(1)	O(17)–C(8)–C(7)	110(1)
O(17)–C(9)–C(10)	108(1)	O(18)–C(10)–C(9)	109(1)
O(18)–C(11)–C(12)	108(1)	O(13)–C(12)–C(11)	108(1)

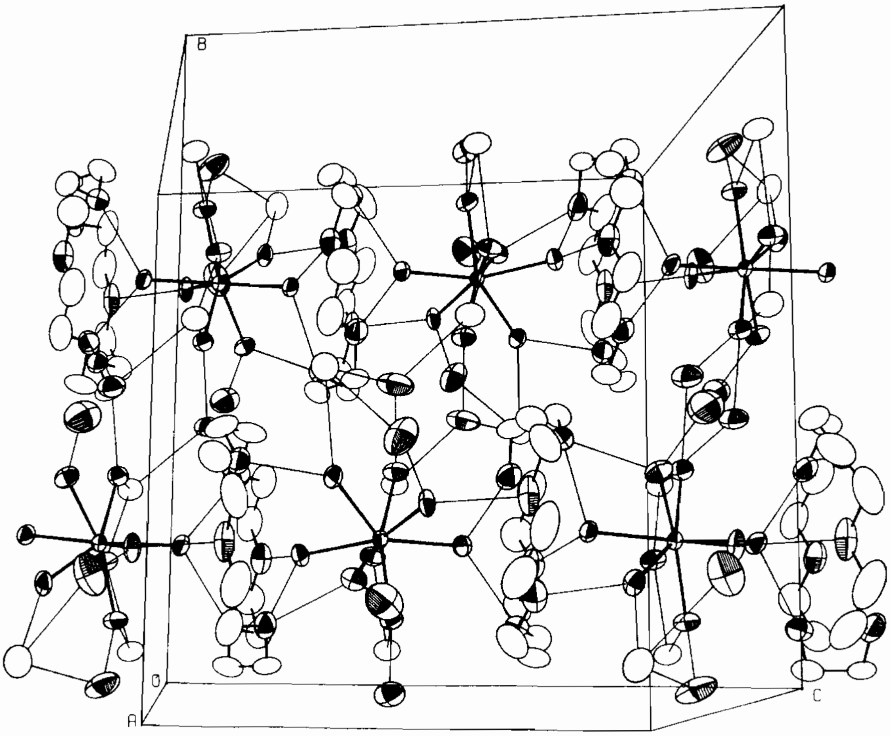

Fig. 2. Cell packing diagram.

The $[Dy(OH_2)_8]^{3+}$ cation in the title complex is best described as a distorted bicapped trigonal prism on the reaction pathway toward dodecahedral symmetry [11]. The shape determining dihedral angles at the 'b' edges are 1.41, 13.6, 38.4, and 39.8° compared to ideal values for the dodecahedron of 29.5° for all four, and for the bicapped trigonal prism of 0.0, 21.8, 48.2, and 48.2° [11]. The ϕ angles for the title complex as defined in reference 11 average 14.1° (ideal value, 14.1°). O(6) and O(8) are the capping atoms in the bicapped trigonal prism and are an average of 2.41(1) Å from Dy. The remaining Dy–O separations average 2.38(2) Å. Of the latter, the two coordination positions which would become 'A' sites in the dodecahedron are the longest (average 2.397(3) Å, O(2), O(4)). In the disordered eight-coordinate $[Dy(OH_2)_7(OHMe)]^{3+}$ cation, found in $[Dy(OH_2)_7(OHMe)][DyCl(OH_2)_2(18\text{-crown-}6)]_2Cl_7 \cdot 2H_2O$ [1], the Dy–O separations averaged 2.39(5) Å (–150 °C). Similar values have been observed for the slightly smaller Y^{3+} ion (0.01 Å difference in $CN = 8$ ionic radii [12]) with distorted dodecahedral geometry in $[Y(OH_2)_8]Cl_3 \cdot 15\text{-crown-}5$: Y–O average = 2.37(4) Å, $Y\text{–}O_A = 2.40(3)$ Å, $Y\text{–}O_B = 2.35(3)$ Å [4] (at –150 °C: 2.36(4), 2.39(4), 2.34(2) Å [5]) and $[Y(OH_2)_8]Cl_3 \cdot 2C_{10}H_8N_2$: 2.38(6), 2.425(6), 2.327(6) Å [13].

The presence of seven hydrogen bonds to the 18-crown-6 molecule results in an interesting distortion in crown conformation (Table IV). The entire molecule, except for one O–C–C–O unit containing O(15) which accepts two hydrogen bonds, follows the D_{3d} conformation normally observed in metal

TABLE IV. Torsion Angles for $[Dy(OH_2)_8]Cl_3\cdot$18-crown-6$\cdot 4H_2O$

O(13)–C(1)–C(2)–O(14)	−63.0
C(1)–C(2)–O(14)–C(3)	−166.7
C(2)–O(14)–C(3)–C(4)	−85.6
O(14)–C(3)–C(4)–O(15)	−62.4
C(3)–C(4)–O(15)–C(5)	−73.6
C(4)–O(15)–C(5)–C(6)	−172.9
O(15)–C(5)–C(6)–O(16)	−67.1
C(5)–C(6)–O(16)–C(7)	174.8
C(6)–O(16)–C(7)–C(8)	172.0
O(16)–C(7)–C(8)–O(17)	57.3
C(7)–C(8)–O(17)–C(9)	179.9
C(8)–O(17)–C(9)–C(10)	−176.1
O(17)–C(9)–C(10)–O(18)	−65.8
C(9)–C(10)–O(18)–C(11)	177.3
C(10)–O(18)–C(11)–C(12)	177.9
O(18)–C(11)–C(12)–O(13)	64.8
C(11)–C(12)–O(13)–C(1)	178.7
C(12)–O(13)–C(1)–C(2)	174.5

complexes and many neutral hydrogen bond donor complexes with 18-crown-6 [14, 15]. This conformation is characterized by gauche O–C–C–O torsion angles of alternating sign (±60°) and C–O–C–C angles of 180°. The distortion of the O(14)–C(3)–C(4)–O(15) unit is evident from the three consecutive g^- angles. (The C–O–C–C angles are >70° to avoid CH···HC overlap [16]). As a result of this distortion O(15) is directed outward and is thus capable of accepting the two hydrogen bonds.

The conformational change caused by the hydrogen bonding is also evident in the C–O–C and C–C–O angles. The C–O–C angles at O(14) and O(15) average 114(1)° with the remainder averaging 111(1)°. Similarly the C–C–O angles for C(3) and C(4) average 111(1)° *versus* 108(1)° for the ten other such angles. The C–O and C–C bond distances average 1.44(2) and 1.51(2) Å, respectively. In free 18-crown-6 at room temperature [17] the C–O and C–C distances and C–O–C and C–C–O angles average 1.411 and 1.507 Å and 114 and 110°, respectively.

The hydrogen bonding has been inferred from the O···O and O···Cl contact geometries listed in Table V. O(2) and O(5) are hydrogen bonded exclusively to crown oxygen atoms. O(1) and O(4) have one such interaction with the crown and one each with an uncoordinated water molecule. O(8) forms the remaining hydrogen bond to the crown ether and also interacts with a chloride anion. O(6) hydrogen bonds only chloride anions, and O(3) and O(7) one chloride anion and one uncoordinated water molecule. Each uncoordinated water molecule accepts one hydrogen bond from the cation (Dy–

TABLE V. Hydrogen Bonding Contact Geometries for $[Dy(OH_2)_8]Cl_3\cdot$18-crown-6$\cdot 4H_2O$

Distances			
O(1)–O(11)	2.66(1)	O(1)–O(16)	2.72(1)
O(2)–O(14)	2.828(9)	O(2)–O(18)	2.876(9)
O(3)–Cl(1)	3.114(8)	O(3)–O(10)	2.732(9)
O(4)–O(12)	2.70(1)	O(4)–O(15)[a]	2.85(1)
O(5)–O(13)[a]	2.76(1)	O(5)–O(15)[a]	2.854(9)
O(6)–Cl(1)	3.072(6)	O(6)–Cl(2)	3.057(6)
O(7)–Cl(2)	3.109(8)	O(7)–O(9)	2.68(1)
O(8)–Cl(3)	3.219(7)	O(8)–O(17)[a]	2.71(1)
O(9)–Cl(2)[b]	3.146(8)	O(9)–Cl(3)	3.137(9)
O(10)–Cl(1)[c]	3.229(8)	O(10)–Cl(3)[d]	3.226(8)
O(11)–Cl(2)[e]	3.12(1)	O(11)–Cl(3)	3.19(1)
O(12)–Cl(1)[e]	3.23(1)	O(12)–Cl(3)[d]	3.244(9)
Angles			
O(11)–O(1)–O(16)	93.1(3)	O(14)–O(2)–O(18)	108.4(3)
Cl(1)–O(3)–O(10)	112.6(3)	O(12)–O(4)–O(15)[a]	109.7(3)
O(13)[a]–O(5)–O(15)[a]	113.4(3)	Cl(1)–O(6)–Cl(2)	119.1(2)
Cl(2)–O(7)–O(9)	117.4(3)	Cl(3)–O(8)–O(17)[a]	76.2(2)
Cl(2)[b]–O(9)–Cl(3)	129.0(3)	Cl(1)[c]–O(10)–Cl(3)[d]	111.8(2)
Cl(2)[b]–O(9)–O(7)	116.9(3)	Cl(1)[c]–O(10)–O(3)	120.7(3)
Cl(3)–O(9)–O(7)	113.4(3)	Cl(3)[d]–O(10)–O(3)	126.0(3)
Cl(2)[e]–O(11)–Cl(3)	115.5(3)	Cl(1)[e]–O(12)–Cl(3)[d]	122.3(3)
Cl(2)[e]–O(11)–O(1)	122.0(3)	Cl(1)[e]–O(12)–O(4)	146.5(3)
Cl(3)–O(11)–O(1)	106.4(3)	Cl(3)[d]–O(12)–O(4)	83.9(3)

[a] Atoms are related to those in Table II by x, $1.5 - y$, $0.5 + z$. [b] $1 - x$, $2 - y$, $-z$. [c] $1 - x$, $1 - y$, $-z$. [d] $1 + x$, y, z. [e] $2 - x, y - 0.5, 0.5 - z$.

$OH_2\cdots OH_2$ = 2.69(3) Å average) and donates two to chloride anions ($H_2O\cdots Cl$ = 3.19(5) Å average). Cl(1) and Cl(2) accept four hydrogen bonds. Cl(3) accepts five hydrogen bonds, one from O(8) and one from each of the uncoordinated water molecules. The Dy–$OH_2\cdots$O(crown) and Dy–$OH_2\cdots Cl^-$ contacts average 2.80(6) and 3.11(6) Å, respectively.

Discussion

In the three structurally characterized complexes of the $[M(OH_2)_8]^{3+}$ cation, chloride anions, and a hydrogen bonded crown ether, polymeric chain like structures have been observed. In the title complex and $[M(OH_2)_8]Cl_3\cdot$15-crown-5 (M = Y [4, 5], Gd [6], Lu [7]) the crown ethers bridge each cation with hydrogen bonds to two cations on either side of the crown ether. The smaller 12-crown-4 in $[Lu(OH_2)_8]Cl_3\cdot$1.5(12-crown-4)$\cdot 2H_2O$ [7] has one crown acting in such a capacity and a second unique ether (with a different conformation) which bridges two cations by hydrogen bonds, but in which all four hydrogen bonds are on the same side of the crown molecule. Each $[Lu(OH_2)_8]^{3+}$ cation is thus hydrogen bonded to three crown ethers. It is possible that more 12-crown-4 molecules can form hydrogen bonds to this cation because of the smaller overall size of this crown ether.

All three crown ethers mentioned above have conformational flexibility allowing maximum hydrogen bonding overlap. For example, two different conformations, C_4 and C_i, were observed for 12-crown-4 in $[Lu(OH_2)_8]Cl_3\cdot$1.5(12-crown-4)$\cdot 2H_2O$. The unusual hydrogen bonding in the title complex (two hydrogen bonds to O(15)) results in an unusual conformation, but even this conformation is based on the most commonly observed D_{3d} form of complexed 18-crown-6 [14, 15]. The D_{3d} conformation directs alternating oxygen atoms toward opposite sides of the crown ether and thus seems suited to the polymeric nature of the title complex.

The hydrogen bonding not only influences overall structure, stoichiometry and crown ether conformation, it also appears to influence metal coordination geometry. The $[M(OH_2)_8]^{3+}$ ion has been structurally characterized eight times in related complexes. In $[M(OH_2)_8]Cl_3\cdot 2C_{10}H_8N_2$ (M = Y [13], Gd [18]) the cation is very close to dodecahedral symmetry. In the four structural characterizations of $[M(OH_2)_8]Cl_3\cdot$15-crown-5 [4–6], this cation is close to dodecahedral geometry but distorted along the reaction pathway leading to a bicapped trigonal prism (and eventually to a square antiprism). In the title complex, the cation is very close to a bicapped trigonal prism with distortions toward dodecahedral symmetry. In $[Lu(OH_2)_8]Cl_3\cdot$1.5(12-crown-4)$\cdot 2H_2O$ [7] this cation is again close to the bicapped trigonal prism but any distortions in this complex are toward the square antiprism. Finally, a square antiprismatic geometry has been observed in $[Lu(OH_2)_8]$[Na(12-crown-4)$_2$]$Cl_4\cdot 2H_2O$ [19].

Supplementary Material

Tables of thermal parameters, least-squares planes, and observed and calculated structure factors are available from the authors on request (12 pages).

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