

## f-Element/Crown Ether Complexes. 5.<sup>1</sup> Structural Changes in Complexes of Lanthanide Chloride Hydrates with 18-Crown-6 Accompanying Decreases in Ln<sup>3+</sup> Ionic Radii: Synthesis and Structures of [M(OH<sub>2</sub>)<sub>7</sub>(OHMe)][MCl(OH<sub>2</sub>)<sub>2</sub>(18-crown-6)]<sub>2</sub>Cl<sub>7</sub>·2H<sub>2</sub>O (M = Y, Dy)

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Received October 16, 1986

Reaction under argon of the hydrated chloride salts of Y<sup>3+</sup> and Dy<sup>3+</sup> with 18-crown-6 in a 1:3 solution of methanol and acetonitrile and crystallization at 5 °C yield crystalline [M(OH<sub>2</sub>)<sub>7</sub>(OHMe)][MCl(OH<sub>2</sub>)<sub>2</sub>(18-crown-6)]<sub>2</sub>Cl<sub>7</sub>·2H<sub>2</sub>O (M = Y, Dy). X-ray crystallographic examinations of these isostructural complexes have been carried out. Both crystallize in the monoclinic space group *I*2/a with cell constants (at -150 °C) *a* = 25.525 (8) Å, *b* = 7.310 (4) Å, *c* = 30.506 (9) Å, β = 109.35 (5)°, and *D*<sub>calcd</sub> = 1.71 g cm<sup>-3</sup> for *Z* = 4 (M = Y) and *a* = 25.715 (7) Å, *b* = 7.348 (1) Å, *c* = 30.603 (5) Å, β = 109.62 (3)°, and *D*<sub>calcd</sub> = 1.95 g cm<sup>-3</sup> for *Z* = 4 (M = Dy). Least-squares refinement of both complexes led to conventional *R* values of 0.060 (using 3358 independent observed [*F*<sub>o</sub> ≥ 5σ(*F*<sub>o</sub>)] reflections) for M = Y and 0.036 (4395 observed reflections) for M = Dy. There are two unique metal atom environments in the asymmetric unit. One M<sup>3+</sup> cation is nine-coordinate, coordinated to the six oxygen atoms of the crown ether, one chlorine "above" the crown, and two water molecules "below". The M-Cl, M-O(crown), and M-O(OH<sub>2</sub>) distances average respectively 2.647 (2), 2.44 (5), and 2.36 (3) Å for M = Y and 2.654 (2), 2.46 (5), and 2.39 (4) Å for M = Dy. The second metal ion is eight-coordinate, coordinated to seven water molecules and one methanol oxygen atom. This cation resides on a crystallographic 2-fold axis and exhibits disorder of two of its water molecules and the methanol group. The average M-O separations for this cation are 2.36 (3) Å (M = Y) and 2.39 (2) Å (M = Dy). Three of the seven uncoordinated chloride ions and the two noncoordinated water molecules are disordered, two of the chloride ions being required to occupy positions across the 2-fold axis from the two water molecules and the same type of disorder being exhibited between the third chloride and the methanol carbon. All water molecules, the methanol moiety, and the uncoordinated chloride ions participate in a complex polymeric hydrogen-bonding network.

### Introduction

Bunzli and Wessner<sup>2</sup> have reported the 1:1 complexes of lanthanide(III) nitrates and 12-crown-4 to be isomorphous from X-ray powder data despite the steady decrease in Ln<sup>3+</sup> ionic radius with atomic number. The crystal structure of Eu(NO<sub>3</sub>)<sub>3</sub>(12-crown-4)<sup>3</sup> revealed the actual coordination: the three nitrate ligands are bidentate on one side of the Eu<sup>3+</sup> ion and the 12-crown-4 is coordinated on the other side. We isolated the isostructural Y analogue in the solid state even though we used hydrated Y(NO<sub>3</sub>)<sub>3</sub> as our starting material.<sup>4</sup> (The ionic radius of Y<sup>3+</sup> falls between those for Dy<sup>3+</sup> and Ho<sup>3+</sup>.)

Metal-crown coordination in related structures of 15-crown-5 complexes has been observed for the larger Ln<sup>3+</sup> ions, La<sup>3+</sup> through Eu<sup>3+</sup>, with the NO<sub>3</sub><sup>-</sup> (La-Nd, Eu)<sup>1,5,6</sup> and ClO<sub>4</sub><sup>-</sup> (La, Sm<sup>8</sup>) anions. The latter two structures also contained coordinated water molecules and a second uncoordinated hydrogen-bonded crown ether. We have attempted to isolate 15-crown-5 complexes of this type for the later lanthanides but thus far have succeeded only in synthesizing and structurally characterizing second-sphere hydrogen-bonded crown complexes of the type [M(OH<sub>2</sub>)<sub>8</sub>]Cl<sub>3</sub>·15-crown-5 (M = Y,<sup>9,10</sup> Gd,<sup>11</sup> Lu<sup>11</sup>).

Early lanthanide, La(NO<sub>3</sub>)<sub>3</sub><sup>12</sup> and Nd(NO<sub>3</sub>)<sub>3</sub><sup>13,14</sup> complexes and

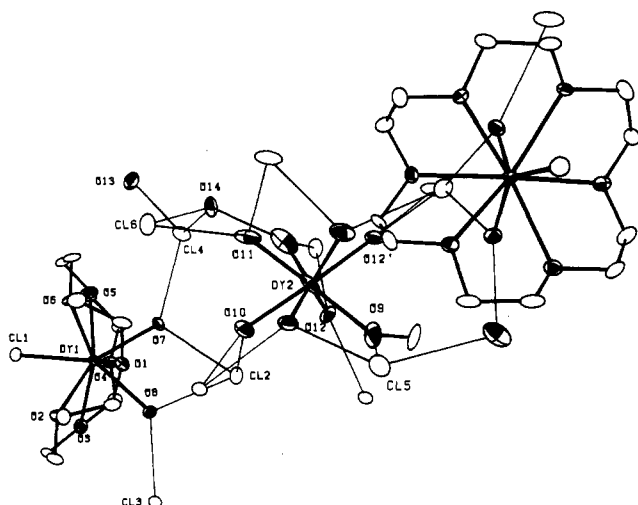
more recently a GdCl<sub>3</sub><sup>15</sup> complex of the larger 18-crown-6 reveal a different type of crown ether coordination, with the metal ion residing in the crown ether cavity. The complexation of hydrated lanthanide chlorides with 18-crown-6 in methanolic solution by Izatt et al.<sup>16</sup> indicated that no reaction took place with a lanthanide ion heavier than Gd<sup>3+</sup>. In our most recent report in this area we extended the list of LnCl<sub>3</sub>·*n*H<sub>2</sub>O salts that would complex 18-crown-6 to Tb, with the synthesis and structures of [MCl(OH<sub>2</sub>)<sub>2</sub>(18-crown-6)]Cl<sub>2</sub>·2H<sub>2</sub>O (M = Sm, Gd, Tb)<sup>17</sup> utilizing a 1:3 methanol-acetonitrile mixture as solvent. This paper details the extension of this work to DyCl<sub>3</sub>·6H<sub>2</sub>O and YCl<sub>3</sub>·6H<sub>2</sub>O, which form 18-crown-6 complexes that appear to have solid-state structures intermediate between [M(OH<sub>2</sub>)<sub>8</sub>]Cl<sub>3</sub>·15-crown-5 and [MCl(OH<sub>2</sub>)<sub>2</sub>(18-crown-6)]Cl<sub>2</sub>·2H<sub>2</sub>O. We also present preliminary findings on the effects of solvent and anion concentration on the observed metal ion coordination.

### Results and Discussion

Lanthanide(III) ions are too small to allow an ideal fit when complexing 18-crown-6.<sup>18-20</sup> The ligand must fold around the ion for full coordination. One would expect, then, to be able to follow the deformation of the crown and resulting effects on structure as the metal ion size is decreased. We have attempted to follow these changes with the mid-to-late hydrated lanthanide chlorides, monitoring as many of the variables as possible. Under identical conditions of reaction (hydrated metal chloride-18-crown-6 (1:1) in methanol-acetonitrile (1:3) heated for 1 h at 60 °C) and crystallization (storage in the original reaction flask at 5 °C), two different types of complexes containing identical [MCl(OH<sub>2</sub>)<sub>2</sub>(18-crown-6)]<sup>2+</sup> ions have formed as the metal size is decreased from Sm<sup>3+</sup> to Y<sup>3+</sup>. For the larger ions, Sm<sup>3+</sup>, Gd<sup>3+</sup>, and Tb<sup>3+</sup>, the isostructural complexes formed have the formula

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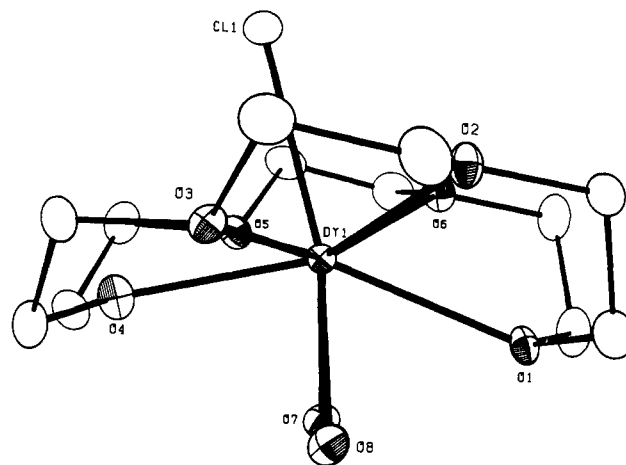
**Figure 1.** Environment of the three cations in the formula unit  $[M(OH_2)_7(OHMe)][MCl(OH_2)_2(18\text{-crown-6})]_2Cl_7 \cdot 2H_2O$  ( $M = Dy$  (shown),  $Y$ ). Metal and oxygen atoms are shaded (50% ellipsoids); hydrogen bonds are indicated as lines joining the non-hydrogen atoms.

$[MCl(OH_2)_2(18\text{-crown-6})]Cl_2 \cdot 2H_2O$ .<sup>17</sup> The 18-crown-6 complexes of  $M = Dy$  and  $Y$  are also isostructural; however, they contain structural elements of both the directly coordinated complexes mentioned above and the second-sphere, hydrogen-bonded complexes obtained when smaller crown ethers are used:  $[M(OH_2)_8]Cl_3 \cdot 15\text{-crown-5}$  ( $M = Y$ ,<sup>9,10</sup>  $Gd$ ,<sup>11</sup>  $Lu$ <sup>11</sup>) and  $[M(OH_2)_8]Cl_3 \cdot 1.5(12\text{-crown-4}) \cdot 2H_2O$ .<sup>22</sup> The structural features of the title complexes detailed below include eight-coordinate  $[M(OH_2)_7(OHMe)]^{3+}$  and nine-coordinate  $[MCl(OH_2)_2(18\text{-crown-6})]^{2+}$  ions participating in a complex hydrogen-bonded network.

When the conditions of crystallization change for  $M = Dy$ , so does the resulting structure. A stoichiometric transformation from 3:2 to 1:1 (metal:crown) appears to take place when the  $Dy$  reaction mixture containing the crystalline product is warmed to room temperature. The crystals redissolve, and a viscous immiscible liquid layer forms. (A similar effect has been observed by Bunzli.<sup>23</sup>) If allowed to slowly evaporate, the hydrogen-bonded complex  $[Dy(OH_2)_8]Cl_3 \cdot 18\text{-crown-6} \cdot 4H_2O$  results.<sup>24</sup> Its structure has several features in common with  $[M(OH_2)_8]Cl_3 \cdot 15\text{-crown-5}$  and  $[Lu(OH_2)_8]Cl_3 \cdot 1.5(12\text{-crown-4}) \cdot 2H_2O$ , including the octa-aquated metal ion and a polymeric hydrogen-bonded chain of cation/crown/cation/crown.

Similar chemistry was not observed when the prelanthanide  $Y$  was used. When the reaction mixture containing crystals of the title complex formed at 5 °C is warmed, the crystals redissolve without the appearance of a viscous liquid and a new crystalline product forms within 24 h. The same higher melting product can be obtained by heating the reaction mixture and allowing crystallization to occur at room temperature. Unlike the results for  $M = Dy$ , however, the new crystals formed for  $M = Y$  are almost identical with those of the title complexes. Very slight differences are observed in the disorder of the  $[M(OH_2)_7(OHMe)]^{3+}$  cation and in the hydrogen bonding even though both forms of this complex are essentially isostructural (see Experimental Section). We have previously observed examples of disorder, and consequent varying hydrogen-bonding patterns in "isostructural" complexes resulting in very different temperature stabilities.<sup>10</sup>

The title complexes are isostructural. The environment of the three cations in the formula unit are presented in Figure 1 for  $M = Dy$ . The  $[M(OH_2)_7(OHMe)]^{3+}$  cation resides on a crystallographic 2-fold axis and is disordered. (The two orientations of this cation have a geometry very close to a bicapped trigonal prism.<sup>25</sup>) In addition,  $Cl(4)$ ,  $Cl(5)$ ,  $Cl(6)$ ,  $O(13)$ , and  $O(14)$  are



**Figure 2.** View of the  $[MCl(OH_2)_2(18\text{-crown-6})]^{2+}$  ion along the pseudo-3-fold axis of the tricapped trigonal prism.

in general positions at 0.5 occupancy. Unreasonably close contacts and analysis of possible hydrogen-bond geometries suggest that  $Cl(4)$  and  $O(13)$ ,  $Cl(5)$  and  $O(14)$ , and  $Cl(6)$  and  $C(13)$  (of the methanol group) must reside on opposite sides of the 2-fold axes in  $I2/a$ . A rather complex network of hydrogen bonding results in which both cations, the uncoordinated chloride anions, and water molecules participate. The remaining cations,  $[MCl(OH_2)_2(18\text{-crown-6})]^{2+}$ , contain nine-coordinate  $M^{3+}$  directly coordinated to an 18-crown-6 molecule.

The geometry of the  $[MCl(OH_2)_2(18\text{-crown-6})]^{2+}$  cations is that of a distorted tricapped trigonal prism<sup>25</sup> (Figure 2), similar to that observed in  $[MCl(OH_2)_2(18\text{-crown-6})]Cl_2 \cdot 2H_2O$  ( $M = Sm, Gd, Tb$ ).<sup>17</sup> The  $M^{3+}$  ions are coordinated to the six crown oxygen atoms, one chlorine atom "above" the crown and two water molecules "below" the crown ether. The crown ether wraps around the metal cation with  $O(1)$  and  $O(4)$  occupying capping positions, along with  $Cl(1)$ . The distortion toward a capped square antiprism leaves  $O(1)$  as the capping atom and the  $M-O(1)$  distance is the longest of all of the  $M-O$  separations in all five determinations of this cation.

Bond distances and angles for the title compounds are given in Table I, and comparative averages from similar structures are compiled in Table II. The expected decrease of  $M-Cl(1)$  and  $M-O$  distances with a corresponding decrease in ionic radii is observed with values ranging from  $Sm-Cl(1) = 2.678$  (3) Å,  $Sm-O(\text{crown}) = 2.55$  (2) Å, and  $Sm-O(OH_2) = 2.45$  (3) Å to  $Y-Cl(1) = 2.647$  (2) Å,  $Y-O(\text{crown}) = 2.44$  (5) Å, and  $Y-O(OH_2) = 2.36$  (3) Å. The  $Tb$  complex appears to be an exception, but very small crystals and a corresponding shortage of observable data resulted in poor refinement and high standard deviations for this structure.<sup>17</sup>

An examination of the  $M-O(\text{crown})$  interactions for the five complexes containing the  $[MCl(OH_2)_2(18\text{-crown-6})]^{2+}$  cation ( $M = Sm, Gd, Tb, Dy, Y$ ) reveals some interesting features not necessarily explained by metal geometry. Despite its capping position, in each case the  $M-O(4)$  separation is significantly shorter than the average of the remaining  $M-O(\text{crown})$  distances. This is best illustrated with the low-temperature structures: for  $M = Dy$ ,  $Dy-O(4) = 2.360$  (5) Å,  $Dy-O(1-3,5,6)$  average 2.478 (7) Å; for  $M = Y$ ,  $Y-O(4) = 2.336$  (6) Å,  $Y-O(1-3,5,6)$  average 2.46 (1) Å. In addition, in each of the five compounds the  $M-O(2)$ ,  $M-O(3)$ , and  $M-O(4)$  distances are shorter than the  $M-O$  distances trans to them ( $M-O(5)$ ,  $M-O(6)$ ,  $M-O(1)$ ). Part of this may be due to distortions toward capped-square-antiprismatic geometry caused by the larger chloride ion, which appears to lean toward  $O(3)$  and  $O(5)$  and thereby flatten that square face.

In all five examples of this cation,  $O(1)$  and  $O(4)$  appear to bear the brunt of any steric effects as the metal ion size is reduced. (A similar effect was noted in ref 12.)  $O(1)$  and  $O(4)$  show large deviations (in the direction of the  $H_2O-M-OH_2$  bond angle) from the mean plane defined by the six crown oxygen atoms, as the crown ether wraps the metal cation and these atoms take capping

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**Table I.** Bond Distances (Å) and Angles (deg) for  $[M(OH_2)_7(OHMe)][MCl(OH_2)_2(18\text{-crown-6})]_2Cl_7 \cdot 2H_2O$ 

atoms	dist		atoms	dist	
	M = Y	M = Dy		M = Y	M = Dy
M(1)–Cl(1)	2.647 (2)	2.654 (2)	M(2)–O(9)	2.343 (9)	2.359 (6)
M(1)–O(1)	2.454 (6)	2.475 (5)	M(2)–O(10)	2.327 (8)	2.372 (6)
M(1)–O(2)	2.451 (5)	2.488 (4)	M(2)–O(11)	2.357 (7)	2.371 (5)
M(1)–O(3)	2.455 (6)	2.472 (4)	M(2)–O(12)	2.40 (1)	2.42 (1)
M(1)–O(4)	2.336 (6)	2.360 (5)	M(2)–O(12) <sup>y</sup>	2.39 (1)	2.41 (1)
M(1)–O(5)	2.476 (5)	2.483 (4)	O(9)–C(13)	1.41 (2)	1.39 (2)
M(1)–O(6)	2.460 (6)	2.473 (4)	O–C av	1.45 (2)	1.45 (1)
M(1)–O(7)	2.333 (6)	2.360 (5)	C–C av	1.49 (1)	1.50 (1)
M(1)–O(8)	2.382 (5)	2.411 (4)			

atoms	angle		atoms	angle	
	M = Y	M = Dy		M = Y	M = Dy
Cl(1)–M(1)–O(1)	127.6 (2)	127.3 (1)	O(4)–M(1)–O(8)	83.4 (2)	83.4 (2)
Cl(1)–M(1)–O(2)	77.4 (1)	77.3 (1)	O(5)–M(1)–O(8)	131.8 (2)	131.6 (1)
O(1)–M(1)–O(2)	66.5 (2)	66.4 (2)	O(6)–M(1)–O(8)	134.2 (2)	133.8 (2)
Cl(1)–M(1)–O(3)	76.0 (1)	75.9 (1)	O(7)–M(1)–O(8)	72.2 (2)	71.8 (1)
O(1)–M(1)–O(3)	117.4 (2)	117.2 (1)	O(9)–M(2)–O(10)	109.8 (3)	109.1 (2)
O(2)–M(1)–O(3)	65.5 (2)	65.0 (1)	O(9)–M(2)–O(11)	144.8 (3)	144.6 (2)
Cl(1)–M(1)–O(4)	86.3 (2)	86.2 (1)	O(9)–M(2)–O(12)	82.5 (4)	82.6 (3)
O(1)–M(1)–O(4)	146.1 (2)	146.4 (2)	O(9)–M(2)–O(12) <sup>y</sup>	82.7 (4)	82.3 (3)
O(2)–M(1)–O(4)	130.3 (2)	130.0 (2)	O(9)–M(2)–O(9) <sup>a</sup>	143.4 (4)	143.2 (3)
O(3)–M(1)–O(4)	65.0 (2)	65.3 (1)	O(9)–M(2)–O(10) <sup>a</sup>	83.1 (3)	83.7 (2)
Cl(1)–M(1)–O(5)	75.7 (2)	76.1 (1)	O(9)–M(2)–O(11) <sup>a</sup>	72.8 (3)	71.1 (2)
O(1)–M(1)–O(5)	118.7 (2)	118.2 (1)	O(10)–M(2)–O(11)	76.2 (3)	76.3 (2)
O(2)–M(1)–O(5)	147.6 (2)	147.8 (1)	O(10)–M(2)–O(12)	79.1 (4)	78.5 (3)
O(3)–M(1)–O(5)	123.5 (2)	124.3 (2)	O(10)–M(2)–O(12) <sup>y</sup>	149.8 (4)	150.4 (3)
O(4)–M(1)–O(5)	65.3 (2)	65.7 (1)	O(10)–M(2)–O(10) <sup>a</sup>	139.5 (4)	139.6 (3)
Cl(1)–M(1)–O(6)	79.7 (2)	80.1 (1)	O(10)–M(2)–O(11) <sup>a</sup>	72.8 (3)	72.5 (2)
O(1)–M(1)–O(6)	66.2 (2)	65.9 (1)	O(11)–M(2)–O(12)	132.0 (4)	131.9 (3)
O(2)–M(1)–O(6)	93.0 (2)	93.2 (1)	O(11)–M(2)–O(12) <sup>y</sup>	109.9 (3)	110.6 (2)
O(3)–M(1)–O(6)	150.4 (2)	150.4 (2)	O(11)–M(2)–O(11) <sup>a</sup>	78.8 (3)	77.9 (2)
O(4)–M(1)–O(6)	130.1 (2)	130.2 (1)	O(12)–M(2)–O(12) <sup>y</sup>	75.4 (5)	76.1 (3)
O(5)–M(1)–O(6)	64.9 (2)	64.5 (1)	O(12)–M(2)–O(9) <sup>a</sup>	66.0 (3)	65.9 (2)
Cl(1)–M(1)–O(7)	143.2 (1)	143.6 (1)	O(12)–M(2)–O(10) <sup>a</sup>	141.4 (4)	141.9 (3)
O(1)–M(1)–O(7)	71.6 (2)	71.5 (2)	O(12)–M(2)–O(11) <sup>a</sup>	130.8 (3)	131.0 (2)
O(2)–M(1)–O(7)	135.7 (2)	135.4 (2)	O(12) <sup>y</sup> –M(2)–O(9) <sup>a</sup>	72.0 (4)	72.3 (3)
O(3)–M(1)–O(7)	127.0 (2)	127.2 (1)	O(12) <sup>y</sup> –M(2)–O(10) <sup>a</sup>	67.4 (4)	66.9 (3)
O(4)–M(1)–O(7)	80.9 (2)	81.2 (2)	O(12) <sup>y</sup> –M(2)–O(11) <sup>a</sup>	137.0 (4)	136.6 (3)
O(5)–M(1)–O(7)	67.6 (2)	67.6 (2)	M(2)–O(9)–C(13)	122.8 (9)	122.5 (7)
O(6)–M(1)–O(7)	82.5 (2)	82.3 (2)			
Cl(1)–M(1)–O(8)	140.4 (2)	140.5 (1)	M(1)–O–C av	118 (2)	118 (2)
O(1)–M(1)–O(8)	69.8 (2)	69.9 (2)	C–O–C av	114 (2)	114 (2)
O(2)–M(1)–O(8)	80.5 (2)	80.6 (1)	O–C–C av	107 (1)	107 (1)
O(3)–M(1)–O(8)	65.0 (2)	65.1 (2)			

<sup>a</sup> Atoms related to those in Tables VI and VII by the crystallographic 2-fold axis (0.5 – x, y, 2 – z).

**Table II.** Series Characteristics for the 18-Crown-6 Complexes of Lanthanide(III) Chloride Hydrates and Comparative Data

complex	M <sup>3+</sup> ionic radius <sup>a</sup>	CN	M(1)–Cl, Å	M(1)–O(crown) av, Å	M(1)–OH <sub>2</sub> av, Å	M(2)–O, av, Å	ref
[La(NO <sub>3</sub> ) <sub>3</sub> (18-crown-6)]	1.36	12		2.72 (6)			12
[Nd(NO <sub>3</sub> ) <sub>3</sub> (18-crown-6)]	1.27	12		2.70 (9)			13
[Nd(NO <sub>3</sub> ) <sub>2</sub> (18-crown-6)] <sub>3</sub> [Nd(NO <sub>3</sub> ) <sub>6</sub> ]		10		2.59 (2)			14
[SmCl(OH <sub>2</sub> ) <sub>2</sub> (18-crown-6)]Cl <sub>2</sub> ·2H <sub>2</sub> O	1.132	9	2.678 (3)	2.55 (2)	2.45 (3)		17
[GdCl(OH <sub>2</sub> ) <sub>2</sub> (18-crown-6)]Cl <sub>2</sub> ·2H <sub>2</sub> O	1.107	9	2.663 (3)	2.52 (3)	2.41 (3)		17
[GdCl <sub>2</sub> (OHEt)(18-crown-6)]Cl	1.107	9	2.695 (3), 2.734 (3)	2.54 (4)	2.414 (6) (OHEt)		15
[TbCl(OH <sub>2</sub> ) <sub>2</sub> (18-crown-6)]Cl <sub>2</sub> ·2H <sub>2</sub> O	1.095	9	2.69 (1)	2.53 (5)	2.36 (4)		17
[Dy(OH <sub>2</sub> ) <sub>7</sub> (OHMe)]-	1.027	8				2.39 (2)	
[DyCl(OH <sub>2</sub> ) <sub>2</sub> (18-crown-6)] <sub>2</sub> Cl <sub>2</sub> ·2H <sub>2</sub> O <sup>b</sup>	1.083	9	2.654 (2)	2.46 (5)	2.39 (4)		this study
[Dy(OH <sub>2</sub> ) <sub>8</sub> Cl <sub>3</sub> ·18-crown-6·4H <sub>2</sub> O]	1.027	8				2.39 (2)	24
[Y(OH <sub>2</sub> ) <sub>7</sub> (OHMe)]-	1.019	8				2.36 (3)	
[YCl(OH <sub>2</sub> ) <sub>2</sub> (18-crown-6)] <sub>2</sub> Cl <sub>7</sub> ·2H <sub>2</sub> O <sup>b</sup>	1.075	9	2.647 (2)	2.44 (5)	2.36 (3)		this study
[Y(OH <sub>2</sub> ) <sub>8</sub> ]Cl <sub>3</sub> ·15-crown-5 <sup>b</sup>	1.019	8				2.36 (4)	10

<sup>a</sup> Radii for CN = 9 (or as indicated) from ref 21. <sup>b</sup> Structure determination carried out at –150 °C.

positions in the tricapped trigonal prism. The deviations range from 0.88 Å (O(1)) and 0.58 Å (O(4)) for M = Sm to 1.19 Å (O(1)) and 0.54 Å (O(4)) for M = Dy and Y. The effect on the individual C–O and C–C distances and C–C–O angles is negligible, but a definite widening of the C–O–C angles involving O(1) and O(4) is observed. These values are 115.1 (6), 117.2 (7)° (O(1), O(4), M = Y) and 115.2 (5), 117.5 (5)° (M = Dy) compared to averages of the remaining C–O–C angles of 112.7

(7)° (M = Y) and 112.7 (4)° (M = Dy).

The result of the folding of the crown ether in the title complexes is clearly seen in the torsion angles given in Table III. The major deviations from the normally observed  $D_{3d}^{18-20}$  conformation for 18-crown-6 involve O(1), O(4), and the C<sub>2</sub>H<sub>4</sub> groups bonded to them.

The contacts and contact geometries of the water molecules and chloride ions are given in Table IV and have been used to

**Table III.** Torsion Angles (deg) for  $[M(OH_2)_7(OHMe)][MCl(OH_2)_2(18\text{-crown-6})]_2Cl_7 \cdot 2H_2O$ 

atoms	angle	
	M = Y	M = Dy
O(1)-C(1)-C(2)-O(2)	51.5	51.0
C(1)-C(2)-O(2)-C(3)	104.4	104.6
C(2)-O(2)-C(3)-C(4)	177.9	178.5
O(2)-C(3)-C(4)-O(3)	55.2	55.0
C(3)-C(4)-O(3)-C(5)	169.8	169.3
C(4)-O(3)-C(5)-C(6)	-178.6	-178.7
O(3)-C(5)-C(6)-O(4)	-52.1	-50.8
C(5)-C(6)-O(4)-C(7)	-140.8	-141.7
C(6)-O(4)-C(7)-C(8)	143.1	143.3
O(4)-C(7)-C(8)-O(5)	53.2	53.5
C(7)-C(8)-O(5)-C(9)	177.3	178.8
C(8)-O(5)-C(9)-C(10)	-172.2	-171.3
O(5)-C(9)-C(10)-O(6)	-51.3	-53.8
C(9)-C(10)-O(6)-C(11)	-179.5	-176.9
C(10)-O(6)-C(11)-C(12)	-112.9	-111.6
O(6)-C(11)-C(12)-O(1)	-48.9	-50.4
C(11)-C(12)-O(1)-C(1)	-98.0	-97.5
C(12)-O(1)-C(1)-C(2)	98.2	99.2

**Table IV.** Hydrogen-Bonding Contact Geometries for  $[M(OH_2)_7(OHMe)][MCl(OH_2)_2(18\text{-crown-6})]_2Cl_7 \cdot 2H_2O$ 

atoms	dist, Å	
	M = Y	M = Dy
O(7)-Cl(2)	3.066 (6)	3.066 (5)
O(7)-Cl(4)	3.044 (6)	3.024 (5)
O(7)-O(13) <sup>b</sup>	2.65 (1)	2.64 (1)
O(8)-Cl(2)	3.050 (7)	3.062 (6)
O(8)-Cl(3)	3.169 (6)	3.179 (5)
O(9)-Cl(5)	3.28 (1)	3.294 (8)
O(9)-Cl(6) <sup>a</sup>	3.01 (1)	3.017 (7)
O(9)-O(14) <sup>a</sup>	2.42 (1)	2.43 (1)
O(10)-Cl(2)	3.008 (8)	3.007 (6)
O(10)-Cl(3) <sup>c</sup>	3.086 (8)	3.081 (6)
O(11)-Cl(3) <sup>d</sup>	3.056 (8)	3.070 (6)
O(11)-Cl(5) <sup>a</sup>	3.21 (1)	3.240 (7)
O(11)-Cl(6)	2.850 (9)	2.870 (7)
O(12)-Cl(3) <sup>f</sup>	3.18 (1)	3.195 (9)
O(12)-Cl(6) <sup>e</sup>	3.25 (1)	3.25 (1)
O(12)-Cl(3) <sup>g</sup>	3.15 (2)	3.15 (1)
O(12)-Cl(2) <sup>a</sup>	2.97 (1)	2.99 (1)
O(13)-Cl(4)	3.07 (1)	3.11 (1)
O(13)-Cl(5) <sup>h</sup>	3.15 (1)	3.19 (1)
O(14)-Cl(4)	3.06 (2)	3.08 (1)
O(14)-Cl(6)	3.22 (2)	3.21 (1)

atoms	angle, deg	
	M = Y	M = Dy
Cl(2)-O(7)-Cl(4)	111.7 (2)	111.6 (2)
Cl(2)-O(7)-O(13) <sup>b</sup>	107.3 (3)	107.0 (3)
Cl(2)-O(8)-Cl(3)	114.2 (2)	115.0 (1)
Cl(6) <sup>a</sup> -O(9)-O(14) <sup>a</sup>	106.7 (5)	107.7 (3)
Cl(2)-O(10)-Cl(3) <sup>c</sup>	110.2 (2)	110.9 (2)
Cl(3) <sup>d</sup> -O(11)-Cl(6)	95.1 (2)	95.6 (2)
Cl(3) <sup>d</sup> -O(11)-Cl(5) <sup>a</sup>	114.4 (2)	114.8 (2)
Cl(3) <sup>f</sup> -O(12)-Cl(6) <sup>e</sup>	102.3 (4)	102.2 (3)
Cl(2) <sup>a</sup> -O(12)-Cl(3) <sup>g</sup>	83.8 (4)	84.0 (3)
Cl(4)-O(13)-Cl(5) <sup>h</sup>	109.7 (4)	109.0 (3)
Cl(4)-O(14)-Cl(6)	122.5 (5)	121.6 (4)

<sup>a</sup> Atoms related to those in Tables VI and VII by 0.5 -x, y, 2 - z. <sup>b</sup> 0.5 - x, 1.5 - y, 1.5 - z. <sup>c</sup> 1 - x, 1 - y, 2 - z. <sup>d</sup> x - 0.5, 1 - y, z. <sup>e</sup> x, 1 + y, z. <sup>f</sup> 1 - x, 2 - y, 2 - z. <sup>g</sup> x - 0.5, 2 - y, z. <sup>h</sup> x, 1.5 - y, z - 0.5.

infer where hydrogen bonds exist. The formula units are associated into dimers (two formula units) in the *ac* plane, and these are linked in chains along the short *b* axis via hydrogen bonds between the  $[M(OH_2)_7(OHMe)]^{3+}$  cations and Cl(3) and Cl(6).

### Conclusions

A structural change in  $LnCl_3 \cdot nH_2O$  complexes with 18-crown-6 occurs between M = Tb and M = Dy. At M = Dy there appears to be a competition between second-sphere (hydrogen-bonded) coordination of the crown ether as observed in  $[M(OH_2)_6]Cl_3$

**Table V.** Crystal Data and Summary of Intensity Data Collection and Structure Refinement for  $[M(OH_2)_7(OHMe)][MCl(OH_2)_2(18\text{-crown-6})]_2Cl_7 \cdot 2H_2O$ 

compd	M = Y	M = Dy
color/shape	clear/irregular	clear/block
mol wt	1380.7	1601.4
space group	<i>I</i> 2/a	<i>I</i> 2/a
temp, °C	-150	-150
cell consts <sup>a</sup>		
<i>a</i> , Å	25.525 (8)	25.715 (7)
<i>b</i> , Å	7.310 (4)	7.348 (1)
<i>c</i> , Å	30.506 (9)	30.603 (5)
β, deg	109.35 (5)	109.62 (3)
cell vol, Å <sup>3</sup>	5371 (4)	5447 (3)
formula units/unit cell	4	4
ρ(calcd), g cm <sup>-3</sup>	1.71	1.95
μ(calcd), cm <sup>-1</sup>	36.5	47.3
diffractometer/scan	Enraf-Nonius CAD4/θ-2θ	Enraf-Nonius CAD4/θ-2θ
range of rel transm factors	53/100%	76/100%
radiation, graphite monochromator	Mo Kα(λ = 0.71073 Å)	Mo Kα(λ = 0.71073 Å)
max cryst dimens, mm	0.40 × 0.65 × 0.65	0.50 × 0.60 × 0.73
scan width	0.80 + 0.35 tan θ	0.80 + 0.35 tan θ
std reflns	(14,0,0), (040), (0,0,16)	(14,0,0), (040), (0,0,16)
decay of stds	±1%	±1%
no. of reflns measd	5215	5236
2θ range, deg	2 < 2θ < 50	2 < 2θ < 50
range of <i>h, k, l</i>	+30, +8, ±36	+30, +8, ±36
reflns obsd [ <i>F</i> <sub>o</sub> ≥ 5σ( <i>F</i> <sub>o</sub> ) <sup>b</sup> ]	3358	4395
computer program <sup>c</sup>	SHELX <sup>28</sup>	SHELX <sup>28</sup>
no. of params varied	316	321
wts	unit	[σ( <i>F</i> <sub>o</sub> ) <sup>2</sup> + 0.000004 <i>F</i> <sub>o</sub> <sup>2</sup> ] <sup>-1</sup>
GOF	8.59	4.19
$R = \sum   F_o  -  F_c   / \sum  F_o $	0.060	0.036
<i>R</i> <sub>w</sub>	0.068	0.039
largest feature on final diff map, e/Å <sup>3</sup>	1.2	1.2

<sup>a</sup> Least-squares refinement of ((sin θ)/λ)<sup>2</sup> values for 25 reflections: θ > 10° (M = Y), 20° (M = Dy). <sup>b</sup> Corrections: Lorentz, polarization, and absorption (empirical, ψ scan). <sup>c</sup> Neutral-atom scattering factors and anomalous dispersion corrections from ref 29.

15-crown-5 and  $[Lu(OH_2)_8]Cl_3 \cdot 1.5(12\text{-crown-4}) \cdot 2H_2O$  and the in-cavity direct coordination found for  $[MCl(OH_2)_2(18\text{-crown-6})]Cl_2 \cdot 2H_2O$ . Indeed both the title complex (M = Dy) and  $[Dy(OH_2)_8]Cl_3 \cdot 18\text{-crown-6} \cdot 4H_2O$  can form under the appropriate conditions of crystallization from the same reaction mixture. The observations for M-O(crown) separations, C-O-C angles, crown oxygen deviations from their mean plane, and crown ether torsion angles tend to support the idea that the bulk of any steric strain in the crown ether produced as a result of the folding of this ligand around a metal ion of decreasing size (La to Lu) is absorbed by two oxygens of the crown ether trans to one another (and staggered with respect to the pair of non-crown metal ligands occupying metal coordination sites on the same side of the crown ether).

The solvent also plays a key role in the nature of the crystalline products. Izatt observed no complexation of 18-crown-6 to a hydrated lanthanide chloride heavier than gadolinium utilizing methanolic solutions,<sup>17</sup> and thus far, we have managed only to recrystallize  $[YCl_2(OH_2)_6]Cl^{26}$  when using only acetonitrile as the solvent.

We are continuing to follow lines of research that we hope will lead to more clues about the nature of crown ether complexation to f elements and allow us to sort through the myriad of variables responsible for observed structures. One current investigation that appears to hold some promise is the study of the effect of chloride ion concentration on the coordination and structure of the

**Table VI.** Final Fractional Coordinates for  $[\text{Y}(\text{OH})_2(\text{OHMe})][\text{YCl}(\text{OH})_2(18\text{-crown-6})]_2\text{Cl}_7\cdot 2\text{H}_2\text{O}$ 

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> (eqv), <sup>b</sup> Å <sup>2</sup>
Y(1)	0.44681 (3)	0.4556 (1)	0.84767 (3)	0.012
Y(2)	0.2500	0.6580 (2)	1.0000	0.036
Cl(1)	0.47417 (8)	0.2667 (3)	0.78445 (7)	0.020
Cl(2)	0.40530 (9)	0.7978 (3)	0.95693 (7)	0.026
Cl(3)	0.61144 (9)	0.7798 (3)	0.96104 (9)	0.030
Cl(4) <sup>a</sup>	0.2626 (2)	0.7539 (8)	0.7963 (2)	0.032
Cl(5) <sup>a</sup>	0.2877 (2)	0.4394 (8)	1.1550 (2)	0.036
Cl(6) <sup>a</sup>	0.2317 (2)	0.1396 (7)	0.8894 (2)	0.032
O(1)	0.4193 (2)	0.3354 (8)	0.9119 (2)	0.017
O(2)	0.5110 (2)	0.2259 (8)	0.8947 (2)	0.019
O(3)	0.5454 (2)	0.5271 (8)	0.8639 (2)	0.018
O(4)	0.4641 (2)	0.7169 (8)	0.8106 (2)	0.020
O(5)	0.3734 (2)	0.5312 (8)	0.7734 (2)	0.019
O(6)	0.3690 (2)	0.2382 (8)	0.8231 (2)	0.017
O(7)	0.3789 (2)	0.6478 (8)	0.8581 (2)	0.020
O(8)	0.4886 (2)	0.6306 (8)	0.9163 (2)	0.019
O(9)	0.2794 (3)	0.759 (1)	1.0772 (3)	0.060
O(10)	0.3256 (3)	0.548 (1)	0.9815 (2)	0.041
O(11)	0.2133 (3)	0.4088 (9)	0.9503 (3)	0.036
O(12) <sup>a</sup>	0.2923 (6)	0.939 (2)	0.9884 (4)	0.035
O(12) <sup>a</sup>	0.1797 (5)	0.885 (2)	0.9912 (4)	(iso)
O(13) <sup>a</sup>	0.2243 (5)	0.754 (2)	0.6897 (4)	0.024
O(14) <sup>a</sup>	0.2052 (6)	0.558 (2)	0.8567 (5)	0.038
C(1)	0.4620 (3)	0.242 (1)	0.9485 (3)	0.020
C(2)	0.4934 (3)	0.118 (1)	0.9273 (3)	0.021
C(3)	0.5692 (3)	0.271 (1)	0.9126 (3)	0.025
C(4)	0.5830 (3)	0.373 (1)	0.8763 (3)	0.022
C(5)	0.5598 (4)	0.657 (1)	0.8349 (3)	0.023
C(6)	0.5176 (4)	0.807 (1)	0.8268 (3)	0.022
C(7)	0.4203 (4)	0.806 (1)	0.7739 (3)	0.024
C(8)	0.3884 (4)	0.655 (1)	0.7437 (3)	0.023
C(9)	0.3401 (4)	0.381 (1)	0.7490 (3)	0.024
C(10)	0.3210 (4)	0.279 (1)	0.7829 (3)	0.026
C(11)	0.3544 (4)	0.137 (1)	0.8577 (3)	0.026
C(12)	0.3642 (3)	0.255 (1)	0.8997 (3)	0.022
C(13) <sup>a</sup>	0.2741 (9)	0.941 (3)	1.0897 (7)	0.037

<sup>a</sup> Atoms are disordered, present at half-occupancy. <sup>b</sup> *U*(eqv) is equal to (*U*<sub>11</sub> + *U*<sub>22</sub> + *U*<sub>33</sub>)/3.

$[\text{MCl}(\text{OH})_2(18\text{-crown-6})]^{2+}$  ion. Preliminary synthetic and X-ray structural results have shown that it is possible to modify the three non-crown coordination sites while leaving the crown ether coordination intact. Utilizing an excess of LiCl in reactions similar to those reported in this paper, we have synthesized and characterized  $[\text{GdCl}_x(\text{OH})_2(18\text{-crown-6})]_2[\text{GdCl}_6]\cdot 2\text{OHMe}$  (*x* = 1 and *y* = 2 or *x* = 2 and *y* = 1).<sup>27</sup> Interestingly, the chloride ion contacts are in coordination sites occupied by O(7) and O(8) in the title complexes. Even more surprising is the observation of an  $[\text{Y}(\text{OH})_2(18\text{-crown-6})]^{3+}$  ion when hydrated yttrium chloride and an excess of LiCl are used.<sup>27</sup> Future reports from our group will highlight these results.

### Experimental Section

**Synthesis and Crystallization of  $[\text{Y}(\text{OH})_2(\text{OHMe})][\text{YCl}(\text{OH})_2(18\text{-crown-6})]_2\text{Cl}_7\cdot 2\text{H}_2\text{O}$ .** Under Ar, 10 mmol of 18-crown-6 in 30 mL of  $\text{CH}_3\text{OH}-\text{CH}_3\text{CN}$  (1:3) was added to a stirring solution of 10 mmol of  $\text{YCl}_3\cdot 6\text{H}_2\text{O}$  in 30 mL of the corresponding solvent. The reaction mixture was heated to 60 °C for 1 h, cooled to 22 °C, and concentrated to 15–30 mL. Crystals suitable for X-ray diffraction analysis formed after 10 days at 5 °C. The crystals redissolve when warmed to room temperature under the solvent mixture and melt within 1 min upon removal from the solvent in air. Longer periods of heating had no effect on the resulting crystalline product. When the solution is allowed to warm to room temperature and the crystals redissolve, crystallization occurs again within 24 h at room temperature. The new crystals do not melt when removed from the solvent. Single-crystal X-ray diffraction data were collected on both sets of crystals at low temperature. Initially they appeared to be isostructural, but as discussed below, slight differences in the disorder of the  $[\text{M}(\text{OH})_2(\text{OHMe})]^{3+}$  cation were found for the two determinations. The latter set were further analyzed; mp 80 °C discolored. Anal. Calcd for  $[\text{Y}(\text{OH})_2(\text{OHMe})][\text{YCl}(\text{OH})_2(18\text{-crown-6})]_2\text{Cl}_7\cdot 2\text{H}_2\text{O}$ : C, 21.75; H, 5.69. Found: C, 21.42; H, 5.78. The

**Table VII.** Final Fractional Coordinates for  $[\text{Dy}(\text{OH})_2(\text{OHMe})][\text{DyCl}(\text{OH})_2(18\text{-crown-6})]_2\text{Cl}_7\cdot 2\text{H}_2\text{O}$ 

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> (eqv), <sup>b</sup> Å <sup>2</sup>
Dy(1)	0.44674 (1)	0.45528 (4)	0.84748 (1)	0.010
Dy(2)	0.2500	0.65887 (7)	1.0000	0.031
Cl(1)	0.47403 (7)	0.2666 (2)	0.78444 (6)	0.018
Cl(2)	0.40517 (7)	0.7977 (3)	0.95691 (6)	0.025
Cl(3)	0.61148 (7)	0.7792 (3)	0.96125 (7)	0.028
Cl(4) <sup>a</sup>	0.2630 (2)	0.7483 (6)	0.7972 (1)	0.028
Cl(5) <sup>a</sup>	0.2880 (2)	0.4422 (6)	1.1552 (1)	0.032
Cl(6) <sup>a</sup>	0.2319 (2)	0.1393 (5)	0.8893 (1)	0.028
O(1)	0.4192 (2)	0.3336 (6)	0.9119 (2)	0.016
O(2)	0.5117 (2)	0.2235 (6)	0.8953 (1)	0.015
O(3)	0.5456 (2)	0.5248 (6)	0.8644 (1)	0.013
O(4)	0.4643 (2)	0.7176 (6)	0.8102 (2)	0.017
O(5)	0.3729 (2)	0.5304 (6)	0.7734 (2)	0.016
O(6)	0.3686 (2)	0.2389 (6)	0.8227 (1)	0.015
O(7)	0.3787 (2)	0.6486 (6)	0.8582 (2)	0.018
O(8)	0.4887 (2)	0.6316 (6)	0.9169 (1)	0.017
O(9)	0.2806 (2)	0.7603 (8)	1.0776 (2)	0.051
O(10)	0.3266 (2)	0.5474 (8)	0.9814 (2)	0.038
O(11)	0.2133 (2)	0.4079 (7)	0.9506 (2)	0.031
O(12) <sup>a</sup>	0.2927 (4)	0.939 (1)	0.9879 (3)	0.025
O(12) <sup>a</sup>	0.1798 (4)	0.886 (1)	0.9922 (3)	0.024
O(13) <sup>a</sup>	0.2231 (4)	0.749 (2)	0.6894 (4)	0.040
O(14) <sup>a</sup>	0.2048 (4)	0.554 (1)	0.8571 (3)	0.028
C(1)	0.4619 (3)	0.241 (1)	0.9489 (2)	0.018
C(2)	0.4945 (3)	0.1179 (9)	0.9278 (2)	0.019
C(3)	0.5691 (3)	0.270 (1)	0.9133 (2)	0.021
C(4)	0.5832 (3)	0.374 (1)	0.8770 (2)	0.019
C(5)	0.5604 (3)	0.6579 (9)	0.8356 (2)	0.021
C(6)	0.5178 (3)	0.8080 (9)	0.8266 (2)	0.019
C(7)	0.4206 (3)	0.8059 (9)	0.7737 (2)	0.019
C(8)	0.3882 (3)	0.656 (1)	0.7430 (2)	0.021
C(9)	0.3405 (3)	0.381 (1)	0.7489 (2)	0.018
C(10)	0.3209 (3)	0.282 (1)	0.7831 (2)	0.020
C(11)	0.3547 (3)	0.133 (1)	0.8577 (2)	0.024
C(12)	0.3645 (3)	0.254 (1)	0.8997 (2)	0.021
C(13) <sup>a</sup>	0.2747 (7)	0.939 (2)	1.0896 (5)	0.040

<sup>a</sup> Atoms are disordered, present at half-occupancy. <sup>b</sup> *U*(eqv) is equal to (*U*<sub>11</sub> + *U*<sub>22</sub> + *U*<sub>33</sub>)/3.

full structure determination reported in this paper resulted from the study of the first set of crystals that melt below room temperature. A description of the minor differences in the two structures is given below. Under identical conditions with only acetonitrile as the solvent, only the starting material,  $[\text{YCl}_2(\text{OH})_2]\text{Cl}$ , could be recovered in crystalline form.

**Synthesis and Crystallization of  $[\text{Dy}(\text{OH})_2(\text{OHMe})][\text{DyCl}(\text{OH})_2(18\text{-crown-6})]_2\text{Cl}_7\cdot 2\text{H}_2\text{O}$ .** Under Ar, 10 mmol of 18-crown-6 in 25 mL of  $\text{CH}_3\text{OH}-\text{CH}_3\text{CN}$  (1:3) was added to a stirring solution of 10 mmol of  $\text{DyCl}_3\cdot 6\text{H}_2\text{O}$  in 25 mL of the corresponding solvent. The reaction mixture was heated to 60 °C for 1 h, cooled to 22 °C, and concentrated to 20–30 mL. Crystallization took place over a period of approximately 4 months at 5 °C. Longer periods of heating had no effect on the resulting crystalline product. When the reaction mixture containing crystals of the title complex under the original solvent is allowed to warm to room temperature, a viscous liquid forms, probably indicating a 3:2 to 1:1 change in metal:crown stoichiometry. A similar effect has been observed by Bunzli in ref 23. If this resulting solution is allowed to slowly evaporate at room temperature, large single crystals of  $[\text{Dy}(\text{OH})_2]_2\text{Cl}_7\cdot 18\text{-crown-6}\cdot 4\text{H}_2\text{O}$  form. The crystal structure of this complex is reported in ref 24.

**X-ray Data Collection, Structure Determination, and Refinement for  $[\text{M}(\text{OH})_2(\text{OHMe})][\text{MCl}(\text{OH})_2(18\text{-crown-6})]_2\text{Cl}_7\cdot 2\text{H}_2\text{O}$  (M = Y, Dy).** Clear single crystals of the title complexes were mounted on a pin and transferred to the goniometer. The crystals were cooled to –150 °C during data collection by using a stream of cold nitrogen gas to prevent decomposition. The space group was determined to be either the centric *I*2/a or the acentric *I*a from the systematic absences. Statistical tests indicated that the space group was centric, and the final refinement of the structure as discussed below bore this out. A summary of data collection parameters is given in Table V.

(28) Sheldrick, G. M., "SHELX, a System of Computer Programs for X-ray Structure Determination As Locally Modified"; 1976.

(29) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1972; Vol. IV, pp 72, 99, 149.

The dysprosium analogue was solved first, and its final fractional coordinates were used as a starting point in the refinement the Y compound. The dysprosium positions were determined via inspection of a Patterson function map. A difference Fourier map phased on the dysprosium atoms readily revealed the positions of the non-hydrogen atoms.

Disorder in the structures was immediately obvious from unrealistically close contacts between some of the atoms related by the 2-fold axis containing M(2). Because of the presence of disorder, an attempt was made to refine these structures in the noncentrosymmetric *Ia*. High correlations between atoms related by the center of symmetry in *I2/a* and the continued presence of disorder led us to conclude that *I2/a* was in fact the correct choice.

There are four pairs of 2-fold-related general positions in *I2/a*. The disorder model used has two atoms in general positions, half-weighted, such that each of these atoms occupies only one position of each 2-fold-related pair of general positions. The two atoms may not reside on the same side of the 2-fold axes. The pairs of atoms involved are as follows: Cl(4), O(13); Cl(5), O(14); Cl(6), C(13); O(12), O(12)'. In addition, the M(2) position may be fractionally disordered about the 2-fold axis. Although the M(2) atom would not refine properly off the 2-fold axis, noticeable anisotropy of the M(2) thermal parameters are noted for both compounds. The resulting atom orientations and hydrogen-bonding network were described earlier. Least-squares refinement with isotropic thermal parameters led to  $R = 0.104$  ( $M = Dy$ ) and  $0.109$  ( $M = Y$ ). The crown hydrogen atoms were placed in calculated positions  $0.95 \text{ \AA}$  from the bonded carbon atom and allowed to ride on that atom with  $B$  fixed at  $5.5 \text{ \AA}^2$ . The methyl and water hydrogen atoms were not located because of the disorder. Refinement of the non-hydrogen atoms (except for O(12),  $M = Y$ ) with anisotropic temperature factors led to the final

$R$  values. The final values of the positional parameters are given in Tables VI and VII.

A low-temperature and a room-temperature structure determination were also carried out on the higher melting form of the Y compound. These determinations were isostructural with the two complexes reported above except for the atoms relating to O(12) and O(12)'. Whereas only two positions were found for O(12) in the low-melting forms, a third refinable position was found in the higher melting form: Two features were found unique to this form of the Y complex. First, different hydrogen-bonding patterns were noted for the three positions related to O(12). In addition, the disorder resulted in two different geometries observed for the  $[M(OH_2)_7(OHMe)]^{3+}$  cation: one a biccapped trigonal prism and the other a square antiprism. The occupancy factors (50% O(12)/50% O(12)' in the structures reported above) refined to 45% O(12), 40% O(12)', and 15% O(12)P.

**Acknowledgment.** We wish to thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work and the NSF Chemical Instrumentation Program for funds used to purchase the diffractometer.

**Supplementary Material Available:** Figures A and B, showing a view of the unit cell contents and H-bonding contacts around  $[M(OH_2)_7(OHMe)]^{3+}$ , and Tables SI-SIX, listing derived hydrogen atom coordinates, thermal parameters, bond distances and angles, and least-squares planes results for geometry calculations (31 pages); Tables SX and SXI, listing observed and calculated structure factors (30 pages). Ordering information is given on any current masthead page.

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## An Unusual Six-Membered Chelate Ring Involving Carboxylic Function to Copper(II) Coordination: Synthesis, Crystal Structure, and Properties of Aqua(((2-carboxyethyl)imino)diacetato)copper(II)

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Received October 28, 1986

The complex  $[Cu^II(H_2O)(HNPDA)]$  (HNPDA = ((2-carboxyethyl)imino)diacetate) has been synthesized and characterized by X-ray diffraction. The title compound crystallizes in the monoclinic system, space group  $P2_1/c$ , with  $a = 10.559$  (3)  $\text{\AA}$ ,  $b = 8.715$  (2)  $\text{\AA}$ ,  $c = 11.217$  (2)  $\text{\AA}$ ,  $\beta = 111.85$  (3)°,  $Z = 4$ ,  $V = 958.1 \text{ \AA}^3$ , and  $D_{meas} = 1.998 \text{ g cm}^{-3}$ . Final  $R = 0.031$  and  $R_w = 0.029$  for 1663 independent observed reflections. Each tetradentate HNPDA<sup>2-</sup> ligand chelates one copper(II) ion with three nearly coplanar and short bonds (Cu-N = 1.997 (3)  $\text{\AA}$ , Cu-O(13) = 1.963 (3)  $\text{\AA}$ , and Cu-O(23) = 1.972 (3)  $\text{\AA}$ ) and a fourth longer bond (Cu-O(5) = 2.488 (3)  $\text{\AA}$ ), making up an interesting  $\beta$ -aminopropionic acid-copper(II) six-membered chelate ring, which is puckered in a boat-type conformation. The in-plane short bond Cu-O(H<sub>2</sub>O) = 1.924 (2)  $\text{\AA}$  and a trans-apical long bond Cu-O(14<sup>i</sup>) = 2.494 (3)  $\text{\AA}$ , involving an O donor atom of the bidentate-bridged acetate arm of a second HNPDA<sup>2-</sup> ligand (referred to by the superscript *i*), complete the tetragonally elongated octahedral coordination of each copper(II) ion. Thus, each ligand molecule links two copper atoms and each copper(II) is bonded to two ligands. The 2<sub>1</sub>-axis-related copper complexes share one oxygen atom, thus forming infinite polynuclear zigzag chains, reinforced by O(4)-H(O4)...O(24<sup>iv</sup>) (symmetry code *iv*:  $x, -1 + y, z$ ) intrachain hydrogen bonds (linking alternating complex entities). In addition, both hydrogen atoms of the coordinated water molecule are involved in interchain hydrogen bonds with two different homologous chains, making up tunnels of irregular hexagonal cross section that run parallel to the [010] axis in the tridimensional network. The potentiometric and conductometric titrations, thermal stability, spectral (IR, reflectance, ESR) properties, and magnetic susceptibility data are interpreted in light of the known crystal structure of this complex.

### Introduction

The studies on amino polycarboxylic acid-metal ion systems in aqueous solution often point out the formation of metal-proton-ligand species  $M_pH_qL_r$ . The literature concerning these

ternary complexes in the solid state is clearly less extensive. Even for the most common amino polycarboxylic acids such as ethylenediaminetetraacetic acid (H<sub>4</sub>EDTA)<sup>2-7</sup> or nitrilotriacetic

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