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f-Element/Crown Ether Complexes.
7.* Low Temperature (−150 °C) Structure of $[Y(OH_2)_8]Cl_3\cdot(15\text{-crown-}5)$

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Abstract

The crystal and molecular structure of $[Y(OH_2)_8]Cl_3\cdot(15\text{-crown-}5)$ has been determined by single-crystal X-ray diffraction at −150 °C. At this temperature the lattice constants (monoclinic, $P2_1/n$) are $a = 9.126(2)$, $b = 17.104(3)$, $c = 15.237(4)$ Å, $\beta = 92.86(2)°$, and $D_{calc} = 1.56$ g cm^{-3} for $Z = 4$. A final R value of 0.035 was obtained via least-squares refinement using 3399 independent observed $[F_o \geqslant 5\sigma(F_o)]$ reflections. The $[Y(OH_2)_8]^{3+}$ cation is a distorted dodecahedron with average Y–OH$_2$ separations of 2.39(4) Å (type A site) and 2.34(2) Å (type B site). The crown ether and the chloride ions are hydrogen bonded to metal coordinated water molecules resulting in a polymeric network. The average HOH···O(crown) and HOH···Cl$^-$ separations are 1.80(8) and 2.15(9) Å, respectively.

Introduction

We recently reported the preparation and structural characterization of $[M(OH_2)_8]Cl_3\cdot(15\text{-crown-}5)$ (M = Y [1], Gd [2], Lu [2]). For M = Y the hydrogen bonded crown ether exhibited high thermal motion but no resolvable disorder. A disorder model was resolved for the isostructural M = Gd and M = Lu analogs. In each case the major crown conformation (60% M = Gd, 75% M = Lu) had five strong hydrogen bonding contacts while the minor conformation (40% M = Gd, 25% M = Lu) appeared to be in a much poorer position for hydrogen bonding with the metal coordinated water molecules. In neither case could the hydrogen atoms be located. It was noted that the occupancy of the major conformation was greater for the complex containing the smaller ion (M = Lu). Due to the nature of this disorder we had no reason to believe that it was thermal in nature and did not attempt a low temperature determination of these structures.

As our investigations of this work continued, we isolated a second set of crystals of $[Y(OH_2)_8]Cl_3\cdot(15\text{-crown-}5)$. These crystals behaved entirely differently from any of the $[M(OH_2)_8]Cl_3\cdot(15\text{-crown-}5)$ complexes so far investigated. Disordered $[Y(OH_2)_8]Cl_3\cdot(15\text{-crown-}5)$ [1] melts at 104–108 °C. The crystalline material used for this study melts rapidly below room temperature. Initial examination via X-ray diffraction (at −150 °C necessary to prevent decomposition) revealed the current sample to be isostructural with the $[M(OH_2)_8]Cl_3\cdot(15\text{-crown-}5)$ complexes previously studied. In order to answer questions about the differences in the two crystalline samples of the same complex, to possibly learn more about the crown ether disorder, and to locate the hydrogen atoms, we carried out a complete structural examination of the title complex at −150 °C.

Experimental

The preparation and crystallization of $[Y(OH_2)_8]Cl_3\cdot(15\text{-crown-}5)$ have been detailed before in ref. 1. We carried out this reaction again in order to obtain better crystals for an X-ray diffraction analysis that would allow us to resolve any crown ether disorder. The observed vibrational spectral bands were essentially identical to those observed in ref. 1. Upon removal from the freezer (−20 °C), however, the clear crystals melted rapidly.

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

A clear single crystal of the title complex was mounted on a pin and transferred to the goniometer. The crystal was cooled to −150 °C during data collection using a stream of cold nitrogen gas. 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 the centric $P2_1/n$ from the systematic absences.

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*For Part 6, see ref. 2.

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

Compound	$[Y(OH_2)_8]Cl_3 \cdot (15\text{-crown-5})$	
Color/Shape	transparent/parallelepiped	
Molecular weight	559.7	
Space group	$P2_1/n$	$P2_1/n$ [1]
Temperature (°C)	−150	22
Cell constants		
a (Å)	9.126(3)	9.202(2)
b (Å)	17.104(3)	17.247(3)
c (Å)	15.237(4)	15.208(3)
β (deg)	92.86(2)	92.39(2)
Cell volume (Å^3)	2375.3	2411.5
Molecules/unit cell	4	4
ρ(calc) (g cm^{-3})	1.56	1.54
μ(calc) (cm^{-1})	27.7	
Range of relative transmission factors	98%/99%	
Radiation, graphite monochromator	Mo Kα (λ = 0.71073)	
Maximum crystal dimensions (mm)	0.40 × 0.40 × 0.60	
Scan width	$0.80 + 0.35 \tan\theta$	
Standard reflections	(6, 0, 0) (0, 12, 0) (0, 0, 14)	
Decay of standards	−1.8%	
Reflections measured	4591	
2θ range, deg	$2 < 2\theta < 50$	
Range of h, k, l	+10, +20, ±18	
Reflections observed $[F_o \geqslant 5\sigma(F_o)]$	3399	
No. parameters varied	244	
Weights	$[\sigma(F_o)^2 + 0.00004F_o^2]^{-1}$	
Goodness of fit	1.11	
R	0.035	
R_w	0.036	

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 [3]. Neutral atom scattering factors for Y, Cl, O, C and H were taken from ref. 4 and the scattering was corrected for the real and imaginary components of anomalous dispersion [4].

The final fractional coordinates for the $[Y(OH_2)_8]^{3+}$ cation and the three Cl^- anions from the room temperature structure [1], were used as a starting point in this refinement. The atomic positions of the crown ether were located from a difference Fourier map. No evidence of disorder was observed. The crown ether conformation corresponds to the major form found in the disordered room temperature structures of $[M(OH_2)_8]Cl_3 \cdot (15\text{-crown-5})$ (M = Gd, Lu) [2]. Least-squares refinement with isotropic thermal parameters led to $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.061$. The hydrogen atoms were located from a difference Fourier map and included with fixed contributions ($B = 5.5$ Å^2). Refinement of the nonhydrogen atoms with anisotropic temperature factors led to final values of $R = 0.035$ and $R_w = 0.036$. A final difference Fourier showed no feature greater than 0.5 e$^-$/Å^3. The weighting scheme was based on $[\sigma(F_o)^2 + pF_o^2]^{-1}$ where $p = 0.00004$; no systematic variation of $w(|F_o| - |F_c|)$ *vs.* $|F_o|$ or $(\sin\theta)/\lambda$ was noted. The final values of the positional parameters are given in Table II.

Results and Discussion

The cation environment and atom labelling scheme for $[Y(OH_2)_8]Cl_3 \cdot (15\text{-crown-5})$ are presented in Fig. 1. This structure carried out at −150 °C is isostructural with the room temperature determinations of $[M(OH_2)_8]Cl_3 \cdot (15\text{-crown-5})$ (M = Y [1], Gd [2], Lu [2]) with the exception of no crown ether disorder in the low temperature structure. Bonding parameters and contacts given in Table III for the hydrogen atoms confirm the hydrogen bonding network suggested from the nonhydrogen contacts only used in refs. 1 and 2. The $[Y(OH_2)_8]^{3+}$ cation is hydrogen bonded to two different crown molecules for a total of five $Y{-}OH_2 \cdots O(\text{crown})$ hydrogen bonds. The remaining eleven water molecule hydro-

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

Atom	*x/a*	*y/b*	*z/c*
Y	0.85746(4)	0.18056(2)	0.21852(2)
Cl(1)	0.6651(1)	0.17107(6)	0.49094(6)
Cl(2)	0.1488(1)	0.66352(6)	0.33602(7)
Cl(3)	0.6942(1)	0.24877(6)	0.93709(6)
O(1)	0.9167(3)	0.1636(2)	0.3681(2)
O(2)	0.8076(3)	0.3119(1)	0.2379(2)
O(3)	0.6280(3)	0.1969(1)	0.2918(2)
O(4)	0.7746(3)	0.0520(1)	0.2417(2)
O(5)	0.6711(3)	0.1613(2)	0.1101(2)
O(6)	1.0897(3)	0.2457(2)	0.2430(2)
O(7)	1.0406(3)	0.0894(2)	0.1837(2)
O(8)	0.9382(3)	0.2295(2)	0.0845(2)
O(9)	0.9109(3)	0.4622(2)	0.3676(2)
O(10)	0.9560(3)	0.4385(1)	0.1902(2)
O(11)	0.6721(3)	0.4628(2)	0.1077(2)
O(12)	0.4451(3)	0.4483(2)	0.2299(2)
O(13)	0.6450(3)	0.3870(2)	0.3610(2)
C(1)	1.0541(4)	0.4490(2)	0.3369(3)
C(2)	1.0568(4)	0.4817(2)	0.2449(3)
C(3)	0.9327(5)	0.4718(2)	0.1036(3)
C(4)	0.7957(5)	0.4359(2)	0.0620(3)
C(5)	0.5429(5)	0.4172(2)	0.0866(3)
C(6)	0.4181(5)	0.4503(2)	0.1355(3)
C(7)	0.4292(4)	0.3730(2)	0.2678(3)
C(8)	0.4891(4)	0.3772(2)	0.3621(3)
C(9)	0.7094(5)	0.4110(3)	0.4438(3)
C(10)	0.8747(5)	0.4100(3)	0.4368(3)
H(1)[O(1)]	1.011	0.196	0.402
H(2)[O(1)]	0.841	0.162	0.405
H(1)[O(2)]	0.868	0.362	0.231
H(2)[O(2)]	0.747	0.326	0.281
H(1)[O(3)]	0.623	0.197	0.360
H(2)[O(3)]	0.537	0.181	0.261
H(1)[O(4)]	0.787	0.025	0.303
H(2)[O(4)]	0.730	0.023	0.190
H(1)[O(5)]	0.669	0.168	0.038
H(2)[O(5)]	0.579	0.157	0.121
H(1)[O(6)]	1.169	0.222	0.215
H(2)[O(6)]	1.113	0.255	0.307
H(1)[O(7)]	1.141	0.100	0.177
H(2)[O(7)]	1.042	0.038	0.206
H(1)[O(8)]	0.881	0.236	0.039
H(2)[O(8)]	1.014	0.255	0.067
H(1)[C(1)]	1.127	0.482	0.376
H(2)[C(1)]	1.068	0.374	0.339
H(1)[C(2)]	1.042	0.542	0.239
H(2)[C(2)]	1.157	0.484	0.227
H(1)[C(3)]	1.006	0.458	0.061
H(2)[C(3)]	0.924	0.544	0.108
H(1)[C(4)]	0.796	0.371	0.066
H(2)[C(4)]	0.787	0.449	−0.003
H(1)[C(5)]	0.527	0.424	0.014
H(2)[C(5)]	0.569	0.356	0.104
H(1)[C(6)]	0.400	0.518	0.120
H(2)[C(6)]	0.326	0.429	0.117
H(1)[C(7)]	0.483	0.320	0.242
H(2)[C(7)]	0.315	0.361	0.268
H(1)[C(8)]	0.458	0.319	0.391
H(2)[C(8)]	0.454	0.426	0.400
H(1)[C(9)]	0.681	0.386	0.501
H(2)[C(9)]	0.681	0.468	0.459
H(1)[C(10)]	0.915	0.421	0.498
H(2)[C(10)]	0.901	0.336	0.426

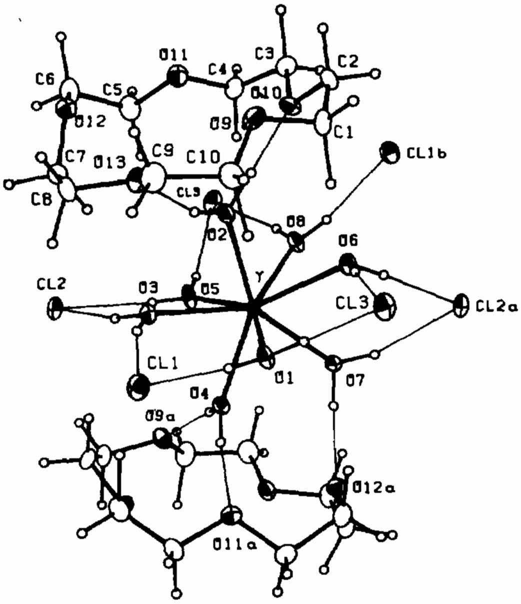

Fig. 1. Cation environment and atom labelling scheme for $[Y(OH_2)_8]Cl_3\cdot$(15-crown-5). The atoms are represented by their 50% probability ellipsoids for thermal motion. The crown ether shown is related to the coordinates in Table II by 1.5 − *x*, *y* − 0.5, 0.5 − *z*. The radii of the hydrogen atoms have been arbitrarily reduced for clarity. The symmetry is indicated in Table III.

gen atoms are hydrogen bonded to chloride anions. Cl(1) has only three such contacts. The average H-OH···O(crown), HOH···Cl^- contacts and corresponding O···O(crown) and O···Cl separations are 1.80(8), 2.15(9), 2.75(4) and 3.08(4) Å, respectively. The average of the 16 O–H···X (O or Cl) angles is 165(8)°. The polymeric network formed by the hydrogen bonding consists of chains of $[M(OH_2)_8]^{3+}$ and 15-crown-5 essentially along *b* with the cations in the direction of *a* and *c* connected via hydrogen bonds to chloride ions. A view of this network and the cell packing (without the chains in the *a* direction) is given in Fig. 2.

Bond distances and angles for the title complex are presented in Table IV. The $[Y(OH_2)_8]^{3+}$ cation is a distorted dodecahedron as determined by the methods used in refs. 5 and 6. The cation geometry is

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

Distances			
H(1)O1–O(1)	1.12	H(2)O1–O(1)	0.91
H(1)O1–Cl(3)[b]	1.97	H(2)O1–Cl(1)	2.13
H(1)O2–O(2)	1.03	H(2)O2–O(2)	0.91
H(1)O2–O(10)	1.68	H(2)O2–O(13)	1.89
H(1)O3–O(3)	1.04	H(2)O3–O(3)	0.97
H(1)O3–Cl(1)	2.06	H(2)O3–Cl(2)[c]	2.21
H(1)O4–O(4)	1.04	H(2)O4–O(4)	1.00
H(1)O4–O(11)[a]	1.76	H(2)O4–O(9)[a]	1.84
H(1)O5–O(5)	1.11	H(2)O5–O(5)	0.86
H(1)O5–Cl(3)[d]	2.09	H(2)O5–Cl(2)[c]	2.22
H(1)O6–O(6)	0.95	H(2)O6–O(6)	1.01
H(1)O6–Cl(2)[a]	2.12	H(2)O6–Cl(3)[b]	2.08
H(1)O7–O(7)	0.95	H(2)O7–O(7)	0.95
H(1)O7–Cl(2)[a]	2.22	H(2)O7–O(12)[a]	1.81
H(1)O8–O(8)	0.85	H(2)O8–O(8)	0.87
H(1)O8–Cl(3)[d]	2.26	H(2)O8–Cl(1)[b]	2.24
O(1)–Cl(1)	3.036(3)	O(1)–Cl(3)[b]	3.082(3)
O(2)–O(10)	2.674(4)	O(2)–O(13)	2.766(4)
O(3)–Cl(1)	3.068(3)	O(3)–Cl(2)[c]	3.164(3)
O(4)–O(11)[a]	2.778(4)	O(4)–O(9)[a]	2.778(4)
O(5)–Cl(3)[d]	3.048(3)	O(5)–Cl(2)[c]	3.072(3)
O(6)–Cl(2)[a]	3.068(3)	O(6)–Cl(3)[b]	3.063(2)
O(7)–Cl(2)[a]	3.133(3)	O(7)–O(12)[a]	2.749(4)
O(8)–Cl(3)[d]	3.100(3)	O(8)–Cl(1)[b]	3.083(3)
Angles			
O(1)–H(1)O1–Cl(3)[b]	168.4	O(1)–H(2)O1–Cl(1)	174.9
O(2)–H(1)O2–O(10)	163.5	O(2)–H(2)O2–O(13)	161.1
O(3)–H(1)O3–Cl(1)	162.1	O(3)–H(2)O3–Cl(2)[c]	165.7
O(4)–H(1)O4–O(11)[a]	166.8	O(4)–H(2)O4–O(9)[a]	154.5
O(5)–H(1)O5–Cl(3)[d]	143.1	O(5)–H(2)O5–Cl(2)[c]	170.3
O(6)–H(1)O6–Cl(2)[a]	174.2	O(6)–H(2)O6–Cl(3)[b]	166.5
O(7)–H(1)O7–Cl(2)[a]	161.1	O(7)–H(2)O7–O(12)[a]	167.8
O(8)–H(1)O8–Cl(3)[d]	168.9	O(8)–H(2)O8–Cl(1)[b]	163.9

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

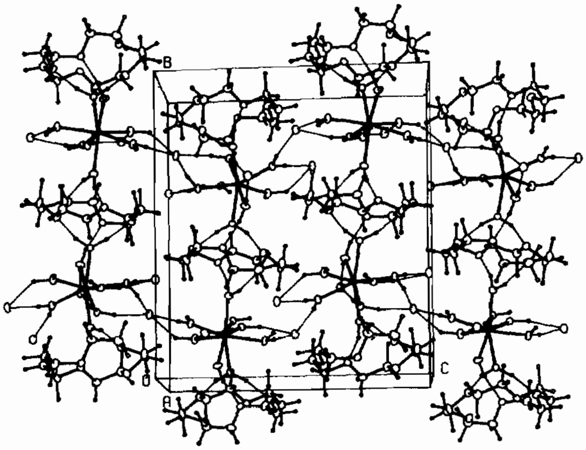

Fig. 2. Cell packing for $[Y(OH_2)_8]Cl_3\cdot$(15-crown-5) depicting the polymeric nature resulting from the hydrogen bonding.

described in more detail in ref. 1. The two types of Y–OH_2 distances average 2.39(4) Å (type A site) and 2.34(2) Å (type B site), are virtually identical to the values observed at 22 °C. As indicated in Table V which compares all the members of this series and two similar structures with the $[M(OH_2)_8]^{3+}$ cation [7, 8], the two other major structural parameters, the $H_2O\cdots O$(crown) and $H_2O\cdots Cl$ separations are also identical at 22 °C (2.76(7), 3.08(4) Å, respectively) and –150 °C (2.75(4), 3.08(4) Å).

The absence of disorder in the crown ether permits a more detailed look at the crown conformation. The average C–C (1.509(7) Å) and C–O (1.432(9) Å) distances and C–O–C (113.1(8)°) angle are not usual for crown ethers [9] and compare nicely with the averages for the same values for the D_{3d} conformation of 18-crown-6 in 18-crown-6·$2(CH_3NO_2)$ [10] (also carried out at –150 °C) of 1.420(4) Å (C–O), 1.500(6) Å (C–C), and 112.0(6)° (C–O–C). There is an interesting variation, however, in the C–C–O angles in the title complex. The O(12)–C(6)–C(5) angle is 112.9(3)°, while the remaining O–C–C angles average 108.0(5)° (108.8(1)° in 18-crown-6·$2(CH_3NO_2)$). An analysis of the crown ether torsion angles (Table VI) indicates further evidence for distortion of this portion of the crown ether molecule. The O–C–C–O torsion angles are all '±g' (±60°) and the C–C–O–C angles are 'a' (±180°) with the exception of C(5)–C(6)–O(12)–C(7) the value of which is –76.0°. The D_{3d} conformation of 18-crown-6 normally found in its complexes with ions and its hydrogen bonded complexes with neutral molecules is $gaag^-aagaag^-aagaag^-$ [11, 12]. For the most part 15-crown-5 in the title complex adopts this conformation but due to the lower symmetry of 15-crown-5 at some point there must be a crossover. This occurs at C(6) such that O(11)–C(5)–C(6)–O(12) is g^- and O(12)–C(7)–C(8)–O(13) is also g^-. A similar crown ether conformation can be found in reference [13] detailing the structure of $CuBr_2(OH_2)_2\cdot$(15-crown-5). The torsion angle sequence is identical to that found here, although less of a distortion from 180° is found for the angle corresponding to C(5)–C(6)–O(12)–C(7) (–118° in [13]).

Oxygen atoms O(10), O(11), O(12), and O(13) are planar to with 0.13 Å. The deviations alternate ±0.1 Å, O(9) is 1.33 Å out of this plane. In 18-crown-6·$2(CH_3NO_2)$ the six oxygen atoms alternate ±0.24 Å from their mean plane.

Conclusions

From Table V we see very little change in the $H_2O\cdots O$ or $H_2O\cdots Cl$ hydrogen bonded contacts for the series $[M(OH_2)_8]Cl_3\cdot$(15-crown-5) (M = Gd, Y,

TABLE IV. Bond Distances (Å) and Angles (deg) for $[Y(OH_2)_8]Cl_3 \cdot (15\text{-crown-}5)$

Distances			
Y–O(1)	2.334(3)	Y–O(2)	2.313(2)
Y–O(3)	2.438(2)	Y–O(4)	2.357(2)
Y–O(5)	2.334(3)	Y–O(6)	2.407(3)
Y–O(7)	2.365(3)	Y–O(8)	2.359(2)
O(9)–C(1)	1.429(5)	O(9)–C(10)	1.433(5)
O(10)–C(2)	1.418(5)	O(10)–C(3)	1.443(5)
O(11)–C(4)	1.431(5)	O(11)–C(5)	1.436(5)
O(12)–C(6)	1.447(5)	O(12)–C(7)	1.423(5)
O(13)–C(8)	1.433(5)	O(13)–C(9)	1.425(5)
C(1)–C(2)	1.510(6)	C(3)–C(4)	1.503(6)
C(5)–C(6)	1.502(6)	C(7)–C(8)	1.513(6)
C(9)–C(10)	1.518(6)		

Angles			
O(1)–Y–O(2)	91.93(9)	O(1)–Y–O(3)	74.30(9)
O(2)–Y–O(3)	69.58(9)	O(1)–Y–O(4)	78.35(9)
O(2)–Y–O(4)	145.04(9)	O(3)–Y–O(4)	75.46(8)
O(1)–Y–O(5)	142.97(9)	O(2)–Y–O(5)	95.0(1)
O(3)–Y–O(5)	74.23(9)	O(4)–Y–O(5)	75.30(9)
O(1)–Y–O(6)	75.35(9)	O(2)–Y–O(6)	73.03(9)
O(3)–Y–O(6)	130.21(8)	O(4)–Y–O(6)	134.04(9)
O(5)–Y–O(6)	141.26(9)	O(1)–Y–O(7)	90.29(9)
O(2)–Y–O(7)	144.51(9)	O(3)–Y–O(7)	144.22(9)
O(4)–Y–O(7)	69.80(9)	O(5)–Y–O(7)	104.3(1)
O(6)–Y–O(7)	73.33(9)	O(1)–Y–O(8)	145.33(9)
O(2)–Y–O(8)	80.67(9)	O(3)–Y–O(8)	131.94(9)
O(4)–Y–O(8)	125.25(9)	O(5)–Y–O(8)	71.67(9)
O(6)–Y–O(8)	70.08(8)	O(7)–Y–O(8)	77.58(9)
C(1)–O(9)–C(10)	113.0(3)	C(2)–O(10)–C(3)	113.2(3)
C(4)–O(11)–C(5)	112.0(3)	C(6)–O(12)–C(7)	114.2(3)
C(8)–O(13)–C(9)	112.9(3)	O(9)–C(1)–C(2)	107.6(3)
O(10)–C(2)–C(1)	108.2(3)	O(10)–C(3)–C(4)	107.8(3)
O(11)–C(4)–C(3)	108.9(3)	O(11)–C(5)–C(6)	108.6(3)
O(12)–C(6)–C(5)	112.9(3)	O(12)–C(7)–C(8)	107.6(3)
O(13)–C(8)–C(7)	107.9(3)	O(13)–C(9)–C(10)	107.6(3)
O(9)–C(10)–C(9)	108.1(3)		

TABLE V. Comparative Aspects of the Series $[M(OH_2)_8]Cl_3 \cdot (15\text{-crown-}5)$ (M = Y, Gd, Lu)

Complex	M^{3+} ionic radius[a]	M–O average (Å)	$M–O_A$ average (Å)[b]	$M–O_B$ average (Å)	$H_2O \cdots O(crown)$[c] average (Å)	$H_2O \cdots Cl$ average (Å)	Reference
$[Gd(OH_2)_8]Cl_3 \cdot (15\text{-crown-}5)$	1.053	2.41(4)	2.44(4)	2.39(4)	2.74(8) (2.8(1))	3.07(3)	2
$[Gd(OH_2)_8]Cl_3 \cdot 2(C_{10}H_8N_2)$	1.053	2.40(7)	2.45(1)	2.35(1)		3.09(5)	7
$[Y(OH_2)_8]Cl_3 \cdot (15\text{-crown-}5)$	1.019	2.37(4)	2.40(3)	2.35(3)	2.76(7)	3.08(4)	1
$[Y(OH_2)_8]Cl_3 \cdot (15\text{-crown-}5)$[d]	1.019	2.36(4)	2.39(4)	2.34(2)	2.75(4)	3.08(4)	this study
$[Y(OH_2)_8]Cl_3 \cdot 2(C_{10}H_8N_2)$	1.019	2.38(6)	2.425(6)	2.327(6)		3.110(5)	8
$[Lu(OH_2)_8]Cl_3 \cdot (15\text{-crown-}5)$	0.977	2.35(4)	2.38(4)	2.32(2)	2.75(6) (3.1(2))	3.08(3)	2

[a] Ionic radii for CN = 8 from ref. 14. [b] Terms A and B for a dodecahedron defined in refs. 5, 6. [c] Minor form of the crown ether in parentheses. [d] Structure determination carried out at –150 °C.

Lu). The normal decrease in $M–OH_2$ separations corresponding to decreasing M^{3+} radius is observed (Gd > Y > Lu). All three of the complexes stable at room temperature were disordered, with the major crown ether conformation (which had better hydrogen bonding contacts) present in only 60% occupancy for M = Gd (cell volume = 2430.0 Å^3) and 75% occupancy for M = Lu (cell volume = 2388.5 Å^3).

TABLE VI. Torsion Angles for $[Y(OH_2)_8]Cl_3$·(15-crown-5)

Atoms	Angle
O(9)–C(1)–C(2)–O(10)	−64.0
C(1)–C(2)–O(10)–C(3)	171.3
C(2)–O(10)–C(3)–C(4)	−163.9
O(10)–C(3)–C(4)–O(11)	68.2
C(3)–C(4)–O(11)–C(5)	−165.8
C(4)–O(11)–C(5)–C(6)	−178.7
O(11)–C(5)–C(6)–O(12)	−60.5
C(5)–C(6)–O(12)–C(7)	−76.0
C(6)–O(12)–C(7)–C(8)	169.0
O(12)–C(7)–C(8)–O(13)	−69.0
C(7)–C(8)–O(13)–C(9)	165.3
C(8)–O(13)–C(9)–C(10)	173.4
O(13)–C(9)–C(10)–O(9)	59.1
C(9)–C(10)–O(9)–C(1)	−162.1
C(10)–O(9)–C(1)–C(2)	157.5

The current determination of $[Y(OH_2)_8]Cl_3$·(15-crown-5) (−150 °C, cell volume = 2375.3 Å^3) exhibits almost identical structural parameters to the 22 °C structure (cell volume = 2411.5 Å^3), however, the crystalline sample used for the current study melts below room temperature.

All of the above suggests that the disorder observed in the higher melting and disordered M = Gd, Y, and Lu structures is indeed static in nature and present only to stabilize the overall packing in the unit cell. The absence of disorder in the low temperature structure of M = Y is therefore, probably not a result of the temperature of data collection, but rather the result of a different mode of crystallization. We plan to continue our studies in this area to further investigate how the method of crystallization affects the structural results obtained.

Supplementary Material

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

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