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f-Element/Crown Ether Complexes.
14.* Synthesis and Crystal Structure of $[Lu(OH_2)_8][Na(12\text{-crown-}4)_2]Cl_4 \cdot 2H_2O$

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Abstract

$[Lu(OH_2)_8][Na(12\text{-crown-}4)_2]Cl_4 \cdot 2H_2O$ crystallizes at 5 °C from a reaction mixture of $LuCl_3 \cdot 6H_2O$ and 12-crown-4 (in a 1:3 solution of CH_3OH: CH_3CN) following the addition of NaCl. The crystal structure of this complex has been determined by single crystal X-ray diffraction techniques. The title complex is monoclinic, $P2_1/c$, with $a = 15.265(2)$, $b = 14.203(2)$, $c = 16.030(1)$ Å, $\beta = 94.570(9)°$, and $D_c = 1.67$ g cm^{-3} for $Z = 4$ formula units. Primarily organic and inorganic zones exist essentially in layers parallel to *bc*. The organic layers consist of $[Na(12\text{-crown-}4)_2]^+$ cations with the oxygen atoms forming a square antiprism around Na^+ (Na–O = 2.49(3) Å average). The $[Lu(OH_2)_8]^{3+}$ cations (also essentially square antiprismatic, Lu–O = 2.34(2) Å), the chloride ions, and the two uncoordinated water molecules are hydrogen bonded forming a network in the *b* and *c* directions. The two unique cations are packed linearly along *a* in a staggered square face to square face arrangement.

Introduction

Much of our current research [1–11] in f-element/crown ether chemistry has focused on obtaining structural results for crown ether complexes of as many of the hydrated lanthanide ions (and Y^{3+}) as possible, in order to investigate subtle effects on structure and bonding that result from the smooth decrease in Ln^{3+} ionic radii [12] from La to Lu. It is equally as important to study the effects of anion and solvent for a given crown ether and metal ion. The influence of the anion can often be structurally decisive, and factors such as the hardness of an anion have been shown to markedly affect extraction coefficients [13]. Chloride ions have been said to be deleterious to the synthesis of crown ether complexes if they are not stabilized by hydrogen bonding from proton solvents or other proton donors [13].

One area of interest regarding chloride counter ions in our research has been the number of tight ion pairs *versus* hydrogen bonded anions. We have utilized hydrated Ln(III) chloride salts in polar solvents. Water is strongly retained by the later lanthanides and water molecules have stabilized the cations by coordination and the anions by hydrogen bonding. We have observed primarily aquated Ln(III) chloride complexes with hydrogen bonded crown ether complexes of 15-crown-5: $[M(OH_2)_8]Cl_3 \cdot 15\text{-crown-}5$ (M = Y [3, 4], Gd [5], Lu [5]), 18-crown-6: $[Dy(OH_2)_8]Cl_3 \cdot 18\text{-crown-}6 \cdot 4H_2O$ [8]; and 12-crown-4: $[Lu(OH_2)_8]Cl_3 \cdot 1.5(12\text{-crown-}4) \cdot 2H_2O$ [11]. When 18-crown-6 coordinates mid to late Ln(III) chlorides directly, one tight ion pair is retained along with two coordinated water molecules, as in $[MCl(OH_2)_2(18\text{-crown-}6)]Cl_2 \cdot 2H_2O$ (M = Sm, Gd, Tb) [6] and $[M(OH_2)_7(OHMe)][MCl(OH_2)_2(18\text{-crown-}6)]_2Cl_7 \cdot 2H_2O$ (M = Dy, Y) [7]. Under anhydrous conditions two tight ion pairs were observed in $[GdCl_2(OHEt)(18\text{-crown-}6)]Cl$ [14]. No chloride anions are in the metal ion's primary coordination sphere in the 12-crown-4 complex, $[Tb(OH_2)_5(12\text{-crown-}4)]Cl_3 \cdot 2H_2O$ [1]. We have attempted to assess the effect of increasing the chloride ion concentration in solution on the overall structure and number of these tight ion pairs. We present here the structure of $[Lu(OH_2)_8][Na(12\text{-crown-}4)_2]Cl_4 \cdot 2H_2O$ which resulted from this line of investigation.

Experimental

Synthesis and Crystallization of $[Lu(OH_2)_8][Na(12\text{-crown-}4)_2]Cl_4 \cdot 2H_2O$

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 $LuCl_3 \cdot 6H_2O$ in 5 ml of the same solvent mixture. The reaction mixture was heated to 60 °C for 1 h at which time 1 mmol of NaCl was added to the reaction mixture. The solution was cooled to 22 °C and the solution volume reduced to 1/3 of its original volume. No crystallization occurred after several weeks at 5 °C. Finally, the mixture was transferred to a test tube and allowed to slowly

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*For Part 13, see ref. 1.

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evaporate at 5 °C. A very large (2.5 × 2.5 × 2.5 mm) crystal formed after four months. One fragment of this crystal, which is stable to the moisture in air, was used for the X-ray diffraction data collection, and others for the melting point analysis. The transparent fragments turned opaque at 80 °C, began discoloring at 289 °C, and were completely dark brown at 360 °C. An elemental analysis was performed on the gummy residue left after evaporation was complete. *Anal.* Calc. for $[Lu(OH_2)_8][Na(12\text{-crown-}4)_2]Cl_4 \cdot 2H_2O$: C, 22.03; H, 6.01. Found: C, 20.46; H, 5.59%.

X-ray Data Collection, Structure Determination and Refinement for $[Lu(OH_2)_8][Na(12\text{-crown-}4)_2]Cl_4 \cdot 2H_2O$

A transparent fragment from a large 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.

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

Compound	$[Lu(OH_2)_8][Na(12\text{-crown-}4)_2]Cl_4 \cdot 2H_2O$
Color/shape	clear/irregular fragment
Molecular wt.	872.3
Space group	$P2_1/c$
Temperature (°C)	20
Cell constants	
a (Å)	15.265(2)
b (Å)	14.203(2)
c (Å)	16.030(1)
β (deg)	94.570(9)
Cell volume (Å^3)	3464.3
Formula units/unit cell	4
D_c (g cm^{-3})	1.67
μ(calc) (cm^{-1})	30.7
Range of relative transmission factors (%)	85/100
Radiation, graphite monochromator	Mo Kα (λ = 0.71073)
Maximum crystal dimensions (mm)	0.10 × 0.13 × 0.20
Scan width	$0.80 + 0.35 \tan\theta$
Standard reflections	14, 0, 0; 0, 10, 0; 0, 0, 12
Decay of standards	±3%
Reflections measured	6594
2θ range (deg)	$2 < 2\theta < 50°$
Range of *h*, *k*, *l*	+18, +16, ±19
Reflections observed $[F_o \geqslant 5\sigma(F_o)]$	4189
No. of parameters varied	361
Weights	$[\sigma(F_o)^2]^{-1}$
GOF[a]	1.31
R	0.034
R_w	0.034

[a] Goodness of fit.

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 [15]. Neutral atom scattering factors for Lu, Na, Cl, O, C and H were taken from reference 16 and the scattering was corrected for the real and imaginary components of anomalous dispersion [16].

The lutetium atom position was determined via inspection of a Patterson function map. A difference Fourier map phased on the lutetium atom readily revealed the positions of the nonhydrogen atoms. Least-squares refinement with isotropic thermal parameters led to $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.060$. 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 $R = 0.034$ and $R_w = 0.034$. A final difference Fourier showed no feature greater than 0.6 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 and Discussion

The addition of NaCl to a reaction mixture containing $LuCl_3 \cdot 6H_2O$ and 12-crown-4 has little effect on cation or anion environment. In the absence of NaCl, $[Lu(OH_2)_8]Cl_3 \cdot 1.5(12\text{-crown-}4) \cdot 2H_2O$ [11] crystallizes, containing $[Lu(OH_2)_8]^{3+}$ cations and hydrogen bonded Cl^- anions, as well as hydrogen bonded 12-crown-4 in the lattice. The structure of $[Na(12\text{-crown-}4)_2]Cl \cdot 5H_2O$ is also known [17]. In the title complex certain aspects of each structure are retained: octaaquated Lu(III) ions, sandwich $[Na(12\text{-crown-}4)_2]^+$ ions, hydrogen bonded chloride anions, and noncoordinated hydrogen bonded water molecules. In addition, as observed in $[Na(12\text{-crown-}4)_2]Cl \cdot 5H_2O$ (but not in $[Lu(OH_2)_8]Cl_3 \cdot 1.5(12\text{-crown-}4) \cdot 2H_2O$), the organic and inorganic portions of the molecules reside in layers (parallel to *bc* in the title complex).

The formula unit, atom labelling, and hydrogen bonding contacts for the eight water molecules coordinated to the Lu(III) cation are depicted in Fig. 1. Bond distances and angles are given in Table III. The separation of organic and inorganic layers parallel to *bc* can be seen in the cell packing diagram

TABLE II. Final Fractional Coordinates for $[Lu(OH_2)_8][Na(12\text{-crown-}4)_2]Cl_4 \cdot 2H_2O$

Atom	*x/a*	*y/b*	*z/c*
Lu	0.46509(2)	0.24752(2)	0.94886(2)
Na	0.9642(2)	0.2509(2)	0.8682(1)
Cl(1)	0.6851(1)	0.4485(1)	1.1018(1)
Cl(2)	0.3365(1)	−0.0411(1)	0.9089(1)
Cl(3)	0.5893(1)	0.4986(1)	0.8233(1)
Cl(4)	0.3124(1)	0.2909(2)	0.6933(1)
O(1)	0.5444(3)	0.2809(3)	0.8329(3)
O(2)	0.5566(4)	0.1164(4)	0.9333(3)
O(3)	0.5503(3)	0.2230(3)	1.0732(3)
O(4)	0.5350(3)	0.3901(3)	0.9770(3)
O(5)	0.3916(3)	0.1589(3)	0.8395(3)
O(6)	0.3803(4)	0.1356(3)	1.0100(3)
O(7)	0.3838(3)	0.3237(3)	1.0498(3)
O(8)	0.3710(3)	0.3488(3)	0.8743(3)
O(9)	0.5585(5)	−0.0351(5)	0.8283(4)
O(10)	0.5543(3)	0.3438(3)	1.2050(3)
O(11)	0.9141(3)	0.3178(3)	1.0004(3)
O(12)	0.8812(3)	0.1312(3)	0.9476(3)
O(13)	0.8308(3)	0.1997(3)	0.7859(3)
O(14)	0.8616(3)	0.3839(3)	0.8394(3)
O(15)	1.0924(3)	0.1873(3)	0.9541(3)
O(16)	1.0306(3)	0.1139(4)	0.7976(3)
O(17)	1.0184(3)	0.2947(3)	0.7294(3)
O(18)	1.0838(3)	0.3672(3)	0.8858(3)
C(1)	0.8539(5)	0.2600(6)	1.0405(4)
C(2)	0.8800(5)	0.1584(5)	1.0329(4)
C(3)	0.7980(5)	0.1084(6)	0.9080(5)
C(4)	0.8045(5)	0.1102(6)	0.8148(5)
C(5)	0.7624(4)	0.2679(6)	0.7760(5)
C(6)	0.8027(5)	0.3618(5)	0.7688(4)
C(7)	0.8205(5)	0.4204(6)	0.9101(5)
C(8)	0.8858(5)	0.4125(5)	0.9849(5)
C(9)	1.1095(5)	0.0926(5)	0.9290(5)
C(10)	1.1132(5)	0.0869(5)	0.8371(5)
C(11)	1.0281(5)	0.1301(6)	0.7103(5)
C(12)	1.0668(5)	0.2229(5)	0.6883(5)
C(13)	1.0651(5)	0.3817(5)	0.7389(4)
C(14)	1.1307(5)	0.3819(6)	0.8128(4)
C(15)	1.1398(5)	0.3465(5)	0.9596(4)
C(16)	1.1678(5)	0.2454(6)	0.9614(5)

(Fig. 2). The organic layer consists of $[Na(12\text{-crown-}4)_2]^+$ cations, with charge separation accomplished by the crown ether ligands. The $[Lu(OH_2)_8]^{3+}$ cations, chloride anions, and uncoordinated water molecules, comprise the inorganic layer and are hydrogen bonded forming a complex network in the *b* and *c* directions. The coordination polyhedra for both the 8-coordinate Na^+ and Lu^{3+} ions can best be described as square antiprisms as discussed below. These coordination polyhedra are packed linearly along *a* in a staggered square face to square face arrangement.

As mentioned above the $[Na(12\text{-crown-}4)_2]^+$ cation is square antiprismatic with all eight oxygen atoms coordinated to the metal ion. The Na–O separations average 2.49(3) Å. The O···O contacts forming the square planes (*s*) average 2.80(2) Å, while those between planes (*l*) average 3.37(6) Å. The *s*/*l* ratio is 0.83 and the Na^+ ion is 1.50 and 1.51 Å from the mean plane of O(11)–O(14) and O(15)–O(18), respectively. Each square face is planar to within

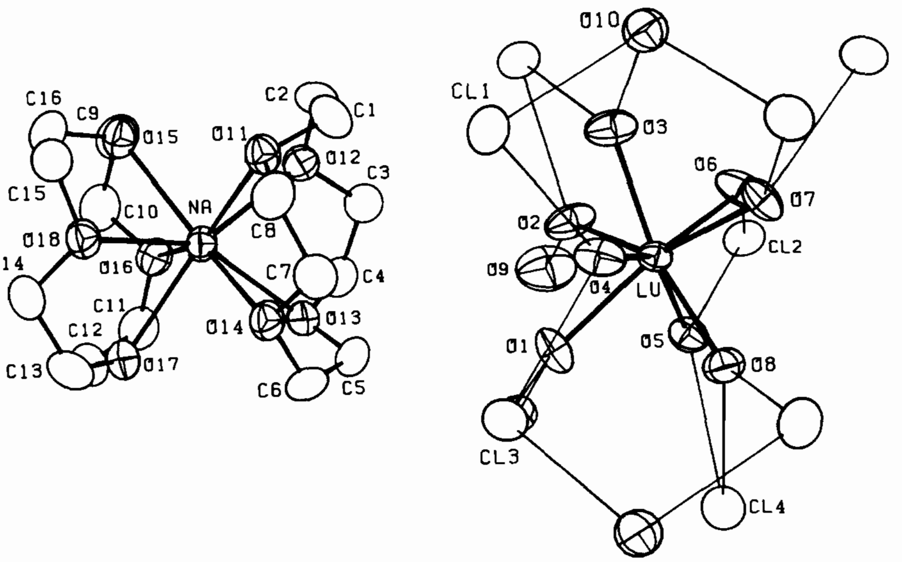

Fig. 1. Formula unit and coordinated water molecule hydrogen bonding contacts for $[Lu(OH_2)_8][Na(12\text{-crown-}4)_2]Cl_4 \cdot 2H_2O$. The atoms are represented by their 50% probability ellipsoids for thermal motion. The symmetries of the contacts are given in Table V.

TABLE III. Bond Distances (A) and Angles (deg) for $[Lu(OH_2)_8][Na(12\text{-crown-}4)_2]Cl_4 \cdot 2H_2O$

Distances			
Lu–O(1)	2.346(4)	Lu–O(2)	2.354(5)
Lu–O(3)	2.319(5)	Lu–O(4)	2.317(5)
Lu–O(5)	2.367(4)	Lu–O(6)	2.316(5)
Lu–O(7)	2.376(4)	Lu–O(8)	2.299(5)
Na–O(11)	2.497(5)	Na–O(12)	2.525(5)
Na–O(13)	2.448(5)	Na–O(14)	2.473(5)
Na–O(15)	2.472(5)	Na–O(16)	2.506(6)
Na–O(17)	2.514(5)	Na–O(18)	2.462(5)
O(11)–C(1)	1.422(8)	O(11)–C(8)	1.429(8)
O(12)–C(2)	1.423(8)	O(12)–C(3)	1.410(8)
O(13)–C(4)	1.422(8)	O(13)–C(5)	1.423(8)
O(14)–C(6)	1.422(7)	O(14)–C(7)	1.436(8)
O(15)–C(9)	1.433(8)	O(15)–C(16)	1.415(8)
O(16)–C(10)	1.420(9)	O(16)–C(11)	1.416(8)
O(17)–C(12)	1.448(8)	O(17)–C(13)	1.427(8)
O(18)–C(14)	1.435(8)	O(18)–C(15)	1.434(8)
C(1)–C(2)	1.50(1)	C(3)–C(4)	1.51(1)
C(5)–C(6)	1.48(1)	C(7)–C(8)	1.502(9)
C(9)–C(10)	1.48(1)	C(11)–C(12)	1.50(1)
C(13)–C(14)	1.490(9)	C(15)–C(16)	1.50(1)
Angles			
O(1)–Lu–O(2)	74.2(2)	O(1)–Lu–O(3)	115.0(2)
O(2)–Lu–O(3)	71.0(2)	O(1)–Lu–O(4)	73.7(2)
O(2)–Lu–O(4)	116.4(2)	O(3)–Lu–O(4)	75.2(2)
O(1)–Lu–O(5)	76.4(2)	O(2)–Lu–O(5)	75.6(2)
O(3)–Lu–O(5)	139.2(2)	O(4)–Lu–O(5)	142.5(2)
O(1)–Lu–O(6)	144.6(2)	O(2)–Lu–O(6)	81.9(2)
O(3)–Lu–O(6)	80.0(2)	O(4)–Lu–O(6)	141.4(2)
O(5)–Lu–O(6)	72.6(2)	O(1)–Lu–O(7)	141.1(2)
O(2)–Lu–O(7)	141.2(2)	O(3)–Lu–O(7)	76.7(2)
O(4)–Lu–O(7)	74.2(2)	O(5)–Lu–O(7)	120.3(2)
O(6)–Lu–O(7)	71.6(2)	O(1)–Lu–O(8)	78.6(2)
O(2)–Lu–O(8)	142.3(2)	O(3)–Lu–O(8)	145.6(2)
O(4)–Lu–O(8)	79.2(2)	O(5)–Lu–O(8)	73.1(2)
O(6)–Lu–O(8)	107.6(2)	O(7)–Lu–O(8)	74.4(2)
O(11)–Na–O(12)	68.2(2)	O(11)–Na–O(13)	105.8(2)
O(12)–Na–O(13)	69.0(2)	O(11)–Na–O(14)	68.6(2)
O(12)–Na–O(14)	105.8(2)	O(13)–Na–O(14)	68.8(2)
O(11)–Na–O(15)	87.1(2)	O(12)–Na–O(15)	83.1(2)
O(13)–Na–O(15)	141.2(2)	O(14)–Na–O(15)	147.6(2)
O(11)–Na–O(16)	147.3(2)	O(12)–Na–O(16)	86.7(2)
O(13)–Na–O(16)	82.8(2)	O(14)–Na–O(16)	141.4(2)
O(15)–Na–O(16)	68.7(2)	O(11)–Na–O(17)	143.3(2)
O(12)–Na–O(17)	145.8(2)	O(13)–Na–O(17)	85.1(2)
O(14)–Na–O(17)	83.9(2)	O(15)–Na–O(17)	106.3(2)
O(16)–Na–O(17)	67.6(2)	O(11)–Na–O(18)	85.6(2)
O(12)–Na–O(18)	142.4(2)	O(13)–Na–O(18)	147.0(2)
O(14)–Na–O(18)	87.8(2)	O(15)–Na–O(18)	68.6(2)
O(16)–Na–O(18)	104.5(2)	O(17)–Na–O(18)	69.0(2)
Na–O(11)–C(1)	114.6(4)	Na–O(11)–C(8)	108.6(4)
C(1)–O(11)–C(8)	115.1(6)	Na–O(12)–C(2)	110.3(4)
Na–O(12)–C(3)	113.5(4)	C(2)–O(12)–C(3)	114.5(6)
Na–O(13)–C(4)	109.5(4)	Na–O(13)–C(5)	115.4(4)
C(4)–O(13)–C(5)	114.9(6)	Na–O(14)–C(6)	109.3(4)
Na–O(14)–C(7)	116.0(4)	C(6)–O(14)–C(7)	114.7(5)
Na–O(15)–C(9)	109.9(4)	Na–O(15)–C(16)	115.8(4)
C(9)–O(15)–C(16)	114.0(6)	Na–O(16)–C(10)	112.7(4)

(continued)

TABLE III. *(continued)*

Angles			
Na–O(16)–C(11)	109.9(4)	C(10)–O(16)–C(11)	115.9(6)
Na–O(17)–C(12)	116.3(4)	Na–O(17)–C(13)	108.4(4)
C(12)–O(17)–C(13)	113.0(5)	Na–O(18)–C(14)	114.7(4)
Na–O(18)–C(15)	110.1(4)	C(14)–O(18)–C(15)	113.5(5)
O(11)–C(1)–C(2)	109.4(6)	O(12)–C(2)–C(1)	111.2(6)
O(12)–C(3)–C(4)	108.3(6)	O(13)–C(4)–C(3)	112.4(6)
O(13)–C(5)–C(6)	108.5(6)	O(14)–C(6)–C(5)	112.2(6)
O(14)–C(7)–C(8)	107.4(6)	O(11)–C(8)–C(7)	112.4(6)
O(15)–C(9)–C(10)	110.7(6)	O(16)–C(10)–C(9)	109.0(6)
O(16)–C(11)–C(12)	113.3(6)	O(17)–C(12)–C(11)	106.8(6)
O(17)–C(13)–C(14)	112.7(6)	O(18)–C(14)–C(13)	107.4(6)
O(18)–C(15)–C(16)	111.3(6)	O(15)–C(16)–C(15)	109.2(6)

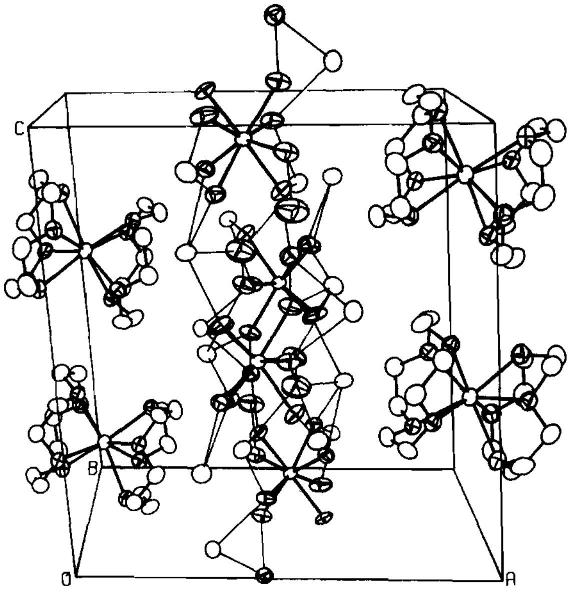

Fig. 2. Cell packing diagram.

0.02 Å. These values are in excellent agreement with three other structures containing this ion: [Na(12-crown-4)$_2$]Cl·5H$_2$O [17] (Na–O = 2.496 Å, *s*/*l* = 0.816, Na is 1.528 Å from each square face), [Na(12-crown-4)$_2$][OH]·8H$_2$O [18] (2.485 Å, 0.83, 1.497 and 1.505 Å) and [Na(12-crown-4)$_2$][ClO$_4$] [19] (2.49(5) Å, 0.82, 1.53(1) Å).

As observed in the previous three structures containing this cation, the crown ether exhibits approximate C_4 symmetry (Table IV). This conformation is well suited for four crown ether contacts on the same side of the molecule as for example in metal complexes where the metal is too large to fit within the cavity [20, 21]. The infrequently observed C_s conformation (e.g., as in CuCl$_2$(12-crown-4) [22]) also directs the four oxygen atoms to the same side, but the C_i conformation observed in the free crown ether [23], UO$_2$(NO$_3$)$_2$(OH$_2$)$_2$·12-crown-4 [24], and for one of the crown ethers in [Lu(OH$_2$)$_8$]Cl$_3$·1.5(12-crown-4)·2H$_2$O [11] is best suited for two oxygen interactions (e.g., hydrogen bonds) on opposite sides of the molecule. The average internal bonding parameters of the crown ethers in the title complex are normal: C–O = 1.426(9) Å, C–C = 1.50(1) Å, C–O–C = 114.4(9)°, O–Cα–Cβ = 108.2(9)°, O–Cβ–Cα = 112.0(8)°.

The [Lu(OH$_2$)$_8$]$^{3+}$ cation also has approximate square antiprismatic geometry. O(1)–O(4) comprise one square face which is planar to within 0.02 Å. The other face (O(5)–O(8)) is planar to within 0.01 Å. The Lu atom resides 1.24 Å out of the former plane and 1.27 Å out of the latter. The other shape

TABLE IV. Torsion Angles for [Lu(OH$_2$)$_8$][Na(12-crown-4)$_2$]Cl$_4$·2H$_2$O

O(11)–C(1)–C(2)–O(12)	–58.8
C(1)–C(2)–O(12)–C(3)	–81.3
C(2)–O(12)–C(3)–C(4)	163.0
O(12)–C(3)–C(4)–O(13)	–59.6
C(3)–C(4)–O(13)–C(5)	–80.0
C(4)–O(13)–C(5)–C(6)	164.6
O(13)–C(5)–C(6)–O(14)	–57.7
C(5)–C(6)–O(14)–C(7)	–82.8
C(6)–O(14)–C(7)–C(8)	163.5
O(14)–C(7)–C(8)–O(11)	–58.4
C(7)–C(8)–O(11)–C(1)	–78.3
C(8)–O(11)–C(1)–C(2)	165.4
O(15)–C(9)–C(10)–O(16)	–61.8
C(9)–C(10)–O(16)–C(11)	168.0
C(10)–O(16)–C(11)–C(12)	–77.2
O(16)–C(11)–C(12)–O(17)	–57.3
C(11)–C(12)–O(17)–C(13)	159.6
C(12)–O(17)–C(13)–C(14)	–81.6
O(17)–C(13)–C(14)–O(18)	–60.8
C(13)–C(14)–O(18)–C(15)	167.9
C(14)–O(18)–C(15)–C(16)	–79.9
O(18)–C(15)–C(16)–O(15)	–55.6
C(15)–C(16)–O(15)–C(9)	161.5
C(16)–O(15)–C(9)–C(10)	–81.6

TABLE V. Hydrogen Bonding Contact Geometries for $[Lu(OH_2)_8][Na(12\text{-crown-}4)_2]Cl_4 \cdot 2H_2O$

Distances			
O(1)–Cl(3)	3.172(5)	O(1)–O(10)[a]	2.722(7)
O(2)–Cl(2)[b]	3.090(5)	O(2)–O(9)	2.732(8)
O(3)–Cl(2)[b]	3.109(5)	O(3)–O(10)	2.718(7)
O(4)–Cl(1)	3.035(5)	O(4)–Cl(3)	3.075(5)
O(5)–Cl(2)	3.188(5)	O(5)–Cl(4)	3.166(5)
O(6)–Cl(2)	3.034(5)	O(6)–Cl(4)[c]	3.357(5)
O(7)–Cl(3)[d]	3.248(5)	O(7)–Cl(4)[c]	3.087(5)
O(8)–Cl(1)[d]	3.036(5)	O(8)–Cl(4)	3.080(5)
O(9)–Cl(3)[e]	3.218(6)	O(9)–Cl(4)[e]	3.196(7)
O(10)–Cl(1)	3.076(5)	O(10)–Cl(3)[d]	3.141(5)
Angles			
Cl(3)–O(1)–O(10)[a]	124.9(2)	Cl(2)[b]–O(2)–O(9)	101.6(2)
Cl(2)[b]–O(3)–O(10)	118.4(2)	Cl(1)–O(4)–Cl(3)	98.9(1)
Cl(2)–O(5)–Cl(4)	133.7(2)	Cl(2)–O(6)–Cl(4)[c]	130.9(2)
Cl(3)[d]–O(7)–Cl(4)[c]	88.7(1)	Cl(1)[d]–O(8)–Cl(4)	107.9(1)
Cl(3)[e]–O(9)–Cl(4)[e]	115.7(2)	Cl(1)–O(10)–Cl(3)[d]	93.0(1)

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

determining parameters include: the average of the sides of the squares s = 2.79(4) Å, the average of the l edges, 2.93(6) Å, the s/l ratio, 0.95, the dihedral angle between the square faces, 2.12°, and the average dihedral angles at the l edges, 51.6°. The distortion of the metal geometry toward dodecahedral symmetry is relatively small as indicated by the dihedral angles at the 'B' edges [25] of 1.3, 10.1, 50.6, and 48.3°, and the angles ϕ, of 20.2 and 22.4°, which assess the planarity of the trapezoids. These compare reasonably well with ideal values reported in references [25–27] for the square antiprism [0.0, 0.0, 52.4, 52.4, 24.5, 24.5°].

The Lu–O separations range from 2.299(5) Å to 2.376(4) Å and average 2.34(3) Å. These are in agreement with the average Lu–O distances in two other complexes containing this cation: $[Lu(OH_2)_8]Cl_3 \cdot$ 15-crown-5 [5] (Lu–O = 2.35(4) Å) and $[Lu(OH_2)_8]$-$Cl_3 \cdot 1.5(12\text{-crown-}4) \cdot 2H_2O$ [11] (Lu–O = 2.33(3) Å). The former has dodecahedral geometry and the latter is a distorted bicapped trigonal prism. The differences observed in the geometry of this cation in the three crystallographically characterized examples may arise from the different packing environments and hydrogen bonding networks.

Finally, the hydrogen bonding contacts indicative of hydrogen bonding (no water molecule hydrogens were located) are given in Table V. O(1), O(2), and O(3) each have one hydrogen bond to an uncoordinated water molecule (O···O average = 2.724(6) Å). The remaining 17 hydrogen bonds are to chloride anions (O···Cl average = 3.14(9) Å). O(10) donates and accepts a total of four hydrogen bonds, O(9) donates two but only accepts one. (This is one possible explanation for the greater thermal motion observed for O(9)). Cl(1) has three hydrogen bonding contacts, Cl(2) has four, and Cl(3) and Cl(4) have five each. As a result of the number of hydrogen bonds to Cl(3) and Cl(4) distortions occur involving these atoms including somewhat longer $O \cdots Cl^-$ contacts and distorted $Cl^- \cdots O \cdots Cl^-$ contact angles.

Supplementary Material

Tables of calculated hydrogen atom positions, thermal parameters, least-squares planes results, and observed and calculated structure factors are available from the authors on request (15 pages).

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References

1 R. D. Rogers, *Inorg. Chim. Acta, 133,* 175 (1987).
2 R. D. Rogers and E. J. Voss, *J. Coord. Chem., Sect. A,* (1987) in press.
3 R. D. Rogers and L. K. Kurihara, *Inorg. Chim. Acta, 116,* 171 (1986).
4 R. D. Rogers and L. K. Kurihara, *Inorg. Chim. Acta, 129,* 277 (1987).

5 R. D. Rogers and L. K. Kurihara, *Inorg. Chim. Acta, 130,* 131 (1987).
6 R. D. Rogers and L. K. Kurihara, *Inorg. Chem., 26,* 1498 (1987).
7 R. D. Rogers and L. K. Kurihara, *Inorg. Chem.,* (1987), in press.
8 R. D. Rogers, *Inorg. Chim. Acta,* (1987) in press.
9 R. D. Rogers and L. K. Kurihara, *J. Less-Common Met., 127,* 199 (1987).
10 R. D. Rogers and L. K. Kurihara, *J. Inclusion Phenom., 4,* 351 (1986).
11 R. D. Rogers, *J. Coord. Chem., Sect. A,* (1987) in press.
12 R. D. Shannon, *Acta Crystallogr., Sect. A, 32,* 751 (1986).
13 R. Hilgenfeld and W. Saenger, in F. Vogtle and E. Weber (eds.), 'Host Guest Complex Chemistry: Macrocycles-Synthesis, Structures, Applications', Springer Verlag, Berlin, 1985, p. 43.
14 F. Forsellini, F. Benetollo, G. Bombieri, A. Cassol and G. DePaoli, *Inorg. Chim. Acta, 109,* 167 (1985).
15 G. M. Sheldrick, 'SHELX', a system of computer programs for X-ray structure determination, University of Cambridge, 1976 (as locally modified).
16 'International Tables for X-ray Crystallography', Vol. IV, Kynoch Press, Birmingham, 1972.
17 F. P. van Remoortere and F. P. Boer, *Inorg. Chem., 13,* 2071 (1974).
18 F. P. Boer, M. A. Neuman, F. P. van Remoortere and E. C. Steiner, *Inorg. Chem., 13,* 2826 (1974).
19 E. Mason and H. A. Eick, *Acta Crystallogr., Sect. B, 38,* 1821 (1982).
20 M. J. Bovill, D. J. Chadwick, I. O. Sutherland and D. Watkin, *J. Chem. Soc., Perkin Trans. 2,* 1529 (1980).
21 J. W. H. M. Uiterwijk, S. Harkema, B. W. van de Waal, F. Gobel and H. T. M. Nibbeling, *J. Chem. Soc., Perkin Trans. 2,* 1843 (1983).
22 F. P. van Remoortere, F. P. Boer and E. C. Steiner, *Acta Crystallogr., Sect. B, 31,* 1420 (1975).
23 P. Groth, *Acta Chem. Scand., Ser. A, 32,* 279 (1978).
24 P. L. Ritger, J. H. Burns and G. Bombieri, *Inorg. Chim. Acta, 77,* L217 (1983).
25 M. G. B. Drew, *Coord. Chem. Rev., 24,* 179 (1977).
26 J. L Hoard and J. V. Silverton, *Inorg. Chem., 2,* 235 (1963).
27 M. A. Porai-Koshits and L. A. Aslanov, *Zh. Strukt. Khim., 13,* 266 (1972).