

## *f*-Element/Crown Ether Complexes. 27.\* The Synthesis and Crystal Structure of [Ce(NO<sub>3</sub>)<sub>3</sub>(OH<sub>2</sub>)(12-crown-4)]·12-crown-4

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**Abstract.** A unique cerium nitrate complex, [Ce(NO<sub>3</sub>)<sub>3</sub>(OH<sub>2</sub>)(12-crown-4)]·12-crown-4, has been crystallized from the reaction of hydrated cerium nitrate and 12-crown-4. It crystallizes in the orthorhombic space group, *Pnma*, with (at -150°C)  $a = 22.901(5)$ ,  $b = 13.547(3)$ ,  $c = 8.422(1)$  Å, and  $D_x = 1.77$  g cm<sup>-3</sup> for  $Z = 4$  formula units. A final *R* value of 0.048 was obtained utilizing 2059 unique observed [ $F_o \geq 5\sigma(F_o)$ ] reflections. The Ce atom resides on a crystallographic mirror plane and is 11-coordinate, coordinated to three bidentate nitrate groups, one water molecule and the four oxygens of one 12-crown-4 molecule. The water molecule hydrogen bonds a second 12-crown-4 unit. Both unique crown molecules and one of the nitrate anions are severely disordered.

**Key words.** 12-crown-4, cerium nitrate complex, X-ray crystal structure.

**Supplementary Data** relating to this article are deposited with the British Library as Supplementary Publication No. SUP 82087 (8 pages).

### 1. Introduction

Complexation reactions of crown ethers and lanthanide salts have been studied extensively under anhydrous conditions. These have been mostly solution studies. Crystallization has proved difficult, possibly due to the lack of strong intermolecular interactions [2]. Recent studies have shown that, by allowing small amounts of water into these systems, crystallization may more readily be realized [3]. This increase in the ease of crystallization appears to be a result of strong hydrogen bonding, although often strong donors such as water molecules can preclude metal/crown complexation. We have investigated reactions of this type utilizing hydrated lanthanide chloride salts with 12-crown-4 in anhydrous solvents which yielded crystalline complexes suitable for X-ray diffraction studies [3]. When too much water is present crown ethers have been found only to accept hydrogen bonds from metal-coordinated water molecules [4]; however, lanthanide/crown ether complexation can often still be realized in spite of competition with the water molecules. The reactions of 12-crown-4 with hydrated lanthanide nitrates illustrates this point.

\* For part 26, see reference [1].

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Under totally anhydrous conditions, but utilizing hydrated salts, Bünzli prepared and isolated anhydrous 12-crown-4 complexes of lanthanide nitrates [2]. He has also reported the crystal structures of one of these ( $M = \text{Eu}[5]$ ). Utilizing hydrated  $\text{Y}(\text{NO}_3)_3$  and 12-crown-4 in an anhydrous solvent mixture of acetonitrile and methanol we prepared and structurally characterized the anhydrous and isostructural  $\text{Y}(\text{NO}_3)_3(12\text{-crown-4})$  [6]. The isostructural Gd complex was confirmed using preliminary unit cell data [7]. Under identical conditions we have observed, as did Bünzli [2], that La and Ce crystallize as monohydrates. In the crystalline form isolated, the extra water molecule results in the crystallization of an extra molecule of 12-crown-4. We intended to structurally characterize the series from La–Pr in order to study how the decreasing size of the lanthanide metal results in a coordination number drop of 11 to 10. We quickly realized, however, that crystals of these complexes form very poorly and contain a tremendous amount of disorder. We thus carried out a study on the best crystal we could obtain of one member of the series to confirm the nature of the complex.

## 2. Experimental

### 2.1. PREPARATION OF $[\text{M}(\text{NO}_3)_3(\text{OH}_2)(12\text{-crown-4})]\cdot 12\text{-crown-4}$ ( $M = \text{La}, \text{Ce}$ )

Acetonitrile and methanol were dried by reflux over  $\text{CaH}_2$  for 4 h. A solution was prepared by mixing the two in a 3:1 ratio and stored over 4 Å molecular sieves until used. A solution of hydrated cerium nitrate salt (1.236 mmol) and 12-crown-4 (1.236 mmol, 0.2 mL) was prepared in 4 mL of the 3:1 solvent mixture. The solution was heated with stirring for 2.75 h at 52°C. The solution was then removed from heat and stirring and allowed to cool to room temperature where it remained overnight. The solution was then refrigerated at 5°C for two days and –5°C for five days. The solvent was reduced in volume with vacuum by half and refrigerated again. Single crystals suitable for crystallographic study were obtained after 24 h at –5°C. Anal. calcd. for  $[\text{Ce}(\text{NO}_3)_3(\text{OH}_2)(12\text{-crown-4})]\cdot 12\text{-crown-4}$ : C, 27.59; H, 4.93; N, 6.04. Found: C, 27.25; H, 5.07; N, 5.79.

In a similar fashion the analogous La complex was prepared. The structure of the La complex was confirmed by comparison of cell parameters and space group with the isostructural Ce complex.

### 2.2. X-RAY DATA COLLECTION, STRUCTURE DETERMINATION AND REFINEMENT FOR $[\text{Ce}(\text{NO}_3)_3(\text{OH}_2)(12\text{-crown-4})]\cdot 12\text{-crown-4}$

A transparent 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. The space group was determined to be either the centric  $Pnma$  or acentric  $Pn2_1a$  from the systematic absences. Statistical tests indicated that the space group was centric and the subsequent solution and successful refinement of the structure in the space group  $Pnma$  despite the presence of disorder confirmed this. A summary of data collection parameters is given in Table I.

Table I. Crystal data and summary of intensity data collection and structure refinement

|   |  |              |
|---|--|--------------|
| Cmpd.   | [M(NO <sub>3</sub> ) <sub>3</sub> (OH <sub>2</sub> )(12-crown-4)]·12-crown-4 | M = La       |
| Color/Shape   | colorless/fragment   |              |
| For. wt.  | 696.6  |              |
| Crystal system  | orthorhombic   | orthorhombic |
| Space group   | <i>Pnma</i>  |              |
| Temp., °C   | -150   |              |
| Cell Constants <sup>a</sup>   |  |              |
| <i>a</i> , Å  | 22.901(5)  | 23.018(4)    |
| <i>b</i> , Å  | 13.547(3)  | 13.286(4)    |
| <i>c</i> , Å  | 8.422(1)   | 8.128(2)     |
| Cell vol., Å <sup>3</sup>   | 2613   |              |
| Formula units/unit cell   | 4  |              |
| <i>D</i> <sub>calc</sub> , g cm <sup>-3</sup>   | 1.77   |              |
| <i>μ</i> <sub>calc</sub> , cm <sup>-1</sup>   | 17.0   |              |
| Diffractometer/Scan   | Enraf-Nonius CAD-4/θ-2θ  |              |
| Range of relative transm. factors, %  | 90/100   |              |
| Radiation, graphite monochromator   | MoK <sub>α</sub> (λ = 0.71073)   |              |
| Max Crystal dimensions, mm  | 0.25 × 0.30 × 0.35   |              |
| Scan width  | 0.80 + 0.35 tan θ  |              |
| Standard reflections  | 14, 0, 0; 0, 12, 0; 008  |              |
| Decay of standards  | ± 4%   |              |
| Reflections measured  | 2627   |              |
| 2θ range, deg   | 2 ≤ 2θ ≤ 50  |              |
| Range of <i>h</i> , <i>k</i> , <i>l</i>   | 0 → 27, 0 → 16, 0 → 10   |              |
| Reflections observed [ <i>F</i> <sub>o</sub> ≥ 5σ( <i>F</i> <sub>o</sub> )] <sup>b</sup>          | 2059   |              |
| Computer programs <sup>c</sup>  | SHELX [8]  |              |
| Structure solution  | Heavy atom techniques  |              |
| No. of parameters varied  | 172  |              |
| Weights   | [σ( <i>F</i> <sub>o</sub> ) <sup>2</sup> ] <sup>-1</sup>                     |              |
| GOF   | 3.8  |              |
| <i>R</i> = Σ    <i>F</i> <sub>o</sub>    -    <i>F</i> <sub>c</sub>   /Σ    <i>F</i> <sub>o</sub> | 0.048  |              |
| <i>R</i> <sub>w</sub>   | 0.053  |              |
| Largest feature of final diff. map  | 0.3e <sup>-</sup> Å <sup>-3</sup>  |              |

<sup>a</sup> Least-squares refinement of ((sin θ)/λ)<sup>2</sup> values for 25 reflections θ > 21°.

<sup>b</sup> Corrections: Lorentz polarization and absorption (empirical, psi scan).

<sup>c</sup> Neutral scattering factors and anomalous dispersion corrections from Ref. [9].

Initially a 20°C data set was collected. It was obvious from this data that the structure was disordered regardless of whether *Pnma* or *Pn2<sub>1</sub>a* was chosen as the space group. A -150°C data set was then collected in the hope of providing better resolution to the disorder problem. Again disorder was clearly evident regardless of the space group chosen. We thus chose the centric *Pnma* and proceeded to resolve the disorder. Ce, O(8), O(2), N(1), O(9) and O(11) reside on a mirror plane in *Pnma*. The nitrate group containing N(1) and O(2) is disordered such that two orientations of O(1) (50% occupancy) are observed. The second nitrate group and its mirror related position and the mirror related positions of the coordinated crown oxygen atoms are normal. The normal C<sub>4</sub> conformation of 12-crown-4 will not support that type of mirror operation and the carbon atoms of this macrocycle are

Table II. Final fractional coordinates for  $[\text{Ce}(\text{NO}_3)_3(\text{OH}_2)(12\text{-crown-4})]\cdot 12\text{-crown-4}$ 

| Atom               | $x/a$      | $y/b$     | $z/c$      | $B_{(\text{eqv})}^a$ |
|--------------------|------------|-----------|------------|----------------------|
| Ce                 | 0.17029(2) | 0.2500    | 1.13832(6) | 0.82                 |
| O(1)               | 0.2355(4)  | 0.3221(7) | 1.362(1)   | 2.0 <sup>c</sup>     |
| O(1) <sup>'b</sup> | 0.2520(4)  | 0.1652(7) | 1.313(1)   | 1.0 <sup>c</sup>     |
| O(2)               | 0.2851(4)  | 0.2500    | 1.532(1)   | 4.53                 |
| O(3)               | 0.1487(2)  | 0.4358(4) | 1.1818(6)  | 1.81                 |
| O(4)               | 0.1231(3)  | 0.3449(4) | 1.3761(7)  | 1.90                 |
| O(5)               | 0.1094(3)  | 0.5022(4) | 1.3909(8)  | 3.48                 |
| O(6)               | 0.2541(2)  | 0.1497(3) | 0.9938(5)  | 1.39                 |
| O(7)               | 0.1443(2)  | 0.1484(4) | 0.8701(6)  | 1.68                 |
| O(8)               | 0.0626(3)  | 0.2500    | 1.1150(8)  | 1.55                 |
| O(9)               | -0.0545(3) | 0.2500    | 1.3630(9)  | 1.73                 |
| O(10)              | -0.0105(4) | 0.4008(7) | 1.160(1)   | 1.2 <sup>c</sup>     |
| O(10) <sup>'</sup> | -0.0245(5) | 0.1021(8) | 1.139(1)   | 1.5 <sup>c</sup>     |
| O(11)              | -0.0430(4) | 0.2500    | 0.919(1)   | 3.9 <sup>c</sup>     |
| N(1)               | 0.2577(4)  | 0.2500    | 1.405(1)   | 2.28                 |
| N(2)               | 0.1266(3)  | 0.4278(5) | 1.3200(8)  | 2.11                 |
| C(1)               | 0.3094(6)  | 0.1988(9) | 0.999(2)   | 1.7 <sup>c</sup>     |
| C(2)               | 0.2470(6)  | 0.097(1)  | 0.837(2)   | 2.4 <sup>c</sup>     |
| C(3)               | 0.1852(6)  | 0.060(1)  | 0.839(2)   | 2.2 <sup>c</sup>     |
| C(4)               | 0.1286(7)  | 0.193(1)  | 0.723(2)   | 2.8 <sup>c</sup>     |
| C(1) <sup>'</sup>  | 0.3045(6)  | 0.299(1)  | 0.921(2)   | 2.0 <sup>c</sup>     |
| C(2) <sup>'</sup>  | 0.2358(6)  | 0.432(1)  | 0.899(2)   | 2.2 <sup>c</sup>     |
| C(3) <sup>'</sup>  | 0.1897(6)  | 0.398(1)  | 0.784(2)   | 2.5 <sup>c</sup>     |
| C(4) <sup>'</sup>  | 0.1041(7)  | 0.291(1)  | 0.762(2)   | 2.9 <sup>c</sup>     |
| C(5)               | -0.0256(3) | 0.3384(6) | 1.417(1)   | 2.10                 |
| C(6)               | -0.0425(4) | 0.4191(6) | 1.302(1)   | 2.57                 |
| C(7)               | -0.0444(6) | 0.416(1)  | 1.011(2)   | 2.5 <sup>c</sup>     |
| C(8)               | -0.0851(8) | 0.324(1)  | 0.971(2)   | 4.7 <sup>c</sup>     |
| C(7) <sup>'</sup>  | -0.080(1)  | 0.110(2)  | 1.042(3)   | 6.2 <sup>c</sup>     |
| C(8) <sup>'</sup>  | -0.068(1)  | 0.153(2)  | 0.906(4)   | 8.0 <sup>c</sup>     |

<sup>a</sup>  $B_{(\text{eqv})} = 4/3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab \cos \gamma \beta_{12} + a \cos \beta \beta_{13} + bc \cos \alpha \beta_{23}]$ .

<sup>b</sup> Primed and unprimed atoms of like number refer to disordered atoms and were refined at 50% occupancy each.

<sup>c</sup> Atom refined isotropically.

disordered (C(1)—C(4), C(1)<sup>'</sup>—C(4)<sup>'</sup> - 50% occupancy). The hydrogen bonded crown ether is also disordered. C(5) and C(6) are related normally by the mirror. O(10), C(7) and C(8) have two orientations, both refined at 50% occupancy. The hydrogen atoms were not included in the final refinement. Refinement of nonhydrogen atoms with anisotropic temperature factors led to the final values of  $R = 0.048$  and  $R_w = 0.053$ . The final values of the positional parameters are given in Table II.

### 3. Discussion

The larger size of the early lanthanides Ce and Pr and the related La is apparently responsible for the structural differences in the title complex and the other struc-

turally characterized lanthanide nitrate/12-crown-4 complexes  $[\text{Eu}(\text{NO}_3)_3(12\text{-crown-4})]$  [5] and  $[\text{Y}(\text{NO}_3)_3(12\text{-crown-4})]$  [6]. The larger early lanthanide ions support the higher coordination number of 11. Coordination of a second crown molecule would be extremely unlikely on steric grounds and thus the best donor molecules left in solution are the unidentate water molecules. Coordination of a water molecule in the title complex brings with it a hydrogen bonded 12-crown-4. A review of the structural reports for the Eu and Y complexes reveals that these already sterically crowded 10-coordinate complexes are unlikely to be able to support the 11-coordinate geometry observed in the title complex.

An ORTEP illustration of  $[\text{Ce}(\text{NO}_3)_3(\text{OH}_2)(12\text{-crown-4})] \cdot 12\text{-crown-4}$  is presented in Figure 1, and bond distances and angles are found in Table III. The 11-coordinate cerium appears to have a distorted 1-6-4 polyhedron [10]. The Ce, water molecule (O(8)) and nitrate atoms N(1) and O(2) reside on a crystallographic mirror plane and severe disorder exists (see Experimental). The three nitrate groups are bidentate (Ce—O = 2.61(2) Å, average) with O(1) disordered.

The coordinated 12-crown-4 is tetradentate with an average Ce—O separation of 2.68(3) Å. This crown ether adopts the normal  $C_4$  conformation normally associated with coordinated 12-crown-4. Unfortunately this conformation cannot support a mirror plane bisecting C—C bonds and the carbon atoms are disordered. The two unique sets of carbon atoms are C(1), C(3), C(4)', C(2)' ( $\alpha$  carbons planar to within 0.065 Å, Ce 2.39 Å out of the plane) and C(1)', C(2), C(4), C(3)' ( $\beta$  carbons planar

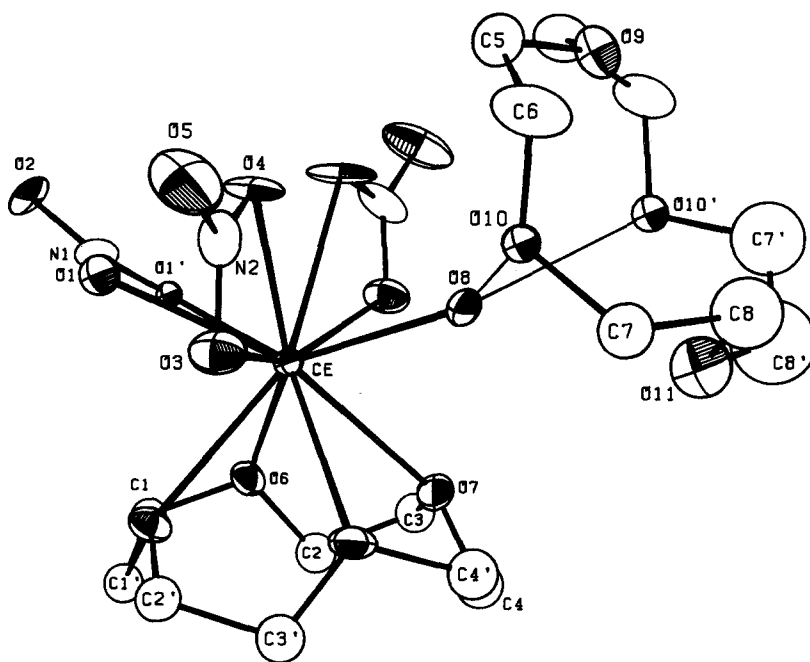


Fig. 1. Structure and atom labelling scheme for  $[\text{Ce}(\text{NO}_3)_3(\text{OH}_2)(12\text{-crown-4})] \cdot 12\text{-crown-4}$ . The atoms labelled (shown with 50% probability ellipsoids) are in the same asymmetric unit. Those atoms designated with primes refer to atoms in the disorder model described in the Experimental section.

Table III. Bond distances (Å) and angles (deg) for [Ce(NO<sub>3</sub>)<sub>3</sub>(OH<sub>2</sub>)(12-crown-4)]·12-crown-4

| Atoms                          | Distance | Atoms                          | Distance |
|--------------------------------|----------|--------------------------------|----------|
| Ce—O(1)                        | 2.593(9) | Ce—O(1)'                       | 2.65(1)  |
| Ce—O(3)                        | 2.592(5) | Ce—O(4)                        | 2.613(6) |
| Ce—O(6)                        | 2.648(4) | Ce—O(7)                        | 2.711(5) |
| Ce—O(8)                        | 2.474(6) | O(1)—N(1)                      | 1.16(1)  |
| O(1)—N(1)                      | 1.39(1)  | O(2)—N(1)                      | 1.24(1)  |
| O(3)—N(2)                      | 1.273(8) | O(4)—N(2)                      | 1.221(9) |
| O(5)—N(2)                      | 1.235(9) | O(6)—C(1)                      | 1.43(1)  |
| O(6)—C(2)                      | 1.51(2)  | O(6) <sup>a</sup> —C(1)'       | 1.48(1)  |
| O(6) <sup>a</sup> —C(2)'       | 1.43(1)  | O(7)—C(3)                      | 1.54(2)  |
| O(7)—C(4)                      | 1.43(2)  | O(7) <sup>a</sup> —C(3)'       | 1.41(2)  |
| O(7) <sup>a</sup> —C(4)'       | 1.53(2)  | C(1)—C(1)'                     | 1.51(2)  |
| C(2)—C(3)                      | 1.50(2)  | C(4)—C(4)'                     | 1.48(2)  |
| C(2)′—C(3)′                    | 1.50(2)  | O(9)—C(5)                      | 1.441(9) |
| O(10)—C(6)                     | 1.43(1)  | O(10)—C(7)                     | 1.49(2)  |
| O(11)—C(8)                     | 1.45(2)  | O(11)—C(8)′                    | 1.43(3)  |
| O(10)′—C(7)′                   | 1.51(3)  | O(10)′—C(6) <sup>a</sup>       | 1.46(1)  |
| C(5)—C(6)                      | 1.50(1)  | C(7)—C(8)                      | 1.60(2)  |
| C(8)′—C(7)′                    | 1.32(4)  |                                |          |
| Atoms                          | Angle    | Atoms                          | Angle    |
| O(1)—Ce—O(1)′                  | 49.5(3)  | O(1)—Ce—O(3)                   | 69.0(2)  |
| O(1)—Ce—O(4)                   | 59.8(2)  | O(1)—Ce—O(6)                   | 96.3(2)  |
| O(1)—Ce—O(7)                   | 157.2(2) | O(1)—Ce—O(8)                   | 129.2(2) |
| O(1)′—Ce—O(3)                  | 118.5(2) | O(1)′—Ce—O(4)                  | 94.4(3)  |
| O(1)′—Ce—O(6)                  | 61.4(2)  | O(1)′—Ce—O(7)                  | 113.6(2) |
| O(1)′—Ce—O(8)                  | 138.5(2) | O(3)—Ce—O(4)                   | 48.3(2)  |
| O(3)—Ce—O(6)                   | 134.6(1) | O(3)—Ce—O(7)                   | 124.7(2) |
| O(3)—Ce—O(8)                   | 79.7(1)  | O(4)—Ce—O(6)                   | 154.7(2) |
| O(4)—Ce—O(7)                   | 142.9(2) | O(4)—Ce—O(8)                   | 69.4(2)  |
| O(6)—Ce—O(7)                   | 61.0(1)  | O(6)—Ce—O(8)                   | 133.3(1) |
| O(7)—Ce—O(8)                   | 73.5(2)  | O(1)—Ce—O(3) <sup>a</sup>      | 111.9(2) |
| O(1)—Ce—O(4) <sup>a</sup>      | 82.4(2)  | O(1)—Ce—O(6) <sup>a</sup>      | 73.9(2)  |
| O(1)—Ce—O(7) <sup>a</sup>      | 122.6(2) | O(1)′—Ce—O(3) <sup>a</sup>     | 68.6(2)  |
| O(1)′—Ce—O(4) <sup>a</sup>     | 69.6(2)  | O(1)′—Ce—O(6) <sup>a</sup>     | 88.1(2)  |
| O(1)′—Ce—O(7) <sup>a</sup>     | 147.2(2) | O(3)—Ce—O(3) <sup>a</sup>      | 152.5(2) |
| O(3)—Ce—O(4) <sup>a</sup>      | 106.9(2) | O(3)—Ce—O(6) <sup>a</sup>      | 72.9(1)  |
| O(3)—Ce—O(7) <sup>a</sup>      | 65.4(2)  | O(4)—Ce—O(4) <sup>a</sup>      | 58.9(2)  |
| O(4)—Ce—O(6) <sup>a</sup>      | 113.5(2) | O(4)—Ce—O(7) <sup>a</sup>      | 107.3(2) |
| O(6)—Ce—O(6) <sup>a</sup>      | 61.7(2)  | O(6)—Ce—O(7) <sup>a</sup>      | 92.1(1)  |
| O(7)—Ce—O(7) <sup>a</sup>      | 61.0(2)  | Ce—O(1)—N(1)                   | 99.6(6)  |
| Ce—O(1)′—N(1)                  | 91.0(5)  | Ce—O(3)—N(2)                   | 97.0(4)  |
| Ce—O(4)—N(2)                   | 97.4(4)  | Ce—O(6)—C(1)                   | 112.9(6) |
| Ce—O(6)—C(2)                   | 124.5(6) | Ce—O(6) <sup>a</sup> —C(1)′    | 120.8(6) |
| Ce—O(6) <sup>a</sup> —C(2)′    | 116.3(6) | Ce—O(7)—C(3)                   | 113.8(6) |
| Ce—O(7)—C(4)                   | 124.4(7) | Ce—O(7) <sup>a</sup> —C(3)′    | 119.3(7) |
| Ce—O(7) <sup>a</sup> —C(4)′    | 110.8(6) | O(1)—N(1)—O(1)′                | 118.5(9) |
| O(1)—N(1)—O(2)                 | 119.8(6) | O(1)′—N(1)—O(2)                | 121.8(5) |
| O(3)—N(2)—O(4)                 | 117.3(6) | O(3)—N(2)—O(5)                 | 119.9(6) |
| O(4)—N(2)—O(5)                 | 122.9(7) | C(1)—O(6)—C(2)                 | 109.9(8) |
| C(3)—O(7)—C(4)                 | 109.4(9) | C(1)′—O(6) <sup>a</sup> —C(2)′ | 111.3(8) |
| C(3)′—O(7) <sup>a</sup> —C(4)′ | 112.0(9) | O(6)—C(1)—C(1)′                | 110(1)   |

Table III. (continued).

| Atoms                          | Angle    | Atoms                           | Angle    |
|--------------------------------|----------|---------------------------------|----------|
| O(6)—C(2)—C(3)                 | 104(1)   | O(7)—C(3)—C(2)                  | 109(1)   |
| O(7)—C(4)—C(4)'                | 106(1)   | O(6) <sup>a</sup> —C(1)'—C(1)   | 108(1)   |
| O(6) <sup>a</sup> —C(2)'—C(3)' | 109(1)   | O(7) <sup>a</sup> —C(3)'—C(2)'  | 109(1)   |
| O(7) <sup>a</sup> —C(4)'—C(4)  | 113(1)   |                                 |          |
| C(5)—O(9)—C(5) <sup>a</sup>    | 112.3(8) | C(6)—O(10)—C(7)                 | 114.8(9) |
| C(8)—O(11)—C(8)'               | 113(1)   | C(6) <sup>a</sup> —O(10)'—C(7)' | 107(1)   |
| O(9)—C(5)—C(6)                 | 106.6(6) | C(5)—C(6)—O(10)                 | 106.2(7) |
| O(10)—C(7)—C(8)                | 112(1)   | O(11)—C(8)—C(7)                 | 102(1)   |
| O(11)—C(8)'—C(7)'              | 115(2)   | O(10)'—C(7)'—C(8)'              | 109(2)   |

<sup>a</sup> Atoms related to those in Table II by the crystallographic mirror plane.

to within 0.055 Å, Ce 2.92 Å out of the plane). All four oxygen atoms are planar by symmetry with the Ce atom residing 1.86 Å above the plane. This same type of disorder was observed and better resolved in the structures of [MCl<sub>2</sub>(OH<sub>2</sub>)<sub>2</sub>(12-crown-4)]Cl (M = Ho–Lu) [3]. Interestingly, the 12-crown-4 molecules in [M(NO<sub>3</sub>)(12-crown-4)] [5, 6] are severely distorted from the normal C<sub>4</sub> conformation and the four oxygen atoms are decidedly nonplanar.

The oxygen atom of the water molecule resides 2.474(6) Å from the metal ion. It is hydrogen bonded to O(10) and O(10)' and their mirror-related positions in the disordered uncomplexed ether. The unique O(8)⋯O(10) and O(8)⋯O(10)' separations are 2.67(1) and 2.83(1) Å, respectively. The disorder in this crown ether was poorly resolved. Portions of the molecule (C(5), C(6), and O(9)) were clearly related by the imposed mirror plane, while the remainder of the atoms exhibited two different conformations. The disorder of this ligand may result from two factors. First, only two oxygen atoms of the ether are hydrogen bonded and the molecule thus does not adopt the normal C<sub>4</sub> conformation. The remainder of the molecule is free to adopt various conformations. Second, a view of the unit cell and a review of intermolecular contacts reveals that there appears to be little steric influence to impose a single conformation.

Although we would have preferred to characterize the entire series of Ln(NO<sub>3</sub>)<sub>3</sub>/12-crown-4 complexes in order to compare subtle structural differences, the current study has halted this investigation. Comparison of structures with as much disorder and esd's as high as the title complex would not be productive. We will, however, continue similar investigations with other ions including mixed ion complexes such as [La(NO<sub>3</sub>)(OH<sub>2</sub>)<sub>4</sub>(12-crown-4)]Cl<sub>2</sub> and [LaCl<sub>2</sub>(NO<sub>3</sub>)(12-crown-4)]<sub>2</sub> [7].

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