

Direct Comparison of the Preparation and Structural Features of Crown Ether and Polyethylene Glycol Complexes of $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$

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The reactions of $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$ in 3/1 $\text{CH}_3\text{CN}/\text{CH}_3\text{OH}$ with 12-crown-4, 15-crown-5, 18-crown-6, dibenzo-18-crown-6, triethylene glycol (EO3), tetraethylene glycol (EO4), pentaethylene glycol (EO5), hexaethylene glycol (EO6), heptaethylene glycol (EO7), 1,5,9,13,17,21-hexathiacyclotetradecane-3,11,19-triol (S6OL), and 1,5,9,13-tetrathiacyclohexadecane-3,11-diol (S4OL) have been investigated. Many of the glycol complexes crystallize identically from H_2O or the organic solvent. Competitive complexation between 12-crown-4 and EO4 favors crystallization of the glycol complex. A crystalline complex with 15-crown-5 directly coordinated to the Nd^{3+} ion could only be isolated by electrocrystallization. The use of LiCl as a salting out agent and the use of an excess of the glycol ligands were also investigated. X-ray structural analysis of the crystalline complexes was carried out. The complexes reported include the following. $[\text{NdCl}_3(15\text{-crown-5})]$: monoclinic, $P2_1/c$, $a = 8.174$ (3) Å, $b = 14.234$ (5) Å, $c = 14.180$ (5) Å, $\beta = 104.80$ (3)°, $D_{\text{calcd}} = 1.93$ g cm^{-3} for $Z = 4$. $[\text{NdCl}(\text{OH})_2(18\text{-crown-6})]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$: orthorhombic, $P2_12_12_1$, $a = 7.438$ (3) Å, $b = 15.994$ (4) Å, $c = 18.966$ (5) Å, $D_{\text{calcd}} = 1.73$ g cm^{-3} for $Z = 4$. $[\text{Nd}(\text{EO4})_2]_4[\text{NdCl}_6]\text{Cl}_9$: tetragonal, $I422$, $a = 17.595$ (6) Å, $c = 17.257$ (4) Å, $D_{\text{calcd}} = 1.74$ g cm^{-3} for $Z = 2$. $[\text{NdCl}_2(\text{OH})_2(\text{EO5})]\text{Cl} \cdot \text{H}_2\text{O}$: monoclinic, $P2_1/c$, $a = 13.412$ (2) Å, $b = 9.780$ (4) Å, $c = 14.461$ (3) Å, $\beta = 102.58$ (1)°, $D_{\text{calcd}} = 1.88$ g cm^{-3} for $Z = 4$. $[\text{NdCl}(\text{OH})_2(\text{EO6})]\text{Cl}_2$: monoclinic, $P2_1/c$, $a = 7.485$ (2) Å, $b = 29.943$ (5) Å, $c = 9.197$ (2) Å, $\beta = 99.99$ (2)°, $D_{\text{calcd}} = 1.80$ g cm^{-3} for $Z = 4$. $[\text{Nd}(\text{OH})_2(\text{EO7})]\text{Cl}_3 \cdot \text{H}_2\text{O}$: monoclinic, $P2_1/c$, $a = 9.053$ (5) Å, $b = 30.216$ (9) Å, $c = 9.691$ (4) Å, $\beta = 113.77$ (7)°, $D_{\text{calcd}} = 1.73$ g cm^{-3} for $Z = 4$. $[\text{Nd}(\text{OH})_2(\text{OHMe})_2]\text{Cl}_3$: orthorhombic, $Pbca$, $a = 12.266$ (2) Å, $b = 12.614$ (2) Å, $c = 19.204$ (1) Å, $D_{\text{calcd}} = 1.97$ g cm^{-3} for $Z = 8$. Except for the 15-crown-5 complex, which is 8-coordinate, and the $[\text{Nd}(\text{EO4})_2]^{3+}$ cation and heptaethylene glycol complex, which are 10-coordinate, the complexes are 9-coordinate tricapped trigonal prismatic. The glycol ligands all exhibit a helical wrapping pattern around the Nd^{3+} ions, while the larger crown ethers attempt to fold around the cations.

Introduction

Bünzli and Pilloud¹ and Barthelemy et al.² have studied the macrocyclic effect vs the chelate effect for complexes of the lanthanides³ with crown ethers and linear polyethers (glymes). Both conclude that the lanthanide podates are less stable than the corresponding crown ethers (which do exhibit a size-related macrocycle effect). Anomalous stability constants with the series of podand complexes were related to possible structural changes from perhaps a cyclic structure to a helical one. Decreasing stability with increasing atomic number was also attributed to a cyclic structure for the podates.

In studies of lanthanide nitrate polyethylene glycol (PEG) complexation, Hirashima⁴⁻¹⁰ also found anomalous trends including a decrease in stability (and consequently percent yield of the complexes) with increasing atomic number. Crystal structures of the triethylene glycol (EO3), tetraethylene glycol (EO4), and pentaethylene glycol (EO5) complexes of $\text{Nd}(\text{NO}_3)_3$ revealed the glycol ligands adopt a rather cyclic "crown-like" conformation.

Our research has focused on the preparation of crystalline complexes of crown ethers and PEG's with lanthanide chlorides and the determination of their structural features. While we have observed a cyclic structure for EO3¹¹ and EO4¹² in a few late-lanthanide complexes, the majority of our work points toward a helical, wrapping nature for PEG complexation. In contrast,

structural characterization of lanthanide chloride complexes of 12-crown-4¹³ result in out-of-cavity complexation of Ln^{3+} to a C_4 crown ether for La^{3+} – Lu^{3+} . Complexes of 18-crown-6¹⁴ with the early lanthanides to mid-lanthanides show the crown folds around the metal cation, distorting the normally observed D_{3d} crown conformation.

In this report we discuss the complexation and structural chemistry of $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$ with 12-crown-4, 15-crown-5, 18-crown-6, dibenzo-18-crown-6, EO3, EO4, EO5, EO6, and EO7. We compare and contrast the ease of preparations and resulting structural differences which may influence the observed complexation behavior.

Results

12-Crown-4. We have recently published¹³ the reaction of $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$ with 12-crown-4 in 3/1 $\text{CH}_3\text{CN}/\text{CH}_3\text{OH}$, from which $[\text{Nd}(\text{OH})_2(12\text{-crown-4})]\text{Cl}_3 \cdot 2\text{H}_2\text{O}$ can be isolated. The complex is 9-coordinate capped square antiprismatic¹⁵ with a C_4 crown ether occupying the uncapped face. Modification of the early-lanthanide coordination sphere has been accomplished by carrying out this reaction in an electrochemical cell. The isolation and structural characterization of $[\text{PrCl}_3(\text{OH})_2(12\text{-crown-4})] \cdot 12\text{-crown-4}$ and $[\text{PrCl}_3(\text{OHMe})(12\text{-crown-4})]$ are reported in ref 16.

15-Crown-5. The direct reaction of 15-crown-5 with $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$ in 3/1 $\text{CH}_3\text{CN}/\text{CH}_3\text{OH}$ produced the second-sphere hydrogen-bonded complexes $[\text{Nd}(\text{OH})_2]_9\text{Cl}_3 \cdot 15\text{-crown-5} \cdot \text{H}_2\text{O}^{17}$ and $[\text{NdCl}_2(\text{OH})_2]_6\text{Cl} \cdot 15\text{-crown-5}$.¹⁷ By carrying out the same reaction but passing a small electric current through $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$ and 15-crown-5 solutions separated by a fine porous glass frit (as discussed in ref 16), we have isolated the anhydrous complex $[\text{NdCl}_3(15\text{-crown-5})]$.

An ORTEP illustration of this anhydrous 8-coordinate complex is presented in Figure 1. The Nd coordination geometry most closely resembles a bicapped trigonal prism¹⁵ with O(1) and O(4) in the capping positions. The Nd–O(1) and Nd–O(4) distances

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Table I. Comparison of Bonding Parameters

| complex | CN | G ^a | Nd-O(av, alcoholic), Å | | Nd-O(av, etheric), Å | | Nd-Cl(av), Å | | Nd-OH ₂ (av), Å | | ref |
|--|----|----------------|------------------------|-----------|-----------------------|-----------|-------------------------------------|----------|----------------------------|-----------|--------|
| | | | capping | prismatic | capping | prismatic | prismatic | other | capping | prismatic | |
| [Nd(OH ₂) ₅ (12-crown-4)]Cl ₃ ·2H ₂ O | 9 | csap | | | | 2.58 (2) | | | 2.548 (7) | 2.46 (3) | 13 |
| [NdCl ₃ (15-crown-5)] | 8 | bctcp | | | 2.630 (8) | 2.55 (4) | 2.70 (1) | | | | d |
| [NdCl(OH ₂) ₂ (18-crown-6)]Cl ₂ ·2H ₂ O | 9 | tctcp | | | 2.58 (1) | 2.58 (2) | 2.706 (4) | | | 2.48 (2) | d |
| [Nd(OH ₂) ₅ (EO3)]Cl ₃ | 9 | tctcp | 2.480 (7) | 2.469 (7) | 2.596 (7) | 2.500 (8) | | | 2.506 (7) | 2.500 (8) | 11 |
| [NdCl(OH ₂) ₃ (EO4)]Cl ₂ ·H ₂ O | 9 | tctcp | | 2.45 (2) | 2.58 (2) | 2.541 (3) | 2.813 (1) | | 2.529 (3) | 2.46 (3) | 12 |
| [Nd(EO4) ₂] ₄ [NdCl ₆]Cl ₆ | 10 | bcsap | | 2.497 (2) | 2.616 (9) | 2.57 (1) | | 2.73 (1) | | | d |
| [NdCl ₂ (OH ₂) ₂ (EO5)]Cl·H ₂ O | 9 | tctcp | 2.516 (5) | 2.504 (5) | 2.556 (4) | 2.57 (3) | 2.749 (2) 2.841 (2) ^b | | | 2.528 (5) | d |
| [NdCl(OH ₂) ₂ (EO6)]Cl ₂ | 9 | tctcp | | 2.477 (3) | 2.534 (7) | 2.52 (1) | 2.740 (2) | | | 2.465 (5) | d |
| [Nd(OH ₂) ₂ (EO7)]Cl ₃ ·H ₂ O | 10 | bcsap | | 2.51 (1) | 2.60 (4) | 2.59 (4) | | | | 2.510 (2) | d |
| [Nd(OH ₂) ₇ (OHMe) ₂]Cl ₃ | 9 | tctcp | | 2.489 (9) | | | | | 2.54 (1) | 2.49 (2) | d |
| [Nd(NO ₃) ₃ (18-crown-6)] | 12 | | | | 2.68 (7) ^c | | | | | | 33, 34 |
| [Nd(NO ₃) ₂ (18-crown-6)] ₃ [Nd(NO ₃) ₆] | 10 | | | | 2.61 (6) ^c | | | | | | 35 |
| [Nd(NO ₃) ₃ (EO3)] | 10 | | 2.50 (1) ^c | | 2.52 (2) ^c | | | | | | 8 |
| [Nd(NO ₃) ₃ (EO4)] | 11 | | 2.51 (3) ^c | | 2.65 (4) ^c | | | | | | 6 |
| [Nd(NO ₃) ₂ (EO5)][NO ₃] | 10 | | 2.485 (3) ^c | | 2.59 (3) ^c | | | | | | 7 |

^a Geometries: csap = capped square antiprism; bctcp = bicapped trigonal prism; tctcp = tricapped trigonal prism; bcsap = bicapped square antiprism. ^b Cl(2) accepts two hydrogen bonds, resulting in a much longer Nd-Cl(2) distance. ^c These values correspond to the average of all Nd-O separations that are etheric or alcoholic and are not subdivided by coordination geometry site type. ^d This study.

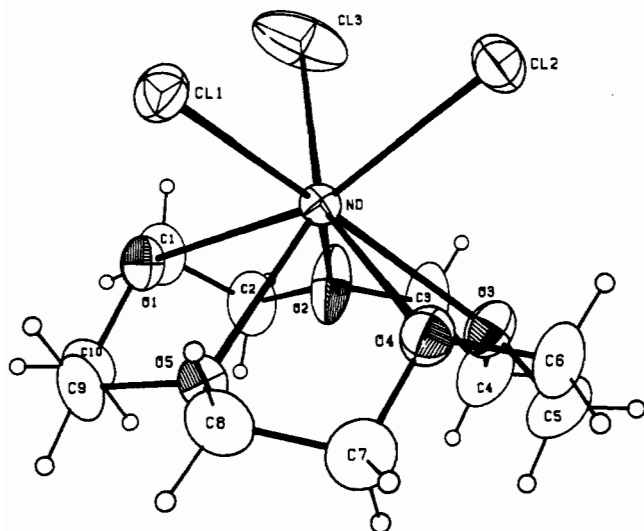


Figure 1. ORTEP illustration of [NdCl₃(15-crown-5)] with 50% probability thermal ellipsoids. The hydrogen atoms have been given arbitrarily reduced radii.

are the longest of the five Nd-O interactions, averaging 2.630 (8) Å (Table I) vs 2.55 (4) Å for the remaining five Nd-O separations. The Nd-Cl separations average 2.70 (1) Å and have a range of only 0.02 Å.

The crown molecule itself is normal. The O-C-C-O torsion angles starting with C(1)-C(2) have the pattern of g⁻ (-60°), g⁻, g⁺, g⁺, g⁻. One C-C-O-C torsion angle between consecutive O-C-C-O angles of like sign deviates toward gauche (the three such angles average 99°), and the remainder are anti (180°). The 15-crown-5 molecule exhibits several conformations in its structurally characterized complexes. The one observed here is the same found in [La(NO₃)₃(15-crown-5)],¹⁸ [La(NO₃)₃(monooza-15-crown-5)],¹⁸ [(NH₄)(15-crown-5)]₂[UO₂Cl₄]·2CH₃CN,¹⁹ one of the crown molecules in [Ba(15-crown-5)]₂Br₂·2H₂O,²⁰ and the hydrogen-bonded ether in [Sm(OH₂)₄(15-crown-5)]-[ClO₄]₃·15-crown-5·H₂O.²¹ A second common conformation has

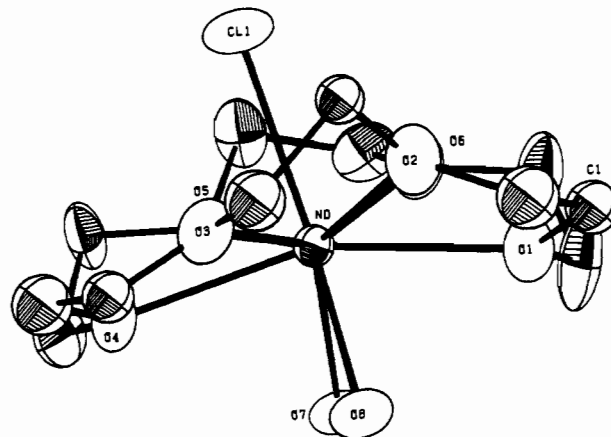


Figure 2. Deformation of 18-crown-6 to fold around Nd³⁺ in [NdCl₂(OH₂)₂(18-crown-6)]Cl₂·2H₂O.

all but two O-C-C-O angles alternating sign ±g with only one C-C-O-C angle forced toward gauche. This latter conformation was observed for the hydrogen-bonded crown molecules in [Nd(OH₂)₉]Cl₃·15-crown-5·H₂O,¹⁷ [NdCl₂(OH₂)₆]Cl·15-crown-5,¹⁷ [ThCl₄(OHMe)₂(OH₂)₂]₂·15-crown-5·CH₃CN,²² and [Y(OH₂)₈]Cl₃·15-crown-5.²³

18-Crown-6. Direct reaction of NdCl₃·6H₂O and 18-crown-6 in 3/1 CH₃CN/CH₃OH produced the complex [NdCl(OH₂)₂(18-crown-6)]Cl₂·2H₂O. A similar procedure was used to prepare the isostructural M = Sm, Gd, and Tb analogues.¹⁴

The Nd complex is depicted in Figure 2. The Nd ion is 9-coordinate tricapped trigonal prismatic¹⁵ with alternating oxygen atoms (O(1), O(3), O(5)) occupying the capping sites. The average Nd-O separation for both capping and prismatic sites is 2.58 (2) Å. The two prismatic Nd-OH₂ distances are a much shorter 2.48 (2) Å average.

The two coordinated water molecules, the two uncoordinated water molecules, and the two uncoordinated chloride anions are hydrogen-bonded in a three-dimensional network. The crown molecule does not adopt the D_{3d} form normally observed in 18-crown-6/metal complexes. This is probably a result of the folding

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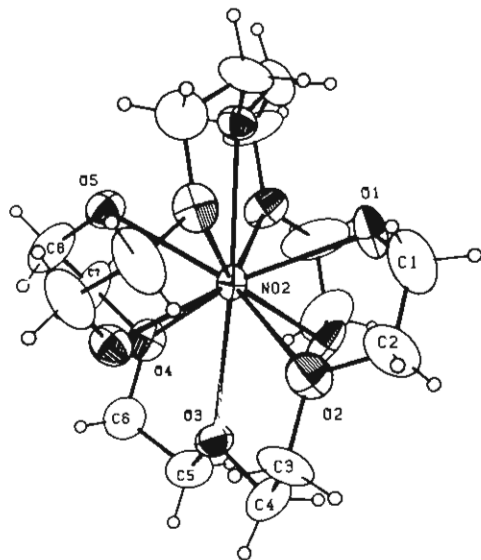


Figure 3. The $[\text{Nd}(\text{EO}4)_2]^{3+}$ cation in $[\text{Nd}(\text{EO}4)_2]_4[\text{NdCl}_6]\text{Cl}_9$.

of the crown around the Nd^{3+} ion. Four oxygen positions, O(2), O(3), O(5), and O(6), are planar with O(1) and O(4) both pulled down toward the O(7)–Nd–O(8) bond angle.

Dibenzo-18-crown-6. All reactions of $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$ in 3/1 $\text{CH}_3\text{CN}/\text{CH}_3\text{OH}$ with dibenzo-18-crown-6 failed. The only crystalline products that could be isolated were the starting salt and dibenzo-18-crown-6 $\cdot 2\text{CH}_3\text{CN}$.²⁴ Addition of an excess of LiCl to this reaction resulted in the isolation of a poorly characterized product containing NdCl_6^{3-} anions and dibenzo-18-crown-6 molecules coordinated to a variety of cation impurities from the LiCl.

EO3. Direct reaction of $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$ with EO3 in a 1/1 ratio in 3/1 $\text{CH}_3\text{CN}/\text{CH}_3\text{OH}$ produced the complex $[\text{Nd}(\text{OH}_2)_5(\text{EO}3)]\text{Cl}_3$ reported in ref 11. The Nd^{3+} ion is 9-coordinate tricapped trigonal prismatic with one alcoholic oxygen atom, one water molecule, and one etheric oxygen atom in capping positions. Crystallization directly from water also produced the same pentahydrate. Addition of an 8-fold excess of LiCl to the Nd salt in a 50/50 mixture of water and EO3 gave both the pentahydrate and a second complex which contains dimeric cations, $[\text{NdCl}_2(\text{OH}_2)_2(\text{EO}3)]_2^{2+}$, a very disordered $[\text{NdCl}_x(\text{OH}_2)_y]$ anion, and disordered Cl^- and H_2O positions. Addition of a 10-fold excess of LiCl to a 1/1 reaction of the salt and EO3 in H_2O again produced the complexed pentahydrate.

EO4. Direct reaction of $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$ with EO4 in 3/1 $\text{CH}_3\text{CN}/\text{CH}_3\text{OH}$ produced the tetrahydrate $[\text{NdCl}(\text{OH}_2)_3(\text{EO}4)]\text{Cl}_2 \cdot \text{H}_2\text{O}$ reported in ref 12. The Nd^{3+} ion is again 9-coordinate tricapped trigonal prismatic with, in this complex, one water molecule and two nonconsecutive etheric oxygen atoms in capping positions. Addition of a 10-fold excess of LiCl gave crystals of the tetrahydrate and precipitates containing two, four, or six molecules of water per formula unit. Reactions in H_2O as solvent produced the complexed tetrahydrate.

Crystallization directly from a solution of EO4 as the solvent produced the new complex $[\text{Nd}(\text{EO}4)_2]_4[\text{NdCl}_6]\text{Cl}_9$. The formula unit of this complex consists of one $[\text{NdCl}_6]^{3-}$ anion, which resides on a crystallographic 422 site, four $[\text{Nd}(\text{EO}4)_2]^{3+}$ cations (Figure 3), each of which resides on a crystallographic 2-fold axis, and nine uncoordinated chloride anions. The cations pack to form large, somewhat circular channels along unit cell axis *c*. These channels contain the $[\text{NdCl}_6]^{3-}$ anions and the disordered Cl(4) positions (Figure 4). At the junction of each set of four large circular channels, a smaller empty channel along *c* is formed. Along *c* each $[\text{NdCl}_6]^{3-}$ position is separated by two disordered Cl(4) positions. A layerlike structure is observed with layers of $[\text{NdCl}_6]^{3-}$ anions separating hydrophobic layers of $[\text{Nd}(\text{EO}4)_2]^{3+}$ cations. The two Cl(4) sites lie in rather elliptical cavities elon-

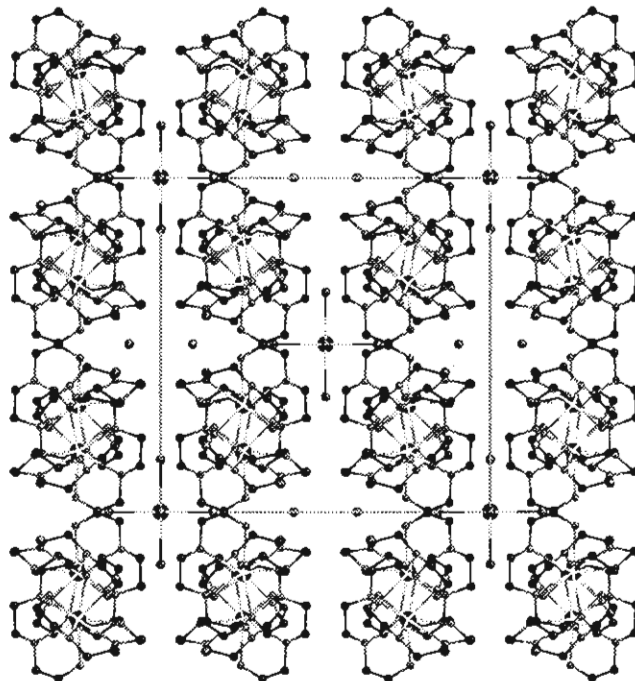


Figure 4. An *yz* slice of $[\text{Nd}(\text{EO}4)_2]_4[\text{NdCl}_6]\text{Cl}_9$. The hydrogen bonding has been omitted. The two positions of Cl(4) shown within elliptical channels are disordered.

gated along *c*. Each site is surrounded by four cations. The disorder is likely a result of the rather large cavity and lack of hydrogen bonding to lock Cl(4) in place. The Cl(3) ions accept hydrogen bonds from both of the alcoholic glycol oxygens and thus lie buried more deeply in the organic layers than do the Cl(4) anions.

The 10-coordinate cation is capped square antiprismatic and resides on a 2-fold axis. The two glycols are coordinated such that the terminal oxygen atoms (O(1), O(5)) occupy diagonal sites in one square plane, the oxygens next to each terminal position (O(2), O(4)) occupy diagonal sites in the opposite square plane, and the central oxygen of each glycol (O(3)) caps the square formed by the etheric oxygen atoms of the glycol and the alcoholic oxygen atoms of the second glycol. Each face is planar to 0.10 Å, the dihedral angle between the planes is 0.46°, and the O(3)–Nd–O(3)^a angle is 175.6 (4)°. The Nd–O(3) distance is the longest observed at 2.616 (9) Å versus 2.57 (1) Å for the remaining Nd–O(etheric) separations and 2.497 (2) Å for the Nd–O(alcoholic) distances (Table I). In the 11-coordinate $[\text{Nd}(\text{NO}_3)_3(\text{EO}4)]$,⁶ the average Nd–O separations are 2.51 (3) Å (alcoholic) and 2.65 (4) Å (etheric).

The O–C–O torsion angles in the glycol have the sequence g^-, g^+, g^+, g^+ . One of each of the two sets of C–O–C angles between consecutive C–C angles of like sign deviates toward gauche. These two angles average 111°. This conformation is identical to that found in $[\text{M}(\text{OH}_2)_4(\text{EO}4)]\text{Cl}_3$ ($\text{M} = \text{Tb}-\text{Yb}, \text{Y}$).¹²

EO5. The reaction of $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$ with EO5 in 3/1 $\text{CH}_3\text{CN}/\text{CH}_3\text{OH}$ gave the dihydrate $[\text{NdCl}_2(\text{OH}_2)(\text{EO}5)]\text{Cl} \cdot \text{H}_2\text{O}$. Every attempt to modify the metal environment by the addition of LiCl has thus far only resulted in recrystallization of the starting salt.

This 9-coordinate complex (Figure 5) is tricapped trigonal prismatic with alternating oxygen atoms along the glycol chain occupying capping positions (O(1), O(3), O(5)). Two chloride ions and one water molecule complete the primary coordination sphere. The alcoholic oxygen atom in a capping position (O(1)) is 2.516 (5) Å (Table I) from Nd compared to 2.504 (5) Å for the Nd–O separation to the terminal oxygen in a prismatic site (O(6)). The two etheric atoms in prismatic sites exhibit the shortest (Nd–O(4) = 2.536 (5) Å) and longest (Nd–O(2) = 2.599 (5) Å) such interactions, giving an average (2.57 (3) Å) which appears slightly longer than the average Nd–O(etheric, capping) distance of 2.556 (4) Å. The Nd–OH₂ separation of 2.528 (5)

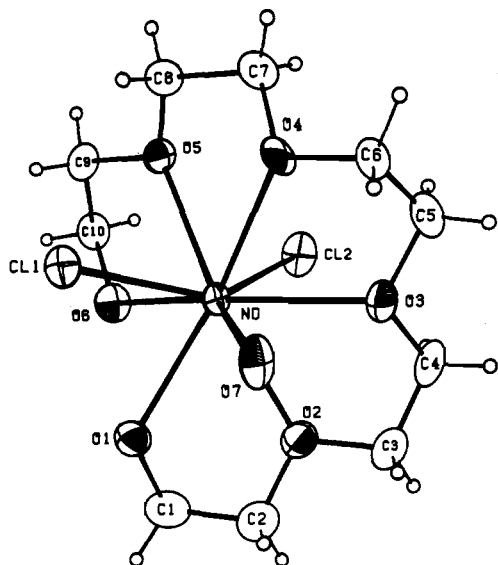


Figure 5. Primary coordination sphere of $[\text{NdCl}_2(\text{OH}_2)(\text{EO}_5)]\text{Cl} \cdot \text{H}_2\text{O}$.

Å is intermediate between the Nd–O(alcoholic) and Nd–O(etheric) distances.

The uncoordinated anions and water molecules lie in channels along *c*. The hydrogen bonding joins these atoms and the Nd complex cations into a three-dimensional network. O(8) accepts a hydrogen bond from O(1) and donates one to the uncoordinated Cl(3) and to the coordinated Cl(2) of a second cation. O(6) donates another hydrogen bond to this same Cl(3) anion while O(7) donates one hydrogen bond to a second Cl(3) anion and one to Cl(2) on a third neighboring cation. Cl(2) accepts hydrogen bonds from a third O(8) atom and from a fourth neighboring cation. The participation of Cl(2) in the hydrogen-bonding network results in a 0.1-Å elongation of the Nd–Cl(2) distance (2.841 (2) Å) vs Nd–Cl(1) (2.749 (2) Å).

The O–C–C–O torsion angles within the PEG chain have the sequence g^-, g^+, g^-, g^+, g^+ . The only C–O–C–C torsion angle which is not anti is C(5)–C(6)–O(4)–C(7) (-105.1°), and it occurs between consecutive O–C–C–O angles of like sign. O(4) has the closest Nd contact of any of the etheric oxygen atoms.

EO6. Reaction of pure EO6, PEG-300, or PEG-400 with $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$ in 3/1 $\text{CH}_3\text{CN}/\text{CH}_3\text{OH}$ produced $[\text{NdCl}(\text{OH}_2)(\text{EO}_6)]\text{Cl}_2$. The addition of an 8-fold excess of LiCl also resulted in isolation of this complex. Crystallization of the monohydrate can also be accomplished directly from H_2O or a 50/50 mixture of water and the pure glycol.

An ORTEP illustration of the $[\text{NdCl}(\text{OH}_2)(\text{EO}_6)]^{2+}$ cation is depicted in Figure 6. The Nd atom is 9-coordinate tricapped trigonal prismatic with alternating etheric oxygen atoms (O(2), O(4), O(6)) in the capping sites. The coordination is completed by one chloride ion and a water molecule. The water molecule exhibits the closest Nd approach at 2.465 (5) Å (Table I), followed by the prismatic alcoholic positions (Nd–O = 2.477 (3) Å, average). The Nd–O(etheric) distances in prismatic sites are next, averaging 2.52 (1) Å, and the average for the Nd–O(capping) separations is 2.534 (7) Å.

There are only four hydrogen-bonding interactions. The two alcoholic oxygen atoms (O(1), O(7)) each donate one hydrogen bond to two uncoordinated Cl(3) anions related by a unit translation along *a*. The water molecule, O(8), donates one hydrogen bond each to two Cl(2) anions related by a center of inversion. These interactions produce hydrogen-bonded chains of dimers which propagate along *a*.

The glycol ligand adopts a conformation very similar to that found for the D_{3d} form of 18-crown-6. The O–C–C–O torsion angles alternate $\pm g$ and the C–O–C–C angles are all anti.

EO7. Crystallization of an EO7 complex is more difficult than for the lower molecular weight PEG's. Reactions of $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$ with EO7 in 3/1 $\text{CH}_3\text{CN}/\text{CH}_3\text{OH}$ most often result in an oil as the solvent is evaporated. By very carefully controlling a slow

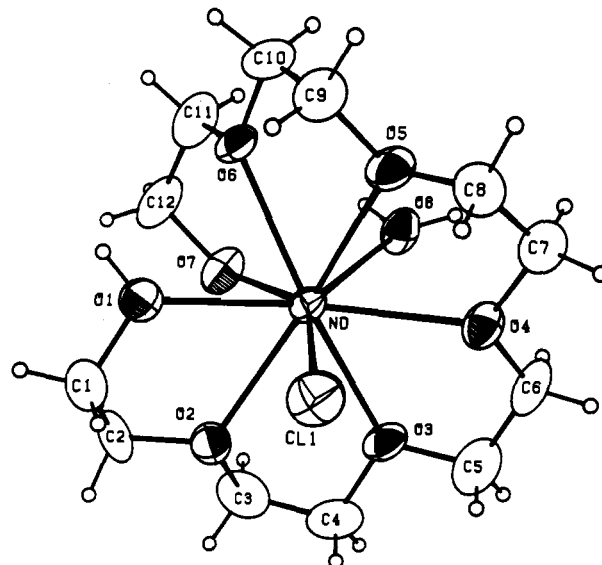


Figure 6. Primary coordination sphere of $[\text{NdCl}(\text{OH}_2)(\text{EO}_6)]\text{Cl}_2$.

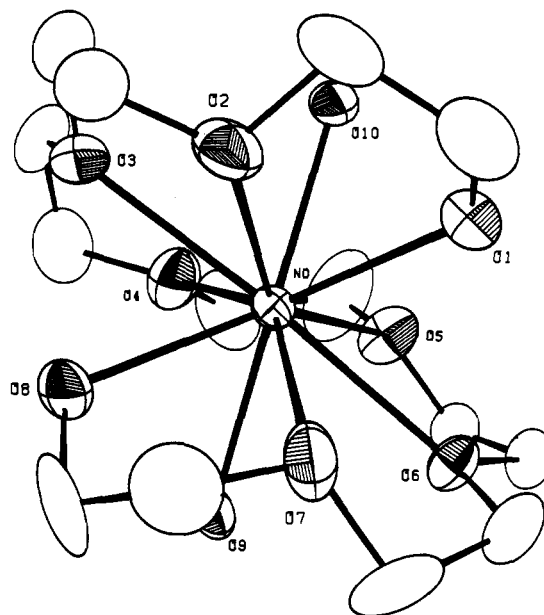


Figure 7. Primary coordination sphere of $[\text{Nd}(\text{OH}_2)_2(\text{EO}_7)]\text{Cl}_3 \cdot \text{H}_2\text{O}$.

evaporation of the solvent, it is possible to isolate crystals of $[\text{Nd}(\text{OH}_2)_2(\text{EO}_7)]\text{Cl}_3 \cdot \text{H}_2\text{O}$.

An ORTEP of the $[\text{Nd}(\text{OH}_2)_2(\text{EO}_7)]^{3+}$ cation clearly showing the wrapping nature of the glycol ligand is given in Figure 7. The Nd ion is 10-coordinate, with the 8-donor glycol and two water molecules completing the coordination sphere. The metal ion geometry is closest to a bicapped square antiprism with O(3) and O(6) in the capping positions. The square faces are planar to 0.16 Å and have a dihedral angle of intersection of only 1.2° . The O(3)–Nd–O(6) angle is $176.4 (2)^\circ$. The average Nd–O distances include 2.51 (1) Å for the alcoholic positions, 2.510 (2) Å for the water molecules, 2.59 (4) Å for the etheric prismatic positions, and 2.60 (4) Å for the capping atoms (Table I).

Of the six hydrogen bonds donated from coordinated atoms, five are to chloride anions and one is to O(11). O(11) donates two hydrogen bonds to two chloride anions. The hydrogen bonding is confined to sheets in *ac* planes. There are no hydrogen-bonding interactions between these sheets. The only formula units in each sheet are those related by unit translations along *a* and *c*. Thus, each unit cell contains a formula unit from four different hydrogen-bonded sheets.

In the glycol ligand there are three sets of consecutive O–C–C–O torsion angles of like sign, giving an overall pattern of $g^+, g^+, g^-, g^+, g^-, g^+$. As observed previously, one of the C–O–C–C

torsion angles between each such pair is forced toward gauche. These three angles average 103° .

S4OL and S6OL. Reactions of crown ethers or PEG's with $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$ usually either produce crystals of a complex or the starting salt, $[\text{NdCl}_2(\text{OH}_2)_6]\text{Cl}$. When 1,5,9,13-tetrathiacyclohexadecane-3,11-diol (S4OL) or 1,5,9,13,17,21-hexathiacyclohexadecane-3,11,19-triol (S6OL) is utilized, however, a novel Nd solvate is isolated, $[\text{Nd}(\text{OH}_2)_7(\text{OHMe})_2]\text{Cl}_3$. The crystallization of this solvate is reproducible and unique to solutions containing S4OL or S6OL.

This solvate is 9-coordinate tricapped trigonal prismatic with water molecules O(2), O(4), and O(6) occupying the capping sites. The Nd–OH₂ separations of these three water molecules average 2.54 (1) Å vs 2.49 (2) Å for the four remaining water molecules and 2.489 (9) Å for the two methanol groups (Table I). The 16 hydrogen bonds to the uncoordinated chloride ions produce an intricate network of hydrogen bonding throughout the unit cell. Both Cl(1) and Cl(3) accept five hydrogen bonds, while Cl(2) accepts six.

12-Crown-4/EO4. The competitive reaction of $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$ in 3/1 $\text{CH}_3\text{CN}/\text{CH}_3\text{OH}$ with 1/1/1 stoichiometry of $\text{Nd}^{3+}/12\text{-crown-4}/\text{EO4}$ produced the tetrahydrate EO4 complex $[\text{NdCl}(\text{OH}_2)_3(\text{EO4})]\text{Cl}_2 \cdot \text{H}_2\text{O}$.

Discussion

Our earlier reports^{11–14,16,17} have dealt with the effects of decreasing size across the lanthanide series on structural features of crown ether and polyethylene glycol complexes. The complexation chemistry has often been complicated by other features which change across the series, such as hydrophilicity. In this paper, we discuss Nd^{3+} , a point in the series where complexation is favored by entropic solvent loss and where the $\text{Ln}^{3+}/\text{OH}_2$ interactions are weaker.²⁵

The isolation of any complex between a crown ether or PEG with $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$ from organic solvents appears to depend on the crystallization conditions. Fast, or even moderately fast, evaporation of 3/1 $\text{CH}_3\text{CN}/\text{CH}_3\text{OH}$ solutions of the salt and ligand (1/1) results in recrystallization of the starting hexahydrate salt. Slow evaporation on the other hand has produced direct complexation for all of the complexes except for 15-crown-5. When the ligand is a PEG, this process first produces a more viscous bottom layer²⁶ which slowly grows, leaching all of the Nd^{3+} (and hence the purple color) from the top layer. Crystallization from this bottom layer produced the 1/1 complexes studied.

The PEG complexes are much easier to prepare. The crown complexes crystallize extremely slowly and typically are deliquescent. The PEG complexes can be prepared using H_2O as solvent. The addition of a salting-out agent, LiCl , enhances crystallization, but for Nd^{3+} does not appear to alter the complex formed. Addition of LiCl to reactions of the mid-lanthanide chlorides with EO4 dramatically changes the isolated complexes.¹² This may be attributed to the high hydration energy of Li^+ , the addition of excess Cl^- , and the fact that the lithium ion does not compete for EO4 complexation.

The only change in coordination environment from that obtained in 1/1 stoichiometric reactions we have accomplished for NdCl_3/PEG complexes has been realized by utilizing the ligand as a solvent. $[\text{Nd}(\text{EO4})_2]_4[\text{NdCl}_6]\text{Cl}_9$ is actually a 5/8 (Nd/EO4) complex. The 1/2 cation is 10-coordinate. It is unlikely that 1/2 complexes with EO5–EO7 could form with coordination numbers 12–16. A 1/2 complex with EO3 should be isolable, however, and we have observed such a complex for the similar La^{3+} and Ce^{3+} , $[\text{MCl}(\text{OH}_2)(\text{EO3})_2]\text{Cl}_2$.²⁷ The larger La^{3+} crystallizes from reaction stoichiometries of 1/1, while, for Ce^{3+} , an excess of glycol must be added to force the higher stoichiometry.²⁷ We have also

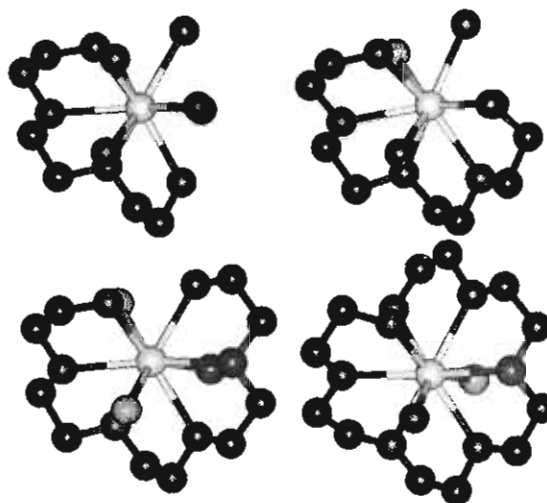


Figure 8. Primary coordination sphere of the 1/1 EO3, EO4, EO5, and EO6 complexes in the same orientation as represented by SYBYL.

isolated a solvent-free 2/1 complex of Cd^{2+} , $[\text{Cd}(\text{EO3})_2][\text{CdI}_4]$.²⁷ The 8-coordinate Cd^{2+} is dodecahedral.

The lack of an easy route to 15-crown-5 complexes of $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$ is surprising. 18-Crown-6 and 12-crown-4 readily form direct complexes; however, under identical reaction conditions, 15-crown-5 yields only hydrogen-bonded hydrates, $[\text{Nd}(\text{OH}_2)_9]\text{Cl}_3 \cdot 15\text{-crown-5} \cdot \text{H}_2\text{O}$ ¹⁷ and $[\text{NdCl}_2(\text{OH}_2)_6]\text{Cl} \cdot 15\text{-crown-5}$.¹⁷ A simple electrocrystallization technique¹⁶ which combines slow ion migration with electrolytic dehydration was used to isolate the anhydrous $[\text{NdCl}_3(15\text{-crown-5})]$.

Although not the last word, and certainly not the only factor to consider, the structures of the isolated complexes reveal some clues to the observed complexation reactions. Within the crown series, the 12-crown-4 and 18-crown-6 complexes are at the extremes. The Nd^{3+} ion sits atop the cavity formed by 12-crown-4 which retains its normally observed C_4 conformation.¹³ This results in a rather unusual capped-square-antiprismatic geometry for Nd^{3+} . It should be noted that the bulkier Cl^- anion probably could not reside either in the capping position or in the capped face and thus the five remaining sites are occupied by water molecules.

18-Crown-6 is very distorted from its commonly observed D_{3d} form as it folds around the Nd^{3+} ion. This flexibility allows Nd^{3+} to attain a tricapped-trigonal-prismatic geometry. The 15-crown-5 complex exhibits features intermediate between the two. The Nd^{3+} ion resides over the 15-crown-5 cavity; however, it does appear that the ether is trying to flex around the cation but it is not large enough to do so. The lower 8-coordinate geometry is supported by three bulky chloride ions in the primary coordination sphere.

One of the most important aspects of this study is that the PEG derivatives in no way, shape, or form mimic crown ethers in complexation of Nd^{3+} . The PEG's wrap the metal ion in a helical fashion, which is clearly seen in the SYBYL²⁸ plots of the crystallographic coordinates for the EO3–EO6 derivatives (Figure 8). Each is 9-coordinate tricapped trigonal prismatic, and in each case the glycol alternates between capping and prismatic coordination sites, starting with one alcoholic end in a prismatic site. As the glycol chain gets longer, it simply displaces another inner-sphere ligand, going from five water molecules in the EO3 complex to one water molecule and one chloride ion in the EO6 complex. Even the observed glycol conformations are quite similar.

While we had hoped to isolate a 9-coordinate complex of EO7, the observed coordination number of 10 was achieved by inclusion of two water molecules in the primary coordination sphere. It appears that the chloride ions are too bulky to be present in the inner sphere. The difficulty in isolating EO7 complexes of the early lanthanides may be related to this change in coordination number. The wrapping of additional donors around the metal ion may limit the useful chain lengths we can use.

(25) Izatt, R. M.; Lamb, J. D.; Christensen, J. J.; Haymore, B. J. *J. Am. Chem. Soc.* 1977, 99, 8344.

(26) The existence of two-phase salt/solvent/PEG systems is well-known: Albertson, P.-A. In *Partition of Cell Particles and Macromolecules*; Almqvist & Wiksell: Stockholm, 1971.

(27) Rogers, R. D.; Etzenhouser, R. E.; Murdoch, J. S. Unpublished results, 1991.

(28) SYBYL: Tripos Associates, St. Louis, MO.

If the structural chemistry can provide any clues to the ready formation of PEG complexes of the lanthanide chlorides versus crown ether complexes in our studies, it would seem to indicate that the glycol flexibility and number of donor atoms are the most important PEG features. One feature which should not be overlooked, however, is the ability of PEG's to donate hydrogen bonding. The intricate hydrogen-bond networks must add some stability to the crystalline complexes and may be one additional factor contributing to the ready isolation of crystalline PEG complexes.

Some of the coordination parameters for the complexes discussed in this paper are summarized in Table I. The ranges in Nd-O separations in the various categories are quite small. After corrections for differences of -0.057 \AA in the 10-coordinate vs 9-coordinate Nd^{3+} ionic radii²⁹ and -0.107 \AA for 11 vs 9-coordinate Nd^{3+} , the maximum range in any one category for the glycol complexes is 0.07 \AA . The crown ether complexes have even narrower ranges which tend to fall at the very high end or exceed the ranges found for the glycol complexes, suggesting a weaker interaction. The Nd-O distances in the NO_3^- derivatives published in the literature tend to be at the low end of each range.

Experimental Section

Preparation of $[\text{NdCl}_3(15\text{-crown-5})]$. A 1-mmol (0.2-mL) sample of 15-crown-5 was dissolved in 10 mL of a 3/1 $\text{CH}_3\text{CN}/\text{CH}_3\text{OH}$ solution, and the mixture was placed in one compartment of an H-cell (10-mL capacity/compartment). A 1-mmol (0.3587-g) amount of $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$ was dissolved in 10 mL of the same solvent, and the solution was placed in the other compartment. The two compartments were separated by a fine-porosity glass frit. Platinum-wire electrodes ($0.1\text{--}0.4 \text{ cm}^2$) were inserted into each compartment and were connected to a variable dc constant-current power supply with a range of $0.1\text{--}0.600 \mu\text{A}$. A current of $50 \mu\text{A}/\text{cm}^2$ was passed through the cell. After a few days, crystals of $[\text{NdCl}_3(15\text{-crown-5})]$ formed in the compartment containing the crown ether solution. Anal. Calcd: C, 25.51; H, 4.28. Found: C, 25.27; H, 4.23.

Preparation of $[\text{NdCl}(\text{OH}_2)_2(18\text{-crown-6})\text{Cl}_2 \cdot 2\text{H}_2\text{O}]$. A 1-mmol (0.3587-g) quantity of $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$ was placed in a reaction tube and dissolved in 4 mL of 3/1 $\text{CH}_3\text{CN}/\text{CH}_3\text{OH}$. A 1-mmol (0.2643-g) sample of 18-crown-6 was then dissolved in the solution, and the resultant mixture was then heated at $56 \text{ }^\circ\text{C}$ with stirring for 4.75 h. The solution was stored at $5 \text{ }^\circ\text{C}$ for 5 days and at $-10 \text{ }^\circ\text{C}$ for 34 days. The solvent volume was reduced by 33% under vacuum. The solution was stored at $20 \text{ }^\circ\text{C}$ for 37 days, at which time crystals of $[\text{NdCl}(\text{OH}_2)_2(18\text{-crown-6})\text{Cl}_2 \cdot 2\text{H}_2\text{O}]$ formed. Anal. Calcd: C, 24.55; H, 5.49. Found: C, 24.32; H, 4.47.

Preparation of $[\text{Nd}(\text{OH}_2)_5(\text{EO3})\text{Cl}_3]$. The original preparation of this complex may be found in ref 11.

(A) In an alternative procedure, 1.5 mmol (0.5388 g) of $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$ was placed in a 1-dram sample vial and dissolved in 2 mL of distilled water. A 15.8-mmol (0.6696-g) quantity of LiCl was then added to the solution followed, after dissolution, by 1.5 mmol (0.2 mL) of triethylene glycol (EO3). The solution was heated with stirring for 1.33 h, with the temperature of the heating bath gradually increasing from 76 to $84 \text{ }^\circ\text{C}$ over the heating period. The solution was stored at $20 \text{ }^\circ\text{C}$ for 1 day, $5 \text{ }^\circ\text{C}$ for 12 h, and $-10 \text{ }^\circ\text{C}$ for 8 days. The solvent volume was to be reduced under vacuum, but crystals of $[\text{Nd}(\text{OH}_2)_5(\text{EO3})\text{Cl}_3]$ immediately formed with no significant reduction of the solvent volume. Crystal composition was confirmed by matching the crystallographic cell parameters. Anal. Calcd: C, 14.68; H, 4.93. Found: C, 13.33; H, 5.26.

(B) A 1-mmol (0.3591-g) sample of $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$ was placed into a 1-dram sample vial, to which was added 1 mL of distilled water. A 10-mmol (0.4298-g) amount of LiCl was added to the solution followed by 7.5 mmol (1 mL) of EO3. The solution was heated with stirring for 1.33 h, with the temperature of the heating bath gradually increasing from 76 to $84 \text{ }^\circ\text{C}$ over the entire heating time. The solution was stored at $20 \text{ }^\circ\text{C}$ for 1 day, $5 \text{ }^\circ\text{C}$ for 12 h, and $-10 \text{ }^\circ\text{C}$ for 8 days. The solvent volume was reduced by 10% under vacuum. Crystals of $[\text{Nd}(\text{OH}_2)_5(\text{EO3})\text{Cl}_3]$ formed after storage at $20 \text{ }^\circ\text{C}$ for 4 days. Anal. Calcd: C, 14.68; H, 4.93. Found: C, 15.31; H, 5.08. Cell parameters matched those of the original sample.

Preparation of $[\text{NdCl}(\text{OH}_2)_3(\text{EO4})\text{Cl}_2 \cdot \text{H}_2\text{O}]$. The original preparation of this complex is given in reference 12.

(A) In an alternative procedure, 1.18 mmol (0.4247 g) of $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$ was placed in a reaction tube, to which was added 5 mL of a 3/1

$\text{CH}_3\text{CN}/\text{CH}_3\text{OH}$ mixture. To the solution was added 10.1 mmol (0.4268 g) of LiCl followed by 1.16 mmol (0.2 mL) of tetraethylene glycol (EO4). The solution was heated with stirring for 1 h. A precipitate formed during this time and was separated from the supernatant by centrifugation. The supernatant was stored at $20 \text{ }^\circ\text{C}$ for 8 days, at which time crystals formed. These were determined to be $[\text{NdCl}(\text{OH}_2)_3(\text{EO4})\text{Cl}_2 \cdot \text{H}_2\text{O}]$ by matching the cell parameters of several crystals.

(B) A 1.16-mmol (0.4161-g) sample of $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$ was placed in a 1-dram sample vial, to which was added 2 mL of distilled water. To the solution was added 12.5 mmol (0.5287 g) of LiCl followed by 1.16 mmol (0.2 mL) of EO4. The solution was heated with stirring for 1.33 h, with the temperature of the heating bath gradually increasing from 76 to $84 \text{ }^\circ\text{C}$ over the heating period. The solution was stored at $20 \text{ }^\circ\text{C}$ for 1 day, $5 \text{ }^\circ\text{C}$ for 12 h, and $-10 \text{ }^\circ\text{C}$ for 8 days. The solvent volume was reduced by 10% under vacuum. The solution was stored at $20 \text{ }^\circ\text{C}$ for 27 days, at which time crystals formed. These crystals were determined to be $[\text{NdCl}(\text{OH}_2)_3(\text{EO4})\text{Cl}_2 \cdot \text{H}_2\text{O}]$ by matching the cell parameters of several crystals.

(C) A 1-mmol (0.3587-g) quantity of $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$ was placed in a reaction tube, to which was added 5 mL of a 3/1 $\text{CH}_3\text{CN}/\text{CH}_3\text{OH}$ mixture. To the solution was added 1 mmol (0.190 mL) of EO4 followed by 1 mmol (0.162 mL) of 12-crown-4. Precipitation occurred soon after the addition of the crown ether. The solution was heated at $60 \text{ }^\circ\text{C}$ with stirring for 1 h. The precipitate was separated from the supernatant by centrifugation and stored at $20 \text{ }^\circ\text{C}$ for 60 days, at which time all the solvent had evaporated. Purple and blue crystals formed in the bottom of the tube. The purple and blue crystals were both confirmed to be $[\text{NdCl}(\text{OH}_2)_3(\text{EO4})\text{Cl}_2 \cdot \text{H}_2\text{O}]$ by matching the cell parameters of several crystals.

Preparation of $[\text{NdCl}_2(\text{OH}_2)(\text{EO5})\text{Cl} \cdot \text{H}_2\text{O}]$. A 1-mmol quantity of pentaethylene glycol (EO5) was added to a stirred solution of 1 mmol of $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$ in 2 mL of 3/1 $\text{CH}_3\text{CN}/\text{CH}_3\text{OH}$. The reaction mixture was heated to $60 \text{ }^\circ\text{C}$ for 1 h, after which time the solution remained clear. The mixture was allowed to evaporate slowly. A two-layer system was observed just prior to crystal formation. Small pink needles formed that were suitable for the crystallographic study. The crystals were found to be deliquescent, which hampered obtaining good analytical results.

Preparation of $[\text{NdCl}(\text{OH}_2)(\text{EO6})\text{Cl}_2]$. (A) A 1-mmol quantity of hexaethylene glycol was added to a stirred solution of 1 mmol of $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$ in 3 mL of 3/1 $\text{CH}_3\text{CN}/\text{CH}_3\text{OH}$. The reaction mixture was heated to $60 \text{ }^\circ\text{C}$ for 1 h, after which time a flaky pale violet precipitate had formed. The mixture was centrifuged while hot and the supernatant decanted. The supernatant was allowed to evaporate slowly. After 10 days, small purple needles had formed that were suitable for study. The crystals were found to be deliquescent, which resulted in inconsistent analyses.

(B) A 1-mmol (0.3587-g) sample of $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$ was placed in a reaction tube, to which was added 5 mL of a 3/1 $\text{CH}_3\text{CN}/\text{CH}_3\text{OH}$ mixture. To the solution was added 8.3 mmol (0.3502 g) of LiCl followed by approximately 1 mmol (0.25 mL) of EO6. The solution was heated at $60 \text{ }^\circ\text{C}$ with stirring for 50 min. A precipitate formed during heating, which was separated from the supernatant with centrifugation. The supernatant was stored at $20 \text{ }^\circ\text{C}$ for 1 day, at which point crystals formed. These crystals were confirmed to be $[\text{NdCl}(\text{OH}_2)(\text{EO6})\text{Cl}_2]$ by matching the cell parameters of several crystals.

(C) A 1-mmol (0.3587-g) quantity of $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$ was placed in a 1-dram sample vial, to which was added 1 mL of distilled water followed by 1 mmol (0.25 mL) of EO6. The solution was heated at $73 \text{ }^\circ\text{C}$ with stirring for 1.75 h and then stored at $5 \text{ }^\circ\text{C}$ for 4 days and $-10 \text{ }^\circ\text{C}$ for 1 day. The solvent volume was to be reduced under vacuum. During solvent reduction, the solution boiled briefly, causing some of the solution to fall into the larger reaction tube. Small crystals formed from the solution in the bottom of the tube. The crystals were determined to be $[\text{NdCl}(\text{OH}_2)(\text{EO6})\text{Cl}_2]$ by matching the cell parameters of several crystals.

Preparation of $[\text{Nd}(\text{OH}_2)_2(\text{EO7})\text{Cl}_3 \cdot \text{H}_2\text{O}]$. A 1-mmol (0.3587-g) sample of $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$ was placed in a reaction tube, to which was added 5 mL of a 3/1 $\text{CH}_3\text{CN}/\text{CH}_3\text{OH}$ mixture followed by 1 mmol (0.290 mL) of heptaethylene glycol (EO7). The solution was heated at $60 \text{ }^\circ\text{C}$ with stirring for 1 h and then stored for 150 days, at which point the solvent had evaporated. Crystals of $[\text{Nd}(\text{OH}_2)_2(\text{EO7})\text{Cl}_3 \cdot \text{H}_2\text{O}]$ formed in the bottom of the tube as the solvent slowly evaporated. Anal. Calcd: C, 26.65; H, 5.75. Found: C, 28.15; H, 6.63.

Preparation of $[\text{Nd}(\text{OH}_2)_7(\text{OHMe})_2\text{Cl}_3]$. (A) A 0.25-mmol (0.0907-g) amount of $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$ was placed in a reaction tube, to which was added 5 mL of a 3/1 $\text{CH}_3\text{CN}/\text{CH}_3\text{OH}$ mixture. A 0.25-mmol (0.1232-g) quantity of 1,5,9,13,17,21-hexathiacyclotetrasacane-3,11,19-triol was added to the solution. The resultant solution was then heated at $58.5 \text{ }^\circ\text{C}$ with stirring for 1.5 h. A small amount of precipitate formed

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Table II. Crystal Data and Summary of Intensity Data Collection and Structure Refinement

| compd | [NdCl ₃ (15-crown-5)] | [NdCl(OH) ₂ (18-crown-6)]Cl ₂ ·2H ₂ O | [Nd(EO4) ₂] ₄ ·[NdCl ₆]Cl ₉ | [NdCl ₂ (OH) ₂ (EO5)]Cl·H ₂ O | [NdCl(OH) ₂ (EO6)]Cl ₂ | [Nd(OH) ₂ (EO7)]Cl ₃ ·H ₂ O | [Nd(OH) ₂ (OHMe) ₂]Cl ₃ |
|--|------------------------------------|--|---|--|--|--|---|
| fw | 470.87 | 586.98 | 2806.8 | 524.91 | 550.95 | 631.03 | 440.79 |
| space group | <i>P</i> 2 ₁ / <i>c</i> | <i>P</i> 2 ₁ 2 ₁ | <i>I</i> 422 | <i>P</i> 2 ₁ / <i>c</i> | <i>P</i> 2 ₁ / <i>c</i> | <i>P</i> 2 ₁ / <i>c</i> | <i>P</i> bc _a |
| <i>T</i> , °C | 20 | 20 | 20 | 20 | 20 | 21 | 18 |
| cell const ^a | | | | | | | |
| <i>a</i> , Å | 8.174 (3) | 7.438 (3) | 17.595 (6) | 13.412 (2) | 7.485 (2) | 9.053 (5) | 12.266 (2) |
| <i>b</i> , Å | 14.234 (5) | 15.994 (4) | | 9.780 (4) | 29.943 (5) | 30.216 (9) | 12.614 (2) |
| <i>c</i> , Å | 14.180 (5) | 18.966 (5) | 17.257 (4) | 14.461 (3) | 9.197 (2) | 9.691 (4) | 19.204 (1) |
| β, deg | 104.80 (3) | | | 102.58 (1) | 99.99 (2) | 113.77 (7) | |
| cell vol, Å ³ | 1595.1 | 2256 | 5342.5 | 1851 | 2030 | 2426 | 2971 |
| no. of formula units/unit cell | 4 | 4 | 2 | 4 | 4 | 4 | 8 |
| radiation, graphite monochromator (λ, Å) | Mo Kα (0.71073) | Mo Kα (0.71073) | Mo Kα (0.71073) | Mo Kα (0.71073) | Mo Kα (0.71073) | Mo Kα (0.71073) | Mo Kα (0.71073) |
| <i>D</i> _{calcd} , g cm ⁻³ | 1.93 | 1.73 | 1.74 | 1.88 | 1.80 | 1.73 | 1.97 |
| <i>μ</i> _{calcd} , cm ⁻¹ | 37.2 | 25.3 | 28.4 | 32.7 | 28.1 | 25.3 | 40.7 |
| range of rel trans factors, % ^b | 87–100 | 97–100 | 80–100 | 89–100 | 73–100 | 76–100 | 77–100 |
| <i>R</i> = Σ <i>F</i> _o - <i>F</i> _c /Σ <i>F</i> _o | 0.035 | 0.043 | 0.042 | 0.040 | 0.036 | 0.047 | 0.042 |
| <i>R</i> _w = [Σw(<i>F</i> _o - <i>F</i> _c) ²]/Σw(<i>F</i> _o) ²] ^{1/2} | 0.040 | 0.049 | 0.048 | 0.042 | 0.038 | 0.056 | 0.059 |

^aLeast-squares refinement of ((sin θ)/λ)² values for 25 reflections with θ > 20°. ^bCorrections: Lorentz-polarization and absorption (empirical, ψ scan).

Table III. Final Fractional Coordinates for [NdCl₃(15-crown-5)]

| atom | <i>x/a</i> | <i>y/b</i> | <i>z/c</i> | <i>B</i> (eqv), Å ² |
|-------|-------------|-------------|-------------|--------------------------------|
| Nd | 0.15958 (4) | 0.24040 (2) | 0.10129 (2) | 1.42 |
| Cl(1) | 0.3384 (2) | 0.3780 (1) | 0.9556 (1) | 2.39 |
| Cl(2) | 0.3344 (3) | 0.1155 (1) | 0.9315 (1) | 2.66 |
| Cl(3) | -0.0508 (3) | 0.2342 (2) | 0.8304 (2) | 5.37 |
| O(1) | -0.0437 (6) | 0.3782 (3) | 1.0282 (3) | 2.03 |
| O(2) | -0.1230 (7) | 0.2014 (4) | 1.0399 (5) | 3.61 |
| O(3) | 0.1329 (6) | 0.0923 (4) | 1.1144 (4) | 2.52 |
| O(4) | 0.4249 (6) | 0.1896 (3) | 1.1510 (3) | 2.28 |
| O(5) | 0.2481 (6) | 0.3444 (3) | 1.1622 (3) | 1.86 |
| C(1) | -0.2207 (9) | 0.3538 (5) | 0.9953 (6) | 2.84 |
| C(2) | -0.2563 (9) | 0.2652 (5) | 1.0390 (7) | 3.05 |
| C(3) | -0.161 (1) | 0.1049 (6) | 1.0547 (9) | 4.46 |
| C(4) | -0.030 (1) | 0.0700 (6) | 1.1342 (7) | 3.94 |
| C(5) | 0.268 (1) | 0.0586 (6) | 1.1932 (6) | 3.43 |
| C(6) | 0.431 (1) | 0.0900 (5) | 1.1725 (6) | 3.27 |
| C(7) | 0.473 (1) | 0.2465 (5) | 1.2387 (6) | 2.62 |
| C(8) | 0.4264 (8) | 0.3439 (5) | 1.2086 (5) | 2.27 |
| C(9) | 0.178 (1) | 0.4370 (5) | 1.1567 (6) | 2.55 |
| C(10) | -0.0068 (9) | 0.4268 (5) | 1.1210 (5) | 2.51 |

^a*B*(eqv) = (4/3)[*a*²β₁₁ + *b*²β₂₂ + *c*²β₃₃ + *ab*(cos γ)β₁₂ + *ac*(cos β)β₁₃ + *bc*(cos α)β₂₃].

which settled to the bottom of the tube after 2 h. The precipitate was separated from the supernatant through centrifugation. The supernatant was stored at 20 °C for 1 day, 5 °C for 15 days, and -10 °C for 54 days. The solvent volume was reduced by 33% under vacuum, and the remaining solution was stored at -10 °C for 21 days. Crystals formed during storage which dissolved when the solution was warmed to 20 °C. The solvent volume was reduced by an additional 33% under vacuum, and the solution was stored at 20 °C for 175 days, at which point a two-layer system formed, consisting of a purple oily droplet below a colorless layer. Crystals of [Nd(OH)₂(OHMe)₂]Cl₃ formed from the oily droplet. Anal. Calcd: C, 5.45; H, 5.03. Found: C, 5.41; H, 5.06.

(B) A 0.5-mmol (0.1794-g) sample of NdCl₃·6H₂O was placed in a reaction tube, to which was added 5 mL of a 3/1 CH₃CN/CH₃OH mixture. To the solution was added 0.5 mmol (0.1655 g) of 1,5,9,13-tetrathiacyclohexadecane-3,11-diol, and the mixture was then heated at 64.5 °C with stirring for 1.5 h. A small amount of precipitate formed during heating, which settled in the bottom of the tube after 2 h. The precipitate was separated from the supernatant through centrifugation. The supernatant was stored at 20 °C for 1 day, 5 °C for 15 days, and -10 °C for 54 days. The solvent volume was reduced by 33% under vacuum, and the solution was stored at -10 °C for 4 days, at which point small crystals formed. These crystals redissolved upon warming the solution to 20 °C, and the solution was returned to storage at -10 °C for 24 days. The solvent volume was reduced by an additional 10% under vacuum, at which point small crystals formed. The solution was placed in a programmable low-temperature bath where the temperature of the sample was lowered from 20 to -25 °C over 3 days. The solution was

Table IV. Final Fractional Coordinates for [NdCl(OH)₂(18-crown-6)]Cl₂·2H₂O

| atom | <i>x/a</i> | <i>y/b</i> | <i>z/c</i> | <i>B</i> (eqv), Å ² |
|-------|------------|-------------|-------------|--------------------------------|
| Nd | 1.0823 (1) | 0.43216 (4) | 0.36323 (4) | 1.47 |
| Cl(1) | 0.8917 (7) | 0.3416 (3) | 0.4578 (2) | 3.09 |
| Cl(2) | 1.3637 (6) | 0.5863 (2) | 0.1884 (2) | 2.97 |
| Cl(3) | 1.3588 (7) | 0.7276 (3) | 0.4118 (2) | 3.37 |
| O(1) | 0.871 (2) | 0.5221 (6) | 0.2873 (6) | 2.79 |
| O(2) | 0.894 (2) | 0.5444 (6) | 0.4258 (6) | 3.31 |
| O(3) | 1.193 (2) | 0.4884 (7) | 0.4832 (5) | 2.87 |
| O(4) | 1.374 (2) | 0.3712 (6) | 0.4104 (6) | 2.79 |
| O(5) | 1.148 (1) | 0.2777 (6) | 0.3287 (5) | 2.22 |
| O(6) | 0.861 (2) | 0.3550 (6) | 0.2787 (6) | 2.80 |
| O(7) | 1.252 (1) | 0.4229 (7) | 0.2525 (4) | 2.38 |
| O(8) | 1.257 (1) | 0.5632 (7) | 0.3412 (5) | 2.65 |
| O(9) | 1.297 (2) | 0.3003 (7) | 0.1588 (6) | 3.69 |
| O(10) | 1.490 (2) | 0.6796 (9) | 0.5631 (6) | 4.45 |
| C(1) | 0.765 (4) | 0.590 (2) | 0.318 (2) | 3.2 (6) ^a |
| C(2) | 0.828 (5) | 0.615 (2) | 0.383 (2) | 4.5 (8) ^a |
| C(3) | 0.902 (4) | 0.546 (2) | 0.506 (1) | 2.7 (5) ^a |
| C(4) | 1.115 (5) | 0.556 (2) | 0.517 (2) | 4.2 (7) ^a |
| C(5) | 1.374 (4) | 0.474 (2) | 0.502 (2) | 3.0 (6) ^a |
| C(6) | 1.438 (5) | 0.391 (2) | 0.480 (2) | 4.2 (7) ^a |
| C(1)' | 0.716 (5) | 0.562 (2) | 0.320 (2) | 4.5 (8) ^a |
| C(2)' | 0.760 (5) | 0.596 (2) | 0.388 (2) | 5.0 (9) ^a |
| C(3)' | 0.959 (5) | 0.586 (2) | 0.491 (2) | 4.4 (7) ^a |
| C(4)' | 1.061 (5) | 0.531 (2) | 0.530 (2) | 4.8 (8) ^a |
| C(5)' | 1.346 (5) | 0.452 (2) | 0.516 (2) | 4.5 (8) ^a |
| C(6)' | 1.407 (6) | 0.365 (2) | 0.489 (2) | 5.8 (9) ^a |
| C(7) | 1.436 (2) | 0.291 (1) | 0.3783 (9) | 3.25 |
| C(8) | 1.280 (2) | 0.2340 (9) | 0.371 (1) | 2.96 |
| C(9) | 0.989 (2) | 0.2243 (9) | 0.3159 (9) | 2.88 |
| C(10) | 0.885 (3) | 0.2681 (9) | 0.2569 (9) | 2.94 |
| C(11) | 0.744 (3) | 0.401 (1) | 0.230 (1) | 3.82 |
| C(12) | 0.823 (3) | 0.486 (1) | 0.220 (1) | 4.32 |

^aIsotropic refinement.

then stored at -10 °C for 10 days, at which point a small amount of white precipitate formed which redissolved at 20 °C. The solution was then stored for 6 months at 20 °C. A two-layer system formed, consisting of an oily purple droplet below a colorless solution. Crystals of [Nd(OH)₂(OHMe)₂]Cl₃ formed from the oily purple droplet. The formulation was confirmed by matching the cell parameters of several crystals with the previously characterized sample.

X-ray Data Collection, Structure Determination, and Refinement. For each crystallographic study, a single crystal was mounted in a thin-walled glass capillary flushed with Ar and transferred to the goniometer of an Enraf-Nonius κ-axis diffractometer. Unless otherwise noted, the space groups were uniquely determined from systematic absences. A summary of data collection parameters for all complexes is given in Table II. Unless otherwise indicated, the geometrically constrained hydrogen atoms

Table V. Final Fractional Coordinates for [Nd(EO4)₂]₄[NdCl₆]Cl₉

| atom | x/a | y/b | z/c | B(eqv), Å ² |
|-------|--------------|--------------|-------------|------------------------|
| Nd(1) | -1.0000 | 0.0000 | -1.0000 | 1.52 |
| Nd(2) | -0.81909 (3) | -0.31909 (3) | -0.7500 | 1.58 |
| Cl(1) | -1.0000 | 0.0000 | -0.8427 (4) | 2.07 |
| Cl(2) | -1.0000 | 0.1559 (3) | -1.0000 | 3.50 |
| Cl(3) | -0.6981 (2) | -0.0841 (2) | -0.6366 (2) | 2.99 |
| Cl(4) | -0.5000 | -0.5000 | -0.904 (1) | 4.44 |
| O(1) | -0.7316 (6) | -0.2486 (4) | -0.6614 (6) | 2.63 |
| O(2) | -0.6879 (6) | -0.3766 (5) | -0.7250 (5) | 2.90 |
| O(3) | -0.7533 (5) | -0.3930 (5) | -0.8631 (5) | 2.20 |
| O(4) | -0.8900 (5) | -0.3320 (6) | -0.8807 (5) | 2.63 |
| O(5) | -0.9585 (5) | -0.3441 (5) | -0.7429 (6) | 2.51 |
| C(1) | -0.669 (1) | -0.286 (1) | -0.627 (1) | 4.53 |
| C(2) | -0.6375 (9) | -0.339 (1) | -0.6776 (9) | 4.98 |
| C(3) | -0.658 (1) | -0.431 (1) | -0.7782 (9) | 4.24 |
| C(4) | -0.6740 (9) | -0.4105 (9) | -0.8594 (9) | 3.22 |
| C(5) | -0.7789 (9) | -0.380 (1) | -0.9418 (7) | 3.25 |
| C(6) | -0.8634 (9) | -0.383 (1) | -0.9381 (8) | 3.38 |
| C(7) | -0.9727 (7) | -0.323 (1) | -0.8761 (8) | 4.39 |
| C(8) | -0.997 (1) | -0.3688 (9) | -0.8089 (8) | 3.35 |

Table VI. Final Fractional Coordinates for [NdCl₂(OH₂)(EO5)]Cl·H₂O

| atom | x/a | y/b | z/c | B(eqv), Å ² |
|-------|-------------|-------------|-------------|------------------------|
| Nd | 0.22869 (3) | 0.37219 (4) | 0.35372 (3) | 1.18 |
| Cl(1) | 0.1002 (2) | 0.3956 (2) | 0.1782 (1) | 1.78 |
| Cl(2) | 0.2596 (2) | 0.4501 (2) | 0.5471 (1) | 2.26 |
| Cl(3) | 0.3399 (2) | 0.8707 (2) | 0.3367 (2) | 2.67 |
| O(1) | 0.3284 (4) | 0.4903 (6) | 0.2484 (4) | 2.07 |
| O(2) | 0.4267 (4) | 0.3580 (6) | 0.4017 (4) | 2.30 |
| O(3) | 0.3077 (4) | 0.1693 (5) | 0.4546 (4) | 1.84 |
| O(4) | 0.1027 (4) | 0.1937 (5) | 0.3847 (4) | 1.86 |
| O(5) | 0.0583 (4) | 0.4552 (5) | 0.3855 (4) | 1.64 |
| O(6) | 0.2024 (4) | 0.6257 (5) | 0.3516 (4) | 2.05 |
| O(7) | 0.2746 (4) | 0.1727 (5) | 0.2599 (4) | 2.12 |
| O(8) | 0.2768 (6) | 0.7248 (7) | 0.1415 (5) | 3.99 |
| C(1) | 0.4339 (7) | 0.523 (1) | 0.2829 (7) | 3.20 |
| C(2) | 0.4858 (7) | 0.402 (1) | 0.3351 (7) | 3.40 |
| C(3) | 0.4739 (7) | 0.2380 (9) | 0.4502 (6) | 2.61 |
| C(4) | 0.4098 (6) | 0.1863 (9) | 0.5119 (6) | 2.32 |
| C(5) | 0.2398 (7) | 0.0874 (9) | 0.4970 (6) | 2.55 |
| C(6) | 0.1447 (6) | 0.0604 (7) | 0.4209 (6) | 2.27 |
| C(7) | 0.0135 (6) | 0.2315 (8) | 0.4177 (6) | 2.10 |
| C(8) | -0.0256 (6) | 0.3622 (7) | 0.3676 (6) | 1.91 |
| C(9) | 0.0272 (6) | 0.5939 (7) | 0.3540 (6) | 1.91 |
| C(10) | 0.1186 (6) | 0.6810 (7) | 0.3857 (5) | 1.79 |

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 Å². If included, the alcoholic or water hydrogen atoms were located from a difference Fourier map and included with fixed contributions (B = 5.5 Å²). All non-hydrogen atoms were refined anisotropically. Structures were refined by utilizing SHELX76³⁰ with neutral-atom scattering factors taken from ref 31. Initial structure solutions were carried out with SHELXS.³² Final fractional coordinates are given in Tables III-IX. Considerations unique to each crystallographic series are discussed below.

[NdCl(OH₂)₂(18-crown-6)]Cl₂·2H₂O. The structure was refined by starting with the coordinates for the isostructural M = Sm complex.¹⁴ Analysis of carbon atoms 1-6 revealed resolvable disorder, whereas only the disorder of C(3) and C(4) was resolvable for M = Sm, Gd, and Tb. The disorder in this complex is 50%/50% (as found for M = Sm), and the two orientations of carbon atoms were refined isotropically only in

Table VII. Final Fractional Coordinates for [NdCl(OH₂)(EO6)]Cl₂

| atom | x/a | y/b | z/c | B(eqv), Å ² |
|-------|-------------|-------------|-------------|------------------------|
| Nd | 0.21653 (5) | 0.37155 (1) | 0.14305 (4) | 1.62 |
| Cl(1) | 0.0593 (3) | 0.33912 (7) | 0.3693 (2) | 3.00 |
| Cl(2) | 0.4347 (3) | 0.47772 (6) | -0.2220 (2) | 2.50 |
| Cl(3) | 0.6489 (3) | 0.32648 (8) | -0.1925 (2) | 3.21 |
| O(1) | -0.0028 (7) | 0.3156 (2) | 0.0213 (6) | 2.85 |
| O(2) | 0.3210 (7) | 0.2913 (2) | 0.1469 (6) | 2.62 |
| O(3) | 0.5227 (6) | 0.3540 (2) | 0.2984 (5) | 2.40 |
| O(4) | 0.3174 (7) | 0.4213 (2) | 0.3664 (5) | 2.25 |
| O(5) | 0.0198 (7) | 0.4371 (2) | 0.1787 (5) | 2.56 |
| O(6) | 0.0046 (6) | 0.4010 (2) | -0.0813 (5) | 2.08 |
| O(7) | 0.3079 (7) | 0.3581 (2) | -0.0998 (5) | 2.80 |
| O(8) | 0.3902 (7) | 0.4356 (2) | 0.0728 (5) | 2.41 |
| C(1) | 0.025 (1) | 0.2694 (3) | 0.049 (1) | 3.37 |
| C(2) | 0.221 (1) | 0.2599 (2) | 0.048 (1) | 3.37 |
| C(3) | 0.516 (1) | 0.2849 (3) | 0.170 (1) | 3.56 |
| C(4) | 0.585 (1) | 0.3091 (3) | 0.3101 (9) | 3.30 |
| C(5) | 0.573 (1) | 0.3764 (3) | 0.439 (1) | 3.89 |
| C(6) | 0.503 (1) | 0.4207 (3) | 0.4333 (9) | 3.36 |
| C(7) | 0.219 (1) | 0.4614 (3) | 0.3878 (8) | 2.93 |
| C(8) | 0.026 (1) | 0.4534 (3) | 0.3253 (9) | 2.86 |
| C(9) | -0.159 (1) | 0.4341 (3) | 0.0875 (9) | 3.27 |
| C(10) | -0.125 (1) | 0.4352 (3) | -0.0684 (9) | 3.32 |
| C(11) | 0.053 (1) | 0.3990 (3) | -0.2252 (8) | 3.25 |
| C(12) | 0.173 (1) | 0.3593 (3) | -0.2335 (8) | 3.24 |

Table VIII. Final Fractional Coordinates for [Nd(OH₂)₂(EO7)]Cl₃·H₂O

| atom | x/a | y/b | z/c | B(eqv), Å ² |
|-------|-------------|-------------|-------------|------------------------|
| Nd | 1.12035 (7) | 0.63297 (2) | 0.22440 (6) | 1.50 |
| Cl(1) | 0.9392 (4) | 0.6473 (1) | -0.3349 (3) | 3.62 |
| Cl(2) | 1.3764 (4) | 0.5476 (1) | 0.7283 (4) | 3.22 |
| Cl(3) | 0.6222 (4) | 0.7103 (1) | 0.2271 (4) | 2.80 |
| O(1) | 1.0496 (9) | 0.6028 (3) | -0.0344 (8) | 2.27 |
| O(2) | 1.228 (1) | 0.5535 (3) | 0.1992 (9) | 3.16 |
| O(3) | 1.405 (1) | 0.6097 (3) | 0.4271 (9) | 2.99 |
| O(4) | 1.299 (1) | 0.6918 (3) | 0.3980 (9) | 2.93 |
| O(5) | 1.075 (1) | 0.7135 (3) | 0.1274 (9) | 2.74 |
| O(6) | 0.8380 (9) | 0.6566 (2) | 0.0412 (8) | 2.05 |
| O(7) | 0.844 (1) | 0.5761 (3) | 0.1636 (9) | 2.49 |
| O(8) | 1.1261 (9) | 0.5869 (3) | 0.4436 (8) | 2.39 |
| O(9) | 0.9592 (9) | 0.6673 (2) | 0.3553 (8) | 1.99 |
| O(10) | 1.3330 (9) | 0.6501 (3) | 0.1283 (8) | 2.33 |
| O(11) | 1.308 (1) | 0.6394 (3) | -0.1604 (9) | 3.24 |
| C(1) | 1.082 (2) | 0.5585 (4) | -0.066 (1) | 3.55 |
| C(2) | 1.238 (2) | 0.5432 (4) | 0.059 (1) | 4.02 |
| C(3) | 1.363 (2) | 0.5371 (5) | 0.327 (2) | 4.53 |
| C(4) | 1.488 (2) | 0.5749 (5) | 0.396 (2) | 4.31 |
| C(5) | 1.518 (1) | 0.6444 (5) | 0.513 (2) | 3.68 |
| C(6) | 1.419 (2) | 0.6812 (5) | 0.539 (1) | 3.91 |
| C(7) | 1.263 (2) | 0.7371 (5) | 0.363 (2) | 5.03 |
| C(8) | 1.193 (2) | 0.7441 (5) | 0.205 (2) | 5.05 |
| C(9) | 0.917 (2) | 0.7303 (4) | 0.060 (1) | 3.00 |
| C(10) | 0.810 (2) | 0.6974 (4) | -0.041 (1) | 2.59 |
| C(11) | 0.711 (2) | 0.6248 (4) | -0.028 (1) | 3.03 |
| C(12) | 0.722 (2) | 0.5927 (5) | 0.097 (2) | 3.47 |
| C(13) | 0.911 (2) | 0.5432 (5) | 0.284 (2) | 4.60 |
| C(14) | 0.982 (2) | 0.5612 (4) | 0.428 (1) | 3.47 |

Table IX. Final Fractional Coordinates for [Nd(OH₂)₇(OHMe)₂]Cl₃

| atom | x/a | y/b | z/c | B(eqv), Å ² |
|-------|-------------|-------------|-------------|------------------------|
| Nd | 0.51152 (4) | 0.28162 (3) | 0.37198 (2) | 1.13 |
| Cl(1) | 0.7405 (2) | 0.0260 (2) | 0.2361 (1) | 2.13 |
| Cl(2) | 0.5640 (2) | -0.2998 (2) | 0.3761 (1) | 2.09 |
| Cl(3) | 0.2709 (2) | 0.0130 (2) | 0.4995 (1) | 1.92 |
| O(1) | 0.6745 (5) | 0.1773 (5) | 0.4032 (3) | 1.92 |
| O(2) | 0.4688 (6) | 0.1693 (5) | 0.4793 (3) | 2.05 |
| O(3) | 0.4761 (6) | 0.4686 (5) | 0.3378 (4) | 2.66 |
| O(4) | 0.6863 (5) | 0.3867 (5) | 0.3609 (3) | 1.89 |
| O(5) | 0.5426 (6) | 0.3820 (5) | 0.4821 (3) | 2.10 |
| O(6) | 0.3748 (6) | 0.2898 (5) | 0.2727 (3) | 2.08 |
| O(7) | 0.6033 (6) | 0.2376 (5) | 0.2581 (3) | 2.02 |
| O(8) | 0.4457 (6) | 0.1002 (5) | 0.3412 (3) | 1.88 |
| O(9) | 0.3266 (5) | 0.3305 (5) | 0.4131 (3) | 2.10 |
| C(1) | 0.4919 (8) | -0.0021 (8) | 0.3554 (6) | 2.24 |
| C(2) | 0.2262 (9) | 0.2692 (9) | 0.4103 (6) | 2.70 |

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alternate least-squares cycles. No hydrogen atoms were included. Refinement of the non-hydrogen atoms with anisotropic temperature factors was carried out except for the disordered atoms.

$[\text{Nd}(\text{EO}4)_2]_4[\text{NdCl}_2]\text{Cl}_3$. The space group was determined to be either the centric $I4/mmm$ or acentric $I4m2$, $I42m$, $I4mm$, or $I422$ from the systematic absences. The subsequent solution and successful refinement of the structure were carried out in the acentric space group $I422$. The alcoholic hydrogen atoms were not included in the final refinement. Two partially occupied sites were observed for the Cl(4) atom. This atom was refined at 50% occupancy. The two possible positions are symmetry related and are surrounded by the $[\text{Nd}(\text{EO}4)_2]^{3+}$ cations, as discussed under Results.

$[\text{NdCl}_2(\text{OH})_2(\text{EO}5)\text{Cl}]\cdot\text{H}_2\text{O}$. The alcoholic and water hydrogen atoms were not included in the final refinement.

$[\text{Nd}(\text{OH})_2(\text{EO}7)\text{Cl}_2]\cdot\text{H}_2\text{O}$. The alcoholic and water hydrogen atoms were not included in the final refinement.

$[\text{Nd}(\text{OH})_2(\text{OHMe})_2]\text{Cl}_3$. The methyl hydrogen atoms were included as rigid groups with rotational freedom at the bonded carbon atom (C-H

= 0.95 Å, $B = 5.5 \text{ \AA}^2$). The remaining hydrogen atoms were not included in the final refinement.

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Supplementary Material Available: Tables SI-SXXXVIII, listing crystal data and data collection and refinement parameters, bond distances and angles, hydrogen atom coordinates, thermal parameters, hydrogen-bonding contact geometries, and torsion angles, and Figures SI-SIV, showing the unit cells for the 18-crown-6, EO6, and EO7 complexes and the Nd^{3+} ion coordination environment in $[\text{Nd}(\text{OH})_2(\text{OHMe})_2]\text{Cl}_3$ (44 pages); tables of observed and calculated structure factors or amplitudes (59 pages). Ordering information is given on any current masthead page.

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Chiral Discriminations and Crystal Packing. Two Diastereomeric Compounds Involving Complex Ions of D_3 Symmetry, Tris(ethylenediamine)cobalt(III) and Tris(oxalato)rhodate(III)

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Factors governing the chiral recognition of three-bladed-propeller type metal complexes were analyzed. Crystal structures of two diastereomeric compounds of $[\text{Co}(\text{en})_3]^{3+}$ (en = 1,2-diaminoethane) and $[\text{Rh}(\text{ox})_3]^{3-}$ (ox = oxalate dianion) have been determined by single-crystal X-ray structure analysis. Crystal I, Δ - $[\text{Co}(\text{en})_3]$ - Δ - $[\text{Rh}(\text{ox})_3]$ is rhombohedral, with $a = 13.069$ (2) Å, $c = 9.877$ (3) Å, space group $R\bar{3}$, and $Z = 3$, and the structure was refined to $R = 0.025$. It is made up of columns of alternating cations and anions along the c axis with the molecular C_3 axes colinear. Crystal II contains optically impure $[\text{Co}(\text{en})_3]^{3+}$ (60% Δ and 40% Λ) and Δ - $[\text{Rh}(\text{ox})_3]^{3-}$. It is monoclinic, with $a = 8.172$ (2) Å, $b = 15.343$ (3) Å, $c = 8.325$ (2) Å, $\beta = 102.99$ (1)°, space group $P2_1$, and $Z = 2$, and the final R value was 0.054. The structure containing Δ - $[\text{Rh}(\text{ox})_3]^{3-}$ accommodates either Δ - or Λ - $[\text{Co}(\text{en})_3]^{3+}$ equally well without any unusually close contacts between the complex ions. All the hydrogen atoms in I and II are involved in hydrogen bonding. The crystal-packing mode is compared with that of reported D_3 -type structures and discussed in the context of chiral recognitions and optical resolution. For those complexes where dispersion forces are dominant, nearly parallel or nearly tetrahedrally tilted arrangements of molecular C_3 axes are often adopted, in agreement with our previous theoretical calculations. When hydrogen bonding is available, this will become a dominant factor. In these cases, the frequently observed C_3 colinear cation-anion mutual orientations afford full use of hydrogen bonding regardless of the chirality of the complex ions or the stacking conformation. Hydrogen bonds perpendicular to the C_3 axes appear to contribute toward successful chiral discriminations.

Introduction

Chirality and optical resolution of chiral compounds are becoming increasingly important in fields related to biology and medicine. However, at present, the molecular basis of optical resolution is poorly understood. To investigate the mechanism of chiral recognitions and discriminations in the crystalline state, we have studied the crystal structures of several different classes of chiral compound including organic molecules with helical morphology,^{1,2} sodium ammonium tartrate³ originally described by Pasteur, and metal complexes.^{4,5} We have been particularly interested in conformationally rigid chiral compounds of high symmetry. Tris-bidentate metal complexes with octahedral coordination exhibit the highest chiral symmetry, D_3 , which facilitates spectroscopic and theoretical analysis of chiral discriminations. These compounds adopt a propeller type structure and exist as optical isomers of Δ (right-handed propeller) and Λ (left-handed propeller) forms, even when the ligand is achiral. Previously, we calculated the chiral discrimination dispersion energy of a model neutral D_3 metal complex, for both an active pair, Δ - Δ or Λ - Λ configuration, and a racemic pair, Δ - Λ configuration, on the basis of an extended monopole model.⁶ The

theoretical analysis showed that there are preferred mutual orientations of the molecules both in the active and racemic system.

The orientations of complexes in the crystalline state were studied and compared in $[\text{Cr}(\text{pd})_3]$ (III)⁴ (pd = 1,2-diaminopropane), and $[\text{Cr}\{(-)\text{bdtp}\}_3]$ (IV)⁵ (bdtp = dimethylethylene dithionato anion). Both compounds were chosen for analysis because they are neutral and devoid of solvent molecules of crystallization: the presence of counterions and solvent molecules contributes to the crystal-packing mode, complicating the analysis of chiral recognition. The theoretical predictions and the observed crystal packings were in reasonable agreement.^{4,5} We have now extended the work to a diastereomeric system, $[\text{Co}(\text{en})_3]^{3+}[\text{Rh}(\text{ox})_3]^{3-}$, where both the cation and the anion possess the simplifying feature of D_3 symmetry. In this system, the complex ions carry electrostatic charges, while the ox and en ligands function as potential hydrogen-bond acceptors and donors, respectively. Thus, not only the shape of the molecules but also electrostatic interactions including hydrogen bonding are expected to play an important role in the chiral discriminations. Two diastereomeric crystals (I and II) were made, and their crystal structures were determined. The crystal packing mode of the structures as well as those of other known diastereomeric D_3 tris(bidentate)metal complexes, K - Δ - $[\text{Ni}(\text{phen})_3]$ - Λ - $[\text{Co}(\text{ox})_3]\cdot 2\text{H}_2\text{O}$ (V)⁷ (phen =

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