Lanthanide polyether complexation chemistry: the interaction of hydrated lanthanide(III) nitrate salts with an acyclic 18-crown-6 analog, pentaethylene glycol†

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The complexation reactions of 1 : 1 molar ratios of $M(NO_3)_3 \cdot nH_2O$ (M = Y, La–Pr, Sm–Lu) and pentaethylene glycol (EO5) in 3 : 1 CH_3CN : CH_3OH were investigated. Crystalline complexes were isolated for all metals investigated and X-ray structural analyses performed. The $M(NO_3)_3$–EO5 complexes structurally characterized are remarkably similar to the corresponding 18-crown-6 complexes. Six structurally unique types of anhydrous complexes with the early- to mid-lanthanides (M = La–Nd, Sm–Dy) were found. For the largest metals studied, the twelve coordinate species $[M(NO_3)_3(EO5)]$ (M = La, Ce) were isolated. A second form of the type $[Ce(NO_3)_2(EO5)]_7[Ce(NO_3)_6][NO_3]_4$ was isolated for M = Ce from the same reaction mixture as the above complex. Praseodymium through dysprosium form ten coordinate species which all have the same basic formula, $[M(NO_3)_2(EO5)][NO_3]$, however, four structurally unique forms have been characterized with the major differences between each arising from the way in which the uncoordinated nitrate anion is hydrogen bonded to the glycol ligand, and the glycol conformation. The smallest lanthanides investigated, M = Ho–Lu, Y, form outer-sphere complexes $[M(OH_2)_3(NO_3)_3] \cdot EO5$. Structural results suggest that the flexibility of the acyclic EO5 ligand allows for the formation of inner sphere complexes across most of the series, whereas the cyclic 18-crown-6 is too constrained to permit such complexation to the mid- to late-lanthanides.

Introduction

The use of macrocyclic polyether ligands as extractants for f-elements has been well investigated,[1] while the use of the analogous open-chain ligands, polyethylene glycols (PEGs), has been widely overlooked. We have previously investigated the use of acyclic polyethers as extractants in novel aqueous biphasic systems formed by salting-out aqueous solutions of high molecular weight PEGs with simple inorganic salts;[2–5] and more recently utilizing a hydrophilic ionic liquid as the species salted-out.[6] In hopes of gaining valuable information on the interaction of f-elements with PEG polymers and on PEG control of an f-element's coordination sphere, we are continuing our solid-state investigation of lanthanide–polyether complexes.

Chloride and nitrate are important anions in f-element separations because they are present at high concentrations in a variety of real world waste systems,[7] and we have previously characterized a large number of lanthanide chloride complexes of crown ethers and PEGs.[8,9] That work demonstrated that in general, the more flexible PEG ligands are able to wrap the lanthanides in a helical fashion while the crown ethers, due to their rigid cavity size, are forced to coordinate in an out-of-cavity fashion or are displaced to hydrogen bonded, outer-sphere locations if the metal ion–cavity size fit was not compatible. The PEG ligands were also able to displace chloride ions from the primary coordination sphere, and very few tight ion pairs were observed. Chloride and H_2O competed for the remaining open coordination sites with results often dictated by steric concerns.

A limited number of lanthanide(III) nitrate–PEG complexes have been previously reported in the literature.[10–16] These results indicate that the glycol ligands wrap the metal ions in a pseudo-planar fashion with two or three directly coordinated nitrate ions depending on the size of the metal. We report here the results obtained with the acyclic 18-crown-6 analog, pentaethylene glycol (EO5), in an effort to systematically characterize the complete lanthanide nitrate series.

Results

Preparation of complexes

The reactions of hydrated lanthanide(III) nitrate salts with pentaethylene glycol in a 1 : 1 molar ratio with a 3 : 1 CH_3CN : CH_3OH solvent resulted in the isolation of crystalline complexes for the entire series (except for M = Pm which was not investigated), as well as for the similar La^{3+} and Y^{3+}. Analytical and structural data have confirmed the formation of seven unique structural forms for this series of complexes. The 12-coordinate complex $[M(NO_3)_3(EO5)]$ is isolated for M = La, Ce. A second structural form which contains both

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12-coordinate and 10-coordinate Ce^{3+} centers, $[Ce(NO_3)_2(EO5)]_7[Ce(NO_3)_6][NO_3]_4$, was isolated for M = Ce from the same reaction mixture as the first form. The lanthanides M = Pr, Nd, Sm–Dy form four different structurally unique complexes of the general type $[M(NO_3)_2(EO5)][NO_3]$ with structural transition points between Nd^{3+}–Sm^{3+}, Eu^{3+}–Gd^{3+}, and Tb^{3+}–Dy^{3+}. The smallest metal ions investigated, M = Ho^{3+}–Lu^{3+} and Y^{3+}, form the hydrogen bonded outer sphere species $[M(NO_3)_3(OH_2)_3] \cdot EO5$.

In general, the crystallization of these complexes occurred very readily. Slow solvent evaporation afforded well formed crystals of all complexes in which direct metal–ligand coordination is present. Diffraction quality crystals of the hydrogen-bonded complexes of the later lanthanides were more difficult to isolate. This is most likely a result of poor packing, possible disorder, and high thermal motion of the uncoordinated glycol ligand.

Structural results

$[M(NO_3)_3(EO5)]$ (M = La, Ce). La^{3+} and Ce^{3+} crystallize as the 12-coordinate anhydrous complexes depicted in Fig. 1 (average bonding parameters are given in Table 1). The glycol ligands wrap the metal ions in an equatorial, crown ether-like fashion (in fact, these complexes are nearly iso-structural with the analogous 18-crown-6 complexes).[17] Two nitrate anions (those containing N(1) and N(3)) coordinate the metal ion in a bidentate fashion on one side of the polyether while the third is coordinated on the other side. The overall arrangement is such that the planes formed by the nitrate ions are twisted with respect to one another.

All three of the bidentate nitrate ions are coordinated in an asymmetric fashion. The differences in the M–ONO_2 separations within each nitrate ion are 0.040 Å, 0.079 Å, and 0.093 Å in the lanthanum complex, and 0.040 Å, 0.068 Å, and 0.079 Å in the cerium complex.

In its most symmetrical possible conformation (analogous to a D_{3d} 18-crown-6 conformation), the glycol O–C–C–O torsion angles would alternate ±60° (±*gauche* (±g)) and all C–O–C–C torsion angles would be 180° (*anti*). The EO5 conformation in these complexes is similar except between O(3) and O(5). The overall O–C–C–O sequence is $g^-g^+g^-g^-g^+$. All C–C–O–C angles are *anti* except for C(5)–C(6)–O(4)–C(7) which approaches a g^- conformation.

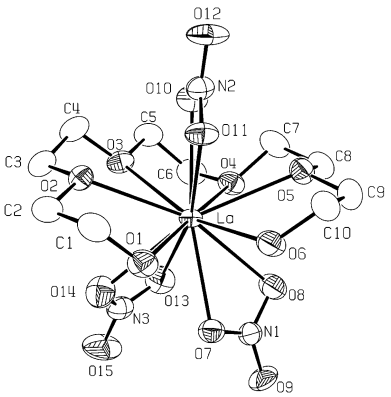

Fig. 1 ORTEP illustration of $[La(NO_3)_3(EO5)]$ with 50% probability thermal ellipsoids.

This angle resides between the two consecutive O–C–C–O angles of like sign.

The M–O separations to the glycol are not equal. The range in M–O(glycol) separations is 0.252 Å and 0.278 Å in the La^{3+} and Ce^{3+} complexes, respectively. In both, the M–O(3) separation is the largest observed at 2.821(3) Å for M = La and 2.824(5) Å for M = Ce. It is not clear whether the EO5 conformation described above is the cause or effect of the long M–O(3) distance.

The hydrogen bonding environment in lanthanide–PEG complexes is typically very important in governing the packing arrangements in the solid-state. In the La^{3+} and Ce^{3+} complexes, the alcoholic O(1) donates a hydrogen bond to a coordinated nitrate oxygen (O(14)) in a symmetry related molecule. (M–O(14) separation is the largest M–ONO_2 separation observed.) The other alcoholic terminus, O(6), donates a hydrogen bond to an uncoordinated nitrate oxygen (O(12)) in a different symmetry related molecule. The overall effect is the formation of hydrogen bonded chains along *b*, an obvious difference in the solid state structures observed for the analogous 18-crown-6 complexes.

$[Ce(NO_3)_2(EO5)]_7[Ce(NO_3)_6][NO_3]_4$. A structural transition point occurs at Ce^{3+} and a rather complex second form was isolated from the same reaction mixture that resulted in the 12-coordinate Ce^{3+} complex above. Although structure solution and refinement of this complex was hampered by severe disorder and the corresponding reduction in scattering ability, results clearly indicate presence of the 10-coordinate form which is found for later members in the series. This behavior is somewhat similar to that observed in the previously published 18-crown-6 complexes, $[M(NO_3)_2(18\text{-crown-}6)]_3[M(NO_3)_6]$ (M = Nd,[18] Gd[19]) in which $[M(NO_3)_6]^{3-}$ anions and ordered and disordered $[M(NO_3)_2(18\text{-crown-}6]^+$ cations are present in the unit cell.

Three unique $[Ce(NO_3)_2(EO5)]^+$ cations and a nitrate ion in the asymmetric unit were readily found and accurately refined. One additional $[Ce(NO_3)_2(EO5)]^+$ cation was found disordered across an inversion center. In addition, one ordered $[Ce(NO_3)_6]^{3-}$ anion which resides on a crystallographic inversion center was observed.

The Ce^{3+}–EO5 coordination environment is very similar to that observed in complexes containing the smaller lanthanides discussed below. In each case, one nitrate ion is displaced from the primary coordination sphere and the glycol ligands wrap cerium in an equatorial fashion. Two nitrates which are present in the primary coordination sphere are coordinated in a much more symmetric fashion compared to the previous cerium complex, with average M–ONO_2 separations of 2.538(4) Å, 2.56(1) Å, and 2.56(1) Å in the three ordered cations with a maximum M–ONO_2 difference of 0.02 Å for the same nitrate ion. Analysis of the torsion angles for the glycol ligands around these three cerium centers reveals a "D_{3d}" like conformation with all O–C–C–O angles alternating ±*gauche* and all C–O–C–C angles *anti*. All of these features would argue that the size of Ce^{3+} is a good fit for the observed coordination modes and coordination number.

$[M(NO_3)_2(EO5)][NO_3]$ (M = Pr, Nd (Type A); Sm, Eu (Type B); Gd, Tb (Type C); Dy (Type D)). All of these

Table 1 Comparison of average bonding parameters in selected lanthanide nitrate–PEG complexes

Compound	CN[a]	IR[b] /Å	M–O (alcoholic)		M–O (etheric)		M–ONO_2		Ref.
			Average/Å	Range/Å	Average/Å	Range/Å	Average/Å	Range/Å	
$[M(NO_3)_3(EO5)]$									
M = La	12	1.36	2.60(4)	0.052	2.75(5)	0.121	2.69(5)	0.123	[c]
M = Ce	12	1.34	2.58(4)	0.058	2.74(6)	0.144	2.66(5)	0.125	[c]
$[M(NO_3)_2(EO5)][NO_3]$									
TYPE A									
M = Pr	10	1.179	2.48(4)	0.055	2.62(5)	0.13	2.54(1)	0.024	[c]
M = Nd	10	1.163	2.46(2)	0.030	2.62(5)	0.12	2.53(4)	0.020	[c]
TYPE B									
M = Sm	10	1.132	2.45(1)	0.020	2.56(5)	0.100	2.49(3)	0.050	[c]
M = Eu	10	1.120	2.44(3)	0.037	2.55(4)	0.084	2.49(3)	0.058	[c]
TYPE C									
M = Gd	10	1.107	2.40(1)	0.020	2.57(4)	0.080	2.46(1)	0.030	[c]
M = Tb	10	1.095	2.40(5)	0.070	2.55(5)	0.090	2.45(3)	0.070	[c]
TYPE D									
M = Dy	10	1.083	2.39(3)	0.046	2.56(5)	0.114	2.44(2)	0.040	[c]
$[Nd(NO_3)_3(EO4)]$	10	1.163	2.51(3)	0.066	2.65(4)	0.089	2.55(2)	0.051	11
$[Nd(NO_3)_2(EO5)][NO_3]$	10	1.163	2.485(5)	0.01	2.59(3)	0.07	2.52(3)	0.08	12
$[Nd(NO_3)_3(EO3)]$	10	1.163	2.495(5)	0.01	2.52(2)	0.04	2.55(2)	0.06	13
$[La(NO_3)_3(EO4)]$	11		2.58(2)	0.05	2.70(3)	0.07	2.64(7)	0.20	14
$[La(NO_3)_3(EO3)]$	10		2.45(2)	0.036	2.502(6)	0.013	2.50(1)	0.034	15
$[La(NO_3)_2(OH_2)(EO3)]_2$	10		2.47(9)	0.225	2.63(3)	0.066	2.70(2)	0.053	16

[a] CN = coordination number. [b] Ionic radii for M^{3+} and CN shown taken from ref. 32. [c] This study.

complexes crystallize as the 10-coordinate species represented in Fig. 2. The decreasing size of the Ln^{3+} ion results in only two inner sphere and one outer sphere nitrate anions, although a 12-coordinate 18-crown-6 complex of Pr^{3+} has previously been characterized.[17] Interestingly, Hirashima[11] has published a Nd^{3+} analog of Type B, rather than the Type A we have observed. This is further confirmation of the structural transition point which occurs between Nd^{3+} and Sm^{3+}.

The coordination geometry of the metal ions most closely approximates a bicapped square antiprism with etheric oxygen atoms O(2) and O(5) in capping positions. Glycol ligands wrap the metal ions in an equatorial fashion with two bidentate nitrate ions in a *trans*-staggered arrangement above and below

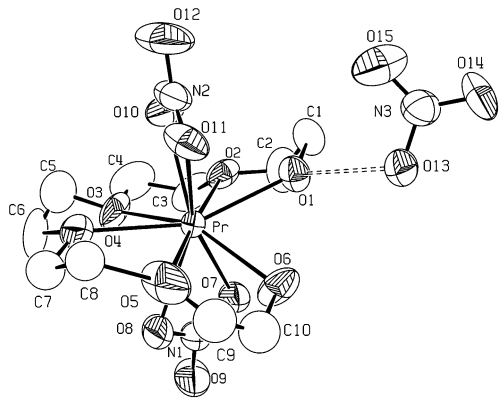

Fig. 2 ORTEP illustration of $[Pr(NO_3)_2(EO5)][NO_3]$ with 50% probability thermal ellipsoids.

the glycol. The nitrate ions are coordinated in a relatively symmetric fashion with maximum differences in M–ONO_2 separations within the same nitrate ion of 0.020 Å, 0.020 Å (Type A); 0.050 Å, 0.058 Å (Type B); 0.030 Å, 0.070 Å (Type C); and 0.040 Å (Type D).

The glycol ligands found in Type A are disordered with C(7)–C(8) and C(9)–C(10) exhibiting ±*gauche* disorder. In Types B and C the same disorder occurs at C(1)–C(2) and C(3)–C(4). This results in two possible glycol conformations (Table 2). The first one is similar to that of D_{3d} 18-crown-6 with O–C–C–O alternating ±g and all C–O–C–C angles *anti*. The second possibility is similar to that observed in the La^{3+} and Ce^{3+} complexes with an overall O–C–C–O sequence of $g^+g^-g^+g^+g^-$. All C–C–O–C angles are *anti* except for the one residing between consecutive O–C–C–O angles of like sign which is forced toward *gauche*. Notably, the disorder in the glycol ligand is only observed for M = Pr–Tb. As the size of the Ln^{3+} ion decreases, the glycol is ultimately (at M = Dy) forced into an ordered, decidedly non-'crown ether like' conformation where the three central O–C–C–O torsion angles are all g^-. This conformation requires two of the intervening C–O–C–C torsion angles to be distorted away from the *anti* conformation toward *gauche* (−94.8° and −97.4°) giving a 'kink' to the glycol ligand. This glycol conformation is unlike any of those observed in previous members of this series and highlights the conformational flexibility of this ligand.

The hydrogen bonding observed in these complexes results in the formation of dimers with the two halves bridged by nitrate anions (Fig. 3). In Types A, C, and D, one oxygen from two uncoordinated nitrate anions each accepts two hydrogen

Table 2 Representative torsion angles

Angles/deg	$[La(NO_3)_3(EO5)]$	$[Pr(NO_3)_2(EO5)]^+$	$[Sm(NO_3)_2(EO5)]^+$	$[Gd(NO_3)_2(EO5)]^+$	$[Dy(NO_3)_2(EO5)]^+$
O(1)–C(1)–C(2)–O(2)	−56.8	57.9	28.0 (39.7)	28.6 (−31.4)	50.5
C(1)–C(2)–O(2)–C(3)	177.7	168.5	166.2 (−176.9)	164.0 (−160.4)	171.7
C(2)–O(2)–C(3)–C(4)	173.4	−166.8	−169.9(−152.8)	−145.0 (175.9)	−177.5
O(2)–C(3)–C(4)–O(3)	60.5	−54.9	−38.5 (−25.1)	−48.4 (21.8)	−56.8
C(3)–C(4)–O(3)–C(5)	175.5	167.3	154.2 (170.6)	172.1 (128.8)	−176.5
C(4)–O(3)–C(5)–C(6)	−179.1	166.4	173.8 (−139.7)	−161.6 (168.4)	−94.8
O(3)–C(5)–C(6)–O(4)	−61.0	63.2	67.3 (−52.8)	42.9	−58.3
C(5)–C(6)–O(4)–C(7)	−88.3	173.4 (150.4)	−179.7 (−109.7)	168.8	−97.4
C(6)–O(4)–C(7)–C(8)	−169.6	−173.8 (120.2)	175.6 (−156.1)	117.8	−175.0
O(4)–C(7)–C(8)–O(5)	−61.3	−61.7 (53.7)	−49.0	45.4	−53.3
C(7)–C(8)–O(5)–C(9)	179.6	−129.5 (179.0)	−168.6	175.8	−175.9
C(8)–O(5)–C(9)–C(10)	−175.4	165.4 (−163.8)	158.9	−177.2	179.6
O(5)–C(9)–C(10)–O(6)	53.1	28.3 (−62.5)	44.5	−38.4	50.0

[a] Torsion angles involving disordered positions appear in parentheses.

bonds (the alcoholic O(1) donates a hydrogen bond to O(13) of the uncoordinated nitrate anion and the other alcoholic oxygen, O(6), donates a hydrogen bond to O(13) in a symmetry related anion). In Type B, however, each uncoordinated nitrate anion accepts hydrogen bonds with two oxygens rather than one, resulting in the arrangement shown in Fig. 3B. Here, the alcoholic O(1) donates a hydrogen bond to O(13) of the uncoordinated nitrate, while the other alcoholic terminus, O(6), donates a hydrogen bond to O(14) of a symmetry related molecule. These differences, although subtle, result in the four crystallographically unique structural types observed.

$[M(OH_2)_3(NO_3)_3]\cdot(EO5)$ (M = Ho–Lu, Y). For smaller, heavier lanthanide complexes, there is no direct glycol–metal interaction observed. The glycol ligand is displaced to a hydrogen bonded outer coordination sphere and interacts with coordinated water molecules *via* hydrogen bonding. Extensive thermal motion and possible disorder in the ligand made positive location of the glycol very difficult, but was eventually accomplished for M = Lu. The major structural features are clear, namely the identity of all inner sphere anions and water molecules, and the lack of a directly coordinated glycol ligand. Identification of the rest of the series was achieved by matching preliminary unit cell data and confirmed with elemental analyses.

This behavior is quite common in Ln^{3+}–crown ether complexes. The structures of $[M(NO_3)_3(OH_2)_3]\cdot 18\text{-crown-6}$ (M = Y, Eu–Lu)[17,20] and $[Dy(OH_2)_8]Cl_3\cdot 18\text{-crown-6}\cdot 4H_2O$[21] have

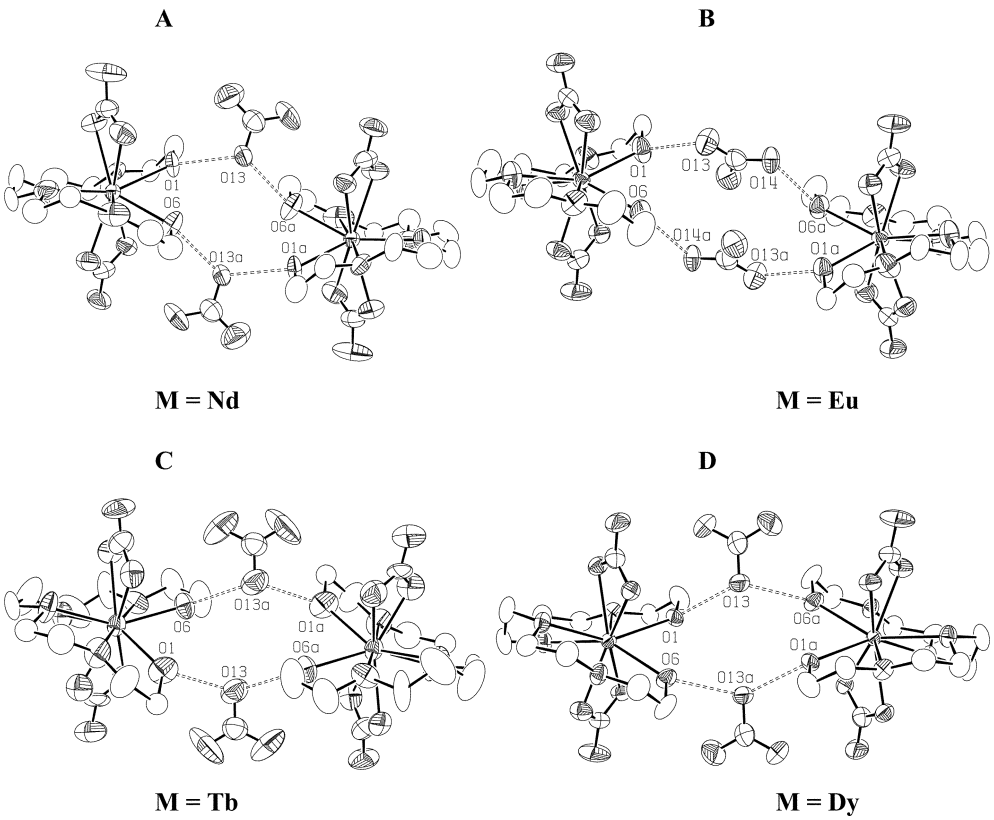

Fig. 3 Hydrogen bonded dimers observed for the four crystallographically unique $[M(NO_3)_2(EO5)][NO_3]$ complexes.

been previously reported. Until very recently, however, we have not observed this type of behavior with the acyclic PEG ligands as direct coordination across the entire series of metals is usually observed.

Discussion

Given the differences in the more rigid, cyclic, 18-crown-6 ligand compared to EO5, the behavior observed for the lanthanide(III) nitrate–EO5 complexes is amazingly similar to that found for 18-crown-6. La^{3+} and Ce^{3+}, the largest metal ions investigated, can accommodate three bidentate nitrate anions and the six glycol oxygen donors in the primary coordination sphere, although the nitrate anions are slightly asymmetric. There is virtually no difference in the macrocyclic complex compared to that of the acyclic one and they appear to be essentially isostructural. The average M–ONO_2 and M–O(etheric) distances in the EO5 complexes and the previously published $[La(NO_3)_3(18\text{-crown-6})]$[20] and $[Ce(NO_3)_3(18\text{-crown-6})]$[22] are also comparable. Neglecting the extra ethyl linkage present in 18-crown-6, the ligand conformation is also identical in the acyclic and macrocyclic complexes. 18-crown-6 adopts a C_2(A) conformation (as defined by Fyles and Gandour[23]).

As the size of the metal ions decrease across the series, the third nitrate is displaced to a hydrogen bonded secondary coordination sphere. The transition point for this behavior occurs at M = Ce and we observe a mixture of the two types of complexes in the same reaction vessel. We often observe mixtures of different structural forms from the same reaction at the structural transition points in our series of lanthanide(III)–polyether complexes.[9] The transition point for this behavior in the analogous 18-crown-6 complexes appears to occur at M = Nd and the structures of both $[Nd(NO_3)_3(18\text{-crown-6})]$[24,25] and $[Nd(NO_3)_2(18\text{-crown-6})][Nd(NO_3)_6]$[18] have been reported.

Four different structural types (A–D above) of the same formula unit ($[M(NO_3)_2(EO5)][NO_3]$) were found for (M = Pr–Dy). The same $[M(NO_3)_2(EO\#)]^+$ core has been repeatedly observed in lanthanide(III) nitrate–PEG complexes, not only for EO5, but also for PEGs of differing chain lengths.[26] These complexes are essentially identical in coordination, but differ in their hydrogen bonding interactions.

An interesting trend in the coordination mode of the nitrate anion is observed near the structural transition points. As the complexes approach a transition point in the series, there appears to be a much greater tendency for the nitrate ions to coordinate in an asymmetric fashion. A transition point is clearly observed at M = Ce and a mixture of complexes is isolated. In the first form (which is isostructural with the earlier M = La complex), the nitrates display pronounced asymmetric coordination. The second form, which contain the same $[M(NO_3)_2(EO5)]^+$ ions present in the M = Pr–Dy complexes, contain nitrates coordinated in a much more symmetric fashion compared to the previous form. In all of the complexes containing two coordinated nitrate ions (M = Pr–Dy), the later member of each isostructural set displays a more asymmetric nitrate coordination compared to that of the earlier member. In addition, there appears to be a steady progression toward asymmetry in moving from M = Pr to M = Tb. In the last of the directly coordinated complexes (M = Dy), the nitrates are coordinated in a less asymmetric fashion, however, there is a distinct deformation of the EO5 conformation which may also indicate increasing steric pressure.

Equatorial conformation of the PEG ligand about the metal center is observed for all of the complexes, differing most recognizably at the last structurally analyzed lanthanide metal, where no disorder is seen and a definite kinking of the ligand occurs. Preferred orientations governed by steric demands on the metal center by both nitrate and PEG donors for coordination sites result in increasing strain as the metal ions become smaller. The increasing steric demand ultimately (for M = Ho–Lu and Y) results in displacement of the glycol from the primary coordination sphere. This behavior is common in crown ether complexes of both chloride and nitrate salts,[7,8,11,27] but not for the acyclic PEG ligands. In our investigations of Ln^{3+} complexes of PEGs of both longer and shorter chain length, we have never observed the displacement of the entire PEG ligand to the outer coordination sphere, although in the study of $[Sm(NO_3)_2(EO6)]_3[Sm(NO_3)_6]$,[26] we did observe a partially coordinated glycol, where 6 of 7 PEG donor atoms were coordinated to Sm^{3+}.

The above results contrast with the results obtained for lanthanide(III) chloride–PEG complexation, where the flexible polyether ligand easily displaces chloride ions. The net result for chloride complexes is a helical wrapping of the metal ion with direct metal–ligand interaction observed even for the smallest lanthanides investigated. Often, all of the chloride ions are displaced and water molecules fill any remaining coordination sites available. In contrast, at least two tight ion pairs are always observed in the analogous nitrate complexes. This may be due to a combination of effects including donor ability of the nitrate anion, the bidentate nature of the nitrate, as well as, the geometrical requirements of the ligands and anions.

Conclusions

Pentaethylene glycol (EO5), when complexed with the lanthanide(III) nitrates, is organized into a pseudo-cyclic, crown ether-like array. In this regard, the EO5 ligand behaves in a remarkably similar fashion to its cyclic analog, 18-crown-6. When the size of the metal ion is too small to accommodate three nitrates and the EO5 ligand in the primary coordination sphere, one nitrate ion is displaced to a hydrogen bonded, secondary coordination sphere. When the size of the metal ion decreases such that additional nitrate ions would have to be displaced to retain EO5 coordination, the glycol is displaced instead, occurring in this series after M = Dy.

For the analogous 18-crown-6 complexes, displacement of the ligand to the secondary coordination sphere occurs after M = Eu, much earlier in the Ln^{3+} series than found for the more flexible PEG molecules. The crown ether cannot distort to accommodate the decreasing ionic radii in the lanthanide series, due to its cyclic nature. The structural rigidity in the crown ligands are greater than that of the PEG analogs and

allow them to be better suited for the coordination of lanthanides as a complete series.

Experimental

Synthesis of complexes

Reagent grade CH_3OH and CH_3CN were distilled over CaH_2 and stored over 4 Å molecular sieves. Hydrated lanthanide(III) nitrate salts (Strem) and pentaethylene glycol (EO5) (Aldrich) were used without further purification.

The following procedure was used for the preparation of all complexes: 1.0 mmol of $M(NO_3)_3 \cdot nH_2O$ (M = La, Ce–Nd, Sm–Lu, Y) was dissolved in 5 mL of 3 : 1 CH_3CN : CH_3OH. 1.0 mmol of pentaethylene glycol (EO5) was then added to the solution. The mixture was heated with stirring for one hour at 60 °C. No precipitate formation was observed for any of the reactions. Slow evaporation of the solutions over a period of approximately two months yielded suitable crystals of each complex. Details for each complex follow.

$[M(NO_3)_3(EO5)]$ (M = La, Ce). M = La: Found: C, 21.23; H, 3.67; N, 7.04. Calc.: C, 21.33; H, 3.94; N, 7.46%. Analyses of the crystalline sample for M = Ce were inconsistent with either of the two formulations crystallographically characterized.

$[M(NO_3)_2(EO5)][NO_3]$ (M = Pr–Tb). M = Pr: Found: C, 21.25; H, 3.87; N, 6.85. Calc.: C, 21.28; H, 3.93; N, 7.44%. M = Nd: Found: C, 21.15; H, 3.88; N, 6.40. Calc.: C, 21.13; H, 3.90; N, 7.39%. M = Sm: Found: C, 21.37; H, 3.80; N, 6.89. Calc.: C, 20.90; H, 3.86; N, 7.31%. M = Eu: Found: C, 20.21; H, 3.73; N, 6.61. Calc.: C, 20.84; H, 3.85; N, 7.29%. M = Gd: Found: C, 20.63; H, 3.91; N, 6.56. Calc.: C, 20.65; H, 3.81; N, 7.23. M = Tb: Found: C, 20.36; H, 4.21; N, 7.00. Calc.: C, 20.59; H, 3.80; N, 7.20%. M = Dy: Found: C, 18.91; H, 4.50; N, 6.23. Calc.: C, 20.47; H, 3.78; N, 7.16%.

$[M(NO_3)_3(OH_2)_3] \cdot (EO5)$ (M = Ho–Lu, Y). M = Ho: Found: C, 18.88; H, 4.41; N, 6.66. Calc.: C, 18.67; H, 4.39; N, 6.53%. M = Er: Found: C, 18.63; H, 4.10; N, 6.09. Calc.: C, 18.60; H, 4.37; N, 6.51%. M = Tm: Found: C, 17.80; H, 3.91; N, 6.00. Calc.: C, 18.56; H, 4.36; N, 6.49%. M = Yb: Found: C, 18.46; H, 4.25; N, 5.68. Calc.: C, 18.44; H, 4.33; N, 6.45%. M = Lu: Found: C, 16.80; H, 4.01; N, 5.35. Calc.: C, 18.38; H, 4.32; N, 4.32%. M = Y: Found: C, 21.17; H, 4.98; N, 7.41. Calc.: C, 19.93; H, 5.09; N, 6.32%.

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 CAD4 diffractometer equipped with MoKα radiation (λ = 0.70173 Å), then collected at 20 °C. A summary of data collection parameters for all complexes studied is given in Table 3. All space groups were uniquely determined from systematic absences except for the $[M(NO_3)_3(OH_2)_3] \cdot (EO5)$ complexes discussed below. Except where noted, geometrically constrained hydrogen atoms were

‡ CCDC reference numbers 633837–633846. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b617452n

Table 3 Crystal data and summary of intensity data collection and structure refinement

	$[La(NO_3)_3(EO5)]$	$[Ce(NO_3)_3(EO5)]$	$[Ce(NO_3)_2(EO5)]_7[Ce(NO_3)_6][NO_3]_4$	$[Pr(NO_3)_2(EO5)][NO_3]$	$[Nd(NO_3)_2(EO5)][NO_3]$	$[Sm(NO_3)_2(EO5)][NO_3]$	$[Eu(NO_3)_2(EO5)][NO_3]$	$[Gd(NO_3)_2(EO5)][NO_3]$	$[Tb(NO_3)_2(EO5)][NO_3]$	$[Dy(NO_3)_2(EO5)][NO_3]$	$[Lu(NO_3)_3(OH_2)_3] \cdot EO5$[d]
FW	563.20[c]	564.42	4277.06	565.20	568.54	574.66	576.26	581.55	583.22	586.80	653.31
Space group cell constants[a]	*Pbca*	*Pbca*	$P2_1/c$	$P2_1/n$	$P2_1/n$	$P2_1/c$	$P2_1/c$	*Pbca*	*Pbca*	$P2_1/n$	$Pn2_1a$
a/Å	12.201(3)	12.177(4)	16.389(7)	11.610(2)	11.610(9)	8.230(2)	8.229(7)	12.378(4)	12.376(8)	11.724(4)	16.744(6)
b/Å	14.308(9)	14.292(3)	28.759(16)	12.439(3)	12.398(9)	14.998(5)	14.975(9)	14.732(6)	14.665(5)	14.009(9)	14.935(9)
c/Å	22.206(4)	22.135(4)	16.460(13)	14.338(9)	14.322(8)	16.074(6)	16.038(9)	21.720(9)	21.715(9)	11.925(11)	8.795(2)
β/deg			94.46(5)	105.91(4)	105.81(9)	97.36(3)	97.40(9)			95.37(6)	
Cell volume/Å^3	3876.5	3852.3	7734.6	1991.3	1983.5	1968	1960	3960.7	3941.1	1950.0	2199
Formula units/unit cell	8	8	2	4	4	4	4	8	8	4	4
D_{calc}, g cm^{-3}	1.93	1.95	1.84	1.89	1.90	1.94	1.95	1.95	1.97	2.00	1.97
μ_{calc}/cm^{-1}	23.3	24.8	24.6	25.3	27.1	31.2	33.1	35.4	37.63	40.6	48.1
Range of relative transmission factors (%)	62/100	67/100	73/100	75/100	64/100	89/100	86/100	69/100	60/100	77/100	81/100
2θ range/deg	$2 \leq 2\theta \leq 50$	$2 \leq 2\theta \leq 50$	$2 \leq 2\theta \leq 50$	$2 \leq 2\theta \leq 50$	$2 \leq 2\theta \leq 50$	$2 \leq 2\theta \leq 50$	$2 \leq 2\theta \leq 50$	$2 \leq 2\theta \leq 50$	$2 \leq 2\theta \leq 50$	$2 \leq 2\theta \leq 50$	
Reflections measured	3830	3821	14 417	3864	3840	3846	3828	3940	3916	3758	
Reflections observed $[F_o \geq 5\sigma(F_o)]$[b]	2558	1974	5271	2159	1423	1574	2461	1679	1330	2263	
Number of parameters varied	262	262	798	258	258	256	316	260	260	262	
GOF	1.43	1.40	8.65	0.96	0.70	0.67	0.61	1.96	1.32	0.70	
R	0.025	0.035	0.061	0.047	0.049	0.046	0.034	0.048	0.045	0.036	
R_w	0.031	0.038	0.068	0.058	0.054	0.048	0.045	0.059	0.052	0.039	

[a] Least squares refinement of $((\sin\theta)/\lambda)^2$ values for 25 reflections $\theta > 15°$. [b] Corrections: Lorentz-polarization and absorption (empirical, psi scan). [c] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = [\Sigma w(||F_o| - |F_c||)^2/\Sigma w(F_o)^2]^{1/2}$. [d] Although we did solve this structure far enough to determine its stoichiometry and coordination, this and the remaining members of this series (M = Ho, Er, Tm, Yb, and Y) gave data sets which were not suitable for publication as final refinements.

placed in calculated positions 0.95 Å from the bonded carbon atom and allowed to ride on that position with B fixed at 5.5 Å^2. The alcoholic hydrogen atoms were not included in the final refinements unless otherwise noted. Structures were rendered with ORTEP-3,[28] refined using SHELX-76,[29] and neutral atom scattering factors were from International Tables.[30] Initial structure solution was carried out using heavy-atom techniques.[31] Subsequent members of an isostructural pair were refined by starting with the non-hydrogen coordinates from the previously determined complex. Any unique considerations for each crystallographic series are discussed below.

$[M(NO_3)_3(EO5)]$ (M = La, Ce). The alcoholic hydrogen atoms were located from difference Fourier maps and included with fixed contributions (B = 5.5 Å^2).

$[Ce(NO_3)_2(EO5)]_7[Ce(NO_3)_6][NO_3]_4$. Data collection and structure solution for this compound were problematic. The crystals had relatively poor scattering ability with only 37% observed reflections for the best data set collected. With the limited data available it was possible to solve the structure with one severely disordered Ce complex cation and one disordered NO_3^- in the asymmetric unit. The $[Ce(NO_3)_6]^{3-}$ anion on a center of inversion, three $[Ce(NO_3)_2(EO5)]^+$ cations, and a nitrate anion were readily found and refined. One $[Ce(NO_3)_2(EO5)]^+$ cation is disordered across an inversion center. For this cation, the cerium atom itself is fractionally disordered. Two cerium positions were included with 0.25 site occupancy factors (50% occupancy each). While it was obvious that this was indeed a $[Ce(NO_3)_2(EO5)]^+$ cation, it was not possible to resolve all of the C, O, and N positions. As much of the electron density as possible was included. The result is a doughnut of atomic positions around an equatorial plane of the cerium atoms and positions suggesting twisted *trans* nitrate anions coordinated to them. A free nitrate ion which is apparently hydrogen bonded to this cerium cation also suffered from disorder, most likely as result of the hydrogen bonding possibilities in the disorder model. Due to the disorder, no hydrogen atom positions were included in the final refinement. The disordered atoms and all other C atoms were refined isotropically only.

$[M(NO_3)_2(EO5)][NO_3]$ (M = Pr, Nd). After the initial refinement, high thermal motion and unreasonable torsion angles were noted for the ethylene units C(7)–C(8) and C(9)–C(10) indicative of +60° (+g) disorder. A 50%/50% disorder model was developed for these carbon atoms which results in either O–C–C–O = 60° (g^+) or O–C–C–O = −60° (g^-). These atoms were isotropically refined at half occupancy in alternate least squares cycles.

$[M(NO_3)_2(EO5)][NO_3]$ (M = Sm, Eu). After all non-hydrogen atoms were located, it became apparent that several of the carbon positions were disordered. Unrealistic C–C and C–O distances and O–C–C–O torsion angles were noted for C(1)–C(2), C(3)–C(4), and C(5)–C(6), but not for C(7)–C(10), although the latter had marginally elevated thermal parameters. Each of the carbon atoms C(1)–C(6) were resolved into two orientations corresponding to +60° (+g) (O–C–C–O) disorder. These positions were refined in alternate least squares cycles with occupancy factors of 0.5. Due to the disorder the hydrogen atoms were not included in the final refinement.

$[M(NO_3)_2(EO5)][NO_3]$ (M = Gd, Tb). High thermal motion was noted for several carbon atoms (especially C(1) and C(4)) and the free nitrate oxygen atoms O(14) and O(15). Two positions each at 50% occupancy were subsequently resolved for C(1) and C(4). This gave O–C–C–O torsion angles of either +60° (+g) for O(1)–C(1)–C(2)–O(2) and O(2)–C(3)–C(4)–O(3). No further glycol disorder could be resolved. Due to the disorder hydrogen atoms were not included in the final refinement.

$[Dy(NO_3)_2(EO5)][NO_3]$. Disorder could not be resolved for the nitrate anion. Only one oxygen (O(13)) is H-bonded, thus leaving no degree of freedom for the O(14) and O(15) positions. This structure was fully ordered and H-atoms were placed in calculated positions. The two alcoholic H-atoms were not included in the final refinement.

$[M(NO_3)_3(OH_2)_3]\cdot(EO5)$. Structure solution and refinement for these complexes were also problematic. The $[M(NO_3)_3(OH_2)_3]$ core was readily found and easily refined for M = Er and Lu (in the space group $Pn2_1a$). Location of the glycol ligand, however, was not trivial. A doughnut of electron density was observed and this electron density appeared to be positioned to interact with the coordinated water molecules *via* hydrogen bonds. We have observed this type of interaction very frequently with crown ether ligands. Location of all glycolic oxygen and carbon atoms was eventually accomplished for M = Lu. High thermal motion, most likely a result of disorder, made refinement of these positions impossible. Identification of the rest of the members of the series was done by matching the unit cell data and elemental analyses.

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