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Effects of Polyethylene Glycol on the Coordination Sphere of Strontium in $SrCl_2$ and $Sr(NO_3)_2$ Complexes

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The reactions of $SrCl_2·6H_2O$ or $Sr(NO_3)_2$ in CH_3CN (in the presence of $NH_4OH(aq)$) with polyethylene glycols (PEGs: triethylene glycol (EO3), tetraethylene glycol (EO4), pentaethylene glycol (EO5), or hexaethylene glycol (EO6)) in 1/1 stoichiometries lead to the isolation of directly coordinated complexes. X-ray structural analyses of nine of these complexes have been carried out. The chlorides crystallize as discrete ions with the strontium cations surrounded by 8−10 oxygen donors and the chloride ions hydrogen bonded in the lattice. The EO3 and EO4 complexes have a 2/1 PEG/Sr^{2+} stoichiometry while the EO5 and EO6 complexes can support only a 1/1 ratio but complete the Sr^{2+} coordination sphere with H_2O molecules. Both a hydrated and an anhydrous form of the EO4 complex were isolated. Cell data for the five $SrCl_2$/PEG complexes are as follows. $[Sr(EO3)_2]Cl_2$ ($C222_1$) (at 19 °C): $a = 8.737(4)$ Å, $b = 18.609(9)$ Å, $c = 12.548(9)$ Å, and $D_{calc} = 1.49$ g cm^{-3} for $Z = 4$. $[Sr(EO4)_2]Cl_2$ ($C2/c$) (at 20 °C): $a = 17.528(9)$ Å, $b = 9.209(3)$ Å, $c = 17.180(9)$ Å, $\beta = 121.13(8)°$, and $D_{calc} = 1.53$ g cm^{-3} for $Z = 4$. $[Sr(EO4)_2]Cl_2·3H_2O$ ($P2_1/n$) (at 19 °C): $a = 12.225(7)$ Å, $b = 18.336(9)$ Å, $c = 12.258(9)$ Å, $\beta = 90.25(5)°$, and $D_{calc} = 1.45$ g cm^{-3} for $Z = 4$. $[Sr(OH_2)_3(EO5)]Cl_2$ ($P\bar{1}$) (at 18 °C): $a = 8.217(9)$ Å, $b = 9.000(8)$Å, $c = 14.514(8)$ Å, $\alpha = 75.55(6)°$, $\beta = 83.33(7)°$, $\gamma = 69.59(9)°$, and $D_{calc} = 1.54$ g cm^{-3} for $Z = 2$. $[Sr(OH_2)_2(EO6)]Cl_2·H_2O$ ($P2_1/n$) (at 18 °C): $a = 9.741(6)$ Å, $b = 16.534(3)$ Å, $c = 13.600(4)$ Å, $\beta = 100.16(4)°$, and $D_{calc} = 1.52$ g cm^{-3} for $Z = 4$. The $Sr(NO_3)_2$/EO4−EO6 complexes all crystallize as tight ion pairs with *trans* nitrates and a nearly equatorial girdle of oxygen donors. To three structurally characterized complexes all have 1/1 PEG/Sr^{2+} stoichiometries and are all 10-coordinate. The achieve 10-coordination, the EO4 complex crystallizes as a monohydrate and in the EO6 complex the ligand is only hexadentate. The $Sr(NO_3)_2$/EO3 complex is also 10-coordinate but achieves this with two coordinated glycols and one bidentate nitrate anion. The second unique anion is hydrogen bonded to the glycols. Cell data for the four $Sr(NO_3)_2$/PEG complexes are as follows. $[Sr(NO_3)(EO3)_2]$ $[NO_3]$ ($P2_1$) (at 20 °C): $a = 8.156(2)$ Å, $b = 9.992(1)$ Å, $c = 13.158(2)$ Å, $\beta = 92.09(1)°$, and $D_{calc} = 1.59$ g cm^{-3} for $Z = 2$. $[Sr(NO_3)_2(OH_2)(EO4)]$ ($P\bar{1}$) (at 18 °C): $a = 7.911(2)$ Å, $b = 9.810(3)$ Å, $c = 10.917(3)$ Å, $\alpha = 92.43(3)°$, $\beta = 94.02(2)°$, $\gamma = 91.75(2)°$, and $D_{calc} = 1.67$ g cm^{-3} for $Z = 2$. $[Sr(NO_3)_2(EO5)]$ ($P\bar{1}$) (at 18 °C): $a = 9.330(9)$ Å, $b = 10.060(9)$ Å, $c = 11.684(5)$ Å, $\alpha = 67.86(8)°$, $\beta = 68.04(8)°$, $\gamma = 68.18(9)°$, and $D_{calc} = 1.65$ g cm^{-3} for $Z = 2$. $[Sr(NO_3)_2(EO6)]$ ($P2_1/c$) (at 19 °C): $a = 16.204(8)$ Å, $b = 10.760(4)$ Å, $c = 12.365(2)$ Å, $\beta = 106.91(4)°$, and $D_{calc} = 1.59$ g cm^{-3} for $Z = 4$. In all nine complexes, the glycols have fairly similar conformations and tend to form pseudocyclized in-cavity crown ether-like complexes. The average Sr−O(alcoholic) and Sr-O(etheric) separations range from 2.526(6) to 2.67(2) Å and from 2.603(1) to 2.74(5) Å, respectively.

Introduction

Radiostrontium present in highly alkaline waste storage facilities poses severe radiological and thermal hazards,[1,2] and the selective removal of these ions directly from alkaline media is difficult with traditional extraction systems. The need for improved separations strategies for strontium and the monitoring requirements of ^{89}Sr and ^{90}Sr in environmental samples has led to an emphasis on the selective removal and analysis of these isotopes. Recent advances in the development of selective extraction technologies (e.g., the SREX process[3,4]) and chromatographic materials (e.g., Sr•Spec[5−9]) have come about by using very selective crown ethers. Other research has focused on acyclic polyethylene glycols (PEGs), glymes or their derivatives, either as extracting ligands[10−13] or as synergists[14−16] in an extraction process. (Acyclic polyethers are thought to wrap Sr^{2+}, giving it a somewhat hydrophobic exterior, thus enhancing transfer to a hydrophobic phase.)

We have recently begun to study the partitioning behavior in high molecular weight PEG-based aqueous biphasic systems

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utilizing crown ethers as extractants.[17,18] PEG-based aqueous biphasic systems are formed by the salting out effect of certain inorganic anions (e.g., SO_4^{2-}, CO_3^{2-}, OH^-) on aqueous PEG.[19,20] The resulting two-phase system is completely aqueous, inexpensive, nonflammable, and nontoxic, thus providing the possibility of cleaner, cheaper, safer separations.[21] Utilizing crown ethers as extractants in these systems sets up a competition between the preorganized macrocycles and the acyclic, flexible PEG molecules.

In order to more fully understand the inorganic and coordination chemistry of Sr^{2+} responsible for its observed extraction behavior, we have investigated the structural chemistry of Sr^{2+}/PEG complexes. Since nuclear waste solutions typically have high concentrations of either chloride or nitrate anions, we have concentrated on the study of $Sr(NO_3)_2$ and $SrCl_2$ salts. The Sr^{2+}/PEG interactions were modeled with low molecular weight PEGs triethylene glycol (EO3) to hexaethylene glycol (EO6) in order to monitor the influence of PEG on the Sr^{2+} coordination sphere as a function of chain length. We compare our structural results with the three Sr^{2+}/PEG,[22-24] four Sr^{2+}/glyme,[25-28] and eight Sr^{2+}/crown ether[29-36] structures available in the literature.

Results

$[Sr(EO3)_2]Cl_2$. Triethylene glycol reacts with $SrCl_2$ to form the 2/1 complex depicted in Figure 1. The Sr^{2+} ion resides on a crystallographic 2-fold axis and has dodecahedral geometry. (The alcoholic oxygen atoms are in B-sites while the etheric oxygen atoms are in A-sites.) A similar coordination geometry was observed for $[Ca(EO3)_2]Cl_2{\cdot}4H_2O$.[37]

The glycol ligands mimic crown ether complexation of Sr^{2+}. These ligands form (as far as possible given their length) equatorial girdles which give the semblance of a crown ether with Sr^{2+} in the cavity. The 2/1 nature of the cation results in a flattening of the mean plane for each set of four donor atoms. The four oxygen atoms of each ligand, alternate ± from their mean plane a maximum of 0.16 Å. Each PEG thus coordinates in a fashion very similar to the template coordination found for PEG/HgX_2 (X = Cl, Br, I) complexes.[38]

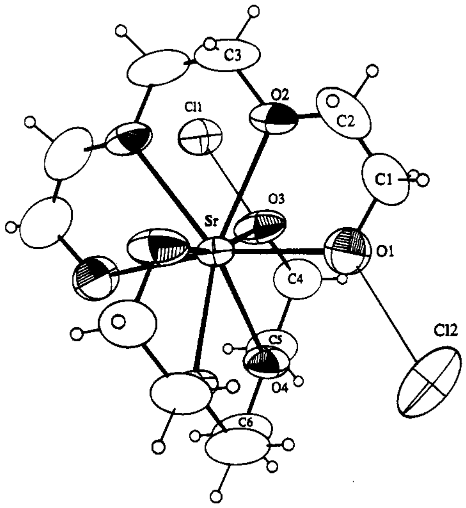

Figure 1. ORTEP illustration of the formula unit in $[Sr(EO3)_2]Cl_2$ with 50% probability ellipsoids. Hydrogen atoms have been arbitrarily reduced.

The crown ether-like behavior is further manifested in the torsion angle sequence $(g^-)(O(1)-C(1)-C(2)-O(2))aa(g^+)aa(g^-)$ where the O−C−C−O angles alternate ±g (±60°) and the C−O−C−C angles are all anti (180°). (In this and subsequent references to torsion angle sequences, the O−C−C−O angles are in parentheses.) This is identical to the conformation found for the same fragment in the common D_{3d} form of 18-crown-6.[39,40]

The alcoholic termini are hydrogen bonded to the chloride anions. Each chloride accepts two hydrogen bonds. Cl(1) bridges cations in linear polymeric chains along *a* where the cations are stacked. Cl(2) bridges cations in zigzag polymeric chains along *c*. The net effect produces 2-dimensional sheets of zigzag polymeric chains of hydrogen bonded columns.

$[Sr(EO4)_2]Cl_2$. The primary coordination sphere depicted in Figure 2 consists of 10-coordinate Sr^{2+} coordinated to two EO4 ligands. The Sr^{2+} ion resides on a 2-fold axis which relates the two glycol ligands. The overall geometry is that of a bicapped dodecahedron with O(3) and its symmetry related position in the capping sites ($O(3)-Sr-O(3)^a$ = 178.9(1)°). All of the remaining etheric oxygen atoms are in B-sites, and all of the alcoholic oxygen atoms are in A-sites.

The glycol ligands again appear to encircle Sr^{2+} rather than wrap around it. The torsion angle sequence does show some deviation from that observed for the EO3 complex and D_{3d} 18-crown-6. The C(7)−C(8) ethyl linkage exhibits ±g disorder; thus the torsion angle sequence may be $(g^+)ag^+(g^+)aa(g^-)aa(g^+)$ or $(g^+)ag^+(g^+)aa(g^-)ag^-(g^-)$. In the former there are only two consecutive O−C−C−O torsion angles of like sign while there are two sets of such in the latter. Whenever there is an occurrence of this, one of the two C−O−C−C torsion angles

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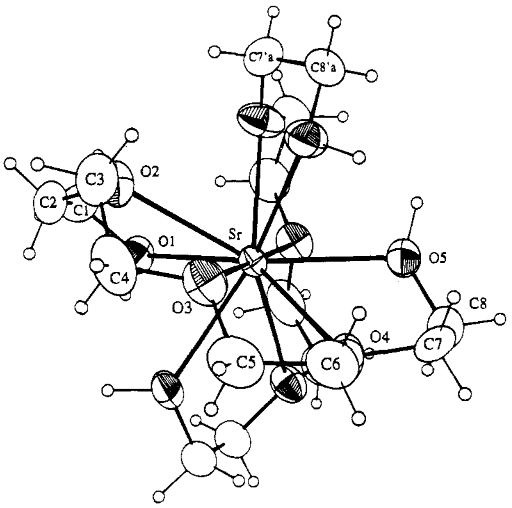

Figure 2. Cation in $[Sr(EO4)_2]Cl_2$.

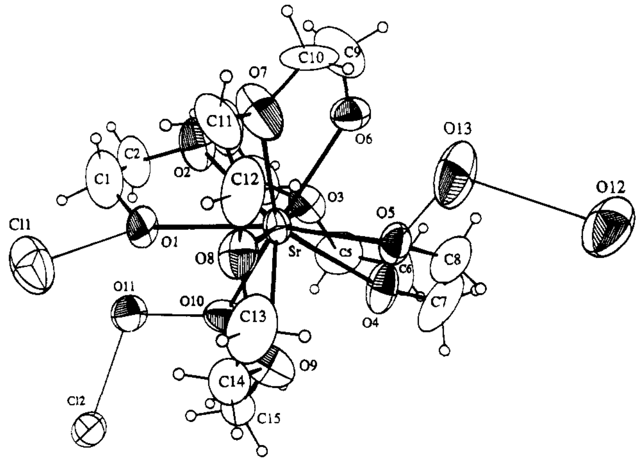

Figure 3. $[Sr(EO4)_2]Cl_2{\cdot}3H_2O$.

between O−C−C−O angles of like sign will be forced toward gauche, usually to a value close to 100°.

Each alcoholic oxygen atom donates a hydrogen bond to chloride anions. Every chloride anion accepts two hydrogen bonds from two different cations, forming polymeric hydrogen bonded chains along *b*.

$[Sr(EO4)_2]Cl_2{\cdot}3H_2O$. The asymmetric unit is depicted in Figure 3. The Sr^{2+} coordination environment is nearly identical to the anhydrous complex described above. The crystallographic symmetry is lower, and thus there are two glycol ligands in the asymmetric unit. The capping positions are O(3) and O(8) (O(3)−Sr−O(8) = 179.0(4)°).

Both glycol ligands have conformations found for the anhydrous complex. The torsion angle sequence for the O(1)−O(5) glycol is $(g^-)ag^-(g^-)aa(g^+)ag^+(g^+)$. The O(6)−O(10) glycol is disordered (C(15)−C(16) exhibits ±g disorder) in a way identical to the anhydrous complex and has an identical torsion angle sequence.

The presence of three water molecules per formula unit results in a complex 3-dimensional network of hydrogen bonds. Each glycol has one end which donates a hydrogen bond to a chloride anion and one end which donates a hydrogen bond to a water molecule. Each water molecule accepts one and donates two hydrogen bonds while Cl(1) accepts four and Cl(2) accepts three hydrogen bonds.

$[Sr(OH_2)_3(EO5)]Cl_2$. This complex is depicted in Figure 4. Unable to support a coordination number of 12, Sr^{2+} crystallizes as a 1/1 complex of EO5 with three water molecules completing the 9-coordination. The coordination geometry is roughly tricapped trigonal prismatic with alternating glycol oxygen atoms in the capping positions (O(2) (etheric), O(4) (etheric), and O(6) (alcoholic)). The primary coordination sphere of Sr^{2+} is very similar to what we observe for mid-to-late lanthanide chloride complexes of EO5 ($[M(OH_2)_3(EO5)]Cl_3{\cdot}H_2O$ (M = Y, Sm−Lu)).[39]

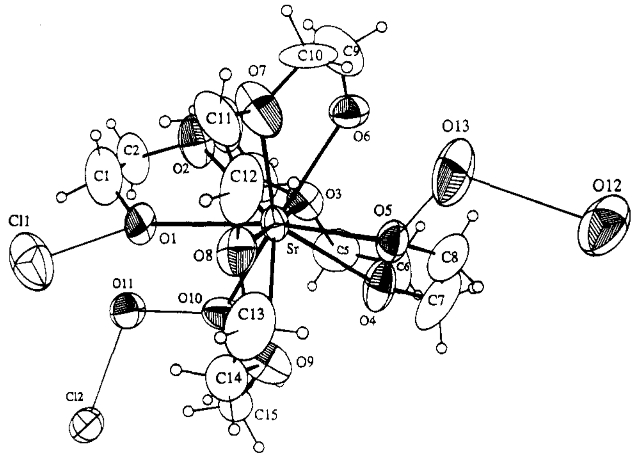

Figure 4. $[Sr(OH_2)_3(EO5)]Cl_2$. Only one conformation of the disordered carbon atoms is shown.

The glycol ligand again has a template coordination resembling a crown ether interaction with Sr^{2+}; however, due to the increased number of donors (from EO3 or EO4 to EO5) and the acyclic nature of the ligand, there is a slight distortion toward helical wrapping. The glycol ligand itself is disordered with C(1)−C(2) and C(9)−C(10) exhibiting ±gauche disorder. The resulting glycol conformations are interesting. In one possible conformation, the torsion angle sequence of D_{3d} 18-crown-6 is observed: O−C−C−O torsion angles alternating ±g and all C−O−C−C torsion angles anti. The remaining possible torsion angle sequences are similar to those observed in $[MCl_2(OH_2)(EO5)]Cl{\cdot}H_2O$ (M = La−Nd)[39] and $[M(OH_2)_3(EO5)]Cl_3{\cdot}H_2O$ (M = Y, Sm−Lu).[39] These conformations are comparable to those observed for the C_2(A) and C_s conformations of complexed 18-crown-6.[40]

The chloride anions again reside in the secondary coordination sphere. The two chloride positions have distinctly different hydrogen bonding interactions. The Cl(1) anion resides on the "underside" (as depicted in Figure 4) of the cation and is hydrogen bonded to both O(7) and O(8) of one cation, alcoholic O(6) and water molecule O(8) of a symmetry related cation, and the water molecule O(7) of a third symmetry related cation. Each Cl(1) anion thus has a total of five hydrogen bonding interactions.

The chloride anion Cl(2) has only three hydrogen bonding interactions. Cl(2) resides on the "upper side" of the cation with hydrogen bonds to the water molecule O(9) and the alcoholic O(1) from one cation and a second interaction with O(9) of a symmetry related molecule. The resulting hydrogen bonding produces 2-dimensional polymeric sheets in *b* oriented along the *ac* diagonal. Interestingly, the cations and anions are layered along *c* such that we find a row of cations, then a row of Cl(1) anions, a row of cations, a row of Cl(2) anions, etc.

$[Sr(OH_2)_2(EO6)]Cl_2{\cdot}H_2O$. The overall structure and geometry of the cation (Figure 5) are very similar to those found for $[Sr(OH_2)_3(EO5)]Cl_2$. The additional glycol donor in the EO6 derivative folds up and displaces the single water molecule that was coordinated "above" the polyether girdle in the EO5 complex. The resulting 9-coordinate geometry is that of a very

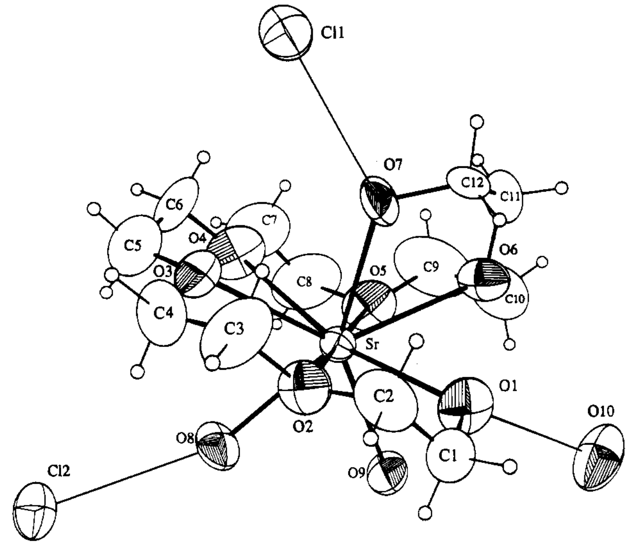

Figure 5. $[Sr(OH_2)_2(EO6)]Cl_2{\cdot}H_2O$.

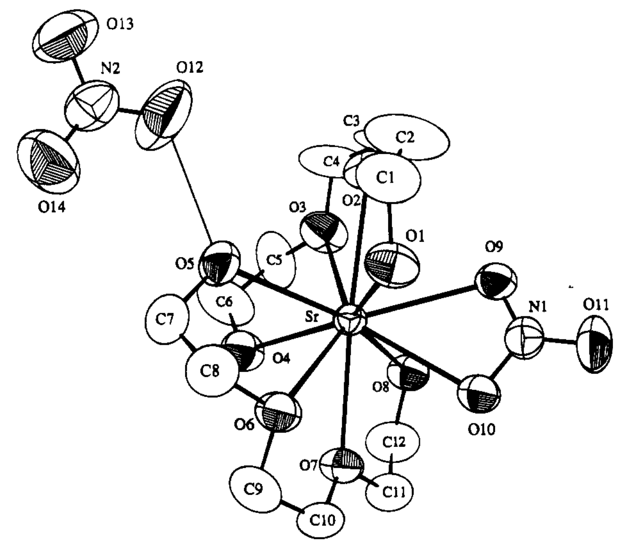

Figure 6. $[Sr(NO_3)(EO3)_2][NO_3]$.

distorted tricapped trigonal prism with alternating polyether oxygens (O(1), O(3), O(5)) in the capping positions. (This is a prominent feature in the 9-coordinate complexes of PEGs with lanthanide(III) chlorides.[41-44])

The EO6 ligand coordinates in a template fashion with the first five oxygens coordinated in a nearly planar fashion (Δ_{max} = 0.25 Å). The sixth oxygen is displaced 1.6 Å out of this plane, and O(7) breaks the crown-like coordination as it bends up to fill the open coordination site. The flexibility of the glycol which leads to the observed behavior is evident in the torsion angle sequence. The fragment O(1) through O(5) displays the sequence observed for D_{3d} 18-crown-6 with alternating O−C−C−O torsion angles of ±60° and anti C−O−C−C torsion angles. The torsion angles around C(7)−C(8), C(9)−C(10), and C(11)−C(12), however, are all −g producing the wrapping pattern shown. In addition, one C−O−C−C torsion angle between each pair of consecutive O−C−C−O torsion angles of like sign is distorted toward gauche (C(7)−C(8)−O(5)−C(9) = −98.0°; C(9)−C(10)−O(6)−C(11) = −85.4°).

Both chloride anions and the uncoordinated water molecule are hydrogen bonded in the secondary coordination sphere. The alcoholic O(1) donates a hydrogen bond to the uncoordinated water molecule O(10), while O(7) hydrogen bonds to Cl(1). The coordinated water molecules and the uncoordinated water molecule each donate one hydrogen bonded to both Cl(1) and Cl(2), resulting in a total of four hydrogen bonding interactions to Cl(1) and three to Cl(2). The hydrogen bonding produces polymeric sheets in *ab*.

$[Sr(NO_3)(EO3)_2][NO_3]$. The asymmetric unit for this complex is depicted in Figure 6. This is the only example of our four $Sr(NO_3)_2$/PEG complexes to have only one tight ion pair, and this may explain the difficulty experienced in obtaining good single crystals for the structural study. Several times the starting salt crystallized mixed in with very small crystals of the complex. A good data set on the small crystals available was finally obtained by collection of the data using the new Siemens CCD area detector known as SMART.

The Sr^{2+} ion is 10-coordinate bicapped square antiprismatic. The bidentate nitrate anion, the four alcoholic PEG termini, and two etheric oxygen atoms (O(3), O(6)) occupy prismatic sites. One etheric oxygen atom from each EO3 ligand caps the two square faces (O(2)−Sr−O(7) = 176.1(2)°). O(9) and O(10) of the anion reside in opposite square faces, as do the two alcoholic termini for a given PEG. This feature of the EO3 chain produces a definite bending of one alcoholic oxygen end of each chain (O(4), O(5)) out of the plane defined by the other three glycol oxygens. Thus the coordination of EO3 is decidedly different from the template mode of coordination found in $[Sr(EO3)_2]Cl_2$.

The EO3 conformation in one chain is obscured by the disorder; however, neither this chain nor the O(5)−O(8) EO3 ligand exhibits the $(g^+)aa(g^-)aa(g^+)$ conformation found in $[Sr(EO3)_2]Cl_2$. Instead, the O−C−C−O torsion angle involving the oxygen which bends out of the plane defined by the other three has the same sign as the O−C−C−O torsion angle next to it. This forces one of the C−O−C−C torsion angles toward gauche (e.g., C(7)−C(8)−O(6)−C(9) = −92.9°). The overall torsion angle sequence for the O(5)−O(8) EO3 ligand is $(g^-){\sim}g^-a(g^-)aa(g^+)a(g^+)$. The O(1)−O(4) glycol exhibits ±g disorder in the C(3)−C(4) and C(5)−C(6) ethylene linkages.

The cations and anions participate in a 3-dimensional network of hydrogen bonds. O(1) and O(5) donate hydrogen bonds to uncoordinated nitrate anions via O(12) and O(13). These interactions exhibit the shortest O···O contacts (2.73(1)−2.79(1) Å). O(4) and O(8) donate hydrogen bonds to the coordinated nitrate of neighboring molecules, one to coordinated O(10) and one to uncoordinated O(11). These hydrogen bonds have longer O···O contacts of 2.953(9) and 2.811(9) Å.

$[Sr(NO_3)_2(OH_2)EO4]$. This complex (Figure 7) is 10-coordinate with the five-donor EO5 ligand, one water molecule, and two bidentate nitrate anions in the primary coordination sphere. Like all of the $Sr(NO_3)_2$/EO4−EO5 complexes we have characterized and unlike all of the $SrCl_2$/PEG complexes, the ions crystallize as tight ion pairs in a *trans*-twisted fashion. (The dihedral angle between the planes formed by the nitrate anions is 93.8°; the N(1)···Sr···N(2) angle is 169.1(2)°.)

The coordination geometry is closer to the lower symmetry 4A,6B-expanded dodecahedron than to either the bicapped dodecahedron or bicapped square antiprism. The latter two geometries require one O−Sr−O angle near 180°, and the closest such angle is only 165.3(2)° (O(1)−Sr−O(4)). The A-sites are occupied by O(3), O(7), O(5), and O(11).

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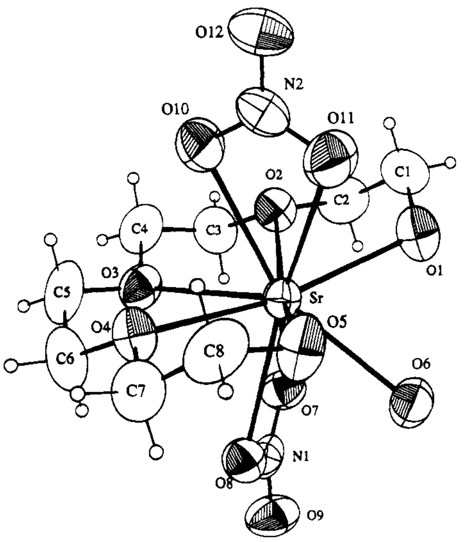

Figure 7. [$Sr(NO_3)_2(OH_2)(EO4)$].

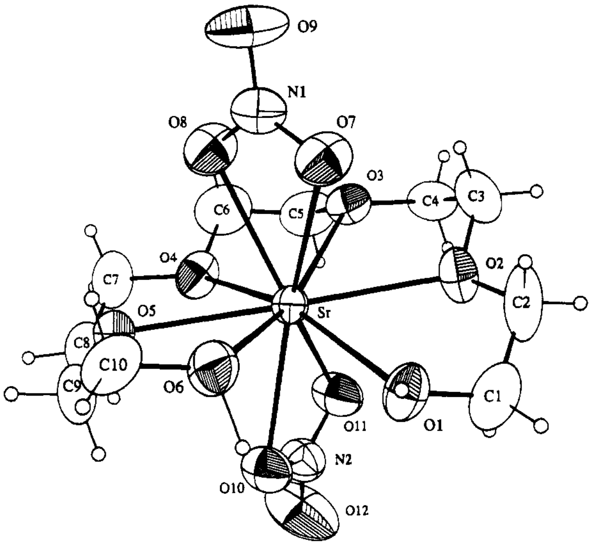

Figure 8. [$Sr(NO_3)_2(EO5)$].

The EO4 ligand coordinates Sr^{2+} in an equatorial crown ether-like array. The one water molecule (O(6)) deviates significantly out of the polyether girdle. The torsion angle sequence is the same as that found for the D_{3d} form of complexed 18-crown-6: $(g^+)aa(g^-)aa(g^+)aa(g^-)$.

The hydrogen bonding from O(1), O(5), and O(6) is ambiguous. The contacts suggest hydrogen bonds to O(8), O(9), O(11), O(12), and possibly O(5) in symmetry related molecules. This hydrogen bonding appears to produce polymeric hydrogen bonded chains which propagate along *b*.

[$Sr(NO_3)_2(EO5)$]. The Sr^{2+} cation is 10-coordinate (Figure 8) with *trans*-twisted ($\delta = 94.6°$) bidendate nitrate anions and the six-donor EO5 ligand in the primary coordination sphere. The metal ion geometry is between a bicapped dodecahedron and a bicapped square antiprism, but appears to be closer to bicapped dodecahedral with the etheric oxygen atoms O(2) and O(5) in capping positions (O(2)−Sr−O(5) = 176.6(2)°). The A-sites are occupied by the nitrate anions (O(7), O(8), O(10), O(11)).

The EO5 coordination is, again, very crown ether-like, coordinating in an equatorial girdle. The torsion angles have the familiar sequence usually found for complexed 18-crown-6 of O−C−C−O torsion angles alternating ±g and C−O−C−C torsion angles all anti. Each alcoholic oxygen atom donates a hydrogen bond to a coordinated nitrate oxygen atom in neighboring molecules. Interactions between O(1) and O(7) in a symmetry related position and between O(6) and O(10) in a second symmetry related site leads to zigzag polymeric hydrogen bonded chains which propagate along *a*.

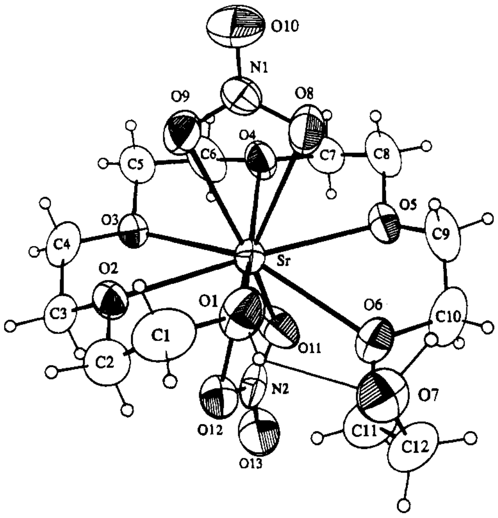

Figure 9. [$Sr(NO_3)_2(EO6)$].

[$Sr(NO_3)_2(EO6)$]. This complex (Figure 9) is very similar to its EO5 analog just described. Sr^{2+} is 10-coordinate with two *trans*-twisted bidentate nitrate anions, but only six of the seven oxygen donors in the PEG ligand coordinate the metal. The glycol encircles Sr^{2+} in the now familiar crown ether-like girdle; however, O(6) deviates more out of this equatorial plane than was observed for the EO5 complex. This is most likely due to distortions caused by swinging the O(7) donor out away from Sr^{2+}, and may be the reason the dihedral angle between the nitrate planes is only 64.0° instead of the nearly 90° observed for the EO4 and EO5 complexes. The overall coordination geometry is again between bicapped square antiprismatic and bicapped dodecahedral, but this time appears to be closer to bicapped square antiprismatic with the etheric O(2) and O(5) as caps (O(2)−Sr−O(5) = 176.9(2)°).

The glycol ligand pseudocyclizes via a hydrogen bond interaction donated by the O(1) alcoholic end and accepted by the uncoordinated O(7) end. This type of displacement of an alcoholic terminus from the primary coordination sphere and pseudocyclization have been observed previously in [$BiCl_3(EO5)$], [$BiI_2(EO5)$][Bi_2I_7]·2MeOH,[45] and [$PbBr(NCMe)(EO6)]_2$-[$PbBr_2(EO6)$][$PbBr_3]_2$.[46] The torsion angle sequence again resembles the D_{3d} form of 18-crown-6. The only exception is the C(10)−O(6)−C(11)−C(12) angle of 73.0° which is not anti. This allows the O(7) donor to swing out away from the metal ion.

The remaining hydrogen bond is between O(7) and O(12) in a symmetry related molecule. These interactions produce polymeric hydrogen bonded chains along *c*.

Discussion

The selective extraction of strontium using crown ethers relies on the precepts of molecular recognition; i.e., the crown ether cavity size and conformational preferences are engineered to fit the requirements of Sr^{2+}. Polyethylene glycols, like all podands, do not possess a fixed cavity; however they are flexible enough to wrap Sr^{2+} in a crown ether-like fashion and still present a hydrophobic exterior for the metal cation. Our

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(46) Rogers, R. D.; Bond, A. H. Unpublished results.

structural results and those of the crown ether and podand structures of Sr^{2+} reveal trends relating to the effects of chain length, number of donor atoms, anion, and metal cation size.

Within our series of nine structures reported here, the obvious differences resulting from choice of anion are clear. The Sr^{2+} cation prefers any oxygen donor to having Cl^- in the primary coordination sphere, and all the chloride structures crystallize with second sphere hydrogen bonded chloride anions. (This has not been the case in our investigation of lanthanide(III) chloride complexes where steric factors tend to influence whether Cl^- is inner or outer sphere.[41-44]) It is also evident that the chelate effect is large enough to make Sr^{2+} prefer PEG coordination over that of water. Thus, 2/1 (PEG/Sr^{2+}) complexes of PEGs up to EO4 (which gives a coordination number of 10) are isolated. A bis-EO5 complex would give Sr^{2+} a coordination number of 12, which is obviously too high, and EO5 and EO6, therefore, coordinate with a 1/1 stoichiometry.

In the $Sr(NO_3)_2$ structures there is a strong preference for tight ion pairs. Only the smallest PEG, EO3 (which can form a 2/1 Sr^{2+} complex and still leave room for at least one tight ion pair), does not have two Sr^{2+}/NO_3^- tight ion pairs. In the EO4−EO6 complexes, the nitrate anions are arranged as far apart as possible in a *trans*-twisted, bidendate orientation. The PEG ligands wrap in an equatorial girdle, and H_2O molecules are included only if necessary to reach coordinative saturation. The preference for at least one tight ion pair is so great that if there are too many PEG donors (as in $[Sr(NO_3)_2(EO6)]$), the extra donors will simply dangle uncoordinated. This same general structure with two *trans*-twisted, bidendate nitrates and six equatorial etheric donors has been observed in $[Sr(NO_3)_2$-(dicyclohexano-18-crown-6)$]$[31] and $[Sr(NO_3)_2(Me_2$-18-crown-6)$]$.[34] A similar orientation for the anions was found for the dimethylpropanoates in [Sr(dmp)$_2$(dicyclohexano-18-crown-6)].[32] (By contrast in our work with $Ln(NO_3)_3$/PEG complexes only two of the three possible tight ion pairs dictate the PEG coordination.[47]) The general effect of the nitrate coordination is to flatten the "girdle" of oxygen donors; thus these complexes resemble crown ether coordination much more than helical wrapping of the cation.

Two other anions have been reported in the literature in Sr^{2+}/podand structures. The NCS^- anion typically forms tight ion pairs but in a monodentate fashion, and the structures of $Sr(NCS)_2$ complexes of EO6,[23] tetraglyme (EG4),[26] EG5,[27] and EG6[28] are somewhat similar to those of our chloride complexes except with NCS^- anions in coordination sites occupied by H_2O molecules. The two exceptions are interesting. In [Sr(NCS)-(EO7)][SCN][24] there is only one tight ion pair—Sr^{2+} preferring the eighth PEG donor rather than the second tight ion pair. (In $[Sr(NO_3)_2(EO6)]$ we saw a preference for the nitrate anion over the seventh PEG donor.) The second exception is $[Sr(NCS)_2(OH_2)_2(EG3)]$.[25] Although there are two tight ion pairs, the glyme molecule coordinates in a pseudocyclic out-of-cavity mode similar to the Sr^{2+}/12-crown-4 coordination in $[Sr(NCS)_2(OH_2)_2$(12-crown-4)$]$.[29] The Sr(3,5-dinitrobenzoate)$_2$ complex of EO4 also is forced into a pseudocyclic out-of-cavity mode of coordination by the nature of the bidentate bridging anions.[22] We have observed similar PEG coordination in several complexes of $BiCl_3$ where the pyramidal covalent $BiCl_3$ moiety dominates.[45]

All of the 18-membered macrocyclic polyether complexes of Sr^{2+} which have been structurally characterized exhibit in-cavity coordination of Sr^{2+} to the six etheric donors.[31-36] The most common coordination numbers are 10 with bidentate anions or 9 with monodentate anions or water molecules completing the coordination sphere. In general, these structures are all very similar to the PEG complexes presented in this report.

We are investigating similar PEG complexes of other group 2 chlorides and nitrates and are beginning to see trends related to cation size. For example the smaller Ca^{2+} can support 2/1 complexes of $CaCl_2$ with EO3 ($[Ca(OH_2)_8][Ca(EO3)_2]Cl_4$[47]) but not with EO4 where $[Ca(OH_2)_3(EO4)]Cl_2$[47] was isolated. $[Ca(NO_3)_2(EO4)]$[47] was isolated as an anhydrous crystalline product and exhibits more bending in the fifth equatorial position rather than the sixth (a water molecule) as in $[Sr(NO_3)_2(OH_2)(EO4)]$. The larger Ba^{2+} supports higher coordination numbers, and all seven EO6 donors coordinate in $[Ba(NO_3)_2(EO6)]$.[47]

Table 1 presents a comparison of the coordination parameters for the title complexes and other polyether complexes of Sr^{2+}. The first group of parameters breaks the Sr−O contacts for the title complexes down by geometric site. The expected trends (e.g., Sr−O capping > Sr−O prismatic) are not always observed due to distortions in metal ion geometry arising from the polydentate nature of the PEG ligands. The relatively high esd's observed when the Sr−O separations are averaged also hinders useful comparisons.

To more effectively compare the title complexes with each other and the literature, part B of Table 1 breaks down the Sr−O separations by type of donor only. Thus, we see the 8-coordinate complex $[Sr(EO3)_2]Cl_2$ exhibits the shortest Sr−O distances as expected. In addition, the Sr−O distances for each complex follow the order of basicity of the ligand $Sr-OH_2$ < Sr−O(alcoholic) < Sr−O(etheric). The $Sr-ONO_2$ separations tend to fall between the alcoholic and etheric separations, although again the esd's of the averages are a bit high due to asymmetry in the bidentate nitrate coordination.

There appears to be no statistical difference between the Sr−O distances in the PEG/Cl^- complexes with no tight ion pairs and those in the PEG/NO_3^- complexes which have one or two tight ion pairs. In fact, given the range in coordination number (8−10), anion type, cyclic versus acyclic polyether, and number of tight ion pairs (0−2), the range in average distances in each category over all the Sr^{2+}/polyether structures is fairly narrow: 0.14 Å for Sr−O(alcoholic) distances (2.526(7)−2.67(2) Å) and 0.15 Å for Sr−O(etheric) separations (2.603(1)−2.75(4) Å). The average Sr−O separations for the monodentate and bidentate ligands exhibit even narrower ranges—the $Sr-OH_2$ range is 0.09 Å, while the $Sr-ONO_2$ range is 0.05 Å.

Conclusions

Strontium(II) will organize PEGs into pseudocyclic crown ether-like equatorial arrays. At least in the limited competitive environment provided in these studies, PEG coordination is preferred over solvation by H_2O. In chloride media it appears that two strategies may be employed to completely wrap Sr^{2+} and give it a hydrophobic exterior prior to extraction. Small PEGs, EO3 or EO4, can complex Sr^{2+} in a 2/1 fashion, or longer PEGs on the order of EO9−EO10 can be utilized to helically wrap the Sr^{2+} cation. In either case a hydrophobic anion would be necessary for extraction to occur. (Recent studies have examined Sr^{2+} extraction with dicarbollides and found that PEGs enhance the extraction from aqueous solution to nitrobenzene.[16,48])

In the absence of a hydrophobic anion, nitrate media may provide a better extraction environment. Here an EO5 ligand could be used to wrap Sr^{2+} and the necessary anions can

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(47) Rogers, R. D.; Bauer, C. B. Unpublished results.

(48) Navratil, J. D. Poster P14.3, International Solvent Extraction Conference—ISEC '93, York, England, 1993.

Table 1. Comparison of Bonding Parameters

A. By Coordination Geometry Site and Oxygen Type

				Sr−O (alcoholic), av, Å				Sr−O(etheric), av, Å				Sr−OH$_2$, av, Å		Sr−ONO$_2$, av, Å		
compound	CN[a]	G[b]	IR,[c] Å	A-site	B-site	capping	prismatic	A-site	B-site	capping	prismatic	B-site	prismatic	A-site	B-site	prismatic
$[Sr(EO3)_2]Cl_2$	8	dod	1.26		2.526(6)			2.603(1)								
$[Sr(EO4)_2]Cl_2 \cdot 3H_2O$	10	bcdod	1.36	2.67(2)					2.73(4)	2.74(2)						
$[Sr(EO4)_2]Cl_2$	10	bcdod	1.36	2.626(2)					2.73(1)	2.762(2)						
$[Sr(OH_2)_3(EO5)]Cl_2$	9	tctp	1.31			2.678(9)	2.626(9)			2.71(3)	2.716(6)		2.61(5)			
$[Sr(OH_2)_2(EO6)]Cl_2 \cdot H_2O$	9	tctp	1.31			2.598(9)	2.571(9)			2.72(1)	2.72(1)		2.61(2)			
$[Sr(NO_3)(EO3)_2][NO_3]$	10	bcsap	1.36				2.67(2)			2.67(1)	2.697(5)					2.700(1)
$[Sr(NO_3)_2(OH_2)(EO4)]$	10	4A,6B-edod	1.36	2.647(6)	2.672(6)			2.699(6)	2.661(6)			2.634(6)		2.67(2)	2.75(4)	
$[Sr(NO_3)_2(EO5)]$	10	bcdod	1.36		2.67(1)				2.79(1)	2.70(3)				2.67(1)		
$[Sr(NO_3)_2(EO6)]$	10	bcsap	1.36				2.556(7)			2.71(3)	2.705(7)					2.67(5)

B. By Oxygen Type Only

			M−O(alcoholic), Å		M−O(etheric), Å		M−OH$_2$, Å		M−ONO$_2$, Å		
compound	CN[a]	IR,[c] Å	av	range	av	range	av	range	av	range	ref
$[Sr(EO3)_2]Cl_2$	8	1.26	2.526(6)	0.013	2.603(1)	0.002					*d*
$[Sr(EO4)_2]Cl_2 \cdot 3H_2O$	10	1.36	2.67(2)	0.060	2.73(3)	0.100					*d*
$[Sr(EO4)_2]Cl_2$	10	1.36	2.626(2)	0.003	2.74(2)	0.043					*d*
$[Sr(OH_2)_3(EO5)]Cl_2$	9	1.31	2.65(3)	0.052	2.71(2)	0.059	2.61(5)	0.130			*d*
$[Sr(OH_2)_2(EO6)]Cl_2 \cdot H_2O$	9	1.31	2.58(1)	0.027	2.72(1)	0.030	2.61(2)	0.036			*d*
$[Sr(NO_3)(EO3)_2][NO_3]$	10	1.36	2.67(2)	0.045	2.68(1)	0.039			2.700(1)	0.002	*d*
$[Sr(NO_3)_2(OH_2)(EO4)]$	10	1.36	2.66(1)	0.025	2.67(2)	0.044	2.634(6)		2.71(5)	0.133	*d*
$[Sr(NO_3)_2(EO5)]$	10	1.36	2.67(1)	0.024	2.74(5)	0.124			2.67(1)	0.026	*d*
$[Sr(NO_3)_2(EO6)]$	10	1.36	2.556(7)		2.71(2)	0.057			2.67(5)	0.133	*d*
[Sr(3,5-dinitrobenzoate)(OH_2)(EO4)][3,5-dinitrobenzoate]	9	1.31	2.67(2)	0.033	2.66(5)	0.117	2.569(4)				22
$[Sr(NCS)_2(EO6)]$	9	1.31	2.606(3)	0.006	2.72(3)	0.076					23
[Sr(NCS)(EO7)][SCN]	9	1.31	2.56(2)	0.000	2.70(2)	0.07					24
$[Sr(NCS)_2(OH_2)_2(EG3)]$[e]	8	1.26			2.66(2)	0.062	2.61(5)	0.092			25
$[Sr(NCS)_2(OH_2)(EG4)]$	8	1.26			2.64(1)	0.035	2.584(6)				26
$[Sr(Ph_2acac)_2(EG4)]$	9	1.31			2.75(3)	0.083					52
$[Sr(NCS)_2(OH_2)(EG5)]$	9	1.31			2.73(5)	0.169	2.614(7)				27
$[Sr(OH_2)_2(EG6)]$-	9	1.31			2.67(5)	0.148	2.588(9)	0.000			
$[Sr(NCS)_2(EG6)][SCN]_2$	9	1.31			2.70(5)	0.147					28
$[Sr(NCS)_2(OH_2)_2$(12-crown-4)]	8	1.26			2.64(3)	0.094	2.54(2)	0.070			29
[Sr(dibutyl phosphate)$_2(OH_2)$(18-crown-6)]	9	1.31			2.75(4)	0.14	2.615(5)	0.01			30
$[Sr(NO_3)_2$(dicyclohexano-18-crown-6)]	10	1.36			2.72(8)	0.19			2.66(2)	0.05	31
[Sr(dimethylpropanoato)$_2$(dicyclohexano-18-crown-6)]	10	1.36			2.73(7)	0.18					32
[CaCl][Sr{$(PhNHCO)_2(COO)_2$-18-crown-6}]	10	1.36			2.70	0.11					34
$[Sr(NO_3)_2(Me_2$-18-crown-6)]	10	1.36			2.70(2)						33
$[Sr(OH_2)_3$(benzo-18-crown-6)]$[ClO_4]_2$	9	1.31			2.68(2)	0.061	2.57(1)	0.025			35
$[Sr(ClO_4)_2$(4′-acetobenzo-18-crown-6)]	8	1.26			2.68(6)	0.17					36
$[Ca(OH_2)_8][Ca(EO3)_2]Cl_4$	8	1.12	2.418(5)		2.477(5)		2.46(7)	0.146			47
$[Ca(EO3)_2]Cl_2 \cdot 4H_2O$	8	1.12	2.41(1)	0.033	2.458(9)	0.022					37
$[Ca(OH_2)_3(EO4)]Cl_2$	8	1.12	2.45(5)	0.108	2.50(2)	0.041	2.42(4)	0.102			47
$[Ca(NO_3)_2(EO4)]$	9	1.18	2.40(1)	0.031	2.48(3)	0.082			2.57(6)	0.223	47
[Ca(picrate)(OH_2)(EO4)][picrate]	8	1.12	2.40(1)	0.029	2.46(3)	0.066	2.383(2)				53, 54
$[Ba(NO_3)_2(EO5)] \cdot H_2O$	10	1.52	2.766(6)	0.011	2.84(1)	0.024			2.86(2)	0.050	47
$[Ba(NO_3)_2(EO6)]$	11	1.57	2.83(6)	0.118	2.87(1)	0.033			2.89(5)	0.115	47

[a] CN = coordination number. [b] Geometry: dod = dodecahedron; bcdod = bicapped dodecahedron; tctp = tricapped trigonal prism; 4A,6B-edod = 4A,6B-expanded dodecahedron; bcsap = bicapped square antiprism. [c] Ionic radius for M^{2+} and coordination number indicated from ref 55. [d] This study. [e] EG3 = triethylene glycol dimethyl ether (triglyme), EG4 = tetraethylene glycol dimethyl ether (tetraglyme), etc.

Table 2. Crystallographic Data

	$[Sr(EO3)_2]Cl_2$	$[Sr(EO4)_2]Cl_2$	$[Sr(EO4)_2]Cl_2 \cdot 3H_2O$	$[Sr(OH_2)_3(EO5)]Cl_2$
a, Å	8.737(4)	17.528(9)	12.225(7)	8.217(9)
b, Å	18.609(9)	9.209(3)	18.336(9)	9.000(8)
c, Å	12.548(9)	17.180(9)	12.258(9)	14.514(8)
α, deg				75.55(6)
β, deg		121.13(8)	90.25(5)	83.33(7)
γ, deg				69.59(9)
V, $Å^3$	2040	2374	2747.7	973.6
Z	4	4	4	2
fw	458.88	546.98	601.03	450.85
space group	$C222_1$ (No. 20)	$C2/c$ (No. 15)	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)
T, °C	19	20	19	18
λ(Mo Kα), Å	0.710 73	0.710 73	0.710 73	0.710 73
ϱ_{calc}, g cm^{-3}	1.49	1.53	1.45	1.54
μ, cm^{-1}	30.6	26.5	23.1	32.1
$R(F_o)^a$	0.041	0.034	0.059	0.056
$R_w(F_o)^b$	0.044	0.034	0.065	0.063

	$[Sr(OH_2)_2(EO6)]Cl_2 \cdot H_2O$	$[Sr(NO_3)(EO3)_2][NO_3]$	$[Sr(NO_3)_2(OH_2)(EO4)]$	$[Sr(NO_3)_2(EO5)]$	$[Sr(NO_3)_2(EO6)]$
a, Å	9.741(6)	8.156(2)	7.911(2)	9.330(9)	16.204(8)
b, Å	16.534(3)	9.992(1)	9.810(3)	10.060(9)	10.760(4)
c, Å	13.600(4)	13.158(2)	10.917(3)	11.684(5)	12.365(2)
α, deg			92.43(3)	67.86(8)	
β, deg	100.16(4)	92.09(1)	94.02(2)	68.04(8)	106.91(4)
γ, deg			91.75(2)	68.18(9)	
V, $Å^3$	2156	1072	843.9	907.5	2062.7
Z	4	2	2	2	4
fw	494.90	511.98	423.87	449.91	493.97
space group	$P2_1/n$ (No. 14)	$P2_1$ (No. 4)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)
T, °C	18	20	18	18	19
ϱ_{calc}, g cm^{-3}	1.52	1.59	1.67	1.65	1.59
μ_{calc}, cm^{-1}	27.9	27.1	34.1	31.8	28.1
λ(Mo Kα), Å	0.710 69	0.710 73	0.710 73	0.710 73	0.710 73
$R(F_o)^a$	0.050	0.046	0.051	0.046	0.048
$R_w(F_o)^b$	0.051	0.064	0.063	0.046	0.055

[a] $\Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $[\Sigma w(||F_o| - |F_c||)^2/\Sigma w(F_o)^2]^{1/2}$.

coordinate above and below the glycol girdle. These complexes will probably suffer from the lack of molecular recognition which introduces selectivity into similar Sr^{2+}/crown ether complexes;[3-9] however, given the large difference in group 1 and 2 cation sizes, appropriate choices of anion, diluents, and PEG length may produce some interesting selectivities.

In our studies involving extraction of Sr^{2+} into aqueous biphasic media based on PEG-2000, the polymer may be too long to effectively wrap any one Sr^{2+} cation. We are currently attempting to model these interactions with polyethylene glycols longer than EO6 to determine if there is a limit to the number of donors before an actual reduction in coordination number, or if it is indeed possible to totally encapsulate Sr^{2+} in a PEG helix. In the meantime, studies of Sr^{2+} extraction into PEG-based aqueous biphasic systems is continuing with crown ethers, small PEGs, and hydrophobic anions.[17,18]

Experimental Section

Synthesis of Complexes. $SrCl_3 \cdot 6H_2O$ (Fisher), $Sr(NO_3)_2$ (Strem), and EO3, EO4, EO5, and EO6 (Aldrich) were used as purchased. Reagent grade NH_4OH (Fisher) (28–30% NH_3) was used without dilution. Reagent grade CH_3CN was distilled from CaH_2 and stored over 4 Å molecular sieves.

$[Sr(EO3)_2]Cl_2$. A 0.5 mmol (0.1333 g) quantity of $SrCl_2 \cdot 6H_2O$ was added to 5 mL of CH_3CN; 0.5 mmol (0.07 mL) EO3 and 1.0 mmol (0.13 mL) NH_4OH were then added and the mixture was heated with stirring for 2 h at 65 °C. A small amount of white precipitate formed during heating. The solution was centrifuged and supernatant was decanted. Slow evaporation of the supernatant afforded colorless plate-shaped crystals. Anal. Calcd: C, 31.41; H, 6.15. Found: C, 32.86; H, 6.61.

$[Sr(EO4)_2]Cl_2$ and $[Sr(EO4)_2]Cl_2 \cdot 3H_2O$. A 0.5 mmol (0.1348 g) quantity of $SrCl_2 \cdot 6H_2O$ was added to 5 mL of CH_3CN; 0.5 mmol (0.08 mL) EO4 and 0.5 mmol (0.07 mL) NH_4OH were added and the solution was heated with stirring for 1 h at 65 °C. Slow evaporation of the solution yielded colorless crystals of a mixture of the two complexes.

Table 3. Final Fractional Coordinates for $[Sr(EO3)_2]Cl_2$

atom	x/a	y/b	z/c	$B(eqv)$,[a] $Å^2$
Sr	0.5000	0.37135(6)	0.7500	3.03
Cl(1)	0.0000	0.2514(2)	0.7500	5.65
Cl(2)	0.8413(6)	0.5000	1.0000	7.45
O(1)	0.625(1)	0.3845(4)	0.9309(7)	6.17
O(2)	0.546(1)	0.2524(4)	0.8542(7)	5.49
O(3)	0.234(1)	0.3566(4)	0.8251(7)	5.57
O(4)	0.364(1)	0.4902(4)	0.8054(7)	4.77
C(1)	0.642(3)	0.3230(7)	0.994(1)	10.99
C(2)	0.633(2)	0.2576(9)	0.948(1)	8.42
C(3)	0.547(2)	0.1892(5)	0.799(1)	7.84
C(4)	0.170(2)	0.4173(6)	0.875(1)	6.16
C(5)	0.205(1)	0.4849(6)	0.820(1)	5.65
C(6)	0.412(1)	0.5533(5)	0.755(2)	6.26

[a] $B(eqv) = (8\pi^2/3)[a^2U_{11}(a^*)^2 + b^2U_{22}(b^*)^2 + c^2U_{33}(c^*)^2 + ab(\cos\gamma)U_{12}a^*b^* + ac(\cos\beta)U_{13}a^*b^* + bc(\cos\alpha)U_{23}b^*c^*]$.

$[Sr(OH_2)_3(EO5)]Cl_2$. A 0.5 mmol (0.1331 g) quantity of $SrCl_2 \cdot 6H_2O$ was added to 5 mL of CH_3CN; 0.5 mmol (0.11 mL) of EO5 and 0.5 mmol (0.07 mL) of NH_4OH were added. The mixture was heated for 1 h with stirring at 62 °C. A small amount of white precipitate which formed was removed and slow evaporation of the supernatant afforded colorless plate-shaped crystals. Anal. Calcd: C, 26.64; H, 6.26. Found: C, 29.14; H, 6.43.

$[Sr(OH_2)_2(EO6)]Cl_2 \cdot H_2O$. A 0.5 mmol (0.1337 g) quantity of $SrCl_2 \cdot 6H_2O$ was added to 5 mL of CH_3CN; 0.5 mmol (0.13 mL) of EO6 and 0.5 mmol (0.07 mL) of NH_4OH were added. The mixture was heated with stirring for 1 h at 65 °C. Slow evaporation of the solution afforded colorless, plate-shaped crystals. Anal. Calcd: C, 29.12; H, 6.52. Found: C, 28.37; H, 5.37.

Table 4. Final Fractional Coordinates for $[Sr(EO4)_2]Cl_2$

atom	*x*/*a*	*y*/*b*	*z*/*c*	*B*(eqv), Å^2
Sr	0.5000	0.60962(5)	0.7500	2.42
Cl(1)	0.43303(7)	1.1135(1)	0.83461(7)	4.94
O(1)	0.4021(2)	0.8422(3)	0.7205(2)	3.98
O(2)	0.4024(2)	0.7157(3)	0.5763(2)	4.01
O(3)	0.5751(2)	0.6068(3)	0.6428(2)	4.39
O(4)	0.6671(2)	0.5024(3)	0.8167(2)	4.79
O(5)	0.5485(2)	0.3817(3)	0.8574(2)	4.05
C(1)	0.3352(3)	0.8762(5)	0.6298(3)	4.26
C(2)	0.3707(3)	0.8606(4)	0.5682(3)	4.27
C(3)	0.4376(3)	0.6863(5)	0.5186(3)	4.89
C(4)	0.5364(3)	0.7070(5)	0.5686(3)	5.70
C(5)	0.6696(3)	0.6062(5)	0.6924(3)	5.51
C(6)	0.7003(3)	0.4830(5)	0.7565(3)	5.56
C(7)	0.6876(8)	0.362(1)	0.8593(7)	3.50
C(8)	0.6431(7)	0.368(1)	0.9166(6)	3.90
C(7)′ [a]	0.6937(8)	0.414(1)	0.8959(8)	4.52
C(8)′	0.6263(7)	0.308(1)	0.8780(7)	4.03

[a] Primed and unprimed atoms of like number are disordered with 50% occupancy each.

Table 5. Final Fractional Coordinates for $[Sr(EO4)_2]Cl_2 \cdot 3H_2O$

atom	*x*/*a*	*y*/*b*	*z*/*c*	*B*(eqv), Å^2
Sr	0.1465(2)	0.2297(1)	0.4119(2)	2.92
Cl(1)	0.0203(6)	0.3820(3)	0.0748(5)	6.55
Cl(2)	−0.1649(5)	−0.0534(3)	0.0729(5)	5.59
O(1)	0.123(1)	0.2577(8)	0.203(1)	4.95
O(2)	0.296(1)	0.1751(8)	0.267(1)	5.90
O(3)	0.233(1)	0.0931(7)	0.454(1)	4.97
O(4)	0.078(1)	0.1516(8)	0.589(1)	5.65
O(5)	0.108(1)	0.3011(7)	0.597(1)	4.09
O(6)	0.339(1)	0.2318(8)	0.519(1)	4.52
O(7)	0.285(2)	0.3406(8)	0.381(1)	7.40
O(8)	0.060(1)	0.3631(7)	0.367(1)	4.61
O(9)	−0.078(1)	0.2489(7)	0.414(1)	5.15
O(10)	0.020(1)	0.1239(7)	0.327(1)	4.66
O(11)	0.032(1)	0.0407(7)	0.149(1)	5.50
O(12)	0.097(1)	0.4723(8)	0.869(1)	7.45
O(13)	0.170(1)	0.4342(7)	0.668(1)	7.06
C(1)	0.204(2)	0.236(1)	0.130(2)	6.94
C(2)	0.260(2)	0.171(1)	0.162(2)	7.15
C(3)	0.354(2)	0.113(1)	0.305(2)	6.73
C(4)	0.283(2)	0.059(1)	0.363(2)	5.79
C(5)	0.164(2)	0.046(1)	0.515(2)	6.54
C(6)	0.135(2)	0.088(1)	0.618(2)	7.43
C(7)	0.049(3)	0.197(1)	0.682(2)	9.06
C(8)	0.101(2)	0.264(1)	0.687(2)	7.06
C(9)	0.412(2)	0.289(1)	0.496(2)	6.38
C(10)	0.368(2)	0.352(1)	0.451(2)	5.67
C(11)	0.239(2)	0.405(1)	0.328(2)	8.06
C(12)	0.130(3)	0.427(1)	0.373(2)	7.19
C(13)	−0.050(3)	0.374(1)	0.394(2)	7.78
C(14)	−0.116(2)	0.309(1)	0.362(2)	5.49
C(15)	−0.139(3)	0.194(2)	0.367(3)	3.5(9)[a]
C(16)	−0.082(4)	0.119(2)	0.361(3)	4(1)[a]
C(15)′ [b]	−0.134(4)	0.169(2)	0.418(3)	5(1)[a]
C(16)′	−0.105(3)	0.142(2)	0.312(3)	4(1)[a]

[a] Isotropic refinement. [b] Primed and unprimed atoms of like number are disordered with 50% occupancy each.

$[Sr(NO_3)(EO3)_2][NO_3]$. A 0.5 mmol (0.1062 g) quantity of $Sr(NO_3)_2$ was added to 5 mL of CH_3CN; 0.5 mmol (0.07 mL) of EO3 and 1.0 mmol (0.13 mL) of NH_4OH were then added and the solution was heated with stirring for 1 h at 60 °C. Slow evaporation of the solution afforded a mixture of the complex and a hydrated form of the starting strontium salt.

Table 6. Final Fractional Coordinates for $[Sr(OH_2)_3(EO5)]Cl_2$

atom	*x*/*a*	*y*/*b*	*z*/*c*	*B*(eqv), Å
Sr	0.1971(1)	1.1234(1)	0.74270(7)	2.57
Cl(1)	−0.1013(4)	1.3032(3)	0.4335(2)	4.76
Cl(2)	0.3652(3)	1.2998(3)	0.9880(2)	4.06
O(1)	0.0995(9)	1.3511(9)	0.8404(6)	5.60
O(2)	−0.1227(9)	1.1911(9)	0.8238(6)	5.55
O(3)	0.0846(9)	0.8752(8)	0.8401(5)	4.83
O(4)	0.3924(9)	0.8081(8)	0.7392(5)	4.37
O(5)	0.520(1)	1.052(1)	0.6605(7)	7.69
O(6)	0.344(1)	1.355(1)	0.6803(7)	7.25
O(7)	0.113(1)	1.0321(9)	0.6031(5)	5.53
O(8)	−0.018(1)	1.3775(8)	0.6264(5)	4.97
O(9)	0.3848(9)	1.0216(8)	0.8881(5)	4.71
C(1)	−0.071(2)	1.351(2)	0.909(1)	2.9(3)[a]
C(2)	−0.201(2)	1.341(2)	0.837(1)	2.9(4)[a]
C(1)′ [b]	−0.071(3)	1.434(3)	0.860(2)	6.0(6)[a]
C(2)′	−0.159(3)	1.329(3)	0.891(2)	5.2(5)[a]
C(3)	−0.176(1)	1.063(2)	0.8869(9)	6.01
C(4)	−0.101(2)	0.916(2)	0.8409(9)	6.48
C(5)	0.167(2)	0.716(1)	0.8214(8)	5.79
C(6)	0.356(2)	0.685(1)	0.8137(9)	5.35
C(7)	0.571(2)	0.771(2)	0.716(1)	6.77
C(8)	0.595(2)	0.902(2)	0.634(1)	7.48
C(9)	0.547(4)	1.198(4)	0.592(2)	8.4(8)[a]
C(10)	0.521(3)	1.320(3)	0.661(1)	3.9(4)[a]
C(9)′	0.599(3)	1.160(3)	0.620(2)	4.0(4)[a]
C(10)′	0.497(3)	1.323(3)	0.622(2)	5.2(5)[a]

[a] Isotropic refinement. [b] Primed and unprimed atoms of like number are disordered with 50% occupancy each.

Table 7. Final Fractional Coordinates for $[Sr(OH_2)_2(EO6)]Cl_2 \cdot H_2O$

atom	*x*/*a*	*y*/*b*	*z*/*c*	*B*(eqv), Å^2
Sr	−0.5690(1)	−0.28687(8)	−0.8351(1)	2.66
Cl(1)	−1.0987(4)	−0.3602(2)	−0.8560(3)	4.83
Cl(2)	−0.3161(4)	−0.5532(2)	−0.6503(3)	4.77
O(1)	−0.561(1)	−0.1627(6)	−0.7171(7)	5.25
O(2)	−0.618(1)	−0.3109(6)	−0.6449(7)	4.52
O(3)	−0.7044(9)	−0.4226(6)	−0.7908(9)	4.72
O(4)	−0.641(1)	−0.4025(7)	−0.9757(8)	6.14
O(5)	−0.529(1)	−0.2585(8)	−1.0251(8)	6.09
O(6)	−0.668(1)	−0.1480(6)	−0.9291(7)	4.78
O(7)	−0.8335(9)	−0.2620(5)	−0.8604(8)	5.15
O(8)	−0.3790(9)	−0.3950(6)	−0.7774(8)	5.18
O(9)	−0.3197(8)	−0.2230(5)	−0.8253(7)	4.75
O(10)	−0.456(1)	−0.0239(6)	−0.7598(9)	7.18
C(1)	−0.546(2)	−0.177(1)	−0.616(1)	5.67
C(2)	−0.647(2)	−0.240(1)	−0.597(1)	5.34
C(3)	−0.712(2)	−0.372(1)	−0.629(1)	7.68
C(4)	−0.693(2)	−0.443(1)	−0.688(1)	6.26
C(5)	−0.708(2)	−0.489(1)	−0.852(2)	7.71
C(6)	−0.736(2)	−0.462(1)	−0.955(2)	7.28
C(7)	−0.635(2)	−0.387(1)	−1.072(2)	8.74
C(8)	−0.531(2)	−0.330(1)	−1.082(1)	8.59
C(9)	−0.595(2)	−0.193(2)	−1.079(2)	10.20
C(10)	−0.600(2)	−0.123(1)	−1.007(2)	7.81
C(11)	−0.818(2)	−0.1404(9)	−0.955(1)	5.38
C(12)	−0.877(1)	−0.1809(9)	−0.873(1)	4.50

$[Sr(NO_3)_2(OH_2)(EO4)]$. A 0.5 mmol (0.1058 g) quantity of $Sr(NO_3)_2$ was added to 5 mL of CH_3CN; 0.5 mmol (0.08 mL) of EO4 and 0.5 mmol (0.07 mL) of NH_4OH were then added. The solution was heated with stirring for 1 h at 65 °C. A small amount of white precipitate which formed was removed by centrifugation. Slow evaporation of the remaining solution yielded colorless crystals. Anal. Calcd: C, 22.67; H, 4.76; N, 6.64. Found: C, 30.59; H, 6.30; N, 4.35. This analysis raised the possibility of the formation of a 2/1 EO4/Sr^{2+} complex; however, we were unable to isolate crystals of such a complex.

$[Sr(NO_3)_2(EO5)]$. A 0.5 mmol (0.1060 g) quantity of $Sr(NO_3)_2$ was added to 5 mL of CH_3CN; 0.5 mmol (0.11 mL) of EO5 and 0.5 mmol (0.07 mL) of NH_4OH were then added. The mixture was heated with stirring for 1 h at 65 °C. A small amount of white precipitate which formed was removed by centrifugation. Slow evaporation of the remaining solution afforded colorless crystals. Anal. Calcd: C, 26.70; H, 4.93; N, 6.23. Found: C, 28.30; H, 5.23; N, 5.56.

$[Sr(NO_3)_2(EO6)]$. A 0.5 mmol (0.1061 g) quantity of $Sr(NO_3)_2$ was added to 5 mL of CH_3CN; 0.5 mmol (0.13 mL) of EO6 and 0.5 mmol (0.07 mL) of NH_4OH were then added. The mixture was heated with stirring for 1 h at 65 °C. Slow evaporation of the solution yielded colorless crystals. Anal. Calcd: C, 29.18; H, 5.31; N, 5.67. Found: C, 28.13; H, 5.54; N, 5.11.

Table 8. Final Fractional Coordinates for $[Sr(NO_3)(EO3)_2][NO_3]$

atom	*x*/*a*	*y*/*b*	*z*/*c*	*B*(eqv), Å^2
Sr	0.59619(7)	0.5000	0.79675(4)	2.75
O(1)	0.3745(8)	0.3554(8)	0.6872(5)	5.01
O(2)	0.4202(9)	0.6248(7)	0.6488(5)	4.85
O(3)	0.6566(9)	0.7600(8)	0.7557(6)	5.78
O(4)	0.9055(7)	0.5800(7)	0.8095(5)	5.19
O(5)	0.7366(8)	0.4488(7)	0.6217(5)	5.03
O(6)	0.7153(8)	0.2512(7)	0.7725(4)	4.53
O(7)	0.7589(8)	0.3852(6)	0.9527(4)	4.24
O(8)	0.6241(8)	0.6328(7)	0.9739(4)	4.35
O(9)	0.2913(8)	0.5587(7)	0.8563(5)	4.33
O(10)	0.3913(7)	0.3803(7)	0.9254(4)	4.49
O(11)	0.1385(8)	0.4397(8)	0.9497(6)	6.25
O(12)	0.717(2)	0.590(1)	0.4443(8)	13.12
O(13)	0.806(1)	0.619(1)	0.2990(6)	9.73
O(14)	0.926(1)	0.482(1)	0.4032(9)	10.72
N(1)	0.2705(9)	0.4617(8)	0.9107(6)	4.11
N(2)	0.820(1)	0.564(1)	0.3830(7)	5.94
C(1)	0.306(2)	0.420(2)	0.599(1)	6.91
C(2)	0.280(2)	0.556(2)	0.606(1)	8.92
C(3)	0.409(3)	0.769(2)	0.673(2)	7.74
C(3)′ [a]	0.427(3)	0.758(2)	0.630(2)	8.00
C(4)	0.565(2)	0.822(1)	0.681(1)	7.79
C(5)	0.826(2)	0.807(2)	0.783(2)	6.19
C(5)′	0.826(3)	0.779(2)	0.722(2)	7.05
C(6)	0.942(1)	0.708(1)	0.776(1)	7.92
C(7)	0.840(1)	0.335(1)	0.6218(7)	5.52
C(8)	0.757(2)	0.223(1)	0.6693(8)	6.19
C(9)	0.840(1)	0.207(1)	0.8460(8)	5.64
C(10)	0.790(1)	0.244(1)	0.9482(7)	4.65
C(11)	0.734(2)	0.435(1)	1.0516(8)	5.64
C(12)	0.735(2)	0.580(1)	1.0498(9)	6.15

[a] Primed and unprimed atoms of like number are disordered with 50% occupancy each.

Table 9. Final Fractional Coordinates for $[Sr(NO_3)_2(OH_2)(EO4)]$

atom	*x*/*a*	*y*/*b*	*z*/*c*	*B*(eqv), Å^2
Sr	0.9793(1)	0.72812(8)	0.68998(8)	3.04
O(1)	1.2336(8)	0.5663(7)	0.6402(6)	4.91
O(2)	1.1659(8)	0.6314(6)	0.8763(5)	4.15
O(3)	0.9202(8)	0.8199(6)	0.9191(5)	4.39
O(4)	0.6777(7)	0.8312(6)	0.7259(5)	4.23
O(5)	0.7566(8)	0.7349(7)	0.4979(6)	5.06
O(6)	1.1290(8)	0.8031(6)	0.4944(6)	4.93
O(7)	1.2177(7)	0.9179(6)	0.7703(6)	4.31
O(8)	1.0029(8)	1.0018(6)	0.6686(6)	4.24
O(9)	1.231(1)	1.1278(6)	0.7142(6)	5.77
O(10)	0.7743(9)	0.5372(6)	0.7965(6)	5.80
O(11)	0.861(1)	0.4787(7)	0.6209(7)	6.32
O(12)	0.7079(9)	0.3374(6)	0.7138(7)	5.63
N(1)	1.151(1)	1.0187(8)	0.7180(6)	3.87
N(2)	0.779(1)	0.4504(7)	0.7102(8)	4.27
C(1)	1.297(1)	0.487(1)	0.739(1)	5.32
C(2)	1.325(1)	0.582(1)	0.8503(9)	5.43
C(3)	1.176(1)	0.716(1)	0.9874(8)	4.95
C(4)	0.998(1)	0.746(1)	1.0149(8)	5.31
C(5)	0.750(1)	0.853(1)	0.9393(9)	5.45
C(6)	0.673(1)	0.922(1)	0.8312(9)	5.41
C(7)	0.584(1)	0.874(1)	0.621(1)	5.72
C(8)	0.586(1)	0.763(1)	0.522(1)	5.71

X−ray Data Collection, Structure Determination, and Refinement

A single crystal of each complex was mounted in a thin-walled glass capillary flushed with Ar and transferred to the Enraf-Nonius CAD-4 diffractometer for analysis. (The data for $[Sr(OH_2)_2(EO6)]Cl_2{\cdot}H_2O$ were collected on a Rigaku AFC7R diffractometer by Molecular Structure Corp. The data for $[Sr(NO_3)(EO3)_2][NO_3]$ were collected using the Siemens CCD area detector, SMART.) A summary of data collection parameters is given in Table 2. For those space groups not uniquely determined by the systematic absences, the higher symmetry centrosymmetric alternative was found to be the correct choice except for $[Sr(NO_3)(EO3)_2][NO_3]$.

Table 10. Final Fractional Coordinates for $[Sr(NO_3)_2(EO5)]$

atom	*x*/*a*	*y*/*b*	*z*/*c*	*B*(eqv), Å^2
Sr	−0.2290(1)	−0.3112(1)	0.79025(8)	2.99
O(1)	−0.1477(7)	−0.5949(6)	0.9294(5)	4.48
O(2)	0.0454(7)	−0.4945(6)	0.6920(5)	4.56
O(3)	−0.0373(7)	−0.2108(6)	0.5470(5)	4.24
O(4)	−0.3636(7)	−0.0577(6)	0.6160(6)	5.14
O(5)	−0.5083(7)	−0.1138(7)	0.8761(7)	5.28
O(6)	−0.3652(7)	−0.3664(6)	1.0414(5)	5.24
O(7)	−0.0074(7)	−0.2897(7)	0.8715(6)	5.66
O(8)	−0.1592(7)	−0.0792(7)	0.7934(6)	5.77
O(9)	0.0332(9)	−0.0831(8)	0.8544(7)	8.23
O(10)	−0.4660(7)	−0.4124(7)	0.8077(6)	5.50
O(11)	−0.2937(8)	−0.3857(7)	0.6234(6)	6.11
O(12)	−0.5049(9)	−0.441(1)	0.6499(7)	11.45
N(1)	−0.0435(9)	−0.1486(8)	0.8397(6)	4.34
N(2)	−0.4242(9)	−0.4133(8)	0.6912(7)	5.07
C(1)	−0.037(1)	−0.694(1)	0.8559(9)	5.98
C(2)	0.105(1)	−0.634(1)	0.7746(9)	5.98
C(3)	0.168(1)	−0.425(1)	0.5983(9)	5.98
C(4)	0.096(1)	−0.319(1)	0.4933(8)	5.15
C(5)	−0.121(1)	−0.109(1)	0.4544(8)	6.09
C(6)	−0.250(1)	0.009(1)	0.5090(9)	6.54
C(7)	−0.497(1)	0.048(1)	0.670(1)	6.72
C(8)	−0.601(1)	−0.032(1)	0.784(1)	7.32
C(9)	−0.600(1)	−0.174(1)	1.002(1)	6.89
C(10)	−0.489(1)	−0.251(1)	1.0868(9)	7.24

The structures were solved utilizing SHELXS[49] and refined with SHELX76.[50] Neutral atom scattering factors and anomalous dispersion corrections were from ref 51. Except for the disordered $[Sr(OH_2)_3(EO5)]Cl_2$ and $[Sr(NO_3)(EO3)_2][NO_3]$ noted below, geometrically constrained hydrogen atoms were placed in calculated positions 0.95 Å from the bonded carbon atom and allowed to ride on that atom with B fixed at 5.5 Å^2. It was possible to locate the alcoholic hydrogen atoms for $[Sr(EO4)_2]Cl_2$, $[Sr(NO_3)_2(EO5)]$, and $[Sr(NO_3)_2(EO6)]$ which were then included with fixed contributions (B = 5.5 Å^2) in the final refinements. All non-hydrogen atoms (except as noted below for disordered structures) were refined anisotropically. Considerations unique to each crystallographic study are discussed below.

$[Sr(EO3)_2]Cl_2$. Relatively high thermal motion was noted for most of the atoms, especially C(1) and C(2); however, no disorder was evident. C(1) and C(2) do exhibit a smaller O(1)−C(1)−C(2)−O(2) torsion angle than expected (−26.5° versus a normal −gauche angle of −60°), and this may be evidence of a minor contribution from unresolvable ±gauche disorder. The final values of the positional parameters are given in Table 3.

$[Sr(EO4)_2]Cl_2$. Disorder was resolved for one ethylene unit (C(7)−C(8)). The two positions resolved for each carbon atom were refined at 50% occupancy in alternate least squares cycles. The disorder amounted to a ±gauche disorder in the one O−C−C−O torsion angle. The final values of the positional parameters are given in Table 4.

$[Sr(EO4)_2]Cl_2{\cdot}3H_2O$. High thermal motion was evident for many of the atoms, especially the carbon atoms. This may be in part responsible for the very low observed/measured ratio of the data. Torsion angle analysis did reveal ±gauche disorder in the C(15)−C(16) ethylene unit. This disorder was resolved into two 50% occupancy groups: C(15)−C(16) and C(15)′−C(16)′. The final values of the positional parameters are given in Table 5.

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Table 11. Final Fractional Coordinates for [Sr$(NO_3)_2$(EO6)]

atom	*x*/*a*	*y*/*b*	*z*/*c*	*B*(eqv), Å^2
Sr	0.76189(6)	0.51048(9)	0.02676(9)	2.90
O(1)	0.7994(5)	0.7418(7)	0.0403(7)	5.09
O(2)	0.8713(4)	0.5933(6)	−0.0829(6)	3.85
O(3)	0.8389(4)	0.3423(7)	−0.0750(6)	3.63
O(4)	0.7647(4)	0.2713(6)	0.0924(6)	4.13
O(5)	0.6435(5)	0.4345(7)	0.1317(6)	4.04
O(6)	0.6308(5)	0.6615(7)	0.0386(7)	4.45
O(7)	0.6851(5)	0.9119(7)	0.0803(7)	5.26
O(8)	0.8286(4)	0.5221(8)	0.2501(6)	5.09
O(9)	0.9189(5)	0.4795(8)	0.1589(7)	5.27
O(10)	0.9632(6)	0.495(1)	0.3401(7)	7.93
O(11)	0.6273(6)	0.3984(8)	−0.1186(7)	5.60
O(12)	0.6731(5)	0.5538(7)	−0.1957(6)	4.37
O(13)	0.5583(5)	0.4545(9)	−0.2856(7)	6.31
N(1)	0.9055(6)	0.502(1)	0.2524(7)	4.13
N(2)	0.6181(6)	0.4682(9)	−0.200(1)	4.30
C(1)	0.8623(9)	0.792(1)	−0.007(1)	6.29
C(2)	0.8618(8)	0.720(1)	−0.114(1)	5.31
C(3)	0.8794(6)	0.514(1)	−0.1724(8)	4.13
C(4)	0.9030(7)	0.387(1)	−0.120(1)	4.41
C(5)	0.8655(8)	0.230(1)	−0.010(1)	4.80
C(6)	0.7914(8)	0.183(1)	0.026(1)	5.82
C(7)	0.6946(7)	0.231(1)	0.130(1)	4.88
C(8)	0.6732(8)	0.329(1)	0.202(1)	5.43
C(9)	0.6187(8)	0.535(1)	0.188(1)	5.81
C(10)	0.5740(8)	0.630(1)	0.104(1)	6.22
C(11)	0.5981(8)	0.757(1)	−0.044(1)	5.68
C(12)	0.6001(7)	0.884(1)	0.009(1)	5.37

[Sr$(OH_2)_3$(EO5)]Cl_2. High thermal motion was noted for several atoms with resolvable disorder observed for the ethylene linkages C(1)−C(2) and C(9)−C(10). The disorder corresponds to a ±gauche conformation of the O−C−C−O fragments. C(1), C(2), C(9), C(10) and C(1)′, C(2)′, C(9)′, C(10)′ were refined at 50% occupancy with isotropic thermal parameters in alternate least squares cycles. Refinement of non-hydrogen atoms was with anisotropic temperature factors except for the disordered ethylene linkages. The final values of the positional parameters are given in Table 6.

[Sr$(OH_2)_2$(EO6)]Cl_2·H_2O. The final values of the positional parameters are given in Table 7.

[Sr(NO_3)(EO3)$_2$][NO_3]. High thermal motion was noted for the carbon atoms in the O(1)−O(4) EO3 molecule. Two carbon positions (C(3) and C(5)) could be resolved into two orientations and were refined in alternate least squares cycles with 50% occupancy. Disorder could not be resolved for C(1), C(2), C(4), or C(6), however, and hydrogen atoms were not included for these atoms. The geometrically constrained hydrogen atoms bonded to C(7)−C(12) were placed in calculated positions 0.95 Å from the bonded carbon atom and allowed to ride on that atom with *B* fixed at 5.5 Å^2. The remaining hydrogen atoms were not included in the final refinement. The final values of the positional parameters are given in Table 8.

[Sr$(NO_3)_2$$(OH_2)$(EO4)], [Sr$(NO_3)_2$(EO5)], and [Sr$(NO_3)_2$(EO6)]. The final values of the positional parameters are given in Tables 9−11, respectively.

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Supplementary Material Available: Tables giving crystal data and details of the structure determinations, bond lengths and angles, anisotropic thermal parameters, and hydrogen atom locations (59 pages). Ordering information is given on any current masthead page.