J. Am. Chem. Soc. 1992, 114, 2960–2967

an agostic structure to overcome the metal unsaturation in the simple carbene formulation. The agostic bond present in $[Tp'(CO)_2W{=}C(Ph)CH_2R][BF_4]$ (R = H, Me) complements the range of saturated and unsaturated agostic ligands represented in Chart IV. In a sense the β-agostic carbene resembles both agostic π-complexes with unsaturation in the organic ligand and Schrock α-agostic carbenes with unsaturation in the metal–carbon bond.

Summary

Reaction of $[Tp'(CO)_2W(PhC_2H)][BF_4]$ with PhC_2H or reaction of $Tp'(CO)IW(PhC_2R)$ (R = H, Me) with $PhC_2H/AgBF_4$ generates cationic bisalkyne complexes $[Tp'(CO)W(PhC_2H)(PhC_2R)][BF_4]$. A crystal structure of $[Tp'(CO)W(PhC_2H)_2][BF_4]$ shows a pseudooctahedral geometry with the two cis phenylacetylene ligands parallel to each other. Structural data and NMR data suggest each alkyne adopts a three-electron donor role with phenyl groups distal to one another. Deprotonation of the bis(phenylacetylene) complex yields an alkyne acetylide complex, $Tp'(CO)_2(PhC_2H)W(C{\equiv}CPh)$, which exists as two isomers in solution, differing in alkyne orientation. Protonation of the acetylide compound with aqueous HCl yields the bisalkyne cation, but decomposition results when HBF_4 is used as a proton source. Hydride addition to the bis(phenylacetylene) complex forms an alkyne η^1-vinyl complex, $Tp(CO)(PhC_2H)W(\eta^1\text{-}CPh{=}CH_2)$, which also exists as two isomers in solution due to different alkyne orientations. NMR data support a formulation containing a σ-vinyl and a four-electron alkyne ligand. Protonation of the η^1-vinyl complex at $C\beta$ results in the formation of an 18-electron alkyne carbene cation, $Tp'(CO)(PhC_2H)W{=}C(Me)Ph][BF_4]$, with the alkyne acting as a four-electron donor. Here $\pi_\perp$ donation from the alkyne ligand is observed rather than agostic bond formation from the carbene substituent. Protonation of the η^2-vinyl complexes $Tp'(CO)_2W(\eta^2\text{-}CPh{=}CHR)$ (R = Me, H) at $C\beta$ of the η^2-vinyl ligand forms β-agostic carbenes $\{Tp'(CO)_2W[{=}C(R)Ph]\}[BF_4]$ (R = Me, Et). An X-ray structure of the methyl derivative revealed a W–C (methyl) distance of 2.49 Å with the W–$C\alpha$–$C\beta$ angle being 91°. Rotation of the methyl group C–H agostic bonds is fast for the methyl derivative. Variable temperature NMR experiments on the ethyl derivative show a barrier of 11.7 kcal/mol for interconversion of enantiomers.

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Supplementary Material Available: Labeled diagrams of **1** and **6** and tables of anisotropic temperature factors and complete bond distances and angles for **1** and **6** (13 pages); listings of observed and calculated structure factors (36 pages). Ordering information is given on any current masthead page.

Alcoholysis of $Bi(NO_3)_3{\cdot}5H_2O$ by Polyethylene Glycols. Comparison with Bismuth(III) Nitrate Crown Ether Complexation

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Abstract: The reactions of $Bi(NO_3)_3{\cdot}5H_2O$ in 3:1 CH_3CN:CH_3OH with 12-crown-4, 18-crown-6, triethylene glycol (EO3), tetraethylene glycol (EO4), pentaethylene glycol (EO5), and hexaethylene glycol (EO6) were studied. The ready isolation of soluble bismuth(III) alkoxides resulted from simple reactions with the inexpensive polyethylene glycols. The $EO3^-$, $EO4^-$, and $EO6^-$ complexes are dimeric, bridged by two alkoxide oxygen atoms. Coordination of each Bi^{3+} ion is completed by two NO_3^- anions and the remaining ether donor atoms. The chain length of EO5 is sufficient to allow both terminal alcohols to participate in bridging two Bi^{3+} centers. The net ionization of one is accomplished by a dually ionized EO5 ligand and a neutral EO5 complex producing a rather complicated structure. The neutral crown ether complexes formed are similar to those isolated for the late lanthanides. The structurally characterized complexes include $[Bi(NO_3)_2(EO3^-)]_2$, $[Bi(NO_3)_2(EO4^-)]_2{\cdot}2MeOH$, $[Bi(NO_3)_2(EO5)][Bi(NO_3)_2(EO5^{2-})Bi(NO_3)_3]{\cdot}2H_2O$, $[Bi(NO_3)_2(EO6^-)]_2$, $[Bi(NO_3)_3(12\text{-}crown\text{-}4)]$, and $[Bi(NO_3)_3(OH_2)_3]{\cdot}18\text{-}crown\text{-}6$. The two covalent Bi–alkoxide interactions activate the Bi^{3+} lone pair resulting in structures with secondary Bi–O contacts surrounding the lone pair site. This results in a very wide range of Bi–O donor contacts. The crown ether complexes do not contain any covalent interactions and do not exhibit lone pair effects. The Bi–O separations have a much narrower range.

Introduction

The chemistry of bismuth has been relatively ignored until recently when the flurry over high T_c oxide–superconducting materials[1-5] renewed interest in bismuth alkoxides as potential precursors for new superconductor formulations.[6-9] Unfortunately, many of the simple alkoxides prepared by alcoholysis have poor solubilities or disproportionate to oxo-centered species.[10,11] The use of chelating alkoxides for a variety of metals[11-21] has received attention lately as a way to reduce the extent of alkoxide bridging; however, thus far only relatively short chain polyethers with one terminal alkyl group have been examined. Polyethylene glycol (PEG) and crown ether complexes of bismuth(III) are virtually nonexistent, with two recent reports discussing the

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structural characterization of the only three bismuth(III) complexes of crown ethers known.[22,23]

We now report the ready isolation of soluble bismuth(III) alkoxides from the simple reactions of $Bi(NO_3)_3 \cdot 5H_2O$ with inexpensive polyethylene glycols (triethylene (EO3)–hexaethylene (EO6)) in 3:1 CH_3CN:CH_3OH. We have also examined similar reactions of bismuth(III) halides which do not result in alcoholysis and reactions with several crown ethers. The resulting structures provide a wealth of information on secondary bonding and lone pair effects in Bi^{3+} complexes. In this contribution we discuss the structural aspects of the bismuth(III) nitrate complexes which include (a) how glycol chain length influences structure, (b) the activation of Bi^{3+} lone pair density by the formation of Bi–O covalent bonds, (c) how a stereochemically active lone pair results in long Bi–O secondary interactions, and (d) how the absence of an active lone pair results in Bi^{3+} complexes very similar to those of the ionic late lanthanides. In the next paper,[24] we provide a detailed examination of the trends in secondary bonding and lone pair effects for a series of related bismuth(III) halide complexes of PEG's and crown ethers.

Results

Synthesis of Complexes. Reactions of $Bi(NO_3)_3 \cdot 5H_2O$ in 3:1 CH_3CN:CH_3OH with triethylene glycol (EO3), tetraethylene glycol (EO4), pentaethylene glycol (EO5), and hexaethylene glycol (EO6) produce bismuth(III) heteroleptic–alkoxide complexes derived from the net ionization of one end of the PEG chain. The EO3, EO4, and EO6 complexes have similar dimeric structures. The EO6 complex has an uncoordinated, dangling $(CH_2)_2O(CH_2)_2OH$ fragment.

The EO5 complex is unique, probably due to the fact that its chain length is just sufficient to encircle a Bi^{3+} ion and allow both terminal oxygens to participate in a bridging mode. The EO5 complex is thus the only one to form a complex with a dually ionized glycol. Since both alkoxide bridges come from one glycol, the second Bi^{3+} ion does not have a coordinated PEG ligand. The charge is balanced by a neutral EO5 complex cation, $[Bi(NO_3)_2(EO5)]^+$. The net ionization of the glycols is again one.

Reactions of $Bi(NO_3)_3 \cdot 5H_2O$ with 12-crown-4 and 18-crown-6 produce neutral complexes similar to those found for the lanthanides. $[Bi(NO_3)_3(12\text{-crown-}4)]$ and $[Bi(NO_3)_3(OH_2)_3] \cdot 18$-crown-6 have been isolated and structurally characterized. The latter is isostructural with the lanthanide complexes Ln = Gd,[25] Y,[26] Er,[26], Yb,[26] and Lu.[26]

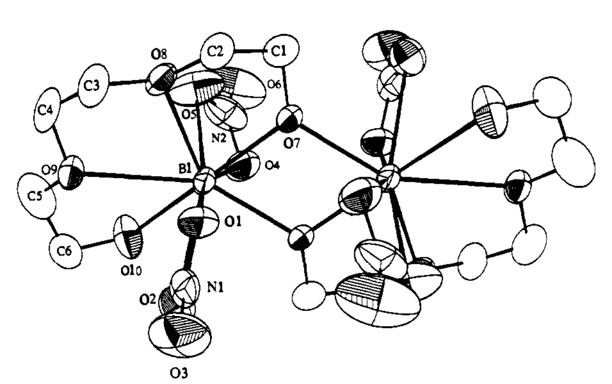

Figure 1. $[Bi(NO_3)_2(EO3^-)]_2$: The atoms are represented by their 50% probability ellipsoids for thermal motion. Hydrogen atoms have been omitted.

The case for the preparation of soluble alkoxides from bismuth(III) halides has not been made. When bismuth(III) halides are utilized, the strong influence of the covalent pyramidal BiX_3 fragment precludes ionization of the PEG ligands and only neutral complexes are isolated. The reactions of $BiCl_3$ or $BiBr_3$ in 3:1 CH_3CN:CH_3OH with 12-crown-4, 15-crown-5, benzo-15-crown-5, EO4, EO5, or EO6 produce complexes consisting of the neutral, pyramidal, BiX_3 unit coordinated very weakly to the oxygen donors of the ligands. The 12-crown-4 complexes are seven-coordinate while all of the remaining complexes are 8-coordinate including two pentadentate EO5 complexes. In stark contrast to our results with the hard lanthanide(III) ions,[27,28] the neutral glycol ligands closely mimic the conformations of analogous crown ethers.

When 18-crown-6 or EO6 is used in these reactions, two completely different 8-coordinate complexes are isolated: the tridentate $[BiCl_3(MeOH)(18\text{-crown-}6)]$ and the ionic $[BiBr_2(18\text{-crown-}6)][BiBr_4]$ and $[BiBr_2(EO6)][BiBr_4]$ (EO6 is hexadentate in this complex). The use of BiI_3 results in the formation of polymeric Bi/I anions which hinder solubility and the isolation of pure complexes. The only completely characterized product thus far observed was formed by reaction with EO5 ($[BiI_2(EO5)][Bi_2I_7] \cdot 2MeOH$) and again the glycol mimics 18-crown-6.

Detailed crystallographic analyses of the bismuth(III) halide complexes reveal some striking examples of secondary bonding and stereochemically active lone pair effects. These results are highlighted in the following paper.[24]

Structure of $[Bi(NO_3)_2(EO3^-)]_2$. An ORTEP illustration of this complex is presented in Figure 1. It crystallizes as a dimer around a crystallographic center of inversion. Except for its lower coordination number (9, a feature of the shorter $EO3^-$ chain length), it has several features in common with all of the dimeric Bi^{3+} alkoxides structures. One end (O(7)) of the glycol has been ionized and bridges two Bi^{3+} centers via short covalent bonds, while the remainder of the polyether oxygen donors encircle one metal ion in a "crown ether-like" girdle. Each Bi^{3+} ion coordination sphere is completed by a second alkoxide bridge from an $EO3^-$ ligand on the adjacent metal ion and two twisted trans-bidentate nitrate anions. The terminal alcohol (O(10)) donates a hydrogen bond to O(4) on a dimer related by a unit translation along *a*, resulting in a polymeric hydrogen-bonded chain of dimers.

The Bi^{3+} environments are similar to the Pb^{2+} environment in $Pb(NO_3)_2(18\text{-crown-}6)$[29] where the Pb^{2+} ion resides exactly in the center of the 18-crown-6 cavity and is additionally coordinated to two trans nitrate anions. The conformation of the ethylene units in the title complex is even organized into the familiar D_{3d} pattern of alternating gauche O–C–C–O torsion angles ±g (±60°) and anti (180°) C–O–C–C angles.[30]

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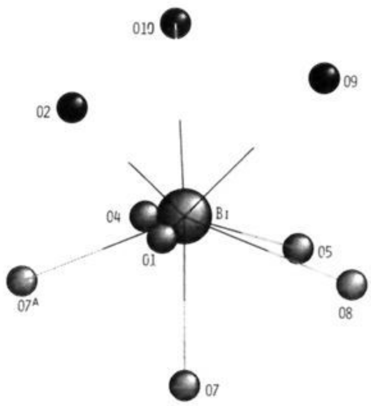

Figure 2. AX_6EY_3 geometry observed for $[Bi(NO_3)_2(EO3^-)]_2$. This representation was generated using the SYBYL molecular modeling software by Tripos Associates, St. Louis, MO. The three more darkly shaded atoms are the designated secondary interactions (Y). The symmetry code $A = 2 - x, 1 - y, 1 - z$.

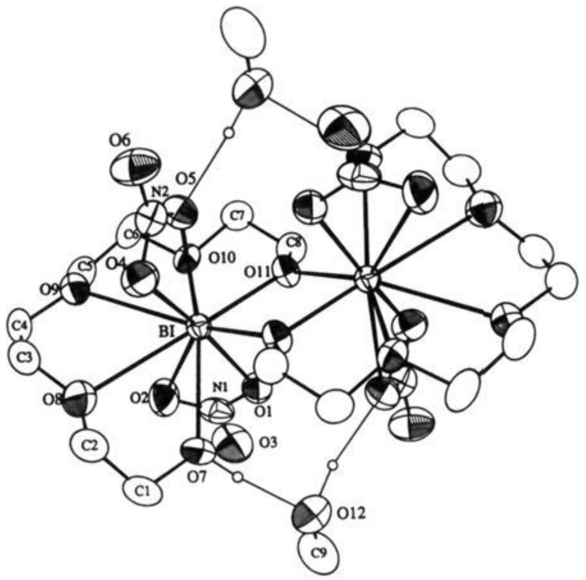

Figure 3. $[Bi(NO_3)_2(EO4^-)]_2 \cdot 2MeOH$.

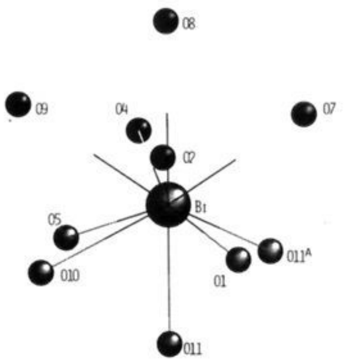

Figure 4. AX_5EY_5 geometry in $[Bi(NO_3)_2(EO4^-)]_2 \cdot 2MeOH$. Symmetry code $A = 1 - x, 1 - y, 1 - z$.

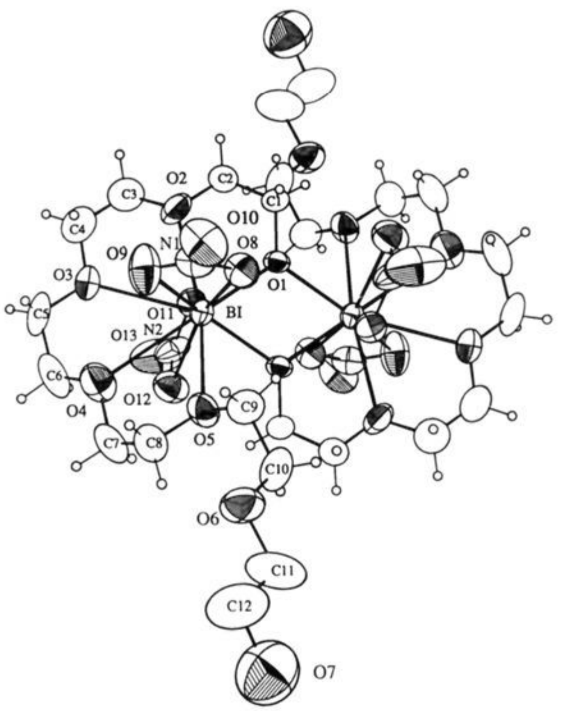

Figure 5. $[Bi(NO_3)_2(EO6^-)]_2$.

Other features of the $EO3^-$ complex common to all four of the alkoxide complexes studied include asymmetrically coordinated, staggered, trans-nitrate anions and a very wide range in Bi···O polyether separations (Table I). The long interactions all reside in an area which surrounds the location of stereochemically active lone pair e^- density. This lone pair e^- density is always trans to the covalent Bi–alkoxide bonds and thus is at first approximation similar to the directed secondary interactions described by Alcock.[31] Because the coordination polyhedra are distorted by the small bite size of the nitrate anions, we will save the full discussion of the differences in these interactions and Alcock's description of secondary bonds for the following paper.

The overall coordination geometry for $[Bi(NO_3)_2(EO3^-)]_2$ comes closest to capped square antiprismatic with O(8) capping the O(1), O(5), O(7), O(9) face. If, however, we take the three longest separations (Bi–O(2) = 2.68 (1) Å, Bi–O(9) = 2.70 (1) Å, Bi–O(10) = 2.70 (1) Å) out of consideration and add a lone pair as the seventh coordination site (following Sawyer and Gillespie[32]), the AX_6EY_3 geometry resembles a distorted Ψ-pentagonal bipyramid (Figure 2). The lone pair and the shorter of the two Bi–alkoxide separations are in the axial positions while the equatorial positions are all bent down away from E. The three longest Bi–O separations surround the general proposed location of the lone pair but do not reside directly over it. We will show this feature to be common to all of the alkoxide structures. In fact it may be a common feature of even very dissimilar structures. The recently communicated structure of potassium bismuth(III) citrate trihydrate has a nearly identical Bi^{3+} coordination sphere.[33]

Structure of $[Bi(NO_3)_2(EO4^-)]_2 \cdot 2MeOH$. The dimeric formula unit for this complex is depicted in Figure 3. The major difference in going from EO3 to EO4 is an increase in the Bi^{3+} coordination number from 9 to 10. The terminal alcohol (O(7)) donates a hydrogen bond to the methanol molecule, which in turn donates a hydrogen bond to a coordinated nitrate oxygen atom (O(5)^a) in the other half of the dimer. As observed for the $EO3^-$ complex, the dimer resides around a center of inversion and the glycol adopts a D_{3d}-like crown ether conformation. The planar Bi_2O_2 core with bridging alkoxides, staggered, trans nitrate anions, and very wide range of Bi–ONO_2 and Bi–O(ether) separations are all similar to those observed in the $EO3^-$ complex.

If one were to describe the overall geometry, it would come closest to a bicapped (O(8), O(11)) square antiprism with the

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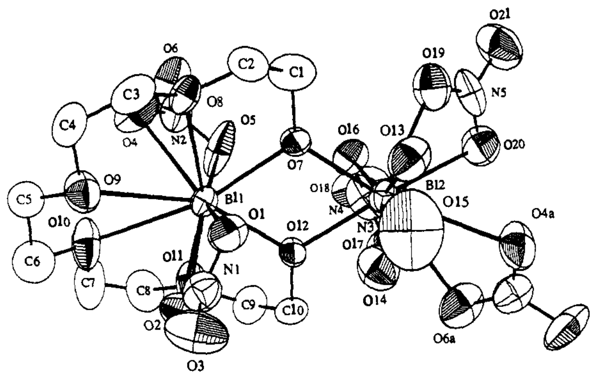

Figure 6. A portion of the polymeric anion in $[Bi(NO_3)_2(EO5)][Bi(NO_3)_2(EO5^{2-})Bi(NO_3)_3]{\cdot}2H_2O$. O(4)^a and O(6)^a coordinated to Bi(2) are related to O(4) and O(6) by x, $^1/_2 - y$, $z - {}^1/_2$.

longest Bi–O distance (O(8), 2.947 (7) Å) trans to the shortest Bi–O separation (O(11), 2.226 (5) Å). A much better description of the structure as AX_5EY_5 reveals a Ψ-octahedral geometry (Figure 4). E is trans to O(11) and its geometric site is surrounded by the five longest Bi–O distances (Bi–O(2) = 2.793 (8) Å, Bi–O(4) = 2.744 (7) Å, Bi–O(8) = 2.947 (7) Å, Bi–O(9) = 2.895 (6) Å).

Structure of $[Bi(NO_3)_2(EO6^-)]_2$. Despite having two additional donor atoms, the Bi^{3+} coordination and geometry (Figure 5) are nearly identical to those observed in the $EO4^-$ complex. This is a result of noncoordination by the O(6) and O(7) donors. The 10-coordinate description of a bicapped square antiprism again has capping atoms with the longest (Bi–O(4) = 2.98 (1) Å) and shortest (Bi–O(1) = 2.227 (8) Å) Bi–O separations.

Again designating the five longest Bi–O separations as secondary (O(3), 2.876 (9) Å; O(4), 2.98 (1) Å; O(5), 2.90 (1) Å; O(9), 2.85 (1) Å; O(12), 2.68 (1) Å) produces an AX_5EY_5 Ψ-octahedral geometry with the five secondary bonds surrounding the E site trans to O(1). This is virtually identical to that found for the $EO4^-$ complex, although the Bi–O(5) distance in this complex is over 0.25 Å longer than the Bi–O(7) separation in the $EO4^-$ complex. While part of this may be due to the presence of a less basic alcoholic oxygen in the latter, most of the lengthening probably results from steric repulsion of the dangling $(CH_2)_2O(CH_2)_2OH$ group.

The conformation of the glycol is interesting. The coordinated portion (O(1)–O(5)) adopts the D_{3d}-like sequence of torsion angles found in the previous complexes. The dangling portion of the molecule ends in a series of three anti torsion angles, essentially giving a straight chain. We would normally expect the terminal alcohol to donate a hydrogen bond; however the closest donors (the terminal NO_3^- oxygen atoms O(10) and O(13) in different dimers) are over 3 Å away. This results in higher thermal motion for the ends of each glycol chain.

Structure of $[Bi(NO_3)_2(EO5)][Bi(NO_3)_2(EO5^{2-})Bi(NO_3)_3]{\cdot}2H_2O$. Just as 18-crown-6 has the perfect cavity size for Pb^{2+}, EO5 has just the right chain length to encircle Bi^{3+} in a crown-like conformation. This allows both terminal oxygen atoms to participate in a single bridge between two bismuth centers. For this to occur, however, the second Bi^{3+} ion cannot supply its own coordinated glycol. The resulting differences in glycol charge and Bi^{3+} stoichiometry in solution produce a complicated structure upon crystallization with a polymeric anion containing a dually ionized EO5 and a monomeric cation containing neutral EO5.

The Bi(1)/Bi(2) coordination environments are shown in Figure 6. For all practical purposes the coordination environment of Bi(1) is identical to that found in the $EO4^-$ and $EO6^-$ complexes. The longest contacts (O(4), 2.86 (2) Å; O(9), 2.85 (1) Å; O(10), 2.88 (1) Å) are opposite the two covalent alkoxide interactions. The glycol conformation has the D_{3d}-like sequence of torsion angles.

The second Bi^{3+} ion in the anion is bonded to the alkoxide bridges at essentially the same separation, but its coordination environment is completed only by nitrate anions. One of these, O(4)^a–O(6)^a, is tetradentate, bridging Bi(2) and Bi(1) in a polymeric chain (Figure 7). Both Bi(1) and Bi(2) are coordinated to O(4).

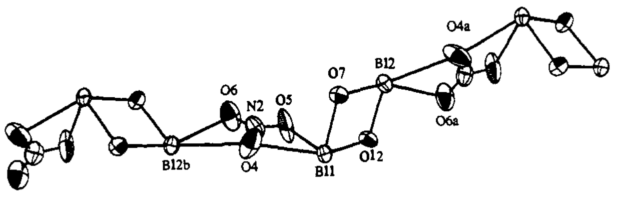

Figure 7. Polymeric chain in the $[Bi(NO_3)_2(EO5^{2-})Bi(NO_3)_3]^-$ anion propagated by a tetradentate nitrate ion as depicted here. The symmetry code a refers to x, $^1/_2 - y$, $z - {}^1/_2$; b refers to x, $^1/_2 - y$, $^1/_2 - z$.

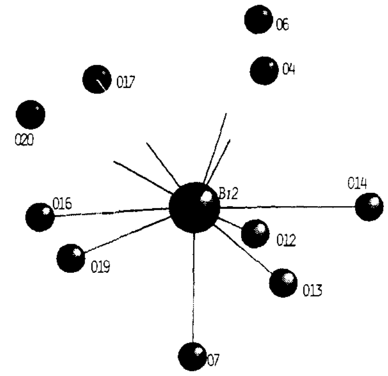

Figure 8. AX_6EY_4 geometry found for Bi(2) in the $[Bi(NO_3)_2(EO5^{2-})Bi(NO_3)_3]^-$ anion.

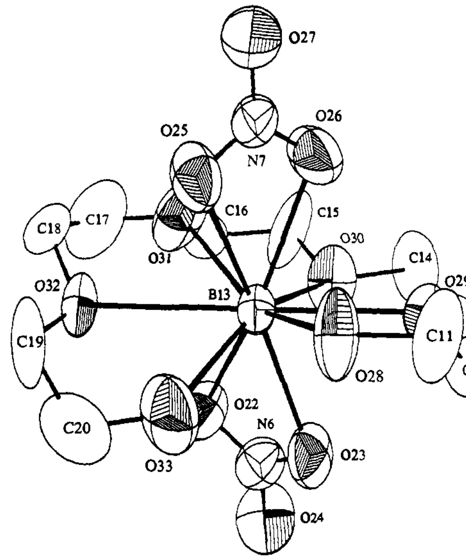

Figure 9. $[Bi(NO_3)_2(EO5)]^+$.

Although Bi(2) is also 10-coordinate, only four of the Bi–O distances should be considered secondary (O(4)^a, 3.00 (2) Å; O(6)^a, 2.84 (1) Å; O(17), 2.86 (1) Å; O(20), 2.94 (1) Å). The remaining Bi(2)–ONO_2 separations average 2.48 (2) Å. The resulting AX_6EY_4 geometry most closely resembles a Ψ-pentagonal bipyramid (Figure 8). As found for the $EO3^-$ complex, the shorter Bi(2)–alkoxide bond (O(7), 2.20 (1) Å) is in the axial position trans to E.

The $[Bi(NO_3)_2(EO5)]^+$ cation, containing the neutral EO5 molecule is represented in Figure 9. The lack of any covalent interactions precludes activation of the lone pair. The nitrate ions are more symmetrically coordinated with a range of Bi–ONO_2 separations of only 0.04 Å. The two alcoholic termini of the EO5 chain are nearly equivalent at 2.47 (2) (O(33)) and 2.43 (1) Å (O(28)) from Bi(3). This value is much shorter than those found for the alcoholic positions in the $EO3^-$ (2.70 (1) Å) or $EO4^-$ (2.644 (6) Å) complexes. The Bi–O (etheric) separations range from

Table I. Comparison of Bonding Parameters

		M–O⁻, Å			M–O(ether), Å			M–ONO₂, Å								
compound	CN	av	range	Δ	av	range	Δ	av	range	Δ	Bi···Bi, Å	O⁻···O⁻, Å	Bi–O⁻–Bi, deg	O⁻–Bi–O⁻, deg	δ (nitrate anions)	ref
$[Bi(NO_3)_2(EO3^-)]_2$	9	2.24 (4)	2.20 (1)–2.28 (1)	0.080	2.70 (1)[a]			2.54 (9)	2.42 (1)–2.68 (1)	0.26	3.708 (1)	2.52 (2)	111.7 (5)	68.3 (5)	41.7	*e*
					2.6 (1)[b]	2.51 (1)–2.70 (1)[b]	0.19[b]									
$[Bi(NO_3)_2(EO4^-)]_2\cdot 2MeOH$	10	2.24 (1)	2.226 (5)–2.252 (8)	0.026	2.644 (6)[a]			2.6 (2)	2.413 (6)–2.793 (8)	0.38	3.7436 (8)	2.46 (1)	113.4 (3)	66.6 (3)	78.2	*e*
					2.8 (2)[b]	2.552 (6)–2.947 (7)[b]	0.40[b]									
$[Bi(NO_3)_2(EO5)]$-	10				2.45 (2)[a]	2.43 (1)–2.47 (2)[a]	0.040[a]	2.51 (2)	2.49 (2)–2.53 (2)	0.040					73.4	
					2.63 (6)[b]	2.55 (2)–2.69 (1)[b]	0.14[b]									
$[Bi(NO_3)_2(EO5^{2-})$-	10	2.25 (4)	2.217 (9)–2.29 (1)	0.073	2.7 (1)	2.61 (1)–2.88 (1)	0.27	2.6 (2)	2.42 (1)–2.86 (2)	0.44	3.7364 (9)	2.45 (1)	113.4 (8)	65.8 (3)	84.5	
$Bi(NO_3)_3]\cdot 2H_2O$	10	2.22 (2)	2.20 (1)–2.23 (1)	0.030				2.7 (2)	2.46 (1)–3.00 (2)	0.54				67.1 (4)		*e*
$[Bi(NO_3)_2(EO6^-)]_2$	10	2.24 (2)	2.227 (8)–2.26 (1)	0.033	2.8 (2)	2.52 (1)–2.98 (1)	0.46	2.6 (2)	2.40 (1)–2.85 (1)	0.45	3.746 (1)	2.47 (2)	113.1 (3)	66.9 (3)	76.7	*e*
$[Bi(NO_3)_3(12\text{-crown-}4)]$	10				2.61 (7)	2.54 (1)–2.68 (2)	0.14	2.46 (6)	2.38 (2)–2.56 (2)	0.18						*e*
$[Bi(NO_3)_3(OH_2)_3]\cdot 18\text{-crown-}6$	9				2.46 (2)[c]	2.439 (8)–2.48 (1)[c]	0.041[c]	2.50 (3)	2.45 (2)–2.54 (2)	0.09						*e*
$[Y(NO_3)_3(12\text{-crown-}4)]$[d]	10				2.46 (4)	2.42 (2)–2.50 (2)	0.080	2.44 (4)	2.37 (2)–2.48 (2)	0.11						34
$[Y(NO_3)_3(OH_2)_3]\cdot 18\text{-crown-}6$[d]	9				2.36 (1)[c]	2.348 (5)–2.371 (7)[c]	0.023[c]	2.40 (2)	2.372 (8)–2.423 (9)	0.051						26

[a] These values are for terminal alcoholic oxygen atoms. [b] These values are for etheric oxygen atoms. [c] These values are for the coordinated H_2O molecules. [d] The difference in the effective ionic radii of Bi^{3+} and Y^{3+} is 0.151 Å.[37] [e] This study.

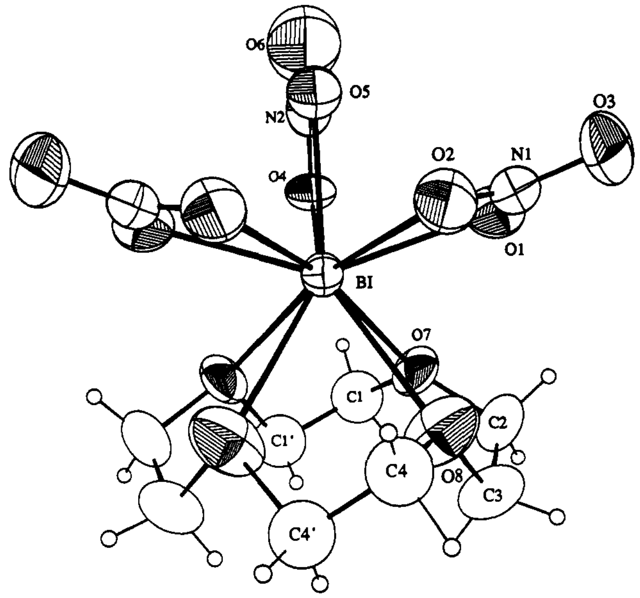

Figure 10. $[Bi(NO_3)_3(12\text{-crown-}4)]$.

2.55 (2) to 2.69 (1) Å, a range of 0.14 Å. The shortening of the alcoholic bonds may represent the initial stages in the ionization of these positions, the formation of covalent bonds, and the activation of the lone pair. The two longest Bi–O distances (Bi–O(32) = 2.69 (1) Å; Bi–O(31) = 2.64 (2) Å) are trans to the shortest (O(28)), while the next two longest (Bi–O(30) = 2.55 (2) Å; Bi–O(29) = 2.56 (1) Å) are trans to the second shortest (O(33)).

Overall Bi(3) comes very close to a bicapped square antiprismatic geometry with O(29) and O(32) in the capping positions. The EO5 ligand coordinates in a fashion expected for 18-crown-6 and its conformation again resembles the D_{3d} form of complexed 18-crown-6. The only deviation occurs in the ethylene group bonding to O(33). From Figure 9 one can see that this position is bent down slightly from where the sixth 18-crown-6 oxygen would reside. This modest difference may arise from the hydrogen bonding of O(28) and O(33) to the two water molecules.

Structure of $[Bi(NO_3)_3(12\text{-crown-}4)]$. The structure of this neutral complex is depicted in Figure 10. The Bi, O(4), O(5), O(6), and N(2) atoms reside on a crystallographic mirror plane; the C(1) and C(4) ethylene linkages are disordered. The crown ether has a C_s conformation.

The 10-coordinate bismuth geometry is best described as a 4A,6B-expanded dodecahedron. The overall structure (and indeed the cell parameters) are very similar to $[M(NO_3)_3(12\text{-crown-}4)]$ (M = Y,[34] Eu[35]), although this structure is much less distorted, probably due to the larger ionic radius of Bi^{3+}. The difference in Bi–O separations in the title complex vs the hard Y^{3+} complex matches this difference in ionic radii (Table I).

Without covalent bonds to activate the lone pair, the ranges in Bi–O separations (0.18 Å, $Bi{-}ONO_2$; 0.14 Å, Bi–O(ether)) are smaller than those observed in the alkoxide complexes.

Structure of $[Bi(NO_3)_3(OH_2)_3]{\cdot}18\text{-crown-}6$. The Bi environment is represented in Figure 11. This complex is isostructural with $[M(NO_3)_3(OH_2)_3]{\cdot}18\text{-crown-}6$ (M = Gd,[25] Y,[26] Er,[26] Yb,[26] Lu[26]). The 9-coordinate bismuth ion resides on a mirror plane with O(1)–O(3), N(1), and O(9). The three water molecules donate three hydrogen bonds to two symmetry related 18-crown-6 molecules. The D_{3d} crown molecules reside around crystallographic centers of inversion, thus creating zigzag polymeric hydrogen bonded chains which propagate along *b*. All six etheric oxygen atoms accept a hydrogen bond.

The overall Bi geometry is closest to a capped square antiprism with O(1) capping the O(2), O(8), O(9), $O(8)^a$ face; however, the small bite of the nitrate anion containing O(1) results in severe distortion. This square face deviates from planarity by as much as 0.26 Å, while the opposite face is planar by symmetry. The two types of Bi–O separations are at the low end of the averages in the previous structures and have narrow ranges.

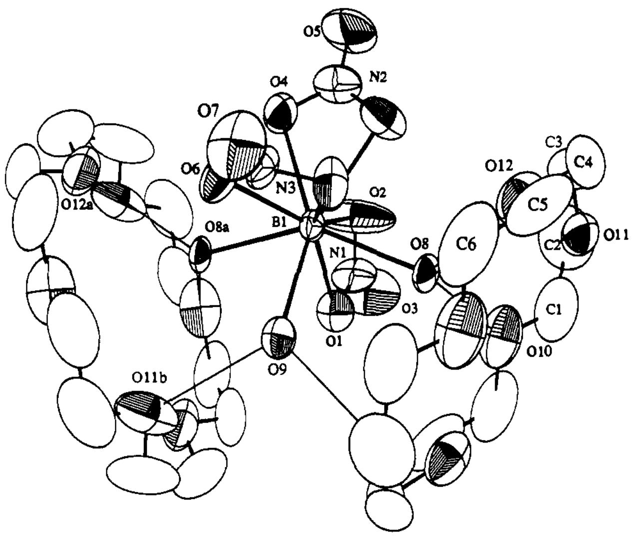

Figure 11. Bi^{3+} environment in $[Bi(NO_3)_3(OH_2)_3]{\cdot}18\text{-crown-}6$. The symmetry codes are $a = x, {}^3/_2 - y, z$ and $b = 2 - x, {}^1/_2 + y, 2 - z$.

Discussion

The heteroleptic alkoxides formed in this study may provide an easier route to the soluble precursor materials than the homoleptic alkoxides previously reported. The combination of donor anions and additional donor atoms in the alkoxide ligands has led to discrete dimers rather than the polymeric structures reported in the literature.[11-13] It appears from the literature that bulky alkoxides may also hold promise.[12,15]

Although not fully described in the three papers reporting the structure of $[Bi(\mu\text{-}\eta^1\text{-}OCH_2CH_2OMe)_2(\eta^1\text{-}OCH_2CH_2OMe)]_\infty$,[11-13] the effect of the Bi^{3+} lone pair is evident and is probably responsible for the observed structures. Each Bi^{3+} ion forms three covalent bonds to three alkoxides (Bi–O = 2.071 (6)–2.230 (6) Å) in the tripodal arrangement expected for $Bi(OR)_3$,[15] BiX_3,[24] $Bi(NR_2)_3$,[36] etc., compounds. The remaining Bi–OR interactions to the alkoxide oxygen atoms are obviously donor interactions similar to the Bi–O(ether) coordination observed in our structures. The Bi–OR separations are reported to range from 2.513 (7) to 2.573 (6) Å. The terminal glycols in our complexes can take part in hydrogen bonding and are unlikely to participate in further Bi–O–Bi bridging.

The four alkoxide structures reported here are testament to the ability of Bi^{3+} to organize flexible polyethylene glycol chains into cyclic crown ether-like structures. This feature of Bi^{3+} complexation chemistry is a result of the formation of covalent interactions which then direct the rest of the Bi^{3+} coordination sphere. This is in direct contrast to the crown ether and PEG structures of the hard ionic lanthanide(III) ions where crown ethers tend to fold around the lanthanides and PEG's wrap the ions in a helical fashion.[27,28]

The four alkoxide complexes have remarkably similar structures. The major deviation occurs for the 9-coordinate $EO3^-$ structure. The Bi_2O_2 core is planar by symmetry in all but the $EO5^{2-}$ complex where it is planar to within 0.033 Å. The Bi···Bi separation is smallest (3.708 (1) Å) for the $EO3^-$ complex vs 3.742 (4) Å average for the three other alkoxides. Similar variations are observed in the $O^-{\cdots}O^-$ separations (2.52 (2) Å ($EO3^-$) vs 2.46 (1) Å average ($EO4^-$, $EO5^{2-}$, $EO6^-$), $Bi{-}O^-{-}Bi$ angles (111.7 (5)°

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

	$[Bi(NO_3)_2(EO3^-)]_2$	$[Bi(NO_3)_2(EO4^-)]_2\cdot$ 2MeOH	$[Bi(NO_3)_2(EO5)]$–$[Bi(NO_3)_2(EO5^{2-})Bi(NO_3)_3]\cdot$ $2H_2O$	$[Bi(NO_3)_2(EO6^-)]_2$	$[Bi(NO_3)_3$(12-crown-4)]	$[Bi(NO_3)_3(OH_2)_3]\cdot$ 18-crown-6
formula wt	964.31	1116.5	1571.6	1228.6	571.21	713.63
space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	*Pnma*	*Pnma*
temp, °C	18	22	22	22	22	22
cell constants[a]						
a, Å	8.004 (4)	8.022 (1)	17.175 (7)	8.117 (2)	15.456 (8)	15.295 (6)
b, Å	8.124 (3)	10.670 (9)	15.887 (6)	11.084 (8)	12.177 (7)	14.273 (5)
c, Å	10.608 (8)	11.428 (6)	16.950 (9)	11.862 (9)	8.529 (3)	11.148 (2)
α, deg	83.62 (5)	69.55 (7)		70.61 (8)		
β, deg	75.00 (6)	83.64 (2)	105.70 (5)	81.32 (5)		
γ, deg	82.98 (4)	71.98 (3)		77.46 (4)		
cell vol, Å^3	659.0	871.6	4452.4	979.1	1605	2433.7
formula units/unit cell	1	1	4	1	4	4
D_{calc}, g cm^{-3}	2.43	2.13	2.34	2.08	2.36	1.95
μ_{calc}, cm^{-1}	127.8	97.03	113.5	86.26	105.2	69.96
range of rel transm factors, %	52/100	35/100	39/100	61/100	42/100	44/100
radiation, graphite monochromator	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)
$R = \sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\|$	0.056	0.036	0.046	0.046	0.075	0.048
R_w	0.069	0.047	0.056	0.053	0.091	0.059

[a] Least-squares refinement of $((\sin\theta)/\lambda)^2$ values for 25 reflections $\theta > 19°$. [b] Corrections: Lorentz-polarization and absorption (empirical, psi scan). [c] Neutral scattering factors and anomalous dispersion corrections.

vs 113.3 (1)° average), and O^-–Bi–O^- angles (68.3 (5)° vs 66.6 (5)° average). In addition the dihedral angle between the trans nitrate anions is smallest for the $EO3^-$ complex (41.7°) vs the 76 (2)° average observed for the 10-coordinate alkoxides. The complex of the neutral EO5 ligand exhibits the largest dihedral angle of 84.5°.

It is apparent from the alkoxide complexes that EO5 has the appropriate chain length to just encircle a Bi^{3+} ion. This is most likely the origin of the structural difference in the $EO5^{2-}$ complex vs $EO3^-$, $EO4^-$, or $EO6^-$. Unfortunately, this is probably the wrong glycol to use to get homogenous solutions of soluble Bi^{3+} alkoxides. With both alkoxide bridges from a single glycol, the second Bi^{3+} ion must be coordinated by other solution species such as water, solvent, or anions. For the purpose of preparing these soluble Bi^{3+} alkoxides, EO4 would seem to be the appropriate choice.

The complex moieties without covalent bonds to Bi^{3+} do not exhibit secondary bonding or lone pair effects. The $[Bi(NO_3)_2(EO5)]^+$ cation, $[Bi(NO_3)_3$(12-crown-4)], and $[Bi(NO_3)_3(OH_2)_3]\cdot$18-crown-6 all exhibit fairly narrow ranges in Bi–O separations. This is consistent with our structural studies of $[Pb(NO_3)$(12-crown-4)$_2$]$[Pb(NO_3)_3$(12-crown-4)], $[PbL_2][Pb(NO_3)_3L]_2$ (L = 15-crown-5 or benzo-15-crown-5), and $[Pb(NO_3)_2$(18-crown-6)][29] in which we did not observe stereochemical activity of any lone pair electron density. The activation of the lone pair and its effect on Bi^{3+} structures is the subject of the following paper where we explore polyether complexes with two or three covalent Bi–X(halide) bonds.

Experimental Section

Reagent quality $Bi(NO_3)_3\cdot 5H_2O$, 12-crown-4, 18-crown-6, EO3, EO4, EO5, and EO6 were used without further purification. CH_3CN and CH_3OH were each distilled from CaH_2 and stored over 4-Å molecular sieves prior to use. All melting points are uncorrected. All samples were dried in vacuo prior to combustion analysis.

$[Bi(NO_3)_2(EO3^-)]_2$. To $Bi(NO_3)_3\cdot 5H_2O$ (0.2419 g, 0.50 mmol) were added 3:1 CH_3CN:CH_3OH (5 mL), EO3 (70 μL, 0.52 mmol), and a magnetic stir bar. The milky white solution was stirred at 60 °C for 1 h followed by centrifugation to remove a formidable quantity of a white precipitate. The solutions were cooled to ambient temperature and stored at 3 °C for 24 h and −10 °C for 82 h. Slow evaporation produced crystals. Crystals were stable to 360 °C. Anal. Calcd: C, 14.95; H, 2.72; N, 5.81. Found for precipitate: C, 7.89; H, 1.49; N, 4.09. Found for crystals: C, 14.94; H, 2.73; N, 4.54.

$[Bi(NO_3)_2(EO4^-)]_2\cdot$2MeOH. To $Bi(NO_3)_3\cdot 5H_2O$ (0.2422 g, 0.50 mmol) were added 3:1 CH_3CN:CH_3OH (5 mL), EO4 (90 μL, 0.52 mmol), and a magnetic stir bar. The white solution was stirred at 60 °C for 1 h followed by centrifugation to remove a moderate quantity of a white precipitate. The supernatant was decanted and stored at 3 °C for 24 h, and after 24 h at −10 °C clear crystals had formed, mp 129.5–140 °C. Anal. Calcd: C, 19.36; H, 3.79; N, 5.02. Found for precipitate: C, 3.12; H, 0.82; N, 3.40. Found for crystals: C, 19.72; H, 3.29; N, 5.41.

$[Bi(NO_3)_2(EO5)][Bi(NO_3)_2(EO5^{2-})Bi(NO_3)_3]\cdot 2H_2O$. To $Bi(NO_3)_3\cdot 5H_2O$ (0.2418 g, 0.50 mmol) were added 3:1 CH_3CN:CH_3OH (5 mL), EO5 (110 μL, 0.52 mmol), and a magnetic stir bar. The milky white solution was stirred at 60 °C for 1 h with subsequent centrifugation to remove an insoluble precipitate. The supernatant was then stored at 3 and −10 °C for 24 and 82 h periods of time. Slow concentration of the solution afforded crystalline material, mp 189–200 °C (dec). Anal. Calcd: C, 15.29; H, 2.95; N, 6.24. Found for precipitate: C, 1.25; H, 0.34; N, 3.38. Found for crystals: C, 16.73; H, 3.14; N, 5.38.

$[Bi(NO_3)_2(EO6^-)]_2$. To $Bi(NO_3)_3\cdot 5H_2O$ (0.2432 g, 0.50 mmol) were added 3:1 CH_3CN:CH_3OH (5 mL), EO6 (130 μL, 0.52 mmol), and a magnetic stir bar. The white solution was stirred for 1 h at 60 °C followed by centrifugation to remove a precipitate. The supernatant was stored at 3 and −10 °C for 24 and 82 h time periods, respectively. Evaporation to dryness afforded no crystalline material, so the solid was dissolved in 3:1 CH_3CN:CH_3OH (5 mL), stirred for 1 h at 60 °C, and stored at 3 and −10 °C for 72 and 20 h time periods. Slow concentration afforded crystalline material, mp 113–117.5 °C. Anal. Calcd: C, 23.46; H, 4.10; N, 4.56. Found for precipitate: C, 0.92; H, 0.58; N, 3.60. Found for crystals: C, 22.23; H, 4.31; N, 4.58.

$[Bi(NO_3)_3$(12-crown-4)]. To $Bi(NO_3)_3\cdot 5H_2O$ (0.0504 g, 0.10 mmol) were added 3:1 CH_3CN:CH_3OH (5 mL) and a magnetic stir bar. The mixture was stirred for 0.5 h at 65 °C followed by the addition of 12-crown-4 (16 μL, 0.10 mmol). Continued stirring at 60 °C for 1 h was followed by centrifugation to remove a small quantity of a white precipitate. The supernatant was then stored at 3 and −10 °C for 24 and 28 h time periods, respectively. Volume reduction by 50% in vacuo followed by further slow concentration afforded crystalline material, mp 235–260 °C (dec). Anal. Calcd: C, 16.82; H, 2.82; N, 7.36. Found for precipitate: C, 1.93; H, 0.48; N, 4.15. Found for crystals: C, 17.02; H, 2.85; N, 6.55.

$[Bi(NO_3)_3(OH_2)_3]\cdot$18-crown-6. To $Bi(NO_3)_3\cdot 5H_2O$ (0.0490 g, 0.10 mmol) were added 3:1 CH_3CN:CH_3OH (5 mL) and a magnetic stir bar. The white solution was stirred at 60 °C for 0.5 h followed by the addition of 18-crown-6 (0.0277 g, 0.10 mmol) with subsequent stirring at 60 °C for 1 h. The reaction solution was centrifuged to remove a white precipitate and the supernatant was then stored at 3 and −10 °C for 48 and 24 h time periods. Slow evaporation of the reaction solution provided diffraction quality crystals, mp 105 °C (dec). Anal. Calcd: C, 20.20; H, 4.24; N, 5.89. Found for precipitate: C, 3.08; H, 0.69; N, 3.97. Found for crystals: C, 19.84; H, 3.67; N, 5.68.

X-ray Data Collection, Structure Determination, and Refinement. Single crystals of the title complexes were mounted in thin-walled glass capillaries, flushed with Ar, and transferred to the goniometer of an Enraf-Nonius CAD-4 diffractometer. The space groups for the two crown ether structures were determined to be either the centric *Pnma* or acentric $Pn2_1a$ from the systematic absences. They were subsequently refined in *Pnma*. The space group for the $EO5^{2-}$ complex was uniquely defined as $P2_1/c$. Solution and successful refinement of the remaining structures were carried in the centric space group $P\bar{1}$. A summary of data collection parameters is given in Table II. Features unique to each refinement are detailed below. The final fractional coordinates for each complex are provided in the supplementary material.

$[Bi(NO_3)_2(EO3^-)]_2$ and $[Bi(NO_3)_2(EO4^-)]_2 \cdot 2MeOH$. The geometrically constrained H atoms were placed in calculated positions 0.95 Å from the bonded carbon atom and allowed to ride on that atom with B fixed at 5.5 Å^2. The alcoholic hydrogen atoms were not included in the final refinement.

$[Bi(NO_3)_2(EO5)][Bi(NO_3)_2(EO5^{2-})Bi(NO_3)_3] \cdot 2H_2O$. After initial structure solution, high thermal motion associated with C(5), C(6), C(16), and the two water molecules led to an investigation of disorder. Disorder was resolved for the C(5)–C(6) ethylene group and the atoms C(16) and O(35). Refinement of the occupancy factors for C(5)–C(6) and C(5)′–C(6)′ led to 54% occupancy of the former and 46% of the latter. Similarly C(16) and C(16)′ refined to 59% and 41% occupancies, respectively. The observed disorder can be traced to conformational disorder of the glycol ligands statistically distributed in the crystal. The water molecule disorder is dictated by hydrogen bonding requirements and is strictly 50/50. Disordered atoms were refined in alternate least-squares cycles.

The 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. The remaining hydrogen atoms were not included in the final refinement. Refinement of non-hydrogen atoms with anisotropic temperature factors except for the disordered C(5), C(5)′, C(6), C(6)′, C(16), and C(16)′ led to the final *R* values.

$[Bi(NO_3)_2(EO6^-)]_2$. Lack of strong hydrogen bonding involving O(7) results in high thermal motion for the terminal portion of the glycol, C(11), C(12), and O(7). The packing forces are obviously not enough to constrain this portion of the chain. It was not possible to resolve a disorder pattern. The high thermal motion is similar to that often observed for organic linear solvent molecules which crystallize in the unit cell.

The 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 (except those for C(11) and C(12)). The unique alcoholic hydrogen atom was not included in the final refinement.

$[Bi(NO_3)_3$(12-crown-4)]. Initial refinement of the title complex in *Pnma* led to high thermal parameters for C(1), C(4), and O(6). C(1) and C(4) were resolved into two positions each disordered across the mirror plane. The disorder is that which is expected for gauche O–C–C–O bonds bisected by a mirror plane. C(1), C(1)′, C(4), and C(4)′ were refined isotropically throughout. O(6) (the uncoordinated nitrate oxygen atom residing on the mirror plane) could not be further resolved and was refined anisotropically. An attempt was made to refine in the acentric $Pn2_1a$; however, because all atoms but C(1) and C(4) fit the mirror symmetry, high correlations were observed between mirror related (in *Pnma*) positions. The bonding parameters resulting from this refinement were unrealistic.

The hydrogen atoms were placed in calculated positions and treated as above. Only the ordered non-hydrogen atoms were refined anisotropically.

$[Bi(NO_3)_3(OH_2)_3] \cdot$18-crown-6. High thermal motion was noted for several atoms, especially O(2) on the mirror plane. We therefore investigated the acentric $Pn2_1a$ as a possible space group choice. High correlations between positions related by the center of inversion and mirror plane (in *Pnma*) prevented anisotropic refinement although the *R* value was comparable to that observed in *Pnma*. The correlations and high estimated standard deviations led us to stay with *Pnma*. Due to the high thermal motion observed, the hydrogen atoms were not included in the final refinement.

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Supplementary Material Available: Lists of crystallographic experimental details, final fractional coordinates, thermal parameters, and bond distances and angles for all compounds (53 pages); a listing of observed and calculated structure factors for all compounds (27 pages). Ordering information is given on any current masthead page.

Complexation Chemistry of Bismuth(III) Halides with Crown Ethers and Polyethylene Glycols. Structural Manifestations of a Stereochemically Active Lone Pair

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Abstract: The reactions of $BiCl_3$ or $BiBr_3$ in 3:1 CH_3CN:CH_3OH with 12-crown-4, 15-crown-5, benzo-15-crown-5, tetraethylene glycol (EO4), or pentaethylene glycol (EO5) produce complexes consisting of the neutral, pyramidal BiX_3 unit coordinated very weakly to the oxygen donors of the ligands. The 12-crown-4 complexes are seven-coordinate while all of the remaining complexes are 8-coordinate including two pentadentate EO5 complexes. The polyethylene glycol (PEG) ligands closely mimic the conformations of analogous crown ethers. When 18-crown-6 is used in these reactions, two completely different 8-coordinate complexes are isolated: the tridentate [$BiCl_3$(MeOH)(18-crown-6)] and the ionic [$BiBr_2$(18-crown-6)][$BiBr_4$]. Reaction of $BiBr_3$ with hexaethylene glycol (EO6) produces an 8-coordinate complex with a hexadentate EO6 ligand analogous to that obtained with 18-crown-6, [$BiBr_2$(EO6)][$BiBr_4$]. The use of BiI_3 results in the formation of polymeric anions which hinder solubility and the isolation of pure complexes. The only completely characterized product was formed by reaction with EO5, [BiI_2(EO5)][Bi_2I_7]·2MeOH. (The glycol mimics 18-crown-6.) Structural analysis of the products appears to support the idea of a stereochemically active lone pair with several directed secondary interactions around the lone pair site. The strong influence of the pyramidal BiX_3 unit and very long Bi–O contacts around locations where an active lone pair would be assumed to reside are taken as evidence of lone pair activity. The structurally characterized complexes include [$BiBr_3$(*12-crown-4*)] (an incomplete characterization), [BiX_3(*15-crown-5*)] (*X* = *Cl*, *Br*), [BiX_3(*benzo-15-crown-5*)] (*X* = *Cl*, *Br*), [$BiCl_3$(*MeOH*)(*18-crown-6*)], [$BiBr_2$(*18-crown-6*)][$BiBr_4$], [BiX_3(*EO4*)] (*X* = *Cl*, *Br*), [$BiCl_3$(*EO5*)] (*form A*), [$BiCl_3$(*EO5*)] (*form B*), [BiI_2(*EO5*)][Bi_2I_7]·*2MeOH*, and [$BiBr_2$(*EO6*)][$BiBr_4$].

Introduction

In the previous paper in this issue, we demonstrated that covalent Bi–O bonds can activate the Bi^{3+} lone pair. With this contribution we attempt to demonstrate that the number of these covalent bonds (one to three) tends to determine the remainder of the Bi^{3+} coordination sphere. We have previously studied the complexation chemistry of crown ethers and polyethylene glycols (PEG's) with lanthanide chloride salts.[1-5] Results obtained are

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