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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.

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

$[Bi(NO_3)_3(OH_2)_3] \cdot 18\text{-crown-}6$. 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

Robin D. Rogers,* Andrew H. Bond, Salvador Aguinaga, and Alain Reyes

Contribution from the Department of Chemistry, Northern Illinois University, DeKalb, Illinois 60115. *Received September 5, 1991*

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 $[BiCl_3(MeOH)(18\text{-crown-}6)]$ and the ionic $[BiBr_2(18\text{-crown-}6)][BiBr_4]$. 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, $[BiI_2(EO5)][Bi_2I_7] \cdot 2MeOH$. (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 $[BiBr_3(12\text{-crown-}4)]$ (an incomplete characterization), $[BiX_3(15\text{-crown-}5)]$ ($X = Cl, Br$), $[BiX_3(benzo\text{-}15\text{-crown-}5)]$ ($X = Cl, Br$), $[BiCl_3(MeOH)(18\text{-crown-}6)]$, $[BiBr_2(18\text{-crown-}6)][BiBr_4]$, $[BiX_3(EO4)]$ ($X = Cl, Br$), $[BiCl_3(EO5)]$ (*form A*), $[BiCl_3(EO5)]$ (*form B*), $[BiI_2(EO5)][Bi_2I_7] \cdot 2MeOH$, 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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* Author for correspondence.

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typical of purely ionic interactions controlled by electrostatic and steric features. The PEG complexes[1,2,4] typically wrap the lanthanide ions in a helical fashion, while the crown ethers[3,5] tend to fold around Ln^{3+}. By carrying out a complete study of the somewhat softer Bi^{3+} ion, we investigated how covalent or partially covalent interactions affect polyether coordination.

The complexation chemistry of bismuth(III) has been relatively ignored. Two recent papers[6,7] present the crystal structures of the only three Bi^{3+} complexes of the common crown ethers structurally characterized, and two other papers,[8,9] the only Sb^{3+} crown complexes. Bismuth(III) does not necessarily always exhibit lone pair effects since only that part of the lone pair electron density in excess of the 6s contribution would have stereochemical impact. Our detailed crystallographic analyses of several bismuth(III) halide crown ether and PEG complexes resulted in some striking examples of secondary bonding and stereochemically active lone pair effects.

Since Hancock has shown for Pb^{2+} that control of this inert pair activity is a useful tool in the control of the complexation chemistry,[10] in this contribution we have attempted to show how classifying these complexes according to their perceived geometries, while convenient, is not enough to thoroughly explain the structural features observed. Even the concept of directed secondary interactions[11] falls short. Only when consideration is given to some stereochemically active lone pair density on Bi^{3+} do the observed trends fall into line.

Synthetic Results

Two series of reactions were investigated. In the first, BiX_3 (X = Cl, Br, I) salts were reacted directly with the crown ether or glycol ligands in 3:1 solutions of CH_3CN:CH_3OH. Slow evaporation of these solutions produced the samples used for the crystallographic analyses including [$BiCl_3$(15-crown-5)], [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)], [BiI_2(EO5)][Bi_2I_7]·2MeOH, and [$BiBr_2$(EO6)][$BiBr_4$]. A partial structure of the BiI_3/EO4 product revealed a dimeric Bi^{3+}/EO4 cation and a polymeric inorganic anion. Most crystalline materials gave satisfactory elemental analyses, the exceptions are noted in the Experimental Section.

Two bromide derivatives were initially prepared in a second type of reaction. $Bi(NO_3)_3 \cdot 5H_2O$ was reacted with the ligands as above and then an excess of LiBr was added to the solutions. The crystallographically studied complexes include [$BiBr_3$(12-crown-4)] and [$BiBr_3$(15-crown-5)]. Both of these were successfully reprepared starting with $BiBr_3$.

The reactions of the halide salts with crown ethers produced immediate precipitates. Elemental analysis of the precipitates usually matched the final formulations derived from the crystal structures. The initial precipitates for the reactions of $Bi(NO_3)_3 \cdot 5H_2O$ followed by addition of excess LiBr did not match their crystalline formulation and were probably contaminated with $BiBr_3$.

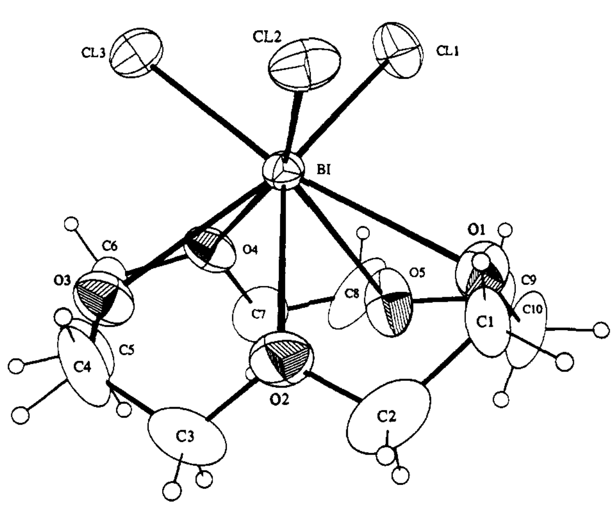

Figure 1. ORTEP illustration of [$BiCl_3$(15-crown-5)] with the atoms represented by their 50% probability thermal ellipsoids. The hydrogen atoms have been arbitrarily reduced.

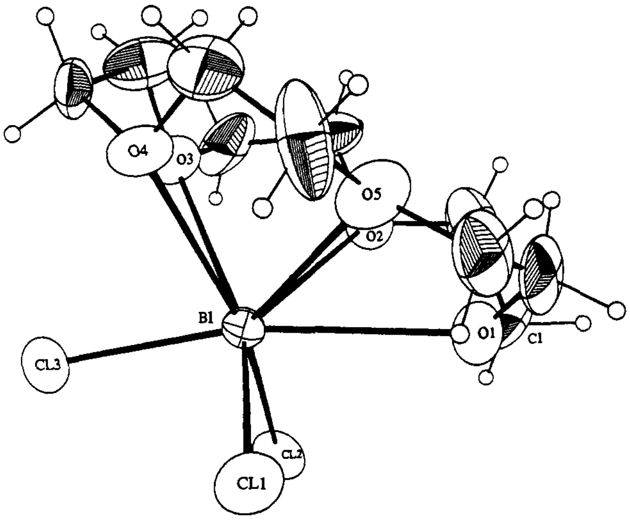

Figure 2. Side view of [$BiCl_3$(15-crown-5)].

Structural Results

[$BiBr_3$(12-crown-4)]. This complex was found to not be isostructural with its chloride analogue.[6] Unfortunately, the 12-crown-4 molecules were disordered by both a rotation of 45° of the four oxygen donors and conformationally in the ethylene groups. Total resolution of the disorder was not possible; however the $BiBr_3$ fragments are totally resolved and the overall nature of the structure is clear. The $BiBr_3$ fragments sit atop a planar arrangement of the crown oxygen atoms. The overall structure is identical to that observed for [$BiCl_3$(12-crown-4)].[6] The crystallographic differences are apparently related only to the crown disorder not observed for the chloride analogue. As our results which follow indicate, it is not so surprising that major differences in the X = Cl and X = Br derivatives occur. Even in the isostructural complexes, subtle differences in the Bi–O interactions observed could easily result in different packing environments.

[BiX_3(15-crown-5)] (X = Cl, Br). These two complexes are isostructural with [$SbCl_3$(15-crown-5)].[8] Each is 8-coordinate and could possibly be described as bicapped trigonal prismatic with one halide (X(3)) and one oxygen atom (O(1)) occupying the capping positions. Invoking a stereochemically active lone pair produces a much better description of the structures as detailed below. An ORTEP illustration of the X = Cl derivative is given in Figure 1.

The pyramidal BiX_3 unit is a major feature of almost all of the complexes we have examined. These units are characterized by strong Bi–X bonds and X–Bi–X angles of ca. 90°. Because of

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the reoccurrence of this unit and its importance in these complexes, we will focus on it here to illustrate the trends found in all the structures. In these two examples, the Bi–Cl and Bi–Br bonds average 2.54 (1) and 2.69 (2) Å (Table I), respectively, while the X–Bi–X angles average 90°. It is interesting to note that the X–Bi–X angles involving the capping position (X(3)) are all less than 90°, while the X(1)–Bi–X(2) angles are greater than 90°.

The presence of the pyramidal BiX_3 unit and the wide range of Bi–O distances (0.14 Å, X = Cl; 0.28 Å, X = Br) have significance in terms of a stereochemically active lone pair on Bi^{3+}. A side view of the X = Cl derivative (Figure 2) reveals a very distorted trigonal prism comprised of Cl(1), Cl(2), and O(2)–O(5). It is clear from this view and an analysis of the Bi–O contacts that if we first ignore the very long distances (for the X = Cl complex: Bi–O(1) = 2.88 (1) Å, Bi–O(2) = 2.91 (1) Å, Bi–O(5) = 2.85 (1) Å) the Bi^{3+} ion is Ψ-octahedral with the basal plane bent slightly down toward X(3). The Bi–O(3), O(4) distances average 2.78 (1) Å (X = Cl), the trans angles average 160 (3)° (X = Cl), the cis angles in the basal plane average 90 (2)° (X = Cl), and the angles involving X(3) average 83 (6)° (X = Cl). In this description a stereochemically active lone pair would reside exactly in the middle of where the three very long Bi–O contacts are found. These three distances average 2.88 (2) Å, over 0.10 Å longer than the remaining two Bi–O separations.

Support for invoking a stereochemically active lone pair to explain these results can also be found in the concept of secondary bonding put forth by Alcock in 1972.[11] Secondary bonds are weak, directed interactions longer than normal bonds but much shorter than van der Waals contacts. (The Bi···O van der Waals contact distance is 3.67 Å.)[11] Further work by Sawyer and Gillespie[12] has shown that the stereosensitivity of the primary bonds and the lone pair can be described in terms of polyhedron using VSEPR theory and that weak interactions form around the direction of maximum electron density of the lone pair, but not directly over it. Crystallographic evidence for this was published by Ziolo and Troup for Me_2TeCl_2[13] with the direct observation of excess lone pair electron density between the two long Te–Cl secondary interactions.

Reconsidering the [$BiCl_3$(15-crown-5)] complex, we can classify the three chlorine positions and the two shortest Bi–O separations as primary (*X*) and the three longest Bi–O distances as secondary (*Y*) resulting in an AX_5EY_3[12] description. We have chosen to indicate these three distances as secondary because they are the longest and they surround the site proposed for the lone pair density. The secondary bonds surround the octahedral site occupied by the lone pair but do not reside directly over it. We believe that the variations in the long Bi–O distances can probably be traced to the competition between wanting to surround the lone pair site equally and the conformational rigidity of the macrocycle.

This same 8-coordinate environment, which we see repeatedly in these complexes, is also observed in $BiCl_3$,[14] $SbCl_3$,[15] and β-$SbBr_3$.[16] Each has three close halide interactions (forming a pyramidal MX_3 group) and five much longer ones resulting in an overall bicapped trigonal prismatic geometry. The three primary bonds in $BiCl_3$ average 2.50 (2) Å with a 0.05 Å range. The five secondary interactions range from 3.216 (9) to 3.450 (9) Å. Bi–Br contacts in α-$BiBr_3$[17] are reported to be 2.66 (2) Å for three primary interactions and 3.32 (6) Å for three secondary contacts, while all six Bi–Br interactions in β-$BiBr_3$[17] are nearly equivalent at 2.81 (2) Å. In the former it is noted that there are two somewhat longer Bi–Br contacts of 3.699 (4) and 4.106 (3) A that would give Bi a coordination number of eight.

Although the structure of [$SbCl_3$(15-crown-5)][8] is isostructural with ours, a strange difference is noted. (The plot of the structure in the paper is labeled incorrectly: O(10) should be O(1), O(13)–O(4), etc.) Two of the three long Sb–O separations (O(13) and O(7)) are opposite the longest Sb–Cl distance (Cl(1)) as expected. We cannot explain why the shortest Sb–O length (O(10)) is located where we would expect the third secondary interaction to be. It is noted, however, that the average Sb–O separation of 2.90 (7) Å is longer than that observed in our complexes and may reflect an expected greater contribution of the Sb lone pair to the nonspherical atomic distribution. In addition, Sb^{3+} is a smaller ion than Bi^{3+} and steric differences could easily distort the M–O separations.

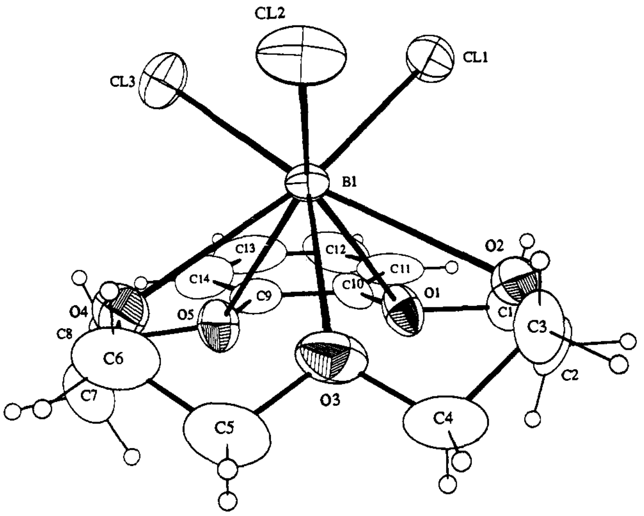

Figure 3. [$BiCl_3$(benzo-15-crown-5)].

An interesting comparison can be made with the structure of [$CrCl_3(OH_2)$(15-crown-5)].[18] This AX_6 structure has a bidentate ether, one water molecule which occupies an octahedral coordination site, and hydrogen bonds to two of the three uncoordinated oxygen atoms.

We have recently characterized the structure of [$NdCl_3$(15-crown-5)].[1] While Nd^{3+} has approximately the same size and charge as Bi^{3+}, it is a much harder ion, it does not have a stereochemically active lone pair, and we do not observe the effects of covalent interactions. The Nd^{3+} complex is 8-coordinate, bicapped trigonal prismatic, two oxygen atoms of the ether occupy the capping positions. The Nd–O capping distances average 2.629 (9) Å, the remaining Nd–O separations, 2.55 (4) Å, a difference of 0.08 Å. The three Nd–Cl contacts are longer than any of the Nd–O separations and average 2.69 (1) Å. There is minimal distortion of the bicapped trigonal prism. Although it is probably of much lesser significance, the 15-crown-5 molecule has the same conformation observed for [BiX_3(15-crown-5)]. The comparison between the Nd^{3+} and Bi^{3+} complexes again argues for a stereochemically active lone pair on Bi^{3+}.

[BiX_3(benzo-15-crown-5)] (X = Cl, Br). The chloride (Figure 3) and bromide complexes are isostructural. Each is 8-coordinate approximately bicapped trigonal prismatic with X(3) and O(2) occupying the capping positions. The individual features of the BiX_3 units, and the coordination around Bi^{3+} are almost identical to that observed for the 15-crown-5 complexes. One small difference is noted in the X–Bi–X angles. In the benzo-15-crown-5 derivatives, the X(1)–Bi–X(2) (92.4 (1)° X = Cl; 92.49 (7)° X = Br) and X(2)–Bi–X(3) (92.4 (1)° X = Cl; 93.31 (8)° X = Br) angles are all just over 90° and the X(1)–Bi–X(3) (87.1 (1)° X = Cl; 87.15 (7)° X = Br) angles are just under 90°. This may be a result of the orientation of the benzo-substituent over the X(1)–Bi–X(3) bond angle.

By use of the Ψ-octahedral description for reference, Cl(1), Cl(2), O(4), and O(5) lie in the basal plane and O(1)–O(3) surround the site expected for an active lone pair. The Bi–O(4), O(5) contacts average 2.81 (1) Å (X = Cl) and 2.82 (2) Å (X = Br) versus Bi–O(1), O(2), O(3) which average 2.839 (4) Å (X

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Table I. Comparison of Bonding Parameters

	CN	M–X,[b] Å			X–M–X,	M–O,[b] Å				M–OH$_2$,	
compound	geom[a]	av	range	Δ	deg	av	range	Δ	capping atoms	MeOH,[b] Å	ref
[BiCl$_3$(12-crown-4)]	7	2.52 (1)			93 (1)		2.652 (8)–2.742 (9)	0.09			6
[BiBr$_3$(12-crown-4)][c]	7	2.72 (4)	2.66 (1)–2.76 (1)	0.10	94 (5)						f
[BiCl$_3$(15-crown-5)]	8 bctp	2.54 (1)	2.523 (5)–2.549 (5)	0.03	90 (2)	2.84 (5)	2.77 (1)–2.91 (1)	0.14	Cl(3), O(1)		f
[BiBr$_3$(15-crown-5)]	8 bctp	2.69 (2)	2.672 (4)–2.714 (4)	0.04	90 (3)	2.9 (1)	2.72 (2)–3.00 (4)	0.28	Br(3), O(1)		f
[BiCl$_3$(benzo-15-crown-5)]	8 bctp	2.53 (2)	2.500 (4)–2.548 (3)	0.05	91 (2)	2.83 (2)	2.793 (9)–2.844 (9)	0.05	Cl(3), O(2)		f
[BiBr$_3$(benzo-15-crown-5)]	8 bctp	2.68 (2)	2.656 (2)–2.694 (2)	0.04	91 (3)	2.85 (3)	2.80 (1)–2.88 (1)	0.08	Br(3), O(2)		f
[BiCl$_3$(MeOH)(18-crown-6)]	7 co	2.54 (2)	2.525 (3)–2.562 (3)	0.04	90.5 (4)	2.79 (1)	2.776 (7)–2.805 (7)	0.03	O(5)	2.549 (9)	f
[BiCl$_3$(OH$_2$)(18-crown-6)]-	7 co	2.51 (3)	2.48 (1)–2.56 (1)	0.0	91 (1)	2.83 (5)	2.76 (2)–2.88 (2)	0.12		2.50 (3)	7
[BiCl$_3$(18-crown-6)]	9	2.495 (9)	2.483 (9)–2.51 (1)	0.03	88.1 (8)	3.0 (1)	2.84 (3)–3.04 (3)	0.20			
[BiCl$_2$(18-crown-6)]-	8 bctp	2.501 (6)			91.0 (2)		2.49 (1)–2.66 (2)	0.17			6
[BiCl$_4$]	6 oh		2.500 (6)–2.966 (6)	0.47							
[BiBr$_2$(18-crown-6)]-	8 bctp	2.666 (5)	2.661 (3)–2.671 (3)	0.01	92.4 (1)	2.62 (9)	2.47 (2)–2.73 (2)	0.26	O(2), O(5)		f
[BiBr$_4$]	6 oh	2.9 (2)	2.677 (3)–3.218 (3)	0.54	90 (8), 169 (7)						
[BiCl$_3$(EO4)]	8 bctp	2.55 (3)	2.516 (3)–2.595 (3)	0.08	89 (2)	2.72 (8)[d]	2.627 (8)–2.828 (8)	0.20	Cl(1), O(3); Cl(4), O(8)		f
						2.82 (5)[e]	2.73 (7)–2.901 (7)	0.16			
[BiBr$_3$(EO4)]	8 bctp	2.70 (2)	2.669 (2)–2.739 (2)	0.07	90 (3)	2.74 (8)[d]	2.66 (1)–2.86 (1)	0.20	Br(1), O(3); Br(4), O(8)		f
						2.83 (5)[e]	2.78 (1)–2.93 (1)	0.15			
[BiCl$_3$(EO5)] (form A)	8 bctp	2.57 (3)	2.530 (5)–2.601 (5)	0.07	88 (4)	2.69 (1)[d]			Cl(1), O(5)		f
						2.76 (5)[e]	2.73 (1)–2.85 (1)	0.12			
[BiCl$_3$(EO5)] (form B)	8 bctp	2.54 (2)	2.515 (5)–2.557 (5)	0.04	89 (2)	2.64 (1)[d]			Cl(2), O(3)		f
						2.88 (2)[e]	2.85 (1)–2.91 (1)	0.06			
[BiI$_2$(EO5)]-	8 bctp	2.89 (1)	2.875 (2)–2.904 (2)	0.03	94.02 (6)	2.61 (1)[d]	2.45 (1)–2.69 (2)	0.24			f
[Bi$_2$I$_7$]·2MeOH						2.67 (5)[e]	2.59 (1)–2.74 (2)	0.15	O(3), O(6)		
	6 oh	3.1 (2)	2.864 (2)–3.443 (2)	0.58	90 (5), 171 (4)						
[BiBr$_2$(EO6)]-	8 bctp	2.67 (2)	2.647 (3)–2.685 (3)	0.04	87.8 (1)	2.43 (1)[d]					f
[BiBr$_4$]						2.69 (9)[e]	2.59 (1)–2.85 (1)	0.26	O(1), O(4)		
	6 oh	2.9 (2)	2.682 (3)–3.184 (3)	0.50	91 (5), 171 (3)						
[Eu(OH$_2$)$_5$(12-crown-4)]-Cl$_3$·2H$_2$O	9 csap					2.54 (2)	2.523 (9)–2.568 (9)	0.04		2.43 (4)	3
[NdCl$_3$(15-crown-5)]	8 bctp	2.69 (1)	2.681 (2)–2.703 (2)	0.02	87 (4)	2.58 (5)	2.508 (5)–2.621 (4)	0.11			1
[SbCl$_3$(15-crown-5)]	8	2.42 (1)	2.405 (1)–2.433 (1)	0.03	91 (2)	2.90 (7)	2.787 (5)–2.997 (4)	0.21			8
[EuCl(OH$_2$)$_2$(18-crown-6)]Cl$_2$·2H$_2$O	9 tctp	2.673 (4)				2.55 (4)	2.491 (9)–2.596 (9)	0.10		2.43 (2)	5, 24
[SbCl$_3$(18-crown-6)]·CH$_3$CN	9	2.38 (1)	2.361 (3)–2.391 (2)	0.03	90.2 (9)	3.2 (2)	2.99 (1)–3.40 (1)	0.41			9
[EuCl(OH$_2$)$_3$(EO4)]Cl$_2$·H$_2$O	9 tctp	2.770 (2)				2.42 (1)[d]	2.404 (6)–2.431 (6)	0.03	O(2), O(4), O(8)	2.43 (5)	2
						2.54 (3)[e]	2.501 (6)–2.565 (6)	0.06			
[Eu(OH$_2$)$_3$(EO5)]Cl$_3$·H$_2$O	9 tctp					2.43 (1)[d]	2.421 (6)–2.447 (6)	0.03	O(1), O(3), O(5)	2.43 (1)	1, 24
						2.50 (2)[e]	2.484 (6)–2.530 (6)	0.05			
[NdCl(OH$_2$)(EO6)]Cl$_2$	9 tctp	2.740 (2)				2.477 (3)[d]	2.474 (5)–2.480 (5)	0.01	O(2), O(4), O(6)	2.465 (5)	1
						2.53 (1)[e]	2.510 (5)–2.543 (5)	0.03			

[a] Coordination geometries include: bctp = bicapped trigonal prism; co = capped octahedron; oh = octahedron; csap = capped square antiprism; tctp = tricapped trigonal prism. [b] The sums of the van der Waals radii are Bi–Cl = 3.90 Å, Bi–Br = 4.00 Å, Bi–I = 4.13 Å, Bi–O = 3.67 Å.[11] [c] This structure is incomplete due to severe ligand disorder. [d] These values are for the alcoholic (terminal) glycol donors. [e] These values are for the etheric glycol donors. [f] This study.

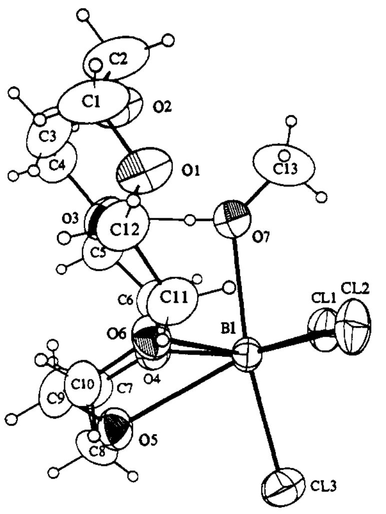

Figure 4. $[BiCl_3(MeOH)(18\text{-crown-}6)]$.

= Cl) and 2.873 (5) Å (X = Br). In these examples, the differences in these average values of 0.03 and 0.05 Å are statistically insignificant, lying well within 3σ of each other; however, the trend is still in evidence.

Part of the reason we see less of a difference in the average values may lie in the fact that O(5) is bonded to the fused aryl and thus the Bi–O(5) separations are longer on steric grounds. We note that the Bi–O(5) distances are significantly longer than the Bi–O(4) separations yet much shorter than the Bi–O(1), O(2), O(3) contacts.

The bonding parameters within the 15-crown-5 and benzo-15-crown-5 molecules are normal. The 15-crown-5 molecules adopt a commonly observed conformation[19] while the conformation of the benzo derivative is identical to that in free benzo-15-crown-5.[20] The unusual features of coordination to the pyramidal BiX_3 fragment have not unduly influenced crown ether conformation for these 15-membered macrocycles.

$[BiCl_3(MeOH)(18\text{-crown-}6)]$. This 7-coordinate complex depicted in Figure 4 is comprised of the pyramidal $BiCl_3$ unit, one coordinated methanol solvent molecule, and a tridentate 18-crown-6 molecule. The coordination environment is similar to that observed for the hydrated Bi^{3+} environment in $[BiCl_3(OH_2)(18\text{-crown-}6)][BiCl_3(18\text{-crown-}6)]$.[7] Similar formulations have been reported for Ti^{3+}, V^{3+}, and Cr^{3+} in $[MCl_3(OH_2)(18\text{-crown-}6)]$ (M = Ti,[21] V[22]) and $[CrCl_3(OH_2)(15\text{-crown-}5)]$.[18] These complexes are all six-coordinate with bidentate ethers.

In all five complexes above, the solvent or water molecule is hydrogen bonded to the uncoordinated ether oxygen atoms. In $[BiCl_3(MeOH)(18\text{-crown-}6)]$, O(7) may donate either a single hydrogen bond to O(3) (as depicted in Figure 4) or a bifurcated hydrogen bond to both O(3) and O(2). The O(7)···O(1) contact of 3.32 (2) Å is most likely too long for a reasonable hydrogen bonding interaction.

The solvent or water to metal distances suggest that these interactions are stronger than those with the ether. While the differences are minor for the Cr^{3+}, V^{3+}, and Ti^{3+} complexes, they are significant for both Bi^{3+} complexes. In the methanol solvate the Bi–O(7) separation of 2.549 (9) Å is 0.24 Å shorter than the average Bi–O(crown ether) distance of 2.79 (1) Å. In $[BiCl_3(OH_2)(18\text{-crown-}6)][BiCl_3(18\text{-crown-}6)]$[7] the $Bi–OH_2$ interaction is even stronger at 2.50 (3) Å, versus the Bi–O(ether) separations which average 2.83 (5) Å (in the 7-coordinate moiety). In both complexes the Bi–Cl bond trans to the water or solvent molecule is significantly longer than the remaining two Bi–Cl separations, as expected for the stronger Bi–solvent interactions.

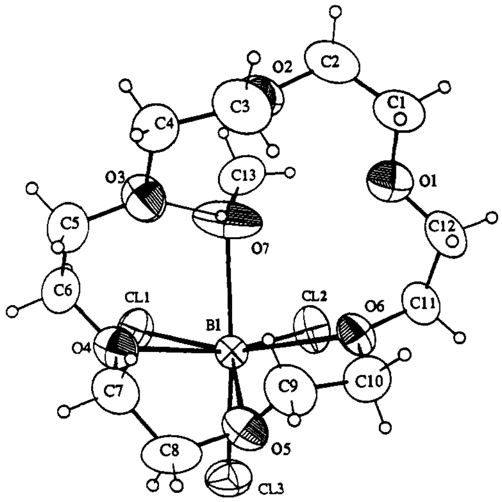

Figure 5. Top view of $[BiCl_3(MeOH)(18\text{-crown-}6)]$.

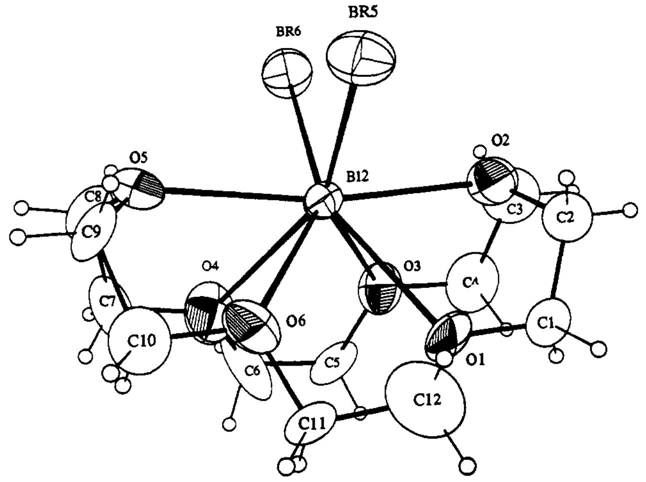

Figure 6. The cation in $[BiBr_2(18\text{-crown-}6)][BiBr_4]$.

The overall Bi^{3+} coordination environment in $[BiCl_3(MeOH)(18\text{-crown-}6)]$ is nearly identical to that found for $[BiX_3(12\text{-crown-}4)]$ (X = Cl,[6] Br). The pyramidal $BiCl_3$ unit is intact with an average Bi–Cl distance of 2.54 (2) Å and an average Cl–Bi–Cl angle of 90.5 (4)°. The three coordinating crown oxygen atoms (O(4)–O(6)) and the solvent oxygen (O(7)) form a plane to within 0.1 Å. The geometry approaches that of a capped octahedron with O(5) capping the triangular face of O(4), O(6), and Cl(3). As in the case of the 12-crown-4 derivatives, if the lone pair is active it must be directed through the crown ether cavity (Figure 5).

If we consider the Bi–O(7) interaction to be primary, this complex is AX_4EY_3. The four primary interactions have a see-saw geometry with the three long crown ether interactions surrounding the open equatorial site in this Ψ trigonal bipyramidal description.

The 18-crown-6 molecule does not adopt its normally observed D_{3d} conformation.[23] Instead it displays a sequence of O–C–C–O torsion angles of g^+, g^+, g^+, g^+, g^+, g^-. While we almost always find one of the C–O–C–C torsion angles between O–C–C–O angles of like sign forced toward gauche, that is true for only three of the four possible groupings in this case. Both angles between O(2)–C(3)–C(4)–O(3) and O(3)–C(5)–C(6)–O(4) are anti, the three C–O–C–C angles forced gauche (C(1)–C(2)–O(2)–C(3), C(5)–C(6)–O(4)–C(7), and C(7)–C(8)–O(5)–C(9)) average 66°. Interestingly, the C(10)–O(6)–C(11)–C(12) angle (between O–C–C–O angles of alternating sign) expected to be anti, is instead

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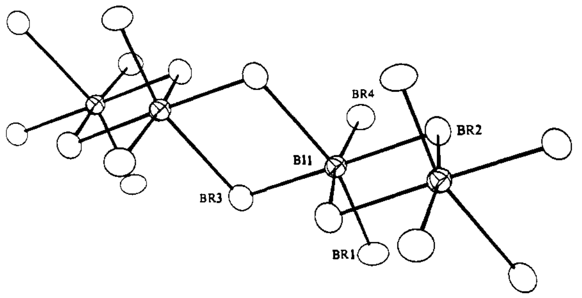

Figure 7. A portion of the polymeric anion in $[BiBr_2(18\text{-crown-}6)][BiBr_4]$.

80.6°. Both deviations from expectations appear explainable in terms of the ligand's coordination. The latter brings O(6) into a position to coordinate Bi^{3+} in an octahedral site (albeit with the longest Bi–O contact) while still providing a large enough hole for any lone pair electron density to protrude into. The former probably allows O(3) into a position close enough to O(7) to accept the hydrogen bond. The O(7)···O(3) contact is the shortest O···O separation at 2.89 (1) Å.

$[BiBr_2(18\text{-crown-}6)][BiBr_4]$. This complex is isostructural with the chloride analogue.[6] The cation is depicted in Figure 6. It is 8-coordinate bicapped trigonal prismatic with O(2) and O(5) occupying the capping positions. Interestingly, the two capping atoms exhibit short Bi–O contacts of 2.47 (2) and 2.55 (2) Å, much shorter than any of the previous complexes have exhibited. There are only two halides in the primary coordination sphere and the coordination geometry is much less distorted than those observed for the 8-coordinate complexes discussed earlier. We believe that this is a result of a coordination environment that has adopted an AX_4EY_4 geometry. Two of the ether oxygen atoms are now primary (O(2), O(5)). The secondary interactions O(1), O(3), O(4), and O(6) surround the open site in a Ψ trigonal bipyramidal geometry.

Support for the contention that a lone pair could extend through the 18-crown-6 ring can be found in the structures of $[MCl(OH_2)_2(18\text{-crown-}6)]Cl_2{\cdot}2H_2O$ (M = Pr,[24] Nd,[1] Sm–Tb[5,24]). In these structures the cations are very similar to that observed for the Bi^{3+} complex; however, a ninth coordination site is observed for the lanthanide compounds, capping the square face formed by the four etheric oxygen positions.

While the four prismatic Bi–O contacts are over 0.07 Å longer than the capping Bi–O separations, even these are shorter than all but one of the Bi–O contacts in the 15-crown-5, benzo-15-crown-5, or 18-crown-6 complexes. This is also true of the chloride analogue and probably reflects the cationic nature of this ion. It is also possible that the presence of only two Bi–X covalent bonds results in less of a contribution to the nonspherical portion of the lone pair.

The folding nature of the 18-crown-6 molecule gives it a conformation which is not recognizable in terms of other coordinated ethers. In general the O–C–C–O torsion angles have the sequence $g^-, g^+, g^-, g^-, g^+, g^-$. The major distortions occur in the C–O–C–C angles involving the capping atoms. Normally at least one of each pair would be anti, however, all four of those involving O(2) and O(5) are forced toward gauche (86° average). This allows O(2) and O(5) to assume capping positions and closer Bi–O approaches. A much greater distortion of the capping atoms, and much less distortion of the crown ether, is observed for the lanthanide complexes where only electrostatic considerations are important.

The related M^{3+}/18-crown-6 complexes are all 9-coordinate, $[SbCl_3(18\text{-crown-}6)]{\cdot}CH_3CN$[9] and the unsolvated moiety in $[BiCl_3(OH_2)(18\text{-crown-}6)][BiCl_3(18\text{-crown-}6)]$.[7] Both Sb^{3+} and Bi^{3+} exhibit much longer M–O contacts and the crown ether retains a semblance of its normal D_{3d} conformation.

We disagree with the interpretation of the anion as presented for the chloride derivative, $[BiCl_2(18\text{-crown-}6)][BiCl_4]$. In the paper describing this complex,[6] the anion was described as a Ψ-octahedral $[Bi_2Cl_8]^{2-}$ anion. We find that the anion is in fact polymeric based on edge sharing octahedra bridged around one center of inversion by Br(2), Br(2)^a and around a second center of inversion via Br(3), Br(3)^b (Figure 7). (A similar anion was observed in $[(\eta^5\text{-}C_5H_5)_2Fe][BiCl_4]$.[25]) It is the long Bi–Br(3)^b interaction (3.218 (3) Å) which occupies the hole suggested for the chloride analogue. This gives a range for the four bridging halides of 2.866 (3)–3.218 (3) Å, well within the range of known Bi–X interactions. The sixth halide around Bi^{3+} is only 0.1 Å longer than the next longest contact. This gives Bi^{3+} an overall distorted octahedral geometry.

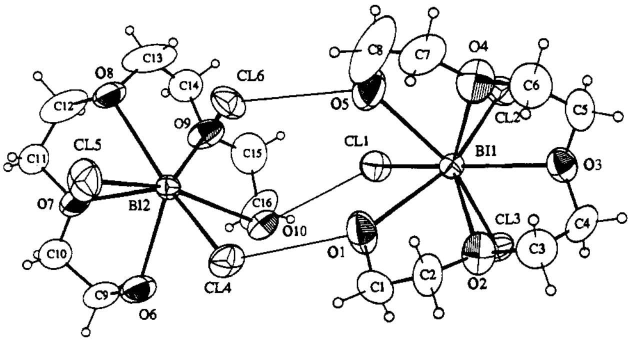

Figure 8. The asymmetric unit (half of a hydrogen bonded tetramer) in $[BiCl_3(EO4)]$.

An active lone pair could be invoked to explain the two long Bi–Br contacts of 3.114 (3) Å (Br(2)^a) and 3.218 (3) Å (Br(3)^b). The pattern of contacts suggest an AX_4EY_2 environment for Bi^{3+} with the two terminal and the two shorter bridging Bi–Br interactions being primary. The terminal Bi–Br contacts (Br(1), 2.677 (3) Å; Br(4), 2.690 (3) Å) are close to the Bi–Br separations in the cation. Several examples of octahedral Bi/Br anions are known. One of these, $Na_7[BiBr_6][Bi_2Br_{10}]$,[26] consists of both isolated $[BiBr_6]^{3-}$ anions with nearly equivalent Bi–Br distances of 2.86 (2) Å and $[Bi_2Br_{10}]^{4-}$ edge bridged octahedra. The Bi–Br distances in the latter range from 2.71 (1) to 3.10 (1) Å.

In the unit cell the polymeric anion chains are arranged in layers with two layers of cations between each layer of anions. The two layers of cations are arranged so that all halide ions are directed toward the other cation layer and all crown ethers are directed toward the anion layers.

$[BiX_3(EO4)]$ (X = Cl, Br). These complexes exist in the unit cell as hydrogen-bonded tetramers. The asymmetric unit consists of two unique bismuth centers and is depicted in Figure 8 for X = Cl. The five donor EO4 ligand completely mimics 15-crown-5 resulting in a structure very similar to that observed for $[BiX_3(15\text{-crown-}5)]$: a pyramidal $BiCl_3$ unit and five oxygen donors, overall a distorted bicapped (Cl(1), O(3); Cl(4), O(8)) trigonal prismatic geometry. One Bi–Cl bond resides directly under the open end of the glycol chain.

The same arguments for an active lone pair can be made for this complex. The coordination environment is again AX_5EY_3 with the secondary interactions O(2), O(3), O(4) for Bi(1) and O(7), O(8), O(9) for Bi(2). The hydrogen bonding, however, adds a complicating factor. X(1), X(4), and X(6) accept hydrogen bonds resulting in significantly longer Bi–X bond lengths for these three positions (2.58 (1) Å average X = Cl) than the remaining three Bi–X separations (2.525 (7) Å average X = Cl). The terminal oxygen O(10) also accepts a hydrogen bond which explains the long Bi(2)–O(10) distance of 2.828 (8) Å (X = Cl).

The Bi(1)–O(3) value of 2.737 (7) Å (X = Cl) is shorter than expected. We believe that the lengthening of Bi(1)–X(1) from the hydrogen bonding is responsible for a shortening of Bi(1)–O(3). The shortest Bi(2)–O contact (Bi(2)–O(6) = 2.627 (8) Å, X =

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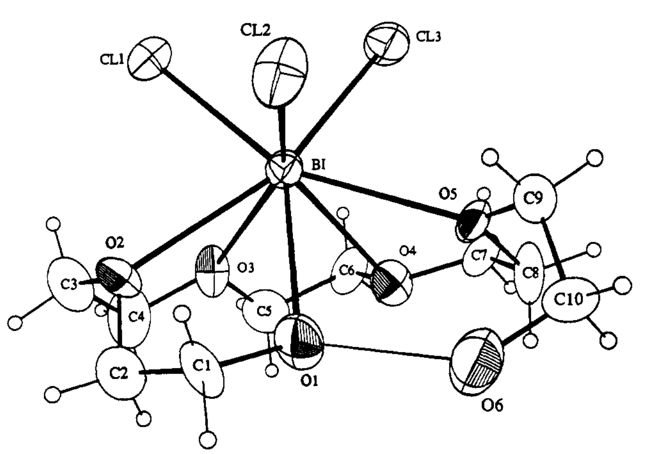

Figure 9. [BiCl$_3$(EO5)] form A.

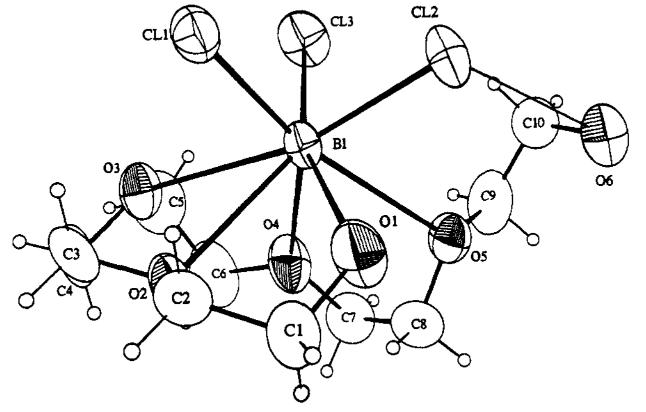

Figure 10. [BiCl$_3$(EO5)] form B.

Cl) is trans to the longest Bi(2)–X bond (X(6), 2.580 (3) Å, X = Cl).

We find the same distortion of the torsion angles involving the capping O(3) as we observed in the [BiBr$_2$(18-crown-6)]$^+$ cation. Both C–O–C–C angles involving O(3) are forced toward gauche (90° average) while the O–C–C–O angles leading to O(3) alternate sign (±g). In this EO4 ligand the remaining C–O–C–C angles are anti and the four O–C–C–O angles alternate ±g.

In the second unique glycol the conformation is different. The O–C–C–O angles have the sequence g$^+$, g$^-$, g$^-$, g$^-$, yet only one C–O–C–C angle is forced gauche. This angle (C(12)–O(8)–C(13)–C(14) = –82.1°) involves the capping oxygen atom (O(8)).

[BiCl$_3$(EO5)] (Form A and B). Both forms of this complex are comprised of pyramidal BiCl$_3$ moieties coordinated to only five of the six EO5 donors. The difference in the two forms is related to the conformation of the uncoordinated alcoholic donor (O(6)). In form A the EO5 ligand cyclizes via an intramolecular O(1)–H···O(6) hydrogen bond (O(1)···O(6) = 2.68 (2) Å) depicted in Figure 9. O(6) donates a hydrogen bond to Cl(1) (O(6)···Cl(1)^a = 3.29 (1) Å) on a Bi^{3+} ion related by a unit translation along *a*, producing polymeric hydrogen bonded chains along *a*. In form B the chain does not cyclize (Figure 10). Instead, O(6) accepts an intermolecular hydrogen bond from O(1) on a symmetry related glycol and O(6) donates an intramolecular hydrogen bond to Cl(2). The hydrogen bonding produces hydrogen-bonded dimers.

In both form A and B, the EO5 ligands, despite having six donors, exactly mimic the coordinaion and geometry of EO4 and 15-crown-5. Both Bi^{3+} ions are 8-coordinate overall, distorted bicapped trigonal prismatic. There are differences within the Bi^{3+} coordination spheres of these two forms with each other and the 15-crown-5 complexes; however, the open chain nature of the ligand, the differing basicities of the donors, and the hydrogen bonding tend to obscure trends which would suggest active lone pairs on the Bi^{3+} ions. These are discussed below.

In form A none of the three chloride ions resides over the open portion of the chain (i.e., over the O(1)–Bi–O(5) angle), a situation we did find for the EO4 complex. The hydrogen bonded Cl(1) is a capping atom (along with O(5)) and exhibits the longest Bi–Cl contact in either form of 2.601 (5) Å. From our previous discussion, we would expect a lengthening of the Bi–O(1), O(4), O(5) distances due to an active lone pair. Only one of these (O(4)) appears appreciably lengthened at 2.85 (1) Å. The Bi–O(1) distance of 2.69 (1) Å is actually the shortest in this form; however, some shortening should be expected due to the alcoholic nature of this donor and its approximate trans position to the hydrogen bond lengthened Cl(1). The Bi–O(5) separation of 2.73 (1) Å is right in the middle of the Bi–O range, but here too it resides approximately trans to the longest Bi–Cl bond. The arguments for an active lone pair are certainly less convincing for this complex.

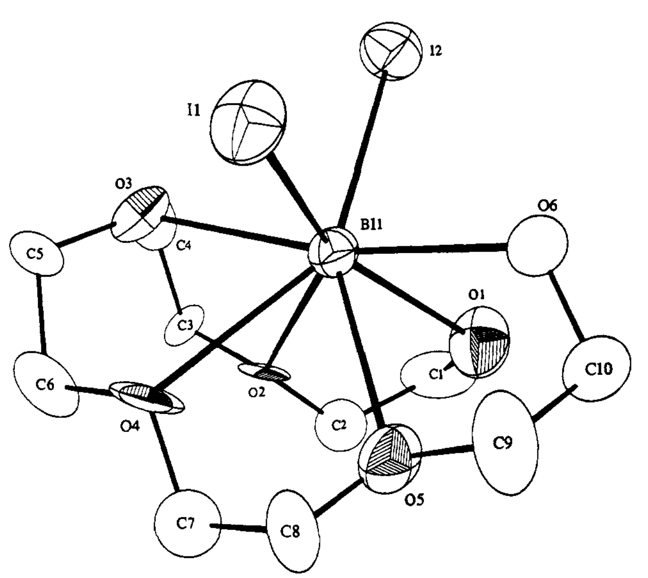

Figure 11. The cation in [BiI$_2$(EO5)][Bi$_2$I$_7$]·2MeOH.

In form B, one chloride ion (Cl(2)) resides directly over the open portion of the chain and accepts a hydrogen bond from O(6). As a hydrogen bond acceptor it exhibits the longest Bi–Cl separation of 2.557 (5) Å.

The capping atoms in form B are Cl(2) and O(3). Consistent with an active lone pair the Bi–O(2), O(3), O(4) distances are long (2.89 (1), 2.85 (1), and 2.89 (1) Å, respectively). The alcoholic contact (Bi–O(1) = 2.64 (1) Å) is 0.05 Å shorter in form B than in form A (where it was in a position that should have been lengthened by a active lone pair!). We believe that the long Bi–O(5) contact (2.91 (1) Å, the longest Bi–O contact in either form) is a consequence of a glycol conformation allowing the O(6) portion of the chain to swing away from the Bi^{3+} center. We note that the shortest Bi–Cl separation in either form, Bi–Cl(1) = 2.515 (5) Å, is trans to O(5).

The glycols in the two forms have different conformations. The conformation in form A is of a type we often see for glycols and crown ethers. The sequence of O–C–C–O torsion angles is g$^-$, g$^-$, g$^+$, g$^-$, g$^-$. All C–O–C–C angles are anti except for one of each pair between O–C–C–O angles of like sign. In form A these two angles average 74°. The sequence of O–C–C–O torsion angles in form B is different (g$^+$, g$^-$, g$^-$, g$^-$, g$^+$), but what makes this conformation somewhat unusual are the C–O–C–C angles from C(6)–O(4) on. Both C(5)–C(6)–O(4)–C(7) and C(6)–O(4)–C(7)–C(8) are anti despite occurring between consecutive O–C–C–O torsion angles of like sign. Additionally, even though O(4)–C(7)–C(8)–O(5) and O(5)–C(9)–C(10)–O(6) alternate sign, C(7)–C(8)–O(5)–C(9) is nearly gauche (–65.6°). This is further evidence that the BiCl$_3$ unit completely controls how the glycol ligands will coordinate even if it means unusual conformations for the organic ligands.

[BiI$_2$(EO5)][Bi$_2$I$_7$]·2MeOH. All six EO5 donor atoms coordinate a BiI$_2$$^+$ cation in a geometry identical to that observed for 18-crown-6 in [BiX$_2$(18-crown-6)][BiX$_4$]. The terminal O(6) and etheric O(3) cap a trigonal prismatic geometry around Bi^{3+} (Figure 11). (The alternate description is AX_4EY_4.) These two

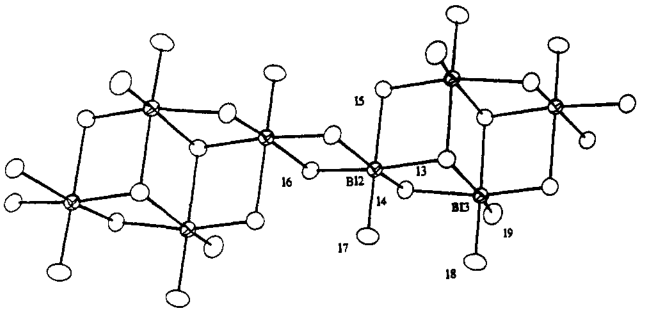

Figure 12. A portion of the polymeric anion in $[BiI_2(EO5)][Bi_2I_7]\cdot 2MeOH$.

atoms exhibit short contacts with the Bi^{3+} ion: 2.45 (1) Å for the alcoholic O(6) and 2.59 (1) Å for the etheric O(3). The four longest Bi–O contacts lie opposite the I–Bi–I bond angle as expected for an active lone pair. These distances range from 2.65 (2) to 2.74 (2) Å.

One of the cation's iodine atoms (I(1)) is in a position where it could accept a hydrogen bond from one of the disordered solvent molecules. The Bi(1)–I(1) distance (2.904 (2) Å) is thus slightly longer than the Bi(1)–I(2) separation of 2.875 (2) Å. O(1) and O(6) both donate hydrogen bonds to the same solvent molecules (O(7)) related by $-x$, $2 - y$, $3 - z$. O(7) in turn donates its hydrogen bond to a second disordered solvent molecule (O(8)). The two possible orientations of O(8) correlate to donation of a hydrogen bond to an iodine of the cation (I(1)) or to an iodine of the anion (I(9)).

The $[Bi_2I_7]^-$ anion is polymeric with the polymer generated by two different centers of inversion. Each Bi^{3+} ion is octahedrally coordinated to six iodine atoms, albeit some with very long contacts. Bi(2) has one short terminal iodine (Bi(2)–I(7) = 2.871 (2) Å) with a very long bridging separation trans to it (Bi(2)–I(5) = 3.416 (1) Å). The remaining four bridging Bi(2)–I separations range from 2.985 (2) to 3.109 (2) Å. The Bi(3) position has two short terminal contacts (I(9), 2.886 (2) Å; I(8), 2.864 (2) Å) and two correspondingly long bridging distances trans to them ($I(3)^a$, 3.443 (2) Å; I(3), 3.417 (2) Å). The two remaining bridging contacts are 2.960 (2) Å ($I(5)^b$) and 3.260 (2) Å (I(4)). As observed in the anions of $[BiX_2(18\text{-crown-}6)][BiX_4]$, the terminal iodines are equivalent to or shorter than the Bi–I contacts in the cation.

The anion can be described as a polymeric chain of tetramers (Figure 12). Each tetramer consists of two triply bridging I(3) ions, each bridging both Bi(3) sites to one Bi(2) position. Each Bi(3) is also singly bridged to the two Bi(2) ions in the tetramer. The tetramers are linked via two iodide bridges between Bi(2) sites in different tetramers. A similar tetramer (although not polymeric) was observed in $[(\eta^5\text{-}C_5H_5)_2Fe][Bi_4Br_{16}]$.[27]

The recently published $(C_{16}H_{36}N)_3Bi_3I_{12}$[28] contains a $[Bi_3I_{12}]^{3-}$ anion consisting of three face-sharing octahedra. The terminal Bi–I separations range from 2.883 (6) to 2.942 (5) Å, while bridging separations of 3.008 (6) to 3.423 (6) Å are observed. Regular isolated $[BiI_6]^{3-}$ octahedral anions are also well-known (e.g., $Rb_5I(I_3)(BiI_6)(H_2O)_2$, Bi–I = 3.073 (6) Å[29]).

The general packing of the cationic and anionic polymeric chains in *ab* planes in the unit cell is essentially the same as observed for $[BiX_2(18\text{-crown-}6)][BiX_4]$. The solvent molecules in the iodide structure reside between the cation layers.

The EO5 ligand is disordered, which obscures most of the conformational information we could obtain from this structure. It is noted, however, that the unusual feature of containing four gauche angles in a row we found for $[BiBr_2(18\text{-crown-}6)][BiBr_4]$ is also found in this structure where EO5 mimics 18-crown-6.

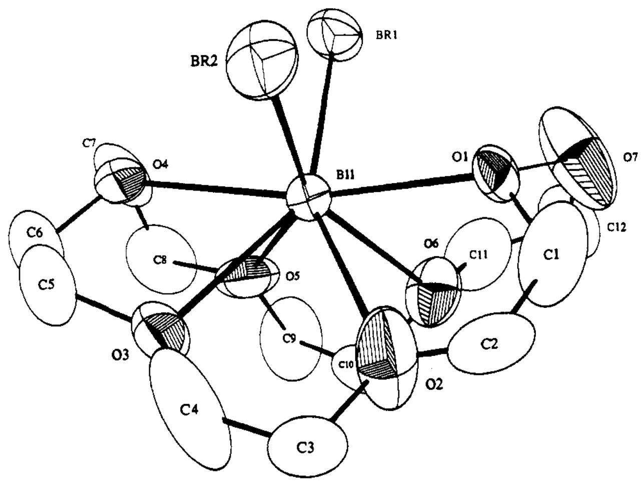

Figure 13. The cation in $[BiBr_2(EO6)][BiBr_4]$.

$[BiBr_2(EO6)][BiBr_4]$. Only six of the seven glycol donors are used in coordinating Bi^{3+} in this complex (Figure 13) producing a structure analogous to that found for the cations in both $[BiBr_2(18\text{-crown-}6)][BiBr_4]$ and $[BiI_2(EO5)][Bi_2I_7]\cdot 2MeOH$. The overall geometry is a regular bicapped trigonal prism with the alcoholic O(1) and etheric O(4) in capping positions. The alcoholic distance, 2.43 (1) Å, is shorter than the etheric separation of 2.59 (1) Å, as expected. The description of this cation as AX_4EY_4 is the same as discussed for the previous cations of this type.

The hydrogen bonding is exclusively donated and accepted by the two terminal alcoholic positions. This cyclizes the glycol via an intramolecular hydrogen bond and forms hydrogen bonded dimers via two intermolecular hydrogen bonds. High thermal motion in the dangling end of the glycol and in several of the ethylene groups tends to obscure conformational information for the glycol chain.

The edge sharing $BiBr_6$ octahedra form polymeric zigzag chains similar to that found for the 18-crown-6 complex. Description of the octahedra as AX_4EY_2 with the terminal bromines (Br(5), Br(6)) and shorter bridging atoms (Br(3), Br(4)) as primary and the longer bridging distances ($Br(3)^a$, $Br(4)^b$) as secondary is again consistent.

Remarkably, the packing of the ions in the unit cell is nearly identical to that observed for the previous two structures with polymeric anions—layers (in *ab*) of anions separated by two layers of cations orientated back-to-back. In this structure the cation layers consist of hydrogen-bonded dimers.

Discussion

For the 4- and 5-donor ligands the complexation chemistry with bismuth halides appears to be very straightforward. The covalent, pyramidal BiX_3 unit remains intact and available coordination sites are taken up by very loosely coordinated oxygen donors. The total domination of the BiX_3 moiety is clearly illustrated by the behavior of the EO4 and EO5 glycols in the solid state. Both EO4 and EO5 (with $BiCl_3$) totally mimic the coordination of crown ethers.

We have shown using the ionic lanthanides[1-5] that when coordination is controlled by purely electrostatic or steric interactions, the glycols would much rather prefer to wrap the cation than adopt a pseudocyclic crown conformation. The structures of $[Eu(OH_2)_5(12\text{-crown-}4)]Cl_3\cdot 2H_2O$,[3] $[NdCl_3(15\text{-crown-}5)]$,[1] $[EuCl(OH_2)_2(18\text{-crown-}6)]Cl_2\cdot 2H_2O$,[5,24] $[Eu(OH_2)_5(EO3)]Cl_3$,[4] $[EuCl(OH_2)_3(EO4)]$,[2] and $[Eu(OH_2)_3(EO5)]Cl_3\cdot H_2O$[1,24] illustrate this point. The Ln^{3+} ion sits atop the crown ether cavity in the 12-crown-4 and 15-crown-5 complexes, and 18-crown-6 strains to fold around the metal cation much as we have observed for Bi^{3+}. The glycols wrap the Ln^{3+} ions in a helical fashion simply occupying one more coordination site in a tricapped trigonal prismatic geometry as the chain length is increased.

The integrity of the $BiCl_3$ core only begins to break down as the number of donors increases to six. For the six-donor glycol,

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[28] Geiser, U.; Wade, E.; Wang, H. H.; Williams, J. M. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1990**, *C46*, 1547.

[29] Lazarini, F. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1977**, *B33*, 1957.

hydrogen bonding stabilizes structures where only five of the six donors are utilized, thus maintaining the $BiCl_3$ unit. The macrocyclic 18-crown-6, however, does not have built-in hydrogen-bond donors, and we thus find several alternative structural types: (a) a solvent hydrogen bond donor to stabilize a partially coordinated ether as in [$BiCl_3$(MeOH)(18-crown-6)] and the 7-coordinate moiety in [$BiCl_3(OH_2)$(18-crown-6)][$BiCl_3$(18-crown-6)],[7] (b) formation of a 9-coordinate complex as in the second unique Bi^{3+} environment in [$BiCl_3(OH_2)$(18-crown-6)][$BiCl_3$(18-crown-6)],[7] or (c) a cationic complex as in [$BiCl_2$(18-crown-6)][$BiCl_4$].[6] In all of the crown ether or PEG complexes of $BiCl_3$ or $SbCl_3$ published or reported here, only the compound in option c violates the integrity of the pyramidal $BiCl_3$ unit, and it has been observed only once. These facts alone can be used as an argument for an active lone pair.

We have further found that the BiX_3 unit is much less inviolate when X = Br or I. The only isolable complex of 18-crown-6 when X = Br is [$BiBr_2$(18-crown-6)][$BiBr_4$]. A similar complex [$BiBr_2$(EO6)][$BiBr_4$] is obtained with EO6, where the glycol is only hexadentate. Perhaps more telling are the complexes with X = I. The same ligand to readily give [$BiCl_3$(EO5)] produced [BiI_2(EO5)][Bi_2I_7]·2MeOH when X = I. Similar complexes containing polymeric Bi/I anions have been isolated for EO4 and EO3, although they have not been completely characterized crystallographically.[24] Thus, even though when X = Br and the number of donors is five or less, the $BiBr_3$ unit remains intact, when X = I there appears to be very little tendency to form complexes of BiI_3.

Of additional interest is how to describe structures of these types as they appear in the literature. We can describe their coordination geometry in terms of all primary and stereochemically significant secondary interactions; however, this does not explain variations found in particular geometric sites. All of the complexes of Bi^{3+} with crown ethers or PEG's except for the 12-crown-4 and two of the 18-crown-6 complexes have an 8-coordinate bicapped trigonal prismatic geometry. This same geometry is found in $BiCl_3$.[14] We could even extend this description to very different types of $BiCl_3$ complexes including [$BiCl_3$[2.2.2]paracyclophane]·C_6H_6.[30] In this latter complex there are three primary Bi–Cl bonds and two secondary Bi–Cl interactions, and three formal coordination sites are occupied by adduct formation with the aromatic rings of the paracyclophane. Formally 8-coordinate, the Bi–Cl primary bonds range from 2.450 (5) to 2.531 (5) Å with the secondary interactions at 2.98 to 3.53 Å.

Unfortunately, this single description of the coordination geometry does not adequately account for the observed trends. Why, for example, are capping positions often much shorter than prismatic sites? Why are there such great variations in Bi–O distances? Even Alcock's[11] description of directed secondary interactions is not totally applicable to these complexes.

The one description that adequately explains the trends observed is one in which lone pair electron density is in part responsible for the observed polyhedra.[12] The observed geometries make sense when all primary bonds and a lone pair determine the geometry, with the much longer secondary interactions surrounding the site where the excess lone pair density resides. Minor variations thus can be attributed to packing effects, steric crowding, or even hydrogen bonding.

Conclusions

All of the crown ether and PEG complexes of BiX_3 have remarkable structural similarities. These similarities go well beyond any expected by electrostatic or steric interactions alone. The structures can best be described in terms of a stereochemically active lone pair which along with the strong primary interactions controls overall coordination geometry. This is supported by the general integrity of the BiX_3 pyramidal moiety and the remarkable ability for this unit to organize acyclic PEG molecules into cyclic crown ether-like ligands despite having very weak Bi–O interactions.

Experimental Section

General Synthetic. Reagent quality $BiCl_3$, $BiBr_3$, BiI_3, $Bi(NO_3)_3\cdot 5H_2O$, and LiBr were used without further purification. The ligands 12-crown-4, 15-crown-5, benzo-15-crown-5, 18-crown-6, EO4, EO5, and EO6 were also used as purchased. CH_3CN and CH_3OH were each distilled over CaH_2, and the 3:1 CH_3CN:CH_3OH solution was stored over 4-Å molecular sieves. All melting points are uncorrected. Samples were dried in vacuo prior to combustion analysis.

[$BiCl_3$(12-crown-4)]. To $BiCl_3$ (0.32 g, 1.0 mmol) in an Ar glovebox were added 3:1 CH_3CN:CH_3OH (5 mL) and a magnetic stir bar. The solution was stirred at ambient temperature for 0.5 h, followed by the addition of 12-crown-4 (0.16 mL, 0.99 mmol) with additional stirring for 1 h at room temperature. An off-white precipitate that formed on cooling to room temperature was centrifuged and the supernatant removed from the Ar atmosphere and stored consecutively at 3 and −10 °C for 14 and 24 h, respectively. The combustion analysis of the precipitate was consistent with the proposed formulation. The precipitate was then mixed with 3:1 CH_3CN:CH_3OH (5 mL), the mixture was stirred at 60 °C for 1 h and centrifuged to remove insoluble matter, and the supernatant was stored at 3 and −10 °C for 20 and 24 h, respectively. Slow concentration of this solution afforded diffraction quality crystals which were confirmed by unit cell parameters to be isostructural with the 12-crown-4 adduct reported in ref 6. Anal. Original precipitate calcd: C, 19.55; H, 3.29. Found: C, 19.58; H, 3.41.

[$BiBr_3$(12-crown-4)]. To $Bi(NO_3)_3\cdot 5H_2O$ (0.0477 g, 0.098 mmol) and LiBr (0.0164 g, 0.189 mmol) were added a 3:1 solution of CH_3CN:CH_3OH (5 mL), 12-crown-4 (16 μL, 0.099 mmol), and a magnetic stir bar. The reaction mixture was stirred at 60 °C for 1 h, during which time a small quantity of a white precipitate formed. The reaction mixture was centrifuged and the supernatant stored consecutively at 3 and −10 °C with no crystal formation. Slow evaporation provided small opaque parallelepiped crystals, mp 133–135 °C. Anal. Calcd: C, 15.38; H, 2.58. Found for precipitate: C, 3.36; H, 0.74; N, 0.30. This indicates the presence of $BiBr_3\cdot nH_2O$ in the original precipitate.

[$BiBr_3$(12-crown-4)] was successfully resynthesized in the following manner. To $BiBr_3$ (0.2244 g, 0.50 mmol) were added a 3:1 CH_3CN:CH_3OH solution (5 mL), 12-crown-4 (81 μL, 0.50 mmol), and a magnetic stir bar. The white reaction mixture was stirred at 60 °C for 1 h during which time copious quantities of a flocculent white precipitate formed. After storage at 3 and −10 °C for approximately 24 h each, slow evaporation afforded large clear parallelepiped crystals, mp 188 °C (dec). Anal. Calcd: C, 15.38; H, 2.58. Found for precipitate: C, 15.52; H, 2.72. Found for crystals: C, 14.27; H, 2.71.

[$BiCl_3$(15-crown-5)]. In an Ar glovebox, 3:1 CH_3CN:CH_3OH (5 mL) and a magnetic stir bar were added to $BiCl_3$ (0.32 g, 1.0 mmol). The milky white solution was stirred at ambient temperature for 0.5 h followed by the addition of 15-crown-5 (0.20 mL, 1.0 mmol). A substantial quantity of a white precipitate formed immediately after addition of the ligand. After 1 h of stirring at room temperature the reaction solution was centrifuged and the supernatant removed from the Ar glovebox and stored at 5 °C for 14 h and −10 °C for 24 h. After approximately 5 months of storage in an Ar atmosphere, colorless parallelepiped crystals of suitable size for the diffraction study were obtained, mp 243–250 °C. Anal. Calcd: C, 22.42; H, 3.77. Found for precipitate: C, 22.51; H, 3.69. Found for crystals: C, 22.43; H, 4.43.

[$BiBr_3$(15-crown-5)]. To $Bi(NO_3)_3\cdot 5H_2O$ (0.0491 g, 0.10 mmol) and LiBr (0.0194 g, 0.22 mmol) were added 3:1 CH_3CN:CH_3OH (5 mL), 15-crown-5 (20 μL, 0.10 mmol), and a magnetic stir bar. The solution was stirred at 60 °C for 1 h. During heating a small amount of a white solid precipitated. The warm solution was centrifuged and the supernatant decanted and stored successively at 3 and −10 °C. Slow evaporation of the reaction solvent provided small clear parallelepiped crystals.

[$BiBr_3$(15-crown-5)] was resynthesized in the following manner. To $BiBr_3$ (0.2246 g, 0.50 mmol) were added 3:1 CH_3CN:CH_3OH (5 mL), 15-crown-5 (99 μL, 0.50 mmol), and a magnetic stir bar. Upon addition of the ligand a formidable quantity of a light tan precipitate formed. The reaction mixture was stirred at 60 °C for 1 h. The precipitate was centrifuged and the supernatant stored at 3 and −10 °C for approximately 24 h time periods. Slow concentration of the reaction solution afforded very small yellow parallelepiped crystals, mp 244–260 °C. Anal. Calcd: C, 17.95; H, 3.02. Found for precipitate: C, 18.56; H, 2.91. Found for crystals: C, 20.05; H, 3.38.

[$BiCl_3$(benzo-15-crown-5)]. To $BiCl_3$ (0.32 g, 1.0 mmol) under Ar were added 3:1 CH_3CN:CH_3OH (5 mL) and a magnetic stir bar. The milky white solution was stirred for 0.5 h at room temperature followed by the addition of benzo-15-crown-5 (0.28 g, 1.0 mmol). The light yellow solution was then stirred at ambient temperature for 1 h. The formation of a large quantity of a light yellow precipitate during heating required that the solid be centrifuged. The supernatant was then removed from the Ar atmosphere and stored at 5 °C for 14 h and −10 °C for 24 h.

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

	[BiBr$_3$(12-crown-4)]	[BiCl$_3$(15-crown-5)]	[BiBr$_3$(15-crown-5)]	[BiCl$_3$-(benzo-15-crown-5)]	[BiBr$_3$-(benzo-15-crown-5)]	[BiCl$_3$-(MeOH)(18-crown-6)]	[BiBr$_2$(18-crown-6)]-[BiBr$_4$]	[BiCl$_3$-(EO4)]	[BiBr$_3$-(EO4)]	[BiCl$_3$-(EO5)] (form A)	[BiCl$_3$-(EO5)] (form B)	[BiI$_2$(EO5)]-[Bi$_2$I$_7$]·2MeOH	[BiBr$_2$-(EO6)]-[BiBr$_4$]
formula weight	624.91	535.61	668.96	583.65	717.0	611.70	1401.4	509.57	642.92	553.62	553.62	2071.4	1179.7
space group	$Pnma$ or $Pnm2_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_1/c$	$P2_1/c$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$Pbca$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
temperature, °C	20	22	18	23	18	22	20	22	18	22	18	18	20
cell constants[a]													
a, Å	30.546 (9)	7.6919 (8)	7.865 (7)	16.300 (2)	16.551 (9)	16.187 (9)	8.294 (9)	7.878 (2)	8.012 (3)	15.150 (4)	8.291 (4)	11.853 (7)	7.897 (5)
b, Å	12.549 (7)	13.280 (5)	13.579 (4)	7.771 (2)	7.964 (4)	8.035 (4)	11.363 (4)	13.439 (5)	13.613 (9)	15.277 (5)	9.034 (3)	12.087 (6)	10.831 (9)
c, Å	8.4039 (9)	15.965 (9)	16.376 (4)	16.304 (2)	16.578 (8)	17.339 (9)	15.299 (4)	14.242 (6)	14.787 (9)	14.810 (3)	12.593 (9)	15.388 (7)	16.198 (7)
α, deg							110.72 (2)	93.13 (3)	93.64 (6)		84.61 (6)	68.95 (4)	100.80 (6)
β, deg				116.83 (1)	115.69 (6)	110.90 (7)	97.26 (5)	90.87 (3)	93.37 (6)		84.25 (6)	82.88 (6)	100.42 (4)
γ, deg							102.84 (5)	92.40 (3)	91.53 (6)		67.52 (4)	70.16 (5)	97.08 (6)
cell volume, Å^3	3221.4	1630.8	1749	1843	1969	2107	1281	1504	1606	3427.7	865.6	1935.4	1321
formula units/unit cell	8	4	4	4	4	4	2	4	4	8	2	2	2
D_{calc}, g cm^{-3}	2.58	2.18	2.54	2.10	2.42	1.93	3.01	2.25	2.66	2.15	2.12	3.55	2.96
μ_{calc}, cm^{-1}	183	108	169	95.4	150	83.8	230	117	184	103	101	202	223
range of rel transm factors, %	14/100	46/100	19/100	52/100	23/100	52/100	13/100	65/100	26/100	38/100	58/100	14/100	13/100
radiation (Å), 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)	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)	Mo Kα (λ = 0.71073)
$R = \sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\|$		0.037	0.050	0.041	0.049	0.038	0.056	0.036	0.044	0.039	0.060	0.048	0.058
R_w		0.048	0.061	0.050	0.054	0.051	0.059	0.053	0.051	0.044	0.075	0.048	0.065

[a] Least-squares refinement of $((\sin\theta)/\lambda)^2$ values for 25 reflection $\theta > 17°$. [b] Corrections: Lorentz–polarization and absorption (empirical, psi scan). [c] Neutral scattering factors and anomalous dispersion corrections.

After 9 months of storage in an Ar atmosphere, large yellow crystalline fragments formed, mp 250–263 °C (dec). Anal. Calcd: C, 28.81; H, 3.46. Found for precipitate: C, 28.96; H, 3.16. Found for crystals: C, 28.69; H, 3.59.

[$BiBr_3$(benzo-15-crown-5)]. To $BiBr_3$ (0.2247 g, 0.50 mmol) were added a 3:1 CH_3CN:CH_3OH solution (5 mL), benzo-15-crown-5 (0.1344 g, 0.50 mmol), and a magnetic stir bar. Upon addition of the ligand a copius quantity of a yellow precipitate formed. The solution was then stirred at 60 °C for 1 h followed immediately by centrifugation to remove the yellow solid. The supernatant was stored successively at 3 and −10 °C for approximately 24 h each. Slow evaporation afforded yellow parallelepiped crystals, mp 243–244 °C. Anal. Calcd: C, 23.45; H, 2.82. Found for precipitate: C, 23.17; H, 2.91. Found for crystals: C, 23.01; H, 3.28.

[$BiCl_3$(MeOH)(18-crown-6)]. To $BiCl_3$ (0.32 g, 1.0 mmol) in an Ar glovebox were added a solution of 3:1 CH_3CN:CH_3OH (5 mL) and a magnetic stir bar. The white solution was stirred for 0.5 h at ambient temperature and followed by the addition of 18-crown-6 (0.27 g, 1.0 mmol). The resulting white solution was stirred at room temperature for 1 h. A microcrystalline white precipitate was then centrifuged and the supernatant removed from the Ar atmosphere and stored at 3 °C. After 14 h large clear parallelepiped crystalline clusters formed, melting range 138–163 °C. Anal. Calcd: C, 25.52; H, 4.62. Found for precipitate: C, 24.67; H, 4.27. Found for crystals: C, 24.69; H, 4.41.

[$BiBr_2$(18-crown-6)][$BiBr_4$]. To $BiBr_3$ (0.2249 g, 0.50 mmol) were added 3:1 CH_3CN:CH_3OH (5 mL), 18-crown-6 (0.1327 g, 0.50 mmol), and a magnetic stir bar. The reaction solution was stirred at 60 °C for 1 h followed by centrifugation to remove a portion of light yellow precipitate. The yellow supernatant was stored at 3 and −10 °C for 24 h each. Slow concentration produced small yellow parallelepiped crystals, mp 201–211 °C. Anal. Calcd: C, 12.41; H, 2.09. Found for precipitate: C, 12.33; H, 2.19.

[$BiCl_3$(EO4)]. The compound was synthesized by the addition of 3:1 CH_3CN:CH_3OH (5 mL), EO4 (90 μL, 0.52 mmol), and a magnetic stir bar to $BiCl_3$ (0.16 g, 0.51 mmol). The solution was then stirred at 60 °C for 1 h. Upon cooling to ambient temperature a very small amount of a white precipitate formed and was centrifuged. The supernatant was stored at 3 and −10 °C for 27 and 46 h, respectively. Slow evaporation produced large clear crystals, mp 133–138 °C. Anal. Calcd: C, 18.86; H, 3.56. Found for precipitate: C, 4.87; H, 0.94. Found for crystals: C, 21.87; H, 4.41.

[$BiBr_3$(EO4)]. To $BiBr_3$ (0.2250 g, 0.50 mmol), were added 3:1 CH_3CN:CH_3OH (5 mL), EO4 (86 μL, 0.50 mmol), and a magnetic stir bar. The yellow solution was then stirred at 60 °C for 1 h. After storage at 3 °C for 48 h and −10 °C for 44 h, slow evaporation yielded crystalline material, mp 109.5–125.5 °C. Anal. Calcd: C, 14.95; H, 2.82. Found for crystals: C, 17.29; H, 3.55.

[$BiCl_3$(EO5)]. The compound was synthesized by the addition of a 3:1 solution of CH_3CN:CH_3OH (5 mL), EO5 (110 μL, 0.52 mmol), and a magnetic stir bar to $BiCl_3$ (0.16 g, 0.51 mmol). The reaction solution was stirred at 60 °C for 1 h followed immediately by centrifugation to remove a small amount of white precipitate. Slow concentration afforded diffraction quality crystals, mp 99–105 °C. Anal. Calcd: C, 21.69; H, 4.01. Found for precipitate: C, 8.71; H, 1.62. Found for crystals: C, 21.12; H, 3.60.

[BiI_2(EO5)][Bi_2I_7]·2MeOH. To BiI_3 (0.2954 g, 0.50 mmol) were added a 3:1 solution of CH_3CN:CH_3OH (5 mL), EO5 (110 μL, 0.52 mmol), and a magnetic stir bar. The deep red solution was stirred at 60 °C for 1 h followed by centrifugation to remove a small amount of a bright red solid. The supernatant was decanted and stored at 3 °C for 24 h. Slow evaporation produced small dark red parallelepiped crystals, melting range 125–167 °C. Anal. Calcd: C, 6.96; H, 1.46. Found for precipitate: C, 10.06; H, 2.01. Found for crystals: C, 8.25; H, 1.46.

[$BiBr_2$(EO6)][$BiBr_4$]. To $BiBr_3$ (0.2236 g, 0.50 mmol) were added a solution of 3:1 CH_3CN:CH_3OH (5 mL), EO6 (125 μL, 0.50 mmol), and a magnetic stir bar. The resulting yellow solution was then stirred at 60 °C for 1 h followed by storage at 3 and −10 °C for 48 and 44 h. Slow evaporation afforded small yellow crystals for the crystallographic study, mp 133–135 °C. Anal. Calcd: C, 12.22; H, 2.22. Found for crystals: C, 13.85; H, 3.82.

X-ray Data Collection, Structure Determination, and Refinement. Single crystals were mounted in thin-walled glass capillaries flushed with Ar and transferred to the goniometer of an Enraf Nonius CAD-4 diffractometer. All space groups except for those of triclinic symmetry and that for [$BiBr_3$(12-crown-4)] were uniquely determined by systematic absences. The triclinic structures were all successfully refined in the centric $P\bar{1}$. A summary of the pertinent features of data collection and refinement is given in Table II.

In each case 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 $Å^2$. Unless noted otherwise, all non-hydrogen atoms were refined anisotropically. Refinements with unique features are discussed below. Final fractional coordinates for all the complexes are given as supplementary material.

[$BiBr_3$(15-crown-5)]. The small poorly formed crystals available for this study greatly reduced the overall quality of the refinement. Higher than expected thermal motion was noted for O(5) and the carbon atoms; however, a disorder model was not resolvable. The carbon atoms were refined isotropically only.

[$BiCl_3$(MeOH)(18-crown-6)]. The methyl hydrogen atoms were included as a rigid group with rotational freedom at the bonded carbon atom (C–H = 0.95 Å, B = 5.5 $Å^2$). The alcoholic hydrogen atom was located from a difference Fourier map and included with fixed contributions (B = 5.5 $Å^2$).

[$BiCl_3$(EO4)], [$BiCl_3$(EO5)] (Form A), [$BiCl_3$(EO5)] (Form B). The alcoholic hydrogen atoms were not included in the final refinement.

[BiI_2(EO5)][Bi_2I_7]·2MeOH. Absorption affects and solvent disorder reduced the overall quality of this structure. Least-squares refinement with isotropic thermal parameters led to R = 0.091. Once the gross structural features were in place, it became clear that several positions of the lighter atoms were disordered. The solvent oxygen O(8) was resolved into two orientations at 50% occupancy each. The attached methyl, C(12), had high thermal motion but could not be resolved into two orientations. Within the polyethylene glycol, disorder was found for two ethylene linkages (C(1)–C(2), C(3)–C(4)) and the oxygen between them (O(2)). The disorder appears to be static in nature, arising from slightly different glycol conformations. C(1), C(2), and O(2) were resolved into two orientations with 50% occupancy each. Analysis of torsion angles reveals the disorder to be the result of O–C–C–O angles of g^+ for C(1)–C(2) versus g^- for C(1)′–C(2)′. The disorder in C(3)–C(4) was not 50/50. The major conformation C(3)–C(4) is present 70% of the time, while C(3)′–C(4)′ is 30% occupied. This requires that C(3) be bonded at some time to both O(2) and O(2)′. We note that the C(3)′–O(2)′ distance precludes both C(3)′ and O(2)′ present in the same glycol ligand. Disordered atoms were refined in alternate least-squares cycles. Due to the disorder, the hydrogen atoms were not included in the final refinement. Refinement of non-hydrogen atoms with anisotropic temperature factors (except for O(8), O(8)′, C(2), C(1)′–C(4)′, and C(7)) led to the final values of R = 0.048 and R_w = 0.048.

[$BiBr_2$(EO6)][$BiBr_4$]. The dangling nature of the C(11)–C(12)–O(7) fragment resulted in high thermal motion for these atoms. In addition, some conformational flexibility is noted for several of the ethylene linkages. This manifests itself in some shortened C–C and C–O distance and high estimated standard deviations for the bonding parameters. A suitable disorder model could not be developed. The alcoholic hydrogen atoms were not located.

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Supplementary Material Available: Lists of crystallographic experimental details, final fractional coordinates, thermal parameters, and bond distances and angles (97 pages); a listing of observed and calculated structure factors or amplitudes (59 pages). Ordering information is given on any current masthead page.