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Defining and Controlling the Aminoethanethiolate Chemistry of Bismuth(III): Synthesis and Comprehensive Characterization of the Homologous Thiolatobismuth Series

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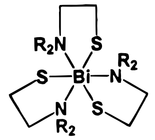
Abstract: Synthetic, spectroscopic (IR, Raman, NMR, APCI-MS), and X-ray crystallographic studies demonstrate that the highly favorable thiolation of bismuth can be controlled by manipulating stoichiometric conditions for the reactions of $BiCl_3$ or $Bi(NO_3)_3$ with aminoethanethiolate anions. With this approach, the first homologous series of mono-, bis-, and tris-thiolated bismuth complexes has been isolated and comprehensively characterized, which includes tris(aminoethanethiolato)bismuth(III) (**1**), bis(aminoethanethiolato)bismuth(III) nitrate (**2**NO_3), and bis(aminoethanethiolato)bismuth(III) chloride (**2**Cl), the corresponding dimethylaminoethanethiolato derivatives (**1(Me)** and **2(Me)**Cl), and dimethylaminoethanethiolatobismuth(III) chloride (**3(Me)**). The acyclic dimethylammoniumethanethiolatobismuth(III) chloride (**4(Me)**) extends the series and represents decoupling of the amine by protonation with retention of monothiolation. The synthetic guidelines are likely to be generally applicable to other metals and other asymmetric ligands.

Introduction

The prominent thiophilicity of the heavy metal elements is responsible for the facile formation of sulfido and thiolato complexes, which are well established for most elements.[1] Thiolatobismuth complexes represent the most extensive class of Bi(III) compounds for which a reliable set of data is available. Nevertheless, the synthesis and chemistry of these compounds remains superficially understood in that most compounds have been isolated under specific conditions and without investigation of other possible reaction products. In most cases, little is known about the relative stability of the identified compounds with respect to other possible structural arrangements. Moreover, there are few examples[2,3] of studies into the reproducible interchange between derivatives or related compounds. In light of recent interest in the potential bioactivity of bismuth compounds,[3,4] we are developing systematic series of structurally simple compounds,[5,6] where there is a variation in antimicrobial bioactivity among the members,[7] which suggests a structure/activity relationship for the bismuth environment. Such realizations highlight the need for universally applicable synthetic procedures which enable control of the coordination chemistry for heavy elements. Moreover, comprehensive structural and spectroscopic characterization of systematic series of compounds represents the most reliable fundamental foundation for rational chemical development. In this context, we now report a comprehensive investigation into aminoethanethiolato complexes of bismuth and, for the first time, demonstrate the ability of bismuth to adopt tris- (**1**), bis- (**2**) and mono- (**3** and **4**) thiolation with the same ligand.



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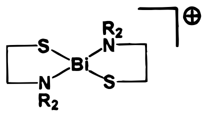

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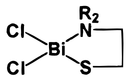

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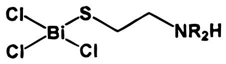

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R = H for compounds labeled **#**

R = Me for compounds labeled **#(Me)**

(Compounds are drawn to illustrate connectivity only; drawings of these compounds aimed at describing bonding features (e.g. Lewis) are not meaningful or are misleading.)

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Table 1. Reaction Conditions, Isolation Conditions, Yields, and Elemental Analyses

compd	reagents (solvents and amounts) [g, mmol]	crystal isolation and period	yield [g, mmol, %]	elemental analysis [% calcd (found)]	comments
1	$BiCl_3$ (1.06, 3.35) $HSCH_2CH_2NH_2{\cdot}HCl$ (1.90, 16.7) KOH (1.88, 33.5) 95% ethanol (150 mL)	4 °C, 4 days	0.55, 1.3, 38	C: 16.47 (16.45) H: 4.15 (4.08) N: 9.61 (9.50)	
1(Me)	$BiCl_3$ (2.10, 6.64) $HSCH_2CH_2NMe_2{\cdot}HCl$ (2.83, 19.9) KOH (2.24, 39.9) 95% ethanol (150 mL)	4 °C, 3 days	0.75, 1.4, 22	C: 27.63 (27.74) H: 5.80 (5.63) N: 8.06 (7.99)	
2NO_3	$Bi(NO_3)_3{\cdot}5H_2O$ (2.44, 5.03) $HSCH_2CH_2NH_2$ (0.78, 10) KOH (0.56, 10) water (150 mL)	ice, 2 hours	0.48, 1.5, 23	C: 11.35 (11.40) H: 2.86 (2.84) N: 9.93 (9.96)	
2$NO_3{\cdot}H_2O$	$Bi(NO_3)_3{\cdot}5H_2O$ (2.52, 5.20) $HSCH_2CH_2NH_2$ (1.20, 15.6) KOH (0.875, 15.6) water (150 mL)	evaporation, 4 days	0.79, 2.4, 35	not determined	light excluded no preconcentration of reaction filtrate
2Cl	$BiCl_3$ (3.02, 9.57) $HSCH_2CH_2NH_2{\cdot}HCl$ (3.26, 28.7) KOH (3.22, 57.4) 95% ethanol (150 mL)	evaporation, 4 days	0.64, 1.6, 17	C: 12.11 (12.28) H: 3.05 (3.00) N: 7.06 (6.86)	light excluded
2(Me) Cl	$BiCl_3$ (2.09, 6.64) $HSCH_2CH_2NMe_2{\cdot}HCl$ (1.88, 13.3) KOH (1.49, 26.6) acetone (150 mL)	4 °C, 1 day	0.94, 2.1, 31	C: 21.22 (21.16) H: 4.45 (4.36) N: 6.19 (6.04)	
4(Me) (1)	$BiCl_3$ (2.10, 6.64) $HSCH_2CH_2NMe_2{\cdot}HCl$ (1.88, 13.3) 95% ethanol (150 mL), THF (50 mL)	precipitation	2.72, 6.47, 97	C: 11.42 (11.98) H: 2.62 (2.77) N: 3.33 (3.42)	$BiCl_3$ dissolved in THF and added dropwise to ligand solution
(2)	$Bi(NO_3)_3{\cdot}5H_2O$ (2.43, 5.01) $HSCH_2CH_2NMe_2{\cdot}HCl$ (2.13, 15.0) water (14 mL)/ acetic acid (6 mL)	precipitation	1.41, 3.35, 67	C: 11.42(11.52) H: 2.62 (2.64) N: 3.33 (3.32)	ligand added to solution of $Bi(NO_3)_3{\cdot}5H_2O$ bulk sample isolated as powder
(3)	crystals from water wash of reaction mixture precipitate of (2)	evaporation, 12 days	0.05, 0.1, 2	C: 11.42 (11.57) H: 2.62 (2.79) N: 3.33 (3.32)	

Experimental Procedure

General Procedures. Melting points were recorded on a Fisher-Johns melting point apparatus and are uncorrected. IR spectra were recorded as Nujol mulls on CsI plates with a Nicolet 510P spectrometer. Raman spectra were obtained for powdered and crystalline samples on a Bruker RFS 100 spectrometer. Chemical analyses were performed by Canadian Microanalytical Service Ltd., Delta, British Columbia. Solution ^1H and ^{13}C NMR data were recorded on a Bruker AC-250 spectrometer. Chemical shifts are reported in ppm relative to TMS and are calibrated to the internal DMSO solvent signal. Atmospheric pressure chemical ionization (APCI) mass spectra were obtained on a VG Quattro triple quadrupole mass spectrometer (VG Organic). Samples were saturated solutions in 95% ethanol [**1**, **2**NO_3], acetonitrile [**1(Me)**, **2(Me)**Cl], or dimethylformamide [**2**Cl, **3(Me)**$\cdot{}^1/_4$**HCl**, **4(Me)**]. Solvent flow [100% acetonitrile (95% ethanol for **1**, **2**NO_3) at 300 μL/min] used a Shimadzu LC-10AT liquid chromatograph pump with a Rheodyne syringe loading sample injector.

Synthetic Procedures. Bismuth chloride, bismuth nitrate pentahydrate, 2-aminoethanethiol hydrochloride, and *N*,*N*-dimethylaminoethanethiol hydrochloride were used as received from Aldrich. Aminoethanethiol (cysteamine) was used as received from Fluka. Potassium hydroxide was used as received from BDH. All reactions were performed under an atmosphere of N_2 (to prevent the oxidation of thiols to disulfides) following standard Schlenk techniques, with the exception of the preparation of compound **4(Me)**. All compounds are air stable, although **2(Me)**Cl changes color over a period of weeks and **2**Cl is light sensitive.

The compounds described below were prepared by a general procedure, with the specific conditions for isolation presented in Table 1. Between 3 and 10 mmol of solid bismuth reagent [$BiCl_3$ or $Bi(NO_3)_3{\cdot}5H_2O$] was added to a solution of an aminoethanethiol (parent or dimethyl derivative), an aminoethanethiol hydrochloride, or a mixture of an aminoethanethiol with KOH, in 95% ethanol, acetone, or water (150 mL), or glacial acetic acid/water (6 mL/14 mL). Most reactions were instantaneous, giving yellow solutions which were stirred overnight, filtered, and reduced in volume on a rotary evaporator (95% ethanol or acetone) or a hot water bath (water) until precipitation began. The solution was then re-filtered and cooled on ice or in the refrigerator (4 °C), or left to evaporate slowly to give crystalline materials (Table 1). Isolated samples were washed with ethanol, acetone, and ether (25 mL each) and dried under vacuum for 1 h. Characterization and spectroscopic data are presented in Tables 1 and 2.

Equimolar reaction mixtures of $BiCl_3$ with $KSCH_2CH_2NMe_2$ (7 mmol, prepared in situ) in 95% ethanol (150 mL) gave a low solubility powder, which was extracted from the reaction precipitate with DMF and recrystallized by removal of solvent in vacuo. Crystals of **3(Me)**$\cdot{}^1/_4$HCl were reproducibly Pasteur separated from a crystalline mixture and characterized by X-ray crystallography, but data for the bulk sample were not reproducible. Although the solubility of compound **4(Me)** is very low, small samples were crystallized from aqueous solution and shown to have the same identity as the bulk reaction mixture precipitate by a variety of techniques.

X-ray Crystallography. X-ray crystallographic data for all compounds were collected on a Rigaku AFC5R diffractometer. Unit cell parameters were obtained from the setting angles of high angle carefully centered reflections. The choice of space groups was based on systematically absent reflections [**1**, **4(Me)**], a statistical analysis of intensity distribution [**2**Cl], or packing considerations and a statistical analysis of intensity distribution [**2(Me)**Cl, **3(Me)**$\cdot{}^1/_4$HCl], and were confirmed by the successful solution and refinement of the structures.

Data were collected by using the $\omega-2\theta$ scan technique. The intensities of three representative reflections were measured after every 150 reflections. Compounds **1**, **2**Cl, and 2**(Me)**Cl showed 3.6%, 15.4%, and 4.8% decreases in intensity, respectively, over the course of the data collection, and a linear correction factor was applied. Compounds **4(Me)** and **3(Me)**$\cdot{}^1/_4$HCl were not corrected for decay. All data were corrected for Lorentz and polarization effects. A correction for secondary extinction was applied to all compounds. An empirical absorption correction based on azimuthal scans of several reflections was applied to each compound.

Table 2. Melting Points, Distinctive Vibrational Bands, Prominent APCI-MS Peaks, and ^{1}H and ^{13}C NMR Data

compd	mp [dp]^a (°C)	distinct IR bands (cm^{-1})	Raman (50−400 cm^{-1})	NMR (DMSO-d_6)^b ^{1}H	NMR (DMSO-d_6)^b ^{13}C	APCI-MS [cone voltage: *m*/*z* (% rel intensity)]
1	87	290 vs, 315 vs, 411 s, 487 s, 505 m, 832 m, 1106 m, 1208 m	100 vs, 123 vs, 177 vs, 211 s, 256 m, 286 s, 321 s	2.24, 3.00, 3.57	31.0, 47.6	5 V: 209 (100), 361 (48) 30 V: 209 (24), 361 (100)
1(Me)	140	266 vs, 346 m, 415 s, 762 vs, 893 vs, 951 m, 1154 s, 1291 s	70 w, 112 s, 162 s, 233 w, 270 vs, 352 m	2.31, 2.80, 3.53	25.3, 44.9, 65.8	5 V: 209 (100), 417 (7) 30 V: 209 (23), 417 (100)
2NO$_3$	[158]	264 vs, 329, 469 s, 618 s, 822 m, 839 m, 968 s, 1319 m	114 vs, 192 m, 216 s, 268 vs, 282 s, 350 vs	3.78, 3.96, 4.13	30.3, 49.1	5 V: 361 (100)
2NO$_3$·H$_2$O	[173]	258 vs, 347 m, 481 s, 839 m, 966 m, 1223 s, 1425 vs, 1602 s, 1636s	86 vs, 117 s, 153 w, 187 m, 210 s, 268 vs, 287 vs, 359 vs	ref 19		
2Cl	[191]	244 s, 317 s, 330 m, 461 s, 722 vs, 964 s, 1011 m, 1082 m	66 vs, 90 vs, 106 vs, 124 vs, 172 s, 212 vs, 246 vs, 279 vs, 322 vs, 371 vs	3.77, 3.96	30.3, 49.0	10 V: 209 (89), 320 (54), 393 (100) 30 V: 284 (75), 320 (100), 393 (7)
2(Me) Cl	[125]	221 vs, 358 s, 426 s, 520 s, 753 vs, 894 vs, 940 s, 992 s, 1245 m	88 m, 103 s, 125 s, 171 m, 218 s, 299 vs, 360 s	2.76, 3.50, 4.32	26.1, 44.9, 66.9	5 V: 209 (100), 417 (2), 453 (2) 30 V: 209 (25), 348 (100), 417 (51), 453 (2)
4(Me)	[205]	335 m, 722 m, 926 s, 1011 m, 1429 m	107 vs, 127 vs, 172 s, 220 s, 247 vs, 334 s	2.77, 3.30, 4.98, 9.02	23.2, 42.7, 60.8	10 V: 209 (100), 348 (79), 384 (9), 417 (4), 421 (57), 453 (4) 30 V: 209 (10), 348 (100), 384 (4), 417 (3)

^{a} Decomposition occurs over a broad range and the temperature given represents the onset of blackening. ^{b} Signals are generally poorly resolved.

Table 3. Crystallographic Data

	1	**2**NO$_3$	**2**Cl	**2(Me)**Cl	**3(Me)**·$^1/_4$HCl	**4(Me)**
formula	$C_6H_{18}BiN_3S_3$	$C_4H_{12}BiN_3O_3S_2$	$C_4H_{12}BiClN_2S_2$	$C_8H_{20}BiClN_2S_2$	$C_4H_{10.25}BiCl_{2.25}NSI$	$C_4H_{11}BiCl_3NS$
fw	437.39	317.45	396.71	452.81	393.19	420.54
crystal color	yellow	light yellow	light yellow	yellow	yellow	yellow
crystal system	monoclinic	trigonal	triclinic	monoclinic	tetragonal	monoclinic
space group	$P2_1/n$ (no. 14)	$P3_121$ (no. 152)	$P\bar{1}$ (no. 2)	$P2_1$ (no. 4)	$I\bar{4}$ (no. 82)	$P2_1/c$ (no. 14)
a (Å)	5.69(1)	8.9331(10)	8.747(2)	8.122(3)	15.082(5)	6.850(2)
b (Å)	11.614(9)	8.9331(10)	9.636(2)	10.107(2)	15.082(5)	13.977(2)
c (Å)	19.562(3)	12.156(4)	5.980(1)	9.295(2)	9.609(7)	11.720(1)
α (deg)	90	90	90.83(2)	90	90	90
β (deg)	91.15(4)	90	101.85(2)	107.3470	90	106.14(1)
γ (deg)	90	120	91.15(2)	90	90	90
V (Å^3)	1292(2)	840.1(3)	493.1(2)	728.3(3)	2186(1)	1077.8(4)
Z	4	4	2	2	8	4
R; R_w	0.043; 0.050	0.0669; 0.1853^a 0.0683; 0.1867^b	0.037; 0.045	0.037; 0.044	0.049; 0.054	0.044; 0.050
GOF	1.23	1.69	1.07	1.14	2.81	4.31

^{a} $R1$; $wR2$ [$I > 2\sigma(I)$]. ^{b} $R1$; $wR2$ [all data].

The structures were solved by direct methods[8] and expanded with use of Fourier techniques.[9] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. Full-matrix least-squares refinement on F was carried out with the teXsan crystallographic package for all structures except **2**NO$_3$, which was refined by full-matrix least-squares refinement on F^2 with use of the SHELX crystallographic package. Neutral atom scattering factors, anomalous dispersion terms (f' and f''), and mass attenuation coefficients were all taken from the International Tables for Crystallography.[10] Crystallographic details are summarized in Table 3 and selected bond lengths are compared in Table 4.

In the structure of **1**, one of the SCH$_2$CH$_2$NH$_2$ groups [S(3).C(6).-C(5).N(3)] is disordered with the carbon atoms in two alternative positions. These disordered atoms were refined under restraints with isotropic thermal parameters. In the structure of **2(Me)**Cl, both of the SCH$_2$CH$_2$N(CH$_3$)$_2$ groups are disordered, and the disordered atoms were refined under restraints. The structure of **1(Me)** is comprehensively disordered and any refinement gives unreliable results. [Crystal data for **1(Me)**: $C_{12}H_{30}BiN_3S_3$, fw 521.55, trigonal, space group $R3$ (no. 146), a = 16.2626(8) Å, c = 6.579(2) Å, V = 1506.9(2) Å, Z = 3.]

Results and Discussion

The database for the thiolate chemistry of bismuth is composed of examples which represent unique complexes for a particular ligand, rather than a series of related compounds establishing fundamental synthetic guidelines and illustrating general chemical properties. Moreover, the difficulties associated with isolation and characterization of bismuth compounds have precluded comprehensive assessment of their relative stability. Isolation yields are often not reported or are low, and are rarely evaluated in terms of other possible reaction products.

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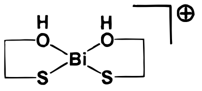
Table 4. Selected Bond Distances (Å) (Bi- - -Cl and Bi- - -S Are Intermolecular Contacts)

	1	**2**NO$_3$	**2**NO$_3$·H$_2$O^{19}	**2**Cl	**2(Me)**Cl	**3(Me)**·$^1/_4$HCl	**4(Me)**
Bi(1)−S(1)	2.748(7)	2.575(8)	2.549(2)	2.608(3)	2.538(9)	2.530(7)	2.669(3)
Bi(1)−S(2)	2.567(5)		2.589(2)	2.569(3)	2.572(9)		
Bi(1)−S(3)	2.654(5)						
Bi(1)−N(1)	2.81(2)	2.48(2)	2.462(5)	2.528(9)	2.84(2)	2.52(2)	
Bi(1)−N(2)	2.83(2)		2.455(6)	2.398(8)	2.67(3)		
Bi(1)−N(3)	2.64(2)						
Bi(1)−O(1)		3.05(2)	3.107(6)				
Bi(1)−O(3)			3.004(6)				
Bi(1)−Cl(1)				3.121(3)	2.618(9)		2.776(4)
Bi(1)−Cl(2)						2.672(7)	2.615(4)
Bi(1)−Cl(3)						2.548(8)	2.636(3)
Bi(1)- - -Cl(1)						3.109(1)	3.001(4)
Bi(1)- - -S(1)	3.686(9)	3.331(10)	3.550(2)	3.479(3)	3.494(9)	3.534(8)	2.927(3)
Bi(1)- - -S(2)			3.517(2)				

The high thiophilicity of bismuth routinely imposes multithiolation,[11,12] the extreme of which is a pentathiolate dianion,[12] but certain ligands have been observed to adopt lower coordination numbers, either coincidentally or preferentially. Thiocarboxylate anions currently present the most varied coordination number for bismuth with examples of mono-,[13] bis,[14] tris-,[15] and tetrathiolate[16] complexes known, but involving a range of ligands and a variety of synthetic procedures.

The potential utility of asymmetric thio-chelate ligands, containing one thiolate moiety and an auxiliary donor to mediate the thiophilicity of bismuth, is demonstrated by reactions of common bismuth salts with mercaptoethanol, which give the bicyclic bis(hydroxyethanethiolato)bismuth complexes **5**Cl, **5**NO$_3$, and **5**CH$_3$CO$_2$[6,17] as the most readily isolated products.[18] Furthermore, the analogous bis(aminoethanethiolato)bismuth complex **2**(NO$_3$)·H$_2$O is the only reported product of the reaction between Bi(NO$_3$)$_3$ and aminoethanethiol in acetic acid,[19] and the penicillamine compound **6** represents a unique example of a monothiolate.[20] To exploit this realization of variable and minimal thiolate coordination, we have performed a comprehensive assessment of the reactions involving BiCl$_3$ or Bi(NO$_3$)$_3$ with aminoethanethiol or dimethylaminoethanethiol at various stoichiometries, in the presence of KOH, which serves to activate the thiol (to a thiolate), and thereby provides a reliable and direct control of the extent of metathesis. In this manner, we have defined the conditions to prepare and characterize homologous series of tris-, bis-, and mono(aminoethanethiolato)bismuth complexes, and have confirmed the solid-state structure of at least one example of each, thereby clarifying and expanding the limited preliminary conclusions arising from previous spectroscopic[19−21] and structural studies.[19,20]



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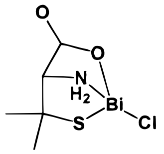

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The aminoethanethiolate and dimethylaminoethanethiolate anions react rapidly with BiCl$_3$ or Bi(NO$_3$)$_3$ to give yellow solutions from which crystalline materials have been isolated by various solution concentrating procedures. Isolates from reactions of the dimethylaminoethanethiolate anion with BiCl$_3$ reflect the respective reaction stoichiometry [3:1 gives **1(Me)**, 2:1 gives **2(Me)**, 1:1 gives **3(Me)**]. In contrast, tris-thiolation to give **1** can only be achieved with the parent aminoethanethiolate ligand by introducing a heavy excess (5:1) of the anionic ligand, and the precise 3:1 stoichiometry affords **2**Cl. The apparent impedance of complete metathesis for the parent ligand is likely due to coordinative interactions from the pendant amines, which inevitably mediate the Lewis acidity of the bismuth center, and are relatively sterically restricted in the methylated (amine) derivative [**2(Me)**Cl]. It is also important to note that the excess ligand is anomalously soluble in the reaction mixture to give **1**, and **2**Cl shows an enhanced solubility in the presence of excess ligand. We interpret these observations

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as indications of the incipient formation of anionic polythiolates of the type $[Bi(SCH_2CH_2NR_2)_4]^-$ and $[BiX(SCH_2CH_2NR_2)_3]^-$, respectively, the lability of which may be responsible for the broad signals observed in NMR spectra (vide infra), and the existence of which contributes to the incompleteness of thiolation.

Reactions involving $Bi(NO_3)_3$ with the methylated ligand typically give oils on evaporation of solvent, so that **2(Me)**NO_3 and **3(Me)**NO_3 have not been isolated, and an insignificant yield of **1(Me)** (identified by Raman spectroscopy) was obtained from a 3:1 reaction stoichiometry. Nevertheless, the parent compound **2**NO_3 is readily obtained both as the previously reported hydrated form[19] and as an unsolvated solid. The former is isolated from relatively dilute solutions containing excess ligand (3:1 stoichiometry) by slow crystal growth over a number of days. Rapid crystal growth from preconcentrated solutions of appropriate stoichiometry give **2**NO_3.

Reactions of $BiCl_3$ with dimethylaminoethanethiol or dimethylaminoethanethiol hydrochloride give **4(Me)** as an essentially quantitative precipitate, independent of stoichiometry.[22] This dramatic thermodynamic preference for coordination of the ammoniumethanethiolate tautomer of the thiol is confirmed by the high yield substitution of nitrate for chloride observed in the 3:1 reaction of $HSCH_2CH_2NMe_2{\cdot}HCl$ with $Bi(NO_3)_3$ (Table 1). Moreover, precipitate mixtures containing **3(Me)** and KCl produce **4(Me)** when washed with water, illustrating the labile and basic nature of the amine chelate interaction.

Except in the case of **4(Me)** (obtained as an analytically pure powder in 97% yield, Table 1), the isolated yields do not generally illustrate quantitative reactions that are sometimes observed for thiolate−bismuth systems,[5] and we expect each reaction mixture to contain all of the metathetical products that have been isolated over the range of stoichiometric conditions. Nevertheless, it is clear that the imposed stoichiometries conveniently and sufficiently enhance formation of one complex over the others to allow for isolation by crystal growth. Compound **3(Me)**$\cdot{}^1/_4$HCl is reproducibly obtained (each sample characterized by X-ray crystallographic analysis) as Pasteur isolated crystals from a powder mixture.

Bismuth thiolates typically exhibit low solubilities in most solvents and strong donor solvents are required to enable any appreciable solvation, usually with the formation of a resilient solvent coordination complex.[5] Complexes involving the asymmetric chelate ligands aminoethanthiolate and hydroxyethanethiolate have substantially higher solubility, perhaps due to the presence of the auxiliary donor site on the ligand, which mimics the role of the donor solvent. As a result, these complexes are more routinely recrystallized and are amenable to solution NMR spectroscopic characterization. ^{1}H and ^{13}C NMR spectra are consistent with the compounds retaining their topological solid state structures in solution, but signals are generally broad, implicating exchange processes, possibly due to the formation of hypervalent anionic complexes and consequential ligand lability.

As is typical for thiolatobismuth compounds, these complexes are thermally sensitive and, except for compounds **1** and **1(Me)**, all decompose (dramatic color change) before melting. The data presented in Table 2 show that each compound exhibits a number of useful features in the IR spectra, but the Raman spectra show very distinctive and intense bands below 400 cm^{-1}, which can be conveniently used as a reliable “fingerprint” identification of crystalline or powder materials.

While electron impact mass spectra of thiobismuth compounds are generally uninformative as a result of their thermal instability, the APCI technique[6] provides characteristic fragments, the most prominent of which are the bisthiolates $\mathbf{2}^+$ and $\mathbf{2(Me)}^+$ (*m*/*z* 361, 417) and atomic bismuth (*m*/*z* 209). Other fragments include the bismuthenium monocycle $[Bi(SC_2H_4NH)]^+$ (*m*/*z* 284), $[Bi(SC_2H_4NH_2)Cl]^+$ (*m*/*z* 320), and $[Bi(SC_2H_4NH_2)Cl + DMF]^+$ (*m*/*z* 393) for **2**Cl and $[Bi(SC_2H_4NMe_2)Cl]^+$ (*m*/*z* 348) for **2(Me)**Cl. A protonated molecular ion is also readily observed for **2(Me)**Cl (*m*/*z* 453) and **3(Me)** (*m*/*z* 384). In addition to other fragments also observed for **1(Me)** and **2(Me)**, spectra of both compounds show a solvent adduct peak $[Bi(SC_2H_4NMe_2)Cl + DMF]^+$ (*m*/*z* 421). Interestingly, **4(Me)** displays the *m*/*z* 417 fragment, suggesting that ligand lability allows for rearrangement to a bicyclic configuration.

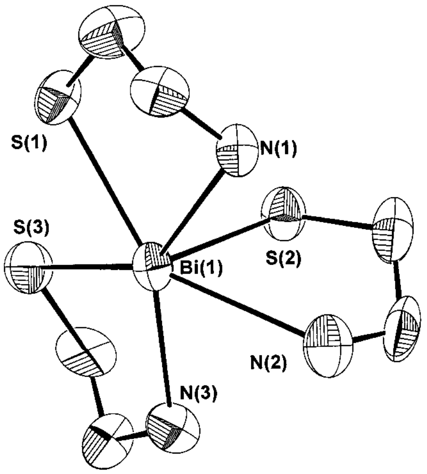

Figure 1. Crystallographic view of $Bi(SCH_2CH_2NH_2)_3$ (**1**).

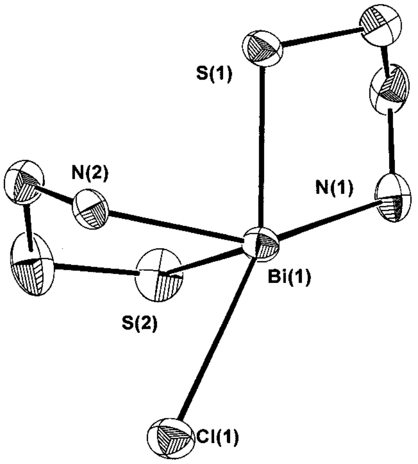

Figure 2. Crystallographic view of $Bi(SCH_2CH_2NH_2)_2Cl$ (**2**Cl).

The solid-state structures of compounds **1**, **1(Me)**, **2**NO_3, **2**$NO_3{\cdot}H_2O$, **2**Cl, **2(Me)**Cl, **3(Me)**$\cdot{}^1/_4$HCl and **4(Me)** have been confirmed by X-ray crystallography (Tables 3 and 4), although the crystal structure of **1(Me)** involves positional disorder which precludes detailed structural discussion. As representatives of each type of complex, crystal structure views of compounds **1**, **2**Cl, **2(Me)**Cl, **3(Me)**$\cdot{}^1/_4$HCl, and **4(Me)** are shown in Figures 1−5, respectively (figures are drawn with 50% probability thermal ellipsoids and H atoms omitted for clarity). The chelate motif of the ligand is evident in all structures except for that of **4(Me)**, in which the pendant amine is protonated rather than coordinated to the Lewis acidic bismuth center. Polymeric packing arrays are made possible by intermolecular Bi- - -Cl and/or Bi- - -S interactions,[22] which are distinctively long. **3(Me)** adopts a 4:1 hydrochloride cluster array (Figure 4) in which the unique chloride anion acquires a tetragonal site,

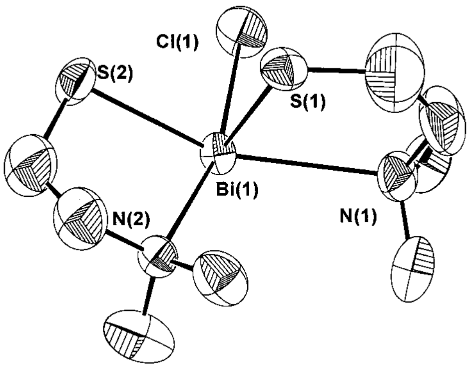

Figure 3. Crystallographic view of Bi$(SCH_2CH_2NMe_2)_2$Cl (**2(Me)**Cl).

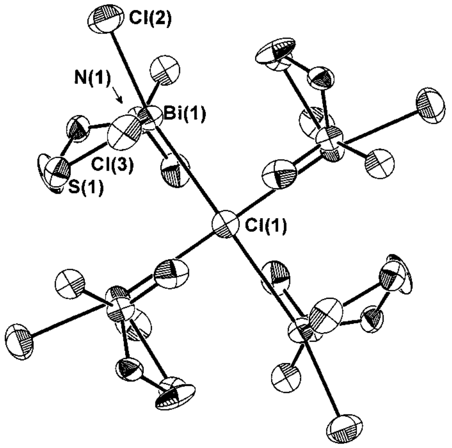

Figure 4. Crystallographic view of the tetramer of Bi$(SCH_2CH_2NMe_2)Cl_2$ (**3(Me)**$\cdot$$^1/_4$HCl).

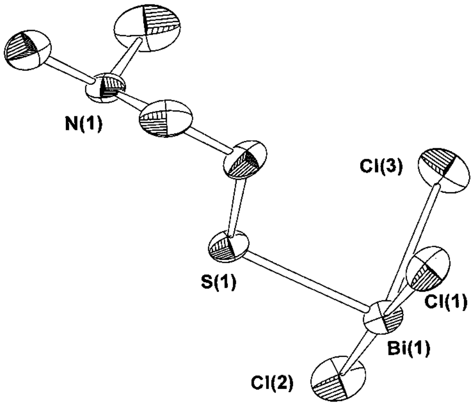

Figure 5. Crystallographic view of Bi$(SCH_2CH_2NHMe_2)Cl_3$ (**4(Me)**).

engaging four bismuth centers and representing the third Bi−Cl (Bi- - -Cl) interaction for each molecule of **3(Me)**.

Bisthiolate complexes involving the parent ligand, **2**NO_3 and **2**Cl, are best interpreted as ionic materials composed of the cation **2**$^+$, on the basis of their relatively long Bi−O [3.05(2) Å] and Bi−Cl [3.121(3) Å] distances, respectively. These interactions are responsible for their polymeric lattice arrays, and the structure of **2**NO_3 only differs from the hydrated solid **2**$NO_3\cdot H_2O$[19] in that water adopts one of two anion contacts observed in the solvent free structure. In surprising contrast to **2**Cl, **2(Me)**Cl has a substantially shorter (more covalent) Bi−Cl interaction [2.618(9) Å], and is best considered molecular in the solid state aside from the intermolecular Bi- - -S contacts. We rationalize these structural differences in terms of the steric hindrance borne by the pendant amines in **2(Me)**Cl relative to those of the parent ligand. The restricted access of the amines in **2(Me)**Cl is evident in the Bi−N bond distances [**2(Me)**Cl: 2.84(2), 2.67(3) Å; **2**NO_3: 2.48(2) Å; **2**Cl: 2.528(9), 2.398(8) Å] and the correspondingly weaker auxiliary amine donation in **2(Me)**Cl, enabling a more competitive coordination of Cl^-. The relative withdrawal of the pendant amines in **2(Me)**Cl may be associated with the distorted cis configuration of the cation moiety, which contrasts the trans configuration adopted in both **2**NO_3 and **2**Cl.

The intermolecular interactions (Bi- - -S) are longest in **1**, enabling an essentially molecular structure in the solid state, with a distorted pentagonal pyramidal geometry at bismuth imposed by two cis equatorial sulfur sites, one apical sulfur site and three equatorial nitrogen sites, and perhaps implicating a stereochemically active lone pair in the other apical position.

The acyclic structure of **4(Me)** contains a six-coordinate, near-octahedral bonding environment for bismuth. A one-dimensional spirocyclic polymeric arrangement results from the association of the bismuth centers by alternating chlorine and sulfur coordinative bridges. The two $Bi-Cl_{terminal}$ bonds [2.615(4) and 2.636(3) Å] are shorter than the $Bi-Cl_{bridging}$ bonds [2.776(4) and 3.001(4) Å]. Likewise, the Bi−S bond [2.669(3) Å] that is trans to the $Bi-Cl_{bridging}$ is significantly shorter than that which is trans to a $Bi-Cl_{terminal}$ [2.927(3) Å].[22] These bond distance comparisons can be interpreted in terms of the bismuth center engaging four covalent bonds (three chlorine and one sulfur) (Figure 5) and two coordinative bonds (one chlorine and one thioether) from a neighboring molecule.

Conclusions

The homologous series of mono-, bis-, and tris-thiolated bismuth complexes presented above establishes the coordinative flexibility of bismuth(III) with aminoethanethiolates and illustrates the ease of stoichiometrically controlling thiolate coordination chemistry. The pendant amine moieties mediate the high thiophilicity of bismuth even in the presence of thiolate moieties (rather than thiols) by coordinatively engaging the bismuth center, so that the stoichiometry of the reaction mixture governs the degree of thiolation in the isolated product, thereby overcoming the astoichiometric multithiolation, typically encountered in reactions of bismuth salts with thiols. The degree of thiolation by the aminoethanethiolate ligand can be further tuned by manipulating the coordination of the auxiliary amine in two ways: the steric imposition of methyl substituents on nitrogen allows for a slightly higher degree of thiolation than the parent ligand, and the amine can be entirely uncoupled from bismuth by protonation, with retention of a monothiolatobismuth complex. These results provide a systematic and comprehensive series of structurally simple thiolatobismuth complexes and the synthetic approach is likely applicable to heavy metals in general.

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Supporting Information Available: Full IR and Raman data for compounds listed in Table 2; crystal data, positional parameters and anisotropic thermal parameters for compounds listed in Table 3 (19 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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