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The Structurally Flexible Bicyclic Bis(2-hydroxyethanethiolato)bismuth(III) Complex: A Model for Asymmetric Monoanionic Chelation of Bismuth(III)

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Reaction of $Bi(NO_3)_3$ with 2-mercaptoethanol gives $[Bi(SCH_2CH_2OH)_2][NO_3]$, **5**($NO_3$), independent of stoichiometry. Other salts or derivatives of **5**, **5**(Cl) and **5**(Br), are readily prepared by anion exchange reactions and can also be obtained by reaction of BiX_3 (X = Cl, Br) with 2-mercaptoethanol. Reaction of $Bi(CH_3COO)_3$ with 2-mercaptoethanol gives the conjugate base of **5** which is readily protonated with glacial acetic acid to give the acetate salt **5**(CH_3COO). The compounds have been characterized by IR, Raman, and NMR spectroscopies and APCI mass spectrometry. X-ray crystallographic studies of **5**(NO_3) [crystal data: $C_4H_{10}O_5BiS_2N{\cdot}H_2O$, $I4_1/a$, $a = 20.337(6)$ Å, $b = 20.337(6)$ Å, $c = 11.303(7)$ Å, $Z = 16$], **5**(Cl) [crystal data: $C_4H_{10}O_2BiS_2Cl$, $P2_1/n$, $a = 8.653(2)$ Å, $b = 10.618(3)$ Å, $c = 10.564(2)$ Å, $\beta = 100.51(2)°$, $Z = 4$], and **5**(CH_3COO) [crystal data: $C_6H_{13}O_4BiS_2$, $P2_1/c$, $a = 8.089(2)$ Å, $b = 16.313(3)$ Å, $c = 8.708(2)$ Å, $\beta = 98.37(3)°$, $Z = 4$] show them to each contain the bicyclic bis(2-hydroxyethanethiolato)bismuth framework **5**. The conformational features of **5** are dramatically different in each of the structures, perhaps reflecting the relative donor capabilities of the anions. The observations reveal a substantial thermodynamic preference for the thiolate−alcohol chelate in a 2:1 stoichiometry over other possible structural arrangements, which is interpreted in terms of hard and soft acid−base theory and mediation of the acidity of the bismuth site by the double hydroxyl coordination.

Introduction

Recent interest in the fundamental chemistry of bismuth has been prompted by a demonstrated bioactivity[1−5] and the need for viable synthetic approaches to new materials.[6−8] A variety of commercial bismuth preparations have been used in the treatment of gastrointestinal disorders, and most contain materials which are classified as bismuth salts, such as bismuth subcitrate and bismuth subsalicylate. The structures of these compounds are complicated,[9] and their chemistry and bioactivity is not understood. Nevertheless, the prevalence of the chelate motif in these compounds has prompted the synthesis of model compounds.[2,10,11]

In this context, we have exploited the thermodynamic preference evident for chelated or cyclic dithia bismuth compounds[12] to develop two systematic series of small, structurally simple heterocyclic compounds (**1**−**4**) (Chart 1) of varying ring size,[13] some of which have been shown to also have antimicrobial[14] and ulcer healing potential.[15] The monocyclic chelation enforced at each bismuth site by the dithiolate ligands in compounds **1**−**4** is in contrast to the multicyclic (bis or tris) chelate complexes observed with monoanionic and oxygen-containing ligands.[2−4,6−8,10−12] This led us to examine reactions of $Bi(NO_3)_3$ and BiX_3 (X = Cl, Br) with the asymmetric diprotic chelate 2-mercaptoethanol,[28] which generally form the bicyclic bis(2-hydroxylthanethiolato)bismuth complex **5** (Chart 2),

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Chart 1

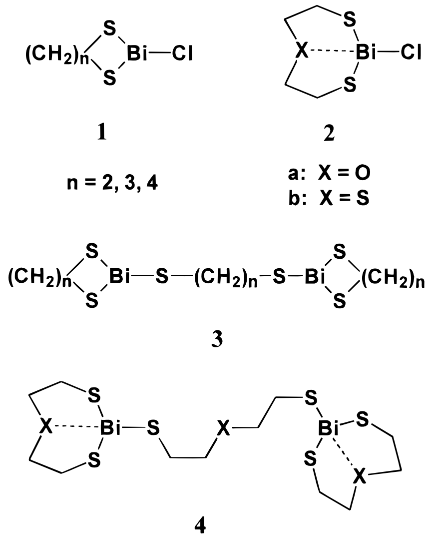
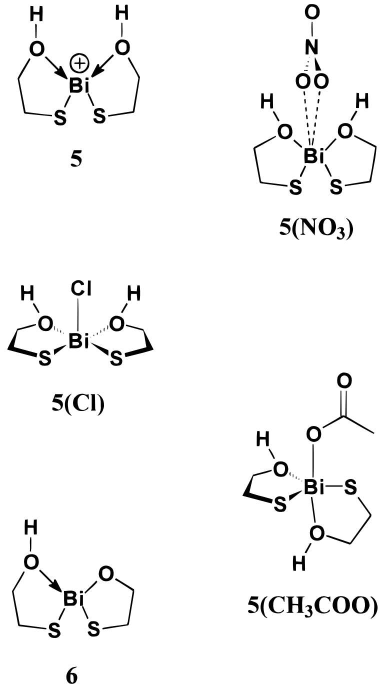


Chart 2



indicating that the bismuth−thiolate interaction is quantitatively favored over the bismuth−alkoxide. The acetate salt of **5** has also been obtained *via* the conjugate base **6**. The series of derivatives show structural flexibility for the bicyclic framework **5**, and the compounds represent simple models for asymmetric monoanionic chelate complexes of bismuth.

Experimental Procedures

General Methods. Bismuth(III) nitrate pentahydrate, bismuth(III) chloride, bismuth(III) bromide, and bismuth(III) acetate were used as received from Aldrich. 2-Mercaptoethanol was used as received from Eastman. Sodium bromide was used as received from Fisher Scientific. Sodium chloride was used as received from BDH. Melting points were recorded on a Fisher-Johns melting point apparatus. Measurements of pH were recorded using a Fisher Accumet Model 620 pH meter. IR spectra were recorded as Nujol mulls on CsI plates using a Nicolet 510P spectrometer. Raman spectra were recorded for powdered and crystalline samples in capillary tubes using a Bruker RFS 100 FT-Raman spectrometer. Atmospheric pressure chemical ionization (APCI) spectra were obtained using a VG Quattro triple quadrupole mass spectrometer (VG Organic). Samples were saturated solutions of each compound in acetonitrile at 25 °C. Solvent flow (100% acetonitrile at 300 μL/min) and sample injection (100 μL) used a Shimadzu LC-6A liquid chromatograph pump with a Rheodyne syringe-loading sample injector. MS/MS spectra used argon collision gas in the second quadrupole resulting in a beam attenuation of approximately 40%. Chemical analyses were performed by Canadian Microanalytical Service Ltd., Delta, BC, Canada and MDS Environmental Services Ltd, Halifax, NS, Canada. Solution 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 solvent signal.

Preparation, Isolation, and Characterization. 5(NO$_3$). Addition of $Bi(NO_3)_3 \cdot 5H_2O$ (4.18 g, 8.61 mmol) to 2-mercaptoethanol (1.50 g, 19.2 mmol) in 95% ethanol gave a yellow solution, instantaneously. Yellow, needlelike crystals of **5**(NO$_3$) formed on slow evaporation of the reaction mixture at room temperature, and these were washed with acetone: yield, 2.89 g, 76%; mp 67−70 °C; solubility in water, 3100 ppm Bi. Anal. Calcd: C, 10.84; H, 2.72. Found: C, 11.03; H, 2.74. IR (cm^{-1}): 1269 (w), 1199 (w), 1161 (w), 1048 (m), 1000 (m), 935 (w), 825 (m), 649 (w), 484 (w), 306 (m). Raman (cm^{-1}): 654 (m), 489 (w), 309 (s), 212 (vs), 136 (s), 93 (m), 71 (m). ^{1}H NMR (DMSO-*d*$_6$): 6 (vbr, OH), 4.13 (tr, CH$_2$O), 3.90 (tr, CH$_2$S). APCI mass spectrum [*m/z* (rel intensity)]: 10 V, 363 (100), 326 (33), 285 (10); 30 V, 363 (8), 285 (100). Varied stoichiometries [Bi(NO$_3$)$_3$:2-mercaptoethanol; 1:1, 1:3, 2:3] gave the same product (confirmed by Raman spectra and melting points) at lower isolated yield, 40, 30, and 50%, respectively.

5(Cl) and 5(Br). In a typical reaction, **5**(NO$_3$) (0.07−0.05 M) was generated *in situ* by the dropwise addition of 2 equiv of 2-mercaptoethanol to a stirrred slurry of Bi(NO$_3$)$_3$ in 95% ethanol. The resulting yellow solution was stirred for 30 min before the addition of NaX [X = Cl (10-fold excess), Br (6-fold excess)], followed by stirring for 24 h. The slurried reaction mixture was filtered using a Buchner funnel, the white precipitate (NaNO$_3$, Raman) was washed with acetone, and the filtrate was allowed to stand at room temperature.

A light yellow precipitate of **5**(Cl) formed over a 48 h period and was recrystallized from boiling acetonitrile producing yellow cubic crystals: yield, 0.29 g, 73%; mp 112−114 °C; solubility in water, 4.2 ppm Bi. Anal. Calcd: C, 12.05; H, 2.53; O, 8.03; S, 16.08. Found: C, 12.21; H, 2.55; O, 7.95; S, 14.97. IR (cm^{-1}): 3264 (s), 1413 (w), 1300 (w), 1279 (m), 1217 (w), 1045 (m), 1002 (m), 936 (m), 827 (m), 667 (m), 650 (w), 324 (m), 303 (m), 279 (m), 246 (s). Raman (cm^{-1}): 667 (w), 650 (w), 481 (w), 320 (s), 227 (vs), 141 (s), 124 (s), 101 (s), 87 (s). ^{1}H NMR (DMSO-*d*$_6$): 5.90 (br, OH), 4.05 (tr, CH$_2$O), 3.77 (tr, CH$_2$S). APCI mass spectrum [*m/z* (rel intensity)]: 10 V, 364 (42), 363 (87), 362 (100), 326 (22), 323 (30), 321 (89), 285 (9); 30 V, 285 (100).

Small yellow, needlelike crystals of **5**(Br) were formed upon slow evaporation of the clear, yellow filtrate: yield, 0.49 g, 22%; mp 185 °C; solubility in water, 0.7 ppm Bi. Anal. Calcd: C, 10.84; H, 2.27. Found: C, 11.05; H, 2.09. IR (cm^{-1}): 3472 (br), 1705 (br), 1271 (w), 1203 (w), 1173 (w), 1070 (w), 1006 (w), 940 (w), 849 (m), 657 (m), 598 (s), 520 (m), 502 (m), 413 (m), 308 (m), 269 (s). Raman (cm^{-1}): 661 (w), 409 (w), 336 (w), 304 (w), 255 (s), 235 (m), 214 (m), 133 (vs), 107 (m), 86 (s). APCI mass spectrum [*m/z* (rel intensity)]: 10 V, 363 (100), 326 (34), 285 (20); 30 V, 363 (68), 285 (100). (Solubility was too low for NMR spectroscopy or p*K*$_a$ measurement, and crystals were not suitable for X-ray analysis).

5(Cl) and **5**(Br) were also prepared by the addition of BiX$_3$ (X = Cl, 2.58 g, 8.18 mmol; X = Br, 2.41 g, 4.98 mmol) to 2-mercaptoethanol (1.29 g, 16.5 mmol; 1.13 g, 14.5 mmol, respectively). The reaction mixture was stirred at room temperature for 1 h and then neutralized with a solution of aqueous Na$_2$CO$_3$ (6 M) before being stirred overnight. The resulting slurry was filtered using a Buchner funnel, rinsed with 10 mL aliquots of acetone, and air dried. The precipitate was characterized by Raman spectroscopy and a melting point determination: yield, 2.46 g, 78% (Cl); 0.41 g, 19% (Br).

6. 2-Mercaptoethanol (1.17 g, 15.3 mmol) was added dropwise to a stirred slurry of bismuth acetate (1.93 g, 5.0 mmol) in acetone (120 mL). The resulting light yellow slurry was stirred for 24 h at room temperature and then filtered using a Buchner funnel, rinsed with 10 mL aliquots of acetone, and air dried: yield, 0.85 g, 2.34 mmol, 47%; mp 180 °C; solubility in water, <2 ppm Bi. Anal. Calcd: C, 13.26;

H, 2.50; S, 17.70. Found: C, 13.31; H, 2.50; S, 18.09. IR (cm^{-1}): 1414 (w), 1287 (m), 1276 (m), 1204 (m), 1167 (m), 1053 (m), 1040 (s), 998 (s), 844 (w), 823 (w), 662 (s), 529 (s), 481 (s), 386 (s), 332 (s), 312 (s), 281 (s). Raman (cm^{-1}): 663 (w), 526 (w), 482 (w), 389 (s), 314 (m), 279 (vs), 261 (s), 236 (s), 175 (s), 147 (m), 119 (s), 83 (s), 49 (w).

5(CH_3COO). **6** (0.14 g, 0.39 mmol) was dissolved in hot CH_3COOH (5 mL), and the solution was allowed to stand and cool to room temperature for 48 h giving needlelike crystals: yield, 0.14 g, 92%; mp 99−100 °C; solubility in water, 220 ppm Bi. IR (cm^{-1}): 3365 (br), 1274 (s), 1209 (m), 1177 (w), 1067 (m), 1047 (s), 1009 (s), 945 (m), 838 (m), 662 (m), 526 (s), 504 (s), 412 (s), 341 (m), 304 (vs), 267 (vs). Raman (cm^{-1}): 670 (w), 658 (w), 478 (w), 322 (s), 272 (s), 237 (s), 161 (m), 133 (s), 112 (vs), 95 (s). ^1H NMR (DMSO-d_6): 4.86 (br, OH), 3.72 (tr, CH_2), 3.72 (tr, CH_2), 3.60 (tr, CH_2), 2.78 (tr, CH_2), 1.86 (s, CH_3). APCI mass spectrum [m/z (rel intensity)]: 10 V, 363 (100), 326 (25), 285 (7); 30 V, 363 (9), 285 (100).

Compounds **5**(NO_3), **5**(Cl), and **5**(CH_3COO) were all determined to have a pK_a value of 3.6.

X-ray crystallography. X-ray crystallographic data for **5**(NO_3), **5**(Cl), and **5**(CH_3COO) were collected on a Rigaku AFC5R diffractometer. Unit cell parameters were obtained from the setting angles of a minimum of 18 carefully centred reflections having $2\theta > 77°$. The choice of space groups was based on systematically absent reflections and confirmed by the successful solution and refinement of the structures.

Data were collected using the $\omega-2\theta$ scan technique. The intensities of three representative reflections were measured after every 150 reflections. Compound **5**(NO_3) showed a 30.2% decrease in intensity over the course of the data collection, and a polynomial decay correction was applied. Compounds **5**(Cl) and **5**(CH_3COO) were not corrected for decay. All data were corrected for Lorentz and polarization effects. A correction for secondary extinction was applied to compounds **5**(NO_3) and **5**(Cl). An empirical absorption correction based on azimuthal scans of several reflections was applied to each compound [transmission factors: **5**(NO_3), 0.85−1.00; **5**(Cl), 0.64−1.00; **5**(CH_3COO), 0.24−1.00].

The structures were solved by direct methods[16] and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms bonded to carbon were placed in geometrically calculated positions and were not refined. Full-matrix least-squares refinement was carried out using the teXsan crystallographic package and/or Shelxl-93. In teXsan, the function minimized is $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F_o)$. In Shelxl-93 the function minimized is $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]$, where $w = [\sigma^2(F_o)^2 + (0.02P)^2 + 10P]^{-1}$ and $P = 1/3(F_o^2 + 2F_c^2)$ for **5**(CH_3COO). For both programs, $R = \sum(|F_o| - |F_c|)/\sum|F_o|$. Neutral atom scattering factors, anomalous dispersion terms (f' and f''), mass attenuation coefficients (teXsan), and absorption coefficients (Shelxl-93) were all taken from ref 17. Crystallographic details are summarized in Table 1, and selected bond lengths and angles are compared in Table 2.

Results and Discussion

As a contribution toward the systematic development of small-molecule Bi(III) compounds, and for comparison with our recent studies[13] involving dithiolate ligands, we have examined metathesis reactions with a simple, small oxy−thio chelate, involving the same elimination of protic acids. Consistent with the reactions of classical bismuth salts and dithiols, a thermodynamic dominance of one structural arrangement is apparent. However, the asymmetric nature of the oxy−thio chelate provides for a dramatically different structural chemistry compared to that of the symmetric dithio chelates.

Table 1. Crystallographic Data

	5(NO_3)	**5**(Cl)	**5**(CH_3COO)
formula	$C_4H_{10}O_5S_2BiN \cdot H_2O$	$C_4H_{10}O_2S_2BiCl$	$C_6H_{13}O_4BiS_2$
fw	443.24	398.68	422.26
λ (CuK_α) (Å)	1.541 78	1.541 78	1.541 78
space group	$I4_1/a$	$P2_1/n$	$P2_1/c$
a (Å)	20.337(6)	8.653(2)	8.089(2)
b (Å)	20.337(6)	10.618(3)	16.313(3)
c (Å)	11.303(7)	10.564(2)	8.708(2)
α (deg)	90	90	90
β (deg)	90	100.51(2)	98.37(3)
γ (deg)	90	90	90
V (Å^3)	4674(3)	954.4(4)	1136.8(4)
Z	16	4	4
T (°C)	23 ± 1	23 ± 1	23 ± 1
D_c (Mg m^{-3})	2.519	2.774	2.467
μ (cm^{-1})	331.91	426.74	337.79
R^a	0.048	0.036	0.082
$R_w{}^a$	0.062	0.045	0.204

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [(\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)]^{1/2}$.

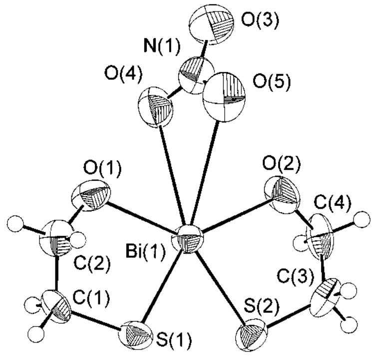


Figure 1. Crystallographic view of $[Bi(SCH_2CH_2OH)_2][NO_3]$, **5**($NO_3$) ($H_2O$ molecule omitted).

Reaction of $Bi(NO_3)_3$ with 2-mercaptoethanol in ethanol occurs rapidly to give **5**(NO_3), in high yield, independent of stoichiometry. An X-ray crystallographic study reveals an essentially ionic structure composed of an almost planar bicyclic framework **5** in which two sulfur atoms and two oxygen atoms adopt a square-planar *cis* arrangement around the bismuth center, as illustrated in Figure 1. The NO_3^- anion forms a third weak chelate between the two hydroxyl oxygen centers, with the nitrogen center in the BiO_2S_2 plane and the two donor oxygen centers of the anion above and below the plane.

Reactions of **5**(NO_3) (generated *in situ*) with NaX (X = Cl, Br) effect rapid anion exchange, and precipitates of **5**(Cl) and **5**(Br) are obtained in high yield from evaporation of the reaction mixtures. Compounds **5**(Cl) and **5**(Br) have also been obtained from the reactions of BiX_3 with 2-mercaptoethanol in ethanol illustrating the thermodynamic preference for the bicyclic framework and the generality of the chelation.

The relative acidity of **5** (pK_a = 3.6) compared to acetic acid (pK_a = 4.75) impedes the formation of **5**(CH_3COO) from the reaction of $Bi(CH_3COO)_3$ with 2-mercaptoethanol which yields **6**, the conjugate base of **5**. Nevertheless, compound **5**(CH_3COO) can be obtained in high yield as needlelike crystals by the reaction of **6** with glacial acetic acid.

X-ray crystallographic studies of **5**(Cl) and **5**(CH_3COO) show that both contain the bicyclic bis(2-hydroxyethanethiolato)bismuth moiety **5**, with a fifth coordination site at bismuth occupied by the chlorine and carbonyl oxygen center of the

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(16) SHELXS-86: Sheldrick, G. M. In *Crystallographic Computing 3*; Sheldrick, G. M., Krüger, C., Goddard, R., Eds.; Oxford University Press: Oxford, U.K., 1985; pp 175−189.

(17) Neutral Atom Scattering Factors (teXsan): *International Tables for Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. IV, Table 2.2A, pp 71−98. All other values taken from: *International Tables for Crystallography*; Wilson, A. J. C., Ed.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1992; Vol. C [Neutral atom scattering factors (Shelxl-93) Table 6.1.1.4 (pp 500−502), anomalous dispersion Table 4..2.6.8 (pp 219−222), mass attenuation (teXsan) Table 4.2.4.3 (pp 200−206), and absorption coefficients (Shelxl-93) Table 4.2.4.2 (pp 193−199)].

Table 2. Selected Bond Lengths (Å) and Angles (deg)

5(NO_3)		**5**(Cl)		**5**(CH_3COO)	
Bi(1)−S(1)	2.639(5)	Bi(1)−S(1)	2.595(3)	Bi(1)−S(1)	2.608(7)
Bi(1)−S(2)	2.655(5)	Bi(1)−S(2)	2.558(4)	Bi(1)−S(2)	2.577(7)
Bi(1)−O(1)	2.63(1)	Bi(1)−O(1)	2.86(1)	Bi(1)−O(1)	2.54(2)
Bi(1)−O(2)	2.63(1)	Bi(1)−O(2)	2.80(1)	Bi(1)−O(2)	2.72(2)
Bi(1)−O(4)	3.01(2)	Bi(1)−Cl(1)	2.589(3)	Bi(1)−O(3)	2.35(2)
Bi(1)−O(5)	3.17(2)				

5(NO_3)		**5**(Cl)		**5**(CH_3COO)	
S(1)−Bi(1)−O(1)	72.8(3)	S(1)−Bi(1)−O(1)	154.2(2)	S(1)−Bi(1)−O(1)	74.4(5)
S(1)−Bi(1)−S(2)	78.1(1)	S(1)−Bi(1)−S(2)	83.7(1)	S(1)−Bi(1)−S(2)	93.7(2)
S(2)−Bi(1)−O(2)	71.4(3)	S(2)−Bi(1)−O(2)	152.3(2)	S(2)−Bi(1)−O(2)	71.6(4)
O(1)−Bi(1)−O(2)	138.4(4)	O(1)−Bi(1)−O(2)	132.9(3)	O(1)−Bi(1)−O(2)	130.7(6)
S(1)−Bi(1)−O(4)	140.6(3)	S(1)−Bi(1)−Cl(1)	94.0(1)	S(1)−Bi(1)−O(3)	73.9(5)
S(1)−Bi(1)−O(5)	139.5(3)				

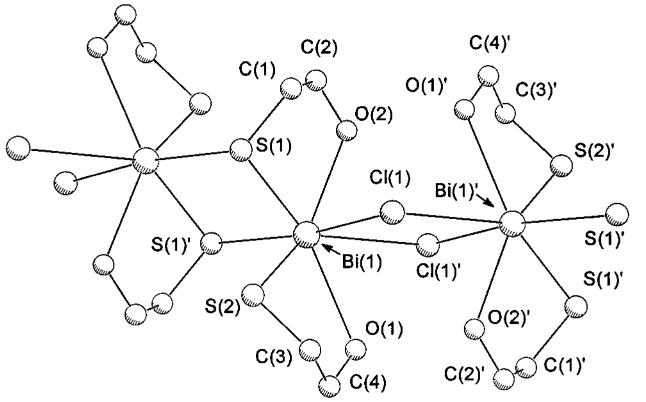

Figure 2. Crystallographic view of [Cl][Bi(SCH_2CH_2OH)$_2$][Cl], **5**(Cl).

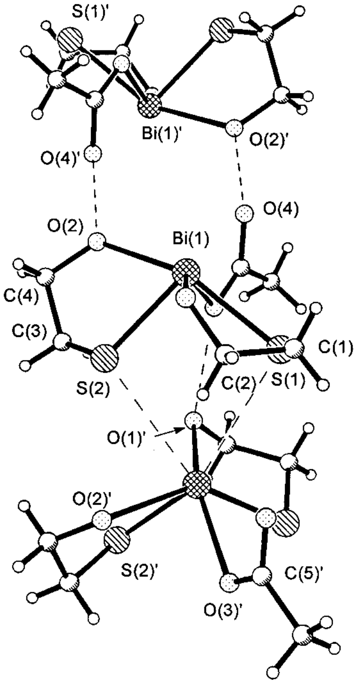

Figure 3. Crystallographic view of [CH_3COO][Bi(SCH_2CH_2OH)$_2$]-[CH_3COO], **5**(CH_3COO).

acetate, respectively. For **5**(Cl), weak intermolecular Bi- - -Cl [3.488(4) Å] and Bi- - -S [3.124(4) Å] interactions render the bismuth site formally seven coordinate and are responsible for a polymeric arrangement (Figure 2) similar to that observed for the dipyridylchlorodithiabismolane **1a**(pyridine)$_2$.[13] The solid-state structure of **5**(CH_3COO) involves intermolecular hydrogen bonding between the hydroxyl group of the chelate ring and the carbonyl moiety of the acetate anion [O- - -O 2.73-(3) Å]. Figure 3 shows the resulting centrosymmetric dimeric arrangement, as well as the weak interdimer Bi- - -S contacts [3.379(8), 3.457(8) Å], which are comparable in length to those observed in related compounds [3.134(7)−3.5910(9) Å].[13]

The Bi−S bond lengths in **5**(NO_3), **5**(Cl), and **5**(CH_3COO) are typical[12,13,18,19] but are slightly longer in **5**(NO_3) than in **5**(Cl), **5**(CH_3COO), and **8**(NO_3)[20] (Chart 3; Table 2). In contrast, the Bi−O bond lengths are substantially shorter in **5**(Cl) than in **5**(NO_3), but in both cases they are at the longer end of the Bi−O$_{\text{dicoordinate}}$ bond length range (2.08−2.86 Å)[2,3,4,6,7,10,21,22] and are more comparable to those of Bi−O$_{\text{tricoordinate}}$ (2.323−3.159 Å),[6,7] which are considered coordinative.

The bicyclic framework **5** adopts quite different conformations illustrated in **5**(NO_3), **5**(Cl), and **5**(CH_3COO), perhaps imposed by the differing donor capabilities of each anion. In **5**(NO_3), the two oxygen [O(1) −0.24(1) Å; O(2) 0.32(1) Å] and two sulfur atoms [S(1) 0.048(5) Å; S(2) 0.044(5) Å] form a slightly twisted plane which essentially contains both the bismuth center (−0.006 Å) and the nitrogen center (0.106 Å) of the anion. While the same five atom plane can be envisaged for **5**(Cl) [O(1) −0.12(1) Å; O(2) 0.15(1) Å; S(1) −0.021(4) Å; S(2) 0.022(4) Å; Bi(1) −0.202 Å], the chlorine center occupies an apical position above this plane, with a typical Bi−Cl bond length.[13,23] The general conformation of **5**(Cl) is similar to that observed for bis(1-oxopyridine-2-thiolato)phenylbismuth, **7**,[21] which involves two dicoordinate sulfur centers and two

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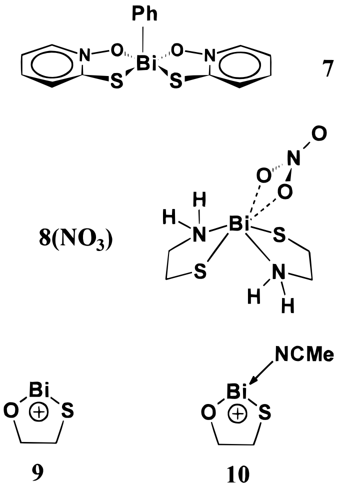
Chart 3



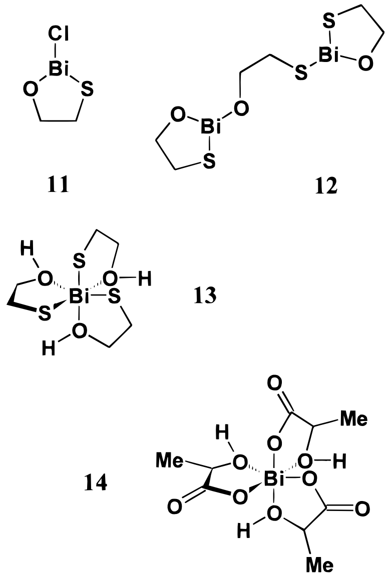
7

8(NO_3)

9

10

Chart 4



11

12

13

14

dicoordinate oxygen centers with realtively short Bi−O bonds [2.51(2), 2.54(1) Å].

In contrast, the cation in **5**(CH_3COO) has a severely twisted structure with the chelating ligands essentially *cis* and one hydroxyl oxygen *trans* to the acetate oxygen. The conformation of the cation in **5**(NO_3) is significantly different from that in the isoelectronic **8**(NO_3) which contains a relatively folded bicyclic bis(2-aminoethanethiolato)bismuth cation with the bismuth center in an apparently apical position,[20] reminiscent of the structure observed for the hydrated tropolonato complex.[2] Also in contrast to **5**(NO_3), the chelate ligands of **8**(NO_3), can formally be considered in a *trans* configuration. We note that the S−Bi−S angles in the bicyclic framework **5** increase with increasing distortion from planarity around the bismuth center, whereas the opposite trend is evident for the O−Bi−O angles.

Although the hydrogen atoms of the hydroxyl moieties could not be located in their respective Fourier maps, the oxygen−oxygen contact distances are representative of hydrogen-bonded moieties. For **5**(NO_3), O(1) and O(4) of a symmetry-related unit have a contact distance of 2.72(2) Å, while O(2) has a contact of 2.65(2) Å to O(6) (a water molecule). For **5**(CH_3COO), two close intermolecular contacts [O(2)- - -O(4)′ and O(2)′- - -O(4) 2.67(3) Å] are responsible for the centrosymmetric dimer arrangement. The closest contact in **5**(Cl) is longer [2.80(2) Å] but still within the hydrogen bond range. The hydroxyl characterization has been confirmed by the observation of a characteristically broad singlet in the solution ^1H NMR spectra, distinct broad bands in the 3400 cm^{-1} region of the infrared spectra, and relatively low pK_a values [3.6 for **5**(NO_3), **5**(Cl), and **5**(CH_3COO)]. The Raman spectra of the series of bicyclic bis(2-hydroxyethanethiolato) complexes show an identical fingerprint in the region 0−450 cm^{-1} for both **5**(NO_3) and **5**(CH_3COO), and a remarkably similar pattern is observed for **5**(Cl).

Further confirmation of the formulas are provided by APCI mass spectrometry on saturated solutions in acetonitrile at cone voltages of 10 and 30 V, which we have found to be a powerful technique for the characterization of bismuth compounds.[13] Assignments described below for the most intense peaks have been confirmed by MS/MS. All spectra show the presence of the molecular cation **5** (*m*/*z* 363) as a dominant peak at a low cone voltage (10 V). The intensity for this ion is substantially reduced at higher cone voltage, and the dominant peak corresponds to the monocyclic fragment oxathiabismolanium cation **9** (*m*/*z* 285), which results from loss of 2-mercaptomethanol, and is present in all spectra at both cone voltages. The acetonitrile complex **10** is also observed in all spectra at low cone voltage but is apparently too labile to exist at the higher cone voltage. Such fragmentation and solvent complexation are consistent with our previous observations for (dithiolato)-bismuth compounds[13] and illustrate the relative stability of cyclic five-membered bismuthenium cations such as **9**.

Salts of **5** are best described as bis chelate complexes of Bi^{3+} involving the hydroxyethanethiolate ligand, with two essentially equivalent intramolecular hydroxyl coordinative interactions responsible for the bicyclic framework. The *cis* orientation of the hydroxyl groups in **5**(NO_3) and **5**(Cl) is consistent with the structure of **7**[21] but is in contrast to **8**(NO_3)[20] and is perhaps imposed by intraligand hydrogen bonding in the transition state during complex formation. The twisted cation structures observed in **5**(CH_3COO) and **8**(NO_3) are possibly due to the presence of substantial intermolecular hydrogen bonding. In general, cations **5** and **8** can be considered as intramolecularly base-stabilized bismuthenium cations and are related to the previously reported solvent stabilized examples.[7,24]

The general and quantitative formation of **5** rather than structures **11**−**13** (Chart 4) is a definitive indication of the preference for thiolate ligation to bismuth over bismuth alkoxide formation, which has its roots in hard and soft acid−base theory,[25] although there are exceptions.[26] Consistently, we note

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(23) See, for example: Willey, B. R.; Barras, J. R.; Rudd, M. C.; Drew, M. G. B. *J. Chem. Soc., Dalton Trans.* **1994**, 3025−3029. Willey, G. R.; Lakin, M. T.; Alcock, N. W. *J. Chem. Soc., Dalton Trans.* **1992**, 1339−1341. Clegg, W.; Compton, N. A.; Errington, R. J.; Fisher, G. A.; Hockless, D. C. R.; Norman, N. C.; Orpen, A. G.; Stratford, S. E. *J. Chem. Soc., Dalton Trans.* **1992**, 3515−3523. Battaglia, L. P.; Bonamartini Corradi, A.; Nardelli, M.; Vidoni Tani, M. E. *J. Chem. Soc., Dalton Trans.* **1978**, 583−587.

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that thioalcohols form alkoxide complexes with harder metals such as titanium.[27] The asymmetric chelate ligand lactate (hydroxycarboxylate) forms a tris chelate complex **14** with bismuth.[11] Therefore, the avoidance of a trithiolate or tris chelate **13** is unexpected as dithiols achieve complete metathesis in the case of bismuth nitrate, resulting in the formation of **3** and **4**.[13] We interpret these observations in terms of the double hydroxyl coordination in derivatives of **5** mediating the acidity of the bismuth site. In comparison, a single intramolecular donation, as observed in compounds **2a**,**b**, is insufficient to prevent trithiolate formation and these compounds are readily transformed into the tethered analogues **4a**,**b**, respectively.[13] The donor sites of the lactate ligand in **14** are both oxygen centers, and therefore, the formation of the bicyclic bis chelate with hydroxyethanethiolate is an expression of the asymmetry due to differing electronegativities and basicities of the donor sites.

Conclusions. The formation of the bis(2-hydroxyethanethiolato)bismuth framework from a variety of sources demonstrates the thermodynamic preference for thiolate ligation at bismuth and highlights the significance of the chelate in mediating the metathesis. Three closely related compounds have been comprehensively characterized and show structural flexibility for the new bicyclic chelate complex. We view these compounds as models for monoanionic chelation of bismuth(III) in the systematic development of bismuth chelate chemistry.

Note Added in Proof. The submission of this work was coincidental with the following: Asato, E.; Kamamuta, K.; Akamine, Y.; Fukami, T.; Nukada, R.; Mikuriya, M.; Deguchi, S.; Yokota, Y. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 639−648. This article describes the syntheses and structures of compounds **5**(NO_3) and **6** and analytical data for compound **13**.

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Supporting Information Available: Listings of crystal data, positional parameters, bond lengths and angles, and anisotropic thermal parameters for **5**(NO_3), **5**(Cl), and **5**(CH_3COO) (15 pages). Ordering information is given on any current masthead page.

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(25) See, for example: Politzer, P. *J. Chem. Phys.* **1987**, *86* (2), 1072−1073. Pearson, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 3533−3539. Pearson, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 6801−6806. Politzer, P. *J. Chem. Phys.* **1987**, *86* (2), 1072−1073.

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(27) Chen, C.-A.; Gau, H.-M. *J. Organomet. Chem.* **1995**, *505*, 17−21. Gau, H.-M.; Chen, C.-A.; Chang, S.-J.; Shih, W.-E.; Yang, T.-K.; Jong, T.-T.; Chien, M. Y. *Organometallics* **1995**, *12*, 1314−1318.

(28) Solution studies have been reported and a 2:1 stoichiometry assigned by an X-ray crystallographic study of the perchlorate salt: Jackson, G. E.; Hancock, R. D. *Polyhedron* **1984**, *3*, 71−73.