A generally applicable synthetic approach for heteroleptic thiolate complexes of bismuth

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Abstract: As part of a systematic development of bismuth coordination chemistry, we are exploiting the thermodynamic and hydrolytic stability of Bi—S bonds. A series of heteroleptic thiolate bismuth complexes have been isolated and characterized. The generally applicable synthetic methodology involves the use of hetero-bifunctional ligands containing a thiolate moiety as an anchor to facilitate coordinate interaction of weak donors (carbonyls, amines, hydroxyls) with bismuth. The bifunctional nature of the ligands is manifested in chelating roles. Important comparisons with established thiolate complexes of bismuth are discussed.

Key words: bismuth, thiolate, heteroleptic, crystallography.

Résumé : Dans le cadre d'un développement systématique de la chimie de coordination du bismuth, on essaye d'exploiter la stabilité thermodynamique et hydrolytique des liaisons Bi—S. On a isolé et caractérisé une série de complexes hétéroleptiques de thiolate de bismuth. La méthode de synthèse généralement applicable implique l'utilization de ligands hétéro-bifonctionnels comportant une portion thiolate agissant comme ancre pour faciliter l'interaction du coordinat des donneurs faibles (carbonyles, amines, hydroxyles) avec le bismuth. La nature bifonctionnelle des ligands se manifeste dans les rôles d'agents chélatant. On discute d'importantes comparaisons avec des complexes bien établis de thiolate de bismuth.

Mots clés : bismuth, thiolate, hétéroleptique, cristallographie.

[Traduit par la Rédaction]

Introduction

Bismuth compounds have been used to treat a variety of medical disorders for over 200 years (1). Most obvious is the widespread gastrointestinal application of the commercially available preparations Pepto-Bismol® and De-Nol®, which contain *"bismuth subsalicylate"* (BSS) and *"colloidal bismuth subcitrate"* (CBS), respectively. However, the mechanisms of bioactivity are not understood and chemical characterization of these compounds remains incomplete. Indeed, the chemical database for bismuth is still superficially developed.

The high thermal and hydrolytic stability of the sulfur–bismuth bond are responsible for the fact that sulfur compounds represent the most extensive series of bismuth complexes for which there is a reliable set of data (2). We have recently developed a series (3, 4) of bismuth thiolates. Their antimicrobial behaviour (5) and ulcer healing capabilities (6) suggest a structure–bioactivity relationship for the bismuth environment. In this context, it is interesting to see that BSS and bismuth nitrate react readily with thiol-based biomolecules to give predictable complexes (7), leading us to speculate that the biochemical fate of bismuth pharmaceuticals begins with thiolation.

It is now necessary to devise universally applicable synthetic procedures that enable rational development of the thiolate coordination chemistry for bismuth in the presence of other donors. To this end, we have examined complexes with hetero-bifunctional ligands bearing a thiolate functionality that serves as an anchor to promote or assist interaction of weaker tethered donors with bismuth. This has enabled us to control the reaction stoichiometry, giving access to series of complexes bearing one (**1**), two (**2**), and three (**3**) thiolate ligands (4, 8). Molecular drawings **1**–**11** illustrate connectivity only, as drawings of these complexes aimed at describing bonding features (e.g., Lewis) are not meaningful or are misleading.

We now report the first systematic preparation and comprehensive characterization of heteroleptic thiolate complexes of bismuth. Facile synthesis and isolation of the chlorodithiolate complexes **4** and **5** (9) highlights their suitability as precursors to dithiolate–aminothiolates **6a** (R = Me) and **7a**, dithiolate–hydroxythiolates **6b** and **7b**, and the dithiolate–esterthiolate **8**. Compound **1b** is also versatile and

Received 4 February 2003. Published on the NRC Research Press Web site at http://canjchem.nrc.ca on 28 May 2003.

This article is dedicated to Professor Donald Arnold in recognition of his outstanding contributions to chemistry in Canada.

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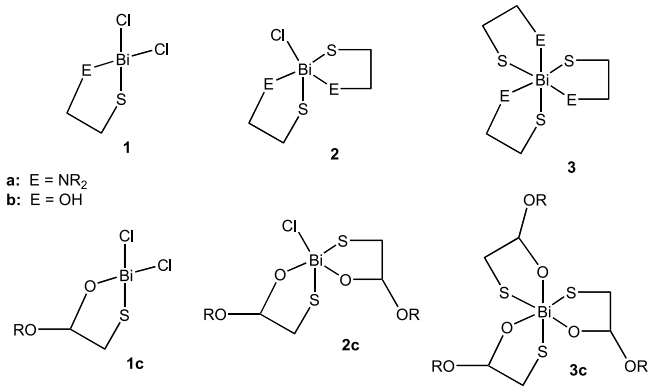
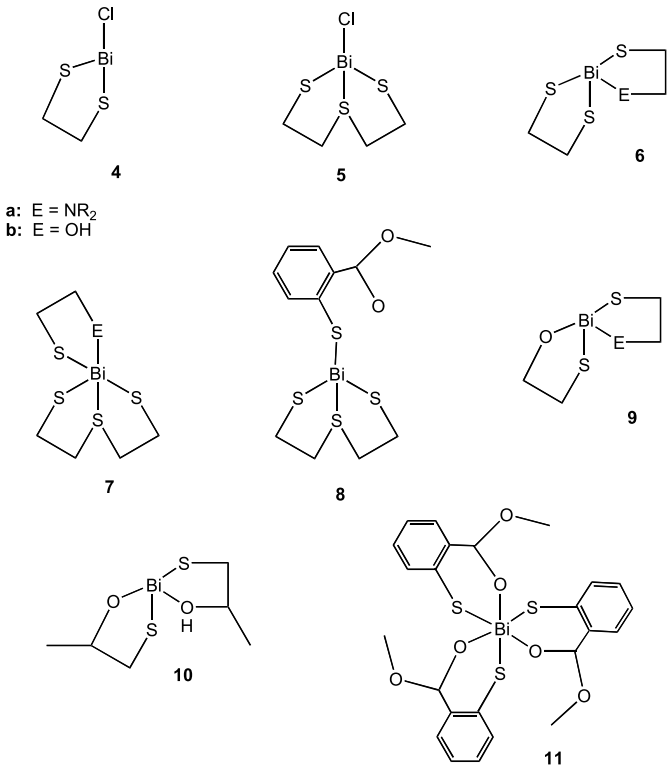
 doi: 10.1139/V03-054 © 2003 NRC Canada



has allowed for the isolation of an oxothiolate–aminothiolate **9a** (R = H). The compounds are rare, resilient examples of amino-, alkoxo-, and ester-complexes of bismuth.



Experimental

General

Bismuth chloride, 2-mercaptoethanol, 2-aminoethanethiol hydrochloride, *N*,*N*-dimethylaminoethanethiol hydrochloride, *N*,*N*-diethylaminoethanethiol hydrochloride, methyl thiosalicylate, and 1,2-ethanedithiol were used as received from Aldrich. Potassium hydroxide was used as received from BDH. All reactions were performed at room temperature under an atmosphere of nitrogen. All isolated products are air stable. Melting points were recorded on an Electrothermal melting point apparatus. IR spectra were recorded as Nujol mulls on CsI plates using a Nicolet 510P spectrometer or a Bruker Vector 22 spectrometer. Raman spectra were obtained for powdered and crystalline samples on a Bruker RFS 100 spectrometer. Vibrational spectra are presented as wavenumber (cm^{-1}) maxima with ranked intensities for each absorption given in parentheses (the most intense peak is given a ranking of 1). Chemical analyses were performed by Canadian Microanalytical Service Ltd., Delta, British Columbia.

Synthetic procedures

Compounds **6**–**8** were prepared according to a general procedure involving the dropwise addition of an ethanolic solution (50 mL) of thiol and KOH to a stirred slurry of **4** or **5** in ethanol (50 mL). The resulting reaction mixtures were allowed to stir overnight at room temperature. The precipitates were suction filtered using a Buchner funnel and washed with two 10 mL aliquots of water. Reagents are presented in Table 1 along with yields, elemental analyses, melting points, and vibrational spectroscopic data for each compound.

Compound **6b** was also obtained by the dropwise addition of 1,2-ethanedithiol to an aqueous solution of bis(2-hydroxyethanethiolato)bismuth(III) chloride (**2b**) (3) (100 mL). The reaction was stirred overnight at room temperature and suction filtered.

Compound **9a** was prepared by addition of a solution of KOH and 2-mercaptoethanol in ethanol (50 mL) to a slurry of bismuth chloride in ethanol (50 mL). The resulting yellow reaction mixture was stirred for 3 h at which point an ethanolic solution (50 mL) containing KOH and 2-aminoethanethiol chloride was added dropwise. This reaction mixture was allowed to stir overnight at room temperature. The reaction mixture was suction filtered.

Compounds **6a**–**9a** were crystallized from filtrates reduced in volume on a rotary evaporator and cooled in the refrigerator (4°C) for 1 day to give yellow needles (**6a**) or left to evaporate slowly over a period of 4 days to give yellow needles (**7a**, **8**) or green-gold plates (**9a**). Compound **6b** was isolated as an analytically pure powder and was recrystallized as green-gold cubic crystals from hot DMF.

X-ray crystallography

Data were collected on a Rigaku AFC5R diffractometer with graphite-monochromated Cu-Kα radiation (λ = 1.54178 Å) and a 12 kW rotating anode generator. The structures were solved by direct methods (SHELXS86 (**6a**), SIR92 (**6b**, **7a**, and **9a**)) or Patterson methods (SIR92 (**8**)). They were refined by full-matrix least-squares on F using 1435 (**6a**) and 468 (**9a**) reflections with $I > 3.00\sigma(I)$ or on F^2 using 1298 (**6b**), 1970 (**7a**), and 1397 (**8**) unique reflections (SHELXL97) (10). Unit cell parameters were obtained from the setting angles of high angle centred reflections. The choice of space groups was based on systematically absent reflections and was confirmed by the successful solution and refinement of the structures.

All data were collected using the ω–2θ scan technique. The intensities of three representative reflections were measured after every 150 reflections. No decay corrections were applied. Data were corrected for Lorentz and polarization effects, and an empirical absorption correction was applied for each structure. Secondary extinction was refined for **6**–**8**. All of the heavy atoms were refined anisotropically for each structure except **9a**, where only Bi and S atoms were made anisotropic (the remainder being refined isotropically). Hy-

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Table 1. Reagents, yields, elemental analyses, melting points, distinctive IR and Raman bands (ranked intensities) for **6–9a**.

Cpd	Reagents (g, mmol)	Yield (g, mmol, %)	Elemental analysis (% calcd. (found))	mp [dp] (°C)	IR bands (cm^{-1})	Raman (cm^{-1})
6a	**4** (3.36, 9.97), $HSCH_2CH_2NMe_3$·HCl (1.41, 9.94), KOH (1.46, 26.0)	1.56, 3.85, 39	C: 17.78 (17.50) H: 3.46 (3.38) N: 3.46 (3.27)	[165–184]	758(1), 994(2), 835(3), 1215(4), 1274(5), 919(6), 1248(7), 1270(8), 946(9), 432(10), 1166(11), 1099(12), 1054(13), 1040(14), 421(15), 1407(16), 1428(17), 528(18), 1143(19), 1123(20)	306(1), 104(2), 2891(3), 131(4), 251(5), 291(6), 76(7), 153(8), 179(9), 89(10), 265(11), 197(12), 2801(13), 357(14), 2918(15), 1157(16), 1288(17), 2945(18), 2833(19), 2966(20)
6b	(1) **4** (1.98, 5.89), $HSCH_2CH_2OH$ (0.60, 7.66), KOH (0.43, 7.70) (2) **2b** (3.87, 9.46), $HSCH_2CH_2SH$ (0.89, 9.40)	2.12, 5.62, 96 3.36, 8.89, 95	C: 12.69 (12.72) H: 2.40 (2.38)	112–114	1054(1), 988(2), 272(3), 331(4), 3222(5), 1293(6), 1279(7), 1413(8), 674(9), 440(10), 643(11), 482(12), 440(13), 1236(14), 1012(15), 929(16),	283(1), 137(2), 123(3), 301(4), 100(5), 185(6), 212(7), 159(8), 79(9), 667(11), 482(12), 644(13)
7b	**5** (0.375, 0.946), $HSCH_2CH_2NH_3$·HCl (0.135, 1.19), KOH (0.151, 2.69)	0.21, 0.48, 51	C: 16.51 (16.56) H: 2.98 (3.19) N: 3.21 (3.16)	[107–145]	269(1), 839(2), 893(3), 1641(4), 811(5), 1166(6), 724(7), 530(8), 1269(9), 414(10), 451(11), 966(12), 1133(13), 1560(14), 1049(15), 657(16)	291(1), 253(2), 315(3), 274(4), 165(4), 2888(5), 2917(6), 178(7), 150(8), 225(9), 204(10), 98(11), 2836(12), 1403(13), 2815(14), 2944(15)
8	**5** (2.00, 5.15), $MeOCOC_6H_4SH$ (0.85, 5.08), KOH (0.34, 6.08), $BiCl_3$ (0.952, 3.02)	1.56, 3.00, 59	C: 27.27 (27.39) H: 2.86 (3.06)	138–140	273(1), 866(2), 875(3), 1716(4), 1423(5), 1136(6), 1274(7), 1437(8), 532(9), 749(10), 307(11), 970(11), 1041(12), 1123(13), 1309(14)	
9a	$HSCH_2CH_2OH$ (0.276, 3.53), KOH (0.350, 6.24), $HSCH_2CH_2NH_3$·HCl (0.278, 3.60), KOH (0.207, 3.68)	0.625, 1.74, 50	C: 13.30 (13.51) H: 2.79 (2.89) N: 3.88 (3.57)	168–173	1035(1), 334(2), 1275(3), 1005(4), 510(5), 1366(6), 317(7), 964(8), 381(9), 833(10), 1052(11), 1418(12), 1205(13), 288(14), 925(15), 1084(16), 271(17), 1160(18), 663(19), 721(20)	

drogen atoms were placed in geometrically calculated positions and not refined, in all cases (Table 2).

A final difference-Fourier map yielded ρ (max) = 1.71 e^- $Å^{-3}$ and ρ (min) = –1.89 e^- $Å^{-3}$ (**6a**), ρ (max) = 1.89 e^- $Å^{-3}$ and ρ (min) = –3.22 e^- $Å^{-3}$ (**6b**), ρ (max) = 1.72 e^- $Å^{-3}$ and ρ (min) = –1.96 e^- $Å^{-3}$ (**7a**), ρ (max) = 1.65 e^- $Å^{-3}$ and ρ (min) = –1.43 e^- $Å^{-3}$ (**8**), and ρ (max) = 1.46 e^- $Å^{-3}$ and ρ (min) = –1.53 e^- $Å^{-3}$ (**9a**). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited.[2]

Results and discussion

Facile hydrolysis of many bismuth element bonds typically results in essentially quantitative precipitation of bismuthyl (BiO^+) salts, and this has impeded studies aimed at

[2] Supplementary data may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0S2, Canada (http://www.nrc.ca/cisti/irm/unpub_e.shtml for information on ordering electronically). CCDC 207453–207457 contain the supplementary data for this paper. These data can be obtained, free of charge, via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax +44 1223 336033; or deposit@ccdc.cam.ac.uk).

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Table 2. Crystallographic data for compounds **6**–**9a**.

	6a	**6b**	**7a**	**8**	**9a**
Formula	$C_6H_{14}BiNS_3$	$C_4H_9BiOS_3$	$C_6H_{14}BiNS_4$	$C_{12}H_{15}BiO_2S_4$	$C_4H_{10}BiNOS_2$
fw	405.34	378.27	437.40	528.47	361.23
λ (Å) (CuK_α)	1.54178	1.54178	1.54178	1.54178	1.54178
Space group	*P*-1	$P2_1/a$	$P2_1/n$	$P2_1$	$P2_1/c$
a (Å)	9.121(2)	9.158(1)	11.748(2)	8.147(2)	8.233(3)
b (Å)	9.266(2)	11.872(2)	5.365(2)	8.736(2)	6.492(4)
c (Å)	7.6099(5)	8.037(1)	19.5313(9)	11.941(2)	16.738(3)
α (°)	104.722(9)	90	90	90	90
β (°)	101.996(9)	90.09(1)	98.354(6)	103.54(2)	111.96(2)
γ (°)	63.51(1)	90	90	90	90
V (Å^3)	553.4(2)	873.9(2)	1217.9(3)	826.3(3)	829.6(5)
Z	2	4	4	2	4
T (°C)	23 ±1	23 ±1	23 ±1	23 ±1	23 ±1
D_c (Mg m^{-1})	2.432	2.875	2.374	2.124	2.892
μ (cm^{-1})	362.44	458.81	345.69	257.12	460.18
R^a	0.049 (obs 3σ data)	0.050 (obs 2σ data)	0.033 (obs 2σ data)	0.044 (obs 2σ data)	0.0570 (obs 3σ data)
$R_w{}^b$	0.047 (obs 3σ data)				0.073 (obs 3σ data)
$wR2^c$		0.164 (all data)	0.125 (all data)	0.124 (all data)	

[a] $R = \Sigma||F_O| - |F_C||/\Sigma|F_O|$.
[b] $R_w = [(\Sigma w(|F_O| - |F_C|)^2/\Sigma|F_O{}^2|)^{1/2}$.
[c] $wR^2 = \{\Sigma[w(F_O{}^2 - F_C{}^2)^2]/\Sigma(F_O{}^2)^2]\}^{1/2}$.

Table 3. Selected bond lengths (Å) listed in order of increasing bond length (i.e., A < B < C < D) for compounds **1–11**.

	Reference	Bi—S_A	Bi—S_B	Bi—S_C	Bi—S_D	Bi—N_A	Bi—N_B	Bi—N_C	Bi—O_A	Bi—O_B	Bi—O_C
1a	4	2.530(7)				2.52(2)					
1c	11	3.021(2)							2.562(6)		
2a	4	2.569(3)	2.608(3)			2.398(8)	2.528(9)		2.86(1)		
2b	3	2.558(4)	2.595(3)						2.80(1)	2.86(1)	
2b	13	2.663(6)	2.853(6)						2.58(2)	2.64(2)	
2c	8	2.849(7)	2.884(6)						2.68(2)	2.77(2)	
3a	4	2.567(5)	2.654(5)	2.748(7)		2.64(2)	2.81(2)	2.83(2)			
3c	8	2.568(2)	2.574(2)	2.608(2)					2.807(5)	2.861(5)	3.071(7)
4·2py	9	2.542(6)	2.545(4)								
6a*		2.542(4) Bi-S3	2.572(4) Bi-S2	2.589(5) Bi-S1		2.72(1) Bi-N1					
6b*		2.532(5) Bi-S1	2.558(5) Bi-S2	2.639(6) Bi-S3					2.77(2) Bi-O1		
5	9	2.541(6)	2.849(5)	3.534(7)							
7a*		2.574(2) Bi-S1	2.592(3) Bi-S4	2.621(3) Bi-S3	3.248(3) Bi-S2	2.723(9) Bi-N1					
8*		2.543(5) Bi-S3	2.550(5) Bi-S1	2.602(5) Bi-S4	3.068(4) Bi-S4				3.55(2) Bi-O1		
11	14	2.597(5)2	2.602(6)	2.606(5)					2.72(2)	2.84(1)	3.08(2)
9a*		2.57(2) Bi-S1	2.58(2) Bi-S2			2.41(7) Bi-N1			2.22(4) Bi-O1		
9b	13	2.527(3)	2.564(3)						2.195(9)	2.577(9)	
10	15	2.582(1)	2.560(1)						2.197(4)	2.589(4)	

Note: Bi-E bond labels are given below the bond distances where distinction is necessary.
*Structures reported in this article.

rational and systematic development of bismuth chemistry. Some complexes involving weakly donating functionalities have been isolated in the absence of moisture, but many conventional types of ligands have yet to be observed coordinated to bismuth. As a result, numerous complexes of bismuth represent unique examples for a particular ligand,

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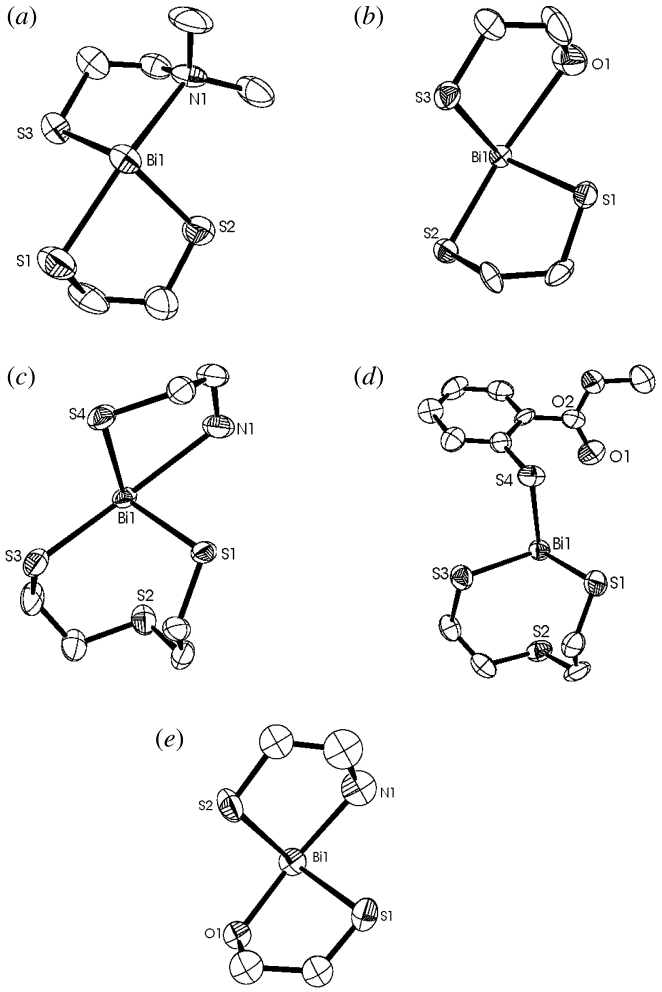
Fig. 1. Crystallographic views of (*a*) **6a**, (*b*) **6b**, (*c*) **7a**, (*d*) **8**, (*e*) **9a**. Thermal ellipsoids are drawn to 50% probability. Hydrogen atoms have been omitted for clarity.



rather than a series of related compounds and general synthetic procedures have not been established to allow for assessment of physical and chemical properties.

A wide range of bismuth thiolate complexes are known due to the high thermal and hydrolytic stability of the sulfur–bismuth bond (2), however, most complexes involve multithiolation. Hetero-bifunctional ligands containing a thiolate moiety and an auxiliary donor have proven effective for developing complexes of bismuth with new donors. Moreover, the chelate interaction of the weaker donor mediates the thiophilicity of the bismuth centre and it is possible to isolate kinetically stable, partially thiolated complexes, so that all three stoichiometric combinations (**1**, **2**, **3**) have been prepared for aminoethanethiolate (4) and esterthiolate (8, 11) complexes.

We have now exploited the features of bifunctional thiolate ligands to develop synthetic procedures for heteroleptic bismuth complexes. The starting materials **4** (12) and **5** (9) that are readily obtained via precipitation, react slowly at room temperature with potassium thiolate solutions in a slurry with little or no change in the visual appearance of the reaction mixture. Nevertheless, the precipitates are characterized as analytically pure metathesis products formed in reasonable yield. Some yields are relatively low, however, conditions to optimize them have not yet been assessed.

Compounds **6**–**9a** have been crystallographically and spectroscopically characterized. Molecular structures are shown in Fig. 1 and selected bond lengths are compared with those of compounds **1**–**5** in Table 3. The spirocyclic environments observed for bismuth in **6a**, **6b**, **7a**, and **9a** confirm auxiliary coordination of the hydroxyl (**6b**), amino (**6a**, **7a**, and **9a**) and alkoxide (**9a**) functional groups to the bismuth centre in each respective example. The structures are consistent with the homoleptic thiolate series **1**–**3** (3, 4, 13), except for compound **8** in that the ester functionality is terminal (Bi-O, 3.55(2) Å; cf. Bi-O 2.56–2.86 Å (8, 11)), showing no evidence of interaction with bismuth. This is an unexpected structural feature, when one compares the structure of tris(thiosalicylato)bismuth **11**, which exhibits a definitively hexacoordinate site for bismuth and typical Bi—O coordinate bond distances (Bi—O 2.72(2)–3.08(2) Å) (14). Although the cross-ring S2—Bi distance is relatively long (3.0688 (4) Å) in **8**, we speculate that this interaction lowers the Lewis acidity of the bismuth center to render the carbonyl donation ineffective.

The structural features of compounds **6**–**9a** represent a useful contribution to the developing database for the chelate–thiolate coordination chemistry of bismuth, as documented in Table 3. Mono-, bis-, and tris-thiolate complexes of bismuth exhibit a narrow range of Bi—S bond distances. The geometry at bismuth varies considerably throughout the series of complexes including a variety of coordination numbers. Nevertheless, most complexes are observed to have Bi—S bond lengths within a narrow range (2.5 to 2.6 Å), so that the thiolate interaction is essentially independent of the number of thiolate ligands, the presence of auxiliary intramolecular coordination to bismuth, or the number of intermolecular interactions at bismuth. The unusually long Bi—S bonds in **1c**, **2b**, and **2c** are likely due to strong intermolecular interactions in the solid state that provide for a dimeric arrangement for **1c** and a polymeric (ribbon-like) structure for **2b** and **2c** (3, 8). The fourth Bi-S contact in **7a** and **8** represent the intramolecular cross-ring thioether donation, which is predictably weaker than those of the thiolates. The relatively weak interactions of the amines are likely made possible by the chelate arrangement. The Bi—N distances are comparable to those of the thiolates despite the smaller size of nitrogen. These observations are consistent with the realization that amine complexes of bismuth are extremely rare and the most reliable comparative data comes from complexes of pyridine derivatives (2), which are in the range of the Bi—N distances listed in Table 3. The relative Bi—O distances are in agreement with the relative Lewis basicity of the oxygen donor in that interactions of hydroxyl (**2b**, **6b**, **9b**, **10**) and carbonyl (**1c**, **2c**, **3c**, **8**, **11**) ligands are longer than interactions with alkoxide (**9a**, **9b**, **10**) functionalities.

Conclusion

The use of thiolates in bifunctional ligands offers a synthetically versatile approach to bismuth complexes involving weak Lewis donors and provides for a general systematic and comprehensive development of bismuth chemistry.

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Acknowledgements

We thank the Natural Sciences and Engineering Research Council of Canada (NSERC), the Killam Trusts, the Canada Research Chairs program, the Canada Foundation for Innovation, the Nova Scotia Research and Innovation Trust Fund and MDS Sciex for funding, the Dalhousie Mass Spectrometry Center for the use of instrumentation, and Douglas Jackson for performing some of the preparative work.

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