Inorg. Chem. **2003**, *42*, 3136–3141

Inorganic Chemistry

Article

Synthesis and Structures of the First Bismuth–Ester Complexes Using Heterobifunctional Thiolate Anchored Ligands and Mass Spectrometric Identification of Ligand-Bridged Derivatives

Glen G. Briand, Neil Burford,* Melanie D. Eelman, T. Stanley Cameron, and Katherine N. Robertson

Department of Chemistry, Dalhousie University, Halifax, Nova Scotia B3H 4J3, Canada

Received November 19, 2002

The first systematic series of bismuth complexes involving ester donors, $Bi(SCH_2C(O)OCH_2CH_3)Cl_2$, $Bi(SCH_2C(O)OCH_3)_2Cl$, and $Bi(SCH_2COOCH_3)_3$, has been isolated and characterized by spectroscopic (IR, Raman) and X-ray crystallographic data. In addition, these and other species have been identified by electron-impact, electrospray, and atmospheric pressure chemical ionization mass sprectometry. The generally applicable synthetic methodology involves the use of heterobifunctional ligands containing a thiolate moiety as an anchor to facilitate coordinate interactions between weak donors (carbonyls) and weak acids (bismuth). The bifunctional nature of the ligands is manifested in both chelating and bridging roles. Important comparisons can be made with the pharmaceutical agent "colloidal bismuth subcitrate" (CBS). The observations allow for a new appreciation of bioactive bismuth compounds, by providing an approach to study the interaction of biorelevant functional groups with bismuth.

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 action for bioactive bismuth compounds are not understood, chemical characterization of the commercial compounds is incomplete, and the chemical database for bismuth is still superficially developed.

We have recently synthesized several systematic series[2−4] of bismuth thiolates and have assessed their antimicrobial behavior as an indicator of bioactivity,[5] exploiting the high thermal and hydrolytic stability of the sulfur−bismuth bond. Indeed, sulfur compounds represent the most extensive series of bismuth complexes for which there is reliable data. Some Bi−S compounds have been evaluated for their ulcer healing potential, and our results suggest a structure/bioactivity relationship for the bismuth environment.[6] It is now necessary to devise universally applicable synthetic procedures that enable rational development of the coordination chemistry for bismuth. In this context, heterobifunctional ligands that include a thiolate anchor provide for control of the reaction stoichiometry and isolation of mono- (**1Cl$_2$**), bis- (**2Cl**), and tris-thiolate (**3**) complexes of bismuth with relatively weak hydroxy (**1aCl$_2$**, **2aCl**, **3a**) and amine (**1bCl$_2$**, **2bCl**, **3b**) Lewis donors. (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.)

In this report we extend this premise to ligands representing functional groups that are prevalent in biosystems, with comprehensive characterization of the first bismuth−ester complexes.[7] Electrospray ionization mass spectrometry (ESI-MS) and X-ray crystallographic data consistently show both chelate and ligand-bridged associated complexes, which allow for important comparisons with the dimeric arrange-

---

* Author to whom correspondence should be addressed. E-mail: neil.burford@dal.ca.

(1) Briand, G. G.; Burford, N. *Chem. Rev.* **1999**, *99*, 2601−2657.

(2) Agocs, L.; Burford, N.; Cameron, T. S.; Curtis, J. M.; Richardson, J. F.; Robertson, K. N.; Yhard, G. B. *J. Am. Chem. Soc.* **1996**, *118*, 895−898.

(3) Agocs, L.; Briand, G. G.; Burford, N.; Cameron, T. S.; Kwiatkowski, W.; Robertson, K. N. *Inorg. Chem.* **1997**, *36*, 2855−2860.

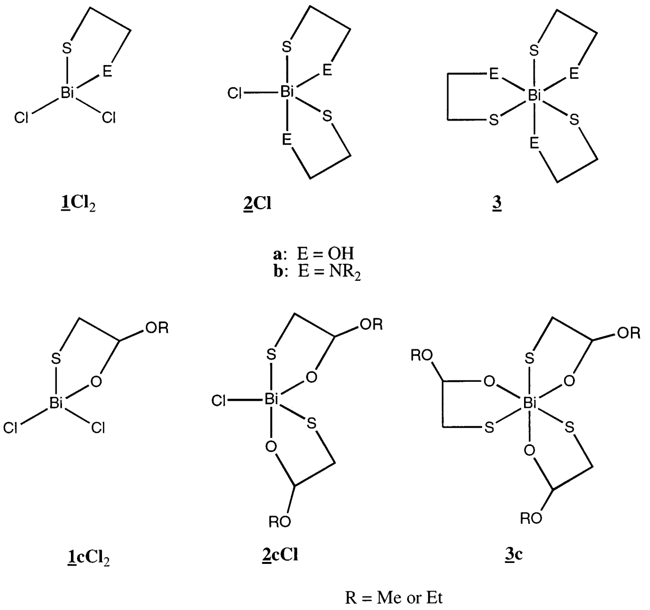
(4) Briand, G. G.; Burford, N.; Cameron, T. S.; Kwiatkowski, W. *J. Am. Chem. Soc.* **1998**, *120*, 11374−11379.

(5) Mahony, D. E.; Lim-Morrison, S.; Bryden, L.; Faulkner, G.; Hoffman, P. S.; Agocs, L.; Briand, G. G.; Burford, N.; Maguire, H. *Antimicrob. Agents Chemother.* **1999**, *43*, 582−588.

(6) Sandha, G. S.; LeBlanc, R.; van Santen, S. J. O. V.; Sitland, T. D.; Agocs, L.; Burford, N.; Best, L.; Mahony, D.; Hoffman, P.; Leddin, D. J. *Dig. Dis. Sci.* **1998**, 43, 2727−2732.

(7) Briand, G. G.; Burford, N.; Cameron, T. S. *Chem. Commun.* **2000**, 13−14.

10.1021/ic0261934 CCC: $25.00



ments reported for the pharmaceutical agent colloidal bismuth subcitrate (CBS).[8−11] Most important is the demonstration of ESI-MS as a powerful tool in the assessment of bismuth coordination chemistry.[12]

Experimental Section

General. Bismuth(III) chloride and methyl thioglycolate 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 and moisture 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. 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 and the most intense peak is given a ranking of 1. Chemical analyses were determined by Canadian Microanalytical Service Ltd., Delta, BC, Canada.

Electron impact (EI) mass spectra were recorded on a CEC 21-110 mass spectrometer. Atmospheric pressure chemical ionization (APCI) and in situ electrospray (ESI) mass spectra were obtained using a VG Micromass Quattro triple quadrupole mass spectrometer. A Shimadzu LC-10AT liquid chromatograph pump with a Rheodyne syringe loading sample injector was used with solvent flow at 300 μL/min. Solutions used for ESI-MS were filtrates collected from reaction mixtures analogous to those used to isolate **$1cCl_2$**, **2cCl**, and **3c** and were directly injected into the ESI or APCI source with a source temperature and cone voltage of 385 K and 50 V, and 473 K and 40 V, respectively. MS/MS spectra were obtained using argon as a collision gas with a collision energy equal to 50 eV. The argon pressure was sufficient to reduce the intensity of the main beam by 1%.

Preparative and Isolation Procedures. $Bi(SCH_2C(O)OCH_2CH_3)Cl_2$ $1cCl_2$ (R = Et). Addition of methyl thioglycolate (5.4 mmol) to a slurry of $BiCl_3$ (5.4 mmol) in absolute ethanol immediately produced a pale yellow solution, which was stirred overnight and suction filtered. On standing for 1 week, the filtrate gave yellow crystalline plates of **$1cCl_2$**, yield 0.63 g, 25%; mp 180 °C dec. Anal. Calcd (found): C 12.04 (12.28); H 1.77 (1.80). IR: 278 (4), 372 (9), 865 (8), 1012 (4), 1110 (11), 1152 (6), 1199 (4), 1266 (10), 1314 (2), 1369 (3), 1383 (5,sh), 1441 (7) 1462 (1,sh), 1662 (6). Raman: 58 (14), 92 (10), 98 (8), 129 (7), 176 (6), 211 (5), 241 (1), 265 (4), 317 (2), 373 (12), 564 (25), 867 (19), 890 (24), 1113 (23), 1156 (22), 1200 (13), 1442 (18), 1665 (20), 2867 (17), 2895 (16), 2910 (3), 2932 (11), 2944 (21), 2976 (15), 2982 (9). EI-MS (rel intensity): 209 (31), 279 (50), 328 (8), 363.5 (100), 398 (19).

$Bi(SCH_2C(O)OCH_3)_2Cl$ 2cCl (R = Me). Addition of $BiCl_3$ (5.3 mmol) to methyl thioglycolate (10 mmol) in 95% ethanol or methanol (150 mL) giving a yellow reaction mixture, which was stirred overnight, suction filtered, and recrystallized from DMF to afford yellow, needle-shaped crystals of **2cCl**, yield 1.1 g, 46%; mp 128 °C. Anal. Calcd (found): C, 15.85 (16.08); H, 2.22 (2.26). IR: 555 (11), 681 (12), 777 (13), 874 (3), 886 (10), 986 (7), 994 (8), 1161 (6), 1206 (6), 1296 (9), 1318 (4), 1676 (2), 1707 (1). Raman: 95 (1), 117 (4,sh), 147 (5), 187 (7), 227 (3), 260 (2), 350 (8), 399 (12), 888 (9), 1392 (13), 2903 (6), 2940 (10), 2959 (11). APCI-MS (rel intensity): 313 (2), 349 (100), 419 (32).

$Bi(SCH_2C(O)OCH_3)_3$ 3c (R = Me). Addition of $BiCl_3$ (5.2 mmol) to methyl thioglycolate (15.7 mmol) and KOH (16 mmol) in 95% ethanol (150 mL) gave a dark yellow reaction mixture, which was stirred overnight, suction filtered, and concentrated by rotary evaporation. Yellow, needle-shaped crystals of **3c** appeared after 2 h at 4 °C and were collected after 1 day, yield 0.71 g, 26%; mp 65 °C. Anal. Calcd (found): C, 20.61 (20.71); H, 2.88 (2.84). IR: 569 (9,sh), 583 (13), 711 (10,sh), 864 (8), 880 (14), 889 (11), 899 (15), 992 (3), 1141 (12), 1204 (4), 1287 (2), 1308 (1), 1397 (5), 1434 (5), 1605w, 1691 (7), 1735 (6). Raman: 95 (2), 146 (5), 195 (6), 221 (9), 266 (3), 292 (1), 334 (7), 402 (11), 580 (20), 714 (21), 769 (22), 885 (15), 907 (16), 990 (14), 1151 (19), 1181 (23), 1296 (24), 1397 (17), 1435 (15), 1696 (14), 2886 (4), 2956 (8), 2976 (10), 2988 (11), 3034 (18). APCI-MS (rel intensity): 313 (4), 419 (100).

X-ray Crystallography. Data were collected on a Rigaku AFC5R diffractometer equipped with graphite-monochromated Mo Kα radiation [$\lambda = 0.71069$ Å] and a 12 kW rotating anode generator. The structures were solved by direct methods (SIR92 for **$1cCl_2$**, SHELXS86 for **2cCl** and **3c**) and refined by full-matrix least squares on F (teXsan) or F^2 (SHELXL) data using 2659 [(F^2) **$1cCl_2$**], 608 [(F) **2cCl**], and 3230 [(F) **3c**)] reflections, respectively. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. Unit cell parameters were obtained from the setting angles of 25 high-angle 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 $\omega-2\theta$ scan technique. The data were corrected for Lorentz and polarization effects. The intensities of three representative reflections were measured after every 150 reflections. A linear decay correction was applied to **3c**. Secondary extinction was refined in **2cCl** and **3c**. Empirical absorption corrections (ψ-scans) were also applied to all structures. In the case of **$1cCl_2$** there was difficulty refining lighter atoms (carbons and oxygens) anisotropically as a result of the large absorption of bismuth. As well,

---

(8) Herrmann, W. A.; Herdtweck, E.; Pajdla, L. *Z. Kristallogr.* **1992**, *198*, 257−264.

(9) Asato, E.; Katsura, K.; Mikuriya, M.; Turpeinen, U.; Mutikainen, I.; Reedijk, J. *Inorg. Chem.* **1995**, *34*, 2447−2454.

(10) Asato, E.; Katsura, K.; Mikuriya, M.; Fujii, T.; Reedijk, J. *Inorg. Chem.* **1993**, *32*, 5322−5329.

(11) Barrie, P. J.; Djuran, M. I.; Mazid, M. A.; McPartlin, M.; Sadler, P. J.; Scowen, I. J.; Sun, H. *J. Chem. Soc., Dalton Trans.* **1996**, 2417−2422.

(12) Burford, N.; Eelman, M. D.; Cameron, T. S. *Chem. Commun.* **2002**, 1402−1403.

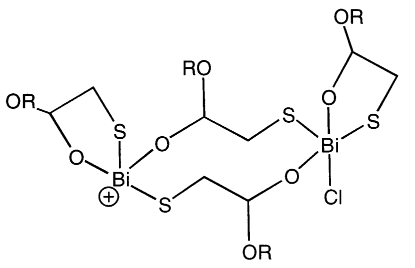
there was high residual electron density near bismuth at the end of the refinement.

Results and Discussion

Facile hydrolysis of many bismuth−element bonds to give essentially quantitative precipitation of bismuth as the bismuthyl unit (BiO^+) has impeded studies aimed at rational and systematic development of bismuth chemistry. Some complexes involving weakly donating functional groups have been isolated in the absence of moisture, but many conventional types of ligands have yet to be observed coordinated to bismuth. In this context, the synthesis and characterization database for complexes of bismuth with weak donors is brief and incomplete, relying on the isolation of the most readily crystallized compounds and determination of their solid state structure by X-ray crystallography. As a result, numerous complexes of bismuth represent unique examples for a particular ligand, rather than a series of related compounds, and general synthetic procedures have not been established to allow for assessment of physical and chemical properties.

Heterobifunctional chelate ligands containing a thiolate moiety and an auxiliary donor have proven effective for developing complexes of bismuth with new donors.[4] 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. Complexes of bismuth involving the heterobifunctional chelating ligands (e.g., aminoethanethiolate or hydroxyethanethiolate) allow for substantially higher solubility, as the auxiliary donor mimics the role of the donor solvent.[3] Therefore, these complexes can be routinely recrystallized and are amenable to studies of solutions by ESI-MS, which we have exploited to identify and isolate the first ester complexes of bismuth.

ESI-MS of reactions between methyl thioglycolate (MTG) and bismuth(III) chloride in absolute ethanol, 95% ethanol, or methanol reveal the presence of mono-, bis-, and tris-ester complexes of the type **1cCl**$_2$, **2cCl**, and **3c** as well as "ligand-bridged" dibismuth complexes **2c·2cCl** and **3c·2c**. The spectral observations are consistent with the isolation and solid state characterization data described for **1cCl**$_2$, **2cCl**, and **3c**.



2c·2cCl

Figure 1 shows the ESI-MS of an equimolar reaction mixture of $BiCl_3$ and MTG in absolute ethanol. The prominent mass peaks that contain bismuth all possess ethoxide functionalities (rather than the methoxide), indicating that quantitative transesterification of the ligand has occurred.[13] HCl resulting from the metathetical thiolation of bismuth is responsible for acidic conditions that facilitate exchange of methoxide for ethoxide from the solvent. With an equilibrium constant typically near unity, this transesterification reaction is driven to completion by the excess of ethanol. Consistently, **2cCl** (R = Me) is the only product isolated from the analogous reaction performed in methanol. Tandem ESI-MS data confirm the identification of **1c**, **2c**, and the sodiated complexes **Na2cCl** and **Na3c**. An adduct **2c·2cCl** is assigned to a peak at *m*/*z* 929, for which we propose the topological ligand-bridged structure based on the solid state structures described below.

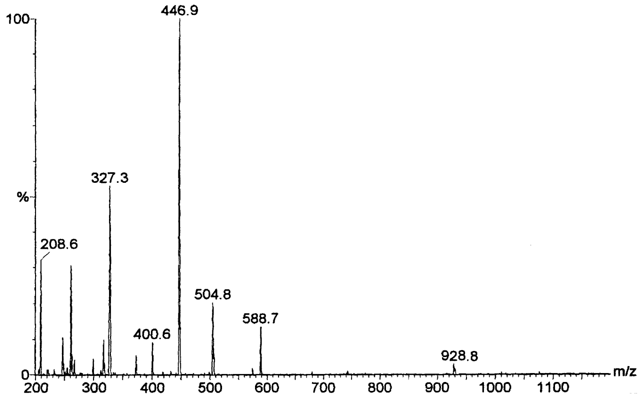


Figure 1. ESI-MS of a reaction mixture containing $BiCl_3$ and MTG in absolute ethanol. Structural assignments for prominent high-mass peaks are based on ESI-MS/MS data and represent monocations: *m*/*z* 327 **1c** (R = Et); *m*/*z* 447 **2c** (R = Et); *m*/*z* 505 **Na2cCl** (R = Et); *m*/*z* 589 **Na3c** (R = Et); *m*/*z* 929 **2c·2cCl** (R = Et).

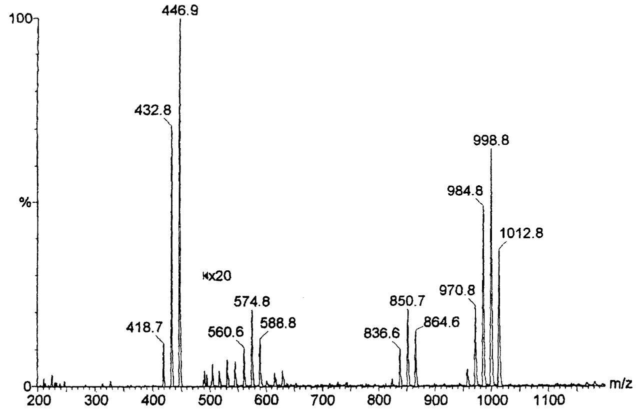
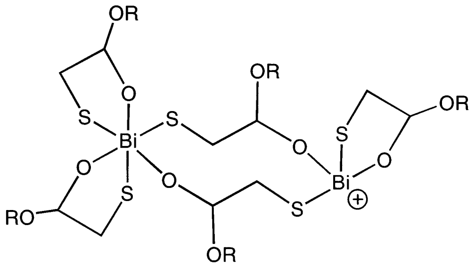


Figure 2. ESI-MS of a reaction mixture containing $BiCl_3$ and 2 equiv of MTG in 95% ethanol. The peak intensity is ×20 from *m*/*z* 475 to 1000. Structural assignments for prominent high-mass peaks are based on ESI-MS/MS data and represent monocations: *m*/*z* 419 **2c** (R = Me); *m*/*z* 433 **2c** (R = Me, Et); *m*/*z* 447 **2c** (R = Et); *m*/*z* 547 **Na3c** (R = Me); *m*/*z* 561 **Na3c** (R = 2Me, Et); *m*/*z* 575 **Na3c** (R = Me, 2Et); *m*/*z* 589 **Na3c** (R = Et); *m*/*z* 943 **3c·2c** (R = Me); *m*/*z* 957 **3c·2c** (R = 4Me, Et); *m*/*z* 971 **3c·2c** (R = 3Me, 2Et); *m*/*z* 985 **3c·2c** (R = Me, 3Et); *m*/*z* 999 **3c·2c** (R = Me, 4Et); *m*/*z* 1013 **3c·2c** (R = Et).

Transesterification of the ligand is mediated in 95% ethanol, as illustrated in Figure 2, which shows an ESI-MS of a reaction mixture involving excess MTG ($BiCl_3$ + 2MTG). All combinations of ethyl (R = Et) and methyl (R = Me) derivatives of **2c** and **Na3c** are observed, as well as the ligand-bridged adduct **3c·2c**.

---

(13) Loudon, G. M. *Organic Chemistry*, 3rd ed.; Benjamin/Cummings Publishing Company, Inc.: 1995.

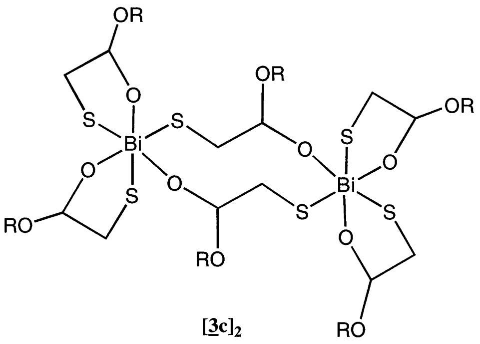


3c·2c

Figure 3 shows the ESI-MS of the reaction mixture involving an excess of KMTG ($BiCl_3$ + 3MTG + 3KOH) in 95% ethanol, in which thiolation of bismuth is facilitated by KCl metathesis, and potassiated complexes are more prevalent than sodiated complexes. Most interesting is the potassiated ligand-bridged dimer **K[3]₂** in this reaction mixture.

Although all three thiolation products (**$1cCl_2$**, **2cCl**, and **3c**) are nominally obtained from reactions of bismuth chloride with MTG, the conditions described in the Experimental Section provide the most facile isolation of [(ethyl ester)-methanethiolato]dichlorobismuth **$1cCl_2$**, bis[(methyl ester)-methanethiolato]chlorobismuth **2cCl**, and tris[(methyl ester)-methanethiolato]bismuth **3c**.

The solid state structures of **$1cCl_2$** (R = Et), **2cCl** (R = Me), and **$[3c]_2$** (R = Me) have been confirmed by X-ray crystallography (Tables 1 and 2).



$[3c]_2$

Figure 4 shows one view of each compound to illustrate the structural similarities and differences. Coordinate interaction of the carbonyl donor with bismuth is apparent in all cases despite the relatively low basicity of the ester carbonyl (pK_b 21.5; cf. OH pK_b 16.5, NR_2 pK_b 9.2, CO_2^- pK_b 9.2) functionality. The interaction is promoted by the chelate arrangement in most cases, but a nonchelate arrangement is evident for **3c** (see below). There are few reported examples of bismuth complexes involving $O_{carbonyl}$ donors. Most also rely on heterobifunctional ligands, and Bi−$O_{carbonyl}$ bond lengths range from 2.31 to 2.46 Å,[14−19] which compares with the range (2.4−2.6 Å) reported for structures of CBS.[8,9,11,20,21] These thiolate anchored complexes exhibit considerably longer Bi−$O_{carbonyl}$ bonds (2.56−2.86 Å) perhaps as a result of the preference for Bi−S bonds.

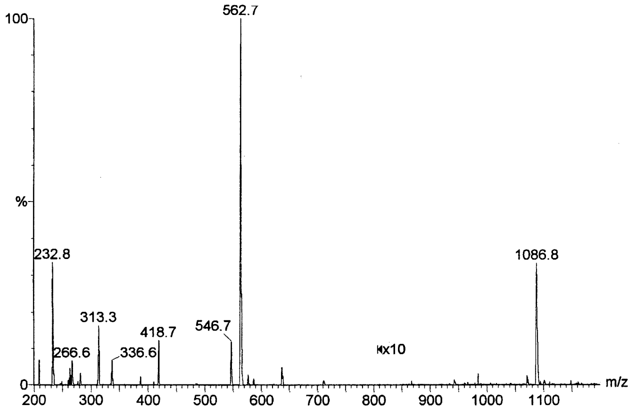


Figure 3. ESI-MS of a reaction mixture containing $BiCl_3$ and 3 equiv of MTG and KOH in 95% ethanol. The peak intensity is ×10 from *m/z* 800 to 1000. Structural assignments for prominent high-mass peaks are based on ESI-MS/MS data and represent monocations: *m/z* 419 **2c** (R = Me); *m/z* 547 **Na3c** (R = Me); *m/z* 563 **K3c** (R = Me); *m/z* 1087 **K[3c]₂** (R = Me).

Table 1. Crystal Data for **$1cCl_2$** (R = Et), **2cCl** (R = Me), and **3c** (R = Me)

	$1cCl_2$ (R = Et)	**2cCl** (R = Me)	**3c** (R = Me)
formula	$C_4H_7BiCl_2O_2S$	$C_6H_{10}BiClO_4S_2$	$C_9H_{15}BiO_6S_3$
fw	399.04	454.70	524.37
λ (Å)	0.71069 (Mo Kα)	0.71069 (Mo Kα)	0.71069 (Mo Kα)
space group	$P2_1/a$	Pa	$P\bar{1}$
a (Å)	8.055(3)	8.092(2)	9.340(1)
b (Å)	10.284(4)	9.13(1)	11.553(3)
c (Å)	11.099(4)	8.128(3)	8.168(1)
α (deg)	90	90	109.81(1)
β (deg)	100.69(4)	102.90(2)	92.98(2)
γ (deg)	90	90	103.38(2)
V (Å^3)	903.5(6)	585.5(6)	798.4(3)
Z	4	2	2
T (°C)	−130 ± 1	23 ± 1	23 ± 1
D_c (Mg m^{-1})	2.993	2.579	2.181
μ (cm^{-1})	202.43	155.99	114.28
final ρ_{max}/ρ_{min} (e$^-$/Å^3)	2.55/−1.94	0.72/−0.69	1.26/−0.80
R^a	0.029 ($I > 2\sigma$)	0.036 ($I > 3\sigma$)	0.030 ($I > 3\sigma$)
$R_w{}^b$		0.027 ($I > 3\sigma$)	0.029 ($I > 3\sigma$)
wR2^c	0.079 (all data)		
GOF	0.99	1.57	1.60

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [(\sum w(|F_o| - |F_c|)^2/\sum|F_o^2|)]^{1/2}$. [c] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum(F_o^2)^2]\}^{1/2}$.

Compounds **$1cCl_2$** and **3c** are dimeric in the solid state, while **2cCl** is polymeric. Compound **$1cCl_2$** (R = Et) associates via μ-thiolate interactions (Figure 4a), and a distorted square pyramidal environment for bismuth is imposed by the chelated carbonyl. Compound **2cCl** (R = Me) forms a one-dimensional array (representative section shown in Figure 4b) with heptacoordination for bismuth

---

(14) Carmalt, C. J.; Farrugia, L. J.; Norman, N. C. *Z. Anorg. Allg. Chem.* **1995**, *621*, 47−56.

(15) Burgess, J.; Fawcett, J.; Parsons, S. A.; Russell, D. R. *Acta Crystallogr.* **1994**, *C50*, 1911−1913.

(16) Diemer, R.; Keppler, B. K.; Dittes, U.; Nuber, B.; Seifried, V.; Opferkuch, W. *Chem. Ber.* **1995**, *128*, 335−342.

(17) Parola, S.; Papiernik, R.; Hubert-Pfalzgraf, L. G.; Jagner, S.; Håkansson, M. *J. Chem. Soc., Dalton Trans.* **1997**, 4631−4635.

(18) Fukin, G. K.; Pisarevskii, A. P.; Yanovskii, A. I.; Struchkov, Yu. T. *Russ. J. Inorg. Chem. (Transl. Zh. Neorg. Khim.)* **1993**, *38*, 1205.

(19) Kyriakidis, C. E.; Christidis, P. C.; Rentzeperis, P. J.; Tossidis, I. A.; Bolos, C. A. *Z. Kristallogr.* **1990**, *193*, 101−110.

(20) Asato, E.; Driessen, W. L.; de Graaff, R. A. G.; Hulsbergen, F. B.; Reedijk, J. *Inorg. Chem.* **1991**, *30*, 4210−4218.

(21) Herrmann, W. A.; Herdtweck, E.; Pajdla, L. *Inorg. Chem.* **1991**, *30*, 2579−2581.

(22) Reglinski, J. In *Chemistry of Arsenic, Antimony, and Bismuth*; Norman, N. C., Ed.; Blackie Academic & Professional: London, 1998.

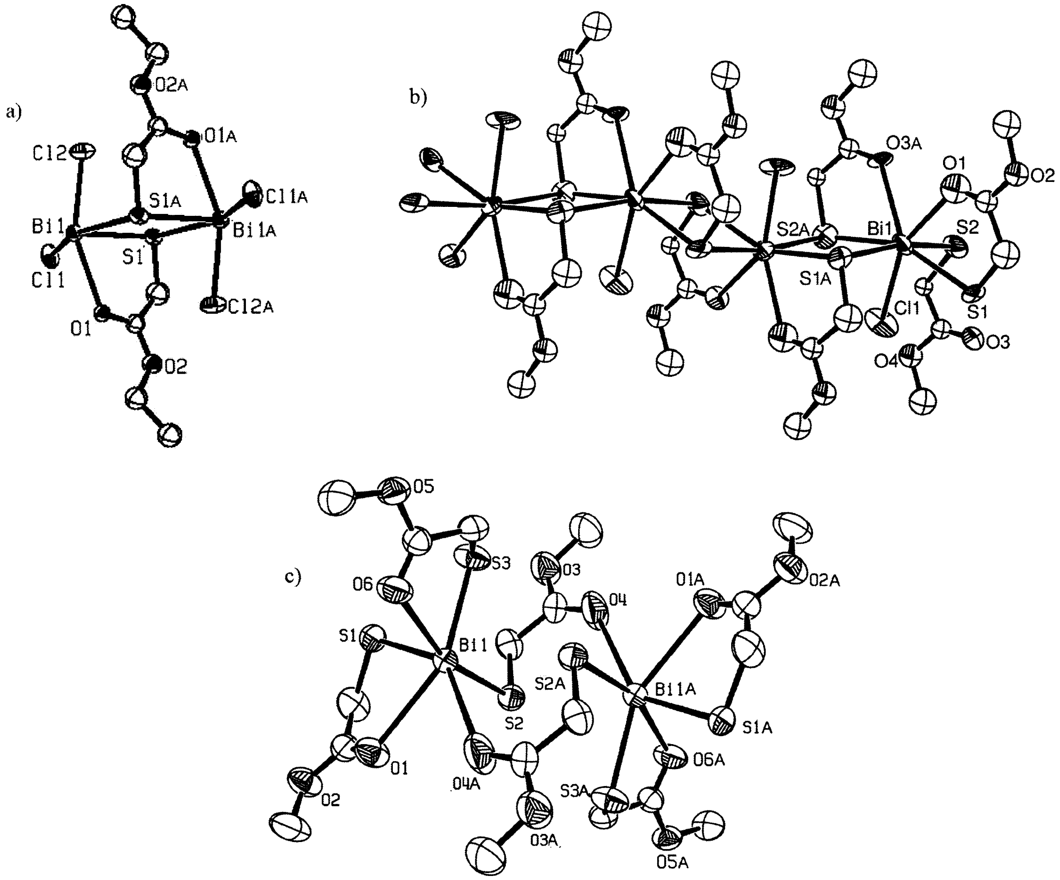


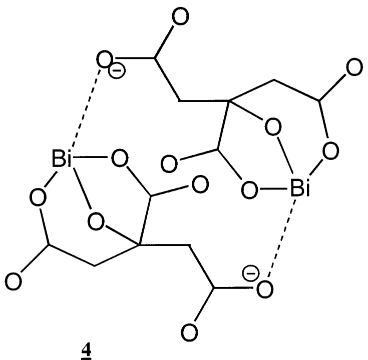
Figure 4. Crystallographic views of (a) **$1cCl_2$**, (b) **2cCl**, and (c) **[3c]$_2$**. Thermal ellipsoids are drawn to 50% probability. Hydrogen atoms have been omitted for clarity.

Table 2. Comparison of Selected Internuclear Distances (Å) for **$1cCl_2$** (R = Et), **2cCl** (R = Me), and **[3c]$_2$** (R = Me)

$1cCl_2$ (R = Et)		**2cCl** (R = Me)		**[3c]$_2$** (R = Me)	
Bi−O1	2.562(6)	Bi−O1	2.68(2)	Bi−O1	2.807(5)
		Bi−O3A	2.77(2)	Bi−O6	2.861(5)
				Bi−O4A	3.071(7)
Bi−S1	3.021(2)	Bi−S1	2.849(7)	Bi−S1	2.568(2)
		Bi−S2	2.884(6)	Bi−S2	2.608(2)
				Bi−S3	2.574(2)
Bi−S1A	3.250(2)	Bi−S1A	2.963(7)	Bi−S2A	3.331(2)
		Bi−S2A	2.861(9)		
Bi−Cl1	2.593(2)	Bi−Cl1	2.535(6)		
Bi−Cl2	2.552(2)				
Bi−Cl1A	3.371(3)				
Bi−Cl2A	3.565(3)				

imposed by four equatorially disposed sulfur centers, two oxygen centers (carbonyl), and one chlorine atom. Although a molecular unit represented by drawing **2** is not discernible in the polymeric solid state structure of **2cCl**, there is a clear analogy with the bis(hydroxyethanethiolate) **2aCl**[3] and bis(aminoethanethiolate) **2bCl**[4] complexes. The structure of **3c** may be viewed as a dimer **[3c]$_2$** (Figure 4c) involving two bridging and four terminal chelate ligands. The bridging ligands exhibit incipient chelation with a longer *μ*-thiolate Bi−S−Bi distance [Bi−S(2A), 3.331(2) Å] than that responsible for the bridging ligand interaction [Bi−S(2), 2.608(2) Å]. Interestingly, the Bi−S distance trend for the series **$1cCl_2$** > **2cCl** > **3c** is counter to that of the Bi−O distance trend (**$1cCl_2$** < **2cCl** < **3c**).

In comparison with the polymeric structure of **2cCl**, substitution of the chloride for a third thiolate in **3c** is manifested in a disruption of the equatorial (square plane, trans) arrangement of the sulfur interactions around bismuth resulting in a distorted facial arrangement of thiolate interactions and consequential relative shortening of Bi−S. The dimeric structure for **[3c]$_2$**, imposed by the pendant ester ligand, is analogous to that observed for CBS (**4**),[10] but is relatively simple due to the presence of methyl groups that preclude the interdimer interactions observed in the latter. In this context, bismuth complexes of the ester functionality are models for the relatively complicated carboxylate chemistry of bismuth.



4

Conclusions

Synthesis and isolation of specific complexes has previously driven understanding of the reaction and structural chemistry of bismuth and many inorganic elements. ESI-MS now allows for a broader evaluation of reaction mixtures with definitive relationships between observations made for gas phase samples and those in the solid state. These results also provide a systematic and comprehensive series of structurally simple esterthiolatobismuth complexes, illustrating the coordinate flexibility of bismuth(III) and confirming the general synthetic applicability of heterobifunctional thiolate coordination chemistry. We now have the opportunity to perform a more comprehensive study of the interactions between bismuth and other biorelevant functional groups including amides [$C(O)NR_2$].

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada, the Killam Trusts, the Canada Research Chairs program, the Canada Foundation for Innovation, the Nova Scotia Research and Innovation Trust Fund, and industrial supporters for funding and Dalhousie Mass Spectrometry Center for the use of instrumentation.

Supporting Information Available: Crystallographic data for **1cCl$_2$** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC0261934