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Spectroscopic, Structural, and Mass Spectrometric Studies on Two Systematic Series of Dithiabismuth(III) Heterocycles: Identification of Bismuthenium Cations and Their Solvent Complexes

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Abstract: General, high-yield metathesis reactions provide two related and comprehensive series of dithiabismuth heterocycles. The compounds are characterized by spectroscopic and X-ray crystallographic analysis. Monocycles 2-chloro-1,3-dithia-2-bismolane (**1**), 2-chloro-1,3-dithia-2-bismane (**2**), 2-chloro-1,3-dithia-2-bismepane (**3**), 2-chloro-1,3,6-trithia-2-bismocane (**4**), and 2-chloro-1,3-dithia-6-oxa-2-bismocane (**5**) are kinetically stable with respect to the tethered bicyclic derivatives 1,2-bis((1,3-dithia-2-bismolan-2-yl)thio)ethane (**6**), 1,3-bis((1,3-dithia-2-bisman-2-yl)thio)propane (**7**), 1,4-bis((1,3-dithia-2-bismepan-2-yl)thio)butane (**8**), bis((1,3,6-trithia-2-bismocan-2-yl)thio)ethyl) sulfide (**9**), and bis(((1,3-dithia-6-oxa-2-bismocan-2-yl)thio)ethyl) ether (**10**). Mass spectrometry provides an excellent means of characterization of compounds of this nature and is responsible for the identification of monocyclic bismuthenium cations as general and dominant dissociation products. In addition, the atmospheric pressure chemical ionization technique reveals solvent coordination chemistry of the bismuthenium cations.

Introduction

Bismuth preparations have been used to treat a variety of medical disorders for over two hundred years[2] with little understanding of their mechanism of activity. Recent developments indicate a special bioactivity for thiabismuth compounds.[3] The prevalence and structural simplicity evident for chelated or cyclic thiabismuth compounds[4−8] highlight them as ideal candidates for systematic study. On this basis we have employed the bismuth metathesis recognized for alcohols (formation of Bi−O bonds)[9] and the preliminary observations of Powell[10] and others[11,12] to generate a comprehensive series of monoheterocyclic bismuth compounds of varying ring size (**1**−**5**), as well as a series of tethered bicyclic systems (**6**−**10**) (Chart 1). Characterization by X-ray crystallography and vibrational spectroscopy establishes the structural simplicity of these compounds. The systematic relationships within the series has allowed for an extensive mass spectrometric study which reveals the prominence of bismuthenium cations.

Experimental Procedure

General Procedures. Bismuth(III) chloride, bismuth(III) nitrate pentahydrate, bismuth oxychloride, 1,2-ethanedithiol, 1,3-propanedithiol, 1,4-butanedithiol, 2-mercaptoethyl ether, and 2-mercaptoethyl sulfide were used as received from Aldrich. Melting points were recorded on a Fisher-Johns melting point apparatus and are uncorrected. 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. Chemical analyses were performed by Fenwick Laboratories, Halifax, Nova Scotia (Perkin-Elmer Elan 5000 ICPMS), and Canadian Microanalytical Service Ltd., Delta, British Columbia. Solution ^{1}H NMR data were recorded on a Bruker AC-250 spectrometer. Chemical shifts are reported in parts per million relative to TMS and are calibrated to the internal solvent signal.

Electron impact (EI) mass spectra were obtained using either a VG ZAB-EQ double-focusing mass spectrometer (VG Organic, Manchester, U.K.) or a VG 20-250 quadrupole mass spectrometer (VG Organic). The spectra were obtained at an ionizing electron energy of 70 eV, using a standard solids probe or a direct probe. Accurate mass measurements were made on the ZAB-EQ instrument at a mass resolution of at least 8000 (10% valley definition) with perfluorokerosine (PFK) as the reference compound. Data acquisition for the ZAB-

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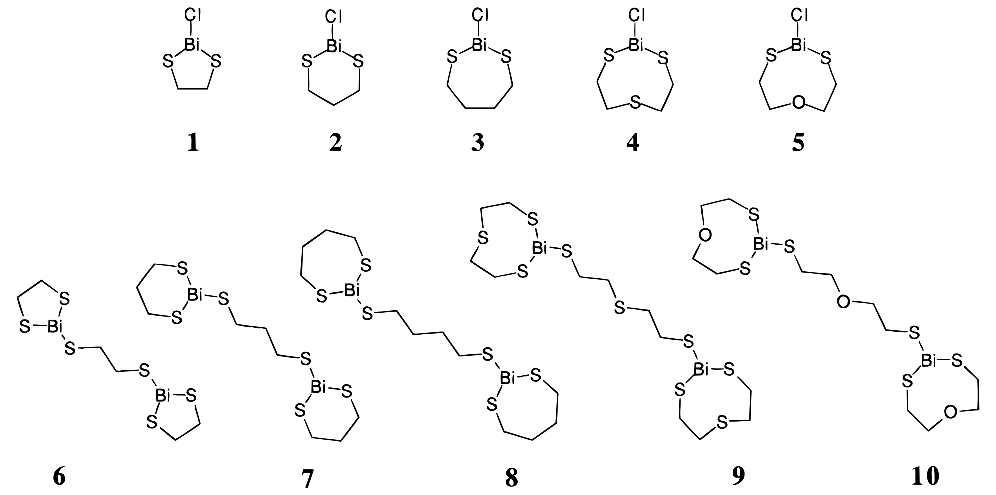
Chart 1



EQ was performed using a Digital VAX 4000 Model 60 computer running Fisons OPUS software. The 20-250 was controlled using a Fisons 11-250J data system running on a Digital PDP11\73 computer.

Atmospheric pressure chemical ionization (APCI) spectra were obtained using either a SCIEX API-III triple quadrupole mass spectrometer (SCIEX, Ontario, Canada) controlled by a Macintosh 950 Quadra computer using SCIEX software, or a VG Quattro mass spectrometer (VG Organic) controlled by a Digital DECpc using Fisons MassLynx software. Solvent flow (1:1 water/acetonitrile at 200 μL/min) and sample injection (10−15 μL) used a Hewlett-Packard Series II 1090 liquid chromatograph pump with autoinjector or a Shimadzu LC-6A with a Rheodyne syringe loading sample injector. MS/MS spectra on either the SCIEX API-III or the VG Quattro used argon collision gas in the second quadrupole, resulting in a beam attenuation of approximately 50%.

General Synthetic Procedure. In a typical reaction, the dithiol was added dropwise to a stirred slurry prepared by mixing bismuth chloride or bismuth nitrate pentahydrate at appropriate stoichiometry (1:1 or 3:2) in ethanol (150 mL). Yellow precipitate formed immediately, and the reaction mixture was allowed to stir at room temperature overnight. The precipitate was filtered using a Buchner funnel, washed with 20 mL aliquots of distilled water, ethanol, and acetone, respectively, and air dried. Yields, chemical analyses, and IR and Raman data for each compound are presented in Table 1.

2-Chloro-1,3-dithia-2-bismolane (**1**),[10] 2-chloro-1,3-dithia-2-bismane (**2**), 2-chloro-1,3-dithia-2-bismepane (**3**), 1,3-bis((1,3-dithia-2-bisman-2-yl)thio)propane (**7**), and 1,4-bis((1,3-dithia-2-bismepan-2-yl)thio)-butane (**8**) were spectroscopically characterized as analytically pure powders. 2-Chloro-1,3,6-trithia-2-bismocane (**4**),[11] 2-chloro-1,3-dithia-6-oxa-2-bismocane (**5**), bis(((1,3,6-trithia-2-bismocan-2-yl)thio)ethyl) sulfide (**9**), and bis(((1,3-dithia-6-oxa-2-bismocan-2-yl)thio)ethyl) ether (**10**) were recrystallized as yellow needles from hot DMSO. 1,2-Bis-((1,3-dithia-2-bismolan-2-yl)thio)ethane (**6**) was recrystallized from hot 1,2-ethanedithiol as dark yellow cubic crystals.

2-Chloro-1,3-dithia-2-bismolane (**1**) was also formed by the reaction of bismuth oxychloride with 1,2-ethanedithiol in HCl (1 M), and was characterized by Raman spectroscopy and chemical analysis, yield 73.0%.

Formation of 6 from 1. **1** (0.58 g, 1.7 mmol) was combined with 1,2-ethanedithiol (0.11 g, 1.1 mmol) in aqueous $NaNO_3$ (0.10 M). The slurry was allowed to stir overnight at room temperature, and the yellow precipitate was filtered, air dried, and characterized by melting point analysis and Raman spectroscopy as **6**, yield 94%.

Formation of 9 from 4. **4** (1.4 g, 3.6 mmol) was combined with 2-mercaptoethyl sulfide (0.72 g, 4.7 mmol) in aqueous $NaNO_3$ (0.12 M). The slurry was allowed to stir overnight at room temperature, and the yellow precipitate was filtered, air dried, and characterized by melting point analysis and Raman spectroscopy as **9**, yield 97%.

Isolation of 2-Chloro-2,2-dipyridyl-1,3-dithia-2-bismolane (11). **1** (0.55 g, 1.4 mmol) was dissolved in hot pyridine (30 mL) and the solution slowly cooled to room temperature, giving white needle-like crystals which were filtered using a Buchner funnel, washed with cold pyridine (10 mL), air dried for 30 min, and characterized as **11**:[10] yield 0.46 g, 1.1 mmol, 81%; dp 130 °C; IR (cm^{-1}) 1412 (s), 1276 (w), 1197 (m), 1185 (s), 1108 (m), 915 (w), 837 (w), 725 (m), 681 (m), 581 (w) cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 1.7 (s, 4H), 7.1 (s, 4H), 7.4 (s, 2H), 8.6 (s, 4H).

X-ray Crystallography. Crystals of **4**, **5**,[13] **6**, **9**, and **11** suitable for crystallography were obtained as described above. The crystals of **9** were twinned, and a fragment was used for data collection. X-ray diffraction data were obtained on Enraf-Nonius CAD-4 and Rigaku AFC5R diffractometers. Unit cell parameters were obtained from the setting angles of a minimum of 20 accurately centered reflections having $\theta > 24°$. The choice of space groups was based on systematically absent reflections and confirmed by the successful solution and refinement of the structures. An empirical absorption correction based on azimuthal scans of several reflections was applied in each case, resulting in transmission factors listed in Table 2. The data were corrected for Lorentz and polarization effects. A correction for secondary extinction was applied to structures **4** and **6**. The structures were solved by direct methods (Shelxs-86 for **4**, **5**, **9**, and **11**; PATTY for **6**).[14] All non-hydrogen atoms were refined anisotropically, except for structure **6** where only Bi and S were made anisotropic. Hydrogen atoms were placed in their geometrically calculated positions but not refined. In the case of compound **11**, the pyridine rings were constrained to have reasonable geometries during refinement. Full-matrix least squares refinement was carried out using the teXsan software package[15] and/or Shelxl-93.[16] For both programs $R = \sum||F_o| - |F_c||/\sum|F_o|$. Atomic scattering factors and corrections for anomalous dispersion were taken from the *International Tables for Crystallography*.[17] All pertinent crystallographic data are summarized in Table 2. Selected bond lengths and angles are presented in Table 3.

Results and Discussion

Powell first recognized the rapid, high-yield reaction between $BiCl_3$ and ethanedithiol, and characterized the product as 2-chloro-1,3-dithiabismolane (**1**) by elemental analysis[10] and infrared spectroscopy,[18] and by formation of a pyridine complex

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[13] The crystals of **5** were of poor quality: $C_4H_8BiClOS_2$, space group *Pmna*, $a = 7.885(4)$ Å, $b = 12.307(5)$ Å, $c = 9.158(9)$ Å, $V = 888.7(10)$ Å$_3$, $D_{calcd} = 2.845$ Mg/m^3, GOF = 1.220, $R = 0.0587$, $R_w = 0.1003$, isostructural with **4**.

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Table 1. Yields, Melting Points, Analyses, and Vibrational Spectral Data for Compounds **1**−**10**

			elemental analysis (%)			IR data (cm^{-1})		Raman data (cm^{-1})	
compd	yield (g (%))	mp [dp] (°C)	C_{calc} (C_{found})	H_{calc} (H_{found})	S_{calc} (S_{found})				
1	102.5 (82)	[120]	7.14 (7.76)	1.20 (1.25)	19.05 (19.35)	237 (s) 330 (s) 436 (m)	638 (m) 665 (m)	76 (s) 105 (s) 126 (s) 145 (s) 200 (s)	279 (s) 324 (vs) 435 (w) 635 (m) 662 (w)
2	5.95 (95)	110	10.24 (10.54)	1.72 (1.72)	14.29 (11.16)	295 (vs) 480 (w) 528 (m)	611 (w) 638 (w) 669 (m)	102 (vs) 164 (s) 300 (vs) 445 (w)	480 (w) 543 (w) 638 (m) 671 (m)
3	4.59 (97)	[100]	13.17 (13.61)	2.21 (2.12)	17.59 (15.12)	286 (w) 304 (m) 370 (w)	388 (w) 420 (w) 639 (w)	68 (s) 89 (vs) 114 (vs) 132 (vs) 194 (s) 255 (vs)	277 (vs) 305 (vs) 371 (m) 461 (w) 505 (w) 641 (m)
4	15.01 (87)	[170]	12.11 (12.34)	2.03 (2.03)	24.25 (23.77)	283 (s) 294 (s) 332 (s) 422 (s) 452 (w)	463 (m) 608 (w) 629 (w) 660 (m) 684 (w)	81 (s) 120 (vs) 163 (s) 190 (s) 225 (s) 294 (vs) 331 (m)	418 (w) 450 (w) 610 (w) 628 (m) 659 (m) 684 (w)
5	4.78 (92)	[190]	12.62 (14.64)	2.12 (2.39)	16.80 (20.65)	224 (s) 256 (s) 293 (s) 316 (m) 366 (w)	471 (m) 509 (w) 538 (w) 666 (m)	74 (s) 118 (vs) 182 (s) 237 (s) 275 (s) 293 (s)	318 (vs) 361 (w) 468 (w) 534 (w) 664 (m)
6	1.27 (97)	[145]	10.38 (10.60)	1.74 (1.72)	27.70 (27.65)	255 (vs) 269 (vs) 302 (m) 318 (s)	433 (s) 634 (m) 662 (m) 672 (w)	71 (s) 86 (s) 104 (s) 132 (s) 159 (s) 179 (s) 196 (s)	258 (vs) 269 (vs) 288 (s) 310 (vs) 428 (m) 633 (m) 660 (w)
7	2.06 (92)	[170]	14.68 (15.11)	2.46 (2.52)	26.12 (22.23)	240 (s) 264 (s) 297 (vs) 307 (w) 319 (s)	430 (m) 636 (w) 663 (w) 677 (m)	86 (s) 136 (s) 165 (s) 181 (s) 230 (s) 240 (s)	278 (vs) 430 (w) 617 (w) 641 (w) 658 (w) 671 (w)
8	2.58 (98)	[140]	18.51 (19.02)	3.11 (3.07)	24.71 (23.62)	256 (vs) 266 (vs) 319 (vs) 350 (m) 378 (m) 429 (s)	526 (w) 570 (w) 659 (m) 673 (m) 669 (m)	83 (vs) 120 (vs) 190 (s) 203 (s) 246 (vs) 267 (vs)	313 (vs) 370 (m) 408 (m) 460 (w) 646 (m)
9	1.28 (67)	[180]	16.47 (16.78)	2.77 (2.71)	32.99 (32.47)	248 (s) 326 (m) 467 (w)	493 (m) 530 (w) 669 (m)	68 (s) 102 (s) 126 (s) 162 (s) 181 (s) 242 (s) 271 (vs)	294 (vs) 332 (m) 425 (w) 620 (m) 656 (w) 682 (m)
10	2.06 (99)	177− 178	17.44 (17.63)	2.93 (2.85)	23.27 (26.65)	283 (vs) 294 (vs) 301 (s) 335 (s) 422 (s) 453 (m)	470 (m) 608 (w) 629 (w) 660 (s) 684 (m)	92 (s) 169 (s) 213 (s) 242 (vs)	271 (s) 303 (s) 491 (w) 666 (m)

characterized in a similar fashion to that of **1**. We have now confirmed these observations with a comprehensive characterization of **1** and **11**. More importantly, we have exploited the general quantitative metathesis reaction to generate a series of cyclic chlorodithiabismuth compounds (**1**−**5**) with increasing ring size (Table 1). As a modification of Powell's procedure all reactions occur in the absence of acid. Moreover, BiOCl is demonstrated to be the actual reactant by the observation of **1** formed in high yield from the reaction of BiOCl with 1,2-ethanedithiol.[19] A formal double metathesis at each bismuth site is inferred in all cases, and the cyclic structures of compounds **1** (as the dipyridyl complex **11**), **4**, and **5**[13] are confirmed by X-ray crystallography (Tables 2 and 3). The spectroscopic data for uncomplexed bismolane **1**, bismane **2**, and bismepane **3**, are consistent with the cyclic structure (X-ray quality crystals were not obtained for these compounds).

When $Bi(NO_3)_3$ is combined with the same dithiols, a complete metathesis is observed to give three Bi−S bonds at each bismuth site, including a cyclic or chelate formation analogous to compounds **1**−**5**. The compounds are assigned

Table 2. Crystallographic Data

	4	**6**	**9**	**11**
formula	$C_4H_8BiClS_3$	$C_6H_{12}Bi_2S_6$	$C_{12}H_{24}Bi_2S_9$	$C_{12}H_{14}BiClN_2S_2$
FW	396.72	694.48	874.82	494.81
crystal description	yellow needle	yellow cube	yellow needle	cream needle
crystal size (mm)	0.40 × 0.15 × 0.10	0.12 × 0.15 × 0.15	0.007 × 0.015 × 0.200	0.10 × 0.15 × 0.30
space group	*Pnma*	$P2_1/c$	$P\bar{1}$	$P2_1$
a/Å	8.1280(9)	8.875(4)	9.757(2)	9.590(3)
b/Å	12.263(5)	17.582(12)	16.625(2)	9.206(3)
c/Å	9.2529(9)	18.250(9)	37.942(3)	9.761(2)
Å/deg	90	90	90.05(2)	90
β/deg	90	96.05(4)	107.84(3)	117.1(2)
γ/deg	90	90	105.81(1)	90
V/Å^3	922.3(6)	2832(3)	1174.9(6)	767.1(4)
Z	4	8	2	2
D_c/(Mg m^{-3})	2.857	3.260	2.473	2.142
μ/(cm^{-1})	199.7	256.48	364.17[a]	118.81
abs corr method	ϕ scan	ϕ scan	ϕ scan	ϕ scan
abs max−min	0.552−1.000	0.676−1.000	0.448−1.000	0.614−1.000
2θ range (deg)	37.0−42.3	24.0−37.0	41.15−58.82	24.58−29.03
no. of observed reflections	493 ($I > 3.00\sigma(I)$)	1897 ($I > 3.00\sigma(I)$)	3718 ($I > 3.00\sigma(I)$)	1051 ($I > 2.00\sigma(I)$)
no. of parameters refined	47	194	209	162 (30 restraints)
Flack parameter				0.018(12)
R	0.029	0.035	0.045	0.019
R_w	0.033	0.035	0.056	0.047
GOF	1.22	1.19	4.26	1.14

[a] Cu Kα.

the tethered bicyclic structures **6**−**10** on the basis of the X-ray structure of **6** and **9**, and the comparative analytical, infrared, Raman, and mass spectral data for the series of compounds **6**−**10**. The observed products are independent of stoichiometry, illustrating a dominant thermodynamic preference for the Bi−S bond formation and suggesting that the chloro-substituted monocyclic derivatives are kinetically stable with respect to the tethered bicyclic analogues **6**−**10** in the presence of excess dithiol. Indeed, compound **1** can be quantitatively tethered to give **6** on introduction of sodium nitrate in the presence of ethanedithiol, which presumably facilitates tethering by promoting Bi−Cl heterolytic bond cleavage. This is a general process allowing for tethering of all heterocycles **1**−**5** and the possibility of the tether having a different chain length than the heterocycle. The observed structure of **6** is consistent with the previously reported structure of the antimony analogue,[20] and is reminiscent of a diazabismuth derivative.[21]

Structural Features. Compounds **1**−**10** have very low solubilities in most solvents, but anomalous is the dissolution of **1** in pyridine. Colorless needle-like crystals of **11** can be obtained, which slowly release pyridine and lose crystallinity. The X-ray structure of **11** (Figure 1) reveals a dipyridyl complex of **1** with the pyridine ligands in a *trans* orientation with respect to a distorted square plane demonstrated by the S_2C_2 chelate ring and two chlorine atoms. The chlorine centers are dicoordinate with essentially equivalent [3.111(4) and 3.231(5) Å] Bi−Cl bonds, providing an alternating Bi−Cl polymeric backbone which links the heterocycles. The bond lengths are substantially longer than terminal Bi−Cl bonds[5,7,22,23] and are comparable with reported bridging bonds.[24] A seventh coordination site is imposed by a contact to a sulfur atom of a neighboring heterocycle. This intermolecular contact is longer [3.443(5) Å] than the two equivalent endocyclic Bi−S bonds [2.545(4) and 2.542(6) Å]. The Bi−N bonds are similar [2.534(8) and 2.592(9) Å] and are typical of N→Bi coordinate bonds.[6,23,25,26]

Compounds **4**, **5**,[13] **6**, and **9** have been crystallized free of solvent and show molecular structures with significant intermolecular and intramolecular interactions. Compounds **4** (Figure 2) and **5** are isostructural and can be viewed as eight-membered heterocycles with a cross-ring 2,6 intramolecular interaction, involving a coordinative donation from sulfur (in **4**, or oxygen in **5**) to bismuth, a structural arrangement that is now well established for many nonmetal elements.[27] Consistent with this bonding model, the two symmetry-related heterocyclic Bi−S bonds [2.541(6) Å] of **4** are slightly shorter than the cross-ring Bi−S bond [2.849(5) Å], and are comparable to the endocyclic Bi−S bonds in **1** [2.545(4) and 2.542(6) Å]. Three intermolecular contacts from chlorine and the sulfur centers of a neighboring molecule impose a seven-coordinate environment for bismuth. The structures are fundamentally analogous to those reported for the phenyl derivative of **5**,[8] and the corre-

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Table 3. Selected Bond Lengths (Å) and Angles (deg)

Bond Distances

4		**6**[a]		**9**		**11**	
Bi−Cl(1)	2.682(5)	Bi(1)−S(1)	2.591(7)	Bi(1)−S(1)	2.597(5)	Bi−Cl(1)	3.111(4)
Bi−S(1)	2.849(5)	Bi(1)−S(2)	2.565(7)	Bi(1)−S(2)	2.559(4)	Bi−N(1)	2.534(8)
Bi−S(2)	2.541(6)	Bi(1)−S(3)	2.633(7)	Bi(1)−S(3)	3.071(5)	Bi−N(2)	2.592(9)
S(1)−C(1)	1.75(2)	S(1)−C(1)	1.82(2)	Bi(1)−S(7)	2.615(4)	Bi−S(1)	2.545(4)
S(2)−C(2)	1.78(2)	S(2)−C(2)	1.81(3)	Bi(2)−S(4)	2.576(4)	Bi−S(2)	2.542(6)
C(1)−C(2)	1.42(2)	C(1)−C(2)	1.42(3)	Bi(2)−S(5)	3.197(5)	S(1)−C(1)	1.82(1)
Bi(1)*−Cl(1)	3.285(6)	S(3)−C(3)	1.79(3)	Bi(2)−S(6)	2.599(4)	S(2)−C(2)	1.83(2)
Bi(1)*−S(2)	3.534(7)	S(4)−C(4)	1.83(3)	Bi(2)−S(9)	2.566(5)	C(1)−C(2)	1.52(2)
		C(3)−C(4)	1.46(4)	Bi(2)−S(8)	3.192(4)	Bi−S(1)*	3.443(5)
		Bi(2)−S(4)	2.635(7)	S(1)−C(1)	1.81(2)	Bi−Cl(1)*	3.231(5)
		Bi(2)−S(5)	2.552(6)	S(3)−C(2)	1.79(2)		
		Bi(2)−S(6)	2.553(7)	S(3)−C(3)	1.82(2)		
		S(5)−C(5)	1.75(3)	S(4)−C(5)	1.84(2)		
		S(6)−C(6)	1.85(3)	S(7)−C(9)	1.81(2)		
		C(5)−C(6)	1.48(3)	C(1)−C(2)	1.51(3)		
		Bi(1)−S(5)	3.170(6)	C(3)−C(4)	1.46(3)		
		Bi(1)−S(4)	3.902(7)	C(5)−C(6)	1.52(3)		
		Bi(1)−S(1)*	3.134(7)	C(9)−C(10)	1.53(2)		
		Bi(1)−S(4)*	3.391(1)	C(11)−C(12)	1.53(3)		
		Bi(2)−S(3)*	3.214(7)	Bi(1)−S(1)*	3.346(5)		
		Bi(2)−S(1)*	3.257(6)	Bi(1)−S(7)*	3.261(5)		
		Bi(2)−S(4)*	3.5910(9)	Bi(2)−S(6)*	3.342(4)		

Bond Angles

4		**6**		**9**		**11**	
Cl(1)−Bi−S(1)	155.3(2)	S(2)−Bi(1)−S(1)	83.8(2)	S(1)−Bi(1)−S(2)	94.2(2)	Cl(1)−Bi−S(1)	157.26(9)
Cl(1)−Bi−S(2)	85.2(1)	S(2)−Bi(1)−S(3)	91.2(2)	S(1)−Bi(1)−S(3)	75.5(1)	Cl(1)−Bi−S(2)	75.3(2)
S(1)−Bi−S(2)	79.0(1)	S(1)−Bi(1)−S(3)	84.7(2)	S(2)−Bi(1)−S(7)	95.6(2)	Cl(1)−Bi−N(1)	82.8(4)
S(2)−Bi−S(2A)	99.4(3)	S(2)−Bi(1)−S(5)	155.9(2)	S(4)−Bi(2)−S(6)	93.9(1)	Cl(1)−Bi−N(2)	101.9(3)
Bi−S(1)−C(1)	101.7(6)	S(3)−Bi(1)−S(1)*	166.6(2)	S(4)−Bi(2)−S(9)	93.5(2)	S(1)−Bi−S(2)	84.8(2)
Bi−S(2)−C(2)	107.5(8)	S(1)*−Bi(1)−S(4)*	74.9(1)	S(6)−Bi(2)−S(5)	74.2(1)	N(1)−Bi−N(2)	173.1(4)
C(1)−S(1)−C(1)	105(1)	S(1)−Bi(1)−S(1)*	82.0(2)	S(6)−Bi(2)−S(9)	81.7(2)	Bi−S(1)−C(1)	100.2(5)
S(1)−C(1)−C(2)	121(1)	S(5)−Bi(2)−S(6)	84.3(2)	S(9)−Bi(2)−S(8)	75.9(1)	Bi−S(2)−C(2)	100.5(5)
S(2)−C(2)−C(1)	123(1)	S(6)−Bi(2)−S(4)	86.4(2)	Bi(1)−S(1)−C(1)	104.0(7)	S(1)−C(1)−C(2)	112.3(9)
		S(5)−Bi(2)−S(4)	104.1(2)	Bi(1)−S(2)−C(4)	96.6(6)	S(2)−C(2)−C(1)	112.3(9)
		S(6)−Bi(2)−S(1)*	78.7(2)	Bi(2)−S(4)−C(5)	100.1(6)		
		S(4)−Bi(2)−S(4)*	90.4(2)	S(3)−C(2)−C(1)	116(1)		
		S(3)−Bi(2)−S(1)*	129.3(3)	S(5)−C(7)−C(8)	114(1)		
				S(7)−C(9)−C(10)	109(1)		
				S(8)−C11−C(12)	109(1)		

[a] Structural parameters for one of two independent molecules in the asymmetric unit.

sponding arsocane[28] and stibocanes[29] with expected bond length and bond angle adjustments.

Two structurally identical molecules are observed in the asymmetric unit for **6**, and its tethered bicyclic structure (Figure 3) is similar to that of **9** (Figure 4) in that they both possess essentially equivalent Bi−S bond lengths within the heterocycle [one molecule of **6**, 2.565(7), 2.591(7), 2.552(7), 2.553(7) Å; **9**, 2.597(5), 2.559(4), 2.576(4), 2.599(4) Å] and for the exocyclic tether linkages [**6**, 2.633(7), 2.635(7) Å; **9**, 2.615(4), 2.566(5) Å]. The cross-ring S→Bi contacts observed in the structure of **4** are also evident in the rings of **9**, although they are slightly longer [**4**, 2.849(5) Å; **9**, 3.071(5), 3.197(4) Å]. In addition, donations from the tether sulfur centers to a bismuth site are observed in both **6** and **9**, which effect the folding or wrapping of the tether. It is interesting to note the five-membered ring motif that is generated by most of the intramolecular interactions and which is likely responsible for the onset of five-membered ring fragmentation in the mass spectra (*vide supra*). The intermolecular and intramolecular contacts provide for six- and seven-coordinate bismuth environments.

Mass Spectrometric Features. Table 4 summarizes the electron ionization (EI) mass spectra for compounds **1**−**5**. Molecular ions are observed for **1**, **4**, and **5**. Figure 5a shows the strong molecular ion $M^{\bullet+}$ for **1** as well as the major fragment ion $[M - Cl]^+$, which have been confirmed by accurate mass measurements ($M^{\bullet+}$, $BiC_2ClH_4S_2$ *m*/*z* 335.9237 $\delta = 2.9$ ppm; $[M - Cl]^+$, $BiC_2H_4S_2$ measured *m*/*z* 300.9550, $\delta = 2.8$ ppm). Compound **4** gives weak $M^{\bullet+}$ ions and major fragment ions at *m*/*z* 336 and 301, which are assumed to have the same structure as $M^{\bullet+}$ and $[M - Cl]^+$ ions from **1**. This suggests a thermodynamic preference for the five-membered heterocycle and implies elimination of SC_2H_4 from $M^{\bullet+}$ and $[M - Cl]^+$ ions of **4** followed by ring closure, as was proposed earlier[8] for the methyl and phenyl analogues. Similarly, compound **5** shows a fragment ion (*m*/*z* 285) which is the oxa analogue of the $[M - Cl]^+$ ion from **1**. The data for compound **1** are consistent with those of a previous report;[12] however, previous reports for compounds **4** and **5**[11] do not describe the intense peaks for $[M - Cl]^+$ or $[M - Cl - SC_2H_4]^+$.

The EI mass spectra of compounds **2** and **3** show ions observed in the spectrum of $BiCl_3$ in addition to the ions corresponding to the organic portion of the molecule, indicative of thermal decomposition. Compounds **6**−**10** behave similarly to bismuth sulfide which is polymeric in the solid state and is not sufficiently volatile to give an EI mass spectrum.

APCI mass spectral data for compounds **1** (Figure 5b), **2**, **4**, and **5** in DMSO and compounds **6**, **7**, **9**, and **10** in acetonitrile with 1% HCl are summarized in Table 5, revealing some general

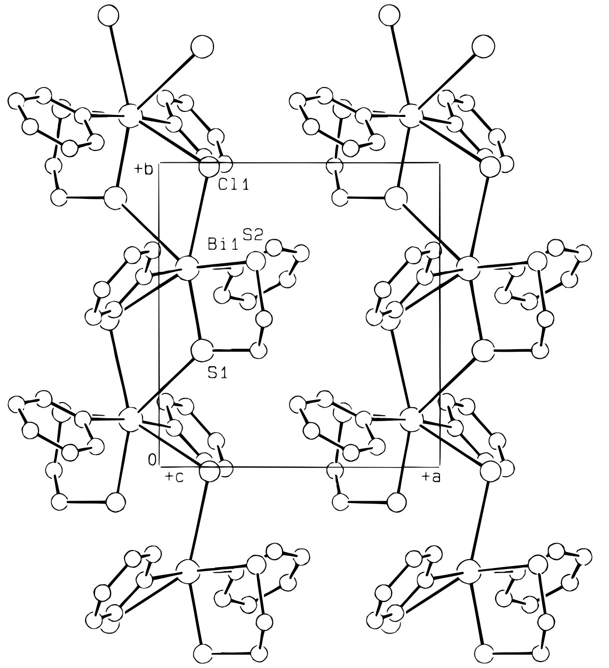

Figure 1. Crystallographic view of the unit cell of compound **11** showing intermolecular contacts.

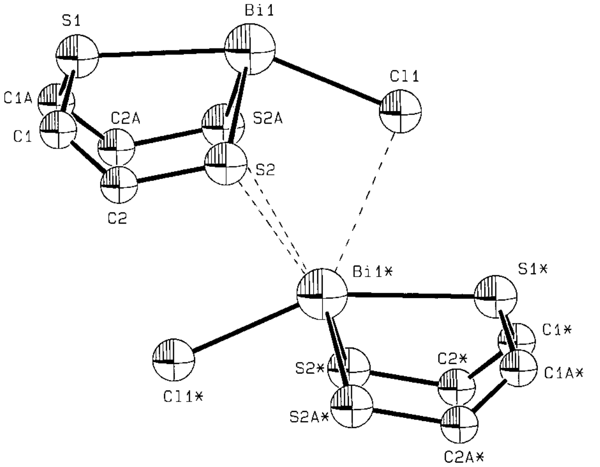

Figure 2. Crystallographic view of two molecules of compound **4** showing intermolecular contacts and the C_s symmetry of the structure.

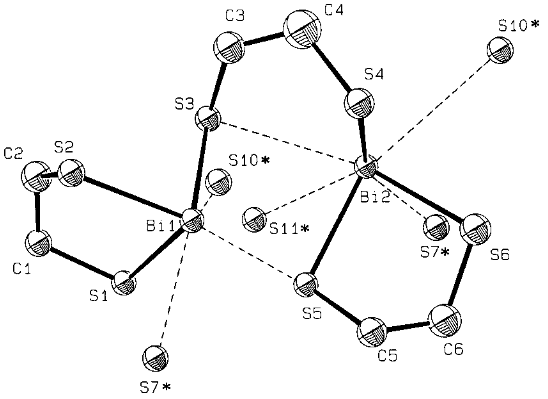

Figure 3. Crystallographic view of one of the two independent molecules of compound **6** showing inter- and intramolecular contacts.

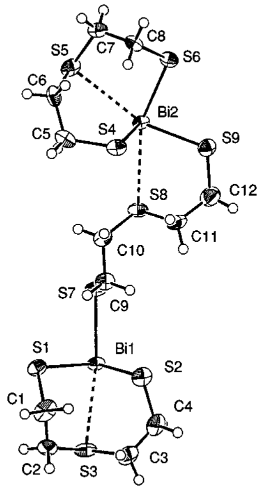

Figure 4. Crystallographic view of compound **9** showing intramolecular contacts.

Table 4. Electron Ionization (70 eV) Mass Spectral Data of **1**–**5**

compd	*m*/*z*	% abundance	ion
1	336	25	$M^{\bullet+}$
	301	30	$[M - Cl]^+$
	273	10	$[BiS_2]^+$
	244	18	$[BiCl]^+$
	241	58	$[BiS]^+$
	209	77	Bi^+
	92	100	$[S_2C_2H_4]^+$
2	314	4	$[BiCl_3]^+$
	279	15	$[BiCl_2]^+$
	244	<1	$[BiCl]^+$
	209	8	Bi^+
	106	100	$[S_2C_3H_6]^+$
3	314	35	$[BiCl_3]^+$
	279	100	$[BiCl_2]^+$
	244	19	$[BiCl]^+$
	209	45	Bi^+
	122	3	$[S_2C_4H_8]^+$
4	396	<1	$M^{\bullet+}$
	361	<1	$[M - Cl]^+$
	336	73	$[ClBiS_2C_2H_4]^+$
	301	30	$[BiC_2H_4]^+$
	241	58	$[BiS]^+$
	209	95	Bi^+
	152	100	$[S_3C_4H_8]^+$
5	380	9	$M^{\bullet+}$
	345	8	$[M - Cl]^+$
	285	5	$[BiSC_2H_4O]^+$
	244	9	$[BiCl]^+$
	241	10	$[BiS]^+$
	209	19	Bi^+
	136	100	$[S_2OC_4H_8]^+$

trends. Dominant in all the spectra are monocyclic cations, which represent $[M - Cl]^+$ for compounds **1**, **2**, **4**, and **5**, and heterolytic Bi–S cleavage of the tether for compounds **6**, **7**, **9**, and **10**. These cations are representative of bismuthenium cations, bismuth analogues of the now well-established series of dicoordinate phosphorus[30] and arsenic cations.[31] They are also observed in the EI mass spectra of **1**, **4**, and **5**, as can be seen in Figure 5 which compares the EI spectrum of compound **1** with the APCI spectrum of compound **1** in DMSO.

Acidified solutions of compounds **6**, **7**, **9**, and **10** also show bismuthenium cations as the dominant species (Figure 6a), and both five-membered (*m*/*z* 301 for **9**; *m*/*z* 285 for **10**) and eight-membered (*m*/*z* 361 for **9**; *m*/*z* 345 for **10**) heterocyclic cations are observed in the spectra of **9** and **10**. A protonated molecular

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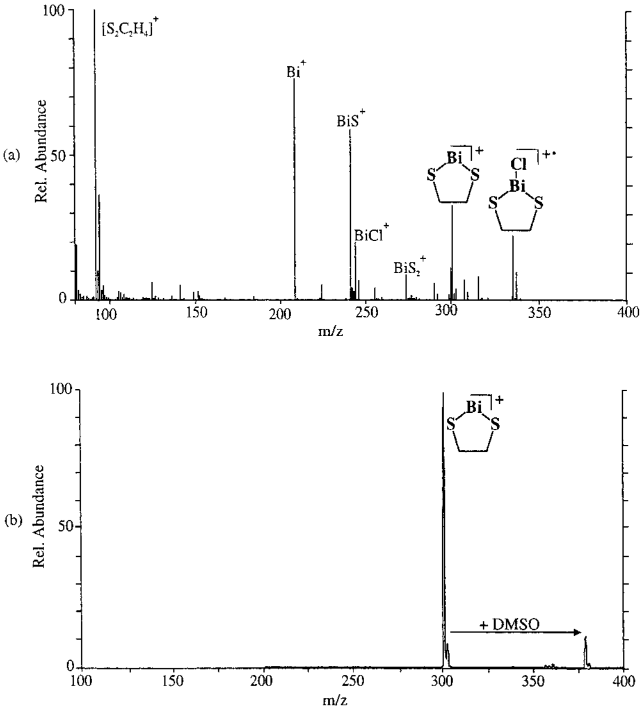

Figure 5. (a) EI mass spectrum of compound **1**. (b) APCI mass spectrum of compound **1** dissolved in DMSO at a cone voltage of 30 V.

Table 5. APCI Spectral Data for Compounds 1, 2, 4, and 5 in DMSO and 6, 7, 9, and 10 in Acetonitrile with 1% HCl

		relative abundance		
compd	*m/z*	SC = 30 V	SC = 10 V	Ion
1	301	100	–	$[M - Cl]^+$
	379	11	100	$[M - Cl + DMSO]^+$
	457	–	17	$[M - Cl + 2DMSO]^+$
2	315	100	–	$[M - Cl]^+$
	393	8	100	$[M - Cl + DMSO]^+$
	471	–	23	$[M - Cl + 2DMSO]^+$
4	301	27	–	$[BiS_2C_2H_4]^+$
	361	100	16	$[M - Cl]^+$
	379	4	100	$[BiS_2C_2H_4 + DMSO]^+$
	439	–	55	$[M - Cl + DMSO]^+$
	457	–	18	$[BiS_2C_2H_4 + 2DMSO]^+$
5	285	12	–	$[BiSOC_2H_4]^+$
	345	100	–	$[M - Cl]^+$
	363	10	16	$[BiSOC_2H_4 + DMSO]^+$
	423	–	100	$[M - Cl + DMSO]^+$
6	301	100		$[BiS_2C_2H_4]^+$
7	209	100		Bi^+
	315	86		$[BiS_2C_3H_6]^+$
9	301	16		$[BiS_2C_2H_4]^+$
	361	100		$[BiS_3C_4H_8]^+$
10	209	8		Bi^+
	285	9		$[BiSC_2H_4O]^+$
	345	100		$[BiS_2OC_4H_8]^+$
	724	1		
	827	1		MH^+

ion was observed for compound **10** (Figure 6a), and the MS/MS spectrum of this ion (Figure 6b) reiterates that the principal fragmentation pathway is the loss of SC_2H_4. Loss of SC_2H_4 or $2SC_2H_5$ from MH^+ may result in a tethered ion with either one or two pendant five-membered heterocycles (at *m/z* 767 and 706, respectively), each containing an oxygen and a sulfur atom. As was observed for the APCI mass spectrum (Table 5), the MS/MS spectrum of $\mathbf{10H}^+$ is dominated by the eight-membered bismuthenium species (*m/z* 345) plus a minor fragment ion due to loss of SC_2H_4 to give the five-membered species at *m/z* 285.

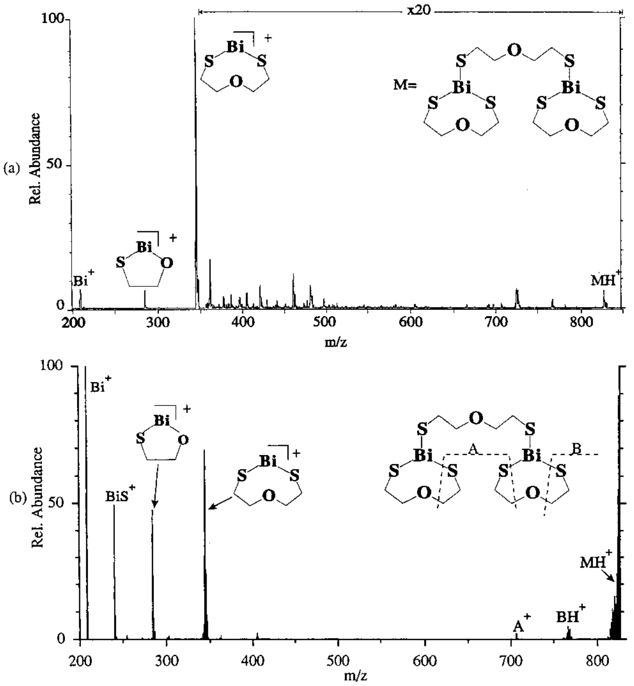

Figure 6. (a) APCI mass spectrum of compound **10** in acetonitrile with 1% HCl. (b) APCI MS/MS spectrum of compound **10**.

Notable in the APCI spectrum of **1** (Figure 5b) is the peak at *m/z* 379 which corresponds to a DMSO complex of the cation, suggestive of a donor stabilization. Similar complexation is also observed for **2**, **4**, and **5** in DMSO solution. Metal ion complexes preformed in solution have been observed by electrospray mass spectrometry.[32] Moreover, a related bismuthenium example has been isolated,[33] and complexes of phosphenium and arsenium cations have been realized.[31,34,35]

By adjusting the sampling cone (SC) voltage of the Quattro mass spectrometer, we were able to effect the acceleration of ions through the region of intermediate pressure where ion–molecule collisions result in a declustering of the solvent molecules and, in the limit, collision-induced decomposition of the ions. For APCI experiments with **1**, **2**, **4**, and **5**, at an SC voltage of 30 V (typical operating condition) the bismuthenium cation $[M - Cl]^+$ is the base peak with a small peak (~10% relative intensity) representing $[(DMSO)M - Cl]^+$. At an SC voltage of 10 V, $[(DMSO)M - Cl]^+$ becomes the base peak and a significant peak for $[(DMSO)_2M - Cl]^+$ complex is observed for compounds **1** and **2**. However, for compounds **4** and **5**, the cross-ring donation from the ether and sulfide, respectively, inhibits complexation of a second solvent molecule, compared to compounds **1** and **2**, and the bis complex is not observed at all for **4** or **5**. Elimination of SC_2H_4 from **4** and **5** in the ion source is observed to occur (confirmed by a precursor ion scan), forming $BiC_2H_4S_2^+$ and $BiC_2H_4OS^+$, respectively. These ions also form DMSO complexes. The identity of these complex ions is confirmed by MS/MS experiments which show sequential loss of the solvent molecule to yield the dicoordinate bismuthenium cation in each case. In addition, the APCI spectra

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for compounds **4** and **5** show the elimination of SC_2H_4 to form the five-membered bismuthenium cations $BiC_2H_4S_2^+$ and $BiC_2H_4OS^+$, respectively. The ions Bi^+ and BiS^+ are observed in the MS/MS spectra of all compounds.

Complex ion formation was also observed in DMSO solutions of compounds **6**, **7**, **9**, and **10**, consistent with the spectra obtained for compounds **1**, **2**, **4**, and **5**, whereas in acetonitrile solutions complex ion formation was found to be variable.

Conclusions

General, high-yield synthesis of two related and comprehensive series of bismuth heterocycles demonstrates a dominant thermodynamic preference for the dianion dithia chelate for bismuth. The chloro-substituted monocycles **1**−**5** are kinetically stable with respect to the tethered bicyclic derivatives **6**−**10**. Mass spectrometry provides an excellent means of characterization of compounds of this nature and is responsible for the identification of monocyclic bismuthenium cations as a general and dominant dissociation product. In addition, the APCI technique exhibits solvent coordination chemistry of the bismuthenium cation.

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Supporting Information Available: Tables giving positional parameters, anisotropic thermal parameters, intramolecular bond distances and angles, and intermolecular bond distances involving non-hydrogen atoms for **4**−**6**, **9**, and **11** (39 pages); tables giving observed and calculated structure factors for **4**−**6**, **9**, and **11** (50 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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