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Complexes of Group 15 Metals with Sterically Hindered Thiolate Ligands. Crystal and Molecular Structures of $[Sb(2\text{-}SC_5H_4N)_3]$, $[Sb(2\text{-}SC_5H_3N\text{-}3\text{-}SiMe_3)_3]$, and $[Bi(2\text{-}SC_5H_3N\text{-}3\text{-}SiMe_3)_3]$

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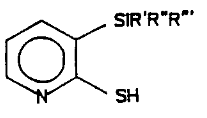
The complexes $[Sb(2\text{-}C_5H_4N)_3]$ (**1**), $[Sb(2\text{-}SC_5H_3N\text{-}3\text{-}SiMe_3)_3]$ (**2**), and $[Bi(2\text{-}SC_5H_3N\text{-}3\text{-}SiMe_3)_3]$ (**3**) were prepared from the reaction of the appropriate metal salt and the ligand in methanol. The structure of **1** consists of a distorted octahedral arrangement of S and N donors, which adopt a facial ligand arrangement. The stereochemically active lone pair of the Sb(III) center occupies a position capping the N_3 face of the octahedron. In contrast, the donor groups in **2** are so disposed that the lone pair occupies an octahedral vertex trans to a sulfur donor, with one nitrogen donor now defining the face capping position. The structure of the bismuth derivative (**3**) is analogous to that of **2**. Crystal data: $C_{15}H_{12}N_3S_3Sb$ (**1**); trigonal $R\bar{3}c$, $a = 12.562$ (2) Å, $c = 37.960$ (4) Å, $V = 5187.6$ (10) Å^3, $Z = 12$, $R = 0.026$; $C_{24}H_{36}N_3Si_3S_3Sb$ (**2**), monoclinic $P2_1/c$, $a = 17.876$ (3) Å, $b = 10.772$ (2) Å, $c = 18.617$ (4) Å, $\beta = 116.08$ (1)°, $V = 3219.8$ (11) Å^3, $Z = 4$, $R = 0.028$; $C_{24}H_{36}N_3Si_3S_3Bi$ (**3**), monoclinic $C2/c$, $a = 24.682$ (4) Å, $b = 12.927$ (2) Å, $c = 24.782$ (4) Å, $\beta = 123.04$ (1)°, $V = 6629.1$ (12) Å^3, $Z = 8$, $R = 0.049$.

The coordination chemistry of transition metals with thiolate ligands has experienced an expansive development in recent years, stimulated in large measure by its relevance to structure, bonding, and function of biologically active reaction centers in metalloproteins and metalloenzymes.[1-3] In contrast, the thiolate chemistry of the main-group metals remains relatively undeveloped.

Although thiolate complexes of the trivalent group 15 metals of general composition $M(SR)_3$ with M = Sb or Bi have been described,[4-12] there is a scarcity of structural data on complexes of this type, as a consequence of their hydrolytic instability in solution and also because of their generally poor solubility properties.[5,7] However, the structural chemistry of group 15 metal-thiolate complexes is potentially of considerable interest by virtue of the tendency of these metal centers to adopt high coordination numbers, the presence of sterically ambivalent lone pairs, and the potential to adopt oligomeric structures.[13-15] Furthermore, bismuth thiolates are of some significance as antitumor agents,[16] fungicides,[17] analytical reagents,[18] catalysts in sulfur vulcanization,[19] and models for bismuth incorporation into metallothioneins.[20]

As part of our continuing investigations of the chemistry of sterically hindered thiolates,[21-34] we have exploited the triorganosilyl group to introduce a substituent which imparts improved solubility and crystallization properties to the complexes. The pyridine-2-thiol derivative A has proved particularly effective



(A)

in the synthesis of a number of unusual transition-metal and main-group-metal thiolates. In this paper, we describe the synthesis and structural characterization of $[Sb(2\text{-}SC_5H_3N\text{-}3\text{-}SiMe_3)_3]$ and $[Bi(2\text{-}SC_5H_3N\text{-}3\text{-}SiMe_3)_3]$ and compare these structures to that of the antimony complex of the underivatized pyridine-2-thiol $[Sb(2\text{-}SC_5H_4N)_3]$,[35] for which a structural redetermination is provided.

Experimental Section

Reactions were carried out under an atmosphere of argon. All solvents were dried and purified by standard techniques. All silicon reagents were purchased from Petrarch Systems. The (triorganosilyl)pyridine-2-thiols were prepared as described in ref 29. The IR spectra were recorded on a Perkin-Elmer 710B spectrometer and were referenced with polystyrene. X-ray crystallographic studies were performed on a Rigaku AFC5S diffractometer. Elemental analyses were performed by Desert Analytics (Phoenix, AZ).

Table I. Selected Crystal Data for the Complexes of This Study

	$C_{15}H_{12}N_3S_3Sb$ (**1**)	$C_{24}H_{36}N_3Si_3S_3Sb$ (**2**)	$C_{24}H_{36}H_3Si_3S_3Bi$ (**3**)
fw	452.22	668.77	756.00
system	trigonal	monoclinic	monoclinic
space group (No.)	$R\bar{3}c$ (167)	$P2_1/c$ (14)	$C2/c$ (15)
a, Å	12.562 (2)	17.876 (3)	24.682 (4)
b, Å	12.562 (2)	10.772 (2)	12.927 (2)
c, Å	37.960 (4)	18.617 (4)	24.782 (4)
β, deg		116.08 (1)	123.04 (1)
V, Å^3	5187.6 (10)	3219.8 (11)	6629.1 (12)
Z	12	4	8
abs coeff, cm^{-1}	19.50	11.75	56.08
R^a	0.026	0.028	0.049
$R_w{}^b$	0.029	0.032	0.059
density (calc), g cm^{-3}	1.737	1.379	1.515

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

Tris(pyridine-2-thiolato)antimony(III) (1). A solution containing antimony(III) acetate (0.298 g, 1.0 mmol), pyridine-2-thiol (0.333 g, 3

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Table II. Atomic Positional Parameters for $[Sb(2\text{-}SC_5H_4N)_3]$ (**1**)

atom	*x*	*y*	*z*
Sb1	0	0	0.201749 (9)
S1	−0.0313 (1)	−0.17366 (9)	0.16409 (2)
N1	0.1135 (3)	−0.1400 (3)	0.21860 (7)
C11	0.0518 (3)	−0.2172 (3)	0.19218 (8)
C12	0.0511 (4)	−0.3264 (4)	0.1872 (1)
C13	0.1152 (5)	−0.3563 (4)	0.2106 (1)
C14	0.1773 (4)	−0.2795 (5)	0.2382 (1)
C15	0.1733 (4)	−0.1731 (4)	0.24114 (9)

Table III. Selected Bond Lengths (Å) and Angles (deg) for $[Sb(2\text{-}SC_5H_4N)_3]$ (**1**)

Sb1–S1	2.470 (1)	S1–C11	1.759 (3)
Sb1–N1	2.837 (3)		
S1–Sb1–S1	89.86 (4)	S1–Sb1–N1b	92.51 (6)
S1–Sb1–N1	59.33 (6)	N1–Sb1–N1a	115.07 (4)
S1–Sb1–N1a	149.07 (6)		

Table IV. Atomic Positional Parameters for $[Sb(2\text{-}SC_5H_3N\text{-}3\text{-}SiMe_3)_3]$ (**2**)

atom	*x*	*y*	*z*
Sb1	0.80764 (2)	0.00180 (4)	0.22421 (2)
S1	0.71651 (9)	−0.0799 (2)	0.28452 (8)
S2	0.8337 (1)	0.1983 (1)	0.29562 (9)
S3	0.66982 (9)	0.0717 (1)	0.11535 (8)
Si1	0.7006 (1)	−0.2378 (2)	0.4385 (1)
Si2	0.8653 (1)	0.4959 (2)	0.2683 (1)
Si3	0.5614 (1)	0.2653 (2)	−0.0417 (1)
N1	0.8769 (3)	−0.0946 (4)	0.3695 (3)
N2	0.9691 (3)	0.1440 (4)	0.2788 (3)
N3	0.8041 (3)	0.1510 (4)	0.1085 (2)
C11	0.8050 (3)	−0.1254 (5)	0.3717 (3)
C12	0.8003 (3)	−0.1854 (5)	0.4360 (3)
C13	0.8783 (4)	−0.2101 (6)	0.5006 (3)
C14	0.9522 (4)	−0.1779 (7)	0.4996 (4)
C15	0.9488 (4)	−0.1222 (6)	0.4328 (4)
C16	0.6327 (4)	−0.1041 (7)	0.4308 (4)
C17	0.6462 (5)	−0.3486 (7)	0.3570 (5)
C18	0.7261 (5)	−0.3125 (8)	0.5369 (5)
C21	0.9213 (3)	0.2398 (5)	0.2799 (3)
C22	0.9358 (3)	0.3647 (5)	0.2692 (3)
C23	1.0073 (4)	0.3855 (6)	0.2583 (3)
C24	1.0575 (4)	0.2887 (6)	0.2578 (4)
C25	1.0350 (4)	0.1703 (6)	0.2671 (3)
C26	0.8673 (5)	0.5049 (7)	0.3690 (4)
C27	0.9066 (6)	0.6447 (6)	0.2493 (5)
C28	0.7578 (5)	0.4765 (8)	0.1869 (6)
C31	0.7201 (3)	0.1637 (5)	0.0715 (3)
C32	0.6775 (3)	0.2436 (5)	0.0065 (3)
C33	0.7275 (3)	0.3104 (5)	−0.0191 (3)
C34	0.8130 (4)	0.2977 (6)	0.0178 (4)
C35	0.8490 (3)	0.2176 (6)	0.0803 (3)
C36	0.5333 (4)	0.3836 (6)	−0.1222 (4)
C37	0.5286 (4)	0.3234 (8)	0.0340 (4)
C38	0.5084 (4)	0.1171 (7)	−0.0863 (4)

Table V. Selected Bond Lengths (Å) and Angles (deg) for $[Sb(2\text{-}SC_5H_3N\text{-}3\text{-}SiMe_3)_3]$ (**2**)

Sb1–S1	2.509 (2)	S1–C11	1.766 (5)
Sb1–S2	2.434 (2)	S2–C21	1.774 (5)
Sb1–S3	2.520 (2)	S3–C31	1.762 (5)
Sb1–N1	2.642 (5)	S1---N1	2.600 (5)
Sb1–N2	3.021 (5)	S2---N2	2.640 (5)
Sb1–N3	2.666 (4)	S3---N3	2.603 (4)
S1–Sb1–S2	93.80 (5)	S2–Sb1–N3	81.3 (1)
S1–Sb1–S3	82.36 (5)	S3–Sb1–N1	142.4 (1)
S2–Sb1–S3	93.66 (6)	S3–Sb1–N2	125.79 (9)
S1–Sb1–N1	60.5 (1)	S3–Sb1–N3	60.2 (1)
S1–Sb1–N2	137.66 (9)	N1–Sb1–N2	84.6 (1)
S1–Sb1–N3	141.6 (1)	N1–Sb1–N3	153.9 (1)
S2–Sb1–N1	83.8 (1)	N2–Sb1–N3	69.3 (1)
S2–Sb1–N2	56.66 (9)		

Table VI. Atomic Positional Parameters for $[Bi(2\text{-}SC_5H_3N\text{-}3\text{-}SiMe_3)_3]$ (**3**)

atom	*x*	*y*	*z*
Bi1	0.31464 (5)	0.16783 (8)	0.09343 (5)
S1	0.3145 (3)	−0.0327 (5)	0.0834 (3)
S2	0.3148 (3)	0.1573 (5)	0.1960 (3)
S3	0.1880 (3)	0.1394 (5)	0.0222 (3)
Si1	0.3944 (4)	−0.2544 (6)	0.1056 (4)
Si2	0.2753 (4)	0.3108 (6)	0.2801 (4)
Si3	0.0427 (4)	0.2287 (7)	−0.0174 (5)
N1	0.425 (1)	0.058 (1)	0.144 (1)
N2	0.382 (1)	0.313 (2)	0.195 (1)
N3	0.2332 (9)	0.326 (2)	0.0692 (9)
C11	0.400 (1)	−0.032 (2)	0.127 (1)
C12	0.435 (1)	−0.127 (2)	0.136 (1)
C13	0.501 (2)	−0.109 (2)	0.168 (1)
C14	0.529 (2)	−0.016 (3)	0.191 (1)
C15	0.491 (2)	0.069 (2)	0.179 (1)
C16	0.344 (1)	−0.259 (2)	0.017 (1)
C17	0.348 (1)	−0.283 (2)	0.145 (1)
C18	0.460 (2)	−0.356 (3)	0.139 (2)
C21	0.348 (1)	0.282 (2)	0.221 (1)
C22	0.335 (1)	0.349 (2)	0.258 (1)
C23	0.363 (1)	0.446 (2)	0.272 (1)
C24	0.398 (1)	0.473 (2)	0.247 (1)
C25	0.409 (1)	0.412 (2)	0.211 (1)
C26	0.294 (1)	0.183 (2)	0.319 (1)
C27	0.193 (2)	0.319 (3)	0.211 (2)
C28	0.291 (2)	0.412 (3)	0.343 (2)
C31	0.177 (1)	0.271 (2)	0.038 (1)
C32	0.118 (1)	0.311 (2)	0.017 (1)
C33	0.118 (1)	0.414 (2)	0.031 (1)
C34	0.170 (1)	0.470 (2)	0.059 (1)
C35	0.228 (1)	0.427 (2)	0.079 (1)
C36	0.055 (2)	0.123 (3)	0.044 (2)
C37	0.023 (2)	0.167 (3)	−0.094 (2)
C38	−0.026 (2)	0.316 (3)	−0.035 (2)

mmol), and triethylamine (0.303 g, 3 mmol) in methanol (25 mL) was stirred at room temperature. The solution was filtered and the filtrate concentrated to about 90% of its original volume. After addition of diethyl ether (10 mL), the solution was allowed to stand at −20 °C for 4 days. Yellow crystals of prismatic habit were collected in 70% yield. Anal. Calcd for $C_{15}H_{12}N_3S_3Sb$: C, 39.8; H, 2.66; N, 9.30. Found: C, 39.6; H, 2.73; N, 9.22.

Tris[3-(trimethylsilyl)pyridine-2-thiolato]antimony(III) (2). A solution containing antimony(III) acetate (0.298 g, 1.0 mmol) and the sodium salt of 3-(trimethylsilyl)pyridine-2-thiol (0.615 g, 3.0 mmol) in methanol (30 mL) was stirred at room temperature for 8 h. The solution was filtered and concentrated to 10 mL. After the solution was allowed to stand for 3 days at −20 °C, yellow crystals of needle habit deposited in 50% yield. Anal. Calcd for $C_{24}H_{36}N_3Si_3S_3Sb$: C, 43.1; H, 5.39; N, 6.29. Found: C, 42.8; H, 5.33; N, 6.18.

Tris[3-(trimethylsilyl)pyridine-2-thiolato]bismuth(III) (3). A methanolic solution (40 mL) of bismuth(III) nitrate hexahydrate (0.485 g, 1.0 mmol), 3-(trimethylsilyl)pyridine-2-thiol (0.549 g, 3.0 mmol), and triethylamine (0.303 g, 3 mmol) was stirred for 5 h. After the solution was

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Table VII. Selected Bond Lengths (Å) and Angles (deg) for $[\mathrm{Bi(2\text{-}SC_5H_3N\text{-}3\text{-}SiMe_3)_3}]$ (**3**)

Bi–S1	2.604 (6)	Bi–N3	2.69 (2)
Bi–S2	2.544 (6)	S1–C11	1.78 (2)
Bi–S3	2.647 (7)	S2–C21	1.76 (2)
Bi–N1	2.69 (2)	S3–C31	1.80 (2)
Bi–N2	2.83 (2)		
S1–Bi–S2	92.4 (2)	S2–Bi–N3	81.8 (4)
S1–Bi–S3	81.8 (2)	S3–Bi–N1	139.7 (4)
S2–Bi–S3	91.0 (2)	S3–Bi–N2	126.4 (4)
S1–Bi–N1	58.0 (4)	S3–Bi–N3	59.4 (4)
S1–Bi–N2	135.4 (4)	N1–Bi–N2	88.7 (6)
S1–Bi–N3	140.5 (5)	N1–Bi–N3	160.7 (6)
S2–Bi–N1	93.0 (5)	N2–Bi–N3	72.7 (6)
S2–Bi–N2	57.9 (4)		

concentrated to 20 mL and carefully layered with diethyl ether (15 mL), it was allowed to stand at room temperature for 6 days. Bright yellow crystals of **3** deposited in 55% yield. Anal. Calcd for $\mathrm{C_{24}H_{36}N_3Si_3S_3Bi}$: C, 38.1; H, 4.77; N, 5.56. Found: C, 38.0; H, 4.83; N, 5.42.

Collection and Reduction of X-ray Data and Solution and Refinement of the Structure. The crystal dara are listed in Table I. A full description of the experimental details and methods of structure solution may be found in the supplementary material.

Data were collected on a Rigaku AFC5S four-circle diffractometer (Mo Kα radiation, λ = 0.71073 Å) using ω–2θ scans and corrected for absorption using ψ scans for a set of reflections with χ angles near 90 or 270°. The structures were solved by the Patterson method and all non-hydrogen atoms located on subsequent difference Fourier maps using the MSC solution and refinement package. Hydrogen atoms were introduced as fixed contributors at their idealized positions with a C–H distance of 0.96 Å. None of the crystals exhibited significant decay under X-ray irradiation. In no instance was a correction for extinction effects introduced. For structures **1** and **2** temperature factors of all non-hydrogen atoms were refined anisotropically. In the case of structure **3** only the Bi, S, Si, and N atoms were refined anisotropically. Tables II and III list atomic positional parameters and selected bond lengths and angles, respectively, for $[\mathrm{Sb(2\text{-}SC_5H_4N)_3}]$, while Tables IV–VII present these data for the structures of $[\mathrm{Sb(2\text{-}SC_5H_3N\text{-}3\text{-}SiMe_3)_3}]$ and $[\mathrm{Bi(2\text{-}SC_5H_3N\text{-}3\text{-}SiMe_3)_3}]$. The metrical parameters for **1** are essentially identical to those previously reported by other authors.[35]

Results and Discussion

The syntheses of the complexes $[\mathrm{Sb(2\text{-}SC_5H_4N)_3}]$ (**1**), $[\mathrm{Sb(2\text{-}SC_5H_3N\text{-}3\text{-}SiMe_3)_3}]$ (**2**), and $[\mathrm{Bi(2\text{-}SC_5H_3N\text{-}3\text{-}SiMe_3)_3}]$ (**3**) were readily effected by reaction of the metal salt with the ligand in methanol. The complexes were pale to deep yellow crystalline solids, which were soluble in common organic solvents such as methylene chloride, acetonitrile, and *N*,*N*-dimethylformamide.

The antimony compounds were susceptible to hydrolysis in solution to yield diaryl disulfides and $\mathrm{Sb_2O_3}$. The presence of the disulfide $[\mathrm{(2\text{-}SC_5H_3N\text{-}3\text{-}SiMe_3)_2}]$ in solutions prepared from **2** was confirmed by mass spectral analysis, which displayed a prominent parent ion $[\mathrm{(2\text{-}SC_5H_3N\text{-}3\text{-}SiMe_3)_2}]^+$.

The infrared spectra of complexes **2** and **3** were dominated by features in the 700–850-cm^{-1} range, attributed to ν(Si–C) of the $\mathrm{SiMe_3}$ substituents. Medium-intensity bands at 355 and 330 cm^{-1} for **1** were attributed to symmetric Sb–S and antisymmetric Sb–S stretching frequencies, respectively. The corresponding vibrations for **2** occur at 345 and 325 cm^{-1}. The bismuth derivative (**3**) exhibits only weak bands in the 250–350-cm^{-1} range, making any assignment tenuous at best.

Complexes **1**–**3** reacted readily with weak electrophilic reagents to give the appropriate sulfides and $\mathrm{MX_3}$ (M = Sb, Bi; X = Cl, I).

$$3\mathrm{MeI} + [\mathrm{Sb(2\text{-}SC_5H_3N\text{-}3\text{-}SiMe_3)_3}] \rightarrow \mathrm{SbI_3} + 3\mathrm{CH_3SC_5H_3N\text{-}3\text{-}SiMe_3}$$

$$3\mathrm{RSCl} + [\mathrm{Bi(2\text{-}SC_5H_3N\text{-}3\text{-}SiMe_3)_3}] \rightarrow \mathrm{BiCl_3} + 3\mathrm{RSC_5H_3N\text{-}3\text{-}SiMe_3}$$

The structure of $[\mathrm{Sb(SC_5H_3N)_3}]$ (**1**), shown in Figure 1, consists of discrete mononuclear units with the Sb atom occupying the crystallographic 3-fold axis which confers C_3 symmetry on the molecule, as previously noted.[35] The antimony environment is six-coordinate and distorted from regular octahedral geometry by the presence of the chelating ligands with sulfur and nitrogen donors and by the influence of the stereochemically active lone pair. The Sb–S distances of 2.470 (1) Å are in the range of distances observed for other examples of Sb–S bonding.[35–38] The Sb–N distances of 2.837 (3) Å are significantly longer than the anticipated single-bond distance of 2.50–2.65 Å[39] but well within the sum of the van der Waals radii.[52] Such long or secondary bonding is a common feature of the structural chemistry of main-group metals[21,38,40] and may be most apparent for complexes of main-group metals with stereochemically active lone pairs.[41]

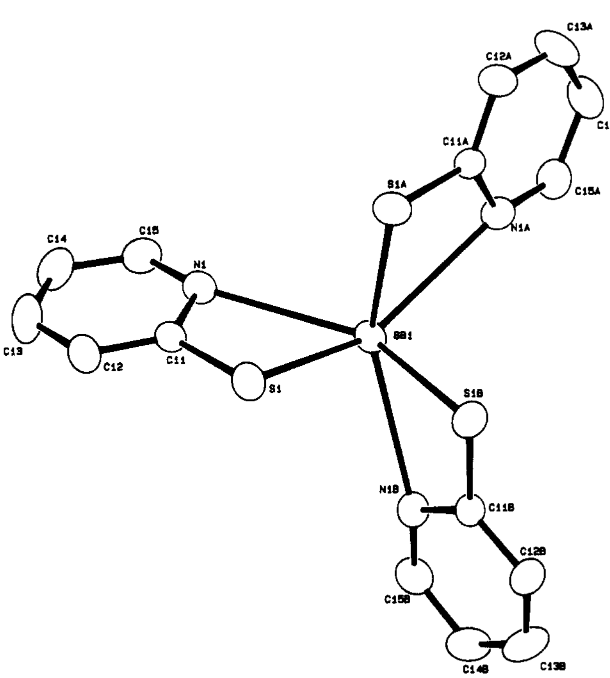

Figure 1. ORTEP view of the structure of $[\mathrm{Sb(2\text{-}SC_5H_4N)_3}]$ (**1**), showing thermal ellipsoids at the 50% probability level.

According to the valence-shell electron-pair repulsion mode,[42,43] the stereochemistry of nontransition elements is governed by repulsions between pairs of valence electrons. For seven electron-pair complexes of the general class $\mathrm{AX_6E}$, where A is a nontransition element, X is a donor atom, and E is the lone pair, the presence of a stereochemically active lone pair is inferred from deviations from local octahedral or approximate octahedral symmetry about the central atom. Although soft donors may lead to a stereochemically inactive lone pair in $\mathrm{AX_6E}$ type complexes,[44] bidentate ligands prevent the attainment of local octahedral symmetry, allowing detection of the stereochemically active lone pair in a seventh coordination position.[14]

The pattern of bond distances, normal Sb–S and long Sb–N, is consistent with the disposition of the one pair in a direction away from the closely coordinated $\mathrm{S_3}$ face and through the centroid of the $\mathrm{N_3}$ face. The tendency is thus toward a trigonal-pyramidal array of sulfur donors and the lone pair, with the lone pair directed along the C_3 axis. The angular distortions associated with the $\mathrm{N_3}$ octahedral face (N1–Sb–N1a = 115.07 (4)°) illustrate that the coordination is considerably splayed in order to accommodate the lone pair. Consequently, the geometry assumed by **1** is best described as capped octahedral with the lone pair in the capping site.

If the secondary metal–nitrogen interactions are ignored, the

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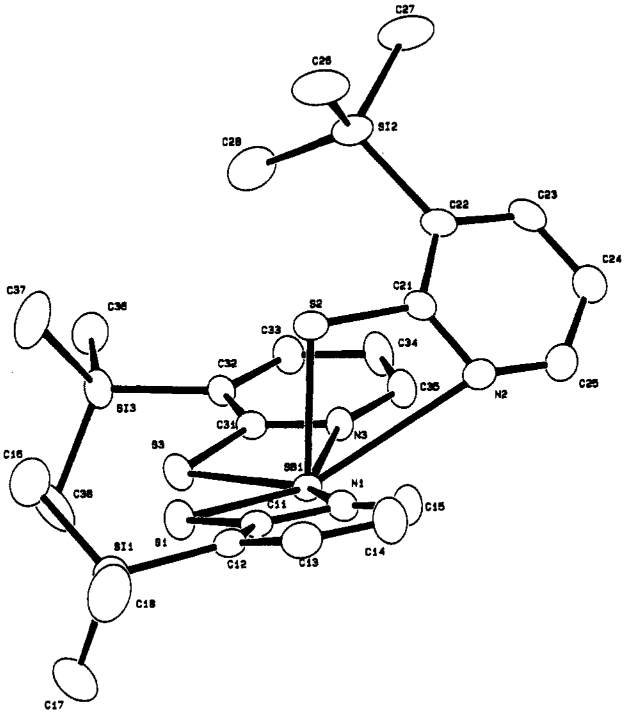
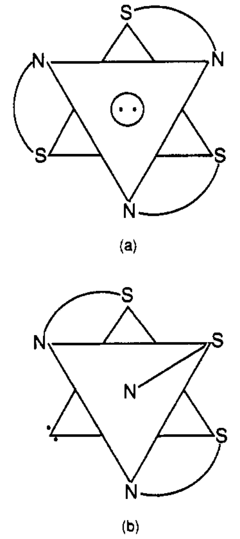


Figure 2. ORTEP view of the structure of $[Sb(2\text{-}SC_5H_3N\text{-}3\text{-}SiMe_3)_3]$ (**2**), showing thermal ellipsoids at the 50% probability level.

geometry of **1**, and those of **2** and **3** also, may be described as trigonal orthogonal, with the MS_3 coordination unit defining the base and the lone pair directed toward the gap formed by the three pyridine nitrogen atoms. This type of geometry is observed for a number of main-group thiolate complexes where there is evidence for a stereochemically active lone pair. The structure of $[Pb(SC_6H_5)_3]$[53] is prototypical of this class. A significant feature of this latter structure is the average dihedral angle between the Pb–S vector and the associated phenyl plane of 50.7°. In contrast, the average angles between the M–S vectors and the C_5N planes for **1**–**3** are 4.5, 3.7, and 7.4°, respectively. Since the ligands are not constrained by steric factors to adopt this orientation in these structures, we conclude that the ligand disposition reflects the interaction between the metals and the pyridine nitrogen donors. This observation is also consistent with the M–N distances which, while long for single-bond interaction, are significantly shorter than the sum of van der Waals radii and thus indicative of secondary bonding.

The consequences of introducing sterically significant substituents on the ligands are illustrated by the structure of $[Sb(2\text{-}SC_5H_3N\text{-}3\text{-}SiMe_3)_3]$ (**2**), shown in Figure 2. The disposition of ligand donors about the Sb center may be described as square pyramidal, with a long-range face-capping interaction provided by N2. The base of the square pyramid is defined by the donor atoms S1, N1, S3, and N3 of two chelating 3-(trimethylsilyl)pyridine-2-thiolate ligands, with the sulfur donor S2 of the third ligand occupying the apical position. The Sb–S distances are inequivalent, with those in the plane at an average distance of 2.515 (3) Å, while the apical Sb–S distance is considerably shorter, 2.434 (2) Å. The in-plane Sb–N distances (2.654 (6) Å, average) fall in the anticipated range for normal Sb–N bond distances, in contrast to those observed for **1**, which are lengthened as a consequence of the steric influence of the lone pair. The third nitrogen donor caps the S2–N1–N3 face on the square pyramid at an Sb–N2 distance of 3.021 (5) Å, which although significantly longer than the other Sb–N distances in **2** and the Sb–N distances of **1**, is shorter than the sum of the van der Waals radii, 3.58 Å. The geometric consequences of capping the S2–N1–N3 face are most apparent in the N1–Sb–N3 angle of 153.9 (1)°, which has expanded from the idealized octahedral limit of 90° to accommodate the face-capping N2 donor.

The Sb atom is displaced 0.24 Å from the S1–N1–S3–N3 plane, and below this plane relative to the apical S2 donor. This disposition of donor groups is consistent with the occupancy of the distal position by the stereochemically active lone pair. If the lone pair is regarded as a coordination site, the coordination geometry of the Sb center of **2** is best described as capped octahedral, with the N2 donor occupying the capping position.



(a)

(b)

Figure 3. Schematic representation of the dispositions of donor groups and stereochemically active lone pairs for (a) $[Sb(2\text{-}SC_5H_4N)_3]$ and (b) $[Sb(2\text{-}SC_5H_3N\text{-}3\text{-}SiMe_3)_3]$.

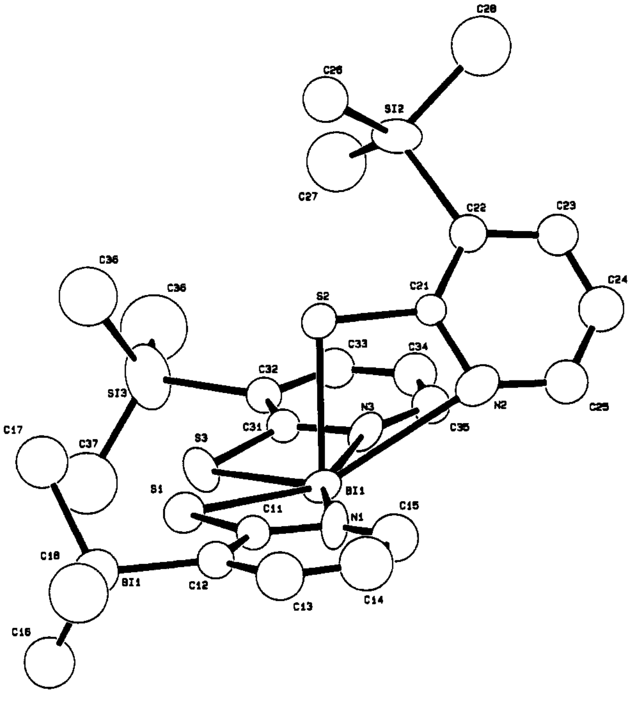


Figure 4. ORTEP view of the structure of $[Bi(2\text{-}SC_5H_3N\text{-}3\text{-}SiMe_3)_3]$ (**3**), showing thermal ellipsoids at the 50% probability level.

The relative disposition of donor groups and lone pairs for structures **1** and **2** is illustrated schematically in Figure 3. The introduction of the bulky $SiMe_3$ units in **2** results in a dramatic structural rearrangement from the geometry observed for **1**. It is evident from the disposition of the $SiMe_3$ groups that the structural rearrangement is not necessitated by a direct steric interaction of the lone pair with the $SiMe_3$ groups. A facial arrangement of sulfur donors with the lone pair positioned along the C_3 axis toward the N_3 face, as observed for **1**, directs the $SiMe_3$ groups below the distal face of the octahedron relative to the lone pair. However, the effect of the lone pair in a capping position of the SbS_3N_3E unit is to expand the N–Sb–N valence angles, concomitantly contracting the S–Sb–S valence angles. Were **2** to adopt the lone-pair capping geometry of **1**, one consequence

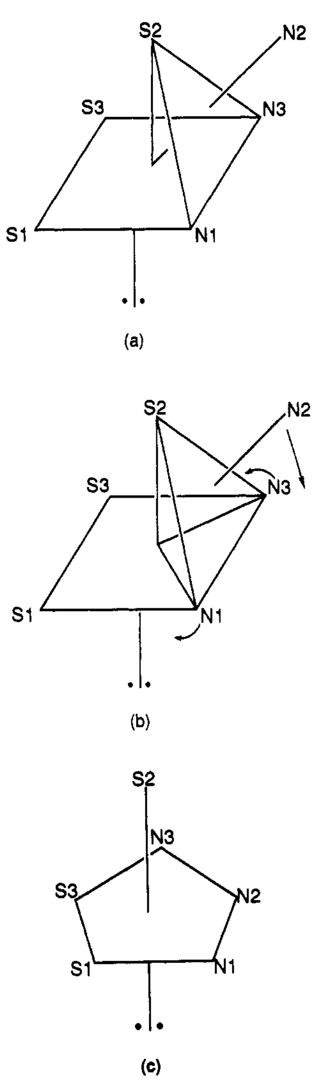


Figure 5. (a) Idealized representation of the capped-octahedral geometry of **2**. (b) Expansion of the N1–M–N3 angle and movement of N2 toward the S1–N1–S3–N3 plane to distort the capped-octahedral geometry toward pentagonal bipyramidal. (c) Idealized pentagonal-bipyramidal geometry with the lone pair in an axial position.

of these angular distortions would be to draw the $SiMe_3$ groups into unfavorably close steric contact. Consequently, the geometry adopted by **2** does not reflect a direct interaction of the lone pair with the $SiMe_3$ groups but rather a need to balance steric interactions between the $SiMe_3$ groups, which are minimized in a facial ligand arrangement by adopting a geometry which places the lone pair in a trans orientation relative to one of the sulfur donors.

The structure of the bismuth derivative, $[Bi(2\text{-}SC_5H_3N\text{-}3\text{-}SiMe_3)_3]$ (**3**), shown in Figure 4, is grossly similar to that of **2**. The average in-plane Bi–S distance of 2.626 (8) Å and the Bi–S distance of 2.544 (6) Å for the apical interaction are significantly shorter than those previously reported for 1,1-dithio acid complexes[13,14,45–47] and for tris(1,5-diphenylthiocarbazonato-*N*,*S*)bismuth(III)[49] but comparable to Bi–S(thiolate) distances in $[CH_3Bi(SCH_2CH_2OCH_2CH_2S)]$ and other alkyl- and arylbismuth thiolate derivatives.[50] The in-plane Bi–N distances are 2.69 (2) Å, while the Bi–N2 capping nitrogen distance is 2.83 (2) Å, a bond length which is significantly shorter than the 3.021 (5) Å distance associated with the antimony derivative **2**. The shorter Bi–N2 interaction most likely reflects the larger covalent radius of Bi relative to that of Sb (ca. 1.55 Å vs 1.45 Å), which allows more effective metal–ligand orbital overlap at this extreme distance. One consequence of the relatively short Bi–N2 distance is to expand the N1–Bi–N3 angle to 160.7 (6)°. Furthermore, N2 has moved toward the S1–N1–S3–N3 plane when compared to the location of the face-capping N2 in complex **2**. As a result, the overall disposition of ligand donors and the lone pair for **3** is intermediate between the capped-octahedral geometry adopted by **2** and pentagonal-bipyramidal geometry, as illustrated in Figure 5.

The disposition of donor groups and the lone pair adopted by **3** is unique for Bi(III) complexes of the BiX_6E class. The most common geometries are regular octahedral, where the lone pairs is stereochemically inactive,[50,51] and the capped octahedral, with the lone pair in the face-capping position.[14,48] A number of irregular geometries have also been described for 1,1-dithio acid derivatives of Bi(III).[14]

The structures of complexes **2** and **3** suggest that sterically encumbering ligands may dramatically influence the geometries of complexes of main-group metals with stereochemically significant lone pairs. We have recently prepared the 6-(dimethylbutylsilyl)pyridine-2-thiol and 3,6-bis(dimethylbutylsilyl)pyridine-2-thiol ligand derivatives and are investigating the stereochemical consequences of introducing increased ligand bulk adjacent to the nitrogen donor groups.

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Registry No. **1** (coordination compound entry), 137091-87-3; **1** (salt entry), 90985-22-1; **2** (coordination compound entry), 137091-88-4; **2** (salt entry), 137091-90-8; **3** (coordination compound entry), 137091-89-5; **3** (salt entry), 137091-91-9.

Supplementary Material Available: Tables of experimental conditions, atomic positional parameters, bond lengths, bond angles, and anisotropic temperature factors for **1**–**3** (33 pages); listings of observed and calculated structure factors for the three complexes (41 pages). Ordering information is given on any current masthead page.

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