Arsenic(III), Antimony(III) and Bismuth(III) Thiobenzoates: Crystal and Molecular Structures of $M(SOCR)_3$ and $PhSb(SOCPh)_2$

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Tris-thiobenzoates, Arsenic, Antimony, Bismuth

Tris-thiobenzoates of arsenic, antimony and bismuth, $M(SOCR)_3$ have been obtained from their oxides and characterized. In the X-ray crystal structure determinations of these, the group 15 atom and the three covalently bonded sulfur atoms are found to constitute a trigonal pyramid, the central atoms lie at a C_3 axis. In the bismuth complex the thiobenzoate ligand tends to chelate. However, three comparatively short intermolecular M---S interactions are significant features for these molecules resulting in stacking of trigonal prisms providing an essentially six coordinate environment around arsenic and antimony and a nine-coordinate one for bismuth. The structure of $PhSb(SOCPh)_2$ can be considered to be distorted trigonal bipyramidal.

Metal carboxylates [1] are known to display interesting structural features arising from the varying modes of bonding of the carboxylate anions. The monothiocarboxylates can be classified as asymetrical sulfur ligands [2] with the potential of binding metal ions depending upon their hardness and softness. Surprisingly, few metal thiocarboxylates [3 - 5] have been prepared so far and even fewer ones [5-9] have been examined for structural details. Amongst group 15 elements, there are two reports on the structures of thioacetate complexes. In antimony tris-thioacetate [10] antimony is found to possess eight-fold coordination, and the resultant geometry is best described as a distorted dodecahedron. A bidentate bonding pattern of the thioacetate group is also present in phenylantimony bis-thioacetate [11] whose geometry is of a distorted square-pyramidal shape.

Our systematic efforts in main group metal complexes of asymmetrical sulfur ligands such as thio-ß-diketonate [12-16] and thiocarbamate [17-29] have provided many discernible and interesting structural features. Thiocarboxylates are the natural extension of this thematic approach [8], and we report here on the synthesis and structure of the tris-monothiobenzoates of arsenic, antimony and bismuth as well as of $PhSb(SOCPh)_2$.

Experimental

All experiments were carried out under anhydrous conditions. Solvents were purified and dried by standard methods. Arsenic, antimony and bismuth oxides (Fluka) were used without further purification. $PhSbCl_2$ and Ph_2SbCl were prepared by literature methods [21], as well as monothiobenzoic acid (b. p. 85 - 87 °C/10 mm Hg) and potassium thiobenzoate [22]. Sulfur was estimated by Messenger's method. IR spectra were recorded in the region 4000-400 cm^{-1} on a JASCO FT/IR-5300 spectrometer on KBr disks. Elemental analyses were carried out on a Perkin-Elmer 240C model analyzer. NMR spectra were recorded in $CDCl_3$ using $SiMe_4$ as an internal reference on a JEOL 270 spectrometer.

Preparation of compounds **1** - **3** *(Table I)*

A solution of the respective thiobenzoic acid in dichloromethane ($\sim$ 20 cm^3) in appropriate molar ratio was added dropwise with constant stirring at room temperature (35 °C) to the suspension of the corresponding oxide in dichloromethane ($\sim$30 cm^3). Within 3 - 4 h the oxide went into solution. From the clear solution the solvent was removed in vacuo and the residue dried for 1 - 2 h at 0.01 mm Hg/30 °C. $As(SOCPh)_3$ (**1a**) and $Sb(SOCPh)_3$ (**2a**) were then crystallized by slow evaporation of their dichloromethane solutions. $Bi(SOCC_6H_4\text{-}o\text{-}Me)_3$ (**3b**) was crystallized from its acetone solution.

Preparation of compounds **4**

The organoantimony chloride solution in dichloromethane ($\sim$20 cm^3) was added to a suspension of the potas-

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Table I. Data concerning the preparation and characterization of compound **1** - **4**.

Reactants (g/mmol)	Product (yield) (g;%)	Nature	m. p. (°C)	Analysis found (calcd) % C	 H	 S
1a As_2O_3 + PhCOSH (0.18; 0.90) (0.74; 5.36)	$As(SOCPh)_3$ (0.84; 96)	White solid	155-7	—	—	20.00 (19.75)
1b As_2O_3 + *o*-MeC_6H_4COSH (0.12; 0.61) (0.59; 3.88)	$As(SOCC_6H_4$-*o*-$Me)_3$ (0.62; 95)	White solid	80	—	—	17.90 (1818)
1c As_2O_3 + *p*-MeC_6H_4COSH (0.17; 0.86) (0.78, 5.13)	$As(SOCC_6H_4$-*p*-$Me)_3$ (0.87; 96)	White solid	128-30	—	—	18.00 (18.18)
2a Sb_2O_3 + PhCOSH (0.58; 1.59) (1.67; 12.10)	$Sb(SOCPh)_3$ (2.07; 98)	White solid	205	47.67 (47.30)	2.86 (2.80)	19.60 (18.0)
2b Sb_2O_3 + *o*-MeC_6H_4COSH (0.14; 0.48) (0.45; 2.96)	$Sb(SOC_6H_4$-*o*-$Me)_3$ (0.55; 92)	Light brown solid	75	—	—	16.00 (16.70)
2c Sb_2O_3 + *p*-MeC_6H_4COSH (0.25; 0.86) (0.78; 5.13)	$Sb(SOCC_6H_4$-*p*-$Me)_3$ (0.95; 97)	Pale yellow solid	140	—	—	17.00 (16.70)
3a Bi_2O_3 + PhCOSH (0.40; 0.86) (0.72; 5.22)	$Bi(SOCPh)_3$ (1.01; 95)	Yellow solid	200^d	39.14 (40.64)	2.27 (2.41)	15.21 (15.48)
3b Bi_2O_3 + *o*-MeC_6H_4COSH (0.35; 0.75) (0.70; 4.60)	$Bi(SOCC_6H_4$-*o*-$Me)_3$ (1.00; 98)	White solid	140	—	—	14.28 (14.50)
3c Bi_2O_3 + *p*-MeC_6H_4COSH (0.18; 0.39) (0.37; 2.43)	$Bi(SOCC_6H_4$-*p*-$Me)_3$ (0.45; 90)	Pale yellow solid	185			13.80 (14.50)
4a $PhSbCl_2$ + PhCOSK (0.44; 1.62) (0.56; 3.15)	$PhSb(SOCPh)_2$ (0.72; 94)	White solid	140	50.31 (50.76)	3.28 (3.17)	13.00 (13.54)
4b Ph_2SbCl + PhCOSK (0.58; 1.86) (0.33; 1.85)	$Ph_2Sb(SOCPh)$ (0.70; 91)	White solid	50	—	—	7.20 (7.75)

Table II. Selected IR absorption bands (cm^{-1}) and NMR data (δ ppm) of complexes **1** - **4**.

	Compound	$\nu C\underline{\cdot\cdot}O$	νPh-C	$\nu C\underline{\cdot\cdot}S$	δSCO	δ ^1H Me	 Ph	δ ^{13}C Me	 Ph
1a	$As(SOCPh)_3$	1630	1209	910	642	—	—	—	—
1b	$As(SOCC_6H_4$-*o*-$Me)_3$	1637	1194	900	648	2.48	6.60 - 7.20	21.23	125.84, 130.29, 131.48, 132.61, 136.14, 138.03
1c	$As(SOCC_6H_4$-*p*-$Me)_3$	1620	1190	920	640	2.36	7.20	—	—
2a	$Sb(SOCPh)_3$	1589	1211	923	644	—	—	—	—
2b	$Sb(SOCC_6H_4$-*o*-$Me)_3$	1597	1205	879	650	2.28	6.44 - 7.28	21.45	125.84, 128.98, 131.80, 132.67, 135.21, 137.71
2c	$Sb(SOCC_6H_4$-*p*-$Me)_3$	1615	1190	920	640	2.36	7.20 - 7.80	—	—
3a	$Bi(SOCPh)_3$	1589	1211	923	646	—	—	—	—
3b	$Bi(SOCC_6H_4$-*o*-$Me)_3$	1556	1195	918	650	2.56	7.08 - 7.76	21.45	125.68, 131.42, 131.86, 132.45, 137.65
3c	$Bi(SOCC_6H_4$-'-$Me)_3$	1556	1211	923	648	2.36	7.20 - 7.80	—	—
4a	$PhSb(SOCPh)_2$	1614	1207	918	648	—	—	—	—
4b	$Ph_2Sb(SOCPh)$	1614	1207	918	648	—	—	—	—

sium salt of monothiobenzoic acid in dichloromethane (~30 cm^3) at room temperature (35 °C) with constant stirring. After ~3 - 4 h of stirring the potassium chloride formed was removed by filtration and the solvent from the filtrate in vacuo. The residue was dried for 1 - 2 h at 0,01 mm Hg/30 °C. $PhSb(SOCPh)_2$ was crystallized from dichloromethane.

Crystallography

Single crystal X-ray diffraction determinations for compounds **1a**, **2a**, **3b**, and **4a** were performed using a Siemens P4 automated diffractometer operating with a graphite monochromator and Mo-Kα radiation (λ = 0.71073 Å) for data collection at 20 °C. Suitable crys-

Table III. Crystal data and data collection parameters.

Compound	**1a**	**2a**	**3b**	**4a**
Chem. formula	$C_{21}H_{15}O_3S_3As$	$C_{21}H_{15}O_3S_3Sb$	$C_{24}H_{21}BiO_3S_3$	$C_{20}H_{15}O_2Sb$
Form. Wght.	486.43	533.26	662.57	473.19
Cryst. Size (mm)	0.6×0.2×0.2	0.28×0.38×0.5	0.28×0.32×0.35	0.18×0.2×0.6
Cryst. System	hexagonal	hexagonal	hexagonal	monoclinic
Space group	R3	R3	R3	P2(1)/*n*
a [Å]	20.418(3)	20.488(2)	21.531(4)	10.901(2)
b [Å]	20.418(3)	20.488(2)	21.531(4)	5.685(2)
c [Å]	4.179(1)	4.245	4.305(1)	30.104(5)
α [°]	90	90	90	90
β [°]	90	90	90	96.76(1)
γ [°]	120	120	120	90
V [$Å^3$]	1508.8(5)	1543.1(2)	1728.4(6)	1852.6(8)
Z	3	3	3	4
p(calcd) [Mg(m^3]	1.606	1.721	1.910	1.696
μ [mm^{-1}]	2.021	1.665	7.947	1.725
F(000)	738	792	960	936
Index range	$-21\le h\le 21$, $-1\le k\le 24$, $-5\le l\le 5$	$-23\le h\le 21$, $-20\le k\le 24$, $-1\le l\le 5$	$-1\le h\le 23$, $-26\le k\le 1$, $-5\le 1\le 5$	$0\le h\le 12$, $0\le k\le 6$, $-35\le l\le 35$
2θ [°]	51.98	49.96	52.00	50.00
Temp. [K]	293(2)	193(2)	293(2)	243
Refl. collected	2516	1434	1616	3444
Refl. unique	1287	870	1443	3260
Refl. observed (4σ)	1256	870	1443	3260
R (int.)	0.0280	0.0280	0.0207	0.0210
No. variables	100	99	95	271
Weighting scheme[1] *x*/*y*	0.0906/0.0000	0.0344/0.0000	0.0409/68.6453	0.0483/0.0000
GOOF	1.046	1.095	1.089	1.144
Final $R(4\sigma)$	0.0420	0.0211	0.0403	0.0325
Final $wR2$	0.1031	0.0516	0.1050	0.0864
Larg. res. peak [e/$Å^3$]	0.527	0.967	0.553	0.655

[1] $w^{-1} = \sigma^2F_o{}^2 + (xP)^2 + yP$; $P = (F_o{}^2 + 2F_o{}^2)/3$.

tals of **1a**, **2a** and **4a** were obtained from CH_2Cl_2 solutions, while **3b** was obtained from acetone solution. Unit cell parameters were refined from the setting angles of 16 - 25 centered reflections by the least-squares method. Lorentz and polarisation corrections were employed as well as empirical absorption correction (Ψ scans). Non-hydrogen atoms were refined anisotropically with hydrogen atoms in calculated positions. Computations were performed with the SHELXTL PLUS [23] or SHELXL 93 [24] program packages. Details of crystallographic data, data collection and structure solution are given in Table II. Refinements were performed on F^2.

Results and Discussion

Arsenic, antimony and bismuth tris-thiocarboxylates, $M(SOCR)_3$, have been prepared in high yields by reacting thiobenzoic acid with the corresponding oxides in appropriate molar ratio at room temperature, in dichloromethane as shown in eq. (1). Very recently the synthesis of $Bi(SOCPh)_3$ was also reported from the reaction of $Bi(OAc)_3/Bi(SPh)_3$ with thiobenzoic acid [5].

$$M_2O_3 + 6\ RCOSH \rightarrow 2\ M(SOCR)_3 + 3\ H_2O \qquad (1)$$

(M = As, Sb and Bi;
R = Ph, *o*-MeC_6H_4 and *p*-MeC_6H_4)

$$Ph_{3-x}\ SbCl_x + x PhCOSK \rightarrow Ph_{3-x}Sb(SOCPh)_x + x KCl \qquad (2)$$

Arylantimony thiobenzoates were obtained by metathesis of the corresponding arylantimony chloride with K[SOCPh] (eq. (2)).

Most of the compounds (see Table I) are white to yellow solids. They are hydrolytically and thermally stable, and those of arsenic and antimony are soluble in common organic solvents. While Bi(SOCPh)$_3$ and Bi(SOCC$_6$H$_4$-p-Me)$_3$ are almost insoluble in polar and nonpolar organic solvents, the ortho methyl substituted complex, Bi(SOCC$_6$H$_4$-*o*-Me)$_3$ is soluble.

Vibrational spectra

Characteristic infrared absorption bands of thiobenzoic acids are found at 1965 [(νC=O)] 1213 [ν(Ph-C)] and 950 cm^{-1} [ν(C$\underline{\cdots}$S)] (see also Table III). In the IR spectra of complexes **1**, **2** and **4** the CO stretching band was found in the frequency range 1589 - 1637 cm^{-1}. Appreciable lowering of the ν(C$\underline{\cdots}$S) absorption (879 - 923 cm^{-1}) indicates a single bond between sulfur and carbon substantiating the coordination of the thiobenzoate only through its sulfur donor atom. In addition the ν(Ph-C) absorption in the region 1190 - 1213 cm^{-1} also reveals monodentate attachment of the ligand because in its chelating mode this absorption is shifted to a higher frequency [3]. Overall the IR data are similar to those of [In(SOCPh)$_4$]$^-$[8] and the dinuclear Cu(I) thiobenzoate complex [7], whose crystal structure shows the presence of a monodentate sulfur bonded ligand, as well as earlier reported complexes of this ligand with soft cations such as Cd(II), Hg(II), Cu(I) and Ag(I) [3]. Bismuth complexes (**3**), on the other hand, exhibit a somewhat lower ν(C=O) absorption (1556 - 1589 cm^{-1}) suggesting the presence of a chelating thiobenzoate ion. However, the positions of ν(C-S) and ν(Ph-C) absorptions are not different from the rest of these complexes.

Crystal and molecular structures

To verify the bonding of the PhCOS ligand, X-ray structure analyses of **1a**, **2a** **3b** and **4a** were performed. The tris(monothioaroyl) complexes **1a**, **2a** and **3b** are isomorphous, crystallizing in the rhombohedrical system, space group R3, with three molecules in the unit cell (see Table II). Selected bond lengths and bond angles are compiled in Table IV. In each case the metal atom occupies a special position on the C$_3$ axis. However, while the ligand is typically S-monodentate for the As and Sb compound, a bidentate behaviour is suggested from the bond lengths for the bismuth complex **3b** (see Figs 1 and 2).

Table IV. Selected bond dimensions of compound **1a**, **2a**, **3b** and **4a**.

A) Bond lengths and intermolecular atom distances without esd's (Å)			
1a:			
As(1)-S(1)	2.283(1)	O(1)-C(1)	1.213(6)
		S(1)-C(1)	1.790(4)
As(1)-S(1B)	3.525	C(1)-C(2)	1.488(6)
2a:			
Sb(1)-S(1)	2.489(1)	O(1)-C(1)	1.214(6)
		S(1)-C(1)	1.773(4)
Sb(1a)-S(1b)	3.509	C(1)-C(2)	1.488(7)
3b:			
Bi(1)-S(1)	2.630(3)	S(1)-C(2)	1.77(2)
		O(1)-C(2)	1.21(2)
Bi(1A)-(S1B)	3.498	Bi(1)-O(1)	2.752(6)
4a:			
Sb(1)-C(1)	2.160(5)	Sb(1)-S(1)	2.487(1)
Sb(1)-S(2)	2.504(2)	S(1)-C(7)	1.766(6)
S(2)-C(14)	1.761(5)	O(1)-C(7)	1.231(7)
O(2)-C(14)	1.237(6)	Sb(1A)-S(1D)	3.769
B) Bond angles (°)			
1a:			
S(1)A-As(1)-S1	93.85(4)	C(1)-S(1)-As(1)	94.5(1)
O(1)-C(1)-C(2)	123.0(4)	O(1)-C(1)-S(1)	120.5(3)
C(2)-C(1)-S(1)	115.9(3)		
2a:			
S(1)A-Sb(1)-S(1)	91.37(3)	C(1)-S(1)-Sb(1)	90.4(2)
O(1)-C(1)-C(2)	122.8(4)	O(1)-C(1)-S(1)	120.6(3)
C(2)-C(1)-S(1)	116.6(4)		
3b:			
C(1)-Bi(1)-S(1)	57.8(2)	O(1)-Bi(1)-O(1A)	120.0(1)
C(1)-Bi(1)-S(1A)	74.2(2)	S(1)-Bi(1)-S(1A)	89.40(9)
S(1)-Bi1-O(1A)	142.6(2)		
4a:			
C(1)-Sb(1)-S(1)	95.3(1)	C(1)-Sb(1)-S(2)	96.2(1)
S(1)-Sb(1)-S(2)	83.96(5)	C(7)-S(1)-Sb(1)	87.6(2)
C(14)-S(2)-Sb(1)	88.2(1)	C(6)-C(1)-Sb(1)	117.1(4)
O(1)-C(7)-S(1)	119.5(4)	O(1)-C(7)-C(8)	121.6(5)
C(8)-C(7)-S(1)	118.8(4)	O(2)-C(14)-C(15)	121.5(5)
O(2)-C(14)-S(2)	119.6(4)	C(15)-C(14)-S(2)	118.9(4)

Inspite of this difference, all these compounds can be considered to have a trigonal pyramidal geometry with respect to the MS$_3$ skeleton. While M---O distances in **1a** and **2a** suggest no bonding contribution, the Bi-O distances in **3b** (2,724 Å) are considerably shorter than the van der Waals interaction (3,47 Å), although definitely longer than a Bi-O single bond length (2,18 Å). Therefore, a weak BiO interaction is suggested. The BiO$_3$ unit is essentially planar as indicated by O-Bi-O angles of 120°, and this leads to a capping of the rectangular faces resulting from the

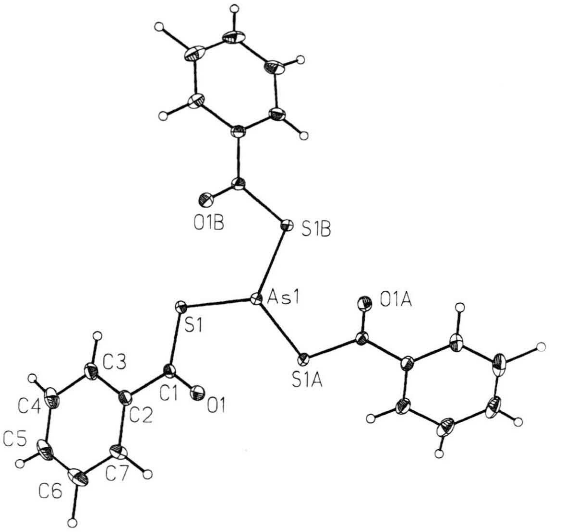

Fig. 1. Molecular structure of $As[S(O)CPh]_3$, **1a**; view down the threefold axis. Thermal ellipsoids represent a 25% probability.

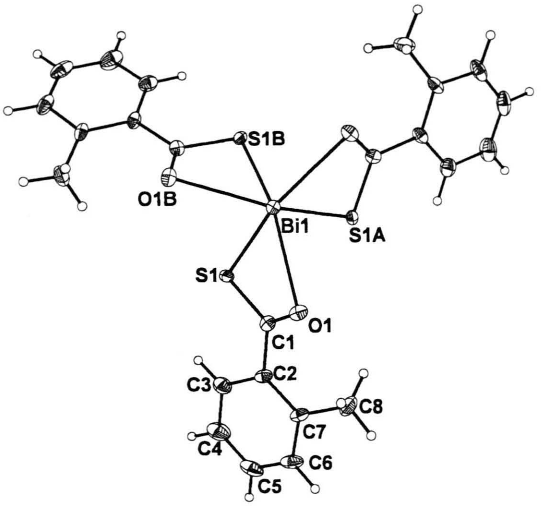

Fig. 2. Molecular structure of $Bi[S(O)C\text{-}C_6H_4\text{-}m\text{-}CH_3]_3$, **3b**. Thermal ellipsoids are shown at the 25% probability level.

intermolecular Bi-S interaction of the molecules **3b** (see Fig. 3). The same type of intermolecular M-S interaction of molecules is found for compounds **1a** and **2a** as depicted in Fig. 4. This results in a stacking of the molecules with formation of a trigonal prismatic arrangement of S atoms about the central atoms As, Sb and Bi. Thus, the intermolecular As-S contacts are 3,525 Å for **1a** (sum of van der Waals radii, sWr, is 3,85 Å), 3,509 Å for **2a** (sWr = 4,05 Å), and 3,498 Å for **3a** (sWr = 4,25 Å), the differences being 0,32, 0,44 and 0,75 Å, respectively. On the other hand, the differences between the M-S bond lengths decrease regularly (1,25, 1,02 and 0,57 Å). As expected, the S-M-S bond angles of the trigonal pyramidal units decrease from 93,85(4)° (As) via 91,37(3)° (Sb) to 89,4(1)° (Bi).

That there is indeed a Bi-O interaction in compound **3a** is revealed not only by a fairly short Bi···O distance but also by the C-O bond lengths: Their lengths are 1,214(6) Å) in **1a** and **2a**, and this bond is elongated to 1,228(8) Å in **3a**. In contrast, the C-S bond lengths become shorter with increasing atomic weight of the central metal atom (1,790, 1,773 and 1,70 Å), suggesting a higher bond order. Nevertheless, the main feature of these three compounds is the trigonal prismatic arrangement of six sulfur atoms around the central metal with three short and three long M-S atomic distances.

This pattern cannot result of course for the phenylantimony compound **4a** which resembles the

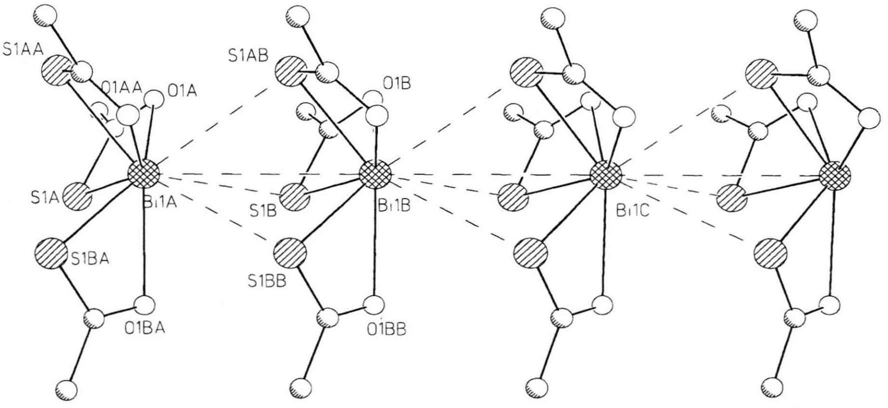

Fig. 3. Intermolecular interactions between **3b** molecules; only the ipso-carbon atoms of the *m*-tolyl group is shown.

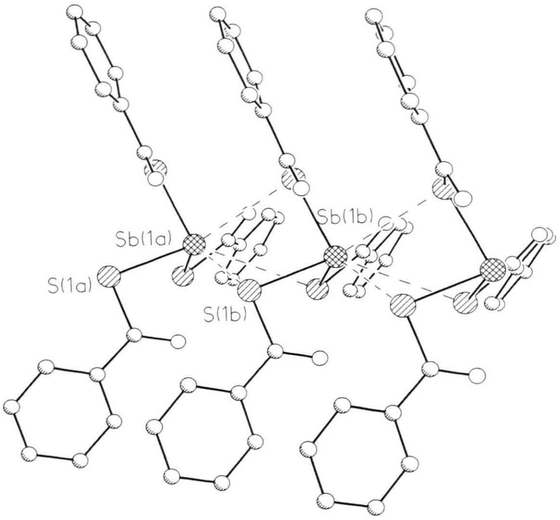

Fig. 4. Intermolecular interactions of $Sb[S(O)CPh]_3$ molecules.

previous examples with regard to an absence of Sb···O bonding (see Fig. 5)

The two Sb-S bonds are significantly different (2,487(1) and 2,504(2) Å. The Sb-C bond length is 2,160(5) Å, and the geometry at the Sb atom is distorted trigonal pyramidal. The S1-Sb-S2 bond angle is quite small (83,96(5)°) while the C-Sb-S bond angles are 95,3(1) and 96,2(1)°. In the crystal the molecular units (see Fig. 5) have intermolecular Sb·(·S contacts to two S atoms resulting in a shorter contact (3,77 Å) and a longer one (3,98 Å). This generates a strand of molecules in the unit cell, the Sb-S-Sb angles being 81,6 and 124°, respectively.

Discussion

Since the monothiocarboxylate units contain one soft and one hard donor atom the most interesting question is, how does the coordination behavior change within the series O_2CR, O(S)CR and S_2CR (R = organyl, NR_2, OR). Structural comparisons of **1a** can be made with arsenic(III) xanthates $As(S_2COR)_3$ [25 - 27] and arsenic diethyldithiocarbaminate $As(S_2CNEt_2)$ [28] which in contrast to **1a** exhibit no intermolecular As-S contacts, most likely due to the fact that S_2CR' units act as asymmetrically bidentate ligands (d(As-S): 2,305 - 2,511 Å for the xanthate, average 2,348 Å for the diethyldithiocarbamate [28]). These bond lengths are shorter than those determined for **1a**. The methyl [25] and the isopropyl xanthates [27] have a distorted octahedral geometry, in contrast to **1a,** due to the chelating behavior of their ligands. While $As(S_2COEt)_3$ adopts an intermediate geometry between an octahedron and a trigonal prism [26], $As(S_2CNEt_2)_3$ [28] shows C_3 point group symmetry [29].

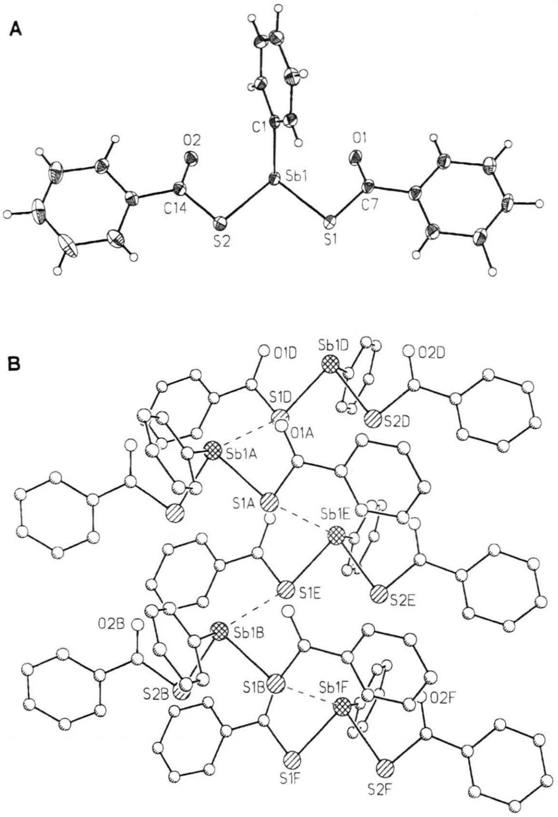

Fig. 5. A) Molecular structure of $PhSb[S(O)Ph]_2$, **4b**, with 25% thermal ellipsoids. B) Intermolecular interactions in the lattice.

The CO bonds in **1a** correspond to a double bond [30] (see also Table III) and, consequently, the C-S bond is comparatively long, corresponding to a single bond. All other bonding parameters are as to be expected.

The Bi complex **3b** differs in its structure particularly due to the weak intramolecular BiO coordination. The tendency of Bi complexes to attain higher coordination numbers in comparison to the Sb complexes is a well known phenomenon as illustrated by the structures of $Bi[O(O)CH]_3$ [32], $Bi[O(O)CCH_3]_3$ [33] or $Bi[O(O)CCMe_3]_3$ [34] where up to nine O atoms coordinate to the Bi center.

As the size of the central atom increases an expansion of the coordination shell can be expected as verified *e.g.* for the series of tris(ethyldithiocarbamato)arsenic, -antimony and -bismuth complexes. The arsenic compound is a molecular compound with C_3 point group symmetry [29] while in the antimony and bismuth complexes weak intermolecular metal sulfur contacts are established expanding the coordination to a dodecahedron [31]. Although the molecular symmetry of $Bi(SOC\text{-}p\text{-}Tol)_3$ is comparable to that of $Bi(S_2CNEt_2)_3$, the intermolecular interaction is quite different since the stacking of the molecules leads to a trigonal prism for the BiS_6 core.

One may envisage that the lone pairs of electrons at As(III), Sb(III) and Bi(III) are directed along the three fold axis of the molecules. However, the bond angles S-M-S are all close to 90°, and it thus appears that the lone pair has a high degree of s-character and is therefore not stereochemically active.

While the molecular structure of $PhSb(SOCPh)_2$ **4b** and $PhSb(OSCMe)_2$ [10] are very similar – **4b** has somewhat longer Sb-S and C=O bonds, while the S-C bond lengths are identical – the main structural differences are significant Sb-O contacts in the thioacetate (Sb···O: 2.808, 2.818(6)Å), leading to a square pyramidal geometry with an apical phenyl group. These molecular units join to a dimer in the solid state (Sb···S': 3.802 Å) in contrast to compound **4b** where two additional Sb···S interactions with neighbouring sulfur atoms are establised (Sb···S 3.769 Å) as depicted in Fig. 5.

The differences in the packing in the crystal are most likely due to the greater space requirements of the phenyl groups compared to the methyl groups allowing a close packing of the SbS_2 units.

The best molecule to be compared with **2a** is the antimony(III) thioacetate $Sb(S(O)CMe)_3$ [10]. Its Sb-S bonds are somewhat longer than in **2a** but shorter than in the xanthates $Sb(S_2COR)_3$ [25 - 27] (2.511 - 2.546 Å) or $Sb(S_2CNEt_2)_3$ (2.57 Å) [31]. It is particularly noteworthy that the intermolecular Sb··S distances are shorter than those of As···S. We attribute this to the particularly strong Lewis acidic character of Sb(III) compounds compared to As(III) compounds [11]. In the antimony(III) acetate, xanthates and diethyldithiocarbamate the ligands are bonded asymmetrically as in **2a**. In case of $Sb(S_2COMe)_3$ [25] there are also intermolecular Sb-S contacts which generate a dimeric unit in contrast to the stacks of **2a**.

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