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Antimony and bismuth dithiocarboxylates of the type $[M(S_2CAr)_3]$ (M = Sb, Bi; Ar = C₆H₅ (Ph), 4-MeC₆H₄

(tol)) have been synthesized. These complexes were characterized by elemental analysis, IR, UV-Vis, and

¹H NMR spectroscopy. X-ray crystal structural analyses of [Sb(S₂Ctol)₃] and [Bi(S₂CPh)₃] showed that the

dithiocarboxylates are asymmetrically chelated to metal atom. The latter acquires a distorted pentagonal

pyramidal geometry as a consequence of the presence of a stereochemically active lone pair of electrons. Pyrolysis of these complexes either in a furnace or in refluxing diphenylether gave M₂S₃ as characterized

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by their XRD pattern and EDAX analysis.

ABSTRACT

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1. Introduction

Group V-chalcogenide materials are of special importance owing to their good photovoltaic properties and high thermo-electric power which allow potential applications in various opto-electronic and thermo-electric cooling devices [1,2]. The compounds, Sb_2S_3 (band gap 1.78–2.5 eV) and Bi_2S_3 (band gap 1.3–1.7 eV), direct band semiconductors, have received considerable attention recently [3,4]. Polymer coated Bi₂S₃ nanoparticles have been used as imaging agent in X-ray computed tomography [5]. Several synthetic strategies have been adopted to prepare M_2S_3 [4,6,7], although use of single source precursors for their preparation appears to be quite promising. The potential of 1,1-dithiolate complexes of antimony and bismuth for the preparation of thin films and nanoparticles of M₂S₃ (M = Sb or Bi) has been realized only recently. Thus complexes, $[Sb(S_2CNRR')_3]$ [8], $[Bi(S_2CNRR')_3]$ [9], $[Bi(S_2COR)_3]$ (R = Me or Et) [10], $[MeBi(S_2COR)_2]$ [11] and $[Bi\{S_2 P(OC_8H_{17})_{2}$ [12], have been used as molecular precursors for the synthesis of M₂S₃. The 1,1-dithiolate complexes have a niche over other precursors like $[M(SR)_3]$ [13,14] and $[Bi\{(SPPr_2^i)_2N\}_3]$ [15] due to their ease of synthesis and cleaner decomposition.

The chemistry of 1,1-dithiolate complexes of arsenic, antimony and bismuth has been an active area of research for nearly half a century [16] and has been dominated by ligands of the type **A**–**C**

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with little attention on dithiocarboxylates (**D**) [17]. The sustained interest in these complexes has been associated due to their numerous applications (catalysts, lubricants, biocides and materials science) and diverse structural features ranging from monomeric to polymeric supramolecular assemblies. Subtle variations in the nature of the organic substituents on the dithiolate group usually result in different structural motifs [16].

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In the above prospective it was considered worthwhile to examine dithiocarboxylates of antimony and bismuth with the following objectives: (a) to identify the kind of structural motifs adopted by this family of 1,1-dithiolate ligands, and (b) to assess their suitability as molecular precursors for the preparation of M₂S₃. The results of this work are described herein.

2. Experimental

All experiments involving antimony and bismuth trichlorides were carried out under anhydrous conditions in Schlenk flasks.



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Fig. 1. Molecular structure of [Sb(S₂Ctol)₃] (ORTEP diagram with 50% probability). Inset shows the line diagram of the molecule.

Solvents were dried by standard procedures. Antimony and bismuth trichlorides were sublimed before use. Dithiocarboxylic acids were prepared by the reported methods [18]. (¹H NMR in CDCl₃, PhCS₂H δ : 6.40 (s, br, SH); 7.39 (br, 2H, H-3, 5); 7.57 (br, 1H, H-4); 8.07 (br, 8.2 Hz, H-2,6). tolCS₂H, δ : 2.38 (s, Me); 4.71 (s, SH); 7.19 (d, 8.3 Hz, 2H, H-3,5); 7.98 (d, 8.2 Hz, 2H, H-2,6) (C₆H₄)). Infrared spectra were recorded as Nujol mulls between CsI plates on a Bomem MB-102 FT IR spectrometer. ¹H NMR spectra were recorded on a Bruker Avance 200 spectrometer as a CDCl₃ solution. Chemical shifts are relative to the internal chloroform peak (δ 7.26 ppm). Electronic spectra were recorded in dichloromethane on a Chemito Spectrascan UV double beam UV–Vis spectropho-



Fig. 2. Molecular structure of [Bi(S2CPh)3] (ORTEP diagram with 50% probability). Inset shows the line diagram of the molecule.

tometer. The TG analyses were performed on a Netzsch STA Luxx instrument which was calibrated with $CaC_2O_4 \cdot H_2O$. Powder X-ray diffraction data were collected on a Philips PW 1820.

2.1. Synthesis

2.1.1. Preparation of [Sb(S₂CPh)₃]

To a benzene solution (60 cm^3) of antimony trichloride (619 mg, 2.71 mmol), a solution of PhCS₂H (1.258 g, 8.15 mmol) and triethylamine (825 mg, 8.15 mmol) in the same solvent was added with stirring. The whole was stirred at room temperature for 4 h. The precipitate was filtered through a G-3 filtration unit and thoroughly washed with methanol to remove Et₃N · HCl, and the orange residue was dried in vacuo (835 mg, 53%). M.p. 175 °C (decomp.). *Anal.* Calc. for C₂₁H₁₅S₆Sb: C, 43.4; H, 2.6; S, 33.1. Found: C, 42.9; H, 2.1; S, 33.5%. UV–Vis λ_{max} : 244, 315 nm. ν (C–S) 722 cm⁻¹, ν (C=S) 1220 cm⁻¹. ¹H NMR in CDCl₃ δ : 7.41 (t, 7.4 Hz, H-3, 5), 7.63 (t, 7.2 Hz, H-4); 8.24 (d, 8 Hz, H-2, 6).

2.1.2. Preparation of [Sb(S₂Ctol)₃]

[Sb(S₂Ctol)₃] was prepared similar to [Sb(S₂CPh)₃] as an orange crystalline solid in 75% yield; m.p. 190 °C (decomp.). *Anal.* Calc. for C₂₄H₂₁S₆Sb: C, 46.2; H, 3.4; S, 30.8. Found: C, 46.0; H, 2.9; S, 30.5%. UV–Vis λ_{max} : 242, 337 nm. ν (C–S) 721 cm⁻¹, ν (C=S) 1222 cm⁻¹. ¹H NMR in CDCl₃ δ : 2.37 (s, Me); 7.17 (d, 7.5 Hz, H-3, 5); 8.16 (d, 7.6 Hz, H-2, 6).

2.1.3. Preparation of $[Bi(S_2CPh)_3]$

[Bi(S₂CPh)₃] was prepared similar to antimony complex as an orange-red solid (pyridine instead of triethylamine was used in the reaction) in 69% yield; m.p. 135 °C (decomp.). *Anal.* Calc. for C₂₁H₁₅BiS₆: C, 37.7; H, 2.3; S, 28.8. Found: C, 38.1; H, 2.3; S, 29.2%. UV–Vis λ_{max} : 242, 324 nm. ν (C–S) 723 cm⁻¹, ν (C=S) 1210 cm⁻¹. ¹H NMR in CDCl₃ δ : 7.40 (t, 7.6 Hz, H-3,5); 7.63 (t, 7.6 Hz, H-4); 8.21 (d, 7.8 Hz, H-2,6).

2.1.4. Preparation of [Bi(S₂Ctol)₃]

[Bi(S₂Ctol)₃] was prepared similar to antimony complex as an orange-red solid in 79% yield; m.p. 185 °C (decomp.). *Anal.* Calc. for C₂₄H₂₁BiS₆: C, 40.5; H, 3.0; S, 27.0. Found: C, 40.2; H, 2.7; S, 26.8%. UV–Vis λ_{max} : 235, 345 nm. ν (C–S) 720 cm⁻¹, ν (C=S) 1224 cm⁻¹. ¹H NMR in CDCl₃ δ : 2.38 (s, Me); 7.20 (d, 8 Hz, H-3, 5); 8.14 (d, 8 Hz, H-2, 6).

Table 1

Crystallographic data and structural refinement details for $[Sb(S_2Ctol_3] \mbox{ and } [Bi(S_2CPh)_3]$

	[Sb(S ₂ Ctol) ₃]	[Bi(S ₂ CPh) ₃]
Chemical formula	C ₂₄ H ₂₁ S ₆ Sb	C ₂₁ H ₁₅ BiS ₆
Formula weight	623.52	668.67
Crystal size (mm)	$0.40 \times 0.20 \times 0.05$	$0.30 \times 0.05 \times 0.05$
Crystal System	monoclinic	monoclinic
Space group	C2/c	C2/c
a (Å)	35.00(3)	31.800(8)
b (Å)	6.388(5)	6.4700(13)
c (Å)	27.250(12)	24.874(7)
β (Å)	120.10(5)	119.30(2)
Volume (Å ³)/Z	5271(7)/8	4463.1 (18)/8
$\mu ({\rm mm^{-1}})/F(000)$	1.533/2496	8.468/2560
θ Range (°)	2.67-27.50	2.60-27.51
Limiting indices	$-25 \leqslant h \leqslant 45$	$-23 \leqslant h \leqslant 41$
	$0 \leqslant k \leqslant 8$	$0 \leqslant k \leqslant 8$
	$-35 \leqslant l \leqslant 30$	$-32 \leqslant l \leqslant 28$
Number of reflections/unique	7111/6022	6071/5137
Number of data/restraints/parameters	6022/0/283	5173/0/253
Final R_1 [I > $2\sigma(I)$]	0.0686, 0.0920	0.0470, 0.0657
R_1 , wR_2 (all data)	0.3056, 0.1352	0.1643, 0.0858
Goodness of fit on F^2	0.906	0.936

2.2. X-ray crystallography

Red crystals of $[Sb(S_2Ctol_3]$ and $[Bi(S_2CPh)_3]$ were grown from dichloromethane/hexane mixture and dichloromethane containing few drops of pyridine, respectively. Addition of pyridine facilitates dissolution of sparingly soluble complexes, possibly by the formation of a labile pyridine adduct. Intensity data were measured on Rigaku AFC7S diffractometer fitted with Mo K α ((λ -0.71069 Å) radiation so that $\theta_{max} = 27.5^{\circ}$. The structure was solved by direct methods [19] and refinement was on F^2 [20] using data corrected for absorption correction effects with an empirical procedure [21,22]. The non-hydrogen atoms were refined with anisotropic displacement parameters and fitted with hydrogen atoms in their calculated positions. Molecular structure was drawn using ORTEP [23]. Crystallographic and structural determination data are listed in Table 1.

2.3. Preparation of M₂S₃

- (a) *Pyrolysis in a furnace:* A weighed quantity of the complex in a quartz boat was heated in a pre-heated furnace at 300 °C under a flowing nitrogen atmosphere for 4 h. After cooling, the residue was analyzed by XRD pattern and EDAX.
- (b) Solvothermal decomposition of complexes: Thermolysis of both antimony and bismuth complexes was carried out in a similar manner. In a typical experiment, diphenylether (25 cm^3) in a three-necked flask was degassed at refluxing temperature under nitrogen for 30 min. To this a weighed quantity of $[\text{Bi}(S_2\text{Ctol})_3]$ (42 mg, 0.06 mmol) was added and the mixture was refluxed for 3 h and gradually cooled. Thorough washing with methanol (5 × 3 cm³) followed by centrifuging and drying under vaccum gave a black residue (10 mg, 65%), which was characterized as Bi_2S_3 by XRD and EDAX analysis.

3. Results and discussion

3.1. Synthesis and spectroscopy

Treatment of antimony and bismuth trichlorides with dithiocarboxylic acid in 1:3 stoichiometry in the presence of triethylamine in benzene afforded orange-red tris dithiocarboxylate complexes of the general formula $[M(S_2CAr)_3]$ (M = Sb or Bi; Ar = Ph or tol) (Scheme 1). The electronic spectra of these complexes exhibited two strong absorptions at ~245 and ~330 nm attributable to π - π^* and n- π^* transitions in the thiocarbonyl group [24]. The band at ~330 was accompanied by an ill-defined shoulder ~350 nm. The IR spectra displayed absorptions due to v(C=S)and v(C-S) stretchings at ~1220 and ~720 cm⁻¹, respectively [25]. ¹H NMR spectra showed characteristic peaks due to aryl protons of the dithiocarboxylate groups. The 2,6-protons of the aryl group are deshielded with respect to the corresponding resonances for the free ligand.

3.2. Crystal structures of [Sb(S₂Ctol)₃] and [Bi(S₂CPh)₃]

The complexes $[Sb(S_2Ctol)_3]$ and $[Bi(S_2CPh)_3]$ are discrete monomers having isomorphous structures (Figs. 1 and 2). Overall molecular geometry can be described as pentagonal pyramidal. All the three dithiocarboxylates are asymmetrically chelated to the central metal atom. The two dithiocarboxylate ligands are nearly coplanar (164.73° for Sb, 163.65° for Bi) while the third ligand is approximately orthogonal to these ligands with S1 at the apex of the pyramid. There is a void opposite to this apical ligand which can be thought of being occupied by stereochemically active lone pair of electrons. This void in associated structures (*e.g.*,



 $(M = Sb, Bi; S^{S} = ArCS_{2}; Ar = phenyl (Ph), p-tolyl (tol))$

Scheme 1.

 $Bi(S_2PMe_2)_3$ [26]) is filled by sulfur atom of a chelating ligand of another molecule giving secondary $M\cdots S$ linkages.

The asymmetry in the M–S bonds of the apical ligand is higher than for the remaining two ligands. The difference in the M–S distances between long and short M–S bonds of a chelating dithiocarboxylate group is greater for antimony complex than the corresponding values for the bismuth derivative. Owing to the anisobidentate chelating ligands, an inverse relationship between M–S and C–S bond distances is evident from Table 2. Thus the shorter M–S distances are associated with longer C–S distances and vice-versa for a four-membered 'MS₂C' chelate ring. The C–S distances (short 1.66 (av.) and long 1.71 (av.) Å) are essentially similar to those reported for dithiocarboxylate complexes [24]. The M–S distances of antimony and bismuth. The S–M–S angles in the chelate are 64° and 63° (av.) for antimony and bismuth com-

 Table 2

 Selected bond distances (Å) and angles (°) for [Sb(S2Ctol)3] and [Bi(S2CPh)3]

	[Sb(S ₂ Ctol) ₃]	[Bi(S ₂ CPh) ₃]
M-S(1)	2.481(3)	2.581(2)
M-S(2)	2.935(3)	2.938(3)
M-S(3)	2.654(3)	2.764(3)
M-S(4)	2.866(4)	2.903(3)
M-S(5)	2.636(3)	2.742(3)
M-S(6)	2.808(3)	2.860(3)
C(1) - S(1)	1.728(9)	1.746(9)
C(1)-S(2)	1.652(9)	1.651(8)
C(8) - S(3)	1.700(10)	1.710(10)
C(8) - S(4)	1.666(11)	1.672(11)
C(15) - S(5)	1.714(10)	1.698(9)
C(15) - S(6)	1.667(11)	1.679(10)
C(1) - C(2)	1.461(12)	1.472(10)
C(8) - C(9)	1.492(13)	1.488(12)
C(15)–C(16)	1.496(14)	1.470(12)
S(1)-M-S(2)	64.70(10)	63.84(8)
S(1)-M-S(3)	84.35(10)	86.07(8)
S(1)-M-S(4)	79.65(11)	80.30(8)
S(1)-M-S(5)	88.32(10)	87.45(8)
S(1)-M-S(6)	84.31(11)	82.79(8)
S(2)-M-S(3)	132.71(10)	132.18(7)
S(2)-M-S(4)	75.66(10)	76.09(8)
S(2)-M-S(5)	132.00(10)	134.10(7)
S(2) - M - S(6)	73.36(10)	77.84(8)
S(3)-M-S(4)	63.73(9)	62.17(8)
S(3)-M-S(5)	77.73(10)	75.33(8)
S(3) - M - S(6)	140.91(9)	137.06(8)
S(4) - M - S(5)	140.41(9)	136.29(8)
S(4) - M - S(6)	148.85(9)	153.21(7)
S(5)-M-S(6)	64.66(9)	62.89(7)
M-S(1)-C(1)	94.6(3)	93.3(3)
M-S(2)-C(1)	81.0(3)	83.3(3)
S(1)-C(1)-S(2)	119.7(5)	119.5(5)
M-S(3)-C(8)	91.2(4)	90.8(4)
M-S(4)-C(8)	84.8(4)	86.9(4)
S(3)-C(8)-S(4)	120.3(7)	120.0(6)
M-S(5)-C(15)	90.4(4)	90.3(3)
M-S(6)-C(15)	85.6(4)	86.7(3)
S(5)-C(15)-S(16)	119.1(7)	120.0(6)

plexes, respectively, as a consequence of a small bite of dithiocarboxylate ligand.

A variety of tris complexes of antimony and bismuth containing 1,1-dithiolates such as xanthates, dithiocarbamates and dithiophosphates have been characterized by X-ray crystallography. The metal atom in these complexes adopts either a regular octahedral geometry or a distorted variance of this configuration (*e.g.*, pentagonal pyramid) depending on whether the lone pair of electron is subdued or is stereochemically active. Both discrete monomers and associated structures formed by a weak secondary $M \cdots S$ interaction have been identified (Table 3) [27–35]. Attempts to rationalize the observed stereochemistry based on factors, such as ligand acidity, ligand bite, nature of the substituents on the ligand or the size of the metal ion, have met with little success. Nonetheless the crystal packing factors, which are difficult to evaluate, seem to play a significant role in determining the stereochemistry of the molecule.

3.3. Thermal studies

The TG curve of $[Sb(S_2CPh)_3]$ showed a single step decomposition at 275 °C with weight loss of 69.4%, suggesting the formation



Fig. 3. XRD pattern of Sb_2S_3 prepared from $[Sb(S_2CPh)_3]$. (a) Heated in a furnace at 300 °C, (b) in diphenylether at 230 °C.

Table 3	
Salient structural features of some 1	.1-dithiolate complexes of antimony and bismuth

Compound	Nuclearity	M–S distance in Å			∠S–M–S in (°)	\angle S–X–S in (°) (X = C or P)	Reference
		M-S _(short)	$M - S_{(long)}$	ΔM–S			
[Sb(S ₂ Ctol) ₃]	monomer	2.48-2.64	2.81-2.93	0.17-0.45	~ 64	119.7	a
[Bi(S ₂ CPh) ₃]	monomer	2.58-2.74	2.86-2.94	0.12-0.36	~63	120	a
[Sb(S ₂ COEt) ₃]	monomer	2.511(2)	3.002(3)	0.49	64.65(6)	123.8(5)	27
$[Sb(S_2COMe)_3]_2$	dimer	2.477-2.591	2.930-3.079	0.36-0.60	64.4 (av.)	123.7 (av.)	28
[Bi(S ₂ COMe) ₃] ₂	dimer	2.596-2.747	2.933-2.998	0.21-0.40	63.5 (av.)	123.8 (av.)	28
$[Sb{S_2CN(CH_2CH_2OH)_2}_3]$	monomer	2.463-2.673	2.763-2.878	0.12-0.41	64.6-66.9	117.5-118.9	29
$[Sb(S_2CNEt_2)_3]_2$	dimer	2.487-2.631	2.886-2.965	0.26-0.48	64.8 (av.)	118.5	30
$[Bi(S_2CNEt_2)_3]_2$	dimer	2.595-2.775	2.908-2.964	0.18-0.36	63.5 (av.)	116.6-120.4	30
$[Sb{S_2P(OMe)_2}_3]$	monomer	2.53	3.00	0.47	72.6	112.5	31
$[Bi{S_2P(OEt)_2}_3]$	monomer	2.758	2.799	0.04	72.0		32
$[Sb(S_2PEt_2)_3]$	monomer	2.503-2.583	2.907-3.137	0.39-0.63	71.0-74.4	110.0-112.8	33
$[Bi(S_2PEt_2)_3]$	monomer	2.753-2.813	2.787-2.858	0.02-0.07	73.1	111.8	34
$[Bi(S_2PPh_2)_3]_2$	dimer	2.456-2.598	2.923-3.187	0.16-0.40	~73	110.4–113.3	35

^a This work.



Fig. 4. XRD pattern of Bi_2S_3 prepared from $[Bi(S_2Ctol)_3]$ (a) heated in a furnace at 300 °C, (b) in diphenylether at 230°.

of Sb_2S_3 (calc. wt loss = 70.8%). The complexes $[Sb(S_2CAr)_3]$ (Ar = Ph or tol) and $[Bi(S_2Ctol)_3]$ when heated in a furnace at 300 °C for 4 h



VAC: HIVac DET: SE Detector 10 µm Vega ©Tescan VAC: HIVac Device: VEGA MV2300T/40 Digital Microscopy Imaging

Fig. 5. SEM of Bi_2S_3 prepared from $[Bi(S_2Ctol)_3]$ by solvothermal decomposition in diphenylether at 230 $^\circ C.$

gave M_2S_3 (M = Sb or Bi) as revealed by their XRD patterns^{1,2} [14]. Thermolysis of $[Sb(S_2CPh)_3]$ and $[Bi(S_2Ctol)_3]$ in diphenylether at 230 °C gave a brownish powder which was characterized as M_2S_3 from their EDAX analyses (Calc. for Sb₂S₃: Sb, 71.7; S, 28.3. Found: Sb, 72.5; S, 27.5%. Calc. for Bi₂S₃: Bi, 81.3; S, 18.7. Found: Bi, 78.4; S, 21.6%) XRD patterns (Figs. 3 and 4).^{1,2} The SEM image (Fig. 5) of these materials showed star like growth pattern of M_2S_3 .

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Appendix A. Supplementary material

CCDC 678137 and 678138 contain the supplementary crystallographic data for $[Sb(S_2Ctol)_3]$ and $Bi(S_2CPh)_3]$. These data can be obtained free of charge from The Cambridge Crystallographic Data

 $^{^1}$ JCPDS File No. 42-1393 (for Sb₂S₃).

² JCPDS File No 17-0320 (for Bi_2S_3).

Centre via http://www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2008.08.022.

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