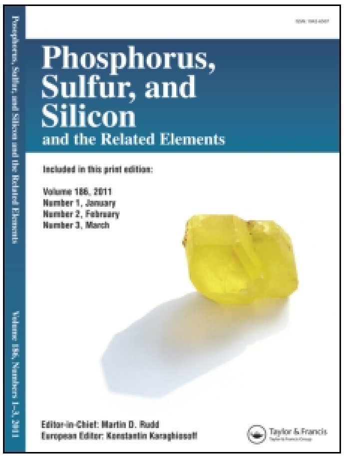

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SYNTHESIS AND CHARACTERIZATION OF SOME DITHIOLATOANTIMONY(III) DIALKYLDITHIOCARBAMATES

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SYNTHESIS AND CHARACTERIZATION OF SOME DITHIOLATOANTIMONY(III) DIALKYLDITHIOCARBAMATES

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Replacement reactions of ethane-1,2-dithiolatoantimony chloride and toluene-3,4-dithiolatoantimony chloride with sodium dialkyldithiocarbamates in 1:1 molar ratios in anhydrous benzene yielded mixed dithiolatodialkyldithiocarbamate derivatives of antimony(III) of the type $\overline{\text{S-A-A-SSb}}\text{S}_2\text{CNR}_2$ [where R = Me, Et and $R_2 = (CH_2)_4$ and -A-A- = $-CH_2-CH_2-$ and $>C_6H_3CH_3$]. Reactions between chloroantimony(III) *bis*(dialkyldithiocarbamates) and sodium dithiolate in 2:1 molar ratios in anhydrous benzene yielded compounds of the type $(R_2NCS_2)_2Sb-SCH_2-CH_2S-Sb\ (S_2CNR_2)_2$ [where R = Me, Et and $R_2 = (CH_2)_4$]. These newly synthesised derivatives are soluble in organic solvents like benzene, chloroform and carbon tetrachloride. These derivatives have been characterised by elemental analysis (C, H, N, Sb and S), melting points as well as IR, ^1H NMR and ^{13}C NMR spectral studies.

Keywords: Dithiolatoantimony; dithiocarbamates; IR spectra; NMR spectra

INTRODUCTION

Several dithiolates[1,2] and tris[3–5] as well as organometallic dithiocarbamate[6,7] derivatives of antimony have been known including X-ray crystal structure of $\overline{SCH_2CH_2SSb}Cl$[2] and $Sb(Et_2NCS_2)_3$[3], $(Pr_2{}^nNCS_2)_3Sb$[4] and $[(CH_2)_4NCS_2]_3Sb$[5] complexes. However, less attention has been paid on mixed dithiocarbamate[8–10] complexes of antimony(III). Recently, we have reported dithiolato-antimony(III) dialkyldithiophosphates[11] and xanthates[12]. We report herein, some new mixed

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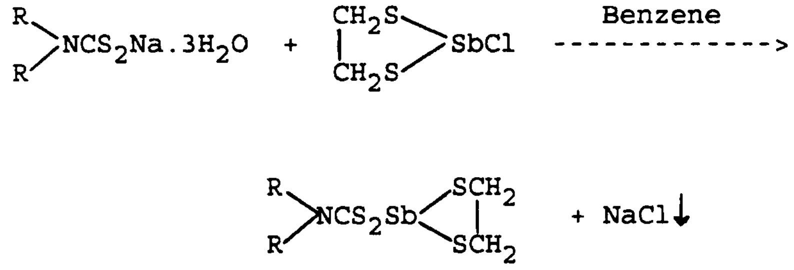
*Corresponding author.

dithiolatoantimony(III) dialkyldithiocarbamate derivatives of the type $\overline{\text{S-A-A-S}}\text{SbS}_2\text{NCR}_2$ and $(R_2NCS_2)_2Sb\text{-}SCH_2\text{-}CH_2S\text{-}Sb(S_2CNR_2)_2$ where, R = Me, Et and $R_2 = (CH_2)_4$ and -A-A-= $-CH_2\text{-}CH_2\text{-}$ and $>C_6H_3CH_3$.

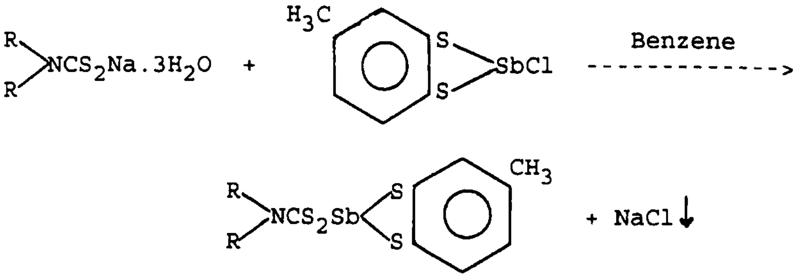
RESULTS AND DISCUSSION

Dithiolatoantimony(III) dialkyldithiocarbamates have been synthesised by following two types of reactions: (i) Reaction of ethane-1,2-dithiolatoantimony chloride and toluene-3,4-dithiolatoantimony chloride with sodium salt of dialkyldithiocarbamates in 1 : 1 molar ratios in anhydrous benzene

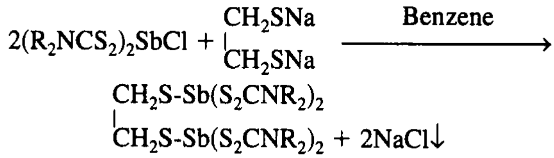
(a)



(b)



(ii) Reaction of chloroantimony(III) *bis*(dialkyldithio-carbamates) with the disodium salt of ethane-1,2-dithiol in 2 : 1 molar ratios in anhydrous benzene



$$2(R_2NCS_2)_2SbCl + \begin{matrix} CH_2SNa \\ | \\ CH_2SNa \end{matrix} \xrightarrow{\text{Benzene}} \begin{matrix} CH_2S\text{-}Sb(S_2CNR_2)_2 \\ | \\ CH_2S\text{-}Sb(S_2CNR_2)_2 \end{matrix} + 2NaCl\downarrow$$

where R = Me, Et and R_2 = $(CH_2)_4$.

These yellow crystalline solids are soluble in common organic solvents like benzene, chloroform and carbon tetrachloride.

IR Spectra

The assignment of the characteristic bands of the IR spectra have been made on the basis of earlier published work[8,10,12,13]. Generally the spectra of the complexes with bidentate dithiocarbamate groups[8,13] show bands at ~1500 & ~1000 cm^{-1} for C.....N and C.....S absorptions respectively. All the above synthesised antimony(III) complexes show a single band in the region 1425–1502 cm^{-1} due to ν C.....N and another band at 900–1020 cm^{-1} due to ν C.....S vibrations, thus, suggesting the bidentate nature of the dithiocarbamate groups in these complexes. A broad band of medium intensity is present in the region 310–320 cm^{-1} which may be assigned to Sb-S stretching vibrations. The characteristic bands observed in the spectra of corresponding tolyldithiolate derivatives in the region 640–730 cm^{-1} may be attributed to an asymmetrically trisubstituted benzene ring.

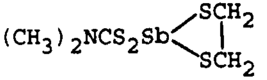
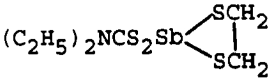
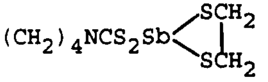
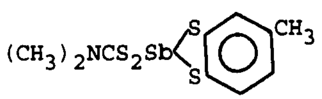
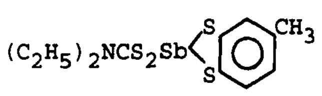
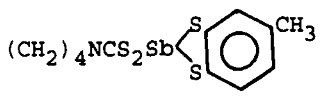
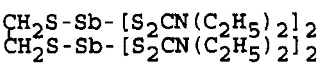
^{1}H NMR Spectra

The ^{1}H NMR spectra of these compounds have been recorded in $CDCl_3$ solutions using TMS as internal standard. These compounds exhibit characteristic signals without any appreciable shifts from reported values[7,8,10,14]. A sharp singlet due to dithiostibacyclopentane ring protons (CH_2S) have been observed at 3.35 to 3.60 δ ppm[11] except compd. no. 1 where a broad singlet is observed. In the corresponding toluene-3,4-dithiolatoantimony(III) derivatives a multiplet due to aromatic ring protons in the region 7.20–7.38 δ ppm and a singlet due to methyl protons on the ring, in the region 2.20–2.26 δ ppm have been observed. In addition, all these compounds also show expected proton resonances due to alkyl protons of dithiocarbamate moieties[12] (Table-I).

^{13}C NMR Spectra

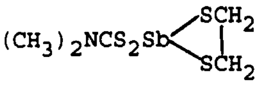
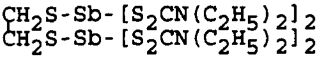
The ^{13}C NMR spectra of only two representative compounds have been recorded. The ^{13}C NMR signals obtained are at reported[8,15,16] values without any appreciable shift (Table-II). The signals for $-NCS_2$ carbon could not be detected as non-protonated carbon atoms give very small peaks at longer relaxation time[15].

TABLE I ^{1}H NMR spectral data of dithiolatoantimony (III) dialkyldithiocarbamates

S. No.	*Compounds*	*^{1}H Chemical Shift (δ ppm)*
1.		3.40, s, 6H (CH_3N) 3.63, s (broad), 4H (CH_2S)
2.		1.21, t, 6H (CH_3); J(CH_2-CH_3) = 9 Hz 3.35, s, 4H (CH_2S) 3.50, q, 4H (CH_2N); J(CH_3-CH_2) = 9 Hz
3.		1.90–2.15, m, 4H (CH_2CH_2N) 3.50, s, 4H (CH_2S) 3.60–3.80, m, 4H (CH_2N)
4.		2.25, s, 3H (Ring CH_3) 3.35, s, 6H (CH_3N) 7.24–7.38, m, 3H (Ring protons)
5.		1.25, t, 6H (CH_3); J(CH_2-CH_3) = 10.5 Hz 2.26, s, 3H (Ring CH_3) 3.75, q, 4H (CH_2N); J(CH_3-CH_2) = 10.5 Hz 7.24–7.38, m, 3H (Ring protons)
6.		1.95–2.1, m, 4H (CH_2CH_2N) 2.26, s, 3H (Ring CH_3) 3.60–3.75, m, 4H (CH_2N) 7.20–7.35, m, 3H (Ring protons)
7.	 $\begin{matrix}CH_2S\text{-}Sb\text{-}[S_2CN(C_2H_5)_2]_2\\CH_2S\text{-}Sb\text{-}[S_2CN(C_2H_5)_2]_2\end{matrix}$	1.24, t, 24H (CH_3); J(CH_2-CH_3) = 8.5 Hz 3.60, s, 4H (CH_2S) 3.80, q, 16H (CH_2N); J(CH_3-CH_2) = 8.5 Hz

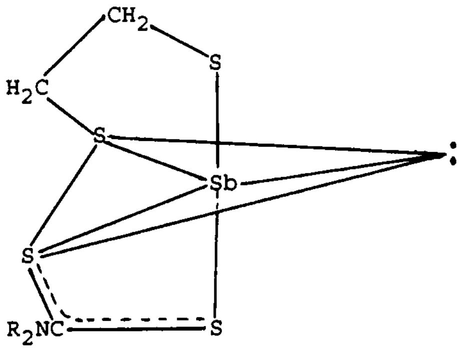
Although it is quite difficult to comment on the molecular structure of these complexes in solid state without actual X-ray crystal structure analysis of at least one of the products, the above studies indicate the bidentate mode of attachment of the dithiocarbamate ligand to metal atom, with a stereochemically active lone

TABLE II ^{13}C NMR spectral data for dithiolatoantimony(III) dialkyldithiocarbamates

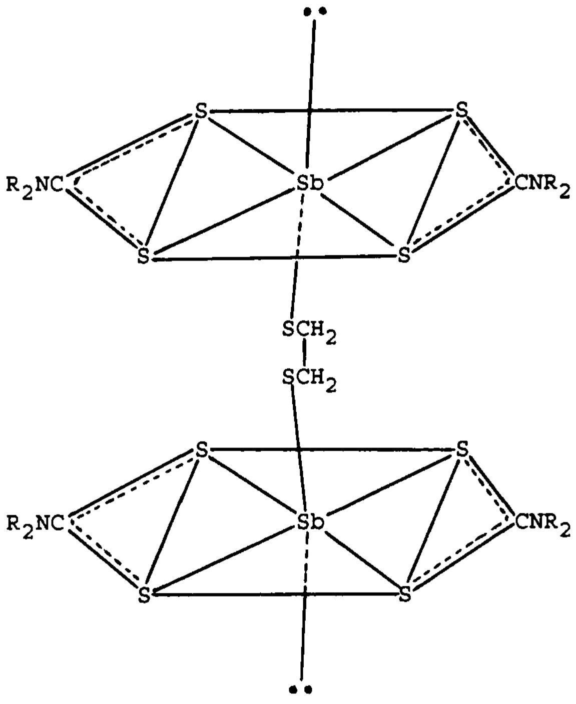
S. No.	*Compound*	*^{13}C Chemical Shift (δ ppm)*
1.		CH_2S, 40.59 CH_3, 44.08
2.	 $\begin{matrix}CH_2S\text{-}Sb\text{-}[S_2CN(C_2H_5)_2]_2\\CH_2S\text{-}Sb\text{-}[S_2CN(C_2H_5)_2]_2\end{matrix}$	CH_3, 12.22 CH_2S, 40.52 CH_2N, 48.46

pair in the coordination sphere[11,16] leading to distorted trigonal bipyramidal and distorted octahedral structure with lone pair occupying one of the equatorial positions as shown in Fig. A and B.

(A)



(B)



EXPERIMENTAL

All the experiments were carried out in moisture free conditions. Benzene, dichloromethane and hexane were dried by standard methods[17]. Ethane-1,2-dithiolatoantimony chloride[2], toluene-3,4-dithiolatoantimony chloride and chloroantimony(III) *bis*(dialkyldithiocarbamates)[8] were prepared by reported methods. Disodium salt of ethane-1,2-dithiol has been prepared by the reaction of ethane-1,2-dithiol with sodium metal in 1:2 molar ratio in anhydrous benzene. Sodium and ammonium dialkyldithiocarbamates (Fluka) were used as such. Antimony was estimated iodometrically[18] and sulfur was estimated gravimetrically as barium sulfate. Carbon, hydrogen and nitrogen were analysed at RSIC, CDRI, Lucknow. The IR spectra were recorded as Nujol mulls on a Perkin Elmer 577 Spectrophotometer in the range 4000-200 cm^{-1}. The ^1H NMR spectra were recorded on EM-360 and Zeol FX-90 Spectrometers using TMS as internal standard. The ^{13}C NMR spectra was recorded at RSIC, IIT, Bombay.

Mixed dithiolatodialkyldithiocarbamate derivatives of antimony(III) (Table-III) were synthesized by one of the following methods (a) and (b).

(a) Reaction Between Sodium Diethyldithiocarbamate and Ethane-1,2-Dithiolatoantimony Chloride in 1:1 Molar Ratio

To the solution of ethane-1,2-dithiolatoantimony chloride (2.22 gm, 8.90 mmol) in benzene (40 ml) was added sodium diethyldithiocarbamate (2.00 gm, 8.87 mmol) and the contents were refluxed for about 3 hours. Sodium chloride (0.44 gms) formed during the reaction was filtered off. The solvent was removed from the filtrate to reduce the volume (~15 ml) under reduced pressure. The contents were kept overnight in refrigerator and the yellow shiny crystals thus obtained were dried under reduced pressure and weighed. [M.P. = 117°C, yield = 3.00 gm, 93%].

(b) Reaction Between Sodium Dithiolate and Chloroantimony(III) bis(Diethyldithiocarbamate) in 1:2 Molar Ratio

To the solution of chloroantimony(III) bis(diethyldithiocarbamate) (1.80 gm, 3.97 mmol) in benzene (30 ml) sodium dithiolate (0.27 gm, 1.95 mmol) was added and the contents were refluxed for about 3 hours. Sodium chloride (0.21 gms) formed during the reaction was filtered off. The solvent was removed from the filtrate to reduce the volume (~10 ml). This was then kept overnight in refrigerator to give yellow crystals. [M.P. = 125°C, yield = 1.79 gm, 97%].

TABLE III Yield, physical and analytical data of dithiolatoantimony(III) dialkyldithiocarbamates

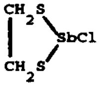
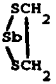
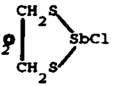
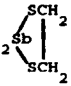
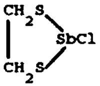
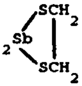
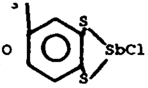
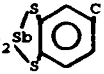
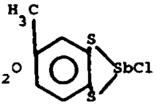
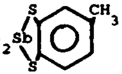
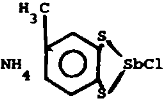
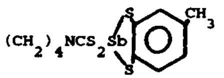
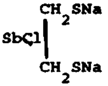
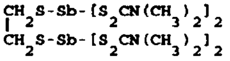
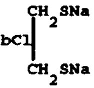
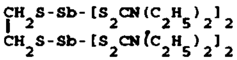
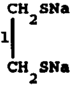
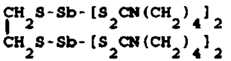
S. No.	*Reactants (gms)*	*Product (yield %)*	*NaCl found (calcd.)*	*M.P. (°C)*	*Found (calcd.) %*				
					Sb	*S*	*C*	*H*	*N*
1.	$(CH_3)_2NCS_2Na.2H_2O$  (1.82) (2.53)	$(CH_3)_2NCS_2$  (67)	0.49 (0.59)	149	37.01 (36.50)	37.81 (38.35)	18.20 (17.98)	3.54 (2.99)	4.36 (4.19)
2.	$(C_2H_5)_2NCS_2Na.3H_2O$  (2.00) (2.22)	$(C_2H_5)_2NCS_2$  (93)	0.44 (0.51)	117	32.16 (33.60)	34.41 (35.38)	23.02 (23.22)	3.91 (3.87)	3.93 (3.87)
3.	$(CH_2)_4NCS_2NH_4$  (1.50) (2.28)	$(CH_2)_4NCS_2$  (60)	0.39 (0.48)	154	32.90 (33.84)	34.69 (35.58)	23.23 (23.34)	3.22 (3.33)	3.67 (3.89)
4.	$(CH_3)_2NCS_2Na.2H_2O$  (0.64) (1.12)	$(CH_3)_2NCS_2$  (97)	0.28 (0.21)	121	31.34 (30.76)	31.23 (32.34)	30.29 (30.32)	3.29 (3.03)	4.00 (3.53)
5.	$(C_2H_5)_2NCS_2Na.3H_2O$  (0.72) (1.00)	$(C_2H_5)_2NCS_2$  (98)	0.20 (0.18)	105	29.62 (28.73)	29.71 (30.20)	33.95 (33.98)	4.19 (3.77)	3.61 (3.30)

TABLE III Yield, physical and analytical data of dithiolatoantimony(III) dialkyldithiocarbamates

S. No.	*Reactants (gms)*		*Product (yield %)*	*NaCl found (calcd.)*	*M.P. (°C)*	*Found (calcd.) %*				
						Sb	*S*	*C*	*H*	*N*
6.	$(CH_2)_4NCS_2NH_4$ (0.54)	 (1.02)	 (99)	0.18 (0.17)	181	30.02 (28.84)	28.98 (30.20)	34.25 (34.11)	3.75 (3.31)	3.65 (3.31)
7.	$[(CH_3)_2NCS_2]_2SbCl$ (1.10)	 $\begin{array}{l} CH_2SNa \\ \mid \\ CH_2SNa \end{array}$ (0.19)	 $\begin{array}{l} CH_2S\text{-}Sb\text{-}[S_2CN(CH_3)_2]_2 \\ \mid \\ CH_2S\text{-}Sb\text{-}[S_2CN(CH_3)_2]_2 \end{array}$ (80)	0.14 (0.16)	185 (Dec.)	28.54 (29.85)	37.80 (39.23)	20.01 (20.60)	3.20 (3.43)	6.54 (6.86)
8.	$[(C_2H_5)_2NCS_2]_2SbCl$ (1.80)	 $\begin{array}{l} CH_2SNa \\ \mid \\ CH_2SNa \end{array}$ (0.27)	 $\begin{array}{l} CH_2S\text{-}Sb\text{-}[S_2CN(C_2H_5)_2]_2 \\ \mid \\ CH_2S\text{-}Sb\text{-}[S_2CN(C_2H_5)_2]_2 \end{array}$ (97)	0.21 (0.23)	125	25.41 (26.23)	33.01 (34.50)	29.16 (28.47)	5.24 (4.74)	5.90 (6.03)
9.	$[(CH_2)_4NCS_2]_2SbCl$ (1.52)	 $\begin{array}{l} CH_2SNa \\ \mid \\ CH_2SNa \end{array}$ (0.23)	 $\begin{array}{l} CH_2S\text{-}Sb\text{-}[S_2CN(CH_2)_4]_2 \\ \mid \\ CH_2S\text{-}Sb\text{-}[S_2CN(CH_2)_4]_2 \end{array}$ (60)	0.18 (0.19)	175 (Dec.)	26.90 (26.48)	33.54 (34.80)	27.10 (28.71)	3.53 (3.91)	5.89 (6.09)

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