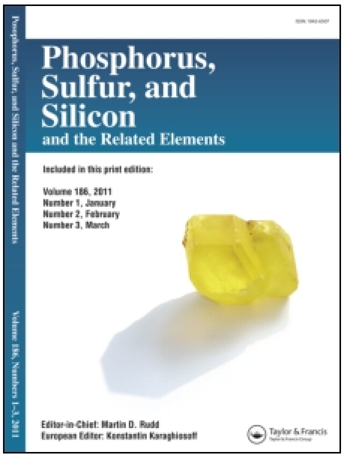

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Sharma, Jyoti , Singh, Yash Pal and Rai, Audhesh Kumar(1994) 'SYNTHESIS AND CHARACTERISATION OF SOME DIPHENYL ANTIMONY(III) COMPLEXES OF CYCLIC-DITHIOCARBAMATES', Phosphorus, Sulfur, and Silicon and the Related Elements, 86: 1, 197 — 202

To link to this Article: DOI: 10.1080/10426509408018404

URL: http://dx.doi.org/10.1080/10426509408018404

Phosphorus, Sulfur, and Silicon, 1994, Vol. 86, pp. 197–202

SYNTHESIS AND CHARACTERISATION OF SOME DIPHENYL ANTIMONY(III) COMPLEXES OF CYCLIC-DITHIOCARBAMATES

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(Received August 25, 1993; in final form December 2, 1993)

Diphenyl-antimony(III) derivatives of cyclic-dithiocarbamates having the general formula

(where X = >NH, CH_3-N<, CH_3-CH< and >CH_2) have been prepared by the reaction of diphenyl-antimony (III) chloride and the sodium salt of the corresponding ligands. The compounds thus prepared were characterised by elemental analysis, molecular weight measurements, IR, ^1H and ^{13}C NMR spectral studies.

Key words: Diphenyl antimony, NMR, IR, antimony sulfur bonds

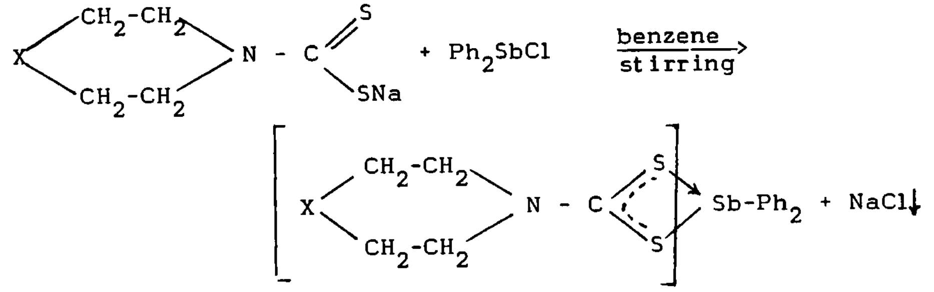
INTRODUCTION

The metal-sulfur bonded compounds have aroused considerable interest during the last few decades largely due to their biological activities and application in agriculture as well as in industry.[1-3]

In this work, the synthesis of some new complexes of diphenyl-antimony with some cyclic-dithiocarbamates is reported. These newly synthesised compounds are characterised on the basis of IR, ^1H and ^{13}C NMR spectral studies.

RESULTS AND DISCUSSION

The interactions of Ph_2SbCl and the sodium salt of the cyclic-dithiocarbamates in 1:1 molar ratio yield the corresponding diphenyl-antimony(III) derivatives.



where X = >CH_2, CH_3—CH< , >NH and >N—CH_3.

All these derivatives are white solids and soluble in common organic solvents like benzene, chloroform, dichloromethane and CS_2 etc. They have been purified by using a mixture of chloroform and hexane. The vapor pressure osmometric molecular weight measurements in chloroform solution at 45°C show the monomeric nature of the derivatives.

IR Spectra

IR spectra of the complexes have been recorded in the region 4000–400 cm^{-1}. The spectra of all these derivatives exhibit a strong band in the region 1450 ± 30 cm^{-1} which may be attributed to $\nu(C \overset{\cdots}{-} N)$. The band present in the region ~1000 cm^{-1} is attributed to ν $(C \overset{\cdots}{-} S)$ mode. However, a small intensity band at ~990 cm^{-1} appears as shoulder band of this main band. The presence of strong band at 1000 ± 20 cm^{-1} indicates that these ligands predominantly act as a bidentate moiety and the presence of a small band also indicates the possibility of the existence of these ligands as a monodentate moiety[4–7] in the solid state. Analysis of the position of the $\nu(C \overset{\cdots}{-} N)$ mode provides further confirmation of such behaviour; this band, in fact, undergoes a shift towards a lower region or remain unchanged,[8] while for bidentate coordination the frequency of this stretching mode would undergo upward shifts.

The presence of a new band at 452 ± 10 cm^{-1} which may be attributed to ν (Sb—S)[9] further supports the bonding of central antimony atom with sulfur. The band due to ν (Sb—C) has been observed in the region 470–447 cm^{-1}.

NMR Spectra

The ^1H NMR spectra of the diphenyl-antimony (III) complexes have been recorded in $CDCl_3$ solution, and are being summarized in Table I. The ^1H NMR spectra of the complexes displays the characteristic proton resonances due to the methyl, ring—CH_2, $>N-CH_3$, $>NH$ and $CH_3-CH<$ protons at their expected positions. The aromatic protons appear in the region δ 6.46–8.50 ppm. The ^{13}C NMR of these complexes were recorded and are summarized in Table II. The comparative study of ^{13}C NMR spectra of the diphenyl-antimony complexes with the free sodium salt of cyclic-dithiocarbamates shows the remarkable up-field shift of the CS_2 carbon atom indicating that the dithiocarbamates act as bidentate moiety.

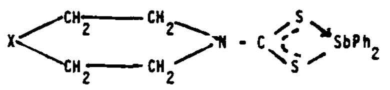
The corrected chemical shift values δ'[11,12] defined as $\delta' = Cp - Cm$ (where Cp and Cm are the chemical shift values of para and meta carbon atom of the phenyl ring respectively) and $\sigma R°$ values[13] are found to be negative in these derivatives (see Table II). The negative values indicate the electron release from metal atom towards phenyl ring through $p\pi - p\pi$ conjugation.

In view of the monomeric nature of these derivatives and the bidentate behaviour of the ligands in the reactions, the following structure in which the central antimony atom requires a trigonal-bipyramidal geometry is proposed in the solution.

TABLE I

^{1}H NMR spectral data of diphenyl-antimony(III) complexes of cyclic dithio-carbamates in ppm (δ). (Value indicated in the table represents the protons in the bold letters)

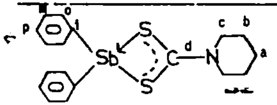
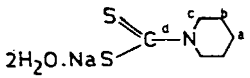
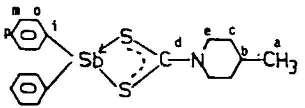
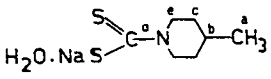
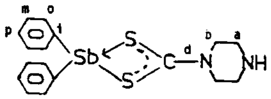
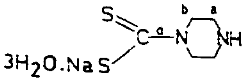
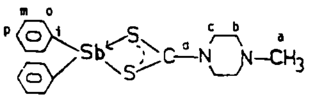
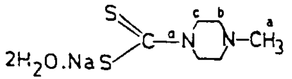
Complexes	$-CH_3$	$CH_2<(CH_2-)(CH_2-)$	$NH<(CH_2-)(CH_2-)$	$Me-\overset{\backslash}{CH}$	$>NH$	$Me-C<(CH_2)(CH_2)$	$Me-N<(CH_2-)(CH_2-)$	$>C-N<(CH_2-)(CH_2-)$	Sb-Ph
$Ph_2Sb[Pipdtc]$	-	1.54(s) (6H)	-	-	-	-	-	3.93(s) (4H)	6.46-8.50 (m)(10H)
$Ph_2Sb[4\text{-}MePipdtc]$	0.85-0.94 (d) (3H)	-	-	1.02-1.73 (m) (1H)	-	2.79,2.96, 3.13 (t) (4H)	-	4.84,5.01 (d) (4H)	7.18-8.09 (m)(10H)
$Ph_2Sb[Pzdtc]$	-	-	2.79,2.90, 2.96 (t) (4H)	-	1.79(s) (1H)	-	-	3.99-4.18 (m) (4H)	7.18-7.69 (m) (10H)
$Ph_2Sb[N\text{-}MePzdtc]$	2.25 (s) (3H)	-	-	-	-	-	2.34,2.40, 2.50 (t) (4H)	3.99,4.05, 4.12 (t) (4H)	7.29-8.14 (m) (10H)

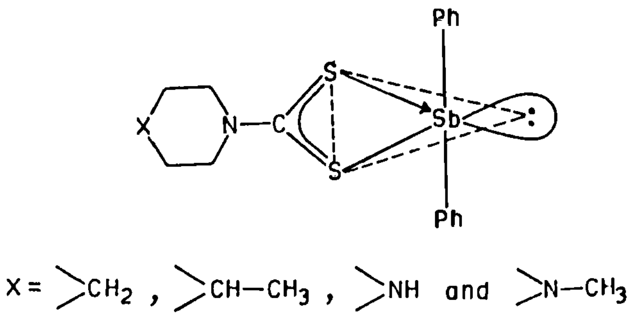


where X = $>CH_2$, $>CH-CH_3$, $>NH$ and $>N-CH_3$ respectively.

TABLE II

^{13}C spectral data of diphenyl-antimony(III) complexes of cyclic-dithio carbamates and Sodium Salt of cyclic-dithio carbamates in ppm (δ)

Complex	C^a	C^b	C^c	C^d	C^e	C^p	C^m	C^o	C^i	δ'	σR°
	23.73	25.68	52.00	199.0	-	126.04	128.8	135.12	147.96	-2.76	-1.2
	23.40	24.8	49.4	211.17	-	-	-	-	-	-	-
	21.02	30.12	33.48	196.60	50.97	128.34	134.73	135.92	148.92	-6.36	-0.28
	20.86	29.64	33.16	211.17	48.81	-	-	-	-	-	-
	45.56	52.76	-	198.9	-	128.77	132.93	135.65	142.20	-4.16	-0.18
	45.13	49.51	-	212.1	-	-	-	-	-	-	-
	54.17	45.29	31.42	196.43	-	128.61	134.89	135.60	142.42	-6.28	-0.28
	53.80	48.02	43.88	212.43	-	-	-	-	-	-	-



However, the possibility of the existence of these ligands as monodentate moieties in the solid state can not be ruled out. This has already been indicated by the i.r. spectra (taken in the solid state).

EXPERIMENTAL

Moisture was carefully excluded throughout the experimental manipulation. The chemicals used were of reagent grade. Diphenylantimony chloride[14] and cyclic-dithiocarbamates[15] have been synthesised by the literature method. Antimony was estimated iodometrically.[16] Nitrogen and sulfur were estimated by Kjeldahl's[16] and gravimetric[16] method, respectively. Molecular weights were determined on Knauer-vapor pressure osmometer in chloroform solution at 45°C. IR spectra of the compound have been recorded as KBr-pellets on a Nicolet Dx-FT-IR spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL-FX-90Q spectrometer in $CDCl_3$/DMSO-d_6 and $CHCl_3$/DMSO solutions respectively using TMS as an internal reference.

Preparation of ligand. The sodium-salt of piperidine-dithiocarbamate was prepared by treating piperidine in dry ether and isopropyl alcohol with carbon disulfide, and adding sodium hydroxide with vigorous stirring for ~4 hours. Molar ratios of amine:CS_2:NaOH are 1:1:1. The crude product was recrystallised from methanol and ether mixture.

TABLE III

Analytical and physical data of diphenyl-antimony(III) complexes

Complex	Reactants in gm		Product, molecular formula (% yield)	NaCl in gm found (calc.)	Analysis		M.P.°C (±1°C)	Mol.wt. found (calc.)
	Na salt of cyclic dithio-carbamate	Ph_2SbCl			Sb% found (calc.)	S% found (calc.)		
$Ph_2Sb(Pipdtc)$	1.09	1.55	$Ph_2Sb(Pipdtc)$ $C_{18}H_{20}NS_2Sb$ (90)	0.28 (0.29)	27.72 (27.90)	14.37 (14.69)	156	432 (436.23)
$Ph_2Sb(4\text{-}MePipdtc)$	1.50	2.17	$Ph_2Sb(4\text{-}MePipdtc)$ $C_{19}H_{22}NS_2Sb$ (95)	0.41 (0.42)	26.92 (27.04)	14.10 (14.24)	138	448 (450.25)
$Ph_2Sb(Pzdtc)$	2.17	2.84	$Ph_2Sb(Pzdtc)$ $C_{17}H_{19}N_2S_2Sb$ (86)	0.52 (0.53)	26.86 (26.98)	14.00 (14.20)	182	445 (451.24)
$Ph_2Sb(N\text{-}MePzdtc)$	2.59	3.44	$Ph_2Sb(N\text{-}MePzdtc)$ $C_{18}H_{21}N_2S_2Sb$ (89)	0.63 (0.65)	27.67 (27.84)	14.38 (14.66)	158	435 (437.22)

Synthesis of  *NCS_2Sb-Ph_2.* Sodium salt of piperidine dithiocarbamate (1.06 g, 4.83 m mol) was added to a benzene solution of Ph_2SbCl (1.51 g, 4.85 m mol). The reaction mixture was stirred for ~4 hours at room temperature (~35°C). The NaCl thus formed, was filtered off and the excess of the solvent was removed from the filtrate under reduced pressure. A white solid was obtained in quantitative yield. The product was purified by redissolving it in chloroform and reprecipitated by adding excess of n-hexane.

The product on analysis was found to have Sb, 27.9; S, 14.45% calc. Sb, 27.9; S, 14.6%.

Following the above method, three other complexes having the molecular formulae $C_{19}H_{22}NS_2Sb$, $C_{17}H_{19}N_2S_2Sb$ and $C_{18}H_{21}N_2S_2Sb$, have also been prepared (Table III).

ACKNOWLEDGEMENT

One of the authors, Ms. Jyoti Sharma is thankful to U.G.C. New Delhi, for financial support.

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