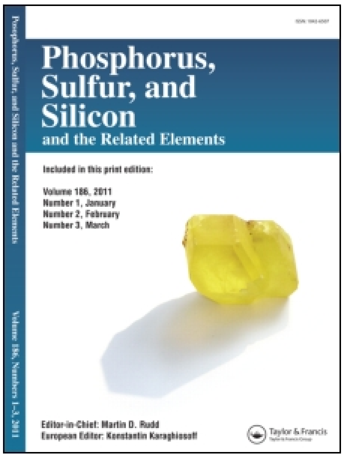


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

ANTIMONY(III) DERIVATIVES WITH 1,l-DITHIOLATO LIGANDS AND THEIR ADDITION COMPLEXES WITH TRIETHYLAMINE

H. P. S. Chauhan[a]; B. Nahar[a]
[a] Institute of Chemical Sciences, Devi Ahilya Vishwavidyalay, Indore, India

To cite this Article Chauhan, H. P. S. and Nahar, B.(1997) 'ANTIMONY(III) DERIVATIVES WITH 1,l-DITHIOLATO LIGANDS AND THEIR ADDITION COMPLEXES WITH TRIETHYLAMINE', Phosphorus, Sulfur, and Silicon and the Related Elements, 128: 1, 119 — 127

To link to this Article: DOI: 10.1080/10426509708031567

URL: http://dx.doi.org/10.1080/10426509708031567

Phosphorus, Sulphur, and Silicon, 1997, Vol. 128, pp. 119–127
Reprints available directly from the publisher
Photocopying permitted by license only

ANTIMONY(III) DERIVATIVES WITH 1,1-DITHIOLATO LIGANDS AND THEIR ADDITION COMPLEXES WITH TRIETHYLAMINE

H. P. S. CHAUHAN* and B. NAHAR

Institute of Chemical Sciences, Devi Ahilya Vishwavidyalay, Takshashila Campus, Khandwa Road, Indore 452001, India

(Received 27 February 1997; In final form 1 May 1997)

Replacement reactions of chloroantimony(III) *bis*(dialkyldithiophosphates) with sodium/ammonium dialkyldithiocarbamates in 1:1 molar ratio in anhydrous benzene yielded dialkyldithiocarbamatoantimony(III) *bis*(dialkyldithiophosphates) of the type $[(RO)_2PS_2]_2SbS_2CX$ [where, R = Pr^i, Bu^i and X = $N(Me)_2$, $N(Et)_2$ and $N(CH_2CH_2)_2$]. Reactions between chloroantimony(III) *bis*(dialkyldithiophosphates) and triethylamine in 1:1 molar ratio in anhydrous dichloromethane yielded addition compounds of the type $[(RO)_2PS_2]_2SbCl \cdot NEt_3$ [where, R = Pr^i and Bu^i].

These newly synthesised derivatives have been characterised by elemental analysis, melting points as well as IR, ^1H NMR and ^{31}P NMR spectral studies.

Keywords: Dithiophosphates; dithiocarbamates; antimony; triethylamine; IR Spectra; NMR Spectra

INTRODUCTION

The 1,1-dithiolato ligands, dialkyldithiophosphates and dialkyldithiocarbamates, are versatile in nature and exhibit remarkable diversities in their bonding patterns and form wide variety of compounds with metals.[1–5] A number of antimony(III) and organoantimony(III) derivatives[6–16] with these ligands are well known including the single crystal X-ray structures of several derivatives.[7–11] In addition to the interest in their structural aspects, antimony derivatives with dithiophosphorus ligands have been known to exhibit antitumor activity.[6] However, less attention has been paid to synthesize mixed sulphur ligand complexes of antimony.[16–18] In continuation to our interest[20–22] in synthetic and structural aspects of mixed sulphur ligand complexes of antimony, we report herein some

---

*Corresponding author.

new mixed dialkyldithiocarbamatoantimony(III) *bis*(dialkyldithiophosphates) and also addition complexes of chloroantimony(III) *bis*(dialkyldithio-phosphates) with triethylamine.

RESULTS AND DISCUSSION

The dialkyldithiocarbamatoantimony(III) *bis*(dialkyldithiophosphates) were synthesised by the reactions of chloroantimony(III) *bis*(dialkyldithiophosphates) with sodium/ammonium dialkyldithiocarbamates in refluxing benzene in 1:1 molar ratio.

$$[(RO)_2PS_2]_2SbCl + XCS_2M \xrightarrow{\textit{Benzene}} [(RO)_2PS_2]_2SbS_2CX + MCl$$

$$\downarrow$$

[where, $R = Pr^i, Bu^i$; $X = N(Me)_2, N(Et)_2, N(CH_2\text{-}CH_2)_2$; $M = Na, NH_4$]

These compounds are low melting, yellow crystalline solids. These are soluble in common organic solvents like benzene, chloroform, carbon tetrachloride, hexane etc.

Chloroantimony(III) *bis*(dialkyldithiophosphates) on treating with triethylamine in dichloromethane at room temperature yielded 1:1 addition compounds.

$$[(RO)_2PS_2]_2SbCl + NEt_3 \xrightarrow{\textit{dichloromethane}} [(RO)_2PS_2]_2SbCl\cdot NEt_3$$

[where $R = Pr^i, Bu^i$]

These light brown coloured solid derivatives are soluble in common organic solvents like benzene, chloroform, carbon tetrachloride etc.

IR SPECTRA

The infrared spectra have been recorded in the range 4000–200 cm^{-1}. The main characteristic features of the IR Spectra with the tentative assignments made on the basis of earlier publications[12,19,20,23] can be summarised as follows:

The bands in the regions 980–1000 cm^{-1} and 820–860 cm^{-1} are assigned to (P)-O-C and P-O-(C) stretching modes of dithiophosphate moieties respectively.

A strong band due to (P = S) present in the spectra of sodium salt of dialkyldithiophosphoric acid in the region 660–690 cm^{-1} is shifted towards lower frequencies in the spectra of all these derivatives and is present at 640–650 cm^{-1}. This shifting indicates most probably a strong bidentate chelation of dithiophosphate ligand with antimony.[20] Bands of medium intensities in the region 520–550 cm^{-1} and 310–330 cm^{-1} are due to (P-S) and (Sb-S) stretching vibrations respectively.

In addition, corresponding dithiocarbamate derivatives exhibit bands in the regions 1500–1520 cm^{-1} and 1020–1030 cm^{-1} due to ($C\overset{\cdots}{-}N$) and ($C\overset{\cdots}{-}S$) stretching vibrations respectively. These are indicative of bidentate nature of dialkyldithiocarbamate[13] ligands in these complexes.

The spectrum of free triethylamine shows bands in the regions 2800–2960 cm^{-1} for ν (C-H) and 1410–1425 cm^{-1} for ν (C-N), however, in the adducts these bands are observed at 2910–3000 cm^{-1} and 1420–1460 cm^{-1} respectively indicating coordination of triethylamine to antimony.[19] A weak band near 400 cm^{-1} in these adducts may be assigned to (Sb-N) stretching vibrations.

NMR SPECTRA

The ^1H NMR Spectra of these derivatives have been recorded in $CDCl_3$ solutions using TMS as internal standard. The ^1H NMR spectra show (Table I) the characteristic proton resonances of the corresponding isopropoxy and isobutoxy groups of dialkyldithiophosphate moieties. Coupling of α protons (protons attached to the carbon atom nearest to phosphorus atom) have been observed with ^{31}P nuclei. The corresponding dialkyldithiocarbamate derivatives, in addition, exhibit signals due to proton resonances of alkyl protons of dialkyldithiocarbamate moieties. In certain cases some of the alkyl protons of dialkyldithiophosphate and dialkyldithiocarbamate moieties exhibit same values of chemical shift; these thus overlap and appear as multiplet e.g. in compound (No. 5, Table I) CH_2O and CH_2N protons and in compound (No. 6, Table I) CH and CH_2 as well as CH_2O and CH_2N protons are appearing as multiplets. In the corresponding adducts of triethylamine proton resonances due to CH_3 and CH_2 protons of triethylamine are also observed in addition to the protons of dialkyldithiophosphate group.

Proton decoupled ^{31}P spectral data (Table I) exhibit only one ^{31}P chemical shift for each compound in the range 90–103 δ PPM indicating the bidentate behaviour of dialkyldithiophosphate[23,24] ligands towards the antimony in all these derivatives.

TABLE I ^1H and ^{31}P NMR spectral data for dialkyldithiocarbamatoantimony(III) *bis*(dialkyldithiophosphates) and chloroantimony(III) *bis*(dialkyldithiophosphates) triethylamine

S.No.	*Compound*	*^1H Chemical shift δPPM*	*^{31}P Chemical shift δPPM*
1.	$[(i\text{-}C_3H_7O)_2PS_2]_2Sb\cdot S_2CN(CH_3)_2$	1.35, d, 24*H*, CH_3, $^3J(HH)$ = 7.5 Hz	
		3.42, s, 6*H*, CH_3N	90.8
		4.83, sep, 4*H*, *CHO*, $^3J(PH)$ = 7.5 Hz	
2.	$[(i\text{-}C_3H_7O)_2PS_2]_2Sb\cdot S_2CN(C_2H_5)_2$	1.30, t, 6*H*, CH_3, $^3J(HH)$ = 7.5 Hz	
		1.35, d, 24*H*, CH_3, $^3J(HH)$ = 7.5 Hz	95.2
		3.81, q, 4*H*, CH_2N, $^3J(HH)$ = 7.5 Hz	
		4.83, sep, 4*H*, *CHO*, $^3J(PH)$ = 7.5 Hz	
3.	$[(i\text{-}C_3H_7O)_2PS_2]_2Sb\cdot S_2CN(CH_2)_4$	1.35, d, 24*H*, CH_3, $^3J(HH)$ = 7.5 Hz	
		2.07, m, 4*H*, CH_2	92.5
		3.82, m, 4*H*, CH_2N	
		4.84, sep, 4*H*, *CHO*, $^3J(PH)$ = 7.5 Hz	
4.	$[(i\text{-}C_4H_9O)_2PS_2]_2Sb\cdot S_2CN(CH_3)_2$	0.92, d, 24*H*, CH_3, $^3J(HH)$ = 8.0 Hz	
		1.88, m, 4*H*, *CH*	–
		3.2, s, 6*H*, CH_3N	
		3.52, dd, 8*H*, CH_2O	
5.	$[(i\text{-}C_4H_9O)_2PS_2]_2Sb\cdot S_2CN(C_2H_5)_2$	0.92, d, 24*H*, CH_3, $^3J(HH)$ = 8.0 Hz	
		1.28, t, 6*H*, CH_3N, $^3J(HH)$ = 8.0 Hz	102.7
		1.88, m, 4*H*, *CH*	
		3.56, m, 12*H*, CH_2O & CH_2N	
6.	$[(i\text{-}C_4H_9O)_2PS_2]_2Sb\cdot S_2CN(CH_2)_4$	0.92, d, 24*H*, CH_3, $^3J(HH)$ = 8.0 Hz	
		1.96, m, 8*H*, *CH* & CH_2	94.7
		3.56, m, 12*H*, CH_2O & CH_2N	
7.	$[(i\text{-}C_3H_7O)_2PS_2]_2SbCl\cdot N(C_2H_5)_3$	1.38, m, 33*H*, CH_3	
		3.12, q, 6*H*, CH_2N, $^3J(HH)$ = 7.5 Hz	–
		4.89, sep, 4*H*, *CHO*, $^3J(PH)$ = 7.8 Hz	
8.	$[(i\text{-}C_4H_9O)_2PS_2]_2SbCl\cdot N(C_2H_5)_3$	1.02, d, 24*H*, CH_3, $^3J(HH)$ = 7.5 Hz	
		1.38, t, 9*H*, CH_3, $^3J(HH)$ = 7.5 Hz	92.6
		2.05, m, 4*H*, *CH*	
		3.15, q, 6*H*, CH_2N, $^3J(HH)$ = 7.5 Hz	
		3.92, dd, 8*H*, CH_2O, $^3J(PH)$ = 7.5 Hz	

s = Singlet, d = doublet, t = triplet, q = quartet, sep = septet, m = multiplet, dd = doublet of doublet.

Although, the actual structures can be established only after single crystal X-ray analysis, the available physicochemical data suggest that both dialkyldithiocarbamate and dialkyldithiophosphate ligands behave as bidentate moieties and therefore following type of distorted capped octahedral structures (A and B) may be proposed tentatively for dialkyldithiocarbamatoantimony(III) *bis*(dialkyldithiophosphates) and addition complexes of chloroantimony(III) *bis*(dialkyldithiophosphates) with triethylamine respectively.

EXPERIMENTAL

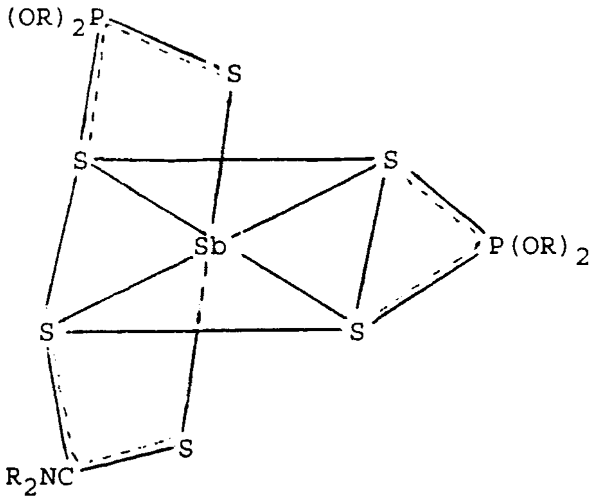
All the experiments were carried out strictly under anhydrous conditions. Triethylamine and solvents (ethanol, isopropanol, isobutanol, benzene, hexane, dichloromethane) were dried by standard methods. Antimony trichloride (Merck) was distilled under reduced pressure before use. Chloroantimony(III) *bis*(dialkyldithiophosphates) were prepared by reported methods.[23] Sodium/ammonium dialkyldithiocarbamates (Fluka) were used as such. Sulphur was estimated gravimetrically as barium sulphate, antimony was estimated iodometrically and nitrogen was estimated by Kjeldahl's method. IR spectral data were recorded in range 4000–200 cm^{-1} as Nujol mulls on a Pye Unican SP3 300 Spectrophotometer. ^1H and ^{31}P NMR spectral data in $CDCl_3$ solutions were recorded at Regional Sophisticated Instrumentation Centre of Indian Institute of Technology, Mumbai.

The mixed dialkyldithiocarbamatoantimony(III) *bis*(dialkyldithiophosphates) and addition complexes of chloroantimony(III) *bis*(dialkyldithiophosphates) and triethylamine have been synthesised by adopting the following methods (a) and (b) respectively (Table II).

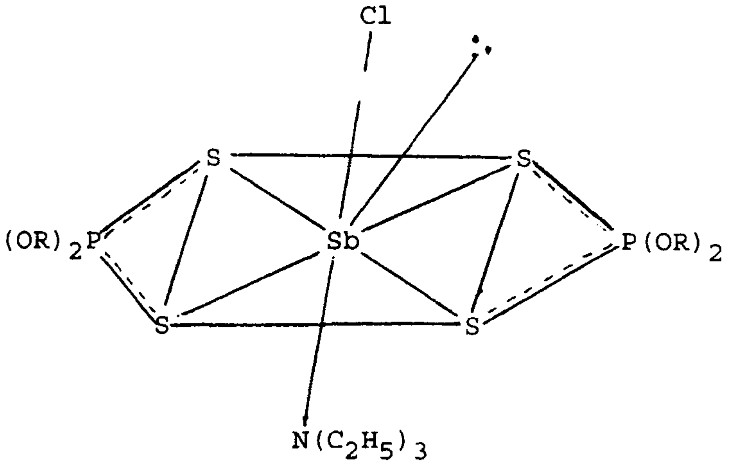
Reaction of chloroantimony(III) *bis*(diisopropyldithiophosphate) with sodium diethyldithiocarbamate in 1:1 molar ratio

To the solution of chloroantimony(III) *bis*(diisopropyldithiophosphate) (2.35g; 4.03 mmol) in benzene (~25 ml) was added sodium diethyldithiocarbamate (0.90g; 4.03 mmol). The contents were heated under reflux for ~3 hours. Precipitated sodium chloride (0.21g) was removed by filtration. On removing the solvent from the filtrate light yellow solid was obtained which was crystallised with hexane to give light yellow crystals.

(Yield - 2.24g; 80%, M.pt 98°C)



[A]



[B]

TABLE II Reactions of chloroantimony(III) *bis*(dialkyldithiophosphates) with dialkyldithiocarbamates and with triethylamine

S. No.	*Reactants*		*Product % yield*	*M.pt. °C*	*Analysis% found (calcd.)*		
	$[(RO)_2PS_2]_2SbCl$ R = (g)	*(g)*			*Sb*	*S*	*N*
1.	i-C_3H_7	$(CH_3)_2NCS_2Na \cdot 2H_2O$	$[(i\text{-}C_3H_7O)_2PS_2]_2Sb \cdot S_2CN(CH_3)_2$	138	18.65	27.97	2.20
	(2.32)	(0.71)	73		(18.25)	(28.79)	(2.09)
2.	i-C_3H_7	$(C_2H_5)_2NCS_2Na \cdot 3H_2O$	$[(i\text{-}C_3H_7O)_2PS_2]_2Sb \cdot S_2CN(C_2H_5)_2$	98	18.05	28.07	1.80
	(2.35)	(0.9)	80		(17.52)	(27.62)	(2.01)
3.	i-C_3H_7	$(CH_2)_4NCS_2NH_4$	$[(i\text{-}C_3H_7O)_2PS_2]_2Sb \cdot S_2CN(CH_2)_4$	120	17.8	28.89	1.96
	(2.23)	(0.63)	71		(17.82)	(28.1)	(2.05)
4.	i-C_4H_9	$(CH_3)_2NCS_2Na \cdot 2H_2O$	$[(i\text{-}C_4H_9O)_2PS_2]_2Sb \cdot S_2CN(CH_3)_2$	140	16.8	26.49	2.32
	(1.78)	(0.5)	62		(16.7)	(26.51)	(1.93)
5.	i-C_4H_9	$(C_2H_5)_2NCS_2Na \cdot 3H_2O$	$[(i\text{-}C_4H_9O)_2PS_2]_2Sb \cdot S_2CN(C_2H_5)_2$	58–60	16.54	25.5	2.10
	(1.28)	(0.45)	74		(16.18)	(25.52)	(1.86)
6.	i-C_4H_9	$(CH_2)_4NCS_2NH_4$	$[(i\text{-}C_4H_9O)_2PS_2]_2Sb \cdot S_2CN(CH_2)_4$	87	16.06	25.19	2.15
	(1.37)	(0.35)	92		(16.22)	(25.59)	(1.86)
7.	i-C_3H_7	$(C_2H_5)_3N$	$[(i\text{-}C_3H_7O)_2PS_2]_2SbCl \cdot N(C_2H_5)_3$	68–70	18.09	18.28	1.94
	(1.65)	(0.28)	83		(17.81)	(18.73)	(2.04)
8.	i-C_4H_9	$(C_2H_5)_3N$	$[(i\text{-}C_4H_9O)_2PS_2]_2SbCl \cdot N(C_2H_5)_3$	94	17.07	17.67	1.92
	(1.70)	(0.26)	98		(16.43)	(17.28)	(1.89)

Reaction of chloroantimony(III) *bis*(diisopropyldithiophosphate) with triethylamine in 1:1 molar ratio

To the solution of chloroantimony(III) *bis*(diisopropyldithiophosphate) (1.65g; 2.83 mmol) in dichloro-methane ($\sim$ 10 ml) was added a solution of triethylamine (0.28g; 2.83 mmol) in dichloromethane ($\sim$ 15 ml) dropwise and a light brown coloured solution was obtained. The contents were then stirred for $\sim$3 hours at room temperature. On removal of solvent, solid light brown product was obtained.

(Yield - 1.60g; 83%, M.pt.68 - 70°C)

Acknowledgements

Financial assistance from MPCST, Bhopal is gratefully acknowledged. We are thankful to Prof. D. Kishore, Banasthali Vidhyapith, Banasthali for scanning IR Spectra.

References

[1] J. R. Wasson, G. M. Woltermann and H. J. Stoklosa, *Top Curr. Chem.*, **35**, 65, (1973).
[2] I. Haiduc and D. B. Sowerby, *Polyhedron*, **14**, 3389, (1995); **15**, 2469, (1996).
[3] I. Haiduc, *Revs. Inorg. Chem.*, **3**, 353, (1981).
[4] R. C. Mehrotra, G. Srivastava and B. P. S. Chauhan, *Coord. Chem. Rev.*, **55**, 207, (1984).
[5] R. CeaOlivares, R. A. Toscano, C. Silvestru, P. G. Garcia, M. L. Cardoso, G. B. Amador and H. Noth, *J. Organometal Chem.*, **493**, 61, (1995).
[6] C. Silvestru, C. Socaceri, A. Bara and I. Haiduc, *Anticancer Res.*, **10**, 803, (1990).
[7] C. Silvestru and I. Haiduc, *Coord. Chem. Review*, **147**, 117, (1996).
[8] C. L. Raston and A. H. White, *J. Chem. Soc. Dalton Trans.*, 791, (1976).
[9] C. A. Kavounis, S. C. Kokkou, P. J. Rentzeperis and P. Karagiannidis, *Acta Crystallogr.*, **B36**, 2954, (1980); **B38**, 2686, (1982).
[10] D. B. Sowerby, I. Haiduc, A. B. Rusu and M. Salojan, *Inorg. Chim. Acta.*, **68**, 87, (1983).
[11] C. Silvestru, M. Curtui, I. Haiduc, M. J. Begley and D. B. Sowerby, *J. Organometal Chem.*, **426**, 49, (1992).
[12] R. Nomura, A. Takabe and H. Matsuda, *Polyhedron*, **6**, 411, (1987).
[13] S. Sharma, R. Bohra and R. C. Mehrotra, *Indian J. Chem.*, **32A**, 59, (1993).
[14] J. Sharma, Y. P. Singh and A. K. Rai, *Phosphorus, Sulphur, Silicon and the Related Elements*, **86**, 197, (1994).
[15] S. Kraft and M. Weiber, *Zeitschrift fur Anorganische Und Allgemeine Cheime*, **607**, 164, (1992).
[16] R. CeaOivares, M. A. MunozHernandez, S. HernandezOrtega and C. Silvestru, *Inorg. Chim. Acta*, **236**, 31, (1995).
[17] G. E. Manoussakis et al. *Inorg. Chim. Acta*, **18**, 35, (1976).
[18] F. M. N. Kheiri, C. A. Tsipis and G. E. Manoussakis, *Inorg. Chim. Acta*, **25**, 223, (1977).
[19] S. Sharma, R. Bohra and R. C. Mehrotra, *J. Indian Chem. Soc.*, **67**, 945, (1990).
[20] H. P. S. Chauhan and S. Lunkud, *Main Group Metal Chem.*, **17**, 313, (1994).

[21] H. P. S. Chauhan and S. Choursia *Indian J. Chem.*, **34A**, 664, (1995).
[22] S. Choursia, B. Nahar and H. P. S. Chauhan *Phosphorus, Sulphur, Silicon and Related Elements*, **1**, 77, (1996).
[23] H. P. S. Chauhan, G. Shrivastava and R. C. Mehrotra, *Polyhedron*, **2**, 359, (1983).
[24] C. Glidewell, *Inorg. Chim. Acta*, **25**, 159, (1977).