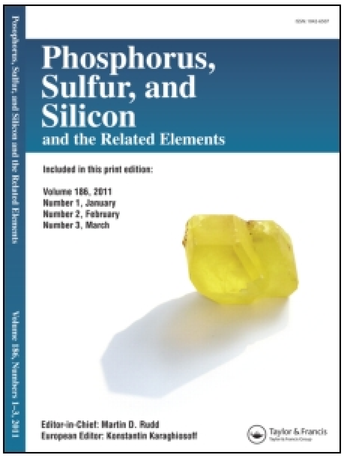

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

0,0-DIALKYL DITHIOPHOSPHATE COMPLEXES OF DIPHENYL ANTIMONY (III)

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To cite this Article Karra, R. , Singh, Y. P. and Rai, A. K.(1989) '0,0-DIALKYL DITHIOPHOSPHATE COMPLEXES OF DIPHENYL ANTIMONY (III)', Phosphorus, Sulfur, and Silicon and the Related Elements, 45: 3, 145 — 150
To link to this Article: DOI: 10.1080/10426508908045010
URL: http://dx.doi.org/10.1080/10426508908045010

Phosphorus, Sulfur, and Silicon, 1989, Vol. 45, pp. 145–150
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0,0-DIALKYL DITHIOPHOSPHATE COMPLEXES OF DIPHENYL ANTIMONY (III)

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Reactions of diphenylantimony chloride with the sodium salts of 0,0-dialkyldithiophosphoric acids in 1:1 molar ratio in benzene solution yield neutral complexes with the general formula $(RO)_2PS_2SbPh_2$ (where $R = CH_3$, C_2H_5, n-C_3H_7, i-C_3H_7, n-C_4H_9, i-C_4H_9). These complexes are monomeric in nature and have been characterized by IR, ^1H, ^{13}C and ^{31}P NMR spectroscopy. The ^{31}P nmr spectral data are consistent with the chelating behaviour of the dithiophosphate moieties.

Key words: 0,0-dialkyldithiophosphates; Diphenyl antimony; Chelates; Monomers; Spectral studies; Five-coordinated antimony.

INTRODUCTION

Although during the last two to three decades, a large amount of work has been carried out on the organic derivatives of organoantimony(III),[1] but most of the work is confined to monoorgano derivatives of Sb(III).[2-5] Recently, publications dealing with the syntheses and X-ray structural analyses of some diorganoantimony derivatives like acetates,[6] dialkyldithiophosphinates,[7] dithiocarbamates[8] etc. have appeared in the literature.

In continuation to our work on monoorgano-antimony(III) dialkyldithiophosphates,[3] we report the syntheses and characterization of some diorganoantimony dithiophosphate derivatives.

RESULTS AND DISCUSSION

The reactions of diphenylantimony chloride or diphenylantimony acetate with the sodium salts of 0,0-dialkylthiophosphoric acids were carried out in 1:1 molar ratio in benzene solution.

(i) $Ph_2SbCl + NaS_2P(OR)_2 \rightarrow Ph_2SbS_2P(OR)_2 + NaCl\downarrow$

(ii) $Ph_2SbOOCCH_3 + NaS_2P(OR)_2 \rightarrow Ph_2SbS_2P(OR)_2 + CH_3COONa\downarrow$

(Where $R = CH_3$, C_2H_5, n-C_3H_7, i-C_3H_7, n-C_4H_9, i-C_4H_9)

These compounds can also be prepared by the reactions of diphenylantimony acetate with the above ligands in 1:1 molar ratio in toluene solution under a fractionating column.

$$Ph_2SbOOCCH_3 + HS_2P(OR)_2 \rightarrow Ph_2SbS_2P(OR)_2 + CH_3COOH\uparrow$$

All these complexes are soluble in common organic solvents and are moisture sensitive. Osmometric molecular weight determination in chloroform solution reveals their monomeric nature.

IR SPECTRA

In the IR spectra of these complexes, the (P)—O—C and P—O—(C) stretching modes have been observed in the regions 970–1030 cm^{-1} and 700–800 cm^{-1}, respectively. The band due to νP—S which is present in the region 680–620 cm^{-1} in the spectra of the ligands, shifted to lower frequencies (by ~30 cm^{-1}) in the corresponding diphenylantimony complexes, indicating the bidentate nature of the ligand in these complexes. The band present in the region 510–550 cm^{-1} may be assigned to νP—S asymmetric and symmetric vibrations.

A medium intensity νSb—C[9,10] band has been observed around ~450 cm^{-1} which is basically a phenyl deformation mode incorporating some Sb—C deformation. Whereas the νSb—S band[11] appeared at ~370 cm^{-1}.

^{1}H NMR SPECTRA

A sharp singlet in the range δ 3.0–3.7 ppm, (Table I) characteristic of the S—H proton in the pmr spectra of the free dithiophosphoric acids is found to be absent in their corresponding diphenylantimony complexes, indicating the removal of —SH proton and the formation of M—S bond. The ^{1}H NMR spectra of these complexes show the characteristic proton resonances due to the alkyl, alkoxy and aromatic protons. The protons attached to the carbon atom of P—O—C linkage do show coupling with the ^{31}P nuclei, due to which a further splitting has been observed e.g. in the complex $(CH_3O)_2PS_2SbPh_2$, instead of a singlet for the methoxy protons, a doublet is obtained. The aromatic protons appear in the range δ 7.1–7.8 ppm.

^{13}C NMR SPECTRA

The ^{13}C NMR spectra of two ligands and their corresponding complexes are being summarised in Table II. The ^{13}C nmr spectra of these complexes exhibit four signals at ~δ 141.2, 135.5, 128.8, ~δ127.8 ppm and have been assigned to C(s), C(m), C(p) and C(o) of phenyl group, respectively. The appearance of only one signal for each of these carbons indicate the equivalent nature of the phenyl groups. The corrected chemical shift values, δ,'[12,13] defined as $\delta' = \delta C_p - \delta C_m$ (where, δC_p and δC_m are the chemical shift values of para- and meta carbon atoms of the phenyl ring) are negative for these complexes. This infers an electron release from metal atom towards phenyl ring through Pπ–Pπ conjugation. The signals for the alkyl carbons were observed at their usual positions with a slight upfield shift as compared to their positions in their corresponding ligands.

^{31}P NMR SPECTRA

^{31}P nmr spectra of these complexes were recorded and are being summarised in Table I. The ^{31}P nmr signals have been observed in the range δ 91.4–99.4 ppm.

TABLE I

^1H and ^{31}P NMR Spectral Data for Diphenylantimony (III) Dialkyldithiophosphates

Complex	Chemical Shifts δ(ppm)				^{31}P NMR (in chloroform) δ(ppm)
	^1H NMR (in $CDCl_3$)			Aromatic	
	$—CH_3$	$>CH_2$	$>CH$		
$[CH_3O]_2PS_2SbPh_2$	3.53 (d) $^3J_{POCH} = 14.3$ Hz	—	—	7.16–7.41 (m)	99.39
$[CH_3CH_2O]_2PS_2SbPh_2$	1.24 (t) $^3J_{HCCH} = 7.9$ Hz	3.88 (dq) $^3J_{HCCH} = 7.9$ Hz $^3J_{POCH} = 7.9$ Hz	—	7.10–7.70 (m)	94.23
$[CH_3\overset{\beta}{CH_2}\overset{\alpha}{CH_2}O]_2PS_2SbPh_2$	0.90 (t) $^3J_{HCCH} = 7.9$ Hz	α CH_2 3.60 (dt) $^3J_{HCCH} = 7.9$ Hz $^3J_{POCH} = 9.9$ Hz β CH_2 1.50 (q)	—	7.31–7.79 (m)	94.66
$[(CH_3)_2CHO]_2PS_2SbPh_2$	1.18 (d) $^3J_{HCCH} = 5.9$ Hz	—	4.71 (m) $^3J_{HCCH} = 5.9$ Hz $^3J_{POCH}$ = Unresolved	7.16–7.38 (m)	91.42
$[CH_3\overset{\gamma}{CH_2}\overset{\beta}{CH_2}\overset{\alpha}{CH_2}O]_2PS_2SbPh_2$	0.89 (t) $^3J_{HCCH} = 7.8$ Hz	α CH_2 3.98 (dt) $^3J_{HCCH} = 7.8$ Hz $^3J_{POCH} = 9.8$ Hz γ β $CH_2—CH_2$ 1.27–1.81 (m) unresolved	—	7.22–7.54 (m)	94.49
$[(CH_3)_2CHCH_2]_2PS_2SbPh_2$	0.78 (d) $^3J_{HCCH} = 5.9$ Hz	3.63 (dd) $^3J_{HCCH} = 5.9$ Hz $^3J_{POCH} = 5.9$ Hz	1.84 (m) unresolved	7.16–7.47 (m)	94.84

d = doublet, t = triplet, dq = double quartet, dt = double triplet, dd = double doublet, m = multiplet

TABLE II

^{13}C NMR Spectral Data for Diphenylantimony (III) Dialkyldithiophosphates

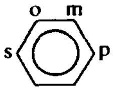
No	Complex	C—ÇH$_3$	C—ÇH$_2$—CH$_3$	O—Ç	C(s)	C(m)	C(p)	C(o)
			Types of C atoms Sb— 					
	(CH$_3$CH$_2$O)$_2$PS$_2$H	16.85(d) J = 6.33 Hz	—	65.07(d) J = 0.27 Hz	—	—	—	—
	(CH$_3$CH$_2$O)$_2$PS$_2$SbPh$_2$	15.44(d) J = 8.55 Hz	—	63.55(d) J = 6.10 Hz	141.18	135.98	128.83	128.39
	(CH$_3$CH$_2$CH$_2$O)$_2$PS$_2$H	11.16(s)	24.05(d) J = 3.66 Hz	70.21(d) J = 6.10 Hz	—	—	—	—
	(CH$_3$CH$_2$CH$_2$O)PS$_2$SbPh$_2$	9.86(s)	22.70(d) J = 8.54 Hz	68.64(d) J = 7.33 Hz	141.18	135.38	128.94	127.85

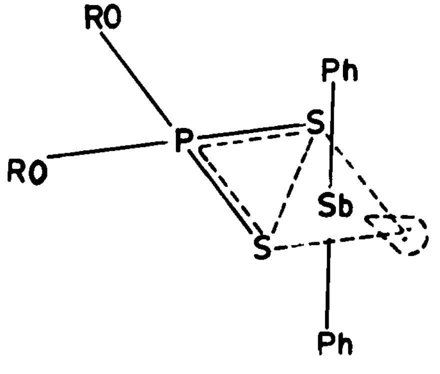
TABLE III

Synthetic and Analytical Data for Diphenylantimony(III) Dialkyldithiophosphates

	Reactants (gms)		Product $(RO)_2PS_2SbPh_2$	% Analyses: Found (Calc.)		Molecular weight:
S. No.	$(RO)_2PS_2Na$	Ph_2SbCl	% yield	Sb	S	Found (Calc.)
1.	$R = CH_3$ 0.68	1.18	96%	28.33 (28.07)	14.51 (14.85)	—
2.	$R = C_2H_5$ 0.54	0.81	91%	26.23 (26.36)	13.79 (13.94)	—
3.	$R = n\text{-}C_3H_7$ 0.97	1.28	95%	25.20 (24.85)	13.18 (13.14)	—
4.	$R = i\text{-}C_3H_7$ 0.74	0.98	95%	25.65 (24.85)	13.35 (13.14)	447 (487)
5.	$R = n\text{-}C_4H_9$ 0.71	0.83	92%	23.58 (23.49)	12.08 (12.43)	489 (515)
6.	$R = i\text{-}C_4H_9$ 0.83	0.98	96%	23.60 (23.49)	12.18 (12.43)	473 (515)

These values are consistent with the chelating nature of dithiophosphoric acids. The ^{31}P signal has earlier been observed at δ 87.30 ppm and δ 88.46 ppm in $Sb[S_2P(iOC_3H_7)_2]_3$[14] and $PhSb[S_2P(iOC_3H_7)_2]_2$[3], respectively. A comparison of these values with the present one indicates that the substitution of ligand with phenyl group increases the ^{31}P chemical shift value. This is due to the deshielding of phosphorus atom in the ligand.

In view of the chelating nature of the ligands and equivalent nature of the phenyl groups attached to antimony atom, following trans-trigonal bipyramidal structure in which axial positions are occupied by phenyl groups and the equatorial positions by ligand and lone pair of electrons, is being tentatively proposed.



EXPERIMENTAL

All reactions were carried out under anhydrous conditions. All the chemicals used were of reagent grade. Antimony trichloride (Fluka, 80°/10 mm) was distilled before use.

The diphenylantimony chloride[15] and 0,0-dialkyldithiophosphoric acids[16] and their sodium salts were prepared by the literature methods.

Sulphur[17] and antimony[17] have been estimated gravimetrically and iodometrically, respectively.

Molecular weights of some representative compounds have been determined on Knauer Vapour Pressure Osmometer in chloroform solution at 45°C.

The IR spectra of some representative compounds are recorded as neat films on Perkin-Elmer-577 spectrophotometer using caesium iodide plates.

^1H, ^{13}C NMR and ^{31}P NMR spectra of the ligands as well as of their diphenylantimony(III) complexes have been recorded in $CDCl_3$ solution on JEOL FX-90 Q spectrometer. TMS was used as an internal reference for ^1H and ^{13}C spectra whereas orthophosphoric acid was used as an external reference for ^{31}P.

All these complexes have been synthesized by the reaction of sodium salts of the ligands with Ph_2SbCl/Ph_2SbOAc. Since same procedure has been followed for the synthesis of these derivatives, the synthesis of one representative complex is being described here and the analytical details of the rest are being summarised in Table-I.

Reaction of diphenylantimony chloride with sodium salt of 0,0-dipropyldithiophosphate in 1:1 molar ratio. A benzene suspension of $(C_3H_7O)_2PS_2Na$ (0.97 gm, 4.14 mM) was added to Ph_2SbCl (1.28 gm, 4.14 mM). The reaction mixture was refluxed for 2 hours. The NaCl thus precipitated was filtered off. After removing the volatile fraction under reduced pressure, a light yellow coloured liquid product was obtained. The product was purified by dissolving in petroleum ether and keeping in a deep freezer over-night. A low melting solid product in 95% yield crystallized out. The product liquefied again during the course of removing the petroleum ether under reduced pressure. Yield 95%, analysis, Found Sb = 25.20%, S = 13.18%. Calculated Sb = 24.85%, s = 13.14%.

This derivative was also prepared by refluxing the 0,0-dipropyldithiophosphoric acid with diphenylantimony acetate in toluene solution in 1:1 molar ratio under a fractionating column. The progress of the reaction was checked by estimating the liberated acetic acid in azeotrope. After the completion of the reaction, the solvent was removed under reduced pressure and the compound was purified as described above.

ACKNOWLEDGEMENT

One of the authors Mrs. R. Karra is thankful to CSIR, New Delhi for financial assistance, and the Head of Chemistry Department for providing the necessary laboratory facilities. Author also gratefully acknowledges the assistance of Shri S. Kumar for recording the NMR spectra.

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