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Chemistry of diorganodithiophosphate (and phosphinate) derivatives with arsenic, antimony and bismuth

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Contents

Abstract

Dialkyldithiophosphates, alkylenedithiophosphates (and dialkyldithiophosphinates) are versatile ligands and exhibit remarkable diversity in their coordination patterns with transition and non-transition metals including arsenic, antimony and bismuth. Their derivatives with these metals have also found applications in a number of ways such as analytical reagents, lubricant additives, regeneration of cracking catalysts and antitumour agents.

In view of the above, a brief review article is being presented on synthetic and structural aspects of dialkyldithiophosphate, alkylenedithiophosphate and dialkyldithiophosphinate derivatives of arsenic, antimony and bismuth and their organometallic moieties.

Starting with a brief introduction and synthesis of ligands, the synthesis of various diorganodithiophosphate (and dialkyldithiophosphinate) derivatives with arsenic, antimony and

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bismuth and their corresponding organometallic moieties and mixed derivatives as well as their properties and reactions have been described. The structural features have been discussed with the help of spectroscopic (IR, NMR and mass) studies. X-ray single crystal structures of a number of tris as well as organometallic derivatives have also been reviewed explaining various types (monodentate, iso and aniso bidentate and tricoordinate-mixed bridging and chelating) of behaviour of the ligands and stereochemistry of the complexes considering various factors such as the presence of the stereochemically active lone pair, small ligand bite and molecular associations. © 1998 Elsevier Science S.A.

Keywords: Alkylenedithiophosphate; Antimony; Arsenic; Bismuth; Dialkyldithiophosphate; Dialkyldithiophosphinate; Mass spectra; NMR spectra; Organometallic derivatives; X-ray structure

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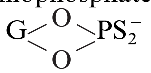
1. Introduction

The ligands containing $>PS_2$ grouping (diorganodithiophosphate and dialkyldithiophosphinate) are known to exhibit remarkable diversity in their coordination patterns. Their interactions with transition metals are well known and in most of the cases these behave as bidentate ligands [1]. A broader diversity of bonding patterns have been observed when such ligands are attached to main group metals and related organometallic moieties [2–4]. Amongst these, arsenic, antimony and bismuth are even more interesting elements because as coordination centre these often exhibit unpredictable structural behaviour due to the presence of a stereochemically active lone pair of electrons [2–7]. However, small ligand bite and molecular associations [4–6] also play an important role in deciding the stereochemistry of the molecules.

The derivatives of arsenic, antimony and bismuth with dithiophosphorus ligands are not only important because of their interesting stereochemistry but also they have been extensively employed in many ways such as analytical reagents [8–12], lubricant additives (to improve extreme pressure and antiwear properties of lubricants) [13–20], catalytic activities for regeneration of cracking catalysts [21–27] and antitumour agents [28].

In view of their interesting stereochemical features and applications, a brief review is being presented on synthetic and structural aspects of diorganodithiophosphate (dialkyldithiophosphate) $(RO)_2PS_2^-$ and their cyclic analogues, i.e. alkylenedithiophosphate  $G{<}\begin{matrix}O\\O\end{matrix}{>}PS_2^-$ and dialkyldithiophosphinate, $R_2PS_2^-$, derivatives of arsenic, antimony and bismuth with particular emphasis on the work reported during the last couple of decades.

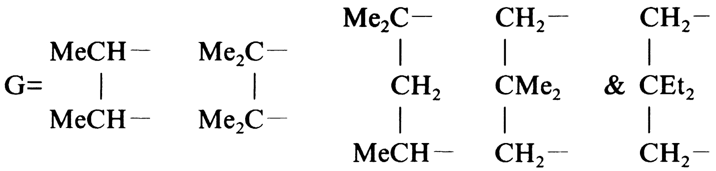
2. General

Dialkyldithiophosphoric acids can be prepared [2,29–33] by the reactions of phosphorus pentasulphide with alcohols (or phenols). Similarly, alkylenedithiophosphoric acids have been prepared recently [34,35] by the reactions of phosphorus pentasulphide with glycols in anhydrous hydrocarbon solvent. For these reactions the glycols should be sterically hindered otherwise polymers are obtained.

$$P_4S_{10}+8ROH\rightarrow 4(RO)_2PS_2H+2H_2S\uparrow$$

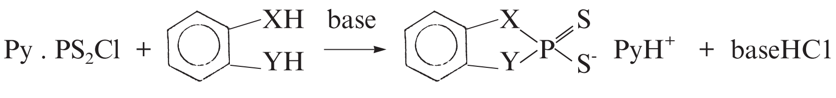
$$P_4H_{10} + 4G\begin{array}{l}OH\\OH\end{array} \longrightarrow 4G\begin{array}{c}O\\O\end{array}PS_2H + 2H_2S\uparrow$$

where



$$G=\begin{array}{c}\mathrm{MeCH}-\\|\\\mathrm{MeCH}-\end{array}\quad\begin{array}{c}\mathrm{Me_2C}-\\|\\\mathrm{Me_2C}-\end{array}\quad\begin{array}{c}\mathrm{Me_2C}-\\|\\\mathrm{CH_2}\\|\\\mathrm{MeCH}-\end{array}\quad\begin{array}{c}\mathrm{CH_2}-\\|\\\mathrm{CMe_2}\\|\\\mathrm{CH_2}-\end{array}\ \&\ \begin{array}{c}\mathrm{CH_2}-\\|\\\mathrm{CEt_2}\\|\\\mathrm{CH_2}-\end{array}$$

Alkylenedithiophosphoric acids can also be prepared by the reaction of Py.PS_2Cl with pyrocatechol or *o*-phenylenediamine in the presence of a tertiary amine [36].

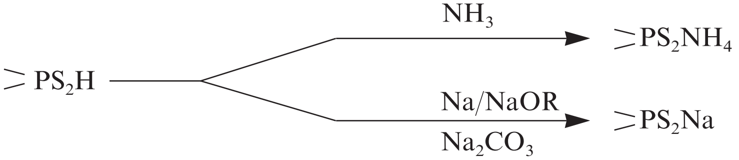


(where X=O, S, NH; Y=O, S, NH; Py=pyridine).

Most of these diorganodithiophosphoric acids can be purified by distillation under reduced pressure. On standing they tend to oxidize to give the corresponding disulphides and other related products [1,2].

Diphenyldithiophosphinic acid can be prepared by the reaction of phosphorus pentasulphide with a Grignard reagent or more conveniently by a modified Friedal–Crafts reaction of phosphorus pentasulphide with benzene in the presence of anhydrous aluminium chloride [37,38].

Most of the time, metal derivatives of these ligands including those of arsenic, antimony and bismuth have been prepared by the reactions of their sodium or ammonium salts with suitable metal precursors. The ammonium salts can be prepared by passing dry ammonia in a hydrocarbon solution of the ligands and sodium salts by the reaction of the ligand with sodium metal, sodium alkoxide or sodium carbonate [29–39].



The salts can also be prepared by the following route [40]

$$\mathrm{(RO)_2P(S)Cl + KSH \rightarrow (RO)_2PS_2K + HCl}$$

The sodium dialkyldithiophosphinates can also be prepared from $\mathrm{R_2P(S)P(S)R_2}$, elemental sulphur and sodium sulphide [41,42].

3. Synthesis of complexes

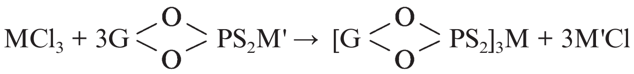
Dialkyldithiophosphate (and phosphinate) and alkylenedithiophosphate derivatives of arsenic, antimony and bismuth can be conveniently synthesized mainly by the following routes.

3.1. Synthesis of metal tris derivatives

3.1.1. By metal chlorides

Arsenic, antimony and bismuth trichlorides on reactions with the corresponding dithio acids or their sodium (or ammonium) salts in 1:3 molar ratio yield the corresponding metal tris (diorganodithiophosphate) (or phosphinate) derivatives [43–55].

$$\mathrm{MCl_3 + 3(RO)_2PS_2M' \rightarrow [(RO)_2PS_2]_3M + 3M'Cl}$$



$$\mathrm{MCl_3 + 3G\overset{O}{\underset{O}{<\;>}}PS_2M' \rightarrow [G\overset{O}{\underset{O}{<\;>}}PS_2]_3M + 3M'Cl}$$

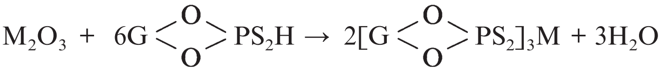
$$\mathrm{MCl_3 + R_2PS_2M' \rightarrow [R_2PS_2]_3M + 3M'Cl}$$
$$\mathrm{(M = As, Sb, Bi;\ M' = H, Na, NH_4)}$$

3.1.2. By metal oxides and alkoxides

Arsenic, antimony and bismuth oxides and alkoxides on treating with parent acids give the corresponding metal tris(diorganodithiophosphates) [47,50,54]

$$\mathrm{M_2O_3 + 6(RO)_2PS_2H \rightarrow 2[(RO)_2PS_2]_3M + 3H_2O}$$

$$\mathrm{M(OR')_3 + 3(RO)_2PS_2H \rightarrow [(RO)_2PS_2]_3M + 3R'OH}$$



$$\mathrm{M_2O_3 + 6G\overset{O}{\underset{O}{<\;>}}PS_2H \rightarrow 2[G\overset{O}{\underset{O}{<\;>}}PS_2]_3M + 3H_2O}$$

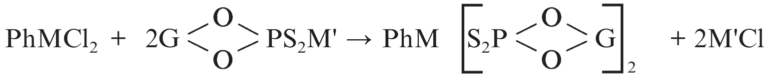
3.2. *Synthesis of mixed derivatives*

3.2.1. *Organometallic derivatives [56–64]*

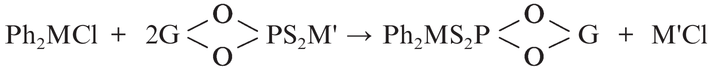
The corresponding organometallic derivatives of arsenic, antimony and bismuth with diorganodithiophosphate (and phosphinate) ligands have been synthesized by the following reaction routes

$$\mathrm{PhMCl_2 + 2(RO)_2PS_2Na \rightarrow PhM[S_2P(OR)_2]_2 + 2NaCl}$$

$$\mathrm{Ph_2MCl + (RO)_2PS_2Na \rightarrow Ph_2MS_2P(OR)_2 + NaCl}$$



$$\mathrm{PhMCl_2 + 2G}\overset{O}{\underset{O}{<\,>}}\mathrm{PS_2M' \rightarrow PhM}\left[\mathrm{S_2P}\overset{O}{\underset{O}{<\,>}}\mathrm{G}\right]_2 \mathrm{+ 2M'Cl}$$



$$\mathrm{Ph_2MCl + 2G}\overset{O}{\underset{O}{<\,>}}\mathrm{PS_2M' \rightarrow Ph_2MS_2P}\overset{O}{\underset{O}{<\,>}}\mathrm{G + M'Cl}$$

$$\mathrm{Ph_2SbOAc + (RO)_2PS_2M' \rightarrow Ph_2SbS_2P(OR)_2 + M'OAc}$$

$$\mathrm{Ph_2SbOAc + Ph_2PS_2M' \rightarrow Ph_2SbS_2P(Ph)_2 + M'OAc}$$

$$\mathrm{Ph_2SbCl_3 + 3(RO)_2PS_2NH_4 \rightarrow Ph_2SbS_2P(OR)_2 + [(RO)_2P(S)S]_2 + 3NH_4Cl}$$

$$\mathrm{O(C_6H_4)_2AsCl + R_2PS_2M' \rightarrow O(C_6H_4)_2AsS_2PR_2 + M'Cl}$$

$$\mathrm{Ph_4MCl + (RO)_2PS_2Na \rightarrow [Ph_4M]^+[S_2P(OR)_2]^- + NaCl}$$

(M = As, Sb; M′ = H, Na, $\mathrm{NH_4}$).

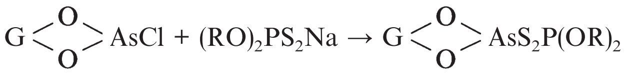
Attempts to prepare $\mathrm{Ph_3M[S_2P(O\text{-}\mathit{i}\text{-}Pr)_2]}$ (M = As, Sb) by the reactions of $\mathrm{Ph_3AsBr_2}$ and $\mathrm{Ph_3SbBr_2}$ with $(\mathit{i}\text{-pro})_2\mathrm{PS_2Na}$ were not successful, but rather than getting the desired product (diisopropyldithiophosphoryl) disulphide, $\mathrm{Ph_3As}$ and $\mathrm{Ph_3Sb}$ were obtained according to the following equation

$$\mathrm{Ph_3MBr_2 + 2(\mathit{i}-PrO)_2PS_2Na \rightarrow Ph_3M + [(\mathit{i}-PrO)_2PS_2]_2 + 2NaCl\downarrow}$$

However, recently Silvestru et al. [65] were successful in preparing $\mathrm{Me_3Sb[S_2PPh_2]_2}$ and have determined its X-ray molecular structure.

3.2.2. *Other mixed derivatives*

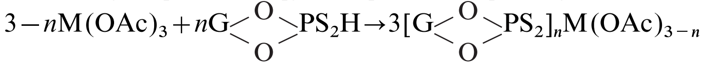
Mixed ligand complexes of arsenic, antimony and bismuth have been synthesized by the following types of reactions [40–42, 47, 50, 54, 66–72]



$$\mathrm{G}\left\langle\begin{matrix}\mathrm{O}\\\mathrm{O}\end{matrix}\right\rangle\mathrm{AsCl} + (\mathrm{RO})_2\mathrm{PS}_2\mathrm{Na} \rightarrow \mathrm{G}\left\langle\begin{matrix}\mathrm{O}\\\mathrm{O}\end{matrix}\right\rangle\mathrm{AsS}_2\mathrm{P}(\mathrm{OR})_2$$

$$MX_3 + n(RO)_2PS_2Na \rightarrow [(RO)_2PS_2]_nMX_{3-n}$$

$$3-nMCl_3 + n[(RO)_2PS_2]_3M \rightarrow 3[(RO)_2PS_2]_nMCl_{3-n}$$

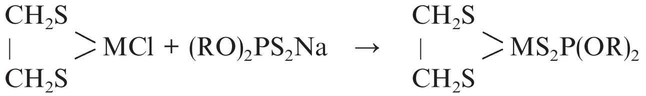


$$3-n\mathrm{M(OAc)}_3 + n\mathrm{G}\left\langle\begin{matrix}\mathrm{O}\\\mathrm{O}\end{matrix}\right\rangle\mathrm{PS}_2\mathrm{H} \rightarrow 3\left[\mathrm{G}\left\langle\begin{matrix}\mathrm{O}\\\mathrm{O}\end{matrix}\right\rangle\mathrm{PS}_2\right]_n\mathrm{M(OAc)}_{3-n}$$

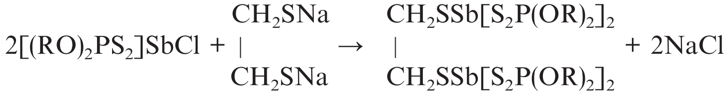
$(n=1, 2)$

$$[(RO)_2PS_2]_3M + X_2 \rightarrow [(RO)_2PS_2]_2MX + [(RO)_2P(S)S]_2$$

(X= Cl, Br, I; M = As, Sb, Bi)



$$\begin{array}{c}\mathrm{CH_2S}\\|\\\mathrm{CH_2S}\end{array}\rangle\mathrm{MCl} + (\mathrm{RO})_2\mathrm{PS}_2\mathrm{Na} \rightarrow \begin{array}{c}\mathrm{CH_2S}\\|\\\mathrm{CH_2S}\end{array}\rangle\mathrm{MS}_2\mathrm{P}(\mathrm{OR})_2$$



$$2[(\mathrm{RO})_2\mathrm{PS}_2]\mathrm{SbCl} + \begin{array}{l}\mathrm{CH_2SNa}\\|\\\mathrm{CH_2SNa}\end{array} \rightarrow \begin{array}{l}\mathrm{CH_2SSb[S_2P(OR)_2]_2}\\|\\\mathrm{CH_2SSb[S_2P(OR)_2]_2}\end{array} + 2\mathrm{NaCl}$$

$$[(RO)_2PS_2]MCl + LNa \rightarrow [(RO)_2PS_2]_2ML + NaCl \ (L = (RO)_2NCS_2^-, ROCS_2^-)$$

$$O(CH_2CH_2S)_2SbCl + KS_2P(OC_2H_5) \rightarrow O(CH_2CH_2S)_2SbS_2P(OC_2H_5)_2 + KCl$$

4. Properties

The diorganodithiophosphate (and phosphinate) derivatives of arsenic(III), antimony(III) and bismuth(III) are light yellow crystalline solids or yellow viscous liquids. These are soluble in common organic solvents such as benzene, chloroform, carbon tetrachloride, hexane, petroleum ether, acetone and alcohols etc. and most are monomeric in nature. Metal tris derivatives are insoluble and stable in water. However, mixed derivatives (halide, acetate, dithiolate and organometallic) are sensitive towards moisture and tend to decompose. The mixed chloride dialkyldithiophosphate derivatives react with water to give the corresponding metal tris derivatives and oxides according to the following reactions [47,50]

$$6[(RO)_2PS_2]_2MCl + 3H_2O \rightarrow 4[(RO)_2PS_2]_3M + M_2O_3 + 6HCl$$

$$3[(RO)_2PS_2]MCl_2 + 3H_2O \rightarrow [(RO)_2PS_2]_3M + M_2O_3 + 6HCl$$

(where M = As, Sb, Bi)

Metal tris(dialkyldithiophosphates) react with excess of ammonia to yield the corresponding metal oxides and ammonium salts of the ligands [47,50].

$$2[(RO)_2PS_2]_3M + 6NH_4OH \rightarrow M_2O_3 + 6(RO)_2PS_2NH_4 + 6H_2O$$

(where M = As, Sb, Bi; R = $i-$Pr)

The diorganodithiophosphate (and phosphinate) derivatives of arsenic(III), antimony(III) and bismuth(III) are stable up to about 100 °C and above this temperature start to decompose. Mixed dichloroantimony(III) diisopropyldithiophosphate on heating disproportionates to give chloroantimony(III) bis(diisopropyldithiophosphate) and antimony(III) trichloride as the first decomposition product [47]

$$2(i-\mathrm{Pro})_2\mathrm{PS}_2\mathrm{SbCl}_2 \rightarrow [(i-\mathrm{Pro})_2\mathrm{PS}_2]_2\mathrm{SbCl} + \mathrm{SbCl}_3$$

Chloroantimony(III) bis(dialkyldithiophosphates) form 1:1 addition complexes with amines like triethyl amine [67]

$$[(\mathrm{RO})_2\mathrm{PS}_2]_2\mathrm{SbCl} + \mathrm{Et}_3\mathrm{N} \rightarrow [(\mathrm{RO})_2\mathrm{PS}_2]_2\mathrm{SbCl.NEt}_3$$

Studies on photometric and polarographic analysis and antiparasitic activities of some metal and organometal dialkyldithiophosphate derivatives have also been reported [2,73].

5. Spectroscopic studies

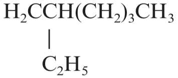
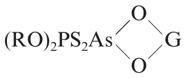
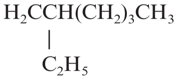
The structural aspects of arsenic(III), antimony(III) and bismuth(III) derivatives with dithiophosphorus ligands have been elucidated by various spectroscopic techniques, e.g. IR, NMR (^{1}H, ^{13}C and ^{31}P) and mass spectra as well as single crystal molecular structure of some of the derivatives. A list of arsenic, antimony and bismuth diorganodithiophosphate (and phosphinate) derivatives along with physicochemical data is given in Table 1. While discussing the structural features of these derivatives one should take into account the possible coordination patterns of these dithiophosphorus ligands [1–6]. These can behave as (I) ionic, (II) monodentate, (III) bidentate [(a) isobidentate, (b) anisobidentate, (c) bridging] and (IV) bimetallic triconnective as shown in Fig. 1.

Ionic behaviour is known for most of the alkali metal derivatives, monodentate behaviour is rare but is known in $\mathrm{Ph_3SnSP(S)(OEt)_2}$ [74] and $\mathrm{O(C_6H_4)_2AsS_2PPh_2}$ [92] whereas anisobidentate coordination is found in closely related organotin compounds $\mathrm{Ph_2Sn[S_2P(O\text{-}\mathit{i}\text{-}Pr)_2]_2}$ [75] and $\mathrm{Ph_2Sn[S_2P(OEt)_2]_2}$ [76], respectively. In most of the derivatives with arsenic(III), antimony(III) and bismuth(III) the ligands exhibit anisobidentate (and isobidentate also in a few cases) behaviour as indicated by most of the spectroscopic techniques. The ligands have also been shown to behave as tricoordinate-mixed chelating and bridging due to molecular associations (Table 2).

5.1. Infrared spectra

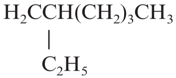
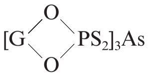
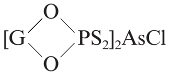
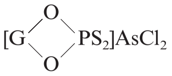
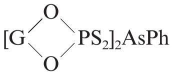
The infrared spectra of arsenic, antimony and bismuth dialkyldithiophosphate [2,34,35,39,43–50,56,57] and alkylenedithiophosphate [54,60,61,72] derivatives exhibit bands at 1020–970 cm^{-1} ν((P)–O–C), 900–800 cm^{-1} ν(P–O–(C)),

Table 1
Diorganodithiophosphate (and phosphinate) derivatives of arsenic, antimony and bismuth

Series no.	Compound		Method of preparation	Physico-chemical and other reported data	Reference
(A) Dialkyldithiophosphates		R = (M. Pt. °C)			
1.	$[(RO)_2PS_2]_3As$	C_2H_5 (52), i-C_3H_7 (100), n-C_3H_7 (liq), i-C_4H_9 (114), C_6H_5,  $H_2C\underset{\displaystyle C_2H_5}{\underset{\vert}{C}}H(CH_2)_3CH_3$	Sections 3.1.1 and 3.1.2	Polarography, photometric analysis, conductivity, mol. wt., Raman, IR, NMR (^1H, ^{31}P)	[2,44–47,77]
2.	$[(RO)_2PS_2]_2AsCl$	C_2H_5, i-C_3H_7, n-C_3H_7, i-C_4H_9	Section 3.2.2	Mol. wt., IR, NMR	[47]
3.	$(RO)_2PS_2AsCl_2$	C_2H_5, i-C_3H_7, n-C_3H_7, i-C_4H_9	Section 3.2.2	Mol. wt., IR, NMR	[47]
4.	 (where G = $-CH_2CH_2-$, $-CHMeCH_2-$, $-CMe_2CH_2CHMe-$, $-CMe_2CMe_2-$)	C_2H_5, i-C_3H_7, n-C_3H_7, i-C_4H_9, C_6H_5	Section 3.2.2	Mol. wt., IR, NMR (^1H, ^{31}P)	[39]
5.	$[Ph_4As]^+[S_2P(OR)_2]^-$	CH_3 (138), C_2H_5 (146), i-C_3H_7 (130), n-C_3H_7 (122), i-C_4H_9 (152)	Section 3.2.1	Conductivity, IR, NMR (^1H, ^{31}P)	[63]
6.	$[(RO)_2PS_2]_2AsPh$	C_2H_5 (liq), i-C_3H_7 (48–50), n-C_3H_7 (liq), C_6H_5 (72–74)	Section 3.2.1	Mol. wt., IR, NMR (^1H, ^{13}C, ^{31}P) (mass spectra and X-ray crystal structure for R = i-C_3H_7)	[55,56]
7.	$[(RO)_2PS_2]_3Sb$	CH_3 (95–96), C_2H_5 (55–56), i-C_3H_7 (78–80), n-C_3H_7 (liq), i-C_4H_9 (123–124), n-C_4H_9 (oil), Sec.C_4H_9 (48–50), C_6H_{11}, C_6H_5,  $H_2C\underset{\displaystyle C_2H_5}{\underset{\vert}{C}}H(CH_2)_3CH_3$	Sections 3.1.1 and 3.1.2	Photometric analysis, mol. wt., conductivity, Raman, IR, NMR (^1H, ^{31}P) (X-ray crystal and molecular structure for R = CH_3, C_2H_5, i-C_3H_7)	[8,13, 44–48,77]

8.	$[(RO)_2PS_2]_2SbCl$	C_2H_5 (100), i-C_3H_7 (92), n-C_3H_7 (liq), i-C_4H_9 (80)	Section 3.2.2	Mol. wt., IR, NMR (^1H, ^{31}P)	[47]
9.	$[(RO)_2PS_2]_2SbBr$	i-C_3H_7 (105)	Section 3.2.2	Mol. wt., IR, NMR	[47]
10.	$[(RO)_2PS_2]_2SbI$	i-C_3H_7 (85)	Section 3.2.2	Mol. wt., IR, NMR	[47]
11.	$(RO)_2PS_2SbCl_2$	C_2H_5 (105), i-C_3H_7 (liq), n-C3H$_7$ (liq), i-C_4H_9 (liq)	Section 3.2.2	Mol. wt., IR, NMR	[47]
12.	$[(RO)_2PS_2]_2SbO$-i-Pr	i-C_3H_7 (76)	Section 3.2.2	Mol. wt., IR, NMR	[47]
13.	$(RO)_2PS_2Sb(O$-i-$Pr)_2$	i-C_3H_7 (liq)	Section 3.2.2	Mol. wt., IR, NMR	[47]
14.	$(RO)_2PS_2\overline{SbCH_2CH_2S}$	i-C_3H_7 (48), i-C_4H_9 (liq)	Section 3.2.2	IR, NMR (^1H, ^{31}P)	[66]
15.	$[(i$-$PrO)_2PS_2]_2SbS_2COR$	C_2H_5, i-C_3H_7, n-C_3H_7, i-C_4H_9, n-C_4H_9	Section 3.2.2	IR, NMR	[68]
16(a)	$[(i$-$PrO)_2PS_2]_2SbS_2CNR_2$	CH_3 (138), C_2H_5 (98), $(CH_2)_2$ (120)	Section 3.2.2	IR, NMR (^1H, ^{31}P)	[69]
16(b)	$[(i$-$BuO)_2PS_2]_2SbS_2CNR_2$	CH_3 (140), C_2H_5 (58–60), $(CH_2)_2$ (87)	Section 3.2.2		
17.	$CH_2SSb[S_2P(OR)_2]_2$ | $CH_2SSb[S_2P(OR)_2]_2$	C_2H_5 (80), i-C_3H_7 (liq), i-C_4H_9 (74)	Section 3.2.2	IR, NMR (^1H, ^{31}P)	[66]
18.	$Ph_2SbS_2P(OR)_2$	CH_3 (104–106), C_2H_5 (oil), i-C_3H_7 (50–52), n-C_3H_7 (oil), i-C_4H_9 (oil), n-C_4H_9 (oil), C_6H_5 (oil)	Section 3.1.2	IR, NMR (^1H, ^{13}C, ^{31}P) (mass spectra and X-ray crystal structure for $R = i$-C_3H_7)	[57,58]
19.	$PhSb[S_2P(OR)_2]_2$	C_2H_5 (78–81), i-C_3H_7 (88), n-C_3H_7 (38), C_6H_5 (108–110)	Section 3.1.2	Mol. wt., IR, NMR (^1H, ^{13}C, ^{31}P) (mass spectra for $R = n$-C_3H_7 and X-ray crystal structure for $R = i$-C_3H_7)	[56]

Table 1 (*continued*)

Series no.	Compound		Method of preparation	Physico-chemical and other reported data	Reference
20.	$[(RO)_2PS_2]_3Bi$	CH_3, C_2H_5 (55), i-C_3H_7 (68), n-C_3H_7 (liq), i-C_4H_9 (160), C_6H_5,  $H_2CCH(CH_2)_3CH_3$ with C_2H_5	Sections 3.1.1 and 3.1.2	Polarography, photometric analysis, gravimetric estimation by spectrophotometry, mol. wt., IR, NMR (^1H,^{31}P) (X-ray structure for $R=CH_3$, i-C_3H_7)	[2,8,44–46, 50,77,83,84]
21.	$[(RO)_2PS_2]_2BiCl$	C_2H_5 (85), i-C_3H_7 (145), n-C_3H_7 (liq), i-C_4H_9 (110)	Section 3.2.2	Mol. wt., IR, NMR (^1H,^{31}P)	[50]
22.	$[(RO)_2PS_2]_2BiBr$	i-C_3H_7 (135)	Section 3.2.2	Mol. wt., IR, NMR	[50]
23.	$[(RO)_2PS_2]_2BiI$	i-C_3H_7 (130)	Section 3.2.2	Mol. wt., IR, NMR	[50]
24.	$(RO)_2PS_2BiCl_2$	C_2H_5 (82), i-C_3H_7 (138), n-C_3H_7 (liq), i-C_4H_9 (90)	Section 3.2.2	Mol. wt., IR, NMR (^1H, ^{31}P)	[50]
(B) Alkylenedithiophosphates		G= (M. Pt. °C)			
1.		–CHMeCHMe– (180), $-CMe_2CMe_2-$, $-CMe_2CH_2CHMe-$ (55), $-CH_2CMe_2CH_2-$ (210), $-CH_2CEt_2CH_2-$ (125)	Section 3.1.1	Mol. wt., IR, NMR	[54]
2.		–CHMeCHMe–	Section 3.2.2	Mol. wt., IR, NMR	[54]
3.		–CHMeCHMe–	Section 3.2.2	Mol. wt., IR, NMR	[54]
4.		–CHMeCHMe– (pasty mass), $-CMe_2CMe_2-$ (158–161), $-CMe_2CH_2CHMe-$ (43–47), $-CH_2CMe_2CH_2-$ (51–55)	Section 3.2.1	Mol. wt., IR, NMR (^1H, ^{31}P)	[60,72]

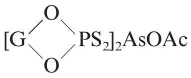
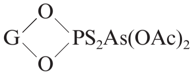
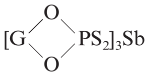
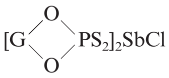
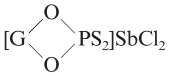
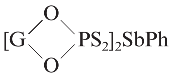
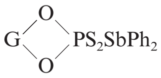
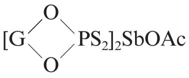
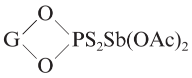
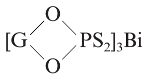
5.		$-CHMeCHMe-$ (130–135 dec.), $-CMe_2CMe_2-$ (180 dec.), $-CH_2CMe_2CH_2-$ (178–180 dec.)	Section 3.2.2	Mol. wt., IR, NMR (^1H, ^{31}P)	[72]
6.		$-CHMeCHMe-$ (100–105 dec.), $-CMe_2CMe_2-$ (130 dec.), $-CH_2CMe_2CH_2-$ (140–145 dec.)	Section 3.2.2	Mol. wt., IR, NMR (^1H, ^{31}P)	[72]
7.		$-CH_2CMe_2CH_2-$ (118), $-CH_2CEt_2CH_2-$ (90)	Section 3.2.2	IR, NMR (^1H, ^{13}C, ^{31}P)	[67]
8.		$-CHMeCHMe-$, $-CMe_2CMe_2-$ (300 dec.), $-CMe_2CH_2CHMe-$ (55), $-CH_2CMe_2CH_2-$ (200), $-CH_2CEt_2CH_2-$ (112)	Sections 3.1.1 and 3.1.2	Mol. wt., IR, NMR (^1H, ^{31}P)	[54]
9.		$-CHMeCHMe-$ (65), $-CH_2CEt_2CH_2-$	Section 3.2.2	Mol. wt., IR, NMR	[54]
10.		$-CHMeCHMe-$, $-CH_2CEt_2CH_2-$	Section 3.2.2	Mol. wt., IR, NMR	[54]
11.		$-CHMeCHMe-$ (105 dec.), $-CMe_2CMe_2-$ (166 dec.), $-CMe_2CH_2CHMe-$ (122–125), $-CH_2CMe_2CH_2-$ (133–137)	Section 3.2.1	Mol. wt., IR, NMR (^1H, ^{31}P)	[60]
12.		$-CMe_2CMe_2-$, $-CMe_2CH_2CHMe-$, $-CH_2CMe_2CH_2-$, $-CH_2CEt_2CH_2-$	Section 3.2.1	Mol. wt., IR, NMR (^1H, ^{13}C, ^{31}P)	[61]
13.		$-CMe_2CMe_2-$ (220 dec.), $-CH_2CMe_2CH_2-$ (170 dec.), $-CH_2CEt_2CH_2-$ (178 dec.)	Section 3.2.2	Mol. wt., IR, NMR (^1H, ^{13}C, ^{31}P)	[72]
14.		$-CHMeCHMe-$ (110 dec.), $-CMe_2CMe_2-$ (190 dec.), $-CH_2CMe_2CH_2-$ (140–145 dec.), $-CH_2CEt_2CH_2-$ (150 dec.)	Section 3.2.2	Mol. wt., IR, NMR (^1H, ^{13}C, ^{31}P)	[72]

Table 1 (*continued*)

Series no.	Compound		Method of preparation	Physico-chemical and other reported data	Reference
15.		–CHMeCHMe– (260), $–CMe_2CH_2CHMe–$ (80 dec.), $–CH_2CMe_2CH_2–$ (290 dec.), $–CH_2CEt_2CH_2–$ (255)	Section 3.1.1	Mol. wt., IR, NMR (^1H, ^{31}P) (X-ray crystal and molecular structure for G = –CHMeCHMe– and $–CH_2CEt_2CH_2–$)	[54,85]
(C) Dialkyldithiophosphinates		R = (M. Pt. °C)			
1.	$R_2AsS_2PPh_2$	CH_3, C_6H_5	Section 3.2.1	IR, NMR	[59]
2.	$O(C_6H_4)_2AsS_2PR_2$	CH_3 (105–117), C_2H_5 (85–88), C_6H_5 (140–141)	Section 3.2.1	IR, NMR (^1H, ^{13}C, ^{31}P), mass spectra (X-ray crystal structure for $R = C_6H_5$)	[64,92]
3.	$Sb(S_2PR_2)_3$	CH_3 (67–68), C_2H_5 (80–82), C_6H_5 (200–202)	Section 3.1.1	IR, NMR (single crystal X-ray structure for $R = C_2H_5$, C_6H_5)	[48,80–82]
4.	$Ph_2SbS_2PR_2$	CH_3 (104–105), C_2H_5 (71–73), C_3H_7 (112–114), C_6H_5 (140–142)	Section 3.2.1	IR, NMR (X-ray crystal structure for $R = C_6H_5$)	[62]
5.	$Me_2SbS_2PMe_2$		Section 3.2.1	X-ray crystal structure	[95]
6.	(p-$MeC_6H_4)_2SbS_2PEt_2$		Section 3.2.1	X-ray crystal structure	[94]
7.	$Me_3Sb(S_2PPh_2)_2$		Section 3.2.1	X-ray crystal structure	[65]
8.	$Bi(S_2PR_2)_3$	CH_3, C_2H_5, C_6H_4	Section 3.1.1	X-ray crystal structure	[81,88–90]
9.	$MeSBi(S_2PPh_2)_2$		Section 3.2.1	X-ray crystal structure	[91]

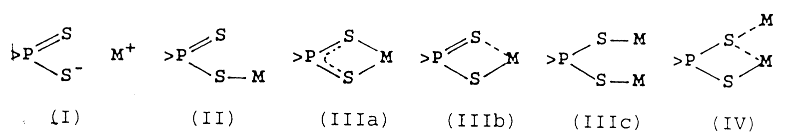
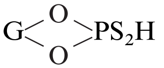


Fig. 1. Structural possibilities of metal diorganodithiophosphate (and phosphinate) derivatives.

575–500 cm^{-1} (ν sym PS_2) or ν(P–S) and 675–625 cm^{-1} (ν asym PS_2) or ν(P=S). The alkylene dithiophosphates in addition exhibit bands at 950–925 cm^{-1} due to dioxaphospholane and dioxaphosphorinane rings [54,60,61,72].

The data cannot distinguish between various structural possibilities since it is not possible to assign P=S and P–S stretching frequencies with certainty [48]. However, the band due to νP=S (ν asym PS_2 by some authors) in the ligands $(RO)_2PS_2H$ or  $G\left<{}^{O}_{O}\right>PS_2H$ and their sodium or ammonium salts appears to shift towards lower frequencies which may be attributed to the bidentate chelation of the ligands to these metals [47,50,54,56,57]. The shifting is observed in the order Bi ~ 50 cm^{-1} > Sb ~ 30 cm^{-1} > As ~ 10 cm^{-1}. Although the frequencies observed in the ranges 500–575 cm^{-1} and 625–675 cm^{-1} probably correspond to ν(sym PS_2) and ν(asym PS_2) [47,50,56] they are little sensitive to distinguish the type of bonding nature of the ligands.

In the spectra of dithiophosphinates bands due to ν(sym PS_2) and ν(asym PS_2) at 400–500 cm^{-1} and 550–640 cm^{-1} have been observed in addition to P–C stretching vibrations at 696–780 cm^{-1}. Although in these compounds there is some mixing of P–S and P–C stretching vibrations, the differences between either ν(P=S) and ν(P–S) or [$\Delta = \nu$(asym PS_2) $-$ ν(sym PS_2)] can be used to determine the coordination behaviour of the ligand as follows [48,62,64]

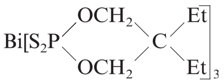
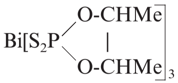
Δ (cm^{-1})	Coordination behaviour of ligand
50–70	Isodentate
70–90	Anisodentate
95 and above	Unidentate

Although infrared data give some indication about the type of coordination behaviour in these derivatives, the data are not sufficient enough to predict exactly the type of coordination and are sometimes misleading. Therefore, further investigation through other spectral studies is essential.

5.2. NMR spectra

The diorganodithiophosphate (and phosphinate) derivatives of arsenic, antimony and bismuth exhibit the usual proton resonances due to the protons of the corresponding ligands. Coupling of phosphorus with α protons (P–OCH) in diorganodithiophosphate ligands and α and β protons (P–CH and P–C–CH) in dialkyldithiophosphinate ligands have been observed [47,48,50,64]. In addition, organometallic moieties exhibit proton resonances due to metal–alkyl protons and

Table 2
Coordination pattern and geometry along the central metal atom in the metal (As, Sb and Bi) diorganodithiophosphates and phosphinates

Series no.	Compound	Coordination pattern of the ligand (from Fig. 1)	Coordination polyhedron	Reference
1.	$Sb[S_2P(OR)_2]$ (R = Me, Et, *i*-Pr)	Bidentate chelating (IIIb)	Distorted octahedron (ψ capped octahedron)	[48,49]
2.	$Sb(S_2PPh_2)_3$	Bidentate chelating (IIIb)	Distorted pentagonal pyramid (ψ pentagonal bipyramid)	[80,81]
3.	$Sb(S_2PEt_2)_3$	Bidentate chelating (IIIb)	Distorted octahedron	[82]
4.	$Bi[S_2P(O\text{-}i\text{-}Pr)_2]_3$	Bidentate chelating (IIIb)	Distorted octahedron (ψ capped octahedron)	[83,84]
5.		Bidentate chelating (IIIb)	Distorted octahedron	[85]
6.		Bidentate chelating (isobidentate) (IIIa)	Less distorted octahedron	[85]
7.	$Bi(S_2PEt_2)_3$	Bidentate chelating (isobidentate) (IIIa)	Octahedron	[88,89]
8.	$Bi(S_2PR_2)_3$ (R = Me,Ph)	Bidentate chelating + bimetallic triconnective (IIIb + IV)	Dimeric pentagonal bipyramid	[81,90]
9.	$MeSBi(S_2PPh_2)_2$	Bidentate chelating (IIIb)	Distorted square pyramid (ψ octahedron)	[91]
10.	$PhM[S_2P(O\text{-}i\text{-}Pr)_2]_2$ (M = As,Sb)	Bidentate chelating (IIIb)	Distorted square pyramid (distorted ψ octahedron)	[56]
11.	$[Ph_2SbS_2PPh_2]_2$	Bimetallic triconnective (IV)	Distorted square pyramid (distorted ψ octahedron)	[62]

12.	$[(p\text{-MeC}_6H_4)_2SbS_2PEt_2]_2$	Bidentate bridging (bimetallic biconnective) (IIIc)	Distorted trigonal bipyramid	[94]
13.	$[Me_2SbS_2PMe_2]_n$	Bimetallic triconnective (IV)	Distorted square pyramid (distorted ψ octahedron)	[95]
14.	$[Ph_2SbS_2P(O\text{-}i\text{-}Pr)_2]_n$	Bimetallic triconnective (IV)	Distorted square pyramid (distorted ψ octahedron)	[58,59]
15.	$O(C_6H_4)_2AsS_2PPh_2$	Monodentate (II)	Pyramid	[92]
16.	$[O(C_6H_4)_2AsS_2PPh_2]_2$	Bimetallic triconnective (IV)	Distorted square pyramid (distorted ψ octahedron)	[64]
17.	$Me_3Sb[S_2PPh_2]_2$	Bidentate chelating (IIIb)	Distorted trigonal bipyramid	[65]

mixed ligand complexes exhibit proton resonances of other types of protons present (Table 2). ^{13}C NMR spectra of some diphenyl antimony(III) alkylenedithiophosphates have been reported to show only two bond coupling with phosphorus whereas three bond coupling is observed in parent dithio acids. The signals of alkylene carbons were observed at the expected positions. The ^{13}C NMR spectra of $O(C_6H_4)_2AsS_2PR_2$ exhibit only one type of organic group bond to phosphorus and the expected phosphorus and carbon coupling.

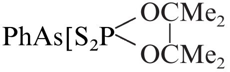
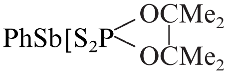
On the basis of analysis of proton decoupled ^{31}P NMR chemical shift values, Glidewell [77] concluded that the different types of bonding modes in metal dithiophosphate complexes can be distinguished as follows

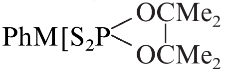
	Bonding pattern	^{31}P NMR chemical shift (ppm)
(i)	Ionic (I)	<101
(ii)	Monodentate (II)	>82
(iii)	Bidentate (IIIa, IIIb, IIIc) (chelating or bridging)	82–101

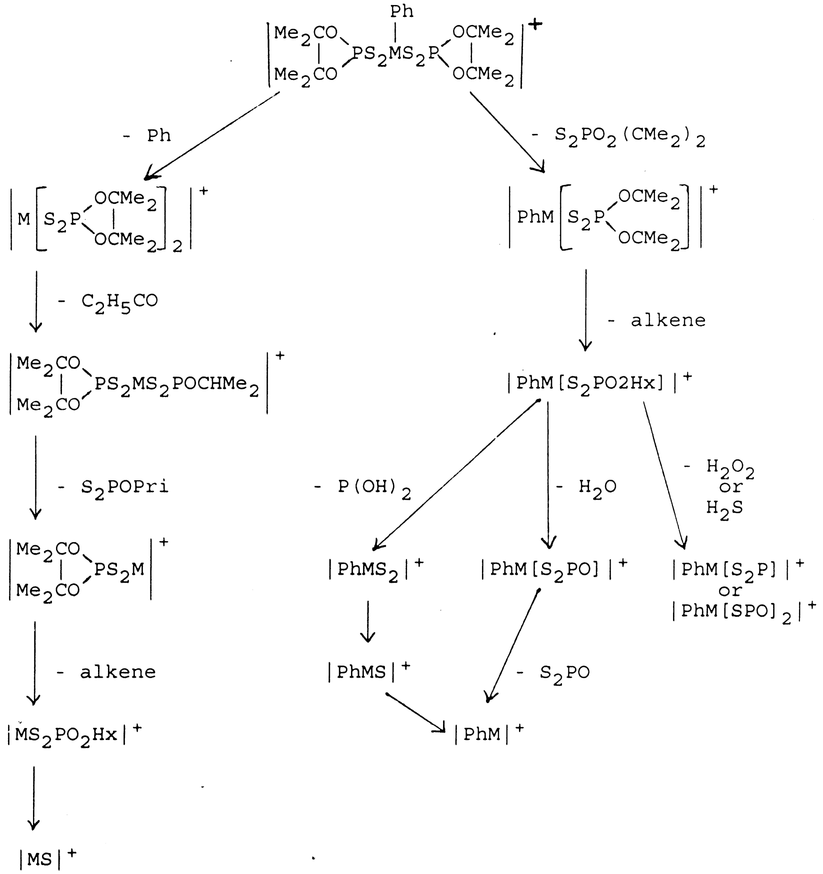
These values are valid with only slight variations in the cases of arsenic, antimony and bismuth derivatives, however, doubts have been made about the universality of the above generalization [78,79]. Therefore, confirmation through more reliable techniques is necessary. In proton coupled ^{31}P NMR spectra the coupling of P with α protons has been observed.

The ^{31}P NMR chemical shift values in cyclic (alkylene) dithiophosphate derivatives exhibit increasing shielding on the transition from a five-membered (dioxaphospholane) to a six-membered (dioxaphosphorinane) ring. On formation of arsenic, antimony and bismuth complexes, a down field shift in the ^{31}P signals has been observed indicating a bidentate chelating nature of the ligands.

5.3. Mass spectra

The spectra of only a few organoarsenic(III) and organoantimony(III) diorganodithiophosphate derivatives, i.e. $Ph_2Sb[S_2P(O\text{-}i\text{-}Pr)_2]$ [58,59], $PhAs[S_2P(O\text{-}i\text{-}Pr)_2]$ [56], $PhSb[S_2P(O\text{-}n\text{-}Pr)_2]$ [58],  $PhAs[S_2P{<}\begin{smallmatrix}OCMe_2\\ |\\ OCMe_2\end{smallmatrix}$ [60],  $PhSb[S_2P{<}\begin{smallmatrix}OCMe_2\\ |\\ OCMe_2\end{smallmatrix}$ [60] and $O(C_6H_4)_2AsS_2PR_2$ [64] have been recorded.

An electron impact fragmentation pattern for $Ph_2Sb[S_2P(O\text{-}i\text{-}Pr)_2]$ is observed that can follow three alternative routes involving the initial loss of either Ph, Ph_2Sb or $SP(O\text{-}i\text{-}Pr)_2$ units. The spectra of  $PhM[S_2P{<}\begin{smallmatrix}OCMe_2\\ |\\ OCMe_2\end{smallmatrix}$ (M = As, Sb) depict no detectable molecular ion peaks which may indicate the pyrolytic decomposition of the derivatives. The fragmentation of complexes appears to start with the initial



[where M = As, Sb; x = 0, 1 2]

Scheme 1. R.K. Gupta, A.K. Rai, R.C. Mehrotra and V.K. Jain, Inorg. Chim. Acta, 88 (1984) 201–207. Reproduced with permission.

loss of a phenyl group or the ligand moiety followed by losses mainly due to alkenes or alkoxy groups (Scheme 1).

In mass spectra [64] of $O(C_6H_4)_2AsS_2PR_2$ (R = Me, Et, Ph) the molecular ion was observed in all the compounds. The expected first fragmentation ion, i.e. $O(C_6H_4)_2As^-$ and $R_2PS_2^-$ was also present, the former always determining the base peak.

5.4. X-ray crystal and molecular structures

X-ray crystal and molecular structures of a number of antimony(III) [4] and bismuth(III) tris(diorganodithiophosphates) and phosphinates as well as a few organometallic (arsenic and antimony) diorganodithiophosphates and phosphinates

Table 3
Comparision of M–S (M = As, Sb, Bi) and P–S bond asymmetries in MS_2P rings of diorganodithiophosphates (and phosphinates)

Series no.	Compound	M–S bond lengths (Å)		Δ (M–S)	P–S bond lengths (Å)		Δ (P–S)	Reference
(A) Antimony(III) tris(diorganodithiophosphates) and phosphinates								
1.	$Sb[S_2P(OMe)_2]_3$	3.008	2.522	0.486	2.029	1.941	0.088	[48]
		3.006	2.535	0.471	2.036	1.941	0.095	
		3.002	2.531	0.471	2.033	1.927	0.106	
		av. = 3.005	av. = 2.529	av. = 0.476	av. = 2.033	av. = 1.936	av. = 0.097	
2.	$Sb[S_2P(OEt)_2]_3$	2.785	2.590	0.195	1.992	1.984	0.008	[49]
		2.838	2.629	0.209	1.983	1.979	0.004	
		2.856	2.583	0.273	1.976	1.927	0.049	
		av. = 2.826	av. = 2.601	av. = 0.225	av. = 1.984	av. = 1.963	av. = 0.021	
3.	$Sb[S_2P(O\text{-}i\text{-}Pr)_2]_3$	3.031	2.521	0.510	2.029	1.945	0.084	[48]
		3.013	2.531	0.482	2.034	1.932	0.102	
		3.000	2.519	0.481	2.044	1.949	0.095	
		av. = 3.015	av. = 2.524	av. = 0.491	av. = 2.036	av. = 1.942	av. = 0.094	
4.	$Sb[S_2PPh_2]_3$	2.978	2.591	0.387	2.048	1.972	0.076	[80,81]
		3.187	2.456	0.731	2.089	1.959	0.130	
		2.923	2.598	0.325	2.044	1.981	0.063	
		av. = 3.029	av. = 2.548	av. = 0.481	av. = 2.060	av. = 1.970	av. = 0.090	
5.	$Sb[S_2PEt_2)_3$	3.137	2.503	0.634	2.056	1.965	0.091	[82]
		3.122	2.583	0.539	2.054	1.960	0.094	
		2.907	2.521	0.386	2.057	1.968	0.089	
		av. = 3.055	av. = 2.535	av. = 0.520	av. = 2.056	av. = 1.964	av. = 0.092	
(B) Bismuth(III) (diorganodithiophosphates) and phosphinates								
6.	$Bi[S_2P(O\text{-}i\text{-}Pr)_2]_3$	2.886	2.714	0.172	1.997	1.959	0.038	[83,84]
		2.876	2.702	0.174	1.991	1.948	0.043	
		2.858	2.690	0.165	2.011	1.955	0.056	
		av. = 2.874	av. = 2.702	av. = 0.171	av. = 2.000	av. = 1.954	av. = 0.046	

Table 3

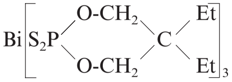
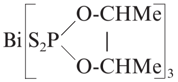
7.		2.837	2.758	0.079	1.980	1.932	0.048	[85]
		2.856	2.712	0.144	2.020	1.969	0.051	
		2.870	2.747	0.123	2.000	1.930	0.070	
		av. = 2.854	av. = 2.739	av. = 0.115	av. = 2.000	av. = 1.944	av. = 0.056	
8.		2.791	2.764	0.027	1.980	1.968	0.012	[85]
9.	$Bi[S_2PEt_2]_3$	2.794	2.782	0.012	2.036	1.999	0.037	[88,89]
10.	$Bi[S_2PPh_2]_3$	2.913	2.754	0.159	2.017	1.987	0.030	[81]
		3.027	2.629	0.398	2.061	1.969	0.092	
		3.020	2.767	0.253	2.007	2.004	0.003	
		av. = 2.987	av. = 2.717	av. = 0.270	av. = 2.028	av. = 1.987	av. = 0.041	
11.	$Bi[S_2PMe_2]_3$	2.891	2.714	0.177	2.031	1.987	0.044	[90]
		3.025	2.641	0.384	2.035	1.969	0.066	
		3.165	2.782	0.383	2.013	2.001	0.012	
		av. = 3.027	av. = 2.712	av. = 0.314	av. = 2.026	av. = 1.985	av. = 0.040	
12.	$MeSBi[S_2PPh_2]_2$	3.112	2.662	0.450	2.051	1.981	0.070	[91]
(C) Phenylarsenic and phenylantimony bis(diisopropyldithiophosphates)								
13.	$PhAs[S_2P(O\text{-}i\text{-}Pr)_2]_2$	3.135	2.310	0.825	2.100	1.900	0.200	[56]
14.	$PhSb[S_2P(O\text{-}i\text{-}Pr)_2]_2$	3.056	2.516	0.540	2.039	1.947	0.092	[56]
(D) Diorganometallic arsenic and antimony dialkyldithiophosphates and phosphinates								
15.	$O(C_6H_4)_2AsS_2PPh_2$	3.402	2.315	1.087	2.091	1.955	0.136	[64,92]

Table 3 (*continued*)

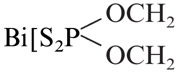
Series no.	Compound	M–S bond lengths (Å)		Δ (M–S)	P–S bond lengths (Å)		Δ (P–S)	Reference
16.	$Ph_2SbS_2PPh_2$	3.441	2.491	0.950	2.081	1.958	0.123	[62]
		3.474						
17.	$(p\text{-}MeC_6H_4)_2SbS_2PEt_2$	3.318	2.485	0.833	2.081	1.965	0.116	[94]
		3.556	2.509	1.047	2.072	1.965	0.107	
		av. = 3.437	av. = 2.497	av. = 0.940	av. = 2.076	av. = 1.965	av. = 0.111	
18.	$[Me_2SbS_2PMe_2]_n$	3.822	2.555	1.267	2.045	1.974	0.071	[95]
		3.158						
19.	$Ph_2SbS_2P(O\text{-}i\text{-}Pr)_2$	3.810	2.540	1.270	2.040	1.943	0.097	[58, 59]
(E) Trimethylantimony(V) bis(diphenyldithiophosphinate)								
20.	$Me_3Sb(S_2PPh_2)_2$	3.744	2.611	1.133	2.051	1.957	0.094	[65]
		3.842	2.611	1.231	2.048	1.965	0.083	
		av. = 3.793	av. = 2.611	av. = 1.182	av. = 2.049	av. = 1.961	av. = 0.088	

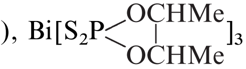
have been produced which are dealt with in the following separate headings (Tables 2 and 3).

5.4.1. Antimony(III) tris(dialkyldithiophosphates) and phosphinates

The structures of $Sb[S_2P(OR)_2]_3$ (R = Me, Et and *i*-Pr) are described as distorted capped octahedral [48,49]. The lone pair occupies a capping position above a triangular face of the octahedron. The longer Sb–S bonds are then rationalized by the interaction of the lone pair with a group of three face sulphur atoms and the other three are the short Sb–S bonds. The geometry about antimony in tris(diphenylphosphino-dithiolato)antimony(III) $Sb(S_2PPh_2)_3$ [80,81] is pentagonal pyramidal that includes two chelating ligands in the basal plane and a third ligand spanning the apical and basal position and the lone pair in the vacant position *trans* to the apical atom. The molecule tris(diethylphosphino-dithiolato)antimony(III) $Sb(S_2PEt_2)_3$ is distorted octahedral with anisobidentate nature of the ligand [82]. The structural distortion has been argued to be caused by a small ligand bite without invoking the lone pair stereochemical activity.

5.4.2. Bismuth (111) tris(diorganodithiophosphates) (and phosphinates)

The crystal structures of $Bi[S_2P(OMe)_2]_3$ and $Bi[S_2P(O\text{-}i\text{-}Pr)]_3]$ are reported [83,84]. The structure of $Bi[S_2P(O\text{-}i\text{-}Pr)_2]_3$ is distorted capped octahedral with three large Bi–S and three small Bi–S bond lengths. The crystal and molecular structure [85] of bismuth tris(2,2-diethyltrimethylenedithio-phosphate),  $\mathrm{Bi[S_2P}\left<\begin{array}{l}\mathrm{OCH_2}\\ \mathrm{OCH_2}\end{array}\right.\mathrm{CEt_2]_3}$, is shown in Fig. 2(a) (ORTEP). The bidentate attachment of the dithiophosphate ligands to bismuth are slightly asymmetrical with three short and three long Bi–S bonds, the configuration of the BiS_6 core is approximately C_{3v}. However, the distortion from a regular octahedron appears to be less pronounced in comparison to $Bi[S_2P(O\text{-}i\text{-}Pr)_2]_3$ (Table 3) and other bismuth complexes with dithio ligands, e.g. $Bi(S_2CNEt_2)_3$ [86] and $Bi(S_2CO\text{-}i\text{-}Pr)_3$ [87].

Preliminary structural data have also been reported for the bismuth tris(butylenedithiophosphate),  $\mathrm{Bi[S_2P}\left<\begin{array}{l}\mathrm{OCHMe}\\ \quad| \\ \mathrm{OCHMe}\end{array}\right.\mathrm{]_3}$ [85]. The ORTEP plot is shown in Fig. 2(b) along with the relevant bond angles and bond lengths. It is interesting that in this case the chelation of the dithiophosphate ligand is almost symmetrical (isobidentate) (Bi–S bond distances are 2.76 and 2.79 Å) and consequently the two P–S bond lengths are also the same (1.98 and 1.97 Å).

Another surprising feature in the structure of $Bi(S_2PEt_2)_3$ [88,89] (shown in Fig. 3) is the almost symmetrical (isobidentate) chelating behaviour of the diethyldithiophosphinate group giving near equality to the two independent Bi–S bonds (2.794 and 2.782 Å). The BiS_2P ring is planar with angles at Bi and P of 73.7 and 120°, respectively. The twist angle between the two planes of the sulphur atom is 34.70°, a value which is almost midway between that of regular octahedral and trigonal-prismatic geometry.

The structures of tris(dimethylphosphinodithiolato) bismuth(III) $Bi[S_2PMe_2]_3$

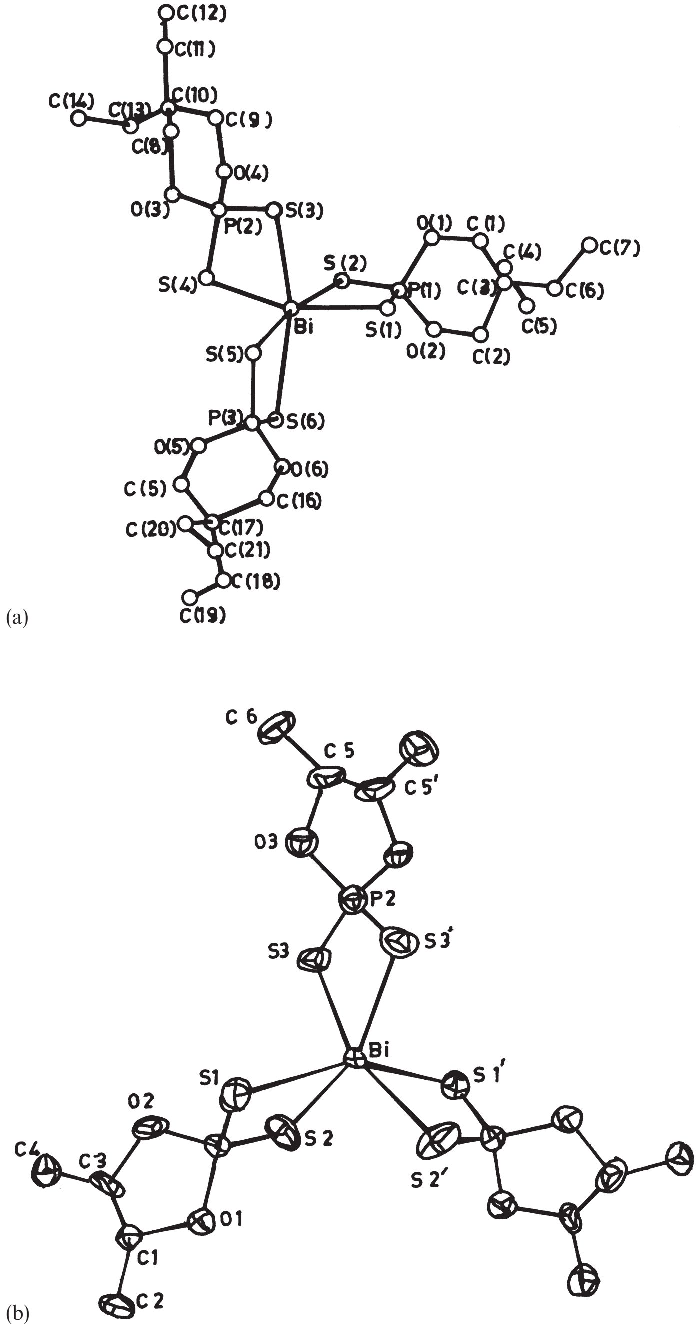


Fig. 2. Ortep plot of (a) Bi$\left[S_2P{<}\begin{matrix}O{-}CH_2\\O{-}CH_2\end{matrix}{>}CEt_2\right]_3$ and (b) Bi$\left[S_2P{<}\begin{matrix}OCHCH_3\\|\\OCHCH_3\end{matrix}\right]_3$. [R. Bohra, H.P.S. Chauhan, G. Srivastava and R.C. Mehrotra, Phosphorus, Sulfur and Silicon, 60 (1991) 167. Reproduced with permission].

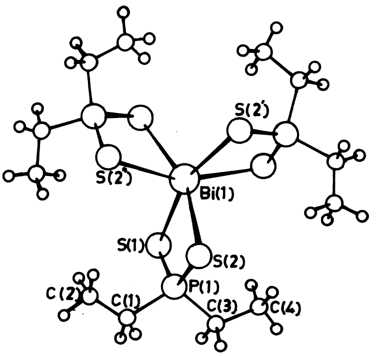


Fig. 3. Molecular structure of $Bi(S_2PEt_2)_3$ showing the atom numbering scheme. [D.B. Sowerby and I. Haiduc, J. Chem. Soc. Dalton Trans., (1987) 1257. Reproduced with permission].

[90] and tris(diphenylphosphino-dithiolato) bismuth(III) $Bi[S_2PPh_2]_3$ [81] are dimeric in the solid. Four of the ligands are bimetallic biconnective (chelating) and two are bimetallic triconnective and bridge between two bismuth atoms via secondary Bi–S bonds (Fig. 4). The mesityl derivative $MeSBi[S_2PPh_2]_2$ is a five-coordinate monomeric species [91] and the steric demands of the mesityl group possibly prevents intermolecular association.

The correlation of stereochemical activity of the lone pair of bismuth in the corresponding diorganodithiophosphate and phosphinate complexes with distortion from regular octahedral structure needs a rather closer look. The view [83,84] that the lone pair is present about the triangular face of the less strongly bonded sulphur atoms should be revised in view of the following.

(i) The dimerization of $Bi(S_2PPh_2)_3$ [81], $Bi(S_2PMe_2)_3$ [90] and also

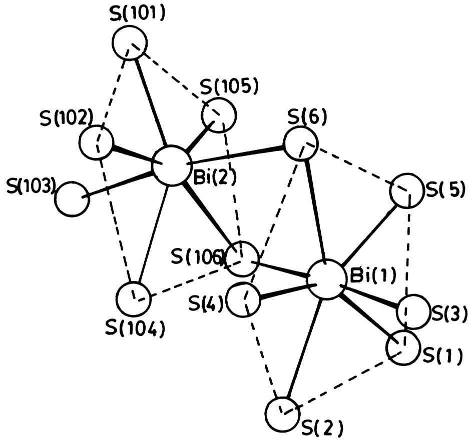
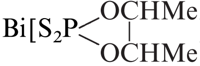
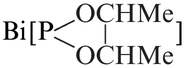


Fig. 4. Schematic representation of the $(BiS_6)_2$ skeleton of $Bi(S_2PPh_2)_3$ (dimer) showing pentagonal bipyramidal coordination. [M.J. Beglay, D.B. Sowerby and I. Haiduc, J. Chem. Soc. Dalton Trans., (1987) 145. Reproduced with permission].

$\mathrm{Bi(S_2CNEt_2)_3}$ [86] with intermolecular Bi–S bonds present at the same position where the lone pair is expected.

(ii) The symmetrical chelation of butylenedithiophosphate [85] and diethyldithiophosphate [88,89] groups in  $\mathrm{Bi[S_2P}{<}\begin{matrix}\mathrm{OCHMe}\\|\\\mathrm{OCHMe}\end{matrix}]_3$ and $\mathrm{Bi(S_2PEt_2)_3}$, respectively, which would indicate stereochemical inactivity of the lone pair.

(iii) In view of the above it is clear that in bismuth(III) tris(diorganodithiophosphate) and phosphinate derivatives three types of geometries occur which cannot be explained with any single argument. (1) Distorted capped octahedral geometries in $\mathrm{Bi[S_2P(OMe)_2]}$ and $\mathrm{Bi[S_2P(O\text{-}\mathit{i}Pr)_2]_3}$ which are well explained by the stereochemical activity of the lone pair. (2) Dimeric structures as in $\mathrm{Bi(S_2PPh_2)_3}$ and $\mathrm{Bi(S_2PMe_2)_3}$ may be explained as the consequences of intermolecular associations. (3) Symmetrical chelation as in $\mathrm{Bi(S_2PEt_2)_3}$ and  $\mathrm{Bi[P}{<}\begin{matrix}\mathrm{OCHMe}\\|\\\mathrm{OCHMe}\end{matrix}]_3$ is difficult to explain. However, this, to some extent, may be explained as a consequence of the ligand properties and less pronounced activity of the lone pair.

5.4.3. Phenylarsenic(III) and phenylantimony(III) bis(diisopropyldithiophosphates)

In the crystal structure of $\mathrm{PhM[S_2P(O\text{-}\mathit{i}\text{-}Pr)_2]_2}$ [56] (where M = As, Sb) (Fig. 5), the two diisopropyldithiophosphate ligands form an approximate basal plane and the phenyl group occupies an axial position in the central atoms square pyramidal geometry. The lone pair of electrons is occupying an axial position *trans* to the phenyl group. The ligands chelate to the central metal atom with unequal M–S bonds. For antimony the difference between two long and two short Sb–S bonds is 0.54 Å, significantly less than the difference in the As–S bonds which is 0.825 Å. The results also confirm the IR observations that the shifting in ν(P=S) is greater in the antimony derivatives than arsenic indicating the tendency of arsenic towards monodentate coordination.

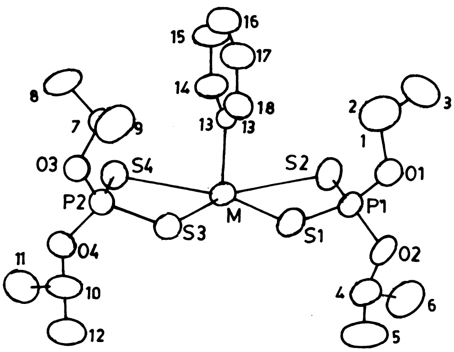


Fig. 5. Structure of $\mathrm{PhM[S_2P(O\text{-}\mathit{i}\text{-}Pr)_2]_2}$ (M = As, Sb). [R.K. Gupta, A.K. Rai, R.C. Mehrotra, V.K. Jain, B.F. Hoskins and E.R.T. Tiekink, Inorg. Chem., 24 (1985) 3280. Reproduced with permission].

5.4.4. Diorganometallic (arsenic and antimony) dialkyldithiophosphates and phosphinates

In the structure [92] of monomeric $O(C_6H_4)_2AsS_2PPh_2$ the coordination of the diphenyldithiophosphinate ligand may be regarded as monodentate leading to a pyramidal geometry with arsenic in the apical position and the s(1) and two carbons in the corner of the basal plane. The phenoxy arsene system is folded over the As–O axis, with a dihedral angle of 154.4°. However, the dimeric association has been recently reported [64] in the same $O(C_6H_4)_2AsS_2PPh_2$ molecule exhibiting a quasitridenic structure based upon intra and intermolecular As–S secondary bonds (3.402 and 3.381 Å, respectively) (Fig. 6(a)). The diphenyl dithiophosphinate group is acting as a bimetallic triconnective bridge.

Similarly, a few other supermolecular dimeric structures such as $[Ph_2SbS_2PPh_2]_2$ [62], $[Ph_2SbAsPh_2]_2$ [93] and $[(P\text{–}MeC_6H_4)_2SbS_2PEt_2]_2$ [94] and polymeric structures such as $[Ph_2SbS_2P(O\text{-}i\text{Pr})_2]_n$ [58,59] and $[Me_2SbS_2PMe_2]_3$ [95] have been determined [4]. In these cases the ligands also exhibit tridentate, mixed chelating and bridging nature. The representation of the skeleton of the dimeric $[Ph_2SbS_2PPh_2]_2$ and polymeric structure of $[Ph_2SbS_2P(O\text{-}i\text{-Pr})_2]_n$ along with some bond distances are shown in Fig. 6(b) and (c), respectively.

In the structure (Fig. 7) of the organoantimony(V) derivative $Me_3Sb(S_2PPh_2)_2$, the central atom is in a trigonal bipyramidal coordination with two sulphur atoms in the axial positions. In addition to the primary Sb–S bonds (2.611 Å) antimony forms two weaker secondary Sb–S interactions (3.744 and 3.842 Å) and the SbS_4 system is almost planar with a *cis* arrangement of the sulphur atoms doubly bonded to phosphorus [65].

6. Concluding remarks

Arsenic, antimony and bismuth derivatives with diorganodithiophosphate (and phosphinate) ligands exhibit broad diversities in their solid state structural chemistry. The geometries are very often unpredictable (Table 2). From the available structural data the following conclusions may be drawn.

(1) Antimony(III) and bismuth(III) tris(diorganodithio-phosphate (and phosphinate) derivatives exhibit monometallic bidentate chelating behaviour. In most cases, the ligand coordination is anisobidentate except in $Bi(S_2PEt_2)_3$ and  $Bi[S_2P{<}\begin{smallmatrix}OCHMe\\ |\\ OCHMe\end{smallmatrix}]_3$ where the ligands are isobidentate in nature. Distortion in the coordination polyhedron (an octahedron in most cases except for $Sb(S_2PPh_2)_3$ which is a pentagonal pyramid) may occur due to the stereochemically active lone pair of electrons or small ligand bite. Dimeric structures in $Bi(S_2PR_2)_3$ (R = Me, Ph) with one of the ligands behaving as a tricoordinate moiety have also been observed.

(2) In mono-organo metal bis(diorganodithiophosphates) (or phosphinates), the ligands behave as anisobidentate chelating moieties. The four sulphur atoms of the

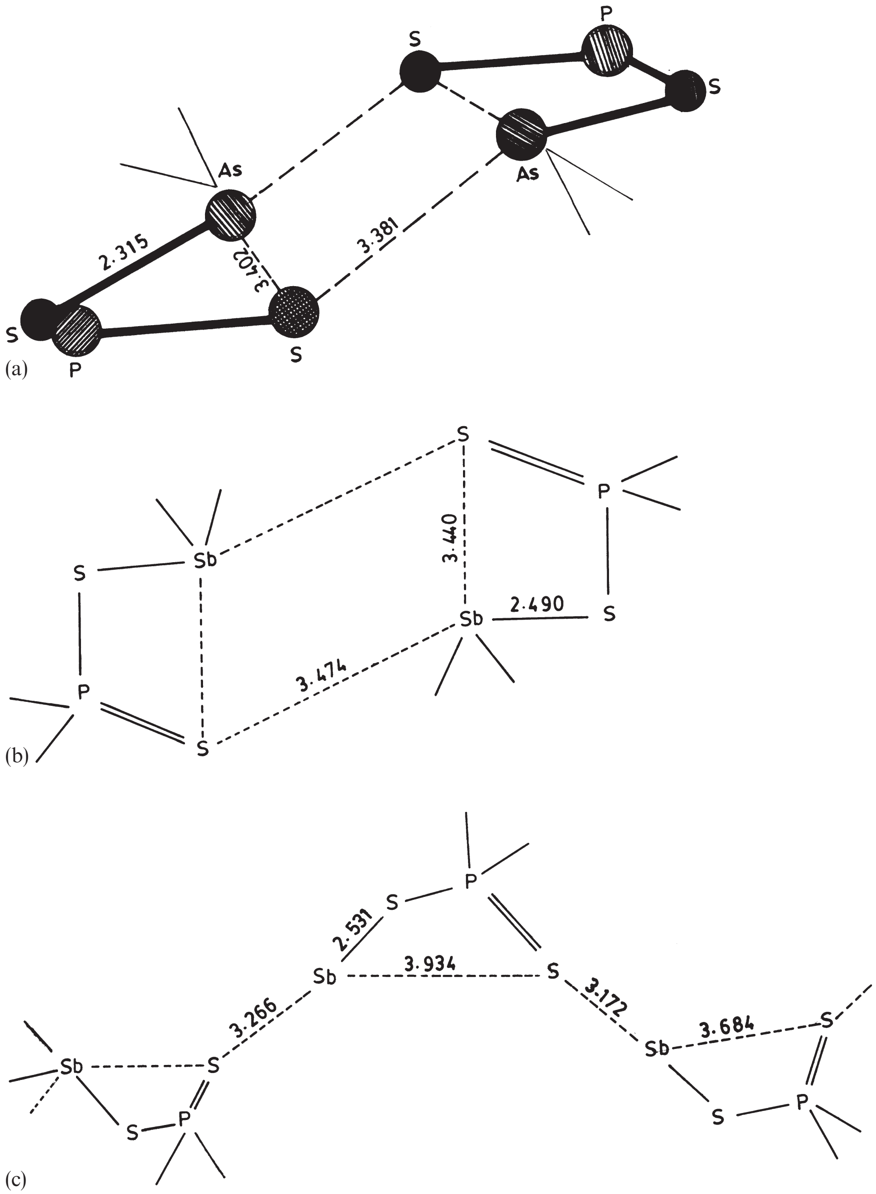


Fig. 6. Schematic representation along with some bond distances (Å) of (a) dimeric $[O(C_6H_4)_2AsS_2PPh_2]_2$, (b) dimeric $[Ph_2SbS_2PPh_2]_2$ and (c) polymeric $[Ph_2SbS_2P(O\text{-}i\text{-}Pr)_2]_n$.

ligands form a square basal plane and the lone pair occupies the position *trans* to the M–C bond.

(3) (a) Diorganoarsenic and antimony derivatives are mostly dimeric or polymeric in nature. These intermolecular associations are due to the mixed chelating and

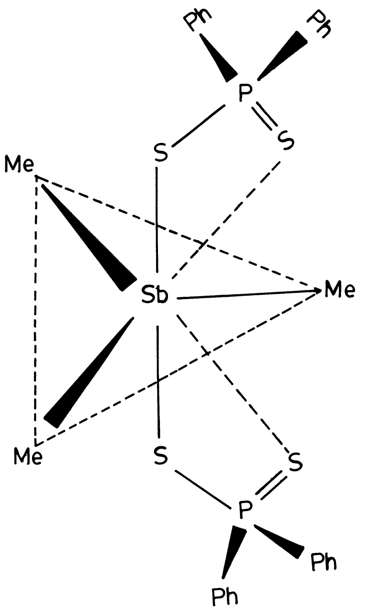


Fig. 7. Structure of $Me_3Sb(S_2PPh_2)_2$.

bridging tricoordinate nature of the ligands. (b) The diphenyldithiophosphinate ligand in $O(C_6H_4)_2AsS_2PPh_2$ is monodentate. Also, proceeding from arsenic to antimony to bismuth, the tendency for strong chelation (monodentate to anisobidentate to isobidentate) increases.

(4) The organoantimony(V) derivative $Me_3Sb(S_2PPh_2)_2$, due to the absence of a lone pair of electrons, exhibits the predicted distorted trigonal bipyramidal structure, with the bidentate chelating ligands.

Thus, the variation in stereochemistry of these metal derivatives depends on various factors, including: (1) the nature of the metal ion — arsenic, antimony and bismuth; (2) the nature of the ligand and nature of the organic group of the ligands; (3) the nature of the organic group and other substituents on the corresponding metal. Future investigation on synthetic and structural aspects, particularly by X-ray diffractometry, of new derivatives with different organic groups on the metals and varying organic groups on the ligands should lead to greater insight into the unusual stereochemical behaviour of these species.

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