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Structural patterns in inorganic and organoantimony derivatives of oxo- and thiodiorganophosphorus ligands

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Contents

Abstract

The structures of inorganic and organoantimony complexes of diorganophosphorus ligands and their thio analogues, determined by X-ray diffraction, are reviewed with particular atten-

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tion given to the coordination geometry around the metal atom and the coordination pattern of the phosphorus ligands.

Keywords: Organoantimony complexes; Diorganophosphorus ligands; Inorganic antimony complexes; Sulphur analogues

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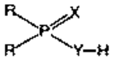
List of abbreviations used

Me	methyl
Et	ethyl
Pr^i	isopropyl
Cy	cyclohexyl
Ph	phenyl

1. Introduction

The metal complexes of oxo- and thiodiorganophosphorus acids, i.e. phosphinates (**1**), phosphates (**2**), and their mono and dithio analogues, represent a research field of continuous interest as a potential source of unexpected structures. This can be the result of both the ability of the organophosphorus ligand to exhibit a large spectrum of coordination patterns, involving one or both chalcogen atoms in multiple interactions with the metal (or organometallic) centre, and of the tendency of the metal to increase its coordination number [1]. As a consequence, several structural types have been established in the solid state, by means of the X-ray diffraction method, ranging from monomeric structures to dimeric and polymeric supramolecular associations. Moreover, the potential ability of the monothio ligands to bind primarily through oxygen or, alternatively, through sulphur to the metal centre (**3** and **4**) broadens even more the structural diversity of this class of compounds.



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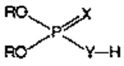

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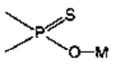
(X, Y = O, S)



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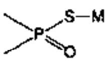

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Related to these aspects, antimony occupies a primary position owing to the variety of structures established for its inorganic and organometallic derivatives. Even for similar types of ligand dramatic changes in the structure were observed, depending on the nature of the organic groups bound to phosphorus, which are quite far from the coordination centre.

The importance of antimony derivatives of phosphorus ligands is related not only to their structural diversity but also to their practical uses. Thus, some inorganic antimony(III) dithiophosphates were reported as passivation agents in the catalytic cracking process of petroleum or as lubricant oil additives [2]. On the contrary, organometallic compounds are currently being investigated as potential antitumour agents [3], and recently two organoantimony derivatives of dithiophosphorus ligands, i.e. $Ph_2SbS_2PPh_2$ and $Ph_2SbS_2P(OPr^i)_2$, were described as the first representatives of a new class of metal compounds exhibiting antitumour properties [4–8].

In this review we summarize the structural peculiarities of antimony derivatives of diorganophosphorus ligands. The classification criteria are (a) the oxidation state of the metal and (b) the inorganic or organometallic nature of the coordination centre. Special attention is paid to the coordination geometry around the metal atom and to the coordination pattern of the phosphorus ligand. For the discussion of the coordination polyhedra around the antimony atom, the covalent and the van der Waals radii of the metal and chalcogen atoms, presented in Table 1, should be taken into account. Thus, secondary (or "semibonding") interactions [12], between antimony and the chalcogen atom doubly bonded to phosphorus in a ligand unit, are considered when $Sb \cdots X$ distances are longer than the sum of covalent radii but significantly shorter than the sum of van der Waals radii. Some relevant phosphorus-sulphur and phosphorus-oxygen bond distances in various organophosphorus acids and related compounds are also given for comparison in Table 2.

All the structural diagrams were redrawn [25] using published atomic coordinates. In some cases, for clarity and better comparison of the structures, only the first carbon atom bonded to the metal or phosphorus (*ipso*-carbon) was presented and, when necessary, the originally published atom numbering scheme was modified in this review to permit direct comparison. The estimated standard deviations (ESDs) for average bond lengths were calculated from the equation

$$\sigma = \left[\sum_{i=1}^{i=N} (x_i - x)^2/(N-1) \right]^{1/2}$$

where x_i is the ith bond length and x is the mean of the N equivalent bond lengths. An analogous formula was used for the calculation of ESDs for average bond angles [26]. In some cases the magnitudes of the ESDs are quite large, thus reflecting the range for the averaged individual values.

Table 1
Covalent and van der Waals radii (ångströms) for antimony and chalcogen atoms

	O		S	
	Covalent radii [9]	van der Waals radii [10]	Covalent radii [9]	van der Waals radii [10]
	0.73	1.50	1.02	1.80
Sb	1.43	2.20 [11]	1.43	2.20 [11]
Sum	2.16	3.70	2.45	4.00

Table 2
Phosphorus–sulphur and phosphorus–oxygen bond distances (ångströms) in some diorganophosphorus acids, their ionic salts, and related compounds

Compound	P−S	P=S	P−O	P=O	Ref.
$Me_2P(O)OH$ ^{a}			1.559(4)	1.495(4)	[13]
$Ph_2P(O)OH$ ^{a}			1.526(6)	1.486(6)	[14]
$Me_2P(S)OH$ ^{b}		1.966(1)	1.580(1)		[15]
$Cy_2P(S)OH$ ^{b}		1.973(1)	1.591(5)		[15]
$Ph_2P(S)OH$ ^{c}		1.956(1)	1.582(2)		[16]
$Et_2PS_2Na \cdot 2H_2O$ ^{d}	2.034(2) 1.993(2)				[17]
$Ph_2P(S)SH$ ^{e}	2.077(1)	1.954(1)			[18]
$(MeO)_2PO_2NH_4$ ^{f}			1.490(5) 1.498(7)		[19]
$(MeO)_2PS_2K$ ^{g}	1.96(1) 1.96(1)				[20]
$[(Pr^{i}O)_2PS_2][Me_2NH_2]$ ^{h}	1.965(6) 1.974(6)				[21]
$(C_6H_5CH_2O)_2PS_2K$ ^{i}	1.969(2) 1.945(2)				[22]
$Ph_2P(S)-S-S-P(S)Ph_2$	2.139(1)	1.930(1)			[23]
$(Pr^{i}O)_2P(S)-S-S-P(S)(OPr^{i})_2$	2.072(2)	1.908(3)			[24]

[a] Polymer chain through O−H · · · O(=P) hydrogen bonds. [b] Dimer through O−H · · · S(=P) hydrogen bonds. [c] Polymer chain through O−H · · · S(=P) hydrogen bonds. [d] Three-dimensional structure through Na · · · S and Na · · · O interactions. [e] Polymer chain through S−H · · · S(=P) hydrogen bonds. [f] Ionic; average P−O(C) length, 1.559(33) Å. [g] Ionic; P−O(C), 1.64(5) Å. [h] Ionic; average P−O(C) length, 1.59 Å. [i] Ionic; average P−O(C) length, 1.619(3) Å.

2. Antimony(III)

So far, as shown in Table 3, molecular structures, determined by X-ray diffractometry, have been reported for both inorganic and organoantimony(III) derivatives of diorganophosphorus ligands. As will be shown, even for the same ligand type, changes in the nature of the organic group bound to phosphorus result in severe modification of the structures. In almost all antimony(III) derivatives the coordination geometry around the central metal atom can be described as pyramidal trigonal with respect to the three covalent bonds (established through pure or almost pure p orbitals of antimony). However, if the secondary Sb · · · S interactions and the possible stereochemical activity of the antimony lone pair of electrons are taken into account, the coordination polyhedron generally becomes a ψ trigonal bipyramid or a ψ octahedron. This alternative will be also discussed.

2.1. *Inorganic compounds*

2.1.1. *Monomeric derivatives*

The expected monomeric structure with 6-coordinated central metal atom is the most common for inorganic antimony(III) derivatives and, with one exception, i.e.

Table 3
Antimony(III) derivatives of diorganophosphorus ligands

Compounds	Coordination pattern of the ligand	Coordination polyhedron
Inorganic derivatives		
Monothiophosphinates		
$Sb(OSPCy_2)_3$	Monometallic biconnective	Distorted octahedron (ψ-capped octahedron)
$Sb(OSPPh_2)_3$	Monometallic biconnective + bimetallic triconnective	Irregular 7-vertex polyhedron (ψ irregular 8-vertex polyhedron)
Dithiophosphinates		
$Sb(S_2PPh_2)_3$	Monometallic biconnective	Distorted pentagonal pyramid (ψ pentagonal bipyramid)
Dithiophosphates		
$Sb[S_2P(OMe)_2]_3$	Monometallic biconnective	Distorted octahedron (ψ-capped octahedron)
$Sb[S_2P(OEt)_2]_3$	Monometallic biconnective	Distorted octahedron (ψ-capped octahedron)
$Sb[S_2P(OPr^i)_2]_3$	Monometallic biconnective	Distorted octahedron (ψ-capped octahedron)
Organometallic derivatives		
Phosphinates		
$Ph_2SbO_2PPh_2$	Bimetallic biconnective	Distorted ψ trigonal bipyramid
Monothiophosphinates		
$Ph_2SbOSPPh_2$	Bimetallic biconnective	Distorted ψ trigonal bipyramid
Dithiophosphinates		
$Me_2SbS_2PMe_2$	Bimetallic triconnective	Distorted ψ octahedron (distorted square pyramid)
p-tolyl$_2SbS_2PEt_2$	Bimetallic biconnective	Distorted ψ trigonal bipyramid
$Ph_2SbS_2PPh_2$	Bimetallic triconnective	Distorted ψ octahedron (distorted square pyramid)
Dithiophosphates		
$PhSb[S_2P(OPr^i)_2]_2$	Monometallic biconnective	Distorted square pyramid (distorted ψ octahedron)
$Ph_2SbS_2P(OPr^i)_2$	Bimetallic triconnective	Distorted ψ octahedron (distorted square pyramid)

$Sb(OSPPh_2)_3$ [27], is achieved in fact for all the compounds investigated by X-ray diffraction, regardless of the nature of the organophosphorus ligand. However, several peculiarities of the reported structures should be noted.

For $Sb(OSPCy_2)_3$ [27] and $Sb[S_2P(OR)_2]_3$ ($R = Me$ [28], Et [29], Pr^i [28]) and for $Sb(S_2PPh_2)_3$ [30], selected interatomic parameters are listed in Tables 4 and 5. In all these compounds the ligands act as monometallic biconnective (bidentate) units, being coordinated to the metal through both chalcogen atoms.

In the monothiophosphinate, $Sb(OSPCy_2)_3$, (Fig. 1(a)) the primary bonds are achieved through oxygen (average Sb—O lengths 2.028(3) Å), while the sulphur atoms doubly bonded to phosphorus are involved in secondary interactions with the metal (average Sb···S lengths 3.23(5) Å) [27]. Similar coordination through

Table 4
Relevant bond lengths (ångströms) and angles (degrees) in monomeric, octahedral, inorganic antimony(III) derivates

Sb(OSPCy$_2$)$_3$ [27]		Sb[S$_2$P(OR)$_2$]$_3$			
			R = Me [28]	R = Et [29]	R = Pr^i [28]
Sb—O (average)	2.028(3)	Sb—S (average)	2.53(1)	2.60(2)	2.52(1)
Sb ··· S (average)	3.23(5)	Sb ··· S (average)	3.005(3)	2.83(4)	3.02(2)
P—O (average)	1.58(1)	P—S (long, average)	2.033(4)	1.98(1)	2.04(1)
P—S (average)	1.96(1)	P—S (short, average)	1.94(1)	1.96(3)	1.94(1)
O—Sb—O (average)	86.5(2.5)	S—Sb—S (average)	88.4(2)	94.1(1.9)	87.5(6)
S ··· Sb ··· S (average)	113.9(10.2)	S ··· Sb ··· S (average)	106.2(2.4)	100.9(4.6)	106.6(4.2)

Table 5
Relevant bond distances (ångströms) and angles (degrees) for the pentagonal pyramidal Sb(S$_2$PPh$_2$)$_3$ [30]

Sb—S(1)$_{ap}$	2.456(1)	P(1)—S(1)	2.089(1)
Sb ··· S(2)$_{eq}$	3.187(1)	P(1)—S(2)	1.959(1)
Sb—S$_{eq}$ (average)	2.595(5)	P—S (long, average)	2.046(3)
Sb ··· S$_{eq}$ (average)	2.95(4)	P—S (short, average)	1.98(1)
S(1)$_{ap}$—Sb—S$_{eq}$ (average)	88.5(9.8)	S$_{eq}$—Sb—S$_{eq}$ (*cis*, average)	72.7(1.5)

oxygen of the monothiophosphinato ligands was observed in all the antimony derivatives investigated by X-ray diffraction, regardless of the oxidation state of the metal, their inorganic or organometallic nature, and the organic groups on phosphorus (see below). This contrasts with the thiocarboxylato analogue, Sb(SOCR)$_3$ (R = Me [31], Ph [32]) and PhSb(SOCMe)$_2$ [33], in which the primary interaction of the monothio ligands is made through the sulphur atom. The borderline hard-soft acid character of Sb(III) and the changes in the electronegativity of the ligands were suggested as responsible for this different behaviour [27].

Although in both Sb(S$_2$PPh$_2$)$_3$ and Sb[S$_2$P(OR)$_2$]$_3$ the dithioligand moieties are monometallic biconnective, some differences should be noted. For the dimethyl- and diisopropyldithiophosphates (Figs. 1(b) and 1(d) respectively), the two groups of short (average Sb—S lengths, 2.53(1) Å (R = Me) and 2.52(1) Å (R = Pr^i)) and long (average Sb ··· S lengths 3.005(3) Å (R = Me) and 3.02(2) Å (R = Pr^i)) metal–sulphur distances are associated with long (single bond; average P—S lengths, 2.033(4) Å (R = Me) and 2.04(1) Å (R = Pr^i)) and short (double bond; average P—S lengths, 1.94(1) Å (R = Me) and 1.94(1) Å (R = Pr^i)) phosphorus–sulphur bonds, the ligand behaving clearly as anisobidentate (Table 4) [28]. Similar considerations can be made for Sb(S$_2$PPh$_2$)$_3$ (Fig. 2), but in this case the anisobidentate character (i.e. the difference between the phosphorus–sulphur and metal–sulphur distances in the same PS$_2$Sb ring) is more pronounced for the ligand moiety containing the sulphur atoms in the apical and equatorial positions of the distorted pentagonal pyramid (Sb—S(1)$_{ap}$, 2.456(1) Å; Sb ··· S(2)$_{eq}$, 3.187(1) Å) than for the other two ligand groups (average Sb—S$_{eq}$ length, 2.595(5) Å; Sb ··· S$_{eq}$, 2.95(4) Å) [30]. By contrast,

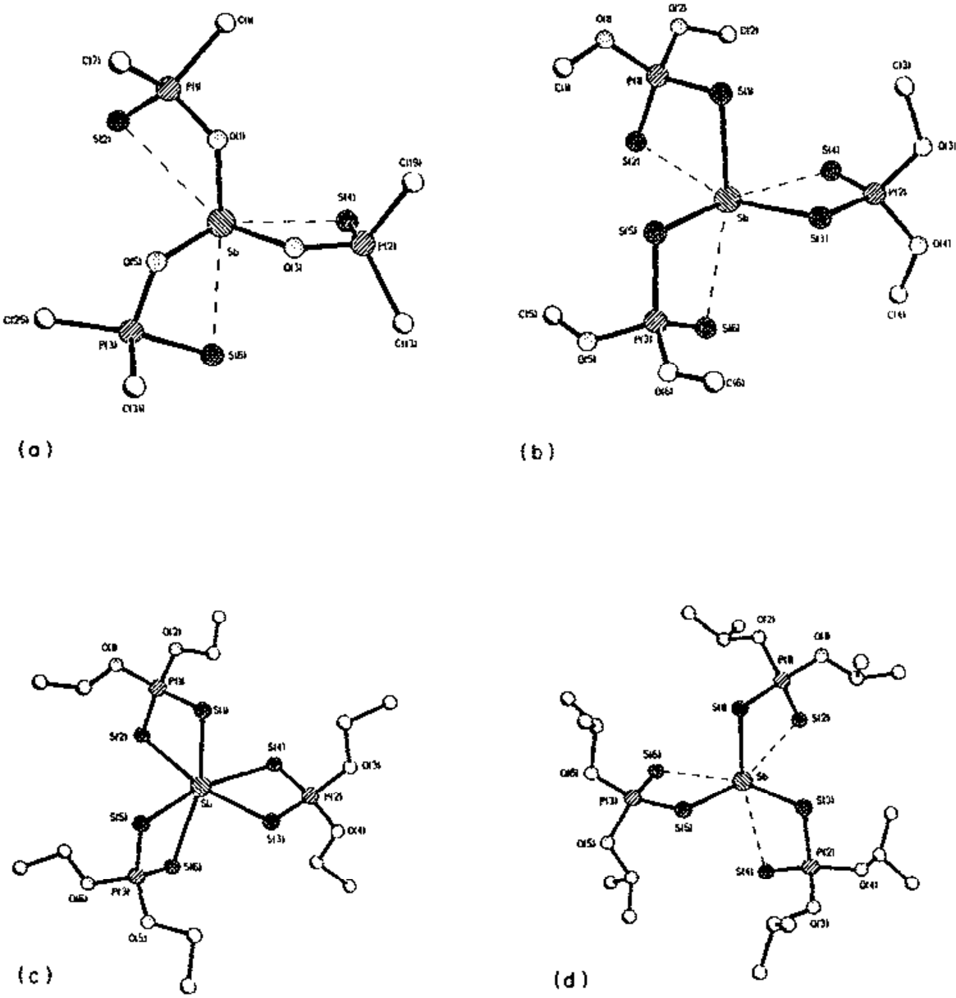

Fig. 1. The molecular structure of (a) $Sb(OSPCy_2)_3$, (b) $Sb[S_2P(OMe)_2]_3$, (c) $Sb[S_2P(OEt)_2]_3$, and (d) $Sb[S_2P(OPr^i)_2]_3$.

in the diethyldithiophosphate (Fig. 1(c)) the difference between antimony–sulphur distances is significantly smaller (short average Sb—S, 2.60(2) Å; long average Sb $\cdots$ S, 2.83(4) Å) and the corresponding phosphorus–sulphur distances in the same ligand unit are practically equal and intermediate (average 1.98(1) and 1.96(3) Å) between single and double phosphorus–sulphur bonds, thus suggesting a more pronounced isobidentate character (Table 4) [29].

Concerning the coordination geometry around antimony, with the exception of $Sb(S_2PPh_2)_3$, all the other derivatives exhibit distorted SbX_3S_3 (X = O or S) octahedra. The distortion is reflected not only by the difference in the antimony–chalcogen distances but also by the angles at antimony (Table 4).

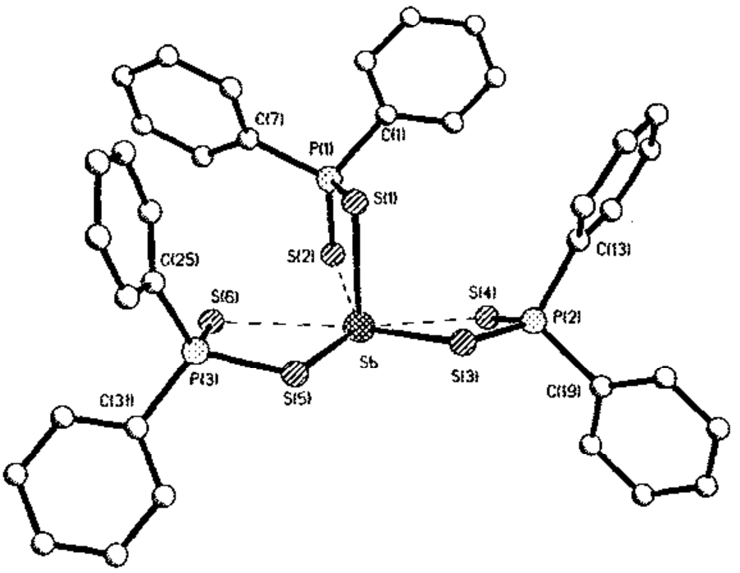

Fig. 2. The molecular structure of $Sb(S_2PPh_2)_3$.

By contrast to the related inorganic Sb(III) derivatives discussed above, the SbS_6 coordination polyhedron in $Sb(S_2PPh_2)_3$ is better described as pentagonal pyramidal (Fig. 2) [30]. This is supported by (i) the shorter apical Sb—S(1) bond distance compared with the other two equatorial primary Sb—S bonds, (ii) the S_{ap}—Sb—S_{eq} and S_{eq}—Sb—S_{eq} angles (Table 5), which fall in the ranges 72.3°–98.2° and 70.9°–74.9° respectively and (iii) the small deviations (ranging between −0.05 Å for Sb and 0.035 Å for S(4)) from the best basal SbS(2)S(3)S(4)S(5)S(6) plane. The smaller apical–equatorial $S(1)_{ap}$—Sb···$S(2)_{eq}$ angle of 72.32(2)° is not unusual since both of these sulphur atoms belong to the same ligand unit.

The coordination geometry around the central antimony atom in the above monomeric derivatives might be alternatively described as a distorted ψ-capped octahedron, with the antimony lone pair of electrons occupying the capping position above the opened S(2)S(4)S(6) triangular face of the octahedron, or as a ψ pentagonal bipyramid in $Sb(S_2PPh_2)_3$, with the lone pair in the axial position *trans* to the shortest Sb—S(1) primary bond. However, so far there is no direct proof concerning the stereochemical activity of the 5s electrons of antimony, and other factors, such as the small X···S bite of the anisobidentate ligand or steric requirements of the phosphorus substituents, might also be responsible for the distortion of the SbX_3S_3 polyhedron.

2.1.2. Dimeric derivatives

By contrast to the above monomeric, inorganic antimony(III) compounds, the related diphenylmonothiophosphinate, $Sb(OSPPh_2)_3$, exhibits a dimeric structure (Fig. 3), built through bridging ligand units [27]. In its monomeric unit all ligands

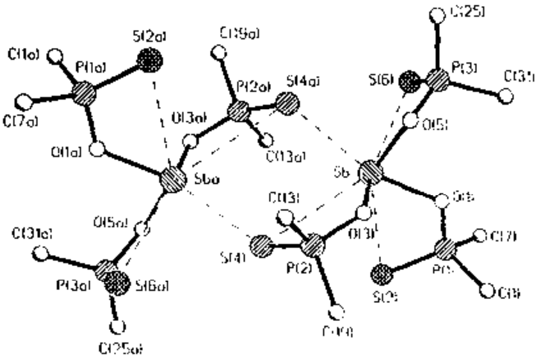

Fig. 3. View of the dimeric $[Sb(OSPPh_2)_3]_2$ association.

are again primarily bonded through oxygen (average Sb—O length, 2.05(1) Å; average P—O length, 1.566(3) Å; average P—S length, 1.96(1) Å). However, while two ligands act as monometallic biconnective moieties, establishing intramolecular secondary bonds through their sulphur atoms doubly bonded to phosphorus (Sb···S(2), 3.223(1) Å; Sb···S(6), 3.164(1) Å), the third monothiophosphinato group exhibits a bimetallic triconnective pattern, leading to dimer formation. Moreover, the intermolecular Sb(a)···S(4) secondary bonding distance is 3.001(1) Å, not only significantly stronger than the intramolecular Sb···S(4) (3.554(1) Å) but also stronger than the other two Sb···S intramolecular interactions (Table 6).

The coordination geometry around antimony is quite complex. The SbO_3 system is pyramidal, with O—Sb—O angles of 81°–88°, as observed for $Sb(OSPCy_2)_3$ [27]. Taking into account the secondary Sb···S interactions, the metal atom lies between two planes: (i) one formed by the three oxygen atoms of its own ligands in the monomeric unit and (ii) the other built by three sulphur atoms of the molecular unit and one sulphur atom of the other molecule in the dimer (Fig. 4). Three of the *cis*-S···Sb···S angles are smaller (70°–86°), while the fourth, i.e.

Table 6
Relevant bond distances (ångströms) and angles (degrees) for the dimeric $[Sb(OSPPh_2)_3]_2$ [27]

Sb—O (average)	2.05(1)	P—O (average)	1.566(3)
Sb···S (average)	3.19(4)	P—S (average)	1.96(1)
Sb···S(4) (intra)	3.554(1)		
Sb(a)···S(4) (inter)	3.001(1)		
O—Sb—O (average)	84.2(2.3)	S(2)···Sb···S(4) (*cis*)	70.5
O—Sb···S[a] (average)	61.2(3.5)	S(4)···Sb···S(4a) (*cis*)	71.5
		S(4a)···Sb···S(6) (*cis*)	86.1
		S(6)···Sb···S(2) (*cis*)	119.8
		S(4)···Sb···S(6)	146.7
		S(2)···Sb···S(4a)	139.3

[a] Within the four-membered SbOSP rings.

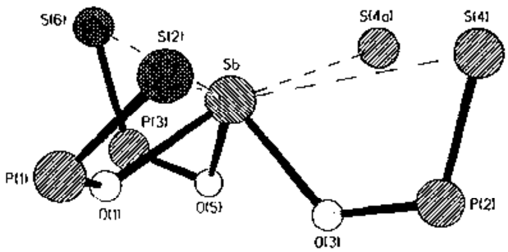

Fig. 4. View of the coordination polyhedron in $[Sb(OSPPh_2)_3]_2$.

S(2) ··· Sb ··· S(6), is larger (ca. 120°) (Table 6). This free space might be occupied by the lone electron pair of antimony, thus explaining the arrangement of the sulphur atoms. The resulting coordination polyhedron is an irregular 7-vertex (or ψ-8 vertex) polyhedron.

2.2. *Organometallic compounds*

Several organoantimony(III) derivatives of organophosphorus acids are described in the literature and some of them were investigated by X-ray diffractometry. A monomeric structure was established for a monoorganoantimony(III) derivative, while diorganoantimony(III) compounds were found to exhibit either dimeric or polymeric associations.

2.2.1. *Monomeric derivatives*

So far, only the molecular structure of a phenylantimony(III) derivative, i.e. $PhSb[S_2P(OPr^i)_2]_2$, has been reported [34]. The compound was described as monomeric (Fig. 5), with monometallic biconnective (anisobidentate) dithiophosphorus ligands (non-equivalent P—S and Sb—S distances) coordinated to the central metal atom (Table 7).

The coordination geometry around antimony is distorted square (trapezoidal) pyramidal, with the carbon atom of the phenyl group in the apical position and the four sulphur atoms forming the basal plane. The distortion is reflected by the open angle formed by the secondary bonded sulphur atoms (average Sb ··· S length, 3.06(1) Å; $S(2)_{eq} \cdots Sb \cdots S(4)_{eq}$, 137.4(1)°). This might be the result either of the small "bite" of the dithio ligand or of the steric effects, since the phenyl ring is bent towards this larger basal side (Fig. 6; Sb—C(13)—C(14), 115.7(6)°; Sb—C(13)—C(18), 122.6(6)°). A similar behaviour was also observed for the mesityl group in $MesBi(S_2PPh_2)_2$ [35].

The antimony lone pair of electrons was suggested to be stereochemically active, occupying the axial position *trans* to the phenyl group. The coordination geometry on the central metal atom would become in this case ψ octahedral, with a quasi-planar SbS_4P_2 system.

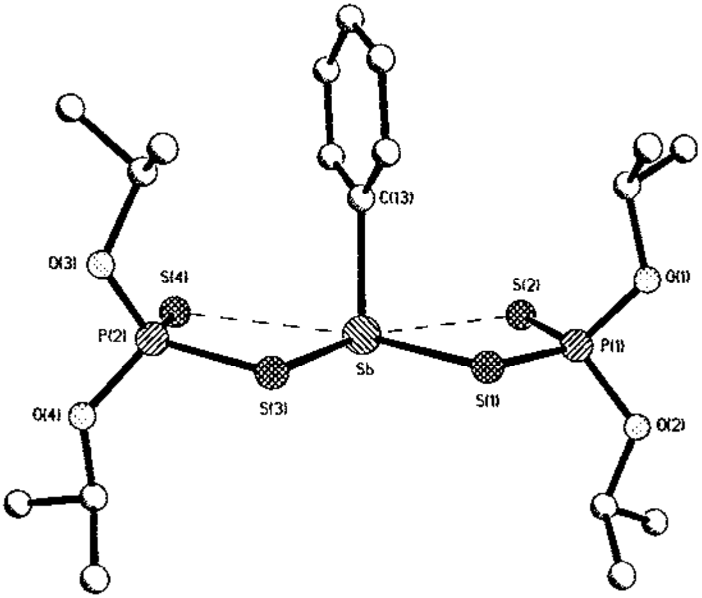

Fig. 5. The molecular structure of $PhSb[S_2P(OPr^i)_2]_2$.

Table 7
Relevant bond distances (ångströms) and angles (degrees) in $PhSb[S_2P(OPr^i)_2]_2$ [34]

Sb—S (average)	2.52(1)	P—S (long) (average)	2.04(1)
Sb···S (average)	3.06(1)	P—S (short) (average)	1.945(4)
Sb—C(13)	2.152(8)		
$C(13)_{ap}$—Sb—S_{eq} (average)	91.1(6.0)	S_{eq}—Sb—S_{eq} (average)	74.2(4.9)
		$S(2)_{eq}$···Sb···$S(4)_{eq}$	137.4(1)

2.2.2. *Dimeric derivatives*

The crystals of *p*-$tolyl_2SbS_2PEt_2$ [36] (Fig. 7(a)) and $Ph_2SbS_2PPh_2$ [37] (Fig. 7(b)) contain discrete dimeric units built through weak, intermolecular Sb···S secondary bonds (Table 8). In both compounds the phosphorus–sulphur distances within a ligand unit might be regarded as basically single (long) and double (short) bonds.

However, significant differences between the structures of these two compounds should be noted. Thus, in the dimeric unit of the *p*-tolyl derivative the dithio ligands act with bimetallic biconnective character, with a long intermolecular interaction between the sulphur doubly bonded to phosphorus and the antimony atom of a neighbouring molecule (Sb(1)···S(4), 3.556 Å; Sb(2)···S(2), 3.318 Å). This leads to an eight-membered, inorganic $Sb_2S_4P_2$ ring, with a twist-chair conformation in which the Sb_2S_4 system is almost planar and the phosphorus atoms are out of plane on opposite sides (Fig. 8(a)).

By contrast, in the dimeric unit of the phenyl derivative additional intramolecular,

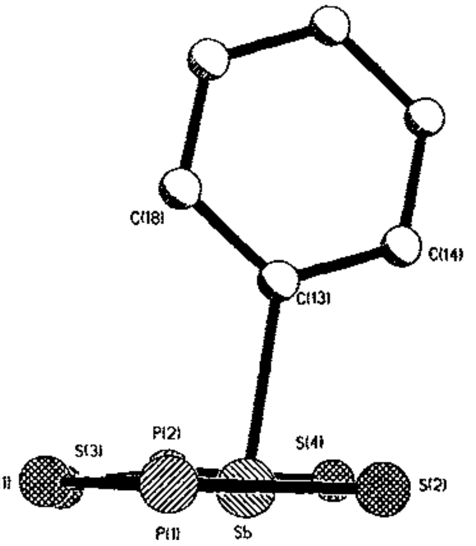

Fig. 6. The phenyl ring orientation in $PhSb[S_2P(OPr^i)_2]_2$.

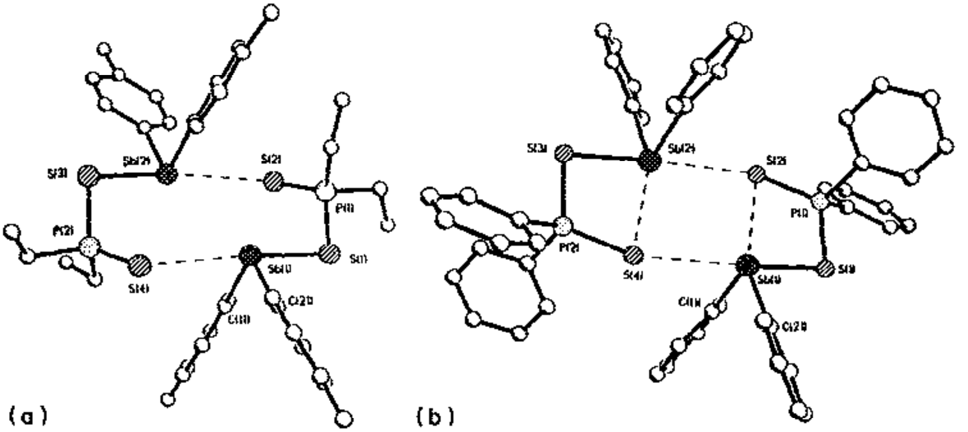

Fig. 7. View of the dimeric association in (a) $[p\text{-tolyl}_2SbS_2PEt_2]_2$ and (b) $[Ph_2SbS_2PPh_2]_2$.

transannular Sb ··· S(=P) interactions were observed, supporting the 3-coordination of the sulphur doubly bonded to phosphorus and, as a consequence, a bimetallic triconnective behaviour of the dithio ligand. The result is a fused tricyclic $Sb_2S_4P_2$ system, in which the eight-membered cyclic contour has again a twist-chair conformation (Fig. 8(b)).

Taking into account only the primary, covalent bonds to antimony, in both compounds the coordination geometry is trigonal pyramidal, with the metal atom in the apical position. If the weak antimony–sulphur interactions are considered, the coordination polyhedra become different.

Table 8
Relevant bond distances (ångströms) and angles (degrees) in $[p\text{-tolyl}_2SbS_2PEt_2]_2$ [36] and $[Ph_2SbS_2PPh_2]_2$ [37]

	$[p\text{-tolyl}_2SbS_2PEt_2]_2$	$[Ph_2SbS_2PPh_2]_2$
Sb−S	2.50(2) [a]	2.490(1)
Sb···S (intra)	3.98(5) [a,b]	3.440(1)
P−S (long)	2.08(1) [a]	2.081(1)
P−S (short)	1.965(4) [a]	1.958(1)
Sb(1)···S(4) (inter)	3.556	3.474
Sb(2)···S(2) (inter)	3.318	3.474
$S(1)_{ax}-Sb(1)\cdots S(4)_{ax}$	173.7	175.9(1)
$S_{ax}-Sb-C_{eq}$	91.9(1.9) [a]	90.9(2.9) [a]
$S(1)_{ax}-Sb(1)\cdots S(2)_{eq}$		68.3(1)
$S(4)_{ax}\cdots S(1)\cdots S(2)_{eq}$		111.5(1)
$C(11)_{eq}-Sb(1)-C(21)_{eq}$	95.6(0.4)	94.2(0.1)
$C(11)_{eq}-Sb(1)\cdots S(2)_{eq}$		94.5(0.1)
$C(21)_{eq}-Sb(1)\cdots S(2)_{eq}$		159.7(0.1)

[a] Averaged values. [b] Non-bonding distances.

(1) There is a distorted ψ trigonal bipyramid in $[p\text{-tolyl}_2SbS_2PEt_2]_2$, with the sulphur atoms in axial positions and two carbon atoms of the *p*-tolyl groups in equatorial positions. The lone pair of electrons seems to be stereochemically active, occupying the third equatorial position and thus compressing the C−Sb−C angles, as suggested by the bond angles at antimony: $S(1)_{ax}-Sb(1)\cdots S(4)_{ax}$, 173.7°; $C(11)_{eq}-Sb(1)-C(21)_{eq}$, 95.6(4)°; $S_{ax}-Sb(1)-C_{eq}$ (range), 89.2°–93.4°.

(2) There is a distorted ψ octahedron in $[Ph_2SbS_2PPh_2]_2$, with S(1) and S(4) in axial positions ($S(1)_{ax}-Sb(1)\cdots S(4)_{ax}$, 175.9(1)°). This coordination geometry might be considered as arising from the above ψ trigonal bipyramid, as a result of an additional intramolecular Sb(1)···S(2) secondary interaction in the equatorial plane. The lone pair would occupy the equatorial position between C(21) and S(2) atoms ($C(21)_{eq}-Sb(1)\cdots S(2)_{eq}$, 159.7(1)°). However, the distortion of the resulting ψ octahedron is very high, as reflected by the axial–equatorial angles of 68.3(1)° for $S(1)_{ax}-Sb(1)\cdots S(2)_{eq}$ and 111.5(1)° for $S(4)_{ax}\cdots Sb(1)\cdots S(2)_{eq}$ (the small S···S bite of the dithio ligand might be also responsible for this behaviour). Therefore, in this case the coordination polyhedron might be alternatively described as a distorted square pyramid (as in the original paper [37]), with S(1), S(2), S(4) and C(21) forming the basal plane and C(11) occupying the apical position. For this description of the coordination geometry around antimony the absence of a stereochemically active lone pair of electrons at antimony (which would have to be directed *trans* to C(11) atom) seems to be supported by the displacement of the metal atom from the basal plane inside the pyramid, towards the apical C(11) atom.

2.2.3. *Polymeric derivatives*

In some other diorganoantimony(III) derivatives the crystals contain various types of chain polymers. Thus, in $Ph_2SbO_2PPh_2$ and $Ph_2SbOSPPh_2$ [38], the ligand is

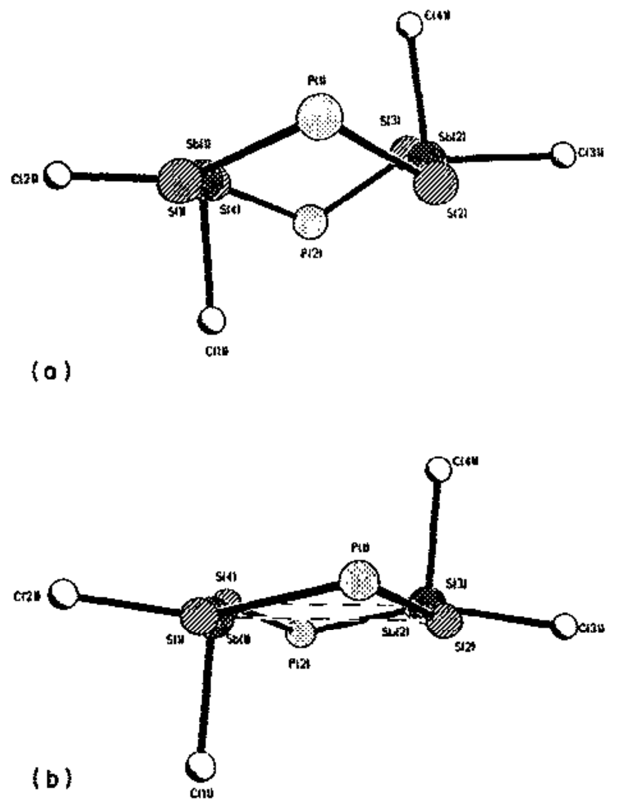

Fig. 8. View of the eight-membered $Sb_2S_4P_2$ ring in (a) $[p\text{-tolyl}_2SbS_2PEt_2]_2$ and (b) $[Ph_2SbS_2PPh_2]_2$.

bimetallic biconnective (Figs. 9(a) and 9(b)). The magnitudes of the Sb—O and P—O bond distances in the phosphinate (Table 9) are consistent with a high degree of delocalization of the π electrons over the PO_2 system (cf. $Ph_2P(O)OH$ [14]: P—O, 1.526(6) Å; P=O, 1.486(6) Å). In the monothiophosphinate (Table 9) the ligand is primarily bonded to antimony through oxygen (Sb(1)—O(1), 2.299(3) Å) and coordinated intermolecularly through the sulphur (Sb(1)—S(4), 2.753(1) Å), but again there is a high delocalization of the π electrons (cf. $Ph_2P(S)OH$ [16] (P—O, 1.582(2); P=S, 1.956(1) Å) and $PhSb(SOCMe)_2$ [33], with the ligands primarily bonded through sulphur (average Sb—S (intra), 2.46(1) Å; Sb—O (intra), 2.81(1) Å; Sb···S (inter), 3.802(2) Å)). In both compounds the Sb(1)···X(2) distances (X = O, S) are significantly larger (4.132 Å and 4.524 Å respectively) than the sum of van der Waals radii, indicating the absence of intramolecular interactions (Table 9).

The coordination geometry around the metal atom can be described as distorted ψ trigonal bipyramidal, with the chalcogen atoms in axial positions and the two carbons in the equatorial ones. The third equatorial position might be occupied by the antimony lone pair of electrons. This is supported by the deviations of the axial

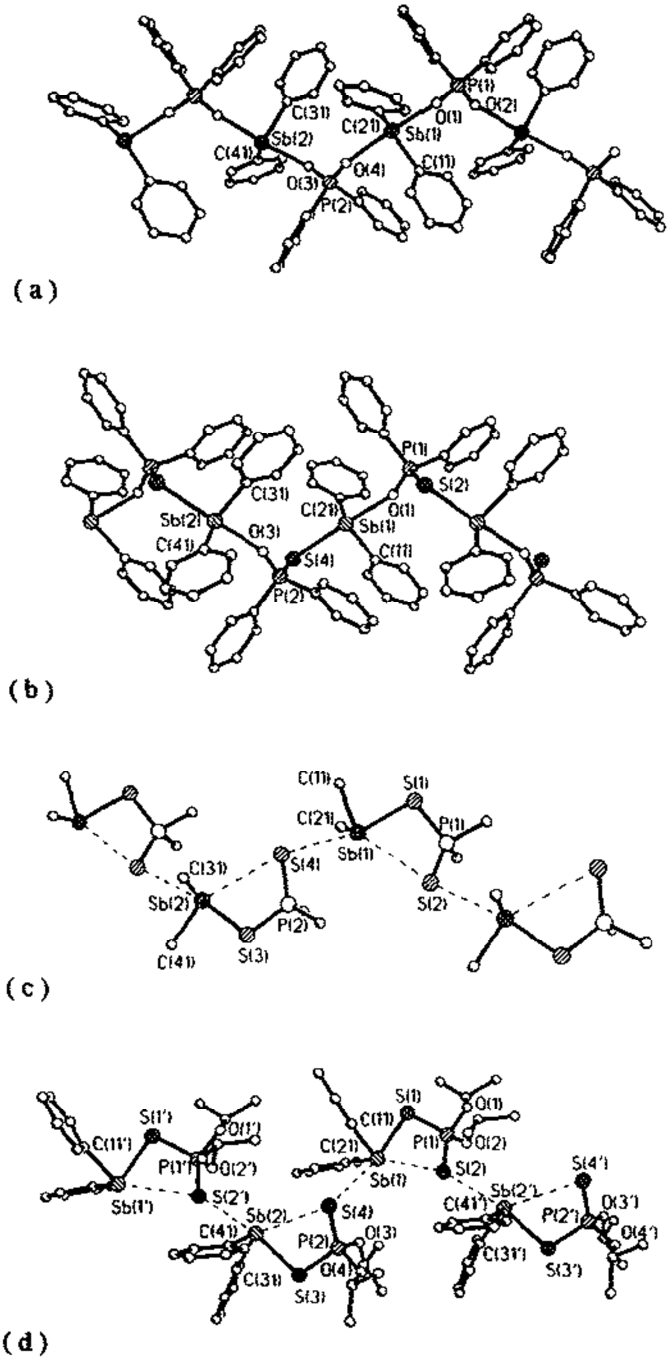

Fig. 9. View of the polymeric association in (a) $[Ph_2SbO_2PPh_2]_n$, (b) $[Ph_2SbOSPPh_2]_n$, (c) $[Me_2SbS_2PMe_2]_n$, and (d) $[Ph_2SbS_2P(OPr^i)_2]_n$.

Table 9
Relevant bond distances (ångströms) and angles (degrees) in $[Ph_2SbOXPPh_2]_n$ (X = O, S) [38] and $[R_2SbS_2PR'_2]_n$ (R = R' = Me [39]; R = Ph, R' = OPr^i [40])

	$[Ph_2SbO_2PPh_2]_n$ X = O	$[Ph_2SbOSPPh_2]_n$ X = S		$[R_2SbS_2PR'_2]_n$ R = R' = Me	$[R_2SbS_2PR'_2]_n$[a] R = Ph, R' = OPr^i
Sb(1)—O(1)	2.23(1)	2.299(3)	Sb(1)—S(1)	2.555(2)	2.54(2)
Sb(1)···X(2) (*intra*)	4.132[b]	4.524[b]	Sb(1)···S(2) (*intra*)	3.822(2)	3.81(18)[c]
P(1)—O(1)	1.49(1)	1.504(3)	P(1)—S(1)	2.045(3)	2.04(1)
P(1)—X(2)	1.51(1)	2.010(3)	P(1)—S(2)	1.974(3)	1.943(1)
Sb(1)—X(4) (*inter*)	2.29(1)	2.753(1)	Sb(1)···S(4) (*inter*)	3.158(2)	3.266(1)
			Sb(2)···S(2) (*inter*)	3.158(2)	3.172(1)
O_{ax}—Sb(1)···X_{ax}	166.7(5)	168.7(1)	$S(1)_{ax}$—Sb(1)···$S(4)_{ax}$	166.5(1)	165.4(2)
O,X_{ax}—Sb(1)—C_{eq}(average)	85.7(1.2)	83.7(3.0)	S_{ax}—Sb(1)—C_{eq}(average)	85.6(3.9)	87.5(5.7)
			$S(1)_{ax}$—Sb(1)···$S(2)_{eq}$	60.7(0.1)	60.3(2.6)
			$S(4)_{ax}$···Sb(1)···$S(2)_{eq}$	127.8(0)	133.7(3.3)
$C(11)_{eq}$—Sb(1)—$C(21)_{eq}$	98.1(6)	95.4(2)	$C(11)_{eq}$—Sb(1)—$C(21)_{eq}$	96.1(3)	97.6(6)
			$C(11)_{eq}$—Sb(1)···$S(2)_{eq}$	146.4(3)	145.4(1)
			$C(21)_{eq}$—Sb(1)···$S(2)_{eq}$	77.9(3)	90.2(4.5)

[a] Averaged values between equivalent bond distances and angles in the two independent molecules of the asymmetric cell unit. [b] Non-bonding distances. [c] Values of 3.934(1) Å and 3.684(1) Å in molecules 1 and 2 respectively.

equatorial and equatorial–equatorial bond angles from the expected values of 90° and 120° (Table 9).

By contrast, the dithio derivatives, $Me_2SbS_2PMe_2$ [39] and $Ph_2SbS_2P(OPr^i)_2$ [40], exhibit different polymeric chains in the crystal. Here the dithio ligand is bimetallic triconnective (Figs. 9(c) and 9(d)), with weak intra- and intermolecular secondary interactions between the sulphur doubly bonded to phosphorus and antimony. This leads to an increase in the coordination number of antimony to 5. The corresponding polyhedron might be considered as distorted ψ octahedral, with axial positions occupied by two sulphur atoms (one belonging to the monomeric unit and the other to a neighbouring molecule in the polymeric chain). The two carbon atoms bonded to antimony and the S(2) atom, providing the intramolecular secondary interaction, are in the equatorial position. The lone pair of electrons, if considered stereochemically active, should occupy the fourth equatorial position, in the free space between C(11) and S(2) atoms ($C(11)_{eq}-Sb(1)\cdots S(2)_{eq}$, 146.4(3)° and 145.4(1)° respectively). The distortion of the coordination polyhedra is reflected by the axial–equatorial angles, of which $S(1)_{ax}-Sb(1)\cdots S(2)_{eq}$ (ca. 60°) and $S(4)_{ax}\cdots Sb(1)\cdots S(2)_{eq}$ (ca. 130°) are the result of the small $S\cdots S$ bite of the dithio ligand unit.

In the original published papers, we have described the coordination geometry of these two organoantimony(III) dithio derivatives as distorted square pyramidal, with the C(21) atom in the apical position and the other carbon atom and three sulphur atoms in equatorial positions. However, in view of the coordination geometry proposed for $[p\text{-tolyl}_2SbS_2PEt_2]_2$ and $[Ph_2SbOXPPh_2]_n$ (X = O, S), which do not contain intramolecular $Sb\cdots S$ or $Sb\cdots O$ secondary interactions, it seems more appropriate to consider the S(1) and S(4) atoms in the axial positions of a distorted trigonal bipyramid (or ψ octahedron).

Other significant differences should be noted concerning the conformation of the polymeric catena in these four compounds. For the phosphinate (Fig. 10(a)) and monothiophosphinate (Fig. 10(b)) it is a helix. For the dithiophosphato derivative (Fig. 10(c)) the helix is strongly distorted, while for the dithiophosphinate (Fig. 10(d)) a zigzag catena can be assumed, with antimony and sulphur atoms almost in the same plane. This might be the result of the intramolecular antimony–sulphur secondary interactions.

3. Antimony(V)

Although the number of antimony(V) compounds containing diorganophophorus ligands investigated by X-ray diffractometry is lower than that of antimony(III) analogues (Table 10), the structural diversity is nevertheless broad. For inorganic compounds, i.e. chloroantimony(V) derivatives, the central metal atom is always 6-coordinated in an octahedral arrangement, while for trimethylantimony(V) derivatives the coordination polyhedron can be described as basically trigonal bipyramidal, with a variable degree of distortion.

Phenylantimony(V) derivatives of diorganodithiophosphorus ligands could not be isolated, all attempts leading to reduction to antimony(III) derivatives and the corresponding disulphanes, $R_2P(S)-S-S-P(S)R_2$ [41].

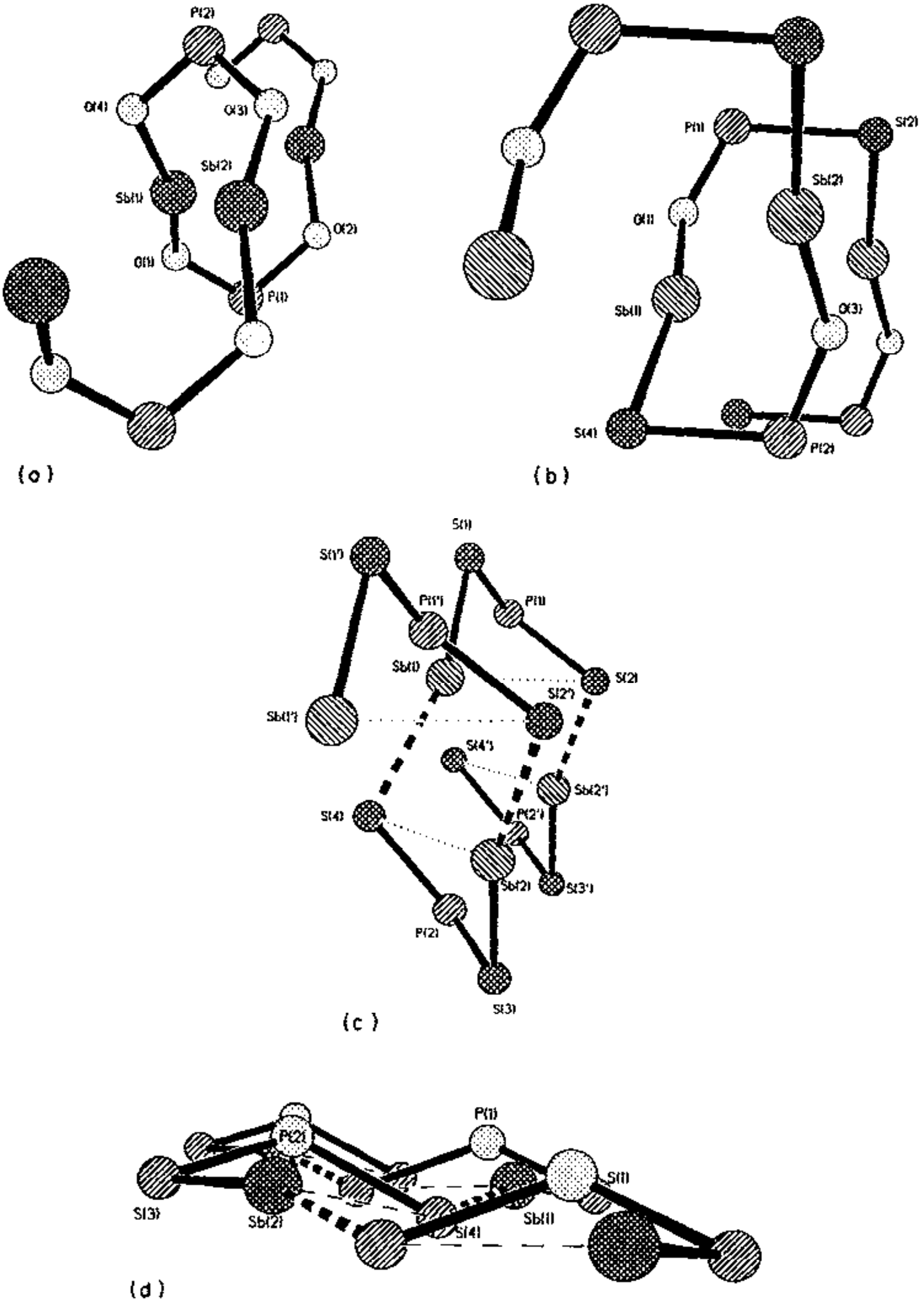

Fig. 10. View of the polymeric catena down the polymer axis in (a) $[Ph_2SbO_2PPh_2]_n$, (b) $[Ph_2SbOSPPh_2]_n$, (c) $[Ph_2SbS_2P(OPr^i)_2]_n$, and (d) $[Me_2SbS_2PMe_2]_n$.

Table 10
Antimony(V) derivatives of diorganophosphorus ligands

Compounds	Coordination pattern of the ligand	Coordination polyhedron
Inorganic derivatives		
Phosphinates		
$[Cl_3Sb(O_2PMe_2)]_2O$	Bimetallic biconnective	Distorted octahedron
$[Cl_4SbO_2PMe_2]_2$	Bimetallic biconnective	Distorted octahedron
Phosphates		
$[Cl_4SbO_2P(OMe)_2]_2$	Bimetallic biconnective	Distorted octahedron
Organometallic derivatives		
Phosphinates		
$[Me_3Sb(OH)(O_2PPh_2)]_n$	Monometallic monoconnective	Distorted trigonal bipyramid
Monothiophosphinates		
$Me_4SbOSPMe_2$	Monometallic monoconnective	Distorted trigonal bipyramid
$Me_3Sb(OSPPh_2)_2$	Monometallic monoconnective	Distorted trigonal bipyramid
Dithiophosphinates		
$Me_3Sb(S_2PPh_2)_2$	Monometallic biconnective	Distorted trigonal bipyramid

3.1. Inorganic compounds

So far only structures of chloroantimony(V) derivatives of oxophosphorus ligands have been reported.

3.1.1. Monomeric derivatives

The reaction between the $[Cl_4SbO_2PMe_2]_2$ dimer and $SbCl_5 \cdot H_2O$ leads to the dinuclear compound $[Cl_3Sb(O_2PMe_2)]_2O$ [42], whose structure is shown in Fig. 11.

In addition to the two bridging dimethylphosphinato groups, which are also present in the starting material (see below), a new oxo bridge is formed between the metal atoms. This converts the initial eight-membered $Sb_2O_4P_2$ ring into two fused six-membered rings, sharing the bridging O(3) and two antimony atoms. The resulting coordination polyhedra around the metal atoms are identical, i.e. slightly distorted octahedra, with O(3) and Cl(3), or Cl(3a), in axial positions ($O(3)_{ax}-Sb(1)-Cl(3)_{ax}$ and $O(3)_{ax}-Sb(1a)-Cl(3a)_{ax}$, 174.1(1)°) and a *fac* arrangement of the three chlorine and three oxygen atoms, respectively.

The isobidentate behaviour of the bimetallic biconnective phosphinato groups is reflected in equal phosphorus–oxygen (average P—O length, 1.544(5) Å) and corresponding antimony–oxygen (average Sb—O length, 2.01(1) Å) bond lengths (Table 11). The phosphorus–oxygen distances in this complex are intermediate between those observed in the free acid $Me_2P(O)OH$ [13] (Table 2), suggesting delocalization of the π electrons over the PO_2 system.

A difference in the Sb—O bond lengths should also be noted: the axial Sb—O(3) bonds in the oxo bridge are significantly shorter (1.942(2) Å) than the equatorial Sb—O(P) bonds (average 2.01(1) Å).

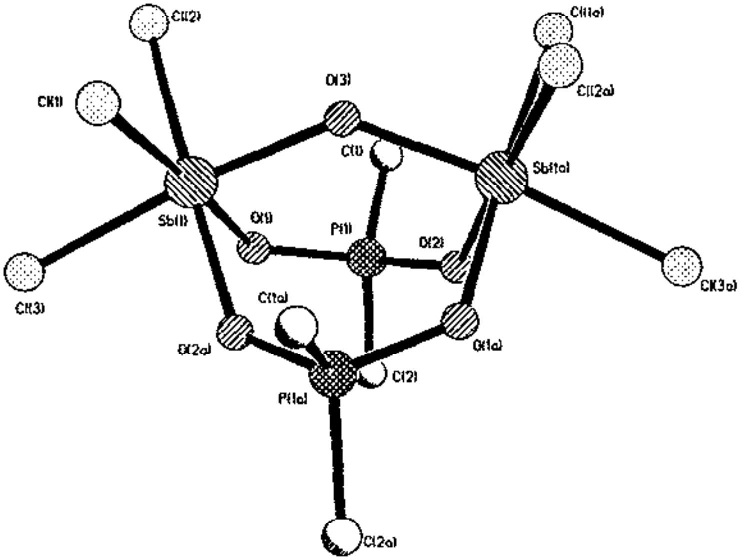

Fig. 11. The molecular structure of $[Cl_3Sb(O_2PMe_2)]_2O$.

Table 11
Relevant bond distances (ångströms) and angles (degrees) in $[Cl_3Sb(O_2PMe_2)]_2O$ [42]

Sb—O (ligand, average)	2.01(1)	P—O (average)	1.544(5)
Sb(1)—O(3)	1.942(2)		
Sb—Cl (average)	2.333(5)		
$O(3)_{ax}$—Sb(1)—$Cl(3)_{ax}$	174.1(1)	$O(3)_{ax}$—Sb(1)—Cl,O_{eq} (average)	90.8(1.0)
X_{eq}—Sb—Y_{eq} [a] (*cis*, average)	90.0(2.3)	$Cl(3)_{ax}$—Sb(1)—Cl,O_{eq} (average)	89.1(4.3)

[a] X, Y = Cl or O atoms.

3.1.2. Dimeric derivatives

Both tetrachloroantimony(V) dimethylphosphinate (R = Me) [43] and dimethylphosphate (R = OMe) [44] display a similar dimeric $[Cl_4SbO_2PR_2]_2$ structure (Fig. 12).

The organophosphorus ligands are isobidentate bridges (average P—O lengths of 1.55(1) Å and 1.505(3) Å and average Sb—O lengths of 2.01(1) Å and 2.028(3) Å for R = Me and OMe respectively) connecting the two metal atoms. In both cases the resulting eight-membered rings have a pseudochair conformation, with the antimony atoms on opposite sides of the plane formed by phosphorus and oxygen atoms. The coordination geometry around antimony is again almost perfectly octahedral (Table 12 gives the axial–equatorial and equatorial–equatorial angles at the central atom), with chlorine atoms in axial positions ($Cl(1)_{ax}$—Sb(1)—$Cl(4)_{ax}$, 175.4(1)° and 172.3(1)° for R = Me and OMe respectively) and *cis*-oxygen atoms in equatorial positions.

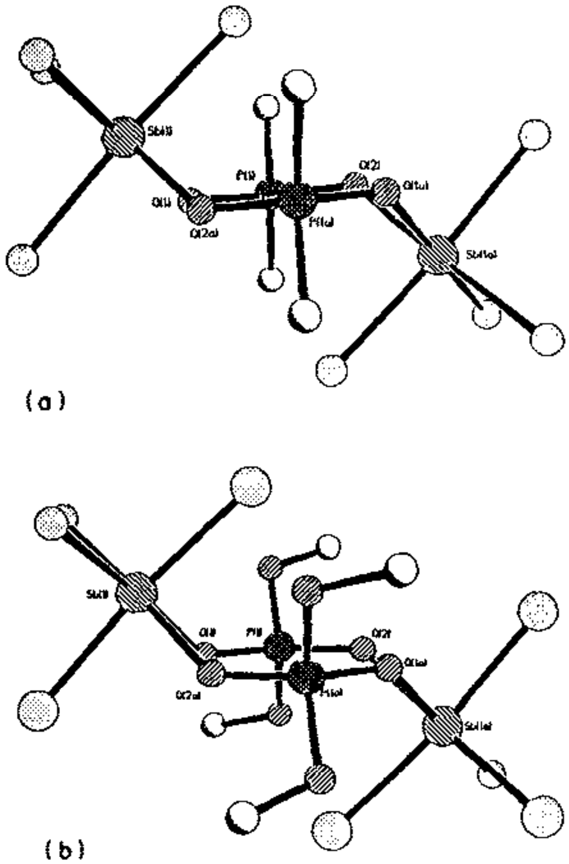

Fig. 12. View of the dimeric association in (a) $[Cl_4SbO_2PMe_2]_2$ and (b) $[Cl_4SbO_2P(OMe)_2]_2$.

Table 12
Relevant bond distances (ångströms) and angles (degrees) in $[Cl_4SbO_2PMe_2]_2$ [43] and $[Cl_4SbO_2P(OMe)_2]_2$ [44]

	$[Cl_4SbO_2PMe_2]_2$	$[Cl_4SbO_2P(OMe)_2]_2$
Sb—O (average)	2.01(1)	2.028(3)
P—O (average)	1.55(1)	1.505(3)
Sb—Cl (average)	2.35(1)	2.32(1)
$Cl(1)_{ax}$—Sb(1)—$Cl(4)_{ax}$	175.4(1)	172.3(1)
$Cl(1)_{ax}$—Sb(1)—Cl,O_{eq} (average)	90.5(4)	91.0(2.0)
$Cl(4)_{ax}$—Sb(1)—Cl,O_{eq} (average)	89.4(3.6)	88.8(4.3)
X_{eq}—Sb—Y_{eq} [a] (average)	90.0(3.0)	90.0(4.8)

[a] X, Y = Cl or O atoms.

3.2. Organometallic compounds

3.2.1. Monomeric derivatives

Monomeric structures were established for $Me_4SbOSPMe_2$ [45], $Me_3Sb(OSPPh_2)_2$ [46], and $Me_3Sb(S_2PPh_2)_2$ [47].

By contrast to the dimeric tetrachloroantimony(V) derivatives described above, the tetramethylstibonium dimethylmonothiophosphinate $Me_4SbOSPMe_2$ [45] is monomeric (Fig. 13). The crystal contains two independent molecules in which the monothiophosphinato ligand seems to be monometallic monoconnective (monodentate), coordinated only through its oxygen atom, while the sulphur atom, doubly bonded to phosphorus, is not involved in any intra- or intermolecular interactions (the Sb ··· S distances of 4.809 Å and 5.014 Å, in molecule 1 and molecule 2 respectively, are significantly larger than the sum of van der Waals radii).

However, in the ligand unit the P—O bond (average 1.514(3) Å) is shortened and the P=S bond (average 1.987(5) Å) is lengthened relative to the free acid (cf. the P—O distance of 1.580(1) Å and the P=S distance of 1.966(1) Å in $Me_2P(S)OH$ [14]), thus suggesting a delocalization of the π electrons over the POS system. On the contrary, the Sb—O distances of 2.532(4) Å and 2.749(4) Å, in molecules 1 and 2 respectively, are significantly larger than the sum of covalent radii or than the Sb—O(P) distances observed in phosphinato derivatives, e.g. an average of 2.01(1) Å in $[Cl_3Sb(O_2PMe_2)]_2O$ [40] or $[Cl_4SbO_2PMe_2]_2$ [41]. The weakness of the antimony–oxygen bond in $Me_4SbPOSPMe_2$ might be correlated with a partial ionic character, which would account for the water solubility of this compound [46].

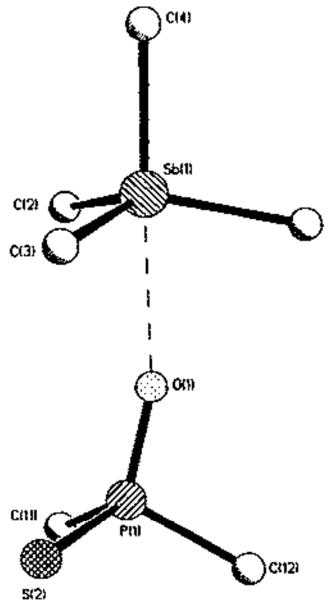

Fig. 13. The molecular structure of $Me_4SbOSPMe_2$.

Even weaker than a normal covalent Sb$-$O bond, this interaction is strong enough to disturb the tetrahedral arrangement of the SbC_4 group, leading to a distorted trigonal bipyramid around antimony (average axial $O(1)_{ax}-Sb-C(4)_{ax}$, 177.1(7)°). The distortion is reflected by the axial–equatorial angles (Table 13) which are larger than 90°, but smaller than 109° (required by a tetrahedral environment at antimony), and by the non-planar arrangement of the equatorial carbon atoms (sum of equatorial angles is 349° and 343.8° in molecules 1 and 2 respectively).

In the case of the monomeric $Me_3Sb(OSPPh_2)_2$ [44] (Fig. 14(a)) the diphenylmonothiophosphinato ligands act again as monometallic monoconnective (monodentate) units (average P$-$O distance of 1.55(1) Å and average P$-$S distance of 1.95(2) Å; cf. the P$-$O distance of 1.582(2) Å and the P=S distance of 1.956(1) Å in $Ph_2P(S)OH$ [15]), with primary bonds to the metal atom through oxygen. The antimony–oxygen bonds (average 2.111(5) Å) are significantly shorter than in the case of $Me_4SbPOSPMe_2$, indicating true Sb$-$O covalent bonds. The Sb$-$O$-$P angles (average 132.4(2.8)°) are large enough to avoid intramolecular Sb ··· S secondary interactions (average non-bonding Sb ··· S distance of 3.96(5) Å, very close to Σr_{vdW}(Sb, S) of ca. 4.0 Å). As a consequence, the coordination polyhedron around antimony is a slightly distorted trigonal bipyramid, with equatorial Sb$-$C bonds in a planar arrangement (sum of equatorial angles of C$-$Sb$-$C, 360°) and axial oxygen atoms ($O(1)_{ax}-Sb(1)-O(3)_{ax}$, 177.7(2)°) (Table 14).

Table 13
Relevant bond distances (ångströms) and angles (degrees) in $Me_4SbOSPMe_2$ [a] [45]

Sb–O	2.64(15) [b]	P–O	1.514(3)
Sb ··· S [c,d]	4.91(14)	P–S	1.987(5)
$O(1)_{ax}-Sb-C(4)_{ax}$ [d]	177.1(7)	$C(4)_{ax}-Sb-C_{eq}$	102.4(2.0)
$C_{eq}-Sb-C_{eq}$ (average)	115.5(2.7)	$O(1)_{ax}-Sb-C_{eq}$ [d]	77.6(2.3)

[a] Averaged values between equivalent bond distances and angles in the two independent molecules of the asymmetric cell unit. [b] Sb$-$O bond distances of 2.532(4) Å and 2.749(4) Å in molecules 1 and 2 respectively. [c] Non-bonding distances. [d] Calculated using the published atomic coordinates.

Table 14
Relevant bond distances (ångströms) and angles (degrees) in $Me_3Sb(OSPPh_2)_2$ [46] and $Me_3Sb(S_2PPh_2)_2$ [47]

	$Me_3Sb(OSPPh_2)_2$ X = O	$Me_3Sb(S_2PPh_2)_2$ X = S
Sb(1)$-$X (average)	2.111(5)	2.611(5)
Sb(1) ··· S (average)	3.96(5) [a]	3.79(7)
P$-$X (average)	1.55(1)	2.050(2)
P$-$S (average)	1.95(2)	1.96(1)
$X(1)_{ax}-Sb(1)-X(3)_{ax}$	177.7(2)	171.1(1)
$X_{ax}-Sb(1)-C_{eq}$ (average)	90.0(3.1)	89.7(3.0)
$C_{eq}-Sb(1)-C_{eq}$ (average)	120.0(3.9)	120.0(9.9)

[a] Non-bonding distances.

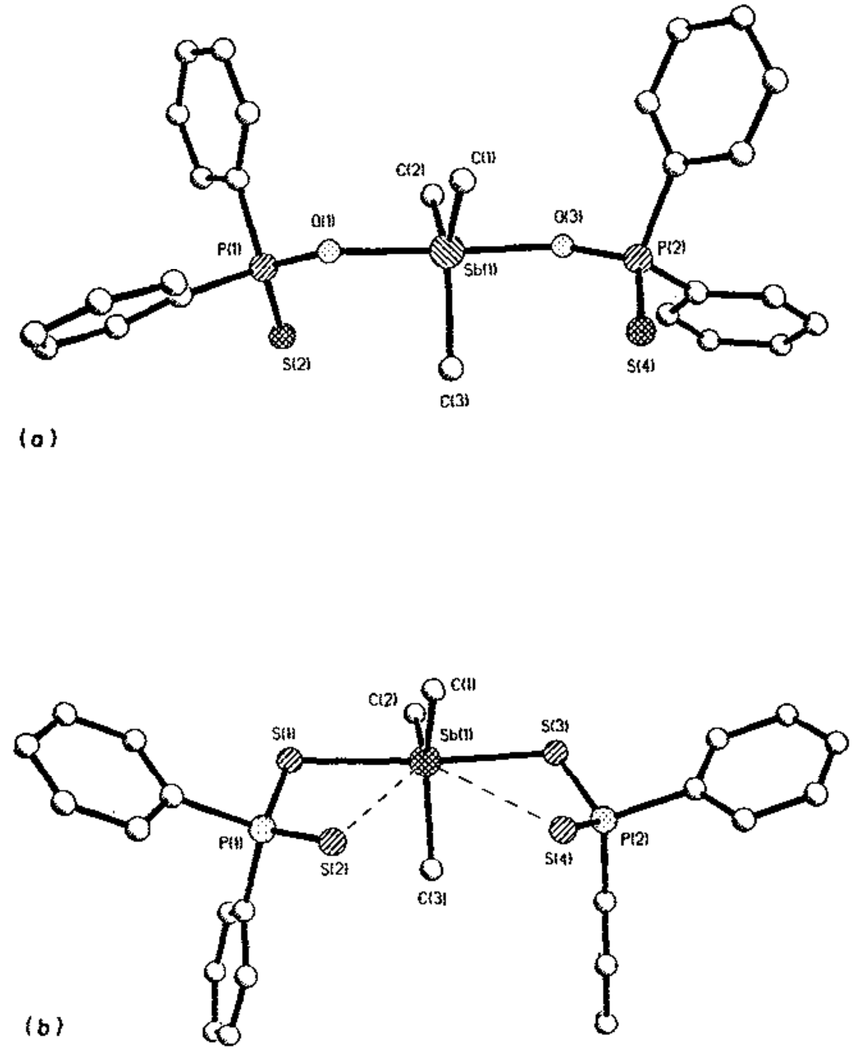

Fig. 14. The molecular structure of (a) $Me_3Sb(OSPPh_2)_2$ and (b) $Me_3Sb(S_2PPh_2)_2$.

By contrast, the structure of the dithio analogue, $Me_3Sb(S_2PPh_2)_2$ [45] is different (Fig. 14(b)). Within the ligand unit the phosphorus–sulphur distances can be assigned to basically single P—S and double P═S bonds (Table 14), thus suggesting a monometallic biconnective (monodentate) coordination pattern which results in a trigonal bipyramidal geometry around antimony (axial sulphur atoms and equatorial carbon atoms). However, although the S—P—S angles (average 116.9(2)°) are of the same magnitude as the O—P—S angles (average 117.5(1)°) in the related monothiophosphinate, a significant difference was observed between Sb—S—P (average 103.4(5)°) and the corresponding Sb—O—P (average 132.4(2.8)°) angles. This results in weak intramolecular Sb ··· S secondary interactions in $Me_3Sb(S_2PPh_2)_2$, i.e. Sb ··· S(=P) distances (average 3.79(7) Å) significantly shorter than Σr_{vdW}(Sb, S). The consequence is an increased distortion of the coordination polyhedron related to the monothiophosphinato analogue, reflected in a smaller $S(1)_{ax}-Sb(1)-S(3)_{ax}$ angle (171.1(1)°) than the corresponding $O(1)_{ax}-Sb(1)-O(3)_{ax}$ angle (177.7(2)°), and a larger equatorial angle, i.e. 131.2(4)° for C(1)—Sb(1)—C(3).

Another significant difference between the structures of these trimethylantimony(V) derivatives should be also noted. In $Me_3Sb(S_2PPh_2)_2$ the SbS_4 system is almost planar, with a *cis* arrangement of the sulphur atoms doubly bonded to phosphorus (Fig. 15(b)). By contrast, in $Me_3Sb(OSPPh_2)_2$ the two ligand units are twisted, bringing the sulphur atoms in a quasi-*trans* position (Fig. 15(a)).

3.2.2. *Polymeric derivatives*

Crystals of $Me_3Sb(OH)(O_2PPh_2)$ were obtained by partial hydrolysis of $Me_3Sb(O_2PPh_2)_2$, during its recrystallization from an MeCN—MeOH mixture [46]. The compound exhibits an unusual chain polymeric structure built through hydrogen bonds (Fig. 16). The diphenylphosphinato ligand is monometallic monoconnective.

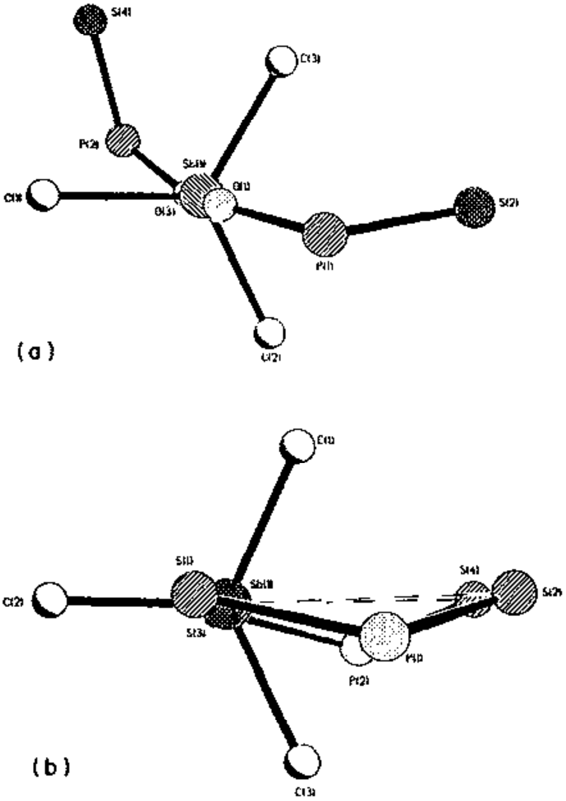

Fig. 15. The orientation of the phosphorus ligands in (a) $Me_3Sb(OSPPh_2)_2$ and (b) $Me_3Sb(S_2PPh_2)_2$.

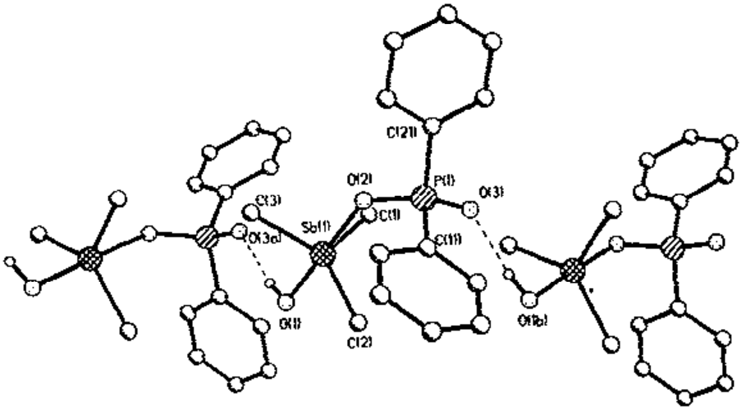

Fig. 16. View of the polymeric association in $[Me_3Sb(OH)(O_2PPh_2)]_n$.

with single P(1)—O(2) (1.528(3) Å) and double P(1)—O(3) (1.490(3) Å) bonds, of the same magnitude as observed in the free acid (Table 2). The O(3) atom is not involved in intra- or intermolecular coordination to the metal atom (Table 15). This type of coordination is less common for a diorganophosphinato group, the bimetallic biconnective (bridging) behaviour being the most common coordination pattern observed so far (see above, for example, $[Ph_2SbO_2PPh_2]_n$ [36] or $[Cl_3Sb(O_2PMe_2)]_2O$ [40], which might be considered as a condensation product of $Cl_3Sb(OH)(O_2PMe_2)$).

The antimony atom is five-coordinated, in a slightly distorted trigonal bipyramidal arrangement, with hydroxylic O(1) and O(2) in axial positions ($O(1)_{ax}$—Sb(1)—$O(2)_{ax}$, 175.7(1)°) and carbon atoms of methyl groups in a planar SbC_3 equatorial arrangement (sum of C—Sb—C angles, 358.4°).

Intermolecular hydrogen bonds (H(1)···O(3a), 1.829 Å) are established between the hydroxylic hydrogen atom and the oxygen atom doubly bonded to phosphorus, thus leading to a supramolecular association of the $Me_3Sb(OH)(O_2PPh_2)$ units in a chain polymeric structure. The resulting polymeric catena has a zigzag conformation, a view down the polymer axis (Fig. 17) showing imaginary staggered planes containing oxygen atoms of the phosphinato ligands, antimony atoms and hydroxylic oxygen atoms.

Table 15
Relevant bond distances (ångströms) and angles (degrees) in $[Me_3Sb(OH)(O_2PPh_2)]_n$ [48]

Sb(1)—O(1)	1.967(3)	O(1)—H(1)	0.869(58)
Sb(1)—O(2)	2.235(2)	P(1)—O(2)	1.528(3)
Sb(1)···O(3)[a] (intra)	3.897	P(1)—O(3)	1.490(3)
Sb(1)···O(3a)[a] (inter)	3.602	H(1)···O(3a) (inter)	1.829
$O(1)_{ax}$—Sb(1)—$O(2)_{ax}$	175.7(1)	O_{ax}—Sb(1)—C_{eq} (average)	90.0(5.5)
C_{eq}—Sb(1)—C_{eq} (average)	119.5(4.2)		

[a] Non-bonding distances.

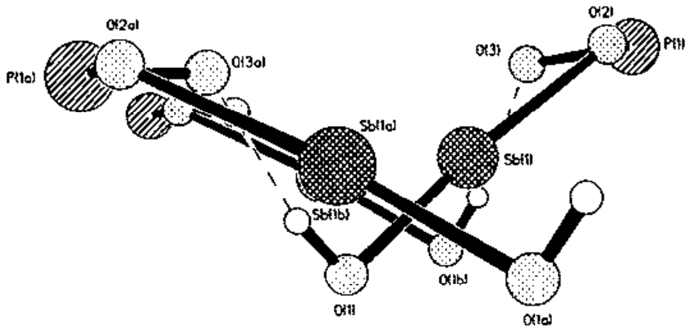

Fig. 17. View of the polymeric catena down the polymer axis in $[Me_3Sb(OH)(O_2PPh_2)]_n$.

4. Concluding remarks

An overview of the structural chemistry of antimony derivatives of oxo- and thiodiorganophosphorus ligands reveals an unexpected, extremely broad solid state structural diversity. A summary of the X-ray diffraction data is presented in Table 16.

The following structural trends might be inferred from the data available so far.

(1) Generally, inorganic antimony(III) derivatives of type SbL_3 (L = anionic diorganophosphorus ligand) exhibit monomeric structures. The ligands are monometallic biconnective, thus leading to distorted octahedral SbX_3S_3 (X = O, S) cores. The distortion of the coordination polyhedron might be the result of either the small ligand bite or the stereoactivity of the antimony lone pair. The ψ pentagonal bipyramidal geometry of the SbS_6 core (with an axial position occupied by the lone pair) found in $Sb(S_2PPh_2)_3$ [30] seems to support the stereochemical influence of the antimony lone pair in such compounds. However, further studies using ligands with a larger X·····Y bite (e.g. $(XPR_2)(YPR'_2)N$, X, Y = O, S) or attempts to coordinate the SbL_3 unit to a transition metal atom might provide direct proof for the activity or inactivity of the lone pair in inorganic, as well as organometallic (see below), antimony(III) derivatives.

(2) The possibility of the SbL_3 unit association into dimeric (as established for $Sb(OSPPh_2)_3$ [27] or $Sb(S_2COMe)_3$ [49]) or polymeric (as reported for $Sb(SOCMe)_3$ and $Sb(O_2CMe)_3$ [31]) structures through additional intermolecular Sb···X (X = O, S) bonds, resulting thus in an increase in the antimony atom coordination number and more complicated coordination polyhedra, has to be also taken into account.

(3) $PhSb[S_2P(OPr^i)_2]_2$ [34] was found to be monomeric, and the antimony lone pair was suggested to occupy the axial position *trans* to the Sb—C bond. However, for other monoorganoantimony(III) derivatives containing ligands with less bulky organic groups attached to phosphorus, associations of the monomeric units might be expected, as reported for the related $PhSb(SOCMe)_2$ [33] or $MeSb(S_2COEt)_2$ [50] derivatives. In these cases the antimony lone pair was suggested to be either stereochemically inactive or placed in an equatorial position bisecting the opened S···Sb···S angle.

Table 16
Summary of the structural types established for antimony derivatives of oxo- and thiodiorganophosphorus ligands

Antimony	Inorganic	Monomeric	$Sb(OSPCy_2)_3$ $Sb[S_2P(OMe)_2]_3$ $Sb[S_2P(OEt)_2]_3$ $Sb[S_2P(OPr^i)_2]_3$ $Sb(S_2PPh_2)_3$
		Dimeric	$[Sb(OSPPh_2)_3]_2$
	Organometallic	Monomeric	$PhSb[S_2P(OPr^i)_2]_2$
		Dimeric	[*p*-tolyl$_2SbS_2PEt_2]_2$ $[Ph_2SbS_2PPh_2]_2$
		Polymeric	$[Ph_2SbO_2PPh_2]_n$ $[Ph_2SbOSPPh_2]_n$ $[Me_2SbS_2PMe_2]_n$ $[Ph_2SbS_2P(OPr^i)_2]_n$
Antimony	Inorganic	Monomeric	$[Cl_3SbO_2PMe_2]_2O$
		Dimeric	$[Cl_4SbO_2PMe_2]_2$ $[Cl_4SbO_2P(OMe)_2]_2$
	Organometallic	Monomeric	$Me_4SbOSPMe_2$ $Me_3Sb(OSPPh_2)_2$ $Me_3Sb(S_2PPh_2)_2$
		Polymeric	$[Me_3Sb(OH)(O_2PPh_2)]_n$

(4) All diorganoantimony(III) derivatives investigated so far were found to exhibit either dimeric or polymeric associations through intermolecular Sb · · · X (X = O, S) bonds, leading to distorted coordination polyhedra around the metal atom which might be thought to be the result of electrostatic repulsion between bond pairs–lone pair of electrons.

(5) In the case of antimony(V) compounds the absence of a metal lone pair results in more predictable, less distorted coordination polyhedra (octahedron or trigonal bipyramid) at the central metal atom. The complexity of the whole structure might arise from either the sensitivity to moisture of the primary formed compounds or the association of the monomeric units. As a general trend, the SbC_3 moiety is planar in the trigonal bipyramidal trimethylantimony(V) derivatives, but sometimes a significant distortion in the C—Sb—C angles might be achieved owing to the tendency of the antimony atom to increase its coordination number (see the structure

of $Me_3Sb(S_2PPh_2)_2$ [45]; similar behaviour was observed for the related $Me_3Sb(S_2CMe_2)_2$ derivative [51]).

The conclusion which can be drawn is that, regardless of the oxidation state of the antimony, changes in (i) the nature of the phosphorus ligand, i.e. phosphinato–phosphato and/or oxo–thio, (ii) the nature of the organic groups on the phosphorus atom, and (iii) the nature of the substituents (inorganic or organic groups) bound to antimony produce important structural changes, ranging from monomeric to dimeric or polymeric supramolecular associations. Moreover, significant structural differences can be observed for compounds belonging to the same class, e.g. different coordination patterns of the phosphorus resulting in different coordination polyhedra and conformation of the polymeric catena in diorganoantimony(III) derivatives. Therefore, the assignment of a solid state structure for a new antimony compound containing phosphorus ligands only on the basis of its similarity with a related compound already studied by X-ray diffractometry might be hazardous. On the contrary, investigation by X-ray diffractometry of new compounds of this class, e.g. containing bulky organic groups on antimony and/or phosphorus atoms, might provide other unexpected structural patterns.

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