Journal of Organometallic Chemistry, 426 (1992) 49–58
Elsevier Sequoia S.A., Lausanne
JOM 22351

Phenylantimony(III) diorganophosphorodithioates: the crystal structure of diphenylantimony(III) di-isopropylphosphorodithioate, $Ph_2SbS_2P(O^iPr)_2$; unusual polymerisation through semibonding

Christian Silvestru, Maria Curtui, Ionel Haiduc
Facultatea de Chimie, Universitatea Babes-Bolyai, R-3400 Cluj-Napoca (Romania)

Michael J. Begley and D. Bryan Sowerby
Department of Chemistry, University of Nottingham, Nottingham NG7 2RD (UK)

(Received July 22, 1991)

Abstract

The diphenylantimony(III) phosphorodithioates, $Ph_2SbS_2P(OR)_2$ where R = Me, Et, ^{i}Pr and Ph, have been prepared and the methyl and isopropyl derivatives obtained as crystalline solids. The compounds have been characterised by infrared and NMR spectroscopy. An X-ray structural determination for the isopropyl compound shows the presence of two independent molecules in the asymmetric unit, with similar but not identical molecular parameters. The ligand in each molecule is strongly bonded to antimony by one sulphur atom (Sb–S 2.54 Å), but there are two weaker Sb–S contacts (*ca.* 3.2 and 3.8 Å) making the ligand effectively tridentate. These interactions generate infinite chains in the solid state, providing an example of a new dithiophosphate structure.

Introduction

Phosphorodithioato, $(RO)_2PS_2^-$, and phosphinodithioato, $R_2PS_2^-$, anions have been extensively used in transition metal coordination chemistry, and in most cases they behave as bidentate ligands [1–3]. A broader diversity of coordination patterns is observed when such ligands are attached to main group metals [1]. Such compounds have been well studied for tin, but only few examples are known for other main group metals [3]. Among these, antimony is an attractive element, because as a coordination centre it often exhibits unpredictable structural behaviour.

Correspondence to: Dr. I. Haiduc, Facultatea de Chimie, Universitatea Babes-Bolyai, R-3400 Cluj-Napoca, Romania, or Dr. D.B. Sowerby, Dept. of Chemistry, University of Nottingham, Nottingham NG7 2RD, UK.

So far, both 'naked' antimony derivatives of dithiophosphorus ligands, $Sb(S_2PR_2)_3$ (where R = alkyl, aryl, alkoxy and aryloxy) [4–7] and organoantimony(III) derivatives, including $Ph_2SbS_2PR_2$ [8] and $PhSb[S_2P(OR)_2]_2$ [9], have been investigated. Extension of our work in this area led us to synthesise the diphenylantimony phosphorodithioates $Ph_2SbS_2P(OR)_2$, where R = Me, Et, ^{i}Pr and Ph. During the course of this work, Karra and coworkers [10] reported the isolation of the compounds with R = Me, Et, Pr, ^{i}Pr, Bu and ^{t}Bu as uncrystallisable oils. We have obtained the methyl and isopropyl derivatives as crystalline solids and have determined the X-ray structure of the latter.

It is perhaps worth noting here that anti-tumour activity of diphenylantimony derivatives of dithiophosphorus ligands [11] compares favourably with that of the corresponding tin compounds [12], suggesting that the former deserve more attention in this respect.

Results and discussion

Diphenylantimony(III) diorganophosphorodithioates have been obtained by reacting diphenylantimony(III) acetate, obtained by a new route, with the appropriate phosphorodithioic acid (eq. 1) or its ammonium salt (eq. 2).

$$Ph_2SbOAc + (RO)_2P(S)SH \rightarrow Ph_2SbS_2P(OR)_2 + HOAc \qquad (1)$$

R = Me, Et and Ph

$$Ph_2SbOAc + (RO)_2P(S)SNH_4 \rightarrow Ph_2SbS_2P(OR)_2 + NH_4OAc \qquad (2)$$

R = ^{i}Pr

In some cases, the phosphorodithioates can also be formed when a diorganoantimony(V) derivative, such as Ph_2SbCl_3, is treated in the ratio 1:3 with an ammonium phosphorodithioate. Antimony is reduced to the +3 oxidation state and the ligand is oxidised to the disulphide.

$$Ph_2SbCl_3 + 3(RO)_2P(S)SNH_4 \rightarrow Ph_2SbS_2P(OR)_2 + [(RO)_2P(S)S]_2 + 3NH_4Cl \qquad (3)$$

Of the four compounds reported here, the methyl and isopropyl derivatives were obtained as pale yellow crystals and the other two as viscous, yellow liquids.

Infrared spectra

Spectra were recorded in the range 4000–400 cm^{-1} and bands associated with PS_2, (P)–O–C and P–O–(C) stretching vibrations are listed in Table 1. These are in accordance with literature values [13]. The (P)–O–C stretching frequency shifts

Table 1

Infrared data (cm^{-1}) for $Ph_2Sb[S_2P(OR)_2]$

R	$\nu_{as}(PS_2)$	$\nu_s(PS_2)$	ν(P–O(R))	ν((P)–OC)
Me [a]	630s	497s	1120s 990s	1175ms
Et [b]	654s	530s 500s	1010s	1155m
^{i}Pr [a]	640s	525m 520s	990s	1130m
Ph [b]	680s	535m	930s, br	1200s

[a] KBr disc. [b] Liquid film.

Table 2
^{1}H NMR data for $Ph_2Sb[S_2P(OR)_2]$

R	Chemical shifts (δ, ppm) and coupling constants (*J*, Hz)	
Me [a]	3.41 d (6H), ^{3}J(POCH) 16	(POC*H*$_3$)
	7.68 m (6H *meta* + *para*), 8.01 m (4H *ortho*)	(SbC$_6$*H*$_5$)
Et [a]	1.21 t (6H), ^{3}J(HCCH) 7	(POCH$_2$C*H*$_3$)
	3.96 dq (4H), ^{3}J(POCH) 9.5, ^{3}J(HCCH) 6.5	(POC*H*$_2$CH$_3$)
	7.29 m (6H *meta* + *para*), 7.58 m (4H *ortho*)	(SbC$_6$*H*$_5$)
^{i}Pr [b]	1.32 d (12H), ^{3}J(HCCH) 6	(POCH(C*H*$_3$)$_2$)
	4.77 m (2H), ^{3}J(HCCH) 6	(POC*H*(CH$_3$)$_2$)
	7.25 m (6H *meta* + *para*), 7.42 m (4H *ortho*)	(SbC$_6$*H*$_5$)
Ph [b]	7.02 m (10H)	(POC$_6$*H*$_5$)
	7.14 m (6H *meta* + *para*), 7.35 m (4H *ortho*)	(SbC$_6$*H*$_5$)

[a] CCl_4 solvent, TMS standard. [b] $CDCl_3$ solvent, HMDSO standard.

to slightly lower wave numbers with increasing length of the alkyl chain. All the compounds show strong absorptions in the 500–550 cm^{-1} and 630–680 cm^{-1} regions, which are assigned to the symmetric and the antisymmetric PS_2 stretching modes respectively. In some cases, the peaks are split but the positions are not influenced by the nature of the organic groups in the ligand.

^{1}H NMR spectra

Data for the proton resonance spectra are collected in Table 2 and confirm the identity of the products: they show no unusual features.

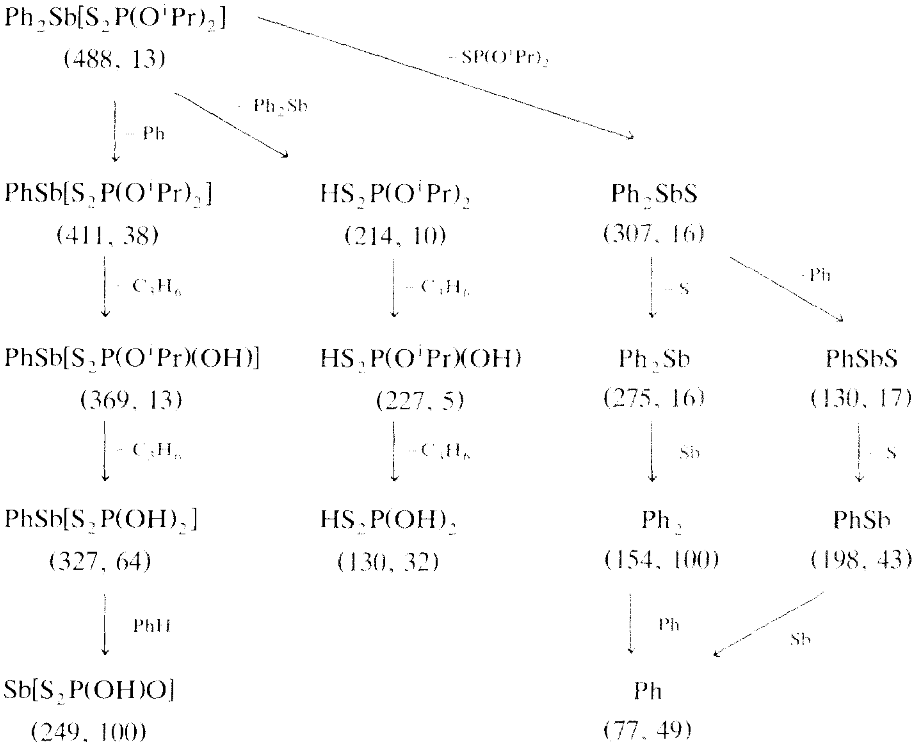
Mass spectrum

The electron impact fragmentation pattern for the di-isopropyl derivative $Ph_2Sb[S_2P(O^{i}Pr)_2]$, is summarised in Scheme 1. Here, figures in parentheses are, respectively, the monoisotopic *m/z* values and the relative abundances. Fragmentation of the parent ion, which is observed, can follow three alternative routes. The major one involves loss of a phenyl group, while in the alternatives either Ph_2Sb or $SP[O^{i}Pr]_2$ units are lost. Loss of C_3H_6 units is important in subsequent stages, and the major low mass fragments are Ph_2, Ph and, more surprisingly, $Sb[S_2P(OH)O]$.

The compounds are monomeric in solution and the infrared data can be interpreted in terms of bidentate dithiophosphate groups. If the solid state structure is also monomeric, antimony would probably adopt pseudo-trigonal bipyramidal coordination with the lone pair in an equatorial position. The ligand could then either span equatorial and axial positions with the phenyl groups also in equatorial and axial sites or, less likely, occupy two equatorial sites, forcing both phenyl groups into axial positions. To resolve this problem, an X-ray structure analysis was carried out on $Ph_2SbS_2P(O^{i}Pr)_2$.

Structure determination

Important bond distances and angles are listed in Table 3, and the structure of the compound is shown in Fig. 1. Crystals of the compound contain two independent formula units and, if interactions only of < 3.0 Å are considered, the molecules are discrete monomers with a unidentate ligand. Metal phosphorodithioates with truly unidentate ligands are, however, rare and the known



Scheme 1.

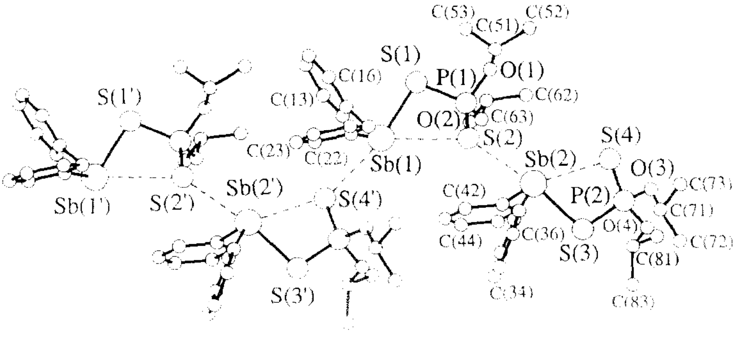


Fig. 1. Molecular structure of $Ph_2SbS_2P(O^iPr)_2$, showing the atom numbering scheme.

examples are mainly derivatives of main group metals, such as $Ph_3SnS_2P(OEt)_2$ [14] and $Ge[S_2P(OMe)_2]_4$ [15]. Monomeric coordination of the phosphorodithioato ligand here is supported by the P–S distances, which fall into groups of two short contacts at 1.94 Å and two longer ones at 2.04 Å. Molecular parameters for the two independent molecules are similar but, as shown in Table 4, there are some differences. An example of this is the variation in the angles describing the

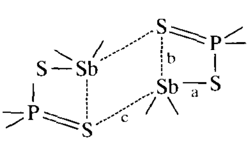


Fig. 2. Schematic representation of the skeleton of $[Ph_2SbS_2PPh_2]_2$, $a = 2.490$, $b = 3.440$ and $c = 3.474$ Å.

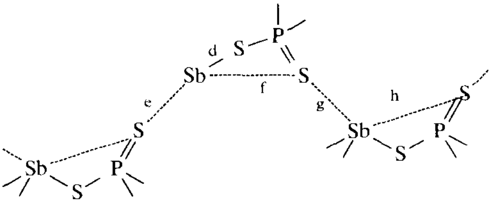


Fig. 3. Schematic representation of the polymeric structure of $Ph_2SbS_2P(O^iPr)_2$, $d = 2.531$, $e = 3.266$, $f = 3.934$, $g = 3.172$ and $h = 3.684$ Å.

distorted pyramidal geometry at antimony between the two phenyl carbon atoms (C(11), C(21) and C(31), C(41) respectively) and the fully bonded sulphur atoms (S(1) and S(3) respectively). At Sb(1), these angles are 98.0(2), 86.9(1) and 93.8(1)°, respectively, compared with 97.2(2), 84.7(1) and 91.9(1)° at Sb(2).

On the other hand, if Sb · · · S contacts of up to 4.0 Å (the sum of the van der Waals' radii) are considered significant, the ligand is best described as tridentate, both chelating the antimony atoms and linking the molecules into infinite zig-zag chains along the a axis. This arrangement represents a novel structure type for dithiophosphorus ligands, but it is related to that of $Ph_2SbS_2PPh_2$ [8].

The relationship between these two structures deserves some comment. Both can be described as consisting of monomeric units, held together by semibonding interactions, as shown by the interatomic contacts, which lie between the single bond Sb–S distance (2.4–2.5 Å) and the sum of the antimony and sulphur van der Waals' radii (*ca.* 4.0 Å). The dimeric structure, which is shown diagrammatically in

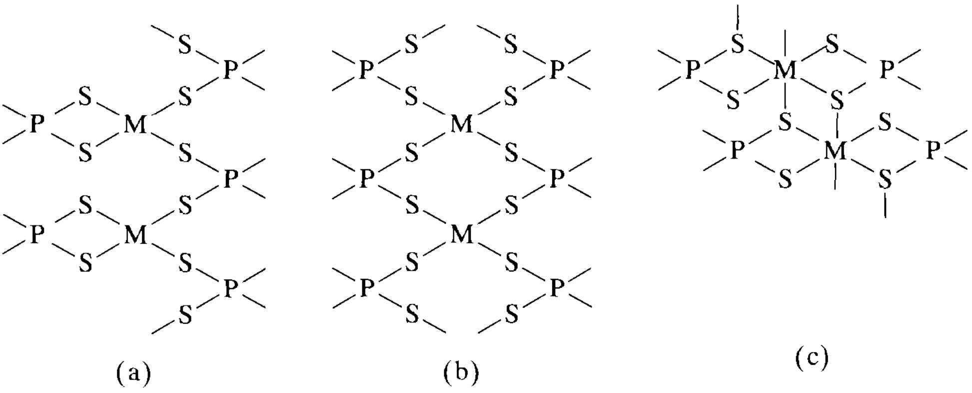

(a) (b) (c)

Fig. 4. Polymerisation modes for $M[S_2P(OR)_2]_2$, (a) M = Zn, R = Et [19], and M = Hg, R = ^{i}Pr [20]; (b) M = Hg, R = Et [21] and (c) M = Pb, R = ^{i}Pr [22].

Table 3

Important bond distances (Å) and angles (deg) for $Ph_2Sb[S_2P(OR)_2]$

Sb(1)–C(11)	2.156(5)	Sb(2)–C(31)	2.161(5)
Sb(1)–C(21)	2.159(5)	Sb(2)–C(41)	2.139(5)
Sb(1)–S(1)	2.531(1)	Sb(2)–S(3)	2.555(1)
Sb(1)···S(2)	3.934(1)	Sb(2)···S(4)	3.684(1)
Sb(1)···S(4′)	3.266(1)	Sb(2)···S(2)	3.172(1)
S(1)–P(1)	2.044(2)	S(3)–P(2)	2.035(2)
S(2)–P(1)	1.942(2)	S(4)–P(2)	1.943(2)
P(1)–O(1)	1.571(4)	P(2)–O(3)	1.573(4)
P(1)–O(2)	1.553(4)	P(2)–O(4)	1.579(4)
O(1)–C(51)	1.431(9)	O(3)–C(71)	1.457(7)
O(2)–C(61)	1.466(7)	O(4)–C(81)	1.466(7)
C(11)–Sb(1)–C(21)	98.0(2)	C(31)–Sb(2)–C(41)	97.2(2)
C(11)–Sb(1)–S(1)	86.9(1)	C(31)–Sb(2)–S(3)	84.7(1)
C(11)–Sb(1)···S(2)	145.3(1)	C(31)–Sb(2)–S(4)	145.5(1)
C(11)–Sb(1)···S(4′)	78.7(1)	C(31)–Sb(2)···S(2)	80.9(1)
C(21)–Sb(1)–S(1)	93.8(1)	C(41)–Sb(2)–S(3)	91.9(1)
C(21)–Sb(1)···S(2)	87.0(1)	C(41)–Sb(2)···S(4)	93.3(1)
C(21)–Sb(1)···S(4′)	89.9(1)	C(41)–Sb(2)···S(2)	93.0(1)
S(2)···Sb(1)···S(4′)	135.96(4)	S(2)···Sb(2)···S(4)	131.41(4)
S(1)–Sb(1)···S(2)	58.39(4)	S(3)–Sb(2)···S(4)	62.14(4)
S(1)–Sb(1)···S(4′)	165.45(4)	S(3)–Sb(2)···S(2)	165.19(4)
Sb(1)–C(11)–C(12)	118.2(4)	Sb(2)–C(31)–C(32)	117.8(4)
Sb(1)–C(11)–C(16)	122.6(5)	Sb(2)–C(31)–C(36)	123.0(5)
Sb(1)–C(21)–C(22)	120.3(4)	Sb(2)–C(41)–C(42)	121.3(4)
Sb(1)–C(21)–C(26)	120.5(4)	Sb(2)–C(41)–C(46)	121.6(4)
Sb(1)–S(1)–P(1)	100.48(6)	Sb(2)–S(3)–P(2)	103.3(6)
Sb(1)···S(2)–P(1)	63.65(6)	Sb(2)···S(4)–P(2)	72.55(6)
Sb(1)···S(2)···Sb(2)	115.59(2)	Sb(2)···S(4)···Sb(1′)	118.24(2)
P(1)–S(2)···Sb(2)	98.62(6)	P(2)–S(4)···Sb(1′)	101.83(6)
S(1)–P(1)–S(2)	116.14(9)	S(3)–P(2)–S(4)	115.31(8)
S(1)–P(1)–O(1)	103.3(2)	S(3)–P(2)–O(4)	104.5(2)
S(1)–P(1)–O(2)	109.7(2)	S(3)–P(2)–O(3)	111.0(2)
S(2)–P(1)–O(1)	116.2(2)	S(4)–P(2)–O(4)	114.5(2)
S(2)–P(1)–O(2)	108.0(2)	S(4)–P(2)–O(3)	109.3(2)
O(1)–P(1)–O(2)	102.6(2)	O(3)–P(2)–O(4)	101.3(2)
P(1)–O(1)–C(51)	127.9(5)	P(2)–O(3)–C(71)	126.4(4)
P(1)–O(2)–C(61)	124.7(4)	P(2)–O(4)–C(81)	122.0(3)
O(1)–C(51)–C(52)	104.1(9)	O(3)–C(71)–C(73)	106.1(6)
O(1)–C(51)–C(53)	116.4(8)	O(3)–C(71)–C(72)	113.9(6)
O(2)–C(61)–C(62)	106.2(7)	O(4)–C(81)–C(82)	107.4(5)
O(2)–C(61)–C(63)	107.8(6)	O(4)–C(81)–C(83)	107.8(6)

Atoms carrying a prime are related to unprimed atoms by the symmetry operation $(1+x, y, z)$.

Fig. 2, is also found in the $\{Sn[S_2P(OPh)_2]_2\}_2$ [16], $[Bi(S_2PPh_2)_3]_2$ [7] and $\{Ag_2[S_2P(OEt)_2]_2\}^{2-}$ [17] structures.

If the four-membered Sb_2S_2 ring of the dimer is opened and the monomeric units rotated, they can be linked into the chain structure of the present compound, which is shown in Fig. 3. Sb···S distances between the monomers, *e* (3.266 Å) and *g* (3.172 Å), are significantly shorter than the sum of the van der Waals' radii. Other examples of phosphorodithioate polymers are known, for example, where polymerisation occurs through either single or double phosphorodithioate bridges

Table 4

Atomic coordinates, with estimated standard deviations in parentheses, for $Ph_2Sb[S_2P(O^iPr)_2]$

Atom	x	y	z	U_{eq}
Sb(1)	0.77707(3)	0.20904(2)	0.27755(2)	0.0413
C(11)	0.8987(4)	0.1408(3)	0.3397(2)	0.0399
C(12)	0.9108(6)	0.0683(3)	0.3250(3)	0.0529
C(13)	0.9796(7)	0.0214(4)	0.3651(4)	0.0670
C(14)	1.0390(6)	0.0460(5)	0.4206(3)	0.0635
C(15)	1.0280(6)	0.1182(5)	0.4354(3)	0.0636
C(16)	0.9592(6)	0.1666(4)	0.3952(3)	0.0561
C(21)	0.8820(5)	0.3102(3)	0.2918(2)	0.0414
C(22)	1.0084(6)	0.3116(4)	0.2863(3)	0.0581
C(23)	1.0734(8)	0.3774(4)	0.2904(4)	0.0674
C(24)	1.0142(8)	0.4412(4)	0.2997(3)	0.0614
C(25)	0.8860(8)	0.4405(4)	0.3050(3)	0.0658
C(26)	0.8217(6)	0.3750(3)	0.3012(3)	0.0568
S(1)	0.6518(1)	0.2320(1)	0.36562(6)	0.0480
S(2)	0.4709(1)	0.3306(1)	0.25747(7)	0.0565
P(1)	0.4782(1)	0.25330(8)	0.31864(6)	0.0421
O(1)	0.3931(4)	0.2641(2)	0.3709(2)	0.0551
C(51)	0.3736(8)	0.3299(6)	0.4040(4)	0.0784
C(52)	0.253(1)	0.3145(9)	0.4332(7)	0.0935
C(53)	0.476(1)	0.3544(8)	0.4460(7)	0.1048
O(2)	0.4236(3)	0.1822(2)	0.2865(2)	0.0518
C(61)	0.4069(6)	0.1124(4)	0.3178(3)	0.0586
C(62)	0.2664(9)	0.1021(6)	0.3164(7)	0.0928
C(63)	0.465(1)	0.0537(5)	0.2841(5)	0.0860
Sb(2)	0.24397(3)	0.26902(2)	0.16456(2)	0.0411
C(31)	0.3121(4)	0.3523(3)	0.1070(2)	0.0410
C(32)	0.2944(7)	0.4245(4)	0.1217(3)	0.0675
C(33)	0.3183(8)	0.4802(5)	0.0824(5)	0.0827
C(34)	0.3645(7)	0.4637(5)	0.0289(5)	0.0714
C(35)	0.3837(7)	0.3931(6)	0.0146(4)	0.0694
C(36)	0.3592(6)	0.3363(4)	0.0532(3)	0.0657
C(41)	0.3531(5)	0.1797(3)	0.1366(2)	0.0401
C(42)	0.4839(5)	0.1853(4)	0.1383(3)	0.0507
C(43)	0.5550(6)	0.1259(4)	0.1250(3)	0.0649
C(44)	0.4991(7)	0.0595(5)	0.1106(4)	0.0699
C(45)	0.3699(7)	0.0528(4)	0.1080(3)	0.0681
C(46)	0.2990(6)	0.1125(4)	0.1216(3)	0.0562
S(3)	0.0724(1)	0.24906(9)	0.07412(6)	0.0463
S(4)	−0.0235(1)	0.14994(8)	0.18836(6)	0.0476
P(2)	−0.0725(1)	0.20631(8)	0.11411(6)	0.0367
O(3)	−0.1680(3)	0.2680(2)	0.1275(2)	0.0446
C(71)	−0.2011(7)	0.3332(4)	0.0904(3)	0.0589
C(72)	−0.270(1)	0.3173(5)	0.0303(4)	0.0819
C(73)	−0.272(1)	0.3819(5)	0.1281(4)	0.0752
O(4)	−0.1530(3)	0.1621(2)	0.0611(2)	0.0422
C(81)	−0.1037(6)	0.0969(4)	0.0332(3)	0.0520
C(82)	−0.187(1)	0.0340(5)	0.0443(5)	0.0769
C(83)	−0.102(1)	0.1127(6)	−0.0329(4)	0.0773

(Figs. 4a–b), triconnective bridges (Fig. 4c) or more complex interactions as in the Pb(S$_2$PEt$_2$)$_2$ structure [18], but the polymerisation in the present compound is unique.

In Ph$_2$SbS$_2$P(O^{i}Pr)$_2$, the fully bonded sulphur atom in each molecule is *ca.* 2.54 Å from antimony but both the chelate (3.934 Å) and bridging (3.266 Å) distances to Sb(1) are weaker than those (3.684 and 3.172 Å, respectively) at Sb(2), again pointing to differences in the two molecules. With these longer contacts, antimony becomes five-coordinate with distorted square pyramidal geometry. The basal atoms at Sb(1) are C(11), S(1), S(2) and S(4′) (at Sb(2) the corresponding atoms are C(31), S(3), S(4) and S(2′)) and the basal angles sum to 360.0 and 359.1°, respectively. The individual angles, however, deviate markedly from the ideal 90° values, ranging from *ca.* 60° for the chelate angle to 134° for that between S(2) (S(4)) and S(4′) (S(2′)). The second phenyl group occupies the apical position in both molecules and angles to the basal atoms are much closer to 90° ideal.

As an alternative description of the antimony geometry, deviations of the five atoms forming the base of the pyramid from the best mean plane through these atoms are: 0.046 Sb(1), −0.017 C(11), −0.003 S(1), −0.014 S(2) and −0.012 Å S(4′) for the first molecule and 0.148 Sb(2), −0.119 C(31), −0.005 S(2′), 0.056 S(3) and −0.080 Å S(4) for the second. In each case the antimony atom is displaced from the plane towards the apical phenyl group, but it is debatable whether this distortion is sufficiently large to indicate stereochemical activity of the antimony lone pair of electrons.

Experimental

Phosphorodithioic acids were obtained by the published method [23] by treating P$_4$S$_{10}$ with the appropriate alcohol, and their ammonium salts were made by passing anhydrous ammonia through a benzene solution of the acid.

Preparation of diphenylantimony(III) chloride. Hydrated diphenylantimony(V) trichloride (8.0 g, 0.02 mol), obtained from the phenylation of SbCl$_5$ with Ph$_4$Sn [24], was dissolved under reflux in ethanol (6 ml) and 10% hydrochloric acid (30 ml). Anhydrous tin(II) chloride (4 g) was added and the mixture refluxed until the solution became clear. An oil separated on cooling and crystallised on standing overnight. The solid Ph$_2$SbCl was filtered off, washed with dilute hydrochloric acid and ethanol (3 ml), and dried in a vacuum. Yield, 5.6 g, 90%, M.p. 63–65°C. Anal. Found: C, 45.8; H, 3.0. C$_{12}$H$_{10}$ClSb calc.: C, 46.3; H, 3.2%.

Preparation of diphenylantimony(III) acetate. Diphenylantimony(III) chloride was refluxed with glacial acetic acid and white crystals separated when the solution was cooled, giving a quantitative yield of the required product. M.p. 133°C. Anal. Found: C, 49.9; H, 3.8. C$_{14}$H$_{13}$O$_2$Sb calc.: C, 50.2; H, 3.9%.

Preparation of diphenylantimony(III) dimethylphosphorodithioate. Dimethylphosphorodithioic acid (0.87 g, 5.5 mmol) was added to a solution of diphenylantimony acetate (1.67 g, 5 mmol) in anhydrous benzene (50 ml), and the mixture stirred under reflux for 2 h. Filtration of the yellow solution was followed by removal of the solvent under vacuum to give a yellow oil. This was dissolved in acetonitrile and on cooling the solution white crystals of the required product were obtained. Yield, 1.1 g, 51%. M.p. 104–106°C. Anal. Found: C, 38.8; H, 3.7. C$_{14}$H$_{16}$O$_2$PS$_2$Sb calc.: C, 38.8; H, 3.7%.

Preparation of diphenylantimony(III) diethylphosphorodithioate. This was prepared similarly in 89% yield from diphenylantimony acetate and the free acid in benzene solution. Removal of the solvent gave a yellowish oil, which was soluble in a range of solvents including benzene, chloroform and carbon disulphide, but it was not possible to obtain crystals of the material either by cooling or slow evaporation of the solvent. The compound was therefore characterised only spectroscopically.

Preparation of diphenylantimony(III) di-iso-propylphosphorodithioate. A solution of diphenylantimony acetate (0.67 g, 2 mmol) in benzene (15 ml) was added to a suspension of ammonium di-isopropylphosphorodithioate (0.46 g, 2 mmol) and the mixture was stirred under reflux for 2 h. The resulting ammonium acetate was filtered to give a clear solution, which was evaporated to dryness under vacuum. The residue was taken up in hot anhydrous acetone which on cooling gave colourless crystals of the product. Yield, 0.83 g, 85%. M.p. 50–52°C. Anal. Found: C, 44.1; H, 4.8, $C_{18}H_{24}O_2PS_2Sb$ calc.: C, 44.2; H, 4.9%.

Preparation of diphenylantimony(III) diphenylphosphorodithioate. The reaction between diphenylphosphorodithioic acid and diphenylantimony acetate in equimolar proportions was carried out in benzene solution as described above for the methyl derivative. Again a yellowish oil was obtained in good yield (91%), but it was not possible to obtain crystals of the compound and it was characterised only by spectroscopy.

Crystal structure determination

Crystal data. $C_{18}H_{24}O_2PS_2Sb$, M 488.8, monoclinic, $a = 10.714(5)$, $b = 18.205(7)$, $c = 22.010(7)$ Å, $\beta = 97.44(2)°$, $U = 4256.9$ Å^3, $Z = 8$, $D_c = 1.52$ g cm^{-3}, $F(000) = 1968$, space group $P2_1/c$, Mo-K_α radiation, $\lambda = 0.7107$ Å, μ(Mo-K_α) 15.8 cm^{-1}, crystal size $0.5 \times 0.3 \times 0.08$ mm^3.

Structure determination. Data were collected on a Hilger and Watts four-circle diffractometer for 7774 reflections of which 5789 with $I > 3\sigma(I)$ were considered observed. The data were corrected for Lorentz and polarisation effects, but an absorption correction was not considered necessary. Crystallographic calculations used the CRYSTALS programs [25] and scattering factors, including the imaginary part for non-hydrogen atoms, were those for neutral atoms [26]. The asymmetric unit contains two complete molecules and positions for the two independent antimony atoms were obtained from a three dimensional Patterson synthesis. Subsequent Fourier syntheses revealed positions for the other non-hydrogen atoms. Refinement by full matrix least squares gave convergence at $R = 10.2\%$ with isotropic thermal parameters. In subsequent cycles of refinement with anisotropic parameters, each molecule was refined in a separate block. A four-coefficient Chebyshev weighting scheme was applied and the hydrogen atoms were placed at their calculated positions. Hydrogen atom positions were refined with isotropic thermal parameters in the final cycles of refinement and final convergence occurred at $R = 4.20\%$ ($R_w = 4.16\%$). Except in the vicinity of the heavy atoms, a final difference Fourier synthesis showed no peaks with an intensity greater than 0.4 e Å^{-3}. Refined values for the atomic coordinates are given in Table 4. A complete list of bond lengths and angles and lists of anisotropic thermal parameters, hydrogen atom positions, and observed and calculated structure factors can be obtained from DBS.

References

1 I. Haiduc, Rev. Inorg. Chem., 3 (1981) 353.
2 K.C. Molloy and J.J. Zuckerman, Acc. Chem. Res., 16 (1983) 386.
3 R.C. Mehrotra, G. Srivastava and B.P.S. Chauhan, Coord. Chem. Rev., 55 (1984) 207.
4 M.J. Begley, D.B. Sowerby and I. Haiduc, J. Chem. Soc., Chem. Commun., (1980) 64.
5 R.O. Day, M.M. Chauvin and W.E. McEwen, Phosphorus Sulfur, 8 (1980) 127.
6 D.B. Sowerby, I. Haiduc, A. Barbul-Rusu and M. Salajan, Inorg. Chim. Acta, 68 (1983) 87.
7 M.J. Begley, D.B. Sowerby and I. Haiduc, J. Chem. Soc., Dalton Trans., (1987) 145.
8 C. Silvestru, L. Silaghi-Dumitrescu, I. Haiduc, M.J. Begley, M. Nunn and D.B. Sowerby, J. Chem. Soc., Dalton Trans., (1986) 1031.
9 R.K. Gupta, A.K. Rai, R.C. Mehrotra, V.K. Jain, B.F. Hopkins and E.R.T. Tiekink, Inorg. Chem., 24 (1985) 3280.
10 R. Karra, Y.P. Singh and A.K. Rai, Phosphorus, Sulfur and Silicon, 45 (1989) 145.
11 C. Silvestru, C. Socaciu, A. Bara and I. Haiduc, Anticancer Res., 10 (1990) 803.
12 I. Haiduc and C. Silvestru, Organometallics in Cancer Chemotherapy, Vol. 1, Main Group Metal Compounds, CRC Press, Boca Raton, FL, 1989, p. 129; I. Haiduc and C. Silvestru, Coord. Chem. Rev., 99 (1990) 253.
13 M. Grayson and E.J. Griffith, Topics in Phosphorus Chemistry, Vol. 6, Wiley, New York, 1969.
14 K.C. Molloy, M.B. Hossain, D. van der Helm, J.J. Zuckerman and I. Haiduc, Inorg. Chem., 18 (1979) 3507.
15 R.K. Chadha, J.E. Drake and A.B. Sarkar, Inorg. Chem., 26 (1987) 2885.
16 J.L. Lefferts, K.C. Molloy, M.B. Hossain, D. van der Helm and J.J. Zuckerman, Inorg. Chem., 21 (1982) 1410.
17 M.G.B. Drew, R.J. Hobson, P.P.E.M. Mumba and D.A. Rice, Inorg. Chim. Acta, 142 (1988) 301.
18 G. Svensson, Ph.D. Thesis, University of Lund (Sweden), 1989.
19 T. Ito, T. Igarashi and H. Hagihara, Acta Crystallogr., Sect. B, 25 (1969) 2303.
20 S.L. Lawton, Inorg. Chem., 10 (1971) 328.
21 Y. Watanabe, Sci. Pap. Inst. Phys. Chem. Res., 74 (1980) 150.
22 S.L. Lawton and G.T. Kokotailo, Inorg. Chem., 11 (1972) 363.
23 J.L. Lefferts, K.C. Molloy, J.J. Zuckerman, I. Haiduc, C. Guta and D. Ruse, Inorg. Chem., 19 (1980) 1662.
24 I. Haiduc and C. Silvestru, Inorg. Synth., 23 (1985) 194.
25 J.R. Carruthers, CRYSTALS, the Oxford Crystallographic Programs, 1975.
26 International Tables for X-ray Crystallography, Vol. 4, Kynoch, Birmingham, 1974.