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Antimony(III) Diorganophosphoro- and Diorganophosphinodithioates: Crystal Structure of $Sb[S_2P(OR)_2]_3$ (R = Me and i-Pr)

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Several antimony(III) tris(dialkylphosphorodithioates) $Sb[S_2P(OR)_2]_3$ (R = Me, Et, i-Pr, n-Bu, i-Bu and sec-Bu) and tris(diorganophosphinodithioates $Sb(S_2PR_2)_3$ (R = Me, Et and Ph) have been prepared by reactions between antimony trichloride and respectively the ammonium and sodium salts of the corresponding acid. The compounds were characterised by infrared and ^1H NMR spectroscopy and the structures of two phosphorodithioates (R = Me and i-Pr) have been determined by X-ray diffraction. Each antimony atom is surrounded by six sulphur atoms from three anisobidentate phosphorodithioate ligands with three atoms at 2.528 and three at 3.010 Å. The overall arrangement is distorted octahedral and although this geometry is consistent with stereochemical activity of the 5s electrons at antimony, it cannot be interpreted as direct proof.

Introduction

Antimony(III) derivatives of potentially bidentate dithiophosphorus ligands are of interest in view of the possible stereochemical consequences of the presence of the lone pair of electrons at the central atom. The structure of antimony(III) tris(diethyldithiocarbamate) [1] for example, can surely be interpreted, in terms of the distortion of the octahedral geometry about antimony, as being consistent with the presence of the lone pair above one of the triangular faces of an SbS_6 octahedron. In view of our interest in the structural chemistry of antimony [2] and dithiophosphorus ligands, [3] we have investigated the antimony(III) phosphorodithioates and phosphinodithioates. Among the first results obtained was the unusual pentagonal pyramidal co-ordination in the structure of antimony(III) tris(diphenylphosphinodithioate) $Sb(S_2PPh_2)_3$, [4] where again it is possible to interpret the structure in terms of stereochemical activity of the lone pair. Here, however, the electron pair is located at the seventh coordination site, *i.e.*, an axial position, in a pentagonal bipyramid.

Antimony(III) phosphoro- and phosphinodithioates have surprisingly been little investigated, and although the preparation [5, 6] and several uses, *e.g.*, as lubricant additives [7] or catalyst decontaminants in petroleum cracking [8] have been reported, no spectral characterisation nor structure determination has been reported. We describe here the preparation and spectra of a number of antimony(III) phosphoro- and phosphinodithioates and the X-ray structures of $Sb[S_2P(OR)_2]_3$ where R = Me and i-Pr. Since completion of this work the structure of the ethyl derivative has been published [9].

Results and Discussion

Antimony(III) dialkylphosphorodithioates were prepared by the reaction of antimony(III) chloride with ammonium dialkylphosphorodithioates, in absolute ethanol, as yellow crystals or liquids:

$$SbCl_3 + 3NH_4S_2P(OR)_2 \rightarrow Sb[S_2P(OR)_2]_3 + 3NH_4Cl \qquad (1)$$

R = Me, Et, i-Pr, n-Bu, i-Bu and sec-Bu

Ammonium salts were preferred as, unlike sodium dialkylphosphorodithioates, they are not hygroscopic and are consequently easier to handle.

The melting points and yields are shown in Table I. No attempts were made to improve the yields although complete evaporation of the filtrate, after

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separation of the first large crop of crystals, yielded further product of lower purity. (This was not included in yield calculation.)

TABLE I. Yields and Melting Points of Compounds Prepared.

Compound R	Yield %	M.p. °C	Observations
Phosphorodithioates $Sb[S_2P(OR)_2]_3$			
Me	54	95–6	(lit. 96–6.5°) [5a]
Et	48	55–6	(lit. 56–7°) [5a]
i-Pr	53	78–80	(lit. 79–80°) [5a, 5b]
n-Bu	50	oil	
i-Bu	68	123–4	(lit. 123–4°) [5b]
sec-Bu	64	45–50	
Phosphinodithioates $Sb(S_2PR_2)_3$			
Me	50	67–8	
Et	52	80–2	
Ph	89	200–2	

TABLE II. Infrared Spectral Data.

Compound	$\nu_{sym}PS_2$	$\nu_{asym}PS_2$	Other vibrations	
Phosphorodithioates $Sb[S_2P(OR)_2]_3$			ν_{P-OR}	ν_{C-O}
R = Me	500	640	1015	1190
Et	515	635	1020	1170
i-Pr	520	640	990	1150
n-Bu	535	645	1000	1150
i-Bu	545	635	1000	1135
sec-Bu	520	635	980	1130
Phosphinodithioates $Sb(S_2PR_2)_3$			ν_{P-R}	
R = Me	440	550	690 760	1390
Et	470	580	730 780	1400
Ph	475, 550	615, 640	1100	1440

The phosphinodithioates were prepared using either the free acid (R = Ph) or the sodium salt (R = Me, Et):

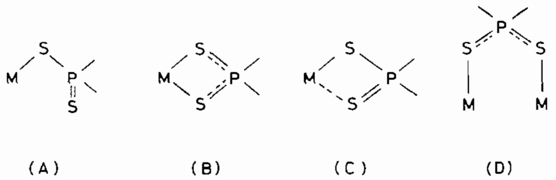
$$SbCl_3 + 3MS_2PR_2 \rightarrow Sb(S_2PR_2)_3 + 3MCl \qquad (2)$$

M = H or Na; R = Me, Et, Ph

The dithiophosphinates are yellow crystals, with the melting points shown in Table I.

Both types of compound described here are stable in air, and soluble in common organic solvents. Prolonged storage results in partial decomposition with formation of Sb_2S_3.

In discussing the structures of antimony(III) derivatives of dithiophosphorus ligands one should take into account the possible co-ordination patterns of these ligands, [3] which can behave as monodentate (A), isobidentate (B), anisobidentate (C) or bridging (D);



Monodentate behaviour is rare, but is known in $Ph_3Sn-SP(S)(OEt)_2$ [10] whereas iso- and aniso-bidentate co-ordination are found in the closely related organotin compounds $Ph_2Sn[S_2P(OPr^i)_2]_2$ [11] and $Ph_2Sn[S_2P(OEt)_2]_2$ [12] respectively. The ligand is again anisobidentate in the thiophosphinate $Sb(S_2PPh_2)_3$ [4] while in $Sb[S_2P(OEt)_2]_3$ [9], the accuracy of the P–S bond distances is too low to distinguish between (B) and (C) although type (C) co-ordination is suggested from the different Sb–S distances.

TABLE III. ^1H NMR Spectral Data (τ in ppm relative to TMS).[a]

R in $Sb[S_2P(OR)_2]_3$	O–C*H*	*O–C–CH*	O–C–C–C*H*
Me	6.42 (d) 6H $^3J_{POCH}$ 16 Hz		
Et	6.03 (dq) 12H $^3J_{HCCH}$ 7 Hz $^3J_{POCH}$ 11 Hz	8.80 (t) 18H $^3J_{HCCH}$ 7 Hz	
i-Pr	5.07 (se) 3H $^3J_{HCCH}$ 6 Hz	8.47 (d) 36H $^3J_{HCCH}$ 6 Hz	
i-Bu	6.24 (dd) 6H $^3J_{HCCH}$ 7 Hz $^3J_{POCH}$ 9 Hz	8.19 (m) 3H $^3J_{HCCH}$ 6 Hz	9.23 (d) 18H $^3J_{HCCH}$ 6 Hz

[a] Abbreviations: d = doublet; dq = double quartet; t = triplet; se = septet; q = quartet; m = multiplet.

Infrared Spectra

The infrared spectra of antimony(III) dialkylphosphorodithioates exhibit absorption bands at 1020–980 cm^{-1} (νP–OR), 1190–1130 cm^{-1} (νC–OR), 545–500 cm^{-1} ($\nu_{sym}PS_2$) and 645–635 cm^{-1} ($\nu_{asym}PS_2$), These data cannot, however, distinguish between the various structural possibilities, since it is impossible to assign with certainty the P–S and P=S stretching frequencies. Thus, bands associated with P–S stretching modes appear in the same region for both transition metal complexes (which contain chelating, bidentate ligands of type (B)) and the free acids $(RO)_2P(S)SH$ and their esters $(RO)_2P(S)SR'$ (which contain groups of type (A) with M = H or R') [13]. The frequencies observed in the ranges 560–500 cm^{-1} and 670–630 cm^{-1}, probably corresponding to $\nu_{sym}PS_2$ and $\nu_{asym}PS_2$ [14, 15] are little sensitive to the nature of the group connected to sulphur.

In the spectra of phosphinodithioates the bands due to P–C vibrations are observed in addition to those due to $\nu_{sym}PS_2$ and $\nu_{asym}PS_2$. The infrared spectral data are listed in Table II.

Normal co-ordinate analyses of the dimethylphosphinodithioato group, both as an anion in the sodium salt $Na^+S_2PMe_2^-$ [16] and as a ligand in a nickel(II) chelate $Ni(S_2PMe_2)_2$ [17] have shown that there is extensive coupling between the P–C and P–S vibrations. A similar analysis of the infrared spectrum of $Ni[S_2P(OR)_2]_2$ (R = Me, Et) [18] showed that vibrations in the 544–520 cm^{-1} region, are also the result of ν_{sym}PS and ν_{sym}PO coupling. Therefore, little structural information concerning the structure of the dithiophosphorus ligands can be derived from the infrared spectra.

Nuclear Magnetic Resonance Spectra

The ^1H NMR spectra of antimony(III) phosphorodithioates are listed in Table III. The ^1H NMR spectrum of $Sb(S_2PEt_2)_3$ contains a double quartet at τ = 7.78 ppm (J_{HH} = 6 Hz; J_{PH} = 10 Hz) due to methylene protons; the signal is split by both *CH*–*CH* and *P*–C–*H* spin-spin coupling. In the spectrum of $Sb(S_2PPh_2)_3$ a multiplet at τ = 2.24–2.63 ppm is observed.

Although the NMR spectra confirm the nature of the compounds investigated, they provide no information about the details of the coordinated ligands. Therefore, X-ray diffraction was used to establish the structural details.

X-ray Structures

Structures have been determined for two of the compounds reported here, *i.e.*, $Sb[S_2P(OR)_2]$ where R = Me and i-Pr. The i-propyl compound was chosen in addition to the methyl derivative as in several cases i-propylphosphorodithioates have structures markedly different from those of the lower alkyl analogues. Such is the case for $Ph_2Sn[S_2P(OR)_2]_2$ R = Et [12] and i-Pr [11], $Pb[S_2P(OR)_2]_2$ R = Et [19] and i-Pr [20], and $Zn[S_2P(OR)_2]_2$ R = Et [21] and i-Pr [22].

Bond distances and angles are summarised in Tables IV and V for the methyl compound and in Tables VI and VII for the i-propyl derivative. Diagrams showing the molecular structure and atom numbering scheme are in Figs. 1 and 2. In each case

TABLE IV. Bond Lengths (A.U.) for $Sb[S_2P(OMe)_2]_3$, with Estimated Standard Deviations in Parentheses.

Sb1	S1	2.522(1)	Sb1	S2	3.008(2)
Sb1	S3	2.535(2)	Sb1	S4	3.006(2)
Sb1	S5	2.531(2)	Sb1	S6	3.002(2)
S1	P1	2.029(2)	P1	S2	1.941(3)
P1	O1	1.558(5)	P1	O2	1.561(5)
O1	C1	1.437(9)	O2	C2	1.442(9)
S3	P2	2.036(2)	P2	S4	1.941(2)
P2	O3	1.572(5)	P2	O4	1.566(5)
O3	C3	1.432(8)	O4	C4	1.425(10)
S5	P3	2.033(2)	P3	S6	1.927(3)
P3	O5	1.551(7)	P3	O6	1.545(8)
O5	C5	1.36(2)	O6	C6	1.21(2)

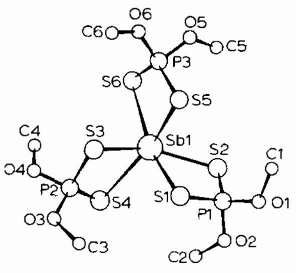


Fig. 1. Molecular structure and atom numbering scheme for $Sb[S_2P(OMe)_2]_3$.

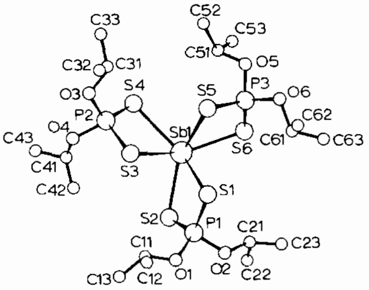


Fig. 2. Molecular structure and atom numbering scheme for $Sb[S_2P(OPr^i)_2]_3$.

TABLE V. Bond Angles (Deg) for $Sb[S_2P(OMe)_2]_3$ with Estimated Standard Deviations in Parentheses.

S1	Sb1	S2	72.64(5)	S1	Sb1	S3	88.50(6)
S1	Sb1	S4	90.21(6)	S1	Sb1	S5	88.17(5)
S1	Sb1	S6	160.76(6)	S2	Sb1	S3	160.90(6)
S2	Sb1	S4	103.67(6)	S2	Sb1	S5	93.83(7)
S2	Sb1	S6	106.43(7)	S3	Sb1	S4	72.68(6)
S3	Sb1	S5	88.43(6)	S3	Sb1	S6	92.36(7)
S4	Sb1	S5	161.08(6)	S4	Sb1	S6	108.40(6)
S5	Sb1	S6	72.66(6)				
Sb1	S1	P1	93.44(7)	Sb1	S2	P1	81.50(8)
S1	P1	S2	112.3(1)	S1	P1	O1	108.8(2)
S1	P1	O2	108.5(2)	S2	P1	O1	115.1(2)
S2	P1	O2	114.1(2)	O1	P1	O2	96.9(3)
P1	O1	C1	121.0(5)	P1	O2	C2	120.4(5)
Sb1	S3	P2	93.10(8)	Sb1	S4	P2	81.74(8)
S3	P2	S4	112.4(1)	S3	P2	O3	108.1(2)
S3	P2	O4	108.6(2)	S4	P2	O3	115.1(2)
S4	P2	O4	114.5(2)	O3	P2	O4	97.0(3)
P2	O3	C3	120.0(4)	P2	O4	C4	120.3(5)
Sb1	S5	P3	92.86(8)	Sb1	S6	P3	81.65(8)
S5	P3	S6	112.8(1)	S5	P3	O5	107.8(3)
S5	P3	O6	109.7(3)	S6	P3	O5	115.5(3)
S6	P3	O6	115.0(4)	O5	P3	O6	94.4(5)
P3	O5	C5	123.5(10)	P3	O6	C6	133.4(12)

TABLE VI. Bond Lengths (A.U.) for $Sb[S_2P(O\text{-}i\text{-}Pr)_2]_3$, with Estimated Standard Deviations in Parentheses.

Sb1	S1	2.521(4)	Sb1	S2	3.031(5)	S3	P2	2.034(6)	P2	S4	1.932(7)
Sb1	S3	2.531(4)	Sb1	S4	3.013(4)	P2	O3	1.55(1)	P2	O4	1.64(1)
Sb1	S5	2.519(4)	Sb1	S6	3.000(5)	O3	C31	1.46(2)	C31	C32	1.39(4)
						C31	C33	1.45(4)	O4	C41	1.35(3)
S1	P1	2.029(6)	P1	S2	1.945(6)	C41	C42	1.34(5)	C41	C43	1.37(4)
P1	O1	1.58(1)	P1	O2	1.58(1)	S5	P3	2.044(6)	P3	S6	1.949(7)
O1	C11	1.40(2)	C11	C12	1.42(3)	P3	O5	1.59(1)	P3	O6	1.58(1)
C11	C13	1.45(3)	O2	C21	1.41(2)	O5	C51	1.46(2)	C51	C52	1.49(3)
C21	C22	1.41(4)	C21	C23	1.45(4)	C51	C53	1.48(3)	O6	C61	1.47(2)
						C61	C62	1.46(3)	C61	C63	1.37(3)

TABLE VII. Bond Angles (Deg) for $Sb[S_2P(O\text{-}i\text{-}Pr)_2]_3$, with Estimated Standard Deviations in Parentheses.

S1	Sb1	S2	71.7(1)	S1	Sb1	S3	87.7(1)
S1	Sb1	S4	159.5(1)	S1	Sb1	S5	86.8(1)
S1	Sb1	S6	95.5(1)	S2	Sb1	S3	93.7(2)
S2	Sb1	S4	111.1(1)	S2	Sb1	S5	158.4(1)
S2	Sb1	S6	105.9(2)	S3	Sb1	S4	72.0(1)
S3	Sb1	S5	88.0(2)	S3	Sb1	S6	160.3(2)
S4	Sb1	S5	90.0(2)	S4	Sb1	S6	102.8(2)
S5	Sb1	S6	72.7(1)				
Sb1	S1	P1	94.9(2)	Sb1	S2	P1	82.1(2)
Sb1	S3	P2	93.8(2)	Sb1	S4	P2	82.2(2)
Sb1	S5	P3	93.8(2)	Sb1	S6	P3	82.2(2)
S1	P1	S2	111.2(3)	S1	P1	O1	108.9(6)

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TABLE VII. *(continued)*

S1	P1	O2	107.8(6)	S2	P1	O1	114.7(6)
S2	P1	O2	116.3(6)	O1	P1	O2	96.9(7)
P1	O1	C11	124.9(13)	O1	C11	C12	113(2)
O1	C11	C13	110(2)	C12	C11	C13	111(2)
P1	O2	C21	121.9(13)	O2	C21	C22	105(2)
O2	C21	C23	111(3)	C22	C21	C23	112(3)
S2	P2	S4	111.6(3)				
S3	P2	O3	109.2(6)	S3	P2	O4	107.6(6)
S4	P2	O3	114.0(6)	S4	P2	O4	116.6(7)
O3	P2	O4	96.7(7)	P2	O3	C31	123.7(12)
O3	C31	C32	105(2)	O3	C31	C33	114(2)
C32	C31	C33	110(3)	P2	O4	C41	133(2)
O4	C41	C42	114(4)	O4	C41	C43	107(3)
C42	C41	C43	116(4)				
S5	P3	S6	111.2(3)	S5	P3	O5	108.2(5)
S5	P3	O6	109.0(5)	S6	P3	O5	115.1(5)
S6	P3	O6	115.6(5)	O5	P3	O6	96.7(6)
P3	O5	C51	120.9(11)	O5	C51	C52	108(2)
O5	C51	C53	105(2)	C52	C51	C53	116(2)
P3	O6	C61	121.0(10)	O6	C61	C62	110(2)
O6	C61	C63	111(2)	C62	C61	C63	111(2)

the antimony atom is surrounded by six sulphur atoms from three chelating phosphorodithioate groups with three short (primary) and three long (secondary) Sb–S distances; the ligands are thus anisobidentate. Within the limits of the determination, the primary and secondary bonds in both compounds are equal, mean values are 2.528 and 3.010 Å respectively.

Unsymmetrical chelation is also reflected in the P–S bond distances which fall into two classes; the short distances (mean 1.939 Å) are associated with sulphur atoms forming long Sb–S interactions while the longer P–S bonds (mean 2.034 Å) are associated with sulphur atoms forming short bonds to antimony. For both compounds the angles between the primary Sb–S bonds are close to 90°, as often found in neutral Sb(III) compounds, but in the i-propyl compound the angles are closed up (mean 87.5°) over those in the methyl analogue (mean 88.4°).

The two P–O bonds at a given phosphorus atom are equal, except for those at P(2) in the i-propyl derivative where the distances are 1.55 and 1.64 Å. In both compounds the mean P–O distance is 1.57 Å. The difference at P(2) is reflected in values of 123.7 and 133° for the appropriate P–O–C angles. However, there is a similar large difference between the angles at P(3) in the methyl compound (123.5 and 133.4°), but the corresponding P–O distances are equal; minor changes in packing are probably responsible for these effects.

The angle at antimony in a given SbS_2P ring has a mean value of 72.4°, as expected with a 'short-bite' ligand, but the S–P–S angles in the methyl compound are somewhat greater (mean 112.5°) than those for the i-propyl (mean 111.3°).

The arrangement of the six sulphur atoms about each antimony atom is best described as distorted octahedral and the diagrams in Figs. 1 and 2 are projections perpendicular to the plane of the primary bonded sulphur atoms, *i.e.*, S(1), S(3) and S(5).

The triangular faces formed by S(1), S(3) and S(5) and S(2), S(4) and S(6) are almost parallel, the angles between them are 178.7 and 177.4° for the methyl and i-propyl derivatives respectively. In each case, the distance between the two planes is 2.656 Å, but in the i-propyl compound the antimony atom is displaced *ca.* 0.02 Å further from the S(1), S(3), S(5) plane (1.519 compared with 1.501 Å) in the methyl compound) thus, accounting for the smaller angles at antimony between the primary bonded sulphur atoms in the i-Pr structure.

Distortion of the octahedron about antimony does not maintain strict three-fold symmetry as shown by a projection of the six sulphur atoms onto a plane. Although the angles between primary bonded sulphurs are within 0.5° of 120°, the second set of sulphur atoms are much less regular. For example, in the methyl compound, the angles between S(2) and S(4), S(2) and S(6) and S(4) and S(6) are 116.4, 121.3 and 122.3°; corresponding angles for the i-propyl compound are 124.0, 121.0 and 115.0°. Twist angles between S(1) and S(2), S(3) and S(4) and S(5) and S(6) then can define the deviation from trigonal symmetry and have values of 43.2, 46.8 and 44.7° for methyl and 43.0, 46.7 and 41.2° for the i-propyl compound.

This type of co-ordination polyhedron has been observed in a number of related antimony(III) complexes with 'short-bite' chelating ligands, including the diethylphosphorodithioate [9] and the diethyldithiocarbamate [1]. These compounds are all formally based on a central antimony atom surrounded by seven pairs of electrons, if it is assumed that the 5s electrons of antimony are stereochemically active. The lone pair then occupies the capping position above one of the triangular faces of an octahedron and the presence of longer Sb–S distances can be rationalised on the basis of interaction between S(2), S(4), and S(6) with the lone pair. On the other hand, stereochemical activity of the lone pair is not necessary to rationalise these structures as a trigonally distorted octahedral arrangement would be highly probable as a direct consequence of anisobidentate character of the dithiophosphate ligand. It is significant that the pentagonal pyramidal structure [4] of the closely related antimony(III) diphenyldithiophosphinate, $Sb(S_2PPh_2)_3$, is based on an alternative polyhedron for a central atom associated with seven pairs of electrons, *i.e.*, a pentagonal bipyramidal. But again, this is not proof that the 5s electrons of antimony are stereochemically active as it is possible to envisage the observed stereochemistry as arising from a combination of factors such as the anisobidentate character of the ligand and the necessity of minimising intra- and inter-molecular interactions. The different structures for the antimony derivatives of $S_2P(OR)_2$ and S_2PPh_2 ligands could well be a consequence of the different steric requirements of the alkoxy and phenyl substituents at phosphorus.

For both compounds there are no intermolecular interactions closer than the sum of the appropriate Van der Waals' radii and the structures consist of discrete molecules.

Experimental

The salts of phosphoro- and phosphino-dithioic acids were prepared following the literature methods. Infrared spectra were recorded as KBr mulls using a Carl Zeiss Jena UR-20 instrument and the ^1H NMR spectra on a Tesla BS 487 spectrometer, in carbon tetrachloride, with tetramethylsilane as internal standard.

All compounds gave correct elemental analyses. Carbon and hydrogen were determined by microcombustion and antimony by X-ray fluorescence, *e.g.*, for $Sb[S_2P(OEt)_2]_3$Sb calcd. 17.97, found 17.62%; for $Sb[S_2P(OPr^i)_2]_3$Sb calcd. 15.98, found 15.50%.)

Preparation of $Sb[S_2P(OMe)_2]_3$

A solution of 2.3 g (0.01 mol) $SbCl_3$ in 15 ml absolute ethanol was treated with 5.3 g (0.03 mol) ammonium dimethylphosphorodithioate, dissolved in 25 ml ethanol. A precipitate of ammonium chloride and antimony dimethylphosphorodithioate was formed. The mixture was stirred for 1 hr, after which the precipitate was filtered, dried and extracted with carbon tetrachloride. Evaporation, followed by recrystallization from acetone, gave 2 g (34%) of pale yellow crystals, m.p. 95–6 °C. A similar procedure was used for the preparation of $Sb[S_2P(OBu^i)_2]_3$.

Preparation of $Sb[S_2P(OR)_2]_3$ ($R = Et, Pr^i, Bu^s$)

In all cases a solution containing 0.03 mol of ammonium dialkylphosphorodithioate (R = Et 6.1 g; R = i-Pr 7.0 g; R = sec-Bu 7.8 g) dissolved in 25 ml absolute ethanol was treated with 2.3 g (0.01 mol) of $SbCl_3$ dissolved in 15 ml absolute ethanol. The precipitate of ammonium chloride was filtered and the filtrate evaporated to give the antimony dialkylphosphorodithioate (R = Et 3.3 g, 48%; R = i-Pr 4.0 g, 52%; R = sec-Bu 5.5 g, 65% yield).

With R = n-Bu, the product was a yellow oil which could not be crystallized.

Preparation of $Sb(S_2PMe_2)_3$

A solution of 2.3 g (0.01 mol) $SbCl_3$ in 15 ml absolute ethanol was treated with 4.5 g (0.03 mol) sodium dimethyldithiophosphinate in 25 ml absolute ethanol. The NaCl precipitate was filtered and the solution evaporated to dryness. The residue was recrystallized from acetone to give 2.5 g (50%) of yellow crystals, m.p. 67–8 °C.

Preparation of $Sb(S_2PEt_2)_3$

Separate solutions of $SbCl_3$ (1.5 g, 0.0065 mol) and $Na_2S_2PEt_2 \cdot 2H_2O$ (4.2 g, 0.019 mol) dissolved in absolute ethanol (25 ml each) were mixed. The yellow precipitate, which separated was filtered and extracted with carbon tetrachloride. Evaporation of the solution gave a solid which on recrystallisation yielded 2.5 g (52%) of yellow crystals, m.p. 78–80 °C.

Preparation of $Sb(S_2PPh_2)_3$

A solution of 1.5 g (0.0065 mol) $SbCl_3$ in 15 ml absolute ethanol was mixed with 4.91 g (0.019 mol) diphenyldithiophosphinic acid in the same solvent (50 ml) and a yellow precipitate deposited immediately. This was filtered, dried and recrystallized from carbon tetrachloride to give 5.1 g (89%) of yellow crystals, m.p. 200–2 °C.

Structure Determinations

Crystal Data

Formula	$Sb[S_2P(OMe)_2]_3$ $C_8H_{18}O_6P_3S_6Sb$	$Sb[S_2P(OPr^i)_2]_3$ $C_{18}H_{42}O_6P_3S_6Sb$
M	593.4	761.4
a (Å)	9.313(5)	11.293(5)
b (Å)	8.506(4)	10.659(5)
c (Å)	28.528(8)	31.195(8)
β (deg)	99.09(2)	97.22(2)
U (Å^3)	2232	3725
Z	4	4
D_c (g cm^{-3})	1.76	1.36
F(000)	1176	1560
Space Group	$P2_1/n$	$P2_1/n$
μ (cm^{-1})	20.1	12.2
Observed reflections	2787	3396
Mo-K$_\alpha$ radiation $\lambda = 0.7107$ Å		

A Hilger and Watts four-circle diffractometer was used to collect the intensity data and reflections with $I > 3\sigma(I)$ were considered observed. The data were corrected for Lorentz and polarisation effects but no absorption correction was necessary. Data reduction and subsequent crystallographic calculations used the CRYSTALS programs [23]; scattering factors were those for neutral atoms [24]. The structure was solved by Patterson and Fourier methods and refined by full matrix least squares to R 8.7% (13.0) with isotropic and R 4.3% (6.6) with anisotropic thermal parameters. The figures in parentheses refer to the i-propyl derivative. Hydrogen atoms were placed at their calculated positions but were not refined in subsequent cycles. Final convergence was at R 3.95 (6.4) after using a four coefficient Chebyshev weighting scheme.

Atomic co-ordinates including the calculated hydrogen atom positions are included in Tables VIII and X for the methyl and i-propyl derivatives respectively, while anisotropic thermal parameters are given in Tables IX and XI. Copies of the observed and calculated structure factors can be obtained from the authors (D.B.S.).

TABLE VIII. Fractional Coordinates ($\times 10^4$) for $Sb[S_2P(OMe)_2]_3$.

Atom	x/a	y/b	z/c	U (iso)	Atom	x/a	y/b	z/c	U (iso)
Sb(1)	5744.9(4)	5805.2(5)	3858.9(1)		O(6)	1969(8)	8928(10)	3274(4)	
S(1)	8049(2)	5694(2)	3499.8(6)		C(6)	2423(18)	10193(19)	3422(8)	
P(1)	7692(2)	3449(2)	3269.8(6)		H(11)	7215	3930	2052	50
S(2)	5852(2)	2629(2)	3402.1(8)		H(12)	6885	5273	2430	50
O(1)	7908(5)	3356(6)	2740(2)		H(13)	5903	3675	2363	50
C(1)	6912(10)	4116(10)	2374(3)		H(21)	10335	1566	4075	50
O(2)	9040(6)	2434(6)	3477(2)		H(22)	9636	3287	4155	50
C(2)	9441(11)	2248(12)	3984(3)		H(23)	8619	1715	4127	50
S(3)	6506(2)	8508(2)	4180.6(6)		H(31)	11110	8554	4738	50
P(2)	7520(2)	7637(2)	4811.6(6)		H(32)	10373	6818	4643	50
S(4)	7476(2)	5357(2)	4831.0(6)		H(33)	9827	8272	4285	50
O(3)	9079(5)	8388(6)	4920(2)		H(41)	5184	8652	5595	50
C(3)	10159(7)	7984(9)	4635(3)		H(42)	5445	6872	5411	50
O(4)	6874(6)	8465(6)	5222(2)		H(43)	4689	8196	5037	50
C(4)	5485(11)	8016(11)	5327(3)		H(51)	602	4615	2577	50
S(5)	4521(2)	7112(3)	3103.3(6)		H(52)	1289	4254	3129	50
P(3)	2571(2)	7236(3)	3336.1(7)		H(53)	2364	4568	2739	50
S(6)	2627(2)	6361(4)	3961.9(7)		H(61)	1821	11135	3338	50
O(5)	1403(6)	6530(11)	2945(2)		H(62)	2620	10208	3810	50
C(5)	1340(16)	4983(25)	2825(6)		H(63)	3469	10458	3356	50

TABLE IX Anisotropic Thermal Parameters ($\times 10^3$) for $Sb[S_2P(OMe)_2]_3$.

Atom	U(11)	U(22)	U(33)	U(23)	U(13)	U(12)
Sb(1)	55.8(2)	64.6(2)	64.3(2)	2.9(2)	10.9(2)	3.0(2)
S(1)	55.1(8)	61.1(9)	78(1)	−6.9(9)	18.2(7)	−4.6(8)
P(1)	70(1)	57.4(9)	71(1)	−2.4(8)	15.5(8)	5.7(8)
S(2)	95(1)	72(1)	121(2)	−11(1)	35(1)	−25(1)
O(1)	90(3)	73(3)	73(3)	−7(2)	12(2)	12(3)
C(1)	124(6)	81(5)	76(4)	−8(4)	9(4)	3(5)
O(2)	102(4)	83(3)	89(3)	5(3)	13(3)	37(3)
C(2)	128(7)	126(8)	101(6)	20(6)	2(5)	49(6)
S(3)	82(1)	51.5(9)	79(1)	6.3(8)	8.0(9)	14.7(8)
P(2)	67(1)	60(1)	63.7(9)	−6.7(8)	11.6(8)	7.5(8)
S(4)	97(1)	60(1)	72(1)	12.2(8)	5.9(9)	13.2(9)
O(3)	74(3)	87(3)	86(3)	−20(3)	11(2)	−6(3)
C(3)	64(4)	83(5)	108(5)	−11(4)	19(4)	8(4)
O(4)	101(4)	95(3)	79(3)	−20(3)	30(3)	8(3)
C(4)	130(7)	106(7)	132(7)	−2(6)	77(6)	9(6)
S(5)	60.5(9)	104(1)	68(1)	20(1)	12.4(8)	9.9(9)
P(3)	56.6(9)	99(1)	85(1)	1(1)	6.4(9)	14(1)
S(6)	68(1)	179(3)	86(1)	16(1)	29(1)	22(1)
O(5)	65(3)	221(8)	108(4)	−17(5)	−2(3)	−8(4)
C(5)	147(11)	275(19)	232(16)	−143(15)	73(11)	−88(13)
O(6)	110(5)	115(6)	277(11)	30(7)	44(6)	45(5)
C(6)	170(13)	113(10)	424(30)	−61(15)	114(16)	10(10)

TABLE X. Fractional Coordinates ($\times 10^3$) for $Sb[S_2P(OPr^i)_2]_3$.

Atom	x/a	y/b	z/c	U (iso)	Atom	x/a	y/b	z/c	U (iso)
Sb(1)	633.87(8)	559.8(1)	362.19(3)		C(53)	635(2)	313(3)	204.1(9)	
S(1)	461.5(3)	613.9(4)	402.9(1)		O(6)	326.1(8)	349(1)	283.1(3)	
P(1)	513.1(5)	794.3(5)	414.6(1)		C(61)	240(1)	412(2)	307.5(7)	
S(2)	660.6(5)	831.0(5)	390.9(2)		C(62)	188(2)	323(3)	335(1)	
O(1)	517(1)	821(1)	464.6(4)		C(63)	152(2)	472(4)	280.1(9)	
C(11)	597(2)	765(2)	497.1(7)		H(1)	650	695	486	50
C(12)	537(3)	700(3)	527.8(8)		H(2)	592	655	552	50
C(13)	678(3)	858(4)	517.8(8)		H(3)	485	759	543	50
O(2)	403(1)	882(1)	399.0(4)		H(4)	481	632	514	50
C(21)	360(3)	897(2)	354.9(8)		H(5)	741	826	542	50
C(22)	386(4)	1022(4)	345.2(9)		H(6)	632	927	532	50
C(23)	233(3)	871(5)	347(1)		H(7)	724	904	496	50
S(3)	740.0(4)	475.5(5)	432.5(1)		H(8)	383	842	330	50
P(2)	890.7(4)	428.8(5)	406.0(2)		H(9)	365	1063	315	50
S(4)	869.5(4)	452.7(6)	344.1(2)		H(10)	352	1092	366	50
O(3)	930(1)	294(1)	420.5(4)		H(11)	480	1045	352	50
C(31)	864(2)	181(2)	405.2(9)		H(12)	191	871	317	50
C(32)	837(4)	121(3)	442(1)		H(13)	183	918	366	50
C(33)	932(3)	97(3)	380(1)		H(14)	219	773	357	50
O(4)	1003(1)	502(1)	433.3(5)		H(15)	787	194	385	50
C(41)	1052(3)	616(3)	429(1)		H(16)	793	37	438	50
C(42)	995(3)	710(4)	447(2)		H(17)	915	97	463	50
C(43)	1172(2)	604(6)	444(1)		H(18)	790	174	461	50
S(5)	538.6(3)	347.1(4)	349.4(1)		H(19)	892	20	369	50
P(3)	461.8(3)	390.7(5)	288.4(1)		H(20)	1012	72	398	50
S(6)	491.2(4)	565.2(5)	274.3(1)		H(21)	959	146	354	50
O(5)	504.8(9)	291(1)	256.0(3)		H(22)	1029	657	396	50
C(51)	630(2)	281(3)	250.0(7)		H(23)	1022	802	446	50
C(52)	671(2)	152(3)	263.2(8)		H(24)	1006	694	483	50

(continued on facing page)

TABLE X. *(continued)*

Atom	x/a	y/b	z/c	U (iso)
H(25)	902	714	442	50
H(26)	1217	695	441	50
H(27)	1184	587	474	50
H(28)	1212	547	426	50
H(29)	695	333	269	50
H(30)	759	134	261	50
H(31)	660	132	295	50
H(32)	623	85	245	50
H(33)	716	312	195	50
H(34)	601	403	198	50
H(35)	581	256	184	50
H(36)	275	483	328	50
H(37)	129	355	353	50
H(38)	253	275	355	50
H(39)	146	251	316	50
H(40)	89	514	294	50
H(41)	187	532	260	50
H(42)	108	404	259	50

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TABLE XI. Anisotropic Thermal Parameters ($\times 10^3$) for $Sb[S_2P(OPr^i)_2]_3$.

Atom	U(11)	U(22)	U(33)	U(23)	U(13)	U(12)
Sb(1)	65.1(5)	83.9(6)	77.6(6)	–5.2(6)	21.7(4)	–5.8(6)
S(1)	77(3)	83(3)	108(3)	–7(2)	45(2)	–4(2)
P(1)	122(4)	85(3)	81(3)	–11(3)	38(3)	–6(3)
S(2)	158(5)	104(4)	125(4)	–24(3)	62(4)	–55(4)
O(1)	179(13)	127(11)	75(8)	–14(8)	39(8)	11(10)
C(11)	172(22)	138(19)	78(14)	–16(14)	25(14)	–1(17)
C(12)	269(34)	346(46)	120(20)	81(26)	43(21)	–81(32)
C(13)	263(35)	313(43)	113(20)	2(25)	14(21)	–89(33)
O(2)	187(13)	97(9)	92(9)	–2(7)	31(9)	44(9)
C(21)	301(37)	90(16)	98(17)	14(13)	26(20)	65(20)
C(22)	449(64)	260(42)	114(22)	21(26)	7(28)	103(43)
C(23)	161(26)	512(80)	235(36)	92(41)	–53(26)	62(38)
S(3)	85(3)	129(4)	81(3)	1(3)	8(2)	–10(3)
P(2)	69(3)	102(4)	134(4)	7(4)	7(3)	–5(3)
S(4)	85(3)	167(5)	134(4)	20(4)	51(3)	25(3)
O(3)	100(9)	89(9)	164(12)	–7(8)	–19(8)	–7(7)
C(31)	135(19)	122(21)	162(23)	32(18)	–32(17)	–28(16)
C(32)	370(49)	127(24)	253(38)	–58(25)	–12(35)	–108(29)
C(33)	331(46)	146(28)	435(59)	–86(33)	209(43)	–4(28)
O(4)	92(9)	116(11)	205(15)	2(11)	–9(9)	–14(8)
C(41)	242(40)	112(22)	215(31)	30(23)	–15(27)	–12(25)
C(42)	200(37)	177(35)	473(68)	12(41)	–98(38)	–66(30)
C(43)	102(18)	933(113)	198(30)	–86(46)	27(19)	–200(39)
S(5)	79(3)	75(3)	82(3)	–7(2)	13(2)	–4(2)
P(3)	65(2)	109(4)	75(3)	–20(2)	16(2)	–0(2)
S(6)	116(4)	129(4)	89(3)	19(3)	14(3)	5(3)
O(5)	79(7)	157(11)	92(8)	–53(8)	25(6)	–6(7)
C(51)	79(13)	218(27)	134(18)	–71(19)	44(12)	–7(15)
C(52)	118(18)	262(34)	143(20)	–59(22)	25(14)	62(20)
C(53)	205(25)	239(32)	182(24)	–54(23)	131(21)	–10(23)
O(6)	59(6)	150(11)	104(8)	–40(8)	14(5)	–1(6)
C(61)	54(9)	145(18)	141(16)	–26(14)	19(10)	18(11)
C(62)	112(17)	212(29)	308(37)	36(27)	109(21)	46(19)
C(63)	134(20)	529(64)	181(25)	110(34)	54(18)	161(31)

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