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CRYSTAL STRUCTURES OF ANTIMONY AND INDIUM PHOSPHINODITHIOATES, $M(S_2PR_2)_3$ ($M = Sb$, $R = Et$; $M = In$, $R = Me$, Ph). IS THE LONE PAIR RESPONSIBLE FOR THE STRUCTURAL DIFFERENCES?

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Abstract—The molecular structures of $Sb(S_2PEt_2)_3$ and $In(S_2PR_2)_3$, R = Me and Ph, have been determined by single crystal X-ray diffraction. Both types of compound display distorted octahedral coordination geometry. In the antimony(III) compound the ligand is anisobidentate (unsymmetric) whereas in the indium compounds the coordinated ligands are basically isobidentate (symmetric). The distortions of the geometry are caused by the small bite of the ligands. An attempt is made to rationalize the structural differences observed without invoking lone pair stereochemical activity in the antimony(III) compound.

The Valence Shell Electron Pair Repulsion (VSEPR) theory frequently invokes the presence of stereochemically active lone pairs of electrons to explain the observed molecular geometry in Main Group element compounds.[1] This works extremely well for simple compounds, built of a central atom surrounded by a number of monodentate ligands, but bidentate ligands often complicate the picture. Thus, 1,1-dithiolates may form a number of primary (covalent) bonds equal to the standard valence of the central atom *and* a number of additional secondary bonds, which increases the coordination number of the central atom, close unsymmetric chelate rings and severely distort the coordination geometry. If the central atom (e.g. a Group 15 element: As, Sb or Bi) has a lone pair of electrons, it is not always clear what its effect would be. Concentrating the discussion upon phosphor-1,1-dithiolates (e.g. phosphinodithioates and phosphorodithioates) some interesting cases can be cited. Thus, antimony(III) tris(diphenylphosphinodithioate), $Sb(S_2PPh_2)_3$, displays a pentagonal pyramidal geometry, with apparently a stereochemically active lone pair in the axial position, completing a ψ-pentagonal bipyramid[2] but antimony(III) phosphorodithioates, $Sb[S_2P(OR)_2]_3$ (R = Me, Et, Pr^i), are distorted octahedral complexes.[3,4]

Among bismuth(III) compounds, the phosphodithioates, $Bi(S_2PR_2)_3$, with R = M[5] and Ph,[2] are dimers. The pentagonal pyramids are joined in pairs through Bi···S weaker interactions; a sulphur atom of a second molecule in an axial position

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occupies a site which in $Sb(S_2PPh_2)_3$ would be assigned to the stereochemically active lone pair. This contrasts with the (distorted) octahedral geometry observed in $Bi(S_2PEt_2)_3$,[6a,b] and in $Bi[S_2P(OR)_2]_3$ (R = Et,[7] Pr^i[8]). The intermolecular Bi···S "secondary bonds"[9] leading to dimerization of $Bi(S_2PR_2)_3$ are characterized by interatomic distances between normal covalent bonds and van der Waals interactions. Other examples include $Bi(S_2COMe)_3$,[10] $Bi(S_2CNEt_2)_3$,[11] and $Bi(S_2COCH_2Ph)_3$,[12] to cite only a few.

Unlike some of their bismuth analogues, antimony(III) phosphodithioates, $Sb(S_2PR_2)_3$, do not dimerize in the solid state, but antimony(III) derivatives of other 1,1-dithiolates do. Examples of Sb···S secondary bond dimers are $Sb(S_2COR)_3$ with R = Me,[10] Et,[13] Pr^i [14] and $Sb(S_2CNR_2)_3$ with R = Et[11] and Bu.[15]

It seems that more insight into the factors determining the molecular geometry of Group 15 metal phosphor-1,1-dithiolates could be gained by comparing their structures with those of metals not possessing lone pairs of electrons, i.e. Group 13 elements. A good selection for such comparisons seems to be the indium–antimony pair. The scope of such a study is, however, limited by the paucity of data about indium compounds. Only an indium phosphorodithioate, $In[S_2P(OEt)_2]_3$,[16] and a phosphinodithioate, $In(S_2PEt_2)_3$,[6b] have been structurally investigated. Structures of indium(III) compounds and indium(III) dithiocarbamates, $In(_2CNR_2)_3$, were only recently reported.[17] We decided therefore to determine the structures of some antimony(III) and indium(III) derivatives by X-ray diffraction, thus filling some existing gaps, and now report the solid state molecular structures of $Sb(S_2PEt_2)_3$ and $In(S_2PR_2)_3$ with R = Me and Ph. The methyl derivative $Sb(S_2PMe_2)_3$ was too unstable and suitable crystals for X-ray determination could not be grown because of decomposition.

RESULTS AND DISCUSSION

The compounds investigated were prepared by double exchange reactions between the metal chlorides and appropriate phosphinodithioato salts and are characterized in the Experimental.

The molecular structures $Sb(S_2PEt_2)_3$, $In(S_2PMe_2)_3$ and $In(S_2PPh_2)_3$ are illustrated in Figs 1, 2 and 3, respectively, with the atom numbering schemes; selected interatomic distances and bond angles are given in Tables 1, 2 and 3.

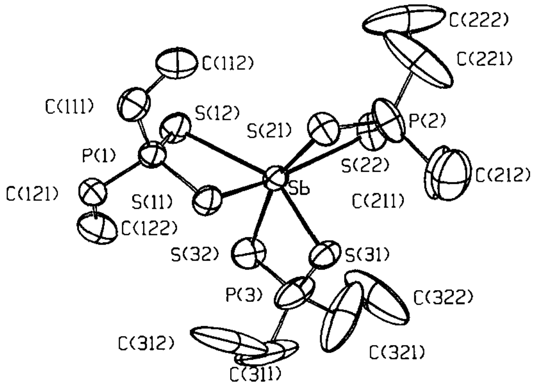


Fig. 1. The molecular structure of $C_{12}H_{30}P_3S_6Sb$ showing the atom labelling; 50% thermal ellipsoids are shown.

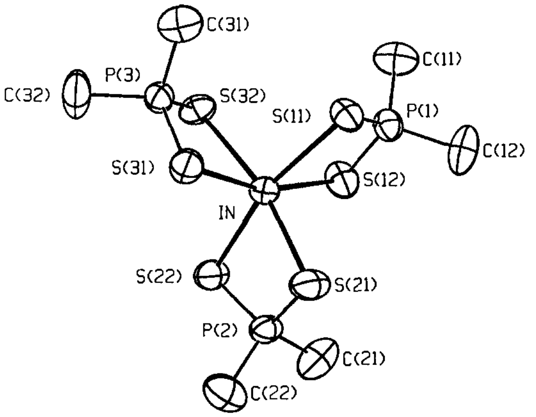


Fig. 2. The molecular structure of $C_6H_{18}InP_3S_6$ showing the atom labelling; 50% thermal ellipsoids are shown.

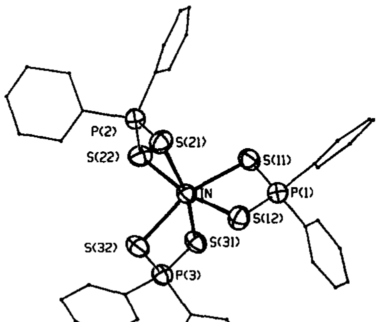


Fig. 3. The molecular structure of $C_{36}H_{30}InP_3S_6$ showing the atom labelling; 50% thermal ellipsoids are shown for the non-C atoms.

Tris(diethylphosphinodithioato)antimony(III), $Sb(S_2PEt_2)_3$, displays a distorted octahedral geometry (Fig. 1) determined by three primary (covalent) Sb—S bonds (2.503, 2.583 and 2.521 Å), the three Sb···S secondary interactions (3.137, 3.122 and 2.907 Å). Each phosphinodithioato ligand forms an unsymmetric four-membered chelate ring, **1**. In the $Sb(S_2PEt_2)_3$ molecule the P—S

Table 1. Selected interatomic distances (Å) and angles (°) in $Sb(S_2PEt_2)_3$[a]

Sb—S(11)	2.503(2)	Sb···S(12)	3.137(3)
Sb—S(21)	2.583(3)	Sb···S(22)	3.122(3)
Sb—S(31)	2.521(3)	Sb···S(32)	2.907(3)
P(1)—S(11)	2.056(3)	P(1)—S(12)	1.965(3)
P(2)—S(21)	2.054(4)	P(2)—S(22)	1.960(4)
P(3)—S(31)	2.057(4)	P(3)—S(32)	1.968(4)
S(11)—Sb···S(12)	71.54(7)	S(11)—Sb···S(22)	157.46(8)
S(21)—Sb···S(22)	71.04(8)	S(12)—Sb···S(31)	150.44(8)
S(31)—Sb···S(32)	74.43(8)	S(21)—Sb···S(32)	161.34(8)
S(11)—Sb—S(21)	86.42(8)	S(11)—Sb···S(32)	95.00(8)
S(11)—Sb—S(31)	87.68(8)	S(12)···Sb—S(21)	111.58(8)
S(21)—Sb—S(31)	87.06(8)	S(22)···Sb—S(31)	91.39(8)
S(12)···Sb···S(22)	115.87(7)		
S(12)···Sb···S(32)	86.38(8)		
S(22)···Sb···S(32)	106.45(8)		
S(11)—P(1)—S(12)	112.1(1)		
S(21)—P(2)—S(22)	112.8(2)		
S(31)—P(3)—S(32)	110.0(2)		
Sb—S(11)—P(1)	95.7(1)	Sb···S(12)—P(1)	79.8(1)
Sb—S(21)—P(2)	92.9(1)	Sb···S(22)—P(2)	79.8(1)
Sb—S(31)—P(3)	92.2(1)	Sb···S(32)—P(3)	83.3(1)

[a] Dotted lines indicate secondary bonds.

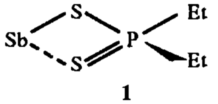
Table 2. Selected interatomic distances (Å) and angles (°) in $In(S_2PMe_2)_3$

In—S(11)	2.643(2)	In—S(12)	2.628(2)
In—S(21)	2.604(2)	In—S(22)	2.602(2)
In—S(31)	2.599(2)	In—S(32)	2.608(2)
P(1)—S(11)	2.013(3)	P(1)—S(12)	2.004(3)
P(2)—S(21)	2.007(3)	P(2)—S(22)	2.010(3)
P(3)—S(31)	2.009(3)	P(3)—S(32)	2.014(3)
S(11)—In—S(12)	77.14(6)	S(11)—In—S(22)	165.33(6)
S(21)—In—S(22)	78.25(6)	S(12)—In—S(31)	163.01(7)
S(31)—In—S(32)	77.77(6)	S(21)—In—S(32)	166.17(6)
S(11)—In—S(21)	92.99(6)	S(12)—In—S(21)	99.87(7)
S(11)—In—S(31)	89.87(6)	S(12)—In—S(22)	92.64(6)
S(11)—In—S(32)	95.76(6)	S(12)—In—S(32)	92.51(6)
S(21)—In—S(31)	91.59(6)		
S(22)—In—S(31)	102.00(6)		
S(22)—In—S(32)	95.18(6)		
S(11)—P(1)—S(12)	109.8(1)		
S(21)—P(2)—S(22)	109.7(1)		
S(31)—P(3)—S(32)	108.7(1)		
In—S(11)—P(1)	86.23(8)	In—S(12)—P(1)	86.84(9)
In—S(21)—P(2)	85.27(9)	In—S(22)—P(2)	85.28(9)
In—S(31)—P(3)	86.10(9)	In—S(32)—P(3)	85.77(8)

Table 3. Selected interatomic distances (Å) and bond angles (°) in $In(S_2PPh_2)_3$ (two independent molecules in the asymmetric unit)

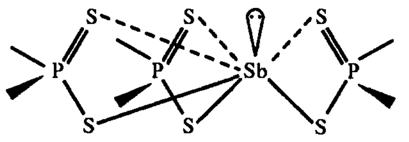
	Unprimed molecule	Primed molecule
In—S(11)	2.622(6)	2.630(7)
In—S(12)	2.604(6)	2.578(7)
In—S(21)	2.566(6)	2.661(8)
In—S(22)	2.588(6)	2.573(6)
In—S(31)	2.609(6)	2.619(8)
In—S(32)	2.621(6)	2.587(7)
P(1)—S(11)	2.015(8)	2.02(1)
P(1)—S(12)	2.015(8)	2.00(1)
P(2)—S(21)	2.018(9)	2.00(1)
P(2)—S(22)	2.003(8)	2.016(9)
P(3)—S(31)	1.988(9)	2.02(1)
P(3)—S(32)	2.012(7)	2.02(1)
S(11)—In—S(12)	78.4(2)	77.7(2)
S(21)—In—S(22)	78.3(2)	77.7(2)
S(31)—In—S(32)	77.8(2)	78.1(2)
S(11)—In—S(32)	161.2(2)	166.8(2)
S(12)—In—S(22)	167.4(2)	167.1(2)
S(21)—In—S(31)	116.7(2)	162.7(2)
S(11)—In—S(21)	99.7(2)	92.6(2)
S(11)—In—S(22)	96.7(2)	92.3(2)
S(11)—In—S(31)	89.4(2)	96.2(2)
S(12)—In—S(21)	91.0(2)	94.6(2)
S(12)—In—S(31)	100.3(2)	101.8(2)
S(12)—In—S(32)	90.3(2)	91.7(2)
S(21)—In—S(32)	95.4(2)	96.1(2)
S(22)—In—S(31)	91.2(2)	87.2(2)
S(22)—In—S(32)	97.2(2)	99.2(2)
S(11)—P(1)—S(12)	110.1(3)	108.6(4)
S(21)—P(2)—S(22)	108.0(4)	109.7(4)
S(31)—P(3)—S(32)	110.4(4)	108.4(4)
In—S(11)—P(1)	84.6(2)	86.0(3)
In—S(12)—P(1)	85.0(2)	87.8(3)
In—S(21)—P(2)	86.3(3)	84.9(3)
In—S(22)—P(2)	86.1(3)	86.9(3)
In—S(31)—P(3)	85.6(3)	84.3(3)
In—S(32)—P(3)	84.8(3)	85.2(3)

bonds (2.056, 2.054 and 2.057 Å) are associated with the primary Sb—S bonds, and the double P═S bonds (1.965, 1.960 and 1.968 Å) are paired with the secondary Sb···S bonds.



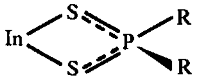
1

The phosphinodithioato ligands are clearly anisobidentate chelating (monometallic biconnective).[18] The S—Sb—S angles between primary bonds are slightly less than 90° (range 86.4–87.7°), suggesting that the central atom uses only *p*-orbitals in determining the coordination geometry. The S···Sb···S angles between the secondary bonds are much larger, corresponding to the corners of the S(12)S(22)S(32) face of the octahedron determined by the three sulphur atoms furthest from the central atom. One feels tempted to suggest that this geometry is caused by the presence of a (stereochemically more or less active) lone pair of electrons pointing towards the S(12)S(22)S(32) face (as shown tentatively in **2**), but it can also be the simple result of the non-equivalence of the antimony–sulphur bonds. An sp^3 hybridization, with one of the orbitals occupied by the lone electron pair is ruled out by the S—Sb—S bond angle, and the presence of the lone pair in a spherically symmetric *s*-orbital of antimony would hardly produce such a distortion. Therefore, it seems that the distortion of the octahedral structure does not necessarily prove stereochemical activity of a lone pair. The presence of ample void space on a coordination site is also observed in cases when no lone pair is present, like in the structure of $Me_2Tl[S(O)PPh_2]$.[19]



2

Indium phosphinodithioates, $In(S_2PR_2)_3$, R = Me and Ph, display more symmetric octahedral geometries, with nearly equal In—S bonds and basically isobidentate phosphinodithioato ligands, forming four-membered chelate rings of type **3**.



3

The differences Δ(P—S) and Δ(M—S) observed between likewise pairs of bonds within the same chelate MS_2P ring can be taken as a measure of asymmetry. Thus, in tris(dimethylphosphinodithioato) indium(III), $In(S_2PMe_2)_3$, the In—S interatomic distances within an InS_2P chelate ring do not differ by more than 0.015 Å and the P—S interatomic distances by more than 0.009 Å (*ca* three standard deviations). Thus, the ligand can be safely described as isobidentate. The S—P—S bond angles are practically tetrahedral (108.7–109.8°). The small S—In—S bond angles in the four-membered chelate rings (77.14–78.25°) are the cause of the observed distortions of the coordination octahedron and they determine the decrease of the S—In—S bond angles of the sulphur atoms located *trans* to each other, from the ideal value of 180° to 163–166°.

The asymmetric unit of tris(diphenylphosphinodithioato)indium(III), $In(S_2PPh_2)_3$, contains two independent molecules, with slightly differing parameters. Thus, in molecule **A** (unprimed) the differences between the In—S bond lengths in a chelate ring are no more than 0.029 Å [In—S(22) 2.588 Å vs In—S(21) 2.566 Å], whereas in molecule **B** (primed) the coordination is less symmetric, and within the same chelate ring the paired In—S bonds differ by at least 0.032 Å [In′—S′(31) 2.619 Å vs In′—S′(32) 2.587 Å] and by as much as 0.088 Å [In′—S′(21) 2.661 Å vs In′—S′(22) 2.573 Å]. It is difficult to explain the significance of these differences, since they are not correlated with the P—S bond lengths observed. It is also worth mentioning that the chelate rings are not identical. In one of them [InS(11)P(1)S(12) in molecule **A** and In′S′(31)P′(3)S′(32) in molecule **B**] the P—S bonds are equal [Δ(P—S) = 0] whereas in the other two chelate rings the P—S pairs differ [average Δ(P—S) = 0.014 Å, in molecule **A** and Δ(P—S) = 0.018 Å in molecule **B**].

The S—P—S bond angles are basically tetrahedral in both molecules (range 108.0–110.4°). In the four-membered chelate rings the bite S—In—S angles are in the range 77.7–78.3° and the bond angles between opposite sulphur atoms (*trans*) are in the range 161.2–167.4° for the two molecules. These deviations from the ideal value of 180° in a regular tetrahedron are a measure of the distortions of the coordination geometry caused by the small bite of the ligands.

In both the methyl and phenyl derivatives, the angles between In—S bonds, which do not belong to the same four-membered chelate ring, may differ by as much as 10° from the ideal value of 90°, but most of them are closer to it.

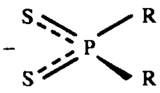
All these data indicate that the coordination geometry can be described as distorted octahedral, the small bite of the ligand causing acute angles in the four-membered chelate rings.

Comparisons with other structures

In the antimony case, the structures available for comparison are those of phosphorodithioates, $Sb[S_2P(OR)_2]_3$, with R = Me, Et and Pr^i, and phosphinodithioate, $Sb(S_2PPh_2)_3$. The tris(diethylphosphorodithioato) derivative differs from the dimethyl and di-isopropyl derivatives in that the former is more symmetric, as reflected in smaller Δ(P—S) and Δ(Sb—S) differences within the four-membered chelate rings (Table 4). Thus, in $Sb[S_2P(OEt)_2]_3$, Δ(P—S) is in the range 0.004–0.049 Å and Δ(Sb—S) in the range 0.195–0.273 Å,[4] whereas in $Sb[S_2P(OR)_2]_3$, with R = Me and Pr^i, Δ(P—S) is in the range 0.084–0.106 Å and Δ(Sb—S) in the range 0.471–0.510 Å.[3] In $Sb(S_2PEt_2)_3$ these differences are in the ranges Δ(P—S) 0.089–0.094 Å and Δ(Sb—S) 0.386–0.634 Å, close to those cited for two of the above phosphorodithioates.[6b] All these compounds display distorted octahedral geometry, except $Sb(S_2PPh_2)_3$ which is pentagonal pyramidal[2] and thus greatly differs from the others, ruling out a rational comparison.

In the indium case, the structures available for comparison are those of $In[S_2P(OEt)_2]_3$ (less accurate)[16] and $In(S_2PEt_2)_3$.[6b] The structures of our compounds, $In(S_2PR_2)_3$, with R = Me and Ph, are quite similar to that of R = Et, with comparable Δ(P—S) and Δ(In—S) values and bond angles (Table 4).

When the indium compounds are compared with chemically analogous antimony compounds, the structural differences are obvious. In indium compounds the ligand is more symmetrically coordinated, with minor Δ(P—S) and Δ(In—S) differences (of the order of a few standard deviations). It could be described as a coordinated anion, **4**. In the antimony(III) derivatives the Δ(P—S) and Δ(Sb—S) differences are major and the ligand can be described as an M—S covalently bonded group **5**, in which the small bite of the ligand brings the second sulphur atom close to the coordination centre M, within a distance shorter than the sum of van der Waals radii.



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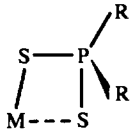


5

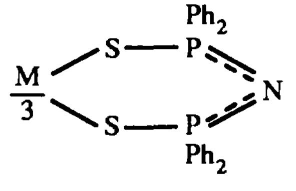
With the hard–soft acid–base concepts in mind, it can be argued that harder elements, with more pronounced metallic character (like indium) coordinate predominantly in a more symmetrical manner, while soft elements, with less pronounced metallic character (like antimony) coordinate as **5**, in a strongly unsymmetric mode. Thus, the differences observed between Group 13 and Group 15 atoms as coordination centres may be rationalized without invoking stereochemically active lone pairs of electrons. We would like to suggest that the VSEPR theory explains the orientation of the primary bonds; the secondary interactions are favoured by the small bite of the ligands, which brings a second atom closer to the coordination centre.

Perhaps more insight into the subject could be

Table 4. Comparison of P—S and M—S bond asymmetries in MS_2 chelate rings (M = Sb, In) of phosphor-1,1-dithiolato ligands

Compound	P—S Bond lengths (Å)		Δ(P—S)	M—S Bond lengths (Å)		Δ(M—S)	Ref.
$Sb(S_2PEt_2)_3$	2.056(3)	1.965(3)	0.091	3.137(3)	2.503(2)	0.634	This work
	2.054(4)	1.960(4)	0.094	3.122(3)	2.583(3)	0.539	
	2.057(4)	1.968(4)	0.089	2.907(3)	2.521(3)	0.386	
$Sb(S_2PPh_2)_3$	2.048(1)	1.972(1)	0.076	2.978(1)	2.591(1)	0.387	2
	2.089(1)	1.959(1)	0.130	3.187(1)	2.456(1)	0.731	
	2.044(1)	1.981(1)	0.063	2.923(1)	2.598(1)	0.325	
$Sb[S_2P(OMe)_2]_3$	2.029(2)	1.941(3)	0.088	3.008(2)	2.522(1)	0.486	3
	2.036(2)	1.941(2)	0.095	3.006(2)	2.535(2)	0.471	
	2.033(2)	1.927(3)	0.106	3.002(2)	2.531(2)	0.471	
$Sb[S_2P(OEt)_2]_3$	1.992(10)	1.984(12)	0.008	2.785(11)	2.590(13)	0.195	4
	1.983(11)	1.979(11)	0.004	2.838(12)	2.629(10)	0.209	
	1.976(11)	1.927(11)	0.049	2.856(18)	2.583(9)	0.273	
$Sb[S_2P(OPr^i)_2]_3$	2.029(6)	1.945(6)	0.084	3.031(5)	2.521(4)	0.510	3
	2.034(6)	1.932(7)	0.102	3.013(4)	2.531(4)	0.482	
	2.044(6)	1.949(7)	0.095	3.000(5)	2.519(4)	0.481	
$In(S_2PMe_2)_3$	2.013(3)	2.004(3)	0.009	2.643(2)	2.628(2)	0.015	This work
	2.010(3)	2.007(3)	0.003	2.604(2)	2.602(2)	0.002	
	2.014(3)	2.009(3)	0.005	2.608(2)	2.599(2)	0.007	
$In(S_2PEt_2)^3$	2.012(2)	2.002(2)	0.010	2.638(1)	2.638(1)	0.000	6
	2.029(2)	2.021(2)	0.008	2.621(1)	2.603(1)	0.018	
	2.023(2)	2.016(2)	0.007	2.628(1)	2.620(1)	0.008	
$In(S_2PPh_2)_3$ molecule **A**	2.015(8)	2.015(8)	0.000	2.622(6)	2.604(6)	0.018	This work
	2.018(9)	2.003(8)	0.015	2.588(6)	2.566(6)	0.022	
	2.012(7)	1.988(9)	0.014	2.621(6)	2.609(6)	0.012	
molecule **B**	2.020(10)	2.000(10)	0.020	2.630(7)	2.578(7)	0.052	
	2.016(9)	2.000(10)	0.016	2.661(8)	2.573(6)	0.088	
	2.020(10)	2.020(10)	0.000	2.619(8)	2.587(7)	0.032	

gained by extending the comparison to complexes of ligands with a larger bite, e.g. dithioimidodiphosphinates, **6**, which do not impose the constraints leading to the distortions observed with phosphor-1,1-dithiolato ligands. Such an attempt has been made in the case of $M(S_2PH_2PNPPh_2S)_3$, with M = In and Bi.[20]



6

EXPERIMENTAL

Preparation of the compounds

Tris(diethylphosphinodithioato)antimony(III), $Sb(S_2PEt_2)_3$. Antimony(III) chloride (0.228 g, 1 mmol) dissolved in benzene (25 cm^3) was treated with $NaS_2PEt_2 \cdot 2H_2O$ (0.636 g, 3 mmol) and stirred for 1 h. The yellow solution was filtered and evaporated in air, and the solid was recrystallized from diethylether, to give 0.45 g (77%) of yellow crystals, m.p. 88°C (lit. 78–80°C,[21] 90–91°C[22]). Found: C, 24.3; H, 5.1. $C_{12}H_{30}P_3S_6Sb$ ($M = 581.43$) requires: C, 24.8; H, 5.2%. ^1H NMR spectrum in $CDCl_3$ (at 200 MHz): $\delta = 1.29$ dt (3H, PCH_2CH_3),

Table 5. Crystal data and structure refinement

	$Sb(S_2PEt_2)_3$	$In(S_2PMe_2)_3$	$In(S_2PPh_2)_3$
Empirical formula	$C_{12}H_{30}P_3S_6Sb$	$C_6H_{18}InP_3S_6$	$C_{36}H_{30}InP_3S_6$
Formula weight	581.43	490.34	862.77
Temperature (K)	291	291	291
Wavelength (λMo-K_α) (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Orthorhombic	Triclinic
Space group	$C2/c$	$P2_12_12_1$	$P\bar{1}$
Unit cell dimensions			
a (Å)	19.384(2)	9.242(1)	10.798(2)
b (Å)	9.327(1)	9.857(1)	13.554(1)
c (Å)	29.016(3)	21.393(2)	26.431(3)
α (°)			85.16(1)
β (°)	107.95(8)		83.83(1)
γ (°)			89.35(1)
Cell volume (Å^3)	4991(2)	1948.9(6)	3832(1)
Z	8	4	4
D_{calc} (g cm^{-3})	1.548	1.671	1.495
Absorption coeff. (mm^{-1})	17.81	20.36	10.69
Abs. correction factors (max, min)	1.22, 0.86	1.08, 0.88	1.22, 0.77
F(000)	2352	976	1744
Crystal size approx. (mm)	0.37 × 0.25 × 0.23	0.35 × 0.25 × 0.20	0.15 × 0.15 × 0.10
2θ range (°)	0–46	0–50	0–46
Index range	$-21 \leqslant h \leqslant 20$ $0 \leqslant k \leqslant 10$ $0 \leqslant l \leqslant 31$	$-2 \leqslant h \leqslant 11$ $0 \leqslant k \leqslant 11$ $0 \leqslant l \leqslant 25$	$-11 \leqslant h \leqslant 11$ $-14 \leqslant k \leqslant 14$ $0 \leqslant l \leqslant 29$
Refl. collected	3247	2380	8375
Independent refl.	3166	2308	8181
R_{int}	0.022	0.014	0.042
Observed refl.	2511	1972	3569
S	1.70	1.20	1.59
R	0.0452	0.0284	0.0713
wR	0.0479	0.0283	0.0700

$^3J_{HH} = 7.5$; $^3J_{PH} = 22.1$ Hz; $\delta = 2.09$ dq (2H, $PC\underline{H}_2CH_3$), $^3J_{HH} = 7.5$; $^3J_{PH} = 10.6$ Hz. ^{13}C NMR spectrum in $CDCl_3$ (at 50 MHz): δ = d ($PCH_2\underline{C}H_3$), $^3J_{PC} = 4.7$ Hz: $\delta = 31.82$ d ($P\underline{C}H_2CH_3$), $^1J_{PC} = 50.2$ Hz. ^{31}P NMR spectrum in $CDCl_3$ (at 121.4 MHz): $\delta = 75.9$ s. IR spectrum (KBr pellets, cm^{-1}): $\nu_{as}(PS_2)$ 570s, $\nu_s(PS_2)$ 460s. Mass spectrum (EI, 70 eV, m/z %): 427(100)$[M-S_2PET_2]^+$, 153(19) $Et_2PS_2^+$, 121(68) ET_2PS^+, 121(6) Sb^+.

Tris(dimethylphosphinodithioato)indium(III), $In(S_2PMe_2)_3$. Clear solutions of $InCl_3$ (0.44 g, 2 mmol in 50 cm^3 water) and $NaS_2PEt_2 \cdot 2H_2O$ (1.104 g, 6 mmol in 50 cm^3 water) were mixed at room temperature and stirred for 0.5 h. The precipitate formed was filtered, washed with water and dried under reduced pressure. Recrystallization from methylene chloride produced white crystals of $In(S_2PMe_2)_3$. Yield: 0.70 g (71%), m.p. 211–213°C (lit. 212–213°C).[23] ^{1}H NMR spectrum (in $CDCl_3$, at 200 MHz): $\delta = 2.17$ d ($P\text{-}C\underline{H}_3$), $^2J_{PH} = 13.2$ Hz. ^{13}C NMR spectrum (in $CDCl_3$, at 50 MHz): $\delta = 28.7$ d ($P\text{-}\underline{C}H_3$), $^1J_{PC} = 50.6$ Hz. ^{31}P NMR spectrum (in $CDCl_3$, at 121.4 MHz): $\delta = 66.6$ s. IR spectrum (KBr pellets, cm^{-1}): $\nu_{as}(PS_2)$ 590vs, $\nu_s(PS_2)$ 490s. Mass spectrum (EI, 70 eV, m/z%): 490(1) M^+, 365(100) $[M\text{-}S_2PMe_2]^+$, 125(21) $Me_2PS_2^+$, 115(64) In^+, 93(18) Me_2PS^+.

Tris(diphenylphosphinodithioato)indium(III), $In(S_2PPh_2)_3$. Aqueous solutions of indium(III) chloride (0.22 g, 1 mmol in 25 cm^3 water) and $NH_4S_2PPh_2$ (0.801 g, 3 mmol in 25 cm^3 water) were mixed and stirred for 0.5 h. The precipitate was filtered and recrystallized from methylene chloride/*n*-hexane (1 : 1 in volumes), to give white crystals of $In(S_2PPh_2)_3$. Yield: 0.84 g (92%), m.p. 230–32°C (lit:[24] no m.p. given). Found: C, 49.7; H, 3.5. $C_{36}H_{30}InP_3S_6$ (M = 862.77) requires: C, 50.1; H, 3.5%. ^{1}H NMR spectrum (in $CDCl_3$, at 200 MHz): $\delta = 7.88$ dm (2H, $P\text{-}C_6\underline{H}_5$ *ortho*), $^3J_{PH} = 15$ Hz; $\delta = 7.43$ m (3H, $P\text{-}C_6\underline{H}_5$ *meta+para*). ^{13}C NMR spectrum (in $CDCl_3$, at 50 MHz): $\delta = 136.1$ d (C_i,

${}^1J_{PC} = 81.1$ Hz) ; $\delta = 131.28$ d (C_o, ${}^2J_{PC} = 12.5$ Hz) ; $\delta = 131.26$ s (C_p), 128.24 d (C_m ${}^3J_{PC} = 13.6$ Hz). ${}^{31}P$ NMR spectrum (in $CDCl_3$, at 121.4 MHz): $\delta = 68.9$ s. IR spectrum (KBr pellets, cm^{-1}) : $\nu_{as}(P_2)$ 630 m, $\nu_s(PS_2)$ 555 m.

Crystal structure determinations

The data were collected on a CAD-4 diffractometer, in the $\omega/2\theta$ scan mode with ω scan width $= 0.8+0.35 \tan \theta$, using graphite monochromated Mo-K_α radiation. In all cases data were corrected for Lorentz and polarization effects. Absorption corrections were applied at a later stage in the refinement.[25] The structures were solved by the standard heavy-atom Patterson method, followed by normal difference Fourier techniques. Refinement was carried out by blocked-matrix least-squares. The programs used were: SHELX-76,[26] SHELXS86[27] and ORTEP.[28] Scattering factors for non-hydrogen atoms were from Ref. 29 and corrections for anomalous dispersion from Ref. 30, and for H-atoms from Ref. 31. In the $Sb(S_2PEt_2)_3$ and in the $In(S_2PMe_2)_3$ structures the H-atoms included in the model were those found in difference synthesis, and refined as fixed contributors with an overall isotropic temperature factor that refined to 0.11(1) and 0.087(6) Å,^{2} respectively. In the $In(S_2PPh_2)_3$ structure H-atoms were included, as fixed contributors, on stereochemical grounds with an isotropic temperature factor of 0.08 Å.^{2}

Further details about the determination of the crystal structures were deposited with the Editor as supplementary material at the Cambridge Crystallographic Data Centre.

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