

# The Crystal Structures of the Tris(diethyldithiophosphinato) Complexes of Bi(III) and In(III)

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The crystal structures of  $\text{Bi}[\text{S}_2\text{P}(\text{C}_2\text{H}_5)_2]_3$  (**1**) and  $\text{In}[\text{S}_2\text{P}(\text{C}_2\text{H}_5)_2]_3$  (**2**) have been determined from single-crystal X-ray diffraction data at 290 K. **1**: space group  $C2/c$  (No. 15),  $a = 19.165(2)$ ,  $b = 9.828(2)$ ,  $c = 27.123(8)$  Å,  $\beta = 94.69(2)^\circ$ ,  $Z = 8$ . Final  $R$  value 0.031 for 2733 observed reflections with  $I > 3\sigma(I)$ . **2**: space group  $P1$  (No. 2),  $a = 9.785(3)$ ,  $b = 10.290(2)$ ,  $c = 13.956(2)$  Å,  $\alpha = 85.26(1)$ ,  $\beta = 75.73(1)$ ,  $\gamma = 66.03(1)^\circ$ ,  $Z = 2$ . Final  $R$  value 0.032 for 3021 observed reflections with  $I > 3\sigma(I)$ . The Bi and In atoms in **1** and **2** are coordinated by six sulfur atoms from three diethyldithiophosphinate ligands in a distorted octahedral environment. The distortion is described by the twist angles,  $\varphi$ , between the two opposite triangular faces of the octahedron along the pseudo-threefold axis. In **1**, the three twist angles are  $31.8(1)$ ,  $36.4(1)$  and  $38.4(1)^\circ$ . The Bi–S bond lengths are unequal, ranging from  $2.753(2)$  to  $2.858(2)$  Å. The deformation of the octahedron is a result of the ligand bite, the crystal packing and a seventh electron pair in the valence shell of bismuth. In **2**, the three-fold symmetry of the molecule is well preserved. This can be seen from the three twist angles of  $39.6(1)$ ,  $42.4(1)$  and  $43.4(1)^\circ$ , which indicate a trigonal distortion of the octahedra. The In–S distances are equal, average  $2.625(13)$  Å. Two of the ethyl groups in **1** and one ethyl group in **2** exhibit orientational disorder of the terminal methyl group.

Substituted dithiophosphorus ligands of the type  $\text{R}_2\text{PS}_2^-$  form complexes with a variety of metals.<sup>1,2</sup> Substitution of one R group for another may lead to changes in structure. The crystal structures of the dithiophosphate complexes  $\text{Bi}[\text{S}_2\text{P}(\text{O}-i-\text{C}_3\text{H}_7)_2]_3$ <sup>3</sup> and  $\text{In}[\text{S}_2\text{P}(\text{OC}_2\text{H}_5)_2]_3 \cdot \text{C}_6\text{H}_6$ <sup>4</sup> and of the dithiophosphinate complexes  $\text{Bi}[\text{S}_2\text{P}(\text{C}_2\text{H}_5)_2]_3$ <sup>5</sup> and  $\text{Bi}[\text{S}_2\text{P}(\text{C}_6\text{H}_5)_2]_3 \cdot \text{C}_6\text{H}_6$ <sup>6</sup> have previously been determined. In order to investigate structural changes brought about by R group variation we have synthesized the complexes  $\text{Bi}[\text{S}_2\text{P}(\text{C}_2\text{H}_5)_2]_3$  (**1**) and  $\text{In}[\text{S}_2\text{P}(\text{C}_2\text{H}_5)_2]_3$  (**2**), and determined their crystal structures.

The bismuth complex of the bidentate diethyldithiophosphinate ligand is of interest in view of the stereochemical effects of the 6 *s* lone pair of electrons in the valence shell of bismuth. According to the valence-shell electron pair repulsion (VSEPR) model,<sup>7,8</sup> six-coordinate bismuth complexes are not expected to possess a regular octahedral structure. Instead, a structure based on coordination number seven with the lone pair occupying the seventh position is predicted by the VSEPR model. In order to make the effects of the lone pair observable, inter-ligand repulsion must be reduced. This is achieved by using the narrow-bite bidentate dithiophosphorus ligand. In  $\text{Bi}[\text{S}_2\text{P}(\text{O}-i-\text{C}_3\text{H}_7)_2]_3$ , the deformation of the bismuth coordination sphere is in accord with a stereochemically active lone pair,<sup>3</sup> while the lone pair is considered to be inactive in the two dithiophosphinate complexes.<sup>5,6</sup>

The indium complex on the other hand is expected to be coordinated by three bidentate diethyldithiophosphinate

ligands in a trigonally distorted octahedron. In the related compound  $\text{In}[\text{S}_2\text{P}(\text{OC}_2\text{H}_5)_2]_3$ <sup>4</sup> the two P–S bonds are of unequal length, which is unexpected since this is not reflected in the In–S distances.

## Experimental

Crystals of **1** and **2** were prepared according to Kuchen *et al.*<sup>9</sup> **1** was then recrystallized as yellow crystals from a 2-propanol solution by slow evaporation, and **2** was recrystallized from a  $\text{CHCl}_3$  solution, yielding colourless crystals. Crystal and structure determination data for the two compounds are given in Table 1. The intensity data measurements were made on an Enraf-Nonius CAD-4 diffractometer at 290 K, using graphite-monochromated  $\text{MoK}\alpha$  radiation ( $\lambda = 0.71069$  Å). Cell constants were determined by a least-squares method from setting angles of 49 and 44 reflections in the ranges  $18 < 2\theta < 36^\circ$  and  $20 < 2\theta < 24^\circ$  for **1** and **2**, respectively. Intensities were measured with the  $\omega/2\theta$  scan technique with  $\Delta\omega = 0.5^\circ + 0.6^\circ \tan\theta$ ,  $\sin\theta/\lambda < 0.60$  Å<sup>-1</sup>. Maximum counting time was 210 sec for **1** and 180 sec for **2**. Three standard reflections were measured every hour of X-ray exposure time for **1** and every two hours for **2**. No significant variation was detected for **2**, but the intensities for **1** decreased by approximately 12%, a correction for this decay being made. Data were corrected for Lorentz, polarization and absorption effects (numerical integration).

Table 1.

Crystallographic data	1	2
Compound	Bi[S <sub>2</sub> P(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> ] <sub>3</sub>	In[S <sub>2</sub> P(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> ] <sub>3</sub>
<i>M<sub>r</sub></i>	668.66	574.50
Crystal system	Monoclinic	Triclinic
Space group	<i>C2/c</i> (No. 15)	<i>P</i> $\bar{1}$ (No. 2)
<i>a</i> /Å	19.165(2)	9.785(3)
<i>b</i> /Å	9.828(2)	10.290(2)
<i>c</i> /Å	27.123(8)	13.956(2)
$\alpha$ /°	90	85.26(1)
$\beta$ /°	94.69(2)	75.73(1)
$\gamma$ /°	90	66.03(1)
<i>V</i> /Å <sup>3</sup>	5092(2)	1244.0(3)
<i>Z</i>	8	2
<i>D<sub>x</sub></i> /g cm <sup>-3</sup>	1.745(1)	1.543(1)
<i>F</i> (000)	2608	584
$\mu$ (MoK $\alpha$ )/cm <sup>-1</sup>	72.2	16.1
Crystal size/mm	0.25×0.20×0.11	0.20×0.15×0.10
Colour	yellow	colourless
Number of faces	9	10
Grid in absorption correction	10×6×16	8×10×12
Range of transmission factor	0.19–0.32	0.70–0.84
<i>h k l</i> range	0→22, 0→11, -32→32	0→9, -9→9, -13→13
Number of reflections measured	5227	4854
Unique reflections	4570	4313
Observed [ <i>I</i> >3 $\sigma$ ( <i>I</i> )]	2733	3021
<i>R<sub>int</sub></i>	0.033	0.045
Extinction coefficient	5.3(6) 10 <sup>3</sup>	1.6(4) 10 <sup>3</sup>
<i>R</i> , <i>R<sub>w</sub></i>	0.031, 0.041	0.032, 0.043
<i>S</i>	1.39	1.30
( $\Delta$ / $\sigma$ ) <sub>average</sub>	0.003(4)	0.002(6)
$\Delta\rho_{\max}/\Delta\rho_{\min}$	0.83/-0.40	0.56/-0.42

### Structure determination and refinement

The systematically absent reflections indicated *Cc* and *C2/c* as possible space groups for **1**, and since *Z* = 8, spacegroup *C2/c* was selected. A subsequent attempt to refine the structure in space group *Cc* gave no improvement. Both structures were solved by Patterson methods. The electron-density difference maps showed the presence of two locations of the methyl groups C8 and C12 in **1** and C4 in **2**. The disorder was interpreted as statistical, with each methyl group distributed over two positions. The occupancy factor sums were constrained to 1.0. All atoms in the ligands with disordered methyl groups have enlarged displacement parameters, which could not be resolved into major disorder sites. Due to the observed disorder, a second full data set for **1** was collected for a crystal obtained in a second preparation. Within the experimental errors the same disorder was found in both crystals.

Refinements were carried out by the full-matrix least-squares method, minimizing  $\sum w(|F_o| - |F_c|)^2$  with  $w = [\sigma_c^2(F_o) + (aF_o)^2]^{-1}$ ,  $a = 0.020$  for **1** and 0.025 for **2**, and  $\sigma_c$  from counting statistics. In the later stages of the refinement, corrections for extinction effects were applied.<sup>10</sup> Anisotropic displacement parameters were used for all non-hydrogen atoms. All hydrogen atoms with the exception of the hydrogen atoms on the disordered ethyl groups were located from difference maps. The positions of the

hydrogen atoms were refined in two cycles with fixed isotropic displacement parameters,  $U_{\text{iso}} = 0.08 \text{ \AA}^2$ . In the final cycles all hydrogen parameters were fixed. The data and the final model were compared by probability-plotting<sup>11</sup> of ordered values of  $\delta R_i = \Delta F_i / \sigma(|F_o|_i)$  vs. those expected for ordered normal deviations [ $\sigma(|F_o|_i) = w^{-1/2}$ ] resulting in plots with slopes of 1.255(2) and 1.232(4), intercepts of 0.090(2) and 0.054(4), and correlation coefficients of 0.9959 and 0.9881 for **1** and **2**, respectively. From these and the related *S* values it is concluded that  $\sigma(|F_o|_i)$  is on average rather well estimated.

Atomic scattering factors and anomalous dispersion corrections were taken from Ref. 12. Calculations were carried out on a VAX 11/780 computer using the crystallographic programs described by Lundgren.<sup>13</sup> Lists of structure factors, anisotropic displacement parameters and hydrogen atom coordinates may be obtained from one of the authors (G.S.) on request. Final atomic coordinates and equivalent isotropic displacement parameters for the non-hydrogen atoms are given in Table 2 for **1** and in Table 3 for **2**, bond distances in Table 4, bond angles in Table 5 and selected torsion angles in Table 6.

### Description of the structures

*Bi*[S<sub>2</sub>P(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>]<sub>3</sub> (**1**). Bismuth coordinates six sulfur atoms from three diethyldithiophosphate ligands in a poly-

**Table 2.** Fractional atomic coordinates and equivalent isotropic displacement parameters for Bi[S<sub>2</sub>P(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>]<sub>3</sub> (1) with e.s.d.'s in parentheses. The occupancy factors are 0.72(2), 0.28(2), 0.40(3) and 0.60(3) for C8A, C8B, C12A and C12B, respectively.

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> <sub>eq</sub> /Å <sup>2</sup> <sup>a</sup>
Bi	0.11451(2)	0.05896(3)	0.12132(1)	0.0581(1)
S1	0.1980(1)	0.1901(2)	0.05840(8)	0.0657(8)
S2	0.1245(1)	-0.1145(2)	0.04089(8)	0.0660(8)
S3	0.1033(2)	0.3013(3)	0.17533(10)	0.0901(11)
S4	-0.0136(1)	0.1824(2)	0.08672(11)	0.0931(11)
S5	0.2272(2)	-0.0296(3)	0.18458(10)	0.0867(11)
S6	0.0671(2)	-0.1656(3)	0.17660(10)	0.0887(11)
P1	0.1848(1)	0.0283(2)	0.01202(8)	0.0542(7)
P2	0.0091(1)	0.3297(3)	0.13694(10)	0.0790(10)
P3	0.1652(2)	-0.1777(2)	0.20810(8)	0.0736(9)
C1	0.1458(5)	0.0819(9)	-0.0487(3)	0.071(3)
C2	0.0793(6)	0.1557(10)	-0.0474(4)	0.095(4)
C3	0.2683(5)	-0.0412(8)	0.0002(4)	0.068(3)
C4	0.3124(6)	-0.0875(10)	0.0457(5)	0.096(5)
C5	0.0075(6)	0.4928(10)	0.1060(5)	0.104(5)
C6	0.0555(8)	0.4978(13)	0.0642(6)	0.128(6)
C7	-0.0632(8)	0.3374(17)	0.1822(5)	0.143(7)
C8A	-0.0754(14)	0.1670(25)	0.1996(9)	0.171(13)
C8B	-0.0512(22)	0.4836(31)	0.2092(14)	0.091(17)
C9	0.2009(7)	-0.3411(10)	0.1960(4)	0.099(5)
C10	0.2175(7)	-0.3699(12)	0.1462(4)	0.106(5)
C11	0.1677(9)	-0.1671(13)	0.2766(4)	0.120(6)
C12A	0.1220(17)	-0.0475(40)	0.2920(11)	0.125(18)
C12B	0.1301(13)	-0.2537(29)	0.3038(9)	0.166(14)

$$^a U_{eq} = 1/3 \sum \sum U_{ij} a_i^* a_j^* a_i a_j$$

**Table 3.** Fractional atomic coordinates and equivalent isotropic displacement parameters for In[S<sub>2</sub>P(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>]<sub>3</sub> (2) with e.s.d.'s in parentheses. The occupancy factors are 0.39(2) and 0.61(2) for C4A and C4B, respectively.

	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> <sub>eq</sub> /Å <sup>2</sup> <sup>a</sup>
In	0.25412(4)	0.28004(3)	0.26682(3)	0.0500(1)
S1	0.3007(2)	0.0676(2)	0.1522(1)	0.0743(7)
S2	0.0438(2)	0.3979(2)	0.1629(1)	0.0819(7)
S3	0.4245(1)	0.1158(1)	0.3833(1)	0.0540(5)
S4	0.0486(1)	0.2505(1)	0.4154(1)	0.0545(5)
S5	0.4884(2)	0.3175(2)	0.1490(1)	0.0658(6)
S6	0.2243(1)	0.5258(1)	0.3302(1)	0.0575(5)
P1	0.1273(2)	0.2074(2)	0.0960(1)	0.0837(8)
P2	0.2246(1)	0.1279(1)	0.4770(1)	0.0470(5)
P3	0.4151(1)	0.5025(1)	0.2243(1)	0.0560(5)
C1	-0.0249(10)	0.1388(10)	0.1116(9)	0.132(5)
C2	-0.0745(10)	0.0910(12)	0.2134(8)	0.143(6)
C3	0.1882(16)	0.2287(15)	-0.0380(7)	0.167(8)
C4A	0.2920(25)	0.2491(25)	-0.0738(16)	0.101(11)
C4B	0.2689(21)	0.1177(20)	-0.1060(11)	0.154(11)
C5	0.2255(6)	-0.0492(5)	0.5020(4)	0.061(2)
C6	0.2543(7)	-0.1323(6)	0.4099(5)	0.085(3)
C7	0.1994(6)	0.1997(5)	0.5975(4)	0.061(2)
C8	0.2113(7)	0.3417(7)	0.5950(5)	0.080(3)
C9	0.5648(6)	0.5067(6)	0.2778(4)	0.068(2)
C10	0.5999(7)	0.4051(7)	0.3613(5)	0.088(3)
C11	0.3780(7)	0.6527(6)	0.1417(4)	0.078(3)
C12	0.2407(8)	0.6857(8)	0.0977(5)	0.104(4)

$$^a U_{eq} = 1/3 \sum \sum U_{ij} a_i^* a_j^* a_i a_j$$

Table 4. Bond distances (Å) in **1** and **2** with e.s.d.'s in parentheses.

	(1)	(2)
M-S1	2.753(2)	2.638(1)
M-S2	2.787(2)	2.638(1)
M-S3	2.813(2)	2.621(1)
M-S4	2.829(3)	2.603(1)
M-S5	2.786(3)	2.620(1)
M-S6	2.858(2)	2.628(1)
P1-C1	1.829(9)	1.852(10)
P1-C3	1.791(9)	1.842(11)
P2-C5	1.808(12)	1.824(5)
P2-C7	1.927(13)	1.813(5)
P3-C9	1.786(11)	1.817(6)
P3-C11	1.856(11)	1.818(6)
S1...S2	3.325(3)	3.294(2)
S3...S4	3.358(4)	3.286(2)
S5...S6	3.338(4)	3.293(2)
P1-S1	2.030(3)	2.012(2)
P1-S2	2.017(3)	2.002(2)
P2-S3	2.029(4)	2.029(2)
P2-S4	2.011(3)	2.021(2)
P3-S5	2.016(4)	2.023(2)
P3-S6	2.003(4)	2.016(2)
C1-C2	1.47(1)	1.50(1)
C3-C4A	1.51(1)	1.11(2)
C3-C4B	—	1.38(2)
C5-C6	1.52(2)	1.508(8)
C7-C8A	1.76(3)	1.509(8)
C7-C8B	1.62(4)	—
C9-C10	1.44(1)	1.507(8)
C11-C12A	1.54(4)	1.515(9)
C11-C12B	1.37(2)	—

hedron described as a distorted octahedron (Fig. 1). The distortion is complicated and differs from the distortions found in other complexes with a  $\text{BiS}_6$  core.<sup>3,5,6,14-16</sup> Octahedral distortion can be described by the twist angles,  $\varphi$ , between the two opposite triangular faces of the octahedron along the pseudo three-fold axis.<sup>17</sup> In a perfect octahedron  $\varphi = 60^\circ$ , and for a trigonal prism  $\varphi = 0^\circ$ . In **1**, the three twist angles are  $31.8(1)$ ,  $36.4(1)$  and  $38.4(1)^\circ$ . The dihedral angle between the two triangular faces (S1-S3-S5 and S2-S4-S6) is  $3.8^\circ$ . The Bi atom lies  $0.065 \text{ \AA}$  from the plane defined by the three P atoms. The six Bi-S bond lengths are in the range  $2.753(2) - 2.858(2) \text{ \AA}$ , values that are in agreement with distances found for other compounds.<sup>3,5,6,14-16</sup> Each ligand is asymmetrically coordinated to the Bi atom so that short Bi-S bonds are associated with long P-S bonds and vice versa. The differences vary from  $0.013(4)$  to  $0.018(4) \text{ \AA}$  for the P-S bonds and  $0.016(3)$  to  $0.072(3) \text{ \AA}$  for the associated Bi-S bonds. The interligand S...S distances are in the range  $3.935(4) - 4.641(4) \text{ \AA}$  (Fig. 5a), which is greater than the sum of the van der Waals radii,  $3.60 \text{ \AA}$ .

Intramolecular repulsion might have some influence on the deformation of the Bi polyhedra since many intramolecular contacts are shorter than normal van der Waals interactions, the shortest being S4-C2,  $3.68(10) \text{ \AA}$ . **1** suffers ligand disorder with two sets of terminal  $\text{CH}_3$  groups

Table 5. Bond angles ( $^\circ$ ) in **1** and **2** with e.s.d.'s in parentheses.

	(1)	(2)
S1-M-S2	73.77(6)	77.28(5)
S3-M-S4	73.06(8)	77.96(4)
S5-M-S6	72.50(8)	77.72(4)
S1-P1-S2	110.5(1)	110.32(9)
S1-P1-C1	110.7(3)	109.2(3)
S1-P1-C3	110.0(3)	112.2(4)
S2-P1-C1	110.2(3)	110.9(3)
S2-P1-C3	110.7(3)	108.6(5)
C1-P1-C3	104.7(5)	105.6(7)
S3-P2-S4	112.5(2)	108.46(7)
S3-P2-C5	109.9(4)	110.6(2)
S3-P2-C7	109.6(5)	112.0(2)
S4-P2-C5	109.2(4)	111.0(2)
S4-P2-C7	109.5(5)	110.3(2)
C5-P2-C7	106.0(7)	104.5(2)
S5-P3-S6	112.3(2)	109.22(8)
S5-P3-C9	110.2(4)	110.8(2)
S5-P3-C11	107.9(5)	111.0(2)
S6-P3-C9	109.6(4)	110.8(2)
S6-P3-C11	111.7(5)	110.8(2)
C9-P3-C11	104.8(5)	104.1(3)
P1-C1-C2	114.4(7)	115.1(6)
P1-C3-C4A	114.6(7)	124.0(18)
P1-C3-C4B	—	124.7(13)
P2-C5-C6	112.8(8)	113.4(4)
P2-C7-C8A	104.6(10)	114.4(4)
P2-C7-C8B	103.8(15)	—
P3-C9-C10	117.8(8)	114.5(4)
P3-C11-C12A	110.2(14)	114.7(4)
P3-C11-C12B	122.2(16)	—
C4A-C3-C4B	—	77.6(16)
C8A-C7-C8B	137.7(16)	—
C12A-C11-C12B	89.5(18)	—

for two of the ligands, markedly influencing some P-C and C-C bond distances (Table 4). As can be seen from the C-C-P-C torsion angles (Table 6) there are two different conformations of the ethyl groups in the molecule. All three ligands have the antiperiplanar, antiperiplanar (*ap,ap*) conformation, but the disordered ligands also adopt the synclinal, antiperiplanar conformation (*sc,ap*).<sup>18</sup> All combinations of disorder cannot occur in one particular ligand molecule since this leads to some unrealistically short intermolecular distances, i.e. C8-C12(-x, -y, -z) =  $2.31(5)$ , C8B-C8B(-x, y, 1/2-z) =  $2.84(9)$  and

Table 6. Selected torsion angles ( $^\circ$ ) in **1** and **2** with e.s.d.'s in parentheses.

	(1)	(2)
C1-P1-C3-C4A	177(1)	-168(4)
C1-P1-C3-C4B	—	-70(2)
C2-C1-P1-C3	-174(1)	171(1)
C5-P2-C7-C8A	165(1)	174(1)
C5-P2-C7-C8B	-46(2)	—
C8-C7-P2-C5	-173(1)	-177(1)
C9-P3-C11-C12A	-166(1)	-172(1)
C9-P3-C11-C12B	-63(1)	—
C10-C9-P3-C11	-169(1)	171(1)

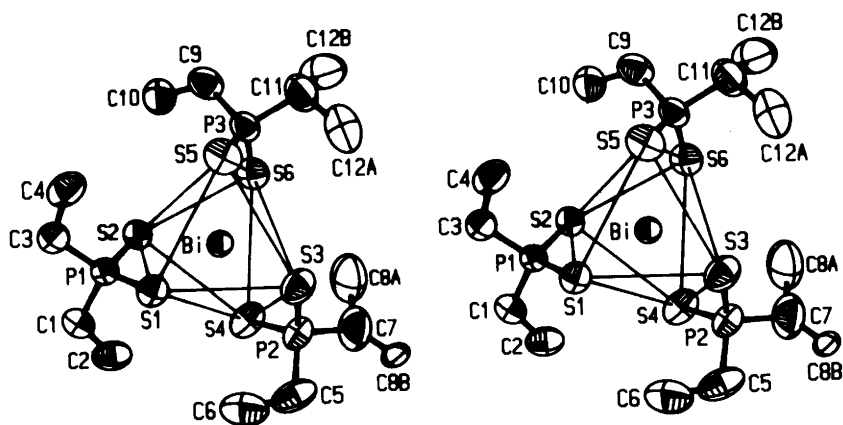


Fig. 1. Stereoscopic view of  $\text{Bi}[\text{S}_2\text{P}(\text{C}_2\text{H}_5)_2]_3$  (**1**) with the atom numbering scheme. The disordered atoms are included. Thermal ellipsoids are drawn at the 50% probability level.

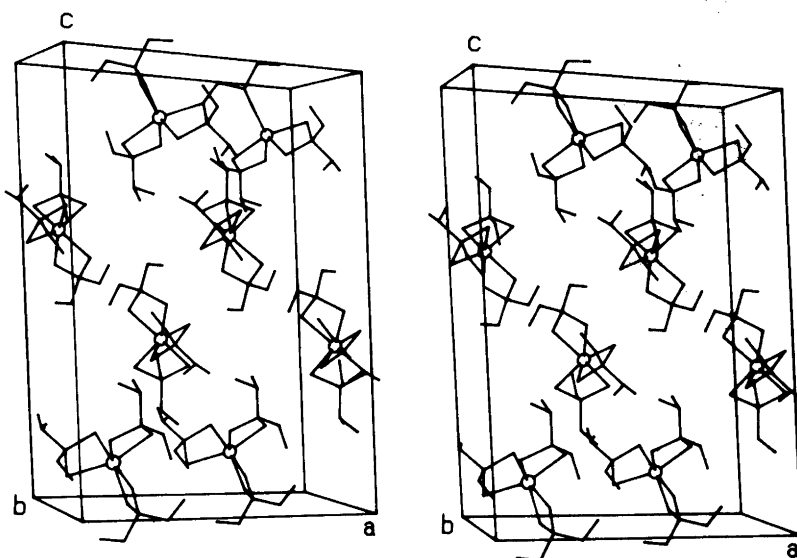


Fig. 2. The unit cell content of  $\text{Bi}[\text{S}_2\text{P}(\text{C}_2\text{H}_5)_2]_3$  (**1**). Disordered atoms are included.

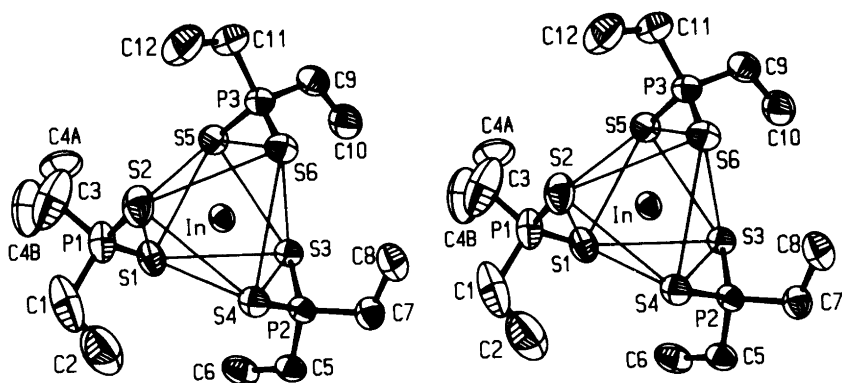


Fig. 3. Stereoscopic view of  $\text{In}[\text{S}_2\text{P}(\text{C}_2\text{H}_5)_2]_3$  (**2**) with the atom numbering scheme. The disordered atom is included. Thermal ellipsoids are drawn at the 50% probability level.

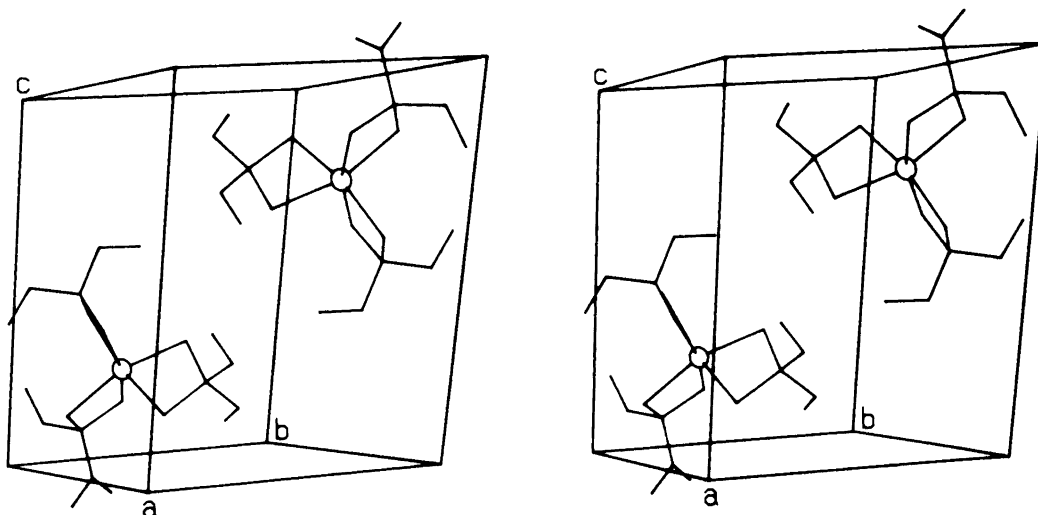


Fig. 4. The unit cell content of  $\text{In}[\text{S}_2\text{P}(\text{C}_2\text{H}_5)_2]_3$  (**2**). The disordered atom is included.

$\text{C8B}-\text{C12B}(-x, y+1, 1/2-z) = 3.00(4) \text{ \AA}$ . A stereoscopic view of the unit cell content is shown in Fig. 2.

$\text{In}[\text{S}_2\text{P}(\text{C}_2\text{H}_5)_2]_3$  (**2**). Indium coordinates six sulfur atoms from three diethyldithiophosphinate ligands in a polyhedron which can be described as a trigonally distorted octahedron (Fig. 3). The close agreement between the three twist angles,  $\varphi = 39.6(1), 42.4(1)$  and  $43.4(1)^\circ$ , clearly shows the almost perfect threefold symmetry (neglecting one of the disordered ethyl groups). The six In-S distances are in the range  $2.603(1)-2.638(1) \text{ \AA}$ , in agreement with distances found in other compounds. This slight variation in the In-S distances has been found in several tris(dithiochelates) of indium,<sup>4,19,20</sup> and an explanation for this has been suggested by Einstein and Jones.<sup>20</sup> The P-S distances are equal, with an average of  $2.017(9) \text{ \AA}$ . **2** suffers ligand disorder of the same type as **1**, with all three ligands having the (*ap, ap*) conformation, and with the disordered ligand also adopting the (*sc, ap*) conformation. The crystal is built up from discrete molecules and is stabilized by Van der Waals interactions only (Fig. 4).

## Discussion

At first sight **1** and **2** do not appear to differ very much (Figs. 1 and 3). The deformation of the coordination polyhedra is, however, different in the two compounds. A comparison of the  $\text{MS}_6$  cores of **1** and **2**, viewed along the pseudo three-fold axis, are shown in Figs. 5a and 5b. The main differences are: (i) The three-fold symmetry is not so well maintained in **1**, and (ii) the metal-S distances in **2** are almost equal, while they are unequal in **1**. These differences are not unexpected since Bi has a seventh stereochemically active lone pair in the valence shell. It is illustrative to compare **1** with the related compounds  $\text{Bi}[\text{S}_2\text{P}(\text{O}-i-\text{C}_3\text{H}_7)_2]_3$  (**3**) and  $\text{Bi}[\text{SP}(\text{C}_6\text{H}_5)_2\text{N}(\text{C}_6\text{H}_5)_2\text{PS}]_3$  (**4**). Figs. 5c-d show the  $\text{BiS}_6$  cores for these compounds,

viewed along the pseudo three-fold axis. Figs. 5b-d show that there are two distinct sets of Bi-S distances in **3** and **4**, while in **1** there is none. Furthermore, in **3** the non-bonding S...S distances in the triangular face S2, S4 and S6 are much longer than in the opposite face S1, S3, S5. Lawton *et al.*<sup>3</sup> attribute the set of long Bi-S distances and the elongated S...S distances to lone-pair repulsion, in accordance with the VSEPR theory. In **4**, there is no elongation of non-bonding S...S distances, and Williams *et al.*<sup>15</sup> concluded that steric crowding by the bulky ligands partially overrides the influence of the lone pair. Another important factor influencing the deformation of the  $\text{BiS}_6$  core is the ligand bite. In **1** and **3** the average bites are  $3.34(2)$  and  $3.28(1) \text{ \AA}$ , respectively, while it is  $4.0(1) \text{ \AA}$  in **4**, thus preventing the lone pair from achieving its full stereochemical influence. In **1** the distortion of the octahedron is complicated and does not resemble the distortions found in **3** and **4**. Our conclusion is that the lone pair influences the bond lengths in the  $\text{BiS}_6$  core, but that intermolecular interactions prevent it from achieving its full stereochemical influence. The most probable position of the seventh electron pair is, however, through the triangular octahedral face made up by S3, S4 and S6, since the corresponding Bi-S bonds are elongated and the inter-ligand S...S distance are the longest in the octahedron. The location of the lone pair is thus different from its position in **3** where it is located on the pseudo-trigonal axis. The weak stereochemical influence of the lone pair is illustrated in the closely related compound  $\text{Bi}[\text{S}_2\text{P}(\text{C}_2\text{H}_5)_2]_3 \cdot \text{C}_6\text{H}_6$ <sup>5</sup> where the lone pair is inactive. The Bi atom is symmetrically coordinated by six sulfur atoms and is also located on a trigonal axis. In  $\text{Bi}[\text{S}_2\text{P}(\text{C}_6\text{H}_5)_2]_3 \cdot \text{C}_6\text{H}_6$ <sup>6</sup> Bi is asymmetrically coordinated by six sulfur atoms from three ligands in a pentagonal pyramidal environment. The empty axial position, which is a probable position for an active lone pair, is however, occupied by a sulfur atom from a neighboring molecule, thus completing the pentagonal bipyramidal conformation. To differentiate

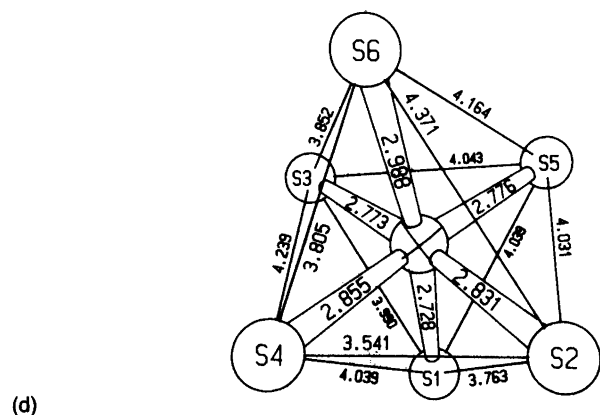
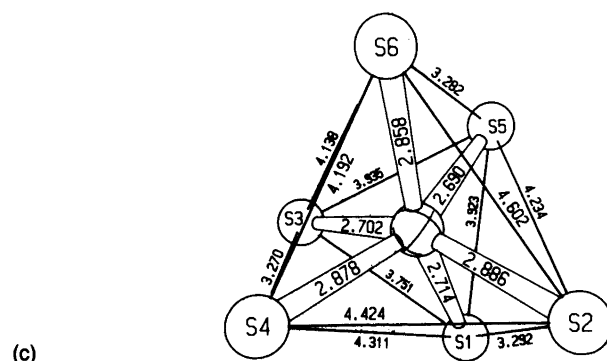
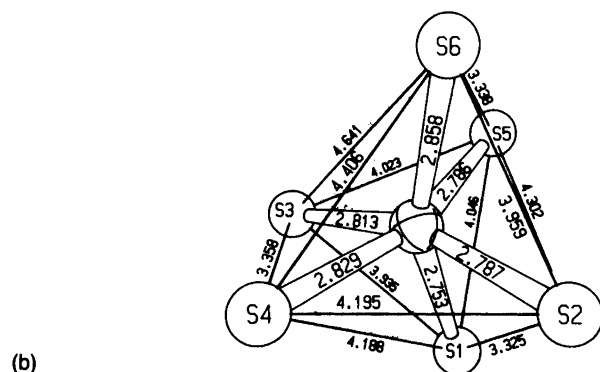
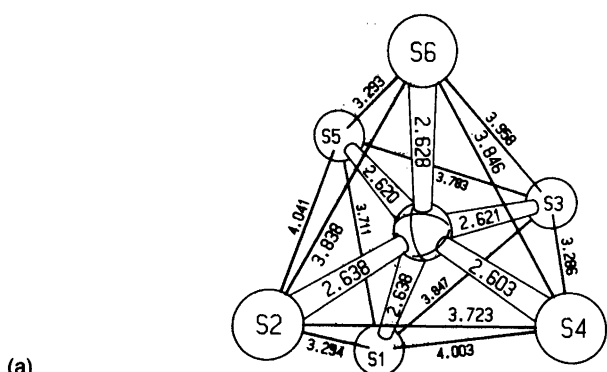


Fig. 5. Perspective views of the  $MS_6$  nucleus of (a)  $In[S_2P(C_2H_5)_2]_3$  (2), (b)  $Bi[S_2P(C_2H_5)_2]_3$  (1), (c)  $Bi[S_2P(O-i-C_3H_7)_2]_3$  (3) Ref. 3 and (d)  $Bi[SPPPh_2NPh_2PS]_3$  (4) Ref. 15 down the pseudo three-fold axis.

between the lone pair and the intra- and intermolecular effects, further studies with other ligands are needed. This work is in progress with the methoxy and ethoxy analogues of 1.

The P-S bond distances in 1 and 2 are all intermediate between those typical for single and double bonds, as is usually found in coordination compounds of this type.<sup>2</sup> In the related compound  $In[S_2P(OC_2H_5)_2]_3$ <sup>4</sup> the P-S bonds are of unequal length, the averages being 1.91(4) and 2.08(5) Å for the shorter and longer bonds, respectively. However, the low accuracy of the latter structure determination makes the results uncertain, the unequal P-S bond lengths not being reflected in unequal In-S bond lengths.

## References

1. Wasson, J. R., Woltermann, G. M. and Stoklasa, H. J. *Fortschr. Chem. Forsch.* 35 (1973) 65.
2. Haiduc, I. *Rev. Inorg. Chem.* 3 (1981) 353.
3. Lawton, S. L., Fuhrmeister, C. J., Haas, R. G., Jarman, C. S. and Lohmeyer, F. G. *Inorg. Chem.* 13 (1974) 135.
4. Coggon, P., Lebedda, J. D., McPhail, A. T. and Palmer, R. A. *J. Chem. Soc. Chem. Commun.* (1970) 78.
5. Sowerby, D. B. and Haiduc, I. *J. Chem. Soc., Dalton Trans.* (1987) 1257.
6. Begley, M. J., Sowerby, D. B. and Haiduc, I. *J. Chem. Soc., Dalton Trans.* (1987) 145.
7. Sidgwick, N. V. and Powell, H. M. *Proc. Roy. Soc., Ser. A* 176 (1940) 153.
8. Gillespie, R. J. and Nyholm, R. S. *Quart. Rev. Chem. Soc.* 11 (1957) 339.
9. Kuchen, W., Metten, J. and Judat, A. *Chem. Ber.* 97 (1964) 2306.
10. Becker, P. J. and Coppens, P. *Acta Crystallogr., Sect. A* 30 (1974) 129.
11. Abrahams, S. C. and Keve, E. T. *Acta Crystallogr., Sect. A* 27 (1971) 157.
12. *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham 1974, Vol. IV, p. 71.
13. Lundgren, J.-O. *Report No. UUIC-B13-4-05*, University of Uppsala, Uppsala, Sweden 1982.
14. Raston, C. L. and White, A. H. *J. Chem. Soc., Dalton Trans.* (1976) 791.
15. Williams, D. J., Quicksall, C. O. and Barkigia, K. M. *Inorg. Chem.* 21 (1982) 2097.
16. Hoskins, B. F., Tiekink, E. R. T. and Winter, G. *Inorg. Chim. Acta* 81 (1984) L33.
17. Stiefel, E. I. and Brown, G. F. *Inorg. Chem.* 11 (1972) 434.
18. Klyne, W. and Prelog, V. *Experientia* 16 (1960) 521.
19. Hauser, P. J., Bordner, J. and Schreiner, A. F. *Inorg. Chem.* 12 (1973) 1347.
20. Einstein, F. W. B. and Jones, R. D. G. *J. Chem. Soc. A* (1971) 2762.

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