

**Discussion.** There are three independent imidazole ligands: *A*, *B* and *C*. The atomic numbering of the ligand is indicated in Fig. 1. Fig. 2 is a stereoscopic projection of one molecular unit. Geometric entities are given in Table 3. The Ni ion is octahedrally surrounded by six imidazole ligands. Contrary to the results of earlier investigations on metal(II) hexakis(imidazole) cations (Santoro, Mighell, Zocchi & Reimann, 1969; Mighell & Santoro, 1971; Strandberg & Lundberg, 1971) no threefold axis is present. The geometry of the cation, however, shows only very slight deviations from the ideal  $\bar{3}$  symmetry. No significant differences in bond distances and angles with respect to reported values and to those of imidazole (Martinez-Carrera, 1966) are found. The cations are surrounded by 12 anions, the shortest anion-cation contacts being F(1)-N(B4 at  $\bar{x} + \frac{1}{2}, y - \frac{1}{2}, \bar{z} + \frac{1}{2}$ ) 3.04 Å, F(2)-N(A4 at  $\bar{x} + 1, \bar{y} + 1, \bar{z} + 1$ ) 2.81 Å and F(3)-N(C4 at  $x + 1, y, z + 1$ ) 3.03 Å. Each anion is surrounded by six cations. The shortest cation-cation contact is C(B3)-C(C3 at  $x + \frac{1}{2}, \bar{y} + \frac{1}{2}, z - 1$ ) 3.50 Å. The very large temperature parameters of the fluoroborate anion are not unusual in hexasolvated coordination compounds in which the anions are very weakly bonded to the cations.

This investigation has been undertaken to support the study of e.p.r. spectra of hexasolvated metals of the first transition series. Reedijk & Nieuwenhuys (1972) described powder-e.p.r. spectra of these compounds and the single-crystal spectra are the subject of investigation at our laboratory (Vermaas, 1975).

All calculations were performed on the IBM 370/158 computer of the University of Leiden with programs

developed in our laboratory, partially based on *ORFLS* (Busing & Levy, 1962) and *ORTEP* (Johnson, 1965).

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### References

- BUSING, W. R. & LEVY, H. A. (1962). *ORFLS*. Oak Ridge National Laboratory Report ORNL-TM-305.  
 CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104-109.  
 GRAAFF, R. A. G. DE (1973). *Acta Cryst.* **A29**, 298-301. *International Tables for X-ray Crystallography* (1962). Birmingham: Kynoch Press.  
 JOHNSON, C. K. (1965). *ORTEP*. Oak Ridge National Laboratory Report ORNL-3794.  
 LEEUWEN, P. W. N. M. VAN & GROENEVELD, W. L. (1967). *Inorg. Nucl. Chem. Lett.* **3**, 145-146.  
 MARTÍNEZ-CARRERA, S. (1966). *Acta Cryst.* **20**, 783-789.  
 MIGHELL, A. D. & SANTORO, A. (1971). *Acta Cryst.* **B27**, 2089-2097.  
 REEDIJK, J. (1969). *Rec. Trav. Chim. Pays-Bas*, **88**, 1451-1470.  
 REEDIJK, J. & NIEUWENHUYSE, B. (1972). *Rec. Trav. Chim. Pays-Bas*, **91**, 533-551.  
 SANTORO, A., MIGHELL, A. D., ZOCCHI, M. & REIMANN, C. W. (1969). *Acta Cryst.* **B25**, 842-847.  
 STRANDBERG, R. & LUNDBERG, B. K. S. (1971). *Acta Chem. Scand.* **25**, 1767-1774.  
 VERMAAS, A. (1975). To be published.

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## $\beta$ -Tetraphosphorus Pentasulphide

BY ALISON M. GRIFFIN AND GEORGE M. SHELDRIK

*University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, England*

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**Abstract.**  $P_4S_5$ , monoclinic,  $P2_1/m$ ,  $a = 6.389$  (3),  $b = 10.966$  (5),  $c = 6.613$  (3) Å,  $\beta = 115.65$  (6)°,  $U = 417.66$  Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 2.26$  g cm<sup>-3</sup>. The structure of a new isomer has been determined by direct methods and refined to an  $R$  of 0.029 for 581 unique diffractometer data. The molecular geometry is analogous to that in  $As_4S_5$ , but quite unlike that in  $\alpha$ - $P_4S_5$  and  $P_4Se_5$ . The cage structure possesses approximate  $mm$  symmetry, and consists of two PPSPS rings fused with two (PS)<sub>3</sub> rings. Mean bond lengths (corrected for libration) and angles for  $mm$  symmetry are: P-S, 2.117 (4), 2.116 (3), 2.130 (4); P-P, 2.295 (5) Å; P-S-P, 115.5 (2), 105.4 (1); S-P-S, 97.6 (2), 107.4 (1), 104.6 (1); S-P-P, 102.2 (2)°.

**Introduction.** Fourier transform <sup>31</sup>P n.m.r. studies (Griffin & Sheldrick, 1976) have recently established the existence of several new molecular phosphorus sulphides. Two isomers of formula  $P_4S_5$  were found;  $\alpha$ - $P_4S_5$  gives an ABCX spectrum consistent with the reported structure (Vos, Olthof, van Bolhuis & Botterweg, 1965), and the new isomer  $\beta$ - $P_4S_5$  gives an A<sub>2</sub>X<sub>2</sub> spectrum consistent with the structure reported here.

Crystals were obtained as elongated golden yellow platelets by cooling of a solution in CS<sub>2</sub>. Intensities were determined with an automated Syntex  $P2_1$  four-circle diffractometer, Cu  $K\alpha$  radiation and graphite

monochromator. 1639 reflexions were measured; after application of  $L_p$  and absorption corrections, equivalent reflexions were averaged to give 581 unique reflexions with  $F > 2.5\sigma(F)$  based on counting statistics. Cell dimensions were obtained from diffractometer measurements of 15 reflexions. The structure was solved by multiresolution  $\Sigma_2$  sign expansion in the space group  $P2_1/m$ ; the choice of  $P2_1/m$  rather than  $P2_1$  was confirmed by the successful refinement of the structure. The structure was refined by full-matrix least-squares calculations, with anisotropic atoms, complex neutral atom scattering factors, and the weighting scheme  $w = 1/[\sigma^2(F) + 0.0002F^2]$  to a final  $R' = \sum w^{1/2} \Delta / \sum w^{1/2} |F_o|$  of 0.031; the corresponding unweighted  $R$  was 0.029. An isotropic extinction parameter  $x$  refined to  $256(34) \times 10^{-8}$ , where  $F_c$  is multiplied by  $[1 - x|F_c|^2/\sin \theta]$ . The results of the final least-squares cycle are given in Tables 1 and 2, and the derived interatomic distances and angles in Tables 3–5.\*

**Discussion.** In  $P2_1/m$  the molecule must possess a crystallographic mirror plane; P(1), P(2) and S(1) are found to lie in special positions in this plane. To a good approximation, the molecule possesses  $mm$

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31242 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. Fractional coordinates ( $\times 10^4$ )

	<i>x</i>	<i>y</i>	<i>z</i>
P(1)	2851 (2)	2500	3388 (2)
P(2)	8706 (2)	2500	7714 (2)
P(3)	4214 (1)	1458 (1)	8575 (1)
S(1)	6449 (2)	2500	4219 (2)
S(2)	7673 (1)	1053 (1)	9179 (1)
S(3)	2231 (1)	1053 (1)	5158 (1)

Table 2. Anisotropic temperature factors ( $\text{\AA}^2 \times 10^4$ )

The anisotropic temperature factor takes the form:

$$\exp [-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{13}hla^*c^* + 2U_{12}hka^*b^*)].$$

	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
P(1)	240 (6)	538 (8)	283 (6)	0	91 (5)	0
P(2)	205 (6)	499 (8)	328 (7)	0	122 (5)	0
P(3)	288 (5)	283 (6)	380 (5)	52 (3)	166 (4)	-2 (3)
S(1)	257 (6)	661 (9)	306 (6)	0	144 (5)	0
S(2)	305 (5)	377 (6)	421 (5)	81 (3)	146 (4)	103 (3)
S(3)	329 (5)	356 (6)	460 (5)	-111 (3)	162 (4)	-104 (3)

Table 3. Bond lengths and librally corrected bond lengths ( $\text{\AA}$ )

P(1)–S(1)	2.120 (1)*	2.125 (3)†	P(2)–S(1)	2.129 (1)*	2.136 (4)†
P(1)–S(3)	2.108 (1)	2.117 (4)	P(2)–S(2)	2.109 (1)	2.116 (4)
P(3)–S(3)	2.105 (1)	2.111 (3)	P(3)–S(3)	2.116 (1)	2.121 (3)
P(3)–P(3')	2.284 (2)	2.295 (5)			

\* Random errors only.

† Including estimated contributions from errors in cell dimensions and librational corrections.

symmetry. The anisotropic temperature factors were found to be in excellent agreement with the rigid-body motion model of Schomaker & Trueblood (1968):  $R_g = [\sum \Delta^2 / \sum U_{ij}^2]^{1/2}$  for the agreement between the observed and calculated  $U_{ij}$  was 0.028. Librational tensors, with respect to axes parallel to  $x^*$ ,  $y$  and  $z$ ,

Table 4. Bond angles ( $^\circ$ )

The estimated standard deviations include contributions for errors in the cell dimensions.

S(1)–P(1)–S(3)	107.4 (1)	S(1)–P(2)–S(2)	107.4 (1)
S(3)–P(1)–S(3')	97.6 (2)	S(2)–P(2)–S(2')	97.6 (2)
S(3)–P(3)–P(3')	102.2 (2)	S(2)–P(3)–P(3')	102.1 (2)
P(1)–S(3)–P(3)	105.5 (1)	P(2)–S(2)–P(3)	105.3 (1)
P(1)–S(1)–P(2)	115.5 (2)	S(2)–P(3)–S(3)	104.6 (1)

Table 5. Non-bonded distances ( $\text{\AA}$ )

Symmetry code

(i)  $x, y, 1+z$ ; (ii)  $1-x, -y, 1-z$ ; (iii)  $x-1, y, z$   
 (iv)  $2-x, -y, 2-z$ ; (v)  $1-x, -y, 2-z$ ; (vi)  $-x, -y, 1-z$

Intermolecular		Intramolecular	
P(3)···P(1 <sup>i</sup> )	3.820	P(3)···P(2)	3.359
S(2)···P(1 <sup>ii</sup> )	4.205	S(1)···P(3)	3.900
S(3)···P(2 <sup>iii</sup> )	3.707	S(2)···P(3')	3.424
S(2)···P(2 <sup>iv</sup> )	4.543	S(3)···P(3')	3.418
S(3)···P(2 <sup>v</sup> )	4.262	S(2)···S(1)	3.416
P(3)···P(3 <sup>v</sup> )	3.627	S(3)···S(1)	3.408
S(2)···P(3 <sup>v</sup> )	3.577	S(2)···S(2')	3.173
S(2)···S(1 <sup>vi</sup> )	4.695	S(3)···S(3')	3.173
S(3)···S(1 <sup>vi</sup> )	3.970		
S(2)···S(2 <sup>iv</sup> )	3.544		
S(3)···S(2 <sup>ii</sup> )	3.704		
S(3)···S(3 <sup>vi</sup> )	3.604		

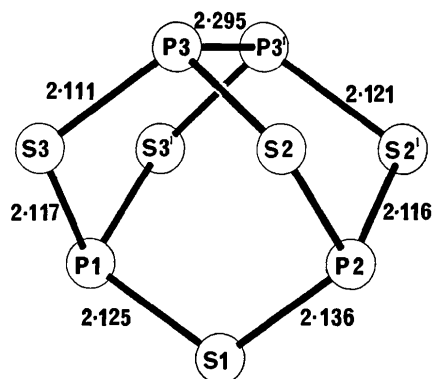


Fig. 1. The molecule of  $\beta$ -P<sub>4</sub>S<sub>5</sub>, showing librally corrected bond lengths ( $\text{\AA}$ ).

were:  $L_{11}$  51(2),  $L_{12}$  0,  $L_{13}$  -1(1),  $L_{22}$  10(1),  $L_{23}$  0,  $L_{33}$  37(1)  $10^{-4}$  rad<sup>2</sup>;  $S_{11}$  0(2),  $S_{12}$  4(1),  $S_{13}$  0(1),  $S_{21}$  4(1),  $S_{22}$  0(2),  $S_{23}$  5(1),  $S_{31}$  0(1),  $S_{32}$  5(1),  $S_{33}$  0(1)  $10^{-4}$  rad Å;  $T_{11}$  165(4),  $T_{12}$  0,  $T_{13}$  23(3),  $T_{22}$  252(4),  $T_{23}$  0,  $T_{33}$  219(4)  $10^{-4}$  Å<sup>2</sup> (relative to an origin at  $x=0.4805$ ,  $y=0.2500$ ,  $z=0.7421$  which makes S symmetric). These values were used in calculating the librational corrected bond lengths given in Table 3 and Fig. 1.

The molecular geometry is quite unlike the rather asymmetric structure found for  $P_4Se_5$  (Penney & Sheldrick, 1971) and  $\alpha$ - $P_4S_5$ . On the other hand  $\beta$ - $P_4S_5$  has the same molecular symmetry, space group, and number of atoms in special positions as  $As_4S_5$  (Whitfield, 1973), but the crystallographic mirror plane in  $As_4S_5$  lies through the atoms corresponding to P(3), P(3') and S(1), *i.e.* it is at right angles to the crystallographic mirror plane in  $\beta$ - $P_4S_5$ . The result is that the cell dimensions and atomic coordinates are quite different in the two structures. The structure of  $\beta$ - $P_4S_5$  may be derived from that of  $P_4S_7$  (Vos *et al.*, 1965) by removing both terminal atoms (attached to P(1) and P(2) in the  $\beta$ - $P_4S_5$  notation). The valence angles at P(1) and P(2) are 2–5° smaller in  $\beta$ - $P_4S_5$  than in  $P_4S_7$  (consistent with lone pair–bond pair repulsion); the valence angles at S are 3–5° larger in  $\beta$ - $P_4S_5$  to

compensate, resulting in the unusually large value of 115.5 (2)° for P(1)–S(1)–P(2) in  $\beta$ - $P_4S_5$ . Ignoring libration, the P–P bond in  $\beta$ - $P_4S_5$  is 0.042 (7) Å shorter than the remarkably long P–P bond in  $P_4S_7$ , whereas the bonds between bridging S and P(1) and P(2) are an average of 0.024 Å longer in  $\beta$ - $P_4S_5$ .

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### References

- GRIFFIN, A. M. & SHELDRIK, G. M. (1976). To be published.  
 PENNEY, G. J. & SHELDRIK, G. M. (1971). *J. Chem. Soc. (A)*, pp. 245–248.  
 SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst. B24*, 63–76.  
 VOS, A., OLTHOF, R., VAN BOLHUIS, F. & BOTTERWEG, R. (1965). *Acta Cryst. 19*, 864–867.  
 WHITFIELD, H. J. (1973). *J. Chem. Soc. Dalton*, pp. 1740–1742.

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## Trimethyllead Acetate

BY GEORGE M. SHELDRIK AND ROBIN TAYLOR

*University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, England*

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**Abstract.**  $C_5H_{12}O_2Pb$ , orthorhombic,  $Pnma$ ,  $a=10.77$  (2),  $b=7.82$  (2),  $c=9.58$  (2) Å,  $U=807$  Å<sup>3</sup>,  $Z=4$ ,  $D_x=2.56$  g cm<sup>-3</sup>. Trimethyllead acetate is isostructural with the analogous Sn compound; planar trimethyllead groups are linked by bridging acetate groups to form infinite chains along **a**, with approximately trigonal bipyramidal coordination of Pb. The two Pb–O distances are significantly different [2.327 (24) and 2.555 (25) Å]. Other mean distances and angles are: Pb–C, 2.181 (25); C–O, 1.223 (30); C–C, 1.519 (36) Å; O–Pb–O, 169.7 (8); O–C–O, 121.5 (24); O–C–C, 119.3 (20)°. The structure was refined to an *R* of 0.052 for 420 unique diffractometer data.

**Introduction.** X-ray crystallographic studies of many apparently tetravalent organotin derivatives [*e.g.*  $(CH_3)_3SnO_2CCH_3$  (Chih & Penfold, 1973),

$(CH_3)_3SnOCH_3$  (Domingos & Sheldrick, 1974) and  $(CH_3)_3SnNCO$ .  $(CH_3)_3SnOH$  (Hall & Britton, 1972)] have established the tendency of Sn to increase its coordination number above four. It is likely that this tendency is continued in the structural chemistry of organolead derivatives, but apart from the structure of  $(C_6H_5)_2PbCl_2$  (Mammi, Buseti & Del Pra, 1967) and the incomplete investigations of  $(CH_3)_3PbCN$  (Chow & Britton, 1971) and  $(CH_3)_2Pb(CN)_2$  (Konnert, Britton & Chow, 1972) there is little crystallographic evidence to confirm this.

Colourless crystals were obtained by recrystallization of a commercial sample of trimethyllead acetate from a methanol/acetone mixture, and were mounted in Lindemann glass capillary tubes. Most proved unsuitable for structural work, but data were eventually collected from two crystals 0.16 × 0.07 × 0.09 mm