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The Crystal Structure of P_4Se_3

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P_4Se_3 belongs to the same space group as the low-temperature modification of P_4S_3 . Its crystal structure, by analogy to that of the latter compound, consists of molecules P_4Se_3 . In both compounds the molecules are located on the planes of symmetry, but their arrangement in these planes is different. The unit cell of P_4Se_3 is twice as large as that of P_4S_3 . The orientation and the position of the molecules was found by interpretation of the [100] and [010] Patterson synthesis combined with trial and error. The co-ordinates were refined by computing Fourier syntheses of the [100] and [010] projection. The average P-P and P-Se bond lengths are 2.25 and 2.24 Å with an e.s.d. of 0.03 and 0.01 Å respectively. The average values of the valence angles Se-P-Se, P-Se-P, Se-P-P and P-P-P are 99.9°, 100.1°, 105.3° and 60.1° respectively. The standard deviation in the individual valence angles is about 1°. Shortest intermolecular distances—about 3.6 Å—are observed between phosphorus atoms.

Introduction

Two phosphorus-selenium compounds, P_4Se_3 and P_2Se_5 , have been reported in the literature (Mai, 1928; Robinson & Scott, 1933; Haq & Samuel, 1937; further references are given in these papers). According to Mai (1926) P_4Se_3 possibly exists in two modifications.

An X-ray investigation of the crystal structures of the phosphorus selenides was undertaken with the object of comparing the structures of these compounds with the recently determined structures of the corresponding sulfides (Vos & Wiebenga, 1955; Leung *et al.*, 1957); P_4Se_3 was investigated first.

Experimental

Materials

P_4Se_3 was prepared by heating white phosphorus and selenium in tetralin (Mai, 1928). The solid reaction product was extracted with tetralin and from the solution thus obtained P_4Se_3 was precipitated by cooling or by addition of ether. After purification by crystallization from benzene, the melting point agreed

with the value reported by Mai (242 °C.). Crystals were grown by slowly cooling the solution in benzene. As the crystals are not stable in moist air, they were transferred into a borosilicate glass capillary in which they could be kept for a long time. Perpendicular to the crystal axis about which the photographs were made, their diameter was approximately 0.1 mm.

Unit cell and space group

Oscillation and Weissenberg photographs, which were made of a number of layer lines about the *b*-axis, indicated an orthorhombic symmetry for the P_4Se_3 crystals. The systematic absences observed were $h0l$ with $h+l$ odd and $hk0$ with k odd, which indicated as probable space group either $Pmnb$ or $P2_1nb$. Because of the absence of piezoelectricity, the crystals were assumed to belong to the centrosymmetric space group $Pmnb$, which was confirmed during the structure analysis. The lattice constants were determined accurately from back reflexion photographs. In Table 1 the lattice constants of P_4Se_3 are compared with those of P_4S_3 (Leung *et al.*, 1957). With 16 units of P_4Se_3 per unit cell the calculated density, 3.17 g.cm.⁻³, was

Table 1. *Crystallographic data for P_4Se_3 and P_4S_3*

P_4Se_3	P_4S_3
Space group $Pmnb$ (or $P2_1nb$)	Space group $Pmnb$ (or $P2_1nb$)
$\alpha = \beta = \gamma = 90^\circ$	$\alpha = \beta = \gamma = 90^\circ$
$a = 9.739 \text{ \AA}$, e.s.d. 0.005 \AA	$a = 9.660 \text{ \AA}$, e.s.d. 0.005 \AA
$b = 11.797$, e.s.d. 0.006	$b = 10.597$, e.s.d. 0.005
$c = 26.270$, e.s.d. 0.013	$c = 13.671$, e.s.d. 0.005
16 molecules per cell	8 molecules per cell
$\lambda(\text{Cu } K\alpha_1) = 1.54051 \text{ \AA}$	
$\lambda(\text{Cu } K\alpha_2) = 1.54433 \text{ \AA}$	

only slightly different from the value, 3.16 g.cm.^{-3} , reported by Mai (1928).

Structure factors

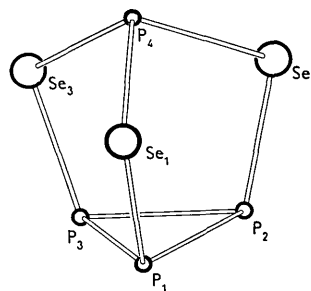
The intensities of the stronger reflexions $h0l$ and $0kl$ were determined from integrated Weissenberg photographs, taken with nickel-filtered copper radiation. The weak intensities were visually estimated on ordinary Weissenberg photographs of long exposure time. Use was made of the multiple-film technique.

Lorentz and polarization factors were taken into account and an approximate correction for absorption was applied, for which the crystal was assumed to be a cylindrical rod ($\mu R \approx 1.2$). In this way the structure factors of 277 $0kl$ and 132 $h0l$ reflexions were obtained.

Determination of the structure

The approximate structure

As is seen from Table 1, P_4Se_3 and P_4S_3 have the same probable space groups but are not isostructural. Because of the equal length of the a -axes the two crystal structures were assumed to be analogous in the x direction. This assumption was supported by a striking similarity of the $[010]$ Patterson syntheses of P_4Se_3 and P_4S_3 ; in both syntheses most of the maxima are located on four lines parallel to the z -axis, with approximate co-ordinates $x = 0$, $x = 0.16$, $x = 0.34$ and $x = 0.5$. Since in P_4S_3 this feature of the Patter-

Fig. 1. Molecule of P_4Se_3 .

son synthesis is due to the location of molecules P_4S_3 on the mirror planes in the unit cell (see Leung *et al.*, 1957, Fig. 5(b)), it was tentatively supposed that the structure of P_4Se_3 also consists of similar molecules lying on the mirror planes in the space group $Pmnb$. If it is assumed that the four independent molecules of the unit cell have the same bond lengths and angles, this model of the structure leaves only one x parameter for the phosphorus atoms and one for the selenium atoms to be determined (see Fig. 4(b)). The first of these was obtained by taking the P-P bond length equal to that in P_4S_3 , the x co-ordinate of the selenium atoms was then chosen such that a reasonable agreement between calculated and observed $h0l$ structure factors was obtained.

The position and the orientation of the four independent molecules was obtained by trial and error, use being made of the information from the $[010]$ and $[100]$ Patterson synthesis, shown in Fig. 2. During this procedure it was assumed that the packing of the molecules resembles that of hexagonal close packing, as in P_4S_3 . When the arrangement of the molecules had been approximately determined, the structure factors $0kl$ and $h0l$ were calculated. The disagreement indices R amounted to 0.4 and 0.3 respectively.

Refinement of the $[100]$ projection

As may be seen from Fig. 3(a), (b), the peaks in the $[010]$ Fourier synthesis show a strong overlap,

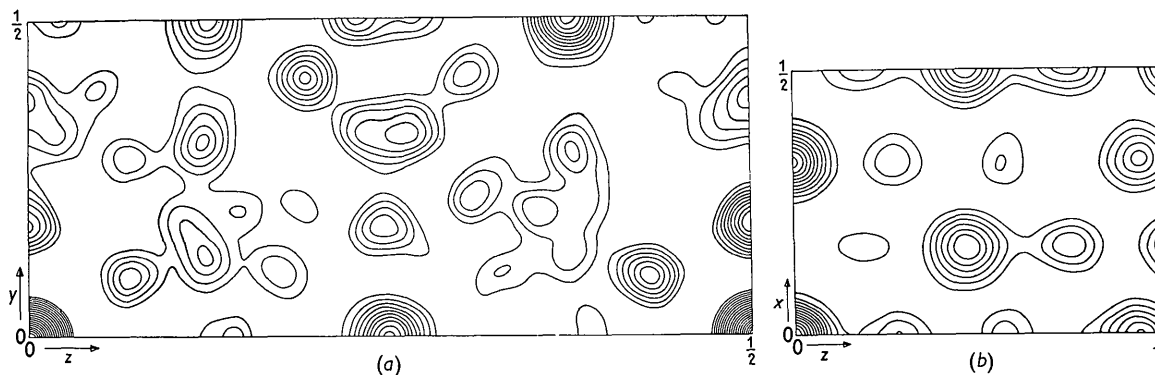


Fig. 2. Projection of the Patterson function along (a) $[100]$ and (b) $[010]$. Only the contour lines for high values of the function are drawn. Contours at arbitrary intervals and not comparable for (a) and (b).

Table 2. *Final co-ordinates**

Molecule	Atom	<i>x</i>	<i>y</i>	<i>z</i>	Molecule	Atom	<i>x</i>	<i>y</i>	<i>z</i>
I	P ₁	0.25	0.086	0.127	III	P ₁	0.25	-0.048	0.325
	P ₂	0.366	0.227	0.0875		P ₂	0.366	-0.010	0.2527
	P ₄	0.25	0.041	0.000		P ₄	0.25	0.239	0.307
	Se ₁	0.25	-0.057	0.0710		Se ₁	0.25	0.107	0.3700
	Se ₂	0.428	0.1592	0.0139		Se ₂	0.428	0.1723	0.2612
II	P ₁	0.75	0.034	0.218	IV	P ₁	0.75	-0.192	0.396
	P ₂	0.866	0.034	0.1443		P ₂	0.866	-0.039	0.3663
	P ₄	0.75	-0.238	0.169		P ₄	0.75	0.032	0.485
	Se ₁	0.75	-0.148	0.2433		Se ₁	0.75	-0.163	0.4822
	Se ₂	0.928	-0.1473	0.1298		Se ₂	0.928	0.0602	0.4355

* For numbering of atoms see Fig. 1. Atoms Se₁, P₁ and P₄ lie on a mirror plane.

while in the [100] Fourier synthesis the non-systematic overlap is small. Therefore the [100] projection was refined first. Four successive Fourier syntheses were computed, the last two of which were compared with the corresponding F_c -syntheses. Finally three F_o-F_c maps were made. The reflexion 008, which showed a strong extinction, was omitted from the F_o-F_c syntheses. The temperature factor was assumed to be isotropic and equal for the different atoms. After each calculation of the structure factors the scale factor and the temperature factor were determined by comparison of the calculated and observed structure factors. The atomic shifts as obtained from the last difference map, were smaller than the estimated standard deviations. After the structure-factor calculation based on the final co-ordinates, the temperature factor was $\exp(-3 \sin^2 \theta / \lambda^2)$ and the disagreement index R amounted to 0.14 for the observed reflexions. The calculated structure factors are compared with the observed ones in Table 3. The final co-ordinates are listed in Table 2.

Refinement of the [010] projection

The scale factor of the reflexions $h0l$ was determined by comparing the intensities of the $00l$ reflexions as observed on the [100] and [010] Weissenberg photographs.

Since the [010] projection shows a strong overlap, the values of the z co-ordinates deduced from the [100] projection were taken as the final ones. The x co-ordinates of the phosphorus and selenium atoms, lying on the mirror planes, are already fixed. Initial values for the x co-ordinates of the remaining atoms were obtained from the distances P₁-P₂₊₃ and Se₁-Se₂₊₃ in the [100] projection, the assumption being made that the phosphorus atoms and the selenium atoms form equilateral triangles (see Fig. 1). These co-ordinates were refined by calculating two successive F_o-F_c syntheses from which the reflexions 600, 008, 303, 305 and 3,0,13 were omitted because of their strong extinction. Only the shifts of the two resolved selenium atoms, I and II in Fig. 3(b), and the one resolved phosphorus atom, III in Fig. 3(b), could be deduced with a reasonable accuracy from these difference maps. Therefore the four independent

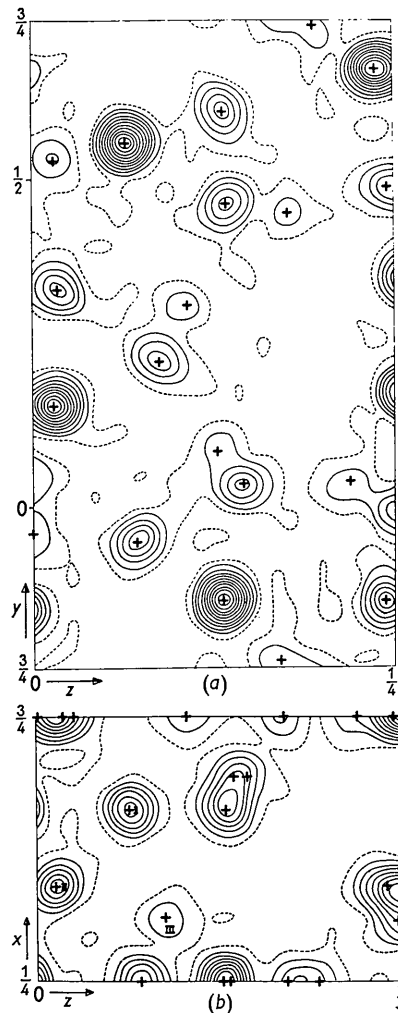


Fig. 3. Electron-density projections along (a) [100] and (b) [010]. Contour lines are at intervals of $10 \text{ e.}\text{\AA}^{-2}$; the broken line is at $5 \text{ e.}\text{\AA}^{-2}$. The crosses indicate the final co-ordinates.

P-P bond lengths perpendicular to the mirror plane were assumed to be equal and were calculated from the position of atom III. After each refinement cycle the distances of the selenium atoms I and II to the mirror planes at 0.75 and 0.25 respectively were

Table 3. *Observed and calculated structure factors*In order to obtain $F_{obs.}$ and $F_{calc.}$ on the absolute scale, the values in the table must be multiplied by 10

hkl	F_o	F_c	hkl	F_o	F_c	hkl	F_o	F_c	hkl	F_o	F_c
002	9	10	0,2,20	—	-2	0,4,23	9	0	0,6,27	—	0
004	11	16	0,2,21	11	-11	0,4,24	—	-1	0,6,28	—	-5
006	17	-18	0,2,22	—	-4	0,4,25	—	1	0,6,29	—	2
008	56	72	0,2,23	9	-10	0,4,26	7	6	0,6,30	5	-7
0,0,10	27	-30	0,2,24	5	-3	0,4,27	8	9	071	18	17
0,0,12	21	23	0,2,25	6	3	0,4,28	8	10	072	12	-11
0,0,14	24	23	0,2,26	4	-3	0,4,29	6	5	073	6	-3
0,0,16	52	52	0,2,27	5	-6	0,4,30	4	-2	074	17	15
0,0,18	23	-23	0,2,28	11	14	0,4,31	—	5	075	—	0
0,0,20	16	-16	0,2,29	—	1	0,4,32	—	1	076	12	11
0,0,22	4	-6	0,2,30	6	3	051	8	8	077	8	10
0,0,24	5	-1	0,2,31	—	-1	052	15	-14	078	22	-22
0,0,26	20	-22	0,2,32	—	6	053	—	1	079	—	2
0,0,28	8	-6	031	25	-26	054	38	41	0,7,10	16	-14
0,0,30	10	6	032	22	23	055	8	-6	0,7,11	11	-11
0,0,32	—	0	033	7	-5	056	43	48	0,7,12	17	-17
011	—	0	034	44	49	057	5	5	0,7,13	6	-4
012	18	21	035	7	7	058	17	16	0,7,14	3	2
013	3	-2	036	5	2	059	6	-10	0,7,15	14	15
014	23	-25	037	26	-24	0,5,10	32	-31	0,7,16	12	-14
015	5	5	038	17	-17	0,5,11	8	4	0,7,17	8	9
016	9	-9	039	—	1	0,5,12	24	26	0,7,18	7	4
017	20	22	0,3,10	14	-14	0,5,13	—	1	0,7,19	9	-2
018	14	-16	0,3,11	—	-3	0,5,14	10	10	0,7,20	5	-5
019	16	17	0,3,12	18	-18	0,5,15	11	12	0,7,21	—	-1
0,1,10	4	2	0,3,13	7	8	0,5,16	18	19	0,7,22	—	2
0,1,11	6	6	0,3,14	7	-9	0,5,17	6	-8	0,7,23	—	-1
0,1,12	41	-46	0,3,15	20	-21	0,5,18	5	7	0,7,24	11	-14
0,1,13	—	4	0,3,16	10	8	0,5,19	6	6	0,7,25	5	-6
0,1,14	23	-26	0,3,17	7	-4	0,5,20	37	41	0,7,26	3	2
0,1,15	—	6	0,3,18	13	13	0,5,21	5	-5	0,7,27	6	-5
0,1,16	20	-23	0,3,19	8	7	0,5,22	12	12	0,7,28	—	-4
0,1,17	12	-14	0,3,20	6	6	0,5,23	8	9	0,7,29	4	2
0,1,18	19	18	0,3,21	8	8	0,5,24	3	-1	080	19	-16
0,1,19	—	4	0,3,22	—	-1	0,5,25	3	-5	081	9	12
0,1,20	18	-20	0,3,23	8	-10	0,5,26	11	-11	082	17	-15
0,1,21	—	0	0,3,24	5	-4	0,5,27	—	3	083	14	15
0,1,22	4	-4	0,3,25	7	5	0,5,28	9	9	084	10	-9
0,1,23	10	10	0,3,26	—	-2	0,5,29	—	-3	085	14	-15
0,1,24	14	-16	0,3,27	12	11	0,5,30	—	-1	086	12	13
0,1,25	7	5	0,3,28	8	-6	0,5,31	—	3	087	16	-15
0,1,26	8	5	0,3,29	—	3	060	37	34	088	12	12
0,1,27	7	8	0,3,30	—	-3	061	13	-12	089	—	4
0,1,28	14	-15	0,3,31	—	-3	062	12	-12	0,8,10	—	4
0,1,29	—	-4	0,3,32	—	3	063	—	0	0,8,11	—	1
0,1,30	—	1	040	14	-20	064	40	44	0,8,12	6	-8
0,1,31	—	-2	041	—	-1	065	8	-13	0,8,13	10	-12
0,1,32	—	2	042	8	-9	066	6	5	0,8,14	8	-10
020	17	15	043	31	-31	067	8	5	0,8,15	11	-13
021	5	-5	044	8	-6	068	53	57	0,8,16	7	-5
022	9	10	045	17	17	069	4	-3	0,8,17	9	12
023	4	3	046	7	-6	0,6,10	6	-6	0,8,18	8	-9
024	18	-17	047	6	-5	0,6,11	8	8	0,8,19	8	-6
025	26	-28	048	37	-41	0,6,12	11	12	0,8,20	—	3
026	6	-5	049	—	-3	0,6,13	7	7	0,8,21	12	-15
027	8	-8	0,4,10	7	5	0,6,14	12	-13	0,8,22	8	7
028	15	-16	0,4,11	—	-6	0,6,15	4	-3	0,8,23	8	-8
029	—	-1	0,4,12	15	15	0,6,16	6	5	0,8,24	10	12
0,2,10	21	-24	0,4,13	27	29	0,6,17	5	-3	0,8,25	7	8
0,2,11	6	5	0,4,14	—	0	0,6,18	11	-11	0,8,26	—	-2
0,2,12	8	-8	0,4,15	—	4	0,6,19	5	3	0,8,27	4	-3
0,2,13	6	-3	0,4,16	18	-16	0,6,20	6	5	0,8,28	4	-4
0,2,14	27	27	0,4,17	—	2	0,6,21	7	-4	091	—	-1
0,2,15	11	-10	0,4,18	6	4	0,6,22	—	-3	092	—	2
0,2,16	17	16	0,4,19	6	-6	0,6,23	—	-3	093	—	0
0,2,17	—	-3	0,4,20	12	12	0,6,24	—	-1	094	—	-3
0,2,18	6	5	0,4,21	—	-3	0,6,25	—	2	095	6	-3
0,2,19	11	-9	0,4,22	—	1	0,6,26	6	-8			

Table 3 (cont.)

<i>hkl</i>	F_o	F_c	<i>hkl</i>	F_o	F_c	<i>hkl</i>	F_o	F_c	<i>hkl</i>	F_o	F_c
096	9	-9	0,12,5	8	9	2,0,20	—	3	6,0,26	8	11
097	16	-18	0,12,6	—	-1	2,0,22	—	1	6,0,28	5	5
098	—	-2	0,12,7	6	7	2,0,24	11	-6	701	—	0
099	9	-10	0,12,8	9	9	2,0,26	—	2	703	7	9
0,9,10	—	2	0,12,9	10	-13	2,0,28	4	-5	705	7	-6
0,9,11	—	0	0,12,10	—	0	2,0,30	—	2	707	2	-2
0,9,12	10	6	0,12,11	—	-1	2,0,32	—	0	709	11	-11
0,9,13	7	5	0,12,12	6	6	301	—	1	7,0,11	7	-5
0,9,14	8	-8	0,12,13	5	4	303	57	72	7,0,13	9	-11
0,9,15	11	-12	0,12,14	7	-8	305	51	-59	7,0,15	5	-6
0,9,16	7	-5	0,12,15	4	3	307	7	7	7,0,17	6	5
0,9,17	7	4	0,12,16	4	2	309	26	-27	7,0,19	4	-1
0,9,18	—	1	0,12,17	5	-4	3,0,11	11	-13	7,0,21	6	-8
0,9,19	—	0	0,13,1	5	9	3,0,13	64	-81	7,0,23	—	-4
0,9,20	—	-2	0,13,2	6	-6	3,0,15	18	-18	7,0,25	—	-1
0,9,21	—	2	0,13,3	—	-4	3,0,17	15	11	7,0,27	—	2
0,9,22	6	-4	0,13,4	10	-10	3,0,19	8	5	800	14	14
0,9,23	5	-6	0,13,5	—	-5	3,0,21	27	-25	802	7	-6
0,9,24	—	-1	0,13,6	—	-2	3,0,23	8	-7	804	9	-8
0,9,25	—	-1	0,13,7	7	8	3,0,25	7	-8	806	4	3
0,9,26	5	3	0,13,8	6	-3	3,0,27	11	-11	808	5	3
0,10,0	33	-37	0,13,9	5	6	3,0,29	15	-12	8,0,10	4	3
0,10,1	8	8	0,13,10	—	2	400	14	19	8,0,12	6	4
0,10,2	9	-11	0,13,11	5	-1	402	7	6	8,0,14	5	-2
0,10,3	9	-9	0,13,12	4	3	404	12	12	8,0,16	—	-4
0,10,4	—	-6	0,13,13	—	-2	406	13	12	8,0,18	6	-7
0,10,5	10	10	0,13,14	3	4	408	8	-3	8,0,20	6	2
0,10,6	8	-6	0,13,15	—	2	4,0,10	13	15	8,0,22	—	2
0,10,7	8	-6	0,13,16	6	-8	4,0,12	—	1	8,0,24	8	5
0,10,8	5	-3	0,14,0	5	-2	4,0,14	3	-4	8,0,26	—	-1
0,10,9	9	11	0,14,1	—	-2	4,0,16	2	6	901	—	0
0,10,10	—	3	0,14,2	—	3	4,0,18	7	10	903	20	-18
0,10,11	12	-10	0,14,3	—	-1	4,0,20	10	-10	905	8	6
0,10,12	5	-6	0,14,4	—	-1	4,0,22	6	-7	907	—	3
0,10,13	—	2	0,14,5	—	0	4,0,24	—	0	909	17	17
0,10,14	14	-12	0,14,6	4	-5	4,0,26	—	0	9,0,11	6	8
0,10,15	7	-11	0,14,7	—	1	4,0,28	—	0	9,0,13	18	18
0,10,16	12	-11	0,14,8	2	-3	4,0,30	—	2	9,0,15	10	10
0,10,17	6	5	0,14,9	2	1	4,0,32	—	-1	9,0,17	—	-4
0,10,18	—	2	0,14,10	—	-1	501	—	0	9,0,19	—	-1
0,10,19	—	4	0,14,11	3	-4	503	4	5	9,0,21	9	9
0,10,20	7	7	0,15,1	3	-2	505	18	18	9,0,23	6	7
0,10,21	—	3	101	—	-3	507	8	-6	10,0,0	28	-30
0,10,22	3	3	103	8	6	509	8	-7	10,0,2	—	0
0,11,1	8	-7	105	10	-10	5,0,11	8	-4	10,0,4	—	-1
0,11,2	14	-12	107	10	9	5,0,13	9	7	10,0,6	—	1
0,11,3	—	5	109	19	20	5,0,15	5	-4	10,0,8	9	-9
0,11,4	—	1	1,0,11	6	7	5,0,17	6	-6	10,0,10	4	2
0,11,5	—	2	1,0,13	9	-7	5,0,19	—	1	10,0,12	4	-4
0,11,6	—	1	1,0,15	8	7	5,0,21	10	7	10,0,14	3	-2
0,11,7	—	0	1,0,17	7	-7	5,0,23	6	-6	10,0,16	3	-8
0,11,8	9	11	1,0,19	5	4	5,0,25	5	5	10,0,18	7	4
0,11,9	8	-10	1,0,21	8	8	5,0,27	5	-6	10,0,20	3	3
0,11,10	—	8	1,0,23	2	6	5,0,29	—	-2	11,0,1	—	0
0,11,11	3	5	1,0,25	—	-2	600	71	-86	11,0,3	7	-5
0,11,12	19	20	1,0,27	7	-9	602	10	-11	11,0,5	—	0
0,11,13	8	-8	1,0,29	—	0	604	15	-17	11,0,7	—	0
0,11,14	8	8	200	31	31	606	6	3	11,0,9	—	1
0,11,15	6	5	202	8	6	608	24	-24	11,0,11	—	1
0,11,16	7	8	204	6	5	6,0,10	8	6	11,0,13	5	4
0,11,17	—	-1	206	12	-12	6,0,12	9	-8	11,0,15	—	1
0,11,18	—	-1	208	6	-2	6,0,14	11	-9	12,0,0	16	18
0,11,19	5	6	2,0,10	12	-12	6,0,16	29	-28	12,0,2	—	3
0,11,20	6	7	2,0,12	8	-6	6,0,18	—	1	12,0,4	5	5
0,12,0	7	6	2,0,14	7	5	6,0,20	13	14	12,0,6	—	0
0,12,1	7	-9	2,0,16	2	2	6,0,22	7	8	12,0,8	4	5
0,12,2	6	-2	2,0,18	4	4	6,0,24	—	3	12,0,10	—	0
0,12,3	5	4									
0,12,4	15	15									

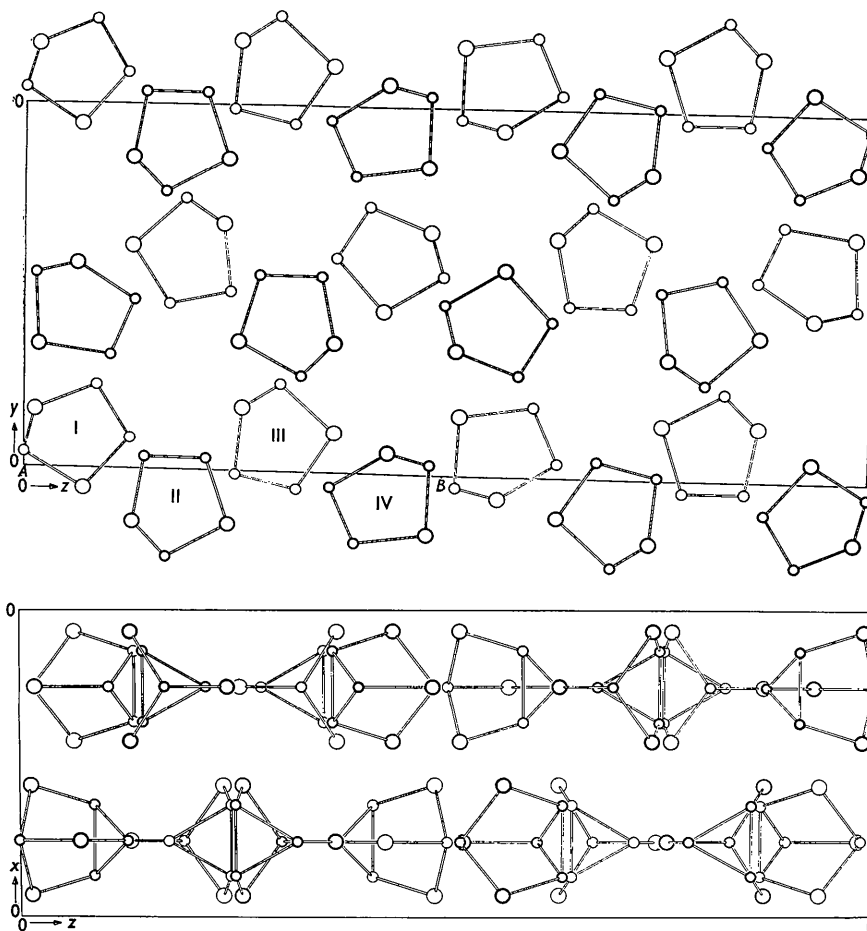


Fig. 4. Projections of the P_4Se_3 structure along (a) [100] and (b) [010]. Small circles: P; large circles: Se.

averaged. The distances of the four selenium atoms in general positions to their nearest mirror plane were taken equal to this average value. A comparison of observed and calculated structure factors showed that it was not necessary to change the temperature factor $\exp(-3 \sin^2 \theta / \lambda^2)$, obtained from the [100] projection. After the last structure-factor calculation the index R for the observed reflexions amounted to 0.16. The calculated values of the structure factors are compared with the observed ones in Table 3.

Accuracy of the co-ordinates

The standard deviations in the co-ordinates due to experimental errors in the structure factors were calculated by applying Cruickshank's formula (1949). The curvatures of the electron-density distribution at the positions of the atoms were determined from Fourier maps. The standard deviations were assumed to be equal for all directions in the [100] projection. Errors due to overlap were neglected. Calculation gave the following values:

[100] projection		[010] projection	
Atom	e.s.d.	Atom	e.s.d. in x direction
Se ('double')	0.007 Å	Resolved Se	0.013
Se ('single')	0.017	Resolved P	0.021
P ('double')	0.017		
P ('single')	0.033		

Discussion

The structure consists of molecules P_4Se_3 roughly arranged in hexagonal close packing (Fig. 4). By comparison of Figs. 4(a) and 5 it is seen that the independent molecules I, II, III and IV of P_4Se_3 and the non-independent molecules 1, 2, 1' and 2' in P_4S_3 are arranged similarly. The distances AB in Fig. 4(a) and EF in Fig. 5 are 13.13 and 12.61 Å respectively. Shortest intermolecular distances were observed between phosphorus atoms; they amount to approximately 3.6 Å.

The bond lengths and angles and their estimated standard deviations are listed in Table 4. In estimating these standard deviations, errors due to inaccuracies

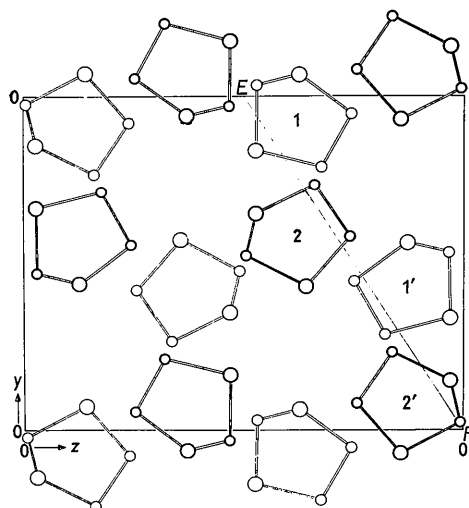


Fig. 5. Projection of the P_4S_3 structure along $[100]$. The molecules 1 and 2 are related to 1' and 2' by the symmetry operation of the glide plane b perpendicular to the c -axis. Small circles: P; large circles: S.

in the cell constants could be neglected. For the calculation of the standard deviations in the bond angles the formula of Cruickshank & Robertson (1953) was used.

Table 4. Bond lengths and angles in the P_4Se_3 molecules

	Mol. I	Mol. II	Mol. III	Mol. IV	e.s.d.
P_1-P_2	2.26 Å	2.23 Å	2.25 Å	2.26 Å	0.03 Å
P_2-P_3	2.26	2.26	2.26	2.26	0.04
P_1-Se_1	2.23	2.25	2.18	2.30	0.04
P_2-Se_2	2.18	2.25	2.25	2.25	0.02
P_4-Se_1	2.20	2.21	2.27	2.30	0.04
P_4-Se_2	2.26	2.28	2.25	2.20	0.02
$Se_1-P_4-Se_3$	100.9°	100.0°	98.5°	97.5°	0.9°
$Se_2-P_4-Se_3$	101	99	101	104	1.4
$P_1-Se_1-P_4$	100	101	100	100	1.3
$P_3-Se_3-P_4$	99.4	99.3	100.2	101.0	0.8
$Se_1-P_1-P_3$	105	105	107	103	1.0
$Se_2-P_2-P_3$	106.1	105.4	105.4	105.6	0.9
$Se_3-P_3-P_1$	106	106	104	106	1.0
$P_1-P_3-P_2$	60.1	59.7	60.0	60.1	0.8
$P_2-P_1-P_3$	60	61	60.0	60	1.3

There are no significant differences between the

molecules. If the bonds of one type are considered to be equivalent, the weighted averages of the bond lengths are 2.25 Å (e.s.d. 0.03 Å) for P-P and 2.24 Å (e.s.d. 0.01 Å) for P-Se. The P-P bond length may be compared with the value 2.235 Å, observed in P_4S_3 . As far as we know the P-Se bond length has not been determined before; the observed value is equal to the sum of the atomic radii of phosphorus and selenium, 1.10 and 1.14 Å respectively. (Pauling, 1945).

The four types of bond angles in the molecule and their weighted average values are as follows

Se-P-Se (99.9°), P-Se-P (100.1°), Se-P-P (105.3°),
P-P-P (60.1°).

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