

## The Crystal and Molecular Structure of Bis(diethyl-dithiophosphato)tellurium(II). A Compound with Three Molecules in the Asymmetric Unit

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The crystal structure of bis(diethylthiophosphato)tellurium(II) has been determined, and refined by three dimensional X-ray methods. The crystals are built up of  $(C_2H_5O)_2P(S)S-Te-S(S)P(OC_2H_5)_2$  molecules, with three crystallographically independent molecules in the asymmetric unit. Each molecule has a P-S-Te-S-P chain in the *trans* form, containing nearly twofold symmetry axes through the tellurium atoms. Average molecular dimensions are Te-S=2.42 Å, P-S=2.08 Å, P=S=1.93 Å and  $\angle S-Te-S=100.2, 96.6, 95.2^\circ$  in molecules I, II and III, respectively. The molecules are joined together in a three dimensional network by weak intermolecular Te...S bonds with bond lengths varying between 3.21 and 3.54 Å. Each tellurium atom participates in two such bonds at an S-Te-S angle of 70.3, 101.0, 91.7° in molecules I, II and III, respectively. As these weak bonds are *trans* to, and nearly collinear with the Te-S bonds, there is a tendency to square planar coordination around tellurium in all three molecules.

It has been shown from work on divalent tellurium compounds with bidentate sulfur containing ligands having a large bite, that symmetric square planar complexes can be prepared (class V).<sup>1,2</sup> However, ligands with small bites give trapezoid planar complexes (class I and II).<sup>1,3</sup> These  $ML_2$  (M=Se,Te) complexes are four-coordinate. In class I, the ligands are aniso-

bidentate. In class II they are essentially monodentate, and four-coordination is achieved through weak, intermolecular P=S...Te bonding.<sup>1</sup>

During the investigation of the IR spectra of dialkyldithiophosphates and dialkyldithiophosphinates of selenium and tellurium,<sup>4</sup> bis(diethylthiophosphato)tellurium(II) was the only compound with a multiplet for the P=S stretching frequency; this may indicate differences in the P=S...Te bond system relative to the other compounds. The only previously known structure of a dialkyldithiophosphate of tellurium is that of bis(dimethylthiophosphato)tellurium(II)<sup>5</sup> which is based on photographic data collection and thus less accurate. It was decided to solve the structure of the bis(diethylthiophosphato)tellurium(II) complex at low temperature to have a more accurate structure determination of such a tellurium complex, and also to find out the actual P=S...Te intermolecular interaction in the above system.

### EXPERIMENTAL

*Preparation of the complex.* This was prepared by published procedures<sup>6</sup> and recrystallized from ethanol as deep orange-red prisms.

*IR-spectrum.* The IR spectrum was obtained in the region from 4000-200  $cm^{-1}$ , using a Perkin-Elmer 683 instrument. The CsI disc technique was used in the solid state, while the spectrum in solution was obtained with  $CCl_4$  as solvent.

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**X-Ray data.** Intensity data and data for determination of unit cell parameters were obtained on an Enraf-Nonius CAD4 diffractometer, at  $-135^{\circ}\text{C}$ . The crystal used had approximate dimensions  $0.29 \times 0.53 \times 0.41$  mm. Unit cell parameters were found from least squares refinement of the setting angles of 25 general reflections with  $2\theta$  between 15 and  $24^{\circ}$ . They are  $a=12.247(4)$ ,  $b=12.656(3)$ ,  $c=20.135(4)$  Å,  $\alpha=101.69(2)$ ,  $\beta=103.29(2)$ ,  $\gamma=104.72(2)^{\circ}$ ,  $Z=6$ ,  $D_x(-135^{\circ}\text{C})=1.757$  g cm $^{-3}$ ,  $D_m(22^{\circ}\text{C})=1.680$  g cm $^{-3}$ ,  $\mu(\text{MoK}\alpha)=21.812$  cm $^{-1}$ . The space group is  $P1$  or  $P\bar{1}$  (no. 1 or 2).

Reflection intensities were recorded using the  $\omega$ -scan technique with scan width  $(1.25+0.35 \text{ tg } \theta)^{\circ}$ , a graphite monochromator and MoK $\alpha$ -radiation ( $\lambda=0.71073$  Å). The scan rate was  $4^{\circ} \text{ min}^{-1}$  for all reflections. 5357 unique reflections of a total of 6898 with  $2\theta < 44^{\circ}$  had  $I > 3\sigma(I)$  and were treated as observed. The intensities were corrected for Lorentz and polarization effects as well as for absorption based on crystal faces and dimensions (min. transm. 0.385, max. transm. 0.781).

Data collection and computer programs used throughout this investigation belong to the Enraf-Nonius Structure Determination Pack, SDP-Plus 1982. The reader is referred to a previous paper<sup>7</sup> for further details.

## STRUCTURE DETERMINATION

The structure was solved by means of direct methods (MULTAN), and refined by full-matrix least-squares iterations assuming the space group to be  $P\bar{1}$ . Attempted refinement in space group  $P1$  was unsuccessful. Anisotropic temperature factors were included for the atoms Te, P, and S. Hydrogen atoms were geometrically placed at C–H=0.95 Å and fixed, their isotropic temperature factors refined and averaged, then attributed the rounded fixed value in the iterations to follow. Before the final L. S. iterations 14 "bad" reflections were rejected, but this did not significantly influence the result. The function minimized is  $\Sigma w(\Delta F)^2$ , the attributed weights correspond to the counting statistics plus 3% of the net intensity (fudge factor=0.03). The refinement converged at  $R=0.029$ ,  $R_w=0.033$  and  $S=1.27$ .

A difference map showed two peaks of ca.  $0.9$  e/Å $^3$ . Those were close to the C22–C23 ethyl group, and might indicate a small disorder in this group. No other peaks above  $0.5$  e/Å $^3$  were observed. Refined atomic coordinates are shown

in Table 1. The final bond lengths and angles are listed in Tables 2 and 3, respectively, while torsional angles and short interatomic non-bonded contacts are listed in Tables 4 and 5. Finally, planes in the molecules, weak intermolecular Te $\cdots$ S bonds and corresponding angles are shown in Tables 6 and 7. Tables of thermal parameters and observed and calculated structure factors are available from the author K.M.M. upon request.

## RESULTS AND DISCUSSION

The three crystallographically independent molecules are shown in Figs 1–3. As can be seen from the figures, the structures are very similar, even if some bond lengths and angles are significantly different. In each molecule, the central tellurium atom is surrounded by four sulfur atoms. Two of these belong to the molecule proper, one from each ligand. The other two belong to two different neighbour molecules and form the weak intermolecular bonds indicated in the figures.

**The  $\text{TeS}_4$  coordination groups.** In these groups which are roughly planar (Table 6), there are two intramolecular short Te–S bonds. Their average length in the three molecules is  $2.420(15)$  Å. This may be compared to  $2.440(5)$  Å found for such a bond in the corresponding bis(dimethyldithiophosphato)tellurium(II)<sup>5</sup> complex and to  $2.38$  Å, the covalent bond length corrected for polarity.<sup>8</sup> There is a very short Te–S bond in molecule II, namely Te2–S22, being only  $2.387(1)$  Å or close to a covalent bond length. The other short Te–S bonds range from  $2.420(1)$ – $2.435(1)$  Å and are significantly longer than a covalent bond. The reason for this is probably the influence of the two weak intermolecular Te–S bonds *trans* to the strong ones above. These bonds have lengths varying from  $3.209(1)$  to  $3.541(1)$  Å, well below the van der Waals contact of  $3.86$  Å.<sup>9</sup> Surprisingly, one of these weak bonds are to a sulfur (S21) atom already strongly bonded to tellurium. In other class II Te and Se complexes, such bonds are always to thiono sulfur atoms ( $\text{P}=\text{S}^5$  or  $\text{C}=\text{S}^1$ ). The Se–Te–S angles vary from  $95.23$  to  $100.18^{\circ}$ . These values are close to those found in class II complexes,<sup>1,5,10</sup> but also close to the valency angle found on tellurium in two-coordinate tellurium compounds.<sup>11</sup> There are thus two

Table 1. Positional parameters and their estimated standard deviations.<sup>a</sup>

Atom	x	y	z	B(A <sup>2</sup> )
Te1	-0.09088(3)	0.92709(3)	0.60072(2)	1.283(8)
Te2	0.57941(3)	0.63616(3)	0.94376(2)	1.590(9)
Te3	0.45748(3)	1.02394(3)	0.72344(2)	1.557(9)
S11	-0.0673(1)	0.7791(1)	0.65691(8)	1.63(3)
S12	-0.2457(1)	0.9762(1)	0.64444(8)	1.53(3)
S13	-0.1569(1)	0.5040(1)	0.61285(8)	2.22(4)
S14	-0.2551(1)	1.1526(1)	0.78545(8)	1.74(3)
S21	0.6330(1)	0.6189(1)	1.06435(7)	1.28(3)
S22	0.7653(1)	0.7657(1)	0.95281(8)	1.56(3)
S23	0.6000(1)	0.7265(1)	1.21563(7)	1.81(4)
S24	1.0116(1)	0.7554(1)	0.92522(8)	1.67(3)
S31	0.2493(1)	0.9388(1)	0.65842(7)	1.57(3)
S32	0.5017(1)	0.8463(1)	0.70703(7)	1.54(3)
S33	0.0876(1)	0.8933(1)	0.49817(8)	1.52(3)
S34	0.5023(1)	0.6444(1)	0.78190(8)	2.11(4)
P11	-0.1842(1)	0.6318(1)	0.58166(8)	1.40(3)
P12	-0.1505(1)	1.0877(1)	0.74402(8)	1.26(3)
P21	0.5872(1)	0.7478(1)	1.12229(7)	1.14(3)
P22	0.8693(1)	0.6617(1)	0.93492(7)	1.16(3)
P31	0.2498(1)	0.9628(1)	0.55979(8)	1.21(3)
P32	0.4773(1)	0.7908(1)	0.79435(8)	1.62(4)
O11	-0.1725(3)	0.6381(3)	0.5065(2)	1.72(8)*
O12	-0.3120(3)	0.6419(3)	0.5683(2)	1.65(8)*
O13	-0.0803(3)	1.0249(3)	0.7880(2)	1.52(8)*
O14	-0.0410(3)	1.1759(3)	0.7360(2)	1.41(7)*
O21	0.6649(3)	0.8646(3)	1.1176(2)	1.35(7)*
O22	0.4648(3)	0.7513(3)	1.0790(2)	1.27(7)*
O23	0.8799(3)	0.5993(3)	0.9951(2)	1.35(7)*
O24	0.7930(3)	0.5531(3)	0.8724(2)	1.29(7)*
O31	0.3461(3)	0.9204(3)	0.5338(2)	1.56(8)*
O32	0.3087(3)	1.0924(3)	0.5689(2)	1.33(7)*
O33	0.3559(4)	0.7970(3)	0.8039(2)	2.49(9)*
O34	0.5702(4)	0.8786(4)	0.8647(2)	2.53(9)*
C11	-0.0915(5)	0.5922(5)	0.4758(3)	1.8(1)*
C12	-0.1600(5)	0.4852(5)	0.4185(3)	1.9(1)*
C13	-0.3720(5)	0.6407(5)	0.6233(3)	2.1(1)*
C14	-0.4990(6)	0.5842(6)	0.5891(4)	3.1(1)*
C15	-0.1350(5)	0.9545(5)	0.8283(3)	1.8(1)*
C16	-0.0879(5)	1.0175(5)	0.9051(3)	2.2(1)*
C17	-0.0562(5)	1.2575(5)	0.6960(3)	2.2(1)*
C18	0.0638(6)	1.3243(6)	0.6968(4)	3.0(1)*
C21	0.7896(5)	0.9130(5)	1.1589(3)	1.8(1)*
C22	0.8266(5)	1.0344(5)	1.1605(3)	2.1(1)*
C23	0.3558(5)	0.6625(5)	1.0717(3)	1.9(1)*
C24	0.2544(5)	0.6868(5)	1.0284(3)	2.1(1)*
C25	0.9514(5)	0.6616(5)	1.0680(3)	1.5(1)*
C26	0.9595(5)	0.5765(5)	1.1087(3)	2.2(1)*
C27	0.7748(5)	0.5547(5)	0.7982(3)	1.9(1)*
C28	0.6894(5)	0.4432(5)	0.7536(3)	2.1(1)*
C31	0.3302(5)	0.8014(5)	0.5041(3)	2.0(1)*
C32	0.4202(7)	0.7962(7)	0.4663(4)	4.1(2)*
C33	0.2619(5)	1.1789(5)	0.5996(3)	1.6(1)*
C34	0.3510(5)	1.2923(5)	0.6120(3)	2.0(1)*
C35	0.2509(6)	0.7167(6)	0.7575(4)	2.9(1)*
C36	0.1821(7)	0.6511(7)	0.7956(4)	4.6(2)*
C37	0.5646(6)	0.9857(6)	0.9023(3)	2.7(1)*
C38	0.6334(5)	1.0087(5)	0.9774(3)	2.0(1)*

<sup>a</sup> Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as:  $(4/3)[a^2B(1,1)+b^2B(2,2)+c^2B(3,3)+ab \cos \gamma B(1,2)+ac \cos \beta B(1,3)+bc \cos \alpha B(2,3)]$ .

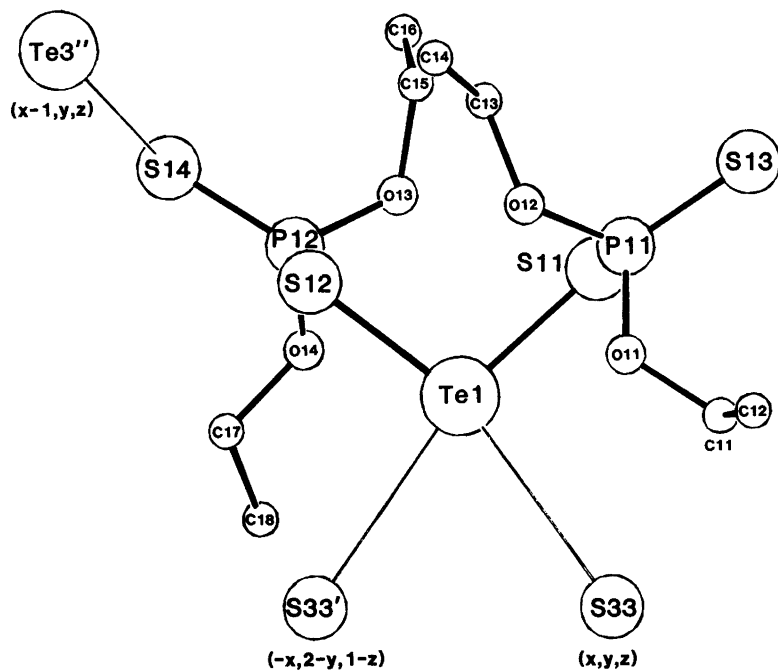


Fig. 1. Molecule I as seen along the normal to the Te1S11S12 plane. Thin lines indicate weak intermolecular bonds. Hydrogen atoms are omitted for the sake of clarity.

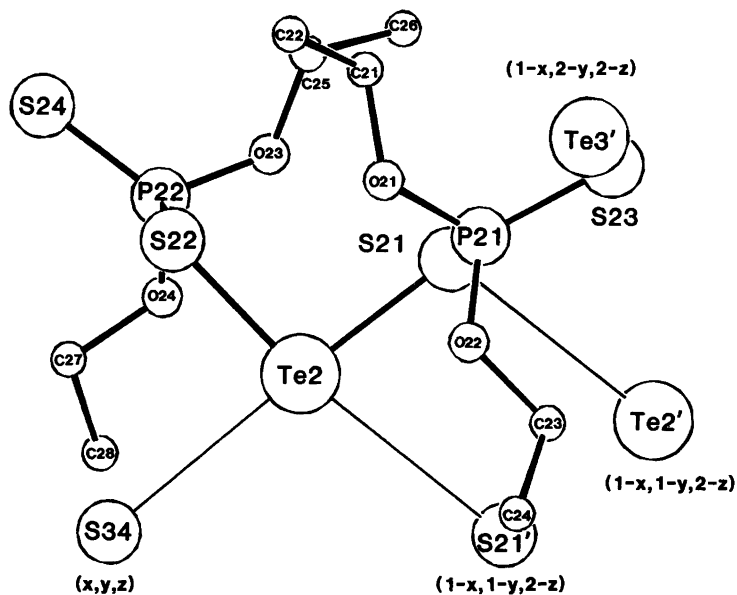


Fig. 2. Molecule II as seen along the normal to the Te2S21S22 plane.

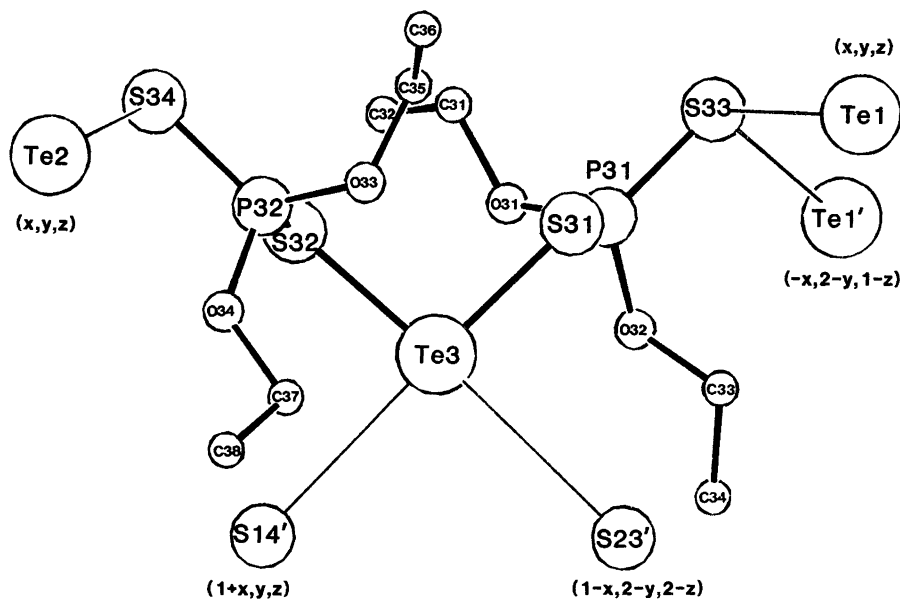


Fig. 3. Molecule III as seen along the normal to the  $\text{Te}_3\text{S}_3\text{S}_2$  plane.

three-center  $\text{S}-\text{Te}\cdots\text{S}$  systems in each molecule. They are almost orthogonal and the average  $\text{S}-\text{Te}\cdots\text{S}$  angle is  $167.0^\circ$ . From the preceding description, the molecules may be classified as trapezoid planar class II complexes of tellurium(II)<sup>1</sup>.

The  $\text{P}-\text{S}$ , the  $\text{P}=\text{S}$  bonds and the  $\text{P}=\text{S}$  stretching frequency. There are two types of  $\text{P}-\text{S}$  bonds in each molecule. The  $\text{P}-\text{S}$  bonds where sulfur is also bonded strongly to tellurium have an average length of  $2.079(6)$  Å. This is a little shorter than a single covalent bond of  $2.10$  Å, the sum of

Table 2. Bond lengths in the molecules I, II and III (Å) and their estimated standard deviations.

	I ( $i=1$ )	II ( $i=2$ )	III ( $i=3$ )
$\text{Te}(i)-\text{S}(i)1$	2.420(1)	2.435(1)	2.424(1)
$\text{Te}(i)-\text{S}(i)2$	2.430(1)	2.387(1)	2.421(1)
$\text{P}(i)1-\text{S}(i)1$	2.079(2)	2.082(2)	2.070(2)
$\text{P}(i)2-\text{S}(i)2$	2.077(2)	2.089(2)	2.076(2)
$\text{P}(i)1-\text{S}(i)3$	1.927(2)	1.929(2)	1.949(2)
$\text{P}(i)2-\text{S}(i)4$	1.939(2)	1.919(2)	1.930(2)
$\text{P}(i)1-\text{O}(i)1$	1.569(4)	1.576(4)	1.564(4)
$\text{P}(i)1-\text{O}(i)2$	1.569(4)	1.568(4)	1.568(4)
$\text{P}(i)2-\text{O}(i)3$	1.561(4)	1.573(4)	1.563(4)
$\text{P}(i)2-\text{O}(i)4$	1.576(4)	1.566(4)	1.586(4)
$\text{O}(i)1-\text{C}(i)1$	1.460(6)	1.461(6)	1.448(6)
$\text{O}(i)2-\text{C}(i)3$	1.464(7)	1.466(6)	1.454(6)
$\text{O}(i)3-\text{C}(i)5$	1.462(6)	1.461(6)	1.400(7)
$\text{O}(i)4-\text{C}(i)7$	1.454(7)	1.463(6)	1.438(7)
$\text{C}(i)1-\text{C}(i)2$	1.488(8)	1.479(8)	1.483(9)
$\text{C}(i)3-\text{C}(i)4$	1.466(8)	1.484(8)	1.499(8)
$\text{C}(i)5-\text{C}(i)6$	1.489(8)	1.489(8)	1.479(10)
$\text{C}(i)7-\text{C}(i)8$	1.492(8)	1.482(8)	1.481(8)

Table 3. Bond angles in the molecules I, II and III (°) and their estimated standard deviations.

	I (i=1)	II (i=2)	III (i=3)
S(i)1-Te(i)-S(i)2	100.18(5)	96.56(5)	95.23(5)
Te(i)-S(i)1-P(i)1	103.15(7)	103.58(7)	100.82(7)
Te(i)-S(i)2-P(i)2	102.12(7)	104.07(7)	104.72(7)
S(i)1-P(i)1-S(i)3	107.71(9)	107.45(9)	106.68(8)
S(i)1-P(i)1-O(i)1	108.6(2)	107.7(2)	110.7(2)
S(i)1-P(i)1-O(i)2	108.2(2)	109.5(1)	109.0(2)
S(i)3-P(i)1-O(i)1	117.4(2)	117.3(2)	116.5(2)
S(i)3-P(i)1-O(i)2	117.8(2)	117.1(2)	116.8(2)
O(i)1-P(i)1-O(i)2	96.3(2)	97.1(2)	96.8(2)
S(i)2-P(i)2-S(i)4	109.56(8)	106.88(8)	106.95(9)
S(i)2-P(i)2-O(i)3	108.4(2)	107.5(2)	109.5(2)
S(i)2-P(i)2-O(i)4	108.2(2)	108.9(2)	109.5(2)
S(i)4-P(i)2-O(i)3	116.9(2)	118.5(2)	117.2(2)
S(i)4-P(i)2-O(i)4	115.6(2)	118.0(2)	110.4(2)
O(i)3-P(i)2-O(i)4	97.4(2)	96.3(2)	103.2(2)
P(i)1-O(i)1-C(i)1	122.5(3)	120.7(3)	122.9(3)
P(i)1-O(i)2-C(i)3	121.2(3)	120.1(3)	122.1(3)
P(i)2-O(i)3-C(i)5	121.0(3)	120.8(3)	119.8(4)
P(i)2-O(i)4-C(i)7	121.3(3)	121.3(3)	127.7(4)
O(i)1-C(i)1-C(i)2	109.5(4)	107.0(4)	107.2(5)
O(i)2-C(i)3-C(i)4	108.7(5)	108.5(4)	107.3(4)
O(i)3-C(i)5-C(i)6	108.8(4)	107.5(4)	111.8(6)
O(i)4-C(i)7-C(i)8	107.4(5)	107.3(4)	106.8(5)

Table 4. Torsional angles in the molecules I, II and III (°).

	I (i=1)	II (i=2)	III (i=3)
S(i)1-Te(i)-S(i)1-P(i)1	91.1	90.0	82.8
S(i)1-Te(i)-S(i)2-P(i)2	82.8	82.3	89.2
Te(i)-S(i)1-P(i)1-S(i)3	171.1	170.3	177.9
Te(i)-S(i)1-P(i)1-O(i)1	43.0	117.5	50.2
Te(i)-S(i)1-P(i)1-O(i)2	119.5	42.1	144.9
Te(i)-S(i)2-P(i)2-S(i)4	173.5	170.4	176.7
Te(i)-S(i)2-P(i)2-O(i)3	122.1	118.6	48.8
Te(i)-S(i)2-P(i)2-O(i)4	46.8	41.6	136.3

the covalent radii of the two atoms corrected for bond polarity. However, the difference is probably not significant. Within limits of error, the P-S bonds are equal to the corresponding bond length of 2.089(7) Å found in [Te{(MeO)<sub>2</sub>PS<sub>2</sub>}]<sub>2</sub>.

The other type of P-S bond is essentially a P=S double bond. The average P=S bond length in the three molecules is 1.932(9) Å, which is normal for such bonds.<sup>12</sup> From the IR spectrum of this complex in the solid state,<sup>4</sup> (repeated in connection with the present work), the  $\nu_{\text{P}=\text{S}}$

absorption was found to be a triplet with frequencies 628, 639 and 649 cm<sup>-1</sup>. It was the only compound in a series of analogous Se(II) and Te(II) compounds not to have just one absorption band for the P=S stretch.<sup>4</sup> By looking at the P=S...Te intermolecular interactions (Figs. 1-3) we find that there are indeed three different types of such interactions. For the P31=S33 bond, S33 participates in two S...Te weak intermolecular bonds. For P12=S14, P21=S23 and P32=S34 bonds, there is only one S...Te bond for each

Table 5. Short interatomic non-bonded contacts in the crystals(Å) and their estimated standard deviations.<sup>a</sup>

Te1-S31	4.016(1)	<i>x, y, z</i>
S11-S12	3.720(2)	<i>x, y, z</i>
S11-S13	3.237(2)	<i>x, y, z</i>
S12-S14	3.281(2)	<i>x, y, z</i>
S21-S21	3.790(3)	1- <i>x, 2-y, 2-z</i>
S21-S22	3.600(2)	<i>x, y, z</i>
S21-S23	3.235(2)	<i>x, y, z</i>
S22-S24	3.221(2)	<i>x, y, z</i>
S31-S32	3.579(2)	<i>x, y, z</i>
S31-S33	3.225(2)	<i>x, y, z</i>
S32-S34	3.221(2)	<i>x, y, z</i>
S23-C34	3.453(6)	1- <i>x, 2-y, 2-z</i>
O11-C34	3.269(7)	$\bar{x}, 2-y, 1-z$
C38-C38	3.55(11)	1- <i>x, 2-y, 2-z</i>

<sup>a</sup> The distances are from an atom in the asymmetric unit (Table 1) to an atom in a molecule whose transformation from the original one is given in the right hand column.

Table 6. Planes in the molecules.<sup>a</sup>

No. of plane	Atoms included	Interplanar angles (°)	
1	Te1, S11, S12, S33', S33	1-2	81.7
2	Te2, S21, S22, S21', S34	1-3	71.1
3	Te3, S31, S32, S14', S23'	2-3	79.9
4	Te1, S11, P11	1-4	95.7
5	Te1, S12, P12	1-5	99.3
6	Te2, S21, P21	2-6	102.4
7	Te2, S22, P22	2-7	84.0
8	Te3, S31, P31	3-8	90.5
9	Te3, S32, P32	3-9	84.8

<sup>a</sup> Atomic displacement from the three first planes (Å), and their estimated standard deviations.

1. Te1-0.090(1); S11-0.032(2); S12, 0.092(1); S33, 0.076(1); S33'-0.046(2).
2. Te2-0.203(1); S21-0.196(2); S22, 0.306(2); S21', 0.213(1); S34-0.120(2).
3. Te3, 0.021(1); S31, 0.303(1); S32-0.326(1); S14', 0.231(2); S23'-0.229(1).

sulfur atom. Finally for the P11=S13 and P22=S24 bonds there are not any S...Te interactions at all. The intermolecular interactions are strong enough to influence the P=S bond strength. With decreasing interaction, the P=S bond lengths are 1.949(2), 1.933(5) and 1.923(6) Å for the three different types of interactions above (the last two values are averages).

The trend is in the expected direction showing that the P=S bond is stronger, the smaller the S...Te interaction. In solution, the spectrum is the same as in the solid state except that the  $\nu_{\text{P=S}}$  is now a singlet absorption with frequency 649 cm<sup>-1</sup>. It indicates that in solution there are no

weak intermolecular bonds and that tellurium atoms will be two-coordinate.

*Other ligand bonds.* The P-O bond length has an average value of 1.579(7) Å. This is not significantly different from the corresponding value found in [Te{(MeO)<sub>2</sub>PS<sub>2</sub>}]<sub>2</sub>; 1.58 Å. It is shorter than the covalent bond length corrected for polarity, 1.65 Å, but it is close to 1.545 Å, the value found in the isolated phosphate ion with  $\pi$ -bond order=1/2.<sup>13</sup> Therefore, there is probably considerable double bond character in the P-O bonds indicating a mesomeric shift of electron density towards the P=S sulfur atoms. One result of this is that the average P-O-C angle is

Table 7. Weak intermolecular Te...S bonds (Å) and corresponding angles (°) in the molecules I, II, III with their estimated standard deviations.

<b>I</b>	
Tel-S33	3.379(1)
Tel-S33'	3.311(1)
S11-Te-S33	96.67(4)
S11-Te-S33'	167.00(4)
S12-Te-S33	161.52(4)
S21-Te-S33'	92.54(4)
S33-Te-S33'	70.32(4)
<b>II</b>	
Te2-S21'	3.541(1)
Te2-S34	3.209(1)
S21-Te2-S21'	76.23(4)
S21-Te2-S34	177.00(4)
S21'-Te2-S22	159.70(4)
S21'-Te2-S34	101.00(4)
S22-Te2-S34	85.63(5)
<b>III</b>	
Te3-S14'	3.294(1)
Te3-S23'	3.454(2)
S14'-Te3-S23'	91.70(4)
S14'-Te3-S31	169.62(4)
S14'-Te3-S32	87.02(4)
S23'-Te3-S31	88.27(4)
S23'-Te3-S32	167.44(4)

121.8°, corresponding to  $sp^2$  hybridization of the oxygen atoms. The average C-O and C-C bond lengths are normal, being 1.456(17) and 1.484(8) Å, respectively. The values of some of the C-O bond lengths and P-O-C angles of the P32 diethyldithiophosphate ligand deviate considerably from the mean. This effect may be due to the slight disorder mentioned above.

*The overall structure of the molecules.* If one ignores the ethyl groups, the molecules have nearly the same structure, the main differences being due to the variations in the S-Te-S angles. They all have nearly twofold symmetry axes through the tellurium atoms intersecting the midpoint of the S-S line of the S-Te-S angle (still ignoring the ethyl groups). In other class II compounds,<sup>5,10</sup> an exact twofold crystallographic axis passes through the tellurium atom. The P-S-Te-S-P chain in the molecules has a *trans* configuration with respect to the central S-Te-S plane, the S-P-S group of the ligands being nearly at right angles to the central TeS<sub>4</sub> plane (Tables 6 and 7). The TeS<sub>4</sub> group is nearly planar in molecule I, but the maximum deviation of an atom from the best plane through the group is more than 0.3 Å in molecules II and III. The phosphorus atoms are essentially tetrahedrally coordinated. On P32 the relative sizes of two of

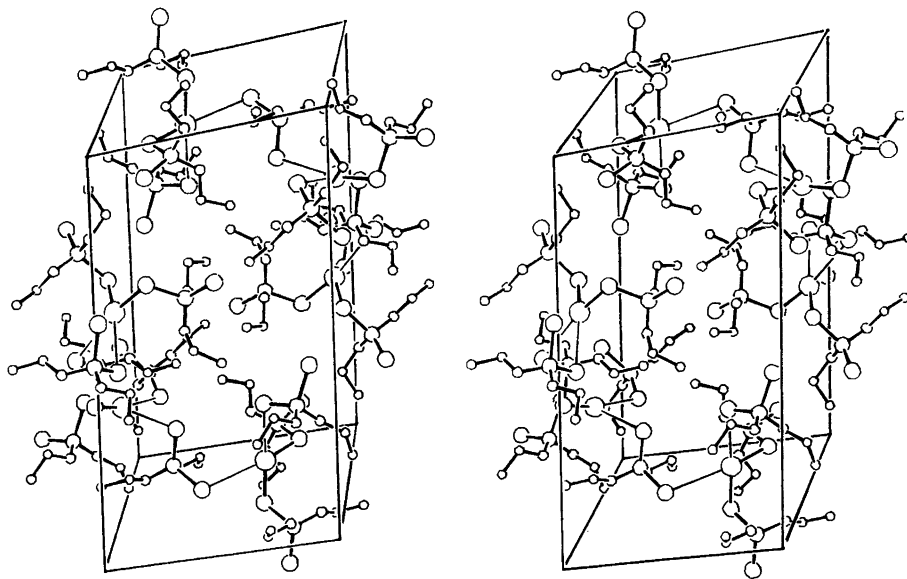


Fig. 4. Stereoview of the molecular packing (excluding hydrogens) in the unit cell. Thin lines indicate weak intermolecular bonds.



the angles deviate from those found on the other phosphorus atoms. This may be a secondary result of the disorder in the ethyl group connected via oxygen to P32.

*Molecular packing.* The molecules are bound together by weak  $\text{Te}\cdots\text{S}$  bonds ranging from 3.209(1) to 3.541(1) Å. In Fig. 4 is shown the resultant polymeric network in the unit cell. The weak  $\text{Te}-\text{S}$  bonds mentioned here are exactly the same as those that complete the four-coordination of the tellurium atoms. From Table 6 it can be seen that the angles between the  $\text{TeS}_4$  coordination planes are not far from  $90^\circ$ , being 81.7, 71.1 and  $79.9^\circ$  for the interplanar angles. A few other short non-bonded contacts are listed in Table 5. They are, except for the  $\text{Te1}\cdots\text{S31}$  contact of 4.016(2) Å, appreciably shorter than the corresponding Van der Waals contacts.

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