

The Crystal and Molecular Structure of the Dimeric Compound of Phenyltellurenyl Imidotetraphenyldithiodiphosphate

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The crystal structure of the title compound has been determined by Patterson and Fourier methods based on 2242 unique observed reflections and refined by full-matrix least-squares methods to a conventional R -factor of 0.062. The compound forms monoclinic crystals with space group $P2_1/n$ and unit cell dimensions $a = 10.557(3)$, $b = 23.836(4)$, $c = 11.604(2)$ Å and $\beta = 101.92(2)^\circ$. Tellurium is bonded to two sulfur atoms, one bond is intramolecular and one intermolecular, in a linear 3c-4e system. This results in the formation of dimers consisting of centrosymmetric 12-membered rings. The coordination around tellurium is distorted square planar. *Trans* to the Te-C(Ph) bond is a weak contact between the two tellurium atoms in the dimer. Te-C(Ph) = 2.109(9), Te-S1 = 2.557(3) and Te-S2' = 2.843(3) Å, while Te...Te' is 3.775(1) Å. The C(Ph)-Te-S1 angle is $89.5(3)^\circ$ and the S1-Te-S2' angle is $174.28(9)^\circ$. The angle S2'-Te-C(Ph) is $84.7(3)^\circ$. The bonding system in the complex is discussed.

The synthesis and crystal structure of a number of three- and four-coordinated complexes of divalent tellurium have been reported.¹⁻¹⁶ The solution of the structure of phenyltellurenyl imidotetraphenyldithiodiphosphate is part of the study of the structures of complexes of divalent tellurium, where the main purpose is to investigate the configuration around tellurium.^{1,2,17-21}

Experimental

Preparation of the complex. 0.188 g (0.5 mmol) PhTe(etu)Br (etu = ethylenethiourea) was thoroughly mixed with 0.275 g (0.55 mmol) $\text{NH}_4(\text{SP}(\text{Ph})_2)_2\text{N}$ in 6 ml CS_2 , first at room temperature and then at the boiling point of the solvent. The colour of the solution changed from yellow to orange. Filtering and reducing the volume to 50% under vacuum resulted in the formation of yellow prisms. Yield: 0.15 g (47%).

Structure analysis. Unit cell parameters (Table 1) were determined from the settings of 25 reflections. An ω -scan mode was used for collection of intensities and the scan width was $1.00 + 0.35 \tan \theta$, plus 25% on each side for background. $\sin \theta/\lambda$ was limited to a maximum of 0.600, equivalent to $\theta = 25^\circ$. 2242 unique reflections from a total of 5164 had $I > 2\sigma(I)$ and were treated as observed. The intensities were corrected for Lorentz and polarization effects, decay and absorption. The intensity variation, based on three reference reflections measured every 2 h of exposure time, was small; total loss of intensity was 2.4% during a total exposure time of 163.4 h. The heavy atoms were

found by use of Patterson and Fourier analysis. Refinements were carried out by full-matrix least-squares techniques, the sum minimized being $\Sigma w(\Delta F)^2$; the attributed weights correspond to the counting statistics plus 2% of the net intensity (fudge factor = 0.020). $w^{-1} = \sigma^2(F) = \sigma^2(I)^2/4LpI$ and $\sigma^2(I) = \sigma^2(I)_{\text{count}} + (0.02I)^2$. Anisotropic temperature factors were applied to all atoms except

Table 1. Crystal data and structural parameters.

Compound	$[\text{PhTeSP}(\text{Ph})_2\text{NP}(\text{Ph})_2\text{S}]_2$
Diffractometer	Enraf-Nonius CAD-4
Radiation	Mo $K\alpha$
Wavelength	0.710 73 nm
Crystal system	Monoclinic
$a/\text{Å}$	10.557(3)
$b/\text{Å}$	23.836(4)
$c/\text{Å}$	11.604(2)
$\beta/^\circ$	101.92(2)
$V/\text{Å}^3$	2856.9
Space group	$P2_1/n$ (No. 14)
M	653.22
Z	4
$F(000)$	1304
$D_{\text{calc}}/\text{g cm}^{-3}$	1.519
$\mu(\text{Mo } K\alpha)/\text{cm}^{-1}$	13.126
Crystal dimensions/mm	0.19 × 0.12 × 0.042
Scan-mode/ $\theta_{\text{max}}/^\circ$	ω -scan/30
Fudge factor	0.020
Scale factor	2.212
No. of independent measurements	5164
No. with $I > 2\sigma(I)$	2242
Transmission factors	0.8553 - 0.9470
$R = \Sigma F_o - F /\Sigma F_o$	0.062
$R_w = [\Sigma w(F_o - F)^2/\Sigma w F_o^2]^{0.5}$	0.040
$S = [\Sigma w(\Delta F)^2/N - n]^{0.5}$	1.223

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hydrogen. The hydrogen atom positions were computed, based on a fixed C–H bond length of 0.95 Å. The hydrogen atoms were included, with isotropic temperature factors, and refined by use of the program HYDRO. A final difference Fourier map showed no peaks above 0.66 eÅ⁻³ and no peaks below -0.655 eÅ⁻³. The shifts in the last cycle of refinements were < 1% of the associated standard deviations. All computer programs used belong to the Enraf-Nonius Structure Determination Package (1987). Crystal and experimental data and final figures of merit are included in Table 1. Tables of observed and calculated structure factors as well as thermal parameters are available from one of the authors (Ø.M.) upon request.

IR spectrum. An IR spectrum of the crystals was obtained using a Perkin Elmer 683 instrument and the CsI disc technique.

Table 2. Fractional atomic coordinates and their e.s.d. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter.

Atom	x	y	z	B/Å ² ^a
Te	0.10779(8)	0.03301(3)	0.13277(6)	3.51(1)
S1	0.3449(3)	0.0079(1)	0.1406(2)	3.67(7)
S2	0.4177(3)	-0.0652(1)	-0.1473(3)	4.11(8)
P1	0.3456(3)	-0.0754(1)	0.1818(2)	2.81(7)
P2	0.1988(3)	-0.1278(1)	-0.0330(2)	2.88(7)
N	0.2402(7)	-0.1142(3)	0.1037(6)	2.8(2)
C1	0.159(1)	0.0645(4)	0.3060(8)	3.3(3)
C2	0.233(1)	0.1122(5)	0.3281(9)	4.9(3)
C3	0.268(1)	0.1322(5)	0.442(1)	6.5(4)
C4	0.232(1)	0.1057(6)	0.535(1)	6.3(4)
C5	0.158(1)	0.0595(6)	0.5114(9)	6.4(4)
C6	0.122(1)	0.0385(5)	0.3983(8)	4.4(3)
C7	0.5084(9)	-0.0986(4)	0.1786(8)	3.2(3)
C8	0.604(1)	-0.0633(4)	0.1583(9)	4.4(3)
C9	0.724(1)	-0.0849(5)	0.1448(9)	4.8(3)
C10	0.746(1)	-0.1413(5)	0.1537(9)	4.6(3)
C11	0.651(1)	-0.1763(5)	0.176(1)	5.1(3)
C12	0.532(1)	-0.1553(5)	0.1891(9)	4.1(3)
C13	0.3199(9)	-0.0834(4)	0.3287(8)	2.8(2)
C14	0.418(1)	-0.0691(5)	0.4259(9)	4.2(3)
C15	0.397(1)	-0.0752(6)	0.539(1)	6.6(4)
C16	0.281(1)	-0.0925(5)	0.5572(9)	6.1(3)
C17	0.185(1)	-0.1073(5)	0.4630(9)	5.4(3)
C18	0.205(1)	-0.1026(5)	0.3506(8)	4.2(3)
C19	0.3289(9)	-0.1660(4)	-0.0797(8)	3.3(3)
C20	0.336(1)	-0.2227(5)	-0.075(1)	5.6(3)
C21	0.442(1)	-0.2507(5)	-0.101(1)	7.3(4)
C22	0.540(1)	-0.2214(7)	-0.131(1)	9.1(4)
C23	0.533(1)	-0.1643(7)	-0.133(1)	7.8(4)
C24	0.4270(9)	-0.1367(5)	-0.1107(9)	4.7(3)
C25	0.0717(9)	-0.1793(4)	-0.0443(8)	2.8(2)
C26	-0.005(1)	-0.1922(5)	-0.1523(9)	4.4(3)
C27	-0.098(1)	-0.2341(5)	-0.160(1)	5.9(4)
C28	-0.111(1)	-0.2632(5)	-0.060(1)	6.5(4)
C29	-0.036(1)	-0.2488(5)	0.047(1)	6.0(4)
C30	0.055(1)	-0.2067(5)	0.055(1)	4.3(3)

$$^a B = (4/3)[a^2 B(1,1) + b^2 B(2,2) + c^2 B(3,3) + abc \cos \gamma B(1,2) + accos \beta B(1,3) + bccos \alpha B(2,3)].$$

Results and discussion

The bond lengths and angles in the molecule are calculated from the coordinates of Table 2 and listed in Table 3, together with the calculated standard deviations. Intermolecular bonds and angles are listed in Table 4. An ORTEP drawing of one molecule (half a dimeric unit) is shown in Fig. 1, while Fig. 2 shows the dimeric ring with the symmetry center in the middle. There are no intermolecular contacts between the dimers, the shortest distance being 3.40(1) Å between C2 and C26. This is shorter than a van der Waals contact,²² and may be due to steric effects. The five phenyl rings are planar, with an average C–C distance of 1.373 Å and an average C–C–C angle of 119.99°. The dihedral angle between the two phenyl rings linked to P1 is 90.1(4)°, and the corresponding angle for the phenyl rings on P2 is 91.0(4)°.

Coordination around tellurium. Each dithiolate ligand bonds to two tellurium atoms through its two sulfur atoms. The resulting S–Te–S system is at right angles to the Te–C (Ph) bond, and forms a nearly linear and asymmetric 3c–4e system. The imidotetraphenyldithiodiphosphinate anion is uninegative and has a delocalized S··S donor system like the dithio ligands in the class I and class II selenium and tellurium complexes.^{23–25} This fact should minimize the effect of electronic differences in the ligands upon the structure of the complex.²⁶ The ligand has a large S–S bite of 3.956(4) Å in this complex, which is well inside the predicted range of 3.67–40.3 Å.²⁶ The distances from tellurium to the three more strongly coordinating atoms are as follows: Te–S1 = 2.557(3), Te–C1 = 2.109(9), Te–S2' =

Table 3. Bond lengths (Å) and angles (°) in the molecule. Estimated standard deviations in parentheses. The five phenyl rings are omitted.

Te–S1	2.557(3)	C1–Te–S1	89.5(3)
Te–C1	2.109(9)	Te–S1–P1	101.1(2)
S1–P1	2.044(4)	S1–P1–C7	104.4(4)
P1–C7	1.81(1)	S1–P1–C13	109.4(4)
P1–C13	1.79(1)	C7–P1–C13	108.5(4)
P1–N	1.580(7)	P1–N–P2	135.1(5)
N–P2	1.589(7)	N–P1–C7	111.6(4)
P2–C19	1.82(1)	N–P1–C13	104.9(4)
P2–C25	1.80(1)	N–P2–C19	109.3(4)
P2–S2	1.996(4)	N–P2–C25	105.0(4)
		N–P2–S2	119.4(3)

Table 4. Additional bond lengths (Å) and angles (°) around the tellurium atom.

Te–S2'	2.843(3)	C1–Te–S2'	84.74(3)
Te–Te'	3.775(1)	C1–Te–Te'	156.9(3)
		S1–Te–S2'	174.28(9)
		Te'–Te–S1	110.62(7)
		Te'–Te–S2'	75.00(6)

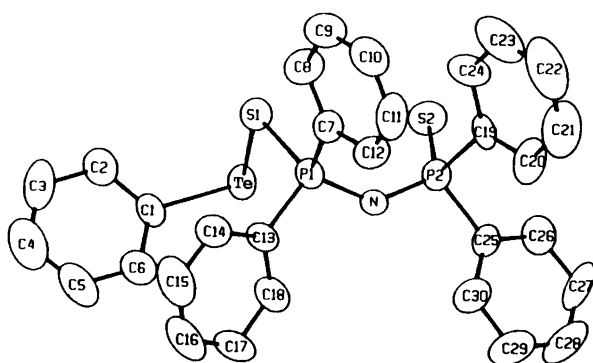


Fig. 1. ORTEP drawing of one molecule of $[\text{PhTeSP}(\text{Ph})_2\text{NP}(\text{Ph})_2\text{S}]_2$.

2.843(3) Å. The geometry of the Te complex may thus be regarded as T-shaped, arising from a trigonal bipyramidal disposition with the two lone pairs in the trigonal plane. Mössbauer studies²⁷ have indicated that only the p-orbitals of the tellurium atom contribute to the bonding in 3c–4e systems. As pointed out by Foss,^{1,28} the tellurium(II) complexes may be regarded as model substances for transition states in nucleophilic displacements at divalent chalcogens. Nucleophilic reactivity may then relate to the ability of the

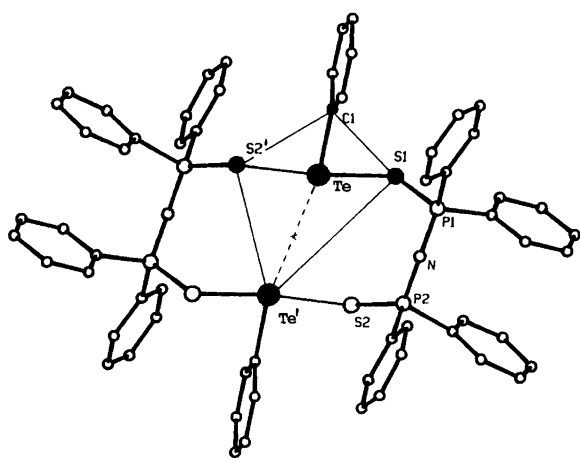


Fig. 2. ORTEP drawing of the dimeric unit of the complex. The atoms in the coordination plane are filled. The T-shape is formed by $\text{S2}'\text{-Te-S1}$ and the possible square-planar configuration is indicated by the thin lines.

reagent to engage a p-orbital in bonding, at the expense of the bond at 180°. In Table 5 angles and bond distances of the present structure are compared to the respective angles and bond distances of $[\text{PhTe}(\text{tu})_2]\text{Cl}$ ²⁹ and $\text{Me}_4\text{N}[\text{PhTe}(\text{SCN})_2]$,³⁰ which are both T-shaped. The average tellurium–sulfur distances are 2.70, 2.59 and 2.68 Å, respectively. Husebye²⁵ has found an average Te–S bond length of 2.69 Å in 11 T-shaped Te(II) complexes containing at least one sulfur atom as a ligand. If the Te' atom is included in the coordination sphere, one obtains the normal, but distorted, square-planar coordination. However, the close Te–Te' distance of 3.775(1) Å (van der Waals Te–Te contact = 4.12 Å²²) could be a result of the ring structure forcing them together.

The imidotetraphenyldithiophosphate ligand. In the dimeric ring there is a pronounced asymmetry in the Te–S and S–P bond lengths. The short Te–S1 bond [2.557(3) Å] is followed by a long S1–P1 bond of 2.044(4) Å, while the long Te–S2' bond [2.843(3) Å] is followed by a short S2'–P2' bond of 1.996(4) Å. The average bond lengths and angles found in this complex agree very well with known structures with this or related ligands. Average S–P and P–N bond lengths of 2.023 and 1.592 Å fit very well with the values found in bis(imidotetraphenyldithiophosphino-S,S')tellurium(II),²⁶ which are 2.022(3) and 1.590(11) Å, respectively, and in bis(imidotetraphenyldithiophosphino-S,S')selenium(II),⁶ where they are 2.021 and 1.578 Å, respectively. This indicates a considerable amount of double-bond character in both bond types.^{31,32} In Table 6 some of the angles in the dimer rings are compared with the respective angles in bis(imidotetraphenyldithiophosphino-S,S')tellurium(II) and bis(imidotetraphenyldithiophosphino-S,S')selenium(II). The angles S–P–N are the same, within accuracy.

Table 6. Comparison of bond angles (°) in the present structure and the tellurium(II) and selenium(II) complexes with the imidotetraphenyldithiophosphino-S,S' ligand.

M–S–P(av)	S–P–N(av)	P–N–P	Ref.
103.9 ^a	118.8	134.8(5)	This work
96.7 ^a	118.8	138.3	26
95.2 ^b	118.1	140.1	6

^aM = Te. ^bM = Se.

Table 5. Comparison of bond angles (°) and distances (Å) in the present structure and the T-shaped Te(II) complexes $[\text{PhTe}(\text{tu})_2]\text{Cl}$ ²⁹ and $\text{Me}_4\text{N}[\text{PhTe}(\text{SCN})_2]$.³⁰

Te–S1	Te–S2	S1–Te–S2	Te–C	S1–Te–C	S2–Te–C	Ref.
2.557(3)	2.843(3)	174.28(9)	2.109(9)	89.53(3)	84.74(3)	This work
2.616(2)	2.766(3)	172.37(8)	2.102(7)	87.9(2)	84.6(2)	29
2.665(2)	2.702(2)	174.94(6)	2.104(5)			30

The IR spectrum. The spectrum in the 1600–200 cm⁻¹ region is similar to the spectra of bis(imidotetraphenyldithiodiphosphino-*S,S'*)tellurium(II)²⁶ and bis(imidotetraphenyldithiodiphosphino-*S,S'*)selenium(II).⁶ Tentative assignments have been made by comparison with these and similar compounds (frequencies in cm⁻¹):^{6,26,32,33} $\nu_{\text{as}}(\text{PNP}) = 1170 \text{ m}$; $\nu(\text{PC}) = 710 \text{ m}$ and 679 s ; $\nu_{\text{s}}(\text{PS}) = 585 \text{ m}$; $\nu_{\text{as}}(\text{PS}) = 555$; $\delta(\text{PNP}) = 528 \text{ m}$; $\delta(\text{NPS}) = 455 \text{ m}$. Husebye suggests that $\nu(\text{P}=\text{S})$ in [Te(S(S)P(EtO)₂)₂] with a very weak P=S...Te interaction is 649 cm⁻¹, and that the stronger the P=S...Te interaction the lower the $\nu(\text{P}=\text{S})$ frequencies.^{2,34} For bis(imidotetraphenyldithiodiphosphino-*S,S'*)tellurium(II), where P=S...Te is much stronger, $\nu_{\text{sym}}(\text{P}=\text{S})$ is 580 cm⁻¹ and $\nu_{\text{as}}(\text{P}=\text{S})$ is 559 cm⁻¹, in excellent agreement with the values found in the present structure. Some of the low-lying absorption bands are probably due to the $\nu_{\text{asym}}(\text{TeS})$ (= 383 m) and $\nu_{\text{sym}}(\text{TeS})$ (= 290 w).^{*} The large separation between them suggests that the S–Te–S angle should be closer to 180° than to 90°,³⁰ as is also found by the structure determination [174.28(9)°]. Absorption bands for the phenyl groups are found with expected frequencies near 1473 m, 1428 s, 1320 m, 1300 w, 1168 m (sh), 1155 w (sh), 1098 s, 1060 w, 1018 m, 990 m, 968 w, 850 w, 605 w.

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* Abbreviations: s, strong; ms, medium strong; m, medium and w, weak.