

The Crystal and Molecular Structure of 4-Methoxyphenyltellurenyl Dimethyldithiophosphate, $\text{CH}_3\text{OPhTeSP}(\text{S})(\text{OCH}_3)_2$

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The crystal and molecular structure of the title compound has been determined by X-ray crystallographic methods based on 3457 unique, observed reflections. The crystals are monoclinic, space group $P2_1/n$ with unit cell dimensions $a = 9.976(1)$, $b = 12.023(1)$, $c = 12.333(1)$ Å, $\beta = 97.22(1)^\circ$. The structure was refined to a conventional R -factor of 0.033. Te is linked to the methoxyphenyl group and the essentially monodentate dimethyldithiophosphate ion. The tellurium valency angle is $94.89(8)^\circ$, and the bond lengths are $\text{Te}-\text{C}(\text{Ph}) = 2.114(3)$ Å and $\text{Te}-\text{S}1 = 2.444(1)$ Å. Roughly *trans* to $\text{Te}-\text{S}1$ one finds a weak intermolecular $\text{Te}\cdots\text{S}2$ bond of length 3.262(1) Å.

The solution of the structure of the title compound, $4\text{-CH}_3\text{OPhTeSP}(\text{S})(\text{OCH}_3)_2$, is part of a study of the configuration in complexes of divalent tellurium containing among the ligands an aryl group and a dithiolate group.^{1,2} The compounds planned for preparation have the general formulas ArTeL and ArTeLX , where $\text{Ar} = 4\text{-methoxyphenyl}$, 4-ethoxyphenyl and phenyl , $\text{L} = \text{alkylxanthates}$, $\text{dialkyldithiophosphates}$, $\text{dialkyldithiocarbamates}$, etc. and X is another sulfur-containing ligand or halogen. The main objective is to investigate the configuration around tellurium in these compounds.^{3,4}

Experimental

Preparation. $\text{CH}_3\text{OPhTeCl}_3$ (0.171 g) was thoroughly mixed with $(\text{CH}_3\text{O})_2\text{PS}_2\text{K}$ (0.311 g) in 4 ml MeOH at room temperature, giving a red, oily solution. To this solution was added 4 ml CS_2 and 10 ml *n*-hexane, leading to two separate layers, one pale yellow and one deep red. The latter was decanted into another beaker, and the volume was reduced by 50% under vacuum. Yield: 0.128 g (32.7%) of deep red plates.

Structure analysis. Unit cell parameters (Table 1) were determined from the settings of 25 reflections. An ω -scan was used for collection of intensities and the scan width was $1.0 + 0.35 \tan\theta$, plus 25% on each side for background. The variation of three standard reflections was used for scaling of intensity data. The data were corrected for Lorentz and polarization effects, as well as for absorption, extinction and anomalous dispersion. The crystal structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares methods. The function minimized is $\sum w(\Delta F)^2$, the attributed weights correspond to the count-

ing statistics plus 3% of the net intensity (fudge factor = 0.03). The expression for the weights is: $w = 4F_{\text{obs}}^2 / \sigma(F_{\text{obs}}^2)^2$ where $\sigma(F_{\text{obs}}^2) = [\sigma(I)^2 + (0.03I)^2]^{0.5}$. Anisotropic temperature factors were applied to all atoms except hydrogen. The hydrogen positions were calculated by using a fixed C-H distance of 0.95 Å, and each hydrogen was kept riding on the carbon to which it was bonded. All hydrogen atoms were given a constant temperature factor ($B = 7.0$ Å²). A final difference map showed two peaks of ca. 1.2 and 1.1 e Å⁻³; these were positioned close to the Te atom. No other

Table 1. Crystal data and structural parameters.

Compound	$\text{CH}_3\text{OPhTeSP}(\text{S})(\text{OCH}_3)_2$
Diffractometer	Enraf-Nonius CAD-4
Radiation (Wavelength/Å)	$\text{MoK}\alpha$ (0.71073)
Crystal system	Monoclinic
$a/\text{Å}$	9.976(1)
$b/\text{Å}$	12.023(1)
$c/\text{Å}$	12.333(1)
$\beta/^\circ$	97.22(1)
$V/\text{Å}^3$	1467.8
Space group	$P2_1/n$ (No. 14)
M	391.90
Z	4
$D_{\text{calc}}/\text{g cm}^{-3}$	1.773
$\mu(\text{MoK}\alpha)/\text{cm}^{-1}$	24.014
Crystal dimensions/mm	$0.5 \times 0.2 \times 0.2$
Scan mode	ω -scan
Fudge factor	0.030
Scale factor	0.152
Maximum value of $\theta/^\circ$	30
No. of reflections	4242
No. with $I > 2\sigma(I)$	3457
Transmission factors	0.5246-0.6020
$R = \sum F_{\text{obs}} - F / \sum F_{\text{obs}}$	0.033
$R_w = [\sum w(F_{\text{obs}} - F)^2 / \sum w(F_{\text{obs}})^2]^{0.5}$	0.039
$S = [\sum w(\Delta F)^2 / (N - n)]^{0.5}$	1.766

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peaks above $0.56 \text{ e } \text{\AA}^{-3}$ were observed. The shifts in the final refinement cycle were $<1\%$ of the associated standard deviations. All computer programs used belong to the Enraf-Nonius structure determination pack (1987). Crystal and experimental data and final figures of merit are included in Table 1. Listings of observed and calculated structure factors as well as anisotropic temperature factors are available from the authors.

Results and discussion

The crystals are built up of 4-methoxyphenyltellurenyl dimethyldithiophosphate molecules. The molecules are connected through weak, intermolecular Te \cdots S2 bonds. The bond lengths and angles in the molecule, calculated from the coordinates of Table 2, are listed in Table 3 together with the calculated standard deviations. An ORTEP drawing of the molecule is shown in Fig. 1. The bond angle C3–Te–S1 is $94.89(8)^\circ$, close to the corresponding angles of $96.77(9)^\circ$ in 4-methoxyphenyltellurenyl thiosulfonate² and $97.24(8)^\circ$ in 4-methoxyphenyltellurenyl methylxanthate.¹ If the weak intermolecular Te \cdots S2' bond of $3.262(1) \text{ \AA}$ is included (sum of van der Waals radii for tellurium and sulfur = 3.86 \AA)⁵ the tellurium atom may be regarded as three-coordinate and the compound as a T-shaped complex (Fig. 2). The three atoms S1, Te and S2' (S2' is given by the symmetry operations $x + 0.5, -y - 0.5, z + 0.5$) are almost colinear, the angle S1–Te–S2' being $172.84(3)^\circ$. The angle S2'–Te–C3 is $87.82(8)^\circ$, and S1, Te, C3 and S2' are nearly coplanar, since S2' is only $0.38(1) \text{ \AA}$ above the plane through C3, Te and S1. Vikane⁶ has examined eight T-shaped phenyltellurenyl compounds and found the average Te–C(Ph) distance to be 2.115 \AA . He concludes that since this is equal to, within accuracy, the Te–C(sp^2) single covalent

Table 3. Bond lengths (in \AA) and angles (in $^\circ$). Estimated standard deviations are given in parentheses.

Te–S1	2.4435(8)	C3–C4	1.387(5)
Te–C3	2.114(3)	C3–C8	1.375(4)
S1–P	2.051(1)	C4–C5	1.368(6)
P–S2	1.933(1)	C5–C6	1.375(5)
P–O1	1.569(3)	C6–C7	1.365(5)
P–O2	1.571(2)	C7–C8	1.387(5)
O1–C1	1.434(5)	C6–O3	1.366(5)
O2–C2	1.436(5)	C9–O3	1.389(5)
S1–Te–C3	94.89(8)	Te–C3–C4	121.2(2)
Te–S1–P	103.33(4)	Te–C3–C8	120.9(2)
S1–P–S2	107.89(5)	C3–C4–C5	120.8(3)
S1–P–O1	109.64(9)	C4–C3–C6	120.4(4)
S1–P–O2	109.27(9)	C5–C6–C7	120.1(3)
S2–P–O1	116.19(9)	C5–C6–O3	115.6(3)
S2–P–O2	116.60(9)	C6–C7–C8	119.1(3)
O1–P–O2	96.8(1)	C7–C8–C3	121.7(3)
P–O1–C1	119.9(2)	C6–O3–C9	119.5(3)
P–O2–C2	120.7(2)	C7–C6–O3	124.2(3)

bond length of 2.11 \AA ,⁷ one may assume that there is an efficient overlap between one tellurium $5p$ orbital and one sp^2 orbital of the phenyl carbon. Most Te(II) complexes are square-planar with the bonding being described by two three-centre, four-electron systems centred at the central tellurium atom and based on mutually perpendicular p -orbitals on tellurium. In the case of a T-shaped Te(II) complex, $L_1\text{--}Te\text{--}L_2$, the fourth ligand position can

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be regarded as empty, presumably because of the strong *trans* influence of the phenyl group.^{6,8–16} $L_1\text{--}Te\text{--}L_2$ constitutes one three-centre, four-electron system, while the other is reduced to a two-centre, two-electron system (Te–Ph). Often a weak intermolecular bond ca. $0.3\text{--}0.5 \text{ \AA}$ shorter

Table 2. Fractional atomic coordinates and their estimated standard deviations. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter.

Atom	x	y	z	B/ \AA^2 ^a
Te	–0.00625(2)	–0.22020(2)	0.13471(2)	4.055(4)
S1	–0.12097(8)	–0.09707(6)	–0.00492(7)	4.21(1)
S2	–0.38904(9)	–0.09883(7)	–0.18020(7)	4.82(2)
P	–0.28446(7)	–0.18889(6)	–0.07048(5)	3.21(1)
O1	–0.3616(2)	–0.2344(2)	0.0236(2)	4.71(4)
O2	–0.2347(2)	–0.3046(2)	–0.1090(2)	4.53(5)
O3	0.3727(3)	–0.4239(2)	–0.1802(2)	7.93(6)
C1	–0.4283(4)	–0.1586(4)	0.0889(3)	7.1(1)
C2	–0.1534(4)	–0.3116(3)	–0.1970(3)	6.10(8)
C3	0.1235(3)	–0.2913(2)	0.0306(2)	3.80(5)
C4	0.1967(3)	–0.2253(3)	–0.0330(3)	4.89(7)
C5	0.2792(4)	–0.2721(3)	–0.1011(3)	5.63(8)
C6	0.2911(4)	–0.3858(3)	–0.1072(3)	5.03(7)
C7	0.2227(4)	–0.4528(3)	–0.0437(3)	6.09(8)
C8	0.1380(4)	–0.4048(3)	0.0241(3)	5.17(7)
C9	0.4050(6)	–0.5362(4)	–0.1815(4)	11.5(1)

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

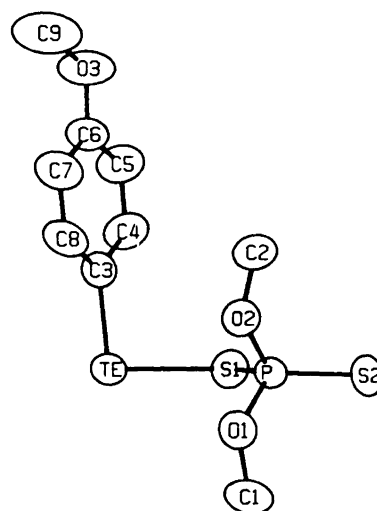


Fig. 1. ORTEP drawing of $p\text{-CH}_3\text{OPhTeSP(S)(OCH}_3)_2$.

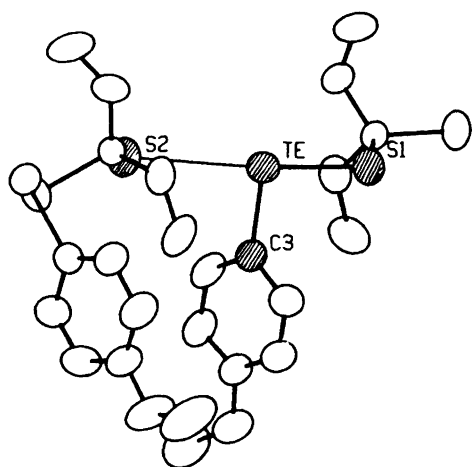


Fig. 2. ORTEP drawing showing the T-shaped configuration around tellurium (shaded) and the intermolecular contact between Te and the neighbouring S2 atom (thin lines).

than a van der Waals contact is found *trans* to aryl in T-shaped tellurium(II) complexes containing an aryl group.⁶ Also, the similar 4-methoxyphenyltellurium methylxanthate has a tendency to four-coordination around tellurium even if the C(sp²)-Te bond has exactly the same length as in the present investigation. The average values for 11 T-shaped Te(II) complexes¹⁶ (only the compounds with L₁ and L₂ binding through S being included) compared to the present structure are as follows (where L₁-Te is denoted *d*₁ and L₂-Te is denoted *d*₂):

	Average ¹⁵	Present compound
$(d_1 + d_2)/2/\text{Å}$	2.708	2.853
$(L_1\text{-Te-L}_2)/^\circ$	175.20	172.84(3)
Te-C(Ph)/Å	2.117	2.114(3)

Increasing asymmetry in a three centre four-electron system like L₁-Te-L₂ causes the sum of the bond lengths (*d*₁ + *d*₂) to increase, and this is in accordance with earlier conclusions.^{6,16} The L₁-Te-L₂ angles are comparable, as are the Te-C(Ph) bond distances. The phenyl ring is nearly planar, with tellurium being 0.023(0) Å above this plane. The alkyl-aryl ether linkage is relatively short.¹⁷ The O3-C9 bond length of 1.389(5) Å is considerably shorter than the corresponding bond lengths of 1.420(5) Å in 4-

methoxyphenyltellurenyl methylxanthate¹ and 1.428(5) Å in 4-methoxyphenyltellurenyl methanethiosulfonate.² In 4-ethoxyphenyltellurenyl methylxanthate the corresponding alkyl-oxygen distance is 1.437(4).¹⁸ The two methoxy groups connected to the phosphorus atom are situated symmetrically on both sides of a plane through S1, P and S2. The C1-O1-P-O2-C2 group is planar, the greatest deviation from planarity being 0.009(4) Å. The short P-O bond lengths of 1.569(3) and 1.571(2) Å imply a considerable amount of double-bond character. This is probably due to overlap of *p*-orbitals of the oxygens with *d*-orbitals on phosphorus, as proposed for phosphates.¹⁹ The short P-S2 bond length of 1.933(1) Å is comparable to the average bond length of 1.95 Å found for the P=S double bond in the phosphorus sulfides,¹⁹ while the long P-S1 bond length of 2.051(1) Å is normal.

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