The Crystal and Molecular Structure of 4-Methoxyphenyltellurenyl Methylxanthate, $CH_3OPhTeSC(S)OCH_3$

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The crystal and molecular structure of the title compound has been determined by X-ray methods based on 2591 unique, observed reflections. The crystals are monoclinic, space group $P2_1/c$ with unit cell dimensions $a = 8.7897(9)$, $b = 17.3453(11)$, $c = 8.0826(9)$ Å and $\beta = 100.144(8)°$. The structure was refined to a conventional R-factor of 0.031. The molecule is L-shaped. Te is linked to the methoxyphenyl group and the essential monodentate methylxanthate. The tellurium valency angle is 97.24 (8)°, and the bond lengths are Te–C(Ph) = 2.114(3) Å and Te–S2 = 2.404(1) Å. Roughly *trans* to these, one finds two weak intermolecular Te···S1 bonds with lengths 3.467(8) and 3.62(1) Å, the longest bond being *trans* to the phenyl group. When the two intermolecular bonds are included in the coordination sphere, tellurium forms a four-coordinated, distorted square-planar complex.

The solution of the structure of the title compound is part of a study of the configuration in complexes of divalent tellurium containing among the ligands at least both an aryl group and a dithiolate group. The compounds have the general formulas ArTeL and ArTeLX (Ar = 4-methoxyphenyl, 4-ethoxyphenyl, phenyl; L = alkylxanthates, dialkylthiophosphates, dialkyldithiocarbamates, etc; X is another sulfur-containing ligand or halogen). The main objective is to investigate the configuration around tellurium in the compounds. Previously, a tendency to square-planar configuration around the central atom has been found in divalent tellurium complexes, as shown by Foss *et al.*[1] and Husebye.[2]

Experimental

Preparation of 4-methoxyphenyltellurenyl methylxanthate has been reported earlier.[3] The direct method involving trituration of 4-methoxytellurenyl methanethiosulfonate with an excess of potassium methylxanthate suspended in warm ether was employed, giving the 4-methoxyphenyltellurenyl methylxanthate as stable, orange-red plates or prisms.

Structure analysis. The coordinates for the tellurium and sulfur atoms were found from a Patterson map, and the positions of the other atoms were found from subsequent Fourier maps. The structure was refined by means of a full-matrix least-squares program which minimizes the quantity $\Sigma w(|F_0|-K|F|)^2$. K is a scale factor and $w^{-1} = \sigma(F_0)$. Anisotropic temperature factors were applied to all atoms except hydrogen, which were refined isotropically. 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. Lists of observed and calculated structure factors as well as anisotropic temperature factors are available from one of the authors (S.H.) on request.

Table 1. Crystal data and structural parameters.

Compound	$CH_3OPhTeSC(S)OCH_3$
Diffractometer	Enraf–Nonius CAD-4
Radiation	Mo$K\alpha$
Wavelength/Å	0.71073
Crystal system	Monoclinic
a/Å	8.7897(9)
b/Å	17.3453(11)
c/Å	8.0826(8)
β/°	100.144(8)
V/Å^3	1213.0
Space group	$P2_1/c$ (No. 14)
M	341.91
Z	4
D_{calc}/g cm^{-3}	1.872
μ(MoK_α)/cm^{-1}	27.615
Scan-mode	ω-scan
Scale factor	0.339
Maximum value of θ/°	30
No. of indep. meas.	356
No. with $I > 2\sigma(I_0)$	2591
Correction for absorption	Empirical
Min. abs. corr. fact.	0.7338
Max. abs. corr. fact.	1.2572
$R = \Sigma\vert F_0-F\vert/\Sigma F_0$	0.031
$R_w = [\Sigma w(F_0-F)^2/\Sigma wF_0^2]^{1/2}$	0.030

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

Atom	*x*	*v*	*z*	$B/Å^{2\,a}$
Te	0.13083(2)	0.57625(1)	0.85621(2)	4.091(4)
S1	0.2251(1)	0.52912(7)	0.2787(1)	5.97(2)
S2	0.1213(1)	0.60143(5)	0.5621(1)	4.54(2)
O1	0.2793(3)	0.4744(1)	0.5877(2)	4.58(5)
O2	0.7518(3)	0.7382(1)	1.1626(3)	5.13(5)
C1	0.3536(5)	0.4081(2)	0.5269(5)	6.2(1)
C2	0.2182(4)	0.5266(2)	0.4790(3)	3.79(6)
C3	0.3430(3)	0.6324(2)	0.9447(3)	3.50(6)
C4	0.4820(4)	0.5994(2)	0.9267(4)	3.85(6)
C5	0.6207(4)	0.6335(2)	0.9936(4)	3.87(6)
C6	0.6214(4)	0.7012(2)	1.0850(3)	3.83(6)
C7	0.4825(4)	0.7350(2)	1.1030(4)	4.52(7)
C8	0.3450(4)	0.7012(2)	1.0334(4)	4.46(7)
C9	0.8976(4)	0.7060(3)	1.1488(5)	6.1(1)

$^aB = 4/3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab\cos\gamma B(1,2) + ac\cos\beta B(1,3) + bc\cos\alpha B(2,3)]$.

Results and discussion

The crystals are built up of 4-methoxyphenyltellurenyl methylxanthate molecules. The molecules are connected through weak, intermolecular Te···S1 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. Intermolecular distances and angles are given in Table 4. Table 5 lists least-squares molecular planes. The bond angle C3TeS2 is 97.24(8)°, which is close to the corresponding angle C2TeS1 of 96.77 (9)° found in the strictly monomeric 4-methoxyphenyltellurenyl methanethiosulfonate.[4] Thus, this compound has an angular structure. If the two weak intermolecular Te···S bonds are included in the coordination sphere, it may be regarded as a distorted square-planar complex of divalent tellurium. This is due to the fact that the four bonds formed by tellurium are nearly coplanar, and that the corresponding bond angles deviate less than 10° from 90° and 180°. In Fig. 2, four molecules with one of the coordination groups ($TeCS_3$) shaded are shown. In the coordination plane, the short Te–C and Te–S bonds are *cis* to each other, but *trans* to and nearly colinear with the two long intermolecular Te–S bonds. Depending on the electron-donating strength of the ligand, four-coordinate tellurium(II) complexes of the type TeL_2 (L is a bidentate dithio ligand) usually form two classes of complexes.[5-12] Both classes have a trapezoid planar configuration around the central atom. With strong electron-donating ligands one obtains class I in which all bonds are intramolecular, while weak donors give class II with two intramolecular bonds and two weak intermolecular bonds roughly *trans* to the others. Dialkylxanthates of divalent tellurium have earlier been cited as examples of

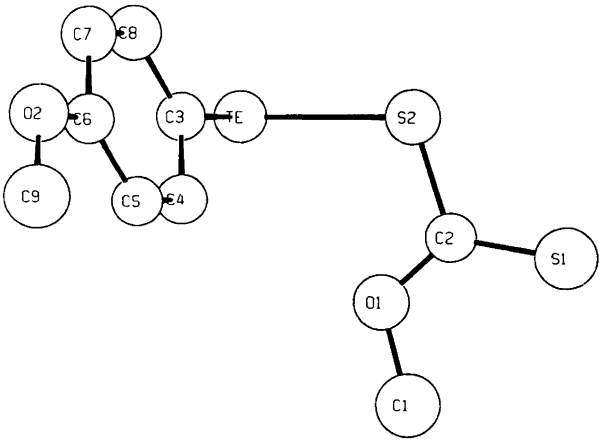


Fig. 1. ORTEP drawing of $4\text{-}CH_3OPhTeSC(S)OCH_3$.

Table 3. Bond lengths (Å) and angles (°). Estimated standard deviations in parentheses.

Te –S2 = 2.4040(9)
Te –C3 = 2.114(3)
S1 –C2 = 1.632(3)
S2–C2 = 1.749(3)
C1–O1 = 1.451(5)
O1–C2 = 1.309(4)
C3–C4 = 1.380(5)
C3–C8 = 1.391(4)
C4–C5 = 1.377(4)
C5–C6 = 1.387(4)
C6–C7 = 1.385(5)
C7–C8 = 1.371(4)
O2–C6 = 1.366(4)
O2–C9 = 1.420(5)

C3–Te –S2 = 97.24(8)
Te –S2–C2 = 108.1(1)
S2–C2–S1 = 117.8(2)
S2–C2–O1 = 115.2(2)
C1–O1–C2 = 118.5(3)
S1 –C2–O1 = 127.0(2)
Te –C3–C4 = 121.2(2)
Te –C3–C8 = 120.0(2)
C3–C4–C5 = 121.3(3)
C3–C8–C7 = 120.6(3)
C4–C5–C6 = 119.6(3)
C5–C6–C7 = 119.5(3)
C5–C6–O2 = 124.5(3)
C4–C3–C8 = 118.6(3)
C6–O2–C9 = 118.4(3)
C6–C7–C8 = 120.4(3)
C7–C6–O2 = 116.0(3)

Table 4. Intermolecular weak bonds and contacts (Å), intermolecular angles (°), and intramolecular contact (Å).

Intermolecular weak bonds and contacts	
Te···S1(I)	3.4668(8)
Te···S1(II)	3.622(1)
Intermolecular angles	
S1(I)–Te–S1(II)	102.79(2)
S1(I)–Te–S2	167.84(3)
S1(II)–Te–C3	74.43(8)
S1(I)–Te–O1	118.41(4)
S1(II)–Te–C3	176.65(7)

S1(I) is given by the symmetry operations *x*, *y*, 1+*z*
S1(II) is given by the symmetry operations −*x*, 1−*y*, 1−*z*

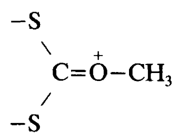
Intramolecular contact	
Te···O1	3.244(2)

Table 5. Best planes.

No. of plane[a]	Atoms included	Δ[b]	Distances (Å) from atoms to plane
1	Te, C3, S2, S1(I), S1(II)	0.128	O1: 2.635(2)
2	C3, C4, C5, C6, C7, C8	0.011	Te: 0.160(0); O2: 0.051(2); C9: 0.066(4)
3	S1, S2, C2, O1	0.004	Te: 0.059; C1: 0.083(4)

[a]Dihedral angle between: plane No. 1 and plane No. 2 101.5(4)°; plane No. 1 and plane No. 3 89.4(3)°. [b]Δ: maximum distance (Å) between all atoms in plane and plane.

class I;[13] however, in the present investigation the structure belongs to class II. The least-squares plane through the phenyl ring shows that O2 and C9 are very close to the plane, while tellurium is 0.160 Å away from it. The strong *trans* influence of the phenyl group[14–15] is reflected in the fact that the Te···S1 bond *trans* to it has a length of 3.62 (1) Å, compared to the other intermolecular Te···S1 bond of 3.467(8) Å, which is *trans* to sulfur. Both are considerably shorter than the sum of van der Waals radii of 4.05 Å.[16] The four-coordination of divalent tellurium is in god agreement with earlier work.[17] With phenyl as one of the ligands one generally finds a three-coordinated, T-shaped configuration around tellurium with the phenyl group at the stem.[14,18] In most cases there is a short intermolecular Te···ligand contact *trans* to phenyl that indicates four-coordination also there.[19–25] The methylxanthate ligand is almost completely planar, and the Te atom is also in this plane. The dihedral angle between the coordination plane and the phenyl group is 101.54(7)°. A dihedral angle of ~100° seems to cause maximum separation between tellurium and one of the *ortho* carbon atoms in the phenyl ring.[26] In 4-nitrobenzyl tellurocyanate,[26] in which tellurium is connected by intermolecular bonds to two neighbouring oxygen atoms, one finds the same pattern as in this structure, with a distorted square-planar configuration but with a bond angle between the strong bonds of only 90.6(1)°. The intermolecular bond *trans* to the benzyl group is the weakest, due to the strong *trans* influence of this group. The average Te–C bond length is 2.114 Å, which is normal[27–28] and equal to the corresponding value found in the present structure. The Te–S2 bond length of 2.4040(9) Å is also normal [ΣR_{cov} (Te–S) = 2.14 Å].[16] In the methylxanthate group the short C2–S1 distance of 1.632(3) Å compared to C2–S2 [1.749 (3) Å] [$\Sigma R_{cov}(C_{sp^2}\text{–}S)$ = 1.78 Å][17] indicates double-bond character in the C2–S1 bond. In the methoxyphenyl end of the molecule there is an alkyl-aryl ether linkage.[29] The C–O–C angle of 118.5(3)° is normal. The corresponding bond lengths are C1–O1 = 1.451(5) Å and O1–C2 = 1.309(4) Å and indicate some double bond character in the latter. This shows some contribution of the resonance form



$$\begin{array}{l} -S \\ \quad\backslash \\ \quad\;\; C=\overset{+}{O}-CH_3 \\ \quad / \\ -S \end{array}$$

The distance Te···O1 is only 3.24(2) Å (corresponding van der Waals contact = 3.58 Å[30]), but this may be due to steric effects since O1 is well out of the bonding plane of tellurium.

Packing in the unit cell. There is a zig-zag pattern of tellurium atoms held together by the two types of intermolecular Te···S1 bonds. Thus, the molecules are held together in chains with the phenyl groups pointing out on both sides, as shown in Fig. 2. Along the chains there are two different non-bonded Te···Te distances, as can be seen in Fig. 2.

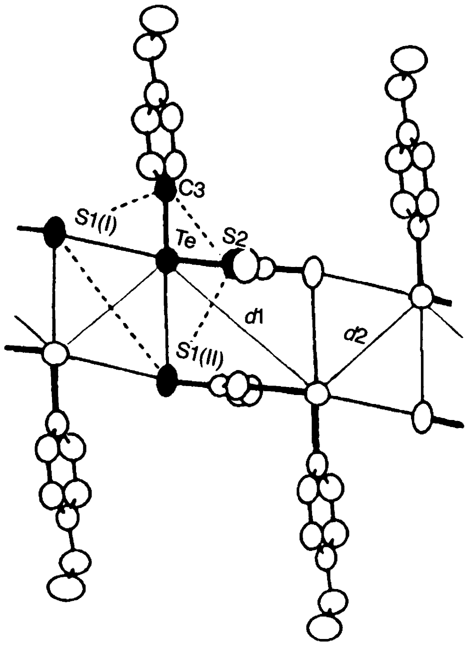


Fig. 2. ORTEP drawing showing the trapezoid planar configuration around tellurium (shaded) and the intermolecular contacts between Te and neighbouring S1 atoms (thin lines). The figure also shows the zig-zag pattern of tellurium atoms with the two non-bonded distances, *d*1 = 6.3858(3) Å and *d*2 = 4.4240(3) Å.

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