

# The Crystal and Molecular Structure of 4-Methoxyphenyltellurenyl Methanethiosulfonate

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We are presently studying the configuration around Te(II) in complexes of divalent tellurium containing among the ligands at least both an aryl group and a dithiolate group.<sup>1</sup> Previously, a tendency to square-planar configuration around the central atom has been found in divalent tellurium complexes, as shown by Foss *et al.* and Husebye.<sup>2,3</sup> The title compound is an intermediate in the formation of some of the complexes mentioned above. Its structure was solved to function as a reference, as this compound cannot be interpreted as a complex of Te(II).

Table 1. Crystal data and structural parameters.

Compound	CH <sub>3</sub> OPhTeS <sub>2</sub> O <sub>2</sub> CH <sub>3</sub>
Diffractionmeter	Enraf-Nonius CAD-4
Radiation	MoK $\alpha$
Wavelength/Å	0.71073
Crystal system	Monoclinic
a/Å	14.1694(16)
b/Å	5.3223(9)
c/Å	15.6908(22)
$\beta$ /°	94.153(10)
V/Å <sup>3</sup>	1180.2
Space group	P2 <sub>1</sub> /n (No. 1014)
M	345.90
Z	4
D <sub>calc</sub> /g cm <sup>-3</sup>	1.947
Abs. coeff./cm <sup>-1</sup>	28.450
Cryst. dim./mm	0.06×0.2×0.2
Scan-mode	$\omega$ -scan
Scale factor	0.421
Maximum $\theta$ /°	30
No. of indep. meas.	3440
No. with $I > 2\sigma(I)$	2292
Transmission factors	0.5193–0.8411
$R = \sum  F_o - F  / \sum F_o$	0.033
$R_w = [\sum w(F_o - F)^2 / \sum wF_o^2]^{0.5}$	0.030

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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 <sup>2</sup> <sup>a</sup>
Te	0.18953(2)	0.36921(5)	-0.12721(2)	3.942(5)
S1	0.32401(7)	0.0981(2)	-0.11606(6)	4.50(2)
S2	0.33099(7)	-0.0276(2)	0.00956(7)	4.24(2)
O1	0.2389(2)	-0.0276(2)	0.0381(2)	6.98(9)
O2	0.3956(3)	-0.2356(6)	0.0087(3)	7.4(1)
O3	-0.1205(2)	-0.4301(5)	-0.2329(2)	4.51(6)
C1	0.3868(3)	0.2091(9)	0.0712(3)	5.1(1)
C2	0.0880(2)	0.0894(7)	-0.1616(2)	3.16(7)
C3	0.0552(3)	0.0576(7)	-0.2460(2)	3.67(8)
C4	-0.0139(3)	-0.1199(8)	-0.2680(2)	4.04(8)
C5	-0.0514(3)	-0.2664(7)	-0.2048(2)	3.41(7)
C6	-0.0175(3)	-0.2361(8)	-0.1205(2)	3.59(8)
C7	0.0512(3)	-0.0593(8)	-0.0990(2)	3.66(8)
C8	-0.1623(3)	-0.5818(9)	-0.1717(3)	5.4(1)

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

## Experimental

Preparation of 4-methoxyphenyltellurenyl methanethiosulfonate has been reported earlier.<sup>4</sup> The crystals are orange-red plates or prisms.

**Structure analysis.** Unit cell parameters (Table 1) were determined from the settings of 25 reflections. The  $\omega$ -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. The variation of three standard reflections was used for scaling of intensity data. The data were corrected for Lorentz and for polarization, absorption, extinction and anomalous dispersion effects. The crystal structure was solved by Patterson and Fourier methods, and refined by full-matrix least-squares, minimizing the function  $\sum w(\Delta F)^2$ . The attributed weights correspond to the counting statistics plus 2% of the net intensity (fudge factor = 0.02).

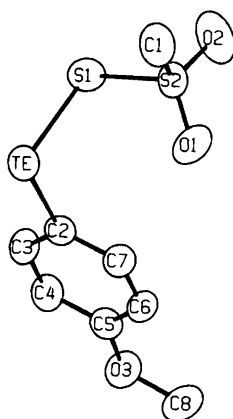


Fig. 1. ORTEP drawing of *p*-CH<sub>3</sub>OPhTeS<sub>2</sub>O<sub>2</sub>CH<sub>3</sub>.

Anisotropic temperature factors were applied for all atoms except hydrogen. Final figures of merits are included in Table 1.

### Results and discussion

The crystals are built up of 4-methoxyphenyltellurenyl methanethiosulfonate molecules. 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 (tables of observed and calculated structure factors, anisotropic temperature factors and hydrogen parameters can be obtained from the authors upon request).

The compound has an angular structure, while Te(II) complexes with monodentate ligands are mostly square-planar or distorted square-planar, executing 3c-4e bonding, as shown by Foss and coworkers.<sup>5</sup> Angle C2-Te-S1 is 96.77

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

Te-S1	2.387(1)	C2-Te-S1	96.77(9)
Te-C2	2.114(3)	Te-S1-S2	104.31(4)
S1-S2	2.077(1)	S1-S2-C1	106.4(2)
S2-C1	1.743(4)	S1-S2-O1	111.3(1)
S2-O1	1.425(3)	S1-S2-O2	103.1(2)
S2-O2	1.437(3)	O1-S2-O2	119.4(2)
C2-C3	1.382(4)	O1-S2-C1	108.6(2)
C2-C7	1.392(4)	O2-S2-C1	107.3(2)
C3-C4	1.386(5)	C5-O3-C8	117.8(3)
C4-C5	1.396(5)	Te-C2-C3	120.4(2)
C5-C6	1.384(4)	Te-C2-C7	120.2(2)
C6-C7	1.378(4)	C3-C2-C7	119.3(3)
O3-C5	1.359(4)	C2-C3-C4	120.3(3)
O3-C8	1.428(5)	C3-C4-C5	120.1(3)
		O3-C5-C4	115.5(3)
		O3-C5-C6	125.2(3)
		C4-C5-C6	119.3(3)
		C5-C6-C7	120.3(3)
		C2-C7-C6	120.6(3)

Table 4. Some distances (Å) and angles (°) in two-coordinate tellurium compounds. In the last entry (present structure), the angle quoted is S1-Te-C2.

Compound	Te-S	S-Te-S	Ref.
Te(S <sub>2</sub> O <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub>	2.35(3) and 2.36(3)	100(2)	9
Te(S <sub>2</sub> O <sub>2</sub> C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub>	2.41(3)	97(2)	10
Te(S <sub>2</sub> O <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub> ) <sub>2</sub>	2.41(4)	96(3)	11
(NH <sub>4</sub> ) <sub>2</sub> Te(S <sub>2</sub> O <sub>3</sub> ) <sub>2</sub>	2.35(3) and 2.36(3)	103(2)	12
BaTe(S <sub>2</sub> O <sub>3</sub> ) <sub>2</sub> ·2H <sub>2</sub> O	2.34(2)	101(1)	13
CH <sub>3</sub> OPhTeS <sub>2</sub> O <sub>2</sub> CH <sub>3</sub>	2.387(1)	96.77(9)	

(9)°, which may be compared with the corresponding angle C3-Te-S2 of 97.24(8)° in the four-coordinate 4-methoxyphenyltellurenyl methylxanthate.<sup>1</sup> In the latter, four-coordination is achieved through the formation of two weak intermolecular Te···S bonds of ca. 3.7 Å. The phenyl group is planar within 0.007 Å, and O3 and C8 are 0.038 Å and 0.073 Å, respectively, below the phenyl plane. Tellurium is 0.084 Å below the plane. The interplanar angle formed with the plane through Te, S1 and S2 is 99.12(7)°, and the Te-C2 bond is, within experimental accuracy, of normal length, viz. 2.114(3) Å.<sup>6,7</sup> In two-coordinate tellurium(II) compounds the Te-S bond lengths vary between 2.34 and 2.41 Å, and the S-Te-S angle between 96° and 103°,<sup>8</sup> as can be seen from Table 4. The upper bond-length limit in this table is 2.41 Å, which is equal to the sum of the respective covalent radii.<sup>14</sup> The S2-C1 bond length of 1.743(4) Å is a bit shorter than that of the normal covalent bond ( $\Sigma R_{\text{cov}}(C_{sp^2}\text{-S}) = 1.78 \text{ Å}$ ),<sup>14</sup> while S2-O1 and S2-O2 with bond lengths of 1.425(3) Å and 1.437(3) Å, respectively, are linked by double bonds. At the methoxyphenyl end of the molecule there is a normal ether linkage.<sup>15</sup> The C<sub>sp<sup>3</sup></sub>-O bond length in this compound is 1.428(5) Å, which may be compared with the corresponding bond length of 1.451(5) Å in 4-methoxyphenyltellurenyl methylxanthate,<sup>1</sup> and the O-C (Ph) bond length is 1.359(4) Å, which may be compared with 1.309(4) Å in the 4-methoxyphenyltellurenyl methylxanthate. Even if the average C-O distances are close in the two compounds, there is a surprisingly large difference in the individual bond lengths.

In this compound there is no intermolecular secondary Te···X bond. There are a few Te-C and S-C intermolecular contacts smaller than a van der Waals distance. The shortest contact is Te···C6, the length being 3.616(3) Å. Thus, tellurium forms an ordinary angular two-coordinate compound.

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