The Crystal and Molecular Structure of the Addition Compound of 4-Ethoxyphenyltellurenyl Methanethiosulfonate and Dimethanesulfonyl Disulfide, $C_2H_5OPhTeS_2O_2CH_3 \cdot (CH_3SO_2S)_2$

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The crystal and molecular structure of the title compound has been determined by X-ray methods based on 4622 unique, observed reflexions. The crystals are triclinic, space group $P\bar{1}$ with unit cell dimensions $a = 5.300(0)$, $b = 13.296(1)$, $c = 16.078(1)$ Å, $\alpha = 108.73(1)$, $\beta = 96.55(1)$ and $\gamma = 97.16(1)°$. The structure was refined to a conventional R-factor of 0.038. Te is linked to the ethoxyphenyl group and the strictly monodentate methanethiosulfonate ion. The resulting molecule is L-shaped. The tellurium valency angle is $97.98(9)°$, and the bond lengths are Te–C(Ph) = 2.104(3) Å and Te–S1 = 2.400(1) Å. In the dimethanesulfonyl disulfide the central S–S bond has a bond length of 2.002(1) Å and the two terminal S–S bonds are 2.136(2) and 2.115(1) Å, respectively. The S–S–S bond angles are 103.48(6) and 103.16(5)° and the dihedral angle SSS/SSS is 92.34(4)°.

The solution of the structure of the title compound, 4-$C_2H_5OPhTeS_2O_2CH_3 \cdot (CH_3SO_2S)_2$, is part of a study of the configuration in complexes of divalent tellurium containing among the ligands both an aryl group and a dithiolate group.[1-4] The main objective is to investigate the configuration around tellurium in the compounds.[5,6]

Experimental

An attempted preparation of 4-ethoxyphenyltellurenyl dithiocarbamate by treatment of $C_2H_5OPhTeS_2O_2CH_3$[7] with an excess of $NH_4SC(S)NH_2$ in CS_2 gave a yellow crystalline product. The results of the structure determination showed that the crystals formed did not consist of the expected product, $C_2H_5OPhTeS_2CNH_2$ [or perhaps $C_2H_5OPhTe(S_2CNH_2)_3$[8]]. Instead the original C_2H_5OPhTe $S_2O_2CH_3$ had cocrystallized with the oxidation product of $CH_3SO_2S^-$ to form the 1:1 addition compound. Thus the disulfide formed during the preparation of C_2H_5OPhTe $S_2O_2CH_3$ must obviously have contaminated the product.

Structure analysis. An Enraf-Nonius CAD4 diffractometer with graphite-monochromated MoKα radiation was used for the determination of cell parameters and for recording of intensity data. The experimental temperature was ~18 °C. Unit cell parameters (Table 1) were determined from the settings of 25 independent reflections with $\lambda(a_1) = 0.70930$ and $\lambda(a_2) = 0.71359$ Å. An ω-scan was used to collect intensities and the scan width was $1.00 + 0.35 \tan\theta$,

plus 25 % on each side for background. Three standard reflections measured every 2 h were used for scaling of intensity data. The intensity data were corrected for Lo-

Table 1. Crystal data and structural parameters.

Compound	$C_2H_5OPhTeS_2O_2CH_3 \cdot (CH_3SO_2S)_2$
Diffractometer	Enraf-Nonius CAD-4
Radiation/Wavelength/Å	MoKα/0.71073
Crystal system	Triclinic
a/Å	5.300(0)
b/Å	13.296(1)
c/Å	16.078(1)
α/°	108.73(1)
β/°	96.55(1)
γ/°	97.16(1)
V/Å³	1050.2
Space group	$P\bar{1}$ (No. 2)
M	582.25
Z	2
D_{calc}/g cm⁻³	1.841
μ(MoKα)/cm⁻¹	20.192
Crystal dimensions/mm	0.40×0.12×0.09
Scan mode/max θ/°	ω-scan/30
Fudge factor	0.030
Scale factor	0.329
No. of independent measurements	6118
No. with $I>2\sigma(I)$	4622
Transmission factors	0.5999–0.8649
$R = \Sigma|F_{obs}-F|/\Sigma F_{obs}$	0.038
$R_w = [\Sigma w(F_{obs}-F)^2 / \Sigma w(F_{obs})^2]^{0.5}$	0.038
$\Sigma = [\Sigma w(\Delta F)^2/N-n]^{0.5}$	1.418

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rentz and polarization effects as well as for absorption, the latter correction being based upon crystal faces and dimensions. Reflections with $I>2\sigma(I)$ were regarded as observed and were used in the calculations. The structure of the complex was solved by interpretation of Patterson and Fourier density maps. The hydrogen atoms were placed geometrically at a fixed C–H distance of 0.95 Å. Refinements were carried out by the full matrix least-squares technique, the sum minimized being $\Sigma w(\Delta F)^2$; the attributed weights correspond to the counting statistics plus 3 % of the net intensity (fudge factor = 0.03). 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 package (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 one of the authors (K.M.M.).]

Results and discussion

The crystals are built up of 4-ethoxyphenyltellurenyl methanethiosulfonate and dimethanesulfonyl disulfide molecules. The bond lengths and angles in the molecules are calculated from the coordinates in Table 2 and listed in

Table 3, together with the calculated standard deviations. An ORTEP drawing of the molecule is shown in Fig. 1. Fig. 2 shows how the molecules are packed in the unit cell, seen in projection along the a-axis. The bond angle S1–Te–C6 is 97.98(9)°, which seems to be normal when tellurium is bonded to an alkoxyphenyl group and a thiosulfonate ligand. In 4-methoxyphenyltellurenyl methanethiosulfonate the corresponding angle is 96.77(9)°.[1] Also, the Te–S distance is very similar; 2.387(1) Å in 4-methoxyphenyltellurenyl methanethiosulfonate[1] and 2.400(1) Å in the present structure. In the ethoxy end of the molecule one finds the normal alkyl–aryl ether linkage,[9] and in the methanethiosulfonate end all angles and bond lengths are similar to those found in 4-methoxyphenyltellurenyl methanethiosulfonate.[1] The pseudohalogen properties of dimethanesulfonyl disulfide have been discussed earlier by Foss.[10] Bond lengths (in Å) and angles (in °) in the sulfur skeletons of $(CH_3SO_2S)_2$,[11] $(PhSO_2S)_2$[12] and $(p\text{-MePhSO}_2S)_2$[12] as given in Table 4 are in good agreement with those in the disulfide of the present study.

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	$B/\text{Å}^{2a}$
Te	0.07160(4)	0.17289(2)	0.11801(1)	3.441(4)
S1	0.2492(2)	0.16036(7)	-0.01515(5)	3.67(2)
S2	0.4410(2)	0.31558(7)	0.01018(5)	3.50(2)
S3	1.1434(2)	0.50719(7)	0.38313(6)	3.61(2)
S4	1.1508(2)	0.53578(7)	0.25993(6)	3.76(2)
S5	0.8138(2)	0.58373(7)	0.23811(6)	3.95(2)
S6	0.8994(2)	0.75223(6)	0.30597(5)	3.30(2)
O1	0.9655(4)	0.0546(2)	0.3370(2)	3.56(5)
O2	0.6190(5)	0.3517(2)	0.0924(2)	5.21(7)
O3	0.5401(5)	0.3111(2)	-0.0705(2)	5.40(7)
O4	0.8894(5)	0.5088(3)	0.4025(2)	6.05(7)
O5	1.2528(6)	0.4112(2)	0.3707(2)	5.63(7)
O6	0.6490(5)	0.7823(2)	0.3044(2)	5.30(7)
O7	1.0600(6)	0.7742(2)	0.3893(2)	4.61(6)
C1	1.3142(8)	0.0763(3)	0.4506(3)	4.76(9)
C2	1.1503(7)	0.1344(3)	0.4072(2)	3.83(8)
C3	0.7822(6)	0.0877(2)	0.2907(2)	2.88(6)
C4	0.5995(7)	0.0055(2)	0.2285(2)	3.31(7)
C5	0.4036(6)	0.0299(3)	0.1790(2)	3.28(7)
C6	0.3848(6)	0.1363(2)	0.1891(2)	2.82(6)
C7	0.5691(7)	0.2177(3)	0.2499(2)	3.23(7)
C8	0.7691(6)	0.1938(3)	0.3005(2)	3.24(7)
C9	0.2039(8)	0.3993(3)	0.0226(3)	4.58(9)
C10	1.3595(8)	0.6158(3)	0.4611(3)	4.49(9)
C11	1.0713(7)	0.8050(3)	0.2386(2)	4.11(8)

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

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

$C_2H_5OPhTeS_2O_2CH_3$

Te –S1	2.400(1)	O1–C3	1.358(4)
Te –C6	2.104(3)	C3–C4	1.394(4)
S1 –S2	2.073(1)	C4–C5	1.371(5)
S2 –O2	1.436(3)	C5–C6	1.388(5)
S2 –O3	1.439(3)	C6–C7	1.386(4)
S2 –C9	1.767(4)	C7–C8	1.393(5)
C1 –C2	1.487(6)	C8–C3	1.380(5)
C2 –O1	1.442(4)		
S1 –Te –C6	97.98(9)	O1–C3–C4	115.5(3)
Te –S1 –S2	103.55(4)	O1–C3–C8	124.9(2)
S1 –S2–O2	110.7(1)	C3–C4–C5	120.3(3)
S1 –S2–O3	104.5(1)	C4–C5–C6	120.8(3)
S1 –S2–C9	106.5(1)	C5–C6–C7	118.7(3)
O2–S2–O3	118.4(2)	C6–C7–C8	121.0(3)
O2–S2–C9	107.9(2)	C7–C8–C3	119.5(3)
O3–S2–C9	108.3(2)	C8–C3–C4	119.7(3)
C1–C2–O1	107.7(3)	C5–C6–Te	120.4(2)
C2–O1–C3	119.0(3)	C7–C6–Te	120.8(3)

$(CH_3SO_2S)_2$

S3–C10	1.751(3)	S5–S6	2.115(1)
S3–O4	1.417(3)	S6–O6	1.433(3)
S3–O5	1.432(3)	S6–O7	1.425(3)
S3–S4	2.136(2)	S6–C11	1.745(4)
S4–S5	2.002(1)		
S3 –S4–S5	103.48(6)	O5–S3–S4	104.1(2)
S4 –S5–S6	103.16(5)	S5–S6–C11	105.5(1)
C10–S3–O4	110.9(2)	S5–S6–O6	102.5(1)
C10–S3–O5	108.6(2)	S5–S6–O7	109.5(1)
C10–S3–S4	104.5(2)	O6–S6–O7	119.5(2)
O4 –S3–O5	119.8(2)	O6–S6–C11	109.8(2)
O4 –S3–S4	107.8(1)	O7–S6–C11	109.0(2)
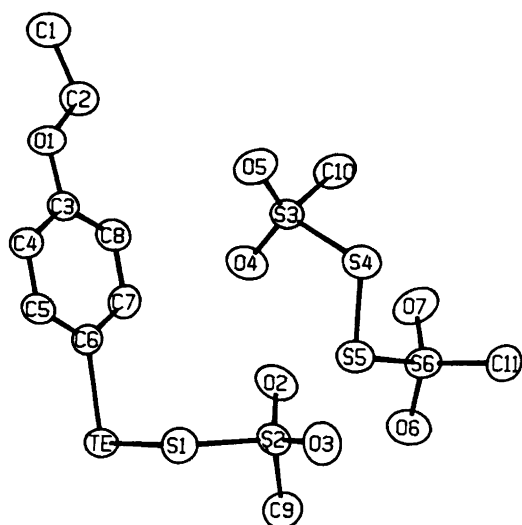
Fig. 1. ORTEP drawing of p-$C_2H_5OPhTeS_2O_2CH_3$ · $(CH_3SO_2S)_2$.

Fig. 2. The unit cell seen in projection along a (c-axis horizontal).

The central S–S bond in the present disulfide is 2.002(1) Å, and is thus significantly shorter than the two terminal bonds, which are 2.115(1) and 2.136(2) Å, respectively (Table 3). The distance between the two dibonded sulfur atoms indicates a π-bond order of ca. 0.48.[13] A comparison of average bond lengths (in Å) and angles (in °) around the Terminal sulfur atoms in $(CH_3SO_2S)_2$,[11] bis(methylsulfon-yldichloromethyl) disulfide[14] and four diarylsulfonyl sulfanes[12] with those from the present study of dimethane-sulfonyl disulfide shows good agreement (Table 5). Truter[15] has discussed the reason for the different bond lengths in oxo-compounds of sulfur, and concludes that many factors contribute to the differences. They include the oxidation state of sulfur, its hybridisation, the electronegativity of all the atoms and the existence of π-bonding. The S–O bond lengths in the present structure (average value 1.427 Å) agree with the average value from the four different dia-rylsulfonyl sulfanes given above. However, these S–O bond lengths are significantly shorter than that observed in the
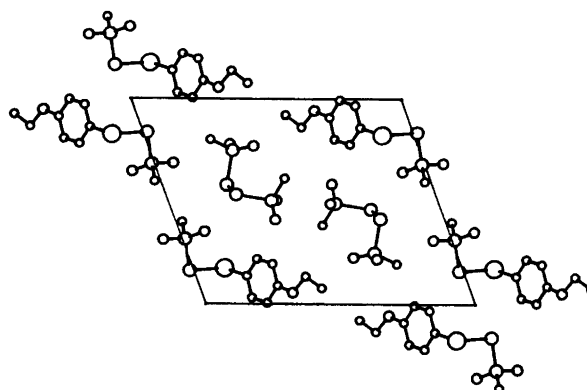
sulfate ion, 1.49 Å,[16] and are also shorter than those found in organic sulfonates. 1.45–1.46 Å,[17] thus indicating some-what more pronounced double-bond character in the for-mer. The large O–S–O angle of 119.7° supports this idea.

Table 4. Bond lengths (Å) and angles (°) in the sulfur skeletons of $(PhSO_2S)_2$,[12] (p-MePhSO_2S)_2$,[12] $(CH_3SO_2S)_2$[11] and the present structure.

Bond angle S–S–S^a	Terminal S–S^a	Central S–S	Ref.
102.32	2.115	2.008(1)	12
103.45	2.121	1.987(1)	12
104.0	2.10(3)	2.06(3)	11
103.32	2.126	2.002(1)	present

^{a}Average value.

Table 5. Comparison of average bond lengths (Å) and angles (°) around the terminal sulfur atoms in $(CH_3SO_2S)_2$,[11] bis(methylsulfonyldichloromethyl) disulfide,[13] four diarylsulfonyl sulfanes[12] and the present structure.

S–O	S–CH$_3$	S–S–O	S–S–C	O–S–O	O–S–C	Ref.
1.48	1.77	103	102	123	112	11
1.424	1.751	–	–	118.7	109.9	13
1.426(1)	1.751(1)	–	–	120.6(1)	109.4	12
1.427	1.748	106.0	106.0	119.7	109.6	present

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