The Crystal and Molecular Structure of Tellurium Di(methylxanthate)

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The structure of tellurium di(methylxanthate), $Te(CH_3OCS_2)_2$ has been determined by three-dimensional X-ray crystallography. The unit cell dimensions are $a = 4.2341(5)$ Å, $b = 14.202(2)$ Å, $c = 17.299(2)$ Å, $\beta = 92.99(2)°$ and $z = 4$. The crystals are monoclinic, space group $C_{2h}^5 - P2_1/c$. Data were collected by means of a Siemens AED-1 diffractometer. The final conventional R-value is 2.96 %.

The structure consists of monomeric molecules in which the central tellurium atoms are coordinated to all four sulfur atoms in a trapezoid planar configuration. The Te−S bond lengths are: Te−S1 = 2.510(1) Å, Te−S2 = 2.841(1) Å, Te−S3 = 2.499(1) Å and Te−S4 = 2.846(1) Å. The corresponding bond angles are: $\angle$ S1−Te−S2 = 66.20(4)°, $\angle$ S1−Te−S3 = 85.18(4)°, $\angle$ S3−Te−S4 = 66.33(4)° and $\angle$ S2−Te−S4 = 142.29(3)°. Weak intermolecular Te···S2 interactions of 3.51 Å tie the molecules into pairs across centres of symmetry.

Previous work on structures of divalent tellurium with bidentate dithio ligands, has shown its preference for a trapezoid planar configuration in complexes with such ligands.[1-4] The same preference has also been demonstrated for divalent selenium [5-8] and in one case such a structure has been found for a divalent sulfur compound.[8]

Two classes of trapezoid planar compounds can be distinguished. Class I consists of essentially monomeric molecules where the central selenium or tellurium atoms are bonded to all four sulfur atoms in the molecule. Class II consists of polymeric networks, where the central atom is strongly bonded to two sulfur atoms in the molecule proper and weakly to two sulfur atoms belonging to different neighbour molecules.

The structure of tellurium di(ethylxanthate)[2] belongs to class I, however, the structures of selenium di(methylxanthate) and its sulfur isomorph both belong to class II.[8] For comparison with the latter two compounds, it was felt worthwhile to undertake the present investigation. Also the high quality of the experimental data obtained here, enabled us to get the most accurate structure determination obtained so far for this type of complex.

EXPERIMENTAL

The preparation of crystals and their space group and unit cell dimensions have been reported earlier.[8] By recrystallization from methanol, deep red crystals are obtained with $a = 4.2341(5)$ Å, $b = 14.202(2)$ Å, $c = 17.299(2)$ Å, $\beta = 92.99(2)°$, $z = 4$ and space group $C_{2h}^5 - P2_1/c$. The observed and calculated densities are 2.18 and 2.19 g/cm^3 respectively.

The crystals are relatively unstable, especially when exposed to X-rays. Small crystals were found to disintegrate in the beam, but crystals with cross sections of 0.1×0.1 mm^2 gave satisfactory intensity data in spite of some decomposition which was evidenced by darkening of crystals during exposure to X-rays.

The intensity measurements were made on a crystal mounted along c, using a Siemens off-line automatic AED-1 diffractometer and Mo$K\alpha$ radiation. Reflections out to $2\theta = 56°$ were collected using the "five value" measurement [9] and the $\theta - 2\theta$ scan technique with scan speed 2.5° per min. with automatic setting of greater speed for strong reflections. An automatic attenuation filter insertion mechanism reduced counting losses. The reflections were scanned between $\theta_1 = \theta - 0.50°$ and $\theta_2 = \theta + 0.50°$ where θ is the Bragg angle for the α_1 peak. Two reference reflections were

measured at intervals of 50 reflections. Out of 2521 reflections measured, 2163 had intensities greater than twice the standard deviations based on counting statistics, only the latter were labelled as observed.

Accurate cell dimensions were determined by least squares methods based on measurements of 20 strong high-order reflections.

The intensities were corrected for Lorentz and polarization effects as well as for absorption ($\mu = 36.7$ cm^{-1}).[10] Crystal dimensions measured as distances from a common origin to crystal faces were: 0.154 mm for $\bar{1}00$, 0.066 mm for $0\bar{1}0$, 0.070 mm for $01\bar{1}$ and $0\bar{1}1$, 0.062 mm for 011 and $0\bar{1}\bar{1}$, and 0.132 mm for 120.

The UV spectrum of tellurium di(methyl-xanthate) in hexane shows the following four absorption bands: I 360 nm, II 297 nm, III 248 nm and IV 212 nm. For comparison, the corresponding disulfide, dimethyldixanthogen gives three absorptions at 361 nm, 278 nm and 240 nm. These latter bands are due to $n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$ and $n \rightarrow \sigma^*$ transitions, respectively, on the ligands.[11]

An IR spectrum was obtained using the KBr disc technique. The following absorption bands have been tentatively assigned: Two strong bands at ν 1220 and 1161 cm^{-1} to stretching vibrations of the $O-C-O$ moiety; a strong band at 1044 cm^{-1} and a weak at 943 cm^{-1} to stretching vibrations in short and long $C-S$ bonds, respectively. The assignments have been done by comparison with the IR spectra of a series of xanthate compounds,[12–14] the corresponding tellurium bis(diethyldithio-carbamate),[15] and the analogous tellurium di(benzylxanthate). The latter compound was from oscillation and Weissenberg films found to be monoclinic with space group $P2_1/c$ and $a = 8.35(5)$ Å, $b = 5.70(2)$ Å, $c = 38.19(4)$ Å, $\beta = 91.8(2)°$ and $Z = 4$.

DETERMINATION AND REFINEMENT OF THE STRUCTURE

The solution of the structure was accomplished by application of a Patterson synthesis which gave the heavy atom position. The positions of the other atoms except hydrogen were then found by successive Fourier syntheses.

The structure was refined by means of a full-matrix least squares program which

Table 1. Atomic coordinates for [Te(CH₃OCS₂)₂]. Standard deviations except for hydrogen in brackets.

	x	y	z
Te	0.33961(6)	0.14848(2)	0.05250(2)
S1	0.3099(3)	0.12768(9)	0.19602(7)
S2	0.0933(3)	−0.02884(8)	0.09587(6)
S3	0.5685(3)	0.30643(9)	0.08587(7)
S4	0.4901(3)	0.25692(9)	−0.07896(7)
O1	0.0798(8)	−0.0241(2)	0.2478(2)
O2	0.7456(8)	0.4131(2)	−0.0207(2)
C1	0.1479(10)	0.0184(3)	0.1819(2)
C2	−0.0698(14)	−0.1155(4)	0.2428(3)
C3	0.6118(10)	0.3310(3)	−0.0102(3)
C4	0.7958(13)	0.4436(4)	−0.0996(3)
H1	−0.130	−0.138	0.301
H2	0.096	−0.167	0.219
H3	−0.283	−0.113	0.205
H4	0.914	0.386	−0.130
H5	0.577	0.462	−0.130
H6	0.959	0.504	−0.097

Table 2. Components of atomic vibration tensors for Te, S, N, O, C ($U \times 10^4$ and H ($U \times 10^3$), in Å² with standard deviations, referred to crystallographic axes. The expression used for the Te, S, N, O, and C atoms is exp $\{-2\pi^2[h^2a^{-2}U_{11} + \cdots + 2hka^{-1}b^{-1}U_{12}\cdots]\}$, while the expression used for hydrogen is exp $[-8\pi^2\bar{U}(\sin^2\theta/\lambda)]$.

	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}		U
Te	490(2)	463(2)	464(2)	7(1)	−25(1)	61(1)	H1	107(24)
S1	904(9)	578(8)	454(6)	128(6)	−115(5)	86(6)	H2	168(31)
S2	777(8)	514(7)	408(5)	−91(6)	−29(5)	28(5)	H3	71(20)
S3	720(8)	508(6)	494(6)	−68(6)	−107(5)	98(5)	H4	58(18)
S4	897(9)	524(7)	482(6)	−123(6)	−44(5)	16(6)	H5	73(20)
C1	495(23)	530(24)	384(20)	69(19)	1(18)	72(17)	H6	84(21)
C2	1064(46)	678(35)	579(31)	−219(32)	147(26)	61(30)		
C3	537(24)	412(23)	536(24)	21(23)	−18(18)	37(19)		
C4	895(38)	617(31)	689(31)	−93(29)	150(26)	149(28)		
O1	975(26)	641(22)	422(16)	−94(18)	41(15)	123(16)		
O2	892(24)	481(18)	650(20)	−134(17)	2(16)	117(17)		

Table 3. Bond lengths (Å) with standard deviations in parentheses. The last column contains RBM corrected bond lengths.

Te — S1	2.510(1)	2.528
Te — S2	2.841(1)	2.849
Te — S3	2.499(1)	2.516
Te — S4	2.846(1)	2.855
C1 — S1	1.709(4)	1.719
C1 — S2	1.638(4)	1.656
C1 — O1	1.335(5)	1.340
C3 — S3	1.717(4)	1.728
C3 — S4	1.650(4)	1.668
C3 — O2	1.314(5)	1.318
C2 — O1	1.445(7)	1.453
C4 — O1	1.458(6)	1.466
C2 — H1	1.092	
C2 — H2	1.103	
C2 — H3	1.088	
C4 — H4	1.103	
C4 — H5	1.070	
C4 — H6	1.105	

Some short intramolecular contacts (Å)

$C_2 - S_2$	2.939(5)	$S_1 - O_1$	2.547(4)
$C_4 - S_4$	2.980(6)	$S_3 - O_2$	2.530(4)
$S_1 - S_2$	2.936(2)		
$S_1 - S_3$	3.390(2)		
$S_3 - S_4$	2.939(2)		

minimizes the quantity $r = \sum w(|F_o| - K|F_c|)^2$. K is a scale factor and w, the weight of a reflection, is the inverse of the variance of F_o. Non-observed reflections with $K|F_c|$ larger than the observable limit are included in the refinement with F_o put equal to the limit.

With anisotropic temperature factors for all atoms, the conventional R factor reached a value of 3.4 %. At this stage of refinement, a difference map revealed the positions of the six hydrogen atoms, and they were included in the refinement with isotropic temperature factors. However, the hydrogen atoms did not refine satisfactorily and their coordinates were fixed at values based on the difference map and a model of the molecule. The final R-value is 2.96 %. A difference map based on the final structure factors revealed no spurious features, the largest peak at 0.6 e/Å³ occurred close to the tellurium atomic position. The observed and calculated structure factors can be obtained from the author Steinar Husebye upon request. Atomic scattering factors were taken from the International Tables [16] and those for tellurium and sulfur were corrected for anomalous dispersion according to Cromer.[17]

Final coordinates and temperature parameters are found in Tables 1 and 2, respectively. Two sets of bond lengths, one uncorrected and the other corrected for rigid-body motion considering the whole molecule as a rigid unit, are found in Table 3. Uncorrected values are used in the discussions throughout this article, because all comparisons are with uncorrected bond lengths. Bond angles are listed in Table 4. Some short intermolecular contacts are listed in Table 5, and some least squares planes through parts of the molecule are shown in Table 6.

Table 4. Bond angles with standard deviations, in degrees.

$\angle$ S1 — Te — S2	66.20(4)	$\angle$ C3 — O2 — C4	118.7(3)
$\angle$ S1 — Te — S3	85.18(4)	$\angle$ S1 — Te — S2'	127.92(4)
$\angle$ S1 — Te — S4	151.51(4)	$\angle$ S2 — Te — S2'	65.14(3)
$\angle$ S2 — Te — S3	151.37(4)	$\angle$ S3 — Te — S2'	141.63(3)
$\angle$ S2 — Te — S4	142.29(3)	$\angle$ S4 — Te — S2'	78.93(3)
$\angle$ S3 — Te — S4	66.33(4)	$\angle$ O1 — C2 — H1	109.58
$\angle$ Te — S1 — C1	90.3(1)	$\angle$ O1 — C2 — H2	109.10
$\angle$ Te — S2 — C1	80.8(2)	$\angle$ O1 — C2 — H3	110.32
$\angle$ Te — S3 — C3	91.1(1)	$\angle$ H1 — C2 — H2	109.10
$\angle$ Te — S4 — C3	81.0(2)	$\angle$ H1 — C2 — H3	109.71
$\angle$ S1 — C1 — S2	122.6(2)	$\angle$ H2 — C2 — H3	109.01
$\angle$ S1 — C1 — O1	113.1(3)	$\angle$ O2 — C4 — H4	108.18
$\angle$ S2 — C1 — O1	124.3(3)	$\angle$ O2 — C4 — H5	111.11
$\angle$ S3 — C3 — S4	121.6(2)	$\angle$ O2 — C4 — H6	108.24
$\angle$ S3 — C3 — O2	112.5(3)	$\angle$ H4 — C4 — H5	110.84
$\angle$ S4 — C3 — O2	125.9(3)	$\angle$ H4 — C4 — H6	107.42
$\angle$ C1 — O1 — C2	118.0(3)	$\angle$ H5 — C4 — H6	110.92

Table 5. Some short intermolecular interatomic distances (Å) with standard deviations in parentheses. The distances are from atoms in the original molecule to atoms in molecules whose transformations are given in the last column.

Te $-$ Te	4.2341(4)	$(x+1,y,z)$
Te $-$ S2	3.513(1)	$(-x,-y,-z)$
Te $-$ S2	3.985(1)	$(1-x,-y,-z)$
Te $-$ S2	4.103(1)	$(x+1,y,z)$
S2 $-$ S2	4.234(2)	$(-x,-y,-z)$
S4 $-$ S2	4.075(2)	$(-x,-y,-z)$

RESULTS AND DISCUSSION

The tellurium di(methylxanthate) molecule is shown in Fig. 1. Except for the hydrogen atoms, the molecule is nearly planar, the maximum deviation of any non-hydrogen atom from the least squares plane based on all atoms in the molecule except hydrogen, is 0.068 Å. Other corresponding deviations are 0.026, 0.009 and 0.016 Å for the least squares planes through ligands 1 (S1, S2), 2 (S3, S4) and the central TeS₄ group, respectively. Tellurium is coordinated to all four sulfur atoms in the molecule, just as in the corresponding ethylxanthate complex. The Te $-$ S bond lengths are: Te $-$ S1 = 2.510(1) Å, Te $-$ S2 = 2.841(1) Å, Te $-$ S3 = 2.499(1) Å and Te $-$ S4 = 2.846(1) Å. Only one of the corresponding bond lengths is significantly different in the less accurately determined tellurium ethylxanthate complex.[ˢ] As in the latter, there is a weak intermolecular Te···S2 bond across a centre of symmetry, being 3.513(1) Å in the present investigation,

Table 6. Least squares planes through parts of the molecule.

a. Atoms defining planes.

　　Plane 1: Te $-$ S1 $-$ S2 $-$ S3 $-$ S4 $-$ C1 $-$ C2 $-$ C3 $-$ C4 $-$ O1 $-$ O2
　　　　　2: S1 $-$ S2 $-$ C1 $-$ C2 $-$ O1
　　　　　3: S3 $-$ S4 $-$ C3 $-$ C4 $-$ O2
　　　　　4: Te $-$ S1 $-$ S2 $-$ S3 $-$ S4

b. In the general equation for a plane, $A_i X + B_i Y + C_i Z - D_i = 0$ where i is the number of the plane, the following constants were calculated:

i	1	2	3	4
A	3.8628	3.8419	3.7997	3.8972
B	-5.7650	-5.8435	-6.2237	-5.5166
C	0.1127	0.6667	0.0715	-0.0660
D	0.4692	0.5855	0.2591	0.5052

c. Interplanar angles in degrees.

1 $-$ 2	1.871	2 $-$ 4	2.834
1 $-$ 3	2.045	3 $-$ 4	3.169
1 $-$ 4	1.245		
2 $-$ 3	2.587		

d. Distances from planes in Å.

Plane No.	Te	S1	S2	S3	S4	C1
1	-0.0074	0.0140	0.0681	-0.0284	-0.0672	0.0173
2	-0.1133	-0.0102	0.0052	-0.1331	-0.2577	-0.0027
3	0.1110	0.1379	0.2815	0.0017	-0.0027	0.2021
4	-0.0041	-0.0146	0.0110	0.0161	-0.0083	-0.0416

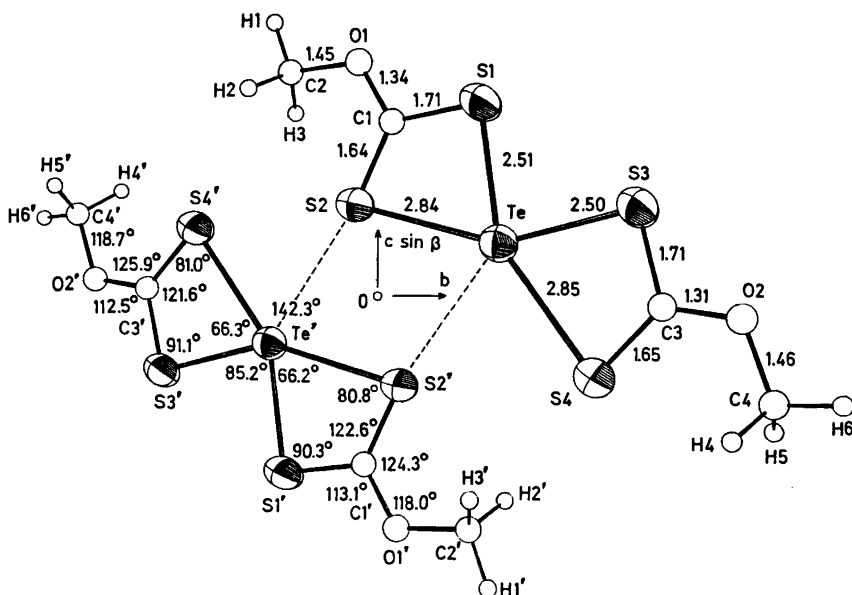| Plane No.	C2	C3	C4	O1	O2
1	-0.0473	-0.0154	0.0444	0.0049	0.0169
2	-0.0185	-0.1760	-0.1783	0.0261	-0.1588
3	0.2102	0.0047	0.0049	0.2109	-0.0086
4	-0.1580	0.0539	0.1640	-0.0788	0.1131

Fig. 1. A pair of molecules related by a center of symmetry as seen along *a*. The heavy atoms are indicated by 50 % probability thermal ellipsoids, and bond lengths (Å) and angles are indicated.

and also here bisecting the wide S2 − Te − S4 angle. However, while this bond in tellurium di(ethylxanthate) was 0.1 Å longer and only 0.65 Å above the TeS$_4$ plane, it is 1.10 Å above that plane in tellurium di(methylxanthate). This tendency to five-coordination is a feature found in all class I complexes of divalent tellurium whose structures are known, *i.e.* tellurium xanthates and dithiocarbamates. This weak association is probably a result of a nucleophilic interaction between non-bonded electron pairs on S2 and the central tellurium atom in a neighbour molecule. Assuming the two lone pairs of electrons on tellurium to be located on both sides of the molecular plane, the interaction is expected to be strongest near the molecular plane in the direction of the large interligand angle S2 − Te − S4 where the screening of the small, positive charge on the tellurium atom has its minimum.

Similar but stronger interactions are observed in several complex salts, for example in some with xenon fluoride cations.[18−19]

The molecules have nearly C_{2v} symmetry, bond lengths and angles in the two halves of the molecule are hardly significantly different. The Te-S bonding in the molecules is of the same type as in the corresponding ethyl-xanthate [2] and in dialkyldithiocarbamates of divalent selenium and tellurium,[4,6,7] probably being of the three-center four-electron type.[23,24] As in those compounds the two three-center systems S1 − Te − S4 and S3 − Te − S2 are not linear, the deviations from linearity are in both cases close to 28.5°. Their average total length is 5.35 Å, in excellent agreement with corresponding values found in the analogous tellurium(II) compounds above,[2,4] and in linear three-center systems in *trans* square planar complexes of divalent tellurium with monodentate thio ligands.[24]

A Mössbauer spectral investigation of tellurium di(methylxanthate) is in progress in order to see if tellurium *s* electrons participate in the bonding.[20] Contribution of orbitals other than two of the 5*p*'s on tellurium in such non-linear three-center systems has earlier been assumed to explain the deviation from linearity.[21−23] In other divalent tellurium compounds with bidentate dithio ligands (diethyl-dithiocarbamate and dimethyldithiophosphate), a small *s*-contribution is indicated from Mössbauer spectra.[20]
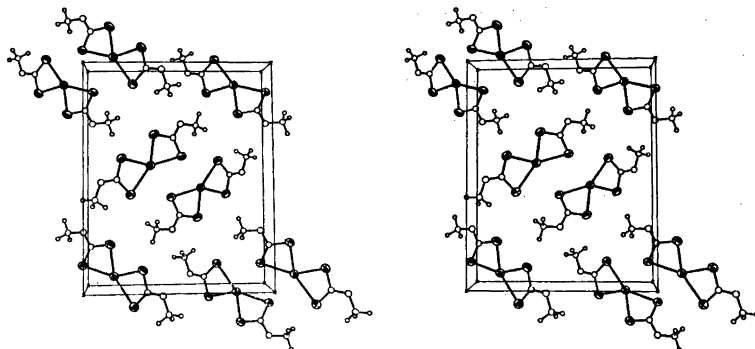
The asymmetry in the Te − S bonds is

Fig. 2. A stereoscopic view of the structure of Te(CH$_3$OCS$_2$)$_2$ showing the unit cell packing. The *b*-axis is horizontal, the *c*-axis is vertical (pointing up along the paper) and the *a*-axis points up from the paper.

reflected in the S – C bonds; a short Te – S bond results in a long S – C bond, and *vice versa*, thus preserving the bond order on the sulfur atoms. In each ligand there is a short and a long C – S bond, the bond lengths being: C1 – S1 = 1.709(4) Å, C1 – S2 = 1.638(4) Å, C3 – S3 = 1.717(4) Å and C3 – S4 = 1.650(4) Å. Compared to a C – S single bond of 1.81 Å, they all have some double bond character as found in most xanthate complexes, and more so than in the corresponding dialkyl-dithiocarbamates,[23] indicating that the resonance form

$$\searrow \overset{+}{O} = C \underset{\underline{S}}{\overset{\overline{S}}{\diagdown}} Te \overset{2+}{\diagup}$$

is of less importance than the resonance form

$$\underset{}{\overset{+}{>N}} = C \underset{\underline{S}}{\overset{\overline{S}}{\diagdown}} Te \overset{2+}{\diagup}.$$

That this is the case has earlier been shown by spectral work.[25] This may explain why the corresponding selenium di-(methylxanthate) complex has a structure quite different from its tellurium analogue.[5] The former has a class II structure while the structure of the latter belongs to class I. In four-coordinate, planar complexes, divalent tellurium is a better acceptor than divalent selenium. When the donor capacity of the ligands decrease (xanthate less effective than dithiocarbamate as indicated by resonance above), there is a switch from the intramolecular, stronger four-coordination (class I) found in selenium dithiocarbamates, to partly intermolecular, weak four-coordination (class II) found in selenium di(methylxanthate). The stronger acceptor capacity of tellurium delays this

switch from class I to II for tellurium complexes so that it occurs between the xanthate and dithiophosphate complexes.[8]

The asymmetry in C – S bond strength is also reflected in the S – C – O angles, in agreement with the VSEPR [26] theory which postulates that electrons in a double bond have greater repulsion effect than electrons in a single bond. Also the C(sp^2) – O bonds show appreciable double bond character, as is usual for xanthates,[11] C1 – O1 and C3 – O2 being 1.340(5) and 1.318(5) Å, respectively. Other bond lengths and angles have normal values.

The packing of the molecules is indicated on Fig. 2. There are several short intermolecular contacts in addition to Te···S2 between the centrosymmetrically related pairs of molecules; these are shown in Table 4. As the *a*-axis is only 4.2341(5) Å, the Te···Te intermolecular non-bonded contacts in the *x* direction will have the same value. This indicates that the Pauling – van der Waals radius for tellurium, 2.20 Å, [27] is too large.

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