

## The Crystal and Molecular Structure of Tellurium Di(ethylxanthate)

STEINAR HUSEBYE

*Chemical Institute, University of Bergen, Bergen, Norway*

The crystal structure of tellurium di(ethylxanthate) has been determined, and refined by three-dimensional X-ray methods. The molecules are nearly planar. Each tellurium atom is bonded to all four sulphur atoms of the molecule, in a distorted square-planar configuration. There are two short and two long Te-S bonds, the bond lengths being: Te-S<sub>1</sub> = 2.49 Å, Te-S<sub>2</sub> = 2.90 Å, Te-S<sub>3</sub> = 2.48 Å and Te-S<sub>4</sub> = 2.86 Å. The corresponding angles are: ∠S<sub>1</sub>-Te-S<sub>2</sub> = 65.5°, ∠S<sub>1</sub>-Te-S<sub>3</sub> = 83.6°, ∠S<sub>3</sub>-Te-S<sub>4</sub> = 66.4° and ∠S<sub>4</sub>-Te-S<sub>2</sub> = 144.5°.

Pairs of molecules are joined across centres of symmetry by two intermolecular Te...S<sub>2</sub> contacts of 3.61 Å.

The structure analysis reported here is part of a study of compounds of divalent tellurium and selenium with dithio and related anions,<sup>1-4</sup> with the main objective of determining the configuration around the tellurium and selenium atoms. The tendency of divalent tellurium to form square-planar complexes involving monodentate sulphur-containing ligands,<sup>5</sup> made it reasonable to inquire whether bidentate dithio anions would form complexes with similar structures. The first structure determined, namely that of tellurium bis(dimethyldithiophosphate),<sup>3</sup> revealed a distorted square-planar configuration around the central tellurium atom.

### CRYSTAL DATA

The preparation of tellurium di(ethylxanthate) was first reported by Foss<sup>6</sup> who also determined the unit cell parameters and the space group.<sup>7</sup> The crystals are monoclinic with  $a = 9.35 \pm 0.03$  Å,  $b = 6.17 \pm 0.02$  Å,  $c = 21.21 \pm 0.03$  Å,  $\beta = 91^\circ$  and  $Z = 4$ . The space group is  $C_{2h}^5 - P2_1/c$ . Crystals were prepared according to the procedure used for divalent tellurium bis(dialkyl-dithiophosphates) and bis(dialkyldithiophosphinates).<sup>1</sup> An aqueous solution of potassium ethylxanthate was added to tellurium dioxide dissolved in hydrochloric acid, in the molar ratio 4:1. The resulting orange-red precipitate was

dissolved in hot alcohol, and deep orange-red needles of tellurium di(ethylxanthate) crystallized out upon cooling. They were recrystallized once from alcohol.

For the structure analysis, intensities of the  $0kl$ ,  $h0l$ , and  $h1l$  reflections were estimated visually from zero-layer and equi-inclination Weissenberg photographs.  $\text{CuK}\alpha$ -radiation was used for all layers. The crystals used for the  $a$  and  $b$  axis photographs had cross-sections of  $0.05 \times 0.04 \text{ mm}^2$  and  $0.05 \times 0.03 \text{ mm}^2$ , respectively. 655 out of 876 accessible reflections with  $\sin \theta \leq 0.985$  were observed and measured. The data were corrected for Lorentz and polarization factors, but no absorption correction was applied.

The least squares refinements were carried out on an IBM 1620<sup>II</sup> computer. The program used was prepared by Mair.<sup>8</sup> Weighting scheme No. 3 in this program was used throughout the refinements.

### STRUCTURE ANALYSIS

Patterson projections along the  $a$  and  $b$  axes yielded the coordinates of the tellurium atom. Fourier analyses, with signs based on the tellurium contributions alone, were then carried out in the two projections. The resulting electron density maps together with the Patterson projections and a model of the ethylxanthate anion,<sup>9</sup> gave the positions of the four sulphur atoms in the molecule. Subsequent Fourier refinement gave the positions of all atoms, and a common temperature factor was then assigned.

The structure factors from the three layers were then brought to the same scale by comparison of reflections common to two layers. The  $00l$  reflections occurring in the  $0kl$  and  $h0l$  layers were removed from the  $0kl$  data, and the  $01l$  reflections occurring in the  $0kl$  and  $h1l$  layers were removed from the  $h1l$  data. The crystal structure was then further refined by means of successive least squares analyses based on the remaining observed reflections.

After a few cycles of refinement, anisotropic temperature factors were assigned to the tellurium atom and the four sulphur atoms. The two reflections 100 and 200 with  $\sin \theta < 0.1$  had to be removed from the data after the first cycle, as the monitored program did not calculate structure factors for reflections with so low values of  $\sin \theta$ . After the fifth refinement cycle, the three layers were rescaled in relation to each other by comparison between the observed and calculated structure factors.

After the eleventh cycle, the coordinates of  $\text{C}_2$  and  $\text{C}_3$  were adjusted to give  $\text{O}_1-\text{C}_2$  and  $\text{C}_2-\text{C}_3$  bond lengths more in agreement with the sum of the covalent radii of the respective atoms.

After the thirteenth and final least squares refinement, the reliability index  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$  had converged to 0.095. A final structure factor calculation based on the parameter output from the last refinement, was then carried out for all reflections with  $\sin \theta \leq 0.985$ . The  $R$ -value for this material, with non-observed reflections included only when  $F_c$  exceeds the observable limit, is 0.098.

The final observed and calculated structure factors are listed in Table 1. The calculated values are based on atomic scattering factors for tellurium by





H	K	L	F0	FC	H	K	L	F0	FC	H	K	L	F0	FC	H	K	L	F0	FC	
-2	1	24	< 56	19	-4	1	19	118	-107	-6	1	16	< 65	-45	-8	1	18	< 52	10	
-2	1	25	< 52	-44	-4	1	20	< 63	-29	-6	1	17	< 63	-31	-8	1	19	71	-67	
-2	1	26	69	-100	-4	1	21	187	-237	-6	1	18	204	-247	-8	1	20	124	-150	
-3	1	1	64	46	-4	1	22	130	150	-6	1	19	59	87	-9	1	1	74	-98	
-3	1	2	343	315	-4	1	23	< 55	17	-6	1	20	107	-135	-9	1	2	< 66	27	
-3	1	3	271	244	-4	1	24	180	218	-6	1	21	< 54	33	-9	1	3	< 65	79	
-3	1	4	371	-320	-4	1	25	< 42	-15	-6	1	22	< 41	20	-9	1	4	< 246	254	
-3	1	5	355	-285	-5	1	1	154	127	-7	1	1	< 63	-17	-9	1	5	65	79	
-3	1	6	971	-979	-5	1	2	422	438	-7	1	2	327	311	-9	1	6	137	139	
-3	1	7	391	-316	-5	1	3	57	-59	-7	1	3	< 63	-14	-9	1	7	64	78	
-3	1	8	83	-67	-5	1	4	73	-74	-7	1	4	421	415	-9	1	8	63	-63	
-3	1	9	141	-119	-5	1	5	53	-32	-7	1	5	211	-201	-9	1	9	< 61	39	
-3	1	10	708	650	-5	1	6	520	-520	-7	1	6	211	-201	-9	1	10	< 223	-245	
-3	1	11	286	-218	-5	1	7	182	131	-7	1	6	< 65	-50	-9	1	11	< 59	45	
-3	1	12	494	446	-5	1	8	315	-288	-7	1	7	< 65	75	-9	1	12	124	< 110	
-3	1	13	59	-15	-5	1	9	< 59	-34	-7	1	8	289	-281	-9	1	13	< 57	27	
-3	1	14	62	34	-5	1	10	155	142	-7	1	9	< 67	30	-9	1	14	130	145	
-3	1	15	64	-34	-5	1	11	176	128	-7	1	10	239	-227	-9	1	15	93	-49	
-3	1	16	554	-554	-5	1	12	463	426	-7	1	11	95	-89	-9	1	16	129	164	
-3	1	17	67	57	-5	1	13	326	309	-7	1	12	< 67	15	-9	1	17	69	95	
-3	1	18	317	-313	-5	1	14	287	260	-7	1	13	87	-64	-9	1	18	47	97	
-3	1	19	75	-71	-4	1	15	67	-44	-7	1	14	264	-278	-10	1	1	60	-30	
-3	1	20	163	138	-4	1	16	196	-183	-7	1	15	84	-75	-10	1	2	59	38	
-3	1	21	62	-59	-4	1	17	66	11	-7	1	16	96	-97	-10	1	3	59	-46	
-3	1	22	154	170	-4	1	18	228	-255	-7	1	17	59	-55	-10	1	4	83	87	
-3	1	23	76	75	-4	1	19	62	-56	-7	1	18	137	-155	-10	1	5	59	-33	
-3	1	24	94	113	-4	1	20	50	-67	-7	1	19	< 55	34	-10	1	6	110	125	
-3	1	25	48	23	-4	1	21	119	-161	-7	1	20	141	-180	-10	1	7	68	49	
-3	1	26	69	92	-4	1	22	114	132	-7	1	21	< 46	31	-10	1	8	66	46	
-4	1	1	202	189	-4	1	23	< 51	31	-8	1	1	67	-45	-10	1	9	54	-45	
-4	1	2	351	341	-4	1	24	159	237	-8	1	2	174	166	-10	1	10	145	-176	
-4	1	3	323	275	-6	1	1	< 57	-49	-8	1	3	153	92	-10	1	11	53	-63	
-4	1	4	254	-222	-6	1	2	339	369	-8	1	4	352	344	-10	1	12	121	-155	
-4	1	5	158	124	-6	1	3	147	-87	-8	1	5	67	85	-10	1	13	47	24	
-4	1	6	644	-625	-6	1	4	269	237	-8	1	6	89	87	-10	1	14	< 42	34	
-4	1	7	< 50	-35	-6	1	5	233	-221	-8	1	7	< 67	36	-11	1	1	54	54	
-4	1	8	159	-118	-6	1	6	331	316	-8	1	8	142	-130	-11	1	2	< 54	-40	
-4	1	9	305	257	-6	1	7	149	135	-8	1	9	< 66	47	-11	1	3	53	-36	
-4	1	10	336	292	-6	1	8	411	-436	-8	1	10	232	-235	-11	1	4	53	41	
-4	1	11	58	34	-6	1	9	90	-64	-8	1	11	< 65	39	-11	1	5	52	-39	
-4	1	12	574	544	-6	1	10	97	-79	-8	1	12	71	-66	-11	1	6	88	103	
-4	1	13	117	91	-6	1	11	147	-125	-8	1	13	76	-69	-11	1	7	48	29	
-4	1	14	309	280	-6	1	12	233	210	-8	1	14	197	-222	-11	1	8	52	65	
-4	1	15	114	-97	-6	1	13	239	238	-8	1	15	< 58	55	-11	1	9	43	-32	
-4	1	16	371	-360	-6	1	14	273	277	-8	1	16	150	171	-11	1	10	53	-82	
-4	1	17	67	51	-6	1	15	< 66	16	-8	1	17	< 55	18						
-4	1	18	320	-332																

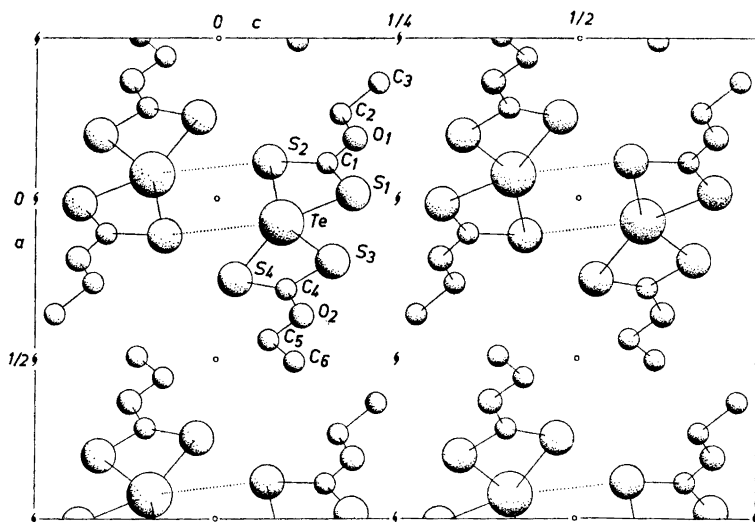


Fig. 1. The molecular arrangement of tellurium di(ethylxanthate) seen along the  $b$  axis. The positive direction of the  $b$  axis points downwards into the page.

Thomas and Umeda,<sup>10</sup> for sulphur by Dawson,<sup>11</sup> and for oxygen and carbon by Hoerni and Ibers.<sup>12</sup> Atomic coordinates and temperature factors from the last refinement cycle are listed in Tables 2 and 3, respectively. Interatomic distances and angles based on the coordinates from Table 2, are listed in Tables 4 and 5.

#### THE PACKING IN THE CRYSTALS AND THE CONFIGURATION AROUND THE CENTRAL TELLURIUM ATOM

The crystals consist of tellurium di(ethylxanthate) molecules, with the tellurium atoms in general, fourfold positions. The molecules are interrelated through centers of symmetry, glide planes and twofold screw axes. Fig. 1 shows the molecular arrangement seen in the projection along the *b* axis. The dotted lines indicate weak intermolecular Te...S<sub>2</sub> bonds which link molecules, related by certain symmetry centers, together in pairs. Such a pair of molecules is shown in Fig. 2, in the projection along the *b* axis. The figure represent the original molecule (Table 2) and the one related to it by the symmetry centre in (0,  $\frac{1}{2}$ , 0).

Table 2. Atomic coordinates for tellurium di(ethylxanthate) in fractions of cell edges. Origin at a centre of symmetry.

	<i>x</i>	<i>y</i>	<i>z</i>
Te	0.0738	0.2377	0.0896
S <sub>1</sub>	-0.0161	0.3940	0.1894
S <sub>2</sub>	-0.1148	0.6065	0.0729
S <sub>3</sub>	0.1979	-0.0209	0.1614
S <sub>4</sub>	0.2512	-0.0660	0.0259
O <sub>1</sub>	-0.1863	0.7037	0.1905
O <sub>2</sub>	0.3658	-0.3081	0.1184
C <sub>1</sub>	-0.1109	0.5862	0.1523
C <sub>2</sub>	-0.2640	0.8980	0.1700
C <sub>3</sub>	-0.3610	0.9780	0.2235
C <sub>4</sub>	0.2819	0.1559	0.0969
C <sub>5</sub>	0.4412	-0.4349	0.0724
C <sub>6</sub>	0.5075	-0.6270	0.1090

The xanthate anions are functioning as bidentate ligands, and the central tellurium atom is bonded to all four sulphur atoms in the molecule. The TeS<sub>4</sub> group is approximately planar. The least squares plane through the five atoms, with tellurium given double weight, is given by the equation: 0.7805*X* + 0.6203*Y* + 0.0763*Z* - 1.5921 = 0, all five atoms lie within 0.05 Å from this plane. The projection of the TeS<sub>4</sub> group in this plane is shown in Fig. 3.

The *cis* S—Te—S angles vary from 65.5 to 144.5°. Also the Te—S bond lengths are quite different, two being about 2.5 Å and the other two being about 2.9 Å. Thus the TeS<sub>4</sub> group represents a rather distorted, square-planar arrangement. The intermolecular, weak Te...S<sub>2</sub> bond, however, points in the middle of the large S—Te—S angle of 144.5°. This fifth sulphur atom is only

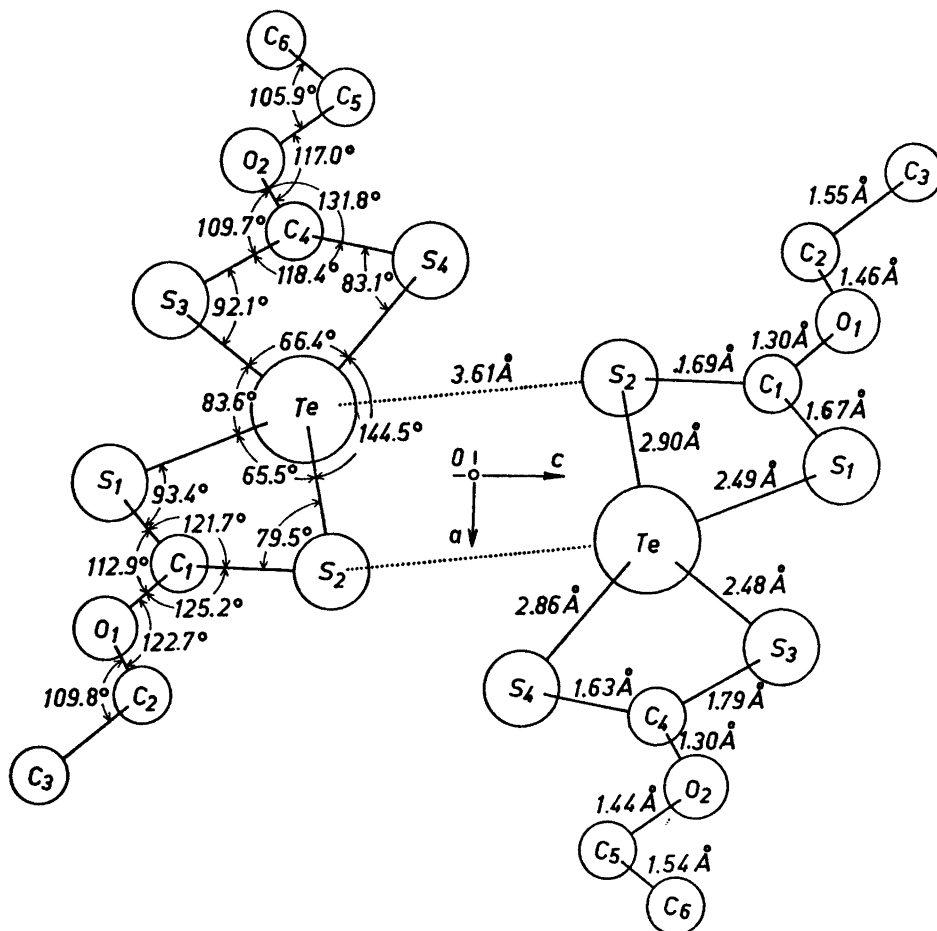


Fig. 2. A pair of tellurium di(ethylxanthate) molecules and the configuration around the tellurium atom seen in the projection along the  $b$  axis.

0.65 Å away from the plane mentioned above, and thus there is in tellurium di(ethylxanthate) a slight tendency toward planar five-coordination around tellurium, the *cis* S—Te—S angles in this case being between 65.5 and 83.6°.

Table 3. Final temperature parameters  $\beta_{ij} \times 10^3$ . The expression used is  $\exp(-h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + kl\beta_{23} + hl\beta_{13} + hk\beta_{12})$ .

	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{23}$	$\beta_{13}$	$\beta_{12}$
Te	11.75	22.95	1.59	0.19	2.40	1.16
S <sub>1</sub>	15.09	27.76	1.40	0.61	2.35	12.46
S <sub>2</sub>	17.55	30.44	1.43	1.29	1.54	19.43
S <sub>3</sub>	13.63	24.29	1.41	-0.17	2.94	5.93
S <sub>4</sub>	16.22	34.05	1.37	-0.45	2.75	18.03

Final temperature parameters  $B$  for the light atoms. The expression used is  $\exp -B (\sin^2 \theta / \lambda^2)$ .

	O <sub>1</sub>	O <sub>2</sub>	C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	C <sub>4</sub>	C <sub>5</sub>	C <sub>6</sub>
$B$	4.27	3.99	4.15	3.92	4.32	4.09	3.60	4.31

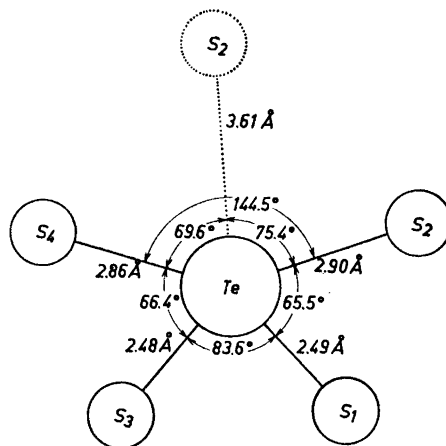


Fig. 3. The projection of the  $\text{TeS}_4$  group in a molecule seen along the normal to the least squares plane through that group. The intermolecular weak  $\text{Te}\cdots\text{S}_2$  bond, is indicated by a dotted line.

There are short intermolecular  $\text{S}_2\cdots\text{S}_4$  and  $\text{S}_2\cdots\text{S}_3$  contacts of 3.74 and 3.75 Å, respectively, between the molecules in Fig. 2. This is close to the van der Waals contact of 3.70 Å. An even shorter  $\text{S}\cdots\text{S}$  contact is found across a screw axis, the  $\text{S}_1\cdots\text{S}_3$  contact being only 3.66 Å. A short  $\text{Te}\cdots\text{S}_4$  contact of 4.01 Å occurs across the centre of symmetry in (0, 0, 0). Other non-bonded distances are listed in Table 5.

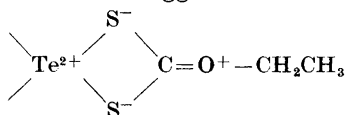
Table 4. Bond lengths and angles in tellurium di(ethylxanthate).

$\text{Te}-\text{S}_1$	$2.486 \pm 0.011 \text{ \AA}$	$\angle \text{S}_1-\text{Te}-\text{S}_2$	$65.5 \pm 0.4^\circ$
$\text{Te}-\text{S}_2$	$2.897 \pm 0.017$	$\angle \text{S}_1-\text{Te}-\text{S}_3$	$83.6 \pm 0.4$
$\text{Te}-\text{S}_3$	$2.480 \pm 0.013$	$\angle \text{S}_1-\text{Te}-\text{S}_4$	$66.4 \pm 0.4$
$\text{Te}-\text{S}_4$	$2.857 \pm 0.014$	$\angle \text{S}_2-\text{Te}-\text{S}_3$	$75.4 \pm 0.3$
$\text{S}_1-\text{C}_1$	$1.67 \pm 0.05$	$\angle \text{S}_2-\text{Te}-\text{S}_4$	$144.5 \pm 0.3$
$\text{S}_2-\text{C}_1$	$1.69 \pm 0.03$	$\angle \text{S}_3-\text{Te}-\text{S}_4$	$69.6 \pm 0.3$
$\text{S}_3-\text{C}_1$	$1.79 \pm 0.04$	$\angle \text{Te}-\text{S}_1-\text{C}_1$	$93.4 \pm 1.3$
$\text{S}_4-\text{C}_1$	$1.63 \pm 0.04$	$\angle \text{Te}-\text{S}_2-\text{C}_1$	$79.5 \pm 1.9$
$\text{C}_1-\text{O}_1$	$1.30 \pm 0.05$	$\angle \text{Te}-\text{S}_3-\text{C}_1$	$92.1 \pm 1.6$
$\text{O}_1-\text{C}_2$	$1.46 \pm 0.07$	$\angle \text{Te}-\text{S}_4-\text{C}_1$	$83.1 \pm 1.9$
$\text{C}_2-\text{C}_3$	$1.55 \pm 0.05$	$\angle \text{S}_1-\text{C}_1-\text{S}_2$	$121.7 \pm 3.0$
$\text{C}_4-\text{O}_2$	$1.30 \pm 0.06$	$\angle \text{S}_2-\text{C}_1-\text{S}_3$	$118.4 \pm 3.3$
$\text{O}_2-\text{C}_5$	$1.44 \pm 0.05$	$\angle \text{S}_1-\text{C}_1-\text{O}_1$	$112.9 \pm 2.6$
$\text{C}_5-\text{C}_6$	$1.54 \pm 0.08$	$\angle \text{S}_2-\text{C}_1-\text{O}_1$	$125.2 \pm 3.7$
		$\angle \text{C}_1-\text{O}_1-\text{C}_2$	$122.7 \pm 2.9$
		$\angle \text{O}_1-\text{C}_2-\text{C}_3$	$109.8 \pm 3.4$
		$\angle \text{S}_3-\text{C}_1-\text{O}_2$	$109.7 \pm 2.4$
		$\angle \text{S}_4-\text{C}_1-\text{O}_2$	$131.8 \pm 3.2$
		$\angle \text{C}_4-\text{O}_2-\text{C}_5$	$117.0 \pm 2.8$
		$\angle \text{O}_2-\text{C}_5-\text{C}_6$	$105.9 \pm 2.8$



## THE STRUCTURE OF TELLURIUM DI(ETHYLXANTHATE)

Not only the  $\text{TeS}_4$  group, but also the whole tellurium di(ethylxanthate) molecule is nearly planar (except for the hydrogen atoms). The least squares plane through all atoms in the molecule (Table 2) except the two methyl carbon atoms, with the tellurium atom given double weight, is closer than 0.1 Å to all atoms, except  $\text{C}_3$  which is 0.16 Å away from it. The plane makes an angle of  $2.0^\circ$  with the  $\text{TeS}_4$  plane mentioned above. This planarity is consistent with the planarity of the xanthate ion and suggests that the canonical form



contributes to the overall structure.<sup>9</sup> The  $\text{>C}-\text{O}$  bond lengths would accordingly be expected to be shorter than a  $\text{C}-\text{O}$  single bond length of 1.43 Å, and likewise a tendency to planar  $sp^2$ -hybridization should occur for  $\text{O}_1$  and  $\text{O}_2$  with  $\text{C}-\text{O}-\text{C}$  angles near  $120^\circ$ . The found  $\text{>C}-\text{O}$  bond lengths of 1.30 Å and  $\text{C}-\text{O}-\text{C}$  angles on  $\text{O}_1$  and  $\text{O}_2$  of  $122.7$  and  $117.0^\circ$ , respectively, (Table 4), are in agreement with the above.

Table 5. Interatomic distances and angles.

Intramolecular distances		Intermolecular distances	
$\text{Te}-\text{C}_1$	3.07 Å	$\text{Te}(\text{I})-\text{S}_2(\text{III})$	$3.605 \pm 0.015$ Å
$\text{Te}-\text{O}_1$	4.35	$\text{Te}(\text{I})-\text{Te}(\text{II})$	4.98
$\text{Te}-\text{C}_4$	3.11	$\text{Te}(\text{I})-\text{Te}(\text{III})$	5.16
$\text{Te}-\text{O}_2$	4.37	$\text{S}_2(\text{I})-\text{S}_4(\text{II})$	4.13
$\text{S}_1-\text{S}_2$	3.31	$\text{S}_2(\text{I})-\text{S}_4(\text{III})$	3.74
$\text{S}_1-\text{S}_2$	2.93	$\text{S}_2(\text{I})-\text{S}_2(\text{III})$	3.75
$\text{S}_3-\text{S}_4$	2.94	$\text{Te}(\text{I})-\text{S}_1(\text{II})$	4.01
$\text{S}_3-\text{S}_4$	5.48	$\text{S}_1(\text{I})-\text{S}_3(\text{IV})$	3.66
$\text{S}_1-\text{O}_1$	2.49		
$\text{S}_3-\text{O}_2$	2.55		
$\text{S}_3-\text{C}_2$	3.04		
$\text{S}_4-\text{C}_5$	3.09		
Intermolecular angles			
$\angle \text{S}_4(\text{I})-\text{Te}(\text{I})-\text{S}_2(\text{III})$		$69.6 \pm 0.4^\circ$	
$\angle \text{S}_2(\text{I})-\text{Te}(\text{I})-\text{S}_2(\text{III})$		$75.4 \pm 0.3$	
$\angle \text{Te}(\text{I})-\text{S}_2(\text{III})-\text{Te}(\text{III})$		$104.6 \pm 0.3$	

The numbers II, III, and IV denote molecules derived from that in Table 2 (I) by centers of symmetry in  $(0, 0, 0)$  and in  $(0, \frac{1}{2}, 0)$ , and by the screw axis  $(0, y, \frac{1}{4})$ , respectively.

The  $\text{Te}-\text{S}_2$  and  $\text{Te}-\text{S}_4$  bonds form an angle of  $144.5^\circ$ , whereas  $\angle \text{S}_1-\text{Te}-\text{S}_3 = 83.6^\circ$ ,  $\angle \text{S}_1-\text{Te}-\text{S}_2 = 65.5^\circ$ , and  $\angle \text{S}_3-\text{Te}-\text{S}_4 = 66.4^\circ$ . The reason for this arrangement is probably the intermolecular  $\text{Te}\cdots\text{S}_2$  bond mentioned above, which bisects the large  $\text{S}_2-\text{Te}-\text{S}_4$  angle. The  $\text{S}_4-\text{Te}\cdots\text{S}_2$  and  $\text{S}_2-\text{Te}\cdots\text{S}_2$  angles are  $69.6$  and  $75.4^\circ$ , respectively, thus on inclusion of this fifth sulphur atom in the  $\text{Te}-\text{S}$  bonding scheme, the  $\text{S}-\text{Te}-\text{S}$  angular arrangement becomes more symmetrical.

In the molecule, the Te—S<sub>1</sub> to Te—S<sub>4</sub> bond lengths are 2.49, 2.90, 2.48, and 2.86 Å, respectively. Thus there are two significantly different pairs of Te—S bonds. The short ones are within the limit of error of the same length as the Te—S bond lengths of 2.47, 2.48, 2.50, and 2.50 Å found in the thiourea complexes *cis*-Te(tu)<sub>2</sub>Br<sub>2</sub>,<sup>13</sup> *cis*-Te(tu)<sub>2</sub>Cl<sub>2</sub>,<sup>13</sup> C<sub>6</sub>H<sub>5</sub>Te(tu)Br<sup>14</sup> and C<sub>6</sub>H<sub>5</sub>Te(tu)Cl,<sup>14</sup> respectively.

The long and short Te—S bonds in the molecule are roughly *trans* to each other, the S<sub>1</sub>—Te—S<sub>4</sub> angle being 149.8° and the S<sub>3</sub>—Te—S<sub>2</sub> angle 149.0°. The bond length sums Te—S<sub>1</sub> + Te—S<sub>4</sub> and Te—S<sub>3</sub> + Te—S<sub>2</sub> are 5.34 and 5.38 Å, respectively. These lengths are close to the average length of 5.36 Å found for linear S—Te—S systems in centrosymmetrical square-planar *trans* tellurium complexes.<sup>5</sup> The deviation from linearity of about 30° in the present case and the great asymmetry in the two Te—S bonds comprising an S—Te—S system, would be expected to cause a significant deviation from the overall length of 5.36 Å.<sup>3,5,13,14</sup> If these three-atom systems are bonded mainly through linear overlap of *p*-orbitals on the tellurium and sulphur atoms,<sup>3,5</sup> one would expect two linear S—Te—S systems at right angles to each other. As the S—Te—S angles in this case are quite different from 90 and 180°, one would expect reduced overlap and a lengthening of the three-atom systems. As the systems retain their "normal" length, other orbitals than the *p*-orbitals in this case probably contribute to the S—Te—S bonding scheme.

The found C<sub>1</sub>—S<sub>1</sub> and C<sub>1</sub>—S<sub>2</sub> bond lengths are 1.67 and 1.69 Å, respectively, while the found C<sub>4</sub>—S<sub>3</sub> and C<sub>4</sub>—S<sub>4</sub> bond lengths are 1.79 and 1.63 Å. In Table 6, bond lengths involving the ethylxanthate *sp*<sup>2</sup> carbon in some xanthates are

Table 6. Bond lengths in Å in the —O—CS<sub>2</sub> group in some ethylxanthate compounds.

Compound	C—S <sub>1</sub>	C—S <sub>2</sub>	C—O
Te[EtOCS <sub>2</sub> ] <sub>2</sub>	1.67 ± 0.05	1.69 ± 0.03	1.30 ± 0.05
As[EtOCS <sub>2</sub> ] <sub>3</sub> <sup>15</sup>	1.79 ± 0.04	1.63 ± 0.04	1.30 ± 0.05
Sb[EtOCS <sub>2</sub> ] <sub>3</sub> <sup>16</sup>	1.66 ± 0.04	1.65 ± 0.04	1.31 ± 0.04
KEtOCS <sub>2</sub> <sup>9</sup>	1.70 ± 0.02	1.59 ± 0.02	1.36 ± 0.03
	1.69	1.67	1.35
	1.72	1.66	1.34
Ni[EtOCS <sub>2</sub> ] <sub>2</sub> <sup>17</sup>	1.73	1.65	1.38

listed for comparison, together with the corresponding values from the present work. The values found for the C—S bond lengths in Table 6, vary from 1.79 to 1.59 Å, as compared to 1.81 and 1.61 Å on the basis of the Pauling<sup>18</sup> carbon and sulphur single and double bond radii, respectively. Thus there obviously is some double bond character in nearly all the C—S bonds listed in Table 6. In tellurium di(ethylxanthate) the pair of C—S bonds in one of the xanthate ligands is different from the corresponding pair in the other. In antimony tri(ethylxanthate),<sup>16</sup> the C—S bond lengths are 1.59 and 1.70 Å for S—Sb bond lengths of 3.00 and 2.52 Å. In the present work, the corresponding lengths are 1.63 and 1.79 Å for the C<sub>4</sub>—S<sub>4</sub> and C<sub>4</sub>—S<sub>3</sub> bonds and 2.86 and 2.48 Å for the S<sub>4</sub>—Te and S<sub>3</sub>—Te bonds. This type of alternating bond lengths is also found in the P—S and S—Te bond lengths of tellurium bis(dimethyldithio-

phosphate).<sup>3</sup> In the other ligand of tellurium di(ethylxanthate), the  $C_1-S_2$  and  $C_1-S_1$  bond lengths are equal within the limit of error, namely 1.69 and 1.67 Å, respectively. But here the  $S_2$  atom is weakly bonded to the tellurium atom of a neighbouring molecule. This probably reduces the  $p\pi$  overlap in the  $S_2-C_1$  bond and causes a lengthening of this bond. The double bond character of the  $C_1-S_1$  bond is then increased at the expense of the  $S_2-C_1$  bond, and the  $C_1-S_1$  bond is consequently shortened. Another effect of the intermolecular  $S_2 \cdots Te$  bonding is the lengthening of the  $S_2-Te$  bond, although the difference of 0.04 Å between the length of this bond and the corresponding  $S_4-Te$  bond may not be significant.

The bond angles around  $C_1$ ,  $C_4$ ,  $O_1$ , and  $O_2$  are consistent with  $sp^2$  hybridization of these atoms. The bond lengths in the ethoxy groups are, within the error limit, equal to the respective single bond lengths.

#### CONCLUSION

Tellurium di(ethylxanthate) can be considered a four-coordinate, planar complex of divalent tellurium. The two xanthate anions function as bidentate ligands, with all four sulphur atoms bonded to the tellurium atom in an irregular, oblique arrangement. The whole molecule is nearly planar. This planarity is probably a result of the tendency of divalent tellurium to form planar complexes, and of the planarity of the ethylxanthate ion.

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