

The Crystal and Molecular Structures of *trans* Square-Planar Complexes of Tellurium Dibromide and Diiodide with Ethylenethiourea

OLAV FOSS, HANS M. KJØGE and KJARTAN MARØY

Chemical Institute, University of Bergen, Bergen, Norway

The crystal and molecular structures of *trans*-dibromo- and *trans*-diiodo-bis(ethylenethiourea)tellurium(II), $\text{Te}(\text{etu})_2\text{Br}_2$ (I) and $\text{Te}(\text{etu})_2\text{I}_2$ (II), have been determined by X-ray methods, and refined by difference syntheses for the [010] and [110] projections. The crystals of the two compounds are isomorphous, space group $C_{2h}^6 - C2/c$ with $Z = 4$, and unit cells, $a = 17.30 \text{ \AA}$, $b = 5.89 \text{ \AA}$, $c = 15.57 \text{ \AA}$, $\beta = 120^\circ$ for I, and $a = 17.17 \text{ \AA}$, $b = 6.24 \text{ \AA}$, $c = 15.97 \text{ \AA}$, $\beta = 119\frac{1}{2}^\circ$ for II. The tellurium atoms lie in centres of symmetry.

The dimensions of the *trans* square-planar TeS_2Br_2 and TeS_2I_2 groups are: $\text{Te}-\text{Br} = 2.78 \pm 0.01 \text{ \AA}$, $\text{Te}-\text{S} = 2.69 \pm 0.015 \text{ \AA}$, $\angle \text{Br}-\text{Te}-\text{S} = 89.2 \pm 0.3^\circ$ in I, and $\text{Te}-\text{I} = 2.97 \pm 0.01 \text{ \AA}$, $\text{Te}-\text{S} = 2.69 \pm 0.02 \text{ \AA}$, $\angle \text{I}-\text{Te}-\text{S} = 89.2 \pm 0.4^\circ$ in II. The $\text{Te}-\text{S}$ bonds have the same length as in the tetrathioureatellurium(II) cation, $\text{Te}(\text{tu})_4^{2+}$. The results indicate that, with single covalent bond radii for ligands, a bonding radius of 1.64 \AA can be assigned to tellurium(II) in square-planar complexes, or alternatively that, in such complexes the Te -ligand bonds are 0.27 \AA longer than single covalent bonds.

Tellurium dibromide can be isolated as a chocolate-brown solid by depositing the violet vapour on to a cooled surface, but the solid when heated disproportionates rapidly into tellurium and the tetrabromide.^{1,2} The greenish-yellow solutions in ether or chloroform slowly deposit tellurium, more rapidly on heating, and instantaneously if a trace of moisture is admitted.² When solutions of tellurium dibromide and pyridine in dry ether were mixed, a white solid precipitated which rapidly became black.² The vapour density of tellurium dibromide is normal up to about 750°C ;³ an electron diffraction study⁴ of the vapour gave a $\text{Te}-\text{Br}$ bond length of 2.51 \AA and $\text{Br}-\text{Te}-\text{Br}$ bond angle of 98° (limits of error, 0.02 \AA and 3°). As for tellurium diiodide, no indication has been obtained for it in the solid state,⁵ although it probably occurs as a dissociation product of the tetraiodide in the vapour phase.⁶

The complexes of tellurium dibromide and diiodide with ethylenethiourea, $\text{Te}(\text{etu})_2\text{Br}_2$ and $\text{Te}(\text{etu})_2\text{I}_2$, the crystal structures of which are reported here, were prepared,⁷ not from the dihalides but from tetrakis(ethylenethiourea)-tellurium(II) salts⁸ by reactions with bromide or iodide ions. The dibromo compound was also obtained, *via* an orthorhombic form, from hydrobromic acid solutions of tellurium dioxide, and ethylenethiourea. The structure of the square-planar tetrathioureatellurium(II) ion, in the anhydrous dichloride and the dichloride dihydrate salts, is described in a preceding article.⁹

CRYSTAL DATA

The crystals of *trans*-dibromobis(ethylenethiourea)tellurium(II), $\text{Te}(\text{etu})_2\text{Br}_2$ (I), and *trans*-diiodobis(ethylenethiourea)tellurium(II), $\text{Te}(\text{etu})_2\text{I}_2$ (II), are isomorphous, space group C_{2h}^6-C2/c with four molecules per unit cell, of dimensions, $a = 17.30 \text{ \AA}$, $b = 5.89 \text{ \AA}$, $c = 15.57 \text{ \AA}$, $\beta = 120^\circ$ for I, and $a = 17.17 \text{ \AA}$, $b = 6.24 \text{ \AA}$, $c = 15.97 \text{ \AA}$, $\beta = 119\frac{1}{2}^\circ$ for II. Twofold molecular symmetry is crystallographically required. The intensity distribution for I, perhaps best observed on oscillation photographs around the *bc* diagonal: *hkl* reflections with $k + l$ even generally stronger than those with $k + l$ odd, indicated⁷ that the tellurium atoms lie in symmetry centres, positions¹⁰ $4c$ or $4d$, of the space group C_{2h}^6-C2/c . This was confirmed through the structure analyses.

Well developed crystals were obtained from dimethylformamide-glacial acetic acid and dimethylformamide-methanol, respectively.⁷ Those of I are reddish-yellow and those of II are red, they appear as prisms or plates extended along the *b* axis, bounded by {100} and {001} with the latter dominant in most cases. In the case of II there is a tendency of twinning.

Intensities were estimated visually from zero-level Weissenberg photographs around the *b* axes and the *ab* diagonals. $\text{CuK}\alpha$ radiation was used (linear absorption coefficients, 279 cm^{-1} for I and 544 cm^{-1} for II). The photographs of I were non-integrated and taken with a double-film technique, those of II were multiple-film, and integrated. The dimensions of the crystals were, *b*-axis photographs of I: prism with cross-section $0.03 \times 0.05 \text{ mm}$, of II: $0.03 \times 0.04 \text{ mm}$; $[1\bar{1}0]$ photographs of I: approximate sphere with diameter 0.13 mm , of II: 0.07 mm . The intensities of II were corrected for absorption: cylindrical crystal¹¹ with $\mu r = 1.0$, and spherical crystal¹² with $\mu r = 2.0$. The *hhl* reflections of II were eventually corrected for secondary extinction:¹³ $2g = 1.2 \times 10^{-5}$ based on two molecules. 118 *h0l* and 146 *hhl* reflections of I were observed with measurable intensities, out of 144 and 179, respectively, accessible with $\text{CuK}\alpha$ radiation; for II the figures were 109 out of 150 *h0l* reflections and 144 out of 198 *hhl* reflections.

The calculated structure factors were based on the Thomas-Fermi scattering curves for tellurium and bromine, that of Thomas and Umeda¹⁴ for iodine, of Viervoll and Ögrim¹⁵ for sulphur, and of Berghuis *et al.*¹⁶ for carbon and nitrogen. Most calculations were made on the IBM 650 computer, using Shiono's programs.¹⁷

THE STRUCTURE ANALYSES

The structure of the dibromo complex, I, was determined first, and of this, the projection along the *b* axis. With tellurium in a centre of symmetry, a Fourier synthesis of the strongest *h0l* reflections (about one third of the observed ones) with positive signs gave the approximate position of bromine, and further Fourier syntheses revealed also the lighter atoms. One of the strong reflections, 004, included in the first synthesis with positive sign later proved to be negative. In the *b*-axis projection of the diiodo complex, II,

Table 1. Atomic coordinates, in fractions of monoclinic cell edges. Origin at a centre of symmetry.¹⁰

Dibromobis(ethylenethiourea)tellurium(II)			
	<i>x</i>	<i>y</i>	<i>z</i>
Te	$\frac{1}{2}$	$\frac{1}{2}$	0
Br	0.3775	-0.079	0.1070
S	0.2224	0.301	0.1540
C ₁	0.152	0.075	0.145
N ₁	0.138	-0.109	0.092
C ₂	0.067	-0.252	0.089
C ₃	0.045	-0.134	0.164
N ₂	0.099	0.077	0.184
Diiodobis(ethylenethiourea)tellurium(II)			
	<i>x</i>	<i>y</i>	<i>z</i>
Te	$\frac{1}{2}$	$\frac{1}{2}$	0
I	0.3835	-0.086	0.1116
S	0.2190	0.302	0.1480
C ₁	0.151	0.086	0.142
N ₁	0.138	-0.091	0.091
C ₂	0.070	-0.231	0.093
C ₃	0.046	-0.110	0.162
N ₂	0.101	0.086	0.184

the iodine position was first found from the *h0l* Patterson map. The projections were refined through repeated difference syntheses.

The *y* coordinates were evaluated from projections along the *ab* diagonals, the repeat distance along which is halved on account of the *C*-centering and thus is 9.14 Å in I and 9.13 Å in II. Such projections, along an *ab* or *bc* diagonal of a monoclinic unit cell, involve all three monoclinic coordinates.¹⁸⁻²⁰ Retaining the *b* and *c* axes, and choosing half the [1 $\bar{1}$ 0] diagonal of the *C*-centered monoclinic cell as the *a* axis of a primitive triclinic cell, the asymmetric unit consists of two quasi-independent half molecules, at $y_t = x + y$, $z_t = z$ and $y_t = x - y$, $z_t = \frac{1}{2} + z$, where y_t , z_t are the triclinic and x, y, z the monoclinic coordinates. The [1 $\bar{1}$ 0] projections thus also served as a check on the *x* and *z* coordinates.

The [1 $\bar{1}$ 0] projections, in contrast to the *b*-axis projections, involve reflections with $k + l$ odd, to which tellurium does not contribute. In the case of I, a Fourier synthesis of the other set of reflections, with positive signs, gave the approximate bromine y_t coordinates. The ambiguity arising from the

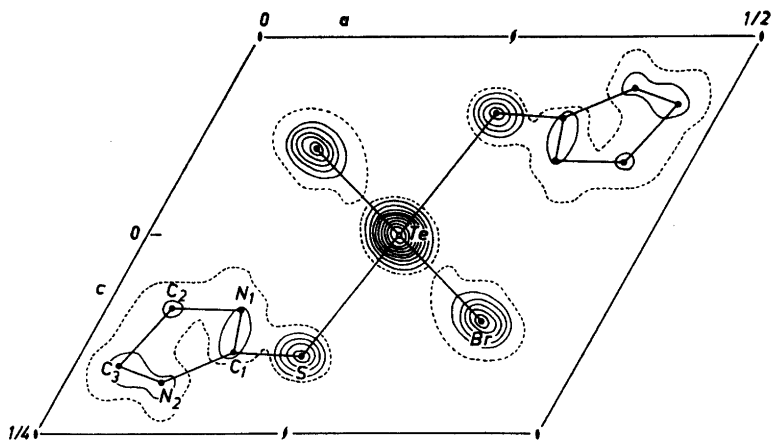


Fig. 1. Electron density projection of *trans*-Te(etu)₂Br₂ along the *b* axis. The 3.5-electron line is dashed. Contour intervals: 8 e . Å⁻² for tellurium and bromine, 4 e . Å⁻² for the other atoms.

presence of false symmetry due to the omission of the $k + l$ odd reflections was resolved by reference to the known x coordinate of bromine. The iodine y_t coordinates of II were first found from the Patterson map. Also these projections were refined through difference syntheses.

The coordinates of the carbon and nitrogen atoms of the ethylenethiourea ring, which in the presence of the heavy atoms can not be determined with any accuracy, were adjusted on the basis of dimensions reported by Wheatley²¹ for ethylenethiourea.

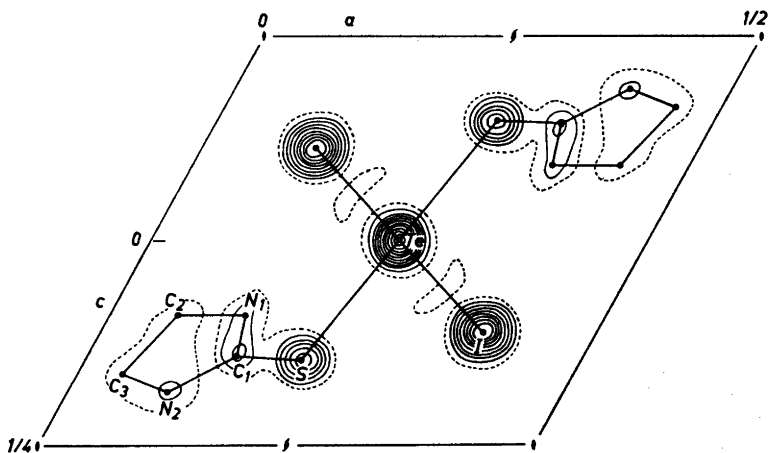


Fig. 2. Electron density projection of *trans*-Te(etu)₂I₂ along the *b* axis. The 4-electron line is dashed. Contour intervals: 10 e . Å⁻² for tellurium and iodine, 4 e . Å⁻² for the other atoms.

Table 2. Observed and calculated $h0l$ and hhl structure factors for dibromobis(ethylene-thiourea)tellurium(II). The signs of the $h0l$ reflections correspond to an origin located at $x = \frac{1}{2}$, and those of the hhl reflections to an origin located at $z = \frac{1}{2}$, relative to the origin of Table 1. The hhl data represent half the absolute values.

l	F_o	F_c	l	F_o	F_c	l	F_o	F_c
<i>h0l</i> zone			<i>60l</i>			<i>10, 0, l</i>		
	00l		0	166	+ 208	10	128	+ 111
2	177	+ 183	2	240	+ 284	12	186	+ 174
4	180	- 186	4	81	+ 96	14	43	+ 44
6	94	+ 99	6	< 21	+ 8	16	< 22	- 12
8	165	+ 159	8	35	+ 33	18	28	+ 25
10	126	+ 123	10	52	+ 52		12, 0, l	
12	67	+ 77	12	55	+ 48	0	25	- 26
14	< 22	+ 7		$\bar{6}0l$		2	93	+ 92
16	< 16	0	2	97	- 101	4	87	+ 92
	20l		4	89	+ 87	6	29	+ 26
0	143	+ 235	6	328	+ 316	8	23	+ 14
2	104	+ 109	8	158	+ 140		$\bar{1}2, 0, l$	
4	< 13	0	10	71	+ 62	2	< 21	- 5
6	235	+ 245	12	38	+ 41	4	179	+ 176
8	181	+ 189	14	26	+ 19	6	184	+ 174
10	< 22	- 21	16	66	+ 66	8	< 21	+ 14
12	< 23	+ 3	18	54	+ 49	10	23	+ 20
14	47	+ 54		80l		12	84	+ 72
16	25	+ 32	0	224	+ 257	14	65	+ 58
	$\bar{2}0l$		2	140	+ 131	16	62	+ 55
2	207	+ 211	4	36	- 41	18	24	+ 22
4	253	+ 269	6	29	+ 27		14, 0, l	
6	78	+ 81	8	92	+ 94	0	44	+ 33
8	19	+ 16	10	46	+ 49	2	82	+ 89
10	99	+ 108	12	< 13	+ 9	4	47	+ 40
12	146	+ 133		$\bar{8}0l$		6	< 15	0
14	48	+ 44	2	126	+ 140		$\bar{1}4, 0, l$	
16	20	- 14	4	49	+ 43	2	< 23	- 19
18	< 15	+ 17	6	34	+ 14	4	77	+ 72
	40l		8	145	+ 136	6	101	+ 117
0	54	- 68	10	219	+ 200	8	76	+ 84
2	93	+ 113	12	84	+ 71	10	73	+ 59
4	194	+ 240	14	< 23	- 12	12	< 23	- 4
6	152	+ 172	16	< 22	+ 22	14	< 22	+ 12
8	53	+ 50	18	53	+ 52	16	77	+ 80
10	< 23	- 16		10, 0, l		18	52	+ 50
12	35	+ 35	0	79	+ 89		16, 0, l	
14	54	+ 56	2	48	+ 34	0	52	+ 47
	$\bar{4}0l$		4	< 22	+ 6	2	41	+ 40
2	90	+ 78	6	69	+ 67	4	< 18	+ 1
4	328	+ 363	8	75	+ 75		$\bar{1}6, 0, l$	
6	397	+ 366	10	< 14	+ 6	2	74	+ 70
8	< 16	+ 13		$\bar{1}0, 0, l$		4	49	+ 46
10	76	- 74	2	142	+ 172	6	29	- 33
12	133	+ 115	4	171	+ 183	8	60	+ 46
14	99	+ 103	6	40	+ 26	10	138	+ 130
16	< 21	+ 25	8	25	- 35	12	48	+ 42
18	16	+ 19						

<i>l</i>	F_o	F_c	<i>l</i>	F_o	F_c	<i>l</i>	F_o	F_c
14	21	- 11	4	77	+ 68	5	95	+ 98
16	< 24	+ 29	5	145	+ 143	6	11	- 21
18	43	+ 36	6	< 6	+ 5	7	70	+ 65
			7	108	+ 110	8	11	+ 16
	18, 0, <i>l</i>		8	75	- 72	9	< 9	+ 2
0	< 16	+ 6	9	12	+ 5	10	< 9	+ 5
			10	19	- 17	11	< 8	+ 3
	18, 0, <i>l</i>		11	11	+ 8	12	11	- 11
2	59	+ 66	12	39	+ 37	13	22	+ 26
4	56	+ 53	13	47	+ 49	14	< 5	+ 4
6	< 21	- 7	14	17	+ 13			
8	21	+ 14	15	31	+ 33		33 <i>l</i>	
10	56	+ 60	16	< 7	- 8	1	64	+ 64
12	55	+ 55	17	10	+ 12	2	15	- 11
14	29	+ 27				3	94	+ 91
16	17	+ 12		22 <i>l</i>		4	23	+ 22
			0	99	+ 98	5	93	+ 90
	20, 0, <i>l</i>		1	60	+ 61	6	< 7	- 13
6	47	+ 41	2	107	+ 108	7	30	+ 26
8	21	+ 18	3	32	- 31	8	17	- 18
10	19	+ 11	4	55	+ 76	9	< 8	- 2
12	18	+ 12	5	50	- 50	10	16	+ 20
14	40	+ 37	6	41	+ 44	11	49	+ 45
			7	< 8	+ 6	12	< 9	+ 6
	<i>hhl</i> zone		8	28	+ 24	13	53	+ 53
	00 <i>l</i>		9	38	+ 36	14	12	- 13
2	80	+ 92	10	33	+ 27	15	19	+ 19
4	82	- 95	11	< 9	+ 4	16	< 6	+ 2
6	48	+ 53	12	45	+ 40			
8	95	+ 87	13	20	- 19		44 <i>l</i>	
10	71	+ 71	14	23	+ 26	0	79	+ 75
12	42	+ 48	15	< 5	- 2	1	33	+ 29
14	9	+ 6				2	50	+ 45
16	< 6	0		22 <i>l</i>		3	51	+ 50
			1	42	+ 44	4	15	+ 4
	11 <i>l</i>		2	10	+ 8	5	19	- 15
0	21	- 28	3	49	- 40	6	27	+ 24
1	87	+ 95	4	33	+ 27	7	36	- 36
2	98	- 119	5	40	- 40	8	32	+ 42
3	50	+ 64	6	131	+ 124	9	< 8	+ 6
4	9	+ 13	7	< 7	- 2	10	23	+ 27
5	86	+ 99	8	78	+ 80	11	10	+ 13
6	62	+ 75	9	40	+ 38	12	17	+ 14
7	74	+ 74	10	15	+ 17			
8	< 7	+ 5	11	21	+ 17		44 <i>l</i>	
9	16	+ 14	12	25	+ 22	1	41	- 41
10	35	- 32	13	26	- 24	2	47	+ 50
11	30	+ 30	14	28	+ 23	3	40	- 38
12	16	- 15	15	15	- 13	4	32	+ 33
13	44	+ 44	16	23	+ 22	5	10	+ 18
14	16	+ 13	17	7	+ 8	6	33	+ 27
15	18	+ 17				7	25	+ 23
16	10	+ 10		33 <i>l</i>		8	37	+ 32
			0	8	- 10	9	14	+ 9
	11 <i>l</i>		1	< 7	+ 4	10	47	+ 43
1	66	+ 60	2	19	+ 28	11	< 9	- 6
2	65	+ 64	3	27	+ 24	12	30	+ 29
3	41	+ 45	4	10	- 9	13	21	- 24

<i>l</i>	<i>F</i> _o	<i>F</i> _c	<i>l</i>	<i>F</i> _o	<i>F</i> _c	<i>l</i>	<i>F</i> _o	<i>F</i> _c
14	13	+ 13	4	41	+ 44	6	8	+ 3
15	< 6	+ 2	5	20	+ 20			
			6	12	- 9		$\overline{66}l$	
	$\overline{55}l$		7	17	+ 20	1	15	- 14
0	25	+ 28	8	37	- 37	2	11	+ 9
1	29	+ 26	9	34	+ 29	3	< 8	+ 6
2	15	- 12	10	< 8	+ 6	4	< 16	+ 8
3	13	+ 13	11	36	+ 34	5	< 8	+ 11
4	< 9	+ 7	12	12	+ 13	6	< 31	+ 32
5	< 25	+ 24	13	15	+ 16	7	< 8	- 6
6	< 8	+ 8	14	< 5	0	8	36	+ 37
7	< 33	+ 29				9	< 7	- 3
8	< 7	+ 6		$\overline{66}l$		10	18	+ 16
9	20	+ 22	0	27	+ 24	11	< 5	+ 4
			1	< 8	- 4			
	$\overline{55}l$		2	31	+ 34		$\overline{77}l$	
1	52	+ 50	3	8	+ 10	2	10	+ 14
2	13	+ 10	4	25	+ 31	3	21	+ 22
3	47	+ 38	5	< 6	0	4	< 5	+ 2

The Fourier maps are reproduced in Figs. 1–4. The final atomic coordinates are listed in Table 1, and observed and calculated structure factors in Tables 2 and 3. In the temperature factor $\exp[-B(\sin^2\theta/\lambda^2)]$ applied to the calculated structure factors, the final values of *B* were, in Å² units: In the *h0l* zone of I, *B* = 3.9 for tellurium, 4.6 for bromine, 3.8 for sulphur, and 4.0 for carbon and nitrogen; in the *h0l* zone of II, *B* = 2.3 for tellurium, 2.8 for iodine, and 2.5 for the other atoms. In the *hhl* zone of I, *B* = 2.8 for tellurium, sulphur, and carbon, 3.6 for bromine, and 3.0 for nitrogen; in the

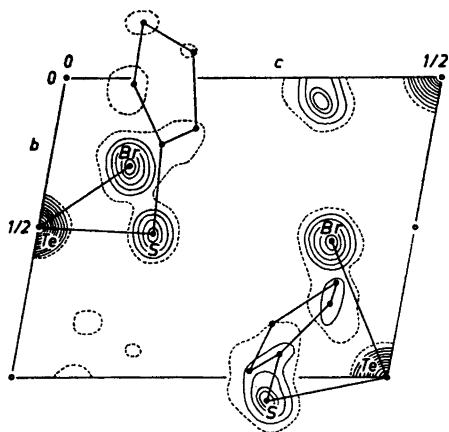


Fig. 3. Electron density projection of *trans*-Te(etu)₂Br₂ along [110]. The 6-electron line is dashed. Contour intervals: 9 e. Å⁻² for tellurium and bromine, 4 e. Å⁻² for the other atoms.

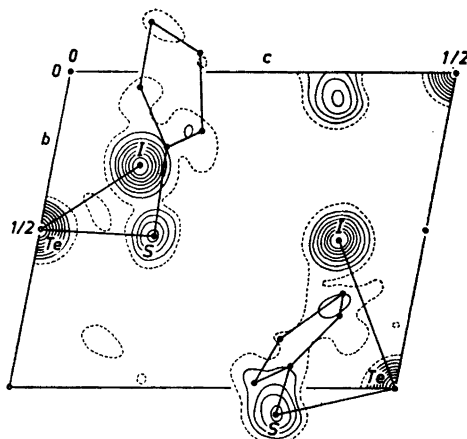


Fig. 4. Electron density projection of *trans*-Te(etu)₂I₂ along [110]. The 6-electron line is dashed. Contour intervals as in Fig. 2.

Table 3. Observed and calculated $h0l$ and hhl structure factors for diiodobis(ethylene-thiourea)tellurium(II). The remarks in the heading of Table 2 apply also here.

l	F_o	F_c	l	F_o	F_c	l	F_o	F_c
	$h0l$ zone							
	00l		2	351	+ 419	14	78	+ 79
2	197	+ 203	4	96	+ 74	16	80	- 77
4	310	- 335	6	101	+ 97	18	< 41	+ 29
6	82	+ 71	8	70	+ 61	20	71	+ 92
8	300	+ 305	10	170	+ 163		$12, 0, l$	
10	203	+ 199	12	103	+ 85	0	67	- 76
12	< 53	+ 33	14	< 25	+ 6	2	192	+ 187
14	< 53	- 18		$\bar{6}0l$		4	183	+ 193
16	39	+ 38	2	188	- 192	6	< 45	- 1
	$20l$		4	< 32	- 2	8	< 34	- 26
0	139	+ 203	6	419	+ 417		$\bar{1}2, 0, l$	
2	31	- 5	8	294	+ 250	2	66	- 81
4	< 33	+ 8	10	< 45	+ 18	4	237	+ 227
6	338	+ 370	12	< 50	- 15	6	284	+ 293
8	270	+ 258	14	63	+ 58	8	< 50	+ 22
10	92	- 93	16	149	+ 148	10	57	- 51
12	52	- 38	18	82	+ 86	12	99	+ 90
14	118	+ 140		$80l$		14	147	+ 138
16	99	+ 105	0	344	+ 355	16	96	+ 95
	$\bar{2}0l$		2	130	+ 90	18	< 40	+ 11
2	325	+ 345	4	116	- 117	20	< 25	- 9
4	351	+ 317	6	79	+ 57		$14, 0, l$	
6	< 33	- 18	8	196	+ 200	0	124	+ 111
8	40	- 21	10	97	+ 90	2	165	+ 154
10	197	+ 196	12	< 31	- 28	4	43	+ 34
12	257	+ 220		$\bar{8}0l$		6	< 33	- 31
14	66	+ 46	2	213	+ 246		$\bar{1}4, 0, l$	
16	63	- 60	4	< 38	- 9	2	< 53	- 27
18	< 29	+ 35	6	79	- 76	4	< 52	+ 10
	$40l$		8	232	+ 187	6	145	+ 141
0	175	- 199	10	327	+ 314	8	169	+ 181
2	158	+ 177	12	109	+ 81	10	106	+ 96
4	331	+ 387	14	75	- 63	12	< 53	- 52
6	179	+ 180	16	< 50	+ 31	14	< 51	- 4
8	< 50	- 16	18	121	+ 128	16	141	+ 156
10	< 53	- 25	20	58	+ 74	18	99	+ 116
12	111	+ 101		$10, 0, l$			$16, 0, l$	
14	119	+ 124	0	< 47	+ 10	0	101	+ 85
	$\bar{4}0l$		2	< 50	- 17	2	< 39	+ 5
2	28	+ 10	4	100	+ 74	4	< 29	- 14
4	457	+ 473	6	173	+ 152		$\bar{1}6, 0, l$	
6	500	+ 462	8	100	+ 95	2	166	+ 173
8	64	- 44	10	< 35	- 24	4	79	+ 71
10	187	- 165		$\bar{1}0, 0, l$		6	84	- 107
12	198	+ 188	2	245	+ 247	8	59	+ 40
14	217	+ 223	4	273	+ 307	10	211	+ 232
16	< 48	+ 20	6	< 44	+ 6	12	102	+ 96
18	< 35	- 15	8	133	- 125	14	47	- 53
	$60l$		10	167	+ 136	16	< 42	+ 14
0	259	+ 291	12	302	+ 298			

<i>l</i>	<i>F</i> _o	<i>F</i> _c	<i>l</i>	<i>F</i> _o	<i>F</i> _c	<i>l</i>	<i>F</i> _o	<i>F</i> _c
18	70	+ 95	2	82	+ 99	2	27	+ 33
	18, 0, <i>l</i>		3	26	+ 34	3	35	+ 35
0	< 33	+ 33	4	106	+ 109	4	< 18	+ 4
	18, 0, <i>l</i>		5	171	+ 169	5	117	+ 135
2	97	+ 110	6	15	- 16	6	< 19	+ 21
4	124	+ 132	7	108	+ 124	7	70	+ 66
6	< 47	+ 8	8	100	- 108	8	< 20	+ 5
8	< 47	- 22	9	< 18	- 9	9	23	- 20
10	72	+ 61	10	< 19	- 11	10	< 19	+ 7
12	104	+ 121	11	< 20	- 9	11	17	- 6
14	68	+ 77	12	62	+ 62	12	< 16	- 6
16	< 35	+ 1	13	61	+ 57	13	36	+ 36
18	< 24	- 9	14	18	+ 14	14	< 11	+ 10
	20, 0, <i>l</i>		15	48	+ 46		33 <i>l</i>	
4	49	+ 50	16	22	- 23	1	45	+ 48
6	97	+ 113	17	< 13	+ 5	2	30	- 29
8	59	+ 62		22 <i>l</i>		3	120	+ 136
10	< 38	- 16	0	106	+ 108	4	29	+ 24
12	< 36	- 8	1	87	+ 91	5	101	+ 109
14	67	+ 84	2	119	+ 128	6	15	+ 7
16	79	+ 105	3	65	- 71	7	< 18	- 3
	<i>hhl</i> zone		4	53	+ 68	8	17	- 17
	00 <i>l</i>		5	81	- 81	9	25	- 19
2	102	+ 101	6	23	+ 24	10	< 20	+ 7
4	176	- 164	7	23	+ 26	11	59	+ 59
6	31	+ 34	8	35	+ 28	12	< 21	+ 7
8	137	+ 141	9	73	+ 64	13	68	+ 67
10	87	+ 87	10	51	+ 41	14	< 17	- 8
12	< 20	+ 14	11	< 19	- 3	15	15	+ 12
14	< 18	- 5	12	44	+ 38	16	< 13	0
16	19	+ 14	13	45	- 40	17	12	- 10
	11 <i>l</i>		14	19	+ 19		44 <i>l</i>	
0	63	- 67	15	< 12	- 2	0	95	+ 103
1	112	+ 106	16	< 8	+ 3	1	51	+ 53
2	170	- 155		22 <i>l</i>		2	47	+ 40
3	88	+ 102	1	86	+ 93	3	55	+ 66
4	39	+ 44	2	14	- 8	4	< 20	+ 16
5	92	+ 97	3	63	- 65	5	41	- 34
6	91	+ 106	4	26	+ 21	6	22	+ 24
7	51	+ 50	5	76	- 84	7	47	- 55
8	18	- 13	6	137	+ 142	8	49	+ 55
9	< 19	+ 11	7	< 17	+ 11	9	21	+ 18
10	61	- 55	8	77	+ 89	10	34	+ 29
11	43	+ 38	9	68	+ 70	11	25	+ 28
12	< 19	- 9	10	< 20	- 1	12	11	+ 4
13	58	+ 48	11	22	+ 15	13	< 8	- 4
14	33	+ 28	12	22	+ 12		44 <i>l</i>	
15	21	+ 15	13	42	- 43	1	44	- 48
16	15	+ 10	14	37	+ 35	2	51	+ 59
17	< 8	0	15	24	- 17	3	59	- 63
	11 <i>l</i>		16	29	+ 27	4	< 19	+ 9
1	21	+ 21	17	17	+ 18	5	17	+ 17
				33 <i>l</i>		6	22	+ 14
			0	25	- 19	7	47	+ 44
			1	40	- 43	8	52	+ 48

<i>l</i>	F_o	F_c	<i>l</i>	F_o	F_c	<i>l</i>	F_o	F_c
9	< 20	+ 9	5	18	+ 13	5	< 17	+ 3
10	63	+ 57	6	< 20	- 7	6	40	+ 44
11	23	- 19	7	17	+ 15	7	< 17	- 6
12	25	+ 20	8	58	- 64	8	< 43	+ 46
13	22	- 22	9	36	+ 35	9	< 15	+ 3
14	< 15	+ 3	10	< 18	0	10	15	+ 9
15	< 13	+ 18	11	37	+ 36	11	< 12	+ 7
16	12	+ 15	12	28	+ 32	12	< 11	- 9
			13	15	+ 13	13	< 8	- 6
	55 <i>l</i>		14	< 12	+ 5			
0	47	- 55	15	< 9	+ 3		77 <i>l</i>	
1	26	+ 24				0	< 11	+ 2
2	31	- 27		66 <i>l</i>		1	< 10	- 4
3	19	+ 10	0	33	+ 32	2	13	- 12
4	22	+ 27	1	< 17	0			
5	35	+ 24	2	43	+ 48		77 <i>l</i>	
6	27	+ 23	3	< 16	+ 6	1	18	+ 14
7	35	+ 31	4	21	+ 23	2	17	+ 21
8	< 15	- 7	5	< 13	- 2	3	26	+ 29
9	16	+ 20	6	< 12	- 8	4	< 12	+ 4
10	18	- 14	7	10	- 4	5	19	+ 21
						6	19	- 22
	55 <i>l</i>			66 <i>l</i>		7	10	+ 7
1	52	+ 55	1	< 18	- 7	8	10	- 9
2	23	+ 17	2	< 18	- 6	9	< 8	+ 6
3	49	+ 43	3	< 18	+ 3			
4	64	+ 74	4	< 18	0			

hhl zone of II, $B = 3.2$ for tellurium and sulphur, 3.8 for iodine, and 3.4 for carbon and nitrogen. The reliability index, R , with non-observed reflections included when $|F_c|$ exceeds the observable limit, is 0.102 and 0.099 for the *h0l* zones of I and II, respectively, and 0.103 and 0.107 for the *hhl* zones. The strong reflection, 200, in the *h0l* zone of I has a markedly higher calculated than observed value; it was omitted in the calculation of R index and difference maps for this zone, and was included in the final electron density map with its calculated value.

The standard deviations of the coordinates of the heavier atoms were estimated from the root-mean-square gradients of the difference maps and the curvatures of peaks in the electron density maps. The values arrived at were, $\sigma(x) = 0.005$ Å, $\sigma(y) = 0.006$ Å, $\sigma(z) = 0.004$ Å for bromine, and $\sigma(x) = 0.012$ Å, $\sigma(y) = 0.016$ Å, $\sigma(z) = 0.010$ Å for sulphur in I; $\sigma(x) = 0.004$ Å, $\sigma(y) = 0.005$ Å, $\sigma(z) = 0.003$ Å for iodine, and $\sigma(x) = \sigma(y) = 0.017$ Å, $\sigma(z) = 0.014$ Å for sulphur in II. The s.d. of the nitrogen and carbon coordinates are probably about 0.05 Å in I and a little larger in II.

RESULTS

Bond lengths and angles involving the heavier atoms, as calculated from the coordinates of Table 1, are listed in Table 4, together with the estimated standard deviations. With tellurium in crystallographic centres of symmetry,

Table 4. Dimensions of the coordination groups.

	Dibromo complex	Diiodo complex
Te—Br	2.779 ± 0.01 Å	
Te—I		2.967 ± 0.01 Å
Te—S	2.686 ± 0.015	2.686 ± 0.02
S—C	1.76 ± 0.05	1.76 ± 0.06
∠ S—Te—Br	89.2 ± 0.3°	
∠ S—Te—I		89.2 ± 0.4°
∠ Te—S—C	105.6 ± 2.1	105.9 ± 2.5

the TeS₂Br₂ and TeS₂I₂ groups are exactly planar. Drawings of the molecules are shown in Fig. 5.

The Te—S bond lengths are the same as in the tetrathioureatellurium(II) cation,⁹ Te(tu)₄²⁺. The covalent single-bond radii²² of tellurium, iodine, bromine, and sulphur being 1.37, 1.33, 1.14, and 1.04 Å, respectively, the Te—ligand bonds are 0.27 Å longer than single covalent bonds. With covalent single-bond radii for ligands, a bonding radius of 1.64 Å can be assigned to tellurium(II) in square-planar complexes.²³

The ethylenethiourea carbon and nitrogen coordinates correspond to the bond lengths, C₁—N₁ and C₁—N₂ = 1.31–1.33 Å, N₁—C₂ and N₂—C₃ = 1.47–1.48 Å, C₂—C₃ = 1.55 Å, and bond angles, S—C₁—N₁ and S—C₁—N₂ = 124°–126°, N₁—C₁—N₂ = 110°–111°, C₁—N₁—C₂ and C₁—N₂—C₃ = 112°–113°, N₁—C₂—C₃ and N₂—C₃—C₂ = 100°–103°, with rather large uncertainties. The deviations of the atoms from the least-squares planes of the ethylenethiourea groups, with sulphur given three times the weight of carbon and nitrogen, are 0.01–0.07 Å in I and 0.01–0.05 Å in II, and are not significant. The least-squares planes of the ethylenethiourea groups make angles of 78° with the TeS₂Br₂ plane in I and 75° with the TeS₂I₂ plane in II.

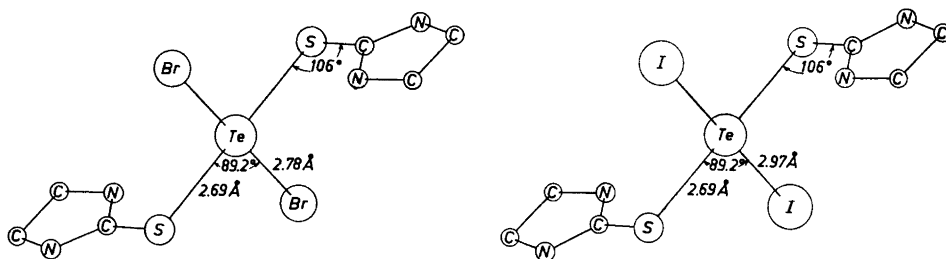


Fig. 5. *trans*-Dibromobis(ethylenethiourea)tellurium(II) (left) and *trans*-diiodobis(ethylenethiourea)tellurium(II) (right) as seen along the *b* crystal axes.

REFERENCES

1. Damiens, A. *Compt. Rend.* **173** (1921) 583; *Bull. Soc. Chim. France* [4] **29** (1921) 1063.
2. Aynsley, E. E. and Watson, R. H. *J. Chem. Soc.* **1955** 2603.
3. Yost, D. M. and Hatcher, J. B. *J. Am. Chem. Soc.* **54** (1932) 151.
4. Rogers, M. T. and Spurr, R. A. *J. Am. Chem. Soc.* **69** (1947) 2103.
5. Blackmore, W. R., Abrahams, S. C. and Kalnajs, J. *Acta Cryst.* **9** (1956) 295.
6. Yost, D. M. and Russel, H. *Systematic Inorganic Chemistry of the Fifth-and-sixth-group Nonmetallic Elements*, Prentice-Hall, New York 1944, p. 297.
7. Foss, O. and Fossen, S. *Acta Chem. Scand.* **15** (1961) 1618.
8. Foss, O. and Fossen, S. *Acta Chem. Scand.* **15** (1961) 1620.
9. Fosheim, K., Foss, O., Scheie, A. and Solheimsnes, S. *Acta Chem. Scand.* **19** (1965) 2336.
10. *International Tables for X-ray Crystallography*, Vol. I. The Kynoch Press, Birmingham 1952, p. 101.
11. Bradley, A. J. *Proc. Phys. Soc. (London)* **47** (1935) 879.
12. Evans, H. T. and Ekstein, M. G. *Acta Cryst.* **5** (1952) 540.
13. Bunn, C. W. *Chemical Crystallography*, Oxford University Press 1946, p. 209.
14. Thomas, L. H. and Umeda, K. *J. Chem. Phys.* **26** (1957) 293.
15. Viervoll, H. and Ögrim, O. *Acta Cryst.* **2** (1949) 277.
16. Berghuis, J., Haanappel, I. M., Potters, M., Loopstra, B. O., MacGillavry, C. H. and Veenendaal, A. L. *Acta Cryst.* **8** (1955) 478.
17. Shiono, R. *IBM 650 Programs for Crystallographic Computing*, Technical Reports Nos. 2 and 9, Computation and Data Processing Center, University of Pittsburgh 1957.
18. MacGillavry, C. H., Hoogschagen, G. and Sixma, F. L. *J. Rec. Trav. Chim.* **67** (1948) 869.
19. Black, P. J. *Acta Cryst.* **8** (1955) 43.
20. Black, P. J. *Acta Cryst.* **8** (1955) 656.
21. Wheatley, P. J. *Acta Cryst.* **6** (1953) 369.
22. Pauling, L. *The Nature of the Chemical Bond*, 3rd Ed., Cornell University Press, Ithaca, New York 1960.
23. Foss, O. *Acta Chem. Scand.* **16** (1962) 779.

Received August 2, 1965.