

The Crystal and Molecular Structures of Complexes of Benzenetellurenyl Chloride and Bromide with Thiourea

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The compounds of benzenetellurenyl chloride and bromide with one molecule of thiourea, $C_6H_5Te(tu)Cl$ (I) and $C_6H_5Te(tu)Br$ (II), form isomorphous crystals, space group $C_{2h}^5-P2_1/n$ with $Z = 4$, and unit cells, $a = 6.32 \text{ \AA}$, $b = 10.62 \text{ \AA}$, $c = 15.16 \text{ \AA}$, $\beta = 90\frac{1}{2}^\circ$ for I; $a = 6.46 \text{ \AA}$, $b = 10.73 \text{ \AA}$, $c = 15.36 \text{ \AA}$, $\beta = 91\frac{1}{2}^\circ$ for II. The crystal and molecular structures have been determined by X-ray methods, and refined by difference syntheses for the $0kl$ and $h0l$ zones.

The tellurium atoms are bonded to one phenyl carbon atom and, in directions approximately normal to the Te-C bond, to one thiourea sulphur atom and one halogen atom. The bond lengths and angles involving tellurium are, Te-S = $2.50 \pm 0.015 \text{ \AA}$, Te-C = $2.12 \pm 0.06 \text{ \AA}$, $\angle S-Te-C = 90 \pm 1^\circ$ in both compounds; Te-Cl = $3.00 \pm 0.015 \text{ \AA}$, $\angle S-Te-Cl = 171.9 \pm 0.5^\circ$, $\angle Cl-Te-C = 84 \pm 1^\circ$ in I, and Te-Br = $3.11 \pm 0.01 \text{ \AA}$, $\angle S-Te-Br = 174.1 \pm 0.5^\circ$, $\angle Br-Te-C = 86 \pm 1^\circ$ in II. The fourth position of square-planar tellurium(II) coordination is approached by a chlorine or bromine atom of an adjacent molecule, at Te...Cl = 3.71 \AA in I and Te...Br = 3.77 \AA in II, in directions which make angles of 164° with the direction of the Te-C bond.

The phenyl group when introduced as a ligand in tellurium(II) complexes leads to structures which may be regarded as based on square-planar four-coordination with one of the positions, opposite to the phenyl group, vacant.¹ The crystal structure of one example, phenylbis(thiourea)tellurium(II) chloride, was described in a preceding article.² The structures of the 1:1 complexes of benzenetellurenyl chloride and bromide with thiourea,³ $C_6H_5Te(tu)Cl$ and $C_6H_5Te(tu)Br$, are reported here. They contain divalent tellurium bonded to a phenyl group, a thiourea molecule and, in *trans* position to the latter, a halogen atom. The tellurium-halogen bonds are rather long, as⁴ in *cis*-dichloro- and *cis*-dibromo-dithioureatellurium(II), $Te(tu)_2Cl_2$ and $Te(tu)_2Br_2$, where the halogen atoms also occur in positions *trans* to thiourea. The present structures illustrate the relative *trans* bond-lengthening order: phenyl > thiourea > halogen, of ligands in tellurium(II) complexes.

The compounds were prepared, not from the benzenetellurenyl halides which apparently are unstable, but from phenyltellurium trichloride and three moles of thiourea, in the case of the bromide in presence of an excess of potassium bromide.³

CRYSTAL DATA

The compounds, C₆H₅Te(tu)Cl (I) and C₆H₅Te(tu)Br (II), crystallize from methanol as orange red, well developed prisms elongated along the *a* axis. The crystals of the two compounds are isomorphous, space group $C_{2h}^5-P2_1/n$ with four molecules per unit cell, of dimensions,³ $a = 6.32 \text{ \AA}$, $b = 10.62 \text{ \AA}$, $c = 15.16 \text{ \AA}$, $\beta = 90\frac{1}{2}^\circ$ for I, and $a = 6.46 \text{ \AA}$, $b = 10.73 \text{ \AA}$, $c = 15.36 \text{ \AA}$, $\beta = 91\frac{1}{2}^\circ$ for II.

The intensities of the $0kl$ and $h0l$ reflections were estimated visually from zero-layer Weissenberg photographs taken with $CuK\alpha$ radiation. Crystals with small cross-sections, about $0.07 \times 0.07 \text{ mm}$, were used in order to minimize absorption. 150 $0kl$ reflections and 112 $h0l$ reflections of I were observed with measurable intensities, out of 201 and 121, respectively, attainable with $CuK\alpha$ radiation. For II, the corresponding figures were 169 out of 207 $0kl$ reflections and 110 out of 125 $h0l$ reflections.

The calculated structure factors were based on the Thomas-Fermi scattering curves for tellurium and bromine, those of Viervoll and Ögrim⁵ for chlorine and sulphur, and of Berghuis *et al.*⁶ for carbon and nitrogen.

Summations were made by means of Beevers-Lipson strips, at 12° intervals along the *a* axes and 6° intervals along the *b* and *c* axes, except for the final electron density maps of II which were summed, at the same intervals, on the IBM 650 computer using Shiono's program.⁷

THE STRUCTURE ANALYSES

The structure of the chloro compound, I, was solved and refined first. The approximate tellurium coordinates were found from the Patterson maps, and Fourier syntheses of 108 of the strongest $0kl$ reflections and 90 of the strongest $h0l$ reflections, with signs based on the tellurium contributions, revealed the sulphur and chlorine positions. The carbon and nitrogen atoms of the thiourea group and the carbon atoms of the phenyl group were placed partly on the basis of the subsequent Fourier maps, and partly from dimensional considerations. Refinement was carried out through repeated cycles of difference syntheses.

The structure of the isomorphous bromo compound, II, was solved through Fourier syntheses of 92 $0kl$ and 99 $h0l$ reflections, with signs calculated from the atomic coordinates of I with bromine substituted for chlorine. Further work proceeded as for I. In presence of the heavy tellurium atom, the carbon and nitrogen coordinates can not be determined with any accuracy, and the coordinates of these atoms were in both compounds adjusted on the basis of the known dimensions of thiourea and phenyl groups.

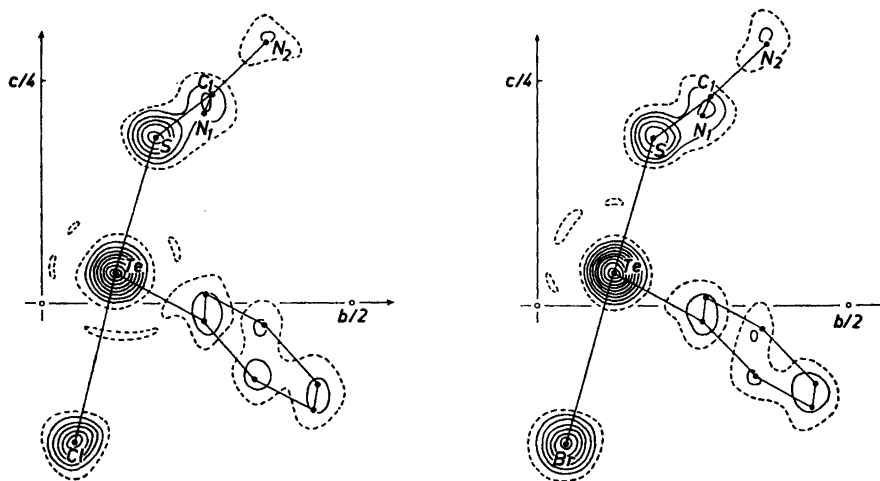


Fig. 1. Electron density projections of chloro(phenyl)thioureatellurium(II) (left) and of bromo(phenyl)thioureatellurium(II) (right) along the a axes, showing one asymmetric unit. The 5-electron lines are dashed. Contour intervals: $12 \text{ e} \cdot \text{\AA}^{-2}$ (left) and $10 \text{ e} \cdot \text{\AA}^{-2}$ (right) for tellurium, $8 \text{ e} \cdot \text{\AA}^{-2}$ for bromine, and $4 \text{ e} \cdot \text{\AA}^{-2}$ for the other atoms.

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

Chloro(phenyl)thioureatellurium(II)			
	x	y	z
Te	0.2570	0.1198	0.0340
Cl	0.321	0.0510	-0.1559
S	0.152	0.1855	0.1855
C ₁	0.358	0.277	0.234
N ₁	0.564	0.264	0.213
N ₂	0.303	0.364	0.292
C ₂	0.058	0.261	-0.020
C ₃	-0.151	0.266	0.010
C ₄	-0.277	0.362	-0.025
C ₅	-0.210	0.445	-0.091
C ₆	-0.001	0.440	-0.121
C ₇	0.125	0.344	-0.086
Bromo(phenyl)thioureatellurium(II)			
	x	y	z
Te	0.2457	0.1242	0.0374
Br	0.319	0.0462	-0.1545
S	0.148	0.1884	0.1871
C ₁	0.356	0.277	0.233
N ₁	0.555	0.265	0.212
N ₂	0.304	0.364	0.291
C ₂	0.048	0.264	-0.016
C ₃	-0.160	0.269	0.010
C ₄	-0.291	0.360	-0.025
C ₅	-0.214	0.446	-0.086
C ₆	-0.006	0.441	-0.112
C ₇	0.125	0.350	-0.077

Table 2. Observed and calculated *Ok**l* and *h*0*l* structure factors for chloro(phenyl)-thioureatellurium(II).

<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
0 <i>kl</i> zone			03 <i>l</i>			14	< 17	+ 12
	00 <i>l</i>		1	82	- 85	15	50	+ 46
2	79*	+133	2	44	+ 41	16	< 14	- 14
4	90*	+124	3	36	- 41	17	38	+ 39
6	86	+ 99	4	119*	-140	06 <i>l</i>		
8	42	- 34	5	66	- 64	0	32	- 33
10	39	- 37	6	81	- 91	1	27	+ 27
12	64	- 57	7	28	+ 23	2	36	- 30
14	78	- 76	8	87	- 94	3	72	+ 70
16	68	- 65	9	20	+ 26	4	27	- 20
18	42	- 42	10	70	- 68	5	78	+ 78
01 <i>l</i>			11	24	+ 18	6	< 16	- 2
1	88*	+125	12	47	- 40	7	93	+ 92
2	40	- 42	13	81	+ 77	8	29	- 26
3	22	+ 27	14	< 18	+ 4	9	99	+108
4	14	- 18	15	33	+ 27	10	19	+ 20
5	90*	+112	16	< 16	+ 12	11	30	+ 26
6	103*	-131	17	16	+ 15	12	< 18	+ 11
7	29	+ 28	18	19	+ 17	13	18	+ 21
8	67	- 71	04 <i>l</i>			14	< 16	- 3
9	65	- 68	0	112*	-127	15	16	+ 19
10	47	- 49	1	47	+ 37	16	22	+ 21
11	57	- 52	2	118*	-141	17	29	- 32
12	50	- 44	3	16	- 13	07 <i>l</i>		
13	50	- 44	4	75	- 76	1	48	+ 51
14	18	+ 9	5	59	- 62	2	51	+ 46
15	54	- 50	6	19	- 23	3	50	+ 55
16	25	+ 21	7	43	+ 45	4	69	+ 71
17	41	- 37	8	30	+ 31	5	26	+ 25
18	< 13	+ 5	9	18	- 18	6	56	+ 46
19	11	- 10	10	49	+ 42	7	< 18	- 12
02 <i>l</i>			11	31	- 27	8	65	+ 65
0	47	- 45	12	74	+ 69	9	< 18	+ 14
1	44	- 41	13	< 18	+ 14	10	55	+ 58
2	23	+ 23	14	74	+ 68	11	31	- 31
3	112*	-154	15	< 17	- 2	12	< 17	+ 1
4	79	- 89	16	48	+ 48	13	32	- 31
5	116*	-152	17	< 13	+ 5	14	21	+ 25
6	< 11	- 4	18	37	+ 38	15	20	- 19
7	111*	-138	05 <i>l</i>			16	< 11	- 7
8	17	+ 12	1	94	-103	08 <i>l</i>		
9	75	- 84	2	65	+ 72	0	65	+ 56
10	47	- 39	3	100	-110	1	< 17	+ 2
11	85	- 86	4	40	+ 38	2	91	+ 99
12	< 18	+ 4	5	39	- 42	3	< 17	+ 14
13	50	- 47	6	33	+ 31	4	88	+ 90
14	< 18	+ 6	7	< 15	- 6	5	< 18	+ 1
15	26	+ 22	8	89	+ 95	6	< 18	- 1
16	25	- 22	9	< 17	+ 6	7	31	+ 29
17	< 15	+ 8	10	21	+ 20	8	< 18	+ 9
18	< 13	+ 5	11	64	+ 65	9	29	+ 23
			12	30	+ 22	10	28	- 25
			13	38	+ 31			

<i>l</i>	F_o	F_c	<i>l</i>	F_o	F_c	<i>l</i>	F_o	F_c
11	< 17	+ 2		0,13, <i>l</i>		8	42	+ 43
12	52	- 57	1	44	- 48	10	34	+ 28
13	< 15	+ 2	2	< 11	- 13	12	69	+ 65
14	32	- 31	3	20	- 14	14	65	+ 71
15	< 10	+ 2	4	17	+ 21	16	69	+ 72
						18	36	+ 46
	09 <i>l</i>			<i>h</i> 0 <i>l</i> zone				
1	58	+ 51		00 <i>l</i>			30 <i>l</i>	
2	< 18	+ 9	2	108*	+ 134	1	60	+ 58
3	73	+ 72	4	112	+ 123	3	114	+ 105
4	36	- 43	6	110	+ 102	5	124	+ 120
5	< 18	- 1	8	49	- 45	7	163	+ 152
6	18	- 16	10	45	- 38	9	83	+ 74
7	< 18	- 10	12	74	- 68	11	40	+ 35
8	20	- 21	14	88	- 83	13	47	+ 43
9	< 17	- 4	16	76	- 76	15	22	- 23
10	30	- 33	18	46	- 45	17	32	- 40
11	30	- 30						
12	< 14	0		10 <i>l</i>			30 <i>l</i>	
13	41	- 44	1	36	- 26	1	23	- 24
14	< 10	- 3	3	67	- 54	3	88	- 83
			5	184	- 190	5	150	- 155
	0,10, <i>l</i>		7	148	- 161	7	75	- 70
0	< 18	- 7	9	77	- 68	9	106	- 108
1	< 18	+ 12	11	90	- 78	11	126	- 121
2	< 18	+ 10	13	57	- 50	13	< 21	- 7
3	41	- 47	15	43	+ 41	15	40	- 33
4	20	+ 28	17	24	+ 22	17	< 14	+ 11
5	53	- 52	19	22	+ 31			
6	< 18	+ 1					40 <i>l</i>	
7	46	- 46		10 <i>l</i>		0	83	+ 88
8	< 16	- 14	1	80*	+ 118	2	154	+ 159
9	51	- 58	3	70*	+ 92	4	32	+ 21
10	< 14	+ 1	5	139*	+ 174	6	< 19	- 7
11	25	- 25	7	126*	+ 152	8	< 21	+ 12
12	17	- 16	9	86	+ 90	10	78	- 83
			11	140	+ 141	12	77	- 76
	0,11, <i>l</i>		13	21	+ 16	14	51	- 50
1	< 17	- 12	15	24	- 18	16	46	- 56
2	30	- 35	17	< 18	+ 3			
3	< 17	- 13	19	47	- 55		40 <i>l</i>	
4	37	- 33				2	96	+ 90
5	< 16	+ 3		20 <i>l</i>		4	110	+ 112
6	39	- 39	0	185*	- 225	6	35	+ 28
7	< 15	- 13	2	194	- 186	8	< 20	- 3
8	41	- 43	4	15	0	10	21	- 19
9	13	+ 15	6	71	- 64	12	74	- 69
10	28	- 25	8	36	+ 29	14	70	- 72
			10	109	+ 101	16	55	- 61
	0,12, <i>l</i>		12	61	+ 55			
0	40	- 52	14	87	+ 81		50 <i>l</i>	
1	17	- 25	16	68	+ 71	1	26	- 34
2	33	- 33	18	42	+ 43	3	91	- 90
3	< 14	+ 6				5	78	- 81
4	17	- 20		20 <i>l</i>		7	85	- 91
5	< 13	- 1	2	70	- 81	9	60	- 63
6	< 13	- 16	4	153*	- 186	11	< 19	- 17
7	25	- 31	6	61	- 63	13	16	- 20
8	< 10	+ 3						

<i>l</i>	<i>F_o</i>	<i>F_c</i>	<i>l</i>	<i>F_o</i>	<i>F_c</i>	<i>l</i>	<i>F_o</i>	<i>F_c</i>
	$\bar{5}0l$						$70l$	
1	27	- 24	4	43	- 48	1	39	+ 47
3	75	+ 63	6	24	+ 27	3	39	+ 44
5	70	+ 59	8	25	+ 22	5	52	+ 58
7	48	+ 45	10	37	+ 39	7	47	+ 59
9	109	+ 116	12	58	+ 74	9	41	+ 49
11	39	+ 41		$\bar{6}0l$			$\bar{7}0l$	
13	< 16	+ 18	2	84	- 87	1	< 18	+ 15
15	24	+ 31	4	74	- 80	3	38	- 36
	$60l$		6	20	- 19	5	20	- 19
0	41	- 43	8	23	- 25	7	50	- 58
2	85	- 87	10	18	+ 16	9	58	- 70
			12	29	+ 35			

The $0kl$ Fourier maps are shown in Fig. 1. The final atomic coordinates are listed in Table 1, and observed and calculated structure factors in Tables 2 and 3. Some strong low order reflections, marked with an asterisk in Tables 2 and 3, have calculated values markedly higher than the observed ones. They were omitted from the last difference syntheses and calculations of scale factors, and were included in the final Fourier maps with their calculated instead of observed values. In the temperature factor $\exp[-B(\sin^2\theta/\lambda^2)]$ applied to the calculated structure factors, the final values of B were, in \AA^2 units: In the $0kl$ zone of I, $B = 2.3$ for chlorine, 1.8 for sulphur, 3.0 for carbon and nitrogen, and $2.0 + 0.5 \cos^2\varphi$ for tellurium, where φ is the angle between the normal of the reflecting plane and the direction of maximum vibration of the atom, the b axis. In the $h0l$ zone of I, $B = 1.5$ for tellurium, 1.8 for chlorine and sulphur, 3.7 for carbon, and 3.0 for nitrogen. In the $0kl$ zone of II, $B = 2.5$ for tellurium, 2.8 for sulphur, and 3.5 for the other atoms, while in the $h0l$ zone, $B = 2.5$ for tellurium and sulphur, and 3.7 for the other atoms.

The reliability index, R , with non-observed reflections included when $|F_c|$ exceeds the observable limit, and with the strong reflections, referred to above, not included, is 0.08 for the $h0l$ zone of II and 0.09 for the three other zones.

The standard deviations of the atomic coordinates were estimated from the root-mean-square gradients of the difference maps and the curvatures of peaks in the electron density maps. Where overlapping occurred, the values were increased relative to those which would otherwise have applied. The resulting s.d. of bond lengths and angles involving the heavier atoms are included in Table 4.

THE BONDING TO TELLURIUM

Table 4 gives bond lengths and angles in the coordination groups, as calculated from the atomic coordinates of Table 1, together with the estimated standard deviations. In the table, Mp denotes the coordinate midpoint of the carbon atoms of the phenyl ring; in view of the rather large uncertainties in the carbon coordinates this midpoint is assumed to give more accurately

<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
10	30	- 28	5	< 12	+ 5	16	58	+ 54
11	16	- 16	6	18	- 22	18	35	+ 35
12	59	- 59	7	13	- 15			
13	< 13	- 1	8	10	+ 10		$\bar{2}0l$	
14	35	- 36	9	< 8	+ 2	2	23	- 17
15	< 10	+ 6				4	145	-164
				0,13, <i>l</i>		6	57	- 74
	09 <i>l</i>		1	43	- 43	8	82	+ 87
1	38	+ 34	2	< 10	- 4	10	65	+ 64
2	< 16	+ 14	3	< 10	- 3	12	49	+ 47
3	75	+ 72	4	27	+ 26	14	52	+ 53
4	63	- 63	5	18	- 23	16	54	+ 54
5	< 16	- 7				18	< 13	+ 11
6	37	- 36		<i>h</i> 0 <i>l</i> zone				
7	30	- 27		00 <i>l</i>			30 <i>l</i>	
8	18	- 23	2	97	+111	1	43	+ 43
9	< 16	- 5	4	71	+ 76	3	57	+ 47
10	35	- 36	6	121	+125	5	125	+120
11	25	- 24	8	61	- 53	7	171	+166
12	< 13	- 5	10	83	- 82	9	54	+ 47
13	43	- 44	12	59	- 51	11	26	+ 27
14	10	+ 7	14	58	- 56	13	53	+ 45
			16	65	- 61	15	31	- 26
	0,10, <i>l</i>		18	25	- 25	17	37	- 33
0	42	- 34						
1	< 16	+ 11		10 <i>l</i>			$\bar{3}0l$	
2	< 16	+ 2	1	9	+ 15	1	< 12	- 6
3	47	- 49	3	28	- 14	3	133	-141
4	20	+ 24	5	230	-238	5	158	-176
5	62	- 63	7	138	-137	7	27	- 24
6	17	- 13	9	32	- 24	9	85	- 94
7	49	- 47	11	87	- 73	11	85	- 87
8	< 15	- 12	13	43	- 40	13	42	+ 36
9	45	- 48	15	66	+ 62	15	< 17	- 9
10	15	+ 15	17	27	+ 23	17	< 13	+ 19
11	22	- 24	19	18	+ 24			
12	12	- 12					40 <i>l</i>	
13	< 8	- 5		$\bar{1}0l$		0	78	+ 80
			1	71	+ 69	2	185	+190
	0,11, <i>l</i>		3	96	+112	4	32	+ 18
1	37	- 33	5	183*	+233	6	< 17	- 8
2	33	- 28	7	95	+ 98	8	43	+ 40
3	< 15	- 7	9	57	+ 58	10	64	- 64
4	33	- 29	11	139	+136	12	77	- 71
5	< 15	- 5	13	20	- 16	14	33	- 33
6	37	- 37	15	53	- 43	16	37	- 37
7	19	- 18	17	< 16	- 5			
8	29	- 30	19	42	- 46			
9	27	+ 30					$\bar{4}0l$	
10	18	- 17	0	20 <i>l</i>		2	54	+ 46
11	31	+ 32	2	224*	-259	4	95	+101
			4	230	-220	6	< 17	+ 4
	0,12, <i>l</i>		6	52	+ 47	8	60	- 51
0	62	- 71	8	67	- 72	10	29	- 29
1	15	- 19	10	< 15	+ 4	12	49	- 55
2	27	- 32	12	124	+118	14	62	- 59
3	13	+ 10	14	60	+ 54	16	37	- 42
4	< 13	- 13		58	+ 54			

l	F_o	F_c	l	F_o	F_c	l	F_o	F_c
	$50l$			$60l$		5	27	+ 31
1	19	- 20	0	19	- 15	7	48	+ 49
3	42	- 45	2	93	- 88	9	42	+ 42
5	52	- 55	4	52	- 57			
7	87	- 89	6	18	+ 19			
9	53	- 50	8	< 17	+ 4		$\bar{7}0l$	
11	< 17	- 9	10	15	+ 18	1	28	- 24
13	26	- 24	12	54	+ 57	3	47	- 52
15	< 9	- 1				5	< 15	- 16
				$\bar{6}0l$		7	43	- 49
			2	56	- 56	9	39	- 47
			4	47	- 50			
			6	22	+ 18		$80l$	
			8	17	+ 16	0	14	+ 16
			10	15	+ 29	2	23	+ 28
			12	26	+ 30			
				$70l$				
			1	22	+ 26		$\bar{8}0l$	
			3	16	+ 17	2	34	+ 40
	$\bar{5}0l$							
1	< 17	+ 5						
3	114	+ 114						
5	51	+ 51						
7	30	+ 33						
9	96	+ 99						
11	< 17	+ 9						
13	20	- 17						
15	< 11	+ 5						

the direction of the tellurium-carbon bond. Drawings of the molecules are reproduced in Fig. 2.

The Te—S bond length, 2.50 Å in both compounds, is a little larger than the sum of the single-bond radii, 2.41 Å, and the lengths, *cf.* Ref. 4, of about 2.37 Å found for this bond in uncomplexed divalent tellurium-sulphur compounds.

The Te—Cl and Te—Br bonds, which occur in *trans* positions to the Te—S bonds, are 0.64 and 0.60 Å, respectively, longer than the sum of the single-bond radii, but considerably shorter than van der Waals contacts.

Table 4. Dimensions of the coordination groups.

	Chloro compound	Bromo compound
Te—Cl	3.00 ± 0.015 Å	
Te—Br		3.11 ± 0.01 Å
Te—S	2.50 ± 0.015	2.50 ± 0.015
Te—C ₁	2.12 ± 0.06	2.12 ± 0.06
S—C ₁	1.78 ± 0.06	1.78 ± 0.06
∠S—Te—Cl	171.9 ± 0.5°	
∠S—Te—Br		174.1 ± 0.5°
∠S—Te—Mp	89.6 ± 1.0	89.8 ± 1.0
∠Cl—Te—Mp	83.6 ± 1.0	
∠Br—Te—Mp		85.9 ± 1.0
∠Te—S—C ₁	109.5 ± 2.0	107.8 ± 2.0
Te...Cl'	3.71 ± 0.015 Å	
Te...Br'		3.77 ± 0.01 Å
∠Mp—Te...Cl'	164.4 ± 1.0°	
∠Mp—Te...Br'		164.2 ± 1.0°

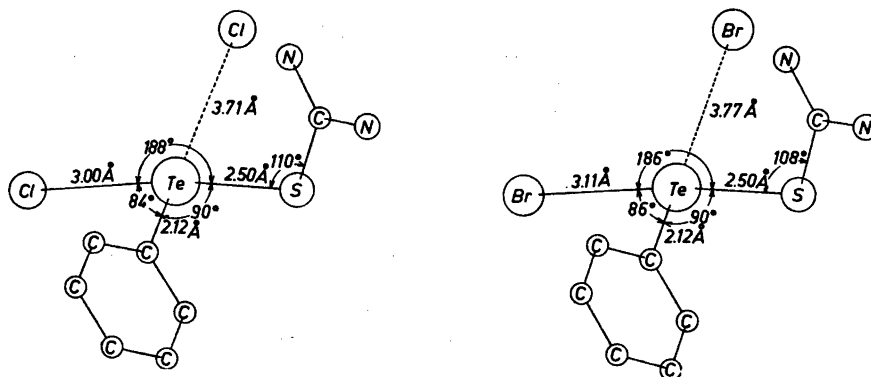


Fig. 2. The molecules as seen along the *b* crystal axes, included a chlorine or bromine atom of an adjacent, symmetry-related molecule.

In *cis*-dichloro- and *cis*-dibromo-dithioureatellurium(II),⁴ Te(tu)₂Cl₂ and Te(tu)₂Br₂, where likewise halogen and thiourea occur in *trans* positions, the Te—S bonds were found to be 2.48 and 2.47 Å, respectively, and Te—Cl = 2.92 Å, Te—Br = 3.05 Å. The sums of the lengths of *trans*-positioned Te—S and Te—Cl bonds are thus 5.50 Å in I and 5.40 Å in *cis*-Te(tu)₂Cl₂, and of *trans*-positioned Te—S and Te—Br bonds, 5.61 Å in II and 5.52 Å in *cis*-Te(tu)₂Br₂. In *trans*-dibromo- and *trans*-diiodo-bis(ethylenethiourea)tellurium(II),⁸ Te(etu)₂Br₂ and Te(etu)₂I₂, Te—S = 2.69 Å while Te—Br = 2.78 Å and Te—I = 2.97 Å, indicating a bonding radius of 1.64 Å for tellurium(II) in centrosymmetric square-planar complexes. There, in *trans*-Te(etu)₂Br₂, the sum of the lengths of the Te—S and Te—Br bonds is 5.47 Å. Thus, although in tellurium(II) complexes with thiourea in *trans* positions to halogen, the Te—S bonds are shorter and the Te—halogen bonds are longer, the sum of the Te—S and Te—halogen bond lengths increases only slightly, relative to the sum in centrosymmetric complexes.

The *trans* bond-lengthening effect of the phenyl group is more pronounced than that of thiourea. In the present compounds, as in phenylbis(thiourea)-tellurium(II) chloride,² the fourth position of square-planar coordination, *trans* to the phenyl group, is virtually vacant. In I, a chlorine atom of an adjacent molecule, related to Cl of Table 1 through the symmetry centre at $\frac{1}{2}, 0, 0$, lies 3.71 Å from tellurium in a direction which makes an angle of 164° with the direction of the Te—C bond. In II, the corresponding bromine atom lies 3.77 Å from tellurium, at an angle of 164°. These atoms, although at such distances as to indicate only very weak bonding interaction with tellurium, approach the fourth coordination site of square-planar structures.

As in *cis*-Te(tu)₂Cl₂ and *cis*-Te(tu)₂Br₂,⁴ the substitution of bromine for chlorine has, within the error, no effect on the length of the Te—S bond *trans* to chlorine or bromine.

The least-squares plane through the coordinate midpoint of the phenyl carbon atoms, and through the heavier atoms, passes at distances of 0.001,

0.071, -0.040 , and -0.033 Å, respectively, from Mp, Te, S, and Cl in I, and at 0, 0.067, -0.038 , and 0.031 Å from Mp, Te, S, and Br in II. The chlorine and bromine atoms of adjacent molecules, referred to above, lie 0.99 and 1.07 Å, respectively, out of these planes. The carbon and nitrogen coordinates correspond to planar phenyltellurium and thiourea groups within 0.02 Å. The phenyltellurium plane makes angles of 52° and 55° , respectively, with the MpTeSCl and MpTeSBr planes, the latter planes make an angle of 69° with the thiourea plane in I and 70° in II. The carbon and nitrogen coordinates give the bond lengths, $C_1-N_1 = 1.35$ and 1.34 Å, $C_1-N_2 = 1.32$ and 1.34 Å, and the bond angles, $S-C_1-N_1 = 123^\circ$ and 125° , $S-C_1-N_2 = 117^\circ$ and 116° , $N_1-C_1-N_2 = 119^\circ$ and 119° , for the thiourea group in I and II, respectively.

Some relatively close non-bonded Te-Te approaches occur, over the symmetry centres at 0,0,0 and $\frac{1}{2}, 0, 0$: 4.25 and 4.13 Å, respectively, in I, and 4.28 and 4.41 Å in II. Zigzagging chains of tellurium atoms, around $x, 0, 0$, thus run through the crystals in the direction of the a axes.

HYDROGEN BONDING

The closest nitrogen-halogen approaches occur between N_1 and the halogen atoms at $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$, where x, y, z are the halogen coordinates of Table 1. These halogen atoms lie 0.29 and 0.28 Å out of the thiourea planes, at N...Cl and N...Br distances of 3.22 and 3.32 Å, respectively, and C-N...Cl and C-N...Br angles of 106° . They probably represent N-H...Cl and N-H...Br hydrogen bonds. The corresponding distances to N_2 are 3.48 and 3.54 Å, respectively, and the angles, 95° and 96° . The halogen atoms at $1 - x, \bar{y}, \bar{z}$ lie 1.69 Å out of the thiourea planes, 3.53 and 3.55 Å from N_1 in I and II, respectively, and at C-N...Cl and C-N...Br angles of 111° and 112° . The standard deviations of the nitrogen-halogen distances are 0.05–0.07 Å. In $Te(tu)_2Cl_2$ and $Te(tu)_2Br_2$,⁴ N-H...Cl approaches of 3.15 to 3.44 Å and N-H...Br approaches of 3.33 to 3.52 Å occur.

The work has been aided by a grant from *Norges Almenvitenskapelige Forskningsråd*.

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Received August 2, 1965.