

The Crystal Structure of Phenylbis(thiourea)tellurium(II) Chloride

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The crystals of the compound, $C_6H_5Te(tu)_2Cl$ where $tu =$ thiourea, have been shown by X-ray analysis to be built up of phenylbis(thiourea)tellurium(II) cations, $C_6H_5Te(tu)_2^+$, and chloride ions. The crystals are orthorhombic, space group $D_{2h}^{14} - P2_12_12_1$ with $Z = 4$, and $a = 11.98 \text{ \AA}$, $b = 20.80 \text{ \AA}$, $c = 5.79 \text{ \AA}$. The structure was refined by least squares for the $hk0$, hkl , and $0kl$ reflections.

Each tellurium atom is bonded to a phenyl carbon atom, at $Te-C = 2.11 \pm 0.04 \text{ \AA}$, and to two thiourea sulphur atoms, at $Te-S_1 = 2.612 \pm 0.014 \text{ \AA}$, $Te-S_2 = 2.741 \pm 0.017 \text{ \AA}$, $\angle S_1-Te-S_2 = 172.0 \pm 0.4^\circ$, $\angle S_1-Te-C$ and $\angle S_2-Te-C = 86.1 \pm 0.8^\circ$. The mean length of the two, nearly linear $Te-S$ bonds is the same as found for $Te-S$ in centrosymmetric, square-planar tellurium(II) complexes.

The structure of the phenylbis(thiourea)tellurium(II) cation may be regarded as based on square-planar coordination with one position, *trans* to the phenyl group, vacant. The fourth ligand would be the chloride ion, which lies at a distance of 3.61 \AA from tellurium in a direction which makes an angle of 163° with the direction of the $Te-C$ bond.

Structures of tellurium(II) complexes reported recently include tetra-thioureatellurium(II) dichloride and the corresponding dihydrate,¹ *trans* square-planar complexes of tellurium dibromide and diiodide with ethylene-thiourea² and of tellurium dimethanethiosulphonate with thiourea,³ *cis* square-planar complexes of tellurium dichloride and dibromide with thiourea,⁴ and trithioureatellurium(II) hydrogendifluoride⁵ where four-coordination arises through dimerization to a binuclear complex ion. The present and a following article report the structures of tellurium(II) complexes containing a phenyl group as one of the ligands. This leads to three-coordination instead of the square-planar four-coordination encountered in the crystals of the compounds referred to above. The crystal structure of phenylbis(thiourea)tellurium(II) chloride is described here, some features of the structure have been briefly reported earlier.⁶

CRYSTAL DATA

The salt, $C_6H_5Te(tu)_2Cl$ where $tu =$ thiourea, crystallizes on addition of a little more than four moles of aqueous thiourea to one mole of methanolic phenyltellurium trichloride.⁷ It may be recrystallized from aqueous thiourea, preferably in presence of a small amount of hydrochloric acid. The nitrate, perchlorate, and thiocyanate have also been obtained.⁷

The crystals are yellow and occur as long orthorhombic prisms elongated in the direction of the c axis. The axial lengths are,⁷ $a = 11.98 \text{ \AA}$, $b = 20.80 \text{ \AA}$, $c = 5.79 \text{ \AA}$, and the space group, from systematic absences, is $D_2^4 - P2_12_12_1$. There are four formula units per unit cell.

Intensities were estimated visually from Weissenberg photographs taken with $CuK\alpha$ radiation: zero-layer and first-layer equi-inclination photographs around the c axis and zero-layer photographs around the a axis, the a -axis photographs gave rather weak intensities. $225 \ hk0$ and $235 \ hkl$ reflections were observed with measurable intensities, out of 312 and 315, respectively, attainable with $CuK\alpha$ radiation. Of the 116 attainable $0kl$ reflections with $l > 1$, only 44 were observed. Small crystals were used in order to minimize absorption ($\mu = 216 \text{ cm}^{-1}$). The hkl intensities were corrected for the effects of spot extension and contraction by the method of Phillips.⁸

THE STRUCTURE ANALYSIS

The approximate tellurium coordinates were found from Patterson line sections at $u = \frac{1}{2}$, $v = \frac{1}{2}$, $w = \frac{1}{2}$, in the projections along the c and a axes. The coordinates found, $x = 0.426$, $y = 0.118$, $z = 0.358$, are very close to the final values. Fourier summations of the 162 strongest $hk0$ reflections and 54 strongest $0kl$ reflections, with signs based on the tellurium contributions, gave the sulphur and chlorine positions. The carbon and nitrogen atoms of the thiourea groups and the carbon atoms of the phenyl group were placed partly on the basis of the subsequent Fourier maps, and partly from dimensional considerations. Difference syntheses brought the reliability index, R , down to 0.14 for the $hk0$ zone and 0.11 for the $0kl$ zone. The former value was reduced to 0.12 through two cycles of least-squares refinement for the $hk0$ data.

The final refinement was carried out by least squares on the IBM 1620 II computer, using Mair's⁹ program and his weighting scheme No. 3 with $a = 96$ and $b = 60$. The refinement comprised 471 observed, independent $hk0$, hkl , and $0kl$ reflections. The strong reflections, 120, 160, 200, 310, and 021, which probably suffer from extinction, were omitted, and likewise the weakest hkl reflections. The $0kl$ and $hk0$ data were used to scale the hkl data before the first cycle, and the scale factors were adjusted after the third cycle. Anisotropic temperature parameters for tellurium, chlorine, and sulphur were introduced in the sixth cycle, and two additional cycles were carried out. Some of the early shifts in the carbon and nitrogen coordinates led to unreasonable molecular dimensions and were not considered genuine. Before the fourth cycle, the carbon and nitrogen coordinates were adjusted on the basis of the known dimensions of thiourea and phenyl groups, and were restored to these values after each subsequent cycle.

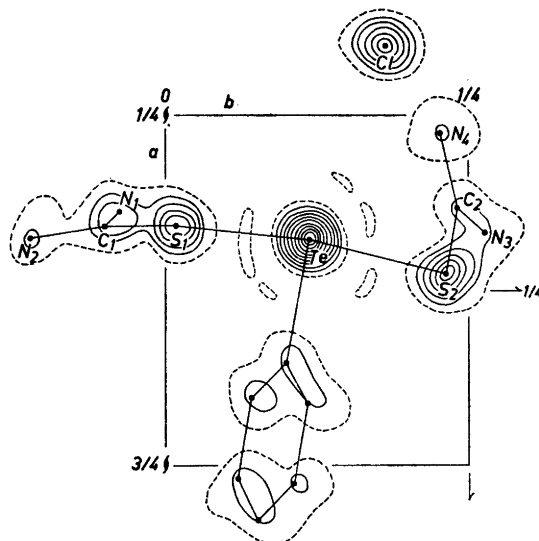


Fig. 1. Electron density projection of phenylbis(thiourea)tellurium(II) chloride along the c axis. The 3-electron line is dashed. Contour intervals: $10 e \cdot \text{\AA}^{-2}$ for tellurium, and $4 e \cdot \text{\AA}^{-2}$ for the other atoms.

The $hk0$ Fourier map is shown in Fig. 1. The final atomic coordinates are listed in Table 1, and the anisotropic temperature parameters in Table 2. The final isotropic parameters, B in $\exp[-B(\sin^2\theta/\lambda^2)]$, were 6.0 \AA^2 for the nitrogen atoms, 3.6 \AA^2 for the thiourea carbon atoms, and 4.8 \AA^2 for the phenyl carbon atoms. These B values were assigned, as averages, before the last least-squares cycle.

Table 1. Atomic coordinates for phenylbis(thiourea)tellurium(II) chloride, in fractions of cell edges. Origin halfway between three pairs of non-intersecting screw axes.

	x	y	z
Te	0.4270	0.1181	0.360
Cl	0.1489	0.1804	0.440
S ₁	0.4079	0.0098	0.585
C ₁	0.409	-0.050	0.366
N ₁	0.391	-0.037	0.144
N ₂	0.426	-0.111	0.428
S ₂	0.4775	0.2313	0.141
C ₂	0.380	0.241	-0.092
N ₃	0.416	0.264	-0.293
N ₄	0.273	0.226	-0.060
C ₃	0.601	0.101	0.367
C ₄	0.654	0.072	0.177
C ₅	0.768	0.061	0.181
C ₆	0.828	0.078	0.376
C ₇	0.775	0.107	0.566
C ₈	0.661	0.118	0.562

Table 3. Observed and calculated $hk0$ and hkl structure amplitudes for phenylbis(thiourea)-tellurium(II) chloride.

k	$ F_o $	$ F_c $	k	$ F_o $	$ F_c $	k	$ F_o $	$ F_c $	k	$ F_o $	$ F_c $
	0k0		11	76	76	10	46	37	11	33	25
2	< 4	7	12	50	52	11	83	94	12	72	68
4	86	99	13	< 13	11	12	< 14	2	13	< 15	9
6	94	114	14	37	28	13	< 14	1	14	38	33
8	147	177	15	28	24	14	42	36	15	41	35
10	65	72	16	33	31	15	67	69	16	47	40
12	67	64	17	23	19	16	34	32	17	< 16	3
14	79	76	18	41	31	17	36	25	18	50	44
16	96	84	19	51	54	18	< 16	9	19	25	23
18	68	71	20	19	19	19	66	66	20	< 14	4
20	43	43	21	23	22	20	< 15	2	21	< 13	14
22	30	21	22	< 14	13	21	< 15	3	22	35	31
24	< 12	7	23	25	24	22	< 14	8	23	< 11	7
26	27	28	24	< 12	10	23	22	23	24	13	13
			25	< 10	2	24	< 11	6			
			26	17	16	25	< 9	5			
	1k0			3k0			5k0			7k0	
1	63	66	1	180	245	1	94	93	1	45	34
2	109	150	2	81	71	2	94	90	2	108	108
3	50	58	3	52	50	3	48	39	3	44	38
4	21	24	4	44	46	4	47	43	4	22	13
5	72	75	5	92	95	5	98	110	5	< 13	3
6	117	144	6	30	26	6	103	109	6	86	88
7	52	61	7	92	92	7	42	35	7	21	22
8	75	84	8	15	5	8	23	16	8	< 14	2
9	57	58	9	116	121	9	116	120	9	< 14	4
10	135	157	10	< 12	5	10	47	40	10	58	53
11	< 12	7	11	24	19	11	56	54	11	19	15
12	32	30	12	15	6	12	73	69	12	73	68
13	51	46	13	84	93	13	36	35	13	< 16	5
14	34	28	14	< 14	7	14	39	34	14	50	50
15	18	7	15	17	15	15	< 16	13	15	< 16	11
16	38	33	16	39	27	16	< 16	3	16	30	24
17	54	47	17	94	89	17	44	41	17	< 16	0
18	66	59	18	30	24	18	32	28	18	34	41
19	< 16	6	19	< 16	7	19	< 15	2	19	19	12
20	46	45	20	< 16	10	20	44	40	20	27	29
21	< 15	10	21	38	37	21	30	34	21	< 12	5
22	< 15	7	22	< 14	8	22	< 13	9	22	< 11	19
23	< 14	3	23	< 13	8	23	< 12	6	23	< 9	1
24	25	24	24	< 12	0	24	< 10	12			
25	< 11	10	25	28	27					8k0	
26	18	18					6k0		0	65	64
	2k0			4k0		0	126	139	1	57	46
0	109	135	0	125	125	1	101	90	2	34	26
1	71	75	1	135	141	2	73	71	3	52	46
2	10	15	2	70	60	3	53	37	4	100	98
3	22	15	3	54	49	4	81	85	5	47	43
4	32	32	4	59	45	5	18	10	6	19	15
5	15	4	5	72	75	6	32	26	7	19	14
6	35	27	6	40	40	7	30	31	8	74	73
7	140	162	7	99	98	8	124	130	9	< 15	0
8	116	139	8	21	15	9	21	9	10	38	32
9	81	89	9	64	62	10	50	47	11	46	45
10	28	23							12	52	55

k	$ F_o $	$ F_c $	k	$ F_o $	$ F_c $	k	$ F_o $	$ F_c $	k	$ F_o $	$ F_c $
13	< 16	16	2	32	30	7	14	12	24	< 15	8
14	22	20	3	46	46	8	19	22	25	< 13	19
15	31	30	4	< 16	0	9	< 9	5			
16	36	36	5	47	49					2k1	
17	21	15	6	22	17	15,k,0			0	62	66
18	20	20	7	39	39	1	14	20	1	77	76
19	30	32	8	< 16	4	2	17	24	2	130	128
20	19	19	9	32	31	3	11	15	3	73	72
21	< 11	12	10	< 15	9				4	79	71
22	21	22	11	< 15	6				5	104	102
			12	29	29	0k1			6	88	73
	9k0		13	49	56	2	136	176	7	32	30
1	70	70	14	< 13	3	3	151	164	8	118	114
2	47	42	15	< 12	12	4	< 8	3	9	75	76
3	< 15	3	16	< 11	10	5	139	128	10	103	93
4	34	28	17	25	26	6	93	98	11	79	69
5	75	75				7	17	20	12	41	39
6	55	54		12,k,0		8	101	90	13	65	66
7	53	52	0	50	55	9	19	10	14	28	22
8	< 16	0	1	< 16	4	10	58	53	15	26	17
9	58	55	2	19	16	11	100	104	16	47	49
10	41	34	3	44	47	12	< 16	9	17	37	41
11	< 16	4	4	38	36	13	24	26	18	38	36
12	< 16	6	5	29	24	14	38	43	19	< 20	21
13	51	51	6	< 15	5	15	54	57	20	< 20	10
14	40	41	7	31	33	16	55	55	21	25	26
15	28	24	8	27	29	17	30	26	22	22	23
16	< 14	11	9	18	15	18	42	44	23	< 16	16
17	26	26	10	25	25	19	40	45	24	19	22
18	< 13	10	11	27	30	20	< 21	19	25	15	22
19	21	20	12	16	21	21	< 19	6			
20	< 10	13	13	19	19	22	< 18	21			
21	24	27	14	< 11	14	23	< 17	15		3k1	
			15	17	21	24	28	27	0	73	80
						25	< 13	4	1	77	77
	10,k,0								2	114	113
0	< 15	7		13,k,0			1k1		3	87	81
1	25	24	1	< 14	5	2	31	34	4	< 11	3
2	28	22	2	32	34	3	13	9	5	87	82
3	77	73	3	21	20	4	127	130	6	67	67
4	33	32	4	21	18	5	153	154	7	92	89
5	55	53	5	21	22	6	77	74	8	26	31
6	< 16	7	6	36	43	7	112	110	9	26	28
7	45	37	7	< 13	10	8	97	96	10	69	67
8	< 16	16	8	< 13	12	9	98	96	11	68	63
9	21	16	9	< 12	2	10	24	24	12	54	53
10	< 16	5	10	31	37	11	48	47	13	38	38
11	55	56	11	< 11	0	12	95	90	14	37	34
12	< 15	7	12	15	14	13	67	61	15	59	62
13	< 15	5	13	16	17	14	53	49	16	< 19	16
14	< 14	8				15	54	50	17	< 20	11
15	32	35		14,k,0		16	28	27	18	40	40
16	17	16	0	31	39	17	35	35	19	37	42
17	< 12	8	1	< 12	7	18	40	45	20	25	34
18	< 11	6	2	< 12	0	19	30	28	21	< 19	6
19	21	29	3	< 12	2	20	< 20	23	22	< 17	13
			4	33	44	21	25	27	23	20	30
	11,k,0		5	< 11	9	22	20	21	24	< 14	7
1	44	42	6	< 11	0	23	< 17	14	25	< 12	12

k	$ F_o $	$ F_c $	k	$ F_o $	$ F_c $	k	$ F_o $	$ F_c $	k	$ F_o $	$ F_c $
	$4k1$		4	67	62	12	24	21	2	46	45
0	128	143	5	24	23	13	39	41	3	40	44
1	120	112	6	103	100	14	36	38	4	24	24
2	41	39	7	73	68	15	20	22	5	35	36
3	99	93	8	35	33	16	28	29	6	24	23
4	81	79	9	59	55	17	< 18	17	7	28	27
5	82	77	10	58	54	18	< 17	27	8	< 19	15
6	70	59	11	58	57	19	20	22	9	19	19
7	24	20	12	34	35	20	< 14	16	10	26	25
8	85	81	13	< 19	8	21	< 13	14	11	31	38
9	77	78	14	52	58				12	< 18	15
10	46	46	15	< 20	12				13	< 17	10
11	51	51	16	35	35		$9k1$		14	< 16	21
12	58	56	17	24	27	0	32	28	15	< 24	30
13	69	65	18	< 19	11	1	< 19	17	16	< 13	18
14	35	34	19	25	32	2	34	30	17	< 12	15
15	< 19	12	20	20	25	3	64	61			
16	51	53	21	< 16	15	4	32	31		$12,k,1$	
17	51	55	22	< 14	14	5	48	50	0	22	19
18	27	30	23	< 12	12	6	34	36	1	30	29
19	24	25				7	44	42	2	25	30
20	20	21		$7k1$		8	39	38	3	21	18
21	22	27	0	77	73	9	36	34	4	19	23
22	< 17	16	1	91	87	10	57	57	5	30	31
23	< 15	9	2	< 16	9	11	50	47	6	29	35
24	< 13	13	3	59	55	12	< 20	20	7	27	29
			4	109	110	13	< 20	23	8	34	35
			5	39	38	14	< 19	7	9	22	22
	$5k1$		6	< 17	10	15	25	30	10	< 17	15
0	59	57	7	27	28	16	20	22	11	16	19
1	109	104	8	62	54	17	< 17	13	12	18	25
2	59	55	9	60	49	18	< 15	18	13	16	23
3	67	59	10	33	36	19	16	15	14	13	14
4	125	120	11	< 19	3	20	< 12	19	15	< 11	17
5	37	36	12	51	51						
6	92	84	13	38	38		$10,k,1$				
7	101	85	14	44	45	0	76	74		$13,k,1$	
8	20	20	15	< 20	7	1	44	44	0	21	25
9	98	85	16	31	32	2	< 20	14	1	17	19
10	67	59	17	38	46	3	40	38	2	21	17
11	44	43	18	22	26	4	24	23	3	21	20
12	60	55	19	< 18	8	5	56	59	4	31	36
13	24	22	20	< 16	18	6	28	19	5	25	29
14	51	47	21	< 15	17	7	29	25	6	< 16	13
15	33	32	22	< 13	19	8	49	46	7	< 16	14
16	< 20	19				9	39	37	8	20	26
17	36	35		$8k1$		10	< 20	9	9	19	27
18	26	24	0	84	80	11	< 19	5	10	< 14	14
19	27	25	1	54	50	12	< 19	21	11	< 13	17
20	19	23	2	63	58	13	41	44			
21	< 17	11	3	38	36	14	< 18	14		$14,k,1$	
22	19	21	4	23	19	15	< 17	17	0	< 15	4
23	17	21	5	44	39	16	< 16	20	1	16	23
24	12	15	6	68	60	17	< 15	24	2	24	32
			7	57	53	18	13	21	3	< 14	13
	$6k1$		8	38	36	19	< 11	5	4	< 14	3
0	42	42	9	33	26				5	< 13	16
1	45	48	10	51	52		$11,k,1$		6	16	24
2	71	67	11	31	29	0	< 20	18	7	< 12	16
3	66	58				1	35	35	8	< 11	7

Table 4. Dimensions of the coordination group.

Te—S ₁ = 2.612 ± 0.014 Å	∠S ₁ —Te—S ₂ = 172.0 ± 0.4°
Te—S ₂ = 2.741 ± 0.017	∠S ₁ —Te—Mp = 86.1 ± 0.8
Te—C ₂ = 2.11 ± 0.04	∠S ₂ —Te—Mp = 86.1 ± 0.8
S ₁ —C ₁ = 1.78 ± 0.07	∠Te—S ₁ —C ₁ = 104.3 ± 2.3
S ₂ —C ₂ = 1.80 ± 0.07	∠Te—S ₂ —C ₂ = 107.5 ± 1.8
Te...Cl = 3.606 ± 0.011	∠Mp—Te...Cl = 163.4 ± 0.8

rium and sulphur atoms, with the tellurium coordinates given four times the weight of the others, passes 0.004 Å from Mp, and -0.037, 0.017, and -0.034 Å from S₁, Te, and S₂, respectively. The arrangement is thus very nearly planar.

The average Te—S bond length, 2.676 Å, is within the error equal to the Te—S bond length in the centrosymmetric Te(tu)₄²⁺ cation, and in the centrosymmetric, *trans* square-planar complexes of tellurium dibromide and diiodide with ethylenethiourea² and of tellurium dimethanethiosulphonate with thiourea:³ the weighted average of eight individual values for Te—S bonds in these compounds is 2.683 Å, with an average deviation of 0.005 Å.

The chloride ion lies -0.78 Å from the MpTeS₁S₂ least-squares plane, 3.61 Å from tellurium in a direction which makes an angle of 163° with the direction of the tellurium-carbon bond. This Te...Cl distance is smaller than the sum of the van der Waals radii, and indicates some, although very weak, bonding interaction between tellurium and chlorine.

The tellurium atom is thus primarily three-coordinated. In view of the tendency of divalent tellurium to form four-coordinated, square-planar complexes, the arrangement may be regarded as based on square-planar coordination with one position, opposite to the phenyl group, vacant. This indicates a pronounced *trans* bond-lengthening effect of the phenyl group.

The carbon and nitrogen coordinates correspond to planar phenyltellurium and thiourea groups, with all atoms within 0.01 Å of the least-squares planes. In the thiourea groups, C—N = 1.33 Å, ∠S—C—N = 118°—123°, ∠N—C—N = 119° and 121°, and in the phenyl ring, C—C = 1.38—1.41 Å and the bond angles, 119°—121°. The phenyltellurium plane is nearly orthogonal (85°) to the MpTeS₁S₂ plane; the thiourea planes make angles of 89° and 46° with the MpTeS₁S₂ plane, and an angle of 84° with each other.

HYDROGEN BONDING

The chloride ions, Cl_A(*x, y, z*) and Cl_B($\frac{1}{2} + x, \frac{1}{2} - y, \bar{z}$) where *x, y, z* are the chlorine coordinates of Table 1, both lie 0.29 Å out of the plane of the S₂ thiourea group, at distances N₃...Cl_B = 3.14 Å and N₄...Cl_A = 3.39 Å, and at C—N...Cl angles of 131° and 127°, respectively. These approaches probably represent N—H...Cl hydrogen bonds. The chloride ion Cl_C($\frac{1}{2} - x, \bar{y}, z - \frac{1}{2}$) lies 0.72 Å out of the plane of the S₁ thiourea group, 3.24 Å from N₁ and 3.29 Å from N₂, at C—N...Cl angles of 101° and 98°, respectively, and at a N₁...Cl

$\cdots N_2$ angle of 41° . N_2 probably also engages to $Cl_D(\frac{1}{2}-x, \bar{y}, \frac{1}{2}+z)$ which lies 1.45 Å out of the plane, 3.41 Å from N_2 , at a $C-N\cdots Cl$ angle of 127° and a $Cl\cdots N_2\cdots Cl_D$ angle of 119° . These distances, 3.14 to 3.41 Å, lie in the range reported for $N-H\cdots Cl$ hydrogen bonds in other thiourea compounds.¹

Each chloride ion thus takes part in five hydrogen bonds, from four different thiourea groups.

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