

The Crystal and Molecular Structures of *cis* Square-Planar Complexes of Tellurium Dichloride and Dibromide with Thiourea

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The compounds, $\text{Te}(\text{tu})_2\text{Cl}_2$ (I) and $\text{Te}(\text{tu})_2\text{Br}_2$ (II) where tu = thiourea, form isomorphous crystals, space group C_{2h}^6-I2/c with four molecules per unit cell, of dimensions, $a = 9.90 \text{ \AA}$, $b = 7.62 \text{ \AA}$, $c = 14.10 \text{ \AA}$, $\beta = 100\frac{1}{2}^\circ$ for I, and $a = 10.10 \text{ \AA}$, $b = 7.74 \text{ \AA}$, $c = 14.67 \text{ \AA}$, $\beta = 100^\circ$ for II. The crystal and molecular structures have been determined by X-ray methods, and refined by difference syntheses for the $h0l$ and $0kl$ projections.

The tellurium atoms lie on twofold axes of symmetry, and are each bonded to two sulphur atoms and two halogen atoms in a distorted square-planar, *cis* arrangement. The TeS_2Cl_2 and TeS_2Br_2 groups have the dimensions: $\text{Te}-\text{S} = 2.48 \pm 0.02 \text{ \AA}$, $\text{Te}-\text{Cl} = 2.92 \pm 0.015 \text{ \AA}$, $\angle\text{S}-\text{Te}-\text{S} = 92.8 \pm 0.7^\circ$, $\angle\text{S}-\text{Te}-\text{Cl} = 87.8 \pm 0.6^\circ$, $\angle\text{Cl}-\text{Te}-\text{Cl} = 92.6 \pm 0.5^\circ$ in I, and $\text{Te}-\text{S} = 2.47 \pm 0.03 \text{ \AA}$, $\text{Te}-\text{Br} = 3.05 \pm 0.01 \text{ \AA}$, $\angle\text{S}-\text{Te}-\text{S} = 95.0 \pm 1.0^\circ$, $\angle\text{S}-\text{Te}-\text{Br} = 86.7 \pm 0.7^\circ$, $\angle\text{Br}-\text{Te}-\text{Br} = 93.0 \pm 0.3^\circ$ in II. The $\text{Te}-\text{S}$ bonds are thus shorter, and the $\text{Te}-\text{halogen}$ bonds, which occur *trans* to the $\text{Te}-\text{S}$ bonds in these *cis* complexes, are longer, than the bonds in corresponding *trans* tellurium(II) complexes, for example in *trans*- $\text{Te}(\text{etu})_2\text{Br}_2$ (etu = ethylenethiourea) where $\text{Te}-\text{S} = 2.69 \text{ \AA}$, $\text{Te}-\text{Br} = 2.78 \text{ \AA}$. The planes through the TeCl_2 and TeBr_2 parts of the groups make angles of 11° and 12° , respectively, with the TeS_2 planes.

The structures of *trans* square-planar complexes of tellurium dibromide and diiodide with ethylenethiourea, $\text{Te}(\text{etu})_2\text{Br}_2$ and $\text{Te}(\text{etu})_2\text{I}_2$, were reported recently.¹ The *cis* form of square-planar complexes of this type occurs in the crystals of the thiourea analogs, $\text{Te}(\text{tu})_2\text{X}_2$, where X = Cl, Br, or I. The crystals of the dichloro, dibromo, and diiodo compounds are isomorphous,^{2,3} the structures of the two former ones are described here.

Of the tellurium dihalide complexes TeL_2X_2 studied so far, those with L = tetramethylthiourea, X = Cl, Br, or I,⁴ with L = ethylenethiourea, X = Br or I,⁵ and with L = propylenethiourea, X = I,⁶ are square-planar

trans in the crystalline state, whereas those with L = thiourea, X = Cl, Br, or I,^{2,3} and with L = propylenethiourea, X = Cl or Br,⁷ are square-planar *cis*. The dichloro complex $\text{Te}(\text{etu})_2\text{Cl}_2$ has not been obtained; of $\text{Te}(\text{etu})_2\text{Br}_2$, a dimorph probably represents the *cis* isomer.⁵

The dihalodithiourea compounds $\text{Te}(\text{tu})_2\text{Cl}_2$ and $\text{Te}(\text{tu})_2\text{Br}_2$ crystallize on addition of about four moles of aqueous thiourea to one mole of tellurium dioxide dissolved in hydrochloric or hydrobromic acid. They were first reported by Vrestal⁸⁻¹⁰ in 1957-60 and, independently, by Foss and Hauge² in 1959. The latter authors pointed out the square-planar *cis* structure.

CRYSTAL DATA

Unit cell and space group data were reported by Nemeč¹¹ in 1958 and, independently, by Foss and Hauge² in 1959. Nemeč¹¹ also gave morphological data and drawings of the crystals.

The crystals of the two compounds, dichlorodithioureatellurium(II), $\text{Te}(\text{tu})_2\text{Cl}_2$ (I), and dibromodithioureatellurium(II), $\text{Te}(\text{tu})_2\text{Br}_2$ (II), are isomorphous, with ² $a = 9.90 \text{ \AA}$, $b = 7.62 \text{ \AA}$, $c = 14.10 \text{ \AA}$, $\beta = 100\frac{1}{2}^\circ$ for I, and $a = 10.10 \text{ \AA}$, $b = 7.74 \text{ \AA}$, $c = 14.67 \text{ \AA}$, $\beta = 100^\circ$ for II. These data, which are considered accurate to within 0.5 %, compare as follows with Nemeč's:¹¹ $a = 9.84 \text{ kX}$, $b = 7.58 \text{ kX}$, $c = 14.11 \text{ kX}$, β (morphological) = $100^\circ 50'$ for I, and $a = 10.04 \text{ kX}$, $b = 7.74 \text{ kX}$, $c = 14.2 \text{ kX}$, β (morphological) = $100^\circ 23'$ for II. The space group is C_{2h}^6-I2/c , and there are four molecules per unit cell; the tellurium atoms lie on twofold axes of symmetry.

Intensities were estimated visually from zero-level Weissenberg photographs around the a and b axes, taken with $\text{CuK}\alpha$ radiation using a double-film technique. The crystals employed had cross-sections of about 0.1 mm (I) and about 0.07 mm (II). 60 $0kl$ reflections and 82 $h0l$ reflections of I were observed with measurable intensities, out of 70 and 83, respectively, attainable with $\text{CuK}\alpha$ radiation; for II, the corresponding figures were 68 out of 77 $0kl$ reflections and 75 out of 92 $h0l$ reflections. The intensities of II were eventually corrected for secondary extinction,¹² with $2g = 4.5 \times 10^{-6}$ and 3.0×10^{-6} , respectively, for the $0kl$ and $h0l$ data.

THE STRUCTURE ANALYSES

The structure of the dichloro compound, I, was worked out first. With four molecules per unit cell, the centrosymmetric space group, $I2/c$, would require that the tellurium atoms lie in special positions, either on the twofold axes or in one of the two sets of symmetry centres. Atoms in the symmetry centres do not contribute to certain sets of reflections, and since no systematically weak sets of reflections were observed, it was considered more probable that the tellurium atoms lie on twofold axes. In the $h0l$ zone, the twofold axes project as centres. A Fourier synthesis of 52 of the strongest $h0l$ reflections, with positive signs, gave a map which revealed the approximate positions of all atoms. Sulphur and chlorine overlapped, but not exactly, and were

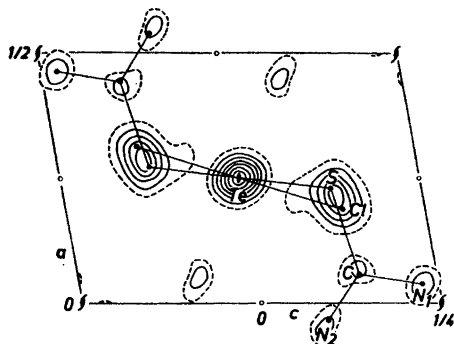


Fig. 1. Electron density projection of *cis*-Te(tu)₂Cl₂ along the *b* axis. The 6-electron line is dashed. Contour intervals: 14 e·Å⁻² for tellurium, 6 e·Å⁻² for chlorine and sulphur, and 2 e·Å⁻² for carbon and nitrogen.

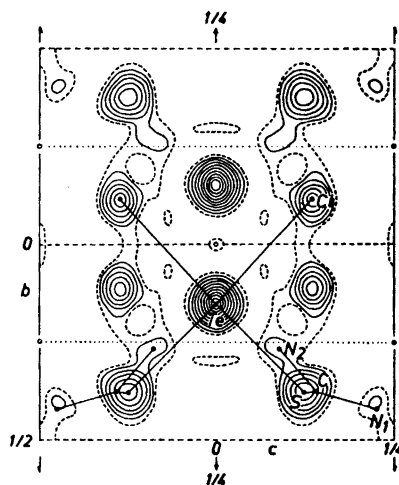


Fig. 2. Electron density projection of *cis*-Te(tu)₂Cl₂ along the *a* axis. The 6-electron line is dashed. Contour intervals: 10 e·Å⁻² for tellurium, 2 and thereafter 4 e·Å⁻² for the other atoms.

distinguished through recourse to the *a*-axis projection, where chlorine was clearly resolved whereas sulphur overlapped with carbon. The *0kl* Patterson map gave the approximate *y* coordinate of tellurium and also the approximate sulphur and chlorine positions; these three atoms gave the signs for a Fourier

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

Dichlorodithioureate tellurium(II)			
	<i>x</i>	<i>y</i>	<i>z</i>
Te	$\frac{1}{2}$	0.1525	0
Cl	0.187	-0.112	0.135
S	0.230	0.377	0.124
C	0.057	0.375	0.141
N ₁	0.036	0.421	0.227
N ₂	-0.037	0.267	0.089
Dibromodithioureate tellurium(II)			
	<i>x</i>	<i>y</i>	<i>z</i>
Te	$\frac{1}{2}$	0.1545	0
Br	0.1820	-0.1167	0.1355
S	0.2305	0.3700	0.1210
C	0.063	0.365	0.138
N ₁	0.043	0.438	0.216
N ₂	-0.038	0.284	0.082

Table 2. Observed and calculated $h0l$ and $0kl$ structure factors for dichlorodithioureate tellurium(II).

l	F_o	F_c	l	F_o	F_c	l	F_o	F_c
<i>h0l</i> zone			2	173	-168	<i>0kl</i> zone		
			4	58	-56			
	00 <i>l</i>		6	28	-31		00 <i>l</i>	
2	98	+142	8	75	-78	2	102	+147
4	36	-39	10	92	-87	4	39	-35
6	113	+130	12	27	-18	6	131	+138
8	222	+229				8	272	+238
10	84	+67		$\bar{6}0l$		10	92	+84
12	32	+25	2	43	-52	12	37	+31
14	88	+72	4	136	-137	14	109	+90
16	55	+55	6	150	-152	16	74	+71
			8	97	-80			
	20 <i>l</i>		10	32	-36		01 <i>l</i>	
0	206	-250	12	94	-85	1	69	+85
2	213	-292	14	63	-64	3	97	+125
4	33	+2	16	39	-41	5	79	+91
6	88	-112				7	92	+96
8	169	-182		80 <i>l</i>		9	29	+34
10	112	-104	0	55	+52	11	51	+48
12	< 24	+3	2	117	+107	13	61	+50
14	34	-38	4	101	+90	15	54	+42
16	63	-60	6	30	+22	17	< 14	+19
			8	35	+32			
	$\bar{2}0l$		10	51	+50		02 <i>l</i>	
2	81	-98				0	57	-61
4	69	-82		$\bar{8}0l$		2	97	-95
6	216	-252	2	61	+59	4	27	-32
8	178	-161	4	94	+92	6	34	-27
10	41	-37	6	106	+101	8	21	-26
12	61	-50	8	69	+64	10	40	-44
14	82	-78	10	80	+74	12	43	-38
16	56	-60	12	50	+52	14	24	-16
			14	38	+44	16	19	+15
	40 <i>l</i>							
0	221	+252		10,0, <i>l</i>			03 <i>l</i>	
2	208	+221	0	64	-59	1	106	-115
4	96	+87	2	50	-50	3	133	-153
6	23	+18	4	49	-47	5	151	-162
8	116	+122	6	31	-31	7	105	-105
10	93	+85				9	80	-76
12	36	+32		$\bar{1}0,0,l$		11	77	-75
14	34	-38	2	56	-60	13	76	-72
			4	65	-66	15	46	-52
	$\bar{4}0l$		6	52	-52			
2	36	+38	8	66	-62		04 <i>l</i>	
4	60	+65	10	44	-50	0	219	-216
6	194	+191	12	30	-46	2	80	-71
8	134	+145				4	31	+3
10	68	+65		12,0, <i>l</i>		6	101	-108
12	68	+55	0	29	+31	8	138	-145
14	89	+80				10	29	-34
16	41	+41		$\bar{1}2,0,l$		12	< 22	-5
			2	29	+40	14	50	-59
	60 <i>l</i>		4	32	+39			
0	123	-112	6	49	+50			

<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
	05 <i>l</i>		4	88	+ 84	11	43	+ 47
1	< 20	+ 4	6	69	+ 68		08 <i>l</i>	
3	< 20	+ 10	8	42	+ 43	0	40	+ 51
5	< 21	+ 15	10	42	+ 52	2	< 21	+ 12
7	< 23	- 5	12	43	+ 48	4	33	- 30
9	23	+ 19		07 <i>l</i>		6	< 19	+ 13
11	< 22	+ 6	1	59	+ 58	8	34	+ 32
13	< 18	- 2	3	76	+ 67		09 <i>l</i>	
	06 <i>l</i>		5	61	+ 66	1	29	- 31
0	54	+ 35	7	30	+ 39	3	30	- 33
2	89	+ 81	9	40	+ 45	5	18	- 24

synthesis of 37 of the strongest *Ok**l* reflections. The two projections were refined through Fourier syntheses and repeated difference syntheses.

The structure of the isomorphous dibromo compound, II, was solved in the same two projections, partly by reference to the dichloro compound. Refinement was made by difference syntheses, although three cycles of least-squares refinement of the *a*-axis projection were carried out on the Ferranti Mercury computer using Curtis' program¹³ and atomic scattering functions of Forsyth and Wells.¹⁴ The results indicated the need for secondary extinction corrections, which were performed for both projections, and refinement of each was concluded through two cycles of difference syntheses. The final structure-factor calculations were made on the IBM 650 computer using Shiono's program.¹⁵

The *a*- and *b*-axis Fourier maps of I are shown in Figs. 1 and 2. The final atomic coordinates are listed in Table 1, and observed and calculated *h*0*l* and *Ok**l* structure factors in Tables 2 and 3. The calculated structure factors are based on the Thomas-Fermi scattering curves for tellurium and bromine, those of Viervoll and Ögrim¹⁶ for chlorine and sulphur, and of Berghuis *et al.*¹⁷ for carbon and nitrogen. In the temperature factor $\exp[-B(\sin^2\theta/\lambda^2)]$ applied to the calculated structure factors, the values of *B* are, in Å² units: In the *h*0*l* zone of I, *B* = 4.0 for all atoms except tellurium; in the *Ok**l* zone, *B* = 4.0 for sulphur, carbon, and nitrogen, and 3.5 for chlorine. For tellurium in the *h*0*l* zone of I, *B* = 2.0 + 1.0 cos² φ , and in the *Ok**l* zone, *B* = 1.8 + 0.5 cos² φ , where φ is the angle between the normal of the reflecting plane and the direction of maximum vibration of the atom. This direction made in the *h*0*l* zone an angle of 60° with the *a* axis in the obtuse angle, and was in the *Ok**l* zone parallel to the *b* axis. In both zones of II, *B* = 1.7 for tellurium, 2.7 for bromine, 2.55 for sulphur, 2.35 for carbon, 2.65 for N₁ and 3.0 for N₂.

The reliability index, *R*, with non-observed reflections included when $|F_c|$ exceeds the observable limit, is 0.11 for the *h*0*l* zone of I and 0.12 for the *Ok**l* zone, 0.10 for the *h*0*l* zone of II and 0.11 for the *Ok**l* zone. The low order reflections of I, 200, 400, 002, $\bar{2}02$, 206, and $\bar{2}06$ in the *h*0*l* zone and 002 in the *Ok**l* zone, have markedly higher calculated than observed values. They were omitted from the last difference syntheses and calculations of scale factors, and were included in the final electron density maps with their cal-

Table 3. Observed and calculated $h0l$ and $0kl$ structure factors for dibromodithiureatellurium(II).

l	F_o	F_c	l	F_o	F_c	l	F_o	F_c
	$h0l$ zone							
	00l		2	217	-237	4	< 26	+ 15
2	126	+138	4	116	-112	6	62	+ 52
4	137	-156	6	< 36	+ 5	8	103	+ 91
6	171	+183	8	73	- 66			
8	299	+316	10	156	-180		$0kl$ zone	
10	57	+ 54	12	49	- 44		00l	
12	< 37	- 24	14	< 23	+ 7	2	121	+138
14	148	+148		$\bar{6}0l$		4	163	-157
16	102	+ 94	2	< 29	- 16	6	153	+183
18	< 20	+ 21	4	203	-234	8	332	+316
	20l		6	177	-154	10	60	+ 54
0	312	-337	8	49	- 42	12	32	- 24
2	355	-394	10	60	- 42	14	142	+148
4	126	-103	12	136	-131	16	96	+ 94
6	66	- 66	14	64	- 64	18	< 17	+ 21
8	273	-298	16	30	- 30		01l	
10	158	-153		80l		1	142	+142
12	48	+ 35	0	36	- 4	3	50	+ 48
14	43	- 33	2	140	+119	5	67	+ 50
16	131	-136	4	156	+169	7	207	+187
	$\bar{2}0l$		6	< 37	+ 25	9	48	+ 32
2	45	+ 33	8	< 35	+ 20	11	< 30	+ 11
4	32	- 43	10	96	+ 81	13	81	+ 61
6	285	-356		$\bar{8}0l$		15	90	+ 71
8	211	-217	2	109	+106	17	< 23	+ 14
10	49	+ 44	4	146	+134		02l	
12	91	- 76	6	80	+ 75	0	59	- 58
14	142	-125	8	50	+ 38	2	109	-113
16	65	- 77	10	132	+130	4	53	- 36
18	< 22	- 18	12	86	+ 76	6	40	- 28
	40l		14	< 29	+ 7	8	28	- 29
0	260	+230	16	59	+ 59	10	46	- 41
2	294	+338		10,0,l		12	59	- 53
4	104	+108	0	73	- 75	14	< 31	- 13
6	66	- 65	2	36	- 23	16	26	- 27
8	154	+173	4	90	- 89		03l	
10	157	+167	6	69	- 72	1	142	-156
12	< 37	+ 20	8	< 22	- 12	3	96	-100
14	< 32	+ 16		$\bar{1}0,0,l$		5	144	-155
16	85	+ 81	2	113	-106	7	159	-154
	$\bar{4}0l$		4	84	- 79	9	97	- 89
2	67	- 51	6	< 36	- 11	11	58	- 43
4	108	+103	8	106	- 89	13	89	- 91
6	287	+279	10	104	- 92	15	84	- 78
8	87	+ 79	12	< 26	- 16	17	34	- 29
10	55	+ 56		12,0,l			04l	
12	129	+102	0	67	+ 54	0	318	-321
14	131	+115	2	48	+ 44	2	78	- 70
16	< 32	+ 30		$\bar{1}2,0,l$		4	114	+109
18	45	+ 34	2	72	+ 76	6	125	-140
0	60l							
	84	- 55						

<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
8	200	-219		06 <i>l</i>		9	51	+ 52
10	< 31	- 9	0	64	+ 49	11	43	+ 36
12	39	+ 33	2	97	+ 99		08 <i>l</i>	
14	83	- 84	4	103	+ 90	0	87	+ 81
16	68	- 77	6	78	+ 71	2	< 30	+ 12
	05 <i>l</i>		8	59	+ 58	4	73	- 86
1	52	- 42	10	58	+ 65	6	26	+ 29
3	83	+ 74	12	54	+ 64	8	68	+ 68
5	51	+ 50	14	38	+ 25	10	< 17	- 24
7	59	- 46		07 <i>l</i>			09 <i>l</i>	
9	32	+ 22	1	89	+ 76	1	24	- 22
11	63	+ 48	3	68	+ 57	3	59	- 78
13	27	- 9	5	69	+ 81	5	38	- 36
15	38	- 23	7	59	+ 44	7	< 16	- 16

culated instead of observed values. The relatively weak reflections of I, 204 in the *h*0*l* zone and 044 in the 0*kl* zone, have near-zero calculated values, and were not included in the calculations of difference and electron density maps.

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 s.d. of the carbon and nitrogen coordinates are probably 0.04–0.06 Å in I and 0.05–0.07 Å in II.

RESULTS

Bond lengths and angles in the coordination groups, from the atomic coordinates of Table 1, are listed in Table 4 together with the estimated standard deviations. Drawings of the molecules are reproduced in Figs. 3

Table 4. Dimensions of the coordination groups.

	Dichloro complex	Dibromo complex
Te–Cl	2.92 ± 0.015 Å	
Te–Br		3.05 ± 0.01 Å
Te–S	2.48 ± 0.02	2.47 ± 0.03
S–C	1.77 ± 0.05	1.76 ± 0.07
∠Cl–Te–Cl	92.6 ± 0.5°	
∠Br–Te–Br		93.0 ± 0.3°
∠Cl–Te–S	87.8 ± 0.6	
	172.3 ± 0.5	
∠Br–Te–S		86.7 ± 0.7
		172.2 ± 0.6
∠S–Te–S	92.8 ± 0.7	95.0 ± 1.0
∠Te–S–C	107.1 ± 1.5	106.9 ± 2.0

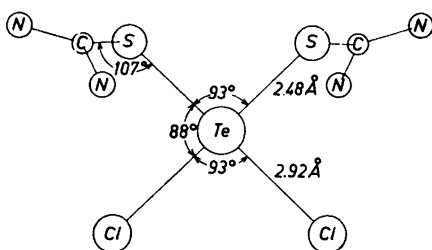


Fig. 3. The *cis*-Te(tu)₂Cl₂ molecule as seen normal to the plane bisecting the slightly diverging TeS₂ and TeCl₂ planes.

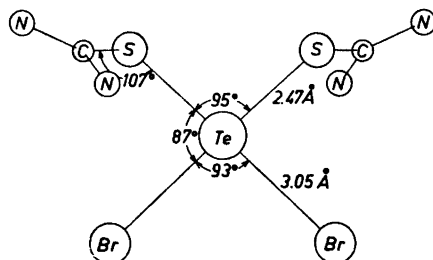


Fig. 4. The *cis*-Te(tu)₂Br₂ molecule seen in the same way as the dichloro analog in Fig. 3.

and 4. A twofold axis of symmetry, passing through the tellurium atom, interrelates the two halves of each molecule.

The TeS₂Cl₂ and TeS₂Br₂ groups are almost but not exactly planar; the angle between the TeS₂ and TeX₂ planes, which intersect in the twofold axis, is 10.7° in I and 11.7° in II. This corresponds to a bending of 7.7° of the Te—Cl bonds out of the TeS₂ plane, and a bending of 8.5° of the Te—Br bonds out of the TeS₂ plane, to opposite sides of the plane in accordance with the molecular twofold axis. The square-planar structure is distorted also with respect to bond angles at tellurium, which deviate from 90° by about 3°. The structures, however, clearly represent approaches toward the exactly planar TeS₂X₂ and TeS₄ arrangements found in centrosymmetric tellurium(II) complexes.^{1,18,19}

In centrosymmetric, *trans* square-planar dibromo- and diiodo-bis(ethylenethiourea)tellurium(II), Te(etu)₂Br₂ and Te(etu)₂I₂, the found bond lengths are,¹ Te—S = 2.69 Å, Te—Br = 2.78 Å, Te—I = 2.97 Å. In the present *cis* Te(tu)₂Br₂ structure, the Te—S bonds are shorter and the Te—Br bonds, which here occur *trans* to the Te—S bonds, are longer; the sum of the lengths of the Te—S and Te—Br bonds, 2.47 + 3.05 Å = 5.52 Å, is a little larger than the sum of the lengths of these bonds in the *trans* Te(etu)₂Br₂ structure, 2.69 + 2.78 Å = 5.47 Å. In the *cis* Te(tu)₂Cl₂ complex the corresponding sum is 2.48 + 2.92 Å = 5.40 Å; no data for a *trans* dichloro complex is available but an estimate on the basis of *trans* Te(etu)₂Br₂, by subtracting the difference between the covalent single-bond radii of bromine and chlorine, would be about 5.3 Å.

It appears that a thiourea group, in *trans* position to halogen in a square-planar tellurium(II) complex, exerts a marked bond lengthening effect on the Te—halogen bond, with a corresponding shortening of the Te—S bond.^{5,20} Although the Te—S and Te—halogen bonds thus become fairly unequal in strength, the sum of their lengths shows only a slight increase relative to the sum in centrosymmetric tellurium(II) complexes, where ligands in *trans* positions are of the same kind.

The Te—S bonds in the *cis* complexes are about 0.1 Å longer than the Te—S bonds in uncomplexed compounds. In tellurium dimethanethio-sulphonate,²¹ dibenzenethio-sulphonate,²² and di-*p*-toluenethio-sulphonate,²³ ammonium telluropentathionate,²⁴ and barium telluropentathionate dihy-

drate,²⁰ the weighted average of the reported Te—S bond lengths is 2.37 Å. The Te—Cl and Te—Br distances, 2.92 and 3.05 Å, are definitely shorter than van der Waals approaches, the sum of the van der Waals radii²⁶ being 4.00 and 4.15 Å, respectively, or with Briegleb's²⁷ value, 1.9 Å instead of 2.20 Å for tellurium, 3.70 and 3.85 Å.

Interchange of bromine for chlorine has, within the error, no effect on the length of the *trans*-positioned Te—S bond.

The rather inaccurate carbon and nitrogen coordinates of the thiourea group give the bond lengths, C—N₁ = 1.32 and 1.32 Å, C—N₂ = 1.35 and 1.35 Å, and the bond angles, S—C—N₁ = 116° and 114°, S—C—N₂ = 121° and 125°, N₁—C—N₂ = 117° and 121°, in I and II, respectively. The least-squares planes of the thiourea groups, with sulphur given three times the weight of carbon and nitrogen, pass at a distance of 0.17 Å from carbon in I and at 0.03 Å in II. Even in the case of I the deviation from planarity may not be significant.

HYDROGEN BONDING

Intermolecular contacts, probably hydrogen-bonded, occur in the dichloro complex between the nitrogen atom N₁ and the chlorine atoms Cl_A($\bar{x}, \frac{1}{2} + y, \frac{1}{2} - z$) and Cl_B($\frac{1}{2} - x, \frac{1}{2} - y, \frac{1}{2} - z$), where x, y, z are the chlorine coordinates of Table 1. The approaches are, N₁...Cl_A = 3.21 Å, ∠C—N₁...Cl_A = 141°, and N₁...Cl_B = 3.39 Å, ∠C—N₁...Cl_B = 113°. The Cl_A and Cl_B atoms lie 0.72 and 0.17 Å, respectively, out of the thiourea least-squares plane; the sum of the three angles at N₁, to C, Cl_A, and Cl_B, is 360°. The nitrogen atom N₂ approaches the chlorine atoms Cl_C($\bar{x}, \bar{y}, \bar{z}$) and Cl_D($x - \frac{1}{2}, \bar{y}, z$), at N₂...Cl_C = 3.44 Å, ∠C—N₂...Cl_C = 148°, and N₂...Cl_D = 3.15 Å, ∠C—N₂...Cl_D = 131°. The Cl_C and Cl_D atoms lie -0.64 and 0.83 Å, respectively, out of the thiourea plane; the sum of the three angles at N₂, to C, Cl_C, and Cl_D, is 358°.

The N—H...Cl distances thus are from 3.15 to 3.44 Å (standard deviations, about 0.04 Å). In dichlorodithioureacadmium,^{28,29} N—H...Cl hydrogen bonds of lengths 3.29 Å occur; in dichlorotetrathiourea nickel,³⁰ of lengths 3.23 and 3.30 Å at C—N...Cl angles of 107° and 106°, respectively, and with the chlorine atoms 0.86 and 1.0 Å out of the thiourea plane. In ionic thiourea-complexed chlorides, *cf.* Ref. 18, reported N—H...Cl distances range from 3.2 to about 3.4 Å.

In the dibromo complex, the corresponding approaches (standard deviations, 0.05–0.06 Å) are, N₁...Br_A = 3.44 Å, N₁...Br_B = 3.50 Å, N₂...Br_C = 3.52 Å, N₂...Br_D = 3.33 Å, at C—N...Br angles of 136°, 119°, 151°, and 128°, respectively. The bromine atoms lie 1.15, 0.15, -0.54, and 1.19 Å, respectively, out of the thiourea plane; the sum of the three angles at N₁, to C, Br_A, and Br_B, is 356° and at N₂, to C, Br_C, and Br_D, 360°. The differences between N—H...Br distances in II and corresponding N—H...Cl distances in I thus are 0.08 to 0.23 Å, with an average of 0.15 Å.

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