

# Crystal and Molecular Structures of *trans* Square-Planar Complexes of Tellurium Dichloride, Dibromide and Diiodide with Tetramethylthiourea, $\text{TeL}_2\text{X}_2$ . Bond Lengths in Centrosymmetric Tellurium(II) Complexes

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The complexes *trans*- $\text{Te}(\text{tmtu})_2\text{Cl}_2$  (1), *trans*- $\text{Te}(\text{tmtu})_2\text{Br}_2$  (2) and *trans*- $\text{Te}(\text{tmtu})_2\text{I}_2$  (3) (tmtu = tetramethylthiourea) crystallize in the triclinic space group  $P\bar{1}$  (No. 2) with  $Z = 2$ . The tellurium atoms lie in centres of symmetry and the asymmetric units consist of two half molecules. The complex *trans*- $\text{Te}(\text{tmtu})_2\text{I}_2$  also occurs in two monoclinic forms, 4 and 5, space group  $P2_1/c$  (alternative  $P2_1/c$ , No. 14) with  $Z = 2$  for 4 and  $Z = 4$  for 5. In 4 but not in 5 the tellurium atoms lie in centres of symmetry. The structures have been determined by X-ray methods and refined to  $R = 0.044$  (1), 0.045 (2), 0.036 (3), 0.033 (4) and 0.043 (5) for 3190, 3672, 4089, 2160 and 3528 observed reflections, respectively. In the centrosymmetric *trans*- $\text{TeS}_2\text{X}_2$  coordination groups of 1–4, bond lengths are Te–S 2.683(2)–2.699(1) Å, Te–Cl 2.586(2) and 2.582(2) Å, Te–Br 2.740(1) and 2.734(1) Å and Te–I 2.950(1)–2.962(1) Å. The S–Te–X angles lie within  $90 \pm 2.0^\circ$ . In the slightly asymmetric *trans*- $\text{TeS}_2\text{I}_2$  group of 5, bond lengths are Te–S 2.765(2) and 2.636(2) Å and Te–I 2.934(1) and 2.978(1) Å with bond angles S–Te–S  $177.29(5)^\circ$  and I–Te–I  $177.92(3)^\circ$ . A survey of bond lengths in centrosymmetric *trans*- $\text{TeL}_2\text{X}_2$  and  $[\text{TeL}_4]\text{X}_2$  complexes gives the mean values Te–Cl 2.584(2), Te–Br 2.746(9), Te–I 2.955(2), Te–S 2.682(3) and Te–Se 2.806(6) Å. These are 0.22, 0.24, 0.26, 0.27 and 0.27 Å larger, respectively, than the sums of the Pauling single-bond radii.

The crystal structures of various *trans*- $\text{TeL}_2\text{X}_2$  complexes have been reported, where L is thio-urea or a substituted thiourea and X is an anionic ligand.<sup>1–8</sup> Two of these complexes contain X = halogen, viz. the bromo and iodo complexes *trans*- $\text{Te}(\text{etu})_2\text{X}_2$  (etu = ethylenethiourea).<sup>1</sup> We report here the structures of *trans*- $\text{Te}(\text{tmtu})_2\text{X}_2$  (tmtu = tetramethylthiourea; X = Cl, Br or I). This series includes the first structurally characterised chloro complex of this type. The iodo complex occurs in three crystalline forms.

## Experimental

**Preparations.** The chloro and bromo complexes and the monoclinic forms of the iodo complex have been reported earlier, together with unit cell and space group data.<sup>9</sup> We have slightly amended the preparative procedures for the former two complexes. The HCl and HI used were ca. 37 and 57% w/w, respectively.

*The complex  $\text{Te}(\text{tmtu})_2\text{Cl}_2$  was prepared by dissolving a mixture of  $\text{Te}(\text{tmtu})\text{Cl}_2$ <sup>10</sup> (1 g) and tmtu*

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(2 g) in hot DMF–HCl (10:1, 20 cm<sup>3</sup>), filtering, and allowing the filtrate to cool, first to room temperature and then in a refrigerator; yield, after filtering and washing rapidly with a little diethyl ether, ca. 0.7 g (50 %).

The complex  $\text{Te}(\text{tmu})_2\text{Br}_2$  was prepared by dissolving a mixture of  $\text{Te}(\text{tmu})\text{Br}_2$ <sup>10</sup> (1.5 g) and tmtu (2.5 g) [or, for recrystallization, a mixture of  $\text{Te}(\text{tmu})_2\text{Br}_2$  (2 g) and tmtu (2 g)] in hot DMF (25 cm<sup>3</sup>), filtering if necessary, and cooling and washing as above; yield ca. 1.5 g (75 %).

The complex  $\text{Te}(\text{tmu})_2\text{I}_2$  (tric.) was obtained by dissolving  $\text{TeO}_2$  (1.6 g, 10 mmol) in hot HCl (5 cm<sup>3</sup>) and adding, with swirling, a solution of tmtu (2.7 g, 20 mmol) in DMF (50 cm<sup>3</sup>) and then a mixture of HI (10 cm<sup>3</sup>) and methanol (50 cm<sup>3</sup>). The resulting solution was kept at room temperature whereupon the complex crystallized; yield, after filtering and washing with diethyl ether containing a little tmtu, ca. 5 g (77 % based on Te). The complex was recrystallized by dissolving 1 g, with gentle heating, in DMF–HI (20:1, 10 cm<sup>3</sup>), filtering if necessary, and adding methanol (10 cm<sup>3</sup>). Yield of dark red crystals, after cooling in a refrigerator and washing as before, ca. 0.7 g. Found: C 19.51; H 3.71; N 8.68; S 9.73. Calc. for  $\text{C}_{10}\text{H}_{24}\text{I}_2\text{N}_4\text{S}_2\text{Te}$ : C 18.60; H 3.75; N 8.67; S 9.93.

The samples of monoclinic  $\text{Te}(\text{tmu})_2\text{I}_2$ , obtained from methanolic tmtu solutions of the chloro or bromo complex and methanolic NaI or KI, were mixtures of the two types of crystals.<sup>9</sup>

*X-Ray structure analyses.* Crystal data, with numbering of complexes, are given in Table 1. Complexes 1 and 2 are isomorphous and the structure of 3 is closely related (see below). The unit cells of complexes 1–3 are not the reduced cells; the cells of 1 and 2 were chosen for morphological reasons<sup>9</sup> and the cell of 3 was based on these. X-ray data were collected on a Siemens AED diffractometer using Nb-filtered  $\text{MoK}\alpha$  radiation ( $\lambda = 0.71069 \text{ \AA}$ ). Unit cell dimensions were determined from the  $2\theta$  values, measured by an  $\omega$ -scan technique,<sup>11</sup> of the  $\text{MoK}\alpha_1$  peaks ( $\lambda = 0.70926 \text{ \AA}$ ) and in most cases also the  $\text{MoK}\alpha_2$  peaks ( $\lambda = 0.71353 \text{ \AA}$ ) of ca. 30 reflections in the  $30 < 2\theta < 50^\circ$  range. Intensities were measured by the five-value  $\theta$ – $2\theta$  scan technique,<sup>12</sup> and  $2\theta_{\text{max}}$  was  $56^\circ$ . Three reference reflections were

measured at intervals of 50 reflections; their intensities decreased by 38, 5, 14, 2 and 1 % for complexes 1–5, respectively. Corrections for decay were made.  $\sigma(I)$  and  $\sigma(F) = \sigma(I)/2(LpI)^{1/2}$  were based on counting statistics and instrument instability. Reflections with  $I > 2\sigma(I)$  were regarded as observed. The “less-than” reflections were assigned the threshold value and included in the refinement when  $|F_c|$  exceeded this value. Lorentz, polarization, and absorption corrections were made, and in the later stages, extinction corrections were applied to the calculated structure factors; the extinction coefficient,  $g$ , was refined together with the scale factor only, and was held fixed in the final cycles.

Calculations were made by use of the “X-Ray 72” programs<sup>13</sup> with local adaptations. Refinements were carried out by the full matrix least-squares method, the sum minimized being  $\Sigma w\Delta^2(F)$  with  $w = 1/\sigma^2(F)$ . Atomic scattering factors, with anomalous dispersion terms included, were taken from Ref. 14. Anisotropic thermal parameters were used for Te, S and halogen, and isotropic parameters for N and C. The hydrogen atoms were ignored. Before the final cycles of refinement, a weight analysis revealed high average  $w\Delta^2(F)$  values for the innermost reflections, and those with  $\sin\theta < 0.1$  were therefore excluded from the refinements.

The structures of complexes 2, 4 and 5 were solved by Patterson and Fourier or difference Fourier techniques, and the coordinates of 2 were used as starting coordinates for the refinement of the isomorphous 1. In complexes 1–3 the Te atoms lie in symmetry centres at 0,0,0 and  $\frac{1}{2}, \frac{1}{2}, 0$ , and the asymmetric units consists of two half molecules. X-ray photographs for complex 3 indicated the structure to be similar to that of 1 and 2; however, with the  $a$  and  $b$  axes as in these, the molecules at  $z = 1$  were translated  $a/2, b/2$  along the  $ab$  diagonal relative to the molecules at  $z = 0$ . That is, the  $c$  axis of complex 3 corresponds to  $[\frac{1}{2}, \frac{1}{2}, 1]$  of 1 and 2 with the direction reversed for obtuse  $\alpha$  and  $\beta$  angles. Refinement for complex 3 began with the coordinates of 2 transformed accordingly and proceeded smoothly.

The largest shift/error ratio in the last cycle was 0.14 for complex 5. Atomic coordinates are listed in Tables 2 and 3. Thermal parameters, torsion angles and planes have been deposited with the Cambridge Crystallographic Data Centre.

Table 1. Crystallographic data.

No.	1	2	3	4	5
Complex	Te(tmtu) <sub>2</sub> Cl <sub>2</sub>	Te(tmtu) <sub>2</sub> Br <sub>2</sub>	Te(tmtu) <sub>2</sub> I <sub>2</sub>	Te(tmtu) <sub>2</sub> I <sub>2</sub>	Te(tmtu) <sub>2</sub> I <sub>2</sub>
Formula	C <sub>10</sub> H <sub>20</sub> Cl <sub>2</sub> N <sub>4</sub> S <sub>2</sub> Te	C <sub>10</sub> H <sub>20</sub> Br <sub>2</sub> N <sub>4</sub> S <sub>2</sub> Te	C <sub>10</sub> H <sub>20</sub> I <sub>2</sub> N <sub>4</sub> S <sub>2</sub> Te	C <sub>10</sub> H <sub>20</sub> I <sub>2</sub> N <sub>4</sub> S <sub>2</sub> Te	C <sub>10</sub> H <sub>20</sub> I <sub>2</sub> N <sub>4</sub> S <sub>2</sub> Te
<i>M</i>	462.96	551.88	645.87	645.87	645.87
System	Triclinic	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group	P1̄ (No. 2)	P1̄ (No. 2)	P1̄ (No. 2)	P2 <sub>1</sub> /n (No. 14)	P2 <sub>1</sub> /n (No. 14)
<i>a</i> /Å	10.619(1)	10.832(1)	11.233(2)	7.998(1)	9.192(1)
<i>b</i> /Å	11.430(1)	11.651(1)	12.055(1)	10.783(1)	18.952(1)
<i>c</i> /Å	9.035(1)	9.025(1)	9.101(1)	11.953(1)	11.866(1)
<i>ω</i> /°	101.90(1)	101.77(1)	122.17(1)	97.74(1)	101.53(1)
<i>β</i> /°	120.03(1)	119.85(1)	101.89(1)	101.89(1)	101.89(1)
<i>γ</i> /°	84.88(1)	83.74(1)	81.02(1)	81.02(1)	81.02(1)
<i>V</i> /Å <sup>3</sup>	928.9(3)	967.1(3)	1019.2(4)	1021.5(2)	2025.5(2)
<i>Z</i>	2	2	2	2	4
<i>D<sub>x</sub></i> /g cm <sup>-3</sup>	1.655	1.895	2.104	2.100	2.118
<i>F</i> (000)	460	532	604	604	1208
<i>μ</i> (MoK $\alpha$ )/cm <sup>-1</sup>	21.7	61.8	47.7	47.9	47.9
Absorption corrections	1.25–1.35	2.62–4.10	1.48–1.82	1.63–1.68	1.23–1.43
Unique reflections	4430	4616	4879	2456	4793
Reflections <i>I</i> > 2 $\sigma$	3190	3672	4089	2160	3528
Extinction coefficient, <i>g</i> × 10 <sup>3</sup>	0.7	0.2	4.0	3.4	3.7
<i>R</i>	0.044	0.045	0.036	0.033	0.043
Max. $\Delta(\rho)$ /e Å <sup>-3</sup>	0.83	1.04	0.84	0.95	0.95

Table 2. Fractional atomic coordinates for triclinic *trans*-Te(tmtu)<sub>2</sub>X<sub>2</sub> with e.s.d.s. in parentheses.

Atom	Molecule A			Molecule B		
	x	y	z	x	y	z
<b>Te(tmtu)<sub>2</sub>Cl<sub>2</sub></b>						
Te	0	0	0	$\frac{1}{2}$	$\frac{1}{2}$	0
Cl	0.27759(19)	0.01769(16)	0.21136(25)	0.22907(19)	0.43940(15)	-0.20245(24)
S	0.04336(19)	0.07589(13)	-0.23357(20)	0.49495(19)	0.43271(14)	0.26441(22)
C(1)	0.1503(6)	-0.0348(5)	-0.2670(7)	0.3499(6)	0.5152(5)	0.2604(7)
N(1)	0.1101(6)	-0.1496(4)	-0.3177(6)	0.3510(6)	0.6344(4)	0.2827(6)
C(2)	0.2136(10)	-0.2466(8)	-0.2580(11)	0.2132(10)	0.6996(7)	0.1830(11)
C(3)	-0.0471(8)	-0.1858(6)	-0.4083(9)	0.4857(9)	0.7049(6)	0.3702(9)
N(2)	0.2800(6)	-0.0061(4)	-0.2441(7)	0.2345(6)	0.4600(4)	0.2332(6)
C(4)	0.3556(8)	0.1088(6)	-0.1380(9)	0.2022(9)	0.3296(6)	0.1510(9)
C(5)	0.3420(9)	-0.0731(7)	-0.3511(10)	0.1409(10)	0.5105(7)	0.3084(11)
<b>Te(tmtu)<sub>2</sub>Br<sub>2</sub></b>						
Te	0	0	0	$\frac{1}{2}$	$\frac{1}{2}$	0
Br	0.28785(7)	0.01187(7)	0.22040(10)	0.22191(7)	0.43692(6)	-0.21763(10)
S	0.04244(17)	0.07476(13)	-0.23347(22)	0.49247(17)	0.43017(14)	0.26112(23)
C(1)	0.1511(6)	-0.0353(5)	-0.2662(7)	0.3484(6)	0.5090(5)	0.2574(7)
N(1)	0.1160(5)	-0.1466(4)	-0.3094(7)	0.3439(5)	0.6274(4)	0.2770(7)
C(2)	0.2235(9)	-0.2414(8)	-0.2483(12)	0.2083(9)	0.6895(7)	0.1826(11)
C(3)	-0.0338(8)	-0.1843(6)	-0.3974(10)	0.4732(8)	0.6976(6)	0.3599(10)
N(2)	0.2757(5)	-0.0061(4)	-0.2463(7)	0.2387(6)	0.4535(4)	0.2364(7)
C(4)	0.3445(8)	0.1072(7)	-0.1484(10)	0.2173(8)	0.3276(6)	0.1641(10)
C(5)	0.3368(8)	-0.0757(7)	-0.3534(11)	0.1504(9)	0.5036(7)	0.3184(11)
<b>Te(tmtu)<sub>2</sub>I<sub>2</sub></b>						
Te	0	0	0	$\frac{1}{2}$	$\frac{1}{2}$	0
I	0.18710(4)	-0.10631(4)	-0.23502(5)	0.34679(4)	0.56427(4)	0.26708(6)
S	0.15209(13)	0.18268(13)	0.25488(21)	0.35909(13)	0.30234(13)	-0.24475(23)
C(1)	0.2796(5)	0.0849(5)	0.2643(6)	0.2172(5)	0.3821(5)	-0.2481(6)
N(1)	0.2738(5)	-0.0169(5)	0.2834(6)	0.1992(5)	0.4795(5)	-0.2789(6)
C(2)	0.3452(7)	-0.1398(7)	0.1903(9)	0.1049(8)	0.5858(8)	-0.2074(10)
C(3)	0.1766(7)	-0.0186(7)	0.3712(10)	0.2802(7)	0.4985(7)	-0.3701(9)
N(2)	0.3866(5)	0.1092(5)	0.2512(6)	0.1242(5)	0.3432(5)	-0.2192(6)
C(4)	0.4006(8)	0.1890(8)	0.1801(10)	0.1457(8)	0.2656(8)	-0.1288(10)
C(5)	0.5025(7)	0.0764(7)	0.3379(9)	-0.0002(8)	0.3461(11)	-0.3081(11)

Table 3. Fractional atomic coordinates for monoclinic *trans*-Te(tmtu)<sub>2</sub>I<sub>2</sub> with e.s.d.s in parentheses.

Atom	x	y	z
Complex 4			
Te	0	0	0
I	-0.19132(5)	0.21069(3)	0.07606(3)
S	0.01018(20)	0.10489(11)	-0.20396(11)
C(1)	0.0534(6)	0.2573(4)	-0.1709(4)
N(1)	0.1979(5)	0.2912(4)	-0.1091(4)
C(2)	0.2178(9)	0.4080(7)	-0.0409(6)
C(3)	0.3456(8)	0.2106(6)	-0.0957(6)
N(2)	-0.0593(5)	0.3449(4)	-0.2096(4)
C(4)	-0.2397(9)	0.3150(7)	-0.2408(6)
C(5)	-0.0083(8)	0.4688(6)	-0.2464(5)
Complex 5			
Te	0.63030(5)	0.38504(2)	0.26181(4)
I	0.60418(6)	0.23098(2)	0.27113(4)
I'	0.65904(6)	0.54155(2)	0.26165(4)
S	0.89015(23)	0.37111(9)	0.17989(17)
S'	0.37688(22)	0.39365(9)	0.33299(15)
C(1)	0.9800(7)	0.3015(3)	0.2548(5)
N(1)	1.0127(7)	0.2988(3)	0.3684(5)
C(2)	1.0112(10)	0.2316(4)	0.4335(7)
C(3)	1.0173(10)	0.3644(4)	0.4409(7)
N(2)	1.0205(7)	0.2473(3)	0.1969(5)
C(4)	0.9530(10)	0.2293(4)	0.0762(7)
C(5)	1.1653(11)	0.2073(5)	0.2430(7)
C(1')	0.2797(7)	0.4570(3)	0.2442(5)
N(1')	0.2563(6)	0.4532(3)	0.1310(5)
C(2')	0.2480(10)	0.5164(4)	0.0552(7)
C(3')	0.2575(10)	0.3842(4)	0.0694(7)
N(2')	0.2278(6)	0.5131(3)	0.2932(4)
C(4')	0.2844(9)	0.5338(4)	0.4155(6)
C(5')	0.0821(10)	0.5467(4)	0.2397(7)

## Results and discussion

The tellurium dihalides TeCl<sub>2</sub>, TeBr<sub>2</sub> and TeI<sub>2</sub> do not occur in the solid state<sup>15</sup> but are stable in the gas phase.<sup>16</sup> The dichloride and dibromide have been studied by gas phase electron diffraction and the following bond lengths and angles found: Te-Cl 2.329(3) Å, Cl-Te-Cl 97.0(6)°<sup>17</sup> and Te-Br 2.51 Å, Br-Te-Br 98°.<sup>18</sup> The sums of the Pauling single-bond radii<sup>19</sup> are Te-Cl 2.36 and Te-Br 2.51 Å.

In square-planar tellurium(II) complexes, tellurium-ligand bonding is of the linear 3c-4e type,<sup>20</sup> and the bonds are longer than single covalent bonds. Two of the tellurium 5p orbitals each form two bonds at 180°. This bonding scheme

Table 4. Bond lengths (Å) and angles (°) in the coordination groups of triclinic *trans*-Te(tmtu)<sub>2</sub>X<sub>2</sub> with e.s.d.s in parentheses. Values for molecule A are listed above values for molecule B.

	X = Cl	X = Br	X = I
Bond lengths			
Te-X	2.586(2)	2.740(1)	2.954(1)
	2.582(2)	2.734(1)	2.962(1)
Te-S	2.687(2)	2.685(2)	2.693(1)
	2.683(2)	2.685(2)	2.687(1)
S-C(1)	1.706(6)	1.726(6)	1.726(5)
	1.721(7)	1.712(7)	1.732(5)
Bond angles			
S-Te-X	88.69(7)	88.55(4)	89.81(4)
	90.33(7)	90.24(4)	90.59(4)
Te-S-C(1)	101.0(2)	101.2(3)	100.8(2)
	99.2(2)	100.2(3)	102.6(2)

was proposed on the basis of bond lengths, angles and *trans*-influences of ligands,<sup>21</sup> and accords with IR and Raman spectra<sup>22</sup> as well as Mössbauer data.<sup>23</sup>

Table 5. Bond lengths (Å) and angles (°) in the coordination groups of monoclinic *trans*-Te(tmtu)<sub>2</sub>I<sub>2</sub> with e.s.d.s in parentheses.

Complex 4			
Bond lengths			
Te-I	2.950(1)	S-C(1)	1.715(5)
Te-S	2.699(1)		
Bond angles			
S-Te-I	92.04(3)	Te-S-C(1)	
	102.9(2)		
Complex 5			
Bond lengths			
Te-I	2.934(1)	Te-I'	2.978(1)
Te-S	2.765(2)	Te-S'	2.637(2)
S-C(1)	1.708(6)	S'-C(1')	1.724(6)
Bond angles			
S-Te-I	90.07(4)	I-Te-S'	88.01(4)
S-Te-S'	177.29(5)	I-Te-I'	177.92(3)
Se-Te-I'	90.68(4)	S'-Te-I'	91.30(4)
Te-S-C(1)	104.6(3)	Te-S'-C(1')	103.3(3)

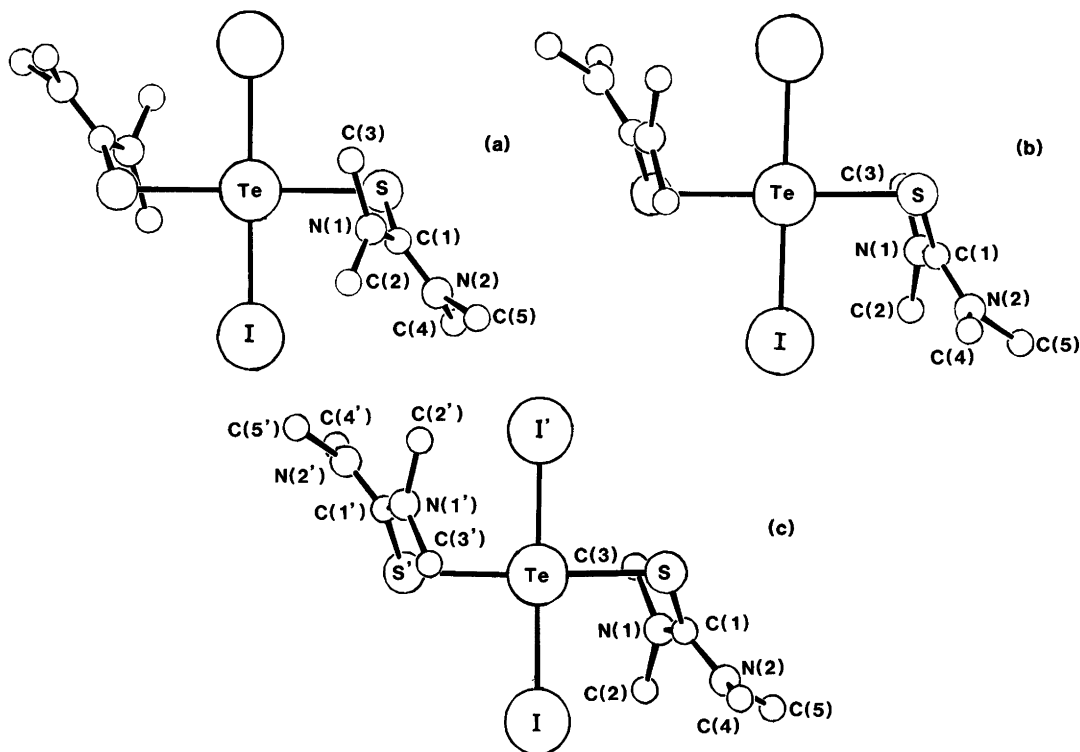


Fig. 1. The *trans*-Te(tmtu)<sub>2</sub> molecule in the three crystalline forms, as seen normal to the coordination plane [TeS plane for (c)]: (a) triclinic, complex 3, molecule A; (b) and (c) monoclinic, complexes 4 and 5, respectively.

Bonds lengths and angles in the coordination groups of *trans*-Te(tmtu)<sub>2</sub>X<sub>2</sub> are listed in Tables 4 and 5, and views of three molecules are shown in Fig. 1. Data for the tmtu ligands are summarized in Table 6, and selected plane angles defining the orientations of the -C(NMe<sub>2</sub>)<sub>2</sub> moieties of the ligands relative to the coordination plane are given in Tables 7 and 8.

In complexes 1–4, the tellurium atoms lie in crystallographic symmetry centres; the TeS<sub>2</sub>X<sub>2</sub> groups are exactly planar and the S–Te–S and X–Te–X systems are exactly linear. In complexes 1–3 the asymmetric units consist of two half molecules, but the differences in bond lengths and angles for the two molecules are very small and their orientations in the unit cell differ only slightly: the angle between the TeS<sub>2</sub>X<sub>2</sub> planes (Table 7) is increased from 9.4° in complex 1 to 15.2° in 3.

In complex 5 the distortions from molecular

centrosymmetry are not large. The Te–I bond lengths differ by 0.044(1) Å and the average length is 2.956 Å, as compared to 2.954(1) and 2.962(1) Å in complex 3 and 2.950(1) Å in 4. The Te–S bond lengths differ more, by 0.128(3) Å, but the average length, 2.701 Å, is practically the same as in complex 3, 2.693(1) and 2.687(1) Å, and in 4, 2.699(1) Å.

The unit cell volumes of the three forms 3–5 of *trans*-Te(tmtu)<sub>2</sub>I<sub>2</sub>, as reflected in the densities  $D_x = 2.104, 2.100$  and  $2.118 \text{ g cm}^{-3}$ , respectively, show that the distortions from centrosymmetry in 5 result in slightly more efficient packing in the crystal.

The dimensions and orientations of the tmtu ligands are discussed elsewhere.<sup>24</sup>

*Bond lengths in centrosymmetric tellurium(II) complexes.* Data for TeL<sub>2</sub>X<sub>2</sub> and [TeL<sub>4</sub>]X<sub>2</sub> complexes are listed in Table 9. The Table contains

Table 6. Ranges of interatomic distances (Å) and angles (°) in the nine independent tetramethylthiourea groups.

	Range	Mean
<b>Bond lengths</b>		
C(1)–N	1.315(7)–1.351(7)	1.333(3)
N–C(Me)	1.457(14)–1.534(11)	1.483(3)
<b>Bond angles</b>		
S–C(1)–N(1)	121.5(5)–123.2(5)	122.0(2)
S–C(1)–N(2)	118.1(5)–119.8(5)	119.1(2)
N(1)–C(1)–N(2)	117.8(6)–119.7(5)	118.2(2)
C(1)–N–C(Me)	120.2(5)–124.8(6)	122.1(2)
C(Me)–N–C(Me)	112.8(7)–116.7(7)	114.7(3)
<b>Non-bonded contacts<sup>a</sup></b>		
S...C(3)	3.039(7)–3.106(8)	3.073(6)
S...C(4)	2.972(9)–3.059(8)	3.014(8)
C(2)...C(5)	2.895(15)–2.970(16)	2.932(8)

<sup>a</sup>Between atoms not bonded to a common atom.

Table 7. Planes for triclinic *trans*-Te(tmtu)<sub>2</sub>X<sub>2</sub>. Planes (1)–(3): molecule A; planes (4)–(6): molecule B. The atoms defining least-squares planes (3) and (6) lie in the planes within error limits.

Planes (1) and (4):	Te, S, X
Planes (2) and (5):	Te, S, C(1)
Planes (3) and (6):	S, C(1), N(1), N(2)

Angles (°) between planes	Planes		
	X = Cl	X = Br	X = I
(1)–(2)	61.7	60.5	53.6
(1)–(3)	82.6	80.9	76.1
(2)–(3)	55.4	53.6	52.7
(4)–(5)	53.8	54.0	59.6
(4)–(6)	79.3	79.0	83.0
(5)–(6)	60.0	57.7	56.5
(1)–(4)	9.4	11.3	15.2
(2)–(5)	18.6	18.8	8.8
(3)–(6)	9.0	8.4	5.0

Distances (Å) of the methyl carbon atoms from the thiourea planes (3) and (6)

Atom	Range	Average
C(2)	0.598–0.779	0.716
C(3)	–(0.455–0.561)	–0.491
C(4)	0.387–0.437	0.417
C(5)	–(0.623–0.707)	–0.675

Table 8. Planes for monoclinic *trans*-Te(tmtu)<sub>2</sub>I<sub>2</sub>. Distances of relevant atoms from least-squares planes are in square brackets.

Complex 4			
Plane (1): Te, S, I			
Plane (2): Te, S, C(1)			
Plane (3): S, C(1), N(1), N(2)			
[C(1) 0.006, C(2) 0.522, C(3) –0.426, C(4) 0.488, C(5) –0.748]			
Angles (°) between planes:			
(1)–(2)	42.3	(1)–(3)	78.4
		(2)–(3)	62.8
Complex 5			
Plane (1): Te, S, I, S', I'			
[Te –0.002, S –0.045, I 0.049, S' –0.048, I' 0.047]			
Plane (2): Te, S, C(1)			
Plane (3): S, C(1), N(1), N(2)			
[C(1) –0.003, C(2) –0.715, C(3) 0.433, C(4) –0.448, C(5) 0.761]			
Plane (4): Te', S', C(1')			
Plane (5): S', C(1'), N(1'), N(2')			
[C(1') –0.006, C(2') 0.679, C(3') –0.505, C(4') 0.400, C(5') –0.743]			
Angles (°) between planes:			
(1)–(2)	39.9	(1)–(3)	73.2
(1)–(4)	46.0	(1)–(5)	73.5
(2)–(4)	6.8	(3)–(5)	3.2
(2)–(3)	55.4	(4)–(5)	54.6

two entries for Te–Cl bonds, three for Te–Br bonds, five for Te–I bonds, twenty for Te–S bonds and ten for Te–Se bonds. Since Te–S bonds are in a majority, TeS<sub>4</sub> groups are included only where the complex is isomorphous with the TeS<sub>2</sub>Se<sub>2</sub> or TeSe<sub>4</sub> analogue; this is the case for complex 9 which is isomorphous with 10, for 12 which is isomorphous with 13 and 14, and for 15 and 17 which are isomorphous with 16 and 18, respectively.

In the last rows of Table 9, the weighted mean bond lengths, with e.s.d.s calculated as in Ref. 28, are compared with the sums of the Pauling single-bond radii.<sup>19</sup> The lengthening of the bonds in the complexes, relative to the single-bond lengths, increases from 0.22 Å for Te–Cl to 0.27 Å for Te–S and Te–Se. This seems to indicate an electronegativity effect.

For Te–S the mean bond length is 2.682(3) Å,

Table 9. Bond lengths (Å) in centrosymmetric square-planar tellurium(II) complexes.

No.	Complex	Te-Cl	Te-Br	Te-I	Te-S	Te-Se	Ref.
1	Te(tmtu) <sub>2</sub> Cl <sub>2</sub>	2.586(2) 2.582(2)			2.687(2) 2.683(2)		This work
2	Te(tmtu) <sub>2</sub> Br <sub>2</sub>		2.740(1) 2.734(1)		2.685(2) 2.685(2)		This work
3	Te(tmtu) <sub>2</sub> I <sub>2</sub> <sup>a</sup>			2.954(1) 2.962(1)	2.693(1) 2.687(1)		This work
4	Te(tmtu) <sub>2</sub> I <sub>2</sub> <sup>b</sup>			2.950(1)	2.699(1)		This work
6	Te(tmsu) <sub>2</sub> I <sub>2</sub> <sup>c,d</sup>			2.954(1)		2.821(1)	25
7	Te(etu) <sub>2</sub> Br <sub>2</sub>		2.764(1)		2.656(1)		1,24
8	Te(etu) <sub>2</sub> I <sub>2</sub>			2.955(1)	2.671(1)		1,24
9	Te(etu) <sub>2</sub> (SCN) <sub>2</sub>				2.651(6) <sup>e</sup> 2.684(7)		2
10	Te(etu) <sub>2</sub> (SeCN) <sub>2</sub>				2.676(6)	2.809(3)	2
11	Te(trtu) <sub>2</sub> (SeCN) <sub>2</sub> <sup>f</sup>				2.670(5)	2.834(2)	3
12	Te(tmtu) <sub>2</sub> (SCN) <sub>2</sub>				2.691(1) <sup>g</sup> 2.685(1)		24
13	Te(tmtu) <sub>2</sub> (SeCN) <sub>2</sub>				2.728(4)	2.815(3)	3
14	Te(tmsu) <sub>2</sub> (SeCN) <sub>2</sub> <sup>c</sup>					2.811(1) <sup>h</sup> 2.814(1)	24
15	[Te(tu) <sub>4</sub> ]Cl <sub>2</sub> <sup>i</sup>				2.685(10) 2.690(10)		26
16	[Te(su) <sub>4</sub> ]Cl <sub>2</sub> <sup>j</sup>					2.814(3) 2.809(4)	27
17	[Te(etu) <sub>4</sub> ]Cl <sub>2</sub>				2.681(1) 2.666(1)		24
18	[Te(esu) <sub>4</sub> ]Cl <sub>2</sub> <sup>k</sup>					2.802(1) 2.773(1)	24
Mean		2.584(1)	2.746(9)	2.955(2)	2.682(3)	2.806(6)	
Single covalent		2.36	2.51	2.70	2.41	2.54	
Δ		0.22	0.24	0.26	0.27	0.27	

<sup>a</sup>Triclinic. <sup>b</sup>Monoclinic dimorph. <sup>c</sup>tmsu = tetramethylselenourea. <sup>d</sup>Isomorphous with complex 4. <sup>e</sup>Te-S(etu).

<sup>f</sup>trtu = trimethylenethiourea. <sup>g</sup>Te-S(tmtu). <sup>h</sup>Te-Se(tmsu). <sup>i</sup>tu = thiourea. <sup>j</sup>su = selenourea.

<sup>k</sup>esu = ethyleneselenourea.

and the values range from 2.651(6) Å in complex 9 to 2.728(4) Å in 13. Not surprisingly, the nature of the thio ligand plays a small but significant role. For the six Te-S(etu) entries in Table 9, the mean is 2.668(4) Å, and for the nine Te-S(tmtu) entries, 2.691(2) Å. If data (not given in Table 9) for the Te-S bond lengths in Te(etu)<sub>2</sub>(S<sub>2</sub>O<sub>2</sub>Ph)<sub>2</sub>,<sup>8</sup> in two forms of Te(etu)<sub>2</sub>

(S<sub>2</sub>O<sub>2</sub>Me)<sub>2</sub>,<sup>5</sup> and in Te(tmtu)<sub>2</sub>(S<sub>2</sub>O<sub>2</sub>Ph)<sub>2</sub><sup>8</sup> and [Te(tu)<sub>2</sub>(tmtu)<sub>2</sub>]X<sub>2</sub> (X = Cl or Br)<sup>29</sup> are included, the means become Te-S(etu) 2.669(4) and Te-S(tmtu) 2.691(2) Å, based on nine and twelve values, respectively. The overall mean of these twenty-one values is 2.681(3) Å.

Structures have been reported for compounds which contain square-planar TeTe<sub>4</sub> coordination



groups, viz. the "pentatellurides" Rb<sub>2</sub>Te<sub>5</sub>,<sup>30</sup> Cs<sub>2</sub>Te<sub>5</sub>,<sup>31</sup> Ga<sub>2</sub>Te<sub>5</sub>,<sup>32</sup> and K<sub>2</sub>SnTe<sub>5</sub>.<sup>33</sup> The central tellurium(II) atoms lie in positions of symmetry *2/m*, *mm*, *4/m*, and *mm*, respectively, and are each bonded to four tellurium atoms in a square-planar arrangement. Te–Te distances are 3.039(1), 3.046(1), 3.027(2), and 3.015(5) and 3.052(5) Å, respectively, for the four compounds. The average distance, 3.036 Å, is 0.30 Å larger than the Pauling Te–Te single-bond length, 2.74 Å.<sup>19</sup> This Δ value may be compared with 0.27 Å for Te–S and Te–Se.

The data of Table 9 give few, if any, indications of *cis*-influence of ligands. Nor is *cis*-influence in tellurium(II) complexes expected on theoretical grounds.<sup>34</sup> The data for the Te(etu)<sub>2</sub>X<sub>2</sub> pairs, complexes 7 and 8 (X = Br or I), and 9 and 10 (X = SCN or SeCN), may indicate *cis*-influence; in each pair, Te–S(etu) is shorter for the more electronegative X. However, for the latter pair the difference may not be significant. In the TeL<sub>2</sub>Br<sub>2</sub> complexes 2 and 7 (L = tmtu or etu), Te–S is shorter where Te–Br is longer. In Te(tmtu)<sub>2</sub>X<sub>2</sub>, complexes 1–4, Te–S appears to be slightly longer for X = I than for X = Cl or Br; the means are 2.693(3) and 2.685(1) Å based on three and four values, respectively. However, for complexes 3, 4 and 6, TeL<sub>2</sub>I<sub>2</sub>, and for 13 and 14, TeL<sub>2</sub>(SeCN)<sub>2</sub>, substitution of tmsu for tmtu does not influence *cis* bond lengths. In complex 17, [Te(etu)<sub>4</sub>]Cl<sub>2</sub>, and 18, [Te(esu)<sub>4</sub>]Cl<sub>2</sub>, the lengths of *cis*-positioned Te–S or Te–Se bonds are markedly different although the ligands are the same in each case.

The synthesis and crystal structures of the [TeX<sub>4</sub>]<sup>2-</sup> salts [Ph<sub>4</sub>As<sub>2</sub>][TeCl<sub>4</sub>], [Et<sub>4</sub>N]<sub>2</sub>[TeBr<sub>4</sub>]·MeCN, and [Et<sub>4</sub>N]<sub>2</sub>[TeI<sub>4</sub>] were reported recently.<sup>35</sup> In the chloro complex the tellurium atoms lie in centres of symmetry, with Te–Cl bond lengths of 2.600(4) and 2.614(4) Å. In the bromo and iodo complexes they lie in positions of *4/mmm* symmetry, with Te–Br 2.753(2) and Te–I 2.985(2) Å. A comparison with *trans*-Te(tmtu)<sub>2</sub>X<sub>2</sub>, complexes 1–4, shows that the Te–X bonds in the dinegative ions are 0.02–0.03 Å longer than in the neutral complexes.

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