

# Complexes of Tellurium Dichloride, Dibromide and Diiodide with Thiourea and Tetramethylselenourea, $\text{TeL}_2\text{X}_2$ . X-Ray Crystal Structures

Olav Foss\* and Knut Maartmann-Moe

Department of Chemistry, University of Bergen, N-5000 Bergen, Norway

Foss, O. and Maartmann-Moe, K., 1987. Complexes of Tellurium Dichloride, Dibromide and Diiodide with Thiourea and Tetramethylselenourea,  $\text{TeL}_2\text{X}_2$ . X-Ray Crystal Structures. – Acta Chem. Scand., Ser. A 41: 121–129.

The X-ray structures of *cis*- $\text{Te}(\text{tu})_2\text{Cl}_2$  (**1**) and *cis*- $\text{Te}(\text{tu})_2\text{Br}_2$  (**2**) (tu = thiourea), determined earlier, have been refined and the structure of *cis*- $\text{Te}(\text{tu})_2\text{I}_2$  (**3**) has been determined. The complexes *cis*- $\text{Te}(\text{tmsu})_2\text{Cl}_2$  (**4**), *cis*- $\text{Te}(\text{tmsu})_2\text{Br}_2$  [two forms, **5** and **6**] and *trans*- $\text{Te}(\text{tmsu})_2\text{I}_2$  (**7**) (tmsu = tetramethylselenourea) have been prepared and their structures determined. They were refined to  $R = 0.020(\mathbf{1}) - 0.049(\mathbf{5})$ . The crystals of **1–3** are isomorphous, as are those of **4** and **5**. In **1–5**, the tellurium atoms lie on two-fold symmetry axes, and in **7** in symmetry centres. In the S–Te–X systems of **1–3**, Te–S bond lengths are 2.457(1), 2.476(1) and 2.521(1); Te–X bond lengths are 2.936(1), 3.038(1) and 3.162(1) Å, and S–Te–X angles are 172.50(2), 171.73(2) and 171.92(2)°, for X = Cl, Br and I, respectively. The Te–S bond lengths reflect the greater relative *trans*-influence of the heavier X. In the Se–Te–X systems of **4** and **5**, bond lengths and angles are Te–Se 2.677(1) and 2.678(1), Te–X 2.753(1) and 2.898(1) Å, and Se–Te–X 172.81(2) and 173.96(2)°, for X = Cl and Br, respectively; for **6**, these values are Te–Se 2.668(1) and 2.677(1), Te–Br = 2.917(1) and 2.898(1) Å, and Se–Te–Br 173.98(2) and 173.40(2)°. At these Te–Cl and Te–Br distances, Cl and Br exert the same *trans*-influence. In the *trans*- $\text{TeSe}_2\text{I}_2$  moiety of **7**, bond lengths and angles are Te–Se 2.821(1), Te–I 2.954(1) Å, and Se–Te–I 92.89(1)°.

The crystal structures of the complexes *cis*- $\text{Te}(\text{tu})_2\text{Cl}_2$  and *cis*- $\text{Te}(\text{tu})_2\text{Br}_2$  (tu = thiourea) were reported some time ago.<sup>1</sup> As part of a study of the relative *trans*-influence of Cl, Br and I in tellurium(II) complexes,<sup>2</sup> we report here refinements of the structures and a determination of the structure of *cis*- $\text{Te}(\text{tu})_2\text{I}_2$ ; the crystals of the three homologues are isomorphous. We also report the preparation and the crystal structures of the tetramethylselenourea (tmsu) complexes,  $\text{Te}(\text{tmsu})_2\text{X}_2$ . These have the *cis* configuration for X = Cl and Br and the *trans* for X = I. The bromo complex was obtained in two crystalline forms, and the iodo complex is isomorphous with one of the three crystalline forms of the tetramethylthiourea (tmtu) analogue.<sup>3</sup>

## Experimental

**Preparations.** The complexes  $\text{Te}(\text{tu})_2\text{X}_2$  were prepared as described previously.<sup>4</sup> The tmsu, obtained from tmtu by the method of Klayman and co-workers,<sup>5</sup> was a gift from Dr. O. Vikane. The HCl, HBr and HI used were ca. 37, 48 and 57 % (w/w), respectively.

**The complex  $\text{Te}(\text{tmsu})_2\text{Cl}_2$ .** A mixture of  $\text{Te}_2(\text{tmsu})_2\text{Cl}_4$ <sup>6</sup> (0.5 g) and tmsu (0.5 g) was dissolved at room temperature in methanol (10 cm<sup>3</sup>) to which a drop of HCl had been added. The solution was filtered and diethyl ether (30 cm<sup>3</sup>) was added with swirling. Crystallization started on scratching the beaker walls, and the beaker was placed in a refrigerator; yield, after filtering and washing with diethyl ether, 0.24 g (31 %) of light red, truncated tetragonal bipyramids. Found: C

\*To whom correspondence should be addressed.

Table 1. Crystallographic data for tu complexes.<sup>a</sup>

	1	2	3
Complex	Te(tu) <sub>2</sub> Cl <sub>2</sub>	Te(tu) <sub>2</sub> Br <sub>2</sub>	Te(tu) <sub>2</sub> I <sub>2</sub>
Formula	C <sub>2</sub> H <sub>8</sub> Cl <sub>2</sub> N <sub>4</sub> S <sub>2</sub> Te	C <sub>2</sub> H <sub>8</sub> Br <sub>2</sub> N <sub>4</sub> S <sub>2</sub> Te	C <sub>2</sub> H <sub>8</sub> I <sub>2</sub> N <sub>4</sub> S <sub>2</sub> Te
<i>M</i>	350.75	439.66	533.65
<i>a</i> /Å	9.878(1)	10.020(1)	10.209(1)
<i>b</i> /Å	7.610(1)	7.727(1)	7.974(1)
<i>c</i> /Å	14.104(1)	14.633(1)	15.500(3)
β/°	100.84(1)	100.46(1)	99.89(1)
<i>V</i> /Å <sup>3</sup>	1041.2(4)	1114.0(3)	1243.0(6)
<i>D<sub>x</sub></i> /g cm <sup>-3</sup>	2.237	2.621	2.851
<i>F</i> (000)	664	808	952
μ(MoKα)/cm <sup>-1</sup>	38.01	106.82	77.78
Crystal volume/mm <sup>3</sup>		0.0023	0.0012
Transmission factors		0.161–0.384	0.393–0.703
Unique reflections	1254	1339	1503
Reflections <i>I</i> > 2σ( <i>I</i> )	1169	1197	1330
No. of variables	67	68	68
Extinction coefficient, <i>g</i> × 10 <sup>7</sup>		7.27	15.05
<i>R</i>	0.020	0.024	0.022
<i>R<sub>w</sub></i>	0.023	0.024	0.023
<i>S</i>	1.475	1.537	1.470
Max. Δ(ρ)/e Å <sup>-3</sup>	0.71	0.97	0.82

<sup>a</sup>In each case: Crystal system monoclinic, space group *I*2/a (alt. *C*2/*c*, No. 15), *Z* = 4; scan rate 1.68–0.39° min<sup>-1</sup>, θ<sub>max</sub> = 28°.

Table 2. Crystallographic data for tmsu complexes.

	4	5	6	7
Complex	Te(tmsu) <sub>2</sub> Cl <sub>2</sub>	Te(tmsu) <sub>2</sub> Br <sub>2</sub>	Te(tmsu) <sub>2</sub> Br <sub>2</sub>	Te(tmsu) <sub>2</sub> I <sub>2</sub>
Formula	C <sub>10</sub> H <sub>24</sub> Cl <sub>2</sub> N <sub>4</sub> Se <sub>2</sub> Te	C <sub>10</sub> H <sub>24</sub> Br <sub>2</sub> N <sub>4</sub> Se <sub>2</sub> Te	C <sub>10</sub> H <sub>24</sub> Br <sub>2</sub> N <sub>4</sub> Se <sub>2</sub> Te	C <sub>10</sub> H <sub>24</sub> I <sub>2</sub> N <sub>4</sub> Se <sub>2</sub> Te
<i>M</i>	556.76	645.67	645.67	739.66
System	Tetragonal	Tetragonal	Monoclinic	Monoclinic
Space group	<i>P</i> 4 <sub>3</sub> 2,2 (No. 96)	<i>P</i> 4 <sub>3</sub> 2,2 (No. 96)	<i>P</i> 2 <sub>1</sub> / <i>c</i> (No. 14)	<i>P</i> 2 <sub>1</sub> / <i>n</i> (No. 14)
<i>a</i> /Å	7.601(2)	7.759(2)	12.218(1)	7.996(1)
<i>b</i> /Å			9.978(2)	10.958(1)
<i>c</i> /Å	33.395(9)	33.809(11)	16.846(6)	11.915(2)
β/°			98.38(2)	97.11(1)
<i>V</i> /Å <sup>3</sup>	1929.4(1.5)	2035.4(1.7)	2031.8(1.5)	1035.9(5)
<i>Z</i>	4	4	4	2
<i>D<sub>x</sub></i> /g cm <sup>-3</sup>	1.917	2.107	2.111	2.371
<i>F</i> (000)	1064	1208	1208	676
μ(MoKα)/cm <sup>-1</sup>	59.27	95.21	95.38	82.76
Crystal volume/mm <sup>3</sup>	0.0041	0.0042	0.0079	0.0040
Transmission factors	0.426–0.571	0.252–0.307	0.133–0.273	0.300–0.385
Scan rate/° min <sup>-1</sup>	3.35–0.75	2.51–0.59	2.51–0.48	3.35–0.50
θ <sub>max</sub> /°	28	28	28	30
No. of reflections <sup>a</sup>	5322	5641	4058	3007
Reflections <i>I</i> > 2σ( <i>I</i> )	3392	2718	2859	2436
No. of variables	87	87	173	89
Extinction coefficient, <i>g</i> × 10 <sup>7</sup>			0.37	2.24
<i>R</i>	0.036	0.049	0.029	0.040
<i>R<sub>w</sub></i>	0.028	0.032	0.033	0.045
<i>S</i>	1.335	1.479	1.914	1.982
Max. Δ(ρ)/e Å <sup>-3</sup>	0.70	1.20	1.52	1.44

<sup>a</sup>Unique reflections for 6 and 7. For 4 and 5, see text.

Table 3. Fractional atomic coordinates for *cis*-Te(tu)<sub>2</sub>X<sub>2</sub> with e.s.d.'s in parentheses.

Atom	x	y	z	B <sub>eq</sub> /Å <sup>2</sup>
<b>Te(tu)<sub>2</sub>Cl<sub>2</sub></b>				
Te	¼	0.15372(3)	0	1.857(3)
Cl	0.18632(6)	-0.11281(9)	0.13556(4)	2.75(1)
S	0.22937(6)	0.37876(9)	0.12144(5)	2.79(1)
N(1)	0.04107(21)	0.4325(4)	0.22356(16)	3.29(5)
N(2)	-0.03955(20)	0.2874(4)	0.08290(17)	3.26(5)
C	0.06085(23)	0.3626(3)	0.14253(17)	2.20(4)
<b>Te(tu)<sub>2</sub>Br<sub>2</sub></b>				
Te	¼	0.15391(3)	0	2.025(5)
Br	0.18373(3)	-0.11672(4)	0.13561(2)	2.833(6)
S	0.23174(8)	0.37667(10)	0.11875(6)	3.07(2)
N(1)	0.04587(28)	0.4314(5)	0.21660(20)	3.86(6)
N(2)	-0.03345(25)	0.2963(5)	0.07880(19)	3.59(6)
C	0.0654(3)	0.3651(4)	0.13810(22)	2.42(6)
<b>Te(tu)<sub>2</sub>I<sub>2</sub></b>				
Te	¼	0.15682(3)	0	2.259(5)
I	0.18417(2)	-0.11375(3)	0.13548(1)	3.081(4)
S	0.23251(8)	0.37727(10)	0.11403(6)	3.49(2)
N(1)	0.0456(3)	0.4249(5)	0.20549(21)	2.76(8)
N(2)	-0.02821(27)	0.3124(5)	0.07158(19)	3.98(7)
C	0.0685(3)	0.3685(4)	0.13058(21)	2.73(6)

Table 4. Fractional atomic coordinates for tetragonal *cis*-Te(tmsu)<sub>2</sub>X<sub>2</sub> with e.s.d.'s in parentheses.

Atom	x	y	z	B <sub>eq</sub> /Å <sup>2</sup>
<b>Te(tmsu)<sub>2</sub>Cl<sub>2</sub></b>				
Te	0.33883(3)	0.33883 <sup>a</sup>	½	3.406(5)
Se	0.11499(6)	0.20038(5)	0.553287(11)	4.792(8)
Cl	0.46403(14)	0.54166(13)	0.562064(25)	5.14(2)
N(1)	-0.0424(4)	0.5327(4)	0.54464(8)	4.04(6)
N(2)	0.0337(4)	0.4595(4)	0.60923(7)	4.40(7)
C(1)	0.0263(4)	0.4211(4)	0.57062(8)	3.52(7)
C(2)	-0.0176(6)	0.7231(5)	0.54933(13)	6.8(1)
C(3)	-0.1231(5)	0.4795(6)	0.50724(10)	6.3(1)
C(4)	0.1539(6)	0.3765(6)	0.63738(11)	6.7(1)
C(5)	-0.0942(6)	0.5801(5)	0.62750(12)	7.2(1)
<b>Te(tmsu)<sub>2</sub>Br<sub>2</sub></b>				
Te	0.33490(5)	0.33490 <sup>a</sup>	½	4.30(1)
Br	0.46666(9)	0.54839(9)	0.563511(17)	6.07(2)
Se	0.11551(9)	0.20027(8)	0.552755(18)	5.92(2)
N(1)	-0.0385(6)	0.5253(6)	0.54562(13)	5.6(1)
N(2)	0.0378(6)	0.4481(6)	0.60902(12)	5.7(1)
C(1)	0.0290(7)	0.4142(7)	0.57051(13)	4.5(1)
C(2)	-0.0160(10)	0.7123(9)	0.55036(22)	8.9(2)
C(3)	-0.1155(8)	0.4768(11)	0.50820(16)	8.0(2)
C(4)	0.1575(10)	0.3666(9)	0.63644(16)	8.5(2)
C(5)	-0.0867(10)	0.5658(9)	0.62746(17)	8.9(2)

<sup>a</sup>y = x by symmetry.

Table 5. Fractional atomic coordinates for monoclinic *cis*-Te(tmsu)<sub>2</sub>Br<sub>2</sub> with e.s.d.'s in parentheses.

Atom	x	y	z	B <sub>eq</sub> /Å <sup>2</sup>
Te	0.241877(22)	0.32209(3)	0.251273(17)	2.903(6)
Br	0.32265(5)	0.52153(6)	0.37060(4)	4.99(1)
Br'	0.18340(5)	0.49422(6)	0.11155(4)	5.06(1)
Se	0.28605(4)	0.14348(6)	0.36943(3)	4.39(1)
Se'	0.17289(4)	0.11685(5)	0.15441(3)	4.16(1)
N(1)	0.5083(3)	0.1869(5)	0.34861(26)	5.8(1)
N(2)	0.4745(3)	0.2049(4)	0.47694(23)	3.7(1)
N(1')	-0.0394(3)	0.2229(4)	0.16218(23)	3.7(1)
N(2')	0.0013(3)	0.1908(4)	0.03463(22)	3.6(1)
C(1)	0.4393(4)	0.1835(5)	0.39986(28)	3.5(1)
C(2)	0.6005(5)	0.2824(9)	0.3556(5)	9.7(2)
C(3)	0.4918(6)	0.1110(10)	0.2752(4)	12.0(2)
C(4)	0.4033(5)	0.2535(7)	0.5333(3)	5.6(1)
C(5)	0.5882(5)	0.1706(6)	0.5127(3)	5.1(1)
C(1')	0.0300(4)	0.1851(4)	0.11342(26)	3.1(1)
C(2')	-0.1158(4)	0.3354(6)	0.1421(4)	5.5(1)
C(3')	-0.0392(5)	0.1706(7)	0.2426(3)	6.2(2)
C(4')	0.0789(5)	0.2054(7)	-0.0222(3)	5.6(1)
C(5')	-0.1147(4)	0.1787(6)	-0.0027(3)	4.8(1)

Table 6. Fractional atomic coordinates for monoclinic *trans*-Te(tmsu)<sub>2</sub>I<sub>2</sub> with e.s.d.'s in parentheses.

Atom	x	y	z	B <sub>eq</sub> /Å <sup>2</sup>
Te	0	0	0	2.288(8)
I	-0.18862(5)	0.21424(4)	0.06733(4)	3.733(8)
Se	0.02375(9)	0.09512(5)	-0.21749(5)	3.32(1)
N(1)	0.2000(6)	0.2981(4)	-0.1170(4)	3.1(1)
N(2)	-0.0586(6)	0.3434(4)	-0.2203(4)	3.3(1)
C(1)	0.0589(6)	0.2614(5)	-0.1798(4)	2.5(1)
C(2)	0.2098(10)	0.4093(6)	-0.0480(6)	4.7(2)
C(3)	0.3501(8)	0.2225(7)	-0.0997(7)	4.5(2)
C(4)	-0.2328(9)	0.3088(7)	-0.2531(7)	4.9(2)
C(5)	-0.0175(10)	0.4658(6)	-0.2532(6)	4.6(2)

21.09; H 4.17; N 10.31. Calc. for C<sub>10</sub>H<sub>24</sub>Cl<sub>2</sub>N<sub>4</sub>Se<sub>2</sub>Te: C 21.57; H 4.35; N 10.06. The crystals dissolve readily in water with rapid blackening, and are hygroscopic in moist air.

*The complex Te(tmsu)<sub>2</sub>Br<sub>2</sub> (mon.)*. A mixture of Te<sub>2</sub>(tmsu)<sub>2</sub>Br<sub>4</sub><sup>6</sup> (0.5 g) and tmsu (0.5 g) was dissolved by heating in methanol (10 cm<sup>3</sup>). The solution was cooled and filtered, and diethyl ether (13 cm<sup>3</sup>) was added to the filtrate. Crystallization started on scratching; yield, after 1 h at room temperature, filtering and washing with diethyl

ether containing a little tmsu, 0.51 g (74 %) of light red, rhomb-shaped plates. Found: C 19.08; H 3.81; N 9.45. Calc. for C<sub>10</sub>H<sub>24</sub>Br<sub>2</sub>N<sub>4</sub>Se<sub>2</sub>Te: C 18.60; H 3.90; N 8.68.

*The complex Te(tmsu)<sub>2</sub>Br<sub>2</sub> (tetr.)* was obtained when crystallization was initiated by adding crushed seed crystals of Te(tmsu)<sub>2</sub>Cl<sub>2</sub> to the filtered methanolic solution, after addition of diethyl ether (10 cm<sup>3</sup>). Yield, after filtering and washing as above, 0.24 g of truncated bipyramids.

**The complex Te(tmsu)<sub>2</sub>I<sub>2</sub>.** A mixture of Te<sub>2</sub>(tmsu)<sub>2</sub>I<sub>4</sub><sup>6</sup> (0.56 g, 0.5 mmol) and tmsu (0.18 g, 2 mmol) was dissolved in warm dimethylformamide/HI (20:1, 10 cm<sup>3</sup>), and methanol (10 cm<sup>3</sup>) was added. Yield, after filtering and washing with methanol and then diethyl ether, ca. 0.65 g (88%) of dark red, thick plates. Anal. C<sub>10</sub>H<sub>24</sub>I<sub>2</sub>N<sub>4</sub>Se<sub>2</sub>Te: C, H, N.

**X-Ray structure analyses.** Crystal data, with numbering of complexes, are given in Tables 1 and 2. Complexes 1–3 are isomorphous, as are 4 and 5. The space group symbol *I2/a* is used for complexes 1–3 instead of the earlier<sup>1,4</sup> *I2/c*, since the origin is chosen to lie in a symmetry centre on glide plane *a* and not on glide plane *c*. X-ray measurements were made on a CAD4 diffractometer using graphite-monochromated MoK $\alpha$  radiation ( $\lambda = 0.71069$  Å). Unit cell dimensions were determined from the diffractometer angles for 19–25 automatically centred reflections. Intensities were recorded by  $\omega/2\theta$  scan for complex 6 and by  $\omega$  scan for the others; the scan width was  $A + 0.35 \tan \theta$ , with  $A = 1.00^\circ$  for 1–4 and 7,  $1.20^\circ$  for 5, and  $0.80^\circ$  for 6, plus 25% on each side for background. For complexes 4 and 5, in order to distinguish with greater certainty between space groups *P4<sub>1</sub>2,2* and *P4<sub>3</sub>2,2*, intensity data for the positive and negative octants of the reciprocal lattice were measured and used. The two octants

include a double set of Friedel pairs for all acentric reflections, plus quartets of equivalent zone reflections. The intensities were corrected for Lorentz and polarization effects, for decay where indicated and for absorption except in the case of complex 1, the crystal of which was small and nearly spherical, with faces which were not clearly defined. Maximum decay corrections were ca. 8% for complex 1 and 14% for 4. Reflections with  $I > 2\sigma(I)$  were regarded as observed and were used in the calculations. These were carried out using the Enraf-Nonius SDP programs. Refinements were carried out by the full matrix least-squares technique, the sum minimized being  $\sum w\Delta^2(F)$  with  $w^{-1} = \sigma^2(F) = \sigma^2(I)/4LpI$  and  $\sigma^2(I) = \sigma^2(I)_{\text{count}} + (0.02I)^2$ . Atomic scattering factors, including anomalous dispersion terms, were taken from Ref. 7. Anisotropic thermal parameters were used for all non-hydrogen atoms. For complexes 2, 3, 6 and 7, an extinction coefficient  $g$  in  $F_{\text{corr}} = F_c(1 + gI_c)^{-1}$  was included as a variable.

The earlier coordinates<sup>1</sup> were used as starting coordinates for the refinements of the structures of complexes 1 and 2, and those of 2 were used for 3. The structures of complexes 5 and 6 were

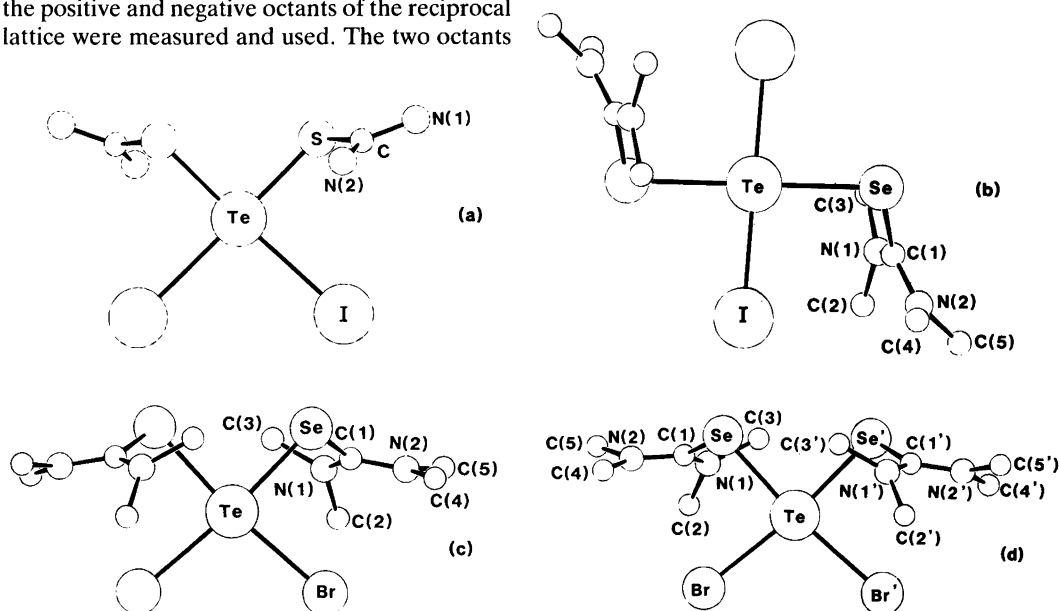


Fig. 1. Views of (a) *cis*-Te(tu)<sub>2</sub>I<sub>2</sub>, (b) *trans*-Te(tmsu)<sub>2</sub>I<sub>2</sub>, and (c) and (d) *cis*-Te(tmsu)<sub>2</sub>Br<sub>2</sub> as it occurs in the tetragonal and monoclinic crystals, respectively.

solved by direct (MULTAN) and Fourier difference methods. For complex **5**, data for the positive octant only were used initially. The coordinates of complex **5** were used as starting coordinates for the refinement of the structure of **4**, and those of the isomorphous form of *trans*-Te(tmtu)<sub>2</sub>I<sub>2</sub><sup>3</sup> were used for **7**. The hydrogen atoms of complexes **1–3** were first placed geometrically and their positions, with individual isotropic thermal parameters, were refined together with the other variables. For complex **3**, seven medium to strong reflections had relatively large  $w\Delta^2(F)$  values and were given zero weight in the last cycles; this was also done for two medium reflections of **2**. For complexes **4**, **6** and **7**, most of the hydrogen atoms were found from Fourier difference maps and the rest were placed geometrically; all were held fixed after a few cycles of refinement, with a common fixed  $B_{\text{iso}}$  for each structure. The fractional hydrogen coordinates of

Table 7. Distances (Å) and angles (°) in *cis*-Te(tu)<sub>2</sub>X<sub>2</sub> with e.s.d.'s in parentheses. Primed atoms related to unprimed ones over molecular two-fold axes.<sup>a</sup>

	X = Cl	X = Br	X = I
<b>Bond lengths</b>			
Te–X	2.936(1)	3.038(1)	3.162(1)
Te–S	2.457(1)	2.476(1)	2.521(1)
S–C	1.750(2)	1.742(3)	1.738(3)
C–N(1)	1.308(3)	1.304(4)	1.303(4)
C–N(2)	1.306(3)	1.306(4)	1.305(4)
<b>Bond angles</b>			
X–Te–X'	92.59(2)	93.01(1)	93.96(1)
X–Te–S	88.37(2)	88.13(2)	87.79(2)
X–Te–S'	172.50(2)	171.73(2)	171.92(2)
S–Te–S'	91.65(3)	91.93(4)	91.57(4)
Te–S–C	106.01(7)	105.85(9)	105.15(9)
S–C–N(1)	115.0(2)	115.1(2)	116.3(2)
S–C–N(2)	123.6(2)	123.1(2)	122.9(2)
N(1)–C–N(2)	121.4(2)	121.9(3)	120.8(3)
<b>Angles between planes<sup>b</sup></b>			
(1)–(2)	10.4	11.4	11.1
(1)–(3)	112.4	110.4	108.8
(3)–(4)	19.5	20.4	24.0

<sup>a</sup>N–H distances: ranges 0.73(3)–0.87(3), 0.70(4)–0.96(5) and 0.77(4)–0.99(5) Å, means 0.81(3), 0.82(5) and 0.88(5) Å, for X = Cl, Br and I, respectively; overall mean 0.83(2) Å. <sup>b</sup>Plane (1): TeSS'; plane (2): TeXX'; plane (3): TeSC; plane (4): SCN(1)N(2). The atoms defining least-squares plane (4) lie in the plane within error limits.

complex **4** were entered for **5** and were held fixed as above. The shifts in the final cycle of refinements were less than one per cent of the asso-

Table 8. Distances (Å) and angles (°) in tetragonal *cis*-Te(tmsu)<sub>2</sub>X<sub>2</sub> with e.s.d.'s in parentheses. Primed atoms as in Table 7.

	X = Cl	X = Br
<b>Bond lengths</b>		
Te–X	2.753(1)	2.898(1)
Te–Se	2.677(1)	2.678(1)
Se–C(1)	1.899(3)	1.888(5)
C(1)–N(1)	1.321(4)	1.314(6)
C(1)–N(2)	1.323(3)	1.330(5)
N(1)–C(2)	1.468(5)	1.471(7)
N(1)–C(3)	1.449(4)	1.449(6)
N(2)–C(4)	1.455(5)	1.457(7)
N(2)–C(5)	1.469(5)	1.468(7)
<b>Bond angles</b>		
X–Te–X'	100.35(4)	98.38(2)
X–Te–Se	86.53(2)	87.35(2)
X–Te–Se'	172.81(2)	173.96(2)
Se–Te–Se'	86.69(2)	87.00(3)
Te–Se–C(1)	94.64(9)	95.44(16)
Se–C(1)–N(1)	120.5(2)	121.0(4)
Se–C(1)–N(2)	118.5(3)	117.8(5)
N(1)–C(1)–N(2)	121.0(3)	121.2(5)
C(1)–N(1)–C(2)	120.8(3)	122.0(5)
C(1)–N(1)–C(3)	123.7(3)	123.6(5)
C(2)–N(1)–C(3)	114.9(3)	113.6(6)
C(1)–N(2)–C(4)	124.1(3)	124.7(5)
C(1)–N(2)–C(5)	120.9(3)	120.4(5)
C(4)–N(2)–C(5)	114.7(3)	114.8(5)
<b>Angles between planes<sup>a</sup></b>		
(1)–(2)	3.1	2.8
(1)–(3)	50.8	50.2
(3)–(4)	55.8	55.7
<b>Distances from selenourea plane<sup>b</sup></b>		
C(1)	0.003(3)	0.002(6)
C(2)	0.743(5)	0.736(8)
C(3)	–0.550(4)	–0.526(7)
C(4)	0.435(5)	0.451(7)
C(5)	–0.583(5)	–0.576(8)
<b>Contacts</b>		
Se...C(3)	3.185(4)	3.176(6)
Se...C(4)	3.125(4)	3.127(5)
C(2)...C(5)	2.887(6)	2.897(9)
Te...C(3)	3.678(4)	3.674(6)

<sup>a</sup>Plane (1): TeSeSe'; plane (2): TeXX'; plane (3): TeSeC(1); plane (4): SeC(1)N(1)N(2). <sup>b</sup>Least-squares plane (4).

ciated standard deviations. Atomic coordinates for non-hydrogen atoms are listed in Tables 3–6. Thermal parameters, hydrogen coordinates, torsion angles and planes have been deposited with the Cambridge Crystallographic Data Centre.

Refinements of the inverted structures of com-

plexes **4** and **5** in the enantiomorphous space group *P4<sub>2</sub>2* gave markedly inferior agreement indexes *R*, *R<sub>w</sub>* and *S*, viz. 0.047, 0.045 and 2.144 for **4** and 0.055, 0.040 and 1.864 for **5**. The *P4<sub>2</sub>2* structure of complex **5** was that arrived at first.

Table 9. Distances (Å) and angles (°) in monoclinic *cis*-Te(tmsu)<sub>2</sub>Br<sub>2</sub> with e.s.d.'s in parentheses. Primed atoms related to unprimed ones over molecular pseudo two-fold axes.

<b>Bond lengths</b>			
Te–Br	2.898(1)	Te–Br'	2.917(1)
Te–Se	2.668(1)	Te–Se'	2.677(1)
Se–C(1)	1.910(3)	Se'–C(1')	1.907(3)
C(1)–N(1)	1.293(5)	C(1')–N(1')	1.319(4)
C(1)–N(2)	1.324(4)	C(1')–N(2')	1.324(4)
N(1)–C(2)	1.466(7)	N(1')–C(2')	1.467(5)
N(1)–C(3)	1.439(7)	N(1')–C(3')	1.452(5)
N(2)–C(4)	1.461(5)	N(2')–C(4')	1.449(5)
N(2)–C(5)	1.471(5)	N(2')–C(5')	1.469(4)
<b>Bond angles</b>			
Br–Te–Br'	100.02(2)	Br–Te–Se	85.97(1)
Br–Te–Se'	173.40(2)	Br'–Te–Se	173.98(2)
Br'–Te–Se'	86.58(1)	Se–Te–Se'	87.43(1)
Te–Se–C(1)	98.29(11)	Te–Se'–C(1')	97.91(10)
Se–C(1)–N(1)	122.4(3)	Se'–C(1')–N(1')	121.0(4)
Se–C(1)–N(2)	117.6(3)	Se'–C(1')–N(2')	118.2(3)
N(1)–C(1)–N(2)	120.0(3)	N(1')–C(1')–N(2')	120.8(3)
C(1)–N(1)–C(2)	122.1(5)	C(1')–N(1')–C(2')	121.4(3)
C(1)–N(1)–C(3)	122.5(5)	C(1')–N(1')–C(3')	124.4(3)
C(2)–N(1)–C(3)	114.9(5)	C(2')–N(1')–C(3')	113.9(4)
C(1)–N(2)–C(4)	123.4(3)	C(1')–N(2')–C(4')	124.3(3)
C(1)–N(2)–C(5)	121.1(3)	C(1')–N(2')–C(5')	121.6(3)
C(4)–N(2)–C(5)	115.3(3)	C(4')–N(2')–C(5')	114.1(3)
<b>Angles between planes<sup>a</sup></b>			
(1)–(2)	0.6		
(1)–(3)	56.9	(1)–(5)	53.4
(3)–(4)	51.3	(5)–(6)	53.6
<b>Distances from selenourea plane<sup>b</sup></b>			
C(1)	0.010(5)	C(1')	0.008(4)
C(2)	0.720(8)	C(2')	0.703(6)
C(3)	–0.567(10)	C(3')	–0.555(7)
C(4)	0.510(7)	C(4')	0.537(7)
C(5)	–0.643(6)	C(5')	–0.616(6)
<b>Contacts</b>			
Se...C(3)	3.179(6)	Se'...C(3')	3.214(4)
Se...C(4)	3.118(4)	Se'...C(4')	3.155(4)
C(2)...C(5)	2.896(7)	C(2')...C(5')	2.899(6)
Te...C(3)	3.682(5)	Te...C(3')	3.735(4)

<sup>a</sup>Planes (1)–(4) as in Table 8; plane (5): TeSe'C(1'); plane (6): Se'C(1')N(1')N(2'). <sup>b</sup>Least-squares plane (4) for C(1)–C(5), (6) for C(1')–C(5').

Table 10. Distances (Å) and angles(°) in monoclinic *trans*-Te(tmsu)<sub>2</sub>I<sub>2</sub> with e.s.d.'s in parentheses.

<b>Bond lengths</b>			
Te—I	2.954(1)	C(1)—N(2)	1.345(5)
Te—Se	2.821(1)	N(1)—C(2)	1.466(6)
Se—C(1)	1.889(4)	N(1)—C(3)	1.452(6)
C(1)—N(1)	1.337(5)	N(2)—C(4)	1.450(6)
		N(2)—C(5)	1.477(6)
<b>Bond angles</b>			
I—Te—Se	92.89(1)	C(1)—N(1)—C(2)	123.2(4)
Te—Se—C(1)	99.38(11)	C(1)—N(1)—C(3)	122.2(4)
Se—C(1)—N(1)	120.9(3)	C(2)—N(1)—C(3)	114.1(3)
Se—C(1)—N(2)	118.8(3)	C(1)—N(2)—C(4)	121.8(4)
N(1)—C(1)—N(2)	120.2(4)	C(1)—N(2)—C(5)	123.0(4)
		C(4)—N(2)—C(5)	114.3(4)
<b>Angles between planes<sup>a</sup></b>			
(1)—(2)	38.3	(2)—(3)	65.4
<b>Distances from selenourea plane<sup>b</sup></b>			
C(1)	−0.011(5)	C(3)	0.387(7)
C(2)	−0.528(8)	C(4)	−0.472(8)
		C(5)	0.700(8)
<b>Contacts</b>			
Se...C(3)	3.134(5)	C(2)...C(5)	2.926(8)
Se...C(4)	3.107(5)	Te...C(3)	4.002(5)

<sup>a</sup>Plane (1): TeISe; plane (2): TeSeC(1); plane (3): SeC(1)N(1)N(2). <sup>b</sup>Least-squares plane (3).

## Results and discussion

Dimensional data are given in Tables 7–10. The three Te(tu)<sub>2</sub>X<sub>2</sub> complexes are isomorphous, as are the Te(tmsu)<sub>2</sub>X<sub>2</sub> complexes **4** and **5**; views of the molecules of **3** and **5–7** are shown in Fig. 1. Complexes **1–6** are *cis* isomers, while **7** is *trans*. In complexes **1–5**, the tellurium atoms lie on two-fold axes: in general positions in **6** and in symmetry centres in **7**. In the two forms **5** and **6** of *cis*-Te(tmsu)<sub>2</sub>Br<sub>2</sub> the molecules are very similar; a molecular pseudo two-fold axis is present in the latter. The *cis* isomers are slightly tetrahedrally distorted; the TeS<sub>2</sub>/TeX<sub>2</sub> or TeSe<sub>2</sub>/TeX<sub>2</sub> dihedral angles are 10.4–11.4° in complexes **1–3** and 0.6–3.1° in **4–6**, and the S—Te—X or Se—Te—X bond angles are 171.73(2)–172.50(2) and 172.81(2)–173.98(2)°, respectively.

*trans*-Influences of ligands. The Te—S bond lengths in *cis*-Te(tu)<sub>2</sub>X<sub>2</sub>, viz. 2.457(1), 2.476(1) and 2.521(1) Å for X = Cl, Br and I, respectively, reflect the greater relative *trans*-influence

of the heavier halides X. The same effect manifests itself in the series Te<sub>2</sub>(tmtu)<sub>2</sub>X<sub>4</sub> and Te<sub>2</sub>(tmsu)<sub>2</sub>X<sub>4</sub>; the Te—S or Te—Se bond lengths increase as the *trans*-ligand X is changed from Cl to Br to I.

In Te(tmsu)<sub>2</sub>X<sub>2</sub>, the geometry is *cis* only for X = Cl or Br. The Te—Cl and Te—Br bonds are shorter, by 0.18–0.12 Å, than in *cis*-Te(tu)<sub>2</sub>Cl<sub>2</sub> and *cis*-Te(tu)<sub>2</sub>Br<sub>2</sub>, which shows that the *trans*-influence of tmsu is smaller than that of tu. Here, the Te—Se bonds for X = Br, viz. 2.678(1) Å in complex **5**, and 2.668(1) and 2.677(1) Å in **6**, are not longer than for X = Cl in **4** [2.677(1) Å]. It appears that at these shorter Te—Cl and Te—Br distances, Cl and Br exert equal *trans*-influence. This aspect is discussed elsewhere.<sup>2</sup>

For thioureas, the order of *trans*-influence in tellurium(II) complexes is tu > ethylenethiourea (etu) ≈ trimethylenethiourea (trtu).<sup>8</sup> Furthermore, selenourea (su) > tu, ethyleneselenourea (esu) > etu, and tmsu > tmtu.<sup>6,8</sup> A comparison of tmsu and trtu can be made: in *cis*-Te(trtu)<sub>2</sub>X<sub>2</sub>, bond lengths are Te—S 2.465(4) and 2.499(5),



and Te–X 2.964(4) and 2.994(2) Å, for X = Cl and Br, respectively,<sup>9</sup> the Te–X distances are longer than for tmsu as the *trans*-ligand in complexes 4–6. The present and previous<sup>6,8</sup> data then indicate the following order of *trans*-influence in tellurium(II) complexes: su > tu ≈ esu > etu ≈ trtu > tmsu > tmtu.

The anionic ligands X = Cl, Br, I, SCN and SeCN have smaller *trans*-influences than the thio- and selenoureas. For the last two anions, SeCN > SCN,<sup>8</sup> but their positions relative to Cl, Br and I are uncertain. In *cis*-Te(trtu)<sub>2</sub>(SCN)<sub>2</sub>,<sup>8</sup> the Te–S (trtu) bond length is 2.530(1) Å, in contrast to 2.499(5) Å for X = Br mentioned above, indicating the order SCN > Br; however, the Te–S(tu) bond length is 2.458(1) Å in *cis*-Te(tu)<sub>2</sub>(SCN)<sub>2</sub>,<sup>8</sup> in contrast to 2.476(1) Å in complex 2, indicating the order Br > SCN.

*Factors affecting cis or trans geometry.* The iodo complex Te(tmsu)<sub>2</sub>I<sub>2</sub> is the only *trans* isomer in the present series. The Te–Se and Te–I bond lengths (Table 10) are as in other centrosymmetric tellurium(II) complexes.<sup>3</sup>

For square-planar PtL<sub>2</sub>X<sub>2</sub> and PdL<sub>2</sub>X<sub>2</sub> complexes, dissimilar *trans*-influence of ligands L and X generally favours formation of the *cis* isomers.<sup>10</sup> This also appears to be the case for TeL<sub>2</sub>X<sub>2</sub> complexes: the *cis* isomers occur in cases where the difference in *trans*-influence of the ligands is largest. With tu at the high end and tmtu at the low end of the L *trans*-influence series, the Te(tu)<sub>2</sub>X<sub>2</sub> complexes (1–3 and X = SCN<sup>8</sup>) are *cis* and Te(tmtu)<sub>2</sub>X<sub>2</sub> (X = Cl, Br, I,<sup>3</sup> SCN<sup>11</sup> or SeCN<sup>12</sup>) are *trans*. The only *trans*-TeL<sub>2</sub>Cl<sub>2</sub> isomer encountered was for L = tmtu,<sup>3</sup> whereas *trans*-TeL<sub>2</sub>I<sub>2</sub> crystallized for L = tmtu,<sup>3</sup> tmsu, etu<sup>11</sup> and probably trtu.<sup>13</sup> Five *cis*- and two *trans*-TeL<sub>2</sub>(SCN)<sub>2</sub> isomers have been isolated, but two *cis*- and four *trans*-TeL<sub>2</sub>(SeCN)<sub>2</sub> isomers.<sup>8</sup>

*The tetramethylselenourea Se–C bond.* This bond lengthens on complexation, as does the S–C bond of tmtu.<sup>11,14</sup> In tmsu itself,<sup>15</sup> the Se–C bond length is 1.863(4) Å. In complex 7, with a Te–Se bond length of 2.821(1) Å, the Se–C bond length is 1.889(4) Å, while in Te<sub>2</sub>(tmsu)<sub>2</sub>Cl<sub>4</sub>,<sup>6</sup> the corresponding values are Te–Se 2.537(1) Å and Se–C 1.920(2) Å. Linear regression of *d*(Se–C) on

*d*(Te–Se) for ten independent tmsu ligands in Te<sub>2</sub>(tmsu)<sub>2</sub>X<sub>4</sub>,<sup>6</sup> the present Te(tmsu)<sub>2</sub>X<sub>2</sub> complexes and *trans*-Te(tmsu)<sub>2</sub>(SeCN)<sub>2</sub>,<sup>11</sup> gave *d*(Se–C) = 2.281–0.142 *d*(Te–Se), with *r* = –0.90. Similarly, for thirteen tmtu ligands in *trans*-Te(tmtu)<sub>2</sub>X<sub>2</sub>,<sup>3</sup> Te<sub>2</sub>(tmtu)<sub>2</sub>X<sub>4</sub><sup>6</sup> and *trans*-Te(tmtu)<sub>2</sub>(SCN)<sub>2</sub>,<sup>11</sup> *d*(S–C) = 2.147–0.159 *d*(Te–S), with *r* = –0.93.

## References

- Foss, O., Johnsen, K., Maartmann-Moe, K. and Marøy, K. *Acta Chem. Scand.* 20 (1966) 113.
- Foss, O., Hermansen, R., Marøy, K. and Moberg, T. *Acta Chem. Scand., Ser. A 41* (1987). 130.
- Foss, O. and Maartmann-Moe, K. *Acta Chem. Scand., Ser. A 40* (1986) 675.
- Foss, O. and Hauge, S. *Acta Chem. Scand.* 13 (1959) 1252; *Ibid.* 15 (1961) 1615.
- Klayman, D. L. and Shine, R. J. *J. Chem. Soc., Chem. Commun.* (1968) 372; *J. Org. Chem.* 34 (1969) 3549; Klayman, D. L. and Griffin, T. S. *J. Am. Chem. Soc.* 95 (1973) 197.
- Eide, J., Foss, O., Maartmann-Moe, K. and Marøy, K. *Acta Chem. Scand., Ser. A 41* (1987). 67.
- Cromer, D. T. and Waber, J. T. *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham 1974, Vol. 4, Table 2.2B; Cromer, D. T. *Ibid.* Table 2.3.1.
- Foss, O., Henjum, J., Maartmann-Moe, K. and Marøy, K. *Acta Chem. Scand., Ser. A 41* (1987). 77.
- Fredin, K. S., Marøy, K. and Slogvik, S. *Acta Chem. Scand., Ser. A 29* (1975) 212.
- Anderson, G. K. and Cross, R. J. *Chem. Soc. Rev.* 9 (1980) 185.
- Foss, O., Maartmann-Moe, K. and Marøy, K. *Acta Chem. Scand., Ser. A 40* (1986) 685.
- Åse, K., Foss, O. and Roti, I. *Acta Chem. Scand.* 25 (1971) 3808.
- Foss, O. In: Andersen, P., Bastiansen, O. and Furberg, S., Eds., *Selected Topics in Structure Chemistry*, Universitetsforlaget, Oslo 1967, pp. 145–173.
- Hough, E. and Nicholson, D. G. *J. Chem. Soc., Dalton Trans.* (1981) 2083.
- Anthoni, U., Borch, G., Larsen, S. and Nielsen, P. H. *Unpublished work*; Larsen, S. and Henriksen, L. *Acta Chem. Scand., Ser. A 38* (1984) 289.

Received July 18, 1986.