# Crystal and Molecular Structures of Dinuclear Complexes of Tellurium Dichloride, Dibromide and Diiodide with Tetramethylthiourea and -selenourea, $Te_2L_2X_4$

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The complexes $Te_2(tmtu)_2Cl_4$ (**1**), $Te_2(tmtu)_2Br_4$ (**2**), $Te_2(tmtu)_2I_4$ (**3**) (tmtu = tetramethylthiourea), $Te_2(tmsu)_2Cl_4$ (**4**), $Te_2(tmsu)_2Br_4$ (**5**), and $Te_2(tmsu)_2I_4$ (**6**) (tmsu = tetramethylselenourea) form isomorphous triclinic crystals, space group $P\bar{1}$ (No. 2) with $Z = 1$. The structures have been determined by X-ray methods and refined to $R = 0.035$ (**1**), 0.038 (**2**), 0.035 (**3**), 0.020 (**4**), 0.045 (**5**) and 0.024 (**6**) for 2511, 2241, 2691, 2439, 2694 and 2546 observed reflections, respectively. The crystals contain planar, dinuclear *af*-S(X)Te($\mu$-X)$_2$Te(X)S or *af*-Se(X) Te($\mu$-X)$_2$Te(X)Se coordination groups, with the two halves of a group related by a symmetry centre. The bridges are asymmetric, owing to the stronger *trans*-influence of the tmtu and tmsu ligands than that of the X ligands. The environment of tellurium(II) is distorted square-planar. In the S–Te–X systems of **1–3**, Te–S bond lengths are 2.425(1), 2.441(2) and 2.473(2) Å, Te–X bond lengths are 3.217(2), 3.284(1) and 3.360(1) Å, and the angles S–Te–X are 171.64(4), 173.18(4) and 175.19(4)°, respectively. In the Se–Te–X systems of **4–6**, Te–Se bond lengths are 2.537(1), 2.550(1) and 2.575(1) Å, Te–X bond lengths are 3.267(1), 3.343(1) and 3.431(1) Å, and the angles Se–Te–X are 172.00(1), 173.29(2) and 174.89(1)°, respectively. The variation in Te–S and Te–Se bond lengths reflects the increase in relative *trans*-influence of the halides from Cl to I and the Te–X bond lengths reflect the greater *trans*-influence of tmsu than of tmtu. The complex $Te_2(tmsu)_2Br_4$ was also obtained in an orthorhombic form, with Te–Se bond length 2.544(1) Å, Te–Br bond length 3.342(1) Å and angle Se–Te–Br 174.36(3)°.

The complexes $Te_2(tmtu)_2Cl_4$ and $Te_2(tmtu)_2Br_4$ (tmtu = tetramethylthiourea) were prepared some time ago,[1] and their crystal structures, based on X-ray film data, were briefly reported.[2] We have prepared the iodo complex, $Te_2(tmtu)_2I_4$, as well as the tetramethylselenourea (tmsu) analogues, $Te_2(tmsu)_2X_4$ (X = Cl, Br or I); we report here the structures of the six complexes, the crystals of which are isomorphous. A dimorph of $Te_2(tmsu)_2Br_4$ with the same molecular structure was also obtained. With formally only three ligands per tellurium atom, and in accordance with the general tendency for tellurium(II) towards planar four-coordination, the complexes are dinuclear in the solid state.

## Experimental

*Preparations.* The tmsu, prepared from tmtu by the method of Klayman and co-workers,[3] was a gift from Dr. O. Vikane. The HCl, HBr and HI used were ca. 37, 48 and 57% (*w*/*w*), respectively.

*The complex $Te_2(tmtu)_2Cl_4$* was prepared from $TeO_2$ dissolved in HCl as described earlier.[1]

*The complex $Te_2(tmtu)_2Br_4$* was prepared by a slightly amended procedure: To $TeO_2$ (1.6 g, 10 mmol) dissolved in hot HBr (10 cm$^3$) were added, with swirling, a hot solution of tmtu (2.7 g, 20 mmol) in dimethylformamide (DMF) (20 cm$^3$)

and then a hot mixture of water (100 cm$^3$), HBr (10 cm$^3$) and methanol (100 cm$^3$). The resulting solution was kept hot for 1–2 h, during which most of the crystallization took place, and was then allowed to cool to room temperature. The crystals were filtered off and washed with methanol to which a little HBr had been added, and then with diethyl ether; yield 2.3–2.9 g (55–69 % based on Te). The complex was recrystallized by dissolving 1 g, with gentle heating, in DMF/HBr (10:1, 20 cm$^3$), filtering if necessary and adding hot methanol (20 cm$^3$); yield, after isolation as before, ca. 0.6 g.

*The complex* $Te_2(tmtu)_2I_4$ was prepared by dissolving $TeO_2$ (1.6 g, 10 mmol) in hot HCl (5 cm$^3$) and adding, with swirling, a hot solution of tmtu (2.7 g, 20 mmol) in DMF (40 cm$^3$) and then a hot mixture of HI (10 cm$^3$) and methanol (200 cm$^3$). The resulting solution was kept hot for ca. 30 min and was then allowed to cool to room temperature; yield, after filtering and washing with methanol and then with diethyl ether, 4.9 g (95 % based on Te). The complex was recrystallized by dissolving 1 g, with gentle heating, in DMF (20 cm$^3$) to which HI (one drop) had been added, filtering and adding hot methanol (20 cm$^3$); yield, after isolation as before, ca. 0.7 g of dark red crystals. Found: C 12.70; H 2.57; N 5.27; S 6.27. Calc. for $C_5H_{12}I_2N_2STe$: C 11.69; H 2.53; N 5.45; S 6.24. The use of lower temperatures and more concentrated solutions led to the isolation of $Te(tmtu)_2I_2$.[4]

*The complex* $Te_2(tmsu)_2Cl_4$. To $TeO_2$ (0.8 g, 5 mmol) dissolved by heating in HCl (5 cm$^3$) were added, with swirling, a solution of tmsu (1.8 g, 10 mmol) in DMF (10 cm$^3$) and then a hot mixture of methanol (50 cm$^3$) and HCl (5 cm$^3$). Crystallization started on scratching the beaker walls. The mixture was allowed to cool to room temperature, with frequent repeated scratching, until no more crystals formed (ca. 3 h); yield, after filtering and washing with methanol containing a little HCl and then with diethyl ether, ca. 1.3 g (69 % based on Te). The product was recrystallized by dissolving 1 g in hot DMF/HCl (10:1, 20 cm$^3$); yield, after isolation as before, 0.4–0.5 g. Anal. $C_5H_{12}Cl_2N_2SeTe$: C, H, N.

*The complex* $Te_2(tmsu)_2Br_4$ *(tric.)*. To $TeO_2$ (0.8 g, 5 mmol) dissolved by heating in HBr (5 cm$^3$) was added, with swirling, a solution of tmsu (2.7 g, 15 mmol) in DMF (30 cm$^3$). The mixture was

*Table 1.* Crystallographic data for $Te_2(tmtu)_2X_4$.[a]

| | **1** | **2** | **3** |
|---|---|---|---|
| Complex | $Te_2(tmtu)_2Cl_4$ | $Te_2(tmtu)_2Br_4$ | $Te_2(tmtu)_2I_4$ |
| Formula | $C_{10}H_{24}Cl_4N_4S_2Te_2$ | $C_{10}H_{24}Br_4N_4S_2Te_2$ | $C_{10}H_{24}I_4N_4S_2Te_2$ |
| $M$ | 661.47 | 839.29 | 1027.27 |
| $a$/Å | 7.985(1) | 8.108(1) | 8.375(1) |
| $b$/Å | 8.543(1) | 8.718(1) | 9.068(2) |
| $c$/Å | 9.412(1) | 9.616(1) | 9.891(2) |
| $\alpha$/° | 107.75(1) | 108.45(1) | 109.14(2) |
| $\beta$/° | 110.84(1) | 109.90(1) | 109.68(1) |
| $\gamma$/° | 93.70(1) | 94.84(1) | 96.10(1) |
| $V$/Å$^3$ | 560.6(2) | 592.0(2) | 648.1(4) |
| $D_x$/g cm$^{-3}$ | 1.959 | 2.354 | 2.632 |
| $F$(000) | 316 | 388 | 460 |
| $\mu$(Mo$K\alpha$)/cm$^{-1}$ | 33.4 | 99.0 | 73.1 |
| Absorption corrections | 1.40–1.72 | 1.86–2.87 | 1.69–2.31 |
| Unique reflections | 2692 | 2852 | 3101 |
| Reflections $I > 2\sigma$ | 2511 | 2241 | 2691 |
| Extinction coefficient, $g \times 10^3$ | 1.8 | 1.2 | 1.6 |
| $R$ | 0.035 | 0.038 | 0.035 |
| Max. $\Delta(\varrho)$/e Å$^{-3}$ | 0.92 | 0.87 | 0.93 |

[a] In each case: Crystal system triclinic, space group $P\bar{1}$ (No. 2), $Z = 1$.

*Table 2.* Crystallographic data for $Te_2(tmsu)_2X_4$.

| | 4 | 5 | 6 | 7 |
|---|---|---|---|---|
| Complex | $Te_2(tmsu)_2Cl_4$ | $Te_2(tmsu)_2Br_4$ | $Te_2(tmsu)_2I_4$ | $Te_2(tmsu)_2Br_4$ |
| Formula | $C_{10}H_{24}Cl_4N_4Se_2Te_2$ | $C_{10}H_{24}Br_4N_4Se_2Te_2$ | $C_{10}H_{24}I_4N_4Se_2Te_2$ | $C_{10}H_{24}Br_4N_4Se_2Te_2$ |
| $M$ | 755.26 | 933.09 | 1121.06 | 933.09 |
| System | Triclinic | Triclinic | Triclinic | Orthorhombic |
| Space group | $P\bar{1}$ (No. 2) | $P\bar{1}$ (No. 2) | $P\bar{1}$ (No. 2) | *Pbca* (No. 61) |
| $a$/Å | 8.060(1) | 8.165(1) | 8.394(1) | 9.118(1) |
| $b$/Å | 8.669(2) | 8.837(2) | 9.153(1) | 11.114(2) |
| $c$/Å | 9.499(1) | 9.700(2) | 9.983(1)) | 23.736(2) |
| $\alpha$/° | 108.27(1) | 109.01(1) | 109.71(1) | |
| $\beta$/° | 111.62(1) | 110.77(1) | 110.58(1) | |
| $\gamma$/° | 92.75(1) | 93.68(1) | 94.96(1) | |
| $V$/Å | 575.8(3) | 605.8(5) | 657.4(4) | 2405.3(8) |
| $Z$ | 1 | 1 | 1 | 4 |
| $D_x$/g cm$^{-3}$ | 2.178 | 2.558 | 2.832 | 2.577 |
| $F$(000) | 352 | 424 | 520 | 1696 |
| $\mu$(Mo$K\alpha$)/cm$^{-1}$ | 64.87 | 127.22 | 100.27 | 128.16 |
| Crystal volume/mm$^3$ | 0.0024 | 0.0090 | 0.0011 | 0.0021 |
| Transmission factors | 0.287–0.608 | 0.035–0.406 | 0.458–0.646 | 0.272–0.440 |
| Scan rate/°min$^{-1}$ | 2.51–0.40 | 1.68–1.55 | 1.68–0.54 | 2.51–0.31 |
| $\theta_{max}$/° | 28 | 30 | 28 | 28 |
| Unique reflections | 2765 | 3454 | 3150 | 2884 |
| Reflections $I > 2\sigma$ | 2439 | 2694 | 2546 | 1637 |
| No. of variables | 138 | 138 | 138 | 101 |
| Extinction coefficient, $g \times 10^7$ | 12.52 | 15.37 | 6.09 | 0.41 |
| $R$ | 0.020 | 0.045 | 0.024 | 0.034 |
| $R_w$ | 0.024 | 0.044 | 0.027 | 0.034 |
| $S$ | 1.507 | 2.477 | 1.536 | 1.244 |
| Max. $\Delta(\varrho)$/e Å$^{-3}$ | 0.61 | 1.30 | 1.20 | 0.43 |

warmed, and a hot mixture of methanol (50 cm$^3$) and HBr (5 cm$^3$) was added. Crystallization started on scratching the beaker walls; yield, after cooling to room temperature, filtering and washing with methanol and then diethyl ether, ca. 2.1 g (90 % based on Te). The product was recrystallized by dissolving 1 g, together with a little tmsu, in hot DMF/HBr (10:1, 20 cm$^3$), filtering if necessary and adding warm methanol (20 cm$^3$); yield, after isolation as before, ca. 0.75 g. Anal. $C_5H_{12}Br_2N_2SeTe$: C, H, N.

*The complex $Te_2(tmsu)_2Br_4$ (o-rh.)* was obtained when 10 mmol of tmsu instead of 15 mmol per 5 mmol of $TeO_2$ was used, as in the preparations of $Te_2(tmsu)_2Cl_4$ and $Te_2(tmsu)_2I_4$. To a solution of $TeO_2$ in HBr as above were added, with swirling, a warm solution of tmsu (1.8 g, 10 mmol) in DMF (10 cm$^3$) and then a hot mixture of water (50 cm$^3$), methanol (50 cm$^3$) and HBr (5 cm$^3$). A brown substance rapidly separated; yield, after filtering and washing with methanol and then diethyl ether, 1.68 g. The product was dissolved by heating in DMF/HBr (10:1, 32 cm$^3$) and warm methanol (32 cm$^3$) was added. On scratching, rapid crystallization set in; yield 1.24 g. The crystals were mostly long, flat, orthorhombic prisms of light brown colour, admixed with some dark plates of the triclinic form. The orthorhombic crystals were subsequently obtained from a triclinic sample by seeding: 0.5 g of the latter was dissolved by heating in DMF/HBr (10:1, 15 cm$^3$) and methanol (15 cm$^3$) was added. On seeding with crushed orthorhombic prisms, rapid crystallization started; yield, after cooling to room temperature and then in a refrigerator, 0.40 g. This product also contained some triclinic crystals.

*Table 3.* Fractional atomic coordinates for $Te_2(tmtu)_2X_4$ with e.s.d.'s in parentheses.

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| $Te_2(tmtu)_2Cl_4$ | | | |
| Te | 0.01975(4) | 0.20138(3) | −0.09760(3) |
| Cl(1) | −0.19849(19) | 0.29282(18) | −0.31846(17) |
| Cl(2) | 0.24946(19) | 0.11380(20) | 0.12589(19) |
| S | 0.25359(16) | 0.43370(13) | −0.04106(13) |
| N(1) | 0.3227(5) | 0.2370(5) | −0.2911(5) |
| N(2) | 0.2737(5) | 0.4987(5) | −0.2913(5) |
| C(1) | 0.2851(5) | 0.3817(5) | −0.2252(5) |
| C(2) | 0.2598(10) | 0.1579(9) | −0.4713(9) |
| C(3) | 0.4113(8) | 0.1325(8) | −0.2010(7) |
| C(4) | 0.1726(8) | 0.6354(7) | −0.2620(7) |
| C(5) | 0.3849(8) | 0.5152(7) | −0.3845(7) |
| $Te_2(tmtu)_2Br_4$ | | | |
| Te | 0.02442(5) | 0.20600(5) | −0.09423(5) |
| Br(1) | −0.20437(10) | 0.29642(9) | −0.31823(9) |
| Br(2) | 0.26201(9) | 0.10606(10) | 0.12715(9) |
| S | 0.26209(21) | 0.43316(19) | −0.04221(18) |
| N(1) | 0.3053(6) | 0.2341(6) | −0.3008(6) |
| N(2) | 0.2760(6) | 0.4958(6) | −0.2903(6) |
| C(1) | 0.2817(7) | 0.3800(7) | −0.2274(7) |
| C(2) | 0.2346(12) | 0.1569(10) | −0.4789(10) |
| C(3) | 0.3935(10) | 0.1274(9) | −0.2153(9) |
| C(4) | 0.1916(10) | 0.6387(9) | −0.2478(9) |
| C(5) | 0.3762(9) | 0.5041(9) | −0.3907(9) |
| $Te_2(tmtu)_2I_4$ | | | |
| Te | 0.02789(4) | 0.20746(4) | −0.09228(4) |
| I(1) | −0.21724(5) | 0.29405(5) | −0.32316(5) |
| I(2) | 0.27618(5) | 0.09413(5) | 0.13086(5) |
| S | 0.26759(19) | 0.42774(16) | −0.04345(16) |
| N(1) | 0.2870(6) | 0.2325(5) | −0.3068(5) |
| N(2) | 0.2720(5) | 0.4892(5) | −0.2853(5) |
| C(1) | 0.2762(6) | 0.3774(6) | −0.2272(6) |
| C(2) | 0.2041(9) | 0.1579(9) | −0.4784(9) |
| C(3) | 0.3705(9) | 0.1295(8) | −0.2312(8) |
| C(4) | 0.2043(9) | 0.6326(9) | −0.2316(8) |
| C(5) | 0.3570(8) | 0.4957(8) | −0.3934(8) |

*The complex* $Te_2(tmsu)_2I_4$. To $TeO_2$ (0.8 g, 5 mmol) dissolved in hot HCl (2.5 $cm^3$) were added, with swirling, a solution of tmsu (1.8 g, 10 mmol) in DMF (50 $cm^3$) and a room-temperature mixture of methanol (50 $cm^3$) and HI (5 $cm^3$). Crystallization started on scratching the beaker walls. After 1–2 h the crystals were filtered off and washed with methanol and then diethyl ether; yield, ca. 2.5 g (89 % based on Te). The product was recrystallized by dissolving 1 g in warm DMF/HI (20:1, 15 $cm^3$), filtering if necessary and adding hot methanol (15 $cm^3$); yield, after cooling to room temperature and then in a refrigerator, ca. 0.9 g. Anal. $C_5H_{12}I_2N_2SeTe$: C, H, N.

The crystals of triclinic $Te_2(tmsu)_2X_4$ were flat prisms or oblong plates of dark violet, almost black colour.

*X-Ray structure analyses.* Crystal data, with numbering of complexes, are given in Tables 1 and 2. Complexes **1**–**6** are isomorphous.

*Complexes* **1–3**, *$Te_2(tmtu)_2X_4$*. The structures of complexes **1** and **2** were solved by Patterson and Fourier methods using two- and partly three-dimensional intensity data estimated visually from Weissenberg photographs taken with Cu$K\alpha$ radiation.[2] For the present work, X-ray data were collected using a Siemens AED diffractometer and Nb-filtered Mo$K\alpha$ radiation ($\lambda$ = 0.71069 Å). Unit cell dimensions were based on the $2\theta$ values of the Mo$K\alpha_1$ peaks ($\lambda$ = 0.70926 Å) and in most cases also the Mo$K\alpha_2$ peaks ($\lambda$ = 0.71353 Å) of ca. 30 reflections in the $38 < 2\theta < 54°$ range. $2\theta_{max}$ for intensities was 56°. Three reference reflections, measured at intervals of 50 reflections, indicated no deterioration of the crystals. The "X-Ray 72" programs[5] were used for calculations. Experimental procedures, treatment of data, scattering factors and details of refinement, including final sin $\theta_{min}$ = 0.1, were as described in Ref. 4.

Refinements of the structures of complexes **1** and **2** started with the coordinates from the earlier work, and those for **2** were used as starting coordinates for the refinement of the structure of

*Table 4*. Fractional atomic coordinates for triclinic $Te_2(tmsu)_2X_4$ with e.s.d.'s in parentheses.

| Atom | *x* | *y* | *z* | $B_{eq}$/Å$^2$ |
|---|---|---|---|---|
| $Te_2(tmsu)_2Cl_4$ | | | | |
| Te | 0.01881(2) | 0.19924(2) | −0.09491(2) | 2.681(3) |
| Cl(1) | −0.20554(11) | 0.29035(9) | −0.31619(9) | 4.49(2) |
| Cl(2) | 0.25337(11) | 0.11254(9) | 0.12533(9) | 4.96(2) |
| Se | 0.25621(3) | 0.44245(3) | −0.03165(3) | 2.959(5) |
| N(1) | 0.3173(3) | 0.2336(3) | −0.2995(2) | 3.31(5) |
| N(2) | 0.2715(3) | 0.4938(3) | −0.3019(2) | 3.15(4) |
| C(1) | 0.2841(3) | 0.3801(3) | −0.2331(3) | 2.53(5) |
| C(2) | 0.2586(6) | 0.1559(5) | −0.4759(4) | 6.0(1) |
| C(3) | 0.4052(4) | 0.1320(4) | −0.2073(4) | 4.70(7) |
| C(4) | 0.1762(5) | 0.6325(4) | −0.2691(4) | 4.60(7) |
| C(5) | 0.3784(4) | 0.5041(4) | −0.3958(3) | 4.50(7) |
| $Te_2(tmsu)_2Br_4$ | | | | |
| Te | 0.02247(4) | 0.20405(4) | −0.09224(4) | 2.630(7) |
| Br(1) | −0.21114(9) | 0.29247(8) | −0.32000(8) | 4.23(2) |
| Br(2) | 0.26418(9) | 0.10836(8) | 0.12852(8) | 4.65(2) |
| Se | 0.26275(8) | 0.44295(7) | −0.03221(6) | 3.03(1) |
| N(1) | 0.3034(6) | 0.2322(6) | −0.3053(5) | 3.3(1) |
| N(2) | 0.2722(6) | 0.4924(5) | −0.2985(5) | 2.9(1) |
| C(1) | 0.2808(6) | 0.3799(6) | −0.2341(6) | 2.4(1) |
| C(2) | 0.2335(11) | 0.1528(9) | −0.4771(8) | 5.8(2) |
| C(3) | 0.3911(8) | 0.1315(8) | −0.2191(8) | 4.7(2) |
| C(4) | 0.1902(9) | 0.6330(8) | −0.2596(8) | 4.8(2) |
| C(5) | 0.3691(8) | 0.4984(8) | −0.3988(7) | 4.4(2) |
| $Te_2(tmsu)_2I_4$ | | | | |
| Te | 0.02497(3) | 0.20752(3) | −0.09044(2) | 3.048(5) |
| I(1) | −0.22448(4) | 0.28911(3) | −0.32865(3) | 4.383(7) |
| I(2) | 0.27757(4) | 0.10151(3) | 0.13460(3) | 4.648(7) |
| Se | 0.26751(5) | 0.44080(5) | −0.03269(4) | 3.623(9) |
| N(1) | 0.2856(4) | 0.2330(4) | −0.3097(3) | 3.63(7) |
| N(2) | 0.2670(4) | 0.4879(4) | −0.2947(3) | 3.46(7) |
| C(1) | 0.2742(5) | 0.3795(4) | −0.2333(4) | 2.98(8) |
| C(2) | 0.2046(7) | 0.1564(6) | −0.4797(5) | 5.5(1) |
| C(3) | 0.3676(6) | 0.1331(5) | −0.2319(5) | 4.9(1) |
| C(4) | 0.1970(7) | 0.6287(5) | −0.2466(6) | 5.3(1) |
| C(5) | 0.3513(6) | 0.4885(5) | −0.4000(5) | 4.7(1) |

*Table 5.* Fractional atomic coordinates for orthorhombic Te$_2$(tmsu)$_2$Br$_4$ with e.s.d.'s in parentheses.

| Atom | $x$ | $y$ | $z$ | $B_{eq}$/Å$^2$ |
|---|---|---|---|---|
| Te | 0.06854(5) | 0.14180(5) | 0.06464(2) | 2.732(8) |
| Br(1) | −0.04375(10) | 0.19375(9) | 0.17046(4) | 4.45(2) |
| Br(2) | 0.16327(9) | 0.08591(8) | −0.04165(3) | 3.59(2) |
| Se | 0.25092(9) | 0.31428(7) | 0.07185(3) | 3.20(1) |
| N(1) | 0.4693(6) | 0.1539(6) | 0.1128(3) | 3.1(1) |
| N(2) | 0.4260(6) | 0.3221(6) | 0.1679(3) | 3.2(1) |
| C(1) | 0.3965(7) | 0.2533(7) | 0.1231(3) | 2.9(1) |
| C(2) | 0.5359(9) | 0.0803(8) | 0.1574(4) | 4.7(2) |
| C(3) | 0.4848(9) | 0.1033(8) | 0.0562(4) | 4.2(2) |
| C(4) | 0.3201(9) | 0.4024(9) | 0.1943(3) | 4.5(2) |
| C(5) | 0.5756(8) | 0.3329(9) | 0.1905(3) | 4.4(2) |

*Table 6.* Distances (Å) and angles (°) in Te$_2$(tmtu)$_2$X$_4$ with e.s.d.'s in parentheses. Primed atoms are related to unprimed ones over symmetry centre in 0,0,0.

| | X = Cl | X = Br | X = I |
|---|---|---|---|
| Bond lengths | | | |
| Te–X(1) | 2.561(2) | 2.703(1) | 2.899(1) |
| Te–X(2) | 2.596(2) | 2.769(1) | 3.017(1) |
| Te–S | 2.425(1) | 2.441(2) | 2.473(2) |
| Te–X(2′) | 3.217(2) | 3.284(1) | 3.360(1) |
| S–C(1) | 1.766(5) | 1.759(7) | 1.751(6) |
| C(1)–N(1) | 1.310(6) | 1.310(8) | 1.323(7) |
| C(1)–N(2) | 1.321(7) | 1.328(9) | 1.318(8) |
| N(1)–C(2) | 1.496(8) | 1.501(10) | 1.474(8) |
| N(1)–C(3) | 1.461(8) | 1.499(11) | 1.471(10) |
| N(2)–C(4) | 1.475(8) | 1.483(10) | 1.483(9) |
| N(2)–C(5) | 1.481(9) | 1.471(11) | 1.483(10) |
| Bond angles | | | |
| X(1)–Te–X(2) | 178.23(6) | 178.00(3) | 176.02(1) |
| S–Te–X(1) | 88.51(5) | 89.61(5) | 91.11(4) |
| S–Te–X(2) | 89.83(5) | 90.42(4) | 91.14(4) |
| S–Te–X(2′) | 171.64(4) | 173.18(4) | 175.19(4) |
| X(1)–Te–X(2′) | 99.76(5) | 97.15(2) | 93.55(2) |
| X(2)–Te–X(2′) | 81.92(5) | 82.86(3) | 84.29(2) |
| Te–X(2)–Te′ | 98.08(4) | 97.14(2) | 95.71(2) |
| Te–S–C(1) | 102.3(1) | 101.8(2) | 102.2(2) |
| S–C(1)–N(1) | 122.2(4) | 122.4(5) | 121.9(5) |
| S–C(1)–N(2) | 116.3(3) | 117.3(4) | 117.9(4) |
| N(1)–C(1)–N(2) | 121.4(5) | 120.3(6) | 120.1(5) |
| C(1)–N(1)–C(2) | 121.2(5) | 121.9(6) | 122.0(5) |
| C(1)–N(1)–C(3) | 124.3(4) | 123.1(5) | 122.7(5) |
| C(2)–N(1)–C(3) | 114.2(5) | 114.9(6) | 115.1(5) |
| C(1)–N(2)–C(4) | 124.3(5) | 123.2(6) | 123.0(6) |
| C(1)–N(2)–C(5) | 121.1(4) | 121.6(6) | 123.0(5) |
| C(4)–N(2)–C(5) | 114.1(5) | 114.6(6) | 113.5(6) |
| Contacts | | | |
| S···C(3) | 3.143(7) | 3.145(9) | 3.129(8) |
| S···C(4) | 3.014(7) | 3.015(9) | 3.001(9) |
| C(2)···C(5) | 2.914(10) | 2.885(11) | 2.913(10) |
| Te···C(3) | 3.622(7) | 3.605(10) | 3.615(9) |

*Table 7.* Distances (Å) and angles (°) in triclinic $Te_2(tmsu)_2X_4$ with e.s.d.'s in parentheses. Primed atoms as in Table 6.

| | X = Cl | X = Br | X = I |
|---|---|---|---|
| Bond lengths | | | |
| Te–X(1) | 2.586(1) | 2.731(1) | 2.927(1) |
| Te–X(2) | 2.593(1) | 2.755(1) | 2.994(1) |
| Te–Se | 2.537(1) | 2.550(1) | 2.575(1) |
| Te–X(2′) | 3.267(1) | 3.343(1) | 3.431(1) |
| Se–C(1) | 1.920(2) | 1.916(4) | 1.912(3) |
| C(1)–N(1) | 1.318(3) | 1.322(5) | 1.332(4) |
| C(1)–N(2) | 1.332(3) | 1.329(5) | 1.325(4) |
| N(1)–C(2) | 1.470(4) | 1.451(7) | 1.462(5) |
| N(1)–C(3) | 1.460(3) | 1.465(6) | 1.458(5) |
| N(2)–C(4) | 1.471(3) | 1.454(6) | 1.466(5) |
| N(2)–C(5) | 1.467(3) | 1.466(5) | 1.460(5) |
| Bond angles | | | |
| X(1)–Te–X(2) | 177.92(2) | 177.58(2) | 175.80(1) |
| Se–Te–X(1) | 88.47(2) | 89.31(2) | 90.69(1) |
| Se–Te–X(2) | 89.72(2) | 90.31(2) | 91.09(1) |
| Se–Te–X(2′) | 172.00(1) | 173.29(2) | 174.89(1) |
| X(1)–Te–X(2′) | 98.94(2) | 96.95(2) | 93.99(1) |
| X(2)–Te–X(2′) | 82.93(2) | 83.53(1) | 84.37(1) |
| Te–X(2)–Te′ | 97.07(2) | 96.47(1) | 95.63(1) |
| Te–Se–C(1) | 99.85(6) | 99.50(11) | 99.64(10) |
| Se–C(1)–N(1) | 122.1(2) | 121.7(3) | 121.5(2) |
| Se–C(1)–N(2) | 116.6(2) | 116.9(3) | 117.8(2) |
| N(1)–C(1)–N(2) | 121.2(2) | 121.4(3) | 120.7(3) |
| C(1)–N(1)–C(2) | 121.8(2) | 122.3(4) | 121.7(3) |
| C(1)–N(1)–C(3) | 123.5(2) | 123.3(4) | 123.2(3) |
| C(2)–N(1)–C(3) | 114.6(3) | 114.4(4) | 115.0(3) |
| C(1)–N(2)–C(4) | 123.4(2) | 124.2(4) | 123.3(3) |
| C(1)–N(2)–C(5) | 121.2(2) | 122.0(3) | 122.1(3) |
| C(4)–N(2)–C(5) | 114.7(2) | 113.2(4) | 114.0(3) |
| Contacts | | | |
| Se···C(3) | 3.231(3) | 3.229(5) | 3.225(5) |
| Se···C(4) | 3.095(3) | 3.107(5) | 3.104(5) |
| C(2)···C(5) | 2.891(6) | 2.931(9) | 2.901(7) |
| Te···C(3) | 3.662(3) | 3.653(5) | 3.643(4) |

C–H bond lengths in the methyl groups: ranges 0.85(4)–1.16(4), 0.82(6)–1.14(6) and 0.86(5)–1.18(5) Å, means 0.98(3), 0.99(2) and 0.98(2) Å for X = Cl, Br and I, respectively; overall mean 0.98(1) Å.

3. The largest shift/error ratio in the last cycle was 0.02 for complexes **1** and **2** and 0.03 for **3**. Atomic coordinates are listed in Table 3.

*Complexes* **4–7**, *$Te_2(tmsu)_2X_4$*. X-Ray diffraction measurements were made on a CAD4 diffractometer using graphite-monochromated Mo$K\alpha$ radiation ($\lambda$ as stated above). Unit cell dimensions were determined from the diffractometer angles for 18–25 automatically centred reflections. Intensities were recorded by $\omega/2\theta$ scan for complexes **4–6** and by $\omega$ scan for **7**; the scan width was $A + 0.35 \tan\theta$, with $A = 1.00°$ for **4**, **6** and **7**, and 1.50° for **5**, plus 25 % on each side for background. The intensities were corrected for Lorentz and polarization effects, decay and absorption. The maximum decay correction, based on three reference reflections measured every 2 h of exposure time, was 7.4 % (for complex **7**). Reflections with $I > 2\sigma(I)$ were regarded as ob-

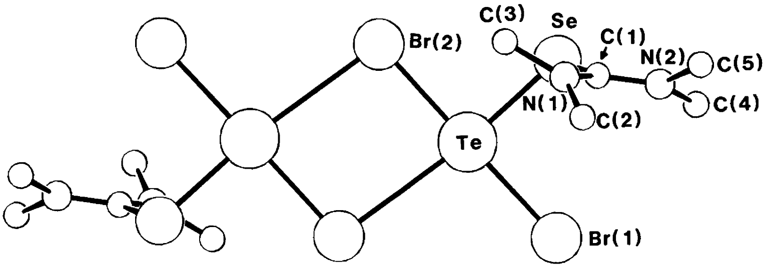

*Fig. 1.* View of a molecule, $Te_2(tmsu)_2Br_4$, in the triclinic crystals.

served and were used in the calculations. These were carried out using the Enraf-Nonius SDP programs. Scattering factors, refinements and weights were as described in Ref. 6.

The structures of complexes **5** and **7** were solved by Patterson and Fourier difference methods, and the coordinates for **5** were used as starting coordinates for the refinements of the structures of **4** and **6**. Anisotropic thermal parameters were used for all non-hydrogen atoms. Hydrogen positions for complex **4** were found from a Fourier difference map; the hydrogen coordinates for **4** were used as starting coordinates for **5** and those for **5** were used for **6**. Hydrogen positions and common $B_{iso}$'s for **4**–**6** were refined together with the other variables. For orthorhombic **7**, most hydrogens were found from a Fourier difference map and the rest were placed geometrically, and were kept fixed after a few cycles of refinement, with a common fixed $B_{iso}$. The shift/error ratios in the last cycles were less than 0.01. Atomic coordinates for non-hydrogen atoms are listed in Tables 4 and 5.

Thermal parameters, hydrogen coordinates for complexes **4**–**7**, torsion angles and planes have been deposited with the Cambridge Crystallographic Data Centre.

## Results and discussion

Bond lengths and angles for $Te_2(tmtu)_2X_4$ and triclinic $Te_2(tmsu)_2X_4$ are given in Tables 6 and 7.

*Table 8.* Distances (Å) and angles (°) in orthorhombic $Te_2(tmsu)_2Br_4$ with e.s.d.'s in parentheses. Primed atoms as in Tables 6 and 7.

| | | | |
|---|---|---|---|
| Bond lengths | | | |
| Te–Br(1) | 2.773(1) | C(1)–N(1) | 1.312(9) |
| Te–Br(2) | 2.738(1) | C(1)–N(2) | 1.336(9) |
| Te–Se | 2.544(1) | N(1)–C(2) | 1.469(9) |
| Te–Br(2′) | 3.342(1) | N(1)–C(3) | 1.464(9) |
| Se–C(1) | 1.924(7) | N(2)–C(4) | 1.457(9) |
| | | N(2)–C(5) | 1.470(8) |
| Bond angles | | | |
| Br(1)–Te–Br(2) | 176.62(3) | Se–C(1)–N(1) | 121.8(5) |
| Se–Te–Br(1) | 91.34(3) | Se–C(1)–N(2) | 116.2(5) |
| Se–Te–Br(2) | 91.54(3) | N(1)–C(1)–N(2) | 121.9(6) |
| Se–Te–Br(2′) | 174.36(3) | C(1)–N(1)–C(2) | 122.9(6) |
| Br(1)–Te–Br(2′) | 94.13(2) | C(1)–N(1)–C(3) | 123.0(6) |
| Br(2)–Te–Br(2′) | 82.95(3) | C(2)–N(1)–C(3) | 114.0(6) |
| Te–Br(2)–Te′ | 97.05(3) | C(1)–N(2)–C(4) | 124.0(6) |
| Te–Se–C(1) | 103.19(22) | C(1)–N(2)–C(5) | 121.6(6) |
| | | C(4)–N(2)–C(5) | 114.1(6) |
| Contacts | | | |
| Se···C(3) | 3.192(8) | C(2)···C(5) | 2.937(12) |
| Se···C(4) | 3.132(7) | Te···C(3) | 3.825(8) |

*Table 9.* Least-squares planes of portions of the Te$_2$(tmtu)$_2$X$_4$ molecules. Primed atoms as in Tables 6–8.

Plane (1): Te, S, X(1), X(2), Te′, S′, X(1′), X(2′);
Plane (2): Te, S, C(1); Plane (3): S, C(1), N(1), N(2)

| | X = Cl | X = Br | X = I |
|---|---|---|---|
| Angles (°) between planes | | | |
| (1)–(2) | 63.6 | 62.5 | 61.3 |
| (1)–(3) | 84.3 | 82.4 | 81.5 |
| (2)–(3) | 53.1 | 51.8 | 51.5 |
| Distances (Å) from planes | | | |
| Plane (1) | | | |
| Te | −0.007 | 0.010 | 0.023 |
| S | 0.019 | 0.026 | 0.040 |
| X(1) | −0.012 | −0.027 | 0.046 |
| X(2) | −0.029 | −0.048 | −0.078 |
| Plane (3) | | | |
| C(1) | 0.010 | 0.009 | 0.001 |
| C(2) | 0.667 | 0.656 | 0.690 |
| C(3) | −0.539 | −0.592 | −0.598 |
| C(4) | 0.473 | 0.456 | 0.432 |
| C(5) | −0.684 | −0.655 | −0.611 |

The six complexes are isomorphous and have the same molecular structure; a view of one molecule is shown in Fig. 1.

The crystals contain planar, dinuclear *af*–S(X)–Te($\mu$–X)$_2$Te(X)S or *af*–Se(X)Te($\mu$–X)$_2$Te(X)Se coordination groups. The two halves of a group are related by a symmetry centre, each half consisting of a T-shaped STeX$_2$ or SeTeX$_2$ unit in which X–Te–X forms the bar of the T. Rather long, bridging Te–X bonds occur *trans* to the Te–S or Te–Se bonds; the environment of tellurium(II) is distorted square-planar.

The X–Te–X systems deviate 1.8–4.2° from linearity. The lengths of the two Te–X bonds differ slightly, viz. by 0.035(2), 0.066(1) and 0.118(1) Å in complexes **1**–**3**, and 0.007(1), 0.024(1) and 0.067(1) Å in **4**–**6**, respectively; the longer bond is a bridging one. The average bond lengths, Te–Cl 2.579(2), Te–Br 2.736(1) and Te–I 2.959(1) Å, for complexes **1**–**3**, and 2.590(1), 2.743(1) and 2.961(1) Å, respectively, for **4**–**6**, are very close to the bond lengths in centrosymmetric *trans*–Te(tmtu)$_2$X$_2$, viz. Te–Cl 2.586(2) and 2.582(2), Te–Br 2.740(1) and 2.734(1), and Te–I 2.954(1), 2.962(1) and 2.950(1) Å.[4]

*Table 10.* Least-squares planes of portions of the Te$_2$(tmsu)$_2$X$_4$ molecules. Primed atoms as in Tables 6–9.

Plane (1): Te, Se, X(1), X(2), Te′, Se′, X(1′), X(2′);
Plane (2): Te, Se, C(1); Plane (3): Se, C(1), N(1), N(2)

| | X = Cl | X = Br[a] | | X = I |
|---|---|---|---|---|
| Angles (°) between planes | | | | |
| (1)–(2) | 64.3 | 62.9 | 74.2 | 61.5 |
| (1)–(3) | 82.7 | 80.8 | 86.8 | 79.4 |
| (2)–(3) | 51.3 | 50.4 | 55.9 | 50.0 |
| Distances (Å) from planes | | | | |
| Plane (1) | | | | |
| Te | 0.023(1) | 0.002(1) | −0.032(1) | −0.020(1) |
| Se | −0.044(1) | −0.047(1) | 0.005(1) | −0.054(1) |
| X(1) | 0.025(1) | 0.039(1) | 0.012(1) | 0.057(1) |
| X(2) | 0.064(1) | 0.079(1) | 0.008(1) | 0.102(1) |
| Plane (3) | | | | |
| C(1) | 0.007(2) | 0.006(5) | −0.024(7) | 0.000(1) |
| C(2) | 0.599(4) | 0.632(9) | −0.514(9) | 0.662(6) |
| C(3) | −0.536(4) | −0.577(7) | 0.508(8) | −0.565(5) |
| C(4) | 0.461(4) | 0.477(7) | −0.537(9) | 0.443(6) |
| C(5) | −0.686(3) | −0.657(7) | 0.751(8) | −0.622(5) |

[a] Data for triclinic form on left, orthorhombic on right.

*Table 11.* Intermolecular contacts (Å) and angles (°) in triclinic $Te_2(tmsu)_2X_4$ across symmetry centre at 0,½,0.[a]

| X | Se···X(1) | C–Se···X(1) |
|---|---|---|
| Cl | 3.569(1) | 157.2(1) |
| Br | 3.641(1) | 157.6(1) |
| I | 3.783(1) | 156.5(1) |

[a] In $Te_2(tmtu)_2X_4$ the S···X(1) distances are longer: 3.671(2), 3.729(2) and 3.866(2) Å.

In the S–Te–X and Se–Te–X systems the bond angles are 171.64(4)–175.19(4)°. The short Te–S and Te–Se bonds and the long Te–X bonds illustrate the greater *trans*-influence of the thiourea or selenourea ligand than of X.[2,7] The Te–X bonds are longer in complexes **4–6** than in **1–3**, owing to the greater *trans*-influence of tmsu than of tmtu, by 0.050(2), 0.059(1) and 0.071(1) Å for X = Cl, Br, and I, respectively. These differences are discussed elsewhere.[8] The Te–S bond lengths, which increase from 2.425(1) Å for X = Cl to 2.473(1) Å for X = I, and the Te–Se bond lengths, which increase from 2.537(1) to 2.575(1) Å, reflect the relatively greater *trans*-influence of heavier X.

The Te–X bonds of the S–Te–X and Se–Te–X systems, which are *trans* to the tmtu oı tmsu ligands, are the long bridging bonds. The strengths of the bonds increase in the order X = Cl, Br and I: In complexes **1–3**, the Te–I bond is 0.143(1) Å longer than Te–Cl; in **4–6** this difference is 0.164(1) Å, whereas the difference in single-bond radii for I and Cl is 0.34 Å. These X atoms also form part of the X–Te–X systems, and the latter are consequently a little more asymmetric for X = I.

The molecular structure of the orthorhombic form of $Te_2(tmsu)_2Br_4$ (**7**) is the same as that of the triclinic form **5**. Bond lengths and angles are listed in Table 8. Only small differences relative to complex **5** are seen. In the Br–Te–Br system, the terminal Te–Br bond rather than the bridging bond is the longer one, and the average Te–Br bond length, 2.756(1) Å, is slightly larger than for complex **5**.

The largest deviation of a Te, S, Se or X atom from the least-squares plane of the dinuclear coordination group, passing through the symmetry centre relating the two halves of the group, is 0.102(1) Å for the bridging I atoms of complex **6** (see Tables 9 and 10).

In complexes **4–6**, short contacts occur between the Se atoms and the X(1) atoms of a neighbouring molecule, at angles of 156.5(1) –157.6(1)° to the C–Se bond (see Table 11). In complex **7**, the shortest intermolecular Se···Br distance is 3.985(1) Å.

With respect to dimensions (Tables 6–8) and orientations relative to the coordination plane, (Tables 9 and 10), the tmtu and tmsu ligands closely resemble those in other tellurium(II) complexes.[4,6] A difference in S–C and Se–C bond lengths may be seen. In *trans*-$Te(tmtu)_2(SCN)_2$, bond lengths are Te–S 2.691(1) and S–C 1.762(3) Å, and in *trans*-$Te(tmsu)_2(SeCN)_2$ bond lengths are Te–Se 2.811(1) and Se–C 1.872(6) Å.[6] The Te–S and Te–Se bonds in the present complexes are shorter, while the ligand S–C and Se–C bonds are longer.

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