*Tellurium dibromide complex*, Te(tmtu)Br$_2$. To 1.6 g of tellurium dioxide, dissolved by heating in 6 ml of concentrated hydrochloric acid, was added 20 ml of water and then 2.7 g of tetramethylthiourea in 40 ml of methanol. The solution was heated, and a hot mixture of 20 ml of 48 – 50 % hydrobromic acid, 100 ml of water and 100 ml of methanol was added under stirring. Crystallization takes place from hot solution as in the case of the dichloride complex. Yield, about 2.7 g of dark red crystals. M. p. 226°. (Found: S 7.61; Te 30.46. Calc. for $C_5H_{12}Br_2N_2STe$: S 7.64; Te 30.41.) More concentrated solutions and lower crystallization temperature [1] gave mixtures of the compound with the tetravalent tellurium complex, Te(tmtu)$_2$Br$_4$.

The crystals of the tellurium dichloride and dibromide complexes are isomorphous. The dimensions of the triclinic unit cells are, for Te(tmtu)Cl$_2$: $a$ = 8.01 Å, $b$ = 8.57 Å, $c$ = 9.43 Å, $\alpha$ = 108°, $\beta$ = 110½°, $\gamma$ = 93½°, and for Te(tmtu)Br$_2$: $a$ = 8.12 Å, $b$ = 8.74 Å, $c$ = 9.65 Å, $\alpha$ = 108½°, $\beta$ = 110°, $\gamma$ = 94½°. There are two formula units per unit cell; densities, calc. 1.94 and 2.33, respectively, found 1.94 and 2.34 g/cm$^3$.

The crystal structure of Te(tmtu)Cl$_2$ has been determined through projections along the $a$ and $b$ axes [4]. The space group is the centrosymmetric one, $C_i^1 - P\bar{1}$. Planar TeSCl$_2$ groups, joined two and two over a centre of symmetry through two unsymmetrical, rather weak Te – Cl – Te bridges, occur in the crystals. Each tellurium atom forms, in a planar, approximately square arrangement, one Te – S bond, two *trans* Te – Cl bonds and a third, longer Te – Cl bond *trans* to the Te – S bond.

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Received October 17, 1961.

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# Complexes of Divalent Tellurium with Tetramethylthiourea

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The tellurium dichloride and dibromide complexes [1], Te(tmtu)Cl$_2$ and Te(tmtu)Br$_2$ where tmtu = tetramethylthiourea, dissolve in warm methanolic tetramethylthiourea to give red solutions from which the compounds, Te(tmtu)$_2$Cl$_2$ and Te(tmtu)$_2$Br$_2$, crystallize on cooling. These are divalent tellurium complexes of the same type as Te(tu)$_2$X$_2$ (tu = thiourea, X = Cl, Br, I, SCN) [2,3] and Te(etu)$_2$X$_2$ (etu = ethylenethiourea, X = Br, I, SCN) [4]. We have also obtained the iodide, Te(tmtu)$_2$I$_2$, in two crystalline forms, and, from the thiourea compounds Te(tu)$_2$Cl$_2$ and Te(tu)$_2$Br$_2$ dissolved in warm methanolic tetramethylthiourea, on cooling, the chloride and bromide of a divalent tellurium cation with two thiourea and two tetramethylthiourea ligands. In all of these Te(tmtu)$_2$X$_2$ complexes, except one of the forms of the iodide, unit cell and space group data indicate that the tellurium atom lies in a centre of symmetry, and they thus represent the *trans* isomer of a square planar complex of this type. *Trans* forms have otherwise been found in the case of Te(etu)$_2$Br$_2$ and Te(etu)$_2$I$_2$ [4] and a series of complexes of divalent tellurium thiosulphonates with thioureas [5].

We have not been able to isolate any salt of a Te(tmtu)$_4^{2+}$ cation, although Te(tu)$_4^{2+}$ and Te(etu)$_4^{2+}$ salts are easily formed [2,6,7]. The reason may lie in the steric requirements of the methyl groups, as may also the preferred occurrence of *trans* forms of the Te(tmtu)$_2$X$_2$ complexes. Scale models indicate, however, that a planar arrangement of four tetramethylthiourea groups around tellurium, or a *cis* arrangement of two groups, should be possible.

The crystals of the dichloride and dibromide complexes are orange yellow to red in colour, those of the diiodide complex dark red, and those of the cation complexes yellow. They are stable in the solid state, but liberate tellurium in presence of water. Single-crystal X-ray data were obtained using Cu*Kα* radiation, $\lambda$ = 1.542 Å; values for axial lengths are probably accurate to within 0.5 %.

*Tellurium dichloride complex,* Te(tmtu)$_2$Cl$_2$. M. p. 167° (decomp.). (Found: Cl 15.57; S 13.82; Te 27.68. Calc. for $C_{10}H_{24}Cl_2N_4S_2Te$: Cl 15.32; S 13.85; Te 27.56.) The crystals occur as triclinic plates {001} with plate edges parallel to the *ab* diagonals and the *a* axis. The unit cell dimensions are, $a$ = 10.64 Å, $b$ = 11.46 Å, $c$ = 9.07 Å, $\alpha$ = 102°, $\beta$ = 120°, $\gamma$ = 84½°, and there are two molecules per unit cell; density, calc. 1.64, found 1.64 g/cm$^3$. A striking feature, for example on oscillation photographs about the *ab* diagonals, are the weak *hkl* reflections for odd values of $h + k$. This indicates that the tellurium atoms are centered on the *c* plane; instead of occupying a twofold set of general positions of the space group $C_i^1 - P\bar{1}$, they are located in symmetry centres at 0,0,0 and ½,½,0. The asymmetric unit thus consists of two half molecules.

*Tellurium dibromide complex,* Te(tmtu)$_2$Br$_2$. M. p. 192° (decomp.). (Found: S 11.64; Te 23.15. Calc. for $C_{10}H_{24}Br_2N_4S_2Te$: S 11.62; Te 23.12.) The crystals are isomorphous with those of the dichloride complex, and show the same morphology and the same intensity distribution: Weak *hkl* reflections when $h + k$ is odd, although less pronounced than in the case of the dichloride complex in accordance with the presence of the heavier bromine in general positions. The unit cell dimensions are, $a$ = 10.89 Å, $b$ = 11.66 Å, $c$ = 9.07 Å, $\alpha$ = 101½°, $\beta$ = 120°, $\gamma$ = 84°, and the density, calc. 1.88 for two molecules per unit cell, found 1.89 g/cm$^3$.

About 2.5 g of tetramethylthiourea in 50 ml of methanol was used per g of Te(tmtu)Cl$_2$ and Te(tmtu)Br$_2$ in preparing the dichloride and dibromide complexes. The methanolic tetramethylthiourea was heated to about 60° and stirred with the powdered substances for some minutes, until no more dissolved, then filtered while warm and allowed to cool to room temperature, in the case of the dichloride complex after addition of a few drops of concentrated hydrochloric acid and about the double volume of ether. The crystals of the dichloride complex were washed on the filter with methanol-ether 1 : 1 and those of the dibromide complex with methanol, containing a little hydrochloric or hydrobromic acid, respectively, and then with ether.

The dibromide complex was also obtained directly from tellurium dioxide and tetramethylthiourea in a molar ratio of 1 : 4 by the procedure [8] which with a molar ratio of 1 : 2 gave a mixture of Te(tmtu)$_2$Br$_4$ and Te(tmtu)Br$_2$. Yield, from 1.6 g (10 mmoles) of tellurium dioxide, 4−5 g (72−91 %). The crystals of the crude product were poorly developed, and twinned; better ones were obtained on recrystallization from methanolic tetramethylthiourea.

*Tellurium diiodide complex,* Te(tmtu)$_2$I$_2$. M. p. 172−3° (decomp.). (Found: I 39.57; S 9.93; Te 19.65. Calc. for $C_{10}H_{24}I_2N_4S_2Te$: I 39.30; S 9.93; Te 19.76.) The samples were mixtures of two types of crystals, which could be picked out under a microscope; they are both monoclinic.

One of the forms occurred as plates {101} bounded by {011} and {110}, often like cut-off, oblique pyramids, with $a$ = 8.00 Å, $b$ = 10.81 Å, $c$ = 11.96 Å, $\beta$ = 97½°, and two molecules per unit cell; density, calc. 2.09, found 2.10 g/cm. The space group, from systematic absences, is $C_{2h}^5 - P2_1/n$, which requires that the tellurium atoms lie in centres of symmetry.

The second type of crystals were prisms {021} terminated by {110}, with {010} developed in most cases, and $a$ = 9.23 Å, $b$ = 18.98 Å, $c$ = 11.94 Å, $\beta$ = 102°. The space group is the same as for the first form, $C_{2h}^5 - P2_1/n$, but there are four molecules per unit cell; density, calc. 2.10, found 2.10 g/cm$^3$, so that no molecular symmetry is required. In view of the finding of only *trans* forms of other tetramethylthiourea complexes, this is probably not the *cis* isomer of the diiodide, but a *trans* dimorph.

The diiodide complex was prepared from warm methanolic tetramethylthiourea solutions of the dichloride or dibromide complex, by addition of methanolic sodium or potassium iodide. It was recrystallized by dissolving it in boiling methanolic tetramethylthiourea (a rather large volume and long heating time is required because of low solubility) and allowing the solution to cool.

The *dichloride,* [Te(tu)$_2$(tmtu)$_2$]Cl$_2$. M. p. 157° (decomp.). (Found: Cl 11.50; S 20.94; Te 20.79. Calc. for $C_{12}H_{32}Cl_2N_8S_4Te$: Cl 11.53; S 20.85; Te 20.74.) The salt forms monoclinic prisms extended along the *c* axis, bounded by {100} and {010} with the former dominant, and terminated by {011}. The unit cell dimensions are, $a$ = 8.83 Å, $b$ = 14.40 Å, $c$ = 9.90 Å, $\beta$ = 94°, and there are two formula units per unit cell; density, calc. 1.63, found 1.63 g/cm$^3$.

The space group, from systematic absences, is $C_{2h}^5 - P2_1/c$, which requires that the tellurium atoms lie in centres of symmetry. This is consistent with the intensity distribution of the *hkl* reflections, those with $k + l$ even being in most cases markedly stronger than those with $k + l$ odd.

The *dibromide*, $[Te(tu)_2(tmtu)_2]Br_2$, is isomorphous with the dichloride, and has $a = 8.78$ Å, $b = 15.02$ Å, $c = 10.04$ Å, $\beta = 94°$, and density, calc. 1.77 for two formula units per unit cell, found 1.79 g/cm³. M. p. 150° (decomp.). (Found: S 18.52; Te 18.09. Calc. for $C_{12}H_{32}Br_2N_8S_4Te$: S 18.22; Te 18.12.) The crystals occurred as short prisms {011}.

The same procedure as above for the dichloride and dibromide complexes was used in preparing the dithioureabis(tetramethylthiourea)tellurium(II) salts; here, about 2 g of tetramethylthiourea in 20 ml of methanol was employed per g of $Te(tu)_2Cl_2$ and $Te(tu)_2Br_2$, and no ether except for the last washings. The methanolic mother liquors, which contain the excess of tetramethylthiourea, can be used for further preparations of the same substance.

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Received October 17, 1961.

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# Complexes of Divalent Tellurium Thiosulphonates with Thioureas

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Thiosulphonates of divalent tellurium, $Te(S_2O_2R)_2$ with R = methyl, phenyl and *p*-tolyl, have been prepared earlier by one of us[1,2], and their crystal structures determined[3-5]. Divalent tellurium in these compounds readily releases the thiosulphonate groups in displacement reactions with thio ions of higher nucleophilic reactivity, such as thiosulphate and dialkyldithiocarbamate ions [1,2]:

$$Te(S_2O_2R)_2 + 2\ YS^- = Te(SY)_2 + 2\ RSO_2S^-$$

This note reports the finding that with thioureas as nucleophiles, in most cases only an addition and not a displacement takes place. Divalent tellurium adds two molecules of thiourea (tu), ethylenethiourea (etu), or tetramethylthiourea (tmtu), to give four-coordinated, planar complexes $Te(tu)_2X_2$, $Te(etu)_2X_2$ and $Te(tmtu)_2X_2$, where X = thiosulphonate. Five representatives are described below, one in two crystalline forms. In all but one of the crystals, unit cell and space group data indicate that the tellurium atom lies in a centre of symmetry. They thus are the *trans* isomers.

The compounds are yellow, with a greenish tinge in the case of the ethylenethiourea derivatives, except the tetramethylthiourea-benzenethiosulphonate complex which is red. In contact with methanol the latter complex gives off tetramethylthiourea, leaving yellow crystals of tellurium dibenzenethiosulphonate. Water destroys the complexes with liberation of tellurium. In the solid, dry state they are quite stable.

Unit cell and space group data were derived from oscillation and Weissenberg photographs, using Cu*Ka* radiation, $\lambda = 1.542$ Å. The values for axial lengths are believed to be accurate to within 0.5 %.

*Dimethanethiosulphonato-dithiourea-tellurium(II)*, $Te(tu)_2(S_2O_2CH_3)_2$, crystallizes from solutions made by dissolving powdered tellurium dimethanethiosulphonate in methanolic thiourea, under stirring and heating to near boiling temperature. Some