

identity was established through single-crystal X-ray photographs showing isomorphism with the tetrachloride complex. M.p., of picked-out crystals, 176–177°.

The crystals are orthorhombic; those of the tetrachloride complex occur as prisms along the *c* axis bounded by {010} and {100} and those of the tetrabromide complex as six-sided plates {010} a little extended along the *c* axis. The axial lengths are, for  $\text{Te}(\text{tmu})_2\text{Cl}_4$ : *a* = 14.74 Å, *b* = 13.87 Å, *c* = 10.06 Å, and for  $\text{Te}(\text{tmu})_2\text{Br}_4$ : *a* = 14.98 Å, *b* = 13.88 Å, *c* = 10.40 Å. There are four molecules per unit cell; densities, calc. 1.72 and 2.19, respectively, found 1.70 and 2.21 g/cm<sup>3</sup>. The space group, from systematic absences, is  $D_{2h}^{15} - Pbca$ , which has eightfold general positions, and requires that the four tellurium atoms lie in centres of symmetry. This is consistent with the intensity distribution of the *hkl* reflections, those with *h* + *k*, *k* + *l* and *l* + *h* even being strongest, particularly in the case of the tetrachloride complex.

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## Complexes of Tellurium Dichloride and Dibromide with One Mole of Tetramethylthiourea

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The tetravalent tellurium complex described in a preceding note<sup>1</sup>,  $\text{Te}(\text{tmu})_2\text{Cl}_4$  where *tmu* = tetramethylthiourea, when dissolved in warm 4 N hydrochloric acid-methanol 2 : 1 (30 ml per g) and the solution kept near boiling temperature, forms a divalent tellurium complex,  $\text{Te}(\text{tmu})\text{Cl}_2$ , which in the course of a few hours separates out as dark red crystals. Presumably tetramethylthiourea acts as the reducing agent, being itself oxidized to the disulphide cation,  $(\text{tmu})_2^{2+}$ , of which salts are known<sup>2,3</sup>.

The tellurium dichloride complex, and the corresponding bromide, may also be prepared directly from tellurium dioxide and tetramethylthiourea, as described below. The X-ray crystallographic data have been obtained from oscillation and Weissenberg photographs; the axial lengths, believed to be accurate to within 0.5 %, are based on  $\lambda(\text{CuK}\alpha) = 1.542 \text{ \AA}$ .

*Tellurium dichloride complex*,  $\text{Te}(\text{tmu})\text{Cl}_2$ . To a warm solution of 1.6 g (10 mmoles) of tellurium dioxide in 20 ml of concentrated hydrochloric acid and 40 ml of water was added 2.7 g (20 mmoles) of tetramethylthiourea dissolved in 40 ml of methanol. The resulting, red solution was heated to near boiling temperature, and kept at this temperature some hours, while crystallization took place; the crystallization starts on scratching of the beaker walls, or on seeding, and is rather slow. Yield, about 2.2 g. M.p. 207°. (Found: Cl 21.32; S 9.69; Te 38.67. Calc. for  $\text{C}_8\text{H}_{12}\text{Cl}_2\text{N}_2\text{STe}$ : Cl 21.44; S 9.70; Te 38.58.) The compound, and the dibromide complex, are stable in the solid state, but liberate tellurium in contact with water like other complexes of divalent tellurium. They were on the filters washed with methanol containing a little concentrated hydrochloric acid or hydrobromic acid, respectively, and then with ether.

**Tellurium dibromide complex,  $\text{Te}(\text{tmtu})\text{Br}_2$ .** 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  $\text{C}_8\text{H}_{12}\text{Br}_2\text{N}_2\text{STe}$ : S 7.64; Te 30.41.) More concentrated solutions and lower crystallization temperature<sup>1</sup> gave mixtures of the compound with the trivalent tellurium complex,  $\text{Te}(\text{tmtu})_2\text{Br}_4$ .

The crystals of the tellurium dichloride and dibromide complexes are isomorphous. The dimensions of the triclinic unit cells are, for  $\text{Te}(\text{tmtu})\text{Cl}_2$ :  $a = 8.01 \text{ \AA}$ ,  $b = 8.57 \text{ \AA}$ ,  $c = 9.43 \text{ \AA}$ ,  $\alpha = 108^\circ$ ,  $\beta = 110\frac{1}{2}^\circ$ ,  $\gamma = 93\frac{1}{2}^\circ$ , and for  $\text{Te}(\text{tmtu})\text{Br}_2$ :  $a = 8.12 \text{ \AA}$ ,  $b = 8.74 \text{ \AA}$ ,  $c = 9.65 \text{ \AA}$ ,  $\alpha = 108\frac{1}{2}^\circ$ ,  $\beta = 110^\circ$ ,  $\gamma = 94\frac{1}{2}^\circ$ . There are two formula units per unit cell; densities, calc. 1.94 and 2.33, respectively, found 1.94 and 2.34 g/cm<sup>3</sup>.

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

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## Complexes of Divalent Tellurium with Tetramethylthiourea

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The tellurium dichloride and dibromide complexes<sup>1</sup>,  $\text{Te}(\text{tmtu})\text{Cl}_2$  and  $\text{Te}(\text{tmtu})\text{Br}_2$  where  $\text{tmtu} =$  tetramethylthiourea, dissolve in warm methanolic tetramethylthiourea to give red solutions from which the compounds,  $\text{Te}(\text{tmtu})_2\text{Cl}_4$  and  $\text{Te}(\text{tmtu})_2\text{Br}_4$ , crystallize on cooling. These are divalent tellurium complexes of the same type as  $\text{Te}(\text{tu})_2\text{X}_2$  ( $\text{tu} =$  thiourea,  $\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{SCN}$ )<sup>2,3</sup> and  $\text{Te}(\text{etu})_2\text{X}_2$  ( $\text{etu} =$  ethylenethiourea,  $\text{X} = \text{Br}, \text{I}, \text{SCN}$ )<sup>4</sup>. We have also obtained the iodide,  $\text{Te}(\text{tmtu})_2\text{I}_2$ , in two crystalline forms, and, from the thiourea compounds  $\text{Te}(\text{tu})_2\text{Cl}_2$  and  $\text{Te}(\text{tu})_2\text{Br}_2$  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  $\text{Te}(\text{tmtu})_2\text{X}_2$  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  $\text{Te}(\text{etu})_2\text{Br}_2$  and  $\text{Te}(\text{etu})_2\text{I}_2$ <sup>4</sup> and a series of complexes of divalent tellurium thio-sulphonates with thioureas<sup>5</sup>.

We have not been able to isolate any salt of a  $\text{Te}(\text{tmtu})_4^{2+}$  cation, although  $\text{Te}(\text{tu})_4^{2+}$  and  $\text{Te}(\text{etu})_4^{2+}$  salts are easily formed<sup>2,6,7</sup>. The reason may lie in the steric requirements of the methyl groups, as may also the preferred occurrence of *trans* forms of the  $\text{Te}(\text{tmtu})_2\text{X}_2$  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  $\text{CuK}\alpha$  radiation,  $\lambda = 1.542 \text{ \AA}$ ; values