

was prepared by treating 0.95 g of powdered tellurium dibenzenethiosulphonate with 15 ml of methanol containing 0.9 g (ca. 90 % excess) of tetramethylthiourea, under stirring and heating to boiling temperature. Undissolved thiosulphonate and some liberated tellurium were filtered off, and the solution allowed to cool to room temperature, after scratching or seeding to start crystallization. The crystals were drained well on the filters and washed with ether. Yield, about 0.2 g (14 %). M p. 121°. (Found: C 35.80; S 26.02. Calc. for $C_{22}H_{34}N_4O_4S_6Te$: C 35.78; S 26.05.)

The crystals show varying habit and many faces, one was a prism extended along the *b* axis, another a thick plate {100} extended along the *bc* diagonal. The dimensions of the monoclinic unit cell are, $a = 10.26 \text{ \AA}$, $b = 10.07 \text{ \AA}$, $c = 15.98 \text{ \AA}$, $\beta = 110^\circ$, and there are two molecules per unit cell; density, calc. 1.58, found 1.58 g/cm³. The systematic absences, and weak *hkl* reflections when $k + l$ is odd, show that the tellurium atoms lie in symmetry centres of the space group $C_{2h}^5 - P2_1/c$.

1. Foss, O. *Acta Chem. Scand.* **5** (1951) 115.
2. Foss, O. *Acta Chem. Scand.* **6** (1952) 521.
3. Foss, O. and Vihovde, E. H. *Acta Chem. Scand.* **8** (1954) 1032.
4. Øyum, P. and Foss, O. *Acta Chem. Scand.* **10** (1956) 279.
5. Foss, O. and Øyum, P. *Acta Chem. Scand.* **9** (1955) 1014.
6. Foss, O. and Marøy, K. *To be published.*
7. Foss, O. and Fossen, S. *Acta Chem. Scand.* **15** (1961) 1620.

Received October 17, 1961.

Complexes of Divalent Tellurium with Propylenethiourea

OLAV FOSS and KJARTAN MARØY

Chemical Institute, University of Bergen, Bergen, Norway

The work reported here and in a following note¹ terminates a series of preparative and preliminary X-ray studies of complexes of divalent tellurium with thioureas, now with propylenethiourea (prt_u) as ligand. Four $Te(prt_u)_2X_2$ complexes are

described, namely with X = chloride, bromide, thiocyanate and methanethiosulphonate; the two former represent the *cis* and the two latter the *trans* isomer of four-coordinated planar complexes of this type. This is the first *trans* thiocyanate found; the established or indicated *trans* isomers of other TeX_2Y_2 complexes are: With thiourea^{2,3} only the methanethiosulphonate, with ethylenethiourea^{3,4} the bromide, iodide, methane- and benzene-thiosulphonate, with tetramethylthiourea^{3,5} the chloride, bromide, iodide and benzenethiosulphonate, and two salts⁵ of a cation with two thiourea and two tetramethylthiourea ligands. The assignment of planar *trans* structure is based on unit cell and space group data, which indicate that in all the above representatives the tellurium atom lies in a crystallographic centre of symmetry, and in some cases on structure analysis.

Propylenethiourea (hexahydropyrimidine-2-thione) was prepared from 1,3-diaminopropane and carbon disulphide^{6,7}, and recrystallized from water. In acid solutions it reduces tetravalent tellurium to divalent, and becomes thereby itself probably oxidized to a disulphide cation, $(prt_u)_2^{2+}$, like other thioureas.

The compounds are yellow, and stable in the solid state, but hydrolyze and liberate tellurium in contact with water. They were on the preparative filters washed with methanol to which in the case of the dichloride complex a little concentrated hydrochloric acid had been added, and then with ether. Single-crystal X-ray data were obtained using $CuK\alpha$ radiation, $\lambda = 1.542 \text{ \AA}$; values for axial lengths are probably accurate to within 0.5 %.

Tellurium dichloride complex, $Te(prt_u)_2Cl_2$. To 1.6 g (10 mmoles) of tellurium dioxide in 15 ml of concentrated hydrochloric acid was added, rapidly under stirring, 4.7 g (40 mmoles) of propylenethiourea in 15 ml of hot water. Crystallization set in on scratching of the beaker walls. Yield, after cooling to room temperature, 3.5 g (81 %). M. p. 199° (decomp.). (Found: Cl 16.54; Te 29.67. Calc. for $C_5H_{16}Cl_2N_4S_2Te$: Cl 16.46; Te 29.61.)

The crystals occur as monoclinic prisms extended along the *b* axis and often flattened along the *c* axis. The unit cell dimensions are, $a = 16.49 \text{ \AA}$, $b = 7.64 \text{ \AA}$, $c = 14.52 \text{ \AA}$, $\beta = 120^\circ$, and there are four molecules per unit cell; density, calc. 1.81, found 1.81 g/cm³. From systematic absences, and a Fourier projection along the *b* axis, the

space group is $C_{2h}^2 - C2/c$. The tellurium atoms lie on twofold axes of symmetry (not in centres of symmetry since there are no systematically weak hkl reflections) and the nearly but not quite planar TeS_2Cl_2 group is *cis*. Its projection along the b axis (twofold axis) is very like the corresponding projection⁸ of the TeS_2Cl_2 group in $\text{Te}(\text{tu})_2\text{Cl}_2$ and⁹ of the TeS_4 group in $\text{Te}(\text{tu})_2(\text{SCN})_2$ which also are *cis* isomers.

Tellurium dibromide complex, $\text{Te}(\text{prtu})_2\text{Br}_2$. To 1.6 g of tellurium dioxide in 5 ml of warm concentrated hydrochloric acid was added, rapidly under stirring, 4.7 g of propylenethiourea in 20 ml of hot water, then 10 ml of methanol and, under stirring, 20 ml of hot ca. 25 % hydrobromic acid. Yield, after scratching or seeding, and cooling to room temperature, 5 g (96 %). M. p. 190° (decomp.). (Found: Br 30.57; Te 24.74. Calc. for $\text{C}_6\text{H}_{16}\text{Br}_2\text{N}_4\text{S}_2\text{Te}$: Br 30.75; Te 24.55.) It can be recrystallized by dissolving 5 g in 30 ml of dimethylformamide at about 60° and adding three to four times the volume of methanol.

The compound forms thick monoclinic plates {100} with $a = 16.11 \text{ \AA}$, $b = 7.91 \text{ \AA}$, $c = 14.31 \text{ \AA}$, $\beta = 117\frac{1}{2}^\circ$, and four molecules per unit cell; density, calc. 2.13; found 2.13 g/cm³. Systematic absences, hkl when $h + k + l$ is odd, $h0l$ when h is odd or l is odd. The $h0l$ and $hk0$ zones of reflections are very similar to the corresponding zones of the dichloride complex, indicating that the compounds are isostructural in the projections along the b and c axes. The space group of the dibromide complex is therefore very probably $C_{2h}^2 - I2/c$, the same as for the dichloride complex, but *I*- instead of *C*-centered once the a axes and β angles in the two compounds are chosen so as to conform dimensionally. This is the same relationship as between the crystals of *racem*-1,2-dithiane- and *racem*-1,2-diselenane-3,6-dicarboxylic acid¹⁰.

The tellurium dithiocyanate complex, $\text{Te}(\text{prtu})_2(\text{SCN})_2$, was prepared from the dichloride complex, and ammonium thiocyanate: 2.2 g of powdered $\text{Te}(\text{prtu})_2\text{Cl}_2$ was dissolved in 50 ml of methanol containing 10 g of ammonium thiocyanate, under stirring and heating to near boiling temperature. Some liberated tellurium was filtered off, and the solution allowed to cool. Yield, 1.8 g (89 %). M. p. ca. 214° (decomp.). (Found: N 17.15; Te 26.84. Calc. for $\text{C}_{10}\text{H}_{16}\text{N}_6\text{S}_4\text{Te}$: N 17.65; Te 26.80.)

The crystals occur as monoclinic prisms {110} with $a = 13.27 \text{ \AA}$, $b = 14.43 \text{ \AA}$, $c = 9.76 \text{ \AA}$, $\beta = 108\frac{1}{2}^\circ$, and four molecules per unit cell; density, calc. 1.78, found 1.78 g/cm³. The systematic absences, and very weak hkl reflections when l is odd, indicate that the tellurium atoms lie in symmetry centres, positions (a) or (b)¹¹, of the space group $C_{2h}^2 - C2/c$.

The tellurium dimethanethiosulphonate complex, $\text{Te}(\text{prtu})_2(\text{S}_2\text{O}_4\text{CH}_3)_2$, crystallized when to 2.8 g of tetrakis(propylenethiourea)tellurium(II) dichloride dihydrate¹ in 8 ml of methanol was added, at room temperature, a filtered solution of 1.4 g (15 % excess) of sodium methanethiosulphonate monohydrate in 8 ml of water. Yield, 2.0 g (86 %). M. p. 172° (decomp.). (Found: N 9.57; Te 21.65. Calc. for $\text{C}_{10}\text{H}_{22}\text{N}_4\text{O}_6\text{S}_4\text{Te}$: N 9.62; Te 21.91.)

The crystals are orthorhombic, and occur as prisms along the c axis bounded by {100} and {001}, with $a = 12.95 \text{ \AA}$, $b = 18.92 \text{ \AA}$, $c = 8.80 \text{ \AA}$, and four molecules per unit cell; density, calc. 1.79, found 1.78 g/cm³. The space group, from systematic absences, is $D_{2h}^{10} - Pccn$, so that twofold molecular symmetry is required. The hkl reflections are weak when $h + k$, $k + l$ and $l + h$ are odd, and not when l is odd, which shows that the tellurium atoms lie, not on twofold axes but in symmetry centres.

1. Foss, O. and Marøy, K. *Acta Chem. Scand.* **15** (1961) 1947.
2. Foss, O. and Hauge, S. *Acta Chem. Scand.* **13** (1959) 1252; **15** (1961) 1615.
3. Foss, O. and Johannessen, I.-J. *Acta Chem. Scand.* **15** (1961) 1943.
4. Foss, O. and Fossen, S. *Acta Chem. Scand.* **15** (1961) 1618.
5. Foss, O. and Johannessen, W. *Acta Chem. Scand.* **15** (1961) 1941.
6. Schacht, W. *Arch. Pharm.* **235** (1897) 441.
7. Staudinger, H. and Niessen, G. *Chem. Ber.* **86** (1953) 1223.
8. Foss, O., Johnsen, K. and Marøy, K. *To be published.*
9. Marøy, K. *To be published.*
10. Foss, O. and Schotte, L. *Acta Chem. Scand.* **11** (1957) 1424.
11. *International Tables for X-ray Crystallography*, Vol. I, The Kynoch Press, Birmingham 1952, p. 101.

Received October 17, 1961.