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/cm^3. 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.

1. Foss, O. and Johannessen, W. *Acta Chem. Scand.* **15** (1961) 1940.
2. Foss, O. and Hauge, S. *Acta Chem. Scand.* **13** (1959) 1252.
3. Foss, O. and Hauge, S. *Acta Chem. Scand.* **15** (1961) 1615.
4. Foss, O. and Fossen, S. *Acta Chem. Scand.* **15** (1961) 1618.
5. Foss, O. and Johannessen, I.-J. *Acta Chem. Scand.* **15** (1961) 1943.
6. Foss, O. and Hauge, S. *Acta Chem. Scand.* **15** (1961) 1616.
7. Foss, O. and Fossen, S. *Acta Chem. Scand.* **15** (1961) 1620.
8. Foss, O. and Johannessen, W. *Acta Chem. Scand.* **15** (1961) 1939.

Received October 17, 1961.

Complexes of Divalent Tellurium Thiosulphonates with Thioureas

OLAV FOSS and INGER-JOHANNE JOHANNESSEN

Chemical Institute, University of Bergen, Bergen, Norway

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 liberated tellurium was filtered off, and the filtrate allowed to cool to room temperature. The compound can also be prepared from the thiourea complexes $Te(tu)_2Br_2$ or $Te(tu)_4Br_2$ and methanolic sodium methanethiosulphonate monohydrate. The crystals were on the filters drained well, and washed with ether; washing with methanol sometimes caused slight blackening. M. p. 130–131° (decomp.). (Found: S 38.52; Te 25.36. Calc. for $C_4H_{14}N_4O_4S_6Te$: S 38.31; Te 25.41.)

The crystals occur as monoclinic prisms extended along the *b* axis, with $a = 12.50$ Å, $b = 5.60$ Å, $c = 12.80$ Å, $\beta = 98°$, and two molecules per unit cell; density, calc. 1.88, found 1.89 g/cm³. The space group, from systematic absences, is $C_{2h}^5 - P2_1/n$; the tellurium atoms lie in centres of symmetry.

From Fourier projections along the *b* and *c* axes [6], the Te–S(thiosulphonate) bonds are 2.68 Å, as compared with 2.36 Å in the parent, uncomplexed compound [3]. The Te–S(thiourea) bonds are 2.65 Å, and the S–Te–S angles of the planar TeS_4 group are 90° within the error.

Dimethanethiosulphonatobis(ethylenethiourea)tellurium(II), $Te(etu)_2(S_2O_2CH_3)_2$, crystallized when to 1.3 g of tetrakis(ethylenethiourea)tellurium(II) dichloride dihydrate [7] dissolved in 20 ml of warm methanol was added a filtered solution of 0.65 g (*ca.* 7 % excess) of sodium methanethiosulphonate monohydrate in 8 ml of methanol. Yield, 1.0 g (89 %). These crystals, and those of the ethylenethiourea-benzenethiosulphonate complex below, were on the filters washed with methanol and then with ether. M. p. 168–169° (decomp.). (Found: S 34.63; Te 23.02. Calc. for $C_8H_{18}N_4O_4S_6Te$: S 34.71; Te 23.02.) Microscopic examination of the samples showed that they consisted of two types of crystals, long prisms and rather small plates, both monoclinic; the latter seemed to predominate in preparations from more dilute methanol solutions.

The prisms were extended along the *b* axis, with $a = 18.35$ Å, $b = 5.41$ Å, $c = 20.16$ Å, $\beta = 102°$, and four molecules per unit cell; density, calc. 1.88, found 1.89 g/cm³. Systematic absences, *hkl* when $h + k$ is odd, *h*0*l* when *h* is odd or *l* is odd. A Fourier projection along the *b* axis has been carried out, which shows that the space group is $C_{2h}^6 - C2/c$, and outlines clearly a centrosymmetric, *trans* molecule.

The plates had edges parallel to the *bc* diagonals, and $a = 9.61$ Å, $b = 10.86$ Å, $c = 10.67$ Å, $\beta = 119°$. There are two molecules per unit cell; density, calc. 1.89, found 1.89 g/cm³. From systematic absences, and weak *hkl* reflections when $k + l$ is odd, the tellurium atoms lie in symmetry centres of the space group $C_{2h}^5 - P2_1/c$. This is thus a dimorph of the *trans* isomer.

Dibenzenethiosulphonatobis(ethylenethiourea)tellurium (II), $Te(etu)_2(S_2O_2C_6H_5)_2$, was prepared like the methanethiosulphonate analog, from 1.6 g of tetrakis(ethylenethiourea)tellurium(II) dichloride dihydrate in 50 ml of warm methanol, to which was added a filtered solution of 1.25 g (*ca.* 15 % excess) of potassium benzenethiosulphonate dihydrate in 20 ml of methanol. Yield, 1.6 g (95 %). M. p. 147° (decomp.). (Found: C 32.09; S 28.40; Te 18.76. Calc. for $C_{18}H_{22}N_4O_4S_6Te$: C 31.87; S 28.36; Te 18.81.)

The crystals are triclinic prisms extended along the *c* axis, with $a = 7.08$ Å, $b = 10.60$ Å, $c = 8.98$ Å, $\alpha = 102\frac{1}{2}°$, $\beta = 91°$, $\gamma = 94°$, and one molecule per unit cell; density, calc. 1.72, found 1.71 g/cm³. The centrosymmetric space group, $C_i^1 - P\bar{1}$, would place the tellurium atom in a centre of symmetry also here.

Dimethanethiosulphonatobis(tetramethylthiourea)tellurium(II), $Te(tmtu)_2(S_2O_2CH_3)_2$. 1.3 g of powdered tellurium dimethanethiosulphonate was dissolved, under stirring and heating to near boiling temperature, in 15 ml of methanol containing 1.2 g (*ca.* 20 % excess) of tetramethylthiourea. Some liberated tellurium was filtered off, and 5 ml of ether added to the warm filtrate. There was a tendency for the product to separate as an oil; crystallization could be effected through scratching of the beaker walls, or by seeding. The crystals were washed on the filters with methanol-ether 1:1 and then with ether. Yield, 1.4 g (60 %). M. p. 85°. (Found: C 23.65; S 31.42; Te 20.68. Calc. for $C_{12}H_{30}N_4O_4S_6Te$: C 23.46; S 31.31; Te 20.77.)

The compound forms prisms extended along the *b* axis and flattened along the *a* axis. They are monoclinic, with $a = 9.52$ Å, $b = 12.62$ Å, $c = 10.46$ Å, $\beta = 98°$, and two molecules per unit cell; density, calc. 1.64, found 1.64 g/cm³. The systematic absences, 0*k*0 when *k* is odd, indicate the space group $C_2^2 - P2_1$ or $C_{2h}^2 - P2_1/m$. The tellurium atoms do not lie in symmetry centres of the latter, since *hkl* reflections are not systematically weak when *k* is odd. There is perfect cleavage along the *b* plane.

Dibenzenethiosulphonatobis(tetramethylthiourea)tellurium(II), $Te(tmtu)_2(S_2O_2C_6H_5)_2$, 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 Å, b = 10.07 Å, c = 15.98 Å, β = 110°, 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 note [1] terminates a series of preparative and preliminary X-ray studies of complexes of divalent tellurium with thioureas, now with propylenethiourea (prtu) as ligand. Four $Te(prtu)_2X_2$ 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 benzenethiosulphonate, with tetramethylthiourea [3,5] the chloride, bromide, iodide and benzenethiosulphonate, and two salts [5] 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, $(prtu)_2^{2+}$, 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 Cu*Kα* radiation, λ = 1.542 Å; values for axial lengths are probably accurate to within 0.5 %.

Tellurium dichloride complex, $Te(prtu)_2Cl_2$. 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 $C_8H_{16}Cl_2N_4S_2Te$: 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 Å, b = 7.64 Å, c = 14.52 Å, β = 120°, 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