The TeS_2Cl_2 and TeS_2Br_2 groups in $Te(tu)_2Cl_2$ and $Te(tu)_2Br_2$ have, according to two-dimensional crystal structure analyses, the dimensions: Te—S = 2.48 Å, Te—Cl = 2.92 Å, ∠S—Te—S = 93°, ∠ Cl—Te—Cl = 93° in the chloride[3]; Te—S = 2.47 Å, Te—Br = 3.05 Å, ∠S—Te—S = 95°, ∠Br—Te—Br = 93° in the bromide[4]. The groups are almost but not exactly planar, the Te—Cl bonds being rotated 8° and the Te—Br bonds 9° out of the S—Te—S plane, to opposite sides of the plane in accordance with the twofold axis of molecular symmetry.

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Tetrathiourea-tellurium(II) Salts

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The salts $Te(tu)_4Cl_2 \cdot 2H_2O$ and $Te(tu)_2Br_4$ (tu = thiourea) were described and unit cell and space group data reported in 1959[1]. The chloride dihydrate crystallizes in the space group $C_{2h}^5-P2_1/c$ with two formula units per unit cell, which shows that the tellurium atom lies in a centre of symmetry and the TeS_4 group of the complex is thus planar. A two-dimensional structure analysis has subsequently been carried out[2]; the Te—S bonds are 2.69 Å and the S—Te—S angles 90°.

Some other salts have later been prepared and characterized, namely an anhydrous chloride, a thiocyanate, nitrate and perchlorate. Vřešťál[3] has independently prepared several tetrathiourea-tellurium(II) salts, and Němec[4] has studied the morphology and unit cells of the chloride dihydrate and perchlorate. Our results are reported below to the extent that they do not duplicate Vřešťál's and Němec's data.

Unit cell dimensions were derived from oscillation and Weissenberg photographs, using Cu*Ka* radiation, $\lambda = 1.542$ Å. Axial lengths are believed to be accurate to within 0.5 %. Densities were determined by flotation in carbon tetrachloride-bromoform mixtures.

The salts are yellow, and stable in the solid state, but become black in contact with water, due to hydrolysis and subsequent dismutation into zero- and tetravalent tellurium. They hydrolyze slightly in contact with 96 % ethanol, and were on the preparative filters in most cases washed with 96 % ethanol containing a little thiourea or concentrated hydrochloric acid, and then with ether. Solutions in aqueous or ethanolic thiourea are fairly stable. The salts dissolve readily in dimethylformamide, to give orange-yellow to orange solutions, apparently stable at room temperature.

Tetrathiourea-tellurium(II) dichloride dihydrate, $Te(tu)_4Cl_2 \cdot 2H_2O$. As reported[1], and confirmed through structure analysis[2], this salt is monoclinic. Němec[4], from morphological study and rotation photographs about three axes, described it as triclinic, obviously because his *a* and *b* axes, the rotation photographs about which[4] "are quite identical, referring not only to the length of axes, but also to the distribution of diffraction spots and their intensities", were not recognized as *bc* diagonals in space group $P2_1/c$.

The salt can be prepared by mixing, at about 80°, a solution of 2.4 g (15 mmoles) of tellurium dioxide in 10 ml of concentrated hydrochloric acid and 10 ml of water, and a solution of 7.5 g (99 mmoles, 10 % excess) of thiourea in 50 ml of water. The mixture is allowed to cool to about 30° and the crystals then filtered off. Yield, 7.9 g (98 %). The mother liquor on further cooling deposits crystals of formamidinium disulphide dichloride. Vřešťál[3] used more dilute solutions. The salt was also prepared as follows: 5.6 g of $Te(tu)_2Cl_2$ was dissolved, under stirring and warming to 40—50°, in a solution of 24 g of thiourea in 160 ml of 48 % ethanol. Some undissolved matter and a little tellurium was filtered off, and the filtrate allowed to stand at room temperature over night. Yield, 5.5 g (64 %). Analytical data for this salt, and for the anhydrous chloride and the perchlorate are given by Vřešťál[3].

Tetrathiourea-tellurium(II) dichloride, Te(tu)$_4$Cl$_2$. Well developed crystals were obtained from a saturated solution of Te(tu)$_2$Cl$_2$ in boiling anhydrous methanol containing an excess of thiourea, by slow cooling.

The salt occurs as thin, triclinic plates {001} extended along the a axis, with the shorter plate edge parallel to the b axis: $a = 5.83$ Å, $b = 7.77$ Å, $c = 10.86$ Å, $\alpha = 95\frac{1}{2}°$, $\beta = 90°$, $\gamma = 119\frac{1}{2}°$. There is one formula unit per unit cell; density, calc. 1.96, found[3] 1.97 g/cm^3. From Fourier projections along the a and b axes[5], the tellurium atom lies in a centre of symmetry of the space group $C_i^1-P\bar{1}$.

Tetrathiourea-tellurium(II) dibromide, Te(tu)$_4$Br$_2$, is isomorphous with the anhydrous chloride, and shows the same morphology. The unit cell dimensions are: $a = 5.95$ Å, $b = 7.86$ Å, $c = 11.10$ Å, $\alpha = 95\frac{1}{2}°$, $\beta = 89\frac{1}{2}°$, $\gamma = 119\frac{1}{2}°$. With one formula unit per unit cell, the calculated density is 2.18; found[1] 2.21 g/cm^3. The space group, from isomorphism with the chloride, is $C_i^1-P\bar{1}$. The incomplete unit cell data reported earlier[1] correspond to a different choice of b axis.

The salt was prepared by dissolving, under stirring and warming to 30–40, 11 g of Te(tu)$_2$Br$_2$ in 300 ml of 10 % aqueous thiourea. After filtering, and addition of 7 g of potassium bromide in 15 ml of water, the salt rapidly crystallized. Yield, 14 g (95 %). (Found: N 18.64; Te 21.59. Calc. for $C_4H_{16}Br_2N_8Te$: N 18.93; Te 21.56.)

Tetrathiourea-tellurium(II) dithiocyanate, Te(tu)$_4$(SCN)$_2$, was obtained from the dithiourea compound, and thiourea: 3 g of Te(tu)$_2$(SCN)$_2$ was dissolved in 75 ml of 10 % aqueous thiourea at about 40°, and the solution filtered and allowed to stand over night at room temperature. Yield, 3.4 g (72 %). The salt can also be prepared from aqueous thiourea solutions of tetrathiourea-tellurium(II) dichloride or dibromide, and ammonium or potassium thiocyanate. (Found: N 25.18; S 34.84; Te 22.92. Calc. for $C_6H_{16}N_{10}S_6Te$: N 25.55; S 35.09; Te 23.27.)

The crystals occur as well developed, monoclinic prisms {011} terminated by {100}, with $a = 7.68$ Å, $b = 14.08$ Å, $c = 9.72$ Å, $\beta = 105°$, and two formula units per unit cell; density, calc. 1.79, found 1.78 g/cm^3. The space group, from systematic absences, is $C_{2h}^5-P2_1/c$, and the tellurium atoms thus lie in centres ofsymmetry.

Tetrathiourea-tellurium(II) nitrate, Te(tu)$_4$(NO$_3$)$_2$, crystallizes from aqueous thiourea solutions of the chloride or bromide, on addition of aqueous potassium nitrate or nitric acid. (Found: S 23.02; Te 22.80. Calc. for $C_4H_{16}N_{10}O_6S_4Te$: S 23.06; Te 22.95.) The salt forms monoclinic prisms extended along the c axis and bounded by {010} and, less dominantly, by {100}, with $a = 6.14$ Å, $b = 24.70$ Å, $c = 7.44$ Å, $\beta = 120°$. The space group, from systematic absences, is $C_{2h}^5-P2_1/c$ and there are two formula units per unit cell; density, calc. 1.89, found 1.88 g/cm^3. Also in this salt, therefore, the cation is centrosymmetric.

The location of the tellurium atoms in centres of symmetry in this and the preceding salt is consistent with the intensity distributions, hkl reflections with $k + l$ even being in most cases markedly stronger than those with $k + l$ odd.

Vřešťál[3] obtained the nitrate as a dihydrate.

Tetrathiourea-tellurium(II) perchlorate, Te(tu)$_4$(ClO$_4$)$_2$. 2 g of the bromide, Te(tu)$_4$Br$_2$, was dissolved in 30 ml of 10 % aqueous thoiurea, some liberated tellurium filtered off, and 5 ml of 60 % perchloric acid added to the filtrate. Yield, after one night in a refrigerator, 1.7 g (80 %).

The salt occurs as triclinic prisms extended along the c axis, with $a = 15.35$ Å, $b = 11.97$ Å, $c = 6.01$ Å, $\alpha = 90°$, $\beta = 91°$, $\gamma = 108°$. There are two formula units per unit cell; density, calc. 2.00, found 2.01 g/cm^3. Vřešťál[3] gives the density as 2.11 g/cm^3. Němec's[4] X-ray data agree well with ours; his b axis corresponds to the short ab diagonal in the above setting.

The TeS$_4$ group of the Te(tu)$_4^{2+}$ ion is thus, from space group requirements of centrosymmetry, exactly planar in five of the above salts: Three salts (chloride dihydrate, thiocyanate and nitrate) crystallize in the monoclinic space group $C_{2h}^5-P2_1/c$ with two formula units per unit cell, and two (anhydrous chloride and bromide) in the triclinic space group $C_i^1-P\bar{1}$ with one formula unit per unit cell.

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Complexes of Divalent Tellurium with Ethylenethiourea

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Divalent tellurium forms square planar complexes with thiourea [1-3]. Of the two possible isomers, *cis* and *trans*, of type $Te(tu)_2X_2$ complexes where tu = thiourea, only one has been encountered in each case. *E.g.*, the crystals of the halides and the thiocyanate (X = Cl, Br, I, SCN) represent the *cis* isomer. In a study of similar complexes with ethylenethiourea (etu) we have not been able to isolate a chloride, $Te(etu)_2Cl_2$, but have obtained at least two forms of the bromide, $Te(etu)_2Br_2$, as well as an iodide and a thiocyanate; these are described below. In one of the bromides, isomorphous with the iodide, the tellurium atom lies in a centre of symmetry, and the arrangement of ligands around tellurium is thus planar *trans*. In the other one, tellurium is located on a twofold axis, and this form, or a possible third one, may be the *cis* isomer.

The ethylenethiourea complexes are stable in the solid state, but like the thiourea complexes, they hydrolyze and become black in contact with water. X-Ray data were obtained from oscillation and Weissenberg photographs; the values for axial lengths are based on $\lambda = 1.542$ Å for Cu*Ka* radiation and are believed to be accurate to within 0.5 %.

Dibromobis(ethylenethiourea)tellurium(II), $Te(etu)_2Br_2$. Two crystalline forms have been obtained pure, an orthorhombic and a monoclinic one. The former was best prepared from tellurium dioxide and ethylenethiourea in a molar ratio of 1 : 6 as follows: 1.6 g (10 mmoles) of tellurium dioxide was dissolved in 50 ml of 48 – 50 % hydrobromic acid and 150 ml of water, the solution was heated almost to boiling, and 6.1 g (60 mmoles) of ethylenethiourea in 60 ml of hot water was added rapidly under stirring. From the resulting, clear solution (filtered immediately after mixing, if necessary) crystallization sets in spontaneously or on scratching of the beaker walls, and may be hastened by occasional stirring; it should take place from hot solution since if the temperature falls below about 50° some tetrakis(ethylenethiourea)tellurium(II) dibromide dihydrate [4] may crystallize and contaminate the product. Yield, 2.6 – 3.8 g (53 – 77 %) depending on the rate of crystallization and temperature when filtering. M.p. 186° (decomp.). (Found: S 13.27; Te 25.98. Calc. for $C_6H_{12}Br_2N_4S_2Te$: S 13.04; Te 25.95.)

The brownish-yellow, *orthorhombic* crystals occur as flat prisms extended along the *c* axis with {010} dominant. The axial lengths are, $a = 14.46$ Å, $b = 31.40$ Å, $c = 12.10$ Å, and the space group, from systematic absences, is $D_{2h}^{24} - Fddd$, which has 32-fold general positions. There are 16 molecules per unit cell; density, calc. 2.38, found 2.38 g/cm³. The intensity distribution: *hkl* reflections with $h+k+l = 2n+1$ or $4n$ in most cases markedly strongest, indicates that the tellurium atoms lie on twofold axes of symmetry.

The substance is practically insoluble in glacial acetic acid, but readily soluble in dimethylformamide to give red, stable solutions. When to a warm solution of the substance in dimethylformamide, preferably less concentrated than corresponding to saturation at room temperature, an about double volume of glacial acetic acid is added, the monoclinic form crystallizes; the orthorhombic one could not be recovered even on seeding.

The *monoclinic* crystals appear a little darker reddish-yellow in colour than the orthorhombic ones. M.p. 192° (decomp.). (Found: S 13.16; Te 26.02.) They occur as prisms or plates extended along the *b* axis, bounded by {100} and {001} with the latter dominant in most cases. The unit cell dimensions are, $a = 17.30$ Å, $b = 5.89$ Å, $c = 15.57$ Å, $\beta = 120°$, and there are four molecules per unit cell; density, calc. 2.38, found 2.38 g/cm³. Systematic absences, *hkl* when $h + k$ is odd, *h0l* when *h* is odd or *l* is odd. These, together with the intensity distribution, perhaps best observed on oscillation photographs about the *bc* diagonal: *hkl* reflections with $k + l$ even generally stronger than those with $k + l$ odd, indicate that the tellurium atoms lie in symmetry centres, positions (*c*) or (*d*) [5], of the space group $C_{2h}^6 - C2/c$.

This has been confirmed by structure analysis [6], through projections along the *b* axis and along the *ab* diagonal, the repeat distance along which is halved on account of the *C*-centering and thus is 9.14 Å. The dimensions of the planar *trans* TeS_2Br_2 group of the centrosymmetric molecule are: Te – S = 2.69 Å, Te – Br = 2.78 Å, and