Reactions of Phenyltellurium Trichloride with Thiourea

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Tellurium dioxide dissolved in hydrochloric or hydrobromic acid reacts with four moles of thiourea to give covalent halides $Te(tu)_2X_2$ (tu = thiourea) and with six moles of thiourea to give salts of the cation $Te(tu)_4^{++}$. These are planar, four-co-ordinated complexes of divalent tellurium [1].

It has been found that phenyltellurium trichloride reacts similarly with thiourea, to give thiourea derivatives of divalent tellurium. The reactions are, with three moles of thiourea:

$$C_6H_5TeCl_3 + 3\ SC(NH_2)_2 = C_6H_5Te[SC(NH_2)_2]Cl + [SC(NH_2)_2]_2^{++} + 2\ Cl^-$$

and with four moles:

$$C_6H_5TeCl_3 + 4\ SC(NH_2)_2 = C_6H_5Te[SC(NH_2)_2]_3^+ + [SC(NH_2)_2]_2^{++} + 3\ Cl^-$$

The following compounds have been prepared and characterized through single-crystal X-ray photographs (Cu$K\alpha$ radiation, $\lambda = 1.542$ Å). Melting points are corrected.

Thiourea-benzenetellurenyl chloride, $C_6H_5Te(tu)Cl$. To 3.11 g (10 mmoles) of phenyltellurium trichloride dissolved in 20 ml of methanol was added 2.28 g (30 mmoles) of thiourea dissolved in 20 ml of warm water. A clear, orange red solution resulted, from which the divalent tellurium compound crystallized on standing. Yield, about 2.5 g (80 %). The product was recrystallized from methanol (2 g dissolved in about 25 ml at boiling temperature). M. p. 166°. (Found: S 9.96; Te 40.11. Calc. for $C_7H_9ClN_2STe$: S 10.14; Te 40.35.)

The crystals are orange red and appear as well developed, monoclinic prisms {011} with $a = 6.32$ Å, $b = 10.62$ Å, $c = 15.16$ Å, $\beta = 90\frac{1}{2}°$. There are four molecules per unit cell; density, calc. 2.06, found 2.07 g/cm³. The space group, from systematic absences, is $C_{2h}^5 - P2_1/n$.

Thiourea-benzenetellurenyl bromide, $C_6H_5Te(tu)Br$. The crystals are isomorphous with those of the chloride, and show the same colour and morphology. The unit cell dimensions are, $a = 6.46$ Å, $b = 10.73$ Å, $c = 15.36$ Å, $\beta = 91\frac{1}{2}°$, and the density, calc. 2.25, found 2.24 g/cm³.

The compound was prepared as described above for the chloride, by dissolving about 3.6 g (30 mmoles) of potassium bromide in the aqueous thiourea solution before mixing with the methanolic phenyltellurium trichloride solution. Yield, about 3.6 g (99 %). M. p. 178° (recrystallized from methanol, 2 g dissolved in about 45 ml at boiling temperature). (Found: Te 35.82. Calc. for $C_7H_9BrN_2STe$: Te 35.37.)

The compounds $C_6H_5Te(tu)X$ dissolve in warm aqueous thiourea to give yellow to orange yellow solutions from which salts of the cation $C_6H_5Te(tu)_3^+$ crystallize on cooling. The chloride was also prepared directly from phenyltellurium trichloride.

Dithiourea-benzenetellurenyl chloride, $C_6H_5Te(tu)_2Cl$. To 3.11 g (10 mmoles) of phenyltellurium trichloride dissolved in 15 ml of methanol was added one drop of conc. hydrochloric acid and, with stirring, 3.8 g (50 mmoles, 25 % excess) of thiourea dissolved in 25 ml of warm water, and then 25 ml of water. On standing, the chloride slowly crystallized, as clusters of yellow needles which ultimately filled the whole liquid. Yield, about 3.4 g (85 %); m. p. 168°. (Found: S 16.30; Te 32.33. Calc. for $C_9H_{13}ClN_4S_2Te$: S 16.34; Te 32.52.) It may be recrystallized from aqueous thiourea, preferrably in presence of a small amount of hydrochloric acid.

The salt forms long orthorhombic prisms elongated in the direction of the c axis. The axial lengths are, $a = 11.98$ Å, $b = 20.80$ Å, $c = 5.79$ Å, and the space group, from systematic absences, is $D_2^4 - P2_12_12_1$. There are four formula units per unit cell; density, calc. 1.81, found 1.81 g/cm³.

The nitrate and perchlorate crystallize on addition of nitric or perchloric acid to aqueous thiourea solutions of the chloride (1 g chloride in 30 ml of warm 10 % thiourea, 3 ml of *ca.* 35 % nitric acid or 2 ml of *ca.* 60 % perchloric acid. Yields on standing to room temperature, about 1 g of each). The salts form long, yellow prisms elongated along the b axis.

Dithiourea-benzenetellurenyl nitrate, $C_6H_5Te(tu)_2NO_3$. M. p. 135°. (Found: S 15.49; Te 29.88. Calc. for $C_8H_{13}N_5O_3S_2Te$: S 15.31; Te 30.46.) Monoclinic, $a = 24.30$ Å, $b = 5.88$ Å, $c = 21.30$ Å, $\beta = 90\frac{1}{2}°$. There are eight formula units per unit cell; density, calc. 1.83, found 1.83 g/cm³. On the basis of the systematic absences, hkl when $h + k$ is odd, $h0l$ when h is odd or l is odd, the space group is either C_{2h}^6—$C2/c$ or C_s^4—Cc.

Dithiourea-benzenetellurenyl perchlorate, $C_6H_5Te(tu)_2ClO_4$. M. p. 136°. (Found: Te 27.97. Calc. for $C_8H_{13}ClN_4O_4S_2Te$: Te 27.96.) Monoclinic prismatic, $a = 12.24$ Å, $b = 5.86$ Å, $c = 22.76$ Å, $\beta = 96°$. There are four formula units per unit cell; density, calc. 1.87, found 1.87 g/cm³. The space group, from systematic absences, is C_{2h}^5—$P2_1/c$.

Dithiourea-benzenetellurenyl thiocyanate, $C_6H_5Te(tu)_2SCN$, was prepared *via* a compound, presumably $C_6H_5Te(tu)SCN$, obtained from phenyltellurium trichloride in the same way as $C_6H_5Te(tu)Br$, by use of 30 mmoles of potassium thiocyanate instead of potassium bromide. The micro-crystalline solid (3 g) which separated on standing at ice temperature, was filtered off and dissolved in 60 ml of warm 10 % aqueous thiourea. On filtering, a clear, orange yellow solution resulted which on standing deposited yellow crystals (2.4 g) of the thiocyanate. M. p. 109°. (Found: S 22.98; Te 30.47. Calc. for $C_9H_{13}N_5S_3Te$: S 23.18; Te 30.75.)

The crystals occur as long, monoclinic prisms extended along the b axis. The unit cell dimensions are, $a = 15.37$ Å, $b = 5.83$ Å, $c = 17.47$ Å, $\beta = 96°$, and the space group, from systematic absences, C_{2h}^5—$P2_1/n$. There are four formula units per unit cell; density, calc. 1.77, found 1.78 g/cm³.

The crystal structures of representatives of the compounds are being studied with a view towards a possible bearing on the transition state in nucleophilic displacements on divalent tellurium, selenium and sulphur.

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Specificity of a Purified Hog Intestinal Maltase Fraction

Competitive Inhibition of Maltase Activity by Other Substrates

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In previous papers the separation of hog intestinal maltase activity into three fractions (maltase I—III) with different enzymatic properties has been described [1-3]. In the present paper the specificity of one of these fractions, *maltase III*, will be further discussed.

Maltase III preparations hydrolyze *phenyl-α-D-glucopyranoside* [2], *isomaltose* (6-(α-D-glucopyranosyl)-D-glucose) [2], *turanose* (3-(α-D-glucopyranosyl)-D-fructose) [2], and *melezitose* (α-D-glucopyranosyl-(1→3)-β-D-fructofuranosyl-(2→1)-α-D-glucopyranoside) [2]. (Melezitose is hydrolyzed to glucose and sucrose). Heat inactivation experiments support the theory that these activities and the maltase activity of the purified maltase III preparation are caused by the same enzyme [2,3].

When two substrates are hydrolyzed by the same enzyme, they act as competitive inhibitors for the hydrolysis of each other. The study of this inhibition usually requires a method for the separate determination of the hydrolysis products of each substrate, when the substrates are present in a mixture [3]. With maltase III, however, the hydrolysis of the other substrates proceeds slowly compared with the hydrolysis of maltose (measured at 0.1388 M substrate concentration the rate for their hydrolysis is 1/20 or less of the rate for the hydrolysis of maltose). When maltose is present in a mixture with one of the other substrates, therefore, it may be assumed that all the glucose produced is derived from maltose, and thus the rate for the hydrolysis of maltose may be measured simply by measuring the increase in reducing power, as if no other substrate were present *.

* This approximation will cause the K_i value measured to be somewhat too high. The error to be expected was calculated from the relative rate of hydrolysis of the different substrates at 0.1388 M substrate concentration and their K_s values. With phenyl-α-D-glycopyranoside as inhibitor the K_i value measured should be about 15 % too high, with *iso*-maltose and turanose about 30 % too high, and with melezitose less than 10 % too high.