Some Thiourea-tellurium(II) Fluorides

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In the course of a study of complexes of divalent tellurium with thiourea [1-4], we have tried to prepare a complex $Te(tu)_2X_2$ (tu = thiourea) with X = fluoride, to complete the series [1,3] of halides of this type. In all attempts, no such fluoride was obtained; instead, tetrathiourea-tellurium(II) salts resulted, and under certain conditions a trithiourea-tellurium(II) salt, $Te(tu)_3(HF_2)_2$. The failure to obtain a difluoro-dithiourea-tellurium(II) complex, together with observations on the relative ease of formation of the corresponding complexes of the other halides, indicate that divalent tellurium belongs to the class of complex formers giving less stable fluoro than chloro, bromo and iodo complexes.

The salts obtained are described below. The preparations were performed in polythene beakers, and the products washed with ethanol containing a little thiourea, and dried on filter paper in air. The salts are yellow; the hydrogenfluorides blacken slowly on prolonged exposure to air or in contact with glass, but remain unchanged when kept in closed polythene bottles. Unit cell and space group data were obtained from oscillation and Weissenberg photographs, using Cu$K\alpha$ radiation, $\lambda = 1.542$ Å; the axial lengths are probably accurate to within 0.5 %.

The dichloro and dibromo complexes crystallize when tellurium dioxide, dissolved in hydrochloric or hydrobromic acid, reacts with four moles of thiourea [1]:

$Te^{IV} + 4\ tu + 2\ X^- = Te(tu)_2X_2 + (tu)_2^{2+}$

where X = halide. With hydrofluoric acid as a solvent, this tellurium dioxide: thiourea molar ratio (1 : 4) gave mainly monoclinic tetrathiourea-tellurium(II) di(hydrogenfluoride) in mixture with some trithiourea-tellurium(II) di(hydrogenfluoride). A molar ratio 1 : 6 gave mainly a triclinic dimorph of the tetrathiourea-tellurium(II) salt admixed with some of the monoclinic one, and a molar ratio 1 : 3 gave only the trithiourea-tellurium(II) salt.

Tetrathiourea-tellurium(II) di(hydrogenfluoride), $Te(tu)_4(HF_2)_2$. To 3.2 g (0.02 moles) of tellurium dioxide dissolved in 25 g of 38–40 % hydrofluoric acid was added, at about 50°, 9.1 g (0.12 moles) of thiourea in 30 ml of water. Yield, after 3 h at room temperature, 7.8 g (76 %). (Found: F 14.95; Te 25.74. Calc. for $C_4H_{18}F_4N_8S_4Te$: F 14.90; Te 25.02.) This sample consisted of the triclinic dimorph with only a small amount of the monoclinic one. The latter was obtained pure in an experiment as above, using 6.1 g (0.08 moles) of thiourea in 30 ml of water: After standing over night a lower layer (3.6 g) of the monoclinic dimorph (Found: F 14.60; Te 25.10) could be separated relatively cleanly from prisms (0.8 g) of the trithiourea-tellurium(II) salt which had grown on top of the layer.

The monoclinic dimorph occurs as short, thick prisms extended along the c axis, with {100} dominant, and $a = 22.32$ Å, $b = 7.92$ Å, $c = 10.16$ Å, $\beta = 91°$. Density, calc. 1.89 for four formula units per unit cell, found 1.90 g/cm³. Systematic absences, hkl when $h + k + l$ is odd, $h0l$ when h is odd or l is odd. These, together with observations that hkl reflections with l odd are in most cases very weak relative to those with l even, indicate that the tellurium atoms lie in symmetry centres of the space group C_{2h}^6-I2/c.

The triclinic dimorph forms plates extended along the a axis, with the c face dominant. With morphological axes, the unit cell dimensions are: $a = 7.59$ Å, $b = 5.84$ Å, $c = 12.41$ Å, $\alpha = 84\frac{1}{2}°, \beta = 116°, \gamma = 116°$. Density, calc. 1.92 for one formula unit per unit cell, found 1.94 g/cm³. The morphology indicates the centrosymmetric space group, $C_i^1-P\bar{1}$, which would require that the tellurium atom lies in a centre of symmetry also in this dimorph.

Tetrathiourea-tellurium(II) difluoride dihydrate, $Te(tu)_4F_2 \cdot 2H_2O$, crystallizes when the above hydrogenfluorides are dissolved in warm aqueous thiourea, and the solution allowed to cool, or on addition of potassium hydrogenfluoride solution to an aqueous thiourea solution of another tetrathiourea-tellurium(II) salt such as the chloride or bromide. (Found: F 7.70; Te 24.63. Calc. for $C_4H_{20}F_2N_8O_2S_4Te$: F 7.51; Te 25.21.) It blackens slowly if kept in a vacuum over sulphuric acid.

The salt occurs as triclinic prisms or plates {001} extended along the a axis, with $a = 5.42$ Å, $b = 8.03$ Å, $c = 11.30$ Å, $\alpha = 103\frac{1}{2}°$, $\beta = 97°$, $\gamma = 72°$. There is one formula unit per unit cell; density, calc. 1.85, found 1.88 g/cm³. The space group $C_i^1 - P\bar{1}$ indicated by the morphology would require centrosymmetry for the cation also here. The intensity distribution along the reciprocal c axis is very similar to that of the triclinic hydrogenfluoride dimorph (c spacings 10.97 and 11.08 Å respectively).

Trithiourea-tellurium(II) di(hydrogenfluoride), $Te(tu)_3(HF_2)_2$. This salt was obtained as prisms growing on top of a layer of the monoclinic tetrathiourea-tellurium(II) salt, as recounted above, and was the only product when a tellurium dioxide: thiourea molar ratio of 1 : 3 was employed (4.5 g thiourea in 15 ml of water in the above procedure). Yield, 2.7 g (52 %). (Found: F 17.36; S 22.23; Te 29.57. Calc. for $C_3H_{14}F_4N_6S_3Te$: F 17.51; S 22.17; Te 29.40.)

The salt forms monoclinic prisms {011} with $a = 5.91$ Å, $b = 20.68$ Å, $c = 11.47$ Å, $\beta = 95°$. The space group, from systematic absences, is $C_{2h}^5 - P2_1/c$. There are four formula units per unit cell; density, calc. 2.06, found 2.05 g/cm³. The crystal structure has been solved, and will be published later.

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The Equilibrium Between Molten FeO—Fe_2O_3 Mixtures and O_2 Gas

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From simple energetic assumptions it is possible to calculate the equilibrium between O_2 gas, Fe(II) and Fe(III) in solid solutions of $Fe_3O_4 - Fe_2O_3$, $Fe_3O_4 - MgFe_2O_4$ and $Fe_3O_4 - FeCr_2O_4$ based on spinel models with a defect cation lattice (cation vacancies and interstitial cations)[1-3]. These and similar models are also applicable[1,2] for the calculation of the equilibrium between oxygen gas and molten oxide mixtures, including a larger part of the range of composition from $FeO - Fe_3O_4$.

In the following a more plausible model will be suggested for the molten oxide mixtures based on a spinel like structure where instead of interstitial cations a corresponding number of oxygen ion vacancies are assumed.

The structure model is thus characterized by a Schottky disorder which can be expressed by

$$\frac{n_{\boxplus}}{n_c} \times \frac{n_{\boxminus}}{n_a} = N_{\boxplus} \times N_{\boxminus} = \text{const.} \qquad (1)$$

where

$n_{\boxplus}$ = number of cation vacancies
$n_{\boxminus}$ = number of anion vacancies
n_c = number of cation positions
n_a = number of anion positions

(The cation and anion vacancies are simultaneously present only in a composition range very close to stoichiometric Fe_3O_4).

The requirement for the model is that

$$\frac{n_c}{n_a} = \frac{3}{4} \qquad (2)$$

where

$n_a = n_{Fe(II)} + n_{Fe(III)} + n_{\boxplus}$
$n_a = n_{O^{2-}} + n_{\boxminus}$