four molecules per unit cell; density, calc. 1.84, found 1.85 g/cm³. The space group, from systematic absences, is $C_{2h}^5 - P2_1/c$. No molecular symmetry is required in these crystals.

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Tetrakis(ethylenethiourea)-tellurium(II) Salts

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In acid solutions tetravalent tellurium reacts with six moles of thiourea to give tetrathiourea-tellurium(II) salts [1,2]. This note describes corresponding salts of divalent tellurium with ethylenethiourea (etu) as ligand, i.e., salts of the cation $Te(etu)_4^{2+}$. They are formed in the same way as the thiourea analogs, two moles of ethylenethiourea reducing tetravalent tellurium to divalent and thereby themselves becoming oxidized to the ethyleneformamidinium disulphide cation, $(etu)_2^{2+}$. The very soluble chloride of this disulphide cation has been described [3]; we have identified it in the mother liquor from tetrakis(ethylenethiourea)tellurium(II) dichloride dihydrate preparations through its reaction product [4,5] with potassium iodide.

In two salts of the $Te(etu)_4^{2+}$ cation namely the anhydrous bromide and the perchlorate, and probably also in the anhydrous chloride, the tellurium atoms lie in centres of symmetry, and the TeS⁴ group is thus exactly planar, as in tetrathioureatellurium(II) salts [1,2].

Like previously described divalent tellurium complexes [1,2,6,7], the present salts hydrolyze and liberate tellurium in presence of water. Acids prevent hydrolysis; e.g., the chloride and bromide can be recrystallized from 2 N hydrochloric and hydrobromic acid, respectively. On the filters the salts were washed with 96 % ethanol containing a little concentrated hydrochloric acid (hydrobromic acid in the case of the bromides) and then with ether.

The following tetrakis(ethylenethiourea)tellurium(II) salts have been characterized through single-crystal X-ray photographs, using $CuK\alpha$ radiation, $\lambda = 1.542$ Å; values for axial lengths are probably accurate to within 0.5 %. The salts are yellow, the chlorides with a greenish, the perchlorate with a brownish tinge.

Dichloride dihydrate, $Te(etu)_4Cl_2 \cdot 2H_2O$. To 1.6 g (10 mmoles) of tellurium dioxide dissolved in 15 ml of concentrated, warm hydrochloric acid were added 6.5 g (a little more than 60 mmoles) of ethylenethiourea in 60 ml of hot water. Crystallization takes place on cooling to room temperature. Yield, 6.1—6.3 g (93—98 %). (Found: S 19.90; Te 19.84. Calc. for $C_{12}H_{28}Cl_2N_8O_2S_4Te$: S 19.94; Te 19.84. Weight loss after one hour at 110°: 5.8 %. Calc. for dihydrate: 5.6 %.) Prisms, extended along the b axis and bounded by {100}, {001} and {101}, with $a = 18.22$ Å, $b = 7.84$, $c = 21.30$ Å, $\beta = 124°$, and four formula units per unit cell; density, calc. 1.69, found 1.70 g/cm³. The space group, from systematic absences, is $C_{2h}^5 - P2_1/c$.

This salt results also when a tellurium dioxide : ethylenethiourea molar ratio of 1 : 4 is used; 4.1 g ethylenethiourea in the above procedure gave 3.2 g yield. In the case of thiourea [1], this molar ratio gives the dichloro complex, $Te(tu)_4Cl_2$.

The *dibromide dihydrate*, $Te(etu)_4Br_2 \cdot 2H_2O$, is isomorphous with the dichloride dihydrate, and has $a = 19.12$ Å, $b = 7.85$ Å, $c = 21.42$ Å, $\beta = 125°$; density, calc. 1.84, found 1.87 g/cm³. The salt was prepared by dissolving 1.6 g (10 mmoles) of tellurium dioxide in 20 ml of 48—50 % hydrobromic and 30 ml of water, and adding at about 50°, rapidly under stirring, 7 g (ca. 70 mmoles) of ethylenethiourea in 100 ml of warm water. The resulting, orange red solution was allowed to cool to room temperature. Yield, about

7 g (96 %). (Found: S 17.42; Te 17.45. Calc. for $C_{12}H_{28}Br_2N_8O_2S_4Te$: S 17.52; Te 17.43.) Under slightly different conditions [6] (60 mmoles of ethylenethiourea, and crystallization from more dilute and hotter solutions) this procedure gives orthorhombic dibromobis(ethylenethiourea)tellurium(II).

The two dihydrates are readily soluble in dimethylformamide, to give yellow to orange red solutions, apparently stable at room temperature. Boiling methanol dissolves per 100 ml about 1.5 g of either of the dihydrates; on cooling, the anhydrous salts crystallize out. Also in contact with the solid dihydrates at room temperature, methanol transfers them to the anhydrous salt.

The *dibromide*, $Te(etu)_4Br_2$, forms short, thick, monoclinic prisms bounded by {100} and {110} and terminated by {001}, with $a = 18.11$ Å, $b = 8.19$ Å, $c = 16.52$ Å, $\beta = 105\frac{1}{2}°$, and four formula units per unit cell; density, calc. 1.96, found 1.95 g/cm³. Systematic absences, hkl when $h + k$ is odd, $h0l$ when h is odd or l is odd. On oscillation photographs about the c axis, reflections on odd layer lines are markedly weaker than on even layer lines, particularly at large scattering angles. This indicates that the tellurium atoms lie in symmetry centres, positions (a) or (b) [8], of the space group $C_{2h}^6 - C2/c$.

The *dichloride*, $Te(etu)_4Cl_2$, is triclinic, with $a = 9.68$ Å, $b = 7.99$ Å, $c = 8.33$ Å, $a = 103°$, $\beta = 99°$, $\gamma = 109\frac{1}{2}°$, and one formula unit per unit cell; density, calc. 1.76, found 1.76 g/cm³. The $h0l$ zone of reflections shows a marked similarity to the $h0l$ zone of the anhydrous bromide ($\beta^* = 75\frac{1}{2}°$ in both salts, and the a and c spacings, halved in the bromide, correspond closely) also with respect to intensity distribution. This may be taken to indicate that the $h0l$ zone also of the chloride is centrosymmetric, *i.e.*, that the space group is $C_i^1 - P\bar{1}$, so that tellurium lies in a centre of symmetry.

The *perchlorate*, $Te(etu)_4(ClO_4)_2$, crystallizes from solutions of the dichloride dihydrate in warm 2 N hydrochloric acid, on addition of perchloric acid and cooling. (Found: S 17.38; Te 17.33. Calc. for $C_{12}H_{24}Cl_2N_8O_8S_4Te$: S 17.45; Te 17.36.) It forms flat prisms or plates {100} extended along the b axis, with $a = 9.61$ Å, $b = 9.78$ Å, $c = 14.64$ Å, $\beta = 92°$. There are two formula units per unit cell; density, calc. 1.78, found 1.78 g/cm³; and the space group, from systematic absences, is $C_{2h}^5 - P2_1/c$. Thus, the tellurium atoms lie in centres of

symmetry, and this agrees with the intensity distribution, hkl reflections with $k + l$ even being markedly strongest.

The *hexachlorotellurite(IV)*, $Te(etu)_4$ $TeCl_6$, resulted from attempts to arrive at the dichloro complex, $Te(etu)_2Cl_2$. To 1.6 g (10 mmoles) of tellurium dioxide in 100 ml of warm concentrated hydrochloric acid was added 4.1 g (40 mmoles) of ethylenethiourea in 50 ml of hot water, and then 50 ml of methanol. Crystallization started on scratching of the beaker walls; to develop well-formed, not too large crystals, the solution was occasionally stirred. Yield, about 3.5 g. (Found: Cl 24.22; S 14.70; Te 28.88. Calc. for $C_{12}H_{24}Cl_6N_8S_4Te_2$: Cl 24.27; S 14.63; Te 29.11.) The salt crystallized unchanged from a solution in warm methanol, but a solution in warm 2 N hydrochloric acid, on cooling, deposited crystals of the dichloride dihydrate.

The crystals of the hexachlorotellurite(IV) are orthorhombic; bipyramidal in appearance, and occur as plates {001} bounded by {110}, sometimes with {011} developed so that the plates become extended along the a axis, or as short prisms {110} terminated by {001}. There is a pronounced tendency of cleavage along the c plane. The axial lengths are, $a = 12.09$ Å, $b = 15.84$ Å, $c = 15.08$ Å, and there are four formula units per unit cell; density, calc. 2.02, found 2.02 g/cm³. Systematic absences, hkl when $h + k$ is odd; furthermore, hkl reflections are very weak when h is odd or k is odd. Of the orthorhombic space groups consistent with these observations, $C_{2v}^{11} - Cmm2$ is perhaps the more probable one, with the tellurium atom of cation as well as anion located on the same twofold axis.

The only trithiourea-tellurium(II) salt encountered was a hydrogenfluoride [2]. In the present work, *tris (ethylenethiourea)tellurium (II) perchlorate*, $Te(etu)_3(ClO_4)_2$, was obtained, as follows: To 1.6 g (10 mmoles) of tellurium dioxide in 5 ml of concentrated hydrochloric acid was added, at room temperature, 20 ml of *ca.* 60 % perchloric acid, and then 4.1 g (40 mmoles) of ethylenethiourea in 30 ml of hot water. Crystallization set in on scratching; yield after cooling to room temperature, 4.0 g. (Found: N 13.32; S 15.20; Te 20.19. Calc. for $C_9H_{18}Cl_2N_6O_8S_3Te$: N 13.28; S 15.20; Te 20.16.) From solutions of the salt in warm methanol (in presence of a little perchloric acid) or in warm 2 N hydrochloric acid, tetrakis(ethylenethiourea)tellurium(II) salts crystallized, as perchlorate or once

from the latter solvent, as the dichloride dihydrate.

The salt forms plates {100} extended along the b axis in most cases, and bounded by {001}. There is perfect cleavage along the a plane, and a persistent tendency of twinning on this plane, but un-twinned crystals were found in a crop from a mother liquor. The unit cell dimensions are, $a = 11.96$ Å, $b = 11.48$ Å, $c = 17.08$ Å, $\beta = 112\frac{1}{2}°$, and there are four formula units per unit cell; density, calc. 1.94, found 1.93 g/cm^3. The space group, from systematic absences, is $C_{2h}^5 - P2_1/c$. The reflections are very weak when $k + l$ is odd (particularly evident on oscillation photographs about the bc diagonal) which is typical for heavy atoms in centres of symmetry in this space group; however, such molecular symmetry is very improbable for stereochemical reasons. The same intensity distribution would result from tellurium atoms in general, fourfold positions x,y,z with x and $z = 0$ or $y = 0$.

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Correction to "A Miniature Solubility Column and its Application to a Study of the Solubility of Red Mercury(II)Oxide in Acid 3 M NaClO₄ Solutions" *

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A systematic error in the $-\log[H^+]$ values quoted in this paper, arising from an arithmetical error, has been detected. Throughout they should be reduced by 0.142 units, e.g., all points in Fig. 2 should be shifted 0.142 units to the left and $-\log[H^+]$ at the intersection of the asymptotes in Fig. 2 should be 3.08 not 3.22. As a result, the published equilibrium constants must be altered as follows:

$$\log {}^*K_1 + \log {}^*K_2 = -6.16 \pm 0.08$$

$$\log {}^*K_{so} = 2.41 \pm 0.10$$

This new value of $(\log {}^*K_1 + \log {}^*K_2)$ agrees with Ahlberg's potentiometric value [1] within the expected limits of error. The values of $\log {}^*K_1 - \log {}^*K_2 = -0.30 \pm 0.30$ and $\log K_{S2} = -3.75 \pm 0.01$ remain unchanged.

In the calculation of the solubility product (pK_{so}) of $Hg(OH)_2$, Lagerström's value [2] of $pK_w = 14.03$ was used. This is applicable to 3 *molal* solution of sodium perchlorate; the measured value for the 3 molar solutions used in the solubility work is 14.22 [3]. Using this and the revised value of $\log {}^*K_{so}$, pK_{so} becomes 26.0.

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