

Some Propylenethiourea-tellurium(II) Salts

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Thiourea^{1,2} and ethylenethiourea³, but not tetramethylthiourea⁴, give cation complexes TeA_4^{2+} where A is an electro-neutral thiourea ligand. Here, we describe two salts, a dichloride dihydrate and a perchlorate, of the cation $\text{Te}(\text{prtu})_4^{2+}$ where prtu = propylenethiourea; unit cell and space group data show that, like in the $\text{Te}(\text{tu})_4^{2+}$ and $\text{Te}(\text{etu})_4^{2+}$ cations¹⁻³, the TeS_4 group is planar. Also, two crystalline modifications of a tris(propylenethiourea)-tellurium(II) perchlorate have been characterized; these represent the third example of a salt of apparently tri-coordinated divalent tellurium, among the prevalingly four-coordinated ones.

Unit cell and space group data were obtained from oscillation and Weissenberg photographs; the values for axial lengths are based on $\lambda = 1.542 \text{ \AA}$ for $\text{CuK}\alpha$ radiation and are believed to be accurate to within 0.5 %.

The *tetrakis dichloride dihydrate*, $\text{Te}(\text{prtu})_4\text{Cl}_2 \cdot 2\text{H}_2\text{O}$, was prepared, like the corresponding thiourea and ethylenethiourea salts, from tellurium dioxide and propylenethiourea in a molar ratio of 1:6. To a warm solution of 1.6 g (10 mmoles) of tellurium dioxide in 10 ml of concentrated hydrochloric acid was added, rapidly with stirring, 7.5 g (ca. 8 % in excess of 60 mmoles) of propylenethiourea in 20 ml of hot water. Yield, after scratching of the beaker walls or seeding, and cooling to room temperature, 6.5–6.7 g (93–96 %). The salt is readily soluble in methanol, and was washed on the filter with a small amount of cold 4 N hydrochloric acid. (Found: Cl 10.09; Te 18.12. Calc. for $\text{C}_{16}\text{H}_{36}\text{Cl}_2\text{N}_8\text{O}_2\text{S}_4\text{Te}$: Cl 10.14; Te 18.25.)

The crystals are yellow with an orange tinge, and form short, monoclinic prisms extended along the *a* axis. The unit cell dimensions are, $a = 9.31 \text{ \AA}$, $b = 18.78 \text{ \AA}$, $c = 9.73 \text{ \AA}$, $\beta = 118^\circ$, and there are two formula units per unit cell; density, calc. 1.55; found 1.55 g/cm³. The space group, from systematic absences, is C_{2h}^2 — $P2_1/c$, 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 strongest.

The *tetrakis perchlorate*, $\text{Te}(\text{prtu})_4(\text{ClO}_4)_2$, crystallizes on addition of dilute perchloric acid to methanol solutions of the dichloride dihydrate. Yield, from 3 g of the latter salt in 15 ml of methanol, and an equal volume of ca. 10 % perchloric acid, 2.9 g (86 %). The crystals showed irregular growth, and better developed ones were obtained on recrystallization from methanol. (Found: N 14.11; Te 16.17. Calc. for $\text{C}_{16}\text{H}_{32}\text{Cl}_2\text{N}_8\text{O}_8\text{S}_4\text{Te}$: N 14.16; Te 16.13.)

The crystals occur as plates {010} or as six-sided prisms along the *a* axis, bounded by {010}, {001} and {011}. They are triclinic, with $a = 10.03 \text{ \AA}$, $b = 9.41 \text{ \AA}$, $c = 9.82 \text{ \AA}$, $\alpha = 118 \frac{1}{2}^\circ$, $\beta = 90 \frac{1}{2}^\circ$, $\gamma = 107^\circ$, and one formula unit per unit cell; density, calc. 1.71, found 1.71 g/cm³. In view of the centrosymmetry shown by the cation in the dichloride dihydrate and the majority of analogous salts¹⁻³, the space group is probably C_i^1 — PI .

The *tris perchlorate*, $\text{Te}(\text{prtu})_3(\text{ClO}_4)_2$, was best prepared from methanol solutions of equal molar amounts of dichlorobis(propylenethiourea)tellurium(II)⁵ and propylenethiourea, or of the former compound and the tetrakis dichloride dihydrate, by addition at room temperature of about one fifth the volume of ca. 60 % perchloric acid. (Found: N 12.43; Te 19.01. Calc. for $\text{C}_{12}\text{H}_{24}\text{Cl}_2\text{N}_6\text{O}_8\text{S}_3\text{Te}$: N 12.45; Te 18.90.) The previously encountered analogs are trithiourea-tellurium(II) di(hydrogenfluoride)² and tris(ethylenethiourea)tellurium(II) perchlorate³.

The salt occurs in two modifications, one monoclinic and one triclinic, both are greenish yellow in contrast to the tetrakis perchlorate which is brownish yellow. The above procedure gave, on seeding, the monoclinic dimorph. It can be recrystallized from methanol; on cooling of the warm solution without seeding the monoclinic dimorph crystallized; on seeding with the triclinic one about equal amounts of the two dimorphs and of the tetrakis perchlorate were obtained. The equilibrium in solution between tellurium(II) cations with three, four and probably also two propylenethiourea ligands showed also when to methanol solutions of the tetrakis dichloride dihydrate was added, at room temperature, about one fifth the volume of ca. 60 % perchloric acid: On scratching

without seeding, the tetrakis perchlorate crystallized, once admixed with a little of the triclinic tris perchlorate. On seeding with one of the tris perchlorates, the dimorph employed for seeding crystallized first, accompanied in the case of the triclinic by the monoclinic one, and then except once when seeding with the monoclinic dimorph, the tetrakis perchlorate.

The monoclinic crystals occur as long prisms {011}, with $a = 12.22 \text{ \AA}$, $b = 14.74 \text{ \AA}$, $c = 14.27 \text{ \AA}$, $\beta = 106 \frac{1}{2}^\circ$, and four formula units per unit cell. The space group, from systematic absences, is $C_{2h}^5 - P2_1/c$.

The triclinic dimorph forms small, relatively thick plates with edges parallel to the a and c axes, and a pronounced ten-

dency of cleavage along the b plane. The unit cell has the dimensions, $a = 12.62 \text{ \AA}$, $b = 10.03 \text{ \AA}$, $c = 10.03 \text{ \AA}$, $\alpha = 96 \frac{1}{2}^\circ$, $\beta = 93^\circ$, $\gamma = 78 \frac{1}{2}^\circ$, and contains two formula units. Densities, calc. and found 1.82 g/cm^3 for both dimorphs.

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