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Complexes of Tellurium Tetrachloride and Tetrabromide with Tetramethylthiourea

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In the course of a study of complexes of divalent tellurium with tetramethylthiourea (tmtu) we have encountered two derivatives of tetravalent tellurium, the presumably six-coordinated complexes $Te(tmtu)_2Cl_4$ and $Te(tmtu)_2Br_4$. The crystals of the two compounds are isomorphous, and unit cell and space group data indicate that the tellurium atom lies in a centre of symmetry. Similar complexes have been described earlier; for example, of tellurium tetrachloride with thiourea [1,2], pyridine and aniline [1], and dimethylaniline [3], and of tellurium tetrabromide with thiourea [2], aniline, dimethylaniline and diphenylamine [4], but no structural data appear to be available.

Tetravalent tellurium in six-coordinated complexes has six bonding electron pairs and one non-bonding one in its valency shell. The stereochemistry of such complexes will depend on whether the lone pair is stereochemically active, in which case a pentagonal-bipyramidal arrangement of six bonding pairs and one lone pair is expected [5], or stereochemically inert [6,7], as in the octahedral [8,9] hexachloro- and hexabromotellurite(IV) ions. Although the centre of symmetry in the tetramethylthiourea complexes does not impose regular octahedral symmetry on the bonding pairs, it is in accord with octahedral symmetry and not with a lone pair in one of seven positions. The compounds would represent the *trans* isomer of octahedral complexes of this type.

The crystals are dark red in colour, and are stable when kept in closed bottles. On prolonged exposure to humid air the surface becomes whitish, and water hydrolyzes them rapidly to white tellurous acid. X-Ray crystallographic data were obtained from oscillation and Weissenberg photographs; the axial lengths quoted below are based on $\lambda = 1.542$ Å for Cu*Ka* radiation and are believed to be accurate to within 0.5 %.

Tellurium tetrachloride complex, $Te(tmtu)_2Cl_4$. To 1.6 g (10 mmoles) of tellurium dioxide in 6 ml of concentrated hydrochloric acid was added, rapidly with swirling, at room temperature, 5.3 g (40 mmoles) of tetramethylthiourea in 20 ml of methanol. The resulting red solution was, to remove some oily material, decanted into another beaker, and 10 ml of methanol was added to the decantate. On standing, the complex slowly crystallized. Yield, 1.8 g (34 %). M.p. 153—154°. (Found: Cl 26.55; S 12.15; Te 23.96. Calc. for $C_{10}H_{24}Cl_4N_4S_2Te$: Cl 26.56; S 12.01; Te 23.90.)

Tellurium tetrabromide complex, $Te(tmtu)_2Br_4$. To 1.6 g (10 mmoles) of tellurium dioxide in 5 ml of concentrated hydrochloric acid and 10 ml of water was added 2.7 g (20 mmoles) of tetramethylthiourea in 20 ml of methanol, and then, rapidly under swirling, a hot mixture of 10 ml of 48—50 % hydrobromic acid, 50 ml of water and 50 ml of methanol. If hydrobromic instead of hydrochloric acid is used to dissolve the tellurium dioxide, rather extensive oil formation occurs on addition of the tetramethylthiourea solution. Yield, after cooling to room temperature, 5.2 g. The product was a mixture of about equal amounts of the tetrabromide complex and the divalent tellurium complex [10] $Te(tmtu)Br_2$; the crystals of the two compounds could be readily discerned and picked out under a microscope. Although the tetrabromide complex thus was not obtained pure and not analyzed,

identity was established through single-crystal X-ray photographs showing isomorphism with the tetrachloride complex. M.p., of picked-out crystals, 176–177°.

The crystals are orthorhombic; those of the tetrachloride complex occur as prisms along the c axis bounded by {010} and {100} and those of the tetrabromide complex as six-sided plates {010} a little extended along the c axis. The axial lengths are, for $Te(tmtu)_2Cl_4$: a = 14.74 Å, b = 13.87 Å, c = 10.06 Å, and for $Te(tmtu)_2Br_4$: a = 14.98 Å, b = 13.88 Å, c = 10.40 Å. There are four molecules per unit cell; densities, calc. 1.72 and 2.19, respectively, found 1.70 and 2.21 g/cm³. The space group, from systematic absences, is D_{2h}^{15} – $Pbca$, which has eightfold general positions, and requires that the four tellurium atoms lie in centres of symmetry. This is consistent with the intensity distribution of the hkl reflections, those with $h + k$, $k + l$ and $l + h$ even being strongest, particularly in the case of the tetrachloride complex.

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Complexes of Tellurium Dichloride and Dibromide with One Mole of Tetramethylthiourea

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The tetravalent tellurium complex described in a preceding note [1], $Te(tmtu)_2Cl_4$ where tmtu = tetramethylthiourea, when dissolved in warm 4 N hydrochloric acid-methanol 2 : 1 (30 ml per g) and the solution kept near boiling temperature, forms a divalent tellurium complex, $Te(tmtu)Cl_2$, which in the course of a few hours separates out as dark red crystals. Presumably tetramethylthiourea acts as the reducing agent, being itself oxidized to the disulphide cation, $(tmtu)_2^{2+}$, of which salts are known [2,3].

The tellurium dichloride complex, and the corresponding bromide, may also be prepared directly from tellurium dioxide and tetramethylthiourea, as described below. The X-ray crystallographic data have been obtained from oscillation and Weissenberg photographs; the axial lengths, believed to be accurate to within 0.5 %, are based on $\lambda(CuK\alpha)$ = 1.542 Å.

Tellurium dichloride complex, $Te(tmtu)Cl_2$. To a warm solution of 1.6 g (10 mmoles) of tellurium dioxide in 20 ml of concentrated hydrochloric acid and 40 ml of water was added 2.7 g (20 mmoles) of tetramethylthiourea dissolved in 40 ml of methanol. The resulting, red solution was heated to near boiling temperature, and kept at this temperature some hours, while crystallization took place; the crystallization starts on scratching of the beaker walls, or on seeding, and is rather slow. Yield, about 2.2 g. M.p. 207°. (Found: Cl 21.32; S 9.69; Te 38.67. Calc. for $C_5H_{12}Cl_2N_2STe$: Cl 21.44; S 9.70; Te 38.58.) The compound, and the dibromide complex, are stable in the solid state, but liberate tellurium in contact with water like other complexes of divalent tellurium. They were on the filters washed with methanol containing a little concentrated hydrochloric acid or hydrobromic acid, respectively, and then with ether.