Complexes of Divalent Tellurium

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Tellurium dioxide dissolved in hydrochloric or hydrobromic acid has been found to react with four moles of aqueous thiourea as follows:

$$\mathrm{Te^{IV}} + 4\ \mathrm{SC(NH_2)_2} + 2\ \mathrm{X^-} \rightarrow \mathrm{Te[SC(NH_2)_2]_2X_2} + [\mathrm{(H_2N)_2C\text{-}S\text{-}S\text{-}C(NH_2)_2}]^{++}$$

where $\mathrm{Te^{IV}}$ represents tetravalent tellurium and X the halide. Tellurium is reduced to the divalent state, by two moles of thiourea which themselves become oxidized to formamidinium disulphide. The divalent tellurium compound crystallizes out on mixing of the tellurium dioxide and thiourea solutions.

The compounds, $\mathrm{Te(tu)_2Cl_2}$ and $\mathrm{Te(tu)_2Br_2}$ (tu = thiourea), dissolve in aqueous thiourea to give yellow solutions from which salts containing the cation $\mathrm{Te(tu)_4^{++}}$ crystallize out. They also dissolve in aqueous potassium thiocyanate to give, similarly, the thiocyanate $\mathrm{Te(tu)_2(SCN)_2}$.

X-Ray crystallographic data have been obtained from oscillation and Weissenberg photographs taken with copper radiation, $\lambda(\alpha) = 1.542$ Å.

Dichloro-dithiourea-tellurium(II), $\mathrm{Te(tu)_2Cl_2}$. Monoclinic prismatic, $a = 9.90$ Å, $b = 7.62$ Å, $c = 14.10$ Å, $\beta = 100\frac{1}{2}°$. There are four molecules per unit cell; density, calc. 2.23, found 2.26 g/cm³. Systematic absences, hkl when $h + k + l$ is odd, $h0l$ when h is odd or l is odd.

From Fourier projections along the b and a axes [1], the space group is the centrosymmetric one, $C_{2h}^6 - I2/c$. The tellurium atom lies on a twofold axis, with the other atoms in general positions. Sulphur and chlorine are bonded to tellurium in a planar or approximately planar, square arrangement, with equal atoms in *cis* positions.

Dibromo-dithiourea-tellurium(II), $\mathrm{Te(tu)_2Br_2}$, is isomorphous with the dichloro compound. The unit cell dimensions are, $a = 10.10$ Å, $b = 7.74$ Å, $c = 14.67$ Å, $\beta = 100°$, and the density, calc. 2.59, found 2.58 g/cm³.

Dithiocyanato - dithiourea - tellurium (II), $\mathrm{Te(tu)_2(SCN)_2}$. Orthorhombic pyramidal, $a = 18.48$ Å, $b = 18.64$ Å, $c = 7.90$ Å. There are eight molecules per unit cell; density, calc. 1.93, found 1.94 g/cm³. The space group, from systematic absences, is $C_{2v}^{19} - Fdd2$, which requires that the tellurium atom lies on a twofold axis.

Presumably the molecular structure is analogous to that of the parent dichloro and dibromo compounds. The slight increase in the length of the c axis relative to the twofold axis of the monoclinic analogs is indicative in this respect. The length, 7.90 Å, excludes the possibility that the atoms of the thiocyanate groups lie on the twofold axis.

The compound was obtained as well developed prisms {110} terminated by {111}, or when prepared from the dibromo compound, as plates {010} elongated in the direction of the c axis; the two forms gave identical X-ray photographs.

Tetrathiourea-tellurium(II) dichloride, $\mathrm{Te(tu)_4Cl_2 \cdot 2H_2O}$. Monoclinic prismatic, $a = 6.01$ Å, $b = 16.49$ Å, $c = 9.95$ Å, $\beta = 98\frac{1}{2}°$. There are two formula units per unit cell; density, calc. 1.84, found 1.86 g/cm³. The space group, from systematic absences, is $C_{2h}^5 - P2_1/c$. The tellurium atom is thereby required to lie in a centre of symmetry, which is also consistent with the intensity distribution of the $0kl$ reflections, those with $k + l$ even being in most cases markedly stronger than those with $k + l$ odd. It follows from the centrosymmetry that the $\mathrm{TeS_4}$ grouping is planar.

The analytical data and the density point to the presence of two moles of crystal water per mole of salt. The crystals occur as six-sided prisms, bounded by {011} and {010} and terminated by {100}.

Tetrathiourea-tellurium (II) dibromide, $\mathrm{Te(tu)_4Br_2}$. The crystals are triclinic, and form thin plates {001} normally elongated in the direction of the a axis. From oscillation and Weissenberg zero-layer photographs about the a and b axes and the shorter ab diagonal, $a = 5.95$ Å, $b = 7.16$ Å, $\gamma = 107°$ or $73°$, $d_{100} = 5.69$ Å, $d_{010} = 6.82$ Å, $d_{001} = 11.05$ Å, $\alpha^* = 84°$, $\beta^* = 88°$. This gives a cell volume of 450 Å³ and one formula unit per unit cell; density, calc. 2.18, found 2.21 g/cm³. If the triclinic space group is the centrosymmetric one, the tellurium atom lies in a centre of symmetry also in this salt.

These are apparently the first instances of complexes of divalent tellurium, apart from the compound $\mathrm{(NH_4)_2TeCl_4}$ reported by Lindner and Apolant [2] in 1924 which may possibly contain the ion $\mathrm{TeCl_4^{--}}$. In the four-co-ordinated state, divalent tellurium has six electron pairs in its valency shell; a square-planar arrangement of the four bonding pairs is in accordance with the two lone pairs occupying *trans* octahedral positions. The square-planar ICl_4^- ion represents an analogous case.

The compounds have a yellow colour, and are quite stable in the solid state. They blacken on contact with water, probably because of hydrolysis and subsequent rearrangement to zero- and tetravalent tellurium, in analogy with the alkaline hydrolysis of other derivatives of divalent tellurium as for example the telluropentathionate ion.

The $Te(tu)_4{}^{++}$ ion is probably the yellow species which forms the basis for the photometric determination [3-6] of tellurium with thiourea. The compounds $Te(tu)_2Cl_2$ and $Te(tu)_2Br_2$ may be the same as those isolated recently from thiourea and the tellurium tetrahalides by Aynsley and Campbell [7], and by these authors formulated with two hydrogen atoms less, as amidinothio derivatives of tetravalent tellurium.

Further preparative andstructural work is being made.

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Gas Chromatographic Separation of 3- and 4-Methyl-1-pentene

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The separation of 3- and 4-methyl-1-pentene by gas chromatography has, according to our knowledge, not been reported yet. Even on very long columns containing various polar or nonpolar liquids as stationary phases, no resolution of the pair was obtained [1]. This is due to the similarity in type and the close boiling points of the two compounds, the difference being only 0.2°C. It is obvious that this separation problem calls for a stationary phase with a highly selective action on the molecules of the two hexenes.

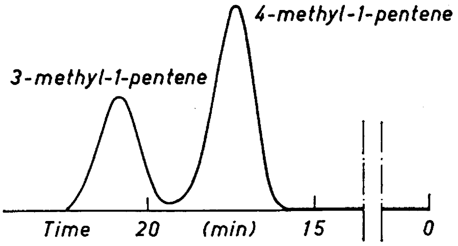

Fig. 1. Mixture of 3- and 4-methyl-1-pentene. Silver nitrate-glycol column, 4 m. Temperature 25°C. Flow of He 50 ml/min.

Such a phase is available in the form of silver nitrate in a suitable solvent, *e.g.* glycol [2,3]. In this case, there exist forces of attraction between the silver ions and the unsaturated hydrocarbons. Thus it was found that the pair in question could be resolved on a 4 m silver nitrate — glycol column containing 17 % of silver nitrate. It should be pointed out, however, that if the content of silver nitrate is appreciably diminished or increased the separation is impaired. The separation of these and other alkenes on a silver nitrate — glycol column will be more fully discussed in a forthcoming paper.

The column was prepared in the following way. Ethylene glycol was saturated with powdered silver nitrate under slight warming and agitation. The solution was decanted from undissolved silver nitrate and mixed with Chromosorb (30—60 mesh). Two parts of Chromosorb were taken to one part of the solution. The mixture was rotated in a round-bottomed flask to ensure thorough mixing of the carrier and the stationary phase. The mixture obtained was packed in two aluminium tubes each 2 m long and with a 4 mm internal diameter.

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