671. *Complexes of Thiourea containing Tellurium.*

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Thiourea forms with tellurium tetrahalides four types of compound, *viz.*, $(CSN_2H_4)_2TeX_4$, $(CSN_2H_5)_2TeX_6$, $(CSN_2H_5)_2TeX_6,2CSN_2H_5X$, and disubstitution compounds of the form $(CSN_2H_3)_2TeX_2$. The last are deposited from ethanol and in the process the solvent is converted into the corresponding ethyl halide.

UREA forms with tellurium tetrahalides unstable urea–tetrahalogenotellurium(IV) complexes and stable uronium pentahalogenotellurites, $(CON_2H_5)TeX_5$.[1] Thiourea and tellurium tetrahalides react quite differently and the products depend upon solvent and the relative concentrations of the reactants.

Dithiourea–tetrahalogenotellurium(IV) complexes, $(CSN_2H_4)_2,TeX_4$ where X = Cl or Br, were prepared by mixing solutions of thiourea and the corresponding tellurium tetrahalide in acetone or in acetic acid, and by shaking solid thiourea (which is insoluble in ether) with ethereal solutions of the tellurium tetrahalides.

Attempts to isolate these compounds from ethanol solutions produced instead diamidinothiodihalogenotellurium(IV) compounds $(CSN_2H_3)_2TeCl_2$ and $(CSN_2H_3)_2TeBr_2$, and ethyl halides. The bromo-compound was formed quantitatively, but the chloro-compound was always obtained mixed with some dithiourea–tetrachlorotellurium(IV), $(CSN_2H_4)_2TeCl_4$.

That $(CSN_2H_3)_2TeCl_2$ and $(CSN_2H_3)_2TeBr_2$ are formed by bonding between the tellurium atom of the halide and the sulphur atom of the thiourea molecule is to be expected from the known properties of thiourea and is proved as follows: when *S*-benzylthiourea reacts with tellurium tetrachloride or tetrabromide in ethanol, *S*-benzylthiourea–tetrahalogenotellurium(IV) compounds, $Ph\cdot CH_2\cdot SCN_2H_3,TeX_4$, are precipitated instead of compounds similar to the dihalogeno-compounds above. Thus the latter are probably formed by way of a two-step scheme:

$$\overset{+}{\mathrm{Te}}\mathrm{X_3}\overset{-}{\mathrm{X}} + \overset{+}{\mathrm{H}}\text{–}\overset{-}{\mathrm{S}}\mathrm{\cdot C(:NH)\cdot NH_2} \longrightarrow \mathrm{TeX_3\text{–}S\cdot C(:NH)\cdot NH_2} + \mathrm{HX}$$

$$\overset{-}{\mathrm{X}}\overset{+}{\mathrm{Te}}\mathrm{X_2\text{–}S\cdot C(:NH)\cdot NH_2} + \overset{+}{\mathrm{H}}\text{–}\overset{-}{\mathrm{S}}\mathrm{\cdot C(:NH)\cdot NH_2} \longrightarrow \mathrm{TeX_2[\cdot S\cdot C(:NH)\cdot NH_2]_2} + \mathrm{HX}$$

followed by subsequent reaction between the hydrogen halide and ethanol to produce an ethyl halide and water. Infrared spectroscopy also supports this structure for $(CSN_2H_3)_2TeX_2$.

The reaction could proceed by way of the addition compound $(CSN_2H_4)_2,TeX_4$ followed by elimination of two molecules of hydrogen halide. This was shown to be unlikely because when $(CSN_2H_4)_2TeBr_4$ was boiled with ethanol $(CSN_2H_3)_2TeBr_2$ was formed extremely slowly.

Water is produced in the reaction and this could cause some hydrolysis of $(CSN_2H_3)_2TeX_2$ or of unchanged tellurium halide. We have shown that these compounds are unaffected by prolonged boiling with ethanol containing small traces of water, provided there is always excess of thiourea present, and that tellurous acid is soluble in the same mixture. Since in our experiments these compounds were always prepared by use of excess of thiourea (thiourea is readily removed by hot ethanol), our samples of $(CSN_2H_3)_2TeX_2$ were not contaminated by decomposition products.

Dithiuronium hexachlorotellurite, $(CSN_2H_5)_2TeCl_6$, can be prepared by mixing solutions of thiourea and tellurium tetrachloride in acetic acid saturated with dry hydrogen chloride. The bromo-analogue is best prepared by cooling hydrobromic acid solutions containing thiourea and a large excess of tellurium tetrabromide.

From the solutions obtained by boiling thiourea and tellurium tetrahalide (or dioxide

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[1] Aynsley and Campbell, *J.*, 1956, 832.

with the appropriate halogen acid the double salts $(CSN_2H_5)_2TeCl_6,2CSN_2H_5Cl$ and $(CSN_2H_5)_2TeBr_6,2CSN_2H_5Br$ have been isolated. Tellurium compounds of this type have not previously been reported. They can also be prepared by boiling $(CSN_2H_3)_2TeX_2$ with excess of the appropriate halogen acid, showing that tellurium tetrahalides and thiuronium halides must have been re-formed. This suggests that the reactions between tellurium tetrahalides and thiourea are reversible. In ethanol removal of the hydrogen halide to form ethyl halide favours the formation of the diamidinothiodihalogeno-compounds; in acetic acid, acetone, and ether the hydrogen halide is not removed so that the dihalogeno-compounds are not formed in these solvents.

EXPERIMENTAL

Analysis.—Tellurium was weighed as the element after reduction of the complex with sulphur dioxide and hydrazine; nitrogen was determined by the micro-Dumas method, and chlorine, bromine, and iodine (as silver salts), fluorine (as lead chlorofluoride), and sulphur (as barium sulphate) by the micro-Parr bomb method.

Dithiourea–tetrahalogenotellurium(IV).—(*a*) Thiourea (1 g.) and tellurium tetrachloride (3 g.), each in acetic acid (100 ml.), were mixed. *Dithiourea–tetrachlorotellurium*(IV) separated immediately as a yellow powder and was dried *in vacuo* (yield 2·6 g.), m. p. 175° (decomp.) [Found: Te, 29·7; Cl, 34·8; N, 13·2. $(CSN_2H_4)_2TeCl_4$ requires Te, 30·2; Cl, 33·7; N, 13·3%]. Addition of water to the solid causes blackening owing to the formation of hydrogen sulphide and consequent reduction to tellurium. (*b*) Thiourea (0·4 g.) and tellurium tetrabromide (1·5 g.), each in acetone (200 ml.), were mixed. *Dithiourea–tetrabromotellurium*(IV) was precipitated (yield 1·5 g.) as an orange-yellow power, m. p. 210° (decomp.) [Found: Te, 22·3; Br, 52·9; N, 9·8. $(CSN_2H_4)_2TeBr_4$ requires Te, 21·2; Br, 53·4; N, 9·4%], which blackens when added to water. These compounds were also prepared by shaking powdered thiourea (insoluble in ether) with excess of an ethereal solution of the appropriate tetrahalide. In the chloride preparation the thiourea first formed a lumpy red-brown solid which on further shaking crumbled to a yellow powder. In both cases the bulk of the thiourea increased remarkably as reaction proceeded.

Diamidinothiodihalogenotellurium(IV).—Thiourea (1 g.) and tellurium tetrabromide (4 g.) were refluxed with ethanol (200 ml.) for 2 hr. *Diamidinothiodibromotellurium*(IV) was precipitated (2·6 g.) as a yellow powder, m. p. 215° (decomp.) [Found: Te, 29·2; Br, 36·5; N, 12·8. $(CSN_2H_3)_2TeBr_2$ requires Te, 29·1; Br, 36·6; N, 12·8%]. With tellurium tetrachloride (1·5 g.) in place of the tetrabromide, a pale yellow powder was obtained with a Te : Cl atomic ratio of 1 : 2·5 [Found: Te, 33·0; Cl, 22·9; N, 14·4. Calc. for $(CSN_2H_3)_2TeCl_2$: Te, 36·5; Cl, 20·4; N, 13·1%]. This was a mixture of $(CSN_2H_3)_2TeCl_2$ and $(CSN_2H_4)_2TeCl_4$, which accounts for the high Te : Cl ratio. Both materials blacken on addition of water and effervesce vigorously with nitric acid, evolving oxides of nitrogen.

The same compounds were also slowly precipitated when cold alcoholic solutions of thiourea and the tellurium tetrahalide were mixed and set aside. A third method of preparation is to reflux the hexahalogenotellurites with ethanol.

In each case fractional distillation of the ethanol mother liquor yielded an ethyl halide in quantities sufficient to account for the halogen removed from the tellurium tetrahalide. Free acid was not detected in the distillate.

Infrared Examination of $(CSN_2H_3)_2TeX_2$.—The infrared spectra, measured in potassium bromide discs between 2 and 15 μ, are very similar. A broad absorption band in the 3 μ region due to N–H stretching vibrations shows maxima at 3348, 3313, 3274, 3168, 3127 cm.$^{-1}$ (cf. crystalline thiourea: 3394, 3287, 3184, 3099 cm.$^{-1}$). Thiourea shows a weak absorption band at 2686 cm.$^{-1}$, which can probably be assigned to S–H stretching. A weaker maximum at 2716 cm.$^{-1}$ occurs for the sample of the dibromide (which is probably a mixture) and not for the dichloride: this lends some support to the view that there is Te–S bonding. Peaks at 1635 (s), 1618 (s), 1519 (sh), 1400 (m), 1362 (sh), 1166 (w), 1099 (w), 1031 (w), 720 (w), and 684 (m) cm.$^{-1}$ (all measured with a rock-salt prism) are shown by the dibromide : values for the dichloride are practically identical. For thiourea, well-defined maxima occur at 1621 (s), 1470 (m), 1414 (s), 1085 (m), and 731 (s) cm.$^{-1}$. The band at 1635 cm.$^{-1}$ may be assigned [2] to $>$C=NH, not present

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[2] Weissberger, " Techniques of Organic Chemistry," Vol. IX., " Chemical Applications of Spectroscopy," Interscience, New York, 1956, p. 532.

in crystalline thiourea: that at 1618 cm.$^{-1}$, due to C–NH$_2$, occurs in both. The band at 1470 cm.$^{-1}$ in thiourea, but not present in the dibromide, may be assigned to the N–C=S group.[3] These considerations further support Te–S–C(:NH)·NH$_2$ as the mode of attachment of the thiourea residue.

Dithiuronium Hexahalogenotellurites.—(*a*) Thiourea (1 g.) and tellurium tetrachloride (3 g.), each dissolved in acetic acid (100 ml.) saturated with dry hydrogen chloride, were mixed, the flask remaining connected to the hydrogen chloride supply. Lemon-yellow plates of dithiuronium hexachlorotellurite were immediately formed. On exposure to air these darkened, depositing tellurium. Since the compound was too unstable for ordinary analysis, it was washed quickly (twice) with acetic acid and, while still wet, transferred to a weighed beaker of water, and the atomic ratio of tellurium to chlorine determined [Found: Te : Cl = 1 : 6].

(*b*) Thiourea (0·5 g.) in concentrated hydrobromic acid (100 ml.) was added to tellurium tetrabromide (3 g.) in 100 ml. of the same acid and the solution boiled. To the hot red solution was added a 10-fold excess (25 g.) of tellurium tetrabromide, which caused the liquid to become dark red. After this was kept overnight, dark red crystals of *dithiuronium hexabromotellurite* separated. Though more stable than the hexachlorotellurite, these crystals decomposed rapidly on drying, but in addition to a determination of the atomic ratio Te : Br as described above, an analysis was attempted [Found: Te : Br ratio = 1 : 6. Te, 17·1; Br, 63·8. $(CSN_2H_5)_2TeBr_6$ requires Te, 16·8; Br, 63·3%]. It is inconvenient to prepare this compound by use of acetic acid saturated with dry hydrogen bromide as solvent owing to the low solubility of tellurium tetrabromide in this liquid.

(*c*) Dithiuronium hexabromotellurite (1 g.) was boiled with concentrated hydriodic acid. Some iodine and tellurium tetraiodide were produced and after being filtered and cooled the solution deposited *dithiuronium hexaiodotellurite* as dark crystals resembling potassium permanganate (4·2 g.). It had m. p. 145° (decomp.) [Found: Te, 11·5; I, 74·0. $(CSN_2H_5)_2TeI_6$ requires Te, 12·2; I, 73·1%].

Double Salts of Dithiuronium Hexahalogenotellurites and Thiuronium Halides.—(*a*) Thiourea (2 g.) and tellurium dioxide (2 g.) were boiled with excess of concentrated hydrochloric acid, and the resulting solution was rapidly filtered. The orange filtrate, on cooling, deposited greenish-yellow crystals of a mixture of unstable $(CSN_2H_5)_2TeCl_6$ with the double salt of this compound and thiuronium chloride. These crystals rapidly darkened in air owing to separation of tellurium, and were discarded. The lemon-yellow mother liquor slowly deposited lemon-yellow crystals of the *double salt.* This material, m. p. 148° (decomp.), is quite stable in air [Found: Te, 17·9; Cl, 38·7; N, 15·8. $(CSN_2H_5)_2TeCl_6,2CSN_2H_5Cl$ requires Te, 17·7; Cl, 39·5; N, 15·6%].

(*b*) With concentrated hydrobromic acid in place of hydrochloric acid, the resulting red solution yielded two quantities of orange crystals which were mixtures but the third and subsequent lots of crystals were the bright red, stable, pure *double salt,* m. p. 155° (decomp.) [Found: Te, 11·8; Br, 59·9; N, 10·5. $(CSN_2H_5)_2TeBr_6,2CSN_2H_5Br$ requires Te, 12·0; Br, 60·3; N, 10·5%].

(*c*) Both double salts were also made by dissolving 1 equiv. of dithiuronium hexachlorotellurite or hexabromotellurite and 2 equiv. of thiourea in the minimum of hot halogen acid and allowing the solution to cool, or by boiling $(CSN_2H_3)_2TeCl_2$ with concentrated hydrochloric acid and $(CSN_2H_3)_2TeBr_2$ with concentrated hydrobromic acid and allowing the solutions to cool.

S-*Benzylthiourea–tetrabromotellurium*(IV).—*S*-Benzylthiuronium chloride (10 g.) was suspended in ethanol, surrounded by a solid carbon dioxide–alcohol freezing mixture, and treated with sodium (1 g.) to liberate the base. After ½ hr., tellurium tetrabromide (25 g.) in ethanol was added. Yellow, amorphous S-*benzylthiourea–tetrabromotellurium*(IV) was precipitated [Found: Te, 20·0; Br, 53·7; N, 4·05. $C_7H_7SCN_2H_4,TeBr_4$ requires Te, 20·7; Br, 53·5; N, 4·65%].

Di-S-*benzylthiuronium Hexahalogenotellurites.*—When *S*-benzylthiourea, liberated from its hydrochloride as described above, was warmed with the theoretical quantity of tellurium dioxide and excess of the appropriate concentrated halogen acid, di-*S*-benzylthiuronium hexahalogenotellurites were formed: -*fluoro*-, unstable white plates which rapidly turn yellow in air [Found: Te, 22·5; F, 19·0; N, 10·1. $(C_7H_7SCN_2H_5)_2TeF_6$ requires Te, 23·9; F, 19·9; N, 9·7%]; -*chloro*-, stable yellow crystals, m. p. 145° [Found: Te, 18·2; Cl, 31·4; N, 8·0

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[3] Bellamy, " The Infra-red Spectra of Complex Molecules," Methuen, London, 1954, p. 294.

$(C_7H_7SCN_2H_5)_2TeCl_6$ requires Te, 18·9; Cl, 31·6; N, 8·3%]; *-bromo-*, stable orange needles, m. p. 158° [Found: Te, 14·0; Br, 51·9; N, 6·3. $(C_7H_7SCN_2H_5)_2TeBr_6$ requires Te, 13·5; Br, 51·1; N, 5·9%]. The hexaiodotellurite could not be prepared, a brown oil being obtained.

On dissolution of the hexafluorotellurite in hot hydrochloric acid and cooling the hexachlorotellurite was obtained. Hot hydrobromic acid converts either the fluoro- or the chloro-analogue into the hexabromotellurite.

Dithiuronium hexahalogenotellurites and their double salts with thiuronium chloride, and di-*S*-benzylthiuronium hexahalogenotellurites, do not effervesce with nitric acid, are insoluble in the common organic solvents, and are rapidly hydrolysed by water forming a precipitate of tellurous acid suspended in a solution of the corresponding halogen acid.

The authors thank Mr. R. E. Dodd for the infrared measurements.

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[*Received, April 25th*, 1958.]