156. *New Complexes containing Tellurium.*

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The preparation of the urea and the diazine salt of the pentahalogenotellurous acids ($HTeX_5$) in which the stability of the $[TeX_5]^-$ anion increases from the chloride through the bromide to the iodide is described. 1 : 1 Addition compounds of tellurium tetrabromide with tetranitrogen tetrasulphide and its tetrahydride and dioxan have also been prepared.

Unstable acids of the form $HTeX_5$, where X = Cl, Br, or I, were prepared by Metzner[1] and, although the corresponding fluorine-containing acid is unknown, metallic fluorides of the form $MTeF_5$ have been reported[2] where M = Na, K, Cs, NH_4, or Ba. On the other hand only one base-containing complex fluoride of the form $(BH)TeX_5$ has been described, *viz.*, pyridinium pentafluorotellurite, $(C_5H_5NH)TeF_5$.[3] Attempts to convert this compound into the corresponding chloride, bromide, and iodide by using the appropriate halogen acid proved unsuccessful and, instead, salts of the form $(BH)_2TeX_6$ were obtained, thus seeming to deny the existence of the chloride, bromide, and iodide of the general formula $(BH)TeX_5$. However, we have been able to prepare crystalline urea complexes of the form $(CON_2H_5)TeX_5$, where X = Cl, Br, or I, in which the stability of the $[TeX_5]^-$ anion increases from the chloride to the iodide, as illustrated by the ready conversion of the chloride into the bromide or iodide and the bromide into the iodide by treatment with the appropriate halogen acid. Attempts to prepare the fluorine compound of this series were unsuccessful.

Compounds of tellurium have also been prepared by using the diazines in which there are two equivalent nitrogen atoms in each six-membered ring available for the formation of complexes. Here the reactions seem to be governed largely by the relative positions of the nitrogen atoms in the molecule. Thus pyrimidine (1 : 3-diazine) and pyrazine (1 : 4-diazine) react with tellurium tetrabromide to form 1 : 1 addition compounds, $(C_4H_4N_2),TeBr_4$. These two compounds are powders which are readily converted into crystalline salts of composition $(C_4H_5N_2)TeBr_5$ on warming with hydrobromic acid. The corresponding chlorides and iodides can be prepared similarly and, as in the urea series, the stability of the $[TeX_5]^-$ anion increases from the chloride to the iodide.

Pyridazine (1 : 2-diazine), on the other hand, forms an unstable addition compound with tellurium tetrabromide which rapidly deposits tellurium. However, when hydrobromic acid solutions of pyridazine and tellurium tetrabromide are mixed, a stable crystalline salt is obtained of the form $(C_4H_5N_2)_2TeBr_6$. Further work on these reactions involving the diazines and similar bases is contemplated. We have also prepared 1 : 1 complexes of tellurium tetrabromide with tetranitrogen tetrasulphide and its tetrahydride, $N_4S_4H_4$, and with dioxan.

Experimental

Analysis.—Tellurium was weighed as the element following reduction of the complex with sulphur dioxide and hydrazine, nitrogen was determined by the micro-Dumas method, and halogens (as silver salts) and sulphur (as barium sulphate) by the micro-Parr bomb method.

Uronium Pentahalogenotellurites.—Urea (0·6 g.), tellurium dioxide (2·0 g.), and the requisite concentrated halogen acid (10 ml.) were heated together to 60° on a water-bath. Except in the case of the fluoride, crystals formed in ½ hr. and were filtered off, recrystallised at least twice from the concentrated acid, washed with a little acid, and finally dried on the water-bath. Slow evaporation of the fluoride solution at laboratory temperatures during several months failed to produce a fluorotellurite. *Uronium pentachlorotellurite* forms yellow crystals which begin

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[1] Metzner, *Compt. rend.*, 1897, **124**, 1448.

[2] Wells and Willis, *Amer. J. Sci.*, 1901, **12**, 190; Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green and Co., London, 1931, Vol. XI, p. 98.

[3] Aynsley and Hetherington, *J.*, 1953, 2802.

to sublime with decomposition at 255° (yield 3·2 g.) [Found: Te, 35·1; Cl, 47·9; N, 7·9. $(CON_2H_5)TeCl_5$ requires Te, 34·9; Cl, 48·5; N, 7·7%].

Uronium pentabromotellurite forms red crystals which darken at 250° and sublime with liberation of elementary tellurium (yield 5·6 g.) [Found: Te, 21·5; Br, 68·7; N, 4·9. $(CON_2H_5)TeBr_5$ requires Te, 21·7; Br, 68·0; N, 4·8%]. *Uronium pentaiodotellurite* consists of dark crystals resembling potassium permanganate which decompose without melting at 300° liberating iodine and tellurium metal (yield 8·0 g.) [Found: Te, 15·3; I, 76·9; N, 3·4. $(CON_2H_5)TeI_5$ requires Te, 15·5; I, 77·1; N, 3·4%]. All three penthalogenotellurites 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.

On dissolution of $(CON_2H_5)TeCl_5$ in hot hydrobromic acid and cooling, red crystals of $(CON_2H_5)TeBr_5$ were deposited. Hot hydriodic acid converts either $(CON_2H_5)TeCl_5$ or $(CON_2H_5)TeBr_5$ into $(CON_2H_5)TeI_5$.

It is not possible to form these salts by dissolving the addition compounds between urea and the tetrahalides of tellurium in the appropriate halogen acid since the complexes are very unstable. Thus, when alcoholic solutions of urea and tellurium tetrabromide were mixed and warmed, a precipitate formed which was filtered off and dried in a vacuum. The product [presumably urea–tetrabromotellurium(IV)], which was an amorphous, orange powder, rapidly lightened in colour and when exposed to the air quickly hydrolysed to tellurous acid.

Diazine–tetrabromotellurium(IV) *Complexes.*—Ethereal solutions of tellurium tetrabromide (2·3 g.) and the appropriate diazine (0·4 g.) were mixed. Precipitates formed immediately, the reactions being almost quantitative. *Pyrimidine–tetrabromotellurium*(IV) (yield 2·6 g.) [Found: Te, 23·6; Br, 61·1; N, 5·0. $(C_4H_4N_2)TeBr_4$ requires Te, 24·0; Br, 60·7; N, 5·3%] and *pyrazine–tetrabromotellurium*(IV) (yield 2·5 g.) [Found: Te, 23·1; Br, 60·2; N, 4·9. $(C_4H_4N_2)TeBr_4$ requires Te, 24·0; Br, 60·7; N, 5·3%] are stable, orange-red, microcrystalline compounds which hydrolyse in water to tellurous acid, are insoluble in the common organic solvents and at 150° darken and liberate tellurium. That from pyridazine is unstable and rapidly turns green, then black owing to the separation of tellurium. If tellurium tetrachloride is substituted for the tetrabromide, the corresponding chlorides can be isolated.

Diazinium Halogenotellurites.—Tellurium tetrabromide (2·3 g.), concentrated hydrobromic acid (10 ml.), and the requisite diazine (0·2 g.) were mixed and warmed to 60° on the water-bath for several hours. On cooling, well defined dark red crystals separated which were filtered off, recrystallised from concentrated hydrobromic acid, washed with a little hydrobromic acid, and dried in a vacuum to give *pyrimidinium pentabromotellurite* (yield 1·3 g.) [Found: Te, 20·4; Br, 65·5; N, 5·1. $(C_4H_4N_2H)TeBr_5$ requires Te, 20·8; Br, 65·9; N, 4·6%] and *pyrazinium pentabromotellurite* (yield 1·3 g.) [Found: Te, 20·6; Br, 65·1; N, 4·7. $(C_4H_4N_2H)TeBr_5$ requires Te, 20·8; Br, 65·9; N, 4·6%]. The product from pyridazine, which was slower to form than the other two, was not the expected pyridazinium pentabromotellurite but *dipyridazinium hexabromotellurite* (yield 1·7 g.) [Found: Te, 16·8; Br, 61·0; N, 8·0. $(C_4H_4N_2H)_2TeBr_6$ requires Te, 16·5; Br, 62·4; N, 7·3%]. These compounds can also be prepared by substituting tellurium dioxide for tellurium tetrabromide in the above preparations or by dissolving the diazine–tetrabromotellurium(IV) complexes in concentrated hydrobromic acid.

Pyrimidinium pentachlorotellurite and pyrazinium pentachlorotellurite, $(C_4H_4N_2H)TeCl_5$, were obtained as yellow crystals by substituting tellurium tetrachloride and hydrochloric acid for tellurium tetrabromide and hydrobromic acid. When pyridazine was used dipyridazinium hexachlorotellurite, $(C_4H_4NH)_2TeCl_6$, was produced. The corresponding iodotellurites were prepared as black crystals by the dissolution of the chlorotellurites or bromotellurites in hot hydriodic acid and cooling. All these diazinium halogenotellurites blacken and decompose between 140° and 200°. They are hydrolysed to tellurous acid with water and are insoluble in the commoner organic liquids.

Complexes of Tellurium Tetrabromide with Tetranitrogen Tetrasulphide and its Tetrahydride.—These were amorphous orange powders prepared by shaking the finely powdered sulphide or its hydride (2·0 g.) for several hours with an ethereal solution of tellurium tetrabromide. The *products* were filtered off, washed with ether and allowed to dry in air (yield 6·5 g.) [Found: Te, 20·0; Br, 50·9; S, 20·3; N, 9·0. $N_4S_4,TeBr_4$ requires Te, 20·2; Br, 51·1; S, 20·2; N, 8·8%] (yield 6·5 g.) [Found: Te, 19·9; Br, 50·6; S, 20·5; N, 8·8; H, 1·0. $N_4S_4H_4,TeBr_4$ requires Te, 20·1; Br, 51·0; S, 20·1; N, 8·8; H, 0·6%]. Both compounds blacken and decompose without melting at 150—151°, are hydrolysed by water to tellurous acid, and are insoluble in organic solvents.

Complex of Tellurium Tetrabromide with Dioxan.—A solution of tellurium tetrabromide in dioxan was allowed to evaporate at laboratory temperature. Red crystals of $C_4H_8O_2,TeBr_4$ were deposited and were purified by redissolving in excess of dioxan, filtering the solution, and allowing the filtrate to evaporate at laboratory temperature. The resulting *complex* has a considerable vapour pressure of dioxan at ordinary temperatures and at 78° it decomposes and evolves dioxan (yield 90%) (Found: Te, 23·7; Br, 60·5; C, 9·1; H, 1·4. $C_4H_8O_2,TeBr_4$ requires Te, 23·8; Br, 60·4; C, 9·0; H, 1·5%). The product is soluble in ether, alcohol, and chloroform but insoluble in benzene. Water hydrolyses it to tellurous acid.

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