563. *New Pyridine Complexes of Tellurium Tetrafluoride.*

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Tellurium tetrafluoride and pyridine in ether yield pyridinetetrafluorotellurium(IV), $(C_5H_5N)TeF_4$: this compound, with aqueous hydrofluoric acid, gives pyridinium pentafluorotellurite, $(C_5H_5NH)TeF_5$. Tellurium dioxide and pyridine in aqueous hydrofluoric acid yield dipyridinium hexafluorotellurite, $(C_5H_5NH)_2TeF_6$. Dipyridinium hexaiodotellurite is formed when any of these complex fluorides, or the hexa-chloride or -bromide, $(C_5H_5NH)_2TeX_6$, is treated with aqueous hydriodic acid.

Of these complex halides, the fluorides are the least stable, the order of stability being $[TeF_5]^-$ and $[TeF_6]^{--} < [TeCl_6]^{--} < [TeBr_6]^{--} < [TeI_6]^{--}$.

Many double chlorides and bromides of tellurium and organic bases have been described. Lenher (*J. Amer. Chem. Soc.*, 1900, **22**, 136) prepared a series of salts of tellurium tetrabromide and tetrachloride with the hydrobromides and hydrochlorides of aliphatic and aromatic amines, the bromides being red and the chlorides invariably yellow. He made salts of the type $(C_5H_5NH)_2TeBr_6$ and $(C_5H_5NH)_2TeCl_6$ by mixing solutions of tellurium dioxide and the amine salt in the appropriate halogen acid.

Lowy and Dunbrook (*ibid.*, 1922, **44**, 614) obtained products of the type $(C_6H_5{\cdot}NH_2)_2TeBr_4$ from solutions of the amines and tellurium tetrabromide in either absolute ether or glacial acetic acid. These compounds dissolved in dilute hydrobromic acid and yielded crystalline complexes containing four molecules of the amine hydrobromide combined with one of tellurium tetrabromide, *e.g.*, $(C_6H_5{\cdot}NH_2,HBr)_4TeBr_4$. Similarly, Morgan and Burgess (*J.*, 1929, 1103) found that tellurium tetrachloride and dimethylamine, in dry ether, formed bisdimethylanilinetellurium tetrachloride, $(C_6H_5{\cdot}NMe_2)_2TeCl_4$.

No mention has, however, been found of fluorides or iodides of this series, and although fluorides of the form $M[TeF_5]$ are reported (Wells and Willis, *Amer. J. Sci.*, 1901, **12**, 190; Mellor, " Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green & Co., London, 1931, Vol. XI, p. 98) where M = Na, K, Cs, NH_4, or Ba; those of the type $M_2[TeF_6]$ are unknown.

We describe here the preparation of a new base, pyridinetetrafluorotellurium(IV), $(C_5H_5N)TeF_4$, and two new complex fluorides, pyridinium pentafluorotellurite, $(C_5H_5NH)TeF_5$, and dipyridinium hexafluoro- and hexaiodo-tellurite, $(C_5H_5NH)_2TeX_6$.

Dissolution of tellurium tetrafluoride and pyridine in dry ether gives white, insoluble $(C_5H_5N)TeF_4$, not $(C_5H_5N)_2TeF_4$ as might be expected by analogy with the chloride and the bromide. This compound is unchanged in dry air, but is instantly decomposed by water to tellurous acid. Above 100° it decomposes without melting. With aqueous hydrofluoric acid it gives pale green crystals of $(C_5H_5NH)TeF_5$ (I). On the other hand, in fairly concentrated aqueous hydrofluoric acid, pyridine and tellurium dioxide give buff-coloured, needle-shaped crystals of $(C_5H_5NH)_2TeF_6$ (II).

The compounds (I) and (II) are rapidly hydrolysed by water to tellurous acid, but are insoluble in and unchanged by ether. Hydrochloric acid converts both salts into dipyridinium hexachlorotellurite, $(C_5H_5NH)_2TeCl_6$; hydrobromic and hydriodic acid give the corresponding salts (Aynsley, *J.*, in the press). Dipyridinium hexaiodotellurite also results from treatment of any of the other complex tellurium halides with hydriodic acid.

The stability of the $[TeX_6]^{--}$ anion (where X = F, Cl, Br, I) increases from the fluoride to the iodide, as illustrated by the ready conversion of any of the higher complex halides into a lower one by treatment with the appropriate halogen acid. The stability of the pentafluorotellurite anion, $[TeF_5]^-$, is of the same order as the hexafluoride anion, $[TeF_6]^{--}$; but its conversion into the lower $[TeX_6]^{--}$ anions (where X = Cl, Br, I), on treatment with the halogen acids seems to deny the existence of the chloride, bromide, and iodide of the series $(C_5H_5NH)TeX_5$, although the free acids, $HTeX_5,5H_2O$, are known (Metzner, *Compt. rend.*, 1897, **124**, 1448).

This order of stability of the complex tellurium halides, *viz.*, $[TeF_5]^-$ and $[TeF_6)^{--} < [TeCl_6]^{--} < [TeBr_6]^{--} < [TeI_6]^{--}$ is the same as that shown by Sharpe (*J.*, 1950, **3444**) for the complex halides of the noble metals, *e.g.*, $[PtF_6]^{--} < [PtCl_6]^{--} < [PtBr_6]^{--}$.

EXPERIMENTAL

Pyridinetetrafluorotellurium(IV).—Tellurium tetrafluoride was dissolved in anhydrous ether and added to a dry ethereal solution of pyridine. The resulting white precipitate of *pyridinetetrafluorotellurium*(IV) was filtered off and washed with ether, and the ether pumped off. It was analysed by dissolving it in cold sodium hydroxide solution and determining the tellurium by reducing it to the element with sulphur dioxide and hydrazine, and the fluorine by Willard and Winter's method after distillation from 50% sulphuric acid [Found: Te, 45·8; F, 26·5; C, 21·2; H, 2·2; N, 4·8. $(C_5H_5N)TeF_4$ requires Te, 45·0; F, 27·0; C, 21·3; H, 1·8; N, 5·0%].

Pyridinium Pentafluorotellurite.—The foregoing compound was dissolved in aqueous hydrofluoric acid, and the solution evaporated on the steam-bath until the pale green *pyridinium pentafluorotellurite* crystallised [Found: Te, 41·6; F, 31·2; C, 20·0; H, 2·0; N, 4·7. $(C_5H_5NH)TeF_5$ requires Te, 42·1; F, 31·5; C, 19·9; H, 2·0; N, 4·6%]. Treatment of this with hydrochloric acid produced yellow needles of dipyridinium hexachlorotellurite [Found: Te, 25·3; Cl, 42·6; C, 24·8; H, 2·7; N, 5·7. Calc. for $(C_5H_5NH)_2TeCl_6$: Te, 25·4; Cl, 42·6; C, 24·0; H, 2·4; N, 5·6%]. Hydrobromic acid similarly converted it into red needles of dipyridinium hexabromotellurite on recrystallisation [Found: Te, 16·4; Br, 62·5; C, 15·7; H, 1·8; N, 3·8. Calc. for $(C_5H_5NH)_2TeBr_6$: Te, 16·6; Br, 62·6; C, 15·7; H, 1·6; N, 3·7%].

On dissolution of $(C_5H_5NH)TeF_5$ in hot hydriodic acid and cooling, small, black needles of *dipyridinium hexaiodotellurite* were deposited [Found: Te, 12·9; I, 71·3; C, 11·5; H, 1·1; N, 2·1. $(C_5H_5NH)_2TeI_6$ requires Te, 12·1; I, 72·7; C, 11·4; H, 1·1; N, 2·7%].

Dipyridinium Hexafluorotellurite.—When pyridine was added to a solution of tellurium dioxide in aqueous hydrofluoric acid, and the solution was evaporated on the steam-bath, buff-coloured needles of *dipyridinium hexafluorotellurite* crystallised [Found: Te, 31·7; F, 28·5; C, 30·1; H, 3·0; N, 7·2. $(C_5H_5NH)_2TeF_6$ requires Te, 31·7; F, 28·4; C, 29·9; H, 3·0; N, 7·0%]. When this was treated with hydrochloric acid dipyridinium hexachlorotellurite was produced [Found: Te, 25·3; Cl, 42·3; C, 23·9; H, 2·7; N, 5·7. Calc. for $(C_5H_5NH)_2TeCl_6$: Te, 25·4; Cl, 42·6; C, 24·0; H, 2·4; N, 5·6%]. Similarly, hydrobromic and hydriodic acid afforded the corresponding hexabromo- and hexaiodo-tellurite. Also, $(C_5H_5NH)_2TeCl_6$ gave the hexabromide and hexaiodide, and $(C_5H_5NH)_2TeBr_6$, the hexaiodide, on treatment with the appropriate acid.

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