40. *Chemical Reactions with Vanadium, Niobium, and Tantalum Pentafluorides.*

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Vanadium pentafluoride reacted with nitryl fluoride and nitrosyl fluoride to form nitronium and nitrosonium hexafluorovanadates. The corresponding hexafluoroniobates and hexafluorotantalates were best prepared from the metal oxide, bromine trifluoride, and dinitrogen tetroxide or nitrosyl chloride. Chloryl hexafluorovanadate was stable only at low temperatures. Dissociation pressures of nitronium and nitrosonium hexafluorovanadates and of nitrosonium hexafluoroniobate were measured. The reactions of the pentafluorides with sulphur dioxide and trioxide and of niobium and tantalum pentafluorides with pyridine were studied.

The reactive molybdenum hexafluoride and vanadium pentafluoride can be satisfactorily examined [1,2] in glass apparatus free from moisture and vacuum grease. The physical properties of vanadium pentafluoride led to the suggestion that it ionises in the liquid state: $2VF_5 \rightleftharpoons VF_4^+ + VF_6^-$. Fairbrother, Frith, and Woolf [3] suggested, as a result of conductivity measurements, that a similar self-ionisation also occurs in molten niobium and tantalum pentafluorides. For all three pentafluorides the physical evidence for self-ionisation is provided by the high values of Trouton's constant and the appreciable electrical conductivities. Supporting indirect chemical evidence is found in the isolation of hexafluoro-vanadates,[4] -niobates,[5] and -tantalates [5] which contain the MF_6^- ions. The influence of such self-ionisation on the chemical properties of these pentafluorides has now been examined by a study of their reactions, mainly with oxides and other fluorides.

Although the hexafluorovanadates are known, no compound containing the " acidic " VF_4^+ ion has been isolated. The formulation [6] of the product of the reaction of iodine pentafluoride with antimony pentafluoride as $IF_4^+SbF_6^-$ suggests that a similar reaction with vanadium pentafluoride might give $VF_4^+SbF_6^-$. However, no such compound was isolated, although it may have been present in a solution of antimony pentafluoride in vanadium pentafluoride. The addition of potassium fluoride to this solution, followed by the removal of all volatile materials, left potassium hexafluoroantimonate. This can be explained in terms of either a simple neutralisation (*a*) or an addition reaction (*b*):

$$K^+VF_6^- + VF_4^+SbF_6^- \rightleftharpoons KSbF_6 + 2VF_5 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (a)$$

$$K^+ + F^- + SbF_5 = KSbF_6 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (b)$$

Similarly, the reactions of vanadium or niobium pentafluoride with boron trifluoride should produce $MF_4^+BF_4^-$ derivatives, but these reactions appeared not to give stable products. This is not surprising since the corresponding derivative of bromine trifluoride, $BrF_2^+BF_4^-$, has not yet been isolated.

To illustrate the formation of the hexafluoro-salts, the reactions of some of these pentafluorides with nitryl, nitrosyl, and chloryl fluorides were studied. With nitryl fluoride, vanadium pentafluoride forms involatile, white nitronium hexafluorovanadate, NO_2VF_6. Previous attempts [7] to produce this compound by the action of bromine trifluoride on mixtures of dinitrogen tetroxide and vanadium trichloride gave products intermediate in composition between the tetrafluoro-oxyvanadate and the hexafluorovanadate. Niobium pentafluoride did not react completely with nitryl fluoride at room

[1] O'Donnell, *J.*, 1956, 4681.
[2] Clark and Emeléus, *J.*, 1957, 2119.
[3] Fairbrother, Frith, and Woolf, *J.*, 1954, 1031.
[4] Emeléus and Gutmann, *J.*, 1949, 2979.
[5] Gutmann and Emeléus, *J.*, 1950, 1046.
[6] Woolf, *J.*, 1950, 3678.
[7] Sharpe and Woolf, *J.*, 1951, 798.

temperature, probably because of the formation of a protective coating of hexafluoroniobate. The nitronium salt is best prepared by the action of bromine trifluoride on dinitrogen tetroxide and niobium pentoxide. Nitronium hexafluoroniobate is a white solid from which all traces of bromine trifluoride cannot be satisfactorily removed. Similar treatment of tantalum pentoxide with dinitrogen tetroxide and bromine trifluoride gives only partial conversion into nitronium hexafluorotantalate and the pure salt could not be isolated.

Nitrosyl fluoride reacts rapidly with vanadium pentafluoride to form nitrosonium hexafluorovanadate, $NOVF_6$. This had been prepared [7] by bromine trifluoride treatment of nitrosyl chloride and vanadium trichloride. Nitrosonium hexafluoro-niobate and -tantalate, $NONbF_6$ and $NOTaF_6$, have now been prepared by treatment with bromine trifluoride of mixtures of nitrosyl chloride with niobium or tantalum pentoxide. Both are white solids which dissolve readily in water and from which all traces of bromine trifluoride cannot be removed. At the temperatures required for complete removal, decomposition is appreciable. The retention of bromine trifluoride may be attributed to solvolysis, *e.g.*, $NONbF_6 + 2BrF_3 \longrightarrow NOBrF_4 + BrF_2,NbF_6$, which occurs with the calcium and barium hexafluoro-niobates and -tantalates.[5]

The direct reaction of chloryl fluoride with other fluorides has led [8,9] to the isolation of the compounds ClO_2F,BF_3, ClO_2F,PF_5, and ClO_2F,SbF_5 which can be formulated as the "chloronium" salts $ClO_2^+BF_4^-$, $ClO_2^+PF_6^-$, and $ClO_2^+SbF_6^-$. With tantalum pentafluoride, chloryl fluoride gives a product containing only 0·48 mole of chloryl fluoride per mole of pentafluoride. Woolf attributed this to the slowness of the reaction at room temperature. Chloryl fluoride has now been allowed to react with vanadium pentafluoride. The reaction products were unstable at room temperature and experiments were made to isolate them at −46° and −78°. They were white solids which decomposed at higher temperatures to the original reactants. The product obtained at −46° contained 0·63 mole of chloryl fluoride per mole of pentafluoride while for the product of isolation at −78° the ratio was 0·97 : 1. This "chloronium hexafluorovanadate" is stable only at low temperatures and probably the low ratio observed by Woolf for the reaction with tantalum pentafluoride is due, not to the slowness of the reaction, but to the instability of the salt at ordinary temperatures. Further information on stability has been obtained from measurements of the dissociation pressures of nitronium and nitrosonium hexafluorovanadates and nitrosonium hexafluoroniobate. From these measurements, the following values have been calculated, simple dissociation being assumed to occur, *e.g.*, $NO_2VF_6(s) \longrightarrow NO_2F(g) + VF_5(g)$:

	ΔH (kcal./mole)	ΔG (50°) (kcal./mole)	ΔS (50°) (cal./deg./mole)
NO_2VF_6	13·75	6·15	23·5
$NOVF_6$	18·00	3·47	35·7
$NONbF_6$	20·5	4·84	48·6

From a consideration of the energetics of these dissociation processes for nitronium and nitrosonium hexafluorovanadates, three terms can be seen to differ; namely, the dissociation energies of nitryl and nitrosyl fluorides, the ionisation energies of the nitronium and nitrosonium ions, and the lattice energies of the original hexafluorovanadates. The difference in the dissociation energies is not likely to be large since in both cases dissociation involves the breaking of a nitrogen–fluorine bond. The other two energy differences will therefore determine the difference in stability, although the two factors cannot be readily separated. These results, together with the observed instability of chloronium hexafluorovanadate, indicate that the order of stability is $NO^+ > NO_2^+ > ClO_2^+$. Nitrosonium hexafluoroniobate is also seen to be more stable than the corresponding hexafluorovanadate. This difference in stability will again be related to the different radii of the VF_6^- and NbF_6^- ions, and to the relative energies of the reaction $MF_6^- \longrightarrow MF_5 + F^-$.

[8] Woolf, *J.*, 1954, 4113.
[9] Schmeisser and Ebenhoch, *Angew. Chem.*, 1954, **66**. 230.

Measurements of the dissociation pressures of nitronium hexafluoroniobate and nitrosonium hexafluorotantalate were not made, as it was not possible to prepare these salts free from bromine trifluoride.

With excess of sulphur dioxide, vanadium pentafluoride reacts quantitatively to form thionyl fluoride and vanadium oxytrifluoride:

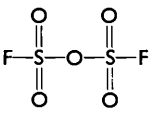
$$VF_5 + SO_2 \longrightarrow VOF_3 + SOF_2$$

Niobuim pentafluoride does not react at room temperature with sulphur dioxide. This difference between the two pentafluorides may be due to their different degrees of self-ionisation. Since excess of liquid sulphur dioxide was employed in both reactions, it seems reasonable to relate the mechanism of the reaction to that of the sulphur dioxide solvent system. The reaction with vanadium pentafluoride may therefore involve, as reaction intermediates, unstable complexes of the type $SO(VF_6)_2$ and $(VF_4)_2SO_3$. Similar complexes of niobium pentafluoride may not be formed so readily. Iodine pentafluoride, whose specific conductivity is of the same order as that of niobium pentafluoride, also does not react with sulphur dioxide.[10]

At room temperature, vanadium pentafluoride reacts readily with sulphur trioxide to form pyrosulphuryl fluoride and vanadium oxytrifluoride, $VF_5 + 2SO_3 \longrightarrow VOF_3 + S_2O_5F_2$. Pyrosulphuryl fluoride boils at 51°, in agreement with Hayek and Koller's value,[11] the latent heat of vaporisation is 7600 cal. mole^{-1} and the Trouton constant 23·5. Scheurer and Le Fave [12] suggested a structure of pyrosulphuryl fluoride involving S–O–F groups, but this seems unlikely since the analogous pyrosulphuryl chloride has [13] the chlorine atoms linked directly to sulphur. The infrared absorption spectrum of pyrosulphuryl fluoride shows that it has S–F and not S–O–F groups as can be seen from the comparison of the principal absorption bands of several sulphur oxyfluorides shown in the Table.

Assignment	Sulphuryl fluoride [14] SO_2F_2	Fluorine fluorosulphate [15] SO_3F_2	Peroxydisulphuryl fluoride [16] $S_2O_6F_2$	Pyrosulphuryl fluoride $S_2O_5F_2$
S–O stretching	1502	1501	1495	1513
	1269	1248	1246	1248
S–F stretching (asymmetric and symmetric)	885	879	—	872
	848	852	848	824
S–O stretching of S–O–F group	—	789	—	—
Unassigned	767	—	755	735

The structure of pyrosulphuryl fluoride therefore appears to be



As distinct from vanadium pentafluoride, niobium and tantalum pentafluorides reacted with sulphur trioxide to produce the addition compounds $NbF_5,2{\cdot}1SO_3$ and $TaF_5,2{\cdot}6SO_3$, which can be formulated as fluorosulphates $NbF_3(SO_3F)_2$ and $TaF_3(SO_3F)_2$ from which excess of sulphur trioxide has been incompletely removed. These compounds are viscous liquids which fume and decompose on exposure to air, and smell slightly of pyrosulphuryl fluoride. From both the niobium and tantalum compounds, thermal decomposition at 175—225° produced sulphuryl fluoride. Their formulation as fluorosulphates follows from a comparison with other fluorosulphates and with the reactions of other fluorides

[10] Aynsley, Nichols, and Robinson, *J.*, 1953, 623.
[11] Hayek and Koller, *Monatsh.*, 1951, **82**, 942.
[12] Scheurer and Le Fave, Abs. 118th Meeting, Amer. Chem. Soc., 1950, 26L.
[13] Gerding and Linden, *Rev. Trav. chim.*, 1942, **61**, 735.
[14] Perkins and Wilson, *J. Chem. Phys.*, 1952, **20**, 1791.
[15] Dudley, Cady, and Eggers, *J. Amer. Chem. Soc.*, 1956, **78**, 290.
[16] Dudley and Cady, *J. Amer. Chem. Soc.*, 1957, **79**, 513.

with sulphur trioxide. Thus, bromine trifluoride and sulphur trioxide form the product $BrF_3,1{\cdot}37SO_3$, a rather viscous liquid which can be formulated as $BrF_2^+SO_3F^-$. All the reactions of this compound show it to be a fluorosulphate.[17] Again, tantalum pentachloride reacts with fluorosulphuric acid [18] to give the fluorosulphate $TaCl_3(SO_3F)_2$. Using niobium pentachloride we obtained an unidentified viscous material and this probably has the formula $NbCl_3(SO_3F)_2$. There is a close resemblance between these compounds and the above pentafluoride derivatives. Finally, the infrared absorption spectrum of the niobium pentafluoride–sulphur trioxide compound, although not well resolved, showed definite bands at frequencies of 767 cm.$^{-1}$ and 1057 cm.$^{-1}$. These bands have been recently assigned to the S–F and to the S–O stretching frequencies respectively of the fluorosulphate group.[19,20] The reactions of the pentafluorides of niobium and tantalum with sulphur trioxide therefore take place through the formation of fluorosulphates:

$$MF_5 + 2SO_3 \longrightarrow MF_3(SO_3F)_2 \longrightarrow MOF_3 + S_2O_5F_2$$

The fluorosulphate derivative of vanadium pentafluoride is evidently unstable and the reaction proceeds to completion. With niobium and tantalum pentafluorides, the fluorosulphates are the stable products. It is not clear why thermal decomposition of the latter should produce sulphuryl rather than pyrosulphuryl fluoride.[21]

The new compounds dipyridinepentafluoroniobium(v), $(C_5H_5N)_2NbF_5$, and dipyridinepentafluorotantalum(v), $(C_5H_5N)_2TaF_5$, have been prepared by the direct reaction of pyridine with each of the pentafluorides. Both compounds are white solids which are stable in air and dissolve readily in water. Attempts were made to convert these pyridine compounds into pyridinium salts by treatment with concentrated aqueous hydrofluoric acid. The pyridinium fluorotantalates $(C_5H_5NH)_3TaF_8,2H_2O$ and $(C_5H_5NH)TaF_6$ have been prepared by Balke.[22] In the present case, repeated treatment of the dipyridine niobium compound with aqueous hydrofluoric acid gave pyridinium hexafluoroniobate, $(C_5H_5NH)NbF_6$, while similar treatment of the tantalum compound gave a product intermediate in composition between pyridinium hexafluorotantalate and dipyridinium heptafluorotantalate. This seems a further instance of the greater stability of the septavalent state of tantalum than of niobium.

Experimental

The preparation and analysis of vanadium pentafluoride have been described.[2] Niobium and tantalum pentafluorides were prepared by direct fluorination of the powdered metals at 350°. Niobium and tantalum were estimated in solutions of the pentafluorides by precipitation with ammonium hydroxide followed by ignition to the pentoxides. Fluorine was determined by precipitation as calcium fluoride (Found: Nb, 49·3; F, 50·4. Calc. for NbF_5: Nb, 49·4; F, 50·6. Found: Ta, 65·3; F, 34·3. Calc. for TaF_5: Ta, 65·6; F, 34·4%).

All reactions were carried out in high-vacuum systems in which the conventional taps and joints were replaced by grease-free capillaries and break-seals. The volatile products of each reaction were separated and purified by fractionation in similar systems and the various fractions were identified by vapour pressures and molecular weights by use of the apparatus previously described.[1] Involatile residues were analysed for vanadium, niobium, or tantalum and fluorine by the above methods. Infrared absorption spectra were determined with a Perkin-Elmer Model 21 double-beam recording spectrophotometer with a sodium chloride optical system.

Reaction with Antimony Pentafluoride.—Antimony pentafluoride, prepared by direct fluorination of the trioxide, gave no visible reaction with excess of vanadium pentafluoride. Fractionation of the liquid mixture gave incomplete separation of the reactants and left no residue.

[17] Woolf, *J.*, 1950, 1053.
[18] Hayek, Puschmann, and Czaloun, *Monatsh.*, 1954, **85**, 359.
[19] Siebert, *Z. anorg. Chem.*, 1957, **289**, 15.
[20] Sharp, *J.*, 1957, in the press.
[21] Hayek, Czaloun, and Krismer, *Monatsh.*, 1956, **87**, 741.
[22] Balke, *J. Amer. Chem. Soc.*, 1905, **27**, 1140.

Addition of dry potassium fluoride to the mixture, followed by the removal of all volatile material, left white potassium hexafluoroantimonate (Found: Sb, 45·9; F, 43·6. Calc. for $KSbF_6$: Sb, 46·0; F, 43·1%).

Reactions with Boron Trifluoride.—Pure boron trifluoride was kept with vanadium pentafluoride at −78° in a sealed apparatus for 20 hr. The volatile products were then separated into fractions condensing at −78° and −184°. The −78° fraction was unchanged vanadium pentafluoride and the −184° fraction boron trifluoride (Found: *M*, 68·5. Calc. for BF_3: *M*, 67·8). The least volatile portion of the reaction mixture was analysed for vanadium (Found: V, 35·6. Calc. for VF_5: V, 34·9%). Similarly, niobium pentafluoride did not react with boron trifluoride since the final portion of the reaction mixture was unchanged niobium pentafluoride (Found: Nb, 49·5. Calc. for NbF_5: Nb, 49·4%).

Reactions with Nitryl Fluoride.—Nitryl fluoride, prepared by direct fluorination of sodium nitrite,[23] reacted rapidly with vanadium pentafluoride at −78° to give an involatile white solid identified as *nitronium hexafluorovanadate* (Found: V, 24·5; F, 53·5. NO_2VF_6 requires V, 24·2; F, 54·1%). This compound was hygroscopic and dissolved instantly in water. A similar reaction of nitryl fluoride with niobium pentafluoride gave very incomplete conversion into nitronium hexafluoroniobate (Found: Nb, 47·8. NO_2NbF_6 requires Nb, 36·7. Calc. for NbF_5: Nb, 49·4%).

Reaction with Nitrosyl Fluoride.—Nitrosyl fluoride was prepared by the direct union of nitric oxide and fluorine carried in a stream of nitrogen in a silica tube, and was made to react immediately in an all-glass apparatus with vanadium pentafluoride. The product was white. involatile nitrosonium hexafluorovanadate, $NOVF_6$ (Found: V, 26·6. Calc. for $NOVF_6$: V, 26·2%).

Preparation of Hexafluoro-niobates and -tantalates with Bromine Trifluoride.—The methods of Woolf and Emeléus [24] were employed. Bromine trifluoride reacted with niobium pentoxide and dinitrogen tetroxide to give *nitronium hexafluoroniobate*, NO_2NbF_6 (Found: Nb, 35·6; F, 45·5. NO_2NbF_6 requires Nb, 36·6; F, 45·1%), a white solid, readily soluble in water and decomposing above *ca.* 60°. Similar treatment with bromine trifluoride of a mixture of niobium pentoxide and nitrosyl chloride gave *nitrosonium hexafluoroniobate*, $NONbF_6$ (Found: Nb, 38·1. $NONbF_6$ requires Nb, 39·2%), a white solid, soluble in water and decomposing above 60—70°. Bromine trifluoride with tantalum pentoxide and dinitrogen tetroxide gave only partial conversion into nitronium hexafluorotantalate, despite vigorous boiling (Found: Ta, 56·5. Calc. for NO_2TaF_6: Ta, 53·1%). However with nitrosyl chloride and tantalum pentoxide, *nitrosonium hexafluorotantalate*, $NOTaF_6$, was formed (Found: equiv., 336; Ta, 54·0. $NOTaF_6$ requires equiv., 325; Ta, 55·7%) as a soluble white solid. All these nitronium and nitrosonium hexafluoro-niobates and -tantalates gave low analytical results for niobium and tantalum, owing to the presence of bromine trifluoride. This could only be completely removed by heating to at least 60°, at which temperature the compounds decomposed.

The dissociation pressures of these salts were measured in the range 25—95° with a modification of the all-glass apparatus previously described for the measurement of the vapour pressure of vanadium pentafluoride. All transfers of the salts were performed in a " dry-box." For nitronium hexafluorovanadate, nitrosonium hexafluorovanadate, and nitrosonium hexafluoroniobate, $\log_{10} p(\text{mm.}) = 9{\cdot}726 - 2725/T$, $13{\cdot}45 - 4048/T$, and $15{\cdot}71 - 4580/T$ respectively.

Reaction with Chloryl Fluoride.—Chloryl fluoride was prepared by Woolf's method,[8] by the reaction of bromine trifluoride with potassium chlorate. As the fluoride thus prepared in glass apparatus is highly reactive and rather impure, its molecular weight could not be determined. Its reactivity with glass was shown by the rapid intensification of the red colour on exposure to glass surfaces at room temperature. In the first preparation, chloryl fluoride was allowed to react immediately with vanadium pentafluoride at −46°. After standing for some hours to ensure completion of the reaction, all substances volatile at −46° were distilled off leaving a white solid which, on warming to room temperature, appeared to decompose. This solid had a V : Cl ratio of 1 : 0·63. The second reaction was performed at −78° and an unstable white solid was obtained which contained vanadium and chlorine in the ratio 1 : 0·97.

Reactions with Sulphur Dioxide.—Excess of dry sulphur dioxide was distilled in a grease- and moisture-free apparatus onto vanadium pentafluoride. There was a vigorous reaction. The

[23] Aynsley, Hetherington, and Robinson, *J.*, 1954, 1119.
[24] Woolf and Emeléus, *J.*, 1950, 1050, 1053.

volatile products were separated into fractions condensing at −132° and −120°, and there remained a pale yellow involatile residue. The −132° fraction (1·66 g.) was thionyl fluoride (Found: *M*, 87·6; b. p. −47°. Calc. for SOF_2: *M*, 86; lit. b. p. −44°). The −120° fraction was sulphur dioxide (Found: *M*, 64·6. Calc. for SO_2: *M*, 64·0). The involatile residue was hygroscopic, dissolved instantly in water, and was vanadium oxytrifluoride (Found: V, 41·1; F, 44·6. Calc. for VOF_3: V, 41·1; F, 46·0%). By estimating from the total amount of vanadium present, the weight of vanadium pentafluoride used in the reaction, the yield of thionyl fluoride was found to be 97·8%.

The reaction of sulphur dioxide with niobium pentafluoride was examined similarly. In this case the only volatile fraction condensed at −120° and was unchanged sulphur dioxide (Found: *M*, 64·7. Calc. for SO_2: *M*, 64·0). The remaining solid was unchanged pentafluoride (Found: Nb, 49·1. Calc. for NbF_5: Nb, 49·4%).

Reactions with Sulphur Trioxide.—Pure, dry sulphur trioxide, prepared from fuming sulphuric acid and phosphoric oxide, reacted readily at room temperature with vanadium pentafluoride to give volatile products condensing at −78° and −46°. A pale yellow involatile hygroscopic solid remained and this was vanadium oxytrifluoride (Found: ratio V : F, 1 : 3·02. Calc. for VOF_3: V : F, 1 : 3·00). The compound which condensed as a white solid at −78° and melted at approximately −50° to a clear liquid was pyrosulphuryl fluoride (Found: *M*, 183. Calc. for $S_2O_5F_2$: *M*, 182·0). Vapour-pressure measurements over the temperature range −28° to 43° gave $\log_{10} p(\text{mm.}) = 8{\cdot}015 - 1662/T$. The −46° fraction was a small excess of vanadium pentafluoride.

The reactions of niobium and tantalum pentafluorides with sulphur trioxide proceeded more slowly, producing in both cases, after several hours, clear viscous liquids. By heating them *in vacuo* to 50° for 2 hr., excess of sulphur trioxide and other volatile materials were removed, the viscous compounds being almost involatile. The negligible volatile fractions were mainly sulphur trioxide together with some less volatile material, but no satisfactory separation was achieved. In the reaction with niobium pentafluoride, a trace of pyrosulphuryl fluoride was also liberated (Found: *M*, 175. Calc. for $S_2O_5F_2$: *M*, 182). Both viscous products fumed in air, reacted vigorously with water, and had a strong odour of pyrosulphuryl fluoride. Analyses of their solutions identified the compounds as NbF_5, $2{\cdot}1SO_3$ (Found: Nb, 25·8; SO_3, 47·7. NbF_5,$2{\cdot}1SO_3$ requires Nb, 25·7; SO_3, 47·3%) and TaF_5,$2{\cdot}6SO_3$ (Found: Ta, 37·5; SO_3, 43·1. TaF_5,$2{\cdot}6SO_3$ requires Ta, 37·4; SO_3, 43·0%). Thermal decomposition at 172° in a sealed tube for 24 hr. produced sulphuryl fluoride (Found: *M*, 102. Calc. for SO_2F_2: *M*, 102). The tantalum compound decomposed at 225°, also producing sulphuryl fluoride (Found: *M*, 103). Measurement of the infrared absorption spectrum of the niobium compound NbF_5,$2{\cdot}1SO_3$ was difficult as the high viscosity and ease of hydrolysis prevented preparation of a sufficiently thin film. The spectrum was therefore not well resolved.

Reactions with Pyridine.—Niobium and tantalum pentafluorides reacted rapidly with dry pyridine to produce white solids which were quite stable to air and dissolved quietly in water. Analyses of their solutions identified the solids as *dipyridinepentafluoroniobium*(v) (Found: Nb, 27·7; F, 27·7. $(C_5H_5N)_2NbF_5$ requires Nb, 26·9; F, 27·5%) and *dipyridinepentafluorotantalum*(v) [Found: Ta, 41·0; F, 22·0. $(C_5H_5N)_2TaF_5$ requires Ta, 41·7; F, 21·8%]. Both compounds decomposed without melting when heated to 100°. Treatment of the niobium compound with concentrated aqueous hydrofluoric acid gave *pyridinium hexafluoroniobate* [Found: Nb, 32·1; F, 40·3. $(C_5H_5NH)NbF_6$ requires Nb, 32·2; F, 39·8%]. Similar repeated treatment of the tantalum compound gave a product intermediate in composition between pyridinium hexafluorotantalate and dipyridinium heptafluorotantalate [Found: Ta, 42·4; F, 29·0. Calc. for $(C_5H_5NH)TaF_6$: Ta, 48·2; F, 30·4. Calc. for $(C_5H_5NH)_2TaF_7$: Ta, 38·2; F, 28·1%]. Further treatment with hydrofluoric acid did not alter the composition.

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