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PREPARATION AND STRUCTURAL PROPERTIES OF SOME FLUOROMETALLATES OF URANIUMAND GROUP V METALS

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LIST OF TABLES AND ILLUSTRATIONS

tion reaction could be studied more easily than in the case of the other metals where bromination is more difficult.

Chapter I is a discussion of the first phase of the work, the study of the bromination of uranium in methanol. This work was carried out to aid in the determination of the optimum conditions for bromination of the metal as well as to study the bromination process itself. It was found that knowledge concerning the nature of the products of the bromination reaction was helpful in determining conditions for the preparation of the fluorometallates. Chapter I also includes some postulations concerning the brominations of niobium, tantalum and vanadium in methanol.

The ammonium fluorometallates of these elements have been prepared previously from methanol solution[11,50]. However, in attempts to repeat the preparations, several impure products were obtained and side reactions were noted. Thus, it was thought best to study, in more detail, the preparation of these ammonium fluorometallates as well as the preparation of the potassium complexes. Chapter II and Chapter III discuss these preparations and give analytical results for the complexes.

Chapter IV is a discussion of the structures of the ammonium and potassium complexes and gives powder diffraction data for them. Chapter V shows the results of magnetic susceptibility measurements. Infrared studies and a discussion of hydrogen bonding in the ammonium complexes are given in Chapter VI.

CHAPTER I

A STUDY OF THE BROMINATION OF THE METALS IN METHANOL

Osthoff and West[64] have chlorinated metals in donor solvents and postulate that the donor solvent coordinates with the metal chloride according to reaction (1) and thus removes the chloride from the metal surface.

$$MCl_{x(surface)} + Et_2O \rightleftharpoons MCl_x{:}OEt_2 \rightleftharpoons MCl_x + Et_2O \quad (1)$$

Ducelliez and Raynaud[29] have brominated manganese in ether solution. Raynaud[68] has brominated zinc in polar, organic solvents and suggests that bromination of metals in donor solvents occurs through the reaction of bromine with the solvent to form HBr, which then reacts with the metals. If Raynaud's postulated reaction is correct, hydrogen evolution should be seen from the reaction of the metals with hydrogen bromide. However, in the bromination of zinc in methanol, the reaction proceeds quickly with no gas evolution. This fact leads to the conclusion that hydrogen bromide is not formed in all brominations of metals in methanol and that another oxidizing agent is present.

In the bromination of the Group V metals studied here and of uranium, gas evolution is seen. Several reactions may be postulated as the source of hydrogen. A study of the stoichiometry of the bromination in methanol seemed necessary to gain an insight into the nature of these reactions. Uranium was used for the study since it is the only one of the

metals studied here which brominates readily in methanol at room temperature and also since much work in uranium chemistry has been done allowing correlations with known reactions in similar solvents such as water or higher alcohols.

The investigation led to the conclusion that the reactions which may be involved in the bromination of uranium in methanol are as follows*:

$$CH_3OH + Br_2 \rightarrow \text{unknown product} \quad (2)$$

$$CH_3OH + HBr \rightarrow CH_3Br + H_2O \quad (3)$$

$$CH_3Br + CH_3OH \rightarrow (CH_3)_2O + HBr \quad (4)$$

$$U^o + 2Br_2 \rightarrow UBr_4 \quad (5)$$

$$2U^o + 6HBr = 2UBr_3 + 3\ H_2 \quad (6)$$

$$U^o + 3UBr_4 \rightarrow 4UBr_3 \quad (7)$$

$$UBr_3 + 2CH_3OH \rightarrow U(OCH_3)_2Br_2 + 1/2\,H_2 + HBr \quad (8)$$

$$UBr_3 + 1/2\ Br_2 \rightarrow UBr_4 \quad (9)$$

$$UBr_4 + 2CH_3OH \rightarrow U(OCH_3)_2Br_2 + 2HBr \quad (10)$$

$$U(OCH_3)_2Br_2 + 2CH_3OH \rightarrow U(OCH_3)_4 + 2\ HBr \quad (11)$$

$$U(OCH_3)_4 \rightarrow \underline{UO_2} + 2(CH_3)_2O \quad (12)$$

$$U(OCH_3)_2Br_2 + Br_2 \rightarrow UO_2Br_2 + 2CH_3Br \quad (13)$$

Each of the above reactions will be discussed in turn giving supporting evidence from the literature or from our experimental results.

First of all, the reaction of bromine with methanol should be discussed. Bhattacharya[10] states that the reaction of bromine and methanol is accelerated by infrared radiation due to the formation of atomic bromine. He gives

*Extent of methanolation of the products is not shown.

acid, and therefore methyl hypobromite, is not formed. Comparison of the reduction potential of hypobromite with that of pervanadyl, both in aqueous solution[16], leads to the conclusion that hypobromous acid is not formed since vanadium is oxidized only to vanadium(IV).

$$H_2O + 1/2Br_2 = HBrO + H^+ + e^- \qquad E^\circ = -1.59 \text{ v.}$$

$$Br^- = 1/2Br_2 + e^- \qquad E^\circ = -1.07 \text{ v.}$$

$$3H_2O + VO^{++} = V(OH)_4^+ + 2H^+ + e^- \qquad E^\circ = -1.00 \text{ v.}$$

Of course, the reducing action of methanol itself may prevent the formation of hypobromous acid or of pervanadyl.

When the bromination solutions are refluxed, the distillate is colorless, does not give a positive test with potassium iodide paper and may be just methanol. Thus it would seem that a high boiling, intermolecular compound may be formed between the methanol and bromine. Another conjecture which may be made concerning a reaction between bromine and methanol is that the presence of specific metal oxides, metal itself, or metal bromides catalyzes such a reaction. Shell and Zimmerman[74] have found an apparent reduction of iodine by zinc halides in methanol solution. However, they give no postulation as to the products formed.

Further work is needed to determine whether a reaction actually does take place between the methanol and the bromine during the bromination of the metal and, if there is such a reaction, what the products are. Quantitative mass spectrometric analysis would be helpful in such a problem.

Reaction (3), that between methanol and hydrobromic acid, is well known[8,63]. Reaction (4) is an equilibrium

reaction[63] and appreciable quantities of ether occur only after the methyl bromide concentration is high. Methyl bromide and very possibly dimethyl ether are also formed in the reaction of the products of the oxidation of uranium (and of the other metals as well) with methanol.

Reaction (5) is postulated since it is known that, at least above 650°, uranium and bromine form uranium tetrabromide[76] if excess bromine is present. The high temperature seemed necessary to carry off the UBr_4 (b.p. = 765° at 740 mm of mercury) in a stream of helium. Thus the metal was not coated with UBr_4. The postulation is made that, in methanol solution, UBr_4 reacts according to reaction (10), $U(OCH_3)_2Br_2$ being soluble in methanol, allowing further bromination of the metal. In support of this Spedding[76] reports that UBr_4 reacts with alcohols to form hydrobromic acid. Spedding[76] does not show the uranium compounds resulting from this reaction of UBr_4 and alcohol, but the presence of methoxy bromides and of the tetramethoxy compound (see reactions 8, 10, 11 and 12) is postulated since it is known that UBr_3 forms UO_2 in water or alcohol[82]. It is known that, in the reaction of UBr_3 with water or alcohol, H_2 is evolved[82], and it is known that the tetramethoxy compound decomposes to UO_2 in water[52]. Our experiments have also shown that the reaction of uranium with hydrogen bromide in methanol, reaction (6), forms a purple solution presumably uranium in the trivalent state, which changes immediately to a green solution giving UO_2 on standing. The UO_2 was identified by its powder pattern. A similar reaction is seen in water[81].

mixture or by weighing the uranium metal itself. The estimate was obtained by weighing the uranium and is, of course, low. However, the postulate that hydrobromic acid is regenerated is not affected.

The postulation that two oxidizing agents, bromine and hydrobromic acid, are present in the reaction mixture is supported by the fact that the amount of hydrogen evolved in the oxidation of a constant amount of uranium varies with the rate of addition of bromine and with the rate of stirring. More hydrogen is evolved with no stirring and slow addition of bromine. The mole ratio of hydrogen evolved to uranium oxidized ranged from 0.6 to 1.0. If hydrobromic acid were the only oxidizing agent this ratio should be at least 1.5, according to reaction (6), and even higher, depending on the amount of hydrogen contributed by reaction (8).

The formation of $K_3UO_2F_5$ upon addition of bromination solutions, prepared under nitrogen using excess bromine, to a potassium fluoride solution indicates that the product of reaction (10) has at least two methoxy groups.

The change of color of the bromination solution from green to orange upon the addition of excess bromine (more bromine than necessary for the oxidation to uranium(IV)) or oxygen shows that the oxidation is stepwise. There remains the possibility that the final product is not UO_2Br_2 as given in reaction (13), but is a methoxy compound. Since the solvent is methanol this seems highly probable. There are several reactions which may be written besides reaction (13).

methanol shows gas evolution. The reaction mixtures are acid to litmus and they fume in moist air, suggesting the presence of hydrogen bromide. Blanchette[11] states that hydrogen bromide is evolved upon evaporation of methanol from the reaction mixture. From these observations and from the fact that tantalum pentachloride decomposes upon standing in alcohol, giving off hydrogen chloride and forming $TaCl_2(OCH_3)_3$[37], the following reactions are postulated for the bromination of these two metals in methanol*.

$$2Ta^{\circ} + 5Br_2 \rightarrow 2TaBr_5 \qquad (17)$$

$$TaBr_5 + {}_xCH_3OH \rightarrow Ta(OCH_3)_xBr_{5-x} + {}_xHBr \qquad (18)$$

$$2Ta^{\circ} + 10HBr \rightarrow 2TaBr_5 + 5H_2 \qquad (19)$$

Blanchette has previously postulated reaction (18) as

$$TaBr_5 \cdot nCH_3OH \rightarrow TaBr_x(OCH_3)_{5-x} + (5-x)HBr \qquad (20)$$

to indicate the solubility of $TaBr_5$ in methanol. It is interesting to note again here that Osthoff and West[64] postulated reaction (1), see page 4, to indicate the solubility of the metal chloride in ether. The possibility of bromides of lower oxidation states reacting with methanol to give hydrogen, as in the case of uranium, has not been indicated or proved.

Blanchette has stated that a large excess of bromine is necessary for the bromination of niobium and tantalum in methanol[11]. However, it has been found that the surface area of the metal is a more important factor. The powdered metals react slowly but metal foil very slightly or not at all even when a large excess of bromine is used. The slowness

*Extent of methanolation is not shown.

of the reaction cannot be explained by oxide formation on the metal surface. An X-ray study of the residue from the reaction mixture showed only metal. Since the reaction of niobium pentachloride with methanol in benzene is vigorous[14], one also cannot postulate the insolubility of niobium pentabromide and slow reaction of niobium pentabromide with methanol as the cause of the slowness of bromination.

Very little can be said concerning the products of the bromination of tantalum and niobium in methanol. Bradley[14] has postulated the reaction

$$Nb(OR)_5 \rightarrow (RO)_4\overset{+}{N}b{-}O + R^- \qquad (21)$$

and states that this reaction occurs more easily for niobium methoxide than for tantalum methoxide. This product could give the $NbOF_5^{-3}$ complex ion readily. It also follows that tantalum forms complexes containing the TaF_8^{-3} ion more readily than niobium does.

Experimentally, by our new method, it was difficult to prepare the niobium and tantalum complexes free from oxide or mixed oxy compounds. If oxide formation occurs in the bromination step, it may be necessary to use a large excess of bromine to (1) speed up the bromination of metal, (2) to hinder the formation of HBr which then can form water by reacting with methanol, and (3) to form methoxy bromides instead of methoxy compounds which hydrolyze much more readily than the bromides.

oxygen to give UO_2Br_2 and Br_2 [61].

Although all brominations of vanadium have been carried out in an air atmosphere, the bromination solutions are green in the presence of excess metal. This points to the presence of methoxy compounds. $VOBr_2$ is yellow-brown and $V(OR)_2Cl_2 \cdot ROH$ is green[15]. This known methoxy chloride, $V(OR)_2Cl_2 \cdot ROH$, is formed by VCl_4 and methanol[15] and supports the postulation of the formation of methoxy bromides. The formation of K_3VOF_5 by reaction of the bromination solution with potassium fluoride suggests the presence of oxy or methoxy bromides of vanadium in the bromination solution.

The bromination of vanadium in isopropanol and in n-butanol gave gas evolution but the reactions were extremely slow. This would indicate that the formation of alkoxy compounds is slow here due to steric effects and thus the bromination itself is hindered perhaps by the insolubility of VBr_3 itself.

CHAPTER II

THE PREPARATION OF THE AMMONIUM FLUOROMETALLATES

Various ammonium fluorometallates of uranium and the Group V metals have been prepared and studied in other laboratories. Discussions concerning these complexes are given under the sections devoted to each metal complex preparation. Specific discussions about the preparations of ammonium fluorometallates from methanol solution are also given in these later sections. Procedures for the preparations and methods of analysis are given in the appendix.

The preparation of the ammonium fluorometallates from methanol was, in general, carried out by the method of Haendler, Johnson and Crocket[43]. That is, the metal bromide solution was added to a rapidly stirred, saturated solution of ammonium fluoride in methanol. A large excess of ammonium fluoride was used. The complexes were filtered off, washed free of bromide with dilute ammonium fluoride in methanol or with methanol and digested at room temperature in ammonium fluoride solution for at least twenty-four hours. The complexes were filtered off, rinsed with methanol and then with ether and air dried.

Several complications arose during the preparations, however, due to the presence of excess bromine. Niobium and tantalum brominate only with difficulty and these reactions were facilitated by the use of a large excess of bromine[11].

formation and may lead to incomplete precipitation of the fluorometallate or to formation of complexes containing fewer ammonium and fluoride atoms. If ammonium complexes are allowed to stand in the presence of bromine, a breakdown of the complexes may occur (reaction 5).

Hydrogen fluoride may be formed as a product of the reaction of bromine where ammonium fluoride, not ammonia, is involved (reaction 5). Complexes containing hydrogen, such as K_3HNbOF_7, are known[47]. This suggests that the presence of HF may lead to varying composition in the fluorometallates.

Monobromoamine is insoluble in ether. Thus the complexes must be washed thoroughly with methanol or ammonium fluoride in methanol before washing with ether.

Further complications arose, particularly in the preparation of the tantalum and niobium complexes, due to the presence of water. One major source of water was from ammonium fluoride. Thus a method was developed for the removal of water from the ammonium fluoride commercially available.

Ammonium fluoride can be made by passing NH_3 gas in excess through an aqueous solution of HF. Ammonium fluoride precipitates upon concentration of the solution[16]. Ammonium fluoride, containing much adsorbed water, and perhaps containing NH_4HF_2, was dissolved in hot 18F ammonium hydroxide. Upon cooling, some ammonium fluoride precipitated. Addition of a 1:3 ether–methanol solution precipitated the major portion of ammonium fluoride. After filtration, the ammonium fluoride was immediately washed well with the ether–methanol

Blanchette[11] to be due to the formation of methoxy compounds which gives fluorometallates on digestion. Another reason for the necessity of a long digestion period for all the complexes may be the presence of a large excess of bromide ion during precipitation of the complex. The formation of bromo-complexes such as $(NH_4)_2UO_2Br_4$[73] can be postulated.

As Blanchette found[11], none of these ammonium complexes can be dried at 100°C without decomposition. Air drying after washing with ether or vacuum drying must be used.

Ammonium Dioxypentafluorouranate(VI), $(NH_4)_3UO_2F_5$.

Bolton in 1866[13] first prepared $(NH_4)_3UO_2F_5$ by reacting ammonium uranate with hydrofluoric acid and purifying by evaporation over sulfuric acid. No analysis is given but the compound's solubility in water and insolubility in alcohol are mentioned. Burger[17], in 1904, prepared the compound from ammonium diuranate, purifying by crystallization from water. Cantone[18], in 1907, prepared it as did Nichols and Merritt[62] in 1911.

Johnson[50], in our laboratories, has prepared $(NH_4)_3UO_2F_5$ from methanol solution and analyzed it, but, although powder diffraction data were taken, the structure of the complex was not established. Ammonium dioxypentafluorouranate(VI) was prepared and analyzed again in hopes that the structure could be elucidated. A discussion of its structure is given in Chapter IV.

The procedure for the preparation of $(NH_4)_3UO_2F_5$ is given in the appendix, as are the procedures used in its

analysis. Table I shows the results of analyses of two preparations of the compound as well as a previous analysis reported by Johnson[50]. The ratio NH_4:U:F for preparations I and II was found to be 2.97:1.00:5.08 and 2.96:1.00:4.96.

Attempts to prepare ammonium fluorometallates of uranium(IV) were unsuccessful. As shown in Chapter I, p.11,

Table I

Analysis of $(NH_4)_3UO_2F_5$

Analysis	Johnson's Results (%)	Preparation I (%)	Preparation II (%)	Theor. (%)
NH_4	13.09 13.22	12.23 12.23 12.89	12.77 12.73	12.88
U	56.83 55.92 56.12	56.29 56.81 56.05	56.85 56.96	56.81
F	22.51 22.63 22.63	22.92 22.80	22.68 22.68 22.11 22.74	22.68

the uranium(IV) compounds formed in the bromination process are readily oxidized to the uranyl compounds leading to uranium in mixed oxidation states even under careful exclusion of air and heat. Oxidation of uranium metal, suspended in ammonium fluoride–methanol solution, with hydrogen bromide gave a green product mixed with UO_2. Attempts to identify the green product by powder diffraction work on the original product and on the product, after leaching with water, failed. Oxidation of uranium, in ammonium fluoride solution, with bromine led

again to a green product mixed with UO_2. The powder pattern of this precipitate was similar but not exactly the same as that for the product from oxidation with hydrogen bromide. It is known[87] that K_3UF_7 has two forms, the ordered tetragonal form which is isostructural with $K_3UO_2F_5$, and the disordered cubic, face-centered form. If $(NH_4)_3UF_7$ were formed in the bromination of uranium in ammonium fluoride solution, it is not known what structure might result. In any case, the patterns of our green precipitates were too complex to use even qualitatively. Many of the lines of the patterns of UO_2 and UF_4 overlap. Thus the UO_2 impurity in the green precipitates prevented the identification of UF_4 from our X-ray data. However, the insolubility in water of the green precipitate suggests green, water insoluble UF_4[53] to be a component of the precipitate in both oxidations. This agrees with the result mentioned in Chapter I, p. 9, where $UF_4 \cdot 1.5H_2O$ was formed with aqueous hydrofluoric acid.

Ammonium Oxyhexafluoroniobate(V), $(NH_4)_3NbOF_6$. De Marignac[25] first prepared $(NH_4)_3NbOF_6$ in 1868 from aqueous solution, but gave no analysis of his product. He states that the complex is cubic. Baker[5] reported the preparation of the compound again in 1879 and claimed that this compound and its potassium analogue were stable at 100°C. No analysis of the preparation was given.

Blanchette[11] prepared the complex, analyzed it and determined its structure as face-centered cubic. Because of difficulty in preparation, we have repeated Blanchette's work.

the preparation in 1875 and used the reaction of hydrated tantalum pentoxide with a concentrated, aqueous solution of ammonium fluoride solution. He states that the complex forms octahedral crystals and is water soluble.

Another attempt was made to prepare an ammonium fluorotantalate from methanol. Table III shows the analyses of the preparations. Blanchette's compound and our preparation I were prepared with ammonium fluoride which had not been dried. Our preparations II and III were prepared when the humidity was above 40%. Preparation IV was prepared when the humidity was 25–30%.

Table III

Analysis of Ammonium Fluorotantalate Preparations

Analysis	Blanchette's Preparation (%)	Preparation I (%)	Preparation II (%)	Preparation III (%)
NH_4	14.31 14.29	8.30 8.39	9.68 9.55	10.67 10.99
Ta	46.32 46.37	58.52 58.79	57.70 57.63	54.46 53.81
F	39.59 39.77	21.91 22.07 22.07	23.97 24.11	26.45 26.92 27.15
F/NH_4	2.64	2.50	2.39	2.35

Analysis	Preparation IV (%)	$(NH_4)_3TaOF_6$ (%)	$(NH_4)_3TaF_8$ (%)
NH_4	13.44 13.49	14.83	14.01
Ta	51.20 50.79	49.56	46.76
F	30.41 30.54	31.23	39.26
F/NH_4	2.15	2.00	2.67

$(NH_4)_3TaF_8$, can be made in a pure state by precipitation from methanol using the bromide solution. As seen in Chapter I, p. 12, $TaBr_5$ may react with methanol to form HBr, which in turn can react with methanol to form water. It is probably the presence of this small amount of water which prevents a successful preparation even though the starting materials are dry. Thus no further attempt was made to prepare a pure tantalum compound.

Ammonium Oxypentafluorovanadate(IV), $(NH_4)_3VOF_5$.

Treatment of vanadium tetroxide with hydrofluoric acid and then with NH_4F yields $(NH_4)_3VOF_5$ according to Petersen[67]. The material is described as blue, almost regular octahedral crystals which are doubly refracting. No analysis was given of the compound. The compound has been prepared from methanol solution in this laboratory by Johnson[50] and again by Blanchette[11]. In both cases the compound was proved by analysis and could not be indexed as cubic.

In another attempt to index the structure of the compound, $(NH_4)_3VOF_5$ was prepared again. Analyses of two preparations and analyses by Johnson[50] and Blanchette[11] are shown in Table IV.

Table IV

Analysis of $(NH_4)_3VOF_5$

Analysis	Blanchette (%)	Johnson (%)	I (%)	II (%)	Theor. (%)
NH_4	25.25 24.85	24.50 24.61	24.28 24.28	24.32 24.39	25.05
V	23.84 23.94	23.50 23.44 22.91	23.22 23.74 23.70	23.84 24.03	23.58
F	46.18 45.18	44.00 44.72 44.60 44.80	44.35 44.10 44.70	43.55 43.75	43.97

Using the results for our preparations, the mole ratio NH_4:V:F was found to be 2.94:1.00:5.09 and 2.88:1.00:4.89.

It was found that upon long standing the complex became dark yellow-green. This might indicate decomposition to $(NH_4)_2VOF_4$, but powder diffraction work showed no change in pattern from that of the original material. Blanchette[11] found such a decomposition at higher temperatures. Although our complex was not heated, the same decomposition may occur slowly at lower temperatures. We found that $(NH_4)_3VOF_5$ could not be dried at 100°C without extensive decomposition.

The high fluoride content of Blanchette's preparation suggests the presence of $(NH_4)_3VF_6$. Indeed, as shown in Chapter IV, the powder patterns of our $(NH_4)_3VOF_5$ show faintly the three strongest lines of $(NH_4)_3VF_6$[65]. Passerini showed

$(NH_4)_3VF_6$ to be grass green[65]. It can be seen from the postulated reactions for the bromination of vanadium in methanol, Chapter I, p. 14, that VBr_3 is a possible intermediate material and might lead to $(NH_4)_3VF_6$ in reaction with ammonium fluoride.

It might be noted here that the character of $(NH_4)_3VOF_6$ when first precipitated is very gelatinous and is yellow-green in color. Upon air drying, the complex becomes powdery and pale blue-green. The color change can be reversed if the dry material is allowed to stand for several hours in methanol. This color change seems to indicate that the complex is methanolated in methanol. The methanol is bonded loosely, however, as can be seen by its easy removal by vacuum or air drying.

CHAPTER III

THE PREPARATION OF THE POTASSIUM FLUOROMETALLATES

As in Chapter II, the preparation of these potassium fluorometallates by other methods and the specific discussions and results regarding the potassium fluorometallates prepared here are discussed under later sections in the chapter. Procedures for the preparations are given in the appendix.

The preparation of the potassium fluorometallates from methanol again involves the addition of the metal bromide solutions to a solution of potassium fluoride in methanol. The procedure differs somewhat from the preparation of the ammonium fluorometallates however. The reasons for a change in procedure are the insolubility of potassium bromide, the formation of insoluble KHF_2 when HBr or excess bromine is present in the bromide solutions, and the stability of the potassium complexes at 110°C.

The solubility of potassium bromide in methanol is 2 grams/100 ml of methanol, about 0.2M; that of potassium fluoride is 10 grams/100 ml of methanol, about 1.7M[66]. Since potassium bromide is somewhat soluble in methanol, it may be readily removed from the complexes by grinding or leaching the material in methanol. The potassium bromide post-precipitates onto the walls of the beaker and on top of the complex as the complex settles out. Thus immediate filtration gives a purer complex. The use of potassium fluoride solutions less concentrated than 0.2M avoids the

to react with the bromine or the hydrogen bromide present.

Precipitation from a water–methanol medium is possible in the case of the uranium complex. However, in the case of all the other potassium complexes prepared here the presence of water caused an entirely different product to be formed. The composition of these products is not known. The purification problem became one of washing out the potassium bromide and potassium hydrogen fluoride. In the case of the niobium and uranium complexes, a water–methanol wash was satisfactory. In washing the other complexes with a water–methanol solution a different product was again formed. Thus methanol seemed to be the only solvent available which was suitable for washing all four potassium fluorometallates prepared here. Extensive washing with methanol, although time consuming, is satisfactory for the purification of the potassium fluorometallates.

Potassium Dioxypentafluorouranate(VI), $K_3UO_2F_5$.

Bolton first reported $K_3UO_2F_5$ in 1866[13]. He used the reaction of uranyl nitrate in aqueous solution with potassium fluoride and purified the complex by washing with cold water. No analysis of the compound was given. Baker[5] again reported the compound in 1880. His analysis is given in Table I. Giolitte reported it in 1905[39]. Zachariasen[86] has prepared the compound by the reaction of concentrated aqueous solutions of potassium fluoride and uranyl nitrate and subsequent crystallization from hot aqueous solution. His

able from that of $K_3UO_2F_5$ suggesting that it is a mixture of $K_3UO_2F_5$ and K_3UF_7, the powder patterns of these two compounds being nearly identical[87]. An analysis showed 25.23% F and 49.33% U. The theoretical for K_3UF_7 is 27.23% F and 48.73% U.

Staritzky[77] has prepared monoclinic, prismatic pentapotassium diuranyl enneafluoride by the reaction of uranyl nitrate and potassium fluoride in dilute aqueous solution. No further details are given on the preparation. It is interesting to note that, in our preparation, even upon extensive leaching with methanol, there was no indication of any formation of $K_5(UO_2)_2F_9$.

Walker[81] has also prepared tripotassium diuranyl heptafluoride dihydrate, $K_3(UO_2)_2F_7 \cdot 2H_2O$, by mixing aqueous solutions of potassium hydrogen fluoride and uranyl nitrate and slowly evaporating at room temperature. The dihydrate is monoclinic. Since KHF_2 is formed from HBr and Br_2 and potassium fluoride in our complex preparations in methanol, it was thought that $K_3(UO_2)_2F_7$ might form. This, however, was not the case. The great insolubility of KHF_2 in methanol apparently eliminates the problem or else our concentrations of potassium, fluoride and of the uranyl group did not approximate those of Walker.

<u>Potassium Oxyhexafluoroniobate(V), K_3NbOF_6</u>. Baker[5] reported the preparation of K_3NbOF_6 by fusing Nb_2O_5 with excess potassium hydrogen fluoride and crystallizing the fused mass from hot water. His analysis of the compound is given

reported the preparation of K_3TaOF_6 [51] by reaction of hydrated tantalum pentoxide with a concentrated, aqueous solution of potassium fluoride and hydrofluoric acid. This preparation is the only one found in the literature. No analysis or structure is given.

Our complex was prepared in the same manner as our niobium complex from methanol solution and was identified by the analysis shown in Table III. Again, procedures and methods of analysis are given in the appendix.

Table III

Analysis of K_3TaOF_6

Analysis	Thesis	Theor. K_3TaOF_6
K	26.43 26.39 27.14	27.39
Ta	42.49 42.14 42.49	42.24
F	26.04 26.28	26.62

The mole ratio of K:Ta:F is 2.91:1.00:5.88.

Potassium Oxypentafluorovanadate(IV), K_3VOF_5. The compound, K_3VOF_5, seems not to have been prepared previously to our work. Simons [75] mentions only the compound K_2VOF_4, prepared by the reaction of VF_4 or VOF_2 with potassium fluoride in aqueous hydrofluoric acid.

CHAPTER IV

STRUCTURAL STUDIES OF THE FLUOROMETALLATES USING THE POWDER DIFFRACTION TECHNIQUE

Powder diffraction data were taken for all the compounds prepared here and the size of the unit cells, which were not previously known, have been determined. Density measurements were taken for use in the calculation of the number of formula-units per unit cell. Data concerning structure are tabulated in Table I. Discussions of the structures, however, are given under the later sections devoted to each complex. The experimental procedure used in the density measurements is given in Section V of the Appendix. Methods of calculation are given in Section VI of the Appendix.

Ammonium Pentafluorodioxyuranate(VI) and Potassium Pentafluorodioxyuranate(VI). Fried[36] has given the crystal structure of $K_3UO_2F_5$ and has determined bond lengths and bond strengths. Zachariasen[86] has recently determined, by Fourier analysis, the crystal structure as tetragonal with "a"= 9.160 Å and "c"= 18.167 Å. The unit cell contains eight formula units. The $UO_2F_5^{\equiv}$ group has the structure of a pentagonal bipyramid with the oxygen atoms at the peaks and the fluorine atoms at the corners of the pentagon. The potassium atoms are arranged between these bipyramids so that K_I is associated with six fluorine atoms, K_{II} with four fluorine atoms and four oxygen atoms, and K_{III} with two oxygen atoms

and six fluorine atoms.

The "d" values found for our preparation of $K_3UO_2F_5$ matched those found by Zachariasen[86] for his preparation of $K_3UO_2F_5$ from aqueous solution. Dunn[30] gives different "d" values for his preparation. It would be interesting to know Dunn's method of preparation and the analysis of his compound.

As noted in Table I, the unit cell of $(NH_4)_3UO_2F_5$ seems to be isostructural with that of $K_3UO_2F_5$ and is tetragonal with "a"= 9.70 Å and "c"= 18.91 Å. The compound contains eight formula units per unit cell. Table II shows the powder diffraction data for $(NH_4)_3UO_2F_5$. "$Sin^2\theta_{obs}$" are determined from the observed θ and "$Sin^2\theta_{calcd}$" are calculated using the values of "a" and "c" given in Table II. These "$Sin^2\theta$" values are included to show the fit of the data to the tetragonal pattern. It was noted that several lines were resolved in the $(NH_4)_3UO_2F_5$ pattern which were only broad lines in the $K_3UO_2F_5$ pattern. This would suggest that $K_3UO_2F_5$ approaches cubic symmetry more closely than does $(NH_4)_3UO_2F_5$. This is also suggested by the fact that the ratio of c/a for the potassium complex is 1.98 where as the ratio is 1.95 for the ammonium complex.

Ammonium Hexafluoroxyniobate(V) and Potassium Hexafluoroxyniobate(V). De Marignac[25] has stated that $(NH_4)_3NbOF_6$ forms cubic crystals. Baker[5] reported it to be isomorphous with the analogous potassium complex. Potassium hexafluoroxyniobate(V) has been indexed by Williams and Hoard[85] using powder diffraction data. K_3NbOF_6 is cubic, face-centered with

Table II

Powder Diffraction Data for $(NH_4)_3UO_2F_5$

"a" = 9.70 Å "c" = 18.91 Å

hkl	I/I$_o$	d$_{obs}$	Sin$^2\theta_{obs}$	Sin$^2\theta_{calcd}$
100	40	9.606(halo)	0.0065	0.0063
112	100	5.507b	0.0196	0.0193
103	2	5.184	0.0221	0.0213
200	50	4.789b	0.0260	0.0253
004	—	—	—	0.0266
220	15	3.444	0.0500	0.0505
204	70	3.380	0.0519	0.0519
116	50	2.867b	0.0723	0.0725
215	—	—	—	0.0731
303	—	—	—	0.0718
224	4	2.753	0.0784	0.0771
107	1	2.597b	0.0881	0.0877
400	7	2.434	0.1004	0.1011
008	7	2.367	0.1060	0.1064
217	2	2.274	0.1149	0.1130
316	10	2.203	0.1224	0.1230
420	25	2.162	0.1272	0.1263
404	—	—	—	0.1276
208	4	2.129	0.1312	0.1316
307	4	2.087	0.1365	0.1383
415	2	2.029b	0.1440	0.1489
424	4	1.978	0.1519	0.1529
228	25	1.942	0.1577	0.1569
219	2	1.880	0.1681	0.1662
309	1	1.756	0.1929	0.1915
1,0.11	10	1.696	0.2065	0.2074

b = Broad

Table III

Powder Diffraction Data for $(NH_4)_3NbOF_6$

"a" = 9.32 Å

hkl	I/I_o	d_{obs}
111	100	5.381
200	67	4.660
220	67	3.293
222	37	2.807
400	50	2.329
331	13	2.137
420	33	2.082
511,333	40	1.792
440	40	1.646
531	17	1.574
600,442	30	1.552
620	23	1.473
533	17	1.421
622	10	1.404
444	3	1.344
711,551	20	1.304
640	7	1.292
642	30	1.244
731,553	20	1.212
800	2	1.165
733	3	1.138

structure of $(NH_4)_3NbOF_6$ having some random character.

Ammonium Hexafluoroxytantalate(V) and Potassium Hexafluoroxytantalate(V). No data has been found in the literature concerning the structures of these ammonium and potassium hexafluoroxytantalates, except the statement by Joly[51] that the ammonium complex forms octahedral crystals.

We have found that $(NH_4)_3TaOF_6$ and K_3TaOF_6 are isomorphous and are face-centered cubic in structure. For $(NH_4)_3TaOF_6$ "a" = 9.31 Å, and for K_3TaOF_6 "a" = 8.90 Å. Each complex contains four formula units per unit cell. The compounds seem to be isostructural with the ammonium and potassium fluoroxyniobates of the same stoichiometry, and again we suggest that the $(NH_4)_3TaOF_6$ and K_3TaOF_6 structures have random character. Table IV and V give the powder diffraction data for $(NH_4)_3TaOF_6$ and for K_3TaOF_6.

Ammonium Pentafluoroxyvanadate(IV) and Potassium Pentafluoroxyvanadate(IV). Petersen[67] described $(NH_4)_3VOF_5$ as almost regular, octahedral crystals. Blanchette[11] and Johnson[50] stated only that $(NH_4)_3VOF_5$ could not be indexed as cubic. No work has been found in the literature concerning K_3VOF_5.

As shown in Table I, both the complexes are tetragonal and contain eight formula units per unit cell. For the $(NH_4)_3VOF_5$ unit cell "a" = 9.17 Å and "c" = 17.64 Å. For the K_3VOF_5 cell, "a" = 8.75 Å and "c" = 17.09 Å. In Tables VI and VII are tabulated the powder diffraction data for these two complexes.

Table V

Powder Diffraction Data for K_5TaOF_6

"a" = 8.90 Å

hkl	I/I_o	d_{obs}
111	50	5.071
200	33	4.400
220	100	3.125
311	17	2.668
222	3	2.559
400	17	2.217
331	20	2.036
420	50	1.999
422	83	1.813
511,333	50	1.709
440	33	1.572
531	50	1.503
600,442	33	1.481
620	67	1.407
533	13	1.357
622	10	1.340
444	17	1.284
711,551	33	1.246
640	10	1.234
642	83	1.196
731,553	50	1.158
733	7	1.088
820,644	3	1.079
822,600	50	1.048
751,555	67	1.028
662	50	1.021
840	33	0.9958
911,753	67	0.9782

Table VII

Powder Diffraction Data for K_5VOF_5

"a" = 8.75 Å "c" = 17.09 Å

hkl	I/I_o	dobs	$\sin^2\theta_{obs}$	$\sin^2\theta_{calcd}$
112	17	4.964	0.0383	0.0373
004	13	4.305b	0.0509	0.0514
105	7	3.157	0.0942	0.0926
220	3	3.090	0.0983	0.0979
204	100	3.022b	0.1027	0.1004
107	10	2.360	0.1684	0.1697
323	7	2.264	0.1830	0.1880
400	3	2.191	0.1954	0.1958
008	5	2.142b	0.2045	0.2056
217	7	2.083	0.2162	0.2186
208	13	1.932	0.2513	0.2546
228	33	1.759b	0.3066	0.3036
219	17	1.699	0.3249	0.3214
336	17	1.670	0.3364	0.3360

b = Broad

Zachariasen[87] has suggested that all of the cubic complexes $(NH_4)_3ZrF_7$, $(NH_4)_3HfF_7$, K_3ZrF_7 and K_3UF_7 are isostructural and that, instead of a distorted octahedron, these MF_7 complexes have the form of a pentagonal bipyramid, their cubic structure still being attributed to random orientation of groups. The K_3NbOF_6 complex is isostructural with $(NH_4)_3ZrF_7$[85]. Thus it would be of interest to determine by single crystal studies whether or not the $NbOF_6^{\equiv}$ structure is really that of a pentagonal bipyramid with the oxygen at one apex.

Since very little work has been carried out concerning the structures of vanadium complexes, it is difficult to speculate about the orientation of atoms in the $VOF_5^{\equiv}$ group. It is known, however, that the complex $(NH_4)_3VF_6$ is cubic[65]. Thus it is suggested here that the $VF_6^{\equiv}$ ion may be in the form of a regular octahedron. If one fluorine atom is replaced with an oxygen atom, it may be seen that the octahedron would be slightly distorted in one dimension giving a tetragonal form instead of a cubic form. This, of course, is a picture much simplified. However, several complexes of vanadium are known in which the coordination number of vanadium may be six. Among these are $(NH_4)_2VF_5 \cdot H_2O$, $NH_4VF_4 \cdot 2H_2O$, $K_2VF_5 \cdot H_2O$, $(NH_4)_2VOF_4 \cdot H_2O$, K_2VF_6, $(NH_4)_2VO_2F_4$ and K_2VOF_5[75] as well as $(NH_4)_3VOF_5$ and K_3VOF_5. If single crystals of several of these complexes could be prepared, a structural study of the series would serve well to elucidate some coordination chemistry of vanadium.

rapid heating of the magnet coils. A one cm. separation of the magnet poles was used.

The volume of the cell was determined by filling with mercury to the mark and weighing. The volume of the cell was 0.5387 ± 0.0006 cm^3. No correction was made for the curved surface of the mercury although the surfaces of the packed solids were flat.

To aid in understanding the discussion of the standardization of the apparatus and the actual determination of the magnetic moments the following equations are given[72].

$K = \Delta w/H_1^2 A/2g$ = volume susceptibility

Δw = change in weight upon application of the magnetic field.

H_1 = applied magnetic field

A = cross-sectional area of the cell

g = gravitational constant

$\chi = K/d$ = gram susceptibility

d = density

$\chi_M = \chi \cdot$ mol. wt. = molar susceptibility

$\mu = \sqrt{n(n+2)} = 2.84\sqrt{\chi_M \cdot T}$ = magnetic moment

The value of the constant $H_1^2 A/2g$ was determined for our apparatus at 27°C by finding the Δw for $HgCo(SCN)_4$ at this temperature. The volume magnetic susceptibility of $HgCo(SCN)_4$, K, was calculated from its mass susceptibility, χ, which has recently been determined by Figgis and Nyholm[34] and which is 16.44×10^{-6} at 20°C. The temperature correction for the susceptibility is given as $d\chi/dt = 0.33\%$ at 20°C. The apparent density of $HgCo(SCN)_4$ was used to calculate K

and was determined from the weight of $HgCo(SCN)_4$ packed into the cell and the volume of the cell. French and Harrison[35] state that "in the case of paramagnetic solids, except in work of extreme accuracy, the error introduced in making this assumption is generally, though not always, negligible". In this case, since no correction was made for the presence of air enclosed in the packed solid, the apparent density was used. No correction was made for enclosed air since the error is small when paramagnetic substances are investigated[35]. Any non-homogeneity of packing of the sample into the cell will cause considerable error, however, since the percentage of sample in the strong field between the poles will differ, thus giving a varying Δw per weight of sample.

Figgis and Nyholm[34], in determining the magnetic susceptibility of $HgCo(SCN)_4$, packed the cell by filling the cell and tapping it 100 times against wood after each addition. In our work the cell was alternately filled and tapped until tapping gave no change in volume of the material and the material had reached the mark on the cell. This procedure gave consistent packing so that the range of apparent density was 1.0795 to 1.2181 gms/cm.^{3}, a variation of $\pm$ 6%.

The constant, H_1^2A/g, for our apparatus was found to be $3030.7 \pm 32.9 cm.^3$. The variation was $\pm$1.1%. Since our apparatus was not temperature controlled, any attempts to attain results better than 1% would be futile.

Determinations of the magnetic susceptibilities of standard and fluorometallate compounds were then undertaken

the complexes contain vanadium(III) and vanadium(V) do not seem plausible since a magnetic moment of about 2.0 β would be expected for a 1:1 mixture, since a highly colored compound would be expected, and since a blue solution is formed appropriate to VO^{++} ion when the compound is dissolved in water.

Table I

The Magnetic Susceptibility of $(NH_4)_3VOF_5$ and of K_3VOF_5

Compound	Susceptibility (magnetons)
$(NH_4)_3VOF_5$	1.72
	1.69
	1.73
	1.59
K_3VOF_5	1.69
	1.69
	1.75

In comparison, the magnetic moment of VCl_4 has been found to be 1.672β (84). Zimmerman(88) has found the magnetic moment of V^{+4} in aqueous solution to be 1.76 β. Bayer(7) gives the moment of two organic complexes of vanadium(IV) as 1.73 β.

Since vanadium(IV) contains only one 3d electron, there are four vacant 3d orbitals available for bond formation. The "ionic" and "covalent" bonding would give the same moment and no conclusion can be drawn from the magnetic data as to the type of bonding present.

Turning to the uranyl group, Pryce's theory aids in the understanding of a lack of paramagnetism in uranyl compounds. The following section is quoted from Bleaney's

article on the paramagnetism of the actinide group[12].

> The UO_2 ion is linear, and it has been suggested that its stability is associated with the formation of a bond involving an f electron. The electronic state of the neutral U atom is $5f^3 6d\ 7s^2$, so that U^{+2} ion may be written as $5f\ 6d\ 7s^2$; it is postulated that these four electrons are used to form dative or electron transfer covalent bonds with the two oxygen atoms. In a simple model using only σ -bonding, a hybrid sp_z orbital (where the O–U–O axis is taken as the z-axis) on each oxygen with its lobe pointing towards the uranium forms the bonding orbital. On the uranium, σ -bonding orbitals can be formed by the use of the substates of 5f and 6d which have $l_z = 0$; these are strongly directional, and two hybrid orbitals, each pointing towards one of the oxygen atoms, can be formed by linear combinations of 5f, 6d and 7s. These hybrid orbitals will have a large overlap with the sp_z orbitals on the oxygens, and will form a strong bond. This uses up all the electrons on the doubly ionized uranium outside the closed shells, and no electrons are left to produce a normal paramagnetism.

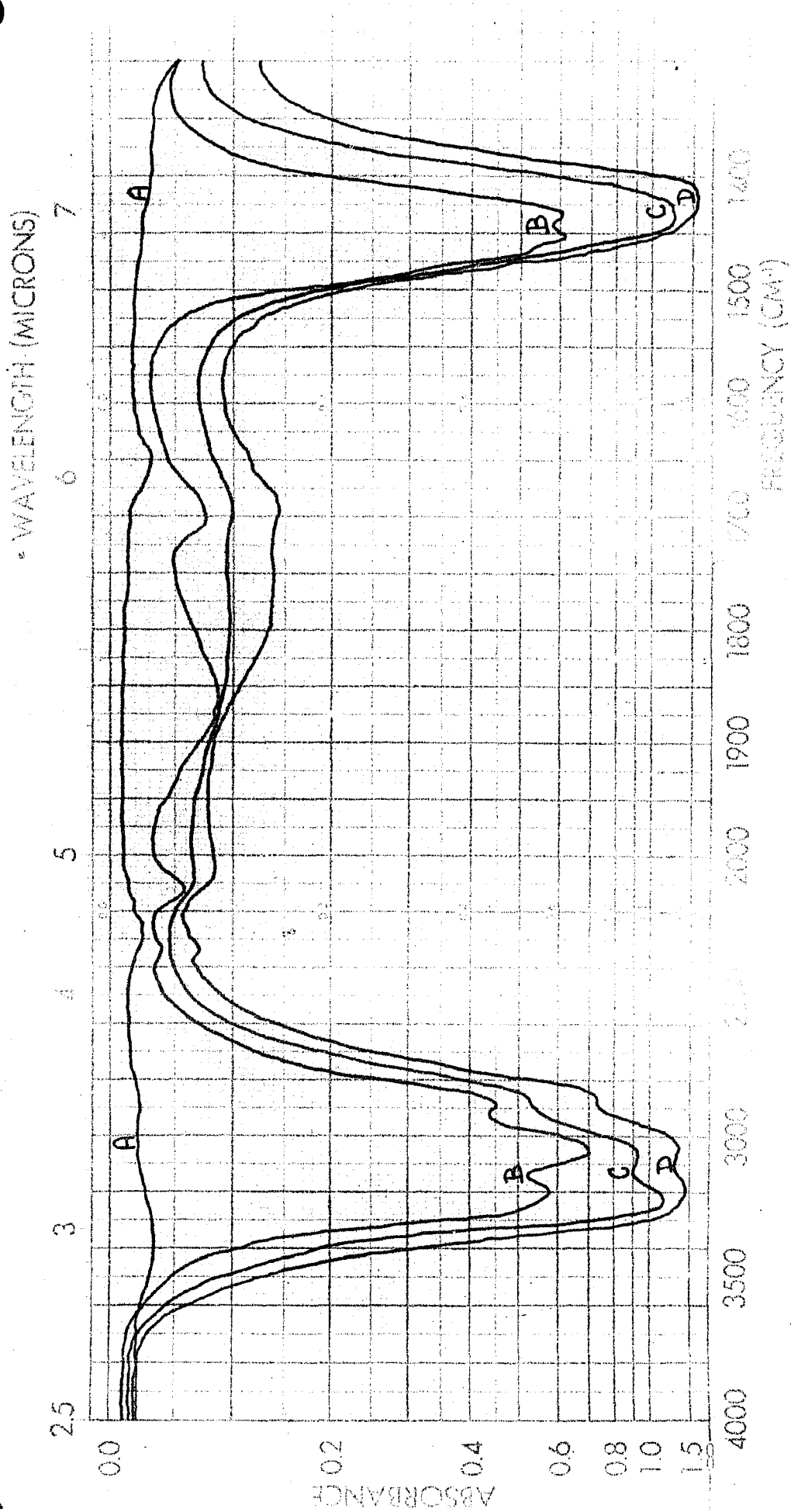

Figure 1

The Infrared Spectra of Some Ammonium Fluorometallates

A $K_3UO_2F_5$ C $(NH_4)_3VOF_5$

B $(NH_4)_3UO_2F_5$ D $(NH_4)_3NbOF_5$

be said that, if present, it is a minor effect. The isomorphism of the ammonium and potassium complexes support this conclusion.

The vanadium and uranium complexes do seem to show some variation in spectra, however, more in the case of ammonium pentafluorodioxyuranate(VI) than in ammonium pentafluoroxyvanadate(IV). For both these compounds the ν_4 peak is shifted upwards to the region of 1470 to 1490 cm^{-1}, this peak in the uranium compound being slightly split and slightly higher than that for the vanadium compound. The area of the ν_3 mode shows a peak at 3240 cm^{-1}, another at 3070 cm^{-1} and a shoulder at 2860 cm^{-1} for the vanadium compound. The uranium complex shows peaks at 3200 cm^{-1}, 3060 cm^{-1} and 2880 cm^{-1}. The $\nu_4 + \nu_6$ mode appears at 1700 cm^{-1} in the spectrum of the uranium compound but is barely discernable in that of the vanadium complex.

It seems that there may be small amounts of hydrogen bonding in the vanadium complex. Again for the vanadium complex, as in the case of the niobium and tantalum compounds, evidence, except for a small splitting in the ν_3 region, is meager to suggest much hydrogen bonding. The isomorphism of $(NH_4)_3VOF_5$ and K_3VOF_5 suggests that hydrogen bonding at least is very weak, not being strong enough to change the structure of the ammonium complex from tetragonal.

In the case of the uranium compound the presence of hydrogen bonding is indicated through the clearness of the $\nu_4 + \nu_6$ peak, the presence of three peaks in the ν_3 mode region

and the slight splitting and shift to a higher frequency of the ν_4 mode. There remains the fact that the $(NH_4)_3UO_2F_5$ is isostructural with $K_3UO_2F_5$, both being tetragonal. Apparently, the stoichiometry of the complex and the sizes of the atoms in the complex, not hydrogen bonding, determine the tetragonal structure. Although hydrogen bonding is present, it is not sufficiently strong to distort the structure of $(NH_4)_3UO_2F_5$ from tetragonal.

Another problem does present itself, however. Zachariasen[86] shows that in $K_3UO_2F_5$ there are three environments around the potassium atoms. K_1 is associated with six fluorine atoms, K_2 to four fluorine atoms and four oxygen atoms and K_3 to six fluorine atoms and two oxygen atoms. Since the ammonium complex is isostructural with the potassium complex it would seem that there are three possible environments for the ammonium ions. Crocket[23] has stated that a possible cause of the large splitting in the ν_4 mode in the spectrum of ammonium trifluorocuprate(II), in comparison with the height of the $\nu_4 + \nu_6$ peak, is the presence of ammonium ions in two unequivalent lattice positions, causing the bending vibration of the ammonium ions to differ. The ν_4 mode in each case is degenerate, however, showing that hydrogen bonding is not present or is very minor.

It can be seen from Figure I that in the infrared spectrum of $(NH_4)_3UO_2F_5$ the extent of splitting of the ν_4 mode is small and can be correlated with the size of the $\nu_4 + \nu_6$ peak and is thus due to hydrogen bonding. Why there

APPENDIX

I. Bromination of the Metals

Table I shows the amounts of material used and the specific conditions for bromination of the various metals used in this research.

Table I

Conditions Used in the Bromination of the Metals

Metal Brominated	Amount of Metal Used (moles)	Amount of Bromine Used (moles Br)	Length of Reflux (hours)	Color of Bromination Solution
Uranium sheet	0.02	0.37	3 – 4	orange
Uranium sheet	0.02	0.13	3 – 4	green + black ppt.
Vanadium chips	0.02	0.15	5 – 6	green–brown to yellow–brown
Niobium powder	0.02	0.10	20	yellow–brown
Tantalum powder	0.02	0,10	20	yellow–brown

The metal was suspended in 100 ml of dry methanol in a 500 ml three–necked, round–bottomed flask attached to a reflux condenser with a drying tube at the top. Bromine was added in slight excess (in small portions in the case of the bromination of uranium since the reaction is exothermic and vigorous). The solution was then refluxed (slowly at first). It can be noted that upon refluxing the distillate gradually

became colorless. The solution was cooled and filtered in a "dry" atmosphere (humidity < 35%) and stored under dry conditions until needed. Filtering may be postponed, of course, and this step incorporated into the preparation of the fluorometallates.

The materials used in the brominations were as follows:

Uranium foil	A.E.C. Found to be spectroscopically.	99% pure
Vanadium chips	Anderson Chemical Co.	99.7% pure.
Niobium powder	A. D. McKay	99.7% pure.
Tantalum powder	A. D. McKay	99.5% pure.
Bromine	Baker & Adamson, ACS Reagent.	
Methyl Alcohol	Fisher Certified Reagent (0.01% H_2O) or Fisher "Karl Fischer" Reagent (0.01% H_2O).	

II. Preparation of the Ammonium Fluorometallates

Table II shows the amounts of material used and the specific conditions for the preparation of the various ammonium fluorometallates used in this research.

In each case, the filtered methanol solution of the metal bromide was added slowly and with rapid stirring to the anhydrous, saturated ammonium fluoride-methanol solution in a polyethylene bottle and then stoppered immediately. After the precipitate settled out, the supernatant was decanted off and more saturated ammonium fluoride-methanol solution added. This procedure of decantation was repeated until the supernatant was colorless. Decantation was used instead of filtration since in most cases the fluorometallates were very

Table II

Conditions Used in the Precipitation of the Ammonium Fluorometallates

Fluorometallate Prepared	Amount of 0.2M bromide used (moles)	Amount of 0.5M NH_4F used (moles)	Length of Digestion (hours)	Color of Product
$(NH_4)_3UO_2F_5$	0.005	0.150	48	pale yellow
$(NH_4)_3VOF_5$	0.010	0.200	48	pale blue-green
$(NH_4)_3NbOF_6$	0.0025	0.200	48	white
$(NH_4)_3TaOF_6$	0.020	0.300	18 days (48 hrs sufficient)	white

gelatinous and extremely difficult to filter. The fluorometallate was then digested in 0.25M ammonium fluoride-methanol solution. After digestion, the precipitate was filtered off, washed with small portions of methanol and then with ether. The complex was dried by aspiration in a vacuum desiccator over silica gel. The samples were stable in air unless the humidity was high and were just stored in screw cap glass vials.

It should be noted here that the procedure was carried out only if the humidity was low, about 35% in the case of the niobium and tantalum compounds.

and again ground in methanol. The procedure was repeated until the filtrate gave negative tests for potassium and fluoride ions. The material was then digested in 0.25M potassium fluoride–methanol solution and finally washed with methanol and ether and oven dried. The complexes were stored in screw–cap glass vials.

The qualitative tests used were the tetraphenyl boron test for potassium[38] and the zirconium alizarinate test[33] for fluoride.

The materials used in the preparation of the potassium fluorometallates were as follows.

Methyl Alcohol	Fisher Certified Reagent (0.01% H_2O) or Fisher "Karl Fisher" Reagent (0.001% H_2O).
KF	Baker and Adamson, anhydrous, granular reagent heated in platinum to the heat of a Meker burner and cooled.
Ether	Mallinckrodt, AR, anhydrous (0.01% H_2O)

IV. Analytical Procedures

A. Ammonia Determination

The sample was placed in concentrated sodium hydroxide solution. The ammonia was distilled into boric acid and titrated with standard hydrochloric acid using methyl purple as indicator[55].

B. Potassium Determination

Potassium was determined gravimetrically as potassium tetraphenylboron according to the method of Geilmann[38]. In cases where the heavy metal ion precipitated in basic solution, the hydrous oxide was removed and the precipitation of potas–

pycnometer was calculated from the weight of the water and the density of water at room temperature. The room temperature was measured using a mercury thermometer, which could be read to ± 0.05°C and which had been checked against a standard thermometer. Any decrease of temperature from its maximum value during the time the pycnometer was allowed to stand was noted by a decrease in volume of the liquid, the capillary not being full. In the few cases where this occurred the determination was repeated.

The volume of the pycnometer was found to be 10.039 ± 0.002 cm^3. The precision was ± 0.02%.

The densities of the compounds were determined by weighing a 0.5 to 1.0 gram sample into the pycnometer, covering the sample with dry benzene, removing the air in the sample by aspiration in a small vacuum desiccator, filling the pycnometer with cold benzene, and continuing as in the procedure for the determination of the volume of the pycnometer.

The densities of water and benzene at the various temperatures were obtained from the International Critical Tables[82a]. Relative densities instead of absolute densities were used since this created no significant error (± 0.003%) in comparison with that inherent in the experimental method itself (± 0.5 to ± 2%).

The densities of sodium chloride and potassium bromide were determined and found to be 2.07 g/cm^3 and 2.64 g/cm^3 respectively. The values found in the International Critical

Tables[82a] are 2.17 g/cm^3 and 2.75 g/cm^3. Our values are 4% low. No explanation has been found for the consistent discrepancy. The smallest sample volume used was in the case of K_3VOF_6, 0.156 cm^3. Here the possible error due to the error inherent in the volume determination was ± 2%. The largest sample volume was 0.383 cm^3, used in the determination of the of the density of $(NH_4)_3NbOF_6$. Here the error due to volume error was ± 0.5%.

VI. The Method of Determination of the Structures of the Ammonium and Potassium Fluoroxymetallates.

The samples were mounted in 0.3 mm. glass capillaries. Powder diffraction patterns were taken using the 57.3 mm. and 114.56 mm. Philips cameras. Copper and iron radiation were used, 1.5418 Å and 1.9373 Å respectively.

Intensities of the patterns for $(NH_4)_3UO_2F_5$, $(NH_4)_3VOF_5$ and K_3VOF_6 were estimated by comparison with a film, for which the intensity of the lines was known by the use of a Welch Densichron. The intensities of the patterns for $(NH_4)_3NbOF_6$, $(NH_4)_3TaOF_6$ and K_3TaOF_6 were estimated by the direct use of the Densichron.

The cubic patterns were calculated using the method of Henry, Lipson, and Wooster[44], giving the best values of "a" in each case.

Each tetragonal pattern was compared with that for $K_3UO_2F_5$[86], the 400 and 008 lines picked out and a pattern calculated. This allowed the correlation of the hkl values

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