O_2Cl_2 complexes. The latter fact also was evidence for two separate products in the reaction of $MoCl_5$ with $(C_6H_5)_3PO$, since the green products exhibited a peak at 967 cm.$^{-1}$, the orange ones did not, and obvious mixtures had a small peak in this region.

The visible spectra of several of the complexes reported here have been studied, and will be the subject of a later communication.

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Synthesis of Fluorometallates in Methanol. Some Structure Relationships. II. Uranium and Group V Metals[1a]

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The complexes $(NH_4)_3UO_2F_5$, $K_3UO_2F_5$, $(NH_4)_3VOF_5$, K_3VOF_5, $(NH_4)_3NbOF_6$, K_3NbOF_6, $(NH_4)_3TaOF_6$, and K_3TaOF_6 were prepared by bromination of the metal in methanol and subsequent precipitation of the fluorometallate by addition of the bromination solution to a solution of the alkali fluoride in methanol. A study of the bromination of uranium in methanol showed that the uranium bromides formed react with methanol to give hydrogen bromide, which further reacts with the metal, hydrogen being evolved. Cell constants of the complexes were determined from X-ray powder data and densities were measured. The uranium complexes were isostructural, as were the vanadium complexes. These complexes appear to be tetragonal and contain eight formula units per unit cell. The niobium and tantalum complexes were isostructural, were face-centered cubic, and contained four formula units per unit cell. Magnetic susceptibility measurements showed that the vanadium complexes contain one unpaired electron per vanadium atom. Infrared studies suggest hydrogen bonding in $(NH_4)_3UO_2F_5$.

Introduction

In previous work,[2,3] alkali fluorometallates of some transition and post-transition metals were prepared from methanol solution. The method of preparation consisted of bromination of the metal in methanol and subsequent addition of the bromination solution to a solution of the alkali fluoride in methanol. The fluorometallates usually precipitate immediately. The present study extends the method to the preparation of some ammonium and potassium oxyfluorometallates of niobium, tantalum, vanadium, and uranium and reports on the structures, magnetic susceptibilities and, in the case of the ammonium complexes, the hydrogen bonding of these complexes.

A study of the bromination of uranium in methanol was carried out to aid in the determination of the optimum conditions for bromination of the metal. Uranium was chosen for this study because it brominates readily at room temperature, in contrast to the other metals. Since structural data were not available for several of the fluorometallates prepared here, powder diffraction data were used to determine the cell constants of these compounds. Density measurements were made to determine the number of formula units per unit cell. Magnetic measurements and infrared spectra were used to aid in the characterization of the complexes.

I. The Bromination of the Metals in Methanol

Experimental

The metal bromides were prepared by the addition of a small excess of bromine to 0.02 mole of the metal suspended in 100 ml. of dry methanol under a dry atmosphere of nitrogen or air. In each case, the reaction mixture was refluxed until the distillate was colorless. Any residue was removed by filtration. The solutions were used immediately for the precipitation of the fluorometallates. It should be noted that the bromination reactions of uranium and vanadium are rapid and exothermic and may require chilling.

Discussion of the Bromination Reaction

Ducelliez and Raynaud[4] have brominated manganese in ether solution. Raynaud[5] has

(1) (a) This work was supported in part by the Atomic Energy Commission; (b) From a thesis submitted to the University of New Hampshire by A. E. Baker in partial fulfillment of the requirements for the degree of Doctor of Philosophy; (c) To whom communications should be addressed.

(2) D. S. Crocket and H. M. Haendler, *J. Am. Chem. Soc.*, **82**, 4158 (1960).

(3) H. M. Haendler, F. A. Johnson, and D. S. Crocket, *ibid.*, **80**, 2662 (1958).

(4) F. Ducelliez and A. Raynaud, *Compt. rend.*, **158**, 576 (1914).

brominated zinc in polar, organic solvents and suggests that bromination occurs through the reaction of bromine with the solvent to form hydrogen bromide, which then reacts with the metal. Osthoff and West[6] have chlorinated metals in donor solvents and postulate that the chloride is removed from the metal surface by reaction 1. The effect of the state of subdivision of the metal on the activity is not known, but may be significant.

$$MCl_{x(\text{surface})} + (C_2H_5)_2O \longrightarrow MCl_x{:}O(C_2H_5)_2 \longrightarrow MCl_x + (C_2H_5)_2O \quad (1)$$

The bromination of uranium in methanol under a dry nitrogen atmosphere showed (1) hydrogen evolution, (2) the formation of an acidic reaction mixture which fumes in moist air, (3) the precipitation of UO_2 when excess bromine is not used, (4) the mole ratio uranium oxidized/hydrogen evolved (as H_2) to be dependent upon the rate of stirring and the rate of addition of bromine, and (5) the mole ratio uranium oxidized/bromine used (as Br) to be as high as 3.6. From these results, from the knowledge that $K_3UO_2F_5$ is formed upon addition of the bromination solution to a methanol solution of potassium fluoride, and from known reactions of uranium and of uranium bromides[7] we have postulated the following reactions to be involved in the bromination of uranium in methanol.

$$U + 2Br_2 \longrightarrow UBr_4 \quad (2)$$

$$2U + 6HBr \longrightarrow 2UBr_3 + 3H_2 \quad (3)$$

$$U + 3UBr_4 \longrightarrow 4UBr_3 \quad (4)$$

$$UBr_3 + 2CH_3OH \longrightarrow U(OCH_3)_2Br_2 + {}^1/_2H_2 + HBr \quad (5)$$

$$UBr_3 + {}^1/_2Br_2 \longrightarrow UBr_4 \quad (6)$$

$$UBr_4 + 2CH_3OH \longrightarrow U(OCH_3)_2Br_2 + 2HBr \quad (7)$$

$$U(OCH_3)_2Br_2 + 2CH_3OH \longrightarrow U(OCH_3)_4 + 2HBr \quad (8)$$

$$U(OCH_3)_4 \longrightarrow UO_2 + 2(CH_3)_2O \quad (9)$$

$$U(OCH_3)_2Br_2 + Br_2 \longrightarrow UO_2Br_2 + 2CH_3Br \quad (10)$$

$$U(OCH_3)_4 + Br_2 \longrightarrow U(OCH_3)_4Br_2 \quad (11)$$

Since hydrogen is evolved here in varying amounts depending upon the reaction conditions, and since in the bromination of zinc in methanol no hydrogen evolution is seen, it is suggested that the reaction mechanism of the bromination of metals in methanol is not as Raynaud suggested but is similar to that suggested by Osthoff and West, except where the bromides actually react with methanol to form methoxy compounds, as seems to be the case with uranium, vanadium, niobium, and tantalum. It is known that UBr_4 reacts with alcohols to form hydrogen bromide,[8] and that UBr_3 forms UO_2 in water or alcohol.[9] The postulation that the bromides of tantalum, niobium, and vanadium react with methanol is supported by the reaction of $TaCl_5$ with methanol to give $TaCl_2(OCH_3)_3$[10] and by the reaction of VCl_4 with methanol to form $V(OCH_3)_2Cl_2 \cdot CH_3OH$.[11]

The bromo compounds of niobium and tantalum are hydrolyzed easily, and the reaction of hydrogen bromide with methanol to form water[12] must be hindered. This is accomplished in the brominations of niobium and tantalum by rapid addition of the bromine to the reaction mixture, the use of excess bromine, and the immediate use of the bromination solution in the precipitation of the fluorometallate.

II. Preparation of the Ammonium and Potassium Fluorometallates

Experimental

Preparation of the Compounds.—The fluorometallates were prepared by the addition of the bromination solution to a large excess of a 0.5 *M* solution of the alkali fluoride in dry methanol.

The ammonium complexes were allowed to settle and washed with dilute ammonium fluoride in methanol by decantation. The complexes then were digested in a dilute solution of ammonium fluoride in methanol for at least 24 hr., filtered, rinsed with methanol and with ether, and dried by vacuum desiccation. Ammonium fluoride for use in the preparation of the tantalum or niobium complexes was dried by successive reprecipitations from methanol solution by the addition of ether.

The potassium complexes were filtered off immediately after precipitation, washed with dilute potassium fluoride solution in methanol, and then with methanol by vigorous shaking and decantation until no loss in weight occurred on further washing. The complexes were digested in a dilute solution of potassium fluoride in methanol for at least 24 hr., filtered, washed with methanol, and dried at 110°.

Preparation of the tantalum or niobium complexes should be carried out only in an atmosphere where the humidity is less than 30%.

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(5) A. Raynaud, *Compt. rend.*, **181**, 1069 (1925).

(6) R. C. Osthoff and R. C. West, *J. Am. Chem. Soc.*, **76**, 4732 (1954).

(7) U. S. Atomic Energy Comm. TID-5290, Books I and II 'Uranium Chemistry," 1958.

(8) F. H. Spedding, A. S. Newton, R. Nottorf, J. Powell, and V. Calkins, U. S. Atomic Energy Comm. TID-5290, Book I, 1958, p. 91–119.

(9) J. C. Warf, U. S. Atomic Energy Comm. TID-5290, Book I, 1958, p. 29–37.

(10) H. Funk and K. Niederlander, *Ber.*, **62**, 1688 (1929).

(11) D. C. Bradley, R. J. Multani, and W. Wardlaw, *J. Chem. Soc.*, 4647 (1958).

(12) G. M. Bennett and F. M. Reynolds, *ibid.*, 131 (1935).

Analytical.—Ammonia was determined by distillation from concentrated sodium hydroxide solution into a saturated solution of boric acid and titration with standard hydrochloric acid using methyl purple as indicator.

Potassium was determined gravimetrically as potassium tetraphenylboron according to the method of Geilmann.[13] In cases where the heavy metal ion precipitated in basic solution, the hydrous oxide was removed and the precipitation of potassium carried out on the filtrate.

Fluoride was determined by the method of Grant and Haendler,[14] where fluosilicic acid is steam-distilled from the sample into dilute sodium hydroxide and titrated oscillometrically with a standard thorium nitrate solution.

Uranium was determined gravimetrically[15] by precipitation with ammonium hydroxide as hydrous oxide after fuming the sample with sulfuric acid. The precipitate was weighed as U_3O_8.

Vanadium was determined volumetrically by titration of a dilute sulfuric acid solution of the sample with permanganate.[16] Addition of a solution of sodium fluoride and of copper sulfate seemed to give a clearer end-point.[17]

Tantalum and niobium were determined gravimetrically by precipitation with cupferron and ignition to the oxide.[18]

Discussion of Results

Tables I and II show the results of the analyses of the complexes. The complexes prepared here are seen from the analyses to be $(NH_4)_3UO_2F_5$, $K_3UO_2F_5$, $(NH_4)_3VOF_5$, K_3VOF_5, $(NH_4)_3NbOF_6$, K_3NbOF_6, $(NH_4)_3TaOF_6$, and K_3TaOF_6.

Complications arose during the preparations due to the presence of excess bromine in the bromination solutions. Bromine and ammonia in ether react to form ammonium bromide and monobromoamine.[19,20] In the preparation of the ammonium fluorometallates it was noted that the bromine color faded to a pale yellow, the color of monobromoamine. The extent of the interference of the reaction of bromine with ammonium fluoride to form monobromoamine and ammonium bromide in the preparation of the ammonium fluorometallates is not known, but a large excess of ammonium fluoride was used to ensure complete precipitation of the fluorometallate.

TABLE I

ANALYSIS OF THE AMMONIUM FLUOROMETALLATES

Formula	Anal. calcd., %		Anal. found, %
$(NH_4)_3UO_2F_5$	U	56.18	56.85, 56.96
	NH_4	12.88	12.77, 12.73
	F	22.68	22.68, 22.68, 22.74
$(NH_4)_3VOF_5$	V	23.58	23.22, 23.74, 23.70
	NH_4	25.05	24.28, 24.28
	F	43.97	44.35, 44.10, 44.70
$(NH_4)_3NbOF_6$	Nb	33.54	33.51, 33.48
	NH_4	19.54	19.01, 19.09
	F	41.84	41.58, 41.75, 42.24
$(NH_4)_3TaOF_6$	Ta	49.56	51.20, 50.79
	NH_4	14.83	13.44, 13.49
	F	31.23	30.41, 30.54

TABLE II

ANALYSIS OF THE POTASSIUM FLUOROMETALLATES

Formula	Anal. calcd., %		Anal. found, %
$K_3UO_2F_5$	U	49.25	49.63, 49.62, 49.77
	K	24.32	23.85, 23.90, 24.04
	F	19.59	19.99, 19.92
K_3VOF_5	V	18.24	18.02, 18.15
	K	42.01	39.96, 40.76, 40.12
	F	34.02	34.15, 34.15
K_3NbOF_6	Nb	27.39	27.19, 26.96, 26.80
	K	34.44	33.75, 34.09
	F	33.51	34.29, 34.10
K_3TaOF_6	Ta	42.24	42.29, 42.14, 42.49
	K	27.39	26.43, 26.39, 27.14
	F	26.62	26.04, 26.28

Bromine and potassium fluoride in methanol react to form nearly insoluble potassium hydrogen fluoride and sparingly soluble potassium bromide. Again a large excess of potassium fluoride was used for complete precipitation of the fluorometallate. Immediate filtration of the potassium fluorometallates after precipitation served to avoid extensive post-precipitation of potassium bromide. Thorough washing with methanol removed potassium hydrogen fluoride.

It should be noted that the analysis of $(NH_4)_3TaOF_6$ shows the compound to be contaminated, probably with oxyfluorides. However, the amount of impurity was not great enough to appear in the powder pattern, and thus the pattern was used to index $(NH_4)_3TaOF_6$. It is doubtful whether a pure compound can be made using our method of preparation because of the formation of water in the bromination step by the reaction of hydrogen bromide and methanol.

III. Structural Studies of the Fluorometallates

Experimental

X-Ray Powder Photographs.—Powder patterns were taken using 57.3 and 114.56 mm. Philips cameras. Copper

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(13) W. Geilmann and W. Gebauhr, *Z. anal. Chem.*, **139**, 161 (1953).

(14) C. L. Grant and H. M. Haendler, *Anal. Chem.*, **28**, 415 (1956).

(15) W. F. Hillebrand, G. E. F. Lundell, H. A. Bright, and J. I. Hoffman, "Applied Inorganic Analysis," John Wiley & Sons, Inc., New York, N. Y., 2nd Ed., 1953, p. 469.

(16) Reference 15, p. 459.

(17) I. M. Issa and M. Hamdy, *Z. anal. Chem.*, **174**, 418 (1960).

(18) F. J. Welcher, "Organic Analytical Reagents," Volume 3, D. Van Nostrand Co., Inc., New York, N. Y., 1947, p. 390.

(19) W. Moldenhauer and M. Burger, *Ber.*, **62**, 1615 (1929).

(20) G. H. Coleman and G. E. Goheen, *Proc. Iowa Acad. Sci.*, **43**, 178 (1936).

TABLE III

STRUCTURES OF SOME AMMONIUM AND POTASSIUM FLUOROMETALLATES

Compound	Structure	Cell Dimensions (Å.)	Density Calcd.	Density Obsd.	Reference
$(NH_4)_3UO_2F_5$	Tetragonal	$a = 9.70$	2.86	2.90	
		$c = 18.91$			
$K_3UO_2F_5$	Tetragonal	$a = 9.160$	4.20	3.93	(22)
		$c = 18.167$		4.267[a]	
$(NH_4)_3NbOF_6$	Face-centered cubic	$a = 9.31$	2.27	2.20	
K_3NbOF_6	Face-centered cubic	$a = 8.88$	3.23	3.01	(23)
$(NH_4)_3TaOF_6$	Face-centered cubic	$a = 9.31$	3.00	2.96	
K_3TaOF_6	Face-centered cubic	$a = 8.90$	4.03	3.97	
$(NH_4)_3VOF_5$	Tetragonal	$a = 9.17$	1.93	1.91	
		$c = 17.64$			
K_3VOF_5	Tetragonal	$a = 8.75$	2.84	2.79	
		$c = 17.09$			

[a] H. Baker, *Ann.*, **202,** 240 (1880).

TABLE IV

X-RAY POWDER DATA FOR $K_3UO_2F_5$[a]

$a = 9.16$ Å. $c = 18.17$ Å.

d_{hkl}	I/I_0	hkl
5.26	100	112
5.08	11	103
4.58	50	200 (004)
4.00	9	211
3.38	20	213 (105)
3.23	100	220, 204
2.86	3	?
2.81	3	?
2.76	40	312 (116)
2.72	11	303
2.63	13	224
2.49	13	107
2.46	3	314
2.32	5	305 (323)
2.29	25	400
2.27	11	008
2.19	15	217 (226)
2.09	15	316 (413) (332)
2.08	15	325
2.05	20	404 (420) (208)
1.97	13	109 (307)
1.89	9	415
1.87	45	424 (228)
1.81	25	219

[a] X-Ray Powder Data File, American Society for Testing Materials.

TABLE V

X-RAY POWDER DATA FOR $(NH_4)_3UO_2F_5$

$a = 9.70$ Å. $c = 18.91$ Å.

d_{hkl}	I/I_0[a]	hkl[b]	10^4Q_{obs}[c]	10^4Q_{calc}
5.51[d]	100	112	330	324
5.18	2	103	372	358
4.79[d]	50	200	436	425
		004	436	447
3.44	15	220	843	850
3.38	70	204	876	872
2.87[d]	50	303	1216	1208
		116	1216	1219
2.75	4	224	1319	1298
2.60[d]	1	107	1483	1477
		314	1483	1510
2.43	7	400	1688	1700
2.37	7	008	1785	1790
2.27	2	217	1934	1902
2.20	10	316	2060	2070
		143	2060	2058
		325	2060	2081
2.16	25	420	2139	2126
		404	2139	2148
2.13	4	208	2206	2215
2.09	4	307	2296	2327
2.03[d]	2	415	2429	2506
		109	2429	2371
1.98	4	424	2556	2573
1.94	25	228	2652	2640
1.88	2	219	2830	2797
1.76	1	309	3242	3221
		20,10	3242	3222
1.70	10	408	3477	3490

[a] Visual estimate. [b] Based on $I4_1/a$. [c] $Q = 1/d^2$. [d] Broad line.

and iron radiations were used. The samples were mounted in 0.3-mm. glass capillaries.

Infrared Spectra.—Infrared spectra were taken using a Perkin–Elmer Model 21 spectrophotometer, with sodium chloride optics. The samples for analysis were prepared as mulls by grinding with halocarbon oil (series 11–14), as described by Crocket and Haendler.[21]

Discussion of Results

Powder diffraction data were taken for the complexes and used for identification of $K_3UO_2F_5$ and K_3NbOF_6, which have been indexed previously,[22,23] and for the indexing of the other

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[21] D. S. Crocket and H. M. Haendler, *Anal. Chem.*, **31,** 629 (1959).

[22] W. H. Zachariasen, *Acta Cryst.*, **7,** 783 (1954).

[23] M. B. Williams and J. L. Hoard, *J. Am. Chem. Soc.*, **64,** 1139 (1942).

TABLE VI

X-RAY POWDER DATA FOR K_3VOF_5

$a = 8.75$ Å. $c = 17.09$ Å.

d_{hkl}	I/I_0[a]	hkl[b]	10^4Q_{obs}[c]	10^4Q_{calc}
4.96	17	112	406	398
4.30[d]	13	200	540	522
		004	540	548
3.16	7	105	1003	987
3.09	3	220	1047	1045
3.02[d]	100	204	1095	1070
2.36	10	107	1795	1808
2.26	7	323	1951	2006
2.19	3	400	2083	2090
2.14[d]	5	008	2180	2191
2.08	7	217	2305	2331
1.93	13	208	2679	2714
		404	2679	2638
1.76[d]	33	228	3232	3236
1.70	17	219	3464	3426
1.67	17	336	3586	3584

[a] Visual estimate. [b] Based on $I4_1/a$. [c] $Q = 1/d^2$. [d] Broad line.

TABLE VII

X-RAY POWDER DATA FOR $(NH_4)_3VOF_5$

$a = 9.17$ Å. $c = 17.64$ Å.

d_{hkl}	I/I_0[a]	hkl[b]	10^4Q_{obs}[c]	10^4Q_{calc}
5.18[d]	100	112	372	366
4.62	38	200	468	476
4.42	50	004	512	514
3.17[d]	63	204	996	990
2.74	3	312	1327	1318
2.69	3	116	1383	1395
2.60	13	224	1481	1466
2.34	6	323	1826	1835
2.29	13	400	1910	1903
2.22[d]	25	008	2023	2057
2.18	3	226	2110	2108
2.10	1	332	2274	2269
2.03	4	404	2420	2417
1.99	4	208	2520	2532
1.89	3	415	2800	2825
1.85	5	424	2919	2893
1.82	5	228	3012	3008

[a] Visual estimate. [b] Based on $I4_1/a$. [c] $Q = 1/d^2$. [d] Broad line.

TABLE VIII

X-RAY POWDER DATA FOR $(NH_4)_3NbOF_6$

$a = 9.31$ Å.

d_{hkl}	I/I_0[a]	hkl[b]	10^4Q_{obs}[c]	10^4Q_{calc}
5.381	100	111	345	346
4.660	67	200	460	462
3.293	67	220	922	923
2.807	37	311	1269	1269
...	...	222	...	1384
2.329	50	400	1844	1846
2.137	13	331	2190	2192
2.082	33	420	2307	2308
...	...	422	...	2769
1.792	40	511, 333	3114	3115
1.646	40	440	3691	3692
1.574	17	531	4037	4038
1.552	30	600, 442	4151	4154
1.473	23	620	4608	4615
1.421	17	533	4953	4961
1.404	10	622	5074	5077
1.344	3	444	5537	5538
1.304	20	711, 551	5882	5884
1.292	7	640	5992	6000
1.244	30	642	6460	6461
1.212	20	731, 553	6807	6807
1.165	2	800	7369	7384
1.138	3	733	7722	7730

[a] Visual estimation. [b] For face-centered cubic cell. [c] $Q = 1/d^2$.

complexes. Table III shows structural data for the complexes and Tables IV-X list the powder diffraction data.

The cubic patterns were calculated using the method of Henry, Lipson, and Wooster.[24] Each tetragonal pattern was compared with that for $K_3UO_2F_5$, which already had been reported.[22] The 400 and 008 lines were identified and a pattern calculated to allow correlation of the *hkl* values with observed lines. Calculations of $Q(4 \sin^2\theta_{calc}/\lambda^2)$ were made and compared with observed values. The best values of a and c were determined by changing each in turn until the difference between values of Q_{calc} and Q_{obs} was as small as possible. Final tabulations were carried out by programs written for the I.B.M. 1620 computer. The space group extinctions in the patterns of the four tetragonal compounds appear to be the same, presumably those of space group $I4_1/a$. The pattern of $K_3UO_2F_5$ is listed in Table IV for comparison. All possible interplanar spacings for this compound were calculated from the unit cell constants. Those in parentheses are reflections whose calculated d values lie close to those observed, but which had not been included in the published A.S.T.M. assignments.

Zachariasen[22] has determined that the UO_2F_5 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 K_I is associated with six fluorine atoms, K_{II} with four fluorine atoms and with four oxygen atoms, and K_{III} with two oxygen atoms and with six fluorine atoms. The inter-

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(24) N. F. M. Henry, H. Lipson, and W. A. Wooster, "The Interpretation of X-Ray Diffraction Photographs," 2nd Ed., St. Martins Press, Inc., New York, N. Y., 1960.

TABLE IX

X-RAY POWDER DATA FOR $(NH_4)_3TaOF_6$

$a = 9.31$ Å.

d_{hkl}	I/I_0[a]	hkl[b]	10^4Q_{obs}[c]	10^4Q_{calc}
5.398	100	111	343	346
4.653	90	200	462	461
3.294	80	220	922	923
2.807	60	311	1269	1269
2.684	5	222	1388	1384
2.325	50	400	1850	1846
2.135	40	331	2194	2192
2.079	55	420	2314	2307
1.897	55	422	2778	2769
1.789	55	511, 333	3125	3115
1.646	15	440	3691	3692
1.573	50	531	4042	4038
1.550	40	600, 442	4163	4153
1.472	30	620	4615	4615
1.418	10	533	4973	4961
1.401	10	622	5094	5076
1.343	5	444	5543	5538
1.304	20	711, 551	5882	5884
1.291	10	640	6000	5999
1.244	15	642	6460	6461
1.212	15	731, 553	6807	6807
1.165	1	800	7369	7384
1.139	1	733	7710	7730
1.129	10	820, 644	7843	7845
1.098	5	822, 660	8292	8307
1.075	10	751, 555	8651	8653
1.068	3	662	8764	8768
1.041	5	840	9225	9230
1.022	10	911, 753	9578	9576
1.016	5	842	9690	9691
0.9920	5	664	10161	10153
0.9763	5	931	10490	10499
0.9504	8	844	11070	11076
0.9364	10	933, 771, 755	11405	11421

[a] Visual estimation. [b] For face-centered cubic cell. [c] $Q = 1/d^2$.

TABLE X

X-RAY POWDER DATA FOR K_3TaOF_6

$a = 8.90$ Å.

d_{hkl}	I/I_0[a]	hkl[b]	10^4Q_{obs}[c]	10^4Q_{calc}
5.071	50	111	389	379
4.400	33	200	516	505
3.125	100	220	1024	1010
2.668	17	311	1405	1389
2.559	3	222	1527	1515
2.217	17	400	2034	2020
2.036	20	331	2412	2399
1.983	50	420	2543	2525
1.813	83	422	3042	3030
1.709	50	511, 333	3423	3409
1.572	33	440	4047	4040
1.503	50	531	4427	4419
1.481	33	600, 442	4560	4545
1.407	67	620	5051	5050
1.357	13	533	5432	5429
1.340	10	622	5568	5555
1.284	17	444	6064	6060
1.246	33	711, 551	6443	6438
1.234	10	640	6566	6565
1.189	83	642	7072	7070
1.158	50	731, 553	7457	7448
1.079	50	820, 644	8591	8585
1.048	67	822, 660	9107	9090
1.028	33	751, 555	9461	9468
1.021	50	662	9597	9595
0.9958	33	840	10084	10099
0.9782	67	911, 753	10450	10478

[a] Visual estimation. [b] For face-centered cubic cell. [c] $Q = 1/d^2$.

planar spacings found for our preparation of $K_3UO_2F_5$ matched those found by Zachariasen for his preparation of $K_3UO_2F_5$ from aqueous solution. Dunn,[25] however gives different interplanar spacings for his preparation.

The powder pattern of our $(NH_4)_3UO_2F_5$ was very similar to that of our $K_3UO_2F_5$ preparation. It was noted, however, that several broad lines of the $K_3UO_2F_5$ pattern were resolved in the $(NH_4)_3UO_2F_5$ pattern. This suggests that in $K_3UO_2F_5$ the ratio c/a approaches the value 2 more closely than it does in the ammonium compound.

The infrared spectra of $(NH_4)_3UO_2F_5$ and $K_3UO_2F_5$ are given in Figure 1. Following the discussions of the infrared spectrum of the ammonium ion by Wagner and Hornig,[26] Waddington,[27] and Crocket and Haendler,[2] it can be seen that the spectrum of ammonium pentafluorodioxyuranate(VI) shows several of the characteristics attributed to the effect of hydrogen bonding. 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

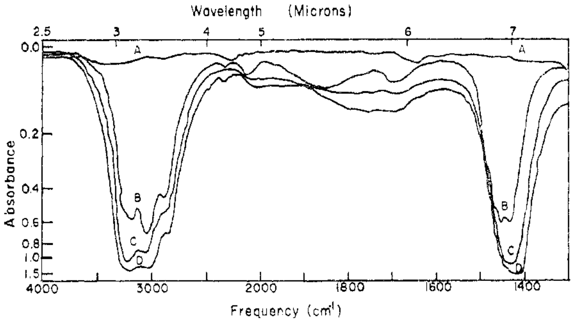

Fig. 1.—Infrared spectra: A = $K_3UO_2F_5$; B = $(NH_4)_3UO_2F_5$; C = $(NH_4)_3VOF_5$; D = $(NH_4)_3NbOF_6$.

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(25) H. W. Dunn, U. S. Atomic Energy Comm. ORNL Report No. 2092, "X-ray Diffraction Data for Uranium Compounds" (1956).

(26) E. L. Wagner and D. F. Hornig, *J. Chem. Phys.*, **18**, 296 (1950).

(27) T. C. Waddington, *J. Chem. Soc.*, 4340 (1958).

region, and the slight splitting and shift to a higher frequency of the ν_4 mode. Since $(NH_4)_3UO_2F_5$ is isostructural with $K_3UO_2F_5$, it would seem that there are three possible environments for the ammonium ions. Crocket and Haendler[2] have stated that a possible cause of the two large peaks in the ν_4 mode area in the spectrum of ammonium tetrafluorocuprate(II) is the presence of ammonium ions in two unequivalent lattice positions, causing the bending vibration of the ammonium ions to differ. The spectrum of the uranium complex is not sufficiently resolved to permit similar conclusions.

Williams and Hoard[23] have indexed K_3NbOF_6 and have suggested that it contains discrete K^+ and $NbOF_6^{-3}$ ions. They further suggest that the $NbOF_6$ group may have the structure of a distorted octahedron, with the niobium atom at the center of a regular octahedron, the six fluorine atoms at the corners of a regular octahedron, and the oxygen atom on the three-fold axis passing through one face of the regular octahedron. To explain the cubic structure of K_3NbOF_6, it is necessary to assume that the structural type for K_3NbOF_6 involves some randomness of atomic arrangement. The niobium and tantalum complexes are isostructural, suggesting that $(NH_4)_3NbOF_6$, $(NH_4)_3TaOF_6$, and K_3TaOF_6 also have some random character.

Zachariasen[28] has found that K_3UF_7 has two structures, the ordered tetragonal form, which is almost indistinguishable from the structure of the $K_3UO_2F_5$, and a disordered cubic form. The cubic form is considered to have some degree of disorder in the positions of the atoms, but the distribution of ionic centers is nearly the same as in the tetragonal form, the structure of the UF_7 group being that of a pentagonal bipyramid. Zachariasen has further suggested that the 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 a random orientation of groups. Since the K_3NbOF_6 complex is isostructural with $(NH_4)_3ZrF_7$,[23] it would be of interest to determine the $NbOF_6$ structure by single crystal studies.

The infrared spectra of $(NH_4)_3NbOF_6$ and $(NH_4)_3TaOF_6$ are very similar. That of $(NH_4)_3NbOF_6$ is given in Figure 1 and shows little evidence for hydrogen bonding. The ν_4 peak is not shifted or split, a $\nu_4 + \nu_6$ mode does not appear clearly, and there is only a very slight splitting of the ν_3 peak. The isomorphism of the ammonium and potassium complexes supports this evidence.

Very little work has been carried out concerning the structures of vanadium complexes, and it is difficult to speculate about the orientation of atoms in the VOF_5 group. It is reported that the complex $(NH_4)_3VF_6$ is cubic,[29] and several other complexes of vanadium are reported in which the coördination number of vanadium may be six. Among these are $(NH_4)_2VF_5 \cdot H_2O$, $(NH_4)VF_4 \cdot 2H_2O$, $K_2VF_5 \cdot H_2O$, $(NH_4)_2VOF_4 \cdot H_2O$, K_2VF_6, $(NH_4)_2VO_2F_4$, and K_2VOF_5.[30] Structural studies of some of these would do much to explain the coördination chemistry of vanadium.

The infrared spectrum of $(NH_4)_3VOF_5$, shown in Figure 1, does show some variation from that of a freely rotating ammonium ion[26,27] in that the ν_4 peak is shifted slightly higher, and the ν_3 mode shows a peak at 3240 cm.$^{-1}$, another at 3070 cm.$^{-1}$, and a shoulder at 2860 cm.$^{-1}$. The $\nu_4 + \nu_6$ mode, which is a main feature in the spectrum of a hydrogen-bonded ammonium ion, is barely discernible. Thus, except for a small splitting in the ν_3 region, evidence is meager to support 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 sufficient to change the structure of the ammonium complex from tetragonal.

Magnetic measurements, using the Gouy method,[31] showed the vanadium complexes prepared here to contain one unpaired electron. The magnetic moment of $(NH_4)_3VOF_5$ was found to be 1.68 ± 0.05 B.M., that of K_3VOF_5 to be 1.71 ± 0.03 B.M.

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[28] W. H. Zachariasen, *Acta Cryst.*, **7**, 792 (1954).

[29] L. Passerini and R. Pirani, *Gazz. chim. ital.*, **62**, 279 (1932).

[30] J. N. Simons, Ed., "Fluorine Chemistry," Vol. II, Academic Press Inc., New York, N. Y., 1954, p. 21.

[31] We are indebted to the Central University Research Fund for a grant toward the construction of this balance.