molecule to assume a planar configuration around the nickel in the 1:1 complex.

Infrared spectra of the three chelating agents give no evidence of an SH stretch. The azothiopyrazolones do show a wide absorption band (1240–1200 cm.$^{-1}$) in the region which has been suggested as representing the C=S bond.[11] This band disappears in the metal derivatives as well as the band at 1560 to 1555 cm.$^{-1}$ which was called a possible N=N stretch.[12] The band at 1240–1200 cm.$^{-1}$ also disappears in the S-methyl derivative of 1-phenyl-3-methyl-4-phenylazo-5-thiopyrazolone. The lack of SH stretch is not surprising since, like the analogous oxygen compounds, this would require the enolization of what could be considered a cyclic thioamide.

A new, strong, multipeaked absorption is found in the metal derivatives in the region 1470–1350 cm.$^{-1}$ which corresponds to the reported[12] broad absorption for the copper derivatives of the analogous oxygen derivatives at 1470–1385 cm.$^{-1}$. This multipeaked absorption is also present in the S-methyl derivative of compound I. The most intense band in this region is at lower frequencies than found in the metal derivatives of the oxygen compounds. This multi-peaked absorption is probably due to the pyrazole ring vibration.

Acknowledgment.—The authors are indebted to the National Science Foundation (NSF-G12306) for financial support in carrying out this investigation.

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Fluoride Complexes of Pentavalent Uranium[1]

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Solid fluoride complexes of pentavalent uranium are formed by heating UF_5 with ammonium or alkali fluorides under anhydrous conditions. A series of complexes having $MF:UF_5$ ratios ($M = NH_4$, Li, Na, K, Rb, and Cs) of 1:1, 2:1 (except Li and Na), and 3:1 (except Li) were characterized by X-ray powder diffraction. These white to pale blue compounds exhibit characteristic absorption in the 1.3 to 1.5 μ region.

Introduction

We reported in a brief communication that UF_5 reacts under anhydrous conditions with NH_4F or alkali fluorides to form complex fluorides of the form MUF_6.[2] That work has been extended and herein we report the synthesis of a series of compounds of pentavalent uranium as well as their X-ray powder diffraction data and spectra.

There are only three cases of elements having a $5f^1$ electronic configuration in chemically tractable valence states: *i.e.*, Pa(IV), U(V), and Np(VI). Additions to the few data on U(V) are of chemical interest as well as having theoretical importance since U(V) absorption spectra in particular can often be interpreted relatively simply.[3]

Few fluoride complexes of U(V) have been characterized previously. Uranium hexafluoride is reduced by NH_3 under certain conditions to give NH_4UF_6[4] and by NO to give $NOUF_6$.[5] Note that Galkin, *et al.*,[6] report that reduction of UF_6 by NH_3 gives UF_5 and a complex of *tetravalent* uranium, NH_4UF_5. Ruedorff and Leutner[7] prepared Na_3UF_8 (contaminated with NaF) from trisodium uranium(IV) fluoride by fluorination at carefully controlled temperatures. However, they could not prepare the analogous potassium uranium(V) compound, but instead always obtained a compound containing U(VI).

A more general approach than either of the above is one which starts with UF_5 and is the one used in this study. All alkali fluorides were found to react with UF_5 to produce complex fluorides containing uranium(V).

Experimental

Materials.—Reagent grade NH_4F, LiF, NaF, and KF were used. Anhydrous UF_6 was distilled. Certified uranium tetrafluoride (99.9%), RbF (99.7%), and CsF (99.7%) were used. The UF_5 was prepared by treatment of UF_4 with gaseous UF_6 in a nickel reactor under anhydrous conditions. Specially prepared UF_4 of high surface area[8] reacted smoothly with UF_6 at 80–100° to yield β-UF_5. Increase in the temperature to 200° yielded α-UF_5. Both forms of UF_5 had the theoretical weight composition

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[1] Work performed under the auspices of the U. S. Atomic Energy Commission.

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[7] W. Ruedorff and H. Leutner, *Ann. Chem.*, **632**, 1 (1960).

[8] J. J. Katz and E. Rabinowitch, "The Chemistry of Uranium," NNES-VIII-5, McGraw-Hill Book Co., New York, N. Y., 1951, p. 385.

and gave X-ray powder patterns agreeing with published values.[9]

Technique.—Screw-cap bombs of Teflon were used to contain the mixtures of UF_5 and ammonium fluoride which were finely ground and mixed thoroughly prior to heating. In the case of the alkali fluorides, a nickel bomb with a copper gasket was used. Preparations were typically made on a 5–20-g. scale and were weighed to 1 mg. Because of their reactivity with moisture, all U(V) compounds were handled in a dry helium atmosphere.

In general, products resulting from heating UF_5 with the heavier alkali fluorides at 350° gave evidence of partial sintering and were generally removed from the reactor as a cake. Usually, a few patches of a green U(IV) impurity were present on the surface of the much lighter colored U(V) compounds and were easily separated. The compounds containing ammonium or the lighter alkali fluorides remained powders.

The X-ray powder diffraction patterns of the products were obtained using Lindemann glass capillaries loaded in an inert atmosphere. A 114.6-mm. powder camera with either Ilford or Kodak AA film was used with filtered copper radiation (λ Cuα = 1.5418 Å.).

The absorption spectra were measured using mineral oil or Fluorolube[10] mulls of compounds which were contained between calcium fluoride disks in a Cary Model 14MR spectrophotometer.

Preparation of Compounds. NH_4F–UF_5 Compounds.—These compounds were prepared in Teflon bombs at the relatively low temperatures of 80–200° using reaction times of 1 to 6 days. Heating an intimate mixture containing a ratio of one mole of NH_4F to one mole of either α or β-UF_5 yielded the compound NH_4UF_6. Alternatively, this white compound was prepared by the treatment of NH_4F with UF_6 at 100° for 18 hr. (first giving yellow NH_4UF_7)[11] followed by heating at 200° for 2 hr. in excess UF_6. The X-ray powder diffraction pattern of NH_4UF_6 showed no lines of the starting materials, UF_5 or NH_4F. The compound lost no weight under vacuum (1 μ) in 2 days at 25°, showing that no free NH_4F was present. The NH_4UF_6 was analyzed by pyrohydrolysis, giving a residue which was weighed as U_3O_8; the distillate was analyzed for NH_4F and HF. *Anal.* Calcd. for NH_4UF_6: U, 64.32; NH_4, 4.86; F, 30.8. Found: U, 64.29; NH_4, 4.9; F, 30.0.

The 2:1 compound, $(NH_4)_2UF_7$, was formed slowly on heating a 2:1 mixture of NH_4F and UF_5 at 80°. Initially a mixture of NH_4UF_6 and $(NH_4)_3UF_8$ was formed. When the mixture was heated for 60 hr. at 200°, the 2:1 compound was formed. $(NH_4)_2UF_7$ gave a diffraction pattern and an absorption spectrum different from that of NH_4UF_6.

The 3:1 compound, $(NH_4)_3UF_8$, was made by heating NH_4F and UF_5 in a 3:1 mole ratio. Again, a unique diffraction pattern and absorption spectrum were found. On heating at 150° under vacuum (1 μ) for 20 hr., 2 moles of NH_4F was removed from $(NH_4)_3UF_8$, forming NH_4UF_6.

An attempt to prepare a 4:1 compound gave a product having the diffraction pattern and the same absorption spectrum as $(NH_4)_3UF_8$. The mixture readily lost one mole of NH_4F at 25° under vacuum and gave the X-ray pattern of 3:1.

LiF–UF_5 Compounds.—Finely-ground LiF and UF_5 were mixed in 1:1, 2:1, 3:1, and 4:1 mole ratios and heated at 300° for 5 days. The X-ray powder diffraction patterns and absorption spectra showed that only the 1:1 complex, $LiUF_6$, had been formed in each case.

NaF–UF_5 Compounds.—Powdered NaF and UF_5 were ground together in integral mole ratios and heated at 350° for several days. The products were fine powders and gave no evidence of sintering.

A 1:1 mole ratio of NaF and UF_5 formed $NaUF_6$ as shown by a distinctive diffraction pattern and absorption spectrum. On the basis of 61 lines, $NaUF_6$ was indexed as fcc, a_0 = 8.608 ± 0.002 Å.

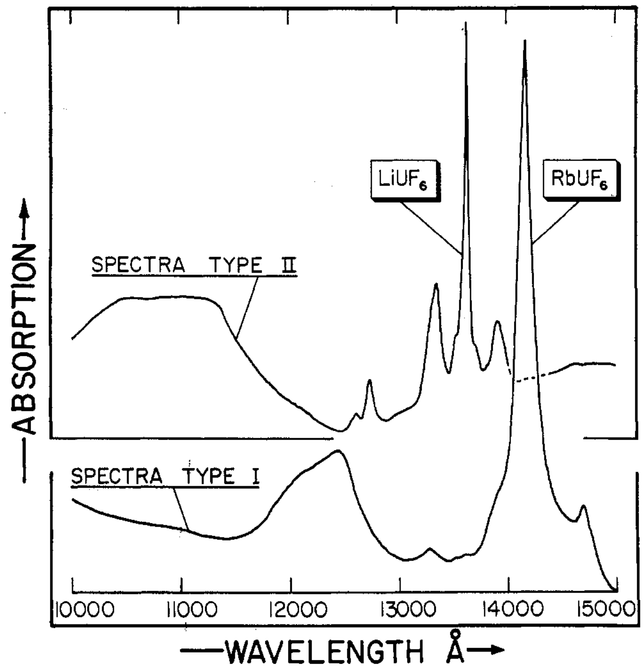

Fig. 1.—Type I: absorption spectrum of $RbUF_6$ (also typical of NH_4UF_6 and KUF_6). Type II: absorption spectrum of $LiUF_6$ (also typical of $NaUF_6$ and $CsUF_6$).

TABLE I

X-RAY POWDER DIFFRACTION DATA FOR MUF_6 COMPOUNDS (TYPE I SPECTRA)

KUF_6		NH_4UF_6		$RbUF_6$	
d	I_{est}	d	I_{est}	d	I_{est}
5.63	100 br	5.81	100 br	5.82	50 br
4.01	100	4.13	80	4.12	100
...	...	3.99	30	3.99	15
3.27	70	3.30	80	3.31	90
2.83	35	{2.96	10	{2.96	10
		2.88	50	2.89	15
2.55	20	2.64	20	2.64	10
2.51	20	2.62	20	2.60	10
2.33	10	2.35	10	2.37	5
2.29	10	2.38	10	2.38	5
{2.15	35	2.20	70 br	{2.20	50
2.13	35			2.18	50
...	...	2.07	30	2.07	40
2.00	35	2.00	10	2.00	30
1.89	25	1.90	30	1.90	15
...	...	1.87	10	1.87	15
...	...	1.85	35	1.84	20
...	...	1.81	30	1.80	40
...	...	1.77	10	1.77	10
1.79	40	1.75	10	1.74	10

Diffraction patterns and absorption spectra of the products formed by heating a 2:1 mole ratio of NaF and UF_5 showed only lines of $NaUF_6$ and Na_3UF_8. Further heating for a week did not show any lines attributable to Na_2UF_7. The absorption spectrum confirmed that a mixture of 1:1 and 3:1 was present.

Heating a mixture of 3NaF and UF_5 gave pale aqua Na_3UF_8. Its X-ray diffraction pattern agreed with that reported for tetragonal Na_3UF_8 by Ruedorff and Leutner[7] and will not be repeated here.

When a mixture containing NaF : UF_5 in a mole ratio of 4:1 was heated, only Na_3UF_8 and unreacted NaF were found by X-ray diffraction.

KF–UF_5 Compounds.—The compounds KUF_6, K_2UF_7, and K_3UF_8 were prepared similarly and characterized by both absorption spectroscopy and X-ray powder diffraction.

RbF–UF_5 Compounds.—The compounds $RbUF_6$, Rb_2UF_7, and Rb_3UF_8 were prepared and characterized as described above.

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[9] W. H. Zachariasen, *Acta Cryst.*, **2**, 296 (1949).

[10] Fluorolube "S," Hooker Electrochemical Co.

[11] B. Volavsek, *Croat. Chem. Acta*, **33**, 181 (1962).

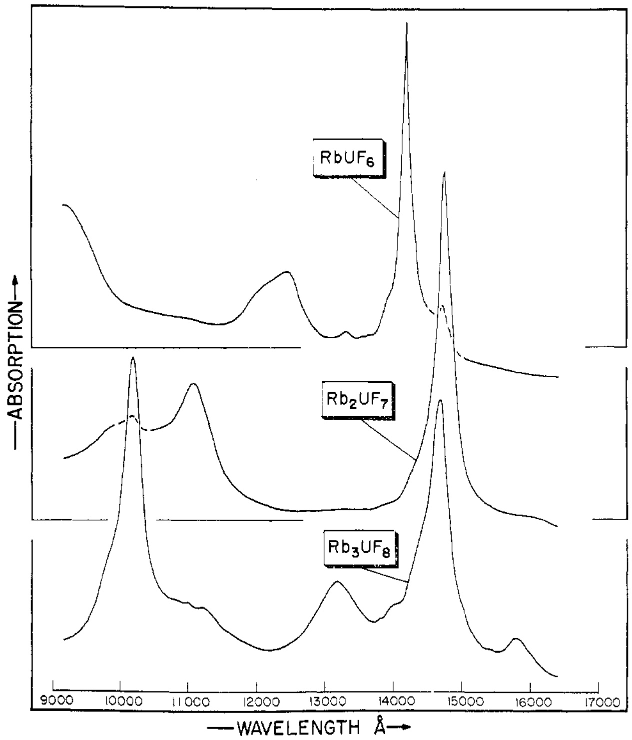

Fig. 2.—Absorption spectra of $RbUF_6$, Rb_2UF_7, and Rb_3UF_8.

CsF–UF$_5$ Compounds.—The compounds $CsUF_6$, Cs_2UF_7, and Cs_3UF_8 were prepared and characterized as described above.

Absorption Spectra.—Representative absorption spectra of the U(V) complex fluorides are given in Fig. 1 and 2.

X-Ray Powder Diffraction Data.—The *d*-values and visually estimated intensities of prominent lines for 1:1, 2:1 (Rb_2UF_7 only), and 3:1 compounds are given in Tables I, II, III, and IV.

TABLE II

X-RAY POWDER DIFFRACTION DATA FOR MUF_6 COMPOUNDS (TYPE II SPECTRA)

$LiUF_6$		$NaUF_6$ fcc, a_0 = 8.608 ± 0.002 Å.		$CsUF_6$	
d	I_{est}	*d*	I_{est}	*d*	I_{est}
4.74	40	4.93	100	5.34	25
4.32	100	4.28	100	4.00	100
3.82	100	3.04	70	3.59	80
2.81	35	2.59	85	2.67	40
2.63	30	2.48	5	2.31	25
2.42	30	2.15	45	2.23	70
2.30	80	1.97	45	2.01	25 br
2.25	20	1.92	90	1.80	20
2.17	20	1.76	50	1.75	30
1.92	25	1.66	40	1.64	35
1.86	20	1.52	30	1.60	20
1.77	60	1.46	45	1.52	30
1.71	25	1.44	45	1.49	25
1.67	30	1.36	25	1.42	20
1.55	20	1.31	20	1.34	15
1.52	20	1.30	15	1.33	10
1.48	20	1.24	10	1.27	10
1.45	20	1.21	25	1.25	5
1.41	10	1.19	20	1.20	15
1.36	20	1.15	35	1.16	5
1.32	20	1.12	35	1.11	5

TABLE III

X-RAY POWDER DIFFRACTION DATA FOR Rb_2UF_7

d	I_{est}	*d*	I_{est}
5.66	10	2.22	25 br
5.37	30	2.17	20 br
4.81	10	2.12	20 br
4.48	20	2.05	30 br
3.65	100	1.95	20
3.51	60 br	1.90	20
3.38	40	1.83	30
3.14	25	1.79	35
3.03	20		

TABLE IV

X-RAY POWDER DIFFRACTION DATA FOR M_3UF_8 COMPOUNDS

Rb_3UF_8		Cs_3UF_8		K_3UF_8		$(NH_4)_3UF_8$	
d	I_{est}	*d*	I_{est}	*d*	I_{est}	*d*	I_{est}
5.48	40			5.27	60	5.56	100
4.77	25			4.58	40	4.77	40
3.37	100	3.50	100 br	3.24	100	3.37	60
2.88	15			2.78	40	2.90	50
2.84	5			2.30	40	2.41	15
2.40	40	2.49	35	2.12	25	2.21	20
2.35	25	2.44	25	2.06	25	2.15	20
2.17	5			1.88	100	1.96	40
2.14	5			1.77	40 br	1.86	30 br
1.95	70	2.03	60	1.56	25	1.63	15
1.93	35			1.54	25	1.61	10
1.89	10 br			1.24	50	1.29	15
1.84	10						
1.70	10						
1.68	20						
1.62	5						
1.59	5						
1.56	5						
1.52	40	1.58	35				
1.49	10						
1.37	5						
1.28	35 br	1.33	20				

Discussion

Direct reaction between UF_5 and NH_4F or the alkali fluorides yields complex compounds of U(V). Compounds having $MF:UF_5$ (M = NH_4, Li, Na, K, Rb, and Cs) ratios of 1:1, 2:1 (except Li and Na), and 3:1 (except Li) were found. No compounds of the type $4MF:UF_5$ were found. This is consistent with the F/U ratio limit of eight frequently observed for U(VI) and U(IV) compounds. For example, in the case of hexavalent uranium the compound having the highest ratio of $NaF:UF_6$ is Na_2UF_8.[12,13] In the case of tetravalent uranium, the compound $(NH_4)_4UF_8$ is the highest found in the NH_4F–UF_4 system.[14]

All of the U(V) compounds show intense and relatively sharp absorption lines in the 1.3–1.5 μ region. In the 1:1 compounds two distinct classes of spectra were observed; within each class the spectra were essentially independent of the cation. The simplest spectra, giving a single, sharp band at 1.42 μ (identified as the $^2F_{5/2}$–$^2F_{7/2}$ transition),[3] were obtained from KUF_6, NH_4UF_6, and $RbUF_6$ (Fig. 1). X-Ray evidence (Table I) shows that the compounds NH_4UF_6 and $RbUF_6$ are isostructural and of very nearly the same cell size. The pattern of KUF_6 is quite similar also. This single band was split into three components in $LiUF_6$, $NaUF_6$, and Cs-

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[12] J. G. Malm and H. Selig, Abstracts, 142nd National Meeting, American Chemical Society, Atlantic City, N. J., Sept., 1962.

[13] I. Sheft, H. H. Hyman, R. M. Adams, and J. J. Katz, *J. Am. Chem. Soc.*, **83**, 291 (1961).

[14] R. Benz, R. M. Douglass, F. H. Kruse, and R. A. Penneman, *Inorg. Chem.*, **2**, 799 (1963).

UF_6 with the prominent peak at 1.36 μ (Fig. 1). The X-ray powder diffraction patterns (Table II) of these compounds are markedly different from NH_4, K, and Rb 1:1 salts. The $NaUF_6$ compound is f.c.c., but $LiUF_6$ and $CsUF_6$ could not be indexed on this basis, even though the absorption spectra show that the U(V)–fluoride species must be in a similar environment in these three compounds.

No compounds were obtained with UF_5 and LiF or NaF in a 2:1 ratio. The X-ray powder patterns of $(NH_4)_2UF_7$, K_2UF_7, Rb_2UF_7, and Cs_2UF_7 showed strong similarities. Since the films were generally of poor quality, data for Rb_2UF_7 only are given (Table III).

UF_5 reacts with all alkali fluorides except lithium to form compounds of the type $3MF \cdot UF_5$. The X-ray powder data for Na_3UF_8 were reported previously.[7] At this 3:1 stoichiometry, the X-ray patterns (Table IV) of the potassium and ammonium compound showed strong similarities, suggesting that K_3UF_8 and $(NH_4)_3UF_8$ are isostructural. In addition, Rb_3UF_8 and Cs_3UF_8 appear isostructural.

The absorption spectra of $RbF \cdot UF_5$ compounds of 1:1, 2:1 and 3:1 ratio are given in Fig. 2. It can be seen that changing the proportion of rubidium to uranium changes the spectrum substantially. In general, the absorption spectrum provided a convenient method of distinguishing mixtures from pure compounds. For example, in the attempt to make Na_2UF_7 by heating a 2:1 mixture of NaF and UF_5, the spectrum of the product showed clearly that $NaUF_6$ and Na_3UF_8 only were formed.

This method of preparing anhydrous fluorides of U(V) is not suitable for producing single crystals. However, we are at present studying the preparation of $RbUF_6$ and $CsUF_6$ from U(V) solutions in ~50% aqueous HF. This technique does yield crystals suitable for single crystal X-ray work.

NOTE ADDED IN PROOF.—R. L. Sherman, Oak Ridge National Laboratory, drew our attention to the close similarity between his powder data for $CsTaF_6$ and ours for $CsUF_6$. Using the rhombohedral $KOsF_6$ structure type[15] to which $CsTaF_6$ and apparently $CsUF_6$ both belong, we have been able to index the $CsUF_6$ pattern. A least-squares fit of our $CsUF_6$ data gave the hexagonal dimensions, $a_0 = 8.036 \pm 0.003$, $c_0 = 8.388 \pm 0.004$ Å. The size of UF_6^- is thus slightly larger than that of TaF_6^- (for $CsTaF_6$, $a_0 = 7.90$, $c_0 = 8.23$ Å.).[16] This is also observed on comparing our data for $NaUF_6$ ($a_0 = 8.608$ Å.) with $NaTaF_6$ ($a_0 = 8.28$ Å.).[16,17] $LiUF_6$ was found to be rhombohedral, isostructural with $LiTaF_6$ ($a_0 = 5.32$, $c_0 = 13.62$ Å.),[17] having unit cell dimensions, $a_0 = 5.262 \pm 0.004$, $c_0 = 14.295 \pm 0.005$ Å. The complete data are available from the authors or from our colleague, Dr. F. H. Kruse, who kindly provided the IBM 7094 computations.

We were not able to index the powder data for KUF_6 or $RbUF_6$ using the structures of the corresponding tantalum compounds. Indeed, $CsUF_6$ and $RbUF_6$ are not isostructural, even though the corresponding tantalum compounds, $CsTaF_6$ and $RbTaF_6$, are isostructural. This finding is also supported by the evidence showing that $RbUF_6$ and $CsUF_6$ give two different classes of spectra.

After completion of our work we became aware of a report[18] issued in 1960 but abstracted only recently [*Chem. Abstr.*, **59,** 8215*d* (1963)] describing the preparation of $LiUF_6$ and KUF_6 by metathesis of $NOUF_6$ with alkali salts.

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