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Synthesis and Characterization of a New Uranium(V) Compound: $H_3O^+UF_6^-$

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The reaction of equimolar amounts of UF_5 and H_2O in hydrogen fluoride results in the partial dissolution of UF_5, yielding a blue-green solution from which the new salt oxonium hexafluorouranate(V) ($H_3O^+UF_6^-$) could be isolated as a green crystalline solid. Calorimetric measurements showed $H_3O^+UF_6^-$ to decompose at about 68 °C and its heat of formation to be equal to -628 ± 2 kcal mol^{-1}. Its ionic nature in the solid state and in HF solutions was demonstrated from vibrational and electronic spectra. The electronic spectrum is closely similar to those of $LiUF_6$, $NaUF_6$, and $CsUF_6$ and differs from those of $RbUF_6$ and KUF_6. This adduct shows a strong ESR signal, with $g = -0.78 \pm 0.10$, characteristic of UF_6^- salts. Based on its x-ray powder diffraction pattern, $H_3O^+UF_6^-$ is cubic with $a = 5.2229 \pm 0.0005$ Å.

Introduction

A recent work of Christe et al.[1] on H_3O^+ salts showed that the oxonium ion associates for instance with arsenic or antimony hexafluoro anions, forming the compounds $H_3O^+AsF_6^-$ or $H_3O^+SbF_6^-$. In previous researches, Bonnet et al.[2] made a DTA study of the solutions of antimony pentafluoride in HF–water mixtures and suggested the existence of ionized compounds $H_3O^+SbF_5OH^-$ and $H_5O_2^+SbF_6^-$. These facts, together with the well-known acidic properties of uranium pentafluoride[3] prompted us to look for the corresponding U(V) salt. This idea was further supported by some previous experimental observations that were made on the x-ray powder patterns obtained during the preparation of the compounds $M^{II}U^V_2F_{12}\cdot4H_2O$ (M^{II} = Co, Ni, Cu).[4] For some UF_5–HF–H_2O mixtures, a small amount of a new solid species was isolated and an x-ray diagram very close to that of $NOUF_6$[5] was obtained, but there was no reason for NO^+ to be present. Unfortunately, the amount of this compound was not sufficient to perform chemical analyses. Since the work of Christe,[1] it has become clear than an oxonium salt might have been obtained. The aim of the present paper is to describe the preparation of this salt (oxonium hexafluorouranate(V)) and some of its properties.

Experimental Section

Materials. Hydrogen fluoride (ultrapure grade) was supplied by Comurhex (Pierrelatte, France) in Monel vessels, under a 200 Torr fluorine pressure and was used without further purification. Uranium pentafluoride (β-UF_5) was prepared by mixing uranium tetrafluoride (Merck, nuclear grade) and uranium hexafluoride (from Comurhex) in liquid HF, at room temperature.[6] The purity of the UF_5 was checked by viewing its x-ray diffraction pattern.

Apparatus. The reactions were carried out in Voltalef (polychlorotrifluoroethylene) vessels, connected to a well-passivated Monel vacuum line. Solid materials were handled in a glovebox, under a dry nitrogen atmosphere.

The infrared spectra were recorded in the range 4000–250 cm^{-1} on a Perkin-Elmer Model 457 spectrophotometer or on a Beckman IR 9 apparatus (4000–400 cm^{-1}). In the far-infrared region, a RIIC (Research and Industrial Instruments Co., London) FS 720 (Fourier transform) spectrophotometer was used. In this case, samples were studied as mulls pressed between polyethylene disks. Otherwise they were pressed into pellets between silver chloride windows.

In the visible and near-infrared regions, spectra were obtained from hydrogen fluoride solutions (contained in transparent Voltalef tubes 4-mm i.d.) or from mulls pressed between calcium fluoride windows, on a Cary 17 spectrophotometer.

The Raman spectra were recorded on a Coderg (Clichy, France) Model T800 spectrophotometer, using the 5145-Å exciting line from a Spectra Physics Model 164 argon laser. Solid samples were studied in sealed glass capillaries (0.5mm i.d) or in a spinning cell in order to reduce the decomposition of the sample by the laser beam. HF solutions were contained in transparent Voltalef tubes.

Accuracies of the measurements were ± 1 cm^{-1} for Raman wavenumbers, ± 5 cm^{-1} for infrared wavenumbers, and ± 1 nm for the visible and near-infrared wavelengths.

Samples sealed in glass capillaries ($\sim$0.5-mm o.d) were used to obtain x-ray diffraction patterns on a Philips diffractometer (114-mm diameter). The exciting radiation was the copper $K\alpha$ line (1.5418 Å).

ESR measurements were carried out with a Varian V4502-15 apparatus, at 77 K, the powdered sample being contained in a quartz tube, sealed under vacuum.

Enthalpimetric and thermal stability measurements were carried out on a microcalorimeter, Model MCB, from Arion Electronique (Grenoble, France). Powdered samples (100–200 mg) were contained in closed Monel cells and a heating rate of 2 K min^{-1} was used.

Chemical analyses were performed as follows. After hydrolysis of the sample, disproportionating U(V) into U(IV) and U(VI), uranium(VI) was determined by polarography in phosphoric acid–lithium perchlorate medium. A subsequent measurement, after oxidation of the sample by nitric acid, led to the total uranium content.

Fluorine was determined by pyrohydrolysis. The sample was heated to 1100 °C, and the evolved hydrogen fluoride was steam-extracted and collected in a sodium hydroxide solution. The fluoride ion concentration was then measured by absorptiometry of the alizarin–cerium complex at 617 nm.

The water content was determined by dissolving a known amount of sample in pyridine and titrating the evolved water with Karl Fischer reagent, using a Prolabo Aquavit titrator.

Preparation of $H_3O^+UF_6^-$. In a typical experiment, uranium pentafluoride (8.59 g, 25.8 mmol) was weighed into a 60-ml Voltalef flask in a drybox. This flask, fitted with a porous Teflon filter on the lid, was then transferred to the vacuum line and evacuated. A 25.8-mmol sample of twice-distilled water (464.3 mg) was weighed into another Voltalef flask which was cooled to −196 °C and carefully evacuated. Hydrogen fluoride (25 ml) was condensed into this vessel.

The mixture was warmed to 25 °C and transferred (in the liquid state) to the UF_5 flask. Upon agitation, the liquid phase showed, after a few minutes, a blue-green color which did not increase notably in the following hours. A solid brownish gray residue (1.9 g) remained in the bottom of the flask. The elemental analysis showed this residue to contain mainly uranium(V), together with a small proportion of U(IV), resulting possibly from the presence of an impurity in the starting material (β-UF_5). The blue solution was then passed through the filter into the flask formerly containing the HF–H_2O mixture. A slow removal of all volatile material in vacuo at 25 °C yielded 5.8 g of a green solid which proved to be oxonium hexafluorouranate(V) (weight calculated for 25.8 mmol: 9.57 g).

Anal. Calcd for $H_3O^+UF_6^-$: H_2O, 4.85; F, 30.0; U, 64.0; U(IV):U(VI), 1:1. Found: H_2O, 3.8 ± 1; F, 30 ± 2; U, 64.8 ± 1; U(IV):U(VI), 1.05 ± 0.02.

Properties of $H_3O^+UF_6^-$

Oxonium hexafluorouranate(V) is a green crystalline solid, slightly soluble in anhydrous hydrogen fluoride which seems to decompose it by retaining water, as upon dissolving $H_3O^+UF_6^-$ in HF, only a slight blue coloration was observed and a gray solid residue appeared. Examination of the visible, near-infrared, and Raman spectra of such solutions showed evidence for the presence of H_3O^+ and UF_6^- species, as will be discussed later.

The calorimetric study indicated that $H_3O^+UF_6^-$ is stable only up to 68 ± 1 °C. At higher temperatures, an endothermic decomposition occurs, which produces a maximum thermal effect at 108 ± 2 °C (in the experimental conditions used).

This decomposition is complete and irreversible; after being heated to 250 °C, a sample shows thermal phenomena neither upon cooling nor during a second heating. X-ray powder diffraction patterns showed the solid decomposition products to be UF_4 and UO_2F_2, suggestive of the decomposition

$$2H_3O^+UF_6^- \rightarrow UF_4 + UO_2F_2 + 6HF$$
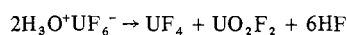
The calibration of the thermograms (thermal effect vs. time) indicated the enthalpy of decomposition to be 18 ± 0.4 kcal mol^{-1}, assuming the formula $H_3O^+UF_6^-$.

As the heats of formation of UF_4(s), UO_2F_2(s), and HF(g) are respectively −443,[7] −391,[8] and −64 kcal mol^{-1},[9] if the reaction written above is assumed to take place, then the heat of formation of the adduct $H_3O^+UF_6^-$ can be deduced from our measurements: ΔH_f = −628 ± 2 kcal mol^{-1}. For the salt $NO^+UF_6^-$, the enthalpy of the reaction

$$NO + UF_6 \rightarrow NOUF_6$$
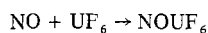
determined by Plurien et al.[10] and the heats of formation of NO[7] and UF_6[11] yield ΔH_f(NOUF$_6$) = −542 kcal mol^{-1}, which is comparable with our value for $H_3O^+UF_6^-$.

The x-ray powder diffraction pattern of $H_3O^+UF_6^-$ is very much similar to that of $NOUF_6$. The corresponding parameters are listed in Table I. $H_3O^+UF_6^-$ is cubic with a = 5.2229 ± 0.0005 Å. This value was obtained using Tournarie's refinement program.[12]

The x-ray powder pattern alone does not permit us to conclude whether the cell is a simple cubic one (like $NOUF_7$[13]) or is cubic centered (like $NOUF_6$[13]). A static or dynamic disorder of at least the H_3O^+ groups is possible.

In one of the syntheses, the diffraction pattern of the sample showed supplementary lines, probably due to a second phase, different from $H_3O^+UF_6^-$ (see Discussion), which was not characterized further.

Low-temperature x-ray powder patterns of $H_3O^+UF_6^-$ indicated that no phase transition occurred between the ambient temperature and −110 °C.

Preliminary ESR measurements at 77 K showed, at a 3-cm wavelength (X band), with a field of about 9000 G, a strong symmetrical line, with a width of approximately 400 G. This line is characteristic of UF_6^- compounds as can be seen from the corresponding value of g, which is −0.78 ± 0.10, very close

Table I. X-Ray Powder Diffraction Data for $H_3O^+UF_6^-$ [a]

hkl	d_{calcd}, Å	d_{obsd}, Å	Intens
100	5.16	5.18	ms
110	3.66	3.63	s
111	2.995	2.995	m
200	2.597	2.609	w
210	2.325	2.330	ms
211	2.123	2.120	s
220	1.840	1.840	m
300, 221	1.735	1.735	ms
310	1.647	1.646	m
311	1.595	1.595	mw
222	1.504	1.504	vw
320	1.445	1.446	mw
321	1.393	1.394	m
410, 322	1.264	1.264	mw
411, 330	1.229	1.231	w
331	1.196	1.197	vw
420	1.167	1.166	vw
421	1.138	1.139	w
332	1.112	1.111	w
422	1.065	1.064	w
500, 430	1.043	1.042	w
510, 431	1.023	1.023	ms
511, 333	1.004 2	1.003 3	vw
520, 432	0.969 1	0.968 7	m
521	0.952 9	0.952 7	w
522, 441	0.908 66	0.908 96	w
530, 433	0.895 23	0.895 32	w
531	0.882 38	0.882 21	w
600, 442	0.870 11	0.869 15	w
611, 532	0.847 00	0.847 14	m
621, 540, 443	0.815 52	0.815 61	m
541	0.805 78	0.805 87	mw
533	0.796 38	0.796 49	w
622	0.787 33	0.787 31	vw
630	0.778 56	0.778 60	m

[a] Simple cubic cell; a = 5.2229 ± 0.0005 Å.

to those published by Rigny et al.[14] for UF_6^- complexes, i.e., −0.768 for $LiUF_6$ and −0.748 for $NOUF_6$. The line width is similar to that of $NOUF_6$ but notably larger (about 10 times) than for complexes like $LiUF_6$ or $NaUF_6$,[14] and this might be correlated to the nonspherical shape of the cation in the NO^+ and H_3O^+ salts.

Vibrational Spectra. The bands observed in the infrared and Raman spectra of $H_3O^+UF_6^-$ are listed in Table II, together with the proposed assignments. Although there were no difficulties in obtaining reproducible infrared spectra, it was very difficult to get stable Raman signals, because of the partial decomposition of $H_3O^+UF_6^-$ caused by the impact of the laser beam, a fact which not only altered the Raman emission but also caused an etching of the glass capillary or the spinning cell.

In the far-infrared region (40–250 cm^{-1}), the spectrum showed no well-defined signals, but two broad bands of weak intensities could nevertheless be observed in the 140–180 and 220–280 cm^{-1} zones. The first may reasonably be attributed to UF_6^- ($\nu_4(F_{1u})$), according to Ryan,[18] whereas the second one may be due to lattice modes.

The wavelengths and relative intensities of the bands observed in the visible and near-infrared regions are summarized in Table III, together with tentative assignments.

Discussion

We have established that the interaction of equimolar amounts of uranium pentafluoride and water in HF solutions renders U(V) partially soluble by producing a stable 1:1:1 adduct (HF, H_2O, UF_5). The oxidation state U(V) for uranium in the ion UF_6^- has been confirmed by ESR spectroscopy. X-ray diffraction measurements of $H_3O^+UF_6^-$ indicate some relationship to $NO^+UF_6^-$. The vibrational spectra show that the adduct is ionic, containing pyramidal

Table II. Bands Observed in the Infrared and Raman Spectra of $H_3O^+UF_6^-$, at 25 °C, and Their Assignments

Infrared				Raman				
		Assign[a]		Freq, cm⁻¹, and rel intens			Assign[a]	
Freq, cm⁻¹	Intens	H_3O^+	UF_6^-	Solid	HF soln		H_3O^+	UF_6^-
3400	s, br	$\nu_1(A_1)$		625 (10)	627 (10)			$\nu_1(A_{1g})$
2950	s, br	$\nu_3(E)$		Not obsd				$\nu_2(E_g)$
1610	s	$\nu_4(E)$		180 sh				
940	vs	$\nu_2(A_1)$		198 (5)	188 (5.4) br			$\nu_5(F_{2g})$
515	m		$\nu_3(F_{1u})$	215 (6)				
				1620 (0.55)			$\nu_4(E)$	

[a] Assignments for the H_3O^+ vibrations were obtained by comparison with the frequencies published by Christe et al.,[15] concerning H_3O^+Sb-F_6^- and $H_3O^+AsF_6^-$ complexes. Assignments for the UF_6^- vibrations were made according to data previously published by Frlec and Hyman,[16] Bougon,[17] and Ryan.[18]

Table III. Wavelengths and Relative Intensities of the Visible and Near-Infrared Bands for $H_3O^+UF_6^-$ Solid and Its Solution in HF

Solid (in Nujol)			HF soln		
Wavelength, nm	Rel intens	Assign[a]	Wavelength, nm	Rel intens	Assign[a]
1270	3.2	$\Gamma_7 \rightarrow \Gamma_{7'}$, $\Delta\nu_3 = +1$	625 sh	6.4	$\Gamma_7 \rightarrow \Gamma_6$, $\Delta\nu_1 = +1$
1337	5.3	$\Gamma_7 \rightarrow \Gamma_{7'}$, $\Delta\nu_4 = +1$	650	10	$\Gamma_7 \rightarrow \Gamma_6$, fund.
1362	10	$\Gamma_7 \rightarrow \Gamma_{7'}$, fund.			
1391	4.0	$\Gamma_7 \rightarrow \Gamma_{7'}$, $\Delta\nu_4 = -1$	727	7.3	$\Gamma_7 \rightarrow \Gamma_{8'}$
1440	~4, br	$\Gamma_7 \rightarrow \Gamma_{7'}$, $\Delta\nu_3 = -1(?)$	795	6.8	
1733	0.3	$\Gamma_7 \rightarrow \Gamma_8$			
1782	0.2				

[a] Assignments were made according to data published by Ryan[18] and Reisfeld and Crosby.[19]

H_3O^+ cations and octahedral UF_6^- anions. These anions appear to be distorted in the solid phase as three bands are observed for the frequency assigned to the UF_6^- $\nu_5(E)$ mode; a splitting of the assigned $\Gamma_{8'}$ energy level also suggests[3] that the anion may be distorted in solution as well. The near-infrared spectrum of $H_3O^+UF_6^-$ is much closer to the spectra of $LiUF_6$, $NaUF_6$, and $CsUF_6$, as described by Penneman et al.,[20] than to the spectra of the KUF_6 or $RbUF_6$ type.

Although the heats of formation of $NO^+UF_6^-$ and H_3O^+-UF_6^- are similar, the latter exhibits a rather low thermal stability; this remark also applies if comparisons are made with the thermal stabilities of $H_3O^+AsF_6^-$ and $H_3O^+SbF_6^-$.[15]

The formation of $H_3O^+UF_6^-$ could reasonably be expected as similar compounds have been obtained by Christe et al.,[15] i.e., $H_3O^+SbF_6^-$ and $H_3O^+AsF_6^-$; nevertheless uranium pentafluoride is a weaker acid than antimony and arsenic pentafluorides in HF and this may explain why the adduct formation was not quantitative. Water is, like the alkali metal fluorides,[20] a basic solute in HF.[21]

A study of U(V) solutions in hydrofluoric acid led Asprey and Penneman[22] to conclude that the hydrates $HUF_6\cdot2.5H_2O$ and $HUF_6\cdot1.25H_2O$ were formed from mixtures containing larger concentrations of water than ours. In their paper these authors made the comment that the necessary presence of water to dissolve UF_5 in HF implied that one of the two released ions, either UF_6^- or H^+, had to be hydrated. The last assumption is in harmony with our work.

The visible and near-infrared absorption spectra we have obtained for $H_3O^+UF_6^-$ are almost identical with those published by Asprey and Penneman,[22] and one might believe that only one species exists and that Asprey and Penneman had synthesized $H_3O^+UF_6^-$. Although we cannot completely exclude this possiblity, the two hydrates obtained by Asprey and Penneman may be hydrates of $H_3O^+UF_6^-$. Our observation of a second distinctive solid phase in one of our syntheses, without notable changes in the observed spectra, is in harmony with the $H_3O^+UF_6^-$ being accompanied by another very much less abundant species which could possibly be $H_3O^+UF_6^-\cdot H_2O$. The latter is analogous to $H_5O_2^+SbF_6^-$ mentioned by Bonnet et al.[2]

In conclusion, $H_3O^+UF_6^-$ is easy to synthesize and is stable at room temperature, although it possesses a low thermal stability. It appears to be completely ionic and may possibly form hydrates.

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Structural Study and Properties of the Alkali Metal, Nitrosyl, and Ammonium Hepta- and Octafluorouranates(VI)

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The thermal decomposition of the heptafluorouranates(VI) of the alkali metals is shown to take place in two steps. The first step gives the octafluorouranates(VI) and UF_6, and the decomposition rate is noticeable at temperatures above 100, 130, 150, and 210 °C for the Na, K, Rb, and Cs salts, respectively. The second step for Na_2UF_8 yields pure NaF and UF_6 above 300 °C, whereas the decomposition temperatures for the K, Rb, and Cs salts are above 300, 350, and 400 °C, respectively. Depending on the decomposition conditions, F_2 and M_2UF_7 (M = K, Rb, Cs) or F_2, UF_6, and M_3UF_8 are formed. The heptafluorouranates(VI) of all the cations studied, except for ammonium, were shown to exhibit dimorphism. The parameters of their cubic form were obtained and are as follows: KUF_7; $a = 5.22$ Å; $RbUF_7$; $a = 5.385$ Å; $CsUF_7$; $a = 5.517$ Å; $NOUF_7$; $a = 5.334$ Å; NH_4UF_7; $a = 5.393$ Å; $NaUF_7(fccub)$, $a = 8.511$ Å, $Z = 4$. The x-ray pattern of the low-symmetry form of $CsUF_7$ just below the solid transition temperature (15 ± 1 °C) was indexed with a tetragonal cell where $a = 5.50$ Å and $c = 5.37$ Å. The x-ray diagrams of the low symmetry form of the other MUF_7 salts were not indexed, whereas those of the octafluorouranates were indexed with orthorhombic cells. The vibrational spectra of the hepta- and octafluorouranates were found to be very dependent on the temperature, and for the same temperature on the cation size. In the solids at high temperature the disordered F positions are likely to be averaged to give pseudo-D_{5h} and O_h symmetry structures for the UF_7^- and UF_8^{2-} ions, respectively. At lower temperature, as the motions are frozen out, the observed spectra for the hepta- and octafluorouranates arise from structures of symmetry no higher than C_{2v} and D_{2d}, respectively. The ions UF_7^- and UF_8^{2-} were characterized in nitrosyl or cesium fluoride HF solutions, which were found to exchange F^- ions with these anions. Based on observation of the chemical exchange between UF_6 and UF_7^- and on a comparative study of the WF_7^- ion, a fluoride ion transfer mechanism is also found for UF_7^- dissolved in acetonitrile. Some trends observed in this study, like the thermal decomposition temperatures or the relative symmetries, are thought to arise from the differences in the cation–anion interaction. This interaction is stronger with smaller cations, which results in more distorted anions, less ionic U–F bonds, and paradoxically less stable complexes.

Introduction

The syntheses and/or properties of hepta- and octa-fluorouranates(VI) have been described by several authors.[2-28] In a previous paper, in which the results of a study of the CsF and NOF/UF_6 systems were reported,[27] it was claimed, mainly from vibrational data, that the heptafluoro and oc-tafluoro anions UF_7^- and UF_8^{2-} could have, at least in the solid state, a structure derived from a slight distortion of the idealized bipyramidal (D_{5h}) and cubic (O_h) structures, re-spectively. In a simultaneous paper,[28] in which x-ray and neutron diffraction work on $NOUF_7$ was reported, it was said that the diffraction patterns could just as well be representative of a monocapped octahedron provided that a statistical oc-cupation of the seventh fluorine atom in the $x'x'x'$ sites was considered. To clear up this apparent discrepancy, a more extensive study was done on this subject in order to obtain a better idea of the structures of the UF_7^- and UF_8^{2-} ions. Some of the corresponding salts were studied both as solids and in solution, using vibrational spectroscopy, x-ray diffraction, and ^{19}F NMR spectroscopy. In addition to the data obtained on the anions themselves or their corresponding alkali metal or nitrosyl salts (such as solid–solid transitions or crystalline structures), some conclusions regarding the effect of the counterion on properties of these salts are given.

Experimental Section

Materials. The compounds UF_6, WF_6, F_2, and HF were purchased from Comurhex; UF_6 was purified from HF by pumping at dry ice temperature; HF was treated with fluorine before use; and F_2 was used without purification. The alkali metal fluorides were purchased from Prolabo and dried either by melting in a crucible followed by cooling in a dry atmosphere or by degassing at 250 °C. NH_4F purchased from Prolabo was used without purification. NOF was produced by first condensing NO, purchased from "l'Air Liquide", and F_2 together at liquid nitrogen temperature in a Monel reactor and then allowing the vessel to warm up to room temperature. In a similar manner, except in Kel-F reactors, the binary mixtures of CsF or NOF with anhydrous HF were obtained by condensing HF onto CsF or NOF. Acetonitrile or SO_2, purchased from Prolabo, was stored over P_2O_5 and introduced onto the sample by vaporization and

condensation. Prior to use, propylene carbonate (4-methyl-2-dioxolone, $C_4H_6O_3$), purchased from Koch-Light Laboratories, was stored over 5 Å molecular sieves from Union Carbide International Co., and poured directly onto the sample in the drybox.

Apparatus. The volatile materials were transferred in a vacuum line made for the most part of Monel Metal tubing equipped with valves purchased from F. W. Co. and with differential gauges from "Etudes et Constructions Aéronautiques". For reactors, depending on the experimental requirements, glass bulbs, Kel-F tubes, Monel cylinders, or high-pressure vessels were used, these vessels being attached to the vacuum line through Monel, Kel-F, or Autoclave Engineer high pressure Monel valves. The nonvolatile solid samples were transferred in a drybox containing P_2O_5 as a desiccant.

X-Ray Diffraction Patterns. The Debye–Scherrer powder patterns were taken using a 114-mm diameter Philips instrument with copper $K\alpha$ radiation (1.5418 Å). The samples were contained in quartz capillaries (~ 0.5 mm) and studies in the temperature range +40 to −180 °C were made possible by use of a Meric cryostat.

Spectra. Infrared spectra were recorded with a Beckman Model IR 9 and a Perkin-Elmer Model 457 in the ranges 4000–400 and 4000–250 cm^{-1}, respectively.

A few measurements were also made in the far-infrared region (400–40 cm^{-1}) using an FS 720 spectrophotometer. Powders were pressed between two thin plates of AgCl 12 mm in diameter or as a Nujol mull between plates of KBr or polyethylene disks. Solutions were studied using Barnes polyethylene molded cells (path length 0.2 mm). These cells were filled in the drybox with a Teflon syringe. The Raman spectra were recorded with a Coderg Model T 800 using the 514.5 nm line of a Model 165 Spectra Physics laser as the exciting light. For these spectra, the neat powders were contained in glass capillaries (~ 2 mm) whereas the solutions were contained in KelF or FEP Teflon tubing (6 mm i.d.). The low-temperature spectra were obtained either with an Air Liquide cryostat for the liquid helium temperature range or a Coderg cryostat for temperatures above liquid nitrogen, in which cases the solid samples were contained in 30 cm long, 4 mm o.d., glass tubes or 8 mm long, ~ 2 mm o.d. capillaries, respectively. The frequency accuracy was estimated to be approx-imately ± 3 cm^{-1} for the infrared spectra and ± 1 cm^{-1} for the Raman spectra. The visible and near infrared spectra which were used for a further identification of the residues from the thermal decomposition of the octafluorouranates were recorded on a Cary 14 instrument. The corresponding powders were studied as Nujol mulls between two CaF_2 plates.