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Synthesis and Characterization of Uranium(V) Fluoride Fluorosulfates and Uranium(V) Oxyfluorosulfate: $UF_3(SO_3F)_2$, $UF(SO_3F)_4$, and $UO(SO_3F)_3$

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The new uranium(V) fluoride fluorosulfate compounds $UF_3(SO_3F)_2$ and $UF(SO_3F)_4$ and uranium(V) oxyfluorosulfate $UO(SO_3F)_3$ have been synthesized. $UF_3(SO_3F)_2$, a pale green solid, resulted from the reaction of UF_5 and $S_2O_6F_2$ in $CFCl_3$ at 40 °C for 20 days; under these conditions the solvent also reacted and was partly transformed into $CFCl_2OSO_2F$ and CF_2Cl_2. The beige solid $UF(SO_3F)_4$ was prepared by mixing UF_6 and SO_3 in $CFCl_3$ at low temperature (<-50 °C) and evaporating the solvent. Its thermal decomposition at 80–100 °C yielded $UO(SO_3F)_3$, a tetragonal gray-beige solid. These three compounds were characterized by chemical analysis. Their thermal stabilities and vibrational and electronic spectra are also reported. The +5 oxidation state of uranium was confirmed by magnetic susceptibility measurements. Despite several attempts under different conditions, no uranium(VI) fluorosulfate or fluoride fluorosulfate was obtained.

Introduction

In an effort to understand the reaction mechanism which led to the synthesis of the previously reported uranium(V) difluoride tris(fluorosulfate), $UF_2(SO_3F)_3$,[1] further experiments were performed. The results of these investigations are reported herein, together with a few properties of the new compounds encountered during these studies.

Experimental Section

Materials and Apparatus. Details concerning the starting materials and the apparatus used for the synthesis and study of these new compounds may be found in a previous publication[1] dealing with $UF_2(SO_3F)_3$. The preparation of uranium pentafluoride (β-UF_5) was described in ref 2. Peroxydisulfuryl difluoride ($S_2O_6F_2$) was prepared according to the Cady method.[3] Fluorine and chlorine trifluoride (pure grade) were supplied by Comurhex (Pierrelatte, France).

Synthesis of $UF_3(SO_3F)_2$. This was carried out in $CFCl_3$ solution, by the reaction of UF_5 and $S_2O_6F_2$, at moderate temperature (40 °C); under these conditions, the blue-green compound $UF_2(SO_3F)_3$ is normally obtained. However, if the products are left in contact for a longer period, the compound turns into a pale green solid, uranium(V) trifluoride bis(fluorosulfate), $UF_3(SO_3F)_2$. It should be pointed out that this compound had been previously detected, in a less pure form, as a product of the reaction of SO_3 with liquid UF_6 at 65 and 90 °C. The impurities consisted mainly of uranyl derivatives, as identified by their fluorescence spectra.[4]

In a typical experiment, uranium pentafluoride (4.808 g, 14.44 mmol) was weighed in a 100-mL glass flask, in a drybox. This flask was then transferred to the vacuum line, evacuated, and cooled to −196 °C. $S_2O_6F_2$ (6.587 g, 33.27 mmol) and $CFCl_3$ (79.25 g) were then condensed onto the UF_5. The mixture was warmed slowly to 40 °C and kept at this temperature for 20 days. Removal of all volatile materials in vacuo yielded 6.262 g of solid $UF_3(SO_3F)_2$ (weight calculated for 14.44 mmol: 7.12 g). Anal. Calcd for $UF_3(SO_3F)_2$: U, 48.27; S, 13.0; F, 19.26; O, 19.47; U(IV)/U(VI) ratio, 1.0. Found: U, 48.4 ± 0.05; S, 13.07 ± 0.05; F, 19.07 ± 0.05; O (by difference), 19.43 ± 0.15; U(IV)/U(VI), 1.01 ± 0.01.

The supernatant $CFCl_3$ solution, examined by ^{19}F NMR spectroscopy, turned out to contain unreacted $S_2O_6F_2$,[5] together with UF_6,[6] $S_2O_5F_2$,[5] CF_2Cl_2,[7] and $CFCl_2OSO_2F$,[8] with the approximate molar ratios as 1:0.32:0.14:0.64:3.58. From the initial amount of UF_5 and that of $UF_3(SO_3F)_2$ produced, 1.74 mmol of UF_6 was expected to be present in the mixture. From this value and the above-mentioned relative concentrations, the amount of $S_2O_5F_2$ was found to be compatible with its concentration in $S_2O_6F_2$ (ca. 2% initially), whereas only 0.6% of $CFCl_3$ was converted to CF_2Cl_2 and 3.4% to $CFCl_2OSO_2F$. On the other hand, 38% of $S_2O_6F_2$ had reacted to yield $UF_3(SO_3F)_2$, and 29% to yield $CFCl_2OSO_2F$. As a whole, if the reaction of the Freon is disregarded as not being within the scope of the present study, it can be concluded that, in these experimental conditions, $S_2O_6F_2$ has reacted with UF_5 to form $UF_3(SO_3F)_2$ and that a fluorination of UF_5 has also taken place.

Synthesis of $UF(SO_3F)_4$. This was also carried out in $CFCl_3$ solution, by reaction of UF_6 and SO_3 at low temperature. If $CFCl_3$ and UF_6 are condensed at −196 °C onto SO_3, upon warming to about −60 °C, a red-brown solution appears, the color of which increases with increasing time. This solution, studied by NMR, appeared to contain mainly UF_6 (δ −769.2 ppm, with respect to internal $CFCl_3$, used as a reference throughout this work), together with a smaller amount (about 3 times less) of $S_2O_6F_2$. It is noticeable that no other NMR line, which could have been assigned to a uranium(VI) fluoride fluorosulfate, was observed in this solution; the small shift which is observed for UF_6 (−769.2 ppm, compared to −764.7 ppm for UF_6 alone in $CFCl_3$) is probably attributable to a solvation of this species by SO_3. Above −50 °C, the red-brown solution decomposes rapidly, yielding a blue-green solid, $UF_2(SO_3F)_3$, which is conveniently prepared in this way in a very pure state. At this stage, the supernatant liquid contains small amounts of UF_6 and $S_2O_6F_2$ dissolved in $CFCl_3$, as shown by NMR and microsublimation, together with traces of other unidentified S–F compounds. However, if the red-brown solution is kept at −50 °C and $CFCl_3$ is pumped off slowly and completely, a beige solid is obtained, which is uranium(V) fluoride tetrakis(fluorosulfate) $UF(SO_3F)_4$. This compound, which is stable at room temperature, is, in turn, rapidly transformed into $UF_2(SO_3F)_3$ by contact with $CFCl_3$.

In a typical experiment, sulfur trioxide (ca. 7 mmol) was condensed into a previously evacuated 100-mL glass flask at −196 °C. $CFCl_3$ (ca. 17 mL) and UF_6 (ca. 3 mmol) were subsequently condensed into the flask. The mixture was brought to −70 °C and left to react and to warm gently to −60 °C, for 2 h. A brown color rapidly appeared which was enhanced by agitating several times. $CFCl_3$ (together with excess UF_6) was eliminated from this solution, maintained at −55 °C, by trapping at liquid nitrogen temperature. When the liquid phase had apparently disappeared, the reaction flask was allowed to warm slowly to room temperature and kept under secondary vacuum for 12 h. The beige solid $UF(SO_3F)_4$ (901 mg) was then left deposited in the flask: weight calculated for 7 mmol of SO_3 = 914 mg, assuming the reaction

$$2UF_6 + 10SO_3 \rightarrow 2UF(SO_3F)_4 + S_2O_6F_2$$

Anal. Calcd for $UF(SO_3F)_4$: U, 36.44; S, 19.60; F, 14.54; O, 29.40. Found: U, 36.80 ± 0.05; S, 19.36 ± 0.05; F, 14.32 ± 0.05; O (by difference), 29.5 ± 0.15. The U(IV)/U(VI) ratio (theoretically equal to 1.0) could only be situated in the domain 1–1.8 because of difficulties encountered in the corresponding polarographic determinations with this particular compound.

Synthesis of $UO(SO_3F)_3$. This species results from the thermal decomposition at 80–100 °C of the beige compound $UF(SO_3F)_4$, in a closed vessel, under nitrogen atmosphere. In a typical experiment, 426 mg of $UF(SO_3F)_4$ was weighed into a 20-mL passivated Monel cylinder, in a drybox; the cylinder was then heated to 100 °C for 2 h. After reaction, the contents of this vessel appeared as a gray-beige solid, which proved to be uranium(V) oxytris(fluorosulfate), $UO(SO_3F)_3$. Anal. Calcd for $UO(SO_3F)_4$: U, 43.19; S, 17.42; F, 10.34; O, 29.03. Found: U, 43.10 ± 0.05; S, 17.52 ± 0.05; F, 10.39 ± 0.05; O (by difference), 29.0 ± 0.15.

Reaction of $UF(SO_3F)_4$ with Fluorine. This reaction was investigated in order to try to obtain uranium(VI) fluorosulfates. It was

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Table I. X-ray Powder Diffraction Data for $UF_3(SO_3F)_2$ and $UO(SO_3F)_3$

$UF_3(SO_3F)_2$		$UO(SO_3F)_3$	
d, Å	Intens	d, Å	Intens
6.32	m	8.23	s
6.10	w	5.71	vw
5.21	ms	4.70	ms
5.03	w	4.09	w
4.62	vw	3.64	m
4.20	s	3.336	s
3.91	w	3.103	w
3.745	ms	2.860	w
3.512	ms	2.733	ms
3.173	m	2.450	vw
3.118	m	2.366	w
3.015	m	2.351	w
2.957	mw	2.277	vw
2.900	w	2.115	m
2.642	mw	2.056	vw
2.583	vw	1.982	m
2.533	w	1.934	vw
2.520	w	1.861	mw
2.408	w	1.829	w
2.360	Trace	1.791	ms
2.336	Trace	1.734	mw
2.268	Trace		
2.241	Trace		
2.139	mw		
2.106	m		
2.056	m		
1.998	m		
1.935	w		
1.907	mw		
1.868	w		
1.849	mw		

carried out in a 35-mL passivated Monel cylinder. $UF(SO_3F)_4$ (330 mg, ca. 0.5 mmol) was weighed into this vessel in a drybox. The cylinder was then transferred to the line and evacuated. Gaseous fluorine (2000 Torr, ca. 4 mmol) was introduced and allowed to react at 50 °C for 20 h. After subsequent pumping, a dry green solid was left in the vessel. From its x-ray pattern and Raman and infrared spectra, this solid was characterized as $UF_2(SO_3F)_3$. A substitution of SO_3F groups by fluorine atoms thus appears to have been the only effect of this reaction. In view of this result, and to avoid a possibly adverse temperature effect on SO_3 displacement, a second trial was made, at room temperature, using chlorine trifluoride as a stronger fluorinating agent.

Reaction of $UF(SO_3F)_4$ with Chlorine Trifluoride. $UF(SO_3F)_4$ was found to react instantaneously at room temperature with gaseous or liquid ClF_3, and uranium was recovered as UF_6. The experiment was achieved with 8 mmol of ClF_3 which was condensed at liquid nitrogen temperature onto 0.16 mmol of $UF(SO_3F)_4$. The mixture yielded a homogeneous solution at room temperature which left no solid residue after being pumped. Its ^{19}F NMR spectrum showed, at −20 °C, the presence of $S_2O_6F_2$, SO_2F_2,[5] $S_2O_5F_2$, and $ClOSO_2F$,[9] with their relative molar ratios as 0.09:0.53:0.57:1. In addition to ClF_3, UF_6 and traces of ClO_2F[10] were also found to be present. The broadness of both the ClF_3 unique line (1100 Hz at 25 °C) and the UF_6 line (2000 Hz at 25 °C), indicated that these species were involved in chemical exchange processes. On the basis of data previously published on the BrF_3–SO_3 system[11-13] and the known F^--acceptor properties of UF_6,[14] a possible mechanism of exchange could be

$$ClF_3 + SO_3 \rightleftarrows ClF_2^+ + SO_3F^-$$

$$UF_6 + SO_3F^- \rightleftarrows UF_7^- + SO_3$$

Probably owing to their low concentration no ionic species were seen in the Raman spectrum of the solution.

A mixture of 8 mmol of ClF_3 and 0.1 mmol of UF_6, to which about 0.5 mmol of SO_3 was added, also showed that both ClF_3 and UF_6 took part in chemical exchanges. Nevertheless, the main effect turned out to be the fluorination of SO_3, since the compounds SO_2F_2, $S_2O_5F_2$, $S_2O_6F_2$, and $ClOSO_2F$, with their relative molar ratios as 0.18:0.20:0.93:1 were found by NMR as well as traces of FSO_3F[5] and ClO_2F.

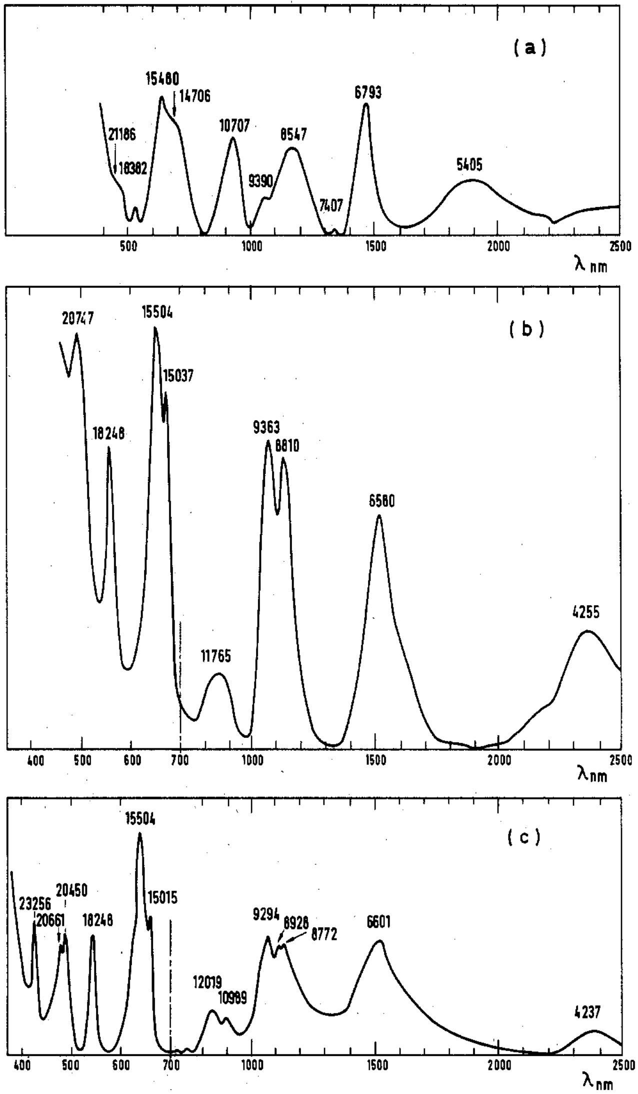

Figure 1. Visible and near-infrared spectra of $UF_3(SO_3F)_2$ (a), $UF(SO_3F)_4$ (b), and $UO(SO_3F)_3$ (c). (Intensities were corrected from the scattering effect dependent background; the frequencies of the maxima, in cm^{-1}, are indicated on the curves.)

Properties of These New Compounds

Thermal Stability. The three compounds are stable at room temperature, in a dry atmosphere, but are readily decomposed by aerial moisture. Calorimetric measurements have shown that $UF_3(SO_3F)_2$ decomposes at 86 ± 1 °C with an enthalpy of decomposition ΔH equal to 4.9 ± 0.2 kcal mol^{-1} to give an amorphous, green, rubber-like compound which could not be further characterized. On the other hand, $UF(SO_3F)_4$ decomposes at 70 ± 1 °C with an exothermic effect ($\Delta H = -4.2 \pm 0.2$ kcal mol^{-1}) to give $UO(SO_3F)_3$. The latter was found to be stable up to 300 °C.

It should be mentioned that the decomposition of $UF_3(SO_3F)_2$ was also investigated by contacting it with $CFCl_3$ at 90 °C for 200 h; after removal of the solvent, a green amorphous compound was obtained in the same way as when the decomposition was carried out in the calorimeter. The difference in appearance between the two resulting solids (a fine powder and rubber-like species) is probably due to the fact that the rubber-like phase contains SO_3.

X-ray Data. The positions and intensities of the lines observed on the x-ray powder diffraction patterns of $UF_3(SO_3F)_2$ and $UO(SO_3F)_3$ are listed in Table I. The X-ray powder pattern of $UF_3(SO_3F)_2$ indicates a rather low symmetry of the lattice and could not be indexed. $UF(SO_3F)_4$ could only be isolated as an amorphous phase. $UO(SO_3F)_3$

Table II. Vibrational Frequencies (cm^{-1}), at 300 K, for $UF_3(SO_3F)_2$, $UF(SO_3F)_4$, and $UO(SO_3F)_3$

$UF_3(SO_3F)_2$				$UF(SO_3F)_4$		$UO(SO_3F)_3$				
Infrared		Raman		Infrared		Infrared		Raman		
Freq	Intens	Freq	Intens	Freq	Intens	Freq	Intens	Freq	Intens	Assign[a]
1430	sh			1485	s			1395	2.2	ν_{SO_3}
1385	vs	1380	<0.5	1382	vs	1383	s	1380	2.2	
1300	vs									
1220	sh			1255	sh	1260	s, br			
1180	vs, br	1183	<0.5	1190	vs, br	1150	s	1150	6.0	
1100	m	1113	1.0					1100	4.5	
1078	sh	1077	1.0	1078	s	1080	s	1042	1.6	
985	m	993	<0.5							*b*
972	sh	980		987	m	982	m			
945	w	930								
		903	0.7							
860	s	862	0.7	850	s	880	s	885	4.6	ν_{S-F}
840	s	840	<0.5			860		870	4.2	
						850				
625	sh	628	10.0	630	m			627[c]		ν_{U-F}
612	s	607	2.4	605	m			606[d]		
596	s	594	sh	585	sh	585	m			Def and lattice modes
580	s							565	8.5	
560	m	557	0.7	558	s	558	s	556	7.0	
548	m	549	0.9							
420	w	430	0.5	420	w	428	w	430	5.2	
		405	<0.5			419	vw	417	3.8	
						402	vw			
		220	1.0					188	2.3	
		208	0.8					160	2.1	
								109	4.9	

[a] Assignments were made by comparison with the data given in ref 15 for the fluorosulfate groups and ref 1 for the U-F vibration. [b-d] These bands, the intensities of which vary from one spectrum to the other, can be attributed to the presence of traces of uranyl compounds (*b*), traces of $UF_3(SO_3F)_2$ (*c*), or traces $UF_2(SO_3F)_3$ (*d*).

exhibits an X-ray pattern much simpler than $UF_3(SO_3F)_2$. The first reflections can be indexed into a cubic-centered cell, with a = 11.44 Å, which is a first approximation of the lattice. An automatic indexation program leads to a related tetragonal cell: a = 16.43 Å, c = 11.43 Å.

Vibrational Data. The bands observed on the infrared and Raman spectra of the three compounds are listed in Table II, together with approximate assignments. Only general features were obtainable for these spectra. Probably owing to a noncrystallized state and/or absorption in the region of the available exciting lines (647.1, 514.5, and 488.0 nm), no Raman spectrum was obtained for $UF(SO_3F)_4$. From these vibrational spectra, the only information that can be obtained, concerning the structure of the new compounds, is that fluorosulfate groups are present, since both the corresponding S–F and S–O stretching vibrations are observed. From the number and location[15] of the bands recorded, it is also likely that bidentate bridging groups are present. A discussion concerning the possible uranium environment has already been made for $UF_2(SO_3F)_2$[1] and will not be repeated here. However, it should be noted that, on the basis of the data obtained by Ryan et al.[16] on β-UF_5, eight-coordination about the uranium atoms is most likely. With such an assumption, one could say that at least one SO_3F group in $UF(SO_3F)_4$ is covalent; this is in agreement with the strong infrared band at 1485 cm^{-1}, which is close to the SO_2 asymmetric stretching vibration found[17] for covalent SO_3F groups. For $UF_3(SO_3F)_2$, one should admit either fluorine bridging or one tridentate group, whereas for $UO(SO_3F)_3$, the eight-fold coordination requires either a tridentate group or oxygen bridging. The infrared spectrum seems to favor this latter hypothesis, since no strong band characteristic of an U–O double bond was observed.

Visible and Near-Infrared Spectra. The electronic absorption spectra of the three compounds are shown on Figure 1. These spectra are characteristic of the crystal field splitting and vibronic coupling effects on the transition $^2F_{5/2} \rightarrow {}^2F_{7/2}$ of the Rn $5f^1$ system[18-23] and thus confirm the +5 oxidation state of uranium found by chemical analyses. Nevertheless, in view of the unknown actual uranium environment, no assignment was given.

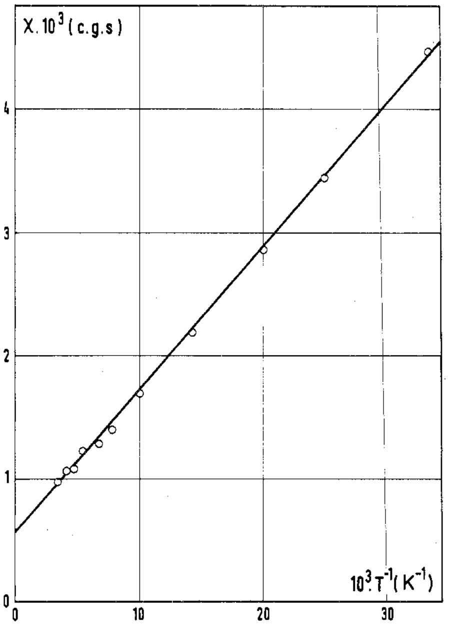

Figure 2. Magnetic susceptibility dependence on temperature for $UF_3(SO_3F)_2$.

Magnetochemistry. The magnetic measurements were made in order to further confirm the oxidation state of uranium.

$UF_3(SO_3F)_2$ has been found to be paramagnetic in the temperature range 5–300 K. The relationship between the magnetic susceptibility χ and the reciprocal temperature T^{-1} is quite linear, as shown in Figure 2, and is indicative of a Curie law $\chi = CT^{-1} + N\alpha$, where C is the Curie constant (C = 0.125

± 0.01 cgsu) and $N\alpha$ is a second-order Zeeman term ($N\alpha = (0.59 \pm 0.05) \times 10^{-3}$ cgsu). The effective magnetic moment μ_e was determined from the Curie constant: $\mu_e = 2.828C^{1/2} = 1.0\ \mu_B$ (μ_B = Bohr magneton). This value is in good agreement with results for other U(V) compounds.[18,24,25] As far as $UF(SO_3F)_4$ is concerned, its magnetic susceptibility appeared to be positive, but very weak, and not to obey a Curie law. In the temperature range studied (6–250 K), the effective moment varied from 1.1 to 2.8 μ_B. $UO(SO_3F)_3$ also exhibits a weakly positive magnetic susceptibility, but this appeared to be appreciably field dependent, rather more than temperature dependent. With a field of 0.9 T, the effective moment varied from 2.7 to 3.5 μ_B, in the temperature range studied (126–293 K), which owing to its field dependence must be considered as meaningless.

ESR measurements were carried out on powdered samples of $UF_3(SO_3F)_2$ and $UF(SO_3F)_4$, at a 3-cm wavelength (x band). They showed no characteristic signal attributable to U(V)[26-28] in the range of field 0.5–1 T, between 293 and 77 K but, at low temperatures, a pseudofine structure consisting of 27 lines appeared for both compounds, superimposed in the case of $UF_3(SO_3F)_2$ onto a very broad line in the region g = 0.5 to 2.[29] Further measurements are now in progress, in order to elucidate the corresponding structural problems.

Conclusion

As far as the initial aim to understand the mechanism which led to the formation of the uranium(V) fluoride fluorosulfates is concerned, it seems reasonable to assume that an initial adduct, only stable at low temperature, is formed between UF_6 and one or several weakly bonded SO_3 molecules. At higher temperature, this adduct can rearrange to give fluorination of SO_3 into $SO_3F\cdot$ which in turn can either coordinate uranium or dimerize into $S_2O_6F_2$.

The presence of a solvent seems to favor the elimination of SO_3 from $UF(SO_3F)_4$ to give successively $UF_2(SO_3F)_3$ and $UF_3(SO_3F)_2$. Attempts to eliminate one more SO_3 molecule were unsuccessful, since, at higher temperature, removal of SO_3 has to compete with the formation of an oxyfluorosulfate.

As a whole, the present study and the previous one[1] have shown that four, three, or two fluorosulfate groups were able to replace stoichiometrically the corresponding number of fluorine atoms in the UF_5 entity. So far, in the absence of single-crystal X-ray diffraction studies, nothing is known concerning the actual coordination of the uranium atom, but vibrational spectroscopy yielded evidences of bidentate bridging fluorosulfate groups. The presence of such groups allows eightfold coordination of the uranium, as recently found by Ryan et al.[16] for β-UF_5. Finally, it is worth noting that, apart from possible uranyl derivatives, no evidence for the existence of uranium(VI) fluorosulfate or fluoride fluorosulfate has been found in the course of these researches.

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Registry No. $UF_3(SO_3F)_2$, 66171-99-1; $UF(SO_3F)_4$, 66197-68-0; $UO(SO_3F)_3$, 66171-98-0; UF_5, 13775-07-0; $S_2O_6F_2$, 13709-32-5; UF_6, 7783-81-5; SO_3, 7446-11-9; fluorine, 7782-41-4; ClF_3, 7790-91-2.

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