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Acid–base reactions of tungsten and uranium oxide fluorides in anhydrous hydrogen fluoride

Yasushi Katayama [a,*], Rika Hagiwara [b], Yasuhiko Ito[b]

[a] *Division of Nuclear Engineering, Graduate School of Engineering, Kyoto University, Sakyo-ku, Kyoto 606-01, Japan*

[b] *Division of Energy Science and Engineering, Graduate School of Engineering, Kyoto University, Sakyo-ku, Kyoto 606-01, Japan*

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Abstract

The acid–base reactions of tungsten oxide tetrafluoride, WOF_4, and uranium dioxide difluoride, UO_2F_2, have been examined in anhydrous hydrogen fluoride (HF). WOF_4 reacts with silver(I and II) fluorides, AgF and AgF_2, to form complex salts, $AgWOF_5$, $AgW_2O_2F_9$ and $AgFW_2O_2F_9$. $AgFW_2O_2F_9$, which is also prepared by the reaction of $AgW_2O_2F_9$ and F_2 in HF, oxidizes elemental xenon to Xe^{II} in HF at room temperature. UO_2F_2 is a weak fluoro base and only forms salts with strong fluoro acids such as arsenic pentafluoride, AsF_5, in HF. The fluoro acidity of UO_2F_2 seems slightly stronger than that of HF, the reaction with AgF giving a 1:1 compound, $AgUO_2F_3$.

Keywords: Acid–base reactions; Tungsten oxide fluorides; Uranium oxide fluorides; Anhydrous hydrogen fluoride; IR spectroscopy; Raman spectroscopy

1. Introduction

Liquid anhydrous hydrogen fluoride (HF) is a good reaction solvent which is often used for the syntheses of inorganic fluorides, especially those with high oxidation states. In addition to its high oxidation potential, one of the advantages of HF is the ability to stabilize fluoro and oxofluoro complexes which are unstable in aqueous media. For example, the hexapositive state of some actinide elements (M) is very stable in aqueous solutions but only as MO_2^{2+}, whereas various fluoro complexes with the same oxidation state are stabilized in HF. On the other hand, oxo complexes of many transition metals including the actinide series are stable in HF since the oxygen ligand is strongly bound to the metal atom through a double bond, thus making substitution by fluorine atoms difficult.

In this preliminary study, the acid–base reactions of tungsten and uranium oxide fluorides with some fluoro bases and acids have been examined.

2. Experimental details

2.1. Reagents

Hydrogen fluoride (Daikin Kogyo, purity 99% or greater) was dried over K_2NiF_6 (Ozark-Mahoning) to remove trace amounts of water. Fluorine (Daikin Kogyo, purity 99.7%), AsF_5 (Matheson), BF_3 (Nippon Sanso) and Xe (Teisan K.K., purity 99.995% or greater) were used as supplied. Germanium tetrafluoride, GeF_4, was prepared by fluorinating powdered Ge metal in a Monel container at 300 °C, and then distilled into another container after initially removing volatile gases at − 196 °C. Silver(I) fluoride, AgF, was prepared by interacting Ag_2O (Wako Chemicals, purity 99% or greater) with HF. Decomposition of the bifluoride, $Ag(HF)_nF$, was effected by heating at 80 °C under vacuum. Silver(II) fluoride, AgF_2, was prepared by fluorinating $AgNO_3$ (Nakarai Tesque, purity 99.95%) in a Monel container at 250 °C. Cesium fluoride (Nakarai Tesque, extra pure reagent) and KF (Wako Chemicals, purity 98% or more) were dried under vacuum at ~300 °C while WOF_4 was prepared by the reaction of WF_6 (Ozark-Mahoning) with quartz wool (Sankyo Denshi) in HF [1]. Purification was effected by sublimation at ~70 °C under reduced pressure. U_3O_8 was obtained by heating UO_2 (Furukawa Denki Kogyo, depleted uranium) in an alumina crucible in air at ~800 °C and UO_2F_2 was subsequently prepared by fluorinating U_3O_8 in a Monel container at 200 °C. No impurity was detected by IR spectroscopy of the gaseous samples. Similarly, no impurity was detected in the solid materials by X-ray powder diffraction.

2.2. Reactions and instrumentation

All reactions were carried out in FEP tube reactors. The reaction procedures and handling of the air-sensitive mate-

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[*] Corresponding author.

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rials were the same as described elsewhere [2]. X-Ray powder photographs were obtained by a Debye-Scherrer camera of 115 mm diameter with a Rigaku apparatus using Cu Kα radiation (Ni-filtered). Samples were usually packed in 0.3 or 0.5 mm o.d. quartz capillaries (Overseas X-ray) sealed by drawing down in a small oxygen burner flame. IR spectra of the gaseous samples contained in a gas cell fitted with AgCl windows were recorded using a Hitachi Perkin-Elmer 621 spectrometer. The spectra of the solid samples sandwiched between two flat AgCl windows were measured on an FT-IR spectrometer (FT/IR-5M, Nippon Spectroscopic). The Raman spectra of the solid samples were obtained using an NR-1000S (Nippon Spectroscopic) instrument employing the 512.5 and 488 nm lines of an Ar laser (NEC) or the 647.1 nm line of a Kr laser (Spectra Physics) as exciting lines. The samples were loaded in 0.5 mm o.d. quartz capillaries in the same manner as for the X-ray powder diffraction samples.

3. Results

3.1. $AgF+2WOF_4$

AgF (50 mg, 0.394 mmol) and WOF_4 (225 mg, 0.816 mmol) were interacted for several hours in HF (~ 1 ml) at room temperature. After removing the HF, an ivory colored solid was obtained. No weight change was observed after reaction. X-Ray diffraction showed the absence of the starting materials. The solid was considered to be the 1:2 complex salt, $AgW_2O_2F_9$, by comparison of its vibrational spectrum with that of $CsW_2O_2F_9$ [3].

3.2. $AgF+WOF_4$

The mixture of AgF (123 mg, 0.962 mmol) and WOF_4 (266 mg, 0.964 mmol) was loaded into one arm (tube A) of a T-shaped reactor and HF (~ 1 ml) condensed onto the mixture at − 196 °C. An ivory colored precipitate was formed after warming tube A to room temperature. The supernatant solution was decanted into the other arm (tube B) of the reactor and the precipitate washed several times with HF condensed back to tube A. Finally, after evaporating HF, an ivory colored solid (~ 270 mg) remained in tube A and a colorless solid in tube B. Additional evacuation of tube B with warming changed the color of the solid to bright yellow (weight, ~ 80 mg). A large weight loss (~ 40 mg) prevented gravimetric determination of its composition. X-ray diffraction showed that the yellow colored solid was AgF while the ivory colored solid was the same as that obtained from the $AgF+2WOF_4$ interaction.

3.3. $AgF+WOF_4$ (slow evacuation of HF)

AgF (107 mg, 0.843 mmol) and WOF_4 (227 mg, 0.823 mmol) were loaded into one arm (tube A) of a T-shaped reactor and HF (~ 1 ml) condensed onto the mixture at − 196 °C. An ivory colored solid was formed as described above. On removing HF very slowly by condensing into the end of the other arm cooled at 0 °C, a colorless crystalline solid was formed in tube A. No weight uptake was observed after the reaction. X-Ray diffraction detected neither AgF nor WOF_4. The solid was considered to be the 1:1 complex salt, $AgWOF_5$, by comparison of its vibrational spectrum with that of $NOWOF_5$ [4].

3.4. AgF_2+2WOF_4

AgF_2 (168 mg, 1.15 mmol) and WOF_4 (640 mg, 2.32 mmol) were interacted in HF (~ 2 ml) in the presence of F_2 at room temperature. After stirring for ~ 24 h, a dark-purple colored solid was obtained. No weight change was observed after the reaction. No phases corresponding to the starting materials were observed in the X-ray powder pattern. The solid is considered to be the 1:2 complex salt, $AgFW_2O_2F_9$, by the comparison of its vibrational spectrum with that of $AgW_2O_2F_9$.

3.5. AgF_2+WOF_4

AgF_2 (103 mg, 0.706 mmol) and WOF_4 (187 mg, 0.678 mmol) were interacted in HF (~ 2 ml) in the presence of F_2 at room temperature. On removing HF very slowly, a dark-purple colored solid was obtained. No weight change was observed after the reaction. This solid was ascribed to a mixture of $AgFW_2O_2F_9$ and unreacted AgF_2 by X-ray diffraction.

3.6. $AgW_2O_2F_9+F_2$

$AgW_2O_2F_9$, prepared as above, was interacted with F_2 in HF (~ 1 ml) at room temperature. The color of the precipitate (ivory) turned to brown after stirring for a while. Additional interaction for 24 h changed the color of the precipitate to dark-purple. X-Ray diffraction of the precipitate detected $AgFW_2O_2F_9$ and AgF_2.

3.7. $AgFW_2O_2F_9+Xe$

$AgFW_2O_2F_9$, prepared as above, was interacted with Xe in HF (~ 1 ml) at room temperature. Over ~ 24 h, the color of the precipitate changed gradually from dark-purple to brown. After removing HF at room temperature, a sublimable and highly reactive colorless solid was crystallized in the upper part of the reaction tube on warming the bottom. The solid was identified as $XeF_2 \cdot WOF_4$ [5] on the basis of its Raman spectrum. X-Ray diffraction showed the residual solid at the bottom of the tube to be a mixture of AgF_2 and $AgW_2O_2F_9$.

3.8. UO_2F_2 + excess AsF_5

UO_2F_2 (190 mg, 0.617 mmol) was interacted with excess AsF_5 in HF (~ 2 ml) at room temperature. The UO_2F_2 dissolved immediately to give a yellow solution. On removing HF slowly, a yellow–green colored solid crystallized. Although a significant weight uptake (81 mg, 0.48 mmol as AsF_5) was observed just after the reaction, X-ray diffraction of the final product showed only a pattern corresponding to UO_2F_2.

3.9. UO_2F_2 + liquid AsF_5 without HF solvent

UO_2F_2 (244 mg, 0.792 mmol) was placed in a reaction tube and AsF_5 (~ 1 ml) was condensed onto it at −77 °C. Under these circumstances, UO_2F_2 did not dissolve. After stirring the mixture for 2 h, a green colored solid was formed. The color of the remaining solid after removing excess AsF_5 at −77 °C faded while the pressure in the tube increased as the temperature was increased. The amount of the gas released was estimated to be ca. 1.3 mmol by tensimetry. IR spectroscopy showed that this gas was pure AsF_5. X-Ray diffraction revealed that the residual solid was UO_2F_2.

3.10. UO_2F_2 + excess BF_3

UO_2F_2 (447 mg, 1.45 mmol) was interacted with excess BF_3 in HF (~2 ml) at room temperature. No color change of the precipitate, gas consumption or weight uptake was observed. X-Ray diffraction identified only UO_2F_2 in the solid.

3.11. UO_2F_2 + excess GeF_4

UO_2F_2 (423 mg, 1.37 mmol) was interacted with excess GeF_4 in HF (~ 2 ml) at room temperature. A green precipitate was formed after stirring the liquid for a while. The color of the solid faded on removing HF. No weight change was observed after the reaction. X-Ray diffraction showed that the residual solid was UO_2F_2.

3.12. CsF + UO_2F_2

CsF (176 mg, 1.16 mmol) and UO_2F_2 (355 mg, 1.15 mmol) were interacted in HF (~ 1 ml) at room temperature. On stirring for several hours, a pale yellow solid was obtained after removing volatile materials at room temperature. A small weight uptake (26 mg, 1.3 mmol as HF) was observed. The X-ray powder pattern of the solid obtained after successive evacuation at ~70 °C was identical with that for $CsUO_2F_3$ prepared from aqueous solution [6]. The Raman spectrum of $CsUO_2F_3$ could not be obtained due to the strong fluorescence of the sample.

3.13. KF + UO_2F_2

KF (32 mg, 0.55 mmol) and UO_2F_2 (172 mg, 0.56 mmol) were interacted in HF (~1 ml) at room temperature. After stirring for several hours, a light greenish solid was obtained after evaporating HF very slowly. X-Ray diffraction showed the solid to be a mixture of $K_3UO_2F_5$ [7] and UO_2F_2. The Raman spectrum of $K_3UO_2F_5$ could not be obtained due to the strong fluorescence of the sample.

3.14. AgF + UO_2F_2

AgF (35 mg, 0.28 mmol) and UO_2F_2 (85 mg, 0.28 mmol) were interacted in HF at room temperature. A light yellow solid was obtained after stirring for 20 h. No weight uptake was observed after removing volatile materials. X-ray diffraction showed no peaks corresponding to the starting materials. The solid is considered to be the 1:1 compound of AgF and UO_2F_2 on the basis of its vibrational spectrum.

3.15. 3AgF + UO_2F_2

AgF (233 mg, 1.84 mmol) and UO_2F_2 (189 mg, 0.614 mmol) were loaded into one arm (tube A) of a T-shaped reactor and allowed to interact in HF (~2 ml) at room temperature. After stirring for several hours, the supernatant solution over the precipitate was decanted into tube B and the precipitate washed several times with HF which was condensed back to tube A. A light yellow solid remained in tube A on removing volatile materials and the colorless solid in tube B was crystallized from the solution used for washing the precipitate. The color of the solid turned to bright yellow an additional evacuation whilst warming tube B. X-Ray diffraction showed the solid in tube A to be a mixture of UO_2F_2 and the 1:1 complex obtained by the interaction of AgF + UO_2F_2. The solid in tube B was AgF alone.

3.16. Excess AgF + UO_2F_2

UO_2F_2 (145 mg, 0.471 mmol) was placed in one arm (tube A) of a T-shaped reactor and AgF (654 mg, 5.15 mmol) in the other arm (tube B). HF (~ 1 ml) was condensed in tube B to prepare a saturated solution of AgF with a small amount of a white precipitate. The solution was decanted to tube A, the mixture stirred for several hours and the supernatant solution then decanted to tube B. In tube A, a bright yellow solid was obtained after evacuating HF with heating so as to decompose $Ag(HF)_nF$. X-Ray diffraction showed the solid to be a mixture of AgF and the 1:1 complex of AgF and UO_2F_2.

4. Discussion

4.1. Acid–base reactions involving WOF_4 in HF

It is known that WOF_4 dissolves to form a monomeric anion, WOF_5^-, and a dimeric anion, $W_2O_2F_9^-$ in HF via the following equilibria [4]:

$$2HF + WOF_4 \rightleftharpoons H_2F^+ + WOF_5^- \qquad (1)$$

Table 1
The X-ray powder diffraction patterns of $AgWOF_5$, $AgW_2O_2F_9$ and $AgFW_2O_2F_9$

$AgWOF_5$		$AgW_2O_2F_9$		$AgFW_2O_2F_9$	
d (Å)	Intensity [a]	d (Å)	Intensity [a]	d (Å)	Intensity [a]
4.92	mw	4.32	w	6.62	w
4.47	s	4.13	s	5.19	vw
4.31	w	3.92	s	4.77	m
4.18	w	3.79	w	4.60	m
3.97	w	3.65	m	4.39	vw
3.75	s	3.50	vw	4.17	s
3.57	s	3.42	s	3.80	s
3.42	s	3.23	m	3.68	mw
3.17	mw	2.59	w	3.33	vs
3.09	m	2.47	vw	3.14	mw
2.81	w	2.42	vw	2.83	m
2.69	w	2.22	vw	2.62	m
2.58	w	2.17	w	2.52	w
2.48	w	2.00	m	2.38	m
2.10	m	1.96	s		
1.88	m				

[a] Abbreviations used: s, strong; m, medium; v, very; w, weak.

$$n\mathrm{HF} + 2\mathrm{WOF_5} \rightleftharpoons \mathrm{W_2O_2F_9} + (\mathrm{HF})_n\mathrm{F} \qquad (2)$$

On the basis of these equilibria, the 1:2 complex salt of AgF and WOF_4, $AgW_2O_2F_9$, is formed in the presence of excess HF while the 1:1 complex salt, $AgWOF_5$, is formed on slow removal of HF, i.e. on shifting the following equilibrium to the left:

$$2\mathrm{AgWOF_5} + n\mathrm{HF} \rightleftharpoons \mathrm{Ag(HF)}_n\mathrm{F} + \mathrm{AgW_2O_2F_9} \qquad (3)$$

$AgW_2O_2F_9$ may also be prepared by interacting stoichiometric amounts of AgF and WOF_4 in HF:

$$\mathrm{AgF} + 2\mathrm{WOF_4} \longrightarrow \mathrm{AgW_2O_2F_9} \qquad (4)$$

The X-ray powder patterns of $AgWOF_5$, $AgW_2O_2F_9$ and $AgFW_2O_2F_9$ are listed in Table 1 while Table 2 shows the vibrational spectra. The spectra of $NOWOF_5$ [4] and $CsW_2O_2F_9$ [3], are also included for comparison. The peaks for WOF_5^- are assigned to C_{4v} symmetry [8]. The vibrational spectra of $AgWOF_5$ and $AgW_2O_2F_9$ are quite similar to those of $NOWOF_5$ and $CsW_2O_2F_9$, respectively.

It has been reported that AgF_2 reacts with strong fluoro acids to give cationic Ag^{II}, $(AgF)_n^{n+}$ and/or Ag^{2+} [9–12]. Two isomers, $AgF^+W_2O_2F_9$ and $Ag^{2+}(WOF_5)_2$, are possible for the 1:2 complex of AgF_2 and WOF_4. The vibrational spectrum of this compound is listed in Table 2. It is evident that this compound contains the $W_2O_2F_9^-$ anion from a comparison of its spectrum with those of $AgWOF_5$ and $AgW_2O_2F_9$. The powerful oxidizing ability discussed below indicates that this compound contains $(AgF)_n^{n+}$ ions. Therefore this compound is concluded to be $AgFW_2O_2F_9$. Its X-ray powder pattern is listed in Table 1.

$AgFW_2O_2F_9$ is stable under an inert gas but irradiation of the compound when sealed in a quartz capillary by an Ar laser (488 and 514.5 nm, 50–250 mW) causes decomposition

Table 2
The vibrational spectra [a] of solid $AgWOF_5$, $AgW_2O_2F_9$, $AgFW_2O_2F_9$ and some related compounds

$AgWOF_5$		$AgW_2O_2F_9$		$AgFW_2O_2F_9$		$NOWOF_5$ [b]		$CsW_2O_2F_9$ [c]		Assignments	
Raman	IR	Raman	IR	Raman	IR	Raman	IR	Raman	IR	WOF_5^- (C_{4v}) [d]	$W_2O_2F_9^-$ [c]
989 (vs)	992 (s, br)	1026 (s)	1009 (s, br)	988 (s)	1010 (s, br)	1001 (s)	1003 (s)	1036 (s)	1048 (vs)	$\nu_1(A_1)$, $\nu(W{=}O)$	$\nu(W{=}O$ out-of-phase$)$
		1021 (s)							1035 (vs)		$\nu(W{=}O$ in-phase$)$
									822 (vw)		
									790 (vw)		
690	692 (ms, sh)	707 (ms)	711 (ms)	690 (m)	711 (ms, sh)	684 (mw)	680 (sh)	700 (m)	704 (s)	$\nu_2(A_1)$, $\nu(W{-}F_t)$	$\nu_s(WF_4$ in-phase$)$
	632 (s, br)		645 (s, br)		645 (s, br)		610 (vs, br)		628 (vs, br)	$\nu_8(E)$, $\nu(WF_4)$	$\nu_{as}(WF_4)$
		610 (w)	597 (s, br)	615 (ms)	602 (s, br)	591 (vw)		610 (vw)		$\nu_5(B_1)$, $\nu(WF_4)$	$\nu_s(WF_4$ out-of-phase$)$
440 (w)	445 (vs)	440 (w)	447 (s)		447		455 (ms)		440 (vs)	$\nu_3(A_1)$, $\nu(WF_4)$	$\nu_{as}(WFW)$
									400 (vw)		
330 (m)		320 (s)		335 (ms)		327 (m)				$\nu_9(E)$, $\rho_w(W{-}F_t)$	
291		282 (w)				292 (sh)				$\nu_4(A_1)$, $\pi(WF_4)$	

[a] Frequencies are given in cm^{-1}. Abbreviations used: sh, sharp; br, broad; s, strong; m, medium; v, very; w, weak.

[b] Spectra reported in Ref. [4]. Peaks corresponding to N–O not listed.

[c] Ref. [3].

[d] Ref. [8].

probably to $AgW_2O_2F_9$ and fluorine, the latter apparently etching the quartz wall of the capillary. The Raman spectrum was obtained using a Kr laser (647.1 nm, 50 mW) beam which did not cause decomposition (Table 2).

Interaction of equimolar amounts of AgF_2 and WOF_4 did not lead to 1:1 complex salts such as $AgFWOF_5$, but gave a mixture of $AgFW_2O_2F_9$ and unreacted AgF_2. WOF_4 is considered to act as a stronger fluoro acid by forming $W_2O_2F_9$ rather than forming WOF_5^-, the latter being unable to form an $(AgF)_n^{n+}$ salt.

The univalent Ag^+ ion is oxidized by F_2 to form cationic Ag^{II} such as Ag^{2+} and $(AgF)_n^{n+}$ in the presence of SbF_5, AsF_5 and BF_3 [9,10]. The formation of $AgF^+W_2O_2F_9^-$ by the reaction of $AgW_2O_2F_9$ with F_2 demonstrates that the fluoro acidity of WOF_4 in forming $W_2O_2F_9^-$ is at least as great as that of BF_3.

$$AgW_2O_2F_9 + \tfrac{1}{2} F_2 \longrightarrow AgFW_2O_2F_9 \qquad (5)$$

The formation of AgF_2 (brown) was observed at the beginning of the reaction. The Ag^+ ion is oxidized to Ag^{II} by F_2 in the presence of a trace amount of WOF_4, formed according to the equilibria expressed by Eqs. (1) and (2). However, AgF_2 would precipitate instead of $AgFW_2O_2F_9$ when the solution is not acidic enough due to the low solubility of $AgW_2O_2F_9$ in HF. Since the reaction rate of AgF_2 and WOF_4 is slow because of the insolubility of the former, $AgFW_2O_2F_9$ is formed very slowly as the fluoro acidity increases on precipitation of AgF_2.

The crystal structure of $H_3O^+W_2O_2F_9^-$ [13] indicates that $W_2O_2F_9^-$ consists of two WOF_4 units linked by a fluorine bridge *trans* to the tungsten–oxygen bonds. At the same time as this work was carried out, Shen also performed a series of reactions between AgF, AgF_2 and WOF_4 [14]. He succeeded in growing a single crystal of $AgW_2O_2F_9$ and determined the crystal structure, indicating two types of fluorine-bridged dimeric anions with slightly different bond angles and conformations relative to each other.

Xenon is oxidized to Xe^{II} by cationic Ag^{II} in HF at room temperature [9]. $AgFW_2O_2F_9$ also oxidizes xenon to Xe^{II} via the following reaction in HF:

$$5AgFW_2O_2F_9 + 2Xe \longrightarrow 2XeF_2\cdot WOF_4 + 4AgW_2O_2F_9 + AgF_2 \qquad (6)$$

Since the fluoro basicity of XeF_2 is greater than that of AgF_2, XeF_2 substitutes AgF_2 in $AgFW_2O_2F_9$ to form $XeF_2\cdot WOF_4$. However, all the Ag^{II} is not consumed in the oxidation of Xe to Xe^{II} due to precipitation of AgF_2 which does not oxidize Xe unless further WOF_4 is added to the solution.

4.2. Acid–base reactions involving UO_2F_2 in HF

Although UO_2F_2 is insoluble in liquid HF, it dissolves in the presence of AsF_5 to generate a solution exhibiting the typical yellow color due to the UO_2^{2+} ion. However, the $UO_2F_2 + AsF_5$ compound formed in HF at −77 °C is not stable at room temperature and decomposes to give the initial starting materials. It is known that the reaction of UO_2F_2 and SbF_5 in HF yields several compounds, $UO_2F_2\cdot nSbF_5$ ($n=2$, 3, 4), of which $UO_2F_2\cdot 2SbF_5$ is the most stable [15,16]. On the basis of the amount of AsF_5 released, the UO_2F_2/AsF_5 ratio in the compound is approximately 1:2. This 1:2 compound is stable only at low temperature.

The compound $UO_2F_2\cdot 3SbF_5$ is considered to be predominantly ionic since its crystal structure shows that it contains monomeric SbF_6^- and dimeric $Sb_2F_{11}^-$ groups [15]. Similarly, $UO_2F_2\cdot 2SbF_5$ is also expected to be an ionic compound containing SbF_6^- groups from the comparison of the IR spectra of $UO_2F_2\cdot 2SbF_5$ with that of $UO_2F_2\cdot 3SbF_5$. The enthalpy change in the decomposition of $UO_2F_2\cdot 2AsF_5$ is estimated from that of $UO_2F_2\cdot 2SbF_5$ at 245 °C [15] taking account of the difference in the fluoride ion affinities of SbF_5 and AsF_5 [17,18]. The estimate here is made assuming (a) the lattice energies of $UO_2F_2\cdot 2SbF_5$ and $UO_2F_2\cdot 2AsF_5$ are approximately the same because of the similarity between the molecular volumes of SbF_6^- and AsF_6^-, and (b) the difference between the enthalpy changes for the decomposition of $UO_2F_2\cdot 2SbF_5$ at room temperature and 245 °C is negligible.

The entropies of $UO_2F_2(s)$, $SbF_5(g)$ and $AsF_5(g)$ are also available [19] while those of $UO_2F_2\cdot 2SbF_5(s)$ and $UO_2F_2\cdot 2AsF_5(s)$ may be evaluated by Latimer's method [20]. The free enthalpy changes of the reactions of UO_2F_2 with SbF_5 and AsF_5 at room temperature may be evaluated by combining the enthalpy changes estimated above and the entropies, from which:

$$UO_2F_2(s) + 2SbF_5(g) \longrightarrow UO_2F_2\cdot 2SbF_5(s) \quad \Delta G^\circ = -169\ \text{kJ mol}^{-1} \qquad (7)$$

$$UO_2F_2(s) + 2AsF_5(g) \longrightarrow UO_2F_2\cdot 2AsF_5(s) \quad \Delta G^\circ = 9\ \text{kJ mol}^{-1} \qquad (8)$$

The ΔG° values agree with the observation that $UO_2F_2\cdot 2SbF_5$ is stable whereas $UO_2F_2\cdot 2AsF_5$ decomposes to UO_2F_2 and AsF_5 at room temperature. The difference in the stabilities is mainly due to the fluoride ion affinities.

UO_2F_2 and BF_3 do not react to give a stable compound. Although the lattice energy of the complex salt of UO_2F_2 and BF_3 is expected to be larger than those of the SbF_6^- and AsF_6^- salts because of the smaller volume of BF_4^-, the fluoride ion affinity of BF_3 is weak compared to AsF_5 and SbF_5, which offsets this advantage for the formation of the complex salt.

Reaction between UO_2F_2 and GeF_4 appears to occur in HF, but the salt is not stable. The fluoro acidity of GeF_4 is probably insufficient to enable two fluoride ions to be accepted to form GeF_6^{2-} and thereby forming the complex salt $UO_2^{2+}GeF_6^{2-}$ despite the advantage of the larger lattice energy which arises from the doubly charged ions. Even if GeF_4 acts as a monobasic fluoro acid, since its fluoro acidity is less than that of

AsF_5, the complex salt $UO_2^{2+}(GeF_5^-)_2$ would not be stabilized.

UO_2F_2 acts as a fluoro base with some strong fluoro acids in HF as described above. On the other hand, it also acts as a fluoro acid to give some compounds with MF (where M is a univalent metal) in aqueous solution [21]. One such compound prepared to date is the anhydrous 1:1 complex $CsUO_2F_3$ [6] whose structure has yet to be determined. The existence of the complex anion $UO_2F_3^-$ has not been claimed in the solid state although the existence was proved in the gaseous phase by Knudsen's effusion method in combination with mass spectrometry [22] and in solution by Raman spectroscopy [23]. The formation of some oxofluoro complex anions is expected in these compounds described here since the uranium atom in UO_2^{2+} is coordinated by ligands which form strong bonds with some covalency [24]. In fact, the anhydrous 3:1 compounds $M_3UO_2F_5$ (M = K, Cs and NH_4) have been well characterized with a pentagonal bipyramidal anion, $UO_2F_5^{3-}$, being found in $K_3UO_2F_5$ [7]. In this anion, five fluorine atoms coordinate to uranium atom within a plane perpendicular to the linear O–U–O axis to form a regular pentagon.

In the reaction of equimolar amounts of CsF and UO_2F_2 in HF, the solvated salt $CsUO_2F_3 \cdot n$HF seems to be formed, in a similar manner to the formation of the hydrate from aqueous solution. This compound loses HF at ~70 °C to give $CsUO_2F_3$. On the other hand, the reaction of equimolar amounts of KF and UO_2F_2 in HF does not yield the 1:1 compound KUO_2F_3, but a mixture of $K_3UO_2F_5$ and unreacted UO_2F_2.

A novel 1:1 compound, $AgUO_2F_3$, is formed by the reaction of equimolar amounts of AgF and UO_2F_2 in HF. The vibrational spectrum listed in Table 3 suggests that $AgUO_2F_3$ contains some oxofluoro anions. If the uranium were present only in the form of bare cationic UO_2^{2+}, a single peak at ca. 900 cm^{-1} would be observed in the Raman spectrum. Thus, the formation of a double salt is excluded from the obvious difference in the spectrum observed for the sample studied. The X-ray powder pattern of $AgUO_2F_3$ is listed in Table 4.

$AgUO_2F_3$ is solvolyzed by washing with HF:

$$AgUO_2F_3 + nHF \rightleftharpoons Ag^+ + (HF)_nF^- + UO_2F_2 \qquad (9)$$

To obtain a pure sample of $AgUO_2F_3$, it is necessary to remove HF very slowly from the system in order to shift the equilibrium to the left. The growth of a single crystal is extremely difficult in HF due to the low solubility of $AgUO_2F_3$.

Reactions of CsF with UO_2F_2 give both the 3:1 and 1:1 compounds in aqueous solution; however, only the latter is formed in HF. The 3:1 compound may be formed by the reaction of KF and UO_2F_2 in both aqueous solutions and HF. The reaction of AgF and UO_2F_2 in HF provides the 1:1 compound alone even in HF saturated with AgF. These observations cannot be explained by the simple comparative chemistry of the stabilities of the ionic salts.

Table 3
The vibrational spectrum of $AgUO_2F_3$ [a]

Raman	IR
	953 (ms)
	935 (ms)
	894 (s, br)
851 (s, sh)	
784 (m, sh)	
	505 (m, sh)
	425 (m, sh)
	412 (m, sh)
	360 (w, sh)

[a] Frequencies are given in cm^{-1}. Abbreviations used: sh, sharp; br, broad; s, strong; m, medium; v, very; w, weak.

Table 4
The X-ray powder diffraction pattern of $AgUO_2F_3$

d (Å)	Intensity [a]	d (Å)	Intensity [a]
9.32	w	2.52	w
7.73	w	2.42	mw
5.47	w	2.15	mw
4.96	vw	2.09	w
4.14	vw	2.01	ms
3.99	w	1.97	m
3.77	m	1.95	w
3.70	m	1.88	m
3.29	m	1.84	m
3.07	s	1.82	w
2.93	w	1.78	w
2.66	mw	1.72	mw
2.62	mw	1.70	w

[a] Abbreviations used: s, strong; m, medium; v, very; w, weak.

It is concluded that the fluoro basicity of UO_2F_2 in HF is weaker than that of AgF_2 from the difference in the reactivity with BF_3, GeF_4 and AsF_5. Although the fluoro acidity of UO_2F_2 in HF does not seem to be substantially greater than that of HF due to the low solubility, the fluoride ion affinity is greater than that of HF [22,25] and the formation of complex salts by strong fluoro bases such as KF, CsF and AgF occurs rather than of Ag(HF)$_n$F.

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