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SYNTHESES AND VIBRATIONAL SPECTRA OF XENON(VI) FLUOROZIRCONATE(IV) AND XENON(VI) FLUOROHAFNATE(IV)

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SUMMARY

Liquid xenon difluoride at 140°C does not react with zirconium or hafnium tetrafluorides, neither does liquid xenon hexafluoride at 60°C. Therefore reactions between the corresponding hydrazinium fluorometalates or ammonium fluorometalates and xenon difluoride and xenon hexafluoride, respectively, were carried out. $N_2H_6ZrF_6$ and $N_2H_6HfF_6$ react with xenon difluoride at 60°C again yielding only the corresponding tetrafluorides, while the analogous reaction with $(NH_4)_2ZrF_6$ and $(NH_4)_2HfF_6$ proceeds at 170°C yielding the corresponding ammonium pentafluorometalates, which are stable and do not react further with excessive xenon difluoride up to 200°C.

The reaction between $N_2H_6ZrF_6$ or $N_2H_6HfF_6$ and xenon hexafluoride proceeds at room temperature yielding a series of thermally unstable compounds of the type $mXeF_6 . MF_4$ (M = Zr,Hf) where $m \leqslant 6$. The final products which are stable at room temperature are $XeF_6 . MF_4$ (M = Zr,Hf). Spectroscopic evidence suggests that these compounds are salts of a XeF_5^+ cation squashed between a polymeric anion of the type $(MF_5)_x^{x-}$.

INTRODUCTION

In the study of the reactions of titanium tetrafluoride with xenon difluoride or xenon hexafluoride a whole series of complex compounds was isolated and identified [1] : $nXeF_2 \cdot TiF_4$ ($n = 1.5, 1, 0.5$), and $nXeF_6 \cdot TiF_4$ ($n = 4, 1, 0.5$). So far only scanty and incomplete data on the $XeF_2 - ZrF_4$ system are available in the literature [2]. In order to complete our work on the systems xenon fluorides - metal fluorides in group IV A of the periodic table, we have extended this study to systems involving zirconium and hafnium tetrafluorides.

RESULTS AND DISCUSSION

To favour the formation of XeF_2-rich complexes, we set out by treating zirconium tetrafluoride and hafnium tetrafluoride with a large excess of liquid xenon difluoride. The removal of the excess of xenon difluoride at room temperature gave only the corresponding tetrafluorides.

To obtain the tetrafluorides in a more reactive form [3] the reactions between the hydrazinium fluorometalates and xenon difluoride were carried out.

$$N_2H_6MF_6 + nXeF_2 \xrightarrow{60^{\circ}C} MF_4 + N_2 + 2Xe + 6HF + (n-2)XeF_2$$

$n \geqslant 10$

$M = Zr, Hf$

The reaction already takes place at 60°C. The final products are again the corresponding tetrafluorides, although they were obtained in more reactive, "molecular" form during the reaction, and could be expected to react immediately further with excess xenon difluoride.

The analogous reactions with ammonium hexafluorometalates of zirconium and hafnium were also carried out.

$$2(NH_4)_2MF_6 + nXeF_2 \xrightarrow{170^{\circ}C} 2NH_4MF_5 + N_2 + 8HF + 3Xe + (n-3)XeF_2$$

$n \geqslant 10$

$M = Zr, Hf$

It was found that at 170°C ammonium pentafluorometalates(IV) are formed. These are stable and do not react further with excess xenon difluoride up to 200°C. Ammonium pentafluorozirconate(IV) and pentafluorohafnate(IV) are, interestingly enough, not the products of the thermal decomposition of the corresponding ammonium hexafluorometalate, but are the products of the reaction with xenon difluoride. This is clearly demonstrated by the high thermal stability of ammonium hexafluorozirconate(IV) and hexafluorohafnate(IV); they decompose only above 300°C [4,5].

The conclusion of all these experiments is that the existence of xenon(II) fluorozirconates(IV) or xenon(II) fluorohafnates(IV) is questionable. We were not able to reproduce the published results [2] although the same synthetic route was used, as well as some different approaches.

In our attempts to isolate xenon(VI) fluorozirconates(IV) or xenon(VI) fluorohafnates(IV), two different synthetic routes were used. Reactions between tetrafluorides and excessive liquid xenon hexafluoride yield a material from which it is difficult to pump away xenon hexafluoride at room temperature. Only after a week of pumping in a good dynamic vacuum was all xenon hexafluoride removed and the starting materials were recovered unchanged.

The reaction between hydrazinium(2+) hexafluorozirconate(IV) or hexafluorohafnate(IV) and xenon hexafluoride proceeds even at room temperature. It yields a whole series of complex compounds of the type $mXeF_6 \cdot MF_4$ where $m \leqslant 6$.

$$N_2H_6MF_6 + nXeF_6 \xrightarrow{25^{\circ}C} mXeF_6 \cdot MF_4 + N_2 + HF + XeF_4 + \text{excess } XeF_6$$

$n \geqslant 16$

$M = Zr, Hf$

The compounds of the type $mXeF_6 \cdot MF_4$ ($M = Zr, Hf$) with $m = 6, 4, 2$ are not stable in a dynamic vacuum at room temperature and decompose to the products of lower xenon hexafluoride content. The end product, which is stable at room temperature, is consequently $XeF_6 \cdot MF_4$ ($M = Zr, Hf$). The isolation of the compounds with higher xenon hexafluoride content presents serious problems because of xenon tetrafluoride, which has rather a low vapour pressure below room temperature.

$XeF_6 \cdot ZrF_4$ and $XeF_6 \cdot HfF_4$ are white solids at room temperature with negligible vapour pressures. They are extremely sensitive already to traces of moisture and their reaction with water is vigorous.

X-ray powder diffraction patterns show that $XeF_6 \cdot ZrF_4$ and $XeF_6 \cdot HfF_4$ are isostructural. This could be expected because of the lanthanide contraction.

The stoichiometry of $XeF_6 \cdot ZrF_4$ and $XeF_6 \cdot HfF_4$ suggests a type of polymeric fluorine bridged octahedral structure $(MF_5)_x^{x-}$ with XeF_5^+ cations placed somewhere between. The Raman spectra (Figure 1) are similar to the spectra of the XeF_5^+ complexes with polymeric anions, we have investigated recently [6,9]. The spectra, Raman and IR (Table 1), were assigned in the usual way by comparison. There are some differences between the published Raman spectra of the XeF_5^+ ion in its complexes with monomeric anions [7,8] and its Raman spectra in the complexes with the polymeric anions. ν_1 is in monomeric complexes appreciable weaker than ν_2 while in our spectra the intensities are comparable. ν_7 is usually at 650 cm^{-1} or even higher, while we find it around 620 cm^{-1}. But the most significant difference is the intensity of ν_4 which is in Raman a weak band or even a shoulder while here it is the strongest band.

These differences could be explained on the basis of the lower symmetry of the XeF_5^+ cation when squashed between polymeric anions [6]. The XeF_5^+ cation deforms to one of the subgroups of its C_{4v} ideal symmetry and redistribution of intensities should occur. If it deforms to a subgroup in which ν_2 and the closely placed ν_4 take the same symmetry representation, interaction between them should occur [6]. The arithmetic mean of ν_2 and ν_4 is approximately the same in the whole series of investigated xenon hexafluoride complexes with polymeric anions (Table 2), thus confirming the proposed explanation.

ν_7 in the Raman spectra is clearly split, as should be expected, while in the infrared spectrum it is the most intense band [10]. Because of its small intensity ν_5 is difficult to observe and assign with certainity, while the degenerate modes of ν_8 and ν_9 are split as expected. Region 430 - 570 cm^{-1} is assigned as stretching modes of Zr - F or Hf - F bonds in accordance with literature data [11,12]. From the spectra we could not decide with certainity between cis or trans binding of the octahedra.

TABLE 1

Vibrational spectra (cm^{-1}) of $XeF_6 \cdot ZrF_4$ and $XeF_6 \cdot HfF_4$

$XeF_6 \cdot ZrF_4$		$XeF_6 \cdot HfF_4$		Assignment
I.R.	R.	I.R.	R.	XeF_5^+
654 sh	659 (91)	654 sh	657 (80)	ν_1
	632 (25)		630 (29)	ν_7
618 vs	619 (16)	617 vs	618 (17)	
	599 (93)	590 sh	597 (82)	ν_2
581 vw,sh	584 (100)	579 sh	581 (100)	ν_4
569 w	571 sh (42)		570 sh	ν (M-F)*
		537 m		
519 vvw	518 (9)	517 sh	524 (9)	
	496 (7)		492 (3)	
		478 sh		
463 m		468 m-s		
			453 (0.2)	
446 sh	442 (2)			
429 sh		430 w		
	420 (3)		424 (2)	ν_8
	400 (4)		401 (4)	
	366 (8)		367 (8)	ν_3
	337 (0.5)		338 (0.1)	
	296 (7)		301 (5)	ν_6
	268 (1)		256 (0.2)	
	229 (2)		227 (1)	ν_9
	210 (1)		205 (1)	

*M = Zr, Hf

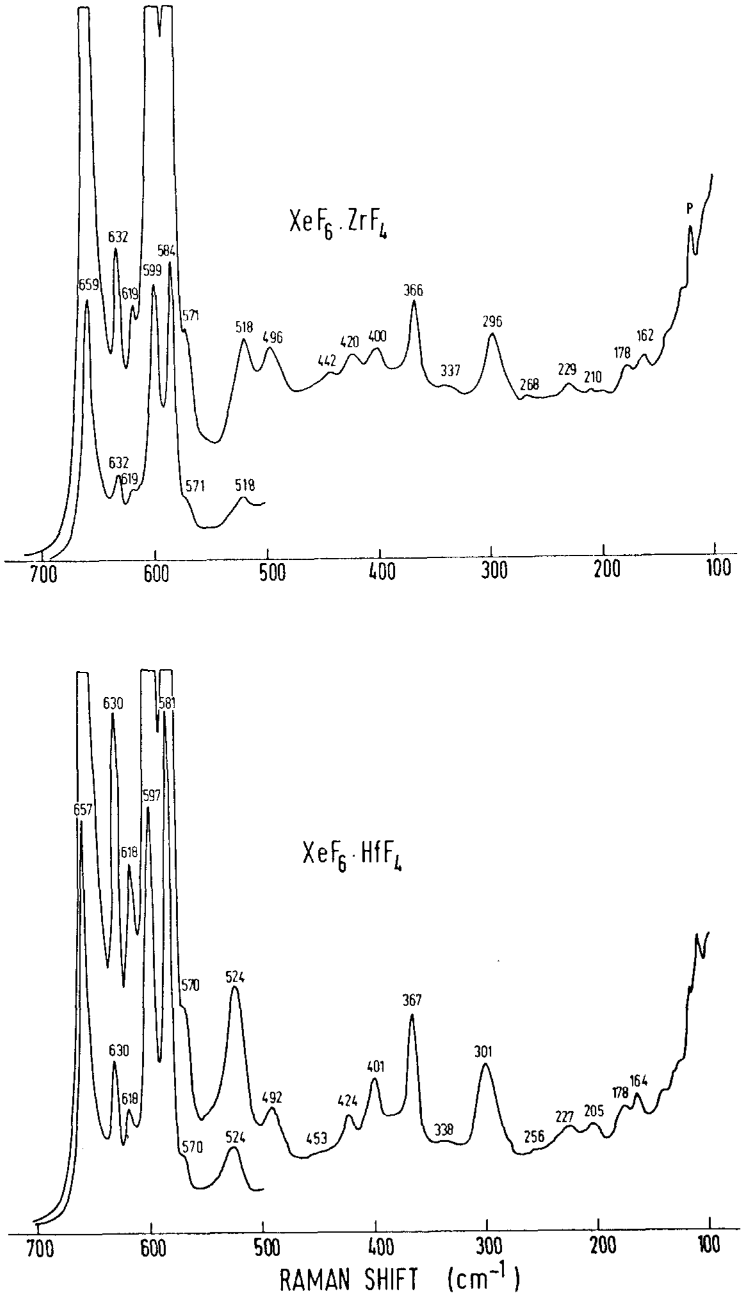

Fig. 1 Raman spectra of $XeF_6 . ZrF_4$ and $XeF_6 . HfF_4$

TABLE 2

Splitting and the arithmetic mean of ν_2 and ν_4

Complex	Splitting (cm^{-1})	Mean (cm^{-1})
$XeF_5^+ZrF_5^-$	15	593.5
$XeF_5^+HfF_5^-$	19	590.5
$XeF_5^+FeF_4^-$ [a]	17	587.5
$XeF_5^+Al_2F_7^-$ [b]	6	588.0
$XeF_5^+GaF_4^-$ [b]	18	589.0

[a] Ref. 9 [b] Ref. 6

EXPERIMENTAL

General apparatus and techniques

Reactions were carried out in argon arc welded nickel pressure and weighing vessels equipped with Teflon packed nickel valves. The volume of the reaction vessel was about 100 ml. They were tested hydrostatically up to 200 atm and were designed also for manipulating solid materials.

All transfers of materials were carried out either in the atmosphere of a dry box or by distillation under vacuum in well dried apparatus.

Raman spectra were recorded using a Spex 1401 double monochromator. As exciting radiation, the 5145 Å line of an Ar^+ laser (Coherent Radiation) was used. Powdered samples were loaded into quartz capillaries in a dry box temporarily plugged with Kel-F grease, and sealed off by a small flame outside the dry box.

IR spectra were recorded using Perkin Elmer 521 and Zeiss UR-20 spectrometers over the range 400-4000 cm^{-1}. The sample was finely powdered and dusted on to silver chloride plates sandwiched in a leak tight brass holder.

X-ray powder photographs were obtained by the Debye-Scherer method on ENRAF (Delft, Holland) using graphite monoshromatized CuK_α radiation. Finely powdered samples were sealed in 0.5 mm thin walled quartz capillaries as described under Raman spectra.

Reagents

Hydrazinium(2+) hexafluorozirconate [13], hydrazinium(2+) hexafluorohafnate(IV) [14], ammonium hexafluorozirconate(IV) [15] and ammonium hexafluorohafnate(IV) [16] were prepared as described elsewhere. Tetrafluorides of zirconium and hafnium were prepared by direct fluorination of corresponding hydrazinium fluorometalates with fluorine under pressure at higher temperatures. Xenon difluoride was prepared by photosynthesis using a near UV lamp [17]. Xenon hexafluoride was prepared by the reaction between xenon and fluorine in the presence of nickel difluoride as catalyst at 120°C [18].

Preparations

In a typical preparation, about 4-6 mmoles of hydrazinium(2+) hexafluorometalate was weighed into the reaction vessel and thoroughly dried in a dynamic vacuum. An excess amount of xenon hexafluoride was sublimed at -196°C on to the hydrazinium(2+) hexafluorometalate and allowed to react for several hours at room temperature. After the reaction was complete, as determined by the amount of nitrogen released, the volatiles were separately pumped off at -196°C (nitrogen), at -100°C (xenon), at -50°C (HF) and at 20°C (excess XeF_6 and XeF_4) as shown by mass spectrometry and infrared spectroscopy. The nonvolatile residual solids were examined by X-ray powder photography, Raman and infrared spectroscopy and were chemically analysed (Table 3).

TABLE 3

Chemical analysis of $XeF_6 \cdot ZrF_4$ and $XeF_6 \cdot HfF_4$

	% M		% F	
	calcd.	found	calcd.	found
$XeF_6 \cdot ZrF_4$	22.11	23.4	46.06	45.7
$XeF_6 \cdot HfF_4$	35.71	35.0	38.02	38.3

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