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SYNTHESES AND VIBRATIONAL SPECTRA OF XENON(VI) FLUOROGALLATE, XENON(VI) FLUOROALUMINATE AND XENON(VI) FLUOROINDATE

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SUMMARY

Liquid xenon difluoride at 140°C does not react with aluminium, gallium, and indium trifluorides, neither does liquid xenon hexafluoride at 60°C. Therefore the reactions between the corresponding hydrazinium fluorometalates ($N_2H_6AlF_5$, $N_2H_6GaF_5$ and $N_2H_5InF_4$) and XeF_2 and XeF_6 were carried out. $N_2H_6AlF_5$, $N_2H_6GaF_5$ and $N_2H_5InF_4$ react with XeF_2 at 60°C (at 25°C in the case of indium) yielding only the corresponding trifluorides, while the reaction with XeF_6 proceeds at room temperature (at −25°C in the case of indium) yielding $XeF_6 . 2AlF_3$, $XeF_6 . GaF_3$ and xenon(VI) fluoroindate(III) contaminated with indium trifluoride. Spectroscopic evidence suggests that these compounds are salts of the XeF_5^+ cation squashed between polymeric anions of the type $(M_2F_7)_x^{x-}$ or $(MF_4)_x^{x-}$.

INTRODUCTION

Systematic studies of the reactions between transition metal fluorides and xenon difluoride [1–3] or xenon hexafluoride [4–8] were recently extended to the elements of the third main group of the periodic table, where only xenon(II) [9] and xenon(VI) fluoroborates [10] were so far known. The study was limited to aluminium, gallium, and indium because their hydrazinium fluorometalates are known [11]. Namely, it was found [12] that hydrazinium fluorometalates are good starting materials for the reaction with xenon hexafluoride because the corresponding metal fluoride formed in situ during the reaction immediately reacts with excess xenon hexafluoride to xenon(VI) fluorometalates. Hydrazine is being oxidized and nitrogen, hydrogen fluoride, xenon and lower xenon fluorides are formed.

RESULTS AND DISCUSSION

Preparation of the complexes by treating aluminium, gallium, and indium trifluorides with a larger excess of liquid xenon difluoride or xenon hexafluoride was unsuccessful. Therefore hydrazinium fluorometalates were taken instead of binary fluorides.

Using hydrazinium fluorometalates of aluminium, gallium and indium for reaction with xenon difluoride, no xenon(II) fluorometalates could be obtained, as was the case in all similar systems studied up to now.

$$N_2H_6MF_5 + nXeF_2 \xrightarrow{60^\circ C} MF_3 + N_2 + 6HF + 2Xe + (n-2)XeF_2$$

$n \geqslant 10$

M = Al, Ga

$$N_2H_5InF_4 + nXeF_2 \xrightarrow{25^\circ C} InF_3 + N_2 + 5HF + 2Xe + (n-2)XeF_2$$

$n \geqslant 10$

Xenon hexafluoride, which is a stronger fluoride ion donor than xenon difluoride, reacts with aluminium, gallium, and indium trifluorides obtained in situ in molecular form by oxidation of corresponding hydrazinium fluorometalate. In order to get pure xenon(VI) fluorometalates not contaminated with trifluorides the reactions should be carried out slowly at as low a temperature as possible. During fast reaction the amount of evolved gases (N_2, Xe, HF) and the heat of reaction developed by oxidation of hydrazinium fluorometalate prevent good contact between molecular trifluoride and xenon hexafluoride. Therefore the final product is only the corresponding trifluoride. However, slow reaction proceeds as follows:

$$N_2H_6AlF_5 + nXeF_6 \xrightarrow{25^\circ C} XeF_6 \cdot 2AlF_3 + N_2 + HF + XeF_4 + \text{little } XeF_2 \text{ and } Xe + \text{excess } XeF_6$$

$n \geqslant 10$

At room temperature $XeF_6 \cdot 2AlF_3$ is a white solid with negligible vapour pressure. It is stable in dynamic vacuum up to 150°C where it begins to loose xenon hexafluoride. The end product of thermal decomposition is aluminium trifluoride as shown by its X-ray diffraction pattern. The purity of $XeF_6 \cdot 2AlF_3$ was checked by mass balance which was followed carefully throughout the experiment, and by chemical analysis which gives the mole ratio Xe : Al : F = 1 : 2 : 12. The X–ray diffraction pattern of the product does not show any lines characteristic of AlF_3.

$$N_2H_6GaF_5 + nXeF_6 \xrightarrow{25^\circ C} XeF_6 \cdot GaF_3 + N_2 + HF + XeF_4 + \text{little } XeF_2 \text{ and } Xe + \text{excess } XeF_6$$

$n \geqslant 10$

At room temperature $XeF_6 \cdot GaF_3$ is a white solid with negligible vapour pressure. It is thermally a little less stable than the aluminium compound and it begins to loose xenon hexafluoride in dynamic vacuum already at 130°C. The decomposition was complete at 150°C, with gallium trifluoride as the final product as shown by its X–ray diffraction pattern. The purity of $XeF_6 \cdot GaF_3$ was checked by mass balance and chemical analysis which gives the mole ratio Xe : Ga : F = 1 : 1 : 9. The X-ray diffraction pattern of $XeF_6 \cdot GaF_3$ does not show any lines of gallium trifluoride.

$$N_2H_5InF_4 + nXeF_6 \xrightarrow{-25^{\circ}C} InF_3 + mXeF_6 \cdot InF_3 + N_2 + HF + XeF_4 + XeF_2 + Xe + \text{excess } XeF_6$$

$n \geqslant 10$

The reaction between hydrazinium(1+) tetrafluoroindate(III) and excess xenon hexafluoride proceeds already below −25°C. Xenon(VI) fluoroindate formed during the reaction is thermally unstable and looses xenon hexafluoride below 0°C. Therefore, it was impossible to remove side reaction products (like XeF_2, XeF_4) and excess xenon hexafluoride without also decomposing xenon(VI) fluoroindate. After more than 15 hours of pumping most of the xenon(VI) fluoroindate was decomposed. The bulk of the sample which was left behind was indium trifluoride with some xenon(VI) fluoroindate(III) always present. This was proven by the X-ray diffraction pattern.

The vibrational spectra of $XeF_6 \cdot 2AlF_3$ and $XeF_6 \cdot GaF_3$ (Table 1) were assigned

TABLE 1
Vibrational spectra (cm^{-1}) of $XeF_6 \cdot 2AlF_3$ and $XeF_6 \cdot GaF_3$

$XeF_6 \cdot 2AlF_3$ I.R.	R.	$XeF_6 \cdot GaF_3$ I.R.	R.	Assignment XeF_5^+
1101 w–m				ν (Al–F)
905 w–m				
744 m				
664 sh				
	654(100)	650 sh	654(100)	ν_1
634 vs,br				ν (Al–F)
	623 (24)	619 vs	621 (28)	ν_7
	591 (92)		598 (60)	ν_2
584 sh	585 (27)	579 w	580 (50)	ν_4
551 s,br		559 w–m		ν (M–F)*
521 s,br		517 m	517 (8)	
494 sh		486 w	490 (2)	
	485 (1)			
453 w	454 (4)			
430 w		420 m		
	436 (8)		417 (3)	ν_8
	414 (4)		395 (2)	
	360 (7)		364 (8)	ν_3
			328 (1)	
	282 (6)		293 (5)	ν_6
	225 (<1)		230 (<1)	ν_9
	207 (<1)		208 (<1)	

*M: Al, Ga

in the usual way by comparison. Besides the published spectra of xenon hexafluoride complexes [13,14,15], the spectra of the complexes $XeF_6.FeF_3$ [8], $XeF_6.ZrF_4$ and $XeF_6.HfF_4$ [16] with polymeric anions were also considered. The bands appearing in all the spectra were assigned to the XeF_5^+–cation, and the bands appearing only in some of the spectra to the corresponding complex anion.

There are some noteworthy differences between the published Raman spectra of the XeF_5^+ ion in its complexes and the Raman spectra we are now presenting (Fig. 1). The differences are not easy to understand, as according to known crystal structures with monomeric anions, the XeF_5^+ cation shows, within standard deviations, hardly any significant differences in size, shape or coordination in different lattices, retaining its approximate C_{4v} symmetry [17,18]. Fluorine bridging contacts with the anionic octahedra seem only to govern the packing within crystals. Absence of splittings and preservation of the selection rules in IR and Raman spectra, where available [14], indicate the influence of site and of field effects to be negligible.

In the complexes which are reported here, the anionic part forms a type of polymeric fluorine bridged octahedral structure $(MF_4)_x^{x-}$ and $(M_2F_7)_x^{x-}$ with XeF_5^+ cations placed somewhere between. The intermolecular forces or fluorine bridges, which only modify the crystal packing in the case of monomeric anions, should result in this case in stresses and consequent deformation of the XeF_5^+ cation (XeF_5^+ is deformed by stronger fluorine bonds; see for instance the structure of $(Xe_2F_{11}^+)AuF_6^-$ [13]). The same type of XeF_5^+ spectrum is found in all the investigated complexes (including $XeF_6.FeF_3$ [8], $XeF_6.ZrF_4$ and $XeF_6.HfF_4$ [16]) without regard to the polymerization mode of the anionic part; the new band in the stretching region in the Raman is very intense and only modes degenerate in C_{4v} symmetry of the unperturbed XeF_5^+ are split. Therefore, the deformation of the cation should essentially determine the spectrum [19], and site symmetry and correlation effects seem to be of lesser influence.

Consequently, the assignment follows the published data [13,14] pretty well, with the differences understandable on the basis of lower symmetry. If, because of the deformation the C_{4v} symmetry is reduced to its subgroups of $C_{2v}(\sigma_v)$, C_2 or C_s (σ_v), ν_4 will take the same representation as closely placed ν_2. Interaction between them should occur and the intensity be shared. Therefore ν_1 which is usually less intense than ν_2 should be relatively more intense, and ν_4, which has been always found as a weak band or even as a shoulder, should gain in intensity and move away from ν_2. The arithmetic mean of ν_2 and ν_4 is almost the same in the whole series of investigated complexes ($590 \pm 2{,}5$ cm^{-1}) [16].

In C_{4v} degenerate ν_7 should be split, but it seems that a component is hidden under the intense bands in the vicinity. It is clearly split in $XeF_5^+MF_5^-$ (M = Zr, Hf) [16]. ν_7 is the most intense band in the infrared in all the studied complexes, which is in accord with the observations of Begun et al. [20] for a series of square pyramida molecules. Because of its small intensity, ν_5 is difficult to observe. The degenerate modes of ν_8 and ν_9 are split as expected.

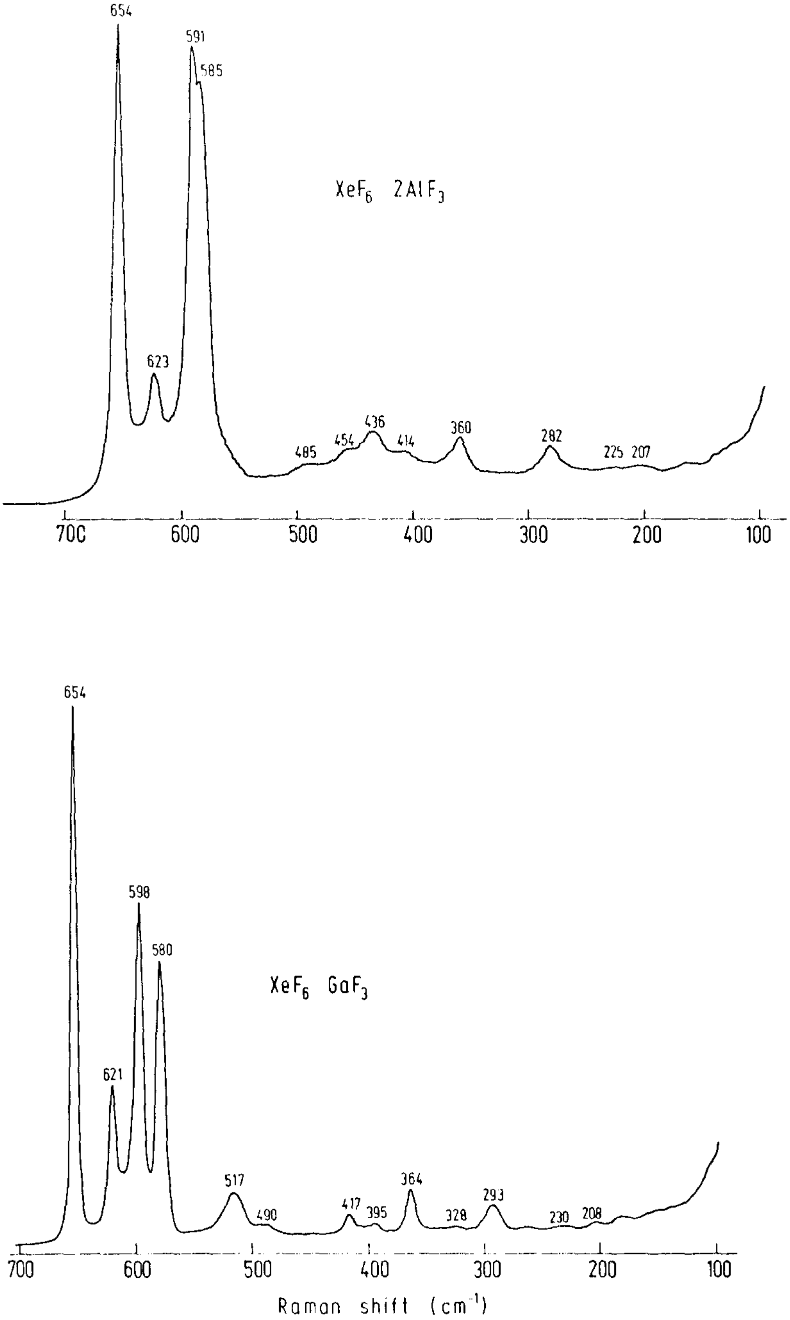

Fig. 1. Raman spectra of $XeF_6.2AlF_3$ and $XeF_6.GaF_3$

There are only a few things which can be said about the anionic part of the spectra with certainity. Fluorides of the investigated elements are poor Raman scatterers in comparison with the XeF_5^+ ion. Strong absorptions in the stretching region of the XeF_5^+ ion (660 – 580 cm^{-1}) in both Raman and IR, may obscure some of the anionic bands. Moreover, the infrared spectra end, because of window material, at 400 cm^{-1}. Therefore, it is difficult to obtain unequivocal proofs for the polymerization type.

For the aluminium and gallium complexes, we expect on the basis of stoichiometry double sheets of $(Al_2F_7)_x^{x-}$ or sheets of $(GaF_4)_x^{x-}$. The infrared spectrum of the aluminium complex shows very broad and strong absorption with multiple peaks (750 – 500 cm^{-1}) which might be the consequence of polymeric structure [21] and which should be assigned to Al–F bond stretchings [22,23]. In the Raman just two very weak bands are associated with Al–F vibrations. The gallium complex shows bands assigned to Ga–F terminal stretching vibrations.

Indium complex is contaminated by an unknown quantity of indium trifluoride. Nevertheless, its Raman spectrum shows the characteristic features of XeF_5^+ squashed between an anionic polymer structure.

EXPERIMENTAL

General apparatus and techniques

Reactions were carried out in argon arc welded nickel pressure and weighing vessels with Teflon packed nickel valves (rated to 100 atm). The majority of the compounds used or prepared during this study are sensitive even to traces of water. Therefore, all transfer of materials was carried out either in a dry box or by distillation under vacuum in well dried apparatus. The vacuum line was constructed of nickel valves and appropriate lines and connectors, and equipped with a Monel-Helicoid gauge for the 0 – 760 torr range.

Raman spectra were obtained using a Spex 1401 double monochromator. As exciting radiation the 5145 Å line of a Coherent Radiation Ar^+ laser and the 6471 Å line of a Coherent Radiation Kr^+ laser were used. Powdered samples were loaded into 2 mm o.d. quartz tubes in the dry box.

Infrared spectra were recorded using Perkin–Elmer 521 and Zeiss UR–20 spectrometers. A 10 cm path length nickel cell with AgCl windows (A.D. McKay, Inc.) was used for gas phase work. Spectra of the solids were obtained by dusting samples onto silver chloride plates which were later sandwiched in a leak tight brass holder.

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

Reagents

Hydrazinium(2+) pentafluoroaluminate(III), pentafluorogallate(III) and hydrazinium(1+) tetrafluoroindate(III) were prepared as described elsewhere [11].

Trifluorides of aluminium, gallium and indium were simply prepared by reacting the corresponding hydrazinium fluorometalate with fluorine under pressure at room temperature. The intentity and the purity of the products was checked by X–ray diffraction and by chemical analysis. Xenon difluoride was prepared by photosynthesis using a near UV lamp [24], xenon hexafluoride was prepared by the reaction between xenon and fluorine in the presence of nickel difluoride as catalyst at 120°C [25]. The purity of both xenon fluorides was checked by i.r. spectroscopy, and in addition, the melting point of xenon difluoride was determined.

Preparations

In a typical preparation hydrazinium fluorometalate (5 mmoles) was weighed into the reaction vessel and thoroughly dried in a dynamic vacuum at room temperature. Then an excess of xenon fluoride (more than 50 mmoles) was added by sublimation at – 196°C. The reaction vessel was than slowly warmed up to room temperature and left at this temperature, or in some reactions with xenon difluoride at higher temperatures (up to 140°C), for several hours. After the reaction was completed the reaction products were separately pumped away: at – 196°C nitrogen, at – 80°C xenon, at – 60°C hydrogen fluoride and at room temperature excessive xenon fluorides.

The mass balance of the experiments were carefully followed throughout the experiment with an accuracy of ± 5 mg.

The thermal decomposition studies were carried out by following weight–loss of the sample when under vacuum as functions of time and temperature. All volatiles were trapped and subsequently examined by mass spectrometry and by gas–phase infrared spectroscopy. The residual solids in the reaction vessel were chemically analysed and examined by Raman and infrared spectroscopy and by X-ray powder photography.

TABLE 2
Chemical analysis of $XeF_6 . 2AlF_3$ and $XeF_6 . GaF_3$

	% M		% F	
	calcd.	found	calcd.	found
$XeF_6 . 2AlF_3$	13.06	12.7	55.17	53.3
$XeF_6 . GaF_3$	18.74	20.5	46.97	45.3

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