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Syntheses, some properties and Infrared and Raman spectra of new xenon(VI) fluorometalates of rare earth elements

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ABSTRACT. — New xenon(VI) fluorometalates(III) and (IV) of rare earth elements (including Y and La) were isolated and characterized: $6XeF_6.YF_3$, $XeF_6.2CeF_4$, $XeF_6.4PrF_4$, $XeF_6.2TbF_4$, $3XeF_6.DyF_3$, $6XeF_6.HoF_3$, $6XeF_6.ErF_3$, $6XeF_6.TmF_3$, $6XeF_6.YbF_3$ and $6XeF_6.LuF_3$. Three approaches, depending on the rare earth element, were used: (1) the interaction of Ln oxide with XeF_6 in excess, (2) the direct interaction of XeF_6 with LnF_4 and (3) the interaction of Ln oxide with the combination of XeF_6 as a fluorobase and KrF_2 as an oxidizing and fluorinating agent in anhydrous HF as a solvent. It was found that xenon(VI) fluorolanthanoates(III) stable at ambient temperatures are formed only for those LnF_3 at the end of the series, where the effective Ln^{3+} nuclear charge is high, and the F^- affinity therefore also large. All LnF_4 which can be obtained by oxidation with XeF_6 or KrF_2 in anhydrous hydrogen fluoride form xenon(VI) fluorolanthanoates(IV). Vibrational spectra are in accordance with the formulation of these compounds as salts of $XeF_5{}^+$ with polymeric ($XeF_6.4MF_4$ and $XeF_6.2MF_4$) or with monomeric anions ($3XeF_6.MF_3$) and salts of $Xe_2F_{11}{}^+$ cation with monomeric anions ($6XeF_6.MF_3$).

INTRODUCTION

Many complexes of XeF_6 with transition element fluorides are known [1] but few studies involving the 3A group (Sc, Y, La) and the lanthanoides have been carried out previously. $XeF_6.ScF_3$ has been prepared [2] and the adducts of the type $XeF_6.LnF_3$ for Ln = La, Pr, Nd, which we have not succeeded to reproduce, have been reported [3]. The findings described here were initiated in 1986 and the preliminary results were first reported at the Fluorine symposium in Paris [4]. Except for promethium and europium, all rare earth elements were examined.

The stoichiometries and particularly the structures of XeF_6 adducts are diverse. There are a few x-ray diffraction structures of $XeF_5{}^+$ solved, and in the numerous cases where they are lacking the conclusions about building blocks, e.g. the presence of monomeric or polymeric coordination anionic

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polyhedra and XeF_5^+ or $Xe_2F_{11}^+$ cations and their symmetry are not easy to answer. Nevertheless, published structures and published vibrational spectra reveal some regularities which may help to answer these questions also in the case of compounds we are here reporting.

EXPERIMENTAL

Starting compounds - As starting materials the following Ln oxides were used: Y_2O_3 (99.99%) and CeO_2 (99%) of the British Drug Houses Ltd.; Y_2O_3 (99.9%) and La_2O_3 (LAB) Merck; Pr_6O_{11} (99.9%), Dy_2O_3 (99.9%) and Ho_2O_3 (99.9%) of Rare Earth Products Ltd.; Nd_2O_3 (99.5%) Koch Light Laboratories Ltd.; Sm_2O_3 (99.9%), Gd_2O_3 (99.9%), Tb_4O_7 (99.9%), Er_2O_3 (99.9%), Tm_2O_3 (99.9%) and Yb_2O_3 (99.9%), Ventron Alfa Produkte; Tb_4O_7 (99.9%) and Lu_2O_3 (99.9%), Alfa Morton Thiokol Inc..

PrF_4 was prepared according to [5] and TbF_4 according to [6]. XeF_6 was synthesized as in [7]. Fluorine was prepared as in [8] and purified as in [9]. KrF_2 was prepared according to [10]. Commercial hydrogen fluoride (Fluka AG, 98%) was purified by K_2NiF_6.

All starting materials used in this work were checked by x-ray powder analysis or Raman spectroscopy.

Instrumentation - The compounds are not stable in air and all manipulations were done in a dry box (MBraun, MB 20G, Garching, Germany; moisture content less than 0.2 ppm).

Debye-Scherrer X-ray powder diffraction patterns of samples in 0.5 mm quartz capillaries were obtained on a PHILIPS PW 1729 (Kassel, Germany) apparatus using graphite-monochromatized CuK_α radiation.

The magnetic susceptibility of powdered samples ($\approx$20 mg) in thin walled capped Kel-F containers was measured by the Faraday method on a modified Newport Instrument magnetic balance in the temperature range rom -196°C to 25°C.

Raman spectra were taken from powdered samples in sealed quartz capillaries in a back-scattering geometry on a Spex-1401 monochromator with exciting lines 514,5 nm or 488 nm of an Ar^+ ion laser (model Coherent Radiation CR-3 and CR INNOVA 70). Spectra were taken at room temperature with as low laser power as purposeful and, in the cases where decomposition could not be avoided, at the temperature of liquid nitrogen (see comments in the Tables III and IV).

Infrared spectra were taken on a Perkin-Elmer FTIR 1710 spectrometer with powdered samples dusted on to the AgCl plates ~~of a~~ leak tight brass-cell.

Preparation - The reactions were carried out in reaction vessels pretreated with fluorine on a nickel vacuum line equipped with a Monel Helicoid pressure gauge (0-1500 Torr, ±3%) (Bristol Babcock Inc.) and nickel valves with Teflon packing.

Nickel vessels with nickel valves were used for reactions with XeF_6. Ln oxide or fluoride (about 2.10^{-3} mol) was weighed in a vessel which was afterwards evacuated and cooled to the temperature of liquid N_2. XeF_6 was condensed into it. The vessel was held at 60°C for several days.

In the case of reactions in which KrF_2 was used, the corresponding amount of Ln oxide was weighed in a FEP reaction vessel fitted out with Teflon valves and Teflon stirring bars. XeF_6 was condensed onto oxide. About 3-4 ml of anhydrous HF (aHF) were condensed onto the mixture. The vessel was cooled in liquid N_2 and an excess of KrF_2 was added by sublimation. The vessel was connected to a ballast volume and warmed up to room temperature. The reaction was carried out at this temperature for several days.

After the reactions were judged to be complete the volatiles were checked at -196°C, -80°C (pressure, IR, mass spectrometry) and pumped out. Volatiles at room temperature (including excess of XeF_6) were pumped out at short intervals and the contents of the vessel determined by weighing until a constant weight was obtained. The end products were checked for unreacted starting materials by x-ray powder analysis. The formation of a complex and its composition was indicated by the increase in weight of the product. The complexes were characterized by chemical analysis, magnetic properties and vibrational spectra.

Chemical analysis - Chemical analyses of isolated XeF_6 compounds are given in Table I. The maximal safe weight for chemical analysis was 100 mg because of violent hydrolysis of $6XeF_6.LnF_3$ compounds in aqueous solutions.

The amount of free (F_f) and total fluoride ions (F_t) was determined by ion selective electrode [11]. F_f corresponds to the fluorine released upon hydrolysis of the compounds to Xe and LnF_3. The metals were determined by complexometric titrations [12].

TABLE I - Chemical analysis in weight %.

	obtained			calculated		
Compound	F_t	F_f	Ln	F_t	F_f	Ln
$6XeF_6.YF_3$	4.52	41.6	6.2	45.80	42.28	5.49
$XeF_6.2CeF_4$	39.1	22.3	40.5	39.26	22.43	41.36
$XeF_6.4PrF_4$	37.4	16.8	49.9	37.56	17.07	50.64
$XeF_6.2TbF_4$	36.4	21.5	44.7	37.20	21.25	44.44
$3XeF_6.DyF_3$	40.9	36.1	16.5	41.76	35.79	17.01
$6XeF_6.HoF_3$*	42.7	40.1	10.9	43.75	40.38	9.74
$6XeF_6.ErF_3$*	40.4	39.0	10.9	43.69	40.33	9.86
$6XeF_6.TmF_3$*	39.6	39.3	13.1	43.65	40.29	9.95
$6XeF_6.LuF_3$	43.0	39.8	11.3	43.49	40.14	10.27

*contaminated with Ln_2O_3

RESULTS AND DISCUSSION

Syntheses - The details of the syntheses are given in the Table II and the pumping curves in Fig. 1 and 2.

Rare earth trifluorides do not react directly with XeF_6. They crystallize in the orthorhombic or in the hexagonal structure or in some cases in both, depending on the reaction conditions [13]. In both types the tridimensional network of atoms does not allow the formation of XeF_5^+ salts. The possible route to the salts is to use other starting materials (e.g. oxides or hydrazinium or ammonium fluorometalates) in order to prepare the trifluorides in situ, in the "active" form, which is able to react further with excessive XeF_6 [14], depending on the Lewis acid strength of the LnF_3. This we expect to parallel the F^- affinity and the effective nuclear charge, which should be inversely proportional to the size of Ln^{3+} ions, other influences being the same [15]. From this we conclude that LaF_3 is the weakest and LuF_3 the strongest Lewis acid in the series and that the strength of YF_3 is comparable with the strength of HoF_3 or ErF_3. Our data (Table II) nicely illustrate the point. The acid strength reaches required value near Dy and the first 3+ valence compound formed with XeF_6 is $3XeF_6.DyF_3$. With all other elements of the series, from Dy on, as well as Y, XeF_6 forms $6XeF_6.LnF_3$ complexes stable at room temperature. The 3+ valence elements before Dy do not form complexes with XeF_6.

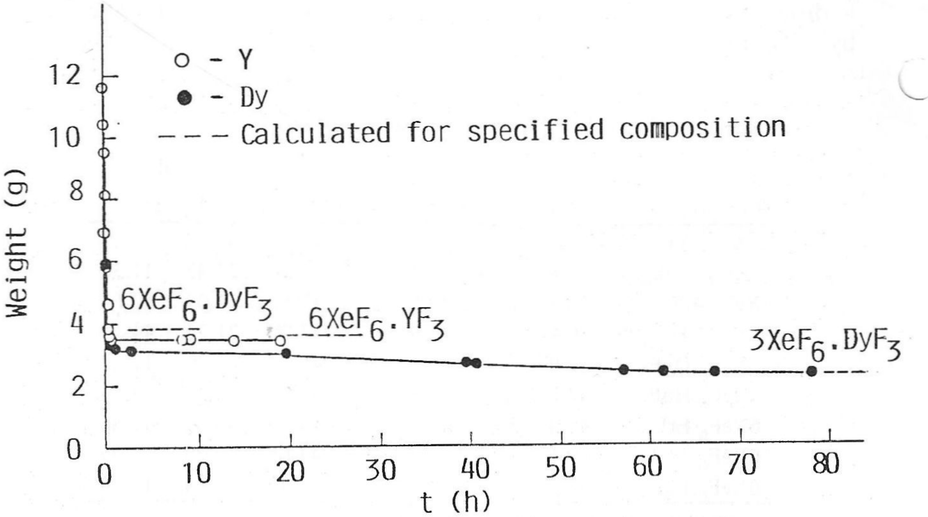

Fig. 1 - Dependence of the total weight of the samples on the time of pumping out volatiles during preparation of $3XeF_6.DyF_3$ and $6XeF_6.YF_3$ at room temperature.

TABLE II - Summary of the preparative reactions.

	Starting compound	Reactant[a]	°C	days	Product[b]	By-products[c]
Y[d]	Y_2O_3	$XeF_6(\geq 20)$	60	10-15	6:1	$XeOF_4+XeF_6$
La	La_2O_3	$XeF_6(\geq 20)$	60	3	LaF_3	$XeOF_4+XeF_6$
Ce[e]	CeO_2	$XeF_6(\geq 10)$	60	1.5	1:2	$XeOF_4+XeF_6$
Pr[f]	Pr_6O_{11}	$XeF_6(\geq 45)$	60	2	PrF_3	$XeOF_4+XeF_6+F_2$
	Pr_6O_{11}	$XeF_6(\geq 50)+KrF_2(\geq 70)+aHF$	25	4	1:4	$XeOF_4+XeF_x+F_2+Kr$
	PrF_4	$XeF_6(\geq 30)$	50	2	1:4	XeF_6
Nd	Nd_2O_3	$XeF_6(\geq 18)$	60	30	NdF_3	$XeOF_4+XeF_6$
	Nd_2O_3	$XeF_6(\geq 25)+KrF_2(\geq 50)+aHF$	25	6	NdF_3	$XeOF_4+XeF_x+F_2+Kr$
Pm	-					
Sm	Sm_2O_3	$XeF_6(\geq 30)$	60	30	SmF_3	$XeOF_4+XeF_6$
Eu	-					
Gd	Gd_2O_3	$XeF_6(\geq 30)$	60	30	GdF_3	$XeOF_4+XeF_6$
Tb[g]	Tb_4O_7	$XeF_6(\geq 30)+KrF_2(\geq 15)+aHF$	25	4	1:2	$XeOF_4+XeF_x+F_2+Kr$
	TbF_4	$XeF_6(\geq 10)$	60	2 h	1:2	XeF_6
Dy[h]	Dy_2O_3	$XeF_6(\geq 19)$	60	30	3:1	$XeOF_4+XeF_6$
Ho[i]	Ho_2O_3	$XeF_6(\geq 35)$	60	30	6:1	$XeOF_4+XeF_6$
Er[i]	Er_2O_3	$XeF_6(\geq 35)$	60	30	6:1	$XeOF_4+XeF_6$
Tm[i]	Tm_2O_3	$XeF_6(\geq 35)$	60	30	6:1	$XeOF_4+XeF_6$
Yb[i]	Yb_2O_3	$XeF_6(\geq 35)$	60	30	6:1	$XeOF_4+XeF_6$
Lu	Lu_2O_3	$XeF_6(\geq 19)$	60	38	6:1	$XeOF_4+XeF_6$

[a] number of moles of the reactant per 1 mole of starting compound is given in parentheses. aHF - anhydrous HF.

[b] X:Y, the composition of the products according to the Table I.

[c] XeF_x, mixture of Xe fluorides.

[d] Y - Commercial oxides have different reactivity and the reaction was incomplete when using the one with lower activity.

[e] Ce, the pumping curve (Fig. 2) levels at a weight corresponding to $XeF_6.2CeF_4$. The compound is diamagnetic (Ce^{4+}). It is stable enough to be characterized. It decomposes in the dynamic vacuum at room temperature and loses 5-8 mg/hour of XeF_6 until the compound $XeF_6.4CeF_4$ is obtained. Checks at -10°C and 0°C indicate that compounds with larger amounts of XeF_6 (e.g. 1:1, 2:1, 4:1) are also possible.

[f] Pr, pumping proceeds over a 4:1 compound and a 1:2 compound to the composition of 1:4, which is stable at room temperature. The 1:4 is paramagnetic and obeys the Currie-Weiss law. The magnetic moment, $\mu_{eff}=2.45$ BM, is in agreement with Pr^{4+} [6]. There is also a 2:1 compound stable at -10°C.

[g] Tb, a 4:1 compound is observed in the dynamic vacuum at 0°C. At room temperature the gradual decomposition by evolution of XeF_6 (at the rate of ca 80 mg/hour) produces the 2:1 compound, which looses ca 30 mg/hour of XeF_6 giving the 1:1 compound, which in its turn, looses ca 13 mg/hour of XeF_6 yielding the 1:2 compound. The reaction of Tb_4O_7 with XeF_6 was incomplete.

[h] Dy, the pumping curve (Fig. 1) changes at the weight corresponding to the 6:1 compound. From this point on the rate of pumping of XeF_6 is ca 20 mg/hour. The

TABLE II, continued:

stable compound in dynamic vacuum at room temperature is $3XeF_6.DyF_3$.

[i] Ho, Er, Tm, Yb, the reactions are not completed even after one month. The crystals of the 6:1 compounds were sifted from the powder of unreacted Ln_2O_3 in the dry box. The separation was not so successful in the case of Yb and the analytical data for this complex are not included in the Table I. Further work is necessary to obtain pure compounds, probably with different starting compounds.

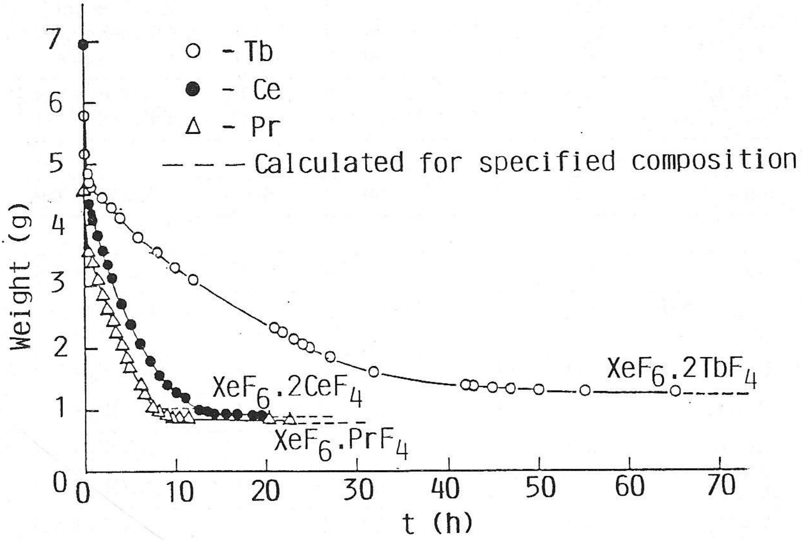

Fig. 2 - Dependence of the total weight of the samples on the time of pumping out volatiles during preparation of $XeF_6.2CeF_4$, $XeF_6.4PrF_4$ and $XeF_6.2TbF_4$ at room temperature.

The 4+ valence fluorides, LnF_4, are stronger Lewis acids than LnF_3 and therefore all lanthanoide elements able to attain 4+ oxidation state are yielding xenon(VI) fluorolanthanoates(IV). In reactions of PrF_4 and TbF_4 the complexes were obtained by using XeF_6 only, which was acting as a fluorobase and in the case of CeO_2 also as a fluorinating agent. With Pr and Tb in lower valence than 4+, XeF_6 is not strong enough oxidant to oxidize the element to 4+, while the 3+ valence states are not able to form complexes. Therefore the combination of XeF_6 as a fluorobase and KrF_2 as an oxidizing and fluorinating agent in aHF is necessary. In this way 4+ valence complexes of Pr were obtained from Pr_6O_{11} and of Tb from Tb_4O_7.

The attempts to prepare Nd^{4+} failed although its compounds, like Cs_2RbNdF_7, are mentioned in the literature [17]. We believe that the main reasons for the failure are: xenon hexafluoride is a weaker fluorobase than alkali metal fluorides and that eventually formed complexes are readily solvolyzed by aHF. No experiments have been done with Pm, because of its radioactivity and with EuF_3 because, analogously to other LnF_3 of lower effective nuclear charge, we expect it to be unable to form a stable XeF_6 complex.

Vibrational spectra - Spectra are given in Tables III and IV and illustrated in Fig. 3. The assignment of stronger bands is made easily by comparison with the spectra of related molecules [18,19,20—22]. Assignment of the weaker bands merits some comment. The frequencies outside the regions observed for XeF_5^+ or $Xe_2F_{11}^+$ ions were assigned to the anionic part. The infrared band of $6XeF_6.MF_3$ complexes at ca 412 cm^{-1} appears in the region observed also for the triply degenerate stretching vibration of the MF_6^{3-} octahedra of Cs_3MF_6 compounds which is shifted to higher frequencies along the lanthanoide series in dependence on the atomic radii (325-400 cm^{-1}) [23]. But, it is definitely a Xe-F vibration, since it appears in all spectra at virtually the same frequencies. The Raman band at ca 376 cm^{-1} is assigned to ν_3 vibration of the XeF_5^+ ion and in $Xe_2F_{11}^+$ ions to

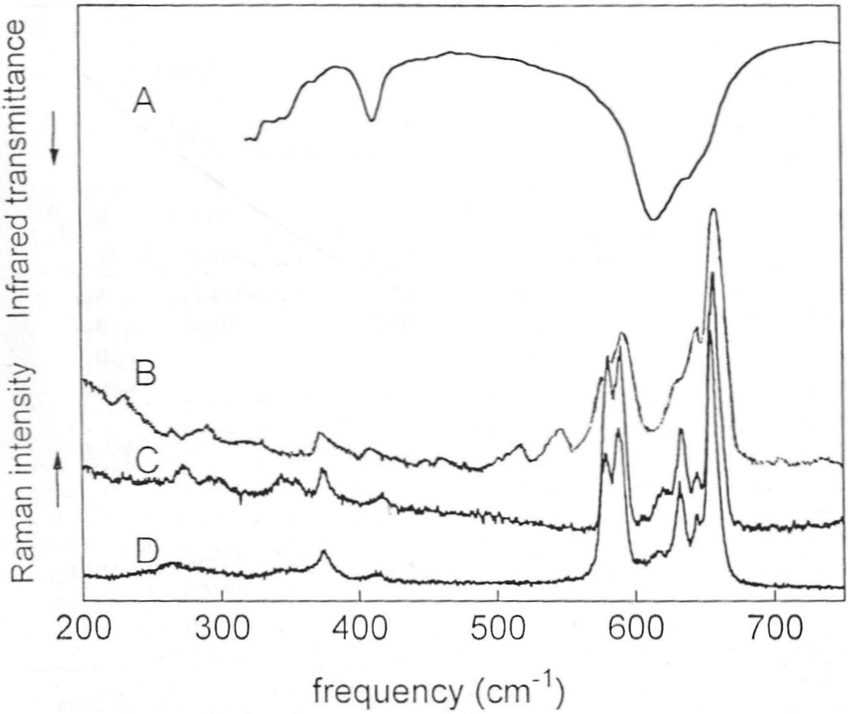

Fig. 3 - Examples of vibrational spectra: A, $6XeF_6.LuF_3$; B, $XeF_6.4PrF_4$; C, $3XeF_6.DyF_3$; D, $6XeF_6.YbF_3$.

the coupling of ν_3 vibrations of the XeF_5^+ units through the symmetric stretching of the bridge XeF_5^+...F... XeF_5^+ [18]. It is therefore also labelled as ν_3. Oxide impurities in $6XeF_6.LnF_3$ (see comments to the Tables I and II) mask some parts of the spectra (Tm compound) or make the determination of some Raman intensities only approximate (Er compound). $XeF_6.4MF_4$ and $XeF_6.2MF_4$ complexes show infrared M-F stretching bands at ca. 420 cm^{-1} which is in accordance with the published data for fluorolanthanoates(IV) [16].

Examination of published X-ray structures of compounds of XeF_5^+ or $Xe_2F_{11}^+$ allows some predictions to be made concerning investigated complexes . In all known cases the structure is influenced by packing forces and the bridging associations are important. Formation of $Xe_2F_{11}^+$ cations

TABLE III - Raman spectra of $XeF_6.2CeF_4$, $XeF_6.TbF_4$, $XeF_6.4PrF_4$ and of $3XeF_6.DyF_3$ in cm^{-1}.[a]

$XeF_6.2CeF_4$		$XeF_6.2TbF_4$		$XeF_6.4PrF_4$		$3XeF_6.DyF_3$		Tentative assignment
IR	R	IR	R[b]	IR[c]	R[b]	IR	R[b]	
								XeF_5^+ bands
656sh	658(100)	650sh	652(100)	650	655(100)		656(100)	$\nu_1(A_1)$
630vs		630vs	635sh		640sh	639sh 617vs	644(21) 634(39) 620(14) 605(?)	$\nu_7(E)$
	600(56)		582(41)		585(56)		590(66)	$\nu_2(A_1)$
590s	585sh	590m	568sh	595	570sh		580(67)	$\nu_4(B_1)$
			405(3)		405(4)	411m 401sh	416(4)	$\nu_8(E)$
	360(5)		365(6)		367(13)	362vw	374(11)	$\nu_3(A_1)$
	290(2)		295(4)		305(7)		301(4)	$\nu_6(B_2)$
			230(4)		230(6)			$\nu_5(B_1)$
			200(3)					$\nu_9(E)$
								Anion bands
	570sh							
	531(6)		535(13)		532(13)			ν(M-F)
			510sh			352w	355(6)	
	488(5)				490(7)	343w	344(7)	
	466(3)						291(4)	
420m		425w		420			272(7)	

[a] s-strong, m-medium, w-weak, v-very, sh-shoulder; Raman intensities are given in parentheses.
[b] Raman spectra taken at the liquid N_2 temperature.
[c] spectrum of poor quality

TABLE IV - Vibrational spectra of $6XeF_6.HoF_3$, $6XeF_6.YF_3$, $6XeF_6.ErF_3$, $6XeF_6.TmF_3$, $6XeF_6.YbF_3$ and $6XeF_6.LuF_3$ in cm^{-1}.[a]

$6XeF_6.YF_3$		$6XeF_6.HoF_3$		$6XeF_6.ErF_3$		$6XeF_6.TmF_3$		$6XeF_6.YbF_3$		$6XeF_6.LuF_3$			Tentative assignment
IR	R	IR	R	IR	R[b,c]	IR	R[c]	IR	R	IR	R	R[b]	
													XeF_5^+ bands
673sh	655(100)		648(100)	667sh 650sh	659(100)	673sh	655(100)		655(100)		654(100)	664(50) 658(100)	$\nu_1(A_1)$
639sh 617vs	635(33)	636sh 617vs	628(24) 617sh	637sh 616vs	649(40)	639sh 616vs	645sh 631(37) 613sh	640sh 617vs	644(19) 632(34) 615(10)	639sh 615vs	644(5) 632(41) 616(5)	647(30) 636(30) 620(10)	$\nu_7(E)$
	588(74)		584(58)		595(60) 590(50)		587(65)		588(59)		588(66)	592(69)	$\nu_2(A_1)$
	580sh		572(53)	564sh	582(70)		577(51)	580sh	578(51)		578(59)	583(54)	$\nu_4(B_1)$
412m	412(3)	410m	408(3)	412m		412m		411m	413(3)	412m	412(3)	417(3)	$\nu_8(E)$
	372(11)		368(15						373(11)	368sh	374(13)	376(10)	$\nu_3(A_1)$
											308(3)	309(3)	$\nu_6(B_2)$
	260(7)		260(9)						262(6)		265(9)	270(7)	$\nu_5(B_1)$
			200(2)						200(2)		205(?)	205(3)	$\nu_9(E)$
						528vw							Anion bands
	342(6)		362(5)						348(3)	348sh		355(4)	
									340(3)	340sh	345(4)	346(4)	
										326sh			ν(M-F)
			284(5)				289(8)		283(3)		287sh		
			236(6)								237sh		
			158(2)									124(3)	lattice
												106(3)	vibrations

[a] s-strong, m-medium, w-weak, v-very, sh-shoulder; Raman intensities are given in parentheses.
[b] Raman spectra taken at the liquid N_2 temperature.
[c] See text.

seems to be governed by such relations [24]. Interactions between Xe and F of the fluorometalate anions are always present [20,21,25,26], and when the charge on the F ligand of the anion (expected to be inversely proportional to the effective nuclear charge of the central atom) is low enough to allow the XeF_6 base to displace the anion ligands in $(XeF_5^+)_3.LnF_6^{3-}$ from their interactions with XeF_5^+, the $Xe_2F_{11}^+$ salts will be formed. This obviously happens in the rare earth series from Ho on (including Y). Therefore, also considering the number of XeF_5^+ ions in $6XeF_6.MF_3$, it is a credible conclusion that these structures consist of $Xe_2F_{11}^+$ ions and monomeric, probably deformed MF_6^{3-} octahedra. XeF_5^+ is expected in $3XeF_6.MF_3$, but it cannot be predicted which of the anionic forms are present, the monomeric MF_6^{3-} or polymeric with coordination numbers larger than 6. Structures of $XeF_6.4MF_4$ and of $XeF_6.2MF_4$ evidently include XeF_5^+ ions and polymeric anions.

In view of such a diversity it is interesting to observe the same kind of vibrational spectra. Infrared spectra are surprisingly similar and the Raman spectra are dominated by two strong bands at ca 653±6 and at ca 583±11 cm^{-1}. Nevertheless, they might be divided into two groups with respect to splitting of bands (Fig. 3), those with monomeric and those with polymeric anions.

But more intriguing is the question of general distribution of Raman intensities. XeF_5^+ complexes with monomeric anions show ν_1 of the XeF_5^+ (axial XeF stretch) significantly weaker than ν_2 (symmetric basal XeF_4 stretch) [18]. In the investigated series ν_1 is stronger than ν_2. This has already been observed in the spectra of XeF_5^+ complexes with polymeric anions [22,27,28] and in $Xe_2F_{11}^+$ compounds with monomeric anions [18]. In the XeF_5^+ complexes with polymeric anions it has been explained as a consequence of mixing of modes due to supposed deformations of the cation [22,27,29] and in $Xe_2F_{11}^+$ compounds probably as the consequence of the coupling of two XeF_5^+ units via the fluorine bridge [18]. Such a distribution of intensities is a confirmation of proposed compositions of $XeF_6.4MF_4$, $XeF_6.2MF_4$ and $6XeF_6.MF_3$ and as a suggestion that $3XeF_6.MF_3$ is formed of polymeric anions and of XeF_5^+ or of $Xe_2F_{11}^+$ cations. Nevertheless, this has to be taken with prudence, because the spectra of three compounds of XeF_5^+ with monomeric anions (PdF_6^{2-} [18], AuF_4^- and AgF_4 [24]) also show stronger ν_1 than ν_2 and demonstrate that in addition to kinematic coupling the electronic effects also have to be taken into account. Therefore, taking into account the discussed structural and spectroscopic information, we are inclined to expect that $3XeF_6.MF_3$ is formed of XeF_5^+ cations and monomeric anions.

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