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Syntheses, infrared and Raman spectra of rare earth(III) fluoroarsenates(V)

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Abstract

Rare earth trifluorides (LnF_3) dissolve in anhydrous hydrogen fluoride (aHF) acidified with AsF_5 at room temperature forming stable solutions of solvated rare earth cations $Ln(HF)_x^{3+}$ and AsF_6^- anions. After the excess of AsF_5 and aHF are pumped away at room temperature $La(AsF_6)_3$, $LnF(AsF_6)_2$ with Ln = Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Y and $Ln_2F_3(AsF_6)_3$ with Ln = Tm, Yb and Lu are isolated, indicating the decreasing stability of $Ln(AsF_6)_3$ and $LnF(AsF_6)_2$ along the series of rare earth metals. This behaviour perfectly reflects the reduced fluorobasicity of rare earth trifluorides along the series. In some selected cases (Ln = La, Nd, Sm and Tm) the isolation of $Ln(AsF_6)_3$ compounds was performed at lower temperatures (263–233 K). The vibrational spectra of all isolated rare earth(III) fluoroarsenates(V) show that deformed AsF_6^- octahedra are present, indicating a covalent contribution to the fluorine bridges between LnF_3 and AsF_5.

Keywords: Raman spectra; Rare earth(III) fluoroarsenates(V); Synthesis

1. Introduction

The pioneering work on rare earth trifluorides as fluorobases in aHF acidified with BF_3 or SbF_5 was done by Alan F. Clifford 40 years ago [1]. Since then, several compounds with LnF_3 as a fluorobase have been prepared by solid-state reactions from intimate mixtures of LnF_3 with another fluoride at elevated temperatures. Compounds of the type $LnFMF_6$, M = Zr [2–4], Nb [5], Mo [6], Hf [7], Sn [8] and Pt [9], and of the type $Ln(MF_5)_3$, M = Tb [10,11], Zr [7,11] and Hf [11,12], were described. The influence of decreasing fluorobasicity of LnF_3 along the series is demonstrated by a group of compounds recently prepared in reactions with AuF_3:$La(AuF_4)_3$ [13], $Ln_2F(AuF_4)_5$, Ln = La to Er [14,15] and $LnF(AuF_4)_2$, Ln = Tm, Yb, Lu [16].

In this paper, we report a new family of compounds synthesized in reactions between rare earth trifluorides and AsF_5 in aHF.

2. Experimental

2.1. Techniques

Infrared spectra were taken on a Perkin-Elmer FTIR 1710 spectrometer on samples powdered between AgCl windows in a leak tight brass-cell. Raman spectra from powder samples were taken in sealed quartz capillaries in back-scattering geometry on a Spex-1401 monochromator with the exciting line of 514.5 nm of an Ar^+-ion laser (Coherent Radiation CR-3 and CR INNOVA 70). Due to rapid decomposition at room temperature, the intensity of the laser beam was set as low as possible (ca. 4 mW on the sample). Most of the compounds are poor Raman scatterers and the spectra obtained are of poor quality with broad Raman signals. The line at 514.5 nm was chosen to diminish the effects of fluorescence. Even repetitive scanning up to 200 times resulted sometimes in poor or unusable spectra (for instance ErF_2AsF_6 and $Yb_2F_3(AsF_6)_3$). The Raman spectrum of a solution in aHF was taken in a FEP test tube in back-scattering geometry. X-ray powder diffraction patterns were obtained using the Debye–Scherrer technique with Ni-filtered CuKα radiation. Samples were loaded into quartz capillaries (0.5 mm) in a dry box.

2.2. Reagents

Rare earth trifluorides purchased from Johnson Matthey, Alfa Products, 99.9% (REO), were used as starting materials. AsF_5 was synthesized by pressure fluorination of arsenic trioxide with elemental fluorine in a nickel reactor at 573 K as previously described [17]. Fluorine was prepared and puri-

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fied as described elsewhere [18,19]. Anhydrous HF (Praxair, 99.9%) was treated with K_2NiF_6 for several hours prior to use. CeF_4 was prepared from CeF_3 under high pressure of elemental fluorine at 623 K [20], while PrF_4 and TbF_4 were prepared from respective oxides with KrF_2 in aHF [21].

2.3. Apparatus

Volatile materials (AsF_5, aHF) were manipulated in an all-Teflon vacuum system equipped with Teflon valves. All nonvolatile products are sensitive to traces of moisture; therefore, they were handled in a dry box (MBraun, Garching, Germany, water content ≤0.2 ppm). The reactions were carried out in FEP or PFA vessels (height = 250 mm with i.d. = 15.5 mm and o.d. = 18.75 mm) equipped with Teflon valves and Teflon-coated stirring bars.

2.4. Syntheses of $LnF_n(AsF_6)_{3-n}$

Three to six mmol of LnF_3 (Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and Y) were loaded in a dry box into FEP or PFA reaction vessels. Then aHF (6–8 ml) was condensed onto LnF_3 from a FEP reservoir containing K_2NiF_6, and excess of AsF_5 was added, both at 77 K. The reaction vessel was warmed up and LnF_3 otherwise insoluble in aHF were readily dissolved due to the presence of AsF_5. All reactions were carried out at room temperature until a clear solution (2–5 h, depending on the excess of AsF_5 and on the lanthanoid in the series) with the typical colour of the particular Ln^{3+} element was obtained. Volatile compounds (aHF and excess of AsF_5) were pumped away at room temperature. First a clear but viscous, highly concentrated solution of the reaction product was obtained. Further removal of the solvent proved difficult because of the very low vapour pressure above the solution. For the heavier lanthanoid elements (Tb–Lu), more dramatic release of gases happened in a short time. Initially, the solid product filled the reaction vessel up to two-thirds of its volume, but the solid volume slowly diminished under vacuum. Pumping was continued at room temperature until the product was losing only 1–3 mg of AsF_5/mmol h. Some characteristic pumping curves are presented in Fig. 1. The detailed reaction conditions for the whole series are given in Table 1.

In order to isolate compounds of the type $Ln(AsF_6)_3$, the volatiles were pumped away at lower temperatures (263–233 K) after reactions were completed at room temperature. It was established from gravimetry (Table 2) that in all four selected cases (La, Nd, Sm and Tm), $Ln(AsF_6)_3$ compounds were synthesized. $La(AsF_6)_3$ was isolated at 263 K, $Nd(AsF_6)_3$ at 253 K, $Sm(AsF_6)_3$ at 243 K and $Tm(AsF_6)_3$ at 233 K. $La(AsF_6)_3$ is stable at room temperature, while $Ln(AsF_6)_3$ with Ln = Nd and Sm lose AsF_5 under dynamic vacuum yielding $LnF(AsF_6)_2$. $Tm(AsF_6)_3$ decomposes immediately at room temperature releasing 1 mmol of AsF_5 for each mmol of $Tm(AsF_6)_3$ forming $TmF(AsF_6)_2$. The weight of the released volatile phase (AsF_5, checked by IR) at 298 K was: calcd.: 845 mg, obtained: 874 mg. Also $TmF(AsF_6)_2$ is unstable under dynamic vacuum at 298 K loosing AsF_5 and yielding $Tm_2F_3(AsF_6)_3$.

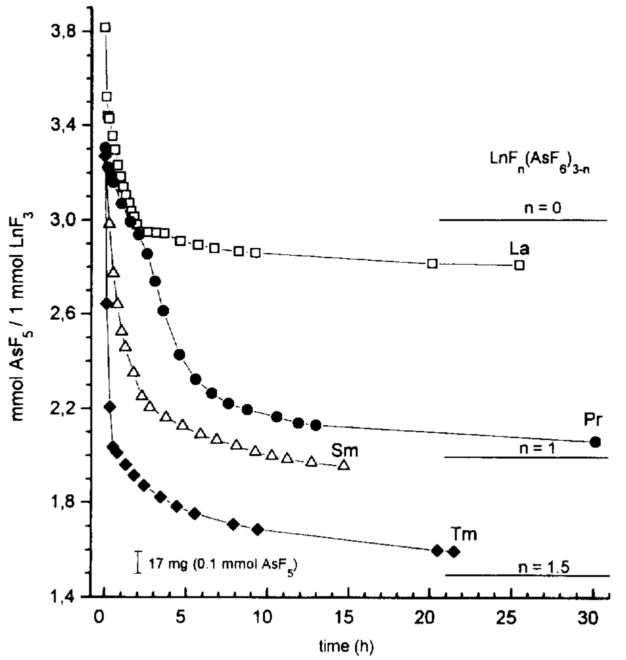

Fig. 1. Examples of pumping curves in the course of the preparation of $LnF_n(AsF_6)_{3-n}$ at room temperature. Weight loss data for the particular experiment were calculated per 1 mmol of LnF_3.

Table 1
Reaction conditions for the syntheses of $LnF_n(AsF_6)_{3-n}$ compounds at room temperatures

LnF_3	LnF_3 (g)	LnF_3 (mmol)	AsF_5 (g)	AsF_5 (mmol)	Final product for chemical analyses
YF_3	0.610	4.18	2.72	16.00	$YF(AsF_6)_2$
LaF_3	1.057	5.40	7.00	41.20	$La(AsF_6)_3$
CeF_3	0.843	4.28	3.24	19.07	$CeF(AsF_6)_2$
PrF_3	0.998	5.04	5.00	29.43	$PrF(AsF_6)_2$
PrF_4	0.467	2.15	1.95	11.49	$PrF(AsF_6)_2$
NdF_3	1.006	4.99	3.49	20.54	$NdF(AsF_6)_2$
SmF_3	0.952	4.59	3.49	20.54	$SmF(AsF_6)_2$
EuF_3	1.092	5.22	5.58	32.82	$EuF(AsF_6)_2$
GdF_3	1.110	5.18	4.88	28.72	$GdF(AsF_6)_2$
TbF_3	1.076	4.98	3.71	21.81	$TbF(AsF_6)_2$
DyF_3	0.711	3.24	2.00	11.77	$DyF(AsF_6)_2$
HoF_3	0.995	4.48	5.58	32.82	$HoF(AsF_6)_2$
ErF_3	0.882	3.93	2.79	16.41	$ErF(AsF_6)_2$
ErF_3	1.155	5.15	5.58	32.82	ErF_2AsF_6
TmF_3	1.051	4.65	4.68	27.54	$Tm_2F_3(AsF_6)_3$
YbF_3	0.687	2.99	7.85	46.20	$Yb_2F_3(AsF_6)_3$
LuF_3	0.998	4.30	4.38	25.78	$Lu_2F_3(AsF_6)_3$

2.5. Solvolysis of $LnF(AsF_6)_2$ in aHF

The isolated $LnF(AsF_6)_2$ compounds do not dissolve again in aHF at room temperature. As a typical example, observations for $DyF(AsF_6)_2$ are given. Three millilitres of aHF were condensed in 1.61 mmol (0.902 g) of $DyF(AsF_6)_2$

Table 2
Reaction conditions for the syntheses of $Ln(AsF_6)_3$ compounds

Compound	LnF_3 (g)	LnF_3 (mmol)	Temperature of pumping (K)	Time of pumping (h)	$Ln(AsF_6)_3$ (g)	
					Calculated	Observed
$La(AsF_6)_3$	0.286	1.46	263	54	1.030	1.016
$Nd(AsF_6)_3$	1.238	6.15	253	110	4.372	4.343
$Sm(AsF_6)_3$	1.354	6.53	243	240	4.682	4.669
$Tm(AsF_6)_3$	1.124	4.97	233	190	3.656	3.679

Table 3
Chemical analyses of $LnF_n(AsF_6)_{3-n}$ compounds isolated at room temperature

Compound	Calculated			Obtained		
	%Ln	%F	%As	%Ln	%F	%As
$YF(AsF_6)_2$	18.30	50.85	30.85	17.2	50.7	31.2
$La(AsF_6)_3$	19.69	48.46	31.85	21.2	49.5	29.2
$CeF(AsF_6)_2$	26.10	45.99	27.91	23.9	45.3	26.2
$PrF(AsF_6)_2$	26.20	45.93	27.87	26.2	46.5	27.5
$PrF(AsF_6)_2$[a]	26.20	45.93	27.87	26.7	45.5	28.0
$NdF(AsF_6)_2$	26.66	45.65	27.69	26.4	44.8	28.3
$SmF(AsF_6)_2$	27.48	45.13	27.39	27.8	45.0	27.3
$EuF(AsF_6)_2$	27.69	45.00	27.31	27.6	43.9	26.8
$GdF(AsF_6)_2$	28.39	44.56	27.05	29.6	44.2	25.9
$TbF(AsF_6)_2$	28.60	44.44	26.96	29.4	42.4	26.2
$DyF(AsF_6)_2$	29.05	44.16	26.79	29.4	44.5	26.6
$HoF(AsF_6)_2$	29.36	43.97	26.67	30.6	42.5	26.4
$ErF(AsF_6)_2$	29.65	43.78	26.57	27.8	43.8	27.5
ErF_2AsF_6	42.43	38.56	19.01	38.8	39.7	21.2
$TmF(AsF_6)_2$[b]	29.86	43.65	26.49	30.0	44.9	25.2
$Tm_2F_3(AsF_6)_3$	35.14	41.49	23.37	33.5	41.9	24.1
$Yb_2F_3(AsF_6)_3$	35.69	41.14	23.17	33.9	42.3	24.1
$Lu_2F_3(AsF_6)_3$	35.94	40.98	23.08	34.6	41.3	23.0

[a] Synthesized from PrF_4.

[b] The compound $TmF(AsF_6)_2$ was obtained at room temperature from $Tm(AsF_6)_3$, which had been isolated at 233 K (see Table 2).

at 77 K. After warming up to 198 K, a clear solution was obtained, which remained completely clear until 265 K (the rate of warming up was 5°C/h). At 265 K, the first precipitation was observed. At 273 K, the amount of precipitate was bigger, and it persisted after cooling to 223 K. Finally, the sample was left at room temperature for two days. The soluble component was shown by chemical analysis to be $Dy(AsF_6)_3$, while a majority of the precipitate is DyF_3.

2.6. *Titration of LnF_3 with AsF_5*

In a few cases (La, Nd, Sm, Tm) additional experiments were performed at room temperature to determine the exact amount of AsF_5 required for the complete dissolution of LnF_3 in aHF. Small portions of AsF_5 gas, monitored by measuring its pressure and weight, were added to the suspension of LnF_3 in aHF.

In a typical run, the procedure was the following: TmF_3 (4.97 mmol) was reacted in aHF with AsF_5 (7.65 mmol) for 24 h. There was no sign of dissolution at this ratio (TmF_3:AsF_5 = 2:3). Additional portions of AsF_5 (1.69 mmol; 0.65 mmol; 3.13 mmol) were added to the solution forming the AsF_5/TmF_3 ratios 1.88, 2.01 and 2.64, respectively. The suspensions were mixed for 8.5 h, 13.5 h and 8.5 h, respectively, before additional AsF_5 was added. When the last portion of AsF_5 (1.79 mmol) was added and the mole ratio TmF_3:AsF_5 = 1:3 was reached within 2.5 h; all TmF_3 dissolved and in the next 2 h a clear solution was obtained.

Chemical analysis of a solution obtained in this way was done in the case of $Nd(AsF_6)_3$: % Nd, 5.8; % AsF_6^-, 22.4. Molar ratio Nd:AsF_6 = 1:2.95.

2.7. *Chemical analyses*

The results of chemical analyses of the compounds isolated at room temperature are given in Table 3. Chemical analyses of the compounds isolated at lower temperatures (233–253 K) are not reliable because of the relatively high equilibrium vapour pressure of AsF_5 above these compounds at 298 K.

The rare earth elements were determined by complexometric titrations [22–24]; total fluoride ion content was determined with an ion selective electrode [25,26]; arsenic was determined by the ICP method [27]; the amount of free fluorine was determined in the solution after hydrolysis with an ion-selective electrode on ORION 960 Autochemistry analyzer [28]; and AsF_6^- species were determined gravimetrically as the insoluble tetraphenylarsonium salt [29,30].

3. Results and discussion

3.1. Reactions of LnF_3 with AsF_5 in aHF

Rare earth trifluorides (LnF_3), are insoluble in aHF, but are readily dissolved in aHF acidified with AsF_5 forming stable solutions of solvated rare earth cations $Ln(HF)_x^{3+}$ [31] and AsF_6^- anions. The reaction proceeds according to the equation:

$$\underset{n \geq 3}{LnF_3 + nAsF_5} \xrightarrow{\text{aHF},298\ \text{K}} Ln(HF)_x(AsF_6)_3 + (n-3)AsF_5$$

The dominant species in the aHF–AsF_5 system at low temperatures (189.6 K) is $As_2F_{11}^-$ [32], while at room temperature, free AsF_5 is in equilibrium with some AsF_6^- and $As_2F_{11}^-$ [33]. Therefore, for synthetic work in solutions of AsF_5 in aHF at room temperature, free AsF_5 needs to be considered as a possible oxidant.

For selected compounds, the stoichiometric ratio $Ln:AsF_6 = 1:3$ was confirmed by titration reactions. It was shown across the whole series of lanthanoids that the last traces of LnF_3 are dissolved in aHF when exactly the mole ratio $Ln:AsF_5 = 1:3$ is reached. An excess in AsF_5 is not necessary. In the Raman spectrum of the solution, only a broad peak around 685 cm^{-1} was observed. This peak can be related to the peak at 685 cm^{-1} reported for $CsAsF_6$ [34], indicating that in the solution, AsF_6^- anions are present. There was no indication of free AsF_5 or $As_2F_{11}^-$ anions. Besides, the chemical analysis of such a solution also supports the molar ratio $Ln:AsF_6 = 1:3$.

Our results are in agreement with some data from the literature. Clifford et al. [1], in his pioneering work in 1957, claimed the existence of $Nd(SbF_6)_3$ in aHF solution. Although PF_5 is a much weaker fluoroacid than AsF_5, a few lanthanoid hexafluorophosphates were described [35–38]. The stabilization of these compounds is achieved through coordination of organic ligands. Recent examples for the stabilization of $Ln(AsF_6)_3$ were achieved through coordination of SO_2 in the compounds $[Ln(SO_2)_n](AsF_6)_3$ [39].

Compounds $Ln(AsF_6)_3$ are less stable in the solid state than in solution because stabilization by the solvent is lacking. Therefore, they can only be isolated at lower temperatures. The basicity of LnF_3 is decreasing along the series being strongest in the case of La and weakest in the case of Lu. Therefore, we were expecting to get the most stable $Ln(AsF_6)_3$ compounds with the biggest Ln^{3+} and the least stable with the smallest Ln^{3+} ion. The fluorobasicity of YF_3 is comparable with that of HoF_3. Concentrated solutions of $Ln(AsF_6)_3$ in aHF exhibit low vapour pressure at room temperature. The removal of the solvent at lower temperatures (233–263 K) under dynamic vacuum is an extremely long process (~100–300 h). Accordingly, we decided to isolate in this way some characteristic $Ln(AsF_6)_3$ compounds (Ln = La, Nd, Sm, Tm) along the series. LaF_3 is the only rare earth trifluoride that forms at room temperature stable $Ln(AsF_6)_3$. The equilibrium vapour pressure of AsF_5 above $La(AsF_6)_3$ at 298 K is practically negligible. Other rare earth trifluorides (e.g., Nd, Sm) form stable $Ln(AsF_6)_3$ only at lower temperatures, while at 298 K, they lose AsF_5 under dynamic vacuum yielding $LnF(AsF_6)_2$. The rare earth trifluorides at the end of the series (e.g., Tm) form stable $Ln(AsF_6)_3$ at temperatures 233 K or lower. At 298 K, they immediately release AsF_5 transforming to $LnF(AsF_6)_2$, which themselves are not stable under dynamic vacuum yielding at 298 K finally $Ln_2F_3(AsF_6)_3$.

If the isolation of rare earth(III) fluoroarsenates(V) (Ln = Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, and Y) is carried out at room temperature $LnF(AsF_6)_2$ type compounds are isolated. In the case of the last three elements in the series (Tm, Yb and Lu), compounds with a lower content of AsF_5 are formed, $Ln_2F_3(AsF_6)_3$. All these compounds have equilibrium vapour pressure of AsF_5 at 298 K. They lose AsF_5 under dynamic vacuum at 298 K with the rate 1–3 mg of AsF_5/mmol h.

All rare earth(III) fluoroarsenates(V) are so soluble in aHF that removal of aHF and AsF_5 leads to very concentrated solutions that suddenly become glassy, rather than providing a crop of crystals [40] (see also Section 2). Although a lot of effort was directed in growing crystals, there was no success. We were not even able to obtain crystalline powders. It is interesting that the same three groups of rare earth elements forming similar types of compounds, as observed in this work, were reported for the system LnF_3/AuF_3 [13–16]. Additionally, we isolated ErF_2AsF_6 by pumping the compound $ErF(AsF_6)_2$ under dynamic vacuum for 234 h at room temperature.

$Ln(AsF_6)_3$ compounds dissolve in aHF at room temperature without forming any precipitate. The compounds $LnF(AsF_6)_2$ also dissolve in aHF to a clear solution but at lower temperature (263 K), while at room temperature some precipitate is formed. It was shown during this work that the only stable species in aHF at room temperature is $Ln(AsF_6)_3$, while all other compounds $LnF_n(AsF_6)_{3-n}$ with $n > 0$ are soluble and stable at temperatures around or below 263 K. They solvolyse in aHF at room temperature forming $Ln(AsF_6)_3$ and LnF_3. ErF_2AsF_6 dissolves in aHF at 263 K or below to a clear solution; thus, showing that also this type of compounds exists, and that they are not a mixture of LnF_3 and $LnF_n(AsF_6)_{3-n}$ with n lower than 2.

LnF_4 are very weak as fluorobases to form $LnF_n(AsF_6)_{4-n}$ compounds. Only in the case of PrF_4, where elemental fluorine is released, does the reaction proceed with formation of $PrF(AsF_6)_2$. Clifford did the reaction between PrO_2 and SbF_5 in aHF and also obtained a compound of Pr^{3+} [1].

Table 4

(a) Infrared and Raman spectra of Y, La, Pr, Nd, Sm, Eu and Gd fluoroarsenates(V) in cm^{-1}

YF(AsF$_6$)$_2$		La(AsF$_6$)$_3$		PrF(AsF$_6$)$_2$		NdF(AsF$_6$)$_2$		SmF(AsF$_6$)$_2$		EuF(AsF$_6$)$_2$		GdF(AsF$_6$)$_2$		Assignment[b]
IR	R[a]	IR	R	IR	R	IR	R	IR	R	IR	R	IR	R	
		1020 vw		1020 vw		1020 vw		1020 vw		1020 vw		1022 vw		
										975 vw				
840 vw				836 vw		841 vw		842 vw		840 w		840 w		
		808 sh												
	782 (2)	796 s			783(4)		787(3)		787(3)		786(3)		780(2)	ν_8, E, ν_{as}(AsF$_4$)
768 vs		759 s	751(4)	767 vs	763 sh	767 vs	766 sh	768 vs		767 vs	767 sh	767 vs		
		750 sh												
							738(2)				740		745(2)	
706 sh	704(10)	704 w	711(10)		697(10)	704 vw	704(10)	702 vw	702(10)	704 sh	704(10)	700 sh	706(10)	ν_1, A$_1$, ν(AsF$_{ax}$)
			702(10)		682(6)		674 sh		678 sh		673 sh		665 sh	
675 vw	660 (2)	655 s		643s		650 m		645 m–s		640 s–m		668 sh		ν_2, A$_1$, ν_{sym}(AsF$_4$)
656 m												645 m–s		
			610(1)						600(1)					ν_5, B$_1$, ν_{as}(AsF$_4$)
575 w		562 m	564(1)	573 w		575 w		577 w		576 w		570 w		ν(LnF)
											545 sh			
529 w		538 sh		528 w		530 w		529 w		528 w	525(4)	528 w		ν_4, A$_1$, ν_{as}(AsF$_{bridge}$)
											512 sh			
		504 m	495(2)				503(2)		483(2)					
427 w														ν_3, A$_1$, δ_{sym}(AsF$_4$)
382 m–s		385 s	378(5)	385 s	380(6)	388 s	380(5)	391m–s	375(7)	375 m–s	375 ?	380 m–s		ν_6, E, δ(F$_{ax}$AsF$_4$)
			372(3)		366(4)			380 m–s						
			346(1)											

(b) Infrared and Raman spectra of Dy, Ho, Er, Tm, Yb, and Lu fluoroarsenates(V) in cm^{-1}

DyF(AsF$_6$)$_2$		HoF(AsF$_6$)$_2$		ErF(AsF$_6$)$_2$		ErF$_2$(AsF$_6$)		Tm$_2$F$_3$(AsF$_6$)$_3$		Yb$_2$F$_3$(AsF$_6$)$_3$		Lu$_2$F$_3$(AsF$_6$)$_3$		Assignment
IR		IR	R	IR	R	IR	R	IR	R	IR	R	IR	R	
						1045 vw						1022 w		
1020 vw				1020 vw		1020 v		1020 vw		1020 vw		974 w		
840 w	838 (2)	839 w				840 vw		840 vw		840 w		843 vw		ν_8, E, ν_{as}(AsF$_4$)
800 sh			786 (4)	800 sh	788(4)				792 (4)				782(4)	
766 vs	767(4)	770 vs	735 (3)	768 vs		772 vs		770 vs	770 sh	768 vs		766 vs	770 sh	
	740(4)		708 (10)											
704 w	704(9)	703 sh	664 sh	704 w	707 (10)	700 sh	705(3)	707 vw	707 (10)	708 sh		704 vw	706 (10)	ν_1, A$_1$, ν(AsF$_{ax}$)
					672(4)		686 (10)		672 sh				685 sh	
645 m		646 m		648 w-m		673 vw		668 w		675 sh		669 sh		ν_2, A$_1$,
	620 (2)					655 m–s		649 m		647 m		655 m		ν_{sym}(AsF$_4$) ν_5, B$_1$,
														ν_{as}(AsF$_4$)
588 w		577 w		576 w		574 w		577 w		574 w		576 w		ν(LnF)
528 w		528 w		528 w		525 w		528 w		527 w		528 w		ν_4, A$_1$, ν_{as}(AsF$_{bridge}$)
			510 (1)									458 w		
424 sh		425 sh				432 w–m				428 w		432 w		ν_3, A$_1$, δ_{sym}(AsF$_4$)
														ν_6, E,
376 m–s	382(10)	380 m	380(4)	376 w–m		385 m–s		372 m	380(6)	382 m		380 m–s	380 (5)	δ(F$_{ax}$AsF$_4$)

[a] Raman intensities are given in parentheses. Infrared intensities: s: strong, m: medium, w: weak, sh: shoulder, br: broad.

[b] Assignment based on the C_{4v} symmetry of the deformed AsF$_6^-$ ion [41]: ν: stretching, δ: deformation, sym: symmetric, as: asymmetric vibration.

3.2. Vibrational spectra

Vibrational spectra of rare earth(III) fluoroarsenates(V) show similar characteristics and fall into the same class (even the spectra of La(AsF_6)$_3$; see Table 4 and Fig. 2). They are assigned primarily to the vibrations of the anion. Nevertheless, they are significantly different from the spectra of the AsF_6^- ion. The strongest Raman (697–711 cm^{-1}) and the strongest infrared band (765–768 cm^{-1}) are shifted to higher frequencies compared with the strongest bands of the octahedral AsF_6^- ion (compare with $CsAsF_6$ [34] in which Raman active symmetrical stretching, $\nu_1(A_{1g})$, appears at 685 cm^{-1} and the infrared degenerate stretching, $\nu_3(F_{1u})$; at 699 cm^{-1}). Considering the composition of the compounds and the fluorine acceptor abilities of AsF_5, this alone suggests, in agreement with the expected shifts in electron density according to 'Gutmann's second rule' [42], partial sharing of a fluorine ion by formation of a fluorine bridge between the lanthanoid atom and As. Consequently, a distorted octahedral AsF_6^- ion of presumably C_{4v} symmetry is indicated. The observed number of bands supports the deduction. Instead of one infrared band of the AsF_6^- ion at ~699 cm^{-1} in the As–F stretching region (see Ref. [34]), four bands, although some of them weak and all of them broad, are observed (~770, ~705, ~650 and ~530 cm^{-1}). They are readily assigned to the vibrations of the bridged anion of C_{4v} symmetry (see Table 4). The bands in spectra of La(AsF_6)$_3$ are in the same frequency regions and have a similar distribution of intensities. The extensive splitting of the strongest infrared band at ca. 760 cm^{-1} ($\Delta = 37$ cm^{-1}) is the result of the changed interactions in the crystal due to different composition, but the doubling of both new components (808/796 and 759/750 cm^{-1}) and the doubling of the strongest Raman band (711/702 cm^{-1}) is obviously caused by correlation effects.

The distribution of frequencies and intensities is in accord with the observations for a series of $MF_2 \cdot 2AsF_5$ compounds, which includes alkaline earth metals and some transition elements [41]. It has been proposed that the spectra are reflecting the relative fluorobasicity and fluoroacidity of the components, which influence the strength of fluorine bridges. With high basicity of a metal fluoride, an ionic compound with octahedral AsF_6^- ions is formed (for instance, the compounds of Sr or Ba), while with lower basicity a F bridge with some degree of covalency distorts the AsF_6^- octahedra to presumably C_{4v} symmetry. The spectra of our compounds are comparable to the spectra of Mg, Co and Ni compounds mentioned above. They indicate low fluorobasicity of rare earth trifluorides, the consequent covalent contribution to the fluorine bridges and appreciably deformed AsF_6^- octahedra.

Identification of the cationic part in the spectra presents a problem; however, in view of LnF_6^{3-} ions absorbing in the infrared between 325 and 392 cm^{-1} [43], matrix-isolated LnF_3 between 480 and 508 cm^{-1} [44] and that a series of $M–F^+$ ions (M: Fe, Cu, Zn, Sn, Cr, Zr, Pb) absorbs in the region between 560 and 620 cm^{-1} [41,45], we tentatively assign the weak and broad band at ca. 570 cm^{-1} to a stretching vibration of the Ln–F bond.

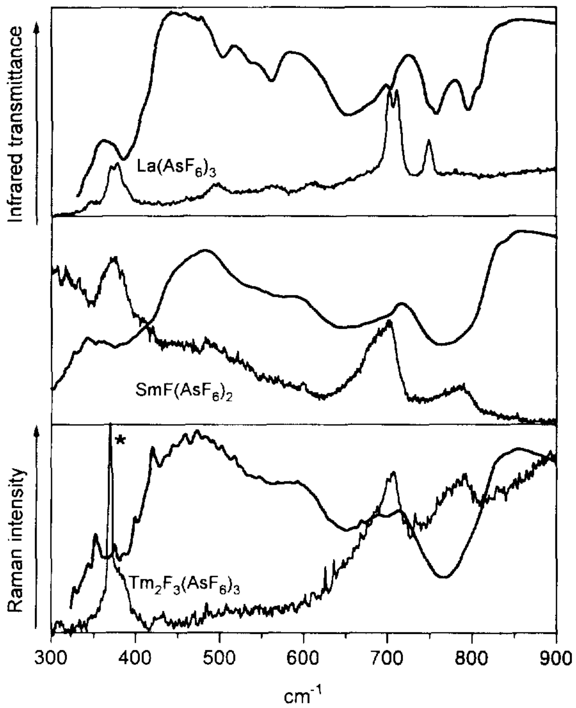

Fig. 2. Examples of infrared and Raman spectra of $LnF_n(AsF_6)_{3-n}$ compounds with $n = 0$, 1 and 1.5; *plasma line.

4. Conclusion

In the system, rare earth trifluorides–AsF_5–aHF, the following compounds, stable at 298 K, are formed: La(AsF_6)$_3$, LnF(AsF_6)$_2$ with Ln = Ce to Er and Y and $Ln_2F_3(AsF_6)_3$ with Ln = Tm, Yb and Lu. All these compounds lose AsF_5 (1–3 mg/mmol h) under dynamic vacuum at 298 K. All rare earth(III) fluoroarsenates(V) dissolve in aHF at lower temperatures (263 K or lower), yielding clear solutions, but solvolyse at 298 K to Ln(AsF_6)$_3$ and LnF_3. All Ln(AsF_6)$_3$ are stable in aHF solutions at 298 K. In solid form, they can be isolated only at lower temperatures (263 to 233 K). Vibrational spectra of rare earth(III) fluoroarsenates(V) show that distorted AsF_6^- octahedra are present, indicating a covalent contribution to the fluorine bridges between LnF_3 and AsF_5.

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