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Metathetical synthesis of $La_2(PdF_6)_3$ and the vibrational spectra of the PdF_6^{2-} anion

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Abstract

Slow mixing of solutions of $La(AsF_6)_3$ in anhydrous hydrogen fluoride (aHF) and Cs_2PdF_6 in aHF at room temperature gives a pure yellow compound $La_2(PdF_6)_3$ insoluble in aHF. The amorphous obtained $La_2(PdF_6)_3$ is very sensitive to moisture and once dry and isolated it solvolyses in contact with fresh aHF. It represents a new type of compound in the systems rare earth (Ln) trifluorides/transition metal (M) tetrafluorides (LnF_3:MF_4 = 2:3). Infrared (615 cm^{-1}) and Raman data (558, 276 and 212 cm^{-1}) show the presence of PdF_6^{2-} anions in $La_2(PdF_6)_3$. K_2PdF_6, Cs_2PdF_6, and Pd_2F_6 were synthesized for comparison and investigated by vibrational spectroscopy. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Lanthanum(III) hexafluoropalladate(IV); Synthesis; Vibrational spectra of PdF_6^{2-}

1. Introduction

The most common method for the preparation of ternary fluorides containing rare earth elements is partial or all solid-state reactions where suitable amounts of binary fluorides or other corresponding starting materials (e.g. chlorides, carbonates) are heated in or without the presence of elemental fluorine. These reactions are usually carried out for some hours at elevated temperature and sometimes at high pressure of fluorine when necessary. Often the whole batch is inhomogeneous and only some crystals were obtained from the reaction mixture and characterization of the product was made by X-ray diffraction analysis.

In the past it has been shown that metathetical reactions in aHF (anhydrous hydrogen fluoride) could be useful for the preparation of new or already known binary fluorides; e.g. mixing of solutions of $M_2M'F_6$ (M = alkali metal, $M' = Ni^{IV}, Mn^{IV}$) in aHF and $M'(AsF_6)_2$ ($M' = Ni^{II}, Mn^{II}$) in aHF yields black and red precipitates of NiF_3 [1] and MnF_3 [2] respectively. Recently, this method was also applied for the preparation of new ternary fluorides [3,4]. This paper reports on metathetical synthesis of a new ternary fluoride in the system LnF_3/MF_4 (Ln = rare earth element, M: transition element) where the synthesis of $La_2(PdF_6)_3$ was achieved as a result of this metathetical approach.

In the course of the preparation of starting materials some new observations were also established for syntheses (already described in the literature [5]) of M_2PdF_6 (M = alkali metal) compounds by reactions between alkali metals and palladium in the presence of fluorine in aHF.

For Pd_2F_6 ($Pd^{II}Pd^{IV}F_6$) and M_2PdF_6 (M = alkali metal) compounds some vibrational data have already been reported [6–10]. In order to make these data more complete and sometimes less abstruse new measurements are presented. A compilation of data for compounds containing PdF_6^{2-} anions and comparison with vibrational spectra of $La_2(PdF_6)_3$ is given.

2. Experimental

2.1. Techniques

Infrared spectra were taken on a Perkin-Elmer FTIR 1710 spectrometer on powdered samples between AgCl windows in a leak tight brass-cell. Raman spectra were recorded on a Renishaw Raman Imaging Microscope System 1000, with He–Ne laser with wavelength 632.8 nm. The Raman spectra of solutions of M_2PdF_6 (M = K, Cs) in aHF were taken in a PFA test tube. X-ray powder diffraction patterns

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were obtained using the Debye–Scherrer technique with Ni-filtered Cu Kα radiation. Samples were loaded into quartz capillaries (0.5 mm) in a dry-box.

2.2. Reagents and apparatus

Volatile materials (AsF_5, aHF) were manipulated in an all Teflon vacuum line equipped with Teflon valves. All non-volatile products are sensitive to traces of moisture. The manipulation of the nonvolatile materials was done in a dry-box (M. Braun). The residual water in the atmosphere within the dry-box never exceeded 1 ppm. The reactions were carried out in PFA vessels (height 250 mm, inner diameter 15.5 mm, outer diameter 18.75 mm) equipped with Teflon valves and Teflon coated stirring bars. Reaction vessels combined from two PFA tubes in a T-shape and with a Teflon valve were used in some experiments. The synthesis of $La_2(PdF_6)_3$ was carried out in a T-shape reaction vessel equipped with two Teflon valves. An additional Teflon valve separated both arms of the T-shape reaction vessel. Prior to their use all reaction vessels were passivated with elemental fluorine.

LaF_3 (Johnson Matthey GmbH, Alfa Products, 99.9% (REO), CsF (Ventron, 99.9%), KF (Ventron, 99.9%) and Pd (Alfa Products, 99.9%) were used as supplied. Purity of CsF was checked by chemical analysis (obtained %F 12.4; calculated %F, 12.51). AsF_5 was synthesised by pressure fluorination of arsenic trioxide with elemental fluorine in a nickel reactor at 573 K as previously described for the syntheses of PF_5 [11]. Fluorine was used as supplied (Solvay, 99.98%). Anhydrous HF (Praxair, 99.9%) was treated with K_2NiF_6 for several hours prior to use.

2.3. Synthesis of Pd_2F_6

Pd_2F_6 was prepared from 0.242 g (2.27 mmol) of Pd and excess of fluorine in aHF at room temperature as described previously [2]. Its purity was checked by chemical analysis (obtained %Pd, 63.9%, %F, 34.6; calculated %Pd, 65.12, %F, 34.88). X-ray powder diffraction pattern of the isolated black product was in agreement with literature data for Pd_2F_6.

2.4. Reactions between Pd, MF ($M = K$, Cs) and F_2 in aHF

Reactions were carried out in a similar method as described in the literature for the syntheses of M_2PdF_6 ($M = Li$, K) compounds [5]. Starting materials were loaded in PFA reaction vessels in a dry-box. Then 6–7 ml aHF was condensed onto the solid at 77 K and the reaction mixture was warmed to room temperature. Fluorine was slowly added at room temperature to the final pressure in reaction vessel as given in Table 1. In the system $CsF/Pd/F_2/aHF$ three experiments with different molar ratios of reactants were performed.

In the case of reactions between equimolar amounts of MF ($M = K$, Cs) and Pd in the presence of fluorine in aHF at room temperature yellow-orange solutions were obtained. Traces of an orange-brown solid were observed at the bottom of reaction vessel in the case of oxidation of Pd with fluorine in aHF made basic with CsF. After recording Raman spectra of both ($M = K$, Cs) yellow-orange solutions (broad band at 580 cm^{-1}) volatile components were pumped away at room temperature and bright yellow precipitates were formed. Isolated yellow products did not change their colour for weeks. The weights of the isolated compounds were 0.429 g (calculated 0.448 g for K_2PdF_6) and 0.474 g (calculated 0.486 g for Cs_2PdF_6) respectively. Chemical analysis confirmed both isolated compounds: (obtained %F, 37.7, %Pd, 34.6, calculated for K_2PdF_6: F%, 38.18, %Pd, 35.63) and (obtained %F, 23.2, %Pd, 22.0, calculated for Cs_2PdF_6: F%, 23.45, %Pd, 21.88). The X-ray powder diffraction pattern of the product in the system $CsF/Pd/F_2/aHF$ was in agreement with literature data for the cubic form of Cs_2PdF_6 [12,13]. The X-ray diffraction powder pattern of the product in the system $KF/Pd/F_2/aHF$ corresponded to hexagonal modification of K_2PdF_6 [12,13].

In the second reaction between CsF, Pd and F_2 in aHF where an excess of CsF was used the procedure was similar. After some time a yellow-orange solution with traces of insoluble solid was also obtained. The solution was decanted away and a yellow precipitate was obtained from it. Overnight the PFA reaction vessel containing the yellow solid was stored in a dry-box. In the morning the solid was

Table 1
Reaction conditions for the oxidation of Pd metal by elemental fluorine in aHF made basic with alkali metal fluorides (MF)

M	MF		Pd metal		Molar ratio $n(MF):n(Pd)$	$P_{(fluorine)}$ (bar)	Time of reaction (days)	Obtained product
	(g)	(mmol)	(g)	(mmol)				
Cs	0.114[a]	0.75	0.030	0.28	2.68:1.00	3.0	3	$Cs_2PdF_6/CsF\cdot nHF$
	0.304	2.00	0.106	1.00	2.00:1.00	3.0	5	Cs_2PdF_6
	0.558[a]	3.67	0.227	2.13	1.72:1.00	1.6	10	Cs_2PdF_6[b]
K	0.174	3.00	0.160	1.50	2.00:1.00	3.0	6	K_2PdF_6

[a] T-shape reaction vessel was used.

[b] Product was isolated from solution decanted from unreacted Pd.

Table 2
Chemical analysis of $La_2(PdF_6)_3$

$La_2(PdF_6)_3$	%La	%Pd	%F	%Cs	%As	n(La):n(Pd):n(F):n(Cs):n(As)
Obtained	29.2	32.9	35.7	0.72	0.49	2 : 2.94 : 17.87 : 0.05 : 0.06
Calculated	29.59	33.99	36.42	0	0	2 : 3 : 18 : 0 : 0

brown and after six days black-brown sticky material was formed.

In the third experiment where a deficit of CsF was used, fluorine was added until the pressure in reaction vessel did not further change. After some time the yellow-orange solution was decanted away from unreacted Pd. Volatile components were pumped away and a yellow precipitate formed. The colour of yellow solid did not change for weeks. The weight of isolated compound was 0.882 g (calculated 0.892 g for Cs_2PdF_6). Chemical analyses showed: (obtained %F, 23.4%, %Pd, 21.7%; calculated for Cs_2PdF_6: %F, 23.45%, % Pd, 21.88%). The X-ray powder diffraction pattern of obtained product was in agreement with literature data for the cubic form of Cs_2PdF_6 [12,13].

2.5. Synthesis of $La_2(PdF_6)_3$

0.358 g (1.83 mmol) of LaF_3 was loaded in a dry-box into one arm of a T-shape PFA reaction vessel equipped with two Teflon valves. Then, aHF (6 ml) was condensed onto LaF_3 from a PFA reservoir containing K_2NiF_6, and 0.943 g (5.55 mmol) of AsF_5 was added, both at 77 K. The reaction vessel was warmed up to 298 K and LaF_3, otherwise insoluble in aHF, readily dissolved due to the presence of AsF_5. The reaction was carried out at room temperature until a clear solution of $La(AsF_6)_3$ in aHF [14] was obtained. The Teflon valve separating both arms of reaction vessel was closed and volatile materials were pumped away from the rest of the PFA reaction vessel.

For the preparation of solution of Cs_2PdF_6 in aHF 0.293 g (2.75 mmol) Pd and 0.837 g (5.51 mmol) CsF were placed in a dry-box into PFA reaction vessel. aHF (7 ml) was condensed onto the reaction mixture at 77 K. After warming the reaction vessel to room temperature fluorine was slowly added to a final pressure of 6 bar. After 10 days a yellow-orange solution with traces of insoluble orange-brown solid was obtained. An excess of fluorine and aHF were pumped away. In a dry-box the obtained, and not completely dry, yellow compound Cs_2PdF_6 (obtained 1.397 g; calculated 1.337 g) was loaded in an empty arm of a T-shape reaction vessel which already contained a solution of $La(AsF_6)_3$ in aHF in the other arm. The aHF was condensed onto the yellow solid and after warming the reaction vessel to room temperature a yellow-orange solution was obtained. The Teflon valve separating both tubes of the T-shape reaction vessel was opened and a solution of Cs_2PdF_6 in aHF was added slowly in small batches to the solution of $La(AsF_6)_3$ in aHF. A yellow and very voluminous precipitate immediately started to form. At the end a very dense suspension was obtained with no visible clear liquid phase above it. Precipitate started to deposit slowly. After 12 h the volume of aHF insoluble solid was 10 times smaller as at the beginning of depositing and above it a colourless liquid phase could be observed. The solution of $CsAsF_6$ in aHF was decanted away from the precipitate in such a way that to leave 1 cm of aHF above the yellow precipitate. Then, aHF was condensed back onto the yellow solid and the rest of the aHF at 77 K. After warming the reaction vessel to room temperature and 10 min of intensive stirring, the yellow compound deposited and liquid phase was decanted again. This was repeated 28 times to wash the yellow solid free of $CsAsF_6$. Finally, volatile materials were pumped away at room temperature. In one arm of a T-shape reaction vessel a yellow material was left (obtained 0.824 g; calculated 0.859 g for $La_2(PdF_6)_3$). The results of chemical analysis are in Table 2. The X-ray diffraction pattern of yellow isolated product did not show any lines.

The X-ray diffraction powder pattern of the brownish material isolated from the decanted solution only gave the pattern of $CsAsF_6$; the colour, however, indicates the presence of a small amount of decomposed $La_2(PdF_6)_3$.

2.6. Chemical analysis

Lanthanum and palladium were determined by complexometric titration [15–17]. Total fluoride ion content was determined with an ion selective electrode [18,19]. Arsenic and cesium were determined by the ICP method [20].

3. Results and discussion

3.1. Synthesis of $La_2(PdF_6)_3$

The metathetic reaction between La(III) and Pd(IV) ternary fluorides is based on the method used for synthesis of NiF_3 [1], and proceeds according to the equation:

$$2La(AsF_6)_{3\,(\text{dissolved in aHF})} + 3Cs_2PdF_{6\,(\text{dissolved in aHF})} \xrightarrow{298\,K} La_2(PdF_6)_3 + 6CsAsF_6$$

Slow mixing of solutions of $La(AsF_6)_3$ in aHF and Cs_2PdF_6 in aHF gives pure yellow $La_2(PdF_6)_3$, insoluble in aHF. The most likely impurity is $CsAsF_6$. Therefore thorough washing of the $La_2(PdF_6)_3$ precipitate with aHF, in which $CsAsF_6$ is rather soluble, is required. From a chemical analysis of

$La_2(PdF_6)_3$ (Table 2) it appears that some very small amounts of $CsAsF_6$ may still be present in the sample even though a thorough separation was performed. However, X-ray powder diffraction pattern showed no detectable lines of $CsAsF_6$.

The mass balance and chemical analysis of the isolated yellow solid correspond to the molar ratio $LaF_3:PdF_4 = 2:3$. Therefore, the product can be written as $La_2(PdF_6)_3$. On the basis of the yellow colour which is typical for compounds containing PdF_6^{2-} anions [5,8,12,21–24] and the vibrational spectra (see Section 3.2), it can be concluded that this is a PdF_6^{2-} compound and not a mixture of LaF_3 and PdF_4. A mixture of white LaF_3 and brick red PdF_4 in the molar ratio 2:3 would be reddish and not yellow. Another possibility for reaction between solutions of $La(AsF_6)_3$ in aHF and Cs_2PdF_6 in aHF would be the formation of a mixture of the PdF_4 and of a compound of the type $LnFMF_6$ (Ln = rare earth element, M = Pd). For palladium such type of compound is not known, but there are examples for other transition elements (M = Zr [25], Hf [26], Nb [27], Mo [28], Pt [29]) described in the literature. In the Raman spectrum there was no sign of a band around 660 cm^{-1} where the strongest band belonging to PdF_4 [8] can be found, so this possibility can be excluded.

$La_2(PdF_6)_3$ is very sensitive to moisture and readily decomposes on exposure to the atmosphere. The dry compound $La_2(PdF_6)_3$ solvolyses in contact with aHF. The product was poorly crystallized and consequently there were no lines in the X-ray diffraction powder pattern.

The described preparation of $La_2(PdF_6)_3$ confirms the usefulness of metathetical synthesis for the preparation of new ternary fluorides between rare earth trifluorides and other transition metal fluorides. In the literature there are already many reports about ternary fluorides between rare earth trifluorides and transition metal tetrafluorides [25–33]. On the basis of the molar ratio $LnF_3:MF_4$ they can be divided into four groups: $LnF_3:MF_4 = 1:1$ ($LnFMF_6$; M = Zr [25], Hf [26], Nb [27], Mo [28], Pt [29]); $LnF_3: MF_4 = 1:2$ (LnM_2F_{11}; M = Zr [30], Hf [26], Th [31]); $LnF_3: MF_4 = 1:3$ (LnM_3F_{15}; M = Zr [26,32,33], Hf [26,33], Tb [33]); and $LnF_3: MF_4 = 1:4$ (LnM_4F_{19}; M = Zr [26]). In this paper the described compound $La_2(PdF_6)_3$ represents a new type where the molar ratio of $LnF_3:MF_4$ corresponds to 1:1.5 (2:3). All previously mentioned compounds in the LnF_3/MF_4 systems were prepared at temperatures higher than 573 K from equimolar amounts of binary fluorides. Since PdF_4 starts to decompose above 473 K to Pd_2F_6 [34], it is questionable if $La_2(PdF_6)_3$ could be prepared in such a way.

3.2. Vibrational spectra

The Raman and infrared spectra of $La_2(PdF_6)_3$ and some other PdF_6^{2-} salts are shown in Figs. 1–4 and vibrational assignments are listed in Table 3. For a regular octahedral PdF_6^{2-} anion, three stretching modes $\nu_1(A_{1g})$, $\nu_2(E_g)$ and $\nu_3(F_{1u})$ and three bending modes $\nu_4(F_{1u})$, $\nu_5(F_{2g})$ and $\nu_6(F_{2u})$ are allowed, where ν_1, ν_2, and ν_5 are Raman active modes, ν_3 and ν_4 are infrared active modes and ν_6 is a silent mode. The strongest band (558 cm^{-1}) in the Raman spectrum of $La_2(PdF_6)_3$ can be readily assigned to the Raman active symmetrical stretching ν_1, and the other two bands (276 and 212 cm^{-1}) are components of the ν_5 bending mode. The

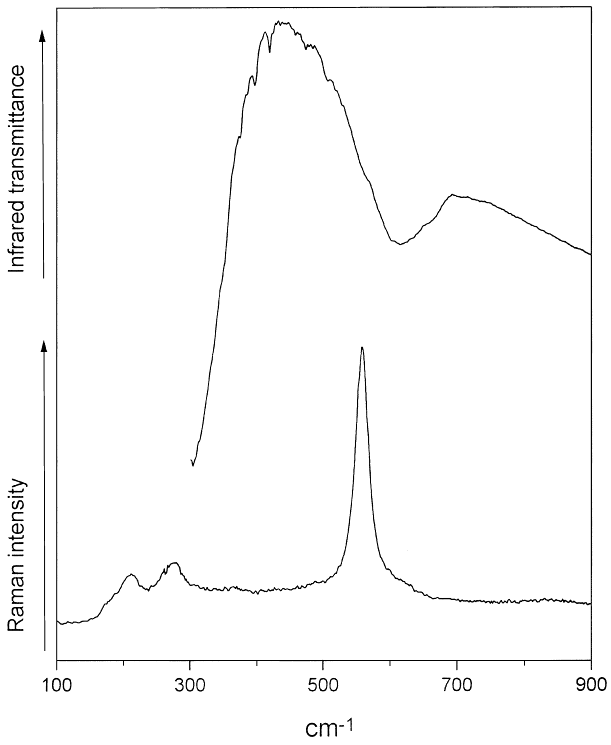


Fig. 1. Vibrational spectra of $La_2(PdF_6)_3$.

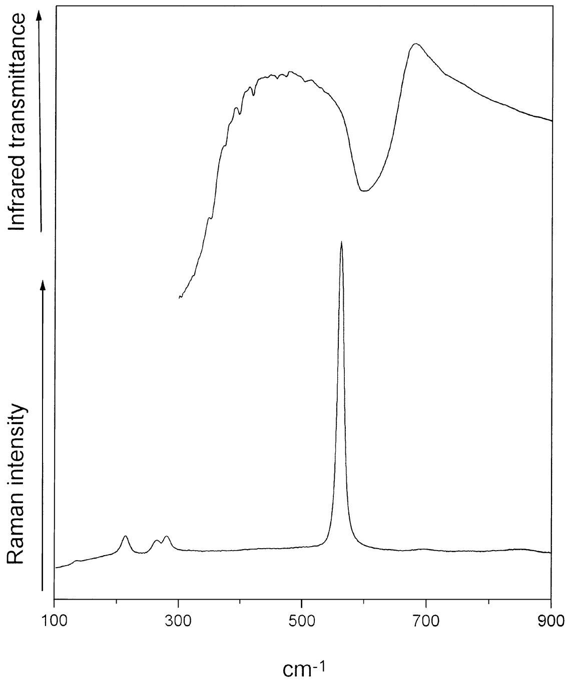


Fig. 2. Vibrational spectra of Pd_2F_6.

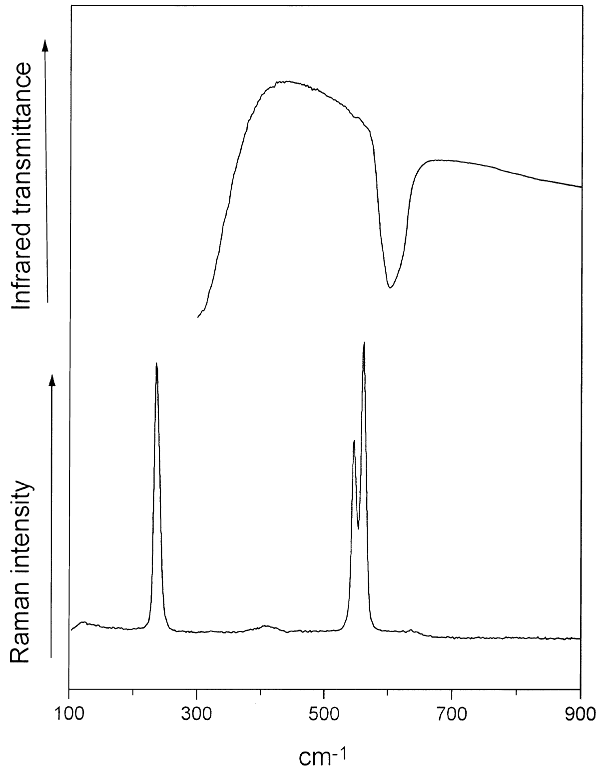


Fig. 3. Vibrational spectra of Cs_2PdF_6.

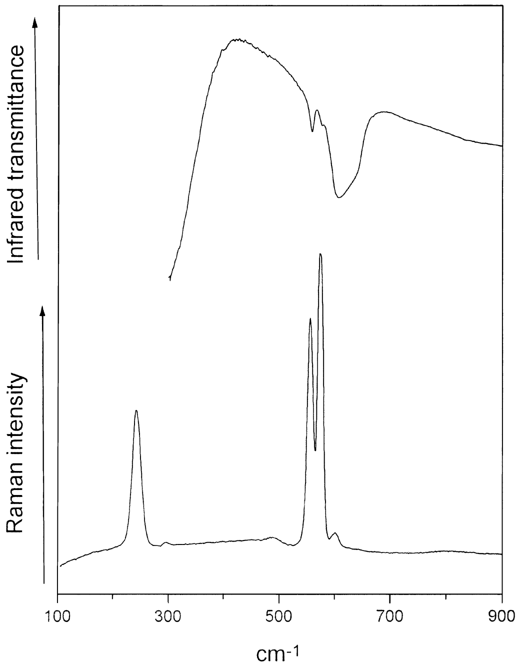


Fig. 4. Vibrational spectra of K_2PdF_6.

splitting of ν_5 is probably caused by site symmetry effects. The ν_2 stretching mode has not been observed. The strongest band (615 cm^{-1}) in the infrared spectrum is assigned to the infrared active degenerate ν_3 stretching mode.

Pd_2F_6 ($Pd^{II}Pd^{IV}F_6$) crystallises in the $R\bar{3}$ space group with $Z = 1$ [35]. From site symmetry considerations it is obvious that the lowering of the $PdF_6{}^{2-}$ symmetry from O_h to C_{3i} should split some degenerate vibrations (Table 4). We observed splitting only for ν_5 in the Raman spectrum, meanwhile in the infrared spectrum (599 cm^{-1}) only a single band was observed. The strongest Raman band (562 cm^{-1}) assigned to ν_1 is in agreement with literature data [8].

Cs_2PdF_6 crystallises in a cubic K_2PtCl_6 structure type (space group $Fm3m$, $Z = 4$) [12,13], but K_2PdF_6 exists in the trigonal (K_2GeF_6-type, space group $P\bar{3}m1$, $Z = 1$) [12,13,21], and hexagonal (K_2MnF_6-type, space group $P6_3mc$, $Z = 2$) [12,13] forms. For the cubic form, the selection rules for the isolated ion should hold. In the Raman spectrum of Cs_2PdF_6 the strongest bands at 561 cm^{-1} and 235 cm^{-1} can be readily assigned to ν_1 and ν_5, respectively,

Table 3
Infrared and Raman spectra of K_2PdF_6, Cs_2PdF_6, Pd_2F_6, $La_2(PdF_6)_3$ and literature data for $(NO)_2PdF_6$ and $(XeF_5)_2PdF_6$ in cm^{-1}

K_2PdF_6[a]		Cs_2PdF_6[a]		Pd_2F_6[a]		$La_2(PdF_6)_3$[a]		$(NO)_2PdF_6$[b]	$(XeF_5)_2PdF_6$[c]	Assignment[g]
Ir[d]	R[e]	IR	R	IR	R	IR	R	R[d]	R	
									634 (4)	
									624 (2)	ν_3
608 (vs) [605][f]	602 (5)	602 (vs) [600]		599 (vs)		615 (s, br)			616 (8)	
577 (w)	575 (100)		561 (100)		562 (100)		558 (100)	573 (s)	558 (67)	ν_1
560 (m) [558]	556 (60)		546 (60)					554 (ms)	535 (92)	ν_2
[295]	295 (2)	[290]							295 (7)	ν_4
					281 (5)		276 (15)		269 (6)	
[236]	242 (40)		235 (90)		265 (3)		212 (10)	243 (ms)	245 (10)	ν_5
					215 (5)					

[a] This work.

[b] [23].

[c] [43].

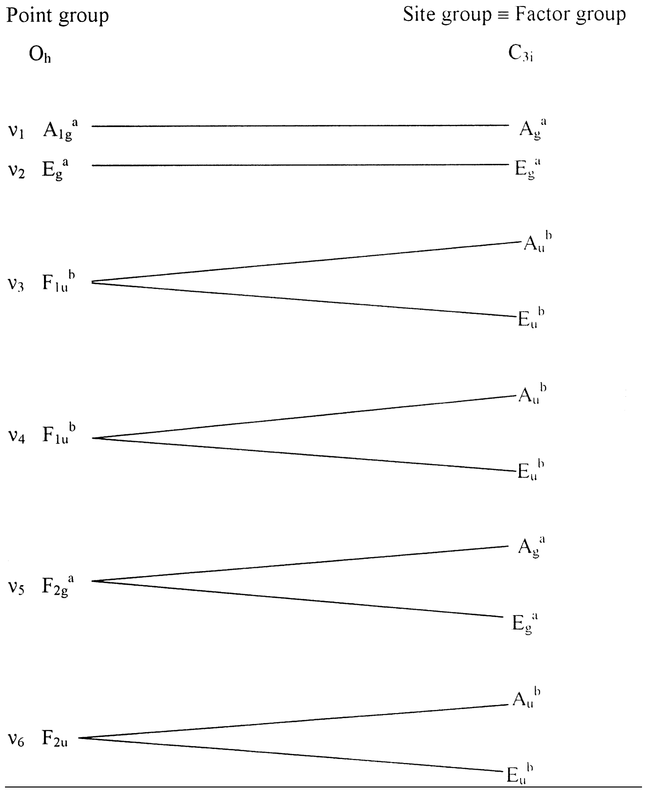
[d] IR intensities and Raman intensities for $(NO)_2PdF_6$: vs: very strong, s: strong, ms: medium strong, m: medium, w: weak, br: broad.

[e] Raman intensities are given in parentheses.

[f] Values in parentheses were given in literature [7] without assignments and data on crystal forms of M_2PdF_6 compounds.

[g] Assignments are made for octahedral symmetry, although in the solid state the actual symmetry is obviously lower (see text).

Table 4
Correlation diagram for the PdF_6^{2-} ions in Pd_2F_6 for $R\bar{3}$ space group and $Z = 1$



[a] Raman active.
[b] Infrared active.

in agreement with literature data for Cs_2PdF_6 [10]. An additional band at 546 cm^{-1} which is surprisingly not mentioned in the same paper [10] belongs to ν_2. The infrared spectrum of Cs_2PdF_6 shows a very intense band (602 cm^{-1}) assigned to ν_3 as previously reported [7]. In the literature there is also a report of a medium strong band at 290 cm^{-1} [7] which can be assigned to ν_4.

The X-ray powder diffraction pattern of our K_2PdF_6 shows only the presence of the hexagonal form of K_2PdF_6. In the hexagonal form of K_2PdF_6 the symmetry of the regular octahedral PdF_6^{2-} ion is reduced. As a consequence not only are splittings of some bands observed, but also some otherwise Raman or infrared inactive bands become active [36]. The strongest Raman bands (575, 556 and 242 cm^{-1}) can be readily assigned to ν_1, ν_2, and ν_5 respectively. Because of the symmetry lowering of the PdF_6^{2-} ion in the hexagonal form of K_2PdF_6, ν_3 and ν_4 became Raman active. The band at 602 cm^{-1} can be assigned to ν_3 and the band at 295 cm^{-1} to ν_4. This violation of the selection rules is similar in the case of the infrared spectrum. The strongest band (608 cm^{-1}) is assigned to ν_3. An additional two bands (577, 560 cm^{-1}), otherwise inactive in infrared spectra of regular octahedral PdF_6^{2-} ion, are assigned to ν_1 and ν_2 respectively. The values of ν_3 and ν_2 are in agreement with literature data [7], meanwhile ν_1 was not described. The same paper also reports two bands at 295 and 236 cm^{-1} which can be assigned to ν_4 and ν_5, respectively.

3.3. Reactions between Pd, MF ($M = K$, Cs) and F_2 in aHF

Oxidation of Pd with fluorine in aHF, made basic with MF ($M = K$ or Cs) yields yellow-orange solutions containing PdF_6^{2-} anions. In the case of reactions between Pd and excess or equimolar amount of CsF in the presence of fluorine in aHF traces of orange-brown solid were observed at the bottom of reaction vessels. An insoluble solid was separated from the solution but attempts to investigate the orange-brown solid by vibrational spectroscopy were unsuccessful due to the small size of the sample. Therefore, future investigations should be made to determine whether traces of these insoluble orange-brown solids are impurities or, because of their insolubility in aHF, this is a compound which possibly contains a polymeric anion (e.g. $CsPdF_5$). When an excess of CsF was used, the same phenomenon was observed. Therefore, the insoluble material could not be unreacted palladium. It is interesting that traces of insoluble orange-brown solid in the solution on the bottom of the reaction vessel were also observed in the synthesis of $(NH_4)_2PdF_6$ [37].

In the case of reaction between Pd and excess of CsF in the presence of fluorine in aHF it was also observed that the isolated solid turned from yellow to brown and finally to black indicating that some decomposition was taking place in the isolated sample. In the Raman spectrum, besides bands belonging to the PdF_6^{2-} anion (561, 546 and 235 cm^{-1}, see Section 3.2), two additional bands at 410 cm^{-1} (medium) and 510 cm^{-1} (weak) were observed. With time, the intensity of the additional bands increased and that of other bands belonging to the PdF_6^{2-} anion decreased. It is interesting that decomposition was also observed in the case of $(NH_4)_2PdF_6$ where the isolated product changed colour from yellow to brown after one night, even if it was stored in a dry-box [37]. One of the causes could be the presence of moisture because the hydrolysis products from Cs_2PdF_6 are brown [12,38]. However in the dry-box, where the reaction vessel with isolated compound was stored, the moisture content was always lower than 1 ppm. Also if the moisture was present in reactants (e.g. CsF), it would react with fluorine at the time of the experiment and form aHF. From the results of all three experiments with different starting molar ratios of CsF and Pd, we can conclude that most likely the cause of the colour change of the isolated sample is the use of an excess of CsF. It is known that reactions between CsF and hydrogen fluoride give compounds CsF·*n*HF where *n* depends on the vacuum conditions and the temperature [39]. In the case of the oxidation of Pd metal with fluorine in aHF in the presence of an excess of CsF, a mixture of CsF·*n*HF and Cs_2PdF_6 is obtained during isolation. With time, CsF·*n*HF can cause the decomposition of yellow Cs_2PdF_6 to an unknown compound. In view of the complexity of the products formed in the M/Pd/F (M: alkali metal) [12,21,39–42] system, a detailed investigation of the decomposition mechanism and of the resulting products was beyond the scope of this study.

When Cs_2PdF_6 was prepared from equimolar amounts of CsF and Pd in the presence of fluorine in aHF or with deficit of CsF, there was no sign of decomposition even after weeks. The colour of the bright yellow solid did not change and the Raman spectrum did not show any additional bands except those belonging to the PdF_6^{2-} anion (see Section 3.2).

4. Conclusions

The described synthesis of $La_2(PdF_6)_3$ and the syntheses reported in the literature [3,4] of some other ternary fluorides present a milder approach for the formation of new ternary fluorides where high temperature reactions are not useful because of the instability of the reactants or the products. For the previously reported preparations of ternary fluorides, side reactions between reactants and the metal reaction vessels must be taken into account when very high temperatures were involved. In the metathetical synthesis, all reactions are carried out in reaction vessels made of PFA, which is very resistant and inert and, therefore, the only contamination should come from a side product. Therefore there is no danger of contamination of the final product by by-products formed between reagents and the reaction vessel material.

Metathetical reactions in liquid aHF offer access not only to intermediate oxidation states of binary fluorides which are sometimes difficult to prepare in high purity [1,2] but also to new ternary fluorides as was shown with synthesis of $La_2(PdF_6)_3$. Therefore, the described metathetical approach deserves more frequent use in the preparation of various binary and ternary fluorides, not only for that described here.

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References

[1] B. Žemva, K. Lutar, L. Chacón, M. Fele-Beuermann, J. Allman, C. Shen, N. Bartlett, J. Am. Chem. Soc. 117 (1995) 10025.
[2] Z. Mazej, K. Lutar, B. Žemva, Acta Chim. Slov. 46 (1999) 229.
[3] C. Shen, L.C. Chacón, N. Rosov, S.H. Elder, J.C. Allman, N. Bartlett, C. R. Acad. Sci. Paris Series IIc 2 (1999) 557.
[4] O. Graudejus, S.H. Elder, G.M. Lucier, C. Shen, N. Bartlett, Inorg. Chem. 38 (1999) 2503.
[5] G. Lucier, S.H. Elder, L.C. Chacón, N. Bartlett, Eur. J. Solid State Inorg. Chem. 33 (1996) 809.
[6] R.D. Peacock, D.W.A. Sharp, J. Chem. Soc. (1959) 2762.
[7] S.V. Zemskov, J.I. Nikonorov, E.D. Pastuhova, V.N. Mitkin, Izv. Sib. Otd. AN SSSR Ser. Khim. Nauk (1976) 83.
[8] N. Bartlett, B. Žemva, L. Graham, J. Fluorine Chem. 7 (1976) 301.
[9] M.J. Reisfeld, J. Molec. Spec. 29 (1969) 120.
[10] V.B. Sokolov, J.V. Drobyševski, V.N. Prusakov, A.V. Ryžkov, S.S. Horošev, Doklad. Akad. Nauk SSSR 229 (1976) 641.
[11] A. Jesih, B. Žemva, Vestn. Slov. Kem. Drus. 33 (1986) 25.
[12] R. Hoppe, W. Klemm, Z. Anorg. Allg. Chem. 268 (1952) 364.
[13] D. Babel, Structural chemistry of octahedral fluorocomplexes of the transition metals, in: C.K. Jørgensen, J.B. Neilands, R.S. Nyholm, D. Reinen, R.J.P. Williams (Eds.), Structure and Bonding, Vol. 3, 1967, p. 3.
[14] M. Fele-Beuermann, K. Lutar, Z. Mazej, S. Milićev, B. Žemva, J. Fluorine Chem. 89 (1998) 83.
[15] G. Schwarzenbach, H. Flaschka, Complexometric Titrations, Methuen, London, 1969, p. 250.
[16] D.D. Perrin, Masking and Demasking of Chemical Reactions, Wiley/Interscience, New York, 1970, p. 33.
[17] R. Pribil, Applied Complexometry, Vol. 5, Pergamon Press, London, 1982, pp. 194–197.
[18] Y. Koryta, Anal. Chim. Acta 61 (1972) 329.
[19] A.K. Covington, Ion-Selective Electrode Methodology, Vol. 2, CRC Press, Boca Raton, FL, 1984, pp. 76–80.
[20] P.W.J.M. Boumans, Inductively Coupled Plasma Emission Spectroscopy, Part 1, Wiley/Interscience, New York, 1987.
[21] N. Bartlett, J.W. Quail, J. Chem. Soc. (1961) 3728.
[22] K. Leary, D.H. Templeton, A. Zalkin, N. Bartlett, Inorg. Chem. 12 (1973) 1726.
[23] W.A. Sunder, A.L. Wayda, D. Distefano, W.E. Falconer, J.E. Griffiths, J. Fluorine Chem. 14 (1979) 299.
[24] H. Henkel, R. Hoppe, Z. Anorg. Allg. Chem. 359 (1968) 160.
[25] O. Graudejus, F. Schrötter, B.G. Müller, R. Hoppe, Z. Anorg. Allg. Chem. 620 (1994) 827.
[26] J.M. Korenev, P.I. Antipov, A.V. Novoselova, Zh. Neorg. Khim. 25 (1980) 1255.
[27] D. Bizot, J. Chassaing, A. Erb, J. Less-Common Metals 79 (1981) 39.
[28] J.C. Couturier, J. Angenault, Y. Mary, M. Quarton, J. Less-Common Metals 138 (1988) 71.
[29] F. Schrötter, B.G. Müller, Z. Anorg. Allg. Chem. 619 (1993) 1431.
[30] J.P. Laval, A. Abaouz, J. Solid State Chem. 100 (1992) 90.
[31] A. Abaouz, A. Taoudi, J.P. Laval, J. Solid State Chem. 130 (1997) 277.
[32] J.P. Laval, J.F. Gervais, L. Fournès, J. Grannec, P. Gravereau, A. Abaouz, A. Yacoubi, J. Solid State Chem. 118 (1995) 389.
[33] A.I. Popov, M.D. Balkovski, P.P. Fedorov, J.M. Kiselev, Zh. Neorg. Khim. 36 (1991) 842.
[34] N. Bartlett, P.R. Rao, Proc. Chem. Soc. (1964) 393.
[35] A. Tressaud, M. Wintenberger, N. Bartlett, P. Hagenmuller, C.R. Acad. Sci. Paris Series C 282 (1976) 1069.
[36] D.H. Brown, K.R. Dixon, C.M. Livingston, R.H. Nuttall, D.W.A. Sharp, J. Chem. Soc. (A) (1967) 100.
[37] J.H. Holloway, E.G. Hope, C.D. Puxley, Eur. J. Solid State Inorg. Chem. 33 (1996) 821.
[38] A.G. Sharpe, J. Chem. Soc. (1953) 197.
[39] G.M. Lucier, C. Shen, S.H. Elder, N. Bartlett, Inorg. Chem. 37 (1998) 3829.
[40] B.G. Müller, Z. Anorg. Allg. Chem. 491 (1982) 245.
[41] E. Alter, R. Hoppe, Z. Anorg. Allg. Chem. 408 (1974) 115.
[42] B. Bachmann, B.G. Müller, Z. Anorg. Allg. Chem. 616 (1992) 7.
[43] C.J. Adams, N. Bartlett, Israel J. Chem. 17 (1978) 114.