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Concerning the nature of $XePtF_6$☆

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Contents

Abstract

Interaction of PtF_6 vapor with a comparable molar quantity of Xe gas, at ≈ 20°C, gives a sticky, red-tinged yellow solid of composition $Xe(PtF_6)_x$, with $1 \leq x \leq 2$, X-ray powder diffraction pattern (XRDP) of which show the presence of $XeF^+PtF_6^-$ $\{a = 8.081(6);$

☆ A contribution to celebrate the 75th birthday of long-time colleague and friend, R.J. Gillespie.

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$b = 11.087(7)$; $c = 7.226(6)$ Å; $\beta = 90.01(5)°$; $V/Z = 161.8(4)$ Å^3} which is isostructural with $XeF^+RuF_6^-$. This implies that first formed $XePtF_6 + PtF_6 \rightarrow XeF^+PtF_6^- + PtF_5$ (non-crystalline). When the product having $x \approx 2$ is warmed ($\leq 60°C$) it is converted to the orange–red, friable solid $XeF^+Pt_2F_{11}^-$: $XeF^+PtF_6^- + PtF_5 \rightarrow XeF^+Pt_2F_{11}^-$. Mixing PtF_6 vapor (diluted with SF_6 gas), with a large excess of Xe gas, with the product mixture quenched at 77 K, gives a mustard yellow solid of composition $\approx XePtF_6$. This does not give an XRDP, and is only weakly paramagnetic. Dissolution of PtF_4, with a large excess of XeF_2 in aHF gives a yellow solution, the ^{19}F NMR spectrum of which reveals PtF_6^{2-}. The diamagnetic, amorphous, aHF-insoluble solid, of composition $\approx XePtF_6$ obtained from that solution is probably a XeF^+ salt of polymeric $(PtF_5^-)_n$. The 1:1 product of $Xe + PtF_6$ is also likely to be of this formulation.

Keywords: $XePtF_6$; Diamagnetic; X-ray powder diffraction pattern

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1. Introduction

After methods had been worked out for the handling of PtF_6 without significant decomposition and loss, it became clear [1] that the stoichiometry of its interaction with Xe, was less simple than deduced from the first preparation [2], at which time it had been concluded to be 1:1. When [1] the Xe was in large excess over the PtF_6, the stoichiometry of the mustard–yellow solid product (see Fig. 2) approached 1:1, but when the PtF_6 exceeded the Xe, the product was a deep red, sticky solid, and approached the composition $Xe(PtF_6)_2$. In the latter case, and whenever the stoichiometry departed markedly from 1:1, X-ray powder diffraction photographs (XRDP) revealed the presence of a microcrystalline phase which was eventually identified as identical with that of the product of the interaction of XeF_2 with PtF_5 1:1 [3]. Vibrational spectroscopic analysis [3] indicated that the appropriate formulation was $XeF^+PtF_6^-$ and this was also supported by a crystal structure [4] of its ruthenium relative coupled to the vibrational analysis [3]. Material of composition $\approx XePtF_6$ has never shown an XRDP. Interaction of XeF_2 with PtF_5 1:2 in BrF_5 solution was shown [3] to form the salt $XeF^+Pt_2F_{11}^-$. The vibrational study [3] showed it to be related to $XeF^+Sb_2F_{11}^-$, an X-ray single crystal structure of which established that formulation [5]. In this study $XeF^+Pt_2F_{11}^-$ is shown to be the friable product obtained when the sticky red 1:2 product of the $Xe + PtF_6$ reaction is warmed ($< 60°C$). The XRDP of $XeF^+PtF_6^-$ is also shown to indicate a close structural relationship with that [4] of $XeF^+RuF_6^-$.

Perhaps the most surprising aspect of the early work [1] was the finding that the pyrolysis of $Xe(PtF_6)_x$ when $1 < x < 2$, gave XeF_4 uncontaminated by XeF_2. This was accompanied by the formation of the diamagnetic Pt(IV) material $XePt_2F_{10}$. Much light was thrown on these observations from the studies [6] of the interaction of liquid XeF_2 with PtF_4 or Pd_2F_6, at 140–150°C, in which both $XePt_2F_{10}$ and $XePd_2F_{10}$ were obtained and found to be closely related, structurally. The production of stoichiometric $XePt_2F_{10}$ from [1] non-stoichiometric $Xe(PtF_6)_x$, with pure XeF_4 as the only observed volatile, was not explained.

From the study [6] of the XeF_2/Pd_2F_6 system it was also found that liquid XeF_2 oxidized the palladium to Pd(IV) to give a diamagnetic yellow solid $XePdF_6$, that vibrational spectroscopy suggested could be $XeF^+PdF_5^-$ (the anion assumed to be a F-bridged polymer or ring).

In spite of the clarification that all of these studies had provided, the nature of $XePtF_6$ and the initial PtF_6 rich product remained unclear. One need was for stoichiometric $XePtF_6$. Another was to find, if possible, a route to crystalline material of that composition. A close approach to the composition $XePtF_6$ has been achieved, but crystalline material has not, even with the use of aHF as solvent. The interaction of XeF_2 with PtF_4 in that solvent, however has provided the platinum relative of $XePdF_6$. This diamagnetic, Pt(IV) material may be the same as $XePtF_6$ from the $Xe + PtF_6$ reaction.

2. Experimental section

2.1. Materials

Fluorine ($>97\%$) and Xenon (99.995%) were supplied by Matheson Gas Products (East Rutherford, NJ), Pt and Pd by Engelhard Industries Division (Newark, NJ). A_2PdF_6 and A_2PtF_6 ($A = Li$, K, Cs) were prepared according to the method recently described [7]. From these salts PdF_4 and PtF_4, respectively, were precipitated using AsF_5 [8], and the $AAsF_6$ washed away with back distilled aHF as previously described [9]. XeF_2 was made photochemically [10]. PtF_6 was prepared by the method of Weinstock and his coworkers [11].

2.2. Apparatus and technique

A nickel vacuum line, fluorine handling equipment and Teflon valves were used as previously described [9]. For all preparations two 1/2 or 1 inch o.d. FEP-tubes (CHEMPLAST Inc., Wayne, NJ), each sealed at one end and drawn down to 3/8 inch o.d. at the other, were joined at right angles to a Teflon Swagelock T compression fitting. This assembly was joined to a Teflon valve by a small section of 3/8 inch o.d. FEP tubing drawn down to 1/4 inch o.d. The reaction system was then connected to the vacuum line via a 1 foot length of 1/4 inch o.d. FEP tubing which facilitates the decantation of solutions from one arm to the other. The T-reactors were evacuated, passivated with fluorine (2 atm) and evacuated again before use.

Anhydrous HF (Matheson, Newark, CA) was condensed from the cylinder into a reservoir FEP tube containing K_2NiF_6 (Ozark-Mahoning Pennwalt, Tulsa, OK) in order to destroy trace quantities of water.

All solid materials were manipulated in the dry Ar atmosphere of a Vacuum Atmospheres Corp. DRILAB.

Analyses for Xe and Pt were carried out as previously described [1,6].

X-ray powder samples were prepared as previously described [9].

Magnetic measurements were carried out on $Xe(PtF_6)_x$ using a Vibrating Sample Magnetometer and those on all other materials were made using a SQUID magnetometer as previously outlined [12].

^{19}F NMR measurements were carried out on a Bruker (VBAMX-400) PFT-spectrometer. The spectra were recorded at room temperature, unlocked and $CFCl_3$ was used as external standard. A signal group consisting of three peaks was observed centered at −351 ppm. The bigger central peak at −351 ppm (arising from the Pt-isotopes with nuclear spin $I=0$; abundance 66.3%) and the two sidebands at −353.8 and −348.2 ppm (arising from the isotope ^{195}Pt with nuclear spin $I=1/2$; abundance 33.7%) are attributed to the $[PtF_6]^{2-}$ ion on the basis of similar spectra from solutions of K_2PtF_6 in aHF, run under similar conditions.

Raman Spectra. A Raman spectrum of the ≈ $XePtF_6$ prepared in aHF, was recorded with a Halo Probe VPT System spectrometer (Kaiser Optical System, Inc., Ann Arbor, MI) using the 532 nm radiation of a Diode-Pumped, Solid-State (DPSS) Laser as exciting wavelength. It consisted of three lines at 657 cm^{-1} (vs), 591 cm^{-1} (s) and 480 cm^{-1} (w).

3. Preparations

3.1. Preparation of ≈ $XePtF_6$ from $Xe + PtF_6$

PtF_6, diluted with SF_6 (1:6), was bled slowly through a length of 1/8 inch copper tubing into a Kel-F vessel while simultaneously flowing xenon into the same vessel through a separate length of tubing but at a faster flow rate. The flow rate of the reactant gases was regulated by passing them each through Monel Nupro SS-4MA metering valves. These valves were each coupled to the 1/8 inch lengths of copper tubing via a 1/4–1/8 o.d. reducing union. The lower portion of approximately 6 inch Kel-F reactor was maintained at 77 K. Thus the product formed by the gas–gas interaction was quickly quenched, along with excess xenon and sulfur hexafluoride diluent. This technique allowed for preparation of the approximately 1:1 product in gram amounts. The resultant, finely divided, mustard–yellow solid was retained on removal of sulfur hexafluoride and xenon at −80°C. Further warming to room temperature produced no other volatiles. Several samples of the product were prepared and analyzed for xenon and/or platinum. Those samples closest in composition to $XePtF_6$ were *a*, *b*, and *c*. Found: Pt, $a=45$, $b=44.6$, c –. Xe, $a=27.5$, $b=26.6$, $c=26.0$. $XePtF_6$ requires Pt = 44.3; Xe = 29.8. $Xe(PtF_6)_2$ requires Pt = 52.1; Xe = 17.5%. These materials neither reacted with aHF (no Xe↑) nor dissolved in it.

Magnetic data for samples *a* and *c* are compared with that of $XeFPtF_6$ in Fig. 1.

Infrared spectra of $Xe(PtF_6)_x$ were obtained by spraying PtF_6 and a large excess of Xe onto a silver chloride window held on a honey-combed silver block attached to the tip of a cryo-cooler (Cryogenic Technology, Inc., Model 21, Waltham, MA) held at 10 K. Product build up of the mustard yellow solid could be seen through the outer AgCl windows of the cell, and this was accompanied by growth of a very strong infrared absorption centered at 650 cm^{-1}. Unreacted PtF_6 was indicated by a sharp ν_3 absorption at 685 cm^{-1}. The only other features attributable to $Xe(PtF_6)_x$ were peaks at 595 (w), 560 (m), 500 (ms) cm^{-1}.

3.2. Identification of $XeFPtF_6$ in the products of the $Xe + PtF_6$ reaction

Many experiments were carried out, at ~20°C, which involved the simple mixing by diffusion of Xe and PtF_6 after a breakseal separating them had been broken (see Fig. 2 for $Xe + PtF_6$ reaction). These reactions [1,13] were followed both tensimetrically, using a sensitive nickel diaphragm gauge as described by Cromer [14] to sense the pressure [15], and gravimetrically. When the quantity of PtF_6 greatly exceeded that of the Xe, the stoichiometry was closer to $Xe(PtF_6)_2$ and the product redder and more sticky than when the Xe was more abundant. In the latter case, the more yellow solid had a composition closer to $XePtF_6$. In most cases, the XRDP showed a distinctive pattern that never varied with the composition. This pattern was eventually identified as being identical with the product of the 1:1 combination of XeF_2 with PtF_5 (prepared [3] from BrF_5 solution), the vibrational spectra [3] of which indicated the formulation $XeF^+PtF_6^-$. The XRDP of the $Xe(PtF_6)_x$ material is given in Table 1.

3.3. Conversion of $Xe + PtF_6$ reaction products to $XeF^+Pt_2F_{11}^-$

The product of one of the PtF_6 rich reactions with Xe, carried out in quartz apparatus by condensing first Xe then PtF_6 into a quartz bulb, gave a product

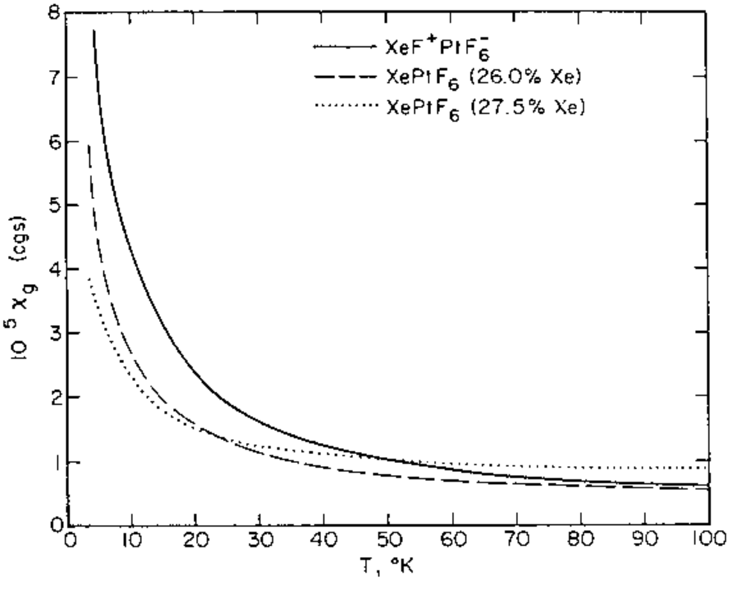

Fig. 1. Gram susceptibility of two samples of $Xe(PtF_6)_x$ compared with $XeF^+PtF_6^-$.

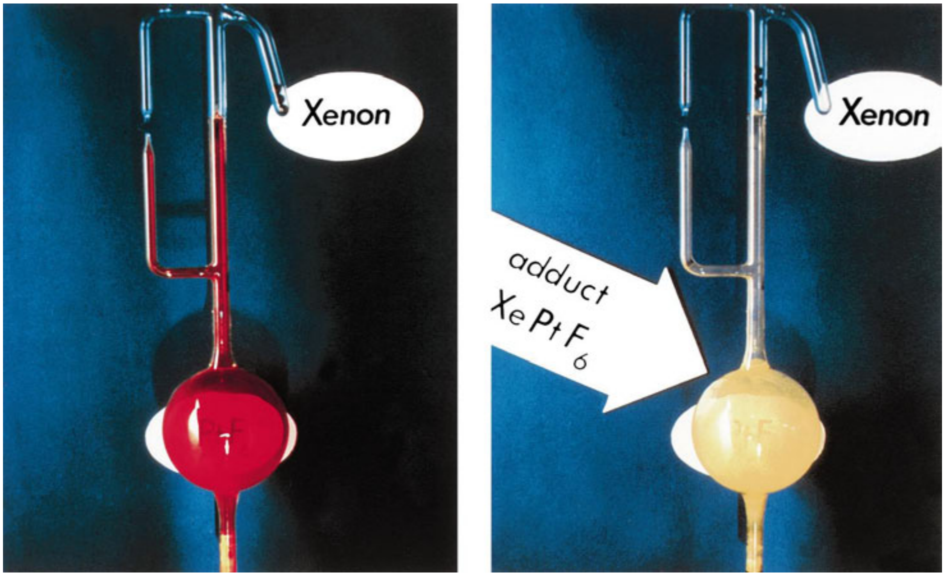

Fig. 2. The $Xe + PtF_6$ reaction: left, the gases separated by a glass break-seal; right, the yellow reaction product formed on breaking the seal. The major product (yellow solid) which is not soluble in aHF, is probably polymeric $(XeF^+)_n(PtF_5)_n^{n-}$.

stoichiometry (by tensimetry) near that of $Xe(PtF_6)_2$. As formed at 20°C, the XRDP of this sticky red solid showed only the pattern of $XeF^+PtF_6^-$. On warming the material (<60°C) it became less glassy in appearance and slightly lighter in color. The solid was found to be markedly more friable than the unwarmed material, and the XRDP showed strongly the pattern of $XeF^+Pt_2F_{11}^-$ which had since been prepared from XeF_2 and PtF_5 (1:2) and vibrationally characterized [3]. The $XeFPtF_6$ pattern is still visible (but weakly) in the $XeFPt_2F_{11}$ sample prepared from the $Xe + PtF_6$. That particular pattern is tabulated in Table 2 where it is compared with that of $XeF^+Ir_2F_{11}^-$, prepared [3] from XeF_2 and IrF_5 (1:2) in BrF_5.

3.4. Interaction of XeF_2 and PtF_4 in aHF at RT

XeF_2 and PtF_4 were placed in separate arms of an FEP T-reactor. HF was condensed in both arms. The XeF_2 dissolved to a colorless solution; the PtF_4 did not. The XeF_2 solution in HF was poured into the limb with the PtF_4 and agitated overnight to yield an orange solution. The solution was decanted and the residue (tan colored) washed once. Removal of volatiles from the solution gave an orange solid. Neither the residue nor the orange solid gave an XRDP. See Table 3 for gravimetry.

3.5. Interaction of XeF_2 and PdF_4 in aHF at RT

The reaction was carried out in the same manner as the reaction of PtF_4 with XeF_2. The PdF_4 was always partially reduced by the XeF_2 solution to leave a black

Table 1
X-ray powder pattern of $XeFPtF_6$ [a]

		$(1/d^2)\times 10^4$				
I_{calc} [b]	I/I_o	Obsd.	Calc.	h	k	l
11	vvw	359	345	1	0	−1
11	vvw	359	345	1	0	1
32	w	489	479	1	2	0
70	s	628	613	2	0	0
86	vvs	687	670	1	2	−1
100	vvs	687	670	1	2	1
35	w	789	766	0	0	2
14	vvw	873	847	0	1	2
7	vvvw	1016	1000	1	1	−2
5	vvvw	1016	1001	1	1	2
3	vvvw	1107	1091	0	2	2
12	vw	1395	1378	2	0	−2
6	vw	1395	1379	2	0	2
7	vw	1487	1460	2	1	−2
2	vw	1487	1460	2	1	2
10	vw	1521	1493	0	4	1
1	vw	1521	1498	0	3	2
24	vs	1933	1895	3	2	−1
15	vs	1933	1895	3	2	1
13	vs	1933	1914	2	4	0
19	m	2139	2106	2	4	−1
10	m	2139	2106	2	4	1
7	vvw	2237	2202	1	2	−3
4	vvw	2237	2202	1	2	3
7	vw	2486	2450	4	0	0
8	vvw	2642	2609	1	3	−3
5	vvw	2642	2609	1	3	3
3	vvw	2714	2680	2	4	−2
2	vvw	2714	2680	3	4	0
5	vvw	2714	2680	2	4	2
11	mw	3123	3082	1	6	0
6	vvw	3438	3390	0	2	4
5	vw	3790	3752	4	4	0
2	vw	3790	3758	2	1	−4
1	vw	3790	3757	0	5	3
1	vw	3790	3759	2	1	4
4	vw	3898	3848	1	6	−2
5	vw	3898	3848	1	6	2
5	vw	3992	3943	4	4	−1
7	vw	3992	3944	4	4	1
9	vwb	4377	4307	3	6	0
4	vwb	4377	4345	5	2	−1
7	vwb	4377	4346	5	2	1
2	vvvw	4558	4517	4	4	−2
1	vvvw	4558	4519	1	4	−4
2	vvvw	4558	4523	3	1	−4
2	vvvw	4558	4517	4	4	2
2	vvvw	4558	4519	1	4	4
1	vvvw	4558	4525	3	1	4
4	vw	6041	6011	2	8	−1
3	vw	6041	6011	2	8	1

[a] Cu–K_α radiation, Ni-filter, with a monoclinic unit cell: $a_o = 8.081(6)$, $b_o = 11.087(7)$, $c_o = 7.226(6)$ Å, $\beta = 90.01(5)°$, $V/Z = 161.8(4)$ Å^3.

[b] I_{calc} obtained (with the program LAZY) using the atom positions from the isostructural [4] $XeFRuF_6$.

Table 2
X-ray powder data (Cu–K_α radiation, Ni filter) for $XeFM_2F_{11}$ (M = Ir, Pt) [a]

		$(1/d^2)\times 10^4$	
$XeFIr_2F_{11}$ I/I_0	$XeFPt_2F_{11}$ I/I_0	$XeFIr_2F_{11}$ Obs.	$XeFPt_2F_{11}$ Obs.
	vw		260
	vvw		354*
	m		447
	m		476*
vw	ms	537	536
	vw		619*
m	vs	653	655
w	s	685	678*
	vvw		736
vvw	vvw	775	775*
s[b]	vs	849	845*
	vw		1011*
	mw		1222
	vvvw		1304
	vvvw		1390*
m	s	1495	1498*
w	vw	1593	1590
vvw	vvwb	1773	1769
mw	m	1953	1930*
w	s	2137	2138*
ms[b]	ms	2333	2341
vvw		2488	
w	vvw	2609	2618*
vvw		2712	
vw		2891	
vw		2976	
	vvw		2895
	vw		3102*
vw	w	3272	3272
ms[b]	vw	3357	3365
w	w	3450	3464
vw		3631	
	vvw		3714
vvw		3816	
	vvw		3875*
m	wb	3999	3999
mw	wb	4099	4094
wb	wb	4384	4374
wb	wb	4560	4540*
vw	vwb	5134	5150
m	vw	5686	5703
vvw	vvw	6594	6611
vw		7507	
vvw	vvw	7700	7729
vvw		7916	
vvw		8162	
vvw		8467	
vvw		10684	
vvvw		11055	
vw		12340	
vvw		12955	
vvw		14919	

[a] The lines marked with an asterisk coincide with those of $XeFPtF_6$ (see Table 1).

[b] For these lines I/I_o is enhanced by preferred orientation.

Table 3
Combining weights for the interaction of XeF_2 with PtF_4 in liquid aHF at ≈ 20°C [a]

	Reactants			Undissolved	Dissolved	$(XeF_2)_x PtF_4$ from decanted solution	Combined XeF_2	mmol XeF_2
Expt no.	aHF	XeF_2	PtF_4	PtF_4	PtF_4			mmol PtF_4
1	1.5 ml	mg **660.2**	**144.1**	**81.8**	62.3	**109.4**	47.1	1.21
		mmol 3.8998	0.5316	0.3018	0.2298		0.2782	
2	0.7 ml	mg **212.5**	**84.8**	**39.3**	45.5	**72.4**	26.9	0.95
		mmol 1.2553	0.3128	0.1450	0.1679		0.1589	
3	1.0 ml	mg **516.5**	**83.8**	**5.1**	78.7	**156.6**	77.9	1.59
		mmol 3.0510	0.3091	0.0188	0.2903		0.4602	
4	0.7 ml	mg **554.7**	**99.8**	**1.1**	98.7	**172.2**	73.5	1.19
		mmol 3.2766	0.3682	0.0040	0.3641		0.4342	
5	1.0 ml	mg **796.8**	**175.2**	**53.8**	121.4	**232.6**	111.2	1.47
		mmol 4.7067	0.6463	0.1985	0.4479		0.6569	

[a] Weights marked in **bold** were actual weights, others were deduced.

residue, which was identified as Pd_2F_6 by XRDP. The XRDP of the yellow solid recovered from the decanted solution gave no pattern. In the preparation giving the smallest yield of Pd_2F_6, PdF_4 (69.8 mg, 0.383 mmol) largely dissolved in aHF (~ 2 ml) containing XeF_2 (670 mg, 3.96 mmol) to leave Pd_2F_6 (12.1 mg, 0.037 mmol). The orange–yellow solution gave a diamagnetic orange yellow solid (127.4 mg) on removal of volatiles. On the basis of 0.309 mmol Pd, the formula weight of the orange solid is 412; required for $XePdF_6$ 351.7 and for $(XeF_2)_2PdF_4$ 521.0. The orange solid did not give an XRDP.

3.6. Interaction of '$XeMF_6$' ($M = Pd$, Pt) and CsF in aHF

The solids obtained from the aHF solutions of the reactions mentioned above were placed in one arm of a T-reactor and cesium fluoride in the other. HF was condensed in both arms. The '$XeMF_6$' gave only a faintly yellow solution, most of the solid remaining undissolved, the color of the residue changing from orange to dark red. Most of the solid dissolved in the CsF–aHF solution within 15–20 min and with agitation overnight dissolution was essentially complete. The solution was decanted, any residue washed once, and all volatiles removed. XRDP of the solids recovered from the decanted solution (and washing) showed the hexagonal form of Cs_2PtF_6 [16] and the cubic form of Cs_2PdF_6 [17].

4. Results and discussion

By diluting PtF_6 with the condensable inert gas SF_6, and co-condensing this mixture (at 77 K) with a large molar excess of Xe, it was possible to bring the stoichiometry of the solid product of the reaction close to $XePtF_6$. The slow warm up from 77 K ensured the opportunity for any unreacted PtF_6 to oxidize Xe, although the reactor design probably resulted in most, if not all, having interacted in the mixed gas stream:

$$PtF_6 \text{ (dil. 1:6 with } SF_6) + Xe \text{ (in excess)} \rightarrow \approx XePtF_6 \tag{1}$$

This mustard–yellow solid gave neither XRDP nor Raman spectra, probably as a consequence of very small crystallite size. It neither reacted with, nor dissolved in aHF. The color indicated that PtF_5, which is red, was absent, and this distinguished the product from that obtained when PtF_6 and Xe were mixed in equimolar quantities. In those circumstances, there was always a red side-product, and the stoichiometry of that product was always between $XePtF_6$ and $Xe(PtF_6)_2$.

Structural information on $XePtF_6$ was not obtained. The paramagnetism of the solids close to that composition, compared with that for $XeFPtF_6$ in Fig. 1, indicate that the material is only weakly paramagnetic. It is possible that this weak paramagnetism could arise from the small quantities of $XeF^+PtF_6^-$ (and PtF_5) that are present even in the best preparations. $XePtF_6$ when pure, therefore, may be the relative of diamagnetic [6] $XePdF_6$.

XRDP of the sticky red-tinged solids, $Xe(PtF_6)_x$ $1 < x < 2$, always exhibited the characteristic pattern of $XeF^+PtF_6^-$. This pattern (given in Table 1) is almost identical with that of $XeF^+RuF_6^-$, the single crystal structure of which [4] established the salt formulation. It can be concluded, therefore, that the initial product of the oxidation of Xe by PtF_6 interacts with additional PtF_6 to generate $XeF^+PtF_6^-$ (and, therefore, PtF_5):

$$XePtF_6 + PtF_6 \rightarrow XeF^+PtF_6^- + PtF_5 \tag{2}$$

PtF_5 does not crystallize easily, and its XRDP has never been observed in the $Xe(PtF_6)_x$ products. The color and sticky character of the solid are, however, consistent [18] with its presence. Chemical evidence for this comes from the formation of the orange–red, friable solid $XeF^+Pt_2F_{11}^-$ [3] when material near to the composition $\sim Xe(PtF_6)_2$ (XRDP of which show only $XeF^+PtF_6^-$) is warmed (at $< 60°C$):

$$XeF^+PtF_6^- + PtF_5 \rightarrow XeF^+Pt_2F_{11}^- \tag{3}$$

From XRDP (see Table 2) it is clear that this salt has the same structure as $XeF^+Ir_2F_{11}^-$. Vibrational spectroscopic evidence for these and other noble-metal relatives, indicates [3] that they are similar to $XeF^+Sb_2F_{11}^-$, which Peacock and his coworkers, from single crystal data [5], showed to be such a salt.

Since $Ag^{2+}_{(g)}$ and $Xe^{2+}_{(g)}$ have similar first electron affinities [19], it is of value to compare the chemistry of Xe(II) with Ag(II). Recently, in these laboratories, it has been shown [20] that PtF_6^- in aHF oxidizes Ag^+ to give $Ag^{2+}PtF_6^{2-}$. Also, Ag(II), like Xe(II), tends to make F-bridged species and will subtract F^- from rather stable MF_6^- to do so. An example is the failure to prepare $Ag(AsF_6)_2$, although aHF solutions of a salt of that stoichiometry can easily be prepared. Removal of aHF, even at $-65°C$, leaves [12] only the $AgF^+AsF_6^-$ salt originally discovered by Gantar et al. [21]. It has similarly not proved possible [22] to prepare $Ag(PtF_6)_2$. It must be noted, however, that $Ag(SbF_6)_2$ does exist [23], in contrast with $Xe(SbF_6)_2$ which does not; $XeF^+Sb_2F_{11}^-$ being preferred [5]. (The SbF_6^- species is probably the most stable MF_6^- ion with respect to F^- loss [15].) It is therefore apparent that the Xe^{2+} species has greater F^- withdrawing power, than Ag^{2+}, and that Xe^{2+} salts are unlikely to be found.

It is surprising that $XeF^+Pt_2F_{11}^-$ was not formed directly as a consequence of the interaction of PtF_6 with the initially formed $XePtF_6$. Indeed, it is reasonable to assume that the highly electrophilic PtF_6 molecule should attack the anion. If the anion of $XePtF_6$ is cyclic or polymeric, i.e. $(PtF_5^-)_n$ (as has been conjectured [6] for $XePdF_6$) the low temperature interaction with a second PtF_6 can be understood. The PtF_6 would capture an electron from the anion but would not form a F bridge to the residual $(PtF_5)_n$, because the Pt in that oligomer is already coordinatively saturated (i.e. pseudo-octahedral). Mechanistically, Eq. (2) can then, perhaps, be represented as:

$$n{*}PtF_6 + (XeF^+)_n(PtF_5^-)_n \rightarrow nXeF^+{*}PtF_6^- + (PtF_5)_n \tag{4}$$

In an attempt to obtain more crystalline $XePtF_6$, aHF was employed as the solvent, at $\sim 20°C$ for the interaction of PtF_4 with XeF_2. Equimolar quantities of the reagents did not provide for dissolution of all of the PtF_4. For that, it was necessary to employ a multifold excess of XeF_2, from which a yellow solution was obtained. An ^{19}F NMR spectrum of this solution showed that it contained the PtF_6^{2-} species. Removal of the solvent and excess XeF_2 gave a diamagnetic solid of approximate composition $XePtF_6$. Like its compositional relative obtained from PtF_6 and Xe, however, this solid did not give an XRDP. The PtF_6^{2-} in the aHF is probably stabilized by the solvated and therefore less strongly polarizing cation $XeF^+_{(solv)}$ which, on removal of aHF gives the strongly polarizing [3,24] naked XeF^+. The last is evidently [6] capable of taking F^- from PdF_6^{2-} to yield PdF_5^-, and would surely interact similarly with PtF_6^{2-} to give PtF_5^- (which would then oligomerize). The insolubility of the diamagnetic $\sim XePtF_6$ in aHF is consistent with it being the XeF^+ salt of cyclic or polymeric $(PtF_5^-)_n$ and therefore akin [6] to $XePdF_6$.

$$2\ XeF_{2(solv)} + PtF_{4(c)} \rightarrow 2\ XeF^+_{(solv)} + PtF^{2-}_{6(solv)} \tag{5}$$

$$(XeF^+)_2PtF_6^{2-} \rightarrow XeF_2 + XeFPtF_5 \tag{6}$$

It should be noted that a single crystal structural analysis of $XeCrF_6$ by Žemva and his coworkers [25] has shown that it is a polymeric F-bridged chain $(CrF_5)_n$ {with six coordinated Cr(IV)} with pendent Xe–F groups, linearly aligned via strong F-bridges, to F ligands of the $(CrF_5)_n$. The $XePdF_6$ and $XePtF_6$ could be structurally similar.

The acidic conditions prevailing in the aHF solvent (containing the rather weak base XeF_2 [26]) were evidently not conducive to the oxidation of Pt(IV) to Pt(V) that liquid XeF_2 itself provides [6]. In this, the Pd system is similar. A solution of XeF_2 in aHF extensively reduced a sample of PdF_4 to Pd_2F_6, part only of the PdF_4 dissolving to give PdF_6^{2-}. Clearly the F^- donor character of XeF_2 is here in competition with its capability to act as a reducing agent towards what is, in PdF_4, a very potent oxidizer and fluorinator:

$$2\ XeF_{2(solv)} + PdF_{4(c)} \rightarrow 2\ XeF^+_{(solv)} + PdF^{2-}_{6(solv)} \tag{7}$$

$$XeF_{2(solv)} + 2\ PdF_{4(c)} \rightarrow XeF_{4(solv)} + Pd_2F_{6(c)} \tag{8}$$

Again, this is in marked contrast to the action of liquid XeF_2 which provided [6] pure $XePdF_6$ from Pd_2F_6. Liquid XeF_2 must be a superior F^- donor than its aHF solution. Perhaps this is a consequence of the weakly polarizing cation $Xe_2F_3^+$, being largely solvolyzed in aHF. It is probably relevant that Gillespie and his coworkers reported [27] an ^{19}F NMR spectrum to demonstrate the existence of $Xe_2F_3^+$ in the solvent BrF_5 but they gave no such evidence for aHF solutions.

The $XeMF_6$ salts (M = Pd or Pt) are the XeF_2 rich relatives of the isostructural XeM_2F_{10} compounds. Pyrolysis of $XePdF_6$, in vacuo at 140–150°C, had provided [6] the first sample of $XePd_2F_{10}$:

$$2\ XePdF_6 \rightarrow XePd_2F_{10} + XeF_2 \tag{9}$$

and the XRDP of this proved to be very like that of the previously described [1] Pt relative obtained, along with XeF_4, by the pyrolysis of $Xe(PtF_6)_x$ ($x = 1.8$) at 165°C.

Since this last material contains $XeFPtF_6$, which decomposes [6] at 150–160°C:

$$2\ XeFPtF_6 \rightarrow XePt_2F_{10} + XeF_4 \qquad (10)$$

the source of the observed XeF_4 is understood, but the fact that the solid residue of the $Xe(PtF_6)_x$ decomposition was pure $XePt_2F_{10}$ requires that the PtF_5 accompanying the $XeFPtF_6$ also be a reactant. As PtF_5 is a good F^- acceptor, it would take up XeF_2 released by $XePtF_6$, in decomposition analogous to Eq. (9):

$$2\ XePtF_6 \rightarrow XePt_2F_{10} + XeF_2;\ XeF_2 + PtF_5 \rightarrow XeFPtF_6 \qquad (11)$$

This being so, as long as the number of moles of $XePtF_6$ is not greater than the number of moles of $XeFPtF_6$ (which must equal PtF_5), the only xenon fluoride evolved would be XeF_4. This was the finding in the early investigation [1], with $x = 1.8$ there being more than enough Pt(V) to oxidize all released Xe(II) to Xe(IV). In accord with this, the XeF_4, which was characterized by its XRDP [28] as well as IR [29], was found to be free of XeF_2. This observation also pointed to the poor F^- donor properties of XeF_4 and led to the finding of a chemical route to the purification of that fluoride [30].

It is highly likely that diamagnetic $Xe(II)Pt(IV)F_6$ (probably as the salt XeF^+ PtF_5^-) is the thermodynamically preferred form of $XePtF_6$, and that made from PtF_6 and Xe, at 20°C or below, is also largely this. The products of the further oxidation by PtF_6 are, however, the Pt(V) derivatives $XeF^+PtF_6^-$, PtF_5 and $XeF^+Pt_2F_{11}^-$. It is evident that the Xe(I) oxidation state is never a viable one, Xe(II) being clearly preferred.

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