Title

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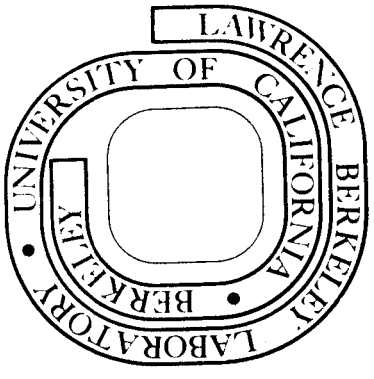

DISCLAIMER

REDOX REACTIONS IN THE XeF_2/PLATINUM FLUORIDE AND XeF_2/PALLADIUM FLUORIDE SYSTEMS AND THE CONVERSION OF XeF_2 TO XeF_4 AND Xe

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(To Professor George H. Cady on his 70th birthday)

SUMMARY

Liquid XeF_2 at 140-150° oxidizes PtF_4: $5XeF_2 + 2PtF_4 \longrightarrow 2Xe_2F_3PtF_6 + Xe\uparrow$. The salt $Xe_2F_3^+PtF_6^-$ loses XeF_2 at 70° *in vacuo*: $Xe_2F_3PtF_6 \longrightarrow XeFPtF_6 + XeF_2\uparrow$. Pyrolysis of $XeF^+PtF_6^-$ at 150-160° yields XeF_4: $XeFPtF_6 \longrightarrow XePt_2F_{10} + XeF_4\uparrow$. The complex $XePt_2F_{10}$ loses XeF_2 at 430°: $XePt_2F_{10} \longrightarrow PtF_4 + XeF_2\uparrow$. $XePt_2F_{10}$ also can be oxidized by liquid XeF_2 at 140-150°: $XePt_2F_{10} + 4XeF_2 \longrightarrow 2Xe_2F_3PtF_6 + Xe\uparrow$. The paramagnetic mixed-valence fluoride Pd_2F_6 is oxidized by $XeF_2(\ell)$ at 140-150°: $Pd_2F_6 + 3XeF_2 \longrightarrow 2XePdF_6 + Xe\uparrow$. The yellow diamagnetic $XePdF_6$, which is thermally stable at room temperature, loses XeF_2 at 140-150°: $2XePdF_6 \longrightarrow XePd_2F_{10} + XeF_2\uparrow$. Both $XePdF_6$ and $XePd_2F_{10}$ may be derived from $XeF_2 + PdF_4$. The complex $XePd_2F_{10}$ is a close structural relative of $XePt_2F_{10}$ and spectroscopic evidence suggests that both are salts of XeF^+ and a polymeric $(M_2F_9)_x^{x-}$ ion. Pyrolysis of $XePd_2F_{10}$ at 280° yields XeF_4: $XePd_2F_{10} \longrightarrow Pd_2F_6 + XeF_4$.

INTRODUCTION

In their early studies of the oxidation of xenon by platinum hexafluoride Bartlett and Jha found [1] that the stoichiometry of the product of that spontaneous reaction varied between $XePtF_6$ and $Xe(PtF_6)_2$. Chemical and physical evidence indicated that the oxidation state of the platinum in $Xe(PtF_6)_x$ was +5. Pyrolysis of $Xe(PtF_6)_x$, at 165°, yielded xenon tetrafluoride as the only identified volatile product, (xenon itself was not

sought). The residue was a red solid of composition $XePt_2F_{10}$, the diamagnetism of which suggested a Pt(IV) compound. There was, however, no proof that this material was even a single phase.

It appeared from these observations that Pt(V) fluorides had (at least under certain circumstances) the capability to oxidize Xe(I) or Xe(II) to Xe(IV).

At the outset of this work, we knew that XeF_2 formed 2:1, 1:1, and 1:2 complexes with PtF_5, which had been characterized [2], respectively, as $Xe_2F_3^+PtF_6^-$, $XeF^+PtF_6^-$ and $XeF^+Pt_2F_{11}^-$. The diamagnetism of the $XePt_2F_{10}$ obtained by Bartlett and Jha indicated that it was probably a Pt(IV) complex, but the stoichiometry rested upon sparse analytical data. A prime goal was therefore to confirm the existence of a 1:2 XeF_2-PtF_4 complex. Whether or not complexes of PtF_4 richer in XeF_2 could be prepared was also of interest and the 1:1 compound particularly so, since it offered the prospect of a valence isomer of $Xe^+PtF_6^-$ [1].

Since Pd(IV) fluorocomplexes are usually structurally similar [3] to their Pt(IV) relatives it appeared probable that XeF_2 with PdF_4 would yield the palladium analogue of $XePt_2F_{10}$ and of any other PtF_4/XeF_2 complex which might occur. Studies of the interactions of XeF_2 both with PtF_4 and with PdF_4 were therefore undertaken. The studies were subsequently broadened to include the interaction of XeF_2 with the mixed-valence palladium fluoride, Pd_2F_6.

RESULTS AND DISCUSSION

To favor the formation of XeF_2-rich complexes, and to encourage the development of crystalline material, we set out by treating PtF_4 with a large excess of liquid XeF_2. We quickly discovered that these mixtures generated xenon as the XeF_2 oxidized the Pt(IV) in an unanticipated reaction:

$$5XeF_2 + 2PtF_4 \longrightarrow 2Xe_2F_3PtF_6 + Xe\uparrow.$$

Removal of the excess XeF_2 provided the Pt(V) salt, $Xe_2F_3^+PtF_6^-$, which had previously been made [2] by mixing XeF_2 and PtF_5, in 2:1 molar ratio, in BrF_5 solution:

$$2XeF_2 + PtF_5 \longrightarrow Xe_2F_3PtF_6$$

Our present findings establish that this salt loses XeF_2 under vacuum at ∿ 70°C:

$$Xe_2F_3Pt_6 \longrightarrow XeFPtF_6 + XeF_2 \uparrow$$

The compound $XeF^+PtF_6^-$, formed in this process, had also been prepared from XeF_2 and PtF_5 in BrF_5 solution and was well characterized structurally [2]. Pyrolysis of the compound at 160°C in a vacuum yielded XeF_4 and $XePt_2F_{10}$:

$$2XeFPtF_6 \longrightarrow XeP_2F_{10} + XeF_4 \uparrow$$

The $XePt_2F_{10}$ proved to be identical with the material of the same composition obtained by Bartlett and Jha [1]. Treatment of $XePt_2F_{10}$ with excess liquid XeF_2 at 140-150° again brought about oxidation of the Pt(IV) to Pt(V):

$$4XeF_2 + XePt_2F_{10} \longrightarrow 2Xe_2F_3PtF_6 + Xe \uparrow.$$

The pyrolysis of $XePt_2F_{10}$, under vacuum at 430°C, yielded no XeF_4, but XeF_2 was evolved:

$$XePt_2F_{10} \longrightarrow 2PtF_4 + XeF_2 \uparrow$$

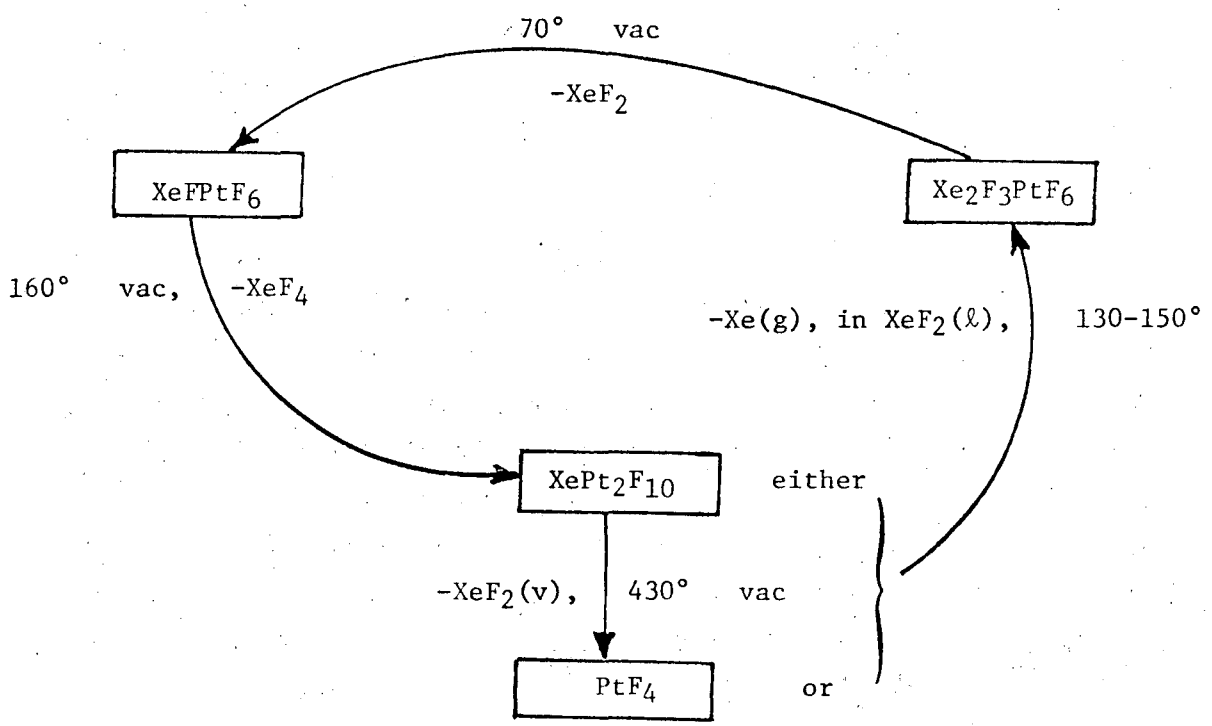

Fig. 1. Conversion of XeF_2 to XeF_4 + Xe using platinum fluorides

The combination of the oxidation of Pt(IV) to Pt(V), by the XeF_2, with the Xe(II) oxidation to Xe(IV) by the Pt(V), has the net effect, as Figure 1 summarizes, of providing for the conversion of two moles of XeF_2 to one of XeF_4 and one of Xe:

$$2XeF_2 \longrightarrow XeF_4 + Xe \uparrow$$

The interaction of liquid XeF_2 at 140-150°C with PdF_4 yielded a diamagnetic yellow material. Changes in slope in a weight-loss time curve indicated that 4:1, 3:1, 2:1 and 1:1 XeF_2: PdF_4 complexes probably occur, however all but the 1:1 complex lose XeF_2 at or below 20°. Our experience with the XeF_2/PtF_4 system suggested that liquid XeF_2 might prove capable of oxidizing the mixed valence palladium fluoride Pd_2F_6 and this proved to be so:

$$(x+1)XeF_2 + Pd_2F_6 + x\ XeF_2.PdF_4 + Xe \uparrow$$

(This is convenient since Pd_2F_6 is much easier to prepare [4] than PdF_4.)

The 1:1 complex, $XePdF_6$, loses XeF_2 in a vacuum at 140-150°:

$$2XePdF_6 \longrightarrow XePd_2F_{10} + XeF_2 \uparrow$$

The solid residue, $XePd_2F_{10}$, proved to be a close structural relative of $XePt_2F_{10}$ (see below), but its pyrolysis proceeded quite differently. Like $XePt_2F_{10}$, $XePd_2F_{10}$ is rather stable thermally, but pyrolysis of $XePd_2F_{10}$ in a vacuum, at 280°, yields XeF_4:

$$XePd_2F_{10} \longrightarrow Pd_2F_6 + XeF_4 \uparrow$$

The net effect of summing these reactions is again to provide for the conversion of XeF_2 into XeF_4 and Xe, as Figure 2 illustrates.

The differences in the conditions which bring about the oxidation of Pt(IV) to Pt(V) by XeF_2 and those which bring about the reduction of Pt(V) to Pt(IV) by XeF_2, are small. It is evident that if there is any thermodynamic obstacle to disproportionation it is not large. Although there are significant differences between the various values quoted [5] for the enthalpies of formation of XeF_2 and XeF_4, a set of calorimetric data, from one laboratory [6], indicates that the standard enthalpy change $\Delta H°(2XeF_{2(g)} \longrightarrow Xe_{(g)} + XeF_{4(g)})$ is 1.9 kcal $mole^{-1}$. The corresponding standard entropy change [5] is -9 cal deg^{-1} $mole^{-1}$. Thus the gaseous difluoride molecule is stable (although not greatly so) towards disproportionation and

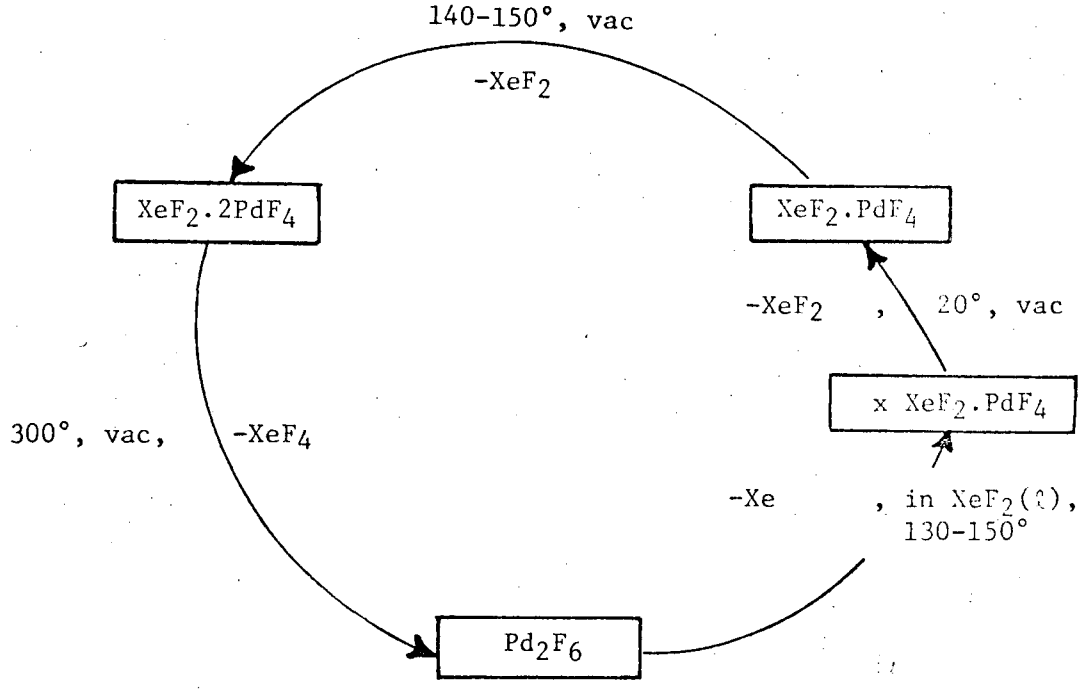

Fig. 2. Conversion of XeF_2 to XeF_4 + Xe using palladium fluorides

the more so the higher the temperature. Because the heats of sublimation [7] of $XeF_{2(c)}$ and $XeF_{4(c)}$ are respectively 13.2 and 14.8 kcals $mole^{-1}$, $\Delta H°(2XeF_{2(c)} \longrightarrow Xe_{(g)} + XeF_{4(c)}) = +13.5$ kcal $mole^{-1}$. This is much less favorable for disproportionation than the gaseous-molecule case, although the corresponding standard entropy change [5] is +16.7 cal deg^{-1} $mole^{-1}$. It is probable that condensed-phase disproportionation of XeF_2 would be aided by the formation of the $XeF_2.XeF_4$ adduct [8] since the enthalpy of formation of this must be exothermic. Therefore the value of $\Delta H°(3XeF_{2(c)} \longrightarrow Xe_{(g)} + XeF_2.XeF_{4(c)})$ is probably less endothermic than 13.5 kcal $mole^{-1}$ and could conceivably be exothermic. However $XeF_2.XeF_4$ plays no part in the cycles we have presented. Evidently the small amount of work necessary to drive the conversion of XeF_2 to XeF_4 is accumulated in the cycles.

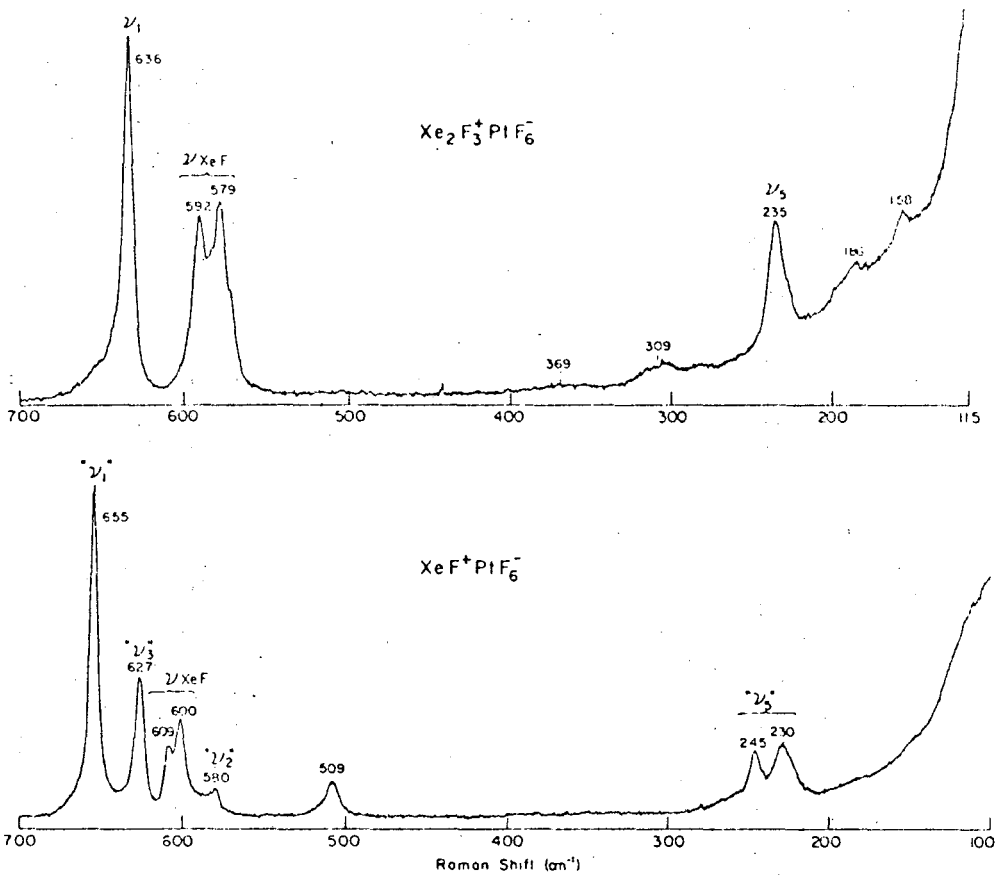

Fig. 3. The Raman spectra of $Xe_2F_3PtF_6$ and $XeFPtF_6$

The initial product in the PtF_4 oxidation by liquid XeF_2 is the salt $Xe_2F_3^+PtF_6^-$. Here we see XeF_2 both as a fluoride ion donor [2] and as an oxidizer. The anion in this salt does not interact strongly with the planar, symmetrical V shaped $(F\text{-}Xe\cdot\cdot F\cdot\cdot\cdot Xe\text{-}F)^+$ ion. When XeF_2 is removed from the $Xe_2F_3^+$ salt (and appreciable work is presumably done in this process) the anion is then subjected to the highly polarizing XeF^+ ion. The crystal structure of $XeF^+RuF_6^-$, which is a close relative of $XeF^+PtF_6^-$ indicates [9] the anion-distorting nature of this cation-anion interaction. The Raman spectra in Figure 3 also give evidence of this change. It will be noted that the ν_3-related mode, which is formally forbidden in the octahedral case, is not seen in $Xe_2F_3^+PtF_6^-$ but appears strongly in $XeF^+PtF_6^-$. Also, ν_5 in $XeF^+PtF_6^-$ is a doublet whereas in $Xe_2F_3^+PtF_6^-$ it is a singlet. There are also appreciable changes in the anion stretching frequencies from one salt to the other. In $Xe_2F_3^+$ each Xe atom has two F atom neighbors coordinated approximately linearly to it and the electron-attracting capability, which such a Xe atom has, is much less than in the XeF^+ case. Indeed the consequence of the interaction of XeF^+, with one of the F-ligands of the anion, is to denude that ligand, and the anion as a whole, of some electron density. The Pt(V) in $XeF^+PtF_6^-$, because of its greater electronegativity, is, potentially at least, a better oxidizer than the Pt(V) in $Xe_2F_3^+PtF_6^-$.

As in the platinum case, the fluoride ion donor capability of XeF_2, coupled with its oxidizing capability, are responsible for the oxidation of Pd_2F_6. The product in liquid XeF_2 is probably the salt $(Xe_2F_3^+)_2PdF_6^{2-}$. The yellow color is characteristic of PdF_6^{2-} salts and the XeF_6 analogue, $4XeF_6.PdF_4$, is known [10] to be the salt $(Xe_2F_{11}^+)_2PdF_6^{2-}$. The electronegativity and oxidizing power of Pd(IV) in PdF_6^{2-} must be lower than in any other Pd(IV) fluorospecies.

In the absence of reliable structural data for $XeF_2.PdF_4$ we are obliged to make educated guesses as to its structure. In all XeF_2 complexes with fluoride ion acceptors, where the XeF_2 is not in molar excess, the combined X-ray crystallographic [9,11] and vibrational spectroscopic evidence [2,12] show the xenon-containing species to be XeF^+. We therefore expect $XeF_2.PdF_4$ to be an XeF^+ salt. A monomeric anion PdF_5^- is, however, not anticipated. In PdF_2 [13], Pd_2F_6 [4,14] and PdF_4 [4] the palladium atom is always octahedrally coordinated by F ligands. In PdF_2 and Pd_2F_6 the ligands are all

equivalent but in PdF_4, two adjacent F ligands in the octahedron are uniquely associated with the central Pd atom, whereas the other 4 ligands are each shared between 2 Pd atoms. This F-bridging in PdF_4 generates a three dimensional lattice and a similar structure is adopted by RhF_4, IrF_4 and PtF_4 [4]. Although there is as yet no known pentafluoride of palladium the pentafluorides of Rh, Ir and Pt are all known and have the same structure. A precise version of this has been described [15] for rhodium pentafluoride. The molecular unit shown in Figure 4 is a fluoride bridged cyclic tetramer in which each Rh atom is octahedrally coordinated in F

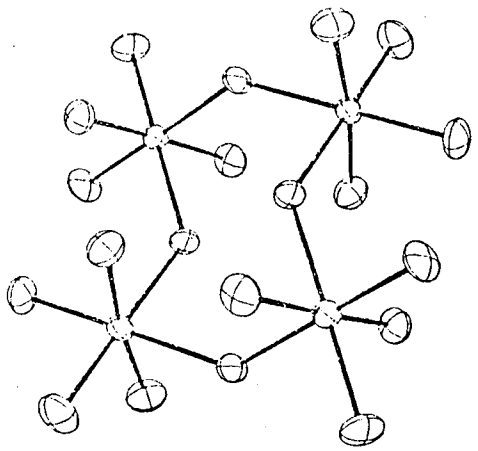

Fig. 4. The RhF_5 tetramer -- a possible model for (PdF_5^-)

atoms. The anticipated PdF_5^- entity in $XeF_2.PdF_4$ may be similar. It is anticipated that the XeF^+ cation, as in the $XeF^+MF_6^-$ salts, will interact strongly with that anion.

The close structural relationship of $XePd_2F_{10}$ to $XePt_2F_{10}$ is supported by the X-ray powder data given in Table 1. We can be confident that essentially the same heavy atom dispositions occur in both compounds. The Raman spectra, furthermore, which are shown in Figure 5, give evidence of an XeF^+ species. That species is characterized [2] in the $XeF^+MF_6^-$ and $XeF^+M_2F_{11}^-$ salts by a band, or pair of bands, in the region 621 - 598 cm^{-1}. The

TABLE 1

X-Ray powder data for $XeF_2.2PdF_4$ and $XeF_2.2PtF_4$

$XeF_2.2PdF_4$		$XeF_2.2PtF_4$	
$10^4\frac{1}{d^2}$	I/I_o	$10^4\frac{1}{d^2}$	I/I_o
140	m	153	w
---	-	185	w
---	-	417	vw
---	-	458	vw
515	vw	529	vw
580	vs	588	s
670	s	672	vs
---	-	691	vw
		777	m
837	vs	847	vs
953	vs	958	vs
1081	vw	1075	w
---	-	1116	vw
1244	w	1235	w
---	-	1328	vw
1355	m	1386	m
1415	w	1451	vw
---	-	1504	vw
---	-	1599	vw
---	-	1626	vw
1728	w	1732	m
1869	m	1869	s
2046	w	2042	m
2096	vw	2103	m
2202	vw	2213	w

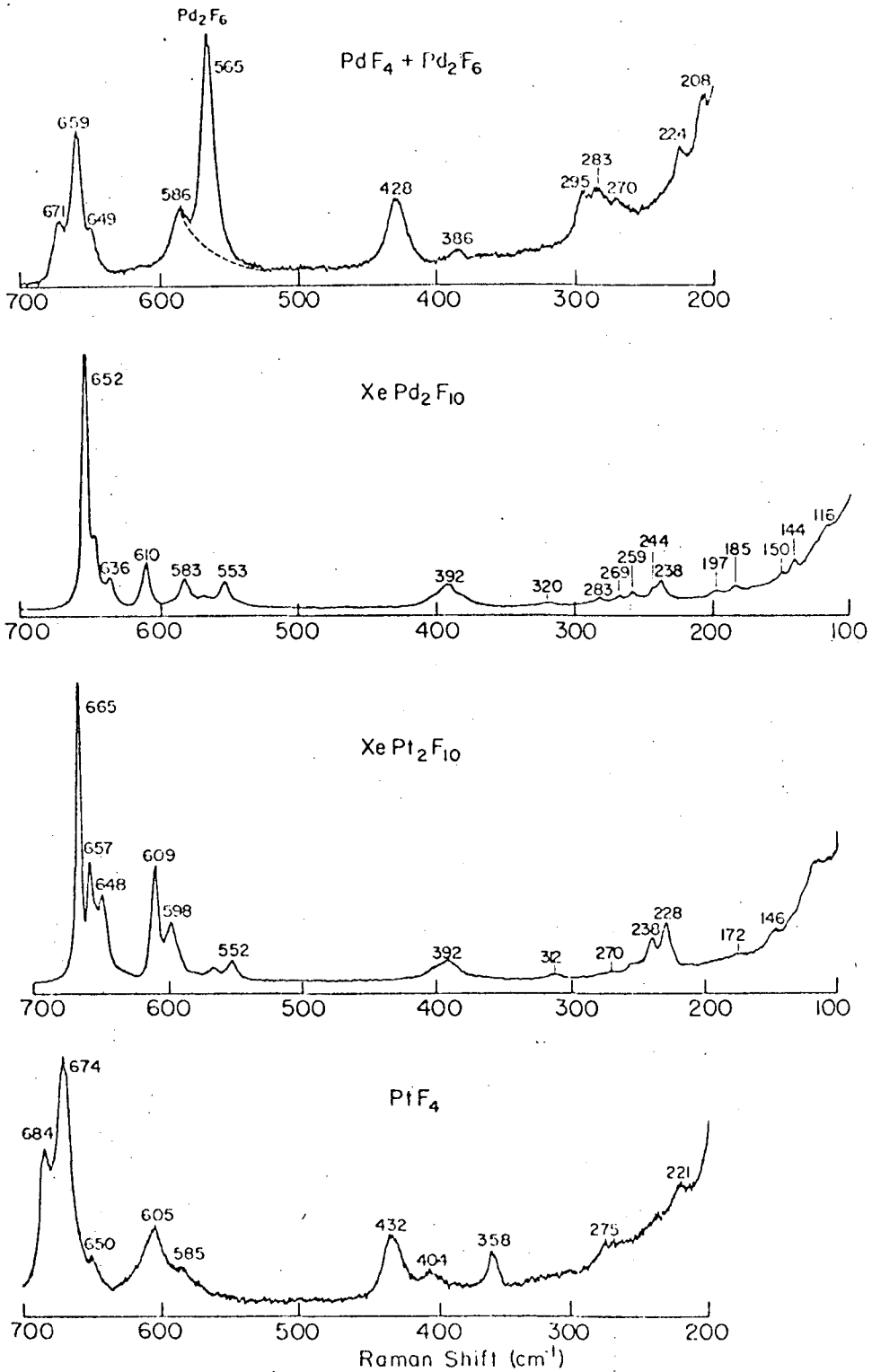

Fig. 5. Raman spectra of PdF_4, Pd_2F_6, $XeF_2.2PdF_4$, $XeF_2.2PtF_4$ and PtF_4

occurence of a band at $\sim$ 610 cm^{-1} in each of the XeM_2F_{10} spectra suggests that XeF^+ is a common component. See also Table 2. There is little likelihood, however, of the anion being $M_2F_9^-$ since again octahedral coordination of M is anticipated and a face sharing of two octahedra has never been confirmed for any polyfluorometal species. The μ fluoro-bridged noble-metal pentafluoride and tetrafluoride structures [15,4] suggest that such an anion would involve each metal atom in μ-fluoro bridging to three other metal atoms. This can give rise to an infinite polymer, but a discrete species could also occur, the simplest of which we would expect to be $M_8F_{36}^{4-}$. We can represent such a species in terms of a distorted cube having M atoms at the corners, 12 bridging F ligands in the edges (M-F-M angles $\neq$ 180°) and 3 unique F atoms per M atom completing the octahedral coordination of each M atom. Such a species can be formed by combining two superimposed $(RhF_5)_4$ type units (see Figure 4). Whatever the structure of the anion, it appears, from the similarity of the Raman spectra of $XeF_6.2PdF_4$ and $XePd_2F_{10}$ ($XeF_2.2PdF_4$) (the data for which are in Table 2) that the same form occurs in both compounds.

Since the break up of the $XePd_2F_{10}$ lattice in vacuo at 280° yields XeF_4 it is evident that sufficient activation energy is available for the redox process at that temperature. In the interaction of liquid XeF_2 with PdF_4 at 140° the thermal energy may fall short of that necessary to activate the redox process, but it is more likely that the redox course is not followed simply because the XeF_2, acting as a fluorobase, quickly stabilizes the Pd(IV) as the PdF_6^{2-} ion:

$$4XeF_2 + PdF_4 \longrightarrow (Xe_2F_3^+)_2PdF_6^{2-}$$

The decomposition of $XePt_2F_{10}$ takes a different course to that of $XePd_2F_{10}$ because Pt(IV) is much less oxidizing than Pd(IV) in an equivalent situation. This in itself is simply a consequence of the tighter binding of the valence electrons of Pd compared with Pt.

These studies have provided new and unexpected insights into a long-standing problem. The question concerning the constitution of $XePtF_6$ remains however. The subtle interrelationships of the platinum and xenon oxidation states which this work has revealed allows for both $Xe(I)Pt(V)F_6$ and $Xe(II)Pt(IV)F_6$ formulations. Fortunately we have recently developed [16] a synthesis which provides material with a composition close to the ideal 1:1 stoichiometry, $XePtF_6$. Coincidentally both this material and $XePdF_6$

TABLE 2

Raman shifts (cm^{-1}) for $XeF_2.2PdF_4$ and $XeF_6.2PdF_4$

XeF^{+*} in $XeFPtF_6$	$XeF_2.2PdF_4$	$XeF_6.2PdF_4$	XeF_5^{+**} in $(XeF_5)_2PdF_6$
		686(1) ·····	{676(3), 660(5)} ν_7
		679(1) ·····	653(100) ν_1
	652(7) ·····	659(7)	
	647(sh,2) ·····	649(5)	
	636(sh,1) ·····	639(sh,2)	
		625(2)	
		618(2) ·····	606(2), ν_4
609, 602 ·····	610(1)		
		608(3) ·····	590(71), ν_2
	583(1), 562(<1), 553(1) ·····	567(1)	
		408(2) ·····	425(3)
		404(sh,2) ·····	396(sh) ν_8
	392(1) ·····	397(sh,1)	
	320(<1)		
		302(1) ·····	309(10), ν_3
	283(<1) ·····	296(1)	
	269(<1) ·····	273(2)	
	259(<1) ·····	258(1)	
	244(<1) ·····	243(1)	
	238(1) ·····	231(1)	
	197(<1) ·····	215(<1)	
	185(<1) ·····	185(1)	

* ref [2]

** C. J. Adams and N. Bartlett, An Investigation of Xenon Hexafluoride and its Complexes by Raman Spectroscopy, to be published.

($XeF_2.PdF_4$) are amorphous to X-rays (whereas $XeFPtF_6$ always reveals its presence, by its characteristic X-ray pattern whenever the stoichiometry of the Xe + PtF_6 reaction product significantly exceeds 1:1). This gives rise to a suspicion that the poor crystal-developing character of both $XePtF_6$ and $XePdF_6$ could signify a structural relationship. However, our recent magnetic measurements for approximately 1:1, $XePtF_6$, suggest that this material is ferrimagnetic whereas $XePdF_6$ is diamagnetic. Absence of structural information is a difficulty, but we are hopeful that this question will soon be resolved.

EXPERIMENTAL

General apparatus and techniques

All of the compounds used or prepared in this work are spoiled by water. All transfer of materials was therefore carried out either in the dry atmosphere of a Vacuum Atmospheres Corp., DRILAB, or by distillation under vacuum in well-dried apparatus. All containers or exposed surfaces were of aluminum, Monel, Kel-F, Teflon or quartz. Vacuum lines were constructed of Autoclave Engineering 30VM6071 Monel valves (rated to 30,000 psi) and appropriate lines and connectors. Normal working pressures were measured with Monel Helicoid gauges -- one for the 0-1500 torr range, and another for the 0-500 psi range.

All of the XeF_2/platinum fluoride and XeF_2/palladium fluoride systems were studied using the same reactor type. This was a 2 3/4 in. length of 3/8 in. Monel tube made by boring out rod to provide a wall and bottom of thickness of 1/16 in. This tube was fitted with a 3/4-1/4 in. Swagelock reducing union. The tube was, depending upon the application, either closed with a 1/4 in. Swagelock cap or by a brass IKS4 Whitey valve (Kel-F tipped stem).

Raman spectra were obtained using a Spex 1401 double monochromator and a detection system which utilized photon counting, in combination with a 647.1 nm laser exciting line from a krypton laser. The Spectrometer was coupled to an on-line computer which allowed the data to be collected, stored, corrected for phototube sensitivity, normalized and plotted. Powdered samples were loaded into 1 mm o.d. quartz X-ray capillaries in the

Drilab, sealed temporarily with a plug of Kel-F grease, and the tube drawn down in a small flame outside the drybox.

Infrared spectra were obtained on a Perkin-Elmer 337 Grating Spectrophotometer over the range 4000-400 cm^{-1}. A 10 cm path length Monel cell with AgCl windows (cut from 1 mm sheet obtained from Harshaw Chemical Co., Cleveland, Ohio) was used for gas phase work. Spectra of solids were obtained from dusted samples of the solids pressed between AgCl sheets (1 mm) in a Kel-F holder.

X-Ray powder photographs were obtained using a General Electric Precision camera (Straumanis loading) with graphite - monochromatized CuK_α radiation. Finely powdered samples were sealed into 0.3-0.5 mm thin-walled quartz capillaries as described under Raman spectra.

Reagents

Platinum tetrafluoride was either prepared after the method given by Sharpe [17] or by pyrolysis of $XePt_2F_{10}$ at 430°. The PtF_4 was characterized by its X-ray powder pattern which is described in ref. [18], and by its Raman spectrum given in Fig. 5.

Palladium tetrafluoride was prepared by a varient of the method of Bartlett and Rao [4] and by the fluorination of $PdGeF_6$. The latter method yields material containing little or no Pd_2F_6. $PdGeF_6$ is prepared by dissolving a 1:1 molar mixture of $PdBr_2$ and germanium tetrabromide (obtained from Ventron Alfa Products, San Leandro, CA) in bromine trifluoride (from The Matheson Co., East Rutherford, N.J.). The $PdBr_2$ was prepared by dissolving palladium sponge (99.99% from Engelhard, Neward, N.J.) in aqueous hydrobromic acid -- bromine mixture. The mixture was heated with an infrared lamp and bromine was added from time to time until all of the Pd metal had dissolved. The resultant solution was passed through a sintered glass filter and was then evaporated to dryness under an infrared lamp. The purple to black solid was further dried by holding it under a vacuum of $\sim 10^{-6}$ torr overnight. The $PdBr_2$, $GeBr_4$ mixture was contained in a Kel-F tube (Argonne Lab. type) and bromine trifluoride was vacuum distilled on to it with the trap at -196°. The mixture was warmed slowly. Onset of reaction was signaled by bromine evolution and was moderated (when necessary) by judicious cooling with liquid N_2. As the reaction proceeded, the evolved

bromine served as a diluent and the vigor of the reaction moderated. When obvious signs of reaction had ceased, the mixture was warmed to ∿ 70° to ensure completion of the reaction, then the volatiles were removed under vacuum. The brown, solid, residue was heated to 200° in a vacuum to ensure complete loss of BrF_3. The resulting solid was heated to 280°, with F_2 (at 780 psi at ∿ 20°), for ∿ 58 hr in a heavy-walled Monel copper-gasketed autoclave, provided with a 30VM6071 valve. The resultant PdF_4, which was a pink powder, showed no X-ray powder lines of Pd_2F_6, the pattern being entirely consistent with that of PdF_4 [4]. The Raman spectrum of PdF_4 is as shown in Figure 5; that of Pd_2F_6 is included since it is a common impurity in PdF_4 and is even produced by pyrolysis, with intense laser sources, in the Raman experiment.

Palladium trifluoride was prepared as described by Sharpe [17].

Xenon difluoride was prepared by a standard procedure [19].

Preparations

In a typical preparation of the XeF_2-rich phases, platinum or palladium fluoride (0.2-0.3 g) was weighed by difference into a Monel tube similar to that described above. An excess of XeF_2 (1-2 g) was then added to the tube. The tube was usually closed with a Swagelock cap, weighed, and then immersed in sand in an electrically heated furnace. Subsequently the cap was exchanged for a valve in the Drilab and XeF_2 and xenon were removed under vacuum. In the first experiments, weight-loss time curves were plotted (care being taken to ensure that a constant sample temperature was maintained while volatiles were being removed). These studies did not give any evidence for compounds richer in XeF_2 than $Xe_2F_3^+PtF_6^-$, but did indicate that 4:1, 3:1 and 2:1 compounds exist in the XeF_2/PdF_4 system although the 1:1 compound $XePdF_6$(nc) proved to be the only one thermally stable at 20°.

The thermal decomposition studies were initially carried out by following weight-loss as functions of time and temperature of the sample when under vacuum. When the lowest temperature for rapid weight-loss had been established it was our practice to hold the sample at this temperature until constant weight was attained. The volatiles were trapped at -196° and were subsequently examined by gas-phase infrared spectroscopy. The residual solids in the Monel tubes were examined by X-ray powder photography, Raman

TABLE 3

Experimental data for the XeF_2/platinum fluoride and XeF_2/palladium fluoride systems

Reactants	Conditions	Products and Characterization
Mix: PtF_4 0.4253 g 1.57 mmole XeF_2 1.8138 g 10.71 mmole	140-150° for ∿ 48 hr, then evacuated at -80°	volatile: Xe (no IR, condensible -196°) 0.0995 g 0.76 mmole
	excess XeF_2 removed in vacuo at ∿ 20°	yellow solid (p): $Xe_2F_3PtF_6$ (X-R1, R1) 0.938 g 1.49 mmole
$Xe_2F_3PtF_6$ 0.8893 g 1.41 mmole	∿ 70° in vacuo for 17 hrs	orange-yellow solid (p): $XeFPtF_6$ (X-R2, R2) 0.6422 1.40 mmole volatile: XeF_2 (IR1) caught in -196° trap
$XeFPtF_6$ 0.3711 g 0.81 mmole	∿ 140° in vacuo for several hours	red-brown solid (d): $XePt_2F_{10}$ (X-R3, R3) 0.2947 g 0.41 mmole volatile: XeF_4 (IR2) caught in -196° trap
$XePt_2F_{10}$ 0.1142 g 0.16 mmole	∿ 430° in vacuo for several hours	light brown solid (d): PtF_4 (X-R4, R4) 0.0771 g 0.28 mmole volatile: XeF_2 (IR1)
Mix: Pd_2F_6 (1) 0.50 1.53 (2) 0.465 g 1.42 mmole XeF_2 2.96 17.48 3.125 g 18.46 mmole	142° for 11 hr, then evacuated at -80°	volatile: Xe (no IR, condensible -196°) (1) 0.19 g 1.45 mmole (2) 0.192 g 1.46 mmole
	excess XeF_2 removed in vacuo at ∿ 20° to constant weight	yellow solid (d): $XePdF_6$ (R5, IR3) (amorphous to X-R) 1.0228 g 2.91 mmole

Mix: PdF_4 0.271 g 1.49 mmole XeF_2 1.480 g 8.74 mmole	150° for 48 hr, excess XeF_2 removed at ∿ 20° to constant weight*	yellow solid as above: $XePdF_6$ (R5, IR3) 0.54 g 1.54 mmole
$XePdF_6$ 1.0228 g 2.91 mmole	140-150 in vacuo for several hours	light brown to pink solid (d): $XePd_2F_{10}$ (X-R5, R6) 0.7513 g 1.41 mmole volatile: XeF_2 (IR1) caught in -196° trap
$XePd_2F_{10}$ 0.3489 g 0.65 mmole	280° in vacuo for 2 hr	black solid (p): Pd_2F_6 (X-R6) 0.2234 g 0.68 mmole volatile: XeF_4 (IR2) caught in -196° trap

p-paramagnetic; d-diamagnetic
X-ray powder data: X-R1 in Table 4; X-R2 in Table 5; X-R3 and 5 in Table 1 and X-R4 in ref [4]; X-R6 in ref [14], where Pd_2F_6 is described as PdF_3.
Raman data: R1 and R2 in Fig. 3, R3,4, and 6 in Fig. 5, R5-see Table 6
Infrared data: for IR1 and 2 see book cited in ref [1]. For IR3 see Table 6.
*Weight-loss time curves for the x $XeF_2.PdF_4$ material indicated the phases $4XeF_2.PdF_4$; $3XeF_2.PdF_4$; $2XeF_2.PdF_4$ and the 1:1 compound.

TABLE 4

X-Ray powder data for $Xe_2F_3^+PtF_6^-$ and related salts

$Xe_2F_3^+IrF_6^-$		$Xe_2F_3^+PtF_6^-$		$Xe_2F_3^+RuF_6^-$	
$10^4\frac{1}{d^2}$	I/I_o	$10^4\frac{1}{d^2}$	I/I_o	$10^4\frac{2}{d^2}$	I/I_o
596	vs	582	vs	596	s
647	vs	642	vs	654	s
693	s	690	s	695	s
726	mw				
811	vs	806	vs	811	s
878	vs	875	vs	883	s
1052	ms	1054	mw	1057	vw
1437	mw				
1513	mw	1507	w		
1715	s	1714	s		
				1744	ms
1814	mw	1789	vvw		
1865	s	1851	ms		
1969	ms	1933	mw	1956	vw
2200	ms	2175	mw	2222	vw
2308	s	2290	s	2330	ms
		2499	w	2515	vvw
2765	s	2754	mw	2911	mw
3221	s	3197	s	3246	mw
		3709	vvw		
3860	w	3846	vw		
				3906	vvw
4019	w				
4049	w	4030	vw	4060	vvw
4185	w				
5295	s			5344	mw
5415	w				
5586	w				
5857	vw				
6690	w				
7230	w				

vs>s>ms>m>mw>w>vw>vvw

TABLE 5

X-Ray powder data for $XeF^+PtF_6^-$ and $XeF^+RuF_6^-$

$XeFPtF_6$			$XeFRuF_6$			hkl
I/I_o	$10^4 \frac{1}{d^2}_{obs}$	$10^4 \frac{1}{d^2}_{calc}$ *	I/I_o	$10^4 \frac{1}{d^2}_{obs}$	$\frac{1}{d^2}_{calc}$ **	
	---	437	m	429	424 432	$\bar{1}11$ 111
m	489	487	ms	480	482	120
s	632	632	s	629	627	200
vs	687	684	vs	674	667 675	$\bar{1}21$ 121
m	788	787	ms	762	761	002
mw	871	869	ms	839	842	012
	---	938	w	923	923	031
vvw	1020	1027	w	999	990 1007	$\bar{1}12$ 112
vvw	1111	1096	w	1084	1075 1083	$\bar{1}31$ 131
		1116			1086	022
			w	1251	1234 1250	$\bar{1}22$ 122
	---	1317	w	1304	1302	040
m	1394	1373	w	1364	1359	230
m	1479	1475	m	1452	1459	140

* $\frac{1}{d^2}$ calculated for $XeFPtF_6$ assuming $\beta = 90°$. Found a = 7.96, b = 11.02, c = 7.13Å.

** The $\frac{1}{d^2}$ calc values for $XeFRuF_6$ are from the cell dimensions obtained in the single crystal study in ref. [9].

TABLE 6

Raman and infrared bands for $XeF_2.PdF_4$

R(cm^{-1})*		649(9)	585(2)	505(1)	385(1)	230(1)
IR(cm^{-1})	655(sh)	635(vs)	580(s)	470(s)		

*all Raman bands were very broad - relative intensities are given in parentheses

and infrared spectroscopy and were also tested for para- or diamagnetism.

The detailed conditions and findings are given in Table 3. The compounds $Xe_2F_3^+PtF_6^-$, $XeF^+PtF_6^-$, $XeF_2.2PtF_4$ ($XePt_2F_{10}$) were identified in the XeF_2/platinum fluoride system. The compounds $XeF_2.PdF_4$(nc) and $XeF_2.2PdF_4$(nc) ($XePd_2F_{10}$) were identified in the XeF_2/palladium fluoride system.

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