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Author's review

Binary Fluorides of Noble-Gases and Their Compounds

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The synthetic work done during the last 25 years in the field of binary fluorides of noble gases (especially xenon and krypton) and their compounds is critically reviewed. Besides, a historical introduction to the noble gas chemistry, its challenges in the future and possible uses of the noble gas compounds are also given.

INTRODUCTION

1.1. General Introduction

Since 1962, when the first xenon compound was reported[1], many books and reviews treating the developments in the noble-gas chemistry have been published. Up to now the most extensive one, dealing with all aspects of the noble-gas chemistry, was written by Bartlett and Sladky[2]. Recently, a review of cationic and anionic complexes of the noble gases was added by Selig and Holloway[3].

The purpose of this review is to summarize the synthetic work done during the last two and a half decades in the field of binary fluorides of noble gases (especially xenon and krypton) and their compounds.

1.2. Historical Introduction

Argon, the most plentiful of the group of noble gases, was isolated and announced as a new element in 1894 by Lord Rayleigh and Sir W. Ramsay. They tried various chemical reagents to form compounds of the new element but without success. Ramsay also sent a 10 ml sample of the gas to his friend H. Moissan, the discoverer of fluorine, so that he should attempt to prepare a fluoride. In 1895, Moissan reported[4] that the reaction between argon and fluorine did not proceed. This experiment was considered the ultimate test for chemical inertness of argon. Some years later, the electronic theory of valence[5,6] supported the proposed chemical inertness of noble gases. The noble-gas valence electron configuration was clearly defined as the configuration to which other elements tended in their chemical bonding.

In 1933, some new reports[7,8,9,10] of unsuccessful experiments to make noble gas compounds were published simultaneously with some theoretical speculations that noble-gas compounds should exist[11,12]. Among these experiments the most promising experiment was made by Yost and Kaye on a suggestion of Pauling, who was convinced that, at least, xenon and fluorine should react. This failure was really unfortunate since a similar experiment, carried out 32 years later but replacing the electric discharge of the early experiment with sunlight[13,14] provided a convenient preparative method for xenon difluoride.

There is no doubt that if xenon had been as abundant as argon we should not have had to wait more than 60 years for the noble-gas chemistry. The legend that the inert gases do not form stable compounds was a rather firmly established chemical dogma until the spring of 1962. At that time Bartlett and Lohmann discovered an oxyfluoride of platinum which proved to be the salt $O_2^+PtF_6^-$ [15]. This formulation indicates that PtF_6 is an oxidizer of unexpected power. Bartlett noted that the ionization potential of xenon atoms is almost identical to that of oxygen molecules ($O_2 = 12.2$ eV, Xe = 12.10 eV). He tried reaction of xenon gas with PtF_6 vapours. Yellow-orange xenon fluoroplatinate(V) was obtained[1,16]. This and the subsequent discovery of xenon fluorides[17,18,19] started a new era of inorganic chemistry.

2. XENON CHEMISTRY

The normal oxidation states are even and range from + 2 to + 8. The oxidation state + 8 is known in the oxide XeO_4, the perxenates XeO_6^{4-} and xenon trioxide difluoride. XeF_8 is not known. The fluorides are readily preparable from the elements and are thermodynamically stable. Among the other binary compounds with the halogens only $XeCl_2$ and $XeBr_2$ are known.

2.1. *Xenon Fluorides*

Three binary fluorides of xenon are known: XeF_2, XeF_4 and XeF_6. Xenon difluoride and xenon hexafluoride form numerous stable complexes with fluoride-ion acceptors. The fluoride ion donor ability of XeF_4 has been shown to be less than that of XeF_2 and XeF_6 : $XeF_6 > XeF_2 \gg XeF_4$ [20] These findings are in agreement with the enthalpies of ionization derived from photoionization studies[21].

	H° (eV)
$XeF_{2(g)} \rightarrow XeF^+_{(g)} + F^-_{(g)}$	9.45
$XeF_{4(g)} \rightarrow XeF_3{}^+_{(g)} + F^-_{(g)}$	9.66
$XeF_{6(g)} \rightarrow XeF_5{}^+_{(g)} + F^-_{(g)}$	9.24

The enthalpy of ionization of XeF_6 is more than 0.6 eV less than anticipated on the basis of XeF_2 and XeF_4 data. This is compatible with the greater stability of XeF_5^+ salts compared with XeF_3^+ and XeF^+. It seems that the pseudo octahedral geometry of XeF_5^+ ion is especially favourable.

Although there is no doubt that XeF_6 is the strongest fluoride ion donor, there is disagreement as to the relative fluoride ion donor abilities of XeF_2 versus XeF_4. On the basis of the length, direction and number of fluorine bridges in the XeF^+ and XeF_3^+ salts it was concluded that the order of fluoride ion donor ability is $XeF_2 < XeF_4 < XeF_6$ [22]. The facts that very few XeF_3^+ salts have been isolated and that they are thermally not so stable as those of XeF_2 do not confirm the last statement.

The simple cation XeF^{+}_{x-1} derived from each of the binary fluorides has been in each case crystallographically defined. Removal of F^{-} from XeF_x in each case leaves one short Xe-F bond trans to the site vacated by F^{-}. The detailed structural arrangements suggest that the non-bonding xenon valence-electron pairs are distributed as shown in Figure 1, with anionic species making their closest approaches to the cations in the directions indicated by the arrows.

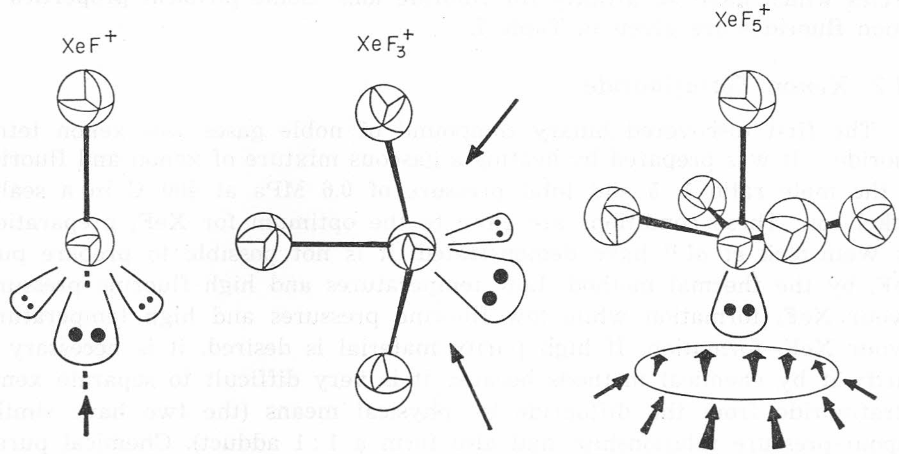

Figure 1. Shapes of the XeF^{+}_{x-1} ions based on steric activity of the non-bonding xenon valence-electron pairs.

(From D. E. McKee, A. Zalkin, and N. Bartlett, *Inorg. Chem.* **12** (1973) 1713.)

2.1.1. Xenon Difluoride

Xenon difluoride was first prepared independently in two laboratories[18,23]. After that, several effective syntheses were reported[24,25,26]. If the thermal method of preparation is used[27,28], a large excess of xenon over fluorine should be employed in order to minimize formation of higher xenon fluorides. A convenient preparation using very simple apparatus, affording a pure product, is the exposure of xenon-fluorine gas mixture to sunlight[13,14,29]. Very pure XeF_2 in bigger quantities (up to 1 kg) can be best prepared by UV irradiation of a gaseous xenon-fluorine mixture in the mole ratio 1 : 2 with addition of about 1 mol % of HF in fluorine as catalyst. The rate of XeF_2 formation is thereby increased by about four times[30].

The thermal reaction between xenon and fluorine to form xenon difluoride is heterogenous and it takes place on the prefluorinated walls of the reaction vessel and/or the surface of added fluoride[31–36]. Among the examined fluorides, nickel difluoride proved to be an excellent catalyst for the xenon-fluorine reaction. In its presence it is possible to synthetize XeF_6 even at 120 °C, starting from the gaseous mixture with the mole ratio $Xe : F_2 = 1 : 5$[37]. Further, it was shown[38] that under certain conditions the reaction between xenon and fluorine could also be homogeneous.

Although xenon difluoride is potentially a strong oxidizer, it is frequently unreactive for kinetic reasons. Its stability in aqueous solution (XeF_2 may be recovered by CCl_4 extraction or fractional distillation) is typical of this kinetic inertness. Neutral or acid solutions decompose rather slowly (the half life being ~ 7h at 0 °C) while in basic solution the decomposition is very fast, the base catalytic effect being roughly in the order of base strength. The hydrolysis products are xenon, oxygen, fluoride ions and hydrogen peroxide. The interaction of XeF_2 with water is not only catalyzed by base but also by species which have an affinity for fluoride ions. Some physical properties of xenon fluorides are given in Table I.

2.1.2. Xenon Tetrafluoride

The first discovered binary compound of noble gases was xenon tetrafluoride[17]. It was prepared by heating a gaseous mixture of xenon and fluorine in the mole ratio 1 : 5 and total pressure of 0.6 MPa at 400 °C in a sealed nickel can. These conditions are close to the optimum for XeF_4 preparation. As Weinstock *et al.*[47] have demonstrated, it is not possible to prepare pure XeF_4 by the thermal method. Low temperatures and high fluorine pressures favour XeF_6 formation while low fluorine pressures and high temperatures favour XeF_2 formation. If high purity material is desired, it is necessary to purify it by chemical methods because it is very difficult to separate xenon tetrafluoride from the difluoride by physical means (the two have similar vapour-pressure relationships and also form a 1 : 1 adduct). Chemical purification could be done from a mixture of xenon fluorides so prepared that the content of XeF_2 is minimal and XeF_6 is the major impurity. XeF_6 could be removed by treating the mixture with sodium fluoride, which forms a complex with it at room temperature[57]. A more general chemical purification[20], which effectively eliminates XeF_2 and XeF_6 simultaneously ,exploits the inferior fluoride ion donor ability of XeF_4 compared to XeF_2 or XeF_6. This purification is appropriate for a XeF_4 sample which contains significant quantities of XeF_2 and XeF_6.

$$\left.\begin{matrix}XeF_2\\ XeF_4\\ XeF_6\end{matrix}\right\}\begin{matrix}+\ AsF_5\ \text{(excess)}\\ \text{in}\ BrF_5\ \text{soln.}\end{matrix}\xrightarrow[-AsF_5,\ -BrF_5]{0\ °C\ \text{in static vacuum}} XeF_4 + (Xe_2F_3)(AsF_6)^- + (XeF_5)^+(AsF_6)^-$$

$$\xrightarrow[20\ °C]{\text{vacuum}} XeF_4$$

Recently, three new methods for the preparation of XeF_4 have been developed[49-52] which give very pure XeF_4 and additional purification is not necessary:

- photochemical reaction between xenon and excess fluorine in the presence of NiF_2 as catalyts[49,50]
- thermal decomposition of XeF_6 in the presence of NaF. (This method can also be used for the preparation of pure fluorine[51])
- pyrolysis of $XeF^+PtF_6^-$ or $XePd_2F_{10}$ at 150 °C [52]:

TABLE I

Some Physical Properties of Xenon Fluorides

	XeF_2	XeF_4	XeF_6
Triple point/K	402.18[a]	390.25[a]	322.38 ($P = 177.51$ mmHg)[b]
$\Delta H_{(sub)}$ (kJ/mol at 298.15 K	55.71 ± 0.07[c]	60.92 ± 0.16[d]	59.1 ± 1.2[e]
ΔH_f (kJ/mol)[f], solid at 298.15 K	—162.76 ± 0.88	—267.11 ± 0.88	—338.2 ± 2.2
Solid density/g/cm³	4.32[g] (calcd.)	4.04[g,h] (calcd.)	3.411 ± 0.015 at 297.55 K[h]
Vapor pressure/mm Hg	$\log P^{a} = \frac{-3057.67}{T} -$	$\log P^{a} = \frac{-3226.21}{T} -$	$\log P^{b} = -(3313.5/T) + 12.5923$
	$-1.23521 \log T +$	$-0.43434 \log T +$	solid XeF_6 between 291.8 and 322.38 K
	$+ 13.969736$	$+ 12.301738$	$\log P = -(3093.9/T) + 11.8397$ solid XeF_6 between 291.8 and 322.38 °K
	valid between 273 and 380 K	valid between 275 and 390.25 K	$\log P = -(6170.88/T) - 23.67815 \log T + 80.77778$ liquid XeF_6 between 322.38 and 350 K
Mean thermochemical bond energy (kJ/mol) at 298.15 K[f]	132.30 ± 0.67	130.33 ± 0.54	125.27 ± 0.67

[a]Ref. (39); [b]Ref. (40); [c]Ref. (41); [d]Ref. (42); [e]Ref. (43); [f]Ref. (44); [g]Ref. (45); [h]Ref. (46).

$$2\,XeFPtF_{6(c)} \rightarrow XeF_{4(g)} + XePt_2F_{10(c)}$$

$$XePd_2F_{10(c)} \rightarrow XeF_{4(g)} + Pd_2F_{6(c)}$$

XeF_4 can be kept in thoroughly dried glass or quartz and can be stored indefinitely in Kel-F, nickel or monel containers. The ultimate products of hydrolysis are Xe, O_2, HF and XeO_3 [53]. The low bond energy of XeF_4 causes it to be a strong oxidative fluorinator (comparable with BrF_3) but it has high kinetic inertness like XeF_2.

2.1.3. *Xenon Hexafluoride*

The preparation of XeF_6 was first described in four independent and almost simultaneous reports[19,54,55,56]. All preparations are carried out in nickel or monel reaction vessels. From the equilibrium constants for the formation of xenon fluorides[47] it can be seen that an excess of fluorine (usually $Xe : F_2 = 1 : 20$) is necessary to minimize the formation of xenon tetrafluoride. In addition, the reaction temperature should be as low as possible, yet consistent with a reasonable reaction rate. In the presence of nickel difluoride as catalyst[37], the activation energy for the xenon-fluorine reaction is lowered and the reaction proceeds rapidly at 120 °C, in contrast with 250 °C without a catalyst[37]. The equilibrium constant for the reaction $XeF_4 + F_2 \rightarrow XeF_6$ is much higher at 120 °C ($K = 330$ atm^{-1}) than at 250 °C ($K = 0.94$ atm^{-1}) [47]. To purify XeF_6, the crude material should be condensed on to NaF which forms a complex with XeF_6 at 50 °C. Impurities ($XeOF_4$, XeF_2, XeF_4) may be removed by pumping on the NaF mixture to constant weight at temperatures up to 50 °C. Na_2XeF_8 is then decomposed at 125 °C under vacuum and pure XeF_6 is collected in a cold trap[57]. Small impurities of XeF_4 in XeF_6 can also be removed by treating it with excess of KrF_2 at room temperature or a little higher[58].

The xenon hexafluoride is much more volatile[40] than either XeF_2 or XeF_4, although much less so than other hexafluorides. Crystalline XeF_6 is effectively $XeF_5^+F^-$. The geometry of the XeF_5^+ and F^- clusters[59,60,61] suggests that the nonbonding xenon(VI) valence electron pair is located on the four-fold axis of the cation, trans to the axial He-F bond. Thus described HeF_5^+ is pseudo-octahedral. The XeF_5^+ unit in $(XeF_6)_x$ polymeric groups is almost indistinguishable from that observed in the XeF_5^+ salts.

XeF_6 is a much more powerful oxidizer and fluorinator than the lower xenon fluorides. It also has lower kinetic stability than XeF_2 and XeF_4. Thus, XeF_6 cannot be stored in glass or quartz but reacts with it exchanging fluorine for oxygen to yield initially $XeOF_4$ and finally xenon trioxide, with silicon tetrafluoride elimination:

$$XeF_6 + x/2\,SiO_2 \rightarrow XeO_xF_{6-2x} + x/2\,SiF_4$$

2.2. *Xenon(II) Compounds*

All known xenon(II) compounds including molecular adducts are listed in Table II. Strong fluoride ion acceptors, such as SbF_5, AsF_5 and metal pentafluorides, some metal tetrafluorides and BF_3 can withdraw a fluoride ion from XeF_2 forming XeF^+ species. The increase in the Xe-F bond energy in the cation formation (195.9 kJ/mol in the cation[21], 133.9 kJ/mol in XeF_2 [62]) contributes to fluoride ion donor ability of the difluoride. Furthermore, one or both of the fluorine ligands of XeF_2 may be substituted by O (e. g. 99,104) or N (100) atoms rendered highly electronegative by pendant electron withdrawing groups forming F—Xe—L or L—Xe—L (with L being $—OSO_2F$, $—OC(O)CF_3$, $—OPOF_2$, $OSeF_5$, $OTeF_5$, $OClO_3$ $—N(OSO_2F)_2$ etc.). Xenon difluoride forms also molecular adducts with other hypervalent species in which the negatively charged F ligands are attracted to the positive centre of the partner molecule of the adduct.

2.2.1. *[XeF^+] and [$Xe_2F_3^+$]*

XeF_2 complexes can be prepared by fusing stoichiometric amounts of the component fluorides under an atmosphere of a dry inert gas or by dissolving them in a non oxidizing or reducing solvent. One component can also be used in excess and removed by vacuum evaporation to constant weight.

Some reactions between binary fluorides in lower oxidation states and XeF_2 have also been carried out in the melt of XeF_2. Under these conditions, the oxidizing as well as the fluorobase properties of the XeF_2 are revealed and Xe(II) complexes of higher oxidation state fluorides are formed:

$$MnF_2 + nXeF_2 \rightarrow XeF_2 \cdot MnF_4 + Xe + (n — 2)\,XeF_2\,^{86}.$$

Xenon(II) compounds have also been prepared from hydrazinium or ammonium fluorometalates instead of binary fluorides[93]. This synthetic route has been extremely useful in the preparation of new xenon(VI) fluorometalates[94,95,96] but it has not yielded xenon(II) fluorometalate which could not be prepared using other synthetic routes. The reaction system XeF_2 — ammonium fluorometalates offers a unique synthetic route for the preparation of ammonium fluorometalates with the metal in higher coordination and oxidation states (e. g. NH_4VF_6 [97], $(NH_4)_3VF_8$ [93], $(NH_4)_4UF_{10}$ [98]).

Xenon difluoride forms with pentafluorides three types of compounds: $2\,XeF_2 \cdot MF_5$, $XeF_2 \cdot MF_5$ and $XeF_2 \cdot 2\,MF_5$. It is also possible that compositions poorer in XeF_2 content could exist[70].

Xenon difluoride forms with tetrafluorides three types of compounds: $2\,XeF_2 \cdot MF_4$, $XeF_2 \cdot MF_4$ and $XeF_2 \cdot 2\,MF_4$. The 2 : 1 compounds between xenon difluoride and tetrafluorides do not exist in a dynamic vacuum at room temperature. Only the 1 : 1 and 1 : 2 compounds are vacuum stable. All appear as the XeF^+ salts with polymeric anions $(MF_5^-)_x$ and $(M_2F_9^-)_x$.

With trifluorides only $2\,XeF_2 \cdot BF_3$ and $XeF_2 \cdot BF_3$ are known.

In XeF_2 rich systems the V-shaped $Xe_2F_3^+$ cation usually occurs. It was first characterized by Bartlett and his coworkers[89] and is planar and symmetrical about the bridging fluorine atom. It is characterized by strong Raman bands in the Xe-F stretch region at cca. 593 and 580 cm^{-1} and in the bend region at 160 cm^{-1}. The XeF^+ ion was first defined structurally by Peacock & Russell[164] and is characterized by strong vibrational bands in the 600—610 cm^{-1} region[89].

2.2.2. *Molecular Adducts of XeF_2*

The first isolated molecular adduct of XeF_2 was $XeF_2 \cdot XeF_4$ which was initially thought to be a second crystalline modification of XeF_4. Since then many other adducts of XeF_2 have been prepared. Some of them are listed in

TABLE II

Xenon(II) Compounds

Ti	V	Cr	Mn	Fe	Co	Ni
$2XeF_2\cdot TiF_4$[79,65,a,b] $3XeF_2\cdot 2TiF_4$[80] $XeF_2\cdot TiF_4$[80] $XeF_2\cdot 2TiF_4$[80]	$2XeF_2\cdot VF_5$[81,d] $XeF_2\cdot VF_5$[92]	$XeF_2\cdot 2CrF_4$[83]	$XeF_2\cdot MnF_4$[86] $XeF_2\cdot 2MnF_4$[86,87]			
Zr	Nb	Mo	Tc	Ru	Rh	Pd
$2XeF_2\cdot ZrF_4$[65,c]	$XeF_2\cdot NbF_5$[82] $XeF_2\cdot 2NbF_5$[82]	$XeF_2\cdot MoF_6$[84,f]	—	$2XeF_2\cdot RuF_5$[67] $XeF_2\cdot RuF_5$[67,82] $XeF_2\cdot 2RuF_5$[67,82]	$XeF_2\cdot RhF_4$[16] $2XeF_2\cdot RhF_5$[89] $XeF_2\cdot RhF_5$[89] $XeF_2\cdot 2RhF_5$[89]	$4XeF_2\cdot PdF_4$[52,l] $3XeF_2\cdot PdF_4$[52] $2XeF_2\cdot PdF_4$[52] $XeF_2\cdot PdF_4$[52] $XeF_2\cdot 2PdF_4$[52]
Hf	Ta	W	Re	Os	Ir	Pt
$2XeF_2\cdot HfF_4$[65,c]	$2XeF_2\cdot TaF_5$[73,e] $XeF_2\cdot TaF_5$[82] $XeF_2\cdot 2TaF_5$[71,82]	$XeF_2\cdot WF_6$[84,f]	—	$2XeF_2\cdot OsF_5$[67] $XeF_2\cdot OsF_5$[67,h]	$2XeF_2\cdot IrF_5$[67] $XeF_2\cdot IrF_5$[67] $XeF_2\cdot 2IrF_5$[67]	$2Xe_2\cdot PtF_5$[67] $Xe_2\cdot PtF_5$[67] $Xe_2\cdot 2PtF_5$[67] $Xe(PtF_6)_x$[1,16,j] $XePt_2\cdot F_{10}$[16]
U						
$XeF_2\cdot UF_6$[85,g]						

Table II to be continued

Table II continued

		B $2XeF_2 \cdot BF_3$[63,k] $XeF_2 \cdot BF_3$[63,k]	C	N	O	F	Ne
		Al	Si XeF_2SiF_6[64,l]	P $2XeF_2 \cdot PF_5$[36,k] $XeF_2 \cdot PF_5$[36,k]	S	Cl	Ar
Cu	Zn	Ga	Ge	As $2XeF_2 \cdot AsF_5$[67] $XeF_2 \cdot AsF_5$[67,n] $2XeF_2(XeF_5AsF_6)$[91] $XeF_2 \cdot XeF_5 \cdot AsF_6$[68,91] $XeF_2 \cdot 2(XeF_5AsF_6)$[68,91]	Se	Br $XeF_2 \cdot 2BrF_5$[74,p]	Kr
Ag	Cd	In	Sn $2XeF_2 \cdot SnF_4$[65,m] $3XeF_2 \cdot 4SnF_4$[66] $XeF_2 \cdot 2SnF_4$[66]	Sb $2XeF_2 \cdot SbF_5$[69,o] $XeF_2 \cdot SbF_5$[69,70] $2XeF_2 \cdot 3SbF_5$[69,70] $XeF_2 \cdot 2SbF_5$[71] $XeF_2 \cdot 3SbF_5$[69] $XeF_2 \cdot 6SbF_5$[70]	Te	I $XeF_2 \cdot IF_5$[75,76] $XeF_2 \cdot 2IF_5$[77,r]	Xe $XeF_2 \cdot XeF_4$[78]
Au $2XeF_2 \cdot AuF_5$[90]	Hg	Tl	Pb	Bi $2XeF_2 \cdot BiF_5$[72] $XeF_2 \cdot BiF_5$[72] $XeF_2 \cdot 2BiF_5$[72]	Po	At	Rn

Foosnotes on the next side

Table II continued: Footnotes

[a] Ref. [79]. The eöistence of the compound was established only by measurements of the electrical conductivity of XeF_2/TiF_4 melt as a function of the composition.

[b] Ref. [65]. The isolation of compound $2\,XeF_2 \cdot TiF_4$ was not confirmed.[80] The reported light yellow colour of $2\,XeF_2 \cdot TiF_4$ might be due to the partial hydrolysis of the isolated material because all öenon(II) and xenon(VI) fluorotitanates(IV) are white solids.[80]

[c] The isolation of $2\,XeF_2 \cdot ZrF_4$ and $2\,XeF_2 \cdot HfF_4$ was not confirmed[95] even using the efficient route of hydrazinium fluorometalates and XeF_2 (thus preparing tetrafluorides in situ in the very reactive, so called »molecular« form.).

[d] The isolation of $2\,XeF_2 \cdot VF_5$ was not confirmed[92]. Stable 2 : 1 compounds were not obtained either in the NbF_5/XeF_2 or TaF_5/XeF_2 systems.

[e] Ref. [73]. The way the compound was isolated and characterized does not support the existence of the 2 : 1 compound, which was neither confirmed by others[82].

[f] The existence of adducts $XeF_2 \cdot MoF_6$ and $XeF_2 \cdot WF_6$ was established from the melting point — composition diagram.

[g] The existence of $XeF_2 \cdot UF_6$ was established from the melting point — composition diagram.

[h] Compound $XeF_2 \cdot 2OsF_5$ was not prepared. Even the 1 : 1 compound is thermally unstable at room temperature and decomposes to $2\,XeF_2 \cdot OsO_5$

$$3\,XeF^+OsF^- \rightarrow Xe_2F_3OsF_6^- + Xe + 2\,OsF_6$$

[i] The interaction of liquid XeF_2 at 140—150 °C with PdF_4 (or Pd_2F_6) 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 all occur but the 1 : 1 complex loses XeF_2 at or below 20 °C.

[j] In the historical oxidation of xenon by platinum bexafluoride it was found[1] that the stoichiometry of the product of spontaneous reaction varied between $XePtF_6$ and $Xe(PtF_6)_2$. Chemical and physical evidence indicated that the oxidation state of platinum in $Xe(PtF_6)_x$was +5. Pyrolysis of $Xe(PtF_6)_x$, at 165 °C, yielded XeF_4 as the only volatile product and the solid, of composition $XePt_2F_{10}$, was diamagnetic, thus suggesting a Pt(IV) compound. The product of spontaneous reaction between xenon and PtF_6 at 20 °C contains $XeF^+PtF_6^-$, as it was shown by X-ray powder photography. When the material of composition $Xe(PtF_6)_2$ was warmed to 60 °C, the product $[XeF^+]\,[Pt_2F_{11}]^-$ was obtained thus indicating that, in addition to $Xe^+FPtF_6^-$, amorphous PtF_5 was also present.

[k] Adduct $2\,XeF_2 \cdot PF_5$, $XeF_2 \cdot PF_5$, $2\,XeF_2 \cdot BF_3$ and $XeF_2 \cdot BF_3$ were not established with certainty and some additional work should be done in these two systems.

[l] The reported compound Xe_2SiF_6 is probably erroneous. The authors claimed to have prepared it from a gaseous mixture of xenon and fluorine in the mole ratio 2 : 1 in a glow discharge.

[m] The existence of the 2 : 1 compound was not confirmed[66]. The existence of $2\,XeF_2 \cdot SnF_4$ was not noticed in the XeF_2/SnF_4 system even during a very careful recording of the course of pumping off the excess of xenon difluoride at 0 °C. It is possible that the compound claimed to be $2\,XeF_2 \cdot SnF_4$ was only $XeF_2 \cdot 2SnF_4$ with some impurities. In favour of this conclusion are the following facts: the published infrared spectrum of the compound reported to be $2\,XeF_2 \cdot SnF_4$ is practically identical with the infrared spectrum of the 1 : 2 compound[66] and the colour of the 2 : 1 compound is reported to be lemon yellow, whereas pure xenon (II) and xenon(VI) fluorostannates are all white solid materials[66,110]

[n] All efforts to prepare a phase richer in AsF_5 than $XeF_2 \cdot AsF_5$ failed and even the 1 : 1 compound loses AsF_5 at room temperature to yield $2\,XeF_2 \cdot AsF_5$ [67].

[o] Ref. [69] and [70]. In the system XeF_2/SbF_5 a whole set of compounds was postulated on the basis of the melting point — composition diagram.

[p] The adduct $XeF_2 \cdot 2BrF_5$ was postulated on the basis of the melting point — composition diagram.

[r] Ref. [77]. It was reported that xenon tetrafluoride interacts with IF_5 to yield IF_7 and an adduct $XeF_2 \cdot 2IF_5$. The authors[76] did not find evidence for an adduct of that composition and, furthermore, they found that XeF_4 dissolves easily in IF_5 but does not form a thermally stable adduct with it. At ambient temperatures there was no evidence of evolution of xenon or of iodine heptafluoride formation.

Table II. In these adducts the individual molecular species have essentially the same size and shape as in a crystal of the pure component. In all of them the F ligands of one molecule show maximum avoidance of other F ligands and are directed towards the positively charged central atom of the other molecule. This provides the best lattice energy for the semi-ionic assembly.

The existence of $XeF_2 \cdot IF_5$ [75,76] and $XeF_2 \cdot XeF_4$ [68] and the isoelectronic relationship and near identity of shape of XeF_5^+ to IF_5 and $XeOF_4$ suggested that XeF_2 might also make adducts with XeF_5^+ salts. $2\,XeF_2 \cdot XeF_5^+AsF_6^-$ [91], $XeF_2 \cdot XeF_5^+AsF_6^-$ and $XeF_2 \cdot (XeF_5^+AsF_6^-)_2$ [68,91] are typical and are conveniently prepared by mixing the component in the appropriate molar proportions either by fusing the components or dissolving them in a suitable solvent. Such adducts are limited to mono anions, in which the fluorine-ligand charge is sufficiently low, so that XeF_2 can effectively compete with the anion in interaction with the XeF_5^+.

2.3. *Xenon(IV) Compounds*

Xenon tetrafluoride is the weakest fluoride ion donor among xenon fluorides and only adducts with the strongest Lewis acids (SbF_5 and BiF_5) have been isolated at room temperature (see Table III). Such adducts were first presented as XeF_3^+ salts on the basis of the crystal structure of $XeF_3Sb_2F_{11}$ [102]. The existence of an adduct $XeF_4 \cdot AsF_5$ has been claimed[101] at low temperatures and in the presence of an excess of AsF_5.

TABLE III

Xenon(IV) Compounds

$XeF_4 \cdot AsF_5$[101]
$XeF_4 \cdot SbF_5$[102,103]
$XeF_4 \cdot 2SbF_5$[102,103]
$XeF_4 \cdot BiF_5$[72]
$XeF_4 \cdot 2BiF_5$[72]

The known xenon(IV) compounds have been prepared by fusing the components or by dissolving them in anhydrous HF, either in stoichiometric amounts or by using excess of one component and removing the excess under vacuum to constant weight.

These complexes are best described in terms of a T-shaped cation, (XeF_3^+) coordinated to the anion via fluorine bridges, the lengths and polar character of which are determined by the Lewis acidity of the anion. The totally symmetric stretching vibration ν_1 of XeF_3^+ is $\sim 643\ cm^{-1}$.

2.4. *Xenon(VI) Compounds*

A number of adducts involving XeF_6 in combination with recognized F^- acceptors (Table IV) and recognized F^- donors have been reported (Table V). High conductivity of XeF_6 in HF solutions, in comparison with those of XeF_2 or XeF_4, indicates the possibility that XeF_6 is extensively ionized in such solutions and is in fact $[XeF_5^+] \cdot F^-_{(solv)}$.

The adducts with fluoride-ion acceptors all appear to be either XeF_5^+ or $Xe_2F_{11}^+$ salts, the prototype structures of which were $XeF_5^+PtF_6^-$ [128] and $Xe_2F_{11}^+AuF_6^-$ [105]. These cations are the Xe(VI) analogues of XeF^+ and $Xe_2F_3^+$.

TABLE IV

Xenon(VI) Compounds with F⁻ Acceptors

Li	Be								
Na	Mg								
K	Ca	Sc $XeF_6\cdot ScF_3^{116,a}$	Ti $4XeF_6\cdot TiF_4^{80,d}$ $XeF_6\cdot TiF_4^{80}$ $XeF_6\cdot 2TiF_4^{80}$	V $2XeF_6\cdot VF_5^{118}$ $XeF_6\cdot VF_5^{88}$ $XeF_6\cdot 2VF_5^{88}$	Cr $XeF_6\cdot CrF_4^{121}$	Mn $4XeF_6\cdot MnF_4^{87}$ $2XeF_6\cdot MnF_4^{87}$ $XeF_6\cdot MnF_4^{87}$ $XeF_6\cdot 2MnF_4^{87}$	Fe $XeF_6\cdot FeF_3^{94,g}$	Co $XeF_6\cdot CoF_3^{94}$
Rb	Sr	Y $3XeF_6\cdot YF_3^{117,b}$	Zr $XeF_6\cdot ZrF_4^{95,e}$	Nb $2XeF\cdot {}_6NbF_5^{119}$ $XeF_6\cdot NbF_5^{119}$	Mo $2XeF_6\cdot MoF_6^{122,f}$ $XeF_6\cdot MoF_6$	Tc	Ru $2XeF_6\cdot RuF_5^{105,h}$ $XeF_6\cdot RuF_5^{124}$	Rh
Cs	Ba	La and Lantanides $4XeF_6\cdot CeF_4^{117,c}$ $XeF_6\cdot 2CeF_4^{117}$ $4XeF_6\cdot PrF_4^{117}$ $XeF_6\cdot 2PrF_4^{117}$ $XeF_6\cdot 4PrF_4^{117}$ $4XeF_6\cdot TbF_4^{117}$ $XeF_6\cdot 2TbF_4^{117}$ $3XeF_6\cdot DyF_3^{117}$ $3XeF_6\cdot HoF_3^{117}$	Hf $XeF_6\cdot HfF_4^{95,e}$	Ta $2XeF_6\cdot TaF_5^{120}$ $XeF_6\cdot TaF_5^{120}$	W	Re	Os	Ir $2XeF_6\cdot IrF_5^{20,i}$ $XeF_6\cdot IrF_5^{20}$
		U $2XeF_6\cdot UF_5^{123}$ $XeF_6\cdot UF_5^{123}$						

Table IV to be continued

Table IV continued

			B $XeF_6 \cdot BF_3{}^{107,163}$	C	N	O	F	Ne
			Al $XeF_6 \cdot 2AlF_3{}^{96,m}$	Si	P $2XeF_6 \cdot PF_5{}^{111}$	S	Cl	Ar
Ni $4XeF_6 \cdot NiF_4{}^{126,j}$ $2XeF_6 \cdot NiF_4{}^{126}$	Cu	Zn	Ga $XeF_6 \cdot GaF_3{}^{96,m}$	Ge $4XeF_6 \cdot GeF_4{}^{108}$ $2XeF_6 \cdot GeF_4{}^{108}$ $XeF_6 \cdot GeF_4{}^{108}$	As $2XeF_6 \cdot AsF_5{}^{111}$ $XeF_6 \cdot AsF_5{}^{107,163}$	Se	Br	Kr
Pd $4XeF_6 \cdot PdF_4{}^{127}$ $2XeF_6 \cdot PdF_4{}^{127}$	Ag $XeF_6 \cdot AgF_3{}^{129,k}$	Cd	In	Sn $4XeF_6 \cdot SnF_4{}^{109,n}$ $2XeF_6 \cdot SnF_4{}^{109}$ $4XeF_6 \cdot 3SnF_4{}^{110}$ $3XeF_6 \cdot 4SnF_4{}^{110}$ $XeF_6 \cdot 4SnF_4{}^{110}$	Sb $2XeF_6 \cdot SbF_5{}^{112}$ $XeF_6 \cdot SbF_5{}^{112}$ $XeF_6 \cdot 2SbF_5{}^{112}$	Te	I	Xe
Pt $2XeF_6 \cdot PtF_5{}^{128}$ $XeF_6 \cdot PtF_5{}^{128}$	Au $2XeF_6 \cdot AuF_5{}^{130}$ $XeF_6 \cdot AuF_5{}^{130}$ $XeF_6 \cdot AuF_3{}^{165,l}$	Hg	Tl	Pb $4XeF_6 \cdot PbF_4{}^{110,n}$ $3XeF_6 \cdot 4PbF_4{}^{110}$ $XeF_6 \cdot 4PbF_4{}^{110}$	Bi $2XeF_6 \cdot BiF_5{}^{113}$ $XeF_6 \cdot BiF_5{}^{114}$	Po	At	Rn

Foosnotes on the next side

Table IV continued: Footnotes

[a] $XeF_6\cdot ScF_3$ has been prepared only by the reaction between $N_2H_5\cdot ScF_4$ and excess of XeF_6 at room temperature. The adduct is stable at 0 ° but it decomposes at 20 °C to ScF_3 and XeF_6. The reaction between so obtained ScF_3 and XeF_6 to form $XeF_6\cdot ScF_3$ is not reversible.

[b] The compound $3\,XeF_6\cdot YF_3$ is the first known monomeric salt of XeF_5^+ with a metal in the +3 valence state. Raman spectroscopy shows that the compound is an XeF_5^+ salt. It can be formulated as $(XeF_5^+)_3YF_6^{3-}$. It has been prepared by the reaction between Y_2O_3 or $N_2H_5YF_4$ and excess XeF_6.

[c] With the lanthanides, two types of XeF_5^+ salts have been synthetized. If the lanthanide is oxidized to the +4 oöidation state, the 4 : 1 and 1 : 2 compounds are formed (in the case of praseodymium also 1 : 4). Only the 1 : 2 compounds are thermally stable at room temperature (1 : 4 in the case of praseodymium). If the lanthanide is not oxidized to the + 4 oxidation state, the 3 : 1 compounds are obtained when the lanthanide trifluoride has the YF_3 structure. When the trifluoride had the LaF_3 structure, no xenon(VI) compounds were preparable.

[d] The evidence for the 2 : 1 compound was found only during the thermal analysis of the compound with the high xenon hexafluoride content. The small difference between the decomposition temperatures of the 4 : 1 and 1 : 1 compounds hampers the isolation of the 2 : 1 compound.

[e] Compounds $XeF_6\cdot MF_4$ ($M = Zr$, Hf) were isolated by using hydrazinium fluorometalates as starting materials for the reaction with XeF_6. The reaction between the corresponding tetrafluorides and XeF_6 did not proceed.

[f] The existence of $2\,XeF_6\cdot MoF_6$ and $XeF_6\cdot MoF_6$ was established only from the melting point — composition diagram.

[g] $XeF_6\cdot FeF_3$ is another example where the use of a hydrazinium salt is essential for the synthesis of an XeF_5^+ salt. Raman spectra establish that it is an XeF_5^+ salt. The anion is probably polymeric $(FeF_4)_n^{n-}$.

[h] The synthesis of $2\,XeF_6\cdot RuF_5$ has not been described. However, the compound is isostructural with the other $2\,XeF_6\cdot MF_5$ where M is Ru, Ir, Pt and Au.

[i] The syntheses of $2\,XeF_6\cdot IrF_5$ and $XeF_6\cdot IrF_5$ have not been described. For the 2 : 1 compound see h). The 1 : 1 compound is isostructural with $XeF_6\cdot MF_5$ where M = Ru, Pt, Nb.

[j] Both nickel compounds have been prepared using XeF_6 and KrF_2 simultaneously. The 4 : 1 compound decomposes at room temperature yielding XeF_6 and the 2 : 1 compound.

[k] The $XeF_6\cdot AgF_3$ compound was synthetized only by simultaneous use of XeF_6 and KrF_2.

[l] The $XeF_6\cdot AuF_3$ compound represents with XeF_6AuF_5 the first instance of XeF_5^+ occurring with two different valence states of a metal.

[m] Compounds $XeF_6\cdot GaF_3$, $XeF_6\cdot 2\,AlF_3$ and $XeF_6\cdot InF_3$ are additional examples of the synthetic route using hydrazinium fluorometalates as the starting materials for the preparation of XeF_5^+ salts. All three compounds are XeF_5^+ salt with polymeric anions. The indium compound is thermally unstable, decomposing at 20 ° to XeF_6 and InF_3.

[n] On the basis of vibrational spectra, the 4 : 1 compounds can be formulated as $Xe_2F_{11}^+$ salts, while the 1 : 4 compounds are XeF_5^+ salt with polymeric anions. The 4 : 3 and 3 : 4 compounds are apparently intermediate compounds with both $Xe_2F_{11}^+$ and XeF_5^+ cations present.

[o] The existence of an adduct $XeF_6\cdot KrF_2$ was not confirmed[168] using the same experimental approach as the authors[115] and also other synthetic routes.

2.4.1. [XeF_5^+] and [$Xe_2F_{11}^+$]

For the preparation of xenon(VI) fluorocomplexes many synthetic schemes have been used, which can be roughly represented by the following three groups:

a) Direct method: The interaction of an excess of xenon hexafluoride with a binary fluoride in a melt of XeF_6 (temperatures higher than 50 °C.) Several complexes have been prepared by oxidizing a lower-valent fluorides in the presence of an excess of XeF_6. In other cases the complexes have been prepared by mixing the component fluorides in a non reducing solvent.

   The stoichiometries of these complexes appear to be determined by the favoured coordination number of M (commonly six as in [MF_6^-], [MF_6^{2-}]) and the formation of either XeF_5^+ or $Xe_2F_{11}^+$. The latter is formed only when the anion is monomeric (MF_x^{n-}) and XeF_6 is available to form a F^- bridge to XeF_5^+.

b) Indirect method: The corresponding binary fluoride is sythetized in situ in a very reactive »molecular form«. In this case xenon hexafluoride is both oxidizer and complexing agent. As starting materials, hydrazinium salts or ammonium fluorocomplexes[94–97] or oxides[117] have been used. Using this synthetic route a whole series of xenon(VI) fluorocomplexes have been isolated (e. g. $XeF_6 \cdot FeF_3$, $XeF_6 \cdot GaF_3$, $XeF_6 \cdot InF_3$, $XeF_6 \cdot 2\,AlF_3$, $XeF_6 \cdot HfF_4$, $XeF_6 \cdot ZrF_4$).

c) Combined Method: In this method, KrF_2 and XeF_6 were used concurrently. This method is efficient in cases where the binary fluoride does not exist in the oxidation state in which the xenon(VI) fluorocomplexes are expected (e. g. xenon(VI) fluoronickelates(IV)[126]) or in the cases where the binary fluoride exists in the oxidation state appropriate for the formation of xenon(VI) fluorocompound, but where this binary fluoride could not be obtained by using only XeF_6 as oxidizer (e. g. xenon(VI) fluoroargentate(III)[129]).

   Xenon hexafluoride forms complexes with monomeric and polymeric anions. In the case of monomeric anions we have the following set of complexes: $Xe_2F_{11}^+\,MF_6^-$, $XeF_5^+\,MF_6^-$, $XeF_5^+\,M_2F_{11}^-$, $(Xe_2F_{11}^+)^2\,MF_6^{2-}$, $(XeF_5^+)_2\,MF_6^{2-}$, $(XeF_5^+)_3\,MF_6^{3-}$. In the case of polymeric anions we have with tetravalent fluorides the following mole ratios: $XeF_6 : MF_4$ 4 : 3, 3 : 4, 1 : 2, 1 : 4[110,87] and with MF_3 1 : 1 and 1 : 2[94,96]. Among all structurally defined xenon(VI) fluorocomplexes, only in the cases of $XeF_6 \cdot AgF_3$ and $XeF_6 \cdot AuF_3$ the anions are not octahedrally coordinated with fluorine.

   The $Xe_2F_{11}^+$ cation behaves vibrationally like two weakly coupled XeF_5^+ species. The F bridging of two XeF_5 groups in the Xe_2F_{11} cation appears to be characterized by a »bridge stretch« at cca. 360 cm^{-1}[105]. For XeF_5^+ of C_{4v} symmetry, nine fundamental vibrations were observed.[166,167]

2.4.2. [XeF_7^-] and [XeF_8^{2-}]

Complexes of XeF_6 with fluoride ion donors, e. g. No_2F, NoF, and alkali metal fluorides (with the exception of LiF) are listed in Table V. With alkali fluorides, complexes of the type $MXeF_7$ and M_2XeF_8 have been reported. They probably contain anions XeF_7^- and XeF_8^{2-}. The XeF_8^{2-} in the fully characterized compound $(NO)_2^+ XeF_8^{2-}$ [134] has an approximately archimedian antiprism geometry, the stereo activity of the non-bonding xenon valence electron pair being only weakly evident. $NF_4^+ XeF_7^-$ decomposes to NF_3, F_2 and XeF_6 and evidence for $(NF_4)_2 XeF_8$ as an intermediate has been given[133].

TABLE V

Xenon(VI) Compounds with F⁻ Donors

$2\,NaF \cdot XeF_6$[57,125]	$NO_2F \cdot XeF_6$[131]
$2\,KF \cdot XeF_6$[125]	$2\,NOF \cdot XeF_6$[132]
$2\,RbF \cdot XeF_6$[106,125]	$NF_4^+ XeF_7^-$[133]
$RbF \cdot XeF_6$[106,125]	$(NF_4^+)_2 XeF_8^{2-}$[133]
$2\,CsF \cdot XeF_6$[106,125]	
$CsF \cdot XeF_6$[106,125]	

3. KRYPTON CHEMISTRY

The chemistry of krypton is limited to that of krypton difluoride and its derivatives. All efforts to confirm the synthesis of krypton tetrafluoride or higher fluorides have failed. Furthermore, there is no firm evidence of the existence of oxides, oxyfluorides or chlorides.

3.1. Krypton Difluoride

Krypton difluoride was first prepared by Turner and Pimentel[135] who prepared it by ultraviolet photolysis of fluorine suspended in a solid mixture of argon and krypton at 20 °K. Because krypton diffluoride is thermodynamically unstable[136], all effective syntheses have to be carried out at lower temperatures (—196 °C). Methods used for the preparation of KrF_2 in the laboratory include electric discharge of a gaseous mixture of krypton and fluorine at low temperature and pressure[137]. The method is claimed to yield about 250 mg KrF_2/h. High frequency discharge in a mixture of krypton and CF_2Cl_2[138] has also been claimed. Other methods involve irradiation of fluorine — krypton mixtures: with 1.5 MeV electrons[139]; with 10 MeV protons[140] or (with low efficiency) exposure to sunlight[141].

A very efficient method for the preparation of KrF_2 on a bigger laboratory scale has been developed (30—40 g/charge)[142]. This is based on the irradiation of a liquified mixture of fluorine and krypton with near UV light at —196 °C. The yield is about 1 g of KrF_2/h.

Properties: krypton difluoride is colourless in the solid and vapour phase. It decomposes at temperatures above —80 °C. The decomposition rate is very much dependent upon the pretreatment of the reaction vessel. If this is well pretreated with KrF_2 before starting, the decomposition of KrF_2 is much lower. Krypton difluoride has the lowest average bond energy of any known fluoride. The atomization energy of KrF_2 ($\Delta H_{at} = 98$ kJ mol^{-1}) is smaller than the dissociation energy of elemental fluorine ($\Delta H_{diss.} = 153$ kJ mol^{-1}), thus indicating that krypton difluoride is closest in activity to atomic fluorine.

TABLE VI

Some Physical Properties of KrF_2

ΔH_{sub}/kJ mol^{-1} [a]	41
$\Delta H_{f}^{\circ}{}_{(g)}$/kJ mol^{-1} [b]	60 ± 3
solid density/g cm^{-3} [c]	3,301 (calcd.)
vapor pressure/mm Hg[a]	10 ± 1 at 257.7 K 29 ± 2 at 273.2 K 73 ± 3 at 288.2 K
mean thermochemical bond energy (kJ mol^{-1})[b]	49.0

[a] Ref. (143); [b] Ref. (136); [c] Ref.(144).

3.2. Krypton(II) Compounds

So far only those krypton-fluorine compounds are known which exhibit a significant amount of ionic character and can be described in terms of $(KrF)^+$ and $(Kr_2F_3)^+$ containing species. The $(Kr_2F_3)^+$ cation consists of two $(KrF)^+$ units joined by a fluorine bridge.

All known krypton compounds are listed in Table VII. They are complexes of KrF_2 with Lewis acid pentafluorides and have the stoichiometries 2 : 1, 1 : 1 and 1 : 2. In addition, there are a number of compounds in which additional KrF_2 units appear to be weakly associated, probably with the cationic part of the compound. Recently, also the first adducts of KrF_2 with tetravalent fluorides have been isolated: $2\,KrF_2 \cdot MnF_4$ and $KrF_2 \cdot MnF_4$[153]. The 1 : 1 compound is most probably $(KrF)^+(MnF_5)^-$ with a polymeric anion. Claims for compounds $2\,KrF_2 \cdot TiF_4$ and $2\,KrF_2 \cdot SnF_4$ have not been supported by any characterizational evidence.

Krypton complexes may be prepared directly by the reaction of KrF_2 with the appropriate pentafluoride or using a solvent. In some cases the pentafluoride has been prepared in situ using KrF_2 as the fluorinating agent. So far no X-ray crystal structure of any KrF_2 complex has been determined and the characterization of the complexes has rested largely on vibrational spectroscopy. Raman spectroscopy has been especially valuable in the studies of these compounds, all of which are of low thermal stability.

Observed Raman and infrared frequencies for Kr(II) compounds are best assigned on the basis of ionic formulations. $(KrF)^+(M_2F_{11})^-$, $(KrF)^+(MF_6)^-$ and $(Kr_2F_3)^+(MF_6)^-$. The appearance of Kr . . . F and M . . .F bridge-stretching and F—Kr . . . F bending modes point to a strong interaction between cation and anion indicative of some covalent character to that bonding. For the $(KrF)^+$ salts the stretching vibration is in the range from 626 cm^{-1} (in the case of $KrF^+\,Sb_2F_{11}^-$) to 597 cm^{-1} (in the case of $KrF_2 \cdot 2\,NbF_5$).

The spectra of the $(Kr_2F_3)^+$ cation have been correlated with those of the $(Xe_2F_3)^+$ species but additional peaks, which have no equivalents in the xenon spectra, suggest that the $(Kr_2F_3)^+$ is less symmetrical than its xenon analogue, with one longer and weaker Kr—F bond and one shorter and stronger Kr—F bond. An alternative interpretation is that this cation involves distorted KrF_2 molecule fluorine bridged to a $(KrF)^+$ cation. KrF_2 is a very strong oxidizer. KrF^+ salts are even more powerful electrophiles since the electron affinity of $(KrF)^+$ is 12.5 eV. This makes it an effective source of F^+, exploited effectively in the synthesis of BrF_6^+ and ClF_6^+ salts.

TABLE VII

Krypton(II) Compounds

Ti	V	Cr	Mn	Fe	Co	Ni
$2KrF_2\cdot TiF_4$[145]	$KrF_2\cdot VF_5$[150]		$2KrF_2\cdot MnF_4$[153] $KrF_2\cdot MnF_4$[153]			
Zr	Nb	Mo	Tc	Ru	Rh	Pd
	$(xKrF_2\cdot KrF)^+\cdot(Nb_2F_{11})^-$[151] $KrF^+\cdot Nb_2F_{11}^-$[152]			$KrF^+\cdot RuF_6^-$[154] $KrF^+\cdot Ru_2F_{11}^-$[154]	$KrF^+\cdot RhF_6^-$[154]	$KrF^+\cdot PdF_6^-$[154]
Hf	Ta	W	Re	Os	Ir	Pt
	$(xKrF_2\cdot KrF^+)\cdot(Ta_2F_{11})^-$[151] $Kr_2F_3^+\cdot TaF_6^-$[151] $KrF^+\cdot TaF_6^-$[152] $KrF^+\cdot Ta_2F_{11}^-$[151]					$KrF^+\cdot PtF_6^-$[147,146] $KrF^+Pt_2F_{11}^-$[154]

Table VII to be continued

Table VII continued

		B $\mathrm{KrF^+ \cdot BF_4^-}$[145]	C	N	O	F	Ne
		Al	Si	P	S	Cl	Ar
Cu	Zn	Ga	Ge	As $\mathrm{(xKrF_2 \cdot Kr_2F_3^+)(AsF_6)^-}$[146,147] $\mathrm{Kr_2F_3^+ \cdot AsF_6^-}$[146,147] $\mathrm{KrF^+ \cdot AsF_6^-}$[146,147]	Se	Br $\mathrm{KrF_2 \cdot BrF_5}$[149]	Kr
Ag	Cd	In	Sn $\mathrm{2KrF_2 \cdot SnF_4}$[145]	Sb $\mathrm{(xKrF_2 \cdot Kr_2F_3)^+ \cdot (SbF_6^-)}$[146] $\mathrm{(xKrF_2 \cdot KrF)^+ \cdot (SbF_6^-)}$[147,148] $\mathrm{Kr_2F_3^+ \cdot SbF_6^-}$[148,146] $\mathrm{KrF^+ \cdot SbF_6^-}$[148,146] $\mathrm{KrF^+ \cdot Sb_2F_{11}^-}$[48,102]	Te	I	Xe $\mathrm{KrF_2 \cdot XeF_6}$[115]
Au $\mathrm{KrF^+ \cdot AuF_6^-}$[90]	Hg	Tl	Pb	Bi $\mathrm{KrF^+BiF_6^-}$[72]	Po	At	Rn

4. RADON CHEMISTRY

There are no stable isotopes of radon and the longest lived »natural« isotope, ^{222}Rn, has a half-life of only 3.83 days. Experimental difficulties arise not only from radiation hazard, but also from the radiation decomposition of the reagents. The most detailed review of radon chemistry, to early 1981, was made by L. Stein[155].

The low first ionization potencial of radon (10.7 eV) and its chemical similarity to xenon indicate that a number of other radon compounds apart from RnF_2 should exist, such as RnF_4, RnF_6, $RnCl_2$, $RnCl_4$, RnO, RnO_2, RnO_3 and $RnOF_4$. The existence of. RnF_4 or RnF_6 and RnO_3 has been claimed.[156] So far no complex compounds containing (RnF), $(Rn_2F_3)^+$ or $(Rn)^{2+}$ have been isolated and fully charazterized. Radon reacts spontaneously at room temperature with many solid compounds that contain oxidizing cations (e. g. XeF^+ and O_2^+ salts). By analogy with xenon, it is bellieved that radon also forms RnF^+ salts.

5. CHEMISTRY OF LIGHTER NOBLE GASES

The first ionization potentials of lighter noble gases Ar (15.76 eV), Ne (21.56 eV) and He (24.59 eV) show that these gases will remain truly inert gases. The only chance is probably for the formation of ArF^+ cation in connection with a high ionization potential anion, which is also a very poor fluoride ion donor. A possible candidate is the $Sb_2F_{11}^-$ ion but AuF_6^- could also serve the purpose. The 2+ oxidation state for krypton and xenon are more stabilized in the diatomic noble-gas fluoride cation $(G—F)^+$. The energy of the bond in KrF^+ is 1.63 eV[62] as compared to XeF^+ which is 2.03 eV[21] and ArF^+ which is 1.655 eV[157].

6. CHALLENGES OF THE NOBLE GAS CHEMISTRY IN THE FUTURE

An extension of noble gas chemistry to other elements than Kr, Xe and Rn is possible only with argon in ArF^+ salts. Further, new oxidation states and a greater range of ligands migth be used in radon chemistry. Otherwise, the extension of the chemical compounds of xenon and krypton in known oxidation states with other electronegative ligands might occur. The high proton affinities of the heavier noble gases[158] (Xe $\geq$ 6 eV; Kr $\geq$ 4 eV) also raise the possibility of $(XeH)^+$ and $(KrH)^+$ salts being preparable. These are of potential value as protonating agents. The greatest extension of noble gas chemistry is expected in the exploitation of noble gas compounds as fluorinating and oxidizing agents.

7. POSSIBLE USES OF THE NOBLE GAS COMPOUNDS

The greatest utility of the noble-gas compounds is derived from the weakness of their bonds and the relative inertness of the reduction product, the noble-gas atom. Their greatest potential value, therefore, lies in their employment as clean oxidizers. The lighter the noble-gas atom the greater is the oxidizing power of the compound. Because of the ready ionization of noble-gas fluorides to form cationc species (XeF^+, KrF^+ etc.), they are fast and efficient electrophilic oxidizers.

The use of XeF_2 as a fluorinating agent for the preparation of some ammonium fluorometalates with metals in higher oxidation state (e. g. $(NH_4)_4UF_{10}$)[98] suggests that it can have a valuable role as a potent electrophilic oxidizing agent in the generation of high oxidation state species. It has also been used as a source of F ligands in the substitution of F ligand into aromatic hydrocarbons[159] and as a route to oxidative reagents which do not contain a noble gas atom (e. g. source of SO_3 radicals)[160]. The interaction of XeF_2 with water as a component in the inetraction has also been an effective route to the synthesis of perbromate[169]. This could be further exploited as an effective [O] atom source: $XeF_2 + H_2O \rightarrow [XeO] + 2\,HF$.

The most spectacular reagents so far have proven to be the GF^+ salts (G = noble gas atom). They act as suppliers of F^+ (synthesis of BrF_6^+[161] etc.).

Reactions between radon and strong oxidizers, such as O_2^+ salts, can be used for scrubbing radon from air. This is of particular value in uranium mines.

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POVZETEK

Pregled dela na sintezi binarnih fluoridov žlahtnih plinov

B. Žemva

Podan je kritični pregled dela na sintezi binarnih fluoridov žlahtnih plinov (posebno ksenona in kriptona) in njunih spojin v obdobju zadnjih 25 let. Poleg tega je podan tudi zgodovinski uvod v kemijo žlahtnih plinov, izziv za bodočnost in možnosti uporabe spojin žlahtnih plinov.