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Fluorine-19 Nuclear Magnetic Resonance Study of the XeF_5^+ Cation and F_5XeSO_3F[1]

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Xenon hexafluoride ionizes to the XeF_5^+ cation in the presence of the Lewis acids SbF_5, AsF_5, and BF_3. The ^{19}F nmr spectrum of XeF_5^+ in solution in SbF_5, BrF_5, HF, and HSO_3F in each case consists of the AX_4 spectrum expected for a square-pyramidal molecule. The reaction between XeF_6 and HSO_3F gives HF and F_5XeSO_3F, which has been isolated as a volatile white solid. The ^{129}Xe–^{19}F coupling constants show a considerable solvent and temperature dependence. Variable-temperature ^{19}F nmr studies of solutions of F_5XeSO_3F in BrF_5 and XeF_6 in BrF_5 and ClF_5 solvents are also reported. A previously observed empirical correlation of the Xe–F coupling constant and the ^{19}F chemical shift is extended to XeF_3^+, XeF_5^+, $XeOF_3^+$, and XeO_2F^+. This correlation shows that the Xe–F couplings in XeF_5^+ and $XeOF_3^+$ are of opposite sign to all previously observed Xe–F coupling constants and are probably negative.

Introduction

Xenon hexafluoride is soluble in anhydrous hydrogen fluoride to give solutions which have an appreciable electrical conductivity. It was suggested that this conductivity is the result of ionization to give the XeF_5^+ ion[2]

$$XeF_6 + HF \rightleftarrows XeF_5^+ + HF_2^- \qquad (1)$$

Only a single ^{19}F nmr signal was, however, obtained from the solution presumably because of rapid fluoride exchange, and therefore no certain conclusions concerning the nature of the ionization could be reached by this method.[3] Subsequently, it was shown by X-ray crystallography that the adducts $XeF_6 \cdot PtF_5$,[4] $XeF_6 \cdot AsF_5$,[4] $2XeF_6 \cdot PdF_4$,[5] and $XeF_6 \cdot RuF_5$[6] can be formulated as $XeF_5^+MF_6^-$ and $(XeF_5^+)_2PdF_6^{2-}$. The XeF_5^+ ion in the crystal has a distorted square-pyramidal structure with C_{4v} symmetry, very similar to the structures of the isoelectronic species IF_5, TeF_5^-,[7,8] and SbF_5^{2-} [8,9] in which the angle between the axial and equatorial fluorines is slightly less than 90° as a consequence of lone pair-bonding pair repulsions.[10] It is reasonable to suppose that other similar complexes such as $XeF_6 \cdot BF_3$,[11] $2XeF_6 \cdot GeF_4$,[12] and $XeF_6 \cdot VF_5$[13] may also be formulated as salts of the XeF_5^+ cation.

The present work was undertaken to study the ionization of XeF_6 in HSO_3F, SbF_5, HF, BrF_5, and ClF_5 solvents and to obtain ^{19}F nmr data for the XeF_5^+ ion and the related fluorosulfate F_5XeSO_3F. We have published a preliminary report of the ^{19}F nmr parameters for XeF_5^+ [14] and have also reported our ^{19}F nmr solution study of the ionization of XeF_6 in HSO_3F to give the XeF_5^+ cation.[1] An earlier report by DesMarteau and Eisenberg[15] that XeF_6 reacts with HSO_3F to give $F_4Xe(SO_3F)_2$ is in error; this work had been carried out using XeF_6 contaminated with significant amounts of XeF_4.[16] The subsequent work of DesMarteau and Eisenberg[17] on the XeF_6-HSO_3F system is in agreement with our earlier results.[1,14]

Results and Discussion

Nmr Spectra of Solutions of XeF_6 and XeF_5^+ Salts in HF, HSO_3F, and BrF_5. We have investigated the systems XeF_6-SbF_5, XeF_6-HSO_3F, XeF_6-SbF_5-HF, XeF_6-SbF_5-HSO_3F, $XeF_5^+SbF_6^-$-HF, $XeF_5^+AsF_6^-$-HF, $XeF_5^+BF_4^-$-HF, and $XeF_5^+Sb_2F_{11}^-$-BrF_5 and found them all to be stable at room temperature over an extended period of time. The ^{19}F nmr spectrum of all these systems consisted of a low-field quintet and a doublet, each with accompanying ^{129}Xe satellites (Figure 1 and Table I). The multiplets comprise an AX_4 spectrum which can only be assigned to XeF_5^+. The relative chemical shifts of the A and X parts of the spectrum are consistent with the proposed geometry; *i.e.*, the A (axial) fluorine occurs at lower field than the X (equatorial) fluorines, as is the case for other C_{4v} molecules such as ClF_5, BrF_5, IF_5, and

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[1] Presented at the First Winter Fluorine Conference, St. Petersburg, Fla., Jan 24–28, 1972, and at the 55th Chemical Institute of Canada Meeting, Quebec City, Canada, June 5–7, 1972.

[2] H. H. Hyman and L. A. Quarterman, "Nobel-Gas Compounds," H. H. Hyman, Ed., University of Chicago Press, Chicago, Ill., 1963, p 275.

[3] (a) J. C. Hindman and A. Svirmickas, ref 2, p 251; (b) T. H. Brown, E. B. Whipple, and P. H. Verdier, ref 2, p 263.

[4] F. Sladky, *MTP (Med. Tech. Publ. Co.) Int. Rev. Sci.: Inorg. Chem., Ser. One,* 3, 1 (1972).

[5] K. Leary, D. H. Templeton, A. Zalkin, and N. Bartlett, *Inorg. Chem.,* 12, 1726 (1973).

[6] N. Bartlett, M. Gennis, D. D. Gibler, B. K. Morrell, and A. Zalkin, *Inorg. Chem.,* 12, 1717 (1973).

[7] A. J. Edwards and M. A. Mouty, *J. Chem. Soc. A,* 703 (1969).

[8] S. H. Martin, R. R. Ryan, and L. B. Asprey, *Inorg. Chem.,* 9, 2100 (1970).

[9] A. Bystrom and K. A. Wilhelm, *Ark. Kemi, Mineral. Geol.,* 3, 411 (1951).

[10] R. J. Gillespie, "Molecular Geometry," Van Nostrand-Reinhold, London, 1972, pp 157–158.

[11] H. Selig, *Science,* 144, 537 (1964).

[12] K. E. Pullen and G. H. Cady, *Inorg. Chem.,* 6, 1300 (1967).

[13] G. J. Moody and H. Selig, *J. Inorg. Nucl. Chem.,* 28, 2429 (1966).

[14] R. J. Gillespie, B. Landa, and G. J. Schrobilgen, *J. Chem. Soc., Chem. Commun.,* 607 (1972).

[15] M. Eisenberg and D. D. DesMarteau, *J. Amer. Chem. Soc.,* 92, 4759 (1970).

[16] D. D. DesMarteau, private communication.

[17] D. D. DesMarteau and M. Eisenberg, *Inorg. Chem.,* 11, 2641 (1972).

Table I. Nmr Parameters for the XeF_5^+ Cation in Various Solvents

Systems			XeF_5^+					Anion		Solvent
			δ, ppm		J, Hz					
						$^{129}Xe-^{19}F$				
Solutes (molal concn)	Solvent	Temp, °C	A	X_4	F–F	A	X_4	Assignments	δ, ppm	δ, ppm
XeF_6 (0.251)	SbF_5	35	−231.7	−108.8	175.7	1512	143.1			126.7
XeF_6 (0.823), SbF_5 (2.30)	HF	26	−226.2	−108.5	176.0	1381	158.8	SbF_6^-	124.1	193.0
		−40	−229.1	−108.1	180.4	1380	180.7		126.3	192.0
$XeF_5^+SbF_6^-$ (4.87)	HF	26	−233.2	−109.6	177.1	1409	156.1	SbF_6^-	123	193.0
$XeF_5^+AsF_6^-$ (5.85)	HF	−10	−231.5	−108.5	178.8	1409	176.0	AsF_6^-–HF	137.8	
$XeF_5^+BF_4^-$ (5.47)	HF	−80	−228.2	−106.2	182.0	1348	182.8	BF_4^-–HF	182.3	
$XeF_5^+Sb_2F_{11}^-$ (satd)	BrF_5	26	−231.7	−108.8	175.7	1512	143.1	F-on-Sb	111.9	−167.3
		26	−226.5	−110.5	179.0	1440	159.0	F-on-Sb	110.7	−40.1
XeF_6 (0.481), SbF_5 (1.40	HSO_3F	−80	−225.4	−108.2	183.0	1425	193.8	SbF_6^-	117.0	−40.8
								$Sb_2F_{11}^-$ [a] F_3	89.4	
								F_2	112.8	
								F_1	136.3	
								$SbF_5(SO_3F)^-$ A	137.5[b]	
								X_4	106.8[b]	
XeF_6 (1.12)	HSO_3F	−90	−226.2	−108.2	178.5	1357	175.0	SO_3F^-–HSO_3F	−40.4	
F_5XeSO_3F (~1.0)	HSO_3F	−81	−228.3	−108.9	178.5	1389	179.6	SO_3F^-–HSO_3F	−40.3	

[a] Numbered according to the uniform numbering system given by P. A. W. Dean and R. J. Gillespie, *J. Amer. Chem. Soc.*, 91, 7260 (1969).
[b] Peaks assigned to fluorine-on-antimony; the fluorine-on-sulfur peak was obscured by the solvent peak.

IOF_5. Table I summarizes the ^{19}F nmr parameters for all the solutions studied.

The spectrum of a solution of XeF_6 in SbF_5 at 35° consists of the AX_4 spectrum of XeF_5^+ together with a single F-on-Sb line arising from fluorine exchange between the anion and the solvent. The ionization of XeF_6 in this system may be represented by the equation

$$XeF_6 + nSbF_5 \rightarrow XeF_5^+ + Sb_nF_{5n+1}^- \qquad (2)$$

A 1:3 mixture of XeF_6 and SbF_5 in HF as solvent gave the same XeF_5^+ spectrum together with a broad line due to SbF_6^- plus the solvent HF line. The ionization of XeF_6 may be represented by the equation

$$XeF_6 + SbF_5 \rightarrow XeF_5^+ + SbF_6^- \qquad (3)$$

Solutions of the compounds $XeF_5^+SbF_6^-$, $XeF_5^+AsF_6^-$, and $XeF_5^+BF_4^-$ in HF all gave the XeF_5^+ spectrum together with the single line due to the solvent and very broad lines due to SbF_6^- and AsF_6^-. No separate line was observed for BF_4^- which undergoes rapid fluorine exchange with the solvent even at −80°.

A saturated solution of $XeF_5^+Sb_2F_{11}^-$ in BrF_5 at room temperature (26°) gave the XeF_5^+ spectrum. Fluorine exchange occurs among the different fluorine environments in BrF_5 and in $Sb_2F_{11}^-$, giving two broad lines due to F-on-Br and F-on-Sb. The $Sb_2F_{11}^-$ ion appears to be at least partly dissociated in BrF_5 so that the mechanism of fluorine exchange can be represented by the equations

$$Sb_2F_{11}^- \rightleftarrows SbF_5 + SbF_6^- \qquad (4)$$

$$BrF_5 + SbF_5 \rightleftarrows BrF_4^+ + SbF_6^- \qquad (5)$$

The room-temperature spectrum of a 1:3 mixture of XeF_6 and SbF_5 in the solvent HSO_3F gave the XeF_5^+ spectrum together with a broad line due to F-on-Sb in addition to the solvent peak. At −80°, the broad F-on-Sb line was resolved into a more complicated spectrum that may be assigned to the anions SbF_6^-, $SbF_5(SO_3F)^-$, and $Sb_2F_{11}^-$.[18,19] The ionization of XeF_6 in this system may be approximately represented by the equations

$$XeF_6 + 3SbF_5 \rightarrow XeF_5^+ + Sb_3F_{16} \qquad (6)$$

$$Sb_3F_{16}^- + 2HSO_3F \rightleftarrows Sb_2F_{11}^- + SbF_5(SO_3F)^- + H_2SO_3F^+ \qquad (7)$$

$$Sb_2F_{11}^- + 2HSO_3F \rightleftarrows SbF_6^- + SbF_5(SO_3F)^- + H_2SO_3F^+ \qquad (8)$$

A solution of XeF_6 in HSO_3F at −90° gave the XeF_5^+ spectrum and a line due to HF, as well as a line due to the solvent undergoing rapid exchange with SO_3F^-. The ionization may be represented by the equation

$$HSO_3F + XeF_6 \rightarrow XeF_5^+ + SO_3F^- + HF \qquad (9)$$

The integrated relative intensities of the equatorial XeF_5^+ fluorines and the HF signal were 4:1 in accord with the above equation. At room temperature the spectrum consisted of only two lines, one arising from the exchanging fluorines of XeF_5^+ and HF and the other from the exchange between SO_3F^- and the solvent. There were no peaks in the spectrum at any temperature that might be assigned to a covalent F_5XeSO_3F molecule, and we conclude that F_5XeSO_3F is completely ionized in solution in HSO_3F.

Preparation of F_5XeSO_3F and the Solution Nmr Spectra of F_5XeSO_3F and XeF_6. The preparation of F_5XeSO_3F has been reported recently.[17] We, too, had independently prepared the compound by the reaction of excess HSO_3F with XeF_6.[1] Removal of excess HSO_3F under vacuum gave a white crystalline solid which sublimes under vacuum and whose elemental analyses were in agreement with the proposed formulation, F_5XeSO_3F. A solution of the compound F_5XeSO_3F in HSO_3F gave a low-temperature spectrum identical with that obtained for XeF_6 in HSO_3F except that no HF peak was observed (Table I).

In BrF_5 solvent at −2° a single broad exchange-averaged peak for F-on-Xe and a sharp line for F-on-S of relative intensities 5:1, respectively, were observed in addition to the solvent peaks (Table II). Exchange averaging of F-on-Xe and F-on-Br environments was fast enough to collapse partially the fluorine-fluorine coupling on the solvent lines. Fluorine exchange among F-on-Xe and F-on-Br environments in F_5XeSO_3F could occur *via* the possible mechanisms

$$F_5XeSO_3F + BrF_5 \rightleftarrows F_4XeSO_3F^+ + BrF_6^- \qquad (10)$$

and/or

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(18) R. C. Thompson, J. Barr, R. J. Gillespie, J. B. Milne, and R. A. Rothenbury, *Inorg. Chem.*, 4, 1641 (1965).

(19) P. A. W. Dean and R. J. Gillespie, *J. Amer. Chem. Soc.*, 91, 7260 (1969).

$$\begin{aligned} &F_5XeSO_3F \rightleftarrows XeF_5^+ + SO_3F^- \\ &XeF_5^+ + BrF_5 \rightleftarrows XeF_6 + BrF_4^+ \end{aligned} \qquad (11)$$

At lower temperatures exchange among F-on-Xe and F-on-Br environments was sufficiently slow to give a well-resolved AX_4 spectrum for the solvent. Further broadening of the F-on-Xe peak occurred, however, even though exchange with the solvent was slow on the nmr time scale. The additional line broadening is attributed to the slowing down of a second exchange process which may be either intramolecular and involve pseudorotation of the presumably distorted octahedral structure of the XeF_5SO_3F molecule as has been proposed for XeF_6[20] or intermolecular and involve the prior dissociation of XeF_5SO_3F to XeF_5^+ and SO_3F^- followed by fluorine exchange according to

$$F_5XeSO_3F + XeF_5^+ \rightleftarrows [F_5Xe\text{- - -}F\text{- - -}XeF_4SO_3F]^+ \rightleftarrows XeF_6 + F_4XeSO_3F^+ \qquad (12)$$

The bridged intermediate is possible in view of the existence of related bridged species such as the fluorine-bridged cations $Xe_2F_3^+$,[21] $Xe_2F_{11}^+$,[22] and $Kr_2F_3^+$.[23]

Similar trends in exchange behavior were also observed for XeF_6 in ClF_5 and BrF_5 solvents and are listed in Table II for comparison. The spectrum of a solution of XeF_6 in ClF_5, a poorer fluoride acceptor than BrF_5, shows that fluorine exchange with the solvent is slow over the entire range of temperatures investigated.

Failure to observe ^{129}Xe-^{19}F coupling in the absence of fluorine exchange with the solvent does not necessarily favor the dissociative type mechanism (12). As, on the basis of an empirical relationship discussed below, the coupling constants are estimated to be relatively small (±500 Hz), the great breadth of the lines at low temperatures would preclude observation of such a coupling.

Solvent Effects. The considerable variations in the ^{129}Xe-^{19}F axial and equatorial coupling constants in going from HSO_3F to less solvating media such as SbF_5 and BrF_5 indicate considerable cation-solvent interactions. Presumably the XeF_5^+ cation is solvated by forming additional bonds with the most basic molecule, *i.e.*, the strongest donor available. As the XeF_5^+ cation becomes more strongly bonded to solvent molecules or accompanying anions, the ^{129}Xe-^{19}F coupling constants decrease. In solutions of $XeF_5^+SbF_6^-$ in HSO_3F and HF, the strongest donor available is presumably the solvent itself. On addition of SbF_5 to HSO_3F or HF, the concentration of the acidium ion $H_2SO_3F^+$ or H_2F^+ is increased, the basicity of the medium decreases correspondingly, and there is a corresponding increase in the coupling constants. In BrF_5 both the solvent and the anions SbF_6^- and $Sb_2F_{11}^-$ are extremely weak bases and the coupling constants increase and are, in fact, equal to those observed in the very weakly basic medium SbF_5. These arguments only apply in the case of the ^{129}Xe-^{19}F equatorial coupling if values obtained at the same temperature are compared since, as will be discussed below, this coupling exhibits a significant temperature dependence.

The lowest values of the axial ^{129}Xe-^{19}F coupling constant were observed for the F_5XeSO_3F-HSO_3F and $XeF_5^+BF_4^-$-HF systems. This is consistent with the fact that SO_3F^- is a very strong base in the HSO_3F solvent system and that BF_4^- is a rather strong base in the HF system, much stronger than either AsF_6^- or SbF_6^- for example.

Table II. Variation of the Fluorine-on-Xenon Line Width with Temperature

Solute (molal concn)	Solvent[a]	Temp, °C	Chem shift, ppm F-on-S	Chem shift, ppm F-on-Xe	Line width of F-on-Xe peak, Hz
F_5XeSO_3F (0.76)	BrF_5	−2[b]	−40.7	−130.0	~120
		−34[c]	−40.7	−129.0	60
		−62[c]	−40.7	−129.2	250
XeF_6 (0.31)	BrF_5	26[d]			
		−40[b]		−110.8	180
		−50[c]		−90	750
XeF_6 (~1.0)	ClF_5	−15[c]		−104.3	35
		−95[c]		−103	500
		−103[c]		−106	1080

[a] F_5XeSO_3F reacts with ClF_5; the spectrum is complex and therefore is not considered here. [b] Fine structure of the solvent lines collapsed due to exchange. [c] Fine structure clearly resolved on the solvent lines. [d] Fluorine-on-bromine and fluorine-on-xenon environments collapsed to a single exchange-averaged peak at −139 ppm (half-width 1210 Hz).

Temperature Dependence of the Equatorial ^{129}Xe-^{19}F Coupling Constant. Whereas both the ^{129}Xe-^{19}F axial and equatorial coupling constants in XeF_5^+ are solvent dependent, it is of interest that only the ^{129}Xe-^{19}F equatorial coupling constant shows a significant temperature dependence. This temperature dependence was studied in some detail for XeF_5^+ in HSO_3F-SbF_5, and the results are given in Figure 2.

A similar temperature dependence has been observed for the boron-fluorine coupling constant of BF_3 in which the coupling constant increases in magnitude with decreasing temperature.[24] A temperature dependence might result, as has been suggested in the case of BF_3, if the coupling constant varies with the vibrational state as a consequence of changes in population of the different vibrational energy states with temperature.

Empirical Correlation of the ^{129}Xe-^{19}F coupling Constant and the ^{19}F Chemical Shift. A number of empirical correlations between ^{19}F chemical shifts and ^{13}C-^{19}F and ^{11}B-^{19}F coupling constants exist in the literature.[25-27] These correlations show an essentially linear relationship between the coupling constant and chemical shift and have been interpreted in terms of p_π-p_π bonding. Frame[28] has shown that a plot of the ^{129}Xe-^{19}F coupling constant *vs.* the ^{19}F chemical shift for xenon fluorides and oxyfluorides yields a similar relationship in which the absolute value of the coupling constant increases monotonically with increasing chemical shift. More recently, Gillespie, *et al.*,[29] have shown that a similar correlation exists for the divalent xenon species XeF^+, $Xe_2F_3^+$, $(FXe)_2SO_3F^+$, $FXeSO_3F$, $FXeOSeF_5$, and XeF_2. Figure 3 shows that this correlation can now be extended to include XeF_3^+, XeF_5^+, $XeOF_3^+$, and XeO_2F^+ [14,30] and thus appears to be generally applicable.

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(20) H. H. Hyman, "Physical Chemistry," Vol. 5, H. Eyring, D. Henderson, and W. Jost, Ed., Academic Press, New York, N. Y., 1970, pp 627-633; see ref 4, pp 20-24.

(21) F. O. Sladky, P. A. Bulliner, and N. Bartlett, *Chem. Commun.*, 1048 (1968).

(22) K. Leary and N. Bartlett, *J. Chem. Soc., Chem. Commun.*, 903 (1972).

(23) R. J. Gillespie and G. J. Schrobilgen, *J. Chem. Soc., Chem. Commun.*, in press.

(24) J. Bacon, R. J. Gillespie, J. S. Hartman, and U. R. K. Rao, *Mol. Phys.*, 18, 561 (1970).

(25) S. A. Fieldhouse and I. A. Peat, *J. Phys. Chem.*, 73, 275 (1969).

(26) J. S. Hartman and G. J. Schrobilgen, *Inorg. Chem.*, **11**, 940 (1972).

(27) N. Muller and D. T. Carr, *J. Phys. Chem.*, 67, 112 (1963).

(28) H. D. Frame, *Chem. Phys. Lett.*, 3, 182 (1969).

(29) R. J. Gillespie, A. Netzer, and G. J. Schrobilgen, *Inorg. Chem.*, in press.

(30) R. J. Gillespie, B. Landa, and G. J. Schrobilgen, *Chem. Commun.*, 1543 (1971).

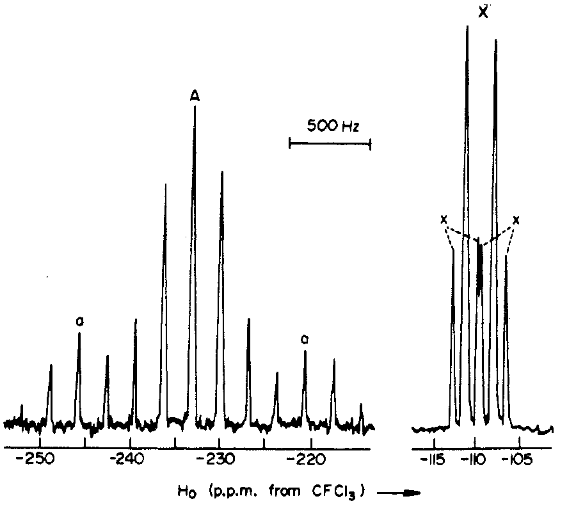

Figure 1. ^{19}F nmr spectrum of the XeF_5^+ cation (4.87 *m* $XeF_5^+SbF_6^-$ in HF solution at 26°): (A) axial fluorine and (a) ^{129}Xe satellites; (X) equatorial fluorines and (x) ^{129}Xe satellites.

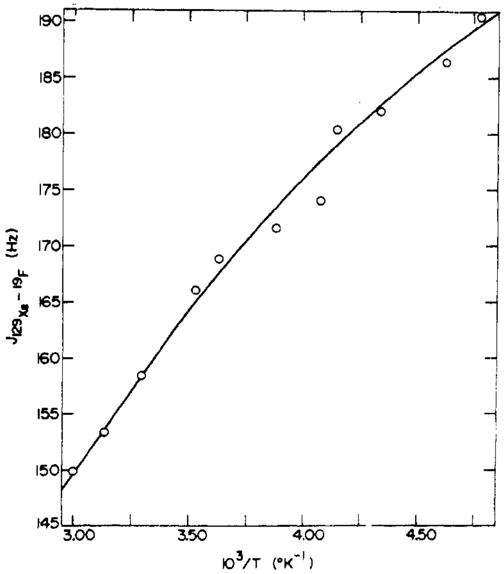

Figure 2. Variation of the equatorial fluorine-xenon-129 coupling constant of the XeF_5^+ cation with $1/T$ (0.481 *m* XeF_6 and 1.40 *m* SbF_5 in HSO_3F solution).

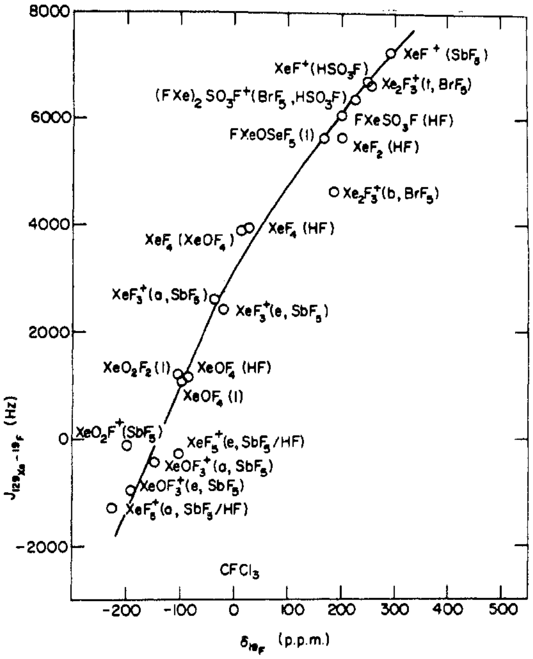

Figure 3. Correlation of the ^{19}F chemical shift ($\delta_{^{19}F}$) and the ^{129}Xe-^{19}F coupling constant ($J_{^{129}Xe-^{19}F}$) for some xenon compounds.

The correlation provides a rationale for the small ^{129}Xe-^{19}F couplings observed for the equatorial fluorines of XeF_5^+ and for XeO_2F^+ if a change in the relative sign of the coupling constant occurs over the series in the vicinity of the equatorial fluorines of XeF_5^+ and XeO_2F^+ (due to the amount of point scatter, the coupling constant could be assigned either sign in these two cases). Accordingly, it is assumed that the signs of the axial ^{129}Xe-^{19}F coupling of $XeOF_3^+$ and the axial ^{129}Xe-^{19}F coupling of XeF_5^+ are negative with respect to those of the remaining species.

The absolute signs of the various Xe-F reduced coupling constants can be arrived at indirectly by considering the series of Sn(IV)-I(VII) hexafluorides which are isoelectronic with the hypothetical Xe(VIII) cation XeF_6^{2+}. A nearly linear relationship is obtained when the square root of the reduced coupling constant j_{X-F}[31] is plotted *vs.* the nuclear charge and the same sign is assumed throughout the series.[32] The absolute value of the reduced coupling constant increases along the series SnF_6^{2-} [33] < SbF_6^- [34,35] < TeF_6[35] < IF_6^+,[36] and since the signs of both Sn(IV)-F[37] and Te(VI)-F[38] couplings have been shown to be negative, negative signs can also be assigned to the reduced coupling constants of the remaining members of the series including XeF_6^{2+}. We, therefore, assign the signs of j_{Xe-F} of Xe(VIII) and Xe(VI), with the exception of $XeOF_4$, XeO_2F_2, and possibly XeF_6 and XeO_2F^+, as negative and j_{Xe-F} of Xe(IV) and Xe(II) as positive.

Correlation of the Nmr Parameters with the Oxidation State of Xenon. Figure 3 also shows that there is a relationship between the formal oxidation state of xenon and the nmr parameters. The species with the xenon atom carrying the higher positive charge have their resonances to lower field and have more negative coupling constants. Since species with a greater partial positive charge on the central xenon are expected to have less polar Xe-F bonds, the overall observed order of ^{19}F chemical shift is the anticipated one, and F-on-Xe(VIII) would be expected to occur to still lower field than F-on-Xe(VI).

In the case of XeF^+, the change in chemical shift between the parent XeF_2 molecule and the fluoro cation is in the same direction as the recently observed positive shifts occurring on formation of the chlorine fluoro and oxyfluoro cations[39] and IF_6^+.[36] In contrast, Xe(IV) and Xe(VI) cations all occur to low field of the parent molecule. A parallel trend is also observed for the ^{129}Xe-^{19}F coupling constant. Clearly, our present understanding of the nature of ^{19}F chemi-

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[31] The reduced coupling constant is taken as $j_{X-F} = J_{X-F}/\gamma_X\gamma_F$ where j_{X-F} is in hertz and γ_X and γ_F are nuclear moments in nuclear magneton units divided by the spin I in units of $\hbar$. In the case where j_{X-F} is negative, $i(j_{X-F})^{1/2}$ instead of $(j_{X-F})^{1/2}$ is taken as the dependent variable.

(32) J. Feeney, R. Haque, L. W. Reeves, and C. P. Yue, *Can. J. Chem.*, 46, 1389 (1968).

(33) P. A. W. Dean and D. F. Evans, *Proc. Chem. Soc., London*, 407 (1964).

(34) R. G. Kidd and R. W. Matthews, *Inorg. Chem.*, 11, 1156 (1972).

(35) E. L. Muetterties and W. D. Phillips, *J. Amer. Chem. Soc.*, 81, 1084 (1959).

(36) M. Brownstein and H. Selig, *Inorg. Chem.*, 11, 656 (1972).

(37) W. McFarlane and R. J. Wood, *Chem. Commun.*, 262 (1969).

(38) G. W. Fraser and R. D. Peacock, *Mol. Phys.*, 17, 291 (1969).

(39) K. O. Christe, J. F. Hon, and D. Pilipovich, *Inorg. Chem.*, 12, 84 (1973).

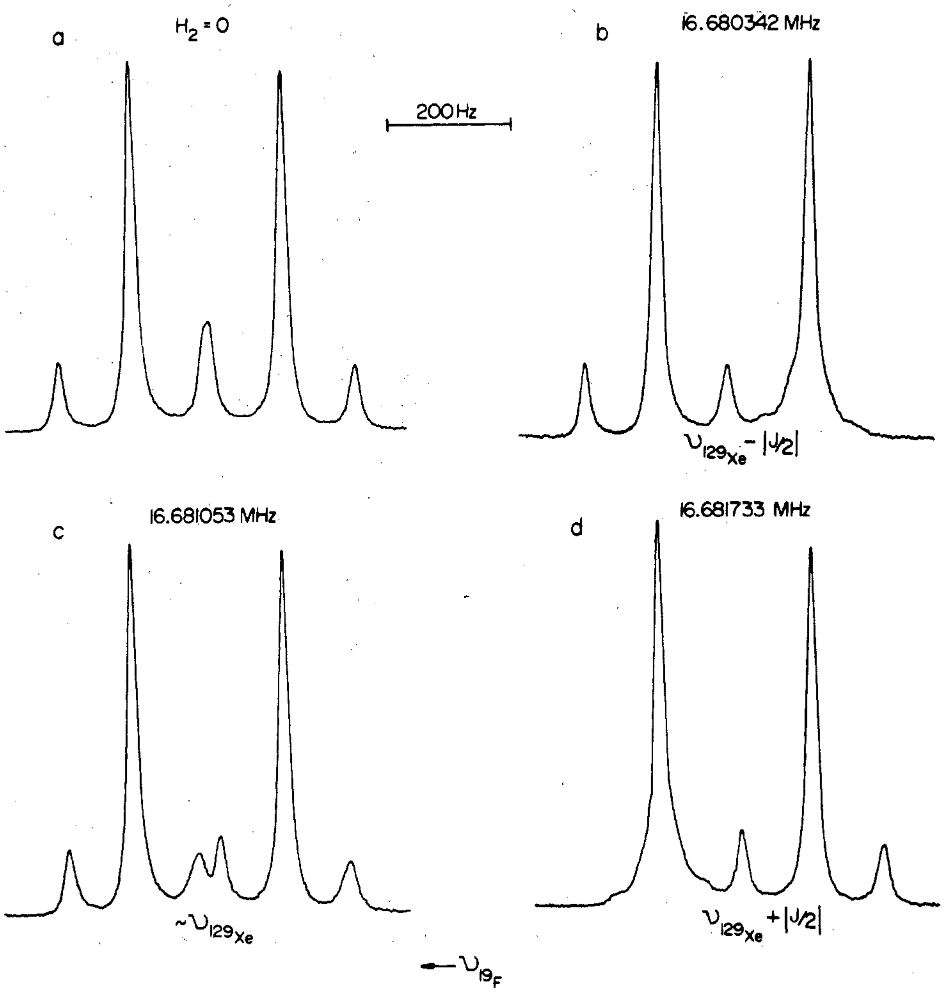

Figure 4. ^{19}F nmr spectra of the equatorial fluorines of the XeF_5^+ cation (~1 *m* F_5XeSO_3F in HSO_3F solution at −81°): a, unperturbed; b–d, with simultaneous irradiation of the ^{129}Xe transitions.

cal shifts and spin–spin coupling constants involving heavy atoms is insufficient to rationalize the latter observation.

Double-Resonance Experiments. A heteronuclear double-resonance experiment is capable of yielding the relative signs of the spin–spin couplings in an AM_4X spin system, such as $^{129}Xe^{19}F_5^+$, as well as the ^{129}Xe shielding constant. Irradiating either of the quintets in the doublet of quintets in the ^{129}Xe spectrum with a small radiofrequency field

$$J_{^{129}Xe-^{19}F_e} < \frac{\gamma H_2}{2\pi} < J_{^{129}Xe-^{19}F_a}$$

leads to selective decoupling of one of the satellite doublets in the ^{19}F spectrum of the equatorial fluorines. By observing the collapse of either the high-frequency or low-frequency pair of ^{129}Xe satellites in the ^{19}F spectrum while irradiating one of the quintets in the ^{129}Xe spectrum, one can infer whether $J_{^{129}Xe-^{19}F_a}$ and J_{FF} have the same or opposite signs.

The results obtained from these double-irradiation experiments are summarized in Figure 4. The separation between successive irradiation frequencies which lead to complete collapse of either pair of ^{129}Xe satellites corresponds to $J_{^{129}Xe-^{19}F_a}$ and it may be concluded that $J_{^{129}Xe-^{19}F_a}$ and J_{FF} are of the same sign and are therefore both negative.

Experimental Section

Nmr Measurements. Fluorine nmr spectra were measured with a Varian DA-60IL spectrometer operating at 56.4 MHz and modified as described previously[19] to record spectra from the first upper side band in the field sweep unlock mode. The spectra were calibrated by the usual audio-side-band method, using a Muirhead-Wigan D-890-A decade oscillator. Side-band frequencies were checked with a General Radio Type 1191 frequency counter. Low-temperature spectra were obtained using a Varian V4540 temperature controller with a low-temperature probe.

Double-resonance experiments were carried out by observing the fluorine resonances at 56.442809 MHz while injecting a variable decoupling frequency in the vicinity of 16.7 MHz across the transmitter coil of the spectrometer probe. Spectra were recorded from the first lower side band in the frequency sweep mode by locking onto the lower side band of the HSO_3F solvent peak. The decoupling field was obtained from a General Radio Co. 1164-A coherent decade frequency synthesizer and an RF Communications Inc. 805 amplifier with an output of 7.4 W. Both the transmitter frequency and the decoupling frequency were accurately determined using a Hewlett-Packard 5246L frequency counter.

Materials. Xenon hexafluoride was prepared by the high-pressure, high-temperature reaction of xenon (Matheson) and fluorine (Matheson) described by Chernick and Malm[40] and further purified by adsorption on dry sodium fluoride.[41] The purity was checked by observing the Raman spectrum and noting the absence of the 543- and 502-cm^{-1} bands of XeF_4 and the 566- and 530-cm^{-1} bands of $XeOF_4$.[42]

Fluorosulfuric acid (Baker and Adamson) and antimony pentafluoride (Ozark-Mahoning) were purified by the standard literature methods. Anhydrous hydrogen fluoride (Harshaw) was used directly from the cylinder.

Arsenic pentafluoride (Ozark-Mahoning) and boron trifluoride (Matheson) were used without further purification.

Bromine pentafluoride (Matheson) was distilled into a Kel-F trap

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[40] J. C. Malm and C. L. Chernick, *Inorg. Syn.*, 8, 258 (1966).

[41] I. Sheft, T. M. Spittler, and F. H. Martin, *Science*, 145, 701 (1964).

[42] Reference 20, p 611.

fitted with Teflon valves and purified by passing fluorine at atmospheric pressure through the liquid until all the Br_2 and BrF_3 had reacted. After degassing several times, the BrF_5 was vacuum distilled and stored over dry sodium fluoride in a Kel-F storage trap.

Chlorine pentafluoride was prepared according to the method of Pilipovich, *et al.*,[43] by reaction of excess fluorine with cesium chlorotetrafluoride and stored in a previously passivated stainless steel container. The purity of both ClF_5 and BrF_5 was checked by recording their ^{19}F nmr spectra at 26°.

Preparation of $XeF_5^+SbF_6^-$, $XeF_5^+Sb_2F_{11}^-$, $XeF_5^+AsF_6^-$, and $XeF_5^+BF_4^-$. The adduct $XeF_5^+SbF_6^-$ was prepared by addition of an excess of XeF_6 to SbF_5 in HF solution. *Anal.* Calcd: F, 45.23; Sb, 26.35; Xe, 28.42. Found: F, 45.34; Sb, 26.13; Xe, 28.26. The $XeF_5^+Sb_2F_{11}^-$ and $XeF_5^+AsF_6^-$ adducts were prepared by addition of an excess of SbF_5 or AsF_5 to an HF solution of XeF_6. *Anal.* Calcd: F, 50.33; As, 18.04; Xe, 31.64. Found: F, 50.48; As, 18.20; Xe, 31.36. The solutions were pumped on, first at −60° and then at room temperature, until constant weight was achieved. The $XeF_5^+BF_4^-$ adduct was prepared by direct combination of XeF_6 with excess BF_3 in a Kel-F trap at room temperature and pumped to constant weight at −78°.

Preparation and Analysis of F_5XeSO_3F. In a typical preparation 1.293 g (5.27 mmol) of XeF_6 was transferred to a Kel-F reaction vessel and dissolved in 3.642 g (36.39 mmol) of HSO_3F, and excess HSO_3F was removed under vacuum at 40°. The resulting white crystalline solid was volatile and slowly pumped off at room temperature. Analytical results are consistent with the formulation F_5XeSO_3F. *Anal.* Calcd: F, 35.04; S, 9.85; Xe, 40.35. Found: F, 34.23; S, 9.56; Xe, 39.92.

Sample Preparation. Stoichiometric samples were prepared by transferring some of the solid adduct from a Kel-F storage trap to a preweighed Kel-F or glass sample tube in a drybox. Fluorosulfuric acid and antimony pentafluoride were syringed into preweighed Kel-F or glass nmr tubes in a drybox. Sample tubes were attached *via* a Kel-F adapter and Teflon valve to a vacuum line with standard 0.25-in. Teflon Swagelok fittings, frozen at liquid nitrogen temperature and evacuated. Xenon hexafluoride, HF, BrF_5, and ClF_5 were distilled directly from their storage vessels into preweighed Kel-F sample tubes through an all Kel-F and Teflon system. Kel-F sample tubes were sealed by immersing in liquid nitrogen, evacuating, and allowing the tube to collapse by heating with a small electrical heating coil.

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Registry No. XeF_6, 13693-09-9; $XeF_5^+SbF_6^-$, 49756-75-4; $XeF_5^+AsF_6^-$, 49756-76-5; $XeF_5^+BF_4^-$, 49756-77-6; $XeF_5^+Sb_2F_{11}^-$, 50432-33-2; F_5XeSO_3F, 38962-10-6; XeF_5^+, 49756-78-7; ^{129}Xe, 13965-99-6.

[43] D. Pilipovich, W. Maya, E. A. Lawton, H. F. Bauer, D. F. Sheehan, N. N. Ogimachi, R. D. Wilson, F. C. Gunderloy, and V. E. Bedwell, *Inorg. Chem.*, 6, 1918 (1967).

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Axial *vs.* Equatorial Bonding in Trigonal-Bipyramidal Complexes. Crystal and Molecular Structure of [Bis(triphenylphosphine)imminium]tetracarbonylcyanoiron(0), $[((C_6H_5)_3P)_2N][Fe(CO)_4CN]$

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The crystal and molecular structure of [bis(triphenylphosphine)imminium]tetracarbonylcyanoiron(0), [PPN][$Fe(CO)_4CN$], has been determined from three-dimensional X-ray data collected by counter methods. The gold-colored salt crystallizes in space group $P2_1/c$ of the monoclinic system with 4 formula units per unit cell of dimensions $a = 10.749$ (4), $b = 12.909$ (6), $c = 26.801$ (9) Å, and $\beta = 97.98$ (5)°; $\rho_{\text{obsd}} = 1.31$ (1), $\rho_{\text{calcd}} = 1.32$ g/cm³. The structure has been refined by full-matrix least-squares methods to a weighted R factor on F of 4.55% for the 2314 independent reflections with $F^2 > 3\sigma(F^2)$. The thermal motion of all nonhydrogen atoms has been treated as anisotropic. The phenyl carbon atoms have been treated as rigid groups with a benzene ring geometry. The $[Fe(CO)_4CN]^-$ ion is a distorted trigonal bipyramid (C_{3v} molecular symmetry), isoelectronic with $Fe(CO)_5$, with the cyanide in an axial position as predicted from a simple π-bonding model which is proposed. The three equatorial iron–carbon bond lengths are 1.769 (8), 1.754 (8), and 1.781 (8) Å. The bond length from the iron to the carbon of the axial carbonyl is 1.723 (8) Å and to the cyanide carbon is 1.928 (8) Å. The axial-equatorial difference in the Fe–C carbonyl bond lengths is 0.045 (12) Å, which agrees well with the latest $Fe(CO)_5$ structural data. The difference between axial cyanide and carbonyl Fe–C bond lengths, 0.205 (12) Å, is largely due to the difference in covalent radii of CN^- and CO. The ions pack in layers with parallel close approach (3.50 Å) of one equatorial carbonyl oxygen and the inversion-related oxygen. The PPN cation has a cisoid conformation with a PNP bond angle of 134.6 (3)°.

Introduction

Although the stereochemical lability of five-coordinate complexes is of interest for several reasons, our interest has remained focused on the use of the high sensitivity of the geometry of these complexes to changes in the bonding. The change in structure of a series of complexes as individual ligands are changed allows a systematic investigation of the various components of the bonding. We have used this technique previously in studying the relative importance of the metal d-electron configuration in determining the geometry of a complex.[2,3] Often the difference in energy between two geometries for a five-coordinate complex is very small and in some cases can be determined by changes as small as crystal or solution environments.[4-7]

The observation of a C_{2v} geometry in $Mn(NO)(CO)_4$, in which the nitrosyl occupies an equatorial coordination site

[1] Alfred P. Sloan Fellow, 1971-1973.

[2] S. A. Goldfield and K. N. Raymond, *Inorg. Chem.*, 10, 2604 (1971).

[3] K. N. Raymond, D. W. Meek, and J. A. Ibers, *Inorg. Chem.*, 7, 1111 (1968).

[4] F. A. Jurnak and K. N. Raymond, to be submitted for publication.

[5] A. Terzis, K. N. Raymond, and T. G. Spiro, *Inorg. Chem.*, 9, 2415 (1970).

[6] K. N. Raymond, P. W. R. Corfield, and J. A. Ibers, *Inorg. Chem.*, 7, 1362 (1968).

[7] J. K. Stalick, P. W. R. Corfield, and D. W. Meek, *J. Amer. Chem. Soc.*, 94, 6194 (1972).