A Raman Spectroscopic Study of Noble-gas Fluoride Adduct Formation with Bismuth Pentafluoride

By **Ronald J. Gillespie, Dominique Martin, and Gary J. Schrobilgen,*** Department of Chemistry, McMaster University, Hamilton, Ontario, Canada L8S 4M1

The fluoride-ion acceptor properties of BiF_5 have been assessed by the preparation of several new adducts of the binary noble-gas fluorides with BiF_5. The adducts $XeF_4{\cdot}BiF_5$, $XeF_4{\cdot}2BiF_5$, $XeF_2{\cdot}BiF_5$, $XeF_2{\cdot}2BiF_5$, $2XeF_2{\cdot}BiF_5$, $KrF_2{\cdot}BiF_5$, and $Cs[Bi_2F_{11}]$ have been prepared and characterized by low-temperature Raman spectroscopy. Although the compounds may be described as ionic to a first approximation, there are rather strong fluoride-bridge interactions between the respective cation and the anion which suggest substantial covalent contributions to the bonding. The present study complements previous studies of adducts between the noble-gas fluorides and AsF_5 and SbF_5. The strength of the cation–anion interactions can be taken as a measure of the acidity of the pentafluoride. It is shown that BiF_5 is a much weaker Lewis acid than SbF_5.

THE relative ordering of Lewis acidities among the Group 5B pentafluorides has been the subject of recent discussions. Although periodic trends alone would predict BiF_5 to be the strongest fluoride-ion acceptor among the Group 5B pentafluorides, Gillespie *et al.*[1] have shown, by means of a conductometric study in $HSFO_3$ solvent, that BiF_5 has an acidity similar to that of AsF_5 and much weaker than that of SbF_5. Surles *et al.*[2] were unable to observe the BiF_6^- ion in anhydrous HF solutions of BiF_5, but only the neutral BiF_5 molecule. That BiF_5 has an appreciable Lewis acidity is, however, indicated by the recent work of Christe *et al.*[3] who have described the purification of HF using reaction (1).

$$H_2O + HF + BiF_5 \rightleftharpoons [H_3O][BiF_6] \qquad (1)$$

Force-constant calculations by Bougon *et al.*[4] for the series of Group 5B MF_6^- anions imply that the fluoride-acceptor strengths increase in the order $BiF_5 < AsF_5 < SbF_5$. The adducts of BiF_5 with the noble-gas fluorides have proved particularly useful in assessing the fluoride-ion acceptor strength of BiF_5. In a recent *X*-ray crystallographic study,[5] we have shown that BiF_5 is a considerably weaker fluoride-ion acceptor towards XeF_4 than SbF_5.

Many of the previous studies of noble-gas fluoride adduct formation have been directed toward the formation of new and interesting noble-gas fluoro- and oxyfluoro-cations with the strongest available acceptors. With the recognition that weak covalent interactions exist between the anions and cations in these compounds (fluorine-bridge interaction), interest has developed in studying the nature of the interaction in these species. As a result, systematic studies of these interactions have been made in both the solid state and in solution for the weak fluoride acceptors, *i.e.* $MoOF_4$ and WOF_4.[6]

In the present study, we report our findings for the intermediate strength fluoride acceptor, BiF_5.

RESULTS AND DISCUSSION

$Cs[BiF_6]$ *and* $[Xe_2F_3][BiF_6]$.—A vibrational force-constant analysis has been performed by Bougon *et al.*[4] for BiF_6^-. The Raman spectrum of $[Xe_2F_3][BiF_6]$ is readily assigned since, unlike compounds of the XeF^+ and XeF_3^+ cations discussed below, no fluorine bridging is expected between the $Xe_2F_3^+$ and BiF_6^- ions. The crystal structure of the analogous $[Xe_2F_3][AsF_6]$ [7] compound has shown that the cation is V-shaped, possessing C_{2v} symmetry, and that the contact distances between the fluorine of the undistorted AsF_6^- ion and the xenon atom are substantially greater than the van der Waals contact distance. Thus, the compound may be regarded as wholly ionic. Assignments analogous to those for $[Xe_2F_3][AsF_6]$ have been made for $[Xe_2F_3][BiF_6]$. The previous vibrational assignments for $[Xe_2F_3][AsF_6]$ and $[Xe_2F_3][SbF_6]$ [8] which were made on the basis of room-temperature data, however, did not fully account for all nine Raman-active vibrational modes which are expected for an $Xe_2F_3^+$ cation having C_{2v} symmetry [see equation (2)]. We have therefore

$$\Gamma = 4A_1 + 3B_1 + A_2 + B_2 \qquad (2)$$

undertaken a more rigorous assignment of $Xe_2F_3^+$. New low-temperature data have also been included for $[Xe_2F_3][SbF_6]$ and $[Xe_2F_3][AsF_6]$ which are of considerably better quality than the previous room-temperature spectra. The assignments and their approximate descriptions are given in Table 1.

$[XeF][BiF_6]$ *and* $[KrF][BiF_6]$.—Unlike $[Xe_2F_3][BiF_6]$ and $Cs[BiF_6]$, $[XeF][BiF_6]$ and $[KrF][BiF_6]$ are expected to possess a rather strong fluorine-bridge interaction between the cation and the anion. Such fluorine bridge interactions have been noted previously for a variety of MF_6^- and $M_2F_{11}^-$ compounds of the xenon fluoro- and oxyfluoro-cations as well as for KrF^+ compounds.[9,10] The normal modes of the MF_6^- ion can be used as a sensitive probe for the detection of fluorine bridging in these compounds. Thus, the isolated MF_6^- ion possesses O_h symmetry and gives rise to six normal modes of vibration [equation (3)] of which only the two T_{1u} modes

$$\Gamma = A_{1g} + E_g + 2T_{1u} + T_{2g} + T_{2u} \qquad (3)$$

are i.r. active and the A_{1g}, E_g, and T_{2g} modes are Raman active. In the case of a wholly ionic $[NgF][BiF_6]$ salt (Ng = noble gas), only four Raman-active modes would be expected with the inclusion of the Xe–F stretch and assuming that the site symmetry for BiF_6^- is

TABLE 1

Raman frequencies (cm^{-1}) and assignments for $[Xe_2F_3][MF_6]$ (M = As, Sb, or Bi)

$[Xe_2F_3][AsF_6]$ [a]	$[Xe_2F_3][SbF_6]$ [a]	$[Xe_2F_3][BiF_6]$	Assignment	Approximate [b] description
598 (98)	591 (66)	589 (60)	ν_5 (b_1)	asym Xe–F str.
588 (100)	582 (100)	580 (73)	ν_1 (a_1)	sym Xe–F str.
471 (<1)	420 (<1)	388 (<1)	ν_6 (b_1)	asym Xe · · · F str.
401 (<1)				
	255 (5)	248 (4)	ν_2 (a_1)	sym i.p. F–Xe · · · F δ
	179 (6)		ν_7 (b_1)	asym i.p. F–Xe · · · F δ
	171 (15)	171 (8)	ν_8 (a_2)	sym o.p. F–Xe · · · F δ
163 (5)	161 (21)	160 (9)	ν_9 (b_2)	asym o.p. F–Xe · · · F δ
		118 (2)	ν_3 (a_1)	sym Xe · · · F str.
		86 (2)	ν_4 (a_1)	sym F · · · Xe · · · F δ
678 (20)	645 (24)	577 (100)	ν_1 (a_{1g})	MF_6^-
667 (4)				
580 (sh)		526 (7)	ν_2 (e_g)	
		520 (6)	ν_2 (e_g)	
	296 (2)	241 (6)	ν_5 (F_{2g})	
367 (7)	293 (2)	239 (7)		
	282 (12)	234 (7)		
		74 (8)		external modes
		59 (9)		
		48 (20)		

[a] Ref. 8. [b] i.p. and o.p. designate ' in-plane ' and ' out-of-plane ' respectively.

O_h. In general, considerably larger numbers of frequencies are always observed than would be predicted from a simple ionic model of $[NgF][MF_6]$ compounds. From Table 1 it is clear that the same conditions apply to $[NgF][BiF_6]$ compounds. In principle, the extra bands may arise from site-symmetry lowering, but, because bands attributable to the F–Ng · · · F group have also been observed, we prefer to regard the additional frequencies as arising from a distortion of the octahedral BiF_6^- anion by formation of a fluorine bridge with the cation. The existence of such fluorine bridges in compounds containing the XeF^+ cations has already been established by means of Raman spectroscopy in a large number of MF_6^- and $M_2F_{11}^-$ compounds including the Group 5A fluoro-anions AsF_6^-, SbF_6^-, and $Sb_2F_{11}^-$ and by *X*-ray crystallography in $[XeF][Sb_2F_{11}]$, $[XeF][AsF_6]$, and $[XeF][RuF_6]$. Recently, we have published the *X*-ray crystal structure of $[XeF_3][BiF_6]$ [5] and have shown the anion to be more strongly fluorine bridged than in the related $[XeF_3][SbF_6]$ structure.[11] These results have led to the conclusion that BiF_6^- is a stronger fluoride-ion donor than SbF_6^- and it is therefore reasonable to expect that $[XeF][BiF_6]$ and $[KrF][BiF_6]$ should be more extensively fluorine bridged than their SbF_6^- analogues.

The vibrational spectra of $[NgF][MF_6]$ compounds can be satisfactorily assigned on the basis of a distorted octahedral anion and a linear F–Ng · · · F group. Ignoring the possibility that the Ng · · · F–Bi bridge angle is less than 180°, which would produce further splitting on the *e* modes, the · · · $F-BiF_5$ portion of structure (I) has been assigned on the basis of C_{4v} symmetry (Table 2). All 11 models of the distorted

$F-Ng^+ \cdots F-BiF_5$

(I)

· · · $F-BiF_5$ octahedron are expected to be Raman active [equation (4)]. The correlation between O_h and C_{4v}

$$\Gamma = 4A_1 + 2B_1 + B_2 + 4E \qquad (4)$$

symmetry has been given by Gillespie and Schrobilgen.[10] The assignment has been guided by comparison with the observed frequencies for the Cs^+ salt as well as by model fluorine-bridged compounds possessing central metal atoms of similar mass such as $[XeF][IrF_6]$, $[XeF][PtF_6]$, and $[KrF][AuF_6]$. The assignments and approximate descriptions of the modes are given for $[XeF][BiF_6]$ and $[KrF][BiF_6]$ in Table 2.

The linear F–Ng · · · F group is expected to give rise to three Raman-active modes, the Ng–F stretching mode, the Ng · · · F stretching mode, and the doubly degenerate F–Ng · · · F bending mode. Recent studies have dealt with the assignment of these modes in several

TABLE 2

Raman frequencies (cm^{-1}) and assignments for $[KrF][BiF_6]$ and $[XeF][BiF_6]$

$[KrF][BiF_6]$	$[XeF][BiF_6]$	Assignment	Approximate description
610 (100)	608 (11)	ν_1 (a_1)	ν(Ng–F)
604 (11)	602 (48)		
600 (25)			
316 (6)	417 (<1)	ν_2 (a_1)	ν(Ng · · · F)
173 (7)	175 (<1)	ν_4 (e)	δ(F–Ng · · · F)
	138 (3)		
592 (35)	590 (12)	ν_8 (e)	F · · · BiF_5 (C_{4v})
580 (40)	588 (100)	ν_1 (a_1)	
547 (3)	545 (4)	ν_2 (a_1)	
541 (9)	541 (9)	ν_5 (b_1)	
	439 (<1)	ν_3 (a_1)	
244 (5)	242 (5)	ν_9 (e)	
233 (3)	228 (4)		
225 (1)	219 (<1)	ν_{11} (e)	
209 (5)	207 (3)		
203 (3)	203 (1)	ν_{10} (e)	
193 (4)	194 (<1)		
184 (5)	186 (<1)	ν_6 (b_1)	
117 (4)	123 (1)	ν_3 (a_1)	
87 (7)	82 (3)		external modes
81 (10)	76 (2)		
63 (8)	72 (2)		
60 (10)	62 (6)		
55 (15)	53 (3)		
44 (12)	44 (2)		
33 (18)			
29 (17)			
21 (27)			

[NgF][MF_6] and [NgF][M_2F_{11}] compounds. It is perhaps noteworthy that the Kr–F and Xe–F stretching frequencies in the BiF_6^- compounds have lower frequencies than in the corresponding SbF_6^- compounds (617 and 615 cm^{-1} respectively) but rather similar frequencies to the corresponding modes in the AsF_6^- compounds (β form, 617 and 601 cm^{-1}; α form, 609 cm^{-1} respectively). This confirms our view that BiF_5 deviates from the anticipated increase in fluoride-ion acceptor strength with increasing atomic number for a Group 5B pentafluoride and is in fact a significantly weaker fluoride-ion acceptor than SbF_5.

In summary, the anion spectrum of BiF_6^- in these compounds can be more satisfactorily assigned on the basis of a distorted C_{4v} symmetry than O_h symmetry. The observation of modes assignable to ν(Ng ··· F) and δ(F–Ng ··· F) in both the KrF^+ and the XeF^+ compounds supports our contention that the origin of the distortion is a fluorine-bridge interaction between the cation and the anion. We therefore conclude that the simple ionic formulation [NgF][BiF_6] is not satisfactory and that a description in terms of the following resonance structures is more appropriate with the contribution from (IIb) being greater in the case of bismuth compounds than in the case of their antimony analogues.

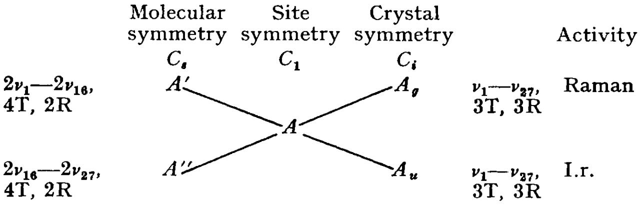
$$\underset{\text{(IIa)}}{\text{F–Ng}^+\ \text{F–MF}_5^-} \qquad \underset{\text{(IIb)}}{\text{F–Ng–F MF}_5}$$

[XeF_3][BiF_6].—We have recently reported the *X*-ray crystal structure of [XeF_3][BiF_6] and shown it to possess several interesting features when compared to its SbF_6^- analogue whose crystal structure is also known.[5] The nature of the fluorine-bridge interaction in both compounds has been used to assess the relative fluoride-ion acceptor strengths of BiF_5 and SbF_5. The bismuth structure possesses one short contact (2.25 Å) between the anion and cation compared to 2.49 Å for the short contact in [XeF_3][SbF_6]. The fluorine in the former case is nearly coplanar with the other atoms of the cation while in [XeF_3][SbF_6] there are two longer fluorine bridges lying nearly perpendicular to two of the triangular faces of the trigonal bipyramid formed by the five electron pairs of the XeF_3^+ cation. In both instances the direction of approach of the bridging fluorine is determined by the tendency of the donated electron pair of the bridging fluorine to avoid other electron pairs in the xenon valence shell. Owing to the weaker fluoride-acceptor strength of BiF_5, the bonding electron pair of the bridging fluorine occupies the middle of the edge of the XeF_3^+ trigonal bipyramid containing the two lone pairs and gives an arrangement more closely resembling square-planar XeF_4. The immediate stereochemistry about the xenon atom in [XeF_3][BiF_6] more closely resembles a square-planar AX_4E_2 structure than a T-shaped AX_3E_2 structure. Since the *X*-ray crystallographic study shows that the molecular point-group symmetry of $F_3Xe \cdots F \cdots BiF_5$ is C_s we have assigned the Raman spectrum of $XeF_4 \cdot BiF_5$ on the basis of this point group. Thus $\Gamma_{vib} = 16A' + 11A''$ and all 27 bands are expected to be active in the Raman and i.r. spectra. A factor-group analysis has also been performed on $XeF_4 \cdot BiF_5$. Taking the crystal space group as $P\bar{1}$ (C_i crystal symmetry) with $Z = 2$, the site symmetry of the $F_3Xe \cdots F \cdots BiF_5$ structural unit within the unit cell is C_1. The appropriate correlations are given in Table 3 and show that no further splitting of the predicted Raman-active modes is expected. Thus 27 Raman-active (and i.r.-active) vibrational bands are expected compared to the 29 bands actually observed in the Raman spectrum. Tentative assignments and approximate descriptions of the vibrational modes are listed in Table 4.

Cs[Bi_2F_{11}], [XeF][Bi_2F_{11}], *and* [XeF_3][Bi_2F_{11}].—Although dinuclear fluorine-bridged anions of arsenic and antimony have been known for some time now, no analogous $Bi_2F_{11}^-$ compounds have previously been reported. We have now synthesized several $Bi_2F_{11}^-$ compounds and have studied their vibrational spectra by Raman spectroscopy.

TABLE 3

Correlation diagram for the vibrational modes of $XeF_4 \cdot BiF_5$ *



* Space group $P\bar{1}$ and $Z = 2$; ref. 5. T and R denote translatory and rotatory (external) modes respectively.

TABLE 4

Raman frequencies (cm^{-1}) and assignments for [XeF_3][BiF_6]

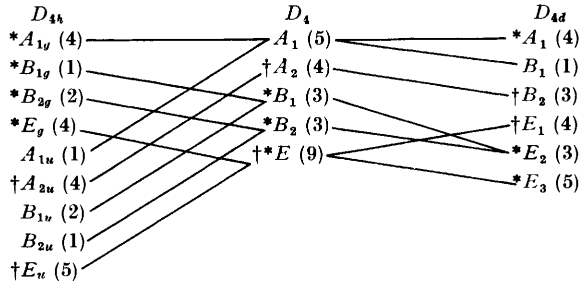
XeF_3^+ [a]	C_{2v}	C_s	Approximate description [b]
645 (100)	ν_1 (a_1)	a'	ν(Xe–F_e)
609 (10)	ν_4 (b_1)	a''	ν_{asym}(Xe–F_a)
557 (83)	ν_2 (a_1)	a'	ν_{sym}(Xe–F_a)
374 (2)	ν_5 (b_1)	a''	ν_{asym}(F_a–Xe–F_a)
253 (3)	ν_6 (b_2)	a'	δ(XeF_3) o.p.
198 (7)	ν_3 (a_1)	a'	δ_{sym}(F_a–Xe–F_a)
[$F_5Bi \cdots F$]$^-$	C_{4v}	C_s	
593 (30) 588 (58)	ν_8 (e)	a' a''	ν_{asym}(BiF_4)
582 (34)	ν_1 (a_1)	a'	ν(BiF_a)
545 (1)	ν_2 (a_1)	a'	ν_{sym}(BiF_4)
542 (1) 534 (17)	ν_5 (b_1)	a''	δ_{sym}(BiF_4) o.p.
246 (8) 231 (5)	ν_9 (e)	a' a''	δ(F_a–BiF_4)
217 (2) 213 (5)	ν_{11} (e)	a' a''	δ(F ··· BiF_4) [c]
187 (3)	ν_6 (b_1)	a''	δ_{asym}(BiF_4) o.p.
377 (1) 170 (2) 152 (2) 130(1) 118 (5) 110 (2)	[c]	a'	ν(Xe ··· F)
		$3a'$	δ(Xe ··· F–Bi) δ(F_e–Xe ··· F) o.p. δ(F_a–Xe ··· F) o.p.
		$2a''$	δ(F_aXe ··· F) i.p. δ(F_eXe ··· F) i.p.

[a] ν_3 (a_1), ν_4 (a_1), ν_7 (b_2), and ν_{10} (e) corresponding to $3a'$ and $2a''$ modes under C_s symmetry are not observed. [b] Axial and equatorial fluorines are denoted by a and e respectively. [c] Vibrational modes attributed to the fluorine bridge.

To date there has been no complete assignment of the vibrational spectrum of any $M_2F_{11}^-$ anion. We have observed a total of 21 Raman-active modes for Cs-$[Bi_2F_{11}]$. Assuming the anion is bent as in [XeF]$[Sb_2F_{11}]$ and $[XeF_3][Sb_2F_{11}]$ the only possibilities for the symmetry of the anion are C_s, C_{2v}, or C_1 symmetry. In each case all the vibrational modes are Raman active. One should therefore observe **33** Raman bands, or more than **33** bands if factor-group splitting is also observed. Alternatively, the Bi · · · F · · · Bi bridge might be linear or near linear. The only other known example of a linear fluorine bridge occurs in $[I_2][Sb_2F_{11}]$.[12] The latter example has been studied by *X*-ray crystallography and shown to possess a linear Sb · · · F · · · Sb arrangement in which the $Sb_2F_{11}^-$ anion possessed D_4 point symmetry. No fluorine bridging exists between the $Sb_2F_{11}^-$ anion and the I_2^+ cation. Three possible molecular point-group symmetries exist for a linear $M_2F_{11}^-$ anion; D_{4h}, D_{4d}, or D_4. The corresponding Raman and i.r. activities are given in Table 5. The point symmetry D_4 would give rise to 20 Raman-active bands compared to the 21 actually observed (Table). The alternative symmetries D_{4d} and D_{4h} would give rise to only 12 and 11 bands, respectively. On the basis of these arguments, $Bi_2F_{11}^-$ in its Cs^+ salt is, like $Sb_2F_{11}^-$ in its I_2^+ salt, perhaps best described as a linear species in which the equatorial fluorines are in a *gauche* conformation (D_4 point symmetry). Davies *et al.*[12] have also noted that there appears to be a tendency for the Sb · · · F · · · Sb angles in $Sb_2F_{11}^-$ to decrease with increasing anion–cation interaction. Since I_2^+ and Cs^+ are both weak electron-pair acceptors they would be expected to be associated with linear $M_2F_{11}^-$ counter ions.

TABLE 5

Raman and infrared activities for the conformations of the linear $Bi_2F_{11}^-$ anion ‡



‡ Raman active (*); i.r. active (†); numbers in parentheses denote the number of bands.

No attempt has been made to similarly assign the spectra of the $Bi_2F_{11}^-$ anion in the XeF^+ and XeF_3^+ salts (Table 6). Detailed assignments, however, have

TABLE 6

Raman frequencies and assignments for $[XeF_3][Bi_2F_{11}]$, $[XeF][Bi_2F_{11}]$, and $Cs[Bi_2F_{11}]$

Frequency/cm^{-1}			Approximate descriptions	
$[XeF_3][Bi_2F_{11}]$	$[XeF][Bi_2F_{11}]$	$Cs[Bi_2F_{11}]$	XeF_3^+	XeF^+
648 (100)			$\nu(Xe{-}F_a)$	
611 (36)	609 (74)		$\nu_{asym}(Xe{-}F_a)$	$\nu(Xe{-}F)$
606 (35)	605 (49)			
574 (98)			$\nu_{sym}(Xe{-}F_a)$	
251 (9)			$\delta\ (XeF_3)$ o.p.	
196 (7)			$\delta_{sym}(F_a{-}Xe{-}F_a)$	
484 (3)	478 (4)		$\nu(Bi \cdots F)$	$\nu(Bi \cdots F)$
444 (9)	465 (5)		$\nu(Xe \cdots F)$	$\nu(Xe \cdots F)$
633 (24)	628 (3)		$Bi_2F_{11}^-$	
624 (8)	621 (4)			
616 (9)	618 (7) 615 (9) 612 (16)	614 (10)		
599 (89)	600 (79)	607 (18) 605 (17) 600 (27)		
587 (82)	587 (16)	592 (8)		
583 (35)	581 (100)	585 (5) 580 (100)		
557 (11)	556 (3) 552 (9) 549 (6)	549 (12)		
534 (28)	545 (5)	540 (7)		
355				
		296 (<1)		
246 (12)		250 (8) 244 (5) 241 (3)		
233 (7)	230 (<1)	234 (3)		
223 (6)	215 (3)	224 (2)		
207 (11)	208 (5)	199 (2)		
182 (5)	186 (2) 180 (2)	189 (1) 180 (4)		
170 (8)		174 (2)		
	144 (2)			
126 (5)	118 (2)	118 (2)		
100 (7)	96 (5)	96 (2)		

been made for the cations and their respective fluorine-bridge modes by analogy with previous assignments for the $Sb_2F_{11}^-$ compounds.

Fluorine-19 *N.M.R. Studies.*—An attempt has been made to characterize the BiF_6^- and $Bi_2F_{11}^-$ anions by ^{19}F n.m.r. spectroscopy. Unlike $[Xe_2F_3][SbF_6]$ and $[Xe_2F_3][AsF_6]$, the bismuth compounds $Cs[BiF_6]$, $Cs[Bi_2F_{11}]$, and $[Xe_2F_3][BiF_6]$ were found to be insoluble in BrF_5 near its freezing point. The XeF^+ salts of BiF_6^- and $Bi_2F_{11}^-$ are soluble but undergo rapid fluorine exchange with BrF_5 at low temperatures.

The XeF^+ salts are soluble in $HSFO_3$ at −80 °C. We observe, in addition to the solvent line, a broad exchange-averaged line whose chemical shift ranges from −20 to −24 p.p.m. The $[Xe_2F_3][BiF_6]$ compound undergoes solvolysis in $HSFO_3$ at −80 °C to give the previously reported $(FXe)_2SO_3F^+$ cation [13] (−218 p.p.m., $w_{\frac{1}{2}} = 400$ Hz) and HF (−118 p.p.m., $w_{\frac{1}{2}} = 300$ Hz). No ^{129}Xe–^{19}F coupling could be observed. A very broad line ($w_{\frac{1}{2}} \approx 5\,000$ Hz) is observed centred at *ca.* −150 p.p.m. which is assigned to fluorine on bismuth(V). In the absence of an electric field gradient at the nucleus, the ^{19}F spectrum of BiF_6^- is expected to consist of ten lines of equal intensity (^{209}Bi, 100% natural abundance, $I = \frac{9}{2}$) arising from ^{209}Bi–^{19}F coupling. A large Bi–F coupling of 2.8 kHz has been found in a solid-state n.m.r. study of $K[BiF_6]$.[14] The broad resonance observed in the present study is consistent with a partially quadrupole-collapsed BiF_6^- spectrum.

EXPERIMENTAL

Materials.—Bismuth pentafluoride (Ozark-Mahoning Co.) was purified by vacuum sublimation at 120 °C. Xenon tetrafluoride,[15] xenon difluoride,[16] and krypton difluoride [17] were prepared as described previously. Caesium fluoride, 99.9% (K and K Laboratories), was dried in a platinum crucible *in vacuo* at 300 °C for several days. The purification of the solvents HF and BrF_5 has been described elsewhere.[10]

Syntheses.—All manipulations were carried out under anhydrous conditions on vacuum lines in which volatile materials came in contact with only Teflon, FEP, or Kel-F surfaces. Materials of low volatility such as XeF_2, BiF_5, CsF, and the adducts were handled in a dry nitrogen atmosphere in a dry-box.

The xenon fluoride adducts were prepared by condensing the solvent on to stoicheiometric quantities of BiF_5 and the xenon fluoride in either a Teflon or Kel-F vessel (note: Kel-F may not be used with the more strongly oxidizing XeF_4 or KrF_2 adducts). This was achieved by weighing a given quantity of BiF_5 into a preweighed reaction vessel followed by the addition of a small excess of xenon fluoride. Owing to the involatility of solid BiF_5 and appreciable vapour pressures of XeF_2 and XeF_4 at room temperature, the final weight of xenon fluoride was adjusted by successive pumpings on the dry mixture. All of the adducts, with the exception of $[Xe_2F_3][BiF_6]$, were prepared in HF solvents (8—10 cm³). The latter adduct showed evidence of displacement by HF solvent to give $[XeF][BiF_6]$ and XeF_2 and was consequently prepared in *ca.* 8 cm³ of BrF_5 solvent. In general, xenon fluoride–BiF_5 mixtures were not very soluble in either BrF_5 or HF at room temperature. By warming to *ca.* 40 °C, however, rapid partial dissolution occurred, giving yellow supernatants and voluminous pale yellow to yellow solids. Only $[XeF][Bi_2F_{11}]$ and $[XeF_3][Bi_2F_{11}]$ were found to have appreciable solubilities in HF at room temperature. When reaction was complete, the solvent was removed *in vacuo* at −48 °C (hexanol slush). Crystalline light yellow solids were isolated. Some typical reactant proportions are as follows: $[XeF][BiF_6]$ (6.40 mmol XeF_2, 6.56 mmol BiF_5); $[Xe_2F_3][BiF_6]$ (3.60 mmol XeF_2, 1.70 mmol BiF_5); $[XeF][Bi_2F_{11}]$ (4.44 mmol XeF_2, 9.16 mmol BiF_5); $[XeF_3][BiF_6]$ (4.50 mmol XeF_4, 4.26 mmol BiF_5); $[XeF_3][Bi_2F_{11}]$ (3.51 mmol XeF_4, 7.21 mmol BiF_5).

The salts $Cs[BiF_6]$ and $Cs[Bi_2F_{11}]$ were also prepared in anhydrous HF. A weighed quantity of CsF was dissolved in HF and then poured through a previously evacuated FEP connecting piece into an evacuated Kel-F vessel containing a stoicheiometric quantity of BiF_5. The amounts used in typical preparations were: $Cs[BiF_6]$ (5.89 mmol CsF, 5.88 mmol BiF_5); $Cs[Bi_2F_{11}]$ (4.41 mmol CsF, 8.91 mmol BiF_5). The remainder of the preparation was identical to that described above for the xenon compounds. Removal of HF solvent *in vacuo* resulted in solid white compounds.

The compound $[KrF][BiF_6]$ was prepared by condensing anhydrous HF (*ca.* 0.3 g) onto BiF_5 (2.27 mmol) in a FEP reaction vessel (6.35 mm outside diameter). An excess of KrF_2 was then condensed into the reaction vessel in increments followed by brief warming and mixing at room temperature. Solid, granular BiF_5 slowly dissolved and eventually disappeared at 1 : 1 stoicheiometry, leaving a fine white precipitate of the adduct. A large excess of KrF_2 was then added followed by brief warming and mixing at room temperature. The tube and contents were cooled to −65 °C (chloroform slush bath) and pumped on until the HF solvent had been removed. Low-temperature Raman spectroscopy revealed only the presence of $[KrF][BiF_6]$ and KrF_2; no $[Kr_2F_3][BiF_6]$ was evident. An excess of KrF_2 was removed by brief pumping at room temperature to give pure $[KrF][BiF_6]$ which was stored at −196 °C until Raman spectra could be obtained. The preparation was also repeated in BrF_5 solvent and gave identical results (BrF_5 solvent was removed at −48 °C). Unlike α-$[KrF][AsF_6]$ and β-$[KrF][AsF_6]$, $[KrF][BiF_6]$ has an appreciable stability at room temperature and, in that respect, resembles $[KrF][SbF_6]$.[10]

Analyses.—Bismuth, fluorine, and caesium analyses were performed by Alfred Bernhardt Mikroanalytisches Laboratorium. The analytical results are consistent with all of the proposed formulations (Found: Bi, 44.3; F, 28.35. Calc. for $[XeF][BiF_6]$: Bi, 44.15; F, 28.1%. Found: Bi, 32.85; F, 26.85. Calc. for $[Xe_2F_3][BiF_6]$: Bi, 32.85; F, 26.85%. Found: Bi, 54.25; F, 28.95. Calc. for $[XeF][Bi_2F_{11}]$: Bi, 54.25; F, 28.95%. Found: Bi, 41.35; F, 33.1. Calc. for $[XeF_3][BiF_6]$: Bi, 41.35; F, 33.1%. Found: Bi, 51.5; F, 32.75. Calc. for $[XeF_3][Bi_2F_{11}]$: Bi, 51.25; F, 32.65%. Found: Bi, 54.7; Cs, 18.0; F, 27.3. Calc. for $Cs[Bi_2F_{11}]$: Bi, 55.0; Cs, 17.5; F, 27.5%).

Raman Spectra.—Raman spectra were obtained with either a Spex Industries model 1 400 or a Coderg model T800 spectrometer using the 5 145 Å radiation from Spectra Physics model 164 argon ion lasers. Spectra were recorded at −196 °C by placing the sample tube inside an unsilvered glass Dewar filled with liquid nitrogen. The Raman shifts are estimated to be accurate to ±2 cm^{-1}. The spectral resolution was 1 cm^{-1}.

We thank the National Research Council of Canada for financial support of this work, the Centre National de la Recherche Scientifique de France for a grant (to D. M.), and N.A.T.O. for travel grants (to D. M. and G. J. S.).

[9/1338 *Received*, 21*st August*, 1979]

REFERENCES

[1] R. J. Gillespie, K. Ouchi, and G. P. Pez, *Inorg. Chem.*, 1969, **8**, 63.

[2] T. Surles, L. A. Quarterman, and H. H. Hyman, *J. Inorg. Nuclear Chem.*, 1973, **35**, 670.

[3] K. O. Christe, W. W. Wilson, and C. J. Schack, *J. Fluorine Chem.*, 1978, **11**, 71.

[4] R. Bougon, T. Bui Huy, A. Cadet, P. Charpin, and R. Rousson, *Inorg. Chem.*, 1974, **13**, 690.

[5] R. J. Gillespie, D. Martin, G. J. Schrobilgen, and D. R. Slim, *J.C.S. Dalton*, 1977, 2234.

[6] J. H. Holloway, G. J. Schrobilgen, and P. Taylor, *J.C.S. Chem. Comm.*, 1975, 40; G. J. Schrobilgen and J. H. Holloway, *Inorg. Chem.*, in the press.

[7] N. Bartlett, B. G. de Boer, F. J. Hollander, F. D. Sladky, D. H. Templeton, and A. Zalkin, *Inorg. Chem.*, 1974, **13**, 780.

[8] R. J. Gillespie and B. Landa, *Inorg. Chem.*, 1973, **12**, 1383.

[9] R. J. Gillespie, B. Landa, and G. J. Schrobilgen, *J. Inorg. Nuclear Chem. Suppl.*, 1976, 179.

[10] R. J. Gillespie and G. J. Schrobilgen, *Inorg. Chem.*, 1976, **15**, **22**.

[11] P. Boldrini, R. J. Gillespie, P. R. Ireland, and G. J. Schrobilgen, *Inorg. Chem.*, 1974, **13**, 1690.

[12] C. C. Davies, R. J. Gillespie, P. R. Ireland, and J. M. Sowa, *Canad. J. Chem.*, 1974, **52**, 2048.

[13] R. J. Gillespie and G. J. Schrobilgen, *Inorg. Chem.*, 1974, **13**, 1694.

[14] E. Fukushima and S. H. Mastin, *J. Magn. Reson.*, 1969, **1**, 648.

[15] J. G. Malm and C. L. Chernick, *Inorg. Synth.*, 1966, **8**, 254.

[16] S. M. Williamson, *Inorg. Synth.*, 1968, **11**, 67.

[17] F. Schreiner, J. G. Malm, and J. S. Hindman, *J. Amer. Chem. Soc.*, 1965, **87**, 25.