The Crystal Structure of Trifluoroxenon(IV) Hexafluorobismuthate(V): the Fluoride-acceptor Strength of Bismuth Pentafluoride

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The crystal structure of $[XeF_3][BiF_6]$ has been determined from three-dimensional *X*-ray counter data. Crystals are triclinic with $a = 5.698(3)$, $b = 7.811(3)$, $c = 8.854(4)$ Å, $\alpha = 99.45(5)$, $\beta = 110.09(5)$, $\gamma = 92.84(5)°$, $U = 362.7$ Å^3, $Z = 2$, and $D_c = 4.69$ g cm^{-3}. The structure has been refined in the space group $P\bar{1}$ to a final conventional R' of 0.097 for 1 238 independent reflections. The structure consists of $[XeF_3]^+$ and $[BiF_6]^-$ ions with a close contact of 2.25(2) Å between the xenon atom of the **T**-shaped cation and fluorine atom of the octahedral anion. The bridging fluorine is shown to be more strongly associated with the xenon in $[XeF_3][BiF_6]$ than in $[XeF_3][SbF_6]$, indicating that BiF_5 is a weaker fluoride acceptor than SbF_5.

THE crystal structures of a number of compounds containing the cations $[XeF]^+$,[1] $[XeF_3]^+$,[2,3] and $[XeF_5]^+$ (ref. 4) have revealed that there are bridging interactions between the anion and cation.[5] The nature and strength of these interactions and their dependence on the nature of the anion are of considerable interest. As no compounds of the inert-gas fluorides with bismuth pentafluoride had been previously prepared and since there is little information on the basicity of $[BiF_6]^-$ or the acidity of BiF_5, we have investigated the formation of adducts of BiF_5 with the fluorides of xenon. An earlier study[6] of the conductivities of various pentafluorides in $HSFO_3$ indicated a decrease in acidity in the order $SbF_5 > AsF_5 > PF_5 > BiF_5$. Indeed BiF_5 was found to have a negligible acidity in solution in $HSFO_3$ in contrast to SbF_5 which is a moderately strong acid. In this paper we report the crystal structure of $[XeF_3][BiF_6]$ and discuss the information that this gives concerning the acid strength of BiF_5.

EXPERIMENTAL

Bismuth pentafluoride (Ozark-Mahoning Co.) was purified by sublimation at 120 °C *in vacuo*. Xenon tetrafluoride was prepared as described previously.[7]

Crystals suitable for single-crystal *X*-ray analysis were grown from HF solution by combining equimolar amounts of XeF_4 and freshly sublimed BiF_5 in HF. Anhydrous HF (*ca.* 3 g) was condensed on to weighed quantities of XeF_4 (4.26 mmol) and BiF_5 (4.26 mmol) in an evacuated Teflon reaction vessel at −196 °C. Neither XeF_4 nor BiF_5 have appreciable solubilities in HF at room temperature and reaction was consequently slow. On warming to 40 °C, vigorous reaction took place, resulting in a slightly soluble, voluminous, pale yellow solid and yellow supernatant. The mixture was cooled to −48 °C, at which temperature excess of HF was removed under dynamic vacuum. The resulting crystalline solid was pumped on at room temperature for several minutes before crystals suitable for single-crystal *X*-ray analysis were selected and introduced into rigorously dried quartz capillaries which were subsequently sealed *in vacuo*.

Crystal Data.—BiF_9Xe, Triclinic, $a = 5.698(3)$, $b = 7.811(3)$, $c = 8.854(4)$ Å, $\alpha = 99.45(5)$, $\beta = 110.09(5)$, $\gamma = 92.84(3)°$, $U = 362.7$ Å^3, $Z = 2$, $D_c = 4.69$ g cm^{-3}, $F_w = 512.3$, $F(000) = 436$, $\lambda(\text{Mo-}K_\alpha) = 0.710\,69$ Å, and $\mu(\text{Mo-}K_\alpha) = 278$ cm^{-1}. The unit-cell parameters were obtained from a least-squares refinement of 15 reflections in the region $20 < 2\theta < 25°$. The structure was successfully refined in the space group $P\bar{1}$ (no. 2).[8]

X-*Ray Measurements.*—A crystal of dimensions *ca.* 0.20 × 0.12 × 0.08 mm was examined on a four-circle Syntex $P2_1$ diffractometer with a fine-focus molybdenum-anode tube and graphite monochromator. The crystal was mounted with its 0.20-mm edge, which was perpendicular to the [010] face, approximately coincident with the ϕ axis of the diffractometer. Data were collected in a similar manner to that described previously.[2] A total of 1 521 reflections was measured with $2\theta < 50°$. Subsequent averaging resulted in a total of 1 238 independent reflections, of which 1 113 had intensities greater than their standard deviations based on counting statistics. Structure factors were computed by application of Lorentz and polarisation corrections.

Solution and Refinement of the Structure.—The positions of the xenon and bismuth atoms were located from the three-dimensional Patterson function. Two cycles of least-squares refinement using an overall scale factor and positional and isotropic thermal parameters gave R 0.18.

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

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Scattering curves for neutral atoms were corrected for anomalous dispersion using values for the real and imaginary parts given in the International Tables.[9] A three-dimensional electron-density map, phased on the heavy-atom positions, gave the locations of all the light atoms. Full-matrix least-squares refinement gave R 0.16. An absorption correction was applied and anisotropic temperature factors were introduced. This led to a final $R' = [\Sigma w(|F_o|^2 - |F_c|^2)/\Sigma w F_o{}^2]^{\frac{1}{2}}$ of 0.096 9 for the 1 238 reflections where $w_{\frac{1}{2}} = (65.6 - 1.23F_o + 0.007\ 3F_o{}^2)^{-1}$ and a final R of 0.087 0 for the 1 113 observed reflections. The largest shift, Δ/σ, was <0.1 in the final cycle of refinement and a final difference-Fourier map showed no peak greater than 0.5 Å^3. Final positional parameters are listed in Table 1 and interatomic distances and angles in Table 2. The $[XeF_3][BiF_6]$ unit is shown in Figure 1. Final observed and calculated structure factors and thermal parameters are in Supplementary Publication No. SUP 22109 (9 pp.).*

TABLE 1

Positional factors ($\times 10^3$) for $[XeF_3][BiF_6]$

	x/a	y/b	z/c
Bi	35.6(2)	340.4(1)	244.9(1)
Xe	484.4(3)	169.3(2)	−221.0(2)
F(1)	274(3)	445(3)	169(3)
F(2)	199(4)	125(3)	246(3)
F(3)	218(4)	438(3)	477(2)
F(4)	−166(5)	536(3)	203(3)
F(5)	157(4)	−233(3)	3(2)
F(6)	−240(4)	217(3)	287(3)
F(7)	302(5)	135(3)	−77(3)
F(8)	627(4)	196(3)	−384(3)
F(9)	178(4)	120(3)	−380(3)

TABLE 2

Interatomic bond lengths (Å) and bond angles (°)

Bond lengths <3.5 Å

Bi–F(1)	1.92(3)	Bi–F(4)	1.98(3)
Bi–F(2)	1.96(2)	Bi–F(5$^{\rm I}$)	2.10(2)
Bi–F(3)	1.96(2)	Bi–F(6)	1.96(3)
Xe–F(1$^{\rm II}$)	3.14(2)	Xe–F(6$^{\rm I}$)	3.14(2)
Xe–F(2$^{\rm III}$)	3.03(2)	Xe–F(7)	1.94(3
Xe–F(4$^{\rm IV}$)	3.03(2)	Xe–F(8)	1.92(3)
Xe–F(5$^{\rm III}$)	2.25(2)	Xe–F(9)	1.81(2)

Bond angles

F(1)–Bi–F(2)	90.2(1.0)	F(2)–Bi–F(6)	89.2(1.0)
F(1)–Bi–F(3)	95.2(1.0)	F(3)–Bi–F(4)	95.1(1.0)
F(1)–Bi–F(4)	90.1(1.1)	F(3)–Bi–F(5$^{\rm I}$)	179.2(9)
F(1)–Bi–F(5$^{\rm I}$)	84.8(9)	F(3)–Bi–F(6)	93.6(1.0)
F(1)–Bi–F(6)	171.2(9)	F(4)–Bi–F(5$^{\rm I}$)	85.7(9)
F(2)–Bi–F(3)	95.0(9)	F(4)–Bi–F(6)	89.0(9)
F(2)–Bi–F(4)	169.8(9)	F(5)–Bi–F(6)	86.5(9)
F(2)–Bi–F(5$^{\rm I}$)	84.1(8)		
F(1$^{\rm II}$)–Xe–F(2$^{\rm III}$)	118.7(6)	F(4$^{\rm IV}$)–Xe–F(6$^{\rm I}$)	119.2(7)
F(1$^{\rm II}$)–Xe–F(4$^{\rm IV}$)	61.1(6)	F(4$^{\rm IV}$)–Xe–F(7)	70.6(1.0)
F(1$^{\rm II}$)–Xe–F(5$^{\rm III}$)	68.0(7)	F(F$^{\rm IV}$)–Xe–F(8)	107.2(1.0)
F(1$^{\rm II}$)–Xe–F(6$^{\rm I}$)	177.8(7)	F(4$^{\rm IV}$)–Xe–F(9)	68.6(8)
F(1$^{\rm II}$)–Xe–F(7)	114.4(9)	F(5$^{\rm III}$)–Xe–F(6$^{\rm I}$)	113.6(7)
F(1$^{\rm II}$)–Xe–F(8)	68.7(9)	F(5$^{\rm III}$)–Xe–F(7)	89.7(9)
F(1$^{\rm II}$)–Xe–F(9)	113.5(8)	F(5$^{\rm III}$)–Xe–F(8)	97.0(1.0)
F(2$^{\rm III}$)–Xe–F(4$^{\rm IV}$)	178.7(7)	F(5$^{\rm III}$)–Xe–F(9)	173.8(1.1)
F(2$^{\rm III}$)–Xe–F(5$^{\rm III}$)	72.8(7)	F(6$^{\rm I}$)–Xe–F(7)	67.5(9)
F(2$^{\rm III}$)–Xe–F(6$^{\rm I}$)	60.9(6)	F(6$^{\rm I}$)–Xe–F(8)	109.3(9)
F(2$^{\rm III}$)–Xe–F(7)	110.4(1.0)	F(6$^{\rm I}$)–Xe–F(9)	65.2(8)
F(2$^{\rm III}$)–Xe–F(8)	71.7(9)	F(7)–Xe–F(8)	173.2(1.0)
F(2$^{\rm III}$)–Xe–F(9)	110.6(8)	F(7)–Xe–F(9)	84.2(1.1)
F(4$^{\rm IV}$)–Xe–F(5$^{\rm III}$)	108.1(7)	F(8)–Xe–F(9)	89.1(1.1)

Roman numerals as superscripts refer to atoms related to the position x, y, z, by the transformations:

I $-x, -y, -z$
II $1 - x, 1 - y, -z$
III $1 - x, -y, -z$
IV $-x, 1 - y, -z$
V $-1 + x, y, z$

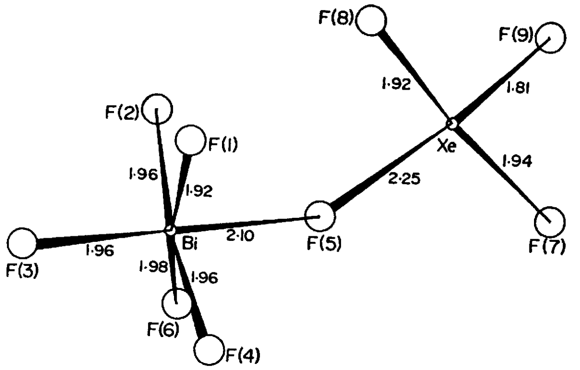

FIGURE 1 The $[XeF_3][BiF_6]$ structural unit

DISCUSSION

The structure can be approximately described as consisting of $[XeF_3]^+$ cations and $[BiF_6]^-$ anions. In the planar T-shaped cation the axial bonds (mean 1.93 Å) are longer than the equatorial bond (1.81 Å) and the mean bond angle is less than 90°, as is expected for an AX_3E_2 species on the basis of valence-shell electron-pair repulsion (VSEPR) theory.[10] The structural parameters for the cation are in good agreement with those obtained by Boldrini *et al.*[2] for α-$[XeF_3][SbF_6]$ and by McKee *et al.*[3] for $[XeF_3][Sb_2F_{11}]$.

There is one short contact (2.25 Å) between F(5) of the $[BiF_6]^-$ anion and the $[XeF_3]^+$ cation. This contact is considerably shorter than the shortest interionic contacts in α-$[XeF_3][SbF_6]$ (2.49 Å) [2] and in $[XeF_3][Sb_2F_{11}]$ (2.50 Å).[3] This fluorine is approximately coplanar with the other atoms of the cation and thus forms a rather distorted square-planar XeF_4 'molecule.' Thus, the structure is appreciably different from those of α-$[XeF_3][SbF_6]$ and $[XeF_3][Sb_2F_{11}]$ where there are two rather longer fluorine bridges which lie approximately perpendicular to two of the triangular faces of the trigonal bipyramid formed by the five electron pairs of the $[XeF_3]^+$ ion. In the latter compounds the direction of approach of the bridging fluorine is dictated by the tendency of the incoming electron pair of fluorine to avoid the other electron pairs in the valence shell of xenon (I). However, in the case of $[XeF_3][BiF_6]$, owing to the stronger Xe–F(5) interaction, the incoming fluoride lone-pair approaches the middle of the edge of the trigonal bipyramid containing the two lone pairs (II), forcing them into an arrangement more closely approximating square-planar XeF_4 (III), *i.e.* an AX_4E_2 species. Thus the overall stereochemistry about the xenon atom is intermediate between a T-shaped AX_3E_2 structure and a square-planar AX_4E_2 structure, *i.e.* between an ionic $[XeF_3][BiF_6]$ structure and a molecular adduct $XeF_4{\cdot}BiF_5$.

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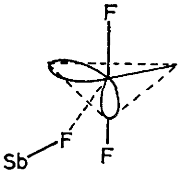
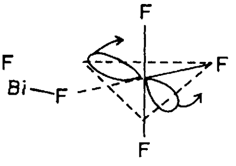
* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1976, Index issue.

[9] 'International Tables for X-Ray Crystallography,' Kynoch Press, Birmingham, 1975, vol. 4.

[10] R. J. Gillespie, 'Molecular Geometry,' Van Nostrand–Reinhold, London, 1972.



(I)



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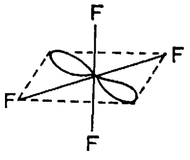

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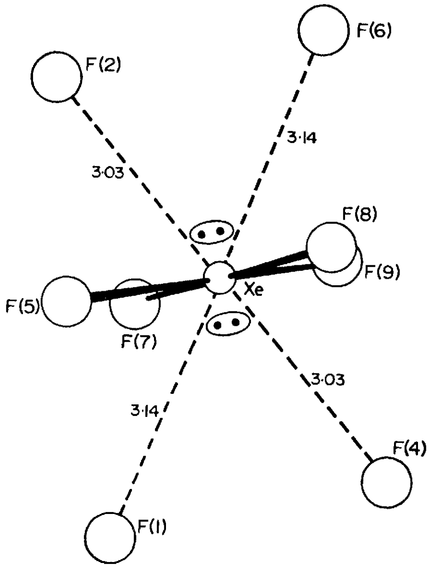

FIGURE 2 The complete co-ordination about the xenon atom

The overall co-ordination of the xenon atom is completed by four long contacts, two at 3.03 Å and two at 3.14 Å. Two of the contacts lie above and two below the $[XeF_4]$ plane (see Figure 2). Each contact subtends angles of *ca.* 65° with its neighbour on the same side of the $[XeF_4]$ plane and 115° with the nearest Xe $\cdots$ F contact on the opposite side. Furthermore, each contact subtends angles of *ca.* 65 and 115° with fluorine atoms of the XeF_4 group. Thus, the four long contacts and the xenon atom are coplanar within 0.02 Å and this plane makes an angle of 90.2° with the $[XeF_4]$ plane. These long contacts are directed towards the centres of four of the faces of the octahedron formed by the six electron pairs comprising the AX_4E_2 stereochemistry of the xenon atom. The two long contacts in α-$[XeF_3][SbF_6]$ [2] are similarly directed towards the centres of the faces of the AX_3E_2 trigonal bipyramid. Although these interactions are weak, their definite characteristic geometry strongly suggests that they are to be regarded as definite fluorine bridges.

It has been pointed out previously that the number of fluorine bridges formed by the cations $[XeF]^+$, $[XeF_3]^+$, and $[XeF_5]^+$ increases in this order and that their strength decreases as shown by their increasing length.[5] It appeared that the bonding capacity of the cation is satisfied by one short strong bridge, by two weaker bridges, or by three or four very weak bridges. The present case is slightly more complicated in that $[XeF_3]^+$ forms one strong bridge to $[BiF_6]^-$ and also four very weak bridges. The formation of a single strong bridge is, however, consistent with an appreciable base strength for the anion, *i.e.* with the increasing tendency to covalent character in the complex.

The length (2.10 Å) of the Bi–F(5) bond that is involved in the bridge to the $[XeF_3]^+$ cation is appreciably greater than the other Bi–F distances (mean 1.96 Å), which are longer than the mean Bi–F (terminal) distances (1.91 Å) [11] in polymeric BiF_5. This is presumably because all except one of these fluorine atoms are involved in bridging interactions with the $[XeF_4]$ unit and because the BiF_6 group has a formal negative charge. The Bi–F(5) bond is relatively weaker than the corresponding Sb–F bond in α-$[XeF_3][SbF_6]$ as is reflected by an increase of the bridge : terminal ratio from 1.03 for α-$[XeF_3][SbF_6]$ to 1.07 : 1 for $[XeF_3][BiF_6]$. The greater weakening of the Bi–F(5) bond reflects the greater strength of the Xe–F(5) bond which has a length of 2.25 Å compared with 2.49 Å in α-$[XeF_3][SbF_6]$. The weakening of the Bi–F(5) bond results in a distortion of the $[BiF_6]^-$ octahedron so that the plane defined by F(1), F(2), F(4), and F(6) is pushed towards the bridging fluorine F(5) as would be expected because of the smaller repulsive effect of the longer weaker Bi–F(5) bond.

In α-$[XeF_3][BiF_6]$ there is an approximate close-packed array of fluorine atoms. This is shown in Figure 3 where the planes corresponding to close-packed atoms lie in the direction of the arrows. It is interesting that the Xe–F–Bi bridge angle of 150° is intermediate between the values of 132 and 180° expected for the limiting cases of the close-packed hexagonal and cubic structures, respectively.[12] This imperfect packing, which gives a relatively high volume per fluorine atom of 20.2 Å^3, is probably a result of the presence of the lone pairs on the xenon atom and the large size of the bismuth atom.

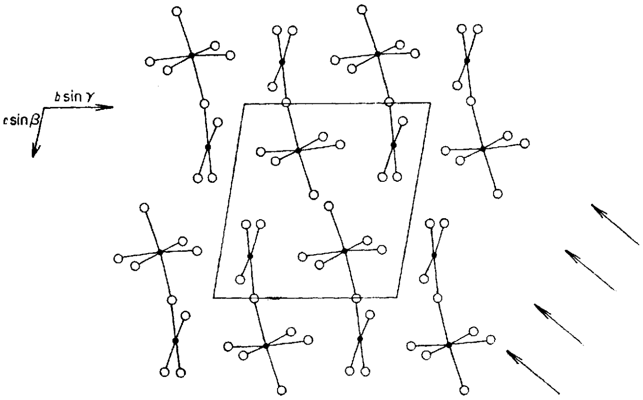

FIGURE 3 Projection of the structure down the *a* axis. The planes of approximately close-packed atoms lie in the directions of the arrows

It may be concluded that the $XeF_4 \cdot BiF_5$ adduct is much less ionic than $XeF_4 \cdot SbF_5$. The latter can be reasonably well described as the ionic compound α-$[XeF_3][SbF_6]$ with relatively weak covalent bridging

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[11] C. Hebecker, *Z. anorg. Chem.*, 1971, **384**, 111.

[12] A. J. Edwards and R. J. C. Sills, *J.C.S. Dalton*, 1974, 1724.

interactions between the ions, while $XeF_4{\cdot}BiF_5$ appears to have considerably more covalent character, *i.e.* it is equally valid to describe it as the molecular adduct $XeF_4{\cdot}BiF_5$. Hence we conclude that BiF_5 is a considerably weaker Lewis acid than SbF_5 towards XeF_4.

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