Volume 12
Number 8
August 1973

Inorganic Chemistry

Contribution from the Inorganic Materials Research Division, Lawrence Berkeley Laboratory, and the Department of Chemistry, University of California, Berkeley, California 94720

Crystal Structure of $[XeF_3^+][Sb_2F_{11}^-]$

D. E. McKEE, A. ZALKIN, and N. BARTLETT*

Received October 1, 1972

Xenon tetrafluoride is a poor fluoride ion donor, forming complexes only with the strongest Lewis acid, antimony pentafluoride. The compound $XeF_4 \cdot 2SbF_5$ is triclinic with $a = 8.237$ (5), $b = 9.984$ (20), $c = 8.004$ (5) Å, $\alpha = 72.54$ (5), $\beta = 112.59$ (7), $\gamma = 117.05$ (21)°, $V = 534.9$ Å^3, $Z = 2$, and $d_c = 3.98$ g cm^{-3}. Refinement has proceeded satisfactorily in space group $P\bar{1}$, using three-dimensional graphite monochromatized Mo Kα X-ray data. With anisotropic temperature factors for all atoms, a final conventional R factor of 0.035, for 1823 independent reflections, for which $I \geqslant 3\sigma(I)$, was obtained. The crystal structure contains discrete $XeF_4 \cdot 2SbF_5$ units and is consistent with the salt formulation, $[XeF_3^+][Sb_2F_{11}^-]$. The T-shaped cation is planar, lying in the same plane as a fourth fluorine atom, which makes a close contact to 2.50 Å to the xenon atom. This F atom, although part of the $Sb_2F_{11}^-$ ion, has a longer Sb–F bond of 1.90 Å. The other Sb–F bonds of the anion are in the range 1.84–1.86 Å. The shape of the cation and the nature of the interaction with the anions are consistent with a trigonal-bipyramidal model for the cation, in which the two nonbonding valence electron pairs occupy equatorial sites.

Experimental Section

The 1:2 XeF_4–SbF_5 complex was made as described in an accompanying paper.[1] Crystals were grown by burying a Pyrex bulb containing a solution of XeF_4 in excess SbF_5, in a sand bath hot enough (~50°) to accomplish complete solution. The temperature of the bath was reduced over a 2-day period to room temperature. The SbF_5 was distilled at room temperature from the yellow crystals under dynamic vacuum to traps held at −196°. Pumping was continued for several days to dry the crystals thoroughly. A Raman spectrum of a conglomerate of crystals showed that they were the 1:2 compound.[1]

Since the compound is highly moisture sensitive, the crystals were manipulated in the dry atmosphere of a Vacuum Atmospheres Corp. Dri-Lab, with the aid of a long focal length microscope mounted externally. Crystals were wedged in 0.3-mm quartz X-ray capillaries. The mouth of each loaded capillary was plugged with Kel-F grease prior to removal from the Dri-Lab. Outside the Dri-Lab, the capillaries were immediately sealed by drawing down in a small flame.

Crystal Data

$XeF_4 \cdot 2SbF_5$ (mol wt 640.8) is triclinic with $a = 8.237$ (5), $b = 9.984$ (20), $c = 8.004$ (5) Å, $\alpha = 72.54$ (5), $\beta = 112.59$ (7), $\gamma = 117.05$ (21)°, $V = 534.9$ Å^3, $Z = 2$, $d_c = 3.98$ g cm^{-3}, and $F(000) = 559.86$. Single-crystal precession and Weissenberg photographs indicated that the space group is triclinic. A Delaunay reduction of the cell chosen failed to show additional symmetry. The structure was successfully refined in the space group $P\bar{1}$.

X-Ray Measurements

A clear, roughly cubic crystal of edge 0.10–0.15 mm was chosen for data collection. A Picker automatic four-circle diffractometer, equipped with a fine-focus Mo anode tube, was used. High-angle reflections were accurately centered at a takeoff angle of ~2° and were used for a least-squares refinement of the cell parameters. Data were collected and treated as described in a recent article.[2] A complete hemisphere of data was collected for $2\theta \leqslant 55°$. Intensities of three standards were collected at intervals of every 200 reflections. A total of 2418 independent intensity data were recorded.

Structure Refinements

The least-squares program used in the structure refinements has been described.[2] Scattering factors for neutral fluorine, xenon, and antimony were used as given by Doyle and Turner.[3] Anamolous dispersion factors were given by Cromer and Liberman.[4]

Since the intensities of the standards were observed to diminish (finally to 85% of their original values) in a regular and nearly isotropic manner, the data were scaled linearly between each pair of standards. Associated with this decrease we also noted a decrease in the parameters b and γ (which were in the end reduced by 0.02 Å and 0.21° from their initial values). Broadening of the ω scans of the standards from 0.10 to 0.35° was also observed. The positions of the heavy atoms were determined from a three-dimensional Patterson synthesis. These positions were subjected to least-squares refinement as xenon atoms, after which it was possible to separate the antimony atoms by exploiting temperature factor differences. The positions were then further refined. A difference Fourier revealed positions for 12 of the 14 fluorine atoms. Least-squares refinement of these positions was followed by another difference Fourier which revealed the positions of the final two fluorine atoms. Refinement of all these positions, with anisotropic temperature factors, resulted in a conventional R factor of 0.06. Weighting schemes were as previously described.[2]

Examination of the observed and calculated structure factors showed that the poorest agreement occurred with the low-angle, high-intensity reflections. Since absorption and extinction corrections could not be reliably made, the lower angle data ($(\sin \theta)/\lambda \leqslant 0.32$) were given zero weight in the final least-squares refinements. This procedure resulted in $R = 0.035$, $R_w = 0.03$, and a standard deviation for an observation of unit weight of 3.7. The number of nonzero weighted data in this refinement was 1823. The positional and thermal parameters, reported in Table I, are from this refinement. Observed structure factors, standard deviations, and differences in Table II are given in the microfilm version of this paper.[5] The highest peak on a final difference Fourier proved to be only 2 e/Å^3. Such peaks

---

(1) D. E. McKee, C. J. Adams, and N. Bartlett, *Inorg. Chem.*, 12, 1722 (1973).

(2) D. D. Gibler, C. J. Adams, M. Fischer, A. Zalkin, and N. Bartlett, *Inorg. Chem.*, 11, 2325 (1972).

(3) P. A. Doyle and P. S. Turner, *Acta Crystallogr., Sect. A*, 24, 390 (1968).

(4) D. T. Cromer and D. Liberman, *J. Chem. Phys.*, 53, 1891 (1970).

(5) Table II, a listing of observed structure factors, will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-73-1713.

Table I. Positional and Thermal Parameters for $[XeF_3^+][Sb_2F_{11}^-]^a$

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Xe	0.29614 (8)	0.74522 (6)	0.18648 (6)	3.01 (2)	2.69 (2)	2.17 (2)	1.54 (2)	1.19 (2)	0.12 (1)
Sb(1)	0.12219 (8)	0.28979 (6)	0.50926 (6)	2.37 (2)	2.56 (2)	1.83 (2)	1.16 (2)	0.87 (2)	−0.37 (1)
Sb(2)	0.35701 (8)	0.22795 (6)	0.20527 (7)	2.75 (2)	2.71 (2)	1.91 (2)	1.16 (2)	1.09 (2)	−0.42 (1)
F(1)	0.1925 (7)	0.2154 (6)	0.3502 (7)	3.2 (2)	3.2 (2)	3.2 (2)	1.0 (2)	1.8 (2)	−0.6 (2)
F(2)	0.1869 (9)	0.4790 (6)	0.3518 (7)	4.7 (3)	3.6 (2)	3.2 (2)	2.4 (2)	1.8 (2)	0.4 (2)
F(3)	0.3785 (8)	0.3544 (7)	0.6376 (8)	3.2 (2)	4.3 (3)	3.8 (2)	1.6 (2)	−0.6 (2)	−1.7 (2)
F(4)	0.318 (1)	0.0264 (6)	0.3119 (8)	5.7 (3)	3.1 (2)	4.3 (3)	2.5 (2)	2.6 (2)	0.7 (2)
F(5)	0.078 (1)	0.0993 (6)	0.6485 (8)	6.1 (3)	3.1 (2)	3.6 (2)	1.9 (2)	3.1 (2)	0.8 (2)
F(6)	0.134 (1)	0.1604 (8)	0.0228 (8)	5.3 (3)	6.1 (3)	2.9 (2)	2.3 (3)	0.2 (2)	−2.1 (2)
F(7)	0.510 (1)	0.2383 (8)	0.0782 (8)	5.0 (3)	5.9 (3)	4.1 (2)	2.6 (3)	3.1 (2)	−0.3 (2)
F(8)	0.057 (1)	0.3681 (8)	0.6462 (8)	7.1 (4)	5.8 (3)	4.1 (2)	3.9 (3)	3.2 (3)	−0.3 (2)
F(9)	0.273 (1)	0.8988 (7)	−0.0048 (7)	5.5 (3)	3.6 (2)	2.5 (2)	1.8 (2)	1.3 (2)	1.0 (2)
F(10)	0.0531 (9)	0.6367 (7)	0.0420 (8)	3.4 (2)	4.6 (3)	3.4 (2)	1.8 (2)	−0.4 (2)	−1.2 (2)
F(11)	0.5350 (8)	0.9022 (6)	0.2669 (8)	3.5 (2)	3.3 (2)	4.6 (3)	1.4 (2)	1.3 (2)	−0.2 (2)
F(12)	−0.1162 (9)	0.2269 (9)	0.3476 (9)	2.8 (2)	6.6 (4)	4.2 (3)	1.3 (2)	0.1 (2)	−2.1 (2)
F(13)	0.5594 (8)	0.2897 (7)	0.4117 (7)	3.4 (2)	5.8 (3)	2.7 (2)	2.2 (2)	0.5 (2)	−1.0 (2)
F(14)	0.3726 (9)	0.4274 (5)	0.1226 (7)	4.7 (3)	2.1 (2)	3.9 (2)	1.2 (2)	2.2 (2)	0.4 (2)

[a] Standard deviations are in parentheses.

were in all cases within 1 Å of atoms. We are confident that they are a result of imperfections in the data and the data treatment. Table III gives chemically significant distances and angles.

Description of Structure

The xenon atom is close-coordinated to three F atoms which define an approximately T-shaped species. The remaining atoms define an Sb_2F_{11} unit which consists of two approximately octahedral SbF_6 groups, sharing a common F atom, such that the angle Sb(1)-F-Sb(2) is 155.4 (2)°. The bridging Sb-F interatomic distances (average distance 2.02 Å) are significantly longer than the nonbridging, with the exception of that F atom (F(2)) which makes a close approach, of 2.50 (1) Å, to the Xe atom. The interatomic Sb-F(2) distance is 1.90 (1) Å. It is of interest that the F atom which makes this close approach to the Xe atom is in cis relationship to the F atom of the Sb(1)-F-Sb(2) bridge.

The Sb_2F_{11} species seen in this structure resembles those previously reported,[6,7] but the XeF_3 species is novel. Only the bridging Sb-F distances differ significantly from 1.85 Å.

As Figure 1 illustrates, all four atoms of the XeF_3 species are in the same plane, but, furthermore, the F(2) atom of the Sb_2F_{11} unit, which makes the close approach of 2.50 Å to the Xe atom, is also in the same plane. Three other contacts, to F(13), F(3), and F(7), of 2.94 (1), 2.97 (1), and 3.04 (1) Å, respectively, are made between formula units, as may be discerned from the stereogram given as Figure 2, in conjunction with Figure 3. (See Figure 4 for a stereogram of the $[XeF_3^+][Sb_2F_{11}^-]$ structural unit.)

Discussion

The observed structure is consistent with the salt formulation $[XeF_3^+][Sb_2F_{11}^-]$. Other Sb_2F_{11} salts reported[6,7] hitherto are $[XeF^+][Sb_2F_{11}^-]$ and $[BrF_4^+][Sb_2F_{11}^-]$. The $Sb_2F_{11}^-$ ion geometry has been discussed by Lind and Christe.[7] The former salt is also of interest in that it defines the Xe(II) cation XeF^+.

Representation of $Sb_2F_{11}^-$ as a resonance hybrid in which $SbF_5(SbF_6^-)$ and $(SbF_6^-)SbF_5$ are major canonical forms accounts for the greater length of the bridging Sb-F bonds compared with the terminal Sb-F bonds. In $[XeF_3^+][Sb_2F_{11}^-]$ as in $[XeF^+][Sb_2F_{11}^-]$,[6] the anion bridge is approximately symmetrical and is consistent with approximately equal contributions from the two canonical forms cited. In $[BrF_4^+][Sb_2F_{11}^-]$[7] the less symmetrical nature of the anion suggests that the end of the anion closest to BrF_4^+ has more SbF_6^- character than the other and, hence, that the corresponding canonical form is more dominant than is the other. This suggests that BrF_4^+ is a more powerfully polarizing cation than either XeF_3^+ or XeF^+.

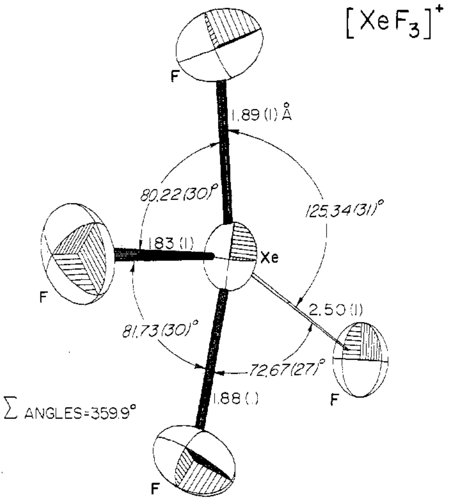

Figure 1. The XeF_3^+ ion and its close contact with the $Sb_2F_{11}^-$ ion.

Although the short in-plane contact of 2.50 (1) Å between the XeF_3^+ ion and the closest F atom (F(2)) of an anion could be represented as an indication of some covalency, the ionic model provides a simple and direct accounting for the observed structural features, if due allowance is made for the polarizing character of the cation.

No matter which bonding model we use for the XeF_3^+ cation,[8] we conclude that two nonbonding valence-electron pairs of the xenon atom are not involved in bonding. If we allow the two nonbonding valence-electron pairs to be sterically active, then they will, with the three F ligands, constitute a five-coordinate arrangement for the xenon atom. As with the majority of five-coordinate non transition element compounds, we might therefore expect the geometry to be based on a trigonal bipyramid.[9] Since the species ClF_3 and BrF_3 (which are electronically related to XeF_3^+) are T shaped,[10,11] we could therefore anticipate that the XeF_3^+ nonbonding pairs would be in the equatorial plane as illus-

---

(6) V. M. McRae, R. D. Peacock, and D. R. Russell, *Chem. Commun.*, 62 (1969).

(7) M. D. Lind and K. O. Christe, *Inorg. Chem.*, 11, 608 (1972).

(8) See article by N. Bartlett, *Endeavour*, 31, 107 (1972), for a simple review of bonding models.

(9) R. J. Gillespie and R. S. Nyholm, *Quart. Rev., Chem. Soc.*, 11, 339 (1957); R. J. Gillespie in "Noble-Gas Compounds," H. H. Hyman, Ed., University of Chicago Press, Chicago, Ill., and London, 1963, pp 333-339.

(10) D. F. Smith, *J. Chem. Phys.*, 21, 609 (1953).

(11) D. W. Magnuson, *J. Chem. Phys.*, 27, 223 (1957).

Table III. Interatomic Distances (Å) and Angles (deg) for $[XeF_3^+][Sb_2F_{11}^-]$ (Standard Deviations 0.01 Å for all Distances)

Intramolecular					
Distances		Angles		Intermolecular distances (≤3.5 Å)[a]	
Xe-F(2)	2.50	F(1)-Sb(2)-F(4)	85.80 (27)	Xe-F(3)$^{\mathrm{II}}$	2.97
F(9)	1.83	F(6)	86.30 (30)	F(4)$^{\mathrm{X}}$	3.17
F(10)	1.88	F(7)	178.81 (37)	F(7)$^{\mathrm{III}}$	3.04
F(11)	1.89	F(13)	85.07 (25)	F(8)$^{\mathrm{V}}$	3.26
Sb(1)-F(1)	2.01	F(14)	84.56 (26)	F(13)$^{\mathrm{II}}$	2.94
F(2)	1.90	F(2)-Sb(1)-F(1)	85.60 (25)	F(1)-F(5)$^{\mathrm{VI}}$	2.91
F(3)	1.85	F(3)	86.26 (32)	F(10)$^{\mathrm{V}}$	3.34
F(5)	1.84	F(5)	171.94 (37)	F(11)$^{\mathrm{II}}$	3.28
F(8)	1.85	F(8)	91.24 (31)	F(2)-F(3)$^{\mathrm{II}}$	3.17
F(12)	1.83	F(12)	89.10 (33)	F(8)$^{\mathrm{V}}$	3.03
Sb(2)-F(1)	2.04	F(3)-Sb(1)-F(1)	85.24 (29)	F(10)$^{\mathrm{V}}$	3.24
F(4)	1.86	F(5)	90.78 (34)	F(13)$^{\mathrm{II}}$	2.91
F(6)	1.84	F(8)	95.29 (35)	F(3)-F(3)$^{\mathrm{II}}$	3.40
F(7)	1.85	F(12)	169.26 (46)	F(7)$^{\mathrm{XI}}$	3.27
F(13)	1.86	F(4)-Sb(2)-F(6)	89.09 (36)	F(11)$^{\mathrm{II}}$	2.78
F(14)	1.86	F(7)	93.58 (31)	F(13)$^{\mathrm{II}}$	3.27
F(1)-F(2)	2.66	F(13)	88.91 (32)	F(14)$^{\mathrm{II}}$	2.84
F(3)	2.62	F(14)	170.35 (38)	Xe$^{\mathrm{II}}$	2.97
F(4)	2.66	F(5)-Sb(1)-F(1)	86.69 (27)	F(4)-F(4)$^{\mathrm{IV}}$	3.45
F(5)	2.65	F(8)	96.50 (32)	F(5)$^{\mathrm{VI}}$	3.02
F(6)	2.66	F(12)	92.52 (37)	F(9)$^{\mathrm{XII}}$	3.00
F(13)	2.64	F(6)-Sb(2)-F(7)	94.70 (32)	F(11)$^{\mathrm{II}}$	3.30
F(14)	2.63	F(13)	171.27 (48)	F(11)$^{\mathrm{XII}}$	2.77
F(2)-F(3)	2.56	F(14)	90.70 (36)	F(12)$^{\mathrm{VI}}$	3.48
F(8)	2.68	F(7)-Sb(2)-F(13)	93.91 (34)	F(5)-F(5)$^{\mathrm{VI}}$	3.06
F(10)	2.64	F(14)	96.05 (32)	F(6)$^{\mathrm{XI}}$	3.06
F(12)	2.62	F(8)-Sb(1)-F(1)	176.76 (36)	F(6)$^{\mathrm{VI}}$	3.47
F(14)	3.07	F(12)	94.49 (39)	F(9)$^{\mathrm{XIII}}$	3.23
F(3)-F(5)	2.63	F(9)-Xe-F(10)	81.73 (30)	F(11)$^{\mathrm{II}}$	3.00
F(8)	2.74	F(11)	80.22 (30)	F(12)$^{\mathrm{VI}}$	3.40
F(13)	3.09	F(2)	154.39 (38)	F(6)-F(6)$^{\mathrm{I}}$	2.98
F(4)-F(6)	2.59	F(10)-Xe-F(11)	161.90 (40)	F(8)$^{\mathrm{VII}}$	3.12
F(7)	2.71	F(2)	72.67 (27)	F(9)$^{\mathrm{V}}$	3.08
F(13)	2.61	F(11)-Xe-F(2)	125.34 (31)	F(9)$^{\mathrm{XII}}$	3.39
F(5)-F(8)	2.76	F(12)-Sb(1)-F(1)	84.76 (29)	F(10)$^{\mathrm{V}}$	2.89
F(12)	2.65	F(13)-Sb(2)-F(14)	89.84 (33)	F(7)-F(9)$^{\mathrm{III}}$	2.99
F(6)-F(7)	2.71	Sb(1)-F(1)-Sb(2)	155.37 (15)	F(9)$^{\mathrm{XII}}$	3.18
F(14)	2.63	Xe-F(2)-Sb(1)	171.64 (13)	F(11)$^{\mathrm{XII}}$	3.31
F(7)-F(13)	2.71			F(11)$^{\mathrm{III}}$	3.29
F(14)	2.76			F(12)$^{\mathrm{XIV}}$	3.04
F(8)-F(13)	2.70			F(14)$^{\mathrm{III}}$	3.12
F(9)-F(10)	2.43			F(8)-F(8)$^{\mathrm{VIII}}$	3.19
F(11)	2.40			F(10)$^{\mathrm{VIII}}$	2.95
F(13)-F(14)	2.63			F(13)$^{\mathrm{II}}$	3.50
				F(9)-F(9)$^{\mathrm{IX}}$	3.32
				F(11)$^{\mathrm{IX}}$	2.83
				F(12)$^{\mathrm{V}}$	2.94
				F(10)-F(10)$^{\mathrm{V}}$	2.67
				F(12)$^{\mathrm{V}}$	3.15
				F(14)$^{\mathrm{V}}$	3.06
				F(11)-F(12)$^{\mathrm{XV}}$	3.25
				F(13)$^{\mathrm{II}}$	2.85
				F(12)-F(13)$^{\mathrm{XVI}}$	3.25
				F(14)-F(14)$^{\mathrm{III}}$	3.01

[a] The crystal chemical unit is at x, y, z and the superscript numerals refer to the following positions: (I) $-x, -y, -z$; (II) $1-x, 1-y, -z$; (III) $1-x, 1-y, -z$; (IV) $1-x, -y, 1-z$; (V) $-x, 1-y, -z$; (VI) $-x, -y, 1-z$; (VII) $x, y, -1+z$; (VIII) $-x, 1-y, 1-z$; (IX) $1-x, 2-y, -z$; (X) $x, 1+y, z$; (XI) $x, y, 1+z$; (XII) $x, -1+y, z$; (XIII) $x, -1+y, 1+z$; (XIV) $1+x, y, z$; (XV) $1+x, 1+y, z$; (XVI) $-1+x, y, z$.

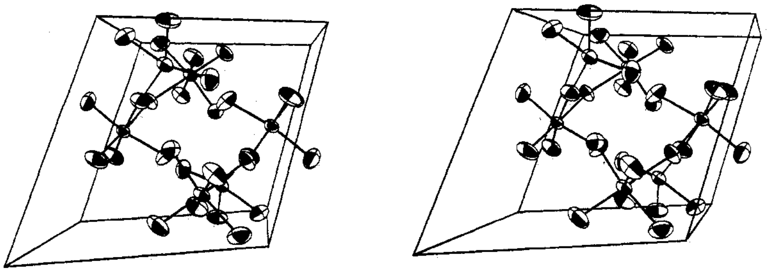

Figure 2. Stereogram showing the arrangement of the $[XeF_3^+][Sb_2F_{11}^-]$ structural units within the unit cell–view along *b*.

trated in Figure 5. Such a cation would be far from spherical in its polarizing effect on anions. Indeed, the screening effects and repulsive effects of the nonbonding electron pairs and the F ligands should result in a negatively charged

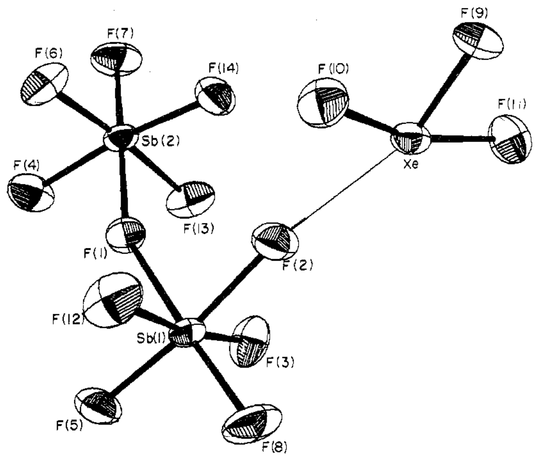

Figure 3. The $[XeF_3^+][Sb_2F_{11}^-]$ structural unit.

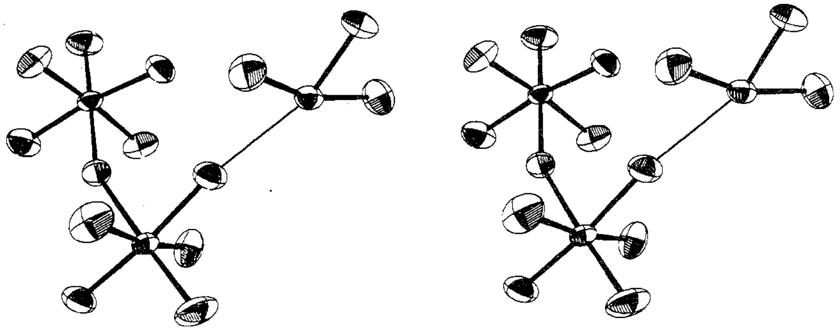

Figure 4. Stereogram of the $[XeF_3^+][Sb_2F_{11}^-]$ structural unit.

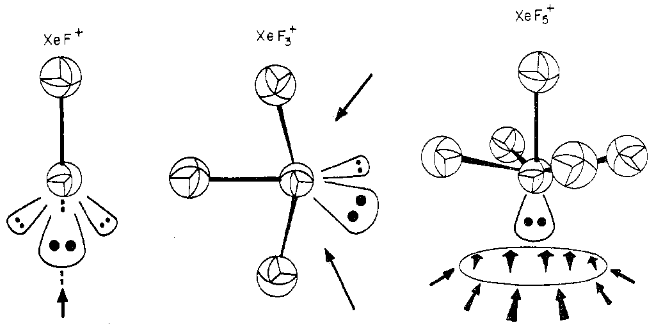

Figure 5. Shapes of the XeF_x^+ ions based on steric activity of the nonbonding xenon valence-electron pairs. (Arrows indicate directions of maximum polarizing effect.) [These models represent the nonbonding xenon electrons in a formalistic way. In the Xe–F$^+$ case the model cannot be realistic since such a cation has cylindrical symmetry. The postulated axial polarizing behavior can also be seen to be a consequence of Xe–F bond formation. Thus we can "synthesize" XeF$^+$ by bringing F$^+$(^{1}D) up to the spherical Xe atom. If we use a p-orbital pair of electrons of the Xe atom to form the Xe–F bond, the electron density will be diminished trans to the bond.]

species (such as a F ligand of an anion) making an approach to the triangular faces containing the two nonbonding electron pairs, as illustrated in Figure 5. It is significant that the F(1)-Xe-F(2) angle of Figure 1 is 154° and not 180° and that all four F atoms close to the Xe atom are in the same plane.

It is instructive to compare XeF_3^+ with XeF^+ and XeF_5^+. In XeF^+ we have three nonbonding valence-electron pairs; therefore, the xenon coordination is pseudotetrahedral as illustrated in Figure 5. This model indicates that a negatively charged species approaching XeF^+ would "see" the greatest positive charge when placed on axis trans to the F ligand. This model accounts for the geometry of the $[XeF^+][Sb_2F_{11}^-]$ arrangement reported by Peacock and his coworkers and for the structure of $XeF^+RuF_6^-$ recently determined in these laboratories.[12] On the other hand, the XeF_5^+ ion possesses only one nonbonding xenon valence-electron pair and the xenon coordination is pseudooctahedral. The crystal structures of the XeF_5^+ salts[12–15] are in excellent accord with the maximum polarizing capability of this ion being directed in a cone about the symmetry axis as shown in Figure 5.

As may be seen from Table IV and Figure 2 the axial bonds in XeF_3^+, ClF_3, and BrF_3 are significantly longer than the equatorial. All bonds in XeF_3^+ are shorter than in XeF_4, where Xe–F = 1.95 Å.[16] Evidently the equatorial F ligand is more strongly bound than the axial ligands. This is in accord with the Pimentel and Rundle models,[17] in which the axial bonds are formulated as three-center bonds (with the bonds amounting to single-electron bonds) and the equatorial bond is represented as an electron-pair bond. Alternatively the greater length of the axial bonds can be attributed, on the basis of the electron-pair repulsion model,[9] to the greater repulsive interaction of the axial F ligands with the nonbonding electron pairs (which are at 90°); the equatorial ligand is at 120° from those electron pairs.

The length of the equatorial Xe–F$^+$ bond compares closely with that of Xe–F$^+$, as predicted[18] on the basis of the Xe–F bonds in XeF_2 being of bond order 0.5, and with that observed[6] in $[XeF^+][Sb_2F_{11}^-]$. This is certainly consistent with an electron-pair representation. The axial Xe–F bonds are significantly shorter than Xe–F in XeF_4, but this shortening can be attributed to increase in the Xe–F bond polarity following the loss of F$^-$ and consequent increase in the effective positive charge of the xenon atom.

We have previously called attention[2] to what appears to be a law of constancy of shape in strictly isoelectronic species. This is particularly well illustrated by the F_{ax}-E-F_{eq} angle (given in parentheses) in the series XeF_5^+ (79 (1)°), IF_5 (80.9 (2)°), TeF_5^- (78.8 (2)°),[19] and SbF_5^{2-} (79.4

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

(13) (a) B. K. Morrell M.Sc. Thesis, University of California, Berkeley, Calif., 1971; (b) F. Hollander, Ph.D. Thesis, University of California, Berkeley, Calif., 1972; (c) N. Bartlett, B. DeBoer, F. Hollander, F. O. Sladky, D. Templeton, and A. Zalkin, submitted for publication in *Inorg. Chem.*

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

(15) N. Bartlett, F. Einstein, D. F. Stewart, and J. Trotter, *J. Chem. Soc. A*, 1190 (1967).

(16) J. A. Ibers and W. C. Hamilton, *Science*, 139, 106 (1963); J. H. Burns, P. A. Agron, and H. A. Levy, *ibid.*, 139, 1208 (1963).

(17) (a) G. C. Pimentel, *J. Chem. Phys.*, 19, 446 (1951); (b) R. E. Rundle, *J. Amer. Chem. Soc.*, 85, 112 (1963).

(18) N. Bartlett and M. Wechsberg, *Z. Anorg. Allg. Chem.*, 385, 5 (1971).

(19) S. H. Mastin, R. R. Ryan, and L. B. Asprey, *Inorg. Chem.*, 9, 2100 (1970).

Table IV. Comparison of ClF_3, BrF_3, and XeF_3^+

	ClF_3	BrF_3	XeF_3^+
E–F_{eq}, Å	1.598	1.721	1.83
E–F_{ax}, Å	1.698	1.810	1.88, 1.89
F_{ax}–E–F_{eq}, deg	87.5	86.2	82, 80
Ref	10	11	Present work

(1)°).[20] We, therefore, believe that molecular IF_3 (the geometry of which is presently unknown) will have the same F_{eq}-E-F_{ax} angle as in XeF_3^+.

The relationship of the XeF_3^+ geometry to the geometries of ClF_3 and BrF_3 calls for further comment since the XeF_3^+ ion has the smallest F_{eq}-E-F_{ax} bond angle of the series even though the Xe-F equatorial and Xe-F axial bonds are more akin than for ClF_3 and BrF_3. Indeed, although the effect is subtle for ClF_3 and BrF_3, there appears to be a general coupling of decrease in the F_{eq}-E-F_{ax} bond angle with increase in the average bond length and decrease in the bond length difference. Of course, for a given F_{eq}-E-F_{ax} bond angle, increase in bond length means an increase in the ligand separation F_{eq}-F_{ax}. The longer the bond length, therefore, the more acute the F_{eq}-E-F_{ax} angle can become before the ligand-ligand repulsive interactions become angle limiting. Thus the F_{eq}-F_{ax} distances in ClF_3, BrF_3, and XeF_3^+ are 2.28, 2.41, and 2.43 Å, respectively. It is, therefore, plausible that the bond angle decrease in this series is simply a consequence of the bond length length increase (*i.e.*, effective central-atom size increase). It can also be argued that the greater bond length difference, seen in the shorter bond length examples, is simply a consequence of the ligand-ligand interactions limiting the F_{eq}-E-F_{ax} angle and forcing an extension of the bonds for those ligands closest to the nonbonding electron pairs—namely, the F_{ax}-E bonds.

Registry No. XeF_4, 13709-61-0; SbF_5, 7783-70-2; $[XeF_3^+][Sb_2F_{11}^-]$, 39797-62-1.

Acknowledgment. This work was supported by the United States Atomic Energy Commission under Contract No. W-7405-eng-48.

---

(20) R. R. Ryan and D. T. Cromer, *Inorg. Chem.*, 11, 2322 (1972).

Contribution from the Inorganic Materials Research Division, Lawrence Berkeley Laboratory, and the Department of Chemistry, University of California, Berkeley, California 94720

Crystal Structures of $[XeF^+][RuF_6^-]$ and $[XeF_5^+][RuF_6^-]$

N. BARTLETT,* M. GENNIS, D. D. GIBLER, B. K. MORRELL, and A. ZALKIN

Received October 1, 1972

Ruthenium pentafluoride forms complexes with XeF_2 and with XeF_6 but not with XeF_4. The compound $XeRuF_7$ is monoclinic with $a = 7.991$, $b = 11.086$, $c = 7.250$ Å (all ±0.006 Å), $\beta = 90.68°$ (±0.05°), $V = 642.2$ Å^3, $Z = 4$, and $d_c = 3.78$ g cm^{-3}. Refinement has proceeded satisfactorily in space group $P2_1/n$, using three-dimensional graphite monochromatized Mo Kα X-ray data. With anisotropic temperature factors for all atoms, a final conventional R factor of 0.07, for 1044 independent reflections, for which $I \geqslant 2\sigma(I)$, was obtained. The crystal contains discrete $XeRuF_7$ units in which the xenon atom is approximately linearly coordinated to two fluorine atoms (F(1)–Xe–F(2) = 177.1 (1.2)°), one of which (F(1)) is bound to the xenon atom alone (Xe–F(1) = 1.872 (17) Å) and the other (F(2)) shared (Xe–F(2) = 2.182 (15) Å) with the ruthenium atom to which it is closely coordinated (Ru–F(2) = 1.919 (13) Å). The other five fluorine atoms complete, with F(2), a distorted octahedral coordination of the Ru atom, with the following Ru–F interatomic distances: F(3), 1.778 (16) Å; F(4), 1.781 (12) Å; F(5), 1.789 (13) Å; F(6), 1.820 (14) Å; F(7), 1.835 (13) Å. The Ru–F(3) bond is trans to the Ru–F(2) bond. The angle Xe–F(2)–Ru = 137.19 (46)°. $XeRuF_{11}$ is orthorhombic with $a = 16.771$ (10), $b = 8.206$ (10), $c = 5.617$ (10) Å, $V = 773.03$ Å^3, $Z = 4$, and $d_c = 3.79$ g cm^{-3}. Data collection and treatment were similar to that in the $XeRuF_7$ case and refinement has proceeded satisfactorily in space group *Pnma*, with a final conventional R factor of 0.042 for the 556 reflections for which $I \geqslant 3\sigma(I)$. The structure reveals discrete XeF_5 and RuF_6 units, with each XeF_5 group coordinated to four RuF_6 groups *via* one F atom on each RuF_6 group. The four Xe···F intergroup contacts are 2.552 (11), 2.601 (9), and (twice) 2.924 (7) Å. This set of four fluorine atoms, together with the five fluorine atoms of the XeF_5 group, pack in a distorted, capped archimedian antiprism arrangement. The RuF_6 group is a slightly distorted octahedron with the following RuF distances: –F(3) (twice), 1.850 (7) Å; F(4), 1.876 (11) Å; F(5), 1.820 (12) Å; F(6), 1.827 (10) Å; F(7), 1.867 (9) Å. The XeF_5 group almost has C_{4v} symmetry, with Xe–F(axial) = 1.793 (8) Å and Xe–F-(equatorial) = (twice) 1.841 (8) and (twice) 1.848 (8) Å. The angle F(axial)–Xe–F(equatorial) = 80°. The crystal structures are consistent with the salt formulations, $[XeF^+][RuF_6^-]$ and $[XeF_5^+][RuF_6^-]$, the observed interactions between cation and anion being attributable to the uniquely polarizing character of each of the cations.

Introduction

An investigation of the products of the interaction of xenon and fluorine with platinum pentafluoride, undertaken by Bartlett and Stewart[1] to help clarify the earlier studies, by Bartlett and Jha,[2] of the Xe-PtF_6 and Xe-RhF_6 systems, revealed that xenon(II) and xenon(VI) fluoride complexes with PtF_5 could be prepared. Curiously, Xe(IV) complexes were not observed. In a subsequent investigation,[3] Bartlett and Sladky confirmed that XeF_4 does not form complexes with the known noble metal pentafluorides and they were able to exploit their finding to provide a chemical purification of xenon tetrafluoride.

Since X-ray crystallographic studies[4] had shown the 1:1 XeF_6 complex with PtF_5 to be the salt $[XeF_5^+][PtF_6^-]$, the absence of a salt $[XeF_3^+][PtF_6^-]$ implied that XeF_6 is a superior fluoride ion donor to XeF_4. On the other hand, the

---

(1) N. Bartlett, F. Einstein, D. F. Stewart, and J. Trotter, *Chem. Commun.*, 550 (1966).

(2) N. Bartlett and N. K. Jha in "Noble-Gas Compounds," H. H. Hyman, Ed., University of Chicago Press, Chicago, Ill., and London, 1963, pp 23–30.

(3) N. Bartlett and F. O. Sladky, *J. Amer. Chem. Soc.*, 90, 5317 (1968).

(4) N. Bartlett, F. Einstein, D. F. Stewart, and J. Trotter, *J. Chem. Soc. A*, 1190 (1967).