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Crystal Structures of $[Xe_2F_3^+][AsF_6^-]$ and $[XeF_5^+][AsF_6^-]$

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Received September 17, 1973

Crystals of $[Xe_2F_3^+][AsF_6^-]$ are pale yellow-green. The crystalline modification which is stable at room temperature is monoclinic with $a = 15.443$ (10) Å, $b = 8.678$ (5) Å, $c = 20.888$ (15) Å, $\beta = 90.13$ (6)°, $V = 2799.3$ Å^3, $Z = 12$, and $d_c = 3.62$ g cm^{-3}. The structure was refined in space group $I2/a$ using three-dimensional Zr-filtered Mo Kα X-ray data. With anisotropic temperature factors for all atoms, a final conventional R factor of 0.048 was obtained for 1024 independent reflections for which $I \geqslant 3\sigma(I)$. The structure indicates the salt formulation $[Xe_2F_3^+][AsF_6^-]$. The structure analysis has not revealed any significant differences between the two crystallographically nonequivalent representatives of each ion in the asymmetric unit. The AsF_6^- species are roughly octahedral, the six As–F distances being in the range 1.56 (3)–1.70 (3) Å and the cis F–As–F bond angles in the range 83 (2)–95 (2)°. The average As–F distance is 1.63 (4) Å. The cation is V shaped $[F{-}Xe{-}F{-}Xe{-}F]^+$ and is planar and symmetrical about the bridging F atom. The average of the terminal Xe–F distances is 1.90 (2) Å, the average bridging distance is 2.14 (2) Å, and the F(terminal)–Xe–F(bridge) angle is not significantly different from 180°. The average bridge Xe–F–Xe angle is 150.2 (8)°. Bonding in the cation can be represented by a resonance hybrid of the canonical forms $(F{-}Xe)^+F^-(Xe{-}F)^+$, $F^-(Xe{-}F)^+(Xe{-}F)^+$, and $(F{-}Xe)^+(F{-}Xe)^+F^-$, with the first form dominant. Crystals of $[XeF_5^+][AsF_6^-]$ are colorless. The unit cell is monoclinic with $a = 5.886$ (3) Å, $b = 16.564$ (10) Å, $c = 8.051$ (4) Å, $\beta = 91.57$ (3)°, $V = 784.6$ Å^3, and $Z = 4$, $d_c = 3.51$ g cm^{-3}. The structure was refined in space group $P2_1/c$ using three-dimensional graphite-monochromatized Mo Kα X-ray data. With anisotropic temperature factors for all atoms a final conventional R factor was obtained of 0.12 for 925 independent reflections for which $I \geqslant \sigma(I)$. The asymmetric structural unit contains one XeF_5^+ and one AsF_6^-. Each cation makes F-bridging contacts to two anions (and *vice versa*) to define $(XeF_5AsF_6)_2$ centrosymmetric rings. Thus each cation is associated with one anion *via* a single F-bridge contact and with the other anion *via* a double F-bridge contact. These three bridging fluorine atom contacts with the cation are arranged approximately symmetrically about the pseudo-fourfold axis of the XeF_5^+ and below its basal plane. The XeF_5^+ has approximately C_{4v} symmetry, with the Xe–F axial distance 1.78 (2) Å, the average Xe–F equatorial distance 1.83 (2) Å, and the average F(axial)–Xe–F(equatorial) angle 80 (1)°. The AsF_6^- group is somewhat distorted from O_h symmetry with bond lengths in the range 1.76 (2)–1.65 (2) Å. The average As–F distance is 1.72 (3) Å. The coordination of the cation is similar to that observed in the $[XeF_5^+]_2[PdF_6^{2-}]$ structure.[1]

Introduction

Complexes of XeF_2 with AsF_5 were first reported by Bartlett and his coworkers.[2] Initially they did not recognize that the 1:1 compound $XeF_2 \cdot AsF_5$ readily loses AsF_5 according to the equation

$$2(XeF_2 \cdot AsF_5) \rightarrow 2XeF_2 \cdot AsF_5 + AsF_5$$

and it was not until the crystal structure determination, reported in detail in this paper, was carried out that the compound first identified[2a] with the composition $XeF_2 \cdot AsF_5$ was recognized as the salt $[Xe_2F_3^+][AsF_6^-]$. Although the compound $XeF_2 \cdot AsF_5$ has been established,[2b] it is only very recently that crystallographic work in these laboratories has established the $[XeF^+][AsF_6^-]$ formulation. Other $[Xe_2F_3^+][MF_6^-]$ salts were made subsequently[2c] but the AsF_6^- salt remains the only one for which a structure determination is available.

Complexes of XeF_6 with F^- acceptors were discovered in three separate laboratories.[3-5] The 1:1 complexes with AsF_5 and BF_3 were formulated on the basis of infrared evidence, by Bartlett, *et al.*,[4] as XeF_5^+ salts. Although the crystal structure determination of $[XeF_5^+][PtF_6^-]$[6] and its relative $[XeF_5^+][RuF_6^-]$[7] gave firm structural support for the vibrational justification[8] for $[XeF_5^+][AsF_6^-]$, it was clear from the powder data that this salt was not isostructural with its transition metal analogs $[XeF_5^+][MF_6^-]$ (M = Ru, Rh, Os, Ir, Pt), in which series an isostructural relationship was assured.[7] It is usual for crystal structures of AsF_6^- salts to differ from those adopted by Sb and transition metal analogs.[9] It appeared probable that the coordination of the XeF_5^+ species in $[XeF_5^+][AsF_6^-]$ would differ from that observed in $[XeF_5^+][PtF_6^-]$ and $[XeF_5^+][RuF_6^-]$. Moreover, although the vibrational data provided strong circumstantial evidence for the salt formulation, firmer evidence was desirable.

The formulation of the $XeF_6 \cdot AsF_5$ complex became a matter of greater interest when Bartlett and Sladky demonstrated[10] that XeF_4 was a poorer fluoride donor than XeF_2 and would not form a complex with AsF_5 under ordinary temperatures and pressures.

Experimental Section

The 2:1 XeF_2–AsF_5 complex was prepared as previously described.[2c] Crystals of the compound (which is rapidly decomposed by water) were grown by sublimation under nitrogen (at ~1 atm) in sealed, dry quartz X-ray capillaries, using the focused beam of a microscope lamp to heat the source material. The 1:1 XeF_6–AsF_5 complex was prepared and single crystals were grown as described by Bartlett and Wechsberg.[8]

Crystal Data. The selected crystal of F_9AsXe_2 (mol wt 508.5) was an approximate parallelepiped of approximate dimensions 0.1 × 0.07 × 0.05 mm, the long edge being parallel with b and the other edges with [101] and [10$\bar{1}$]. Precession and Weissenberg photographs established the lattice to be monoclinic and cell parameters were obtained from high-angle measurements on an XRD5 diffracto-

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meter: $a = 15.443$ (10) Å, $b = 8.678$ (5) Å, $c = 20.888$ (15) Å, $\beta = 90.13$ (6)°, $V = 2799.3$ Å^3, $Z = 12$, $d_c = 3.62$ g cm^{-3}. Observed reflections obeyed the relationships hkl ($h + k + l = 2n$) and $h0l$ ($h = 2n$ ($l = 2n$)) and indicated the space group to be either $I2/a$ or Ia. (The space groups $I2/a$ and Ia are the same groups as $C2/c$ and Cc, respectively, which are the groups listed in ref 11.)

The selected crystal of $F_{11}AsXe$ (mol wt 415.2) was a plate of approximate dimensions 0.28 × 0.16 × 0.04 mm which was bounded by (010), ($0\bar{1}0$), ($\bar{1}01$), ($\bar{1}0\bar{1}$), and the capillary wall. The b axis was normal to the plate and approximately parallel to the axis of the capillary. Precession photographs established monoclinic symmetry and the systematic absences $h0l$ ($l \neq 2n$) and $0k0$ ($k \neq 2n$) indicated, uniquely, the space group $P2_1/c$ (No. 14).[11] Least-squares refinement of data from carefully centered high-angle reflections gave $a = 5.886$ (3) Å, $b = 16.564$ (10) Å, $c = 8.051$ (4) Å, $\beta = 91.564$ (35)°, $V = 784.6$ Å^3, $Z = 4$, and $d_c = 3.51$ g cm^{-3}.

X-Ray Measurements. F_9AsXe_2. Diffraction data were collected at room temperature (24.5 ± 1.5°) using Zr-filtered Mo Kα radiation, λ 0.7107 Å, with a manually operated single-crystal orienter on a GE diffractometer. The crystal was mounted with the b axis parallel to the ϕ axis of the orienter. Intensity measurements were made by the stationary-crystal, stationary-counter technique, using a takeoff angle of 4° and 10-sec counts. Backgrounds (also for 10 sec) were measured at $2\theta \pm 1°$ for reflections up to 30° and at $2\theta \pm 1.5°$ beyond this point. Backgrounds were large. At small diffraction angles the background depended markedly upon 2θ and it was found to be more reliable, for such data, to obtain the background value from an empirical plot of background dependence on 2θ. Data for 1519 independent reflections were obtained, in the range $2\theta \leqslant 45°$. Of these, 1024 met the criterion $I \geqslant 3\sigma(I)$. Several standard reflections were used to monitor the experiment at approximately 3-hr periods during the data collection. The standards showed no significant change in the course of data collection.

Correction for absorption ($\mu = 112$ cm^{-1}) was made by the analytical method of DeMeulenaer and Tompa[12] using a program developed by Templeton and Templeton.[13] The usual corrections were made for Lorentz and polarization effects.

$F_{11}XeAs$. Diffraction data were collected at room temperature (23 ± 1°) on a Picker/Nuclear four-circle diffractometer. Intensity data were collected with a θ–2θ scan technique with Mo Kα radiation, monochromatized with a graphite monochromator ($2\theta_m$ 12.02°). A base width for the scan of 1.1° was used, which was centered on the predicted Mo Kα_1 position and was augmented on the high-2θ side to allow for the α_1–α_2 separation. Each peak was scanned at a speed of 1°/min and background measurements were counted for 10 sec at each end of the scan. Attenuators were automatically inserted in the diffracted beam when the count rate exceeded 10,000 cps. Reflections were collected in the hemisphere $+h,\pm k,\pm l$ for 2θ 0–50° (($\sin\theta)/\lambda = 0.596$). Three reflections were monitored periodically during the data collection and variously decayed to between 43 and 63% of their original values. The data were corrected for this decay with a single (average value) function. A total of 1382 independent data were recorded of which 925 had $I > \sigma(I)$.

Because of the high X-ray absorption ($\mu = 90.8$ cm^{-1}) and the large size and irregular shape of the crystal, an absorption correction was made by numerical integration. The correction varied by a factor 2.5 between extremes. Standard deviations of the intensities were calculated by $\sigma(I) = (\sigma^2(I_{av}) + q^2I^2)^{1/2}$, where q (here 0.11) is a factor introduced to reduce the weights given to intense reflections, and $\sigma(I_{av})$ was calculated from counting statistics or from the deviation of the individual reflections from the average, whichever was larger. Lorentz and polarization factors were then applied.

For both structures atomic scattering factors for neutral F, Xe, and As given by Doyle and Turner[14] and the values of the dispersion corrections, for Xe and As, of Cromer and Liberman[15] were used. Calculations were performed on our CDC 6600 and CDC 7600 computers.[16]

Structure Determinations. F_9AsXe_2. At the outset, the composition of the material was thought to be F_7AsXe, Z was assumed to be 16, and the space group was assumed to be $I2/a$. Study of the Patterson function revealed four sets of heavy atoms, each in the general position. There was, however, some uncertainty as to which of xenon and arsenic should be assigned to the positions. Least-squares refinement, with all four eightfold sets of heavy atoms assigned as xenon, proceeded to a conventional R factor of 0.24. The relative magnitudes of the thermal parameters indicated one of the atoms to be arsenic and a Fourier synthesis revealed an additional heavy atom on an inversion center, the peak height of which indicated it to be arsenic. The Fourier synthesis also showed 14 independent sites appropriate for F atoms. Full-matrix least-squares refinement, with all atoms assigned anisotropic thermal parameters, resulted in a conventional R factor of 0.048 for 1024 independent nonzero data ($I \geqslant 3\sigma(I)$), with R (including zero weight data) = 0.091 for 1735 data. The weighted R factor $R_w = 0.070$. The q factor used was 0.08. The standard deviation of an observation of unit weight was 1.36. A difference Fourier revealed a number of small peaks (generally close to the heavy-atom locations) all of which were <0.65 e Å^{-3}. The atomic parameters from the last refinement are given in Table I. The observed structure factors, standard deviations, and differences are given in Table II.[17]

This analysis therefore established that the unit cell contained 24 Xe, 12 As, and 108 F atoms and thus revealed the composition of the complex to be $2XeF_2 \cdot AsF_5$, not $XeF_2 \cdot AsF_5$.

$F_{11}AsXe$. Zachariasen's criterion[18] of 18 Å^3 per fluorine atom indicated that the number of formula units in the unit cell should be 4.

The three-dimensional Patterson function revealed the positions of the two heavy atoms in the asymmetric unit (each in general position 4e). Four cycles of least-squares refinement, with the atoms assigned isotropic thermal parameters, brought the conventional R factor to 0.29. A subsequent electron density map revealed 11 additional major peaks which were designated as fluorine. Six of these were in an octahedral relationship to the As atom and five were in a square-pyramidal arrangement about the xenon atom. Least-squares refinement proceeded initially with the thermal parameters isotropic for the F atoms and anisotropic for Xe and As; then all atoms were allowed anisotropic thermal parameters. An analysis of the weighted ΔF's showed that the intense reflections had been given too much weight in the refinements and that the parameter q in the standard deviation of an intensity needed adjustment. Values of q from 0.05 to 0.20 were tried, and $q = 0.11$ was chosen as best. Zero weight was assigned when $F^2 < \sigma(F^2)$. The final refinement yielded a conventional R factor of 0.12 for 925 reflections, including zero-weighted reflections $R = 0.14$. The weighted R factor $R_w = 0.13$. The standard deviation of an observation of unit weight was 1.57. The final shifts of all parameters were less than 2% of their estimated standard deviations. The final difference map showed smearing of electron density, about the Xe and As atoms, in the b direction; the peak heights were 7 e/Å^3 near Xe and 4 e/Å^3 near As. Other peaks were 2 e/Å^3 or less. These peaks and the high value found necessary for q probably arise because of the pronounced intensity decay noted during data collection.

The atomic coordinates and thermal parameters are given in Table III, and the structure factors, their standard deviations, and final differences are given in Table IV.[17]

Descriptions of the Structures

The atomic arrangements in the two structures are com-

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(11) "International Tables for X-Ray Crystallography," Vol. I, Kynoch Press, Birmingham, England, 1952. See Table I for the general positions for the unconventional space group $I2/a$.

(12) J. DeMeulenaer and H. Tompa, *Acta Crystallogr.*, 19, 1014 (1965).

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

(16) The following programs were used in the solution of these structures: RLFACS, a program for reduction of raw data from the Picker automatic diffractometer; HORSE, our modification of Hamilton's GONO9 program for absorption correction; INCOR and SORT, general data reduction programs; FORDAP, A. Zalkin's Fourier analysis program; LSLONG and LESQ, modifications of the Ganzel-Sparks-Trueblood least-squares program; DATLOK, D. J. St. Clair's unpublished weighting scheme analysis program; DISTAN and DISMAT, crystallographic bond distance and angle programs, the latter of which calculates standard deviations using the correlation matrix from least squares; ORTEP, C. Johnson's (1965) thermal ellipsoid plotting program; LSPLAN, our modification of the least-squares planes program from the University of Pittsburgh; LIST1 and LISTAP, data presentation programs.

(17) See paragraph at end of paper regarding supplementary material.

(18) W. H. Zachariasen, *J. Amer. Chem. Soc.*, 70, 2147 (1948). It should be noted that this criterion does not apply well to XeF_2, where the unit cell volume, divided by the number of F atoms in the cell, is 32.5 Å^3 (S. Siegel and E. Gebert, *ibid.*, 85, 240 (1963)). Nor does the criterion apply to XeF_2 complexes—evidently Xe(II) is much too big to fit into an octahedral hole.

Table I. Coordinates and Thermal Parameters for $[Xe_2F_3^+][AsF_6^-]^{a-c}$

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Xe(1)	0.1399 (1)	0.2975 (2)	0.55644 (9)	3.9 (1)	4.0 (1)	4.9 (1)	0.44 (8)	0.32 (8)	−0.61 (7)
Xe(2)	−0.0486 (1)	0.0457 (2)	0.22164 (9)	4.9 (1)	3.03 (8)	4.46 (9)	−0.09 (8)	0.09 (8)	0.37 (7)
Xe(3)	0.8389 (1)	0.3861 (2)	0.11007 (9)	4.1 (1)	5.0 (1)	4.6 (1)	0.81 (8)	−0.37 (8)	0.49 (8)
As(1)	0.4268 (2)	0.7646 (3)	0.4152 (1)	5.3 (2)	3.8 (1)	4.7 (2)	−0.2 (1)	−0.3 (1)	−0.2 (1)
As(2)	0.250	0.250	0.250	4.1 (3)	4.5 (2)	4.6 (2)	0.5 (2)	−0.1 (2)	0.6 (2)
F(1)	0.250	0.361 (3)	0.500	6.2 (18)	7.8 (17)	8.7 (17)	0	2.9 (14)	0
F(2)	0.041 (1)	0.251 (2)	0.6088 (8)	6.5 (13)	9.7 (13)	5.3 (9)	−1.3 (10)	1.9 (9)	−1.4 (8)
F(3)	0.025 (1)	−0.079 (2)	0.2706 (3)	7.5 (13)	5.6 (10)	6.6 (10)	1.2 (8)	−1.8 (9)	0.9 (7)
F(4)	0.865 (1)	0.182 (2)	0.161 (1)	6.3 (15)	6.1 (11)	16.3 (19)	−0.9 (9)	−3.8 (14)	5.9 (12)
F(5)	0.808 (2)	0.561 (2)	0.063 (1)	9.2 (17)	8.6 (14)	11.7 (16)	3.4 (11)	2.1 (13)	5.7 (12)
F(6)	0.341 (2)	0.705 (3)	0.460 (1)	10.1 (21)	13.2 (22)	14.2 (20)	1.0 (15)	6.8 (17)	2.2 (16)
F(7)	0.479 (2)	0.607 (3)	0.425 (2)	13.2 (26)	5.3 (12)	28.1 (36)	0.1 (15)	3.8 (26)	5.2 (18)
F(8)	0.507 (2)	0.815 (4)	0.366 (1)	11.2 (23)	17.5 (25)	9.4 (15)	−0.5 (18)	4.4 (15)	4.2 (16)
F(9)	0.366 (2)	0.917 (3)	0.397 (2)	6.3 (16)	7.9 (15)	29.6 (38)	1.5 (12)	−3.0 (21)	6.1 (19)
F(10)	0.472 (2)	0.852 (4)	0.475 (1)	18.3 (32)	14.0 (22)	13.5 (21)	1.2 (21)	−6.8 (22)	−5.5 (17)
F(11)	0.371 (2)	0.678 (4)	0.360 (1)	19.1 (34)	17.6 (27)	9.4 (17)	−7.1 (24)	−3.9 (19)	−4.4 (17)
F(12)	0.152 (2)	0.212 (3)	0.243 (2)	5.4 (16)	12.3 (20)	23.6 (31)	−1.9 (13)	−1.3 (19)	−2.7 (20)
F(13)	0.220 (2)	0.324 (4)	0.319 (1)	9.1 (22)	22.2 (30)	11.3 (18)	8.5 (21)	−1.2 (16)	−4.3 (19)
F(14)	0.231 (2)	0.409 (4)	0.213 (2)	10.6 (23)	11.6 (20)	29.3 (37)	5.7 (16)	1.7 (23)	12.4 (23)

[a] Estimated standard deviations of the least significant digit(s) are given in parentheses here and in Tables III, V, and VI. [b] The form of the temperature factor (B_{ij} in units of Å^2) is $T = \exp[-0.25(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.
[c] For space group $I2/a$ the general positions are $(x, y, z; \bar{x}, \bar{y}, \bar{z}; {}^1/_2 + x, \bar{y}, z; {}^1/_2 - x, y, \bar{z}) + (0, 0, 0; {}^1/_2, {}^1/_2, {}^1/_2)$.

Table III. Coordinates and Thermal Parameters for $[XeF_5^+][AsF_6^-]^a$

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Xe	0.1957 (3)	0.1101 (1)	0.2501 (2)	5.76 (9)	8.41 (11)	5.05 (8)	0.22 (9)	0.01 (5)	0.22 (6)
As	0.6068 (6)	0.1067 (2)	0.7009 (3)	4.16 (15)	5.47 (15)	3.03 (12)	0.07 (15)	−0.31 (11)	−0.43 (10)
F(1)	0.081 (4)	0.1888 (10)	0.126 (2)	6.3 (11)	6.6 (9)	4.7 (8)	0.5 (9)	0.0 (7)	1.2 (7)
F(2)	0.456 (4)	0.1590 (11)	0.187 (2)	6.3 (12)	7.6 (11)	6.4 (10)	−3.1 (10)	1.6 (9)	1.9 (8)
F(3)	0.179 (4)	0.0607 (11)	0.050 (2)	6.4 (11)	8.1 (10)	3.6 (7)	1.1 (9)	−1.5 (7)	−0.8 (7)
F(4)	−0.109 (3)	0.0830 (16)	0.269 (2)	3.5 (9)	14.7 (18)	5.3 (9)	−2.5 (11)	0.4 (7)	1.3 (10)
F(5)	0.161 (4)	0.1882 (11)	0.405 (2)	7.4 (13)	7.9 (10)	4.4 (8)	1.7 (10)	−2.5 (8)	−1.3 (7)
F(6)	0.474 (4)	0.0869 (10)	0.509 (2)	7.7 (12)	7.6 (9)	2.9 (6)	0.2 (9)	−2.7 (7)	−0.7 (6)
F(7)	0.377 (3)	0.1625 (12)	0.756 (2)	3.9 (9)	7.4 (11)	7.1 (10)	2.1 (9)	1.2 (8)	−1.3 (7)
F(8)	0.486 (3)	0.0176 (11)	0.772 (2)	4.6 (9)	7.0 (9)	3.9 (7)	−1.2 (8)	−0.0 (6)	1.2 (6)
F(9)	0.834 (3)	0.0457 (9)	0.643 (2)	3.8 (8)	5.8 (8)	5.7 (9)	1.3 (7)	1.5 (7)	0.6 (7)
F(10)	0.734 (4)	0.1875 (10)	0.620 (3)	7.2 (13)	5.9 (9)	7.4 (11)	−1.5 (9)	1.0 (10)	−0.6 (7)
F(11)	0.741 (4)	0.1226 (11)	0.888 (2)	8.1 (13)	9.8 (12)	2.8 (7)	0.7 (10)	−2.0 (8)	−1.9 (7)

[a] Thermal parameters as in Table I.

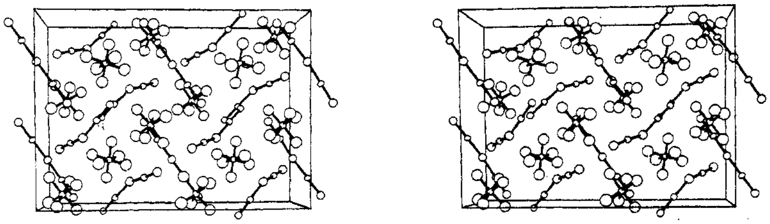

Figure 1. Stereoscopic view of the $[Xe_2F_3^+][AsF_6^-]$ unit cell, showing the arrangement of the ions (the unique axis, *b*, is normal to the plane of the paper and *a* is vertical).

patible with the salt formulations $[Xe_2F_3^+][AsF_6^-]$ and $[XeF_5^+][AsF_6^-]$.

$[Xe_2F_3^+][AsF_6^-]$. The stereoscopic view given in Figure 1 shows the arrangement of the $Xe_2F_3^+$ and AsF_6^- ions within the unit cell.[19] There are two crystallographically nonequivalent ions of each type. The dimensions of the ions are detailed in Table V. The $Xe_2F_3^+$ ions are planar V-shaped species and the two crystallographically distinct forms are not significantly different from one another. Each cation [F-Xe-F-Xe-F]$^+$ is symmetrical about the bridging fluorine atom, the average Xe-F-Xe angle being 150.2 (8)° and each F-Xe-F component being essentially linear. The terminal Xe-F interatomic distances average to 1.90 (3) Å whereas the bridging Xe-F distances average to 2.14 (3) Å. Figure 2 represents the averaged cation.

The interaction of the cations, one with another, as may be seen from Figure 1, generates a three-dimensional network within the cavities of which the AsF_6^- ions are held. The network is a result of two short contacts of ~3.0 Å each, involving interaction of the bridging F atom of one cation with one terminal fluorine atom on each of two other cations. Thus each bridging F atom of each cation is coordinated to two XeF groups, at 2.14 Å, to define the cation, and two other F atoms (of two other cations) are coordinated at ~3.0 Å to define the network. The plane defined by the bridging F atom and the two close terminal F atoms at ~3.0 Å is perpendicular to the plane defined by the cation containing the bridging F atom. The close atomic contacts of the bridging F atom are detailed in Table VI. Note that the alignment of the bridging F atom with the Xe-F groups at 2.14 Å and with each of the F-Xe groups at ~3.0 Å is

[19] The figures represent isotropic F atoms, since the anisotropic thermal parameters given in Tables I and III may not be realistic. The data for the structures were not of high quality and, furthermore, the descriptions of the crystals for the absorption corrections were less exact than we would have liked.

Table V

Some Angles in $Xe_2F_3{\cdot}AsF_6$

Atoms	Angle, deg	Atoms	Angle, deg
	$F{-}Xe{-}F{-}Xe{-}F^+$ Ion		
F(1)-Xe(1)-F(2)	177 (2)	Xe(1)-F(1)-Xe(1)	150.3 (8)
F(3)-Xe(2)-F(4)	179 (1)	Xe(2)-F(4)-Xe(3)	150.0 (6)
F(4)-Xe(3)-F(5)	176 (2)		
	AsF_6^- Octahedron		
F(12)-As(2)-F(13)	83 (2)	F(7)-As(1)-F(11)	88 (2)
F(12)-As(2)-F(14)	88 (2)	F(8)-As(1)-F(9)	94 (2)
F(13)-As(2)-F(14)	88 (2)	F(8)-As(1)-F(10)	91 (2)
F(6)-As(1)-F(7)	94 (2)	F(8)-As(1)-F(11)	95 (2)
F(6)-As(1)-F(9)	86 (2)	F(9)-As(1)-F(10)	93 (2)
F(6)-As(1)-F(10)	94 (2)	F(9)-As(1)-F(11)	85 (2)
F(6)-As(1)-F(11)	80 (2)	F(6)-As(1)-F(8)	175 (3)
F(7)-As(1)-F(8)	86 (2)	F(7)-As(1)-F(9)	173 (3)
F(7)-As(1)-F(10)	95 (2)	F(10)-As(1)-F(11)	174 (3)

Interatomic Distances in $[Xe_2F_3^+][AsF_6^-]$

Atoms	Dist, Å	Atoms	Dist, Å
	$F{-}Xe{-}F{-}Xe{-}F^+$ Ions		
Xe(1)-F(2)	1.93 (2)[a]	Xe(2)-F(4)	2.18 (2)[b]
Xe(1)-F(1)	2.14 (1)[b]	Xe(3)-F(5)	1.87 (2)[a]
Xe(2)-F(3)	1.87 (2)[a]	Xe(3)-F(4)	2.11 (2)[b]
	AsF_6^- Octahedra[c,d]		
As(1)-F(6)	1.70 (3) [1.79]	F(7)-F(8)	2.23 (4)
As(1)-F(7)	1.60 (3) [1.72]	F(7)-F(10)	2.37 (4)
As(1)-F(8)	1.67 (3) [1.76]	F(7)-F(11)	2.24 (5)
As(1)-F(9)	1.67 (2) [1.79]	F(8)-F(9)	2.45 (4)
As(1)-F(10)	1.61 (3) [1.73]	F(8)-F(10)	2.35 (4)
As(1)-F(11)	1.63 (3) [1.75]	F(8)-F(11)	2.42 (4)
As(2)-2F(12)	1.56 (3) [1.67]	F(9)-F(10)	2.37 (4)
As(2)-2F(13)	1.65 (3) [1.76]	F(9)-F(11)	2.22 (4)
As(2)-2F(14)	1.61 (2) [1.75]	F(12)-F(13)	2.14 (4)
F(6)-F(7)	2.41 (4)	F(12)-F(13)	2.40 (5)
F(6)-F(9)	2.29 (4)	F(12)-F(14)	2.20 (4)
F(6)-F(10)	2.42 (5)	F(12)-F(14)	2.28 (4)
F(6)-F(11)	2.15 (4)	F(13)-F(14)	2.27 (5)
		F(13)-F(14)	2.34 (5)

[a] Terminal fluorines. [b] Bridging fluorines. [c] As(1) is in the general position; As(2) is on a center of symmetry. [d] The thermal parameters (given in Table I) indicate librational motion of the AsF_6^- ion. The As-F distances corrected for librational motion are given in brackets.

Table VI. Coordination of the Bridging F Atom in the $Xe_2F_3^+$ Ion (Distances in Å; Angles in deg)

F(1) in F(2)-Xe(1)-F(1)-Xe(1)-F(2)		F(4) in F(3)-Xe(2)-F(4)-Xe(3)-F(5)	
F(1)-Xe(1)	2.14 (1)	F(4)-Xe(2)	2.18 (2)
		F(4)-Xe(3)	2.11 (2)
F(1)-Xe(1)-F(2)	177 (2)	F(4)-Xe(2)-F(3)	179 (1)
		F(4)-Xe(3)-F(5)	176 (2)
F(1)-F(5)	3.05 (3)	F(4)-F(2)	2.98 (3)
		F(4)-F(3)	3.03 (3)
F(1)-F(5)-Xe(3)	173 (1)	F(4)-F(2)-Xe(1)	153 (1)
		F(4)-F(3)-Xe(2)	172 (1)
F(1)-F(6)	3.41 (4)	F(4)-F(13)	3.40 (4)
F(1)-F(6)-As(1)	136 (1)	F(4)-F(13)-As(2)	125 (1)

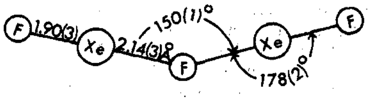

Figure 2. The $Xe_2F_3^+$ ion.

essentially linear. The arrangement of the two Xe atoms and the two F atoms about each bridging F atom can be viewed as grossly distorted tetrahedral. The next nearest atoms to the bridging F atom are F ligands of AsF_6^- ions, which are at distances of 3.4 Å or greater.

The departures of the anions in $[Xe_2F_3^+][AsF_6^-]$ from octahedral symmetry are not statistically significant. Indeed the Raman spectrum of $[Xe_2F_3^+][AsF_6^-]$ indicates[2c] the anion to be close to the octahedral ideal whereas the spectrum of $[XeF_5^+][AsF_6^-]$[8,20] suggests a more distorted anion.

$[XeF_5^+][AsF_6^-]$. The atomic arrangement revealed by the structure analysis shows XeF_5 and AsF_6 groups which make close contacts to define the $(XeF_5AsF_6)_2$ rings shown in Figure 3. These rings have a form which is almost identical with that of the rings in the $(XeF_5)_2PdF_6$ structure.[1] In this unit each XeF_5 group makes bridging contacts to two AsF_6 groups, *via* one F ligand on one AsF_6 group and two F ligands on the other. Three F ligands (in cis relationship to one another) of each AsF_6 group each have bridging interaction with xenon. The intraionic distances and angles are listed in Table VII.

The XeF_5 group has essentially the same shape and size as the XeF_5 group in XeF_5PtF_6,[6] XeF_5RuF_6,[7] $(XeF_5)_2PdF_6$,[1] and crystalline XeF_6[21] and, as in those cases, is consistent with its designation as XeF_5^+ (see ref 1). The AsF_6 group, although distorted somewhat from the ideal octahedral symmetry of AsF_6^-, is nevertheless close enough in size and shape to be so designated. The average As-F distance is 1.72 Å with an average deviation of 0.03 Å. This is larger than the value for the $[Xe_2F_3^+][AsF_6^-]$ case in which As-F = 1.63 Å with an average deviation of 0.04 Å. Evidently there is appreciable librational motion of the AsF_6^- species in $[Xe_2F_3^+][AsF_6^-]$ as indicated by improved consistency after riding-motion correction. After this correction the average As-F distance is 1.74 Å with an average deviation of 0.03 Å. In $[XeF_5^+][AsF_6^-]$ the corrected As-F distance is 1.74 Å with an average deviation of 0.02 Å.

Discussion

These structures confirm that both xenon difluoride and xenon hexafluoride donate fluoride ion to generate the AsF_6^- ion. The discovery that XeF_2 and XeF_6 each form complexes with AsF_5, but that XeF_4 does not, was made by Bartlett and Sladky[10] and they exploited this finding to effect a chemical purification of XeF_4. With AsF_5, XeF_2 forms not only $[Xe_2F_3^+][AsF_6^-]$ but also a 1:1 complex which is $[XeF^+][AsF_6^-]$,[2,7] and XeF_6 forms $[XeF_5^+][AsF_6^-]$ and $[Xe_2F_{11}^+][AsF_6^-]$,[8,10] whereas XeF_4 does not form any complex under normal conditions of temperature and pressure. Evidently XeF_4, as Bartlett and Sladky had supposed, must be an inferior F^- donor compared with either XeF_2 or XeF_6. Only SbF_5 (which is the best F^- acceptor) forms XeF_3^+ salts[22,23] with XeF_4.

It is not, at first sight, surprising that XeF_4 is less effective than XeF_2 as a fluoride ion donor, since the greater positive charge[24] on the xenon atom in XeF_4, relative to that for the XeF_2 case, is anticipated to contribute to a greater ionization energy $[\Delta H(XeF_x \rightarrow XeF_{x-1}^+ + F^-)]$ for XeF_4. Moreover, the greater size of the XeF_3^+ ion relative to XeF^+ should result in a smaller lattice energy for a salt $[XeF_3^+][A^-]$. However, Berkowitz and his coworkers have determined[25] the ionization enthalpies for the xenon fluorides, and although the XeF_4 ionization enthalpy is greater than for XeF_2, it is only slightly so, the values being 9.66 eV for XeF_4 and 9.45

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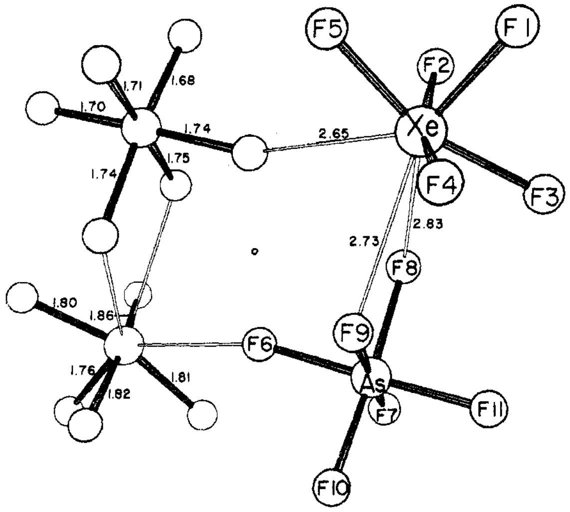

Figure 3. Configuration and bond distances for $[XeF_5^+][AsF_6^-]$. Perspective view roughly perpendicular to the *bc* plane showing the cation-anion clusters about the center of symmetry at $^1/_2, 0, ^1/_2$. Estimated standard deviation for all bond lengths shown is 0.02 Å.

Table VII. Interatomic Distances (Å) and Angles (deg) within the Asymmetric Structural Unit of $[XeF_5^+][AsF_6^-]$[a]

Xe–F(1)	1.76	F(1)–Xe–F(2)	80	F(6)–As–F(7)	90
F(2)	1.82	F(3)	80	F(8)	87
F(3)	1.80	F(4)	82	F(9)	89
F(4)	1.86	F(5)	79	F(10)	90
F(5)	1.81	F(6)	141	F(7)–As–F(8)	92
F(6)	2.65	F(8)[b]	139	F(10)	92
F(8)	2.83	F(9)[b]	148	F(11)	92
F(9)	2.73	F(2)–Xe–F(3)[b]	89	F(8)–As–F(9)	85
As–F(6)	1.74 [1.77][c]	F(5)	89	F(11)	91
F(7)	1.71 [1.74]	F(3)–Xe–F(4)	86	F(9)–As–F(10)	90
F(8)	1.74 [1.75]	F(4)–Xe–F(5)	90	F(11)	89
F(9)	1.75 [1.77]	Xe–F(6)–As	158	F(10)–As–F(11)	91
F(10)	1.68 [1.71]	Xe–F(8)–As	110	F(6)–Xe–F(8)	63
F(11)	1.70 [1.73]	Xe–F(9)–As	114	F(9)	70
				F(8)–Xe–F(9)	50

[a] Estimated standard deviations are, for all values shown, 0.02 Å for distances and 1° for angles. [b] Atom related by center of symmetry at $^1/_2, 0, ^1/_2$. [c] Values in brackets are distances corrected for libration of AsF_6^- assuming riding motion of each light atom on the heavier.

eV for XeF_2. Presumably the ionization of XeF_4 is aided by a steric factor. If all nonbonding xenon electron pairs are visualized as being sterically active (which assumption is in accord with the observed stereochemistry[23]), XeF_2 is a five-coordinate, trigonal-bipyramidal molecule and its simple ion XeF^+ is pseudotetrahedral. Xenon tetrafluoride is more crowded than XeF_2, since it is pseudooctahedral; hence conversion to the trigonal-bipyramidal XeF_3^+ cation[23] may offer a more significant reduction in the ligand and nonbonding pair repulsions than in the XeF_2-XeF^+ case.

The chemical evidence[8,10] and the data[25] of Berkowitz and his coworkers $[\Delta H(XeF_6 \rightarrow XeF_5^+ + F^-) = 9.24 \text{ eV}]$ confirm that XeF_6 is the best fluoride ion donor of the xenon fluorides. In xenon hexafluoride, the ligand and nonbonding pair crowding is presumably much more severe than in the XeF_4 case. The seven-coordinate molecule[26] generates a pseudooctahedral cation on ionization. The evident steric activity of the nonbonding xenon valence electron pair in $[XeF_5^+][AsF_6^-]$ again conforms to the pseudooctahedral model, as Figures 3 and 4 demonstrate.[27] There is, presumably, an appreciable decrease in the coordination sphere interactions accompanying the change $XeF_6 \rightarrow XeF_5^+ + F^-$.[28] This decrease in the ligand-ligand and ligand-nonbonding pair interactions must more than offset those features which are less favorable to ionization in the XeF_6 case, *i.e.*, (1) the greater charge on xenon in XeF_6 relative to XeF_4 or XeF_2 and (2) the greater size of the XeF_5^+ ion relative to XeF_3^+ or XeF^+.

Xenon difluoride yields salts of the simple cation XeF^+ with the best fluoride ion acceptors, and several salts of this cation have been described[2,7,29] and its high electron affinity and its powerfully polarizing nature have been emphasized.[7,26] The simple cation in $[XeF^+][AsF_6^-]$[30] and $[XeF^+][RuF_6^-]$[7] has a bond length of 1.88 Å, which is slightly shorter than the terminal Xe-F bonds in the $Xe_2F_3^+$ cation[2] which has been defined in this study. The shape and dimensions of the $Xe_2F_3^+$ cation conform to its representation as a resonance hybrid of canonical forms $(F\text{-}Xe)^+F^-(Xe\text{-}F)^+$, $F^-(Xe\text{-}F)^+(Xe\text{-}F)^+$, and $(F\text{-}Xe)^+(F\text{-}Xe)^+F^-$, with the first form dominant. Indeed on this basis the salt $[Xe_2F_3^+][AsF_6^-]$ approximates to $[(XeF)^+]_2F^-AsF_6^-$. Fluoride ion is much more electron rich than any F^- ligand in AsF_6^-. It is, therefore, not surprising that the XeF^+ species should interact more strongly with F^- than with AsF_6^-, as the $[Xe_2F_3^+][AsF_6^-]$ structure, shown in Figure 2, demonstrates. It is of interest that recent work in these laboratories[31] has established XeF_2 complexes with PdF_4 of compositions 2:1, 1:1, and 1:2, which Raman and infrared data indicate are

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(26) R. M. Gavin, Jr., and L. S. Bartell, *J. Chem. Phys.*, 48, 2460 (1968); L. S. Bartell and R. M. Gavin, Jr., *ibid*, 48, 2466 (1968); R. D. Burbank and N. Bartlett, *Chem. Commun.*, 645 (1968).

(27) Note, in Figure 4, that the sites for the nonbonding pairs of the XeF_5^+ ions, which lie on the pseudo-fourfold axes of the cations, are related by the center of symmetry of the $(XeF_5AsF_6)_2$ rings. The pseudo-fourfold axis of one cation is tilted away from the other; this tilting would reduce the nonbonding-nonbonding pair interactions.

(28) There are a number of reasons for accepting the view that the bonding in the xenon fluorides maintains (approximately) the xenon octet while simultaneously satisfying the tendency of fluorine to adopt an octet (see N. Bartlett, *Endeavour*, 31, 107 (1972)). Accordingly, each of the Xe-F bonds in the molecules (following J. Bilham and J. W. Linnett, *Nature* (*London*), 301, 1323 (1964)) is a single-electron bond whereas in a species such as $Xe\text{-}F^+$ the bond is an electron-pair bond. The formation of an electron-pair bond must assist in the ionization process $XeF_x \rightarrow XeF_{x-1}^+ + F^-$, but this presumably would be approximately the same for each xenon fluoride. In the ionization of both XeF_2 and XeF_4, separation of a linear F-Xe-F system into F^- and $(Xe\text{-}F)^+$ occurs. Presumably, the separation of a fluoride ion from these fluorides is also assisted by the repulsive interactions of the F^- with the other ligand species and the nonbonding xenon valence electron pairs. Thus the XeF_2 molecule may be visualized as a trigonal bipyramid with three equatorial nonbonding "pairs." In the cation these three "pairs" have moved in toward the molecular axis along which the F^- has departed and they help shield the positive charge of the cation from the anion. Similarly, the removal of F, as F^-, from a corner of the square XeF_4 molecule, is visualized as being accompanied by a relocation of the two Xe "pairs" at the poles of the molecule. This relocation brings the "pairs" toward one another (as they become equatorial "pairs" of the trigonal-bipyramidal cation) and toward the departing F^-. Although XeF_6 is not octahedral, it is not far removed from that shape and we can allow that each F ligand has another F ligand at least approximately trans to it. In the ionization of XeF_6, then, as in the other cases, we can assume that the removal of F^- is associated with the development of an electron-pair Xe-F bond on the axis trans to it. But if we accept the structural evidence on XeF_5^+ as supportive of steric activity of the nonbonding Xe valence-electron pair, the sterically active "pair" occupies the coordination site vacated by F^-. Perhaps, here, we have the major reason for the unexpected fluoro basicity of XeF_6.

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

(30) A. Zalkin, D. L. Ward, D. H. Templeton, and N. Bartlett, to be submitted for publication.

(31) B. Zemva and N. Bartlett, to be submitted for publication; N. Bartlett, B. Zemva, and A. Tressaud, Abstracts, Seventh International Fluorine Symposium, Santa Cruz, Calif., July 15-20, 1973, Paper I-49.

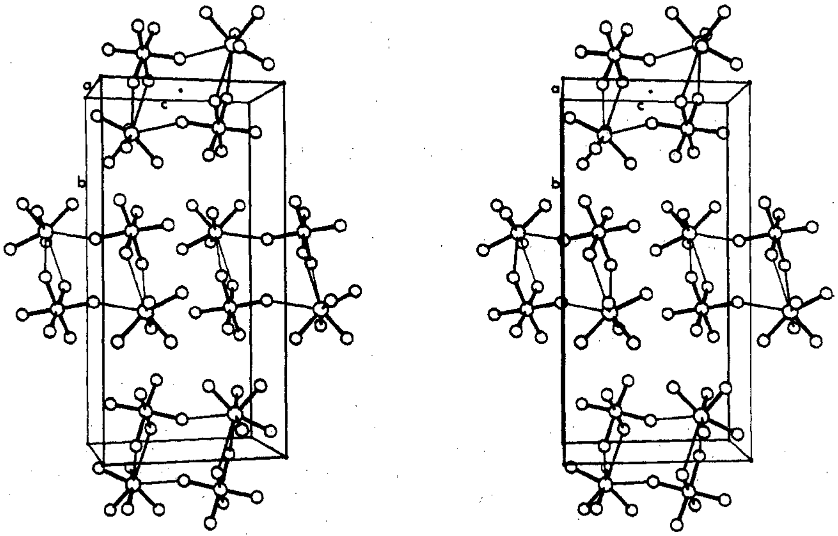

Figure 4. Stereoscopic view of the $[XeF_5^+][AsF_6^-]$ structure.

$(XeF)^+$ salts. There are also thermogravimetric data which suggest compounds $(XeF_2)_4{\cdot}PdF_4$; these may well be $[(Xe_2F_3)^+]_2[PdF_6^{2-}]$. Thus the $Xe_2F_3^+$ ion may even be stable in a doubly charged anion lattice.

The twofold coordination of the bridging F atom in $Xe_2F_3^+$ is reminiscent of the bridging F atom in $F_3H_2^-$.[32] The relationship of the latter to $F_4H_3^-$ and $F_5H_4^-$ [33] poses the question of the possible existence of the species $F_4Xe_2^{2+}$ and $F_5Xe_4^{3+}$. The dipositive cation may indeed be possible in the environment of a very favorable dinegative anion such as PdF_6^{2-}. The existence of a phase $(XeF_2)_3PdF_4$ has been indicated but structural data are not yet available to settle whether the compound is $(Xe_3F_4)^{2+}PdF_6^{2-}$ or $(Xe_2F_3)^+(XeF)^+PdF_6^{2-}$.

Efforts to prepare the bridged species $Xe_2F_7^+$ by adding XeF_4 to $[XeF_3^+][SbF_6^-]$ failed,[23] but the bridged cation $Xe_2F_{11}^+$ has been recognized as a stable ion for several years.[8] Although crystals of $[Xe_2F_{11}^+][AsF_6^-]$ have been grown from the melt and from bromine pentafluoride solution and have provided unit cell and space group information,[8] no satisfactory crystal was found in our studies to warrant a structural study. Fortunately suitable single crystals of $[Xe_2F_{11}^+][AuF_6^-]$ have been obtained and the structure is reported in the accompanying paper.[34] Since the unit cell and space group of $[XeF_5^+][AuF_6^-]$[20] are the same as for $[XeF_5^+][AsF_6^-]$ (indeed the salts are almost isodimensional), it is possible that the structure of $[Xe_2F_{11}^+][AsF_6^-]$ will be similar to that seen in the gold compound.

The structure of $[XeF_5^+][AsF_6^-]$ (Figures 3 and 4) is not like those of $[XeF_5^+][RuF_6^-]$[7] and $[XeF_5^+][PtF_6^-]$[6] in that each XeF_5^+ is coordinated to only three F atoms of two anions whereas in the other salts the cation is coordinated to four F ligands of four separate anions. Nevertheless, as has been discussed previously,[1] the XeF_5^+ size and shape are not significantly different from those seen in the other XeF_5^+ salts (including XeF_6 itself). Moreover, the XeF_5^+ coordination in $[(XeF_5)^+]_2[PdF_6^{2-}]$[1] is almost exactly the same as that seen here.

It is not yet known why certain octahedral anion salts (*e.g.*, AsF_6^-, AuF_6^-, PdF_6^{2-}) should show different cation coordination than others [*e.g.*, RuF_6^-,[7] PtF_6^-,[6] IrF_6^-,[10] SbF_6^- [35]]. The XeF_5^+ case is not an isolated one. It is usual for AsF_6^- salts of the alkali metals to be of NaCl type whereas for SbF_6^-, PtF_6^-, IrF_6^-, and RuF_6^- the CsCl lattice is preferred.[9] Even $[IF_6^+][AsF_6^-]$ has an NaCl lattice,[36] whereas for $[IF_6^+][MF_6^-]$ (M = Ru, Pt, Sb) a CsCl type is preferred.[37] It seems that the coordinating character of the F ligand of AsF_6^- is not the same as for SbF_6^-, whereas the latter species appears to be similar to the majority of the transition metal MF_6^- species. Certainly the AsF_6^- anion is smaller than the other MF_6^- mentioned. Also AuF_6^- is the smallest MF_6^- anion of the third transition series.[38] The structure type changes may, therefore, simply be related to the effective F ligand size although this in itself may be related to changes in the hybridization of the F ligand oribtals and the special arrangement of the formally nonbonding electrons of the F ligand.

Acknowledgments. The work relating to $[Xe_2F_3^+][AsF_6^-]$ was carried out by N. B. during the tenure of a Miller Visiting Professorship (1967-1968) and was also supported by the National Science Foundation under Contract No. GP-7153X. The remainder of the work was supported by the Atomic Energy Commission.

Registry No. $[Xe_2F_3^+][AsF_6^-]$, 50432-32-1; $[XeF_5^+][AsF_6^-]$, 49756-76-5.

Supplementary Material Available. Tables II and IV, listings of structure factor amplitudes, will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th 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-74-780.

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[35] X-Ray powder photographs of $[XeF_5^+][SbF_6^-]$ are almost identical with those of the Pt, Ir, and Ru relatives, whereas, the $[XeF_5^+][AsF_6^-]$ pattern is distinctly different (although very like that of $[XeF_5^+][AuF_6^-]$).

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