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.

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

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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

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[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).

vibrational spectroscopic studies[5] of the $XeF_2 \cdot MF_5$ complexes indicated that they were, at least approximately, the salts $[FXe^+][MF_6^-]$. On this basis, XeF_4 was seen to be inferior as a fluoride ion donor to both XeF_2 and XeF_6.

Crystal structure support for the $[FXe^+][MF_6^-]$ salt formulation was clearly desirable to confirm this peculiar fluoride ion donor behavior of the binary xenon fluorides. However, the $[FXe][MF_6]$ compounds were also of interest to us because the compounds $[FXe][PtF_6]$ and $[FXe][RhF_6]$ are formed when xenon interacts with the appropriate hexafluoride in excess[2,5]

$$Xe + 2MF_6 \rightarrow [FXe][MF_6] + MF_5$$

The ruthenium compound $[FXe][RuF_6]$ was chosen as the representative of the $[FXe][MF_6]$ class, since the X-ray scattering factor for Ru is less dominant than the Ir or Pt factors and the RuF_5 complex is more readily prepared and handled than its RhF_5 relative. To provide for a direct comparison of the XeF^+ and XeF_5^+ species, the crystal structure of $[XeF_5^+][RuF_6^-]$ was also carried out. A secondary purpose of the latter study was to improve the description of the XeF_5^+ ion, since the precision of the $[XeF_5^+][PtF_6^-]$ structure determination[4] was rather low.

Experimental Section

The 1:1 XeF_2-RuF_5 complex was made by fusion, at 120°, of the components, which were prepared as previously described.[5] Crystals of the compound were grown by slow solidification of minute quantities of the fused material contained in closed quartz X-ray capillaries. An electrically heated tube, with a smooth temperature gradient from 100 to 120° along its length, provided for the crystal development.

The 1:1 XeF_6-RuF_5 complex was prepared by fluorinating a sample of the 1:1 XeF_2-RuF_5 complex with excess gaseous fluorine (460 Torr) at 350° overnight. The X-ray powder photograph and the melting point (152°) agreed with the findings of Bartlett and Gibler.[6] Crystals were grown in quartz X-ray capillaries by sublimation under reduced pressure. This was accomplished by placing quartz capillaries, open end being uppermost and each containing a minute amount of the compound, in a Pyrex tube which was evacuated and held at approximately 94°. The quartz capillaries were unloaded from the container in a dry nitrogen atmosphere and were sealed by drawing down in a small flame.

Crystal Data

$XeRuF_7$ (mol wt 365.36) is monoclinic with $a = 7.991$, $b = 11.086$, $c = 7.250$ Å (all ±0.006 Å), $\beta = 90.68 \pm 0.05°$, $V = 642.2$ Å^3, $Z = 4$, and $d_c = 3.78$ g cm^{-3}. Single-crystal precession photographs established the following conditions limiting possible reflections: hkl, none; $h0l$, $h + l = 2n$; $0k0$, $k = 2n$. These indicated the space group $P2_1/n$ (an alternate setting of space group No. 14 in ref 7). The structure was successfully refined in this space group. (The equivalent positions for this setting are as follows: $x, y, z; \bar{x}, \bar{y}, \bar{z}; {}^1/_2 - x, {}^1/_2 + y, {}^1/_2 - z; {}^1/_2 + x, {}^1/_2 - y, {}^1/_2 + z$.)

$XeRuF_{11}$ (mol wt 441.35) is orthorhombic with $a = 16.771$, $b = 8.206$, $c = 5.617$ Å (all ±0.010 Å), $V = 773.03$ Å^3, $Z = 4$, and $d_c = 3.79$ g cm^{-3}. Single-crystal precession and Weissenberg photographs established the following conditions limiting possible reflections: hkl, none; $0kl$, $k + l = 2n$; $hk0$, $h = 2n$. These indicated space groups $Pnma$ or $Pn2_1a$. The structure was successfully refined in the former group (No. 62 in ref 7).

X-Ray Measurements

A Picker automatic four-circle diffractometer, equipped with a fine-focus Mo anode tube, was used for data collection. For each crystal 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.[8] The only differences from the previously described procedure for the data treatment were in the choices for the value of q, the arbitrary factor, employed to prevent the relative error for large counts becoming unrealistically small. A value $q = 0.05$ was assumed for the treatment of the data from each crystal.

$XeRuF_7$. The crystal used was an irregularly shaped, roughly oval tablet ~0.3 × 0.2 × 0.1 mm. Two unique data sets, $\bar{h}kl$ and hkl, were collected for $2\theta \leqslant 60°$. Intensities of two standards were collected at intervals of every 60 reflections. A total of 4137 intensity data were recorded which were averaged to yield a data set of 1887 independent reflections. The absorption coefficient μ is 78.04 cm^{-1}. The crystal was lost (by hydrolytic decomposition) before a precise description, appropriate for an absorption correction, had been made of it.

$XeRuF_{11}$. A tablet of dimensions 0.15 × 0.10 × 0.06 mm (with c^* approximately parrallel to the capillary axis) was selected for the data collection. Intensity data were collected for the sets of reflections $\bar{h}kl$ and $h\bar{k}l$, for $2\theta \leqslant 55°$. Intensities of three strong reflections were used as standards and were recorded every 150 reflections. They showed no change during the period of data collection. A total of 2948 intensity data were recorded which were averaged to give a set of 960 independent reflections. The absorption coefficient μ is 65.76 cm^{-1}. No absorption correction was made.

Structure Refinements

The least-squares program used in the structure refinements was as previously described.[8] Scattering factors for neutral fluorine, ruthenium, and xenon were used as given by Cromer and Mann.[9]

$XeRuF_7$. The positions of the heavy atoms were determined from a three-dimensional Patterson synthesis. The peak intensities did not support unequivocal assignment of the xenon or ruthenium atoms to the two sets of positions. Both possibilities were subjected to least-squares refinement and although the agreement factor was roughly the same for the two cases, one showed large temperature factor anomalies. A difference Fourier based on the other case revealed six peaks, assignable to fluorine atoms, in a near-octahedral disposition about the Ru atom, with a seventh peak, attributable to a F atom, approximately 2 Å away from the Xe atom. Another least-squares refinement including these fluorine atoms resulted in a conventional R factor of 0.20 which improved to 0.13 when the heavy atoms were allowed anisotropic temperature factors. Further full-matrix refinements with all atoms anisotropic gave $R = 0.09$, $R_w = 0.11$.

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 ($((\sin\theta)/\lambda \leqslant 0.20)$) were given zero weight in the final least-squares refinements. This procedure resulted in $R = 0.07$, $R_w = 0.08$, and a standard deviation for an observation of unit weight of 1.28. The number of nonzero-weighted data in this refinement was 1044. A final difference Fourier revealed one peak (3 e/Å^3) 0.8 Å from the Xe atom position and two peaks (each 2 e/Å^3) symmetrically disposed at ~1 Å from the Ru atom position. These features could be a consequence of our failure to correct the intensity data for absorption effects. This same deficiency in the data is even more likely to be responsible for the peculiar anisotropies in the atomic thermal parameters. The positional and thermal parameters, reported in Table I, are from the last refinement. The F_o and F_c data for $[XeF][RuF_6]$ (Table VI) and $[XeF_5][RuF_6]$ (Table VII) are given in the microfilm version of this paper.[10]

$XeRuF_{11}$. Since X-ray powder patterns and Raman spectra indicated $F_{11}XeRu$ to be isostructural with the platinum compound, initial atomic parameters were taken from the platinum structure.[4] A three-dimensional Patterson analysis verified the heavy-atom positions. A difference Fourier established the positions of the fluorine atoms to be similar to the arrangement in the $[XeF_5^+][PtF_6^-]$ structure. Three cycles of a full-matrix least-squares refinement employing 737 reflections having $I \geqslant \sigma(I)$ yielded $R = 0.083$. Allowing anisotropic parameters for heavy atoms reduced R to 0.074. Finally, a full-matrix refinement with all atoms anisotropic gave a conventional

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(5) F. O. Sladky, P. A. Bulliner, and N. Bartlett, *J. Chem. Soc. A*, 2179 (1969).

(6) N. Bartlett and D. D. Gibler, unpublished findings.

(7) "International Tables for X-Ray Crystallography," Vol. 1, Kynoch Press, Birmingham, England, 1952.

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

(9) D. T. Cromer and B. Mann, *Acta Crystallogr., Sect. A*, **24**, 321 (1968).

(10) Tables VI and VII, listings of observed and calculated 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-73-1717.

Table I. Final Positional and Thermal Parameters for $XeRuF_7$

Atom	x	y	z	B_{11}[a]	B_{22}	B_{33}	B_{12}	B_{23}	B_{13}	Rmsd[c]
Ru	0.2493 (2)[b]	0.0358 (1)	0.7785 (2)	2.90 (5)	3.39 (6)	6.29 (7)	0.26 (4)	1.13 (4)	0.37 (5)	0.2303
Xe	0.2432 (1)	0.2160 (1)	0.3294 (1)	3.14 (4)	4.73 (6)	4.75 (4)	0.26 (4)	0.77 (3)	0.36 (4)	0.2308
F(1)	0.1952 (32)	0.3329 (25)	0.1503 (28)	14.97 (1.28)	15.11 (1.73)	11.31 (1.16)	8.58 (1.31)	5.93 (1.04)	8.11 (1.23)	0.4173
F(2)	0.3118 (22)	0.0787 (22)	0.5232 (22)	10.08 (1.02)	10.29 (1.13)	8.19 (70)	4.26 (84)	4.19 (69)	3.67 (73)	0.3466
F(3)	0.1905 (21)	−0.0049 (24)	0.0059 (24)	8.89 (1.02)	12.93 (1.26)	8.85 (79)	−0.93 (94)	3.09 (73)	1.94 (88)	0.3595
F(4)	0.4175 (19)	−0.0683 (14)	0.7697 (26)	6.81 (80)	7.52 (80)	13.52 (1.03)	4.97 (68)	1.68 (71)	2.37 (75)	0.3427
F(5)	0.0855 (20)	0.1457 (14)	0.7677 (31)	7.14 (46)	7.01 (84)	16.51 (1.33)	4.31 (69)	3.55 (84)	1.55 (86)	0.3593
F(6)	0.1025 (21)	−0.0768 (17)	0.6919 (30)	6.73 (82)	10.44 (1.17)	16.35 (1.38)	−4.34 (77)	−0.92 (83)	−5.59 (1.12)	0.3764
F(7)	0.3910 (16)	0.1529 (15)	0.8676 (28)	5.00 (61)	8.84 (1.04)	14.75 (1.19)	−3.25 (63)	−1.29 (65)	−3.57 (94)	0.3477

[a] The form of the anisotropic thermal ellipsoid is $\exp(-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - 2\beta_{12}hk - 2\beta_{13}hl - 2\beta_{23}kl)$. The $B_{ij} = 4\beta_{ij}/a_i^*a_j^*$, where a_i^* and a_j^* are the ith and jth reciprocal cell lengths. [b] Number in parentheses is the estimated standard deviation in the least significant digit. [c] Root-mean-square displacement.

Table II. Final Positional and Thermal Parameters for $[XeF_5^+][RuF_6^-]$[a]

Atom	x	y	z	B_{11}[a]	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	Rmsd
Ru	0.54318 (7)	1/4	0.2205 (2)	2.29 (5)	1.83 (5)	2.12 (6)	0	−0.17 (4)	0	0.1623
Xe	0.34978 (6)	1/4	0.7009 (2)	2.09 (4)	3.16 (5)	2.93 (5)	0	−0.37 (4)	0	0.1859
F(3)	0.5417 (4)	0.4754 (8)	0.227 (1)	5.0 (4)	2.3 (2)	4.3 (4)	−0.3 (2)	−0.8 (3)	0.6 (3)	0.2213
F(4)	0.4880 (6)	1/4	0.511 (2)	3.6 (5)	3.8 (4)	2.6 (5)	0	−0.0 (3)	0	0.2044
F(5)	0.5921 (6)	1/4	−0.069 (2)	3.2 (5)	5.8 (6)	4.2 (6)	0	1.3 (4)	0	0.2359
F(6)	0.6392 (6)	1/4	0.374 (2)	2.1 (4)	4.3 (5)	4.7 (6)	0	−0.6 (4)	0	0.2160
F(7)	0.4443 (5)	1/4	0.068 (2)	2.9 (4)	3.2 (4)	2.1 (4)	0	−0.3 (3)	0	0.1869
F(8)	0.3457 (5)	0.0939 (8)	0.464 (1)	6.1 (5)	3.4 (3)	3.6 (4)	0	−1.6 (3)	0	0.2355
F(9)	0.3128 (5)	0.0955 (9)	0.911 (2)	5.2 (4)	4.3 (4)	4.8 (4)	−0.9 (3)	0.1 (3)	0.8 (3)	0.2459
F(10)	0.2456 (6)	1/4	0.629 (3)	1.3 (4)	7.3 (7)	8.4 (9)	0	−2.3 (5)	0	0.2675

[a] See footnotes to Table I.

R factor of 0.062. At this point limiting the refinement to the 556 reflections where $I \geqslant 3\sigma(I)$ reduced R to 0.042, $R_w = 0.078$, and a standard deviation for an observation of unit weight 1.08. The highest peak on a final difference Fourier proved to be only 0.04 of the intensity of one fluorine peak in the original Fourier. Final positional and thermal parameters are given in Table II.[10]

Description of Structures

$XeRuF_7$. The crystal structure consists of an ordered arrangement of discrete [FXe][FRuF$_5$] units, the closest contact between units being 2.90 (27) Å, which is a contact between fluorine atoms F(7) and F(1) bound to ruthenium and xenon, respectively.

The xenon atom in the formula unit is linearly coordinated to two fluorine atoms (angle F(1)-Xe-F(2) = 177.08 (1.23)°). One fluorine atom (F(1)) is close to the xenon atom (Xe-F(1) = 1.872 (17) Å) and the other (F(2)), although more distant from the xenon atom (Xe-F(2) = 2.182 (15) Å), makes a close contact with the ruthenium atom (Ru-F(2) = 1.919 (13) Å). The other five fluorine atoms, of the formula unit, complete a distorted octahedral coordination of the ruthenium atom. The closest contacts between a xenon of one formula unit and fluorine atoms in neighboring units exceed 3.1 Å. The geometry of the formula unit is shown in Figure 1. The arrangement of the structural units in the lattice is illustrated in Figure 2. Interatomic distances and angles are given in Table III.

$XeRuF_{11}$. The structural analysis shows each xenon atom to be close-coordinated by five fluorine atoms in an approximately square-pyramidal arrangement. Each ruthenium atom is surrounded by six fluorine atoms in a distinct, approximately octahedral RuF_6 group. The XeF_5 and RuF_6 groups are so arranged that each XeF_5 group is nearly equidistant from four RuF_6 groups, such that one F atom from each RuF_6 group is less than 3.0 Å distant from the xenon atom. The four F atoms from the four separate RuF_6 groups are approximately coplanar. They are arranged about the pseudo-fourfold axis of the XeF_5 group, in a staggered configuration with respect to the basal fluorine atoms of that group. The xenon coordination in fluorine atoms can therefore be described as a distorted, capped archimedian antiprism. The important interatomic distances and the group geometries and dispositions are illustrated in Figure 3 and the group arrangements in the crystal lattice may be seen from

Table III. Interatomic Distances (Å) and Angles (deg) for $[XeF^+][RuF_6^-]$ (All F–F Contacts ≥2.5 Å)

Ru-F(2)	1.919 (13)[a]	*1.971*[b]	F(2)-Ru-F(4)	85.65 (76)
Ru-F(3)	1.778 (16)	*1.838*	F(2)-Ru-F(5)	89.36 (98)
Ru-F(4)	1.781 (12)	*1.837*	F(2)-Ru-F(6)	91.30 (105)
Ru-F(5)	1.789 (13)	*1.853*	F(2)-Ru-F(7)	89.21 (98)
Ru-F(6)	1.820 (14)	*1.899*	F(3)-Ru-F(4)	94.27 (121)
Ru-F(7)	1.835 (13)	*1.896*	F(3)-Ru-F(5)	90.73 (93)
Xe-F(1)	1.872 (17)	*1.968*	F(3)-Ru-F(6)	88.22 (109)
Xe-F(2)	2.182 (15)	*2.224*	F(3)-Ru-F(7)	91.28 (113)
Xe-F(5)	3.163 (13)		F(4)-Ru-F(6)	91.25 (104)
Xe-F(6)	3.171 (15)		F(4)-Ru-F(7)	90.77 (82)
Xe-F(7)	3.172 (13)		F(5)-Ru-F(6)	89.08 (123)
Xe-F(4)	3.256 (12)		F(5)-Ru-F(7)	88.93 (86)
Xe-F(3)	3.483 (29)		F(1)-Xe-F(2)	177.08 (123)
Xe-F(5)	3.506 (20)		Xe-F(2)-Ru	137.19 (46)
Xe-F(7)	3.625 (21)			

[a] Estimated standard deviations in parentheses. [b] Italicized bond length values are adjusted for riding of the F atom on the heavy atom in the bond.

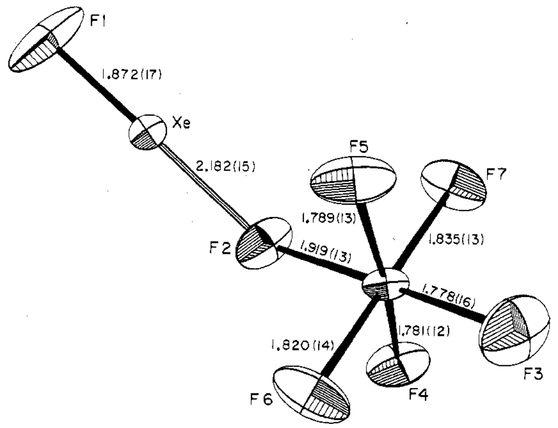

Figure 1. The $[XeF^+][RuF_6^-]$ structural unit (distances in angstroms and standard deviations in parentheses).

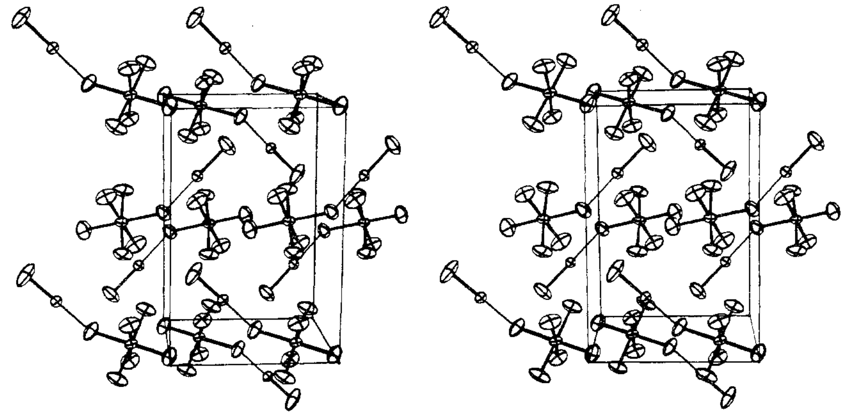

Figure 2. Stereoscopic view to show packing of the [XeF][RuF_6] units in the crystal lattice.

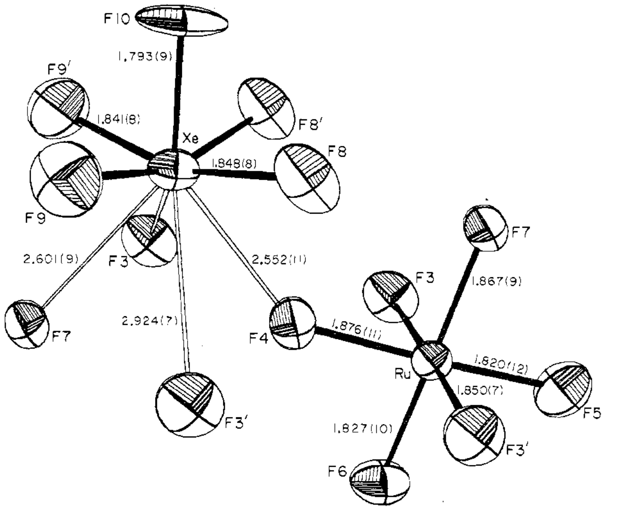

Figure 3. The XeF_5^+ and RuF_6^- structural units and the coordination of XeF_5^+ (distances in angstroms and standard deviations in parentheses).

the stereoscopic view given in Figure 4. Interatomic distances and angles are given in Table IV.

Discussion

Comparison of the two structures reveals that the RuF_6 group is more distorted in $XeRuF_7$ than in $XeRuF_{11}$. The average Ru-F distance in the former is 1.81 Å and the longest bond (1.91 Å) is associated with the fluorine atom, F(2), which makes a close approach (2.19 Å) to the xenon atom. The shortest bond (Ru-F(3)) is trans to RuF(2). It appears that the RuF_6 distortion in $XeRuF_7$ is due primarily to the interaction of that group with the Xe-F group. In the $XeRuF_{11}$ case, the average Ru-F distance in the RuF_6 group is 1.85 Å and the greatest deviations from this value are only ±0.03 Å. It is seen that the fluorine atoms (F(4), F(3), F(3′)) which make closer contacts, each with a Xe atom of the four close XeF_5 groups, are associated with the longer Ru-F bonding. The separation of a RuF_6 group from a xenon atom in the $XeRuF_{11}$ case (closest contact Xe· · ·F(4) = 2.55 Å) is much greater than in the $XeRuF_7$ case (Xe· · ·F(2) = 2.19 Å). Another feature which appears to be common to the two structures is the angle Ru-F· · ·Xe which is approximately 140° in the $XeRuF_7$ and for three of the four associations in the $XeRuF_{11}$ case (the fourth is 155°).

The structure of $XeRuF_{11}$ indicates the formulation [XeF_5^+][RuF_6^-]. Such a formulation is compatible with the bond lengths in the RuF_6^- group. Although no alkali hexafluororuthenate(V) structure has been worked out in detail, it is known[11] that the hexafluororuthenates(V) are almost isodimensional with the other noble metal hexafluorometalates(V) (M = Rh, Os, Ir, Pt). The M-F distance in $KOsF_6$[12] is 1.82 Å and in $O_2^+PtF_6^-$ is 1.83 Å.[13]

The close similarity in shape of the XeF_5 species with that of IF_5 and TeF_5^-, as shown in Table V, supports its formulation as a cation. The angle F(axial)-Xe-F(equatorial) is ~80° for all three isoelectronic species. The bond length shortening in the sequence TeF_5^-, IF_5, XeF_5^+ may be attributed to the increase in the nuclear charge Te → Xe.[14] The

Table IV. Interatomic Distances (Å) and Angles (deg) for [XeF_5^+][RuF_6^-]

Ru-F(3)	1.850 (7)[a]	*1.867*[b]	F(4)-Ru-F(7)	87.76 (53)
Ru-F(4)	1.876 (11)	*1.886*	F(4)-Ru-F(6)	91.40 (61)
Ru-F(5)	1.820 (12)	*1.842*	F(5)-Ru-F(6)	91.36 (56)
Ru-F(6)	1.827 (10)	*1.844*	F(5)-Ru-F(7)	89.48 (61)
Ru-F(7)	1.867 (9)	*1.872*	F(6)-Ru-F(7)	179.16 (81)
Xe-F(3)	2.924 (7)		F(4)-Ru-F(5)	177.25 (79)
Xe-F(4)	2.552 (11)		F(3)-Xe-F(10)	129.59 (30)
Xe-F(7)	2.601 (9)		F(8)-Xe-F(8)	87.78 (25)
Xe-F(8)	1.848 (8)	*1.863*	F(8)-Xe-F(9)	88.44 (41)
Xe-F(9)	1.841 (8)	*1.861*	F(8)-Xe-F(10)	78.59 (43)
Xe-F(10)	1.793 (8)	*1.829*	F(9)-Xe-F(10)	79.43 (51)
			F(7)-Xe-F(10)	140.57 (65)
			F(4)-Xe-F(10)	142.26 (69)
			Ru-F(7)-Xe	154.86 (29)
			Ru-F(3)-Xe	139.91 (22)
			Ru-F(4)-Xe	144.26 (34)

[a] Estimated standard deviations in parentheses. [b] Italicized bond length values are adjusted for riding of the F atom on the heavy atom in the bond.

Table V. Comparison of XeF_5^+ with Isoelectronic Species

		IF_5		
	TeF_5^-	Gas	In $IF_5 \cdot XeF_2$	XeF_5^+
$E\text{-}F_{ax}$, Å	1.84 (2)	1.844 (25)	1.862 (10)	1.793 (8)
$E\text{-}F_{eq}$, Å	1.96 (2)	1.869 (5)	1.892 (5)	1.845 (9)
$F_{ax}\text{-}E\text{-}F_{eq}$, deg	78.8 (17)	81.9 (1)	80.9 (2)	79.0 (5)
Ref	*a*	*b*	*c*	*d*

[a] A. J. Edwards and M. A. Mouty, *J. Chem. Soc. A*, 703 (1969). [b] A. G. Robiette, R. H. Bradley, and P. N. Brier, *Chem. Commun.*, 1567 (1971). [c] G. R. Jones, R. D. Burbank, and N. Bartlett, *Inorg. Chem.*, 9, 2264 (1970). [d] Present work.

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(14) The bond angle constancy for the isoelectronic pair SF_3^+ and PF_3 has been established and is discussed in a recent paper[8] from this laboratory.

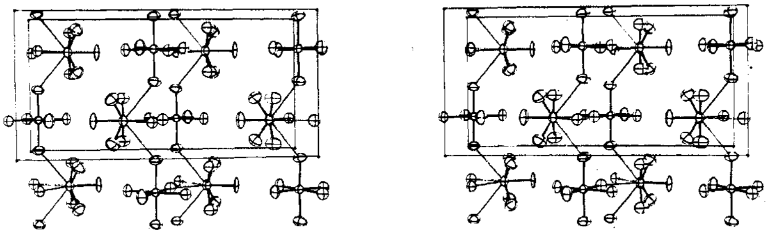

Figure 4. Stereoscopic view showing the arrangement of XeF_5^+ and RuF_6^- units in the crystal lattice.

XeF_5^+ species also occurs in the salts $[XeF_5^+][AsF_6^-]$ and $[XeF_5^+]_2[PdF_6^{2-}]$, the structures of which are reported in accompanying papers.[15,16] Crystalline XeF_6 may be formulated as $[XeF_5^+]F^-$.[17,18] It should be noted that the XeF_5^+ species occurring in those structures are similar in shape to that seen in $[XeF_5^+][RuF_6^-]$, but the coordination of the cation is often different. In both $[XeF_5^+][AsF_6^-]$[15] and $[XeF_5^+]_2[PdF_6^{2-}]$,[16] the xenon atom of the cation is associated with only two MF_6 anion species, the xenon atom being close to two F atoms of one anion and one F atom of another, these three F atoms forming an approximately triangular set. This set is approximately symmetrically disposed about the pseudo-fourfold axis and below the base of the XeF_5^+ ion pyramid.

Since the xenon atom in $[XeF_5^+]$ retains a nonbonding valence electron pair[19,20] we can suppose that this pair occupies a spatially directed orbital, such that the Xe atom is pseudooctahedrally coordinated with five F atoms and the sterically active valence-electron pair. With the "nonbonding pair" sterically active and projecting along the fourfold axis, the effective positive charge of the cation would be shielded along that axis. Negatively charged species would then be attracted most strongly when positioned off axis, as illustrated in Figure 5 (left). The fluorine ligands of the XeF_5 will themselves tend to be neutral or negatively charged; hence any negatively charged species will tend to be distributed below the basal plane of the XeF_5^+ ion and off axis, as observed.

As far as the $XeRuF_7$ compound is concerned it should be noted first that this is one of a series of isomorphous compounds which were formulated by Bartlett and his coworkers on the basis of vibrational spectroscopic evidence,[5] as the salts $[XeF^+][MF_6^-]$ (M = Sb, Ru, Rh, Ir, Pt). The structure observed for $XeRuF_7$ is in remarkable agreement with that postulated[5] on the basis of the spectroscopic evidence for $[XeF^+][MF_6^-]$. We might expect the effective center of positive charge of $[Xe\text{-}F]^+$ to lie near the xenon nucleus. If, however, we allow that each octet of electrons about each atom in the cation is distributed as represented by an electron-pair repulsion model[21] or by a Linnet spin-quartet description,[22] the positive charge is seen to be least shielded on the molecular axis (as illustrated in Figure 5 (right)). We would, therefore, anticipate that any interaction with one negatively charged ligand (L) would result in a linear disposition $F\text{-}Xe^+\cdots L$.

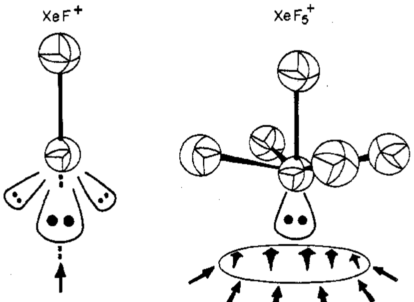

Figure 5. Representation of the influence of nonbonding valence-electron pairs, of the Xe atom, upon the polarizing character of XeF^+ and XeF_5^+ ions. (Arrows indicate directions of maximum polarization of anions by the cations.)

The valence-bond model proposed by Coulson[23] for XeF_2 is probably the most informative description to apply to $XeRuF_7$. Following the XeF_2 description,[23] where the dominant canonical forms in the resonance hybrid are $(F\text{-}Xe)^+F^-$ and $F^-(Xe\text{-}F)^+$, the anticipated canonical forms for $XeRuF_7$ are $(F\text{-}Xe)^+(RuF_6)^-$ and $F^-(Xe\text{-}F)^+RuF_5$. Since the Xe-F(1) bond (1.88 Å) is much shorter than the Xe-F bond in XeF_2 (2.01 Å), it is evident that the canonical form $[FXe]^+[RuF_6]^-$ must be dominant (see ref 24).

Although the rather short cation-anion contacts in $[XeF^+][RuF_6^-]$ and in $[XeF_5^+][RuF_6^-]$ could be interpreted as evidence of some covalency, we believe that the ionic formulations, with due allowance for the polarizing influence and symmetry of the cation, provide simple and sufficient explanations.

Registry No. $[XeF^+][RuF_6^-]$, 39796-97-9; $[XeF_5^+][RuF_6^-]$, 39796-98-0.

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(19) The Xe-F bond shortening accompanying the loss of F^- from XeF_6 (where Xe-F = 1.89 Å[20]) may be associated in part with the transition of the nonbonding pair from an orbital which approximates to Xe 6s to a spatially directed orbital (*e.g.*, an sp hybrid). Thus the F ligands in XeF_5^+ would not only experience less ligand crowding than in XeF_6 but would experience a higher effective nuclear charge at the Xe atom than in XeF_6. Moreover it can be argued that the ligand crowding in XeF_6 tends to inhibit steric activity of the "nonbonding pair," which, therefore, tends to be in a Xe 6s type orbital. Release of F^- provides for the steric activity of the "pair" and accompanying Xe-F bond strength enhancement. Conversely the tendency of the "nonbonding" valence-electron pair in XeF_6 to steric activity may well be responsible for the relative ease of fluoride ion donation by XeF_6.

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