Title
THE CRYSTAL STRUCTURES OF [XeF]+[RuF6]- AND [XeF5]+ [Ruf]-

Author
Bartlett, N.

Publication Date
1972-08-01

Submitted to Inorganic Chemistry

LBL-850
Preprint

THE CRYSTAL STRUCTURES OF $[XeF]^+[RuF_6]^-$ AND $[XeF_5]^+[RuF_6]^-$

N. Bartlett, M. Gennis, D. D. Gibler,
B. K. Morrell and A. Zalkin

August 1972

AEC Contract No. W-7405-eng-48

LBL-850

DISCLAIMER

Contribution from The Lawrence Berkeley Laboratory and The Department of Chemistry; University of California, Berkeley, California 94720

THE CRYSTAL STRUCTURES OF $[XeF]^+[RuF_6]^-$ and $[XeF_5]^+[RuF_6]^-$

by

N. Bartlett, M. Gennis, D. D. Gibler, B. K. Morrell and A. Zalkin

ABSTRACT

Ruthenium pentafluoride forms complexes with XeF_2 and with XeF_6 but not with XeF_4. The compound $XeRuF_7$ is monoclinic with $\underline{a}$ = 7.991, $\underline{b}$ = 11.086, $\underline{c}$ = 7.250 (all ± 0.006)Å, $\underline{\beta}$ = 90.68 (± 0.05)°, $\underline{V}$ = 642.2 Å^3, $\underline{z}$ = 4, $\underline{d}_c$ = 3.78 g cm^{-3}. Refinement has proceeded satisfactorily in space group $\underline{P2_1/n}$, using three dimensional graphite monochromatized MoKα X-ray data. With anisotropic temperature factors for all atoms, a final conventional R factor of 0.07, for 1044 independent reflections, for which $I \geq 2\sigma(I)$, 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 Ru-F interatomic distances: -F(3), 1.778(16); -F(4), 1.781(12); -F(5), 1.789(13); -F(6), 1.820(14) and -F(7), 1.835(13), the

Ru-F(3) bond being *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, d_c = 3.79 g cm^{-3}. Data collection and treatment was 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 $I \geq 3\sigma(I)$. 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 inter-group 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 Ru-F distances: -F(3)(twice), 1.850(7); -F(4), 1.876(11); -F(5), 1.820(12); -F(6), 1.827(10) and Ru-F(7), 1.867(9) Å. The XeF_5 group almost has C_{4v} symmetry, with Xe-F(axial) = 1.793(8) 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 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 behaviour of the binary xenon fluorides. However, the $FXeMF_6$ compounds were also of interest to us because the compounds $FXePtF_6$ and $FXeRhF_6$ are formed when xenon interacts with the appropriate hexafluoride in excess[2,5]:

$$Xe + 2MF_6 \rightarrow FXe\ MF_6 + MF_5 \quad .$$

The ruthenium compound, $FXeRuF_6$ was chosen as the representative of the $FXeMF_6$ 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 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, (all ± 0.006) Å, β = 90.68 ± 0.05°, V = 642.2 Å^3, z = 4, d_c = 3.78 g cm^{-3} and F(000) = 636.30. Single crystal precession photographs established the following conditions limiting possible reflections: $h\,k\,\ell$ none; $h\,0\,\ell$, $h + \ell = 2n$; $0k0$: $k = 2n$. These indicated the space group $P2_1/n$ (an alternate setting of space group No. 14 in the International Tables[7]). The structure was successfully refined in this space group. (The equivalent positions for this setting are: 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.)

$XeRuF_{11}$ (mole wt 441.35) is orthorhombic with a = 16.771, b = 8.206, c = 5.617 (all ± 0.010) Å, V = 773.03 Å^3, z = 4, d_c = 3.79 g cm^{-3}. Single crystal precession and Weisenberg photographs established the following conditions limiting possible reflections: $h\,k\,\ell$, none: $0\,k\,\ell$, $k + \ell = 2n$; $h\,k\,0$, $h = 2n$, indicating space groups $Pnma$ or $Pn2_1a$ The structure was successfully refined in the former group (No. 62 in the International Tables[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 take-off 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 proceedure 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 oval tablet, ~ 0.3 × 0.2 × 0.1 mm. Two unique data sets, the -h, k, ℓ and the h, k, ℓ were collected for $2\theta \leq 60°$. Intensitites 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 $\mu = 78.04\ cm^{-1}$, but, because of the irregular shape of the crystal and the absence of faces, no absorption correction was made.

$XeRuF_{11}$.- A tablet of dimensions 0.15 × 0.10 × 0.06 mm (with c^* approximately parallel to the capillary axis) was selected for the data collection. Intensity data were collected for the sets of reflections: -h, k, ℓ and h, -k, ℓ, for $2\theta \leq 55°$. Intensities of three strong reflections were used as standards and were recorded every 150 relfections. 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 $\mu = 65.76\ cm^{-1}$ 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_2 = 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 ($\sin\theta/\lambda \leq 0.20$) was given zero weight in the final least-squares refinements. This proceedure resulted in R = 0.07, R_2 = 0.08 and a standard deviation for an observation of unit weight of 1.28. The number of non-zero weighted data in this refinement was 1044. The positional and thermal parameters, reported in the Tables I, are from this refinement[10]. The F_o and F_c data for $XeFRuF_6$ (Table VI) and XeF_5RuF_6 (Table VII) are given in the microfilm version of this paper.

$XeRuF_{11}$.- 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 $I \geq \sigma(I)$ 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 R factor of 0.062. At this point limiting the refinement to the 556 reflections where $I \geq 3\sigma(I)$, reduced R to 0.042, $R_2 = 0.078$ 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 $FXeFRuF_5$ 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-four-fold 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 1(b) and the group arrangements in the crystal lattice may be seen from the stereoscopic view given in Figure 3. Interatomic distances and angles are given in Table VI.

(Place Figures 1(a), 1(b), 2 and 3 here)

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 <u>trans</u> 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 distances 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 3 of the 4 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 hexafluorometallates(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 $\sim 80°$ 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 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 the 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 occuring 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 3 F atoms forming an approximately triangular set. This set is approximately symmetrically disposed about the pseudo four-fold axis and below the base of the XeF_5^+ ion pyramid.

Since the xenon atom in $[XeF_5]^+$ retains a non-bonding valence electron pair[19,20] we can suppose that this pair occupies a spacially directed orbital, such that the Xe atom is pseudo-octahedrally coordinated with 5 F atoms and the sterically active valence-electron pair. With the 'non-bonding pair' sterically active and projecting along the four-fold 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 4(a). 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 to 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 4(b)). We would, therefore, anticipate that any interaction with one negatively charged ligand(L) would result in a linear disposition $F\text{-}Xe^{+}\ldots L$.

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.

ACKNOWLEDGMENTS

This work was supported by the U. S. Atomic Energy Commission. One of us (M.G.) is grateful to the Atomic Energy Commission for a Summer Studentship (1970).

REFERENCES

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., The University of Chicago Press, Chicago 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).
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, Alan Zalkin, and Neil Bartlett, Inorg. Chem., in press.
9. D. T. Cromer and B. Mann, Acta Cryst., A24, 321 (1968).
10. Tables VI and VII 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, by referring to code number INORG-00-0000. Remit check or money order for $0.00 for photocopy or $0.00 for microfiche.
11. D. Babel, Structure and Bonding, 3, 11, (1967).
12. M. A. Hepworth, K. H. Jack, and G. J. Westland, J. Inorg. Nucl. Chem., 2, 79 (1956).

13. J. A. Ibers and W. C. Hamilton, J. Chem. Phys., 44, 1748 (1966).

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.

15. N. Bartlett, B. DeBoer, F. Hollander, F. O. Sladky, D. Templeton, and A. Zalkin, accompanying paper.

16. A. Zalkin, K. Leary, D. Templeton and N. Bartlett, accompanying paper.

17. R. D. Burbank, G. R. Jones, Science, 168, 248 (1970).

18. Ibid, Science, 161, 485 (1971).

19. The Xe-F bond shortening accopanying the loss of F^- from XeF_6 (where Xe-F = 1.89 Å [20]) may be associated in part with the transition of the non-bonding pair from an orbital which approximates to Xe 6s to a spacially 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 'non-bonding 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 tendancy of the 'non-bonding' valence-electron pair in XeF_6 to steric activity may well be responsible for the relative ease of fluoride ion donation by XeF_6.

20. R. M. Gavin, Jr., and L. S. Bartell, J. Chem. Phys., 48, 2460 (1968).

21. R. J. Gillespie, in "Noble Gas Compounds", H. H. Hyman, Ed., Chicago

University Press, Chicago, Ill., and London, 1963, pp. 333-8.

22. J. W. Linnett, "The Electronic Structure of Molecules", London: Methuen and Co., Ltd., New York: John Wiley and Sons, Inc., 1964, Chapter 3.

23. C. A. Coulson, J. Chem. Soc., 1442 (1964).

24. N. Bartlett, M. Wechsberg, G. R. Jones, and R. D. Burbank, Inorg. Chem., 11, 1124 (1972).

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	.2493(2)[b]	.0358(1)	.7785(2)	2.90(5)	3.39(6)	6.29(7)	.26(4)	1.13(4)	.37(5)	.2303
Xe	.2432(1)	.2160(1)	.3294(1)	3.14(4)	4.73(6)	4.75(4)	.26(4)	.77(3)	.36(4)	.2308
F_1	.1952(32)	.3329(25)	.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)	.4173
F_2	.3118(22)	.0787(22)	.5232(22)	10.08(1.02)	10.29(1.13)	8.19(70)	4.26(84)	4.19(69)	3.67(73)	.3466
F_3	.1905(21)	-.0049(24)	.0059(24)	8.89(1.02)	12.93(1.26)	8.85(79)	- .93(94)	3.09(73)	1.94(88)	.3595
F_4	.4175(19)	-.0683(14)	.7697(26)	6.81(80)	7.52(80)	13.52(1.03)	4.97(68)	1.68(71)	2.37(75)	.3427
F_5	.0855(20)	.1457(14)	.7677(31)	7.14(46)	7.01(84)	16.51(1.33)	4.31(69)	3.55(84)	1.55(86)	.3593
F_6	.1025(21)	-.0768(17)	.6919(30)	6.73(82)	10.44(1.17)	16.35(1.38)	-4.34(77)	- .92(83)	-5.59(1.12)	.3764
F_7	.3910(16)	.1529(15)	.8676(28)	5.00(61)	8.84(1.04)	14.75(1.19)	-3.25(63)	-1.29(65)	-3.57(94)	.3477

[a] The form of the anisotropic thermal ellipsoid is $\exp(-\beta_{11}\underline{h}^2 - \beta_{22}\underline{k}^2 - \beta_{33}\underline{\ell}^2 - 2\beta_{12}\underline{hj} - 2\beta_{13}\underline{h\ell} - 2\beta_{23}\underline{k\ell})$. The B_{ij} in the table = $4\beta_{ij}/\underline{a}_i^*\underline{a}_j^*$, where $\underline{a}_i^*$ and $\underline{a}_j^*$ are the i^{th} and j^{th} 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 $XeF_5^+RuF_6^-$

Atom	x	y	z	B_{11}[a]	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	rmsd[c]
Ru	.54318(7)[b]	1/4	.2205(2)	2.29(5)	1.83(5)	2.12(6)	0	-.17(4)	0	.1623
Xe	.34978(6)	1/4	.7009(2)	2.09(4)	3.16(5)	2.93(5)	0	-.37(4)	0	.1859
F_3	.5417(4)	.4754(8)	.227(1)	5.0(4)	2.3(2)	4.3(4)	-.3(2)	-.8(3)	.6(3)	.2213
F_4	.4880(6)	1/4	.511(2)	3.6(5)	3.8(4)	2.6(5)	0	-.0(3)	0	.2044
F_5	.5921(6)	1/4	-.069(2)	3.2(5)	5.8(6)	4.2(6)	0	1.3(4)	0	.2359
F_6	.6392(6)	1/4	.374(2)	2.1(4)	4.3(5)	4.7(6)	0	- .6(4)	0	.2160
F_7	.4443(5)	1/4	.068(2)	2.9(4)	3.2(4)	2.1(4)	0	- .3(3)	0	.1869
F_8	.3457(5)	.0939(8)	.464(1)	6.1(5)	3.4(3)	3.6(4)	0	-1.6(3)	0	.2355
F_9	.3128(5)	.0955(9)	.911(2)	5.2(4)	4.3(4)	4.8(4)	-.9(3)	.1(3)	.8(3)	.2459
F_{10}	.2456(6)	1/4	.629(3)	1.3(4)	7.3(7)	8.4(9)	0	-2.3(5)	0	.2675

a, b, c See TABLE I.

TABLE III

INTERATOMIC DISTANCES (Å) AND ANGLES (DEG.)

FOR $XeF^+RuF_6^-$

(All F-F contacts > 2.5Å)

Ru-F_2	1.919(13)[a]	F_2-Ru-F_4	85.65(76)
Ru-F_3	1.778(16)	F_2-Ru-F_5	89.36(98)
Ru-F_4	1.781(12)	F_2-Ru-F_6	91.30(1
Ru-F_5	1.789(13)	F_2-Ru-F_7	89.21(98)
Ru-F_6	1.820(14)	F_3-Ru-F_4	94.27(121)
Ru-F_7	1.835(13)	F_3-Ru-F_5	90.73(93)
		F_3-Ru-F_6	88.22(109)
Xe-F_1	1.872(17)	F_3-Ru-F_7	91.28(113)
Xe-F_2	2.182(15)	F_4-Ru-F_6	91.25(104)
Xe-F_5	3.163(13)	F_4-Ru-F_7	90.77(82)
Xe-F_6	3.171(15)	F_5-Ru-F_6	89.08(123)
Xe-F_7	3.172(13)	F_5-Ru-F_7	88.93(86)
Xe-F_4	3.256(12)		
Xe-F_3	3.483(29)	F_1-Xe-F_2	177.08(123)
Xe-F_5	3.506(20)		
Xe-F_7	3.625(21)	Xe-F_2-Ru	137.19(46)

[a] Estimated Standard deviations in parentheses.

TABLE IV

INTERATOMIC DISTANCES (Å) AND ANGLES (DEG.)

FOR $XeF_5^+RuF_6^-$

$Ru-F_3$	1.850(7)[a]	F_4-Ru-F_7	87.76(53)
$Ru-F_4$	1.876(11)	F_4-Ru-F_6	91.40(61)
$Ru-F_5$	1.820(12)	F_5-Ru-F_6	91.36(56)
$Ru-F_6$	1.827(10)	F_5-Ru-F_7	89.48(61)
$Ru-F_7$	1.867(9)	F_6-Ru-F_7	179.16(81)
		F_4-Ru-F_5	177.25(79)
$Xe-F_3$	2.924(7)		
$Xe-F_4$	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)	F_8-Xe-F_9	88.44(41)
$Xe-F_9$	1.841(8)	F_8-Xe-F_{10}	78.59(43)
$Xe-F_{10}$	1.793(8)	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.

TABLE V

COMPARISON OF XeF_5^+ WITH ISOELECTRONIC SPECIES

	TeF_5^-	IF_5 (gas)	IF_5 (in $IF_5 \cdot XeF_2$)	XeF_5^+
E-F_{ax}(Å)	1.84(2)	1.844(25)	1.862(10)	1.793(8)
E-F_{eq}(Å)	1.96(2)	1.869(5)	1.892(5)	1.845(9)
F_{ax}-E-F_{eq}(°)	78.8(17)	81.9(1)	80.9(2)	79.0(17)
Reference	a	b	c	Present work

Number in parentheses is the Estimated Standard Deviation in the least significant digit.

[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).

Table VI

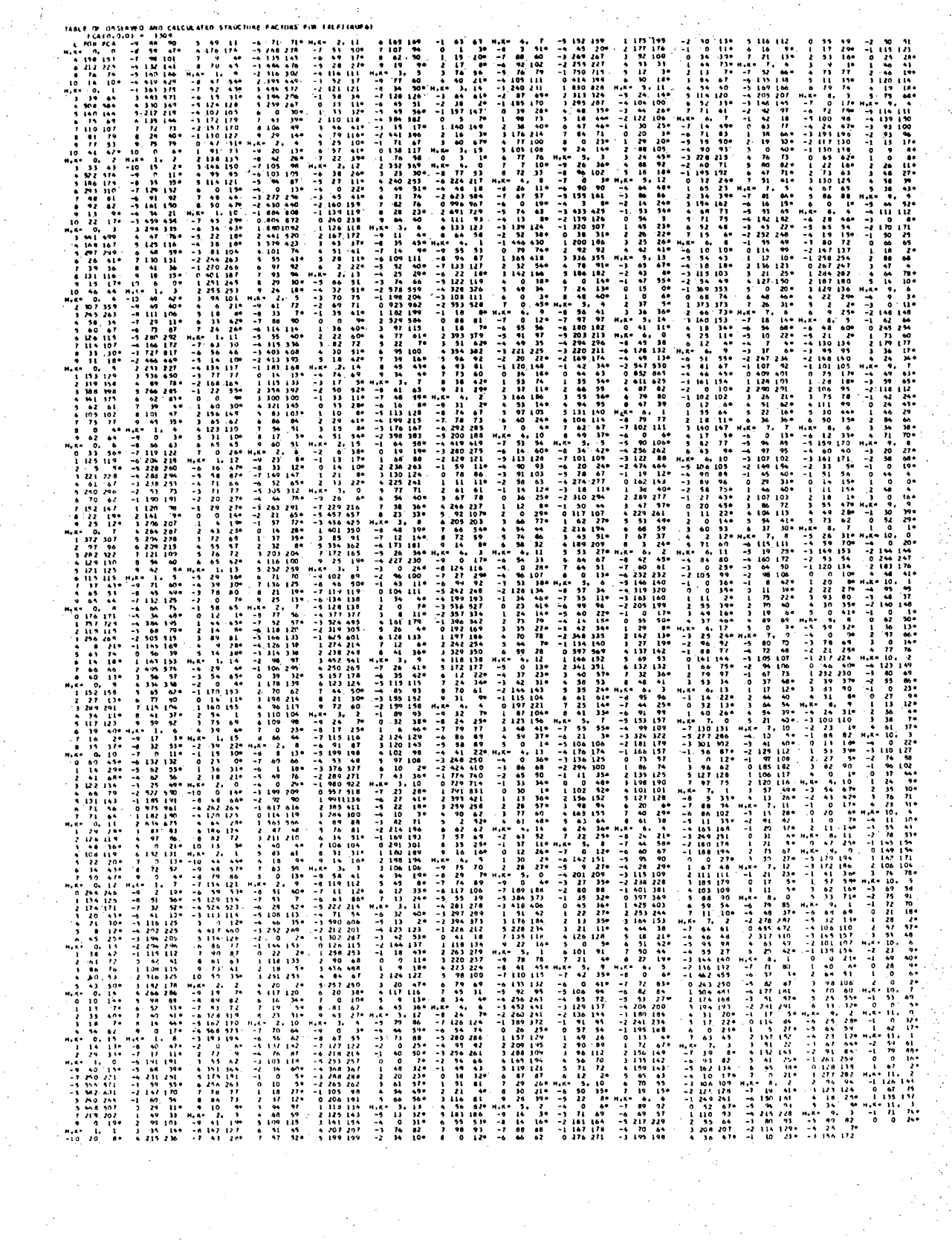
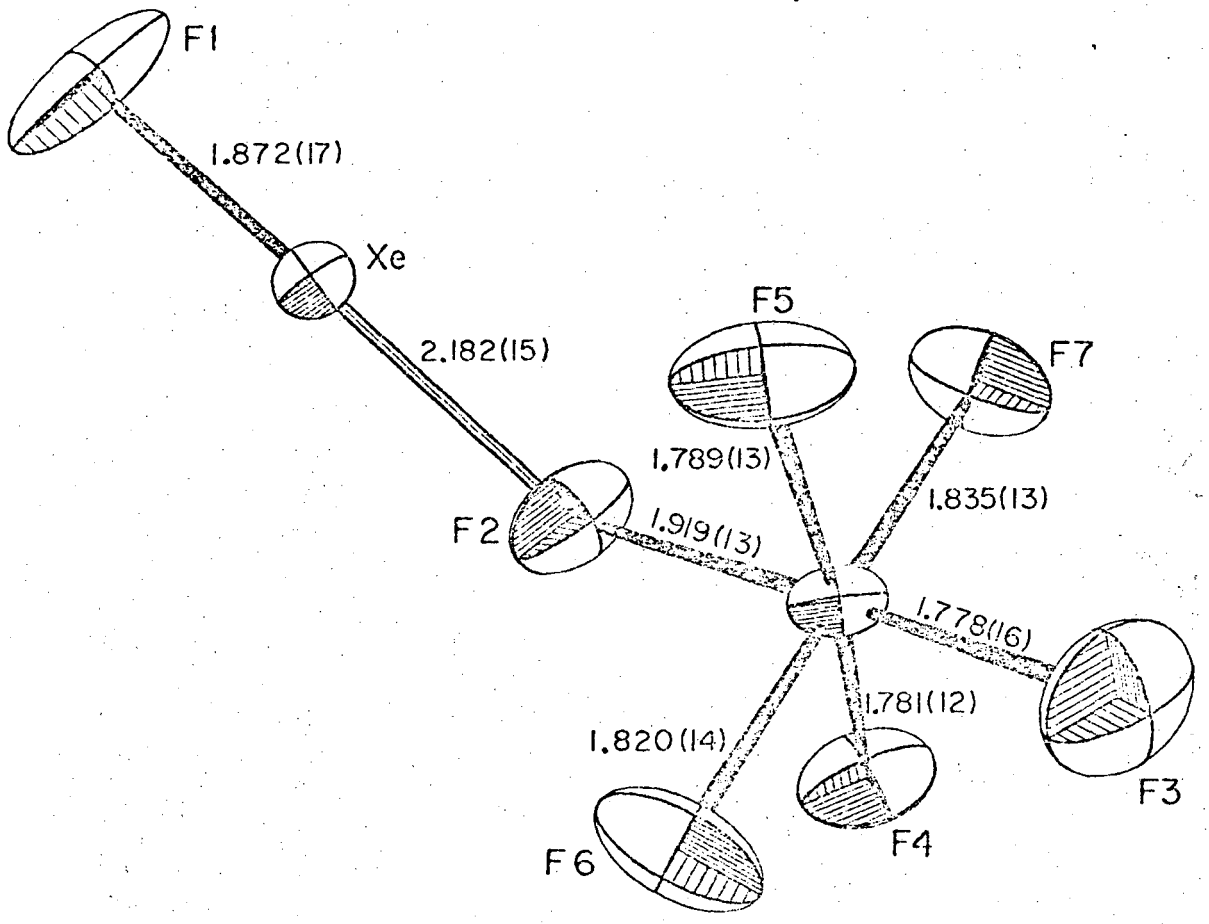


Table VII

OBSERVED STRUCTURE FACTORS, STANDARD DEVIATIONS, AND DIFFERENCES (X 5.0) FOR
XE RU F(0,0,0) = 3841
SG = ESTIMATED STANDARD DEVIATION OF FOB. DEL = /FOB/-/FCA/. * INDICATES ZERO WEIGHTED DATA.

H FOB SG DEL	H FOB SG DEL	H FOB SG DEL	H FOB SG DEL	H FOB SG DEL	H FOB SG DEL	H FOB SG DEL	H FOB SG DEL
K,L= 0, 0	3 204 14 -7	15 104263 -15*	11 148 18 -13	20 246 17 13	17 377 12 3	12 0 73 -38*	10 704 21 11
2 390 17 -91	4 79 19 -15*	16 149 26 -15	12 148 9 -5	K,L= 3, 2	14 346 14 0	13 78 21 -9*	11 234 17 9
4 366 12 -50	5 862 49 -31	17 34 74 -25*	13 123 21 -12	1 107 11 10	16 362 15 -7	14 120 22 -16	12 198 12 -6
6 777 24-105	6 197 17 -9	18 123124 -5*	14 68 32 -7*	2 964 20 28	18 0 44 -48*	15 84 22 10*	13 0 60 -25*
8 193 9 3	7 75 43 1*	19 85101 -27*	15 72 57 -6*	3 738 28 23	20 202 11 13	16 150 13 -1	14 49 73 25*
101206 38 -93	8 105 94 -8*	20 129 14 10	K,L= 6, 1	4 138 9 -10	K,L= 1, 3	17 174 23 -12	15 201 15 -14
12 169 9 -6	9 167 23 -14	21 69147 9*	1 341 14 -4	5 132 15 -1	0 146 24 1	K,L= 5, 3	16 247 31 -20
14 73 75 36*	10 300 13 -8	K,L= 2, 1	2 95 18 -8*	6 208 12 5	1 239 10 11	0 74 27 -26*	17 61 65 -15*
16 367 12 11	11 267 11 -6	1 390 14 14	3 57 68 10*	7 419 18 -15	2 674 21 30	1 253 11 9	18 27 85 0*
18 119 11 9	12 144 9 14	2 131 22 8	4 81 30 21*	8 388 23 -10	3 49 15 1*	2 156 8 11	19 89 20 10*
20 465 15 41	13 0 47 -10*	3 71 26 -3*	5 79 91 25*	9 147 9 -8	4 705 22 23	3 272 11 1	K,L= 3, 4
K,L= 1, 0	14 110 19 23	4 754 50 -31	6 30 66 4*	10 57 66 37*	5 91 8 10	4 136 8 3	1 41 42 35*
1 23 76 -20*	15 355 15 -4	5 38 48 -0*	7 113 16 -7	11 81 64 -5*	6 406 13 16	5 78 31 23*	2 573 17 4
21322 69-120	16 178 10 4	6 878 57 -80	8 95 41 -21*	12 184 11 -8	7 82 14 18	6 73 29 8*	3 652 20 26
3 384 13 -31	17 0 72 -71*	7 194 7 -10	9 230 15 -11	13 327 13 -13	8 510 16 17	7 239 10 7	4 241 9 -1
4 83112 -17*	18 67 33 7*	8 72 28 -12*	10 65 39 -2*	14 0 48 -7*	9 25 47 -0*	8 111 13 11	5 118 10 11
5 16 81 -11*	K,L= 5, 0	9 335 13 -21	11 238 11 -9	15 73 37 -6*	10 183 9 9	9 322 20 -12	6 357 12 10
6 361 12 -26	1 0 88 -25*	10 185 9 -16	12 19 49 -3*	16 120 38 21*	11 13 48 -16*	10 102 28 5*	7 405 14 13
7 760 23 -59	2 0 95 -14*	11 316 11 -15	K,L= 7, 1	17 225 11 19	12 494 19 -14	11 126 15 -7	8 429 17 2
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]



XBL 725-3040

Figure 1(a) The $XeF^{+}RuF_{6}^{-}$ Structural Unit (distances in Ångströms and standard deviations in parentheses).

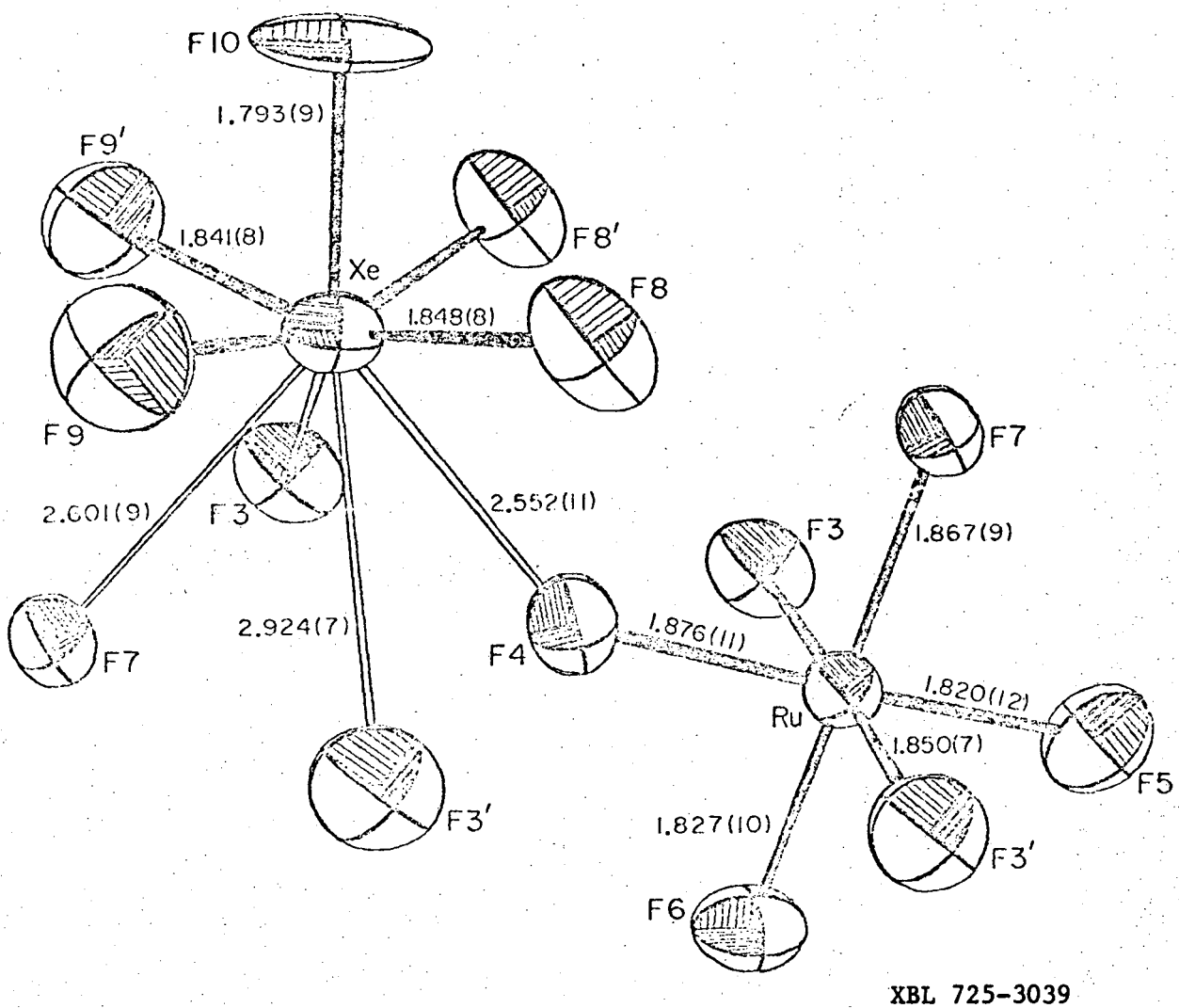
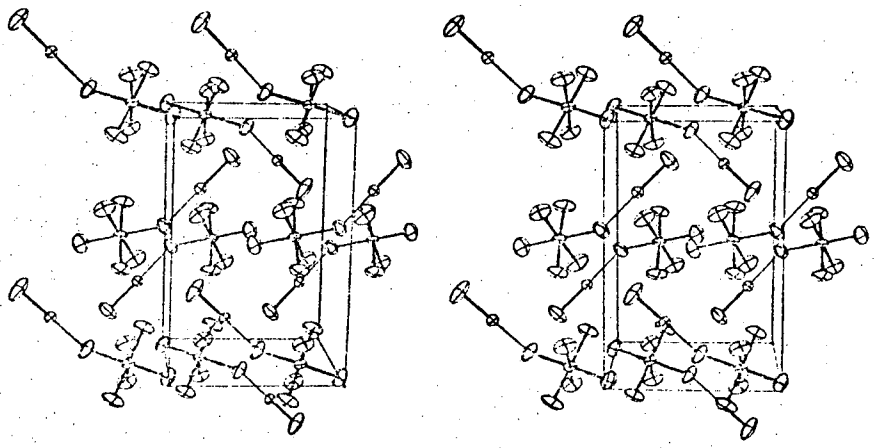
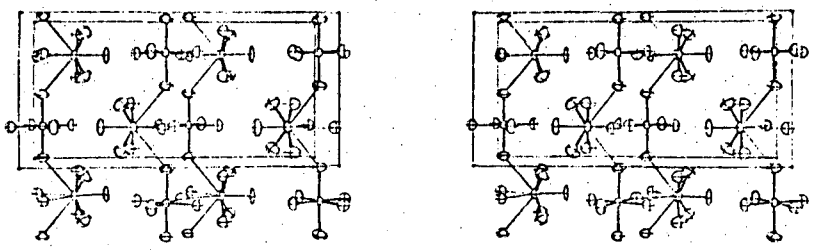


Figure 1(b) The XeF_5^+ and RuF_6^- Structural Units and the Coordination of XeF_5^+ (distances in Ångströms and standard deviations in parentheses).



XBL 725-6298

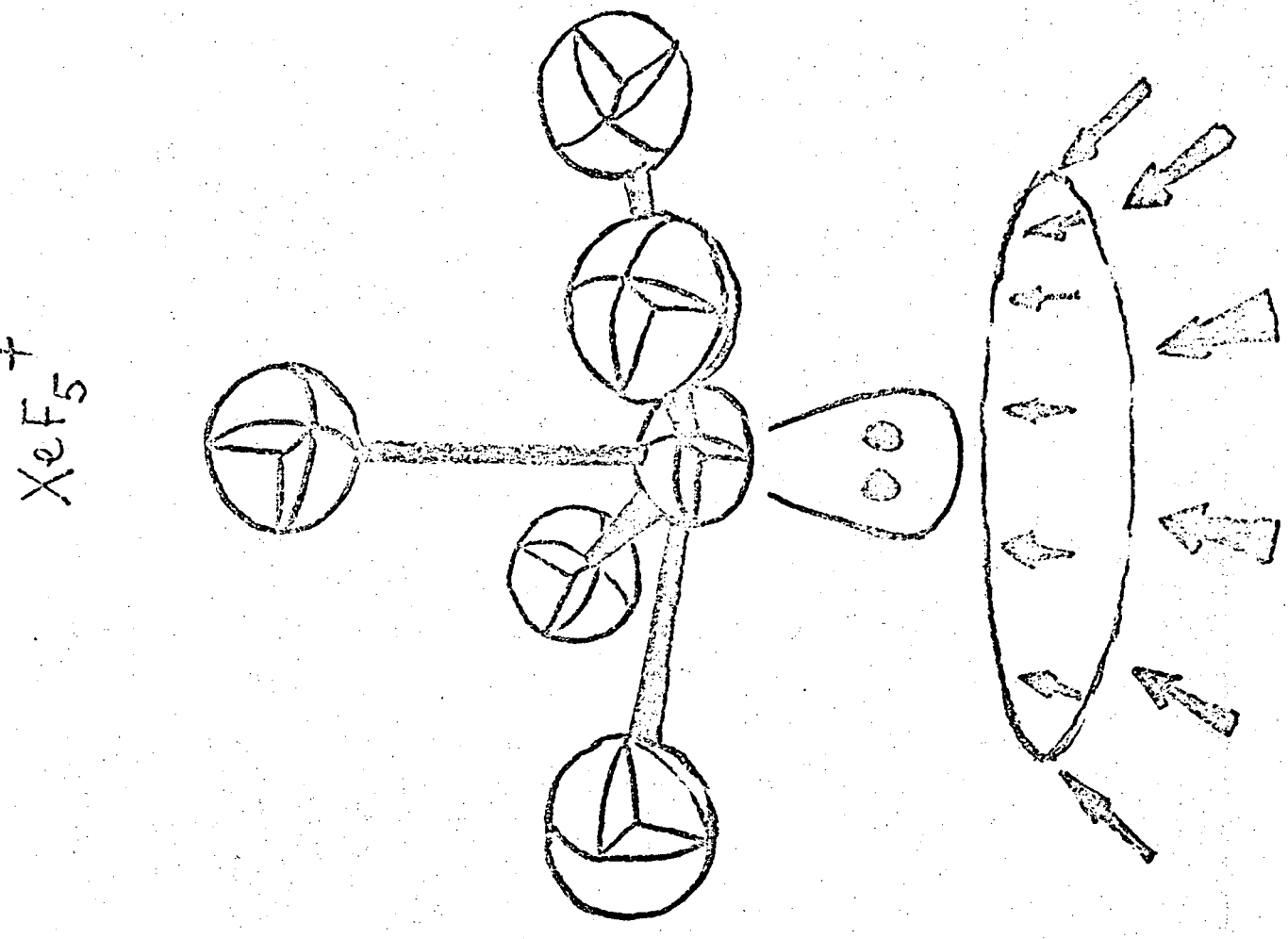
Figure 2 Stereoscopic View to Show Packing of the $XeFRuF_6$ Units in the Crystal Lattice.

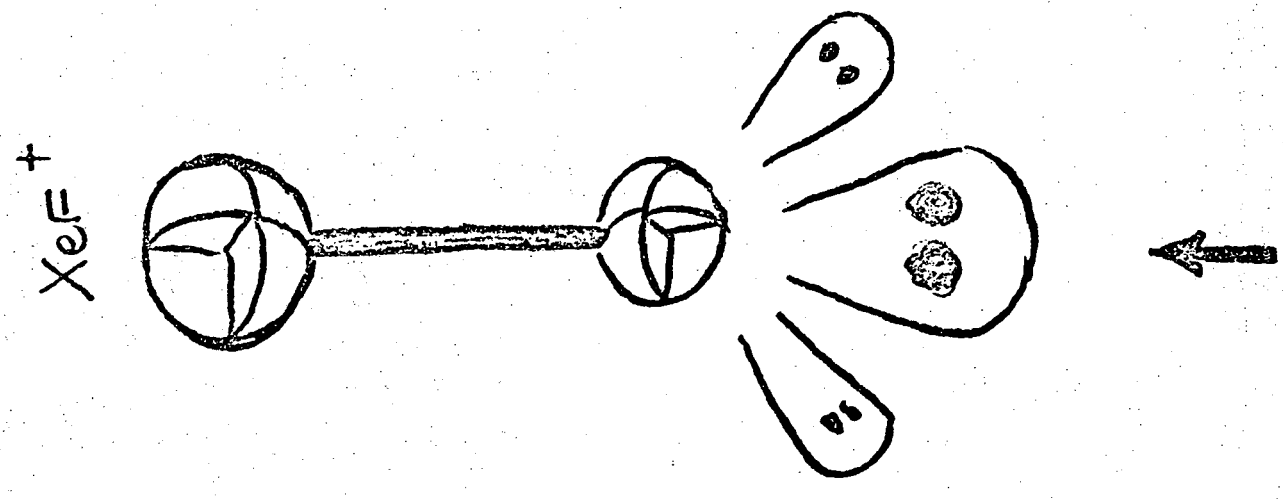


XBL 725-6299

Figure 3 Stereoscopic View Showing the Arrangement of XeF_5^+ and RuF_6^- Units in the Crystal Lattice.

Figure 4 Representation of the influence of non-bonding valence-electron pairs, of the Xe atom, upon the polarizing character of the XeF^+ and XeF_5^+ ions. (Arrows indicate directions of maximum polarization of anions by the cations.)


XeF_5^+


XeF^+

TECHNICAL INFORMATION DIVISION
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720