Xenon Difluoride as a Fluoride Ion Donor and the Crystal Structure of $[Xe_2F_3]^+[AsF_6]^-$

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XENON DIFLUORIDE adducts, $XeF_2,2MF_5$, where M = Sb or Ta, have been reported.[1] The Pt^V material, $Xe(PtF_6)_2$, obtained in the interaction Xe + PtF_6(excess),[2] may also be represented as an XeF_2 adduct.

We have found that the noble-metal pentafluorides give, with XeF_2, three adduct types: $2XeF_2,MF_5$, XeF_2,MF_5, and $XeF_2,2MF_5$ (where M = Pt, Ir, Os,† Ru, and Rh). The adducts of each type form an isomorphous series. On the other hand, arsenic pentafluoride forms only the adducts $2XeF_2,AsF_5$ and XeF_2,AsF_5, The new adducts were prepared from bromine pentafluoride solutions. On the basis of Raman and i.r. spectroscopy they can be formulated as the salts $[Xe_2F_3]^+[MF_6]^-$, $XeF^+[MF_6]^-$, and $XeF^+[M_2F_{11}]^-$. A single-crystal *X*-ray structure determination of $2XeF_2,AsF_5$, m.p. 99°, together with the vibrational spectra, has established the ionic formulation of the 2 : 1 adducts as $[Xe_2F_3]^+[MF_6]^-$.

Suitable small crystals of $2XeF_2,AsF_5$ were obtained by sublimation under nitrogen (at ~1 atmos.) in sealed quartz *X*-ray capillaries. A tablet measuring <0·1 mm. in any dimension was used for the intensity data. The crystals are monoclinic with unit-cell dimensions: $a = 15{\cdot}443$, $b = 8{\cdot}678$, $c = 20{\cdot}888$ Å, $\beta = 90{\cdot}13°$, $V = 2799$ Å^3. The space group is $I2/a$, and $Z = 12$. Three-dimensional data, amounting to 1182 non-zero independent reflections, were obtained. Two xenon and one arsenic atoms were located with a three-dimensional Patterson map, and the remaining atomic positions from subsequent electron-density maps. Full-matrix least-squares refinement led to a final conventional *R*-value of 0·066.

The geometric arrangement is best represented by $Xe_2F_3^+$ and AsF_6^- ions. There are two crystallographically nonequivalent representatives of each ion in the structure, but the structure analysis has not revealed any significant differences between the two representatives. The AsF_6^- species are approximately octahedral, the six As–F distances being in the range 1·62 ± 0·04 to 1·70 ± 0·04 Å and the *cis*-F–As–F bond angles in the range 84 ± 2° to 97 ± 2°. The average of nine As–F distances is 1·67 Å and is identical to the value obtained by Bartlett and Beaton[3] for As–F in the salt $IF_6^+AsF_6^-$.

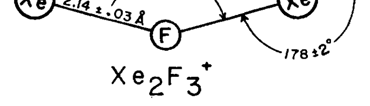

FIGURE. *Bond lengths and angles in* $Xe_2F_3^+$.

The cation is of particular interest since it contains a bridging fluorine atom. The V-shaped $[F–Xe–F–XeF]^+$ cation, shown in the Figure, is planar to within the accuracy of the structure determination, and symmetrical about the bridging fluorine atom. The internuclear separations suggest that the cation is approximately $F–Xe^+F^-Xe–F^+$ since the terminal Xe–F distances, of 1·9 Å, equal the distance quoted[4] for the isoelectronic I–F molecule and are 0·1 Å shorter than those given[5] for Xe–F in XeF_2. The cation geometry is similar to that observed[6,7] in the symmetrical, planar, V-shaped ions I_5^- and $[F–H–F–H–F]^-$. The terminal internuclear distances are the shorter in both ions but as is usual in fluorine bridging, the V angle of 130–139° in the latter is >>90°. In I_5^- the bridge angle is 95°, which is close to the requirement[6] if *p*-valence orbitals alone, are involved in the multicentre bonding.

Although the noble-metal analogues are not isomorphous with $Xe_2F_3^+AsF_6^-$ the i.r. and Raman spectra indicate a very close similarity to it and demonstrate that all contain $[MF_6]^-$. The ν_1, ν_2, ν_3, and ν_5 $[MF_6]^-$ fundamental modes are observed and their frequencies are similar to those of the alkali-metal salts. The $Xe_2F_3^+$ is characterized by strong Raman bands in the Xe–F stretch region at ~593 and 580 cm.$^{-1}$ and in the bend region at 160 cm.$^{-1}$. The vibrational spectra of the $XeF^+[MF_6]^-$ salts are characterized by a strong doublet at ~602 and 608 cm.$^{-1}$, but otherwise show a close relationship to the alkali-metal salt spectra. The 602, 608 cm.$^{-1}$ doublet is

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† XeF_2,OsF_5 dismutates at ~20° to give OsF_6, Xe and the 2 : 1 adduct. The 1 : 2 adduct is unknown.

attributed to XeF^+ stretch. The doublet may arise from crystallographic nonequivalence of separate cations, but it is more probable that it arises from an interaction with the anion or another cation. A stretching frequency of 604 cm.$^{-1}$ has been reported[8] for the IF molecule, which is isoelectronic with XeF^+. Although the vibrational spectra of the $XeF^+[M_2F_{11}]^-$ salts‡ are more complex, the Raman spectra are again characterized by strong bands in the 600—610 cm.$^{-1}$ region, attributable to the XeF^+ ion.

Evidently XeF_2, like all other nonmetal fluoride-ion donors, is capable of donating one fluoride ion only.

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‡ The fluorine bridged $[Ta_2F_{11}]^-$ has recently been established by Edwards and Jones.[9]

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