

The Crystal Structure of $\text{XeF}_2 \cdot 2\text{SbF}_5$

By (MRS.) V. M. McRAE, R. D. PEACOCK, and D. R. RUSSELL*

(Department of Chemistry, The University, Leicester LE1 7RH)

THE first reported adducts of XeF_2 included a yellow compound corresponding to the composition $\text{XeF}_2 \cdot 2\text{SbF}_5$.¹ It was suggested that this had an essentially covalent structure with possible fluorine bridging. The crystal structure of the adduct has now been determined by *X*-ray diffraction methods, and shown to be consistent with a formulation approximating to $[\text{XeF}]^+[\text{Sb}_2\text{F}_{11}]^-$.

A suitable small crystal was obtained by slowly cooling the molten adduct in an evacuated glass capillary tube. The crystal was monoclinic, $a = 8.07$, $b = 9.55$, $c = 7.33$ Å, $\beta = 105.8^\circ$, $U = 543$ Å³; $D_c = 3.69$ for $\text{XeSb}_2\text{F}_{12}$, $M = 602.8$, and $Z = 2$, space group $P2_1$. 838 independent reflexion intensities were measured by an integrating

microdensitometer from Weissenberg and precession photographs, taken with $\text{Mo-}K_\alpha$ radiation. At the present stage of refinement R is 0.11 with anisotropic Xe and Sb atoms and isotropic F atoms. The atomic arrangement is shown in the Figure.

From the distribution of bond lengths it can be argued that the crystal structure is derived from an ionic formulation $[\text{XeF}]^+[\text{Sb}_2\text{F}_{11}]^-$. The Xe-F bond length, 1.84 ± 0.04 Å, is less than found in XeF_2 (2.0 Å) and compares with the value 1.90 ± 0.03 observed in $[\text{Xe}_2\text{F}_3]^+[\text{AsF}_6]^-$.² The overall geometry of the $[\text{Sb}_2\text{F}_{11}]^-$ unit is very similar to that of $[\text{Nb}_2\text{F}_{11}]^-$ both in terminal and bridging F bond lengths.⁴

The next shortest xenon-to-fluorine contact at 2.23 Å is so much less than the sum of the estimated van der Waals radii (3.5 Å, by using 2.2 Å for Xe taken from its crystal structure⁵ at 58° K) that this must be taken as evidence of

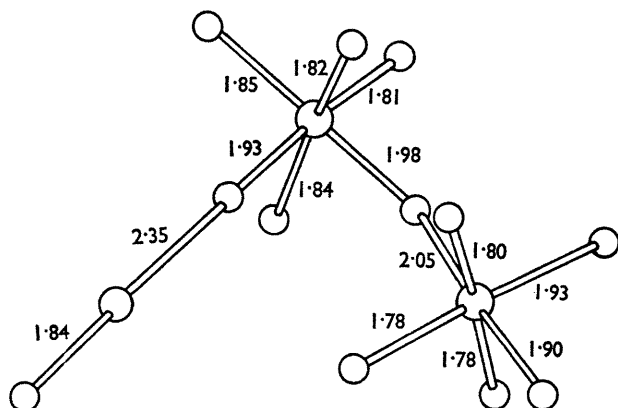


FIGURE. The molecular structure of $\text{XeF}_2 \cdot 2\text{SbF}_5$, *e.s.d.'s* bond lengths 0.04 Å

considerable bond formation. Eight further fluorine atoms lie at distances ranging from 3.2–3.5 Å from the xenon, which is probably a better representation of the non-bonding Xe-F contact (this is 3.4 Å in XeF_2). The Xe-F-Sb angle of 147° is very similar to the fluorine bridge angle in the Sb_2F_{11} unit (150°), in which the Sb-F bond lengths involved in fluorine bridging (1.98, 2.05 ± 0.04 Å) are significantly longer than the terminal Sb-F bonds (average 1.83 ± 0.04 Å), as is usual. We prefer to use the notation $[\text{XeF}]^+[\text{Sb}_2\text{F}_{11}]^-$ as a formalism only, and to regard the compound as an essentially covalent molecule. Large variations in bond lengths involving heavy elements have been noted before in the case of mercury.⁶ The discrepancy between the bond lengths in the Xe-F-Sb unit reflects the greater affinity of antimony for fluorine over xenon.

For similar reasons the representation of the cation³ in $[\text{Xe}_2\text{F}_3]^+[\text{AsF}_6]^-$ as $\text{FXe}^+\text{F}^-\text{XeF}^+$ must be treated cautiously, since the difference between terminal and bridging Xe-F distances of only 0.24 Å is of the same order as the corresponding difference found in fluorine-bridged, covalent polymers such as Nb_4F_{20} .⁷

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