Crystal Structure of $[Xe_2F_{11}]^+[AuF_6]$

By Kevin Leary, Allan Zalkin, and Neil Bartlett*

(*Lawrence Berkeley Laboratory and Department of Chemistry, University of California, Berkeley, California* 94720)

Summary The crystal structure of $[Xe_2F_{11}]^+[AuF_6]^-$ shows the anion to be essentially octahedral and the cation to be approximately two XeF_5^+ ions linked by a fluoride ion.

Recently we reported[1] the novel oxidation state (+5) of gold. We have now solved the crystal structure of the $[Xe_2F_{11}]^+[AuF_6]^-$ salt. *Crystal data:* $F_{17}AuXe_2$, $M = 782{\cdot}5$, orthorhombic, $a = 9{\cdot}115(6)$, $b = 8{\cdot}542(25)$, $c = 15{\cdot}726(20)$ A°, $U = 1224$ Å^3, $Z = 4$, $D_c = 4{\cdot}24$ g cm^{-3}, space group *Pnma*. Structural analysis employing three dimensional Mo-K_α X-ray data from four different crystals has proceeded routinely to a final conventional R factor of 0·035 for 862 independent reflections for which $I \geqslant 3\sigma(I)$ ($R = 0{\cdot}052$ for the 1140 data including zero weight data).

TABLE

Anion		Cation			
F(9)–Au–F(9)′	179·1(3)°	F(1)–Xe(1)–F(2)	79·6(4)°	F(4)–Xe(2)–F(6)	79·4(4)°
F(8)	90·4(4)	F(3)	79·0(4)	F(5)	81·1(5)
F(8)–Au–F(11)	91·6(6)	F(2)–Xe(1)–F(2)	86·8(3)	F(6)–Xe(2)–F(6)	88·6(3)
F(12)	88·0(5)	F(3)	87·1(4)	F(5)	87·4(6)
F(10)–Au–F(11)	89·2(5)	F(3)–Xe(1)–F(3)	91·1(3)	F(5)–Xe(2)–F(5)	89·9(3)
F(12)	91·2(6)	Xe(2)–F(7)–Xe(1)	169·2(2)		
Interionic distances and angles					
Xe(1)–F(8)	2·64(1)	F(1)–Xe(1)–F(7)	147·6(6)°	F(4)–Xe(2)–F(7)	146·3(7)°
F(9)	3·27(1)	F(8)	136·3(6)	F(12)	139·8(7)
Xe(2)–F(12)	2·64(1)	F(9)	132·2(3)	F(9)	135·9(2)
F(9)	3·52(1)				

As may be seen from the Figure, the anion is essentially octahedral. This is in keeping with the t_{2g}^6 configuration of Au^V and is as anticipated from the vibrational spectroscopic[1] and Mössbauer studies.[2]

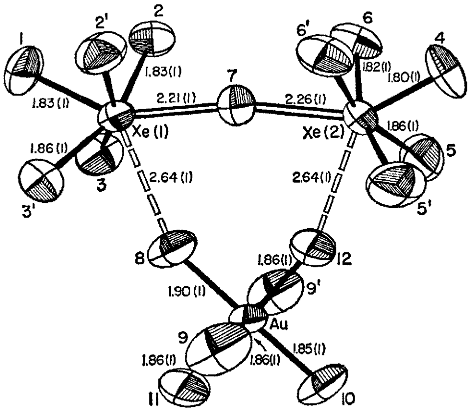

FIGURE. *The structural unit of* $[Xe_2F_{11}]^+[AuF_6]^-$ (*estimated standard deviations in parentheses*)

The cation consists of two approximately square-based pyramidal XeF_5 groups linked by a common fluorine atom F(7). It is of interest that this bridging F atom subtends approximately the same angle (*ca.* 146°) to each of the axial XeF bonds, as do the F atoms which make close approach to the XeF_5^+ ion in its salts.[3–5] Furthermore, the approach of the angle Xe(1)–F(7)–Xe(2) [169·2(2)°] to linearity, indicates that the canonical form $XeF_5^+F^-XeF_5^+$ is a major one in the resonance-hybrid description of the cation.

Although each XeF_5 group in the complex cation departs significantly from the ideal C_{4v} symmetry of the XeF_5^+ cation,[3] each is still characterized by F_{axial}–Xe–$F_{equatorial}$ angles of *ca.* 80°. On the other hand, the *cis* $F_{equatorial}$–Xe–$F_{equatorial}$ angles, in the XeF_5 species of $Xe_2F_{11}^+$, are not equivalent. The greatest *cis* angle, of each XeF_5 equatorial set, is that furthest from the bridging F atom F(7). It may be that the close approach of the bridging F(7) atom (approximately F^- in character) deflects the non-bonding Xe^{VI} valence-electron pair from an axial position in each of the pseudo-octahedral XeF_5^+-like components of $Xe_2F_{11}^+$.

Raman data show that the complex $4XeF_6 \cdot PdF_4$[6] contains essentially the same cation as $[Xe_2F_{11}]^+[AuF_6]^-$ and may, therefore, be formulated as $[Xe_2F_{11}]_2[PdF_6]^{2-}$. The spectra of the $[Xe_2F_{11}]^+$ salts are very like those of the corresponding $[XeF_5]^+$ salts but the $[Xe_2F_{11}]^+$ ion is characterized by a 'bridge stretch' at *ca.* 360 cm^{-1}.

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[1] K. Leary and N. Bartlett, *Chem. Comm.*, 1972, 903.

[2] G. Kaindl, K. Leary, and N. Bartlett, to be published. (The Au 197 Mössbauer spectra of $Xe_2F_{11}^+AuF_6^-$ exhibits a sharp single line shifted 2·28 mm per sec. relative to gold metal. The singularity is in accord with the octahedral symmetry of the anion and the shift with the +5 oxidation state.)

[3] N. Bartlett, K. Leary, D. Templeton, and A. Zalkin, "The Crystal Structure of $(XeF_5^+)_2PdF_6^{2-}$," submitted for publication to *Inorg. Chem.*

[4] N. Bartlett, M. Gennis, D. D. Gibler, B. K. Morrell, and A. Zalkin, "The Crystal Structures of $XeF^+RuF_6^-$ and $XeF_5^+RuF_6^-$," submitted for publication to *Inorg. Chem.*

[5] N. Bartlett, B. DeBoer, F. Hollander, F. O. Sladky, D. Templeton, and A. Zalkin, "The Crystal Structures of $Xe_2F_3^+AsF_6^-$ and $XeF_5^+AsF_6^-$," to be published.

[6] K. Leary and N. Bartlett, to be published.