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THE CRYSTAL STRUCTURE OF $\text{Xe}_2\text{F}_{11}^+\text{AuF}_6^-$ AND THE RAMAN SPECTRUM OF $\text{Xe}_2\text{F}_{11}^+$

by

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Summary: Two novel ions are described by the crystal structure of $\text{Xe}_2\text{F}_{11}^+\text{AuF}_6^-$. The anion is essentially octahedral. The cation can be approximately described as two XeF_5^+ ions linked by a fluoride ion.

In a recent communication from these laboratories¹ we reported the novel oxidation state (+5) of gold, as represented in the AuF_6^- ion. We have now solved the crystal structure of the $\text{Xe}_2\text{F}_{11}^+\text{AuF}_6^-$ salt.

Crystal data: $\text{F}_{17}\text{AuXe}_2$, $M = 782.5$, orthorhombic, $a = 9.115(6)$, $b = 8.542(25)$, $c = 15.726(20)$ Å, $V = 1224$ Å³, $z = 4$, $D_c = 4.24$ g cm⁻³, space group $Pnma$. The estimated errors in the cell dimensions reflect changes of these dimensions in the course of the data collection. Three dimensional Mo K α X-ray data, from four different crystals were collected on a four-circle automatic diffractometer. Absorption corrections were applied and the data averaged. Solution of the three dimensional Patterson function, followed by least-squares refinement, located the heavy atoms. A difference Fourier revealed the F atoms. Final least-squares refinements, including anisotropic temperature factors for all atoms, yielded a

conventional R factor of 0.035 for 862 independent reflections for which $I \geq 3\sigma(I)$ ($R = 0.052$ for the 1140 data including zero weight data). The standard deviation of an observation unit weight = 1.36. The structure reveals Xe_2F_{11} and AuF_6 units which are sufficiently well separated to justify the salt formulation. The structural unit is shown in the Figure. Each ion in this structure is described for the first time.

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 spectroscopic¹ and Mössbauer studies². The average Au-F interatomic distance of 1.86 Å in the anion is slightly shorter than the average Pt-F distance of 1.89 Å reported³ for the anion in $\text{XeF}_5^+\text{PtF}_6^-$.

Although proof³ that $\text{XeF}_6 \cdot \text{PtF}_5$ was the salt $\text{XeF}_5^+\text{PtF}_6^-$, suggested that $2\text{XeF}_6 \cdot \text{PtF}_5$ was probably $\text{Xe}_2\text{F}_{11}^+\text{PtF}_6^-$, efforts to obtain suitable single crystal crystals of this and related compounds^{4,5,6} had failed hitherto⁷. As may be seen from the Figure, the cation consists of two approximately square-based pyramidal XeF_5 groups linked by a common fluorine atom (F7). It is of interest that this bridging F atom subtends approximately the same angle ($\sim 146^\circ$) to each of the axial XeF bonds, as do the F atoms which make close approach to the XeF_5^+ ion in its salts^{8,9,10}. Furthermore, the approach of the angle $\text{Xe}(1)\text{-F}(7)\text{-Xe}(2)$ [$169.2(2)^\circ$] to linearity, indicates that the bridge bond may be close to the ionic form $\text{XeF}_5^+\text{F}^-\text{XeF}_5^+$.

Although each XeF_5 group in the complex cation departs significantly from the ideal C_{4v} symmetry of the XeF_5^+ cation⁸, each is still

characterized by $F_{\text{axial}}\text{-Xe-}F_{\text{equatorial}}$ angles of $\sim 80^\circ$. On the other hand, the cis $F_{\text{equatorial}}\text{-Xe-}F_{\text{equatorial}}$ angles, in the XeF_5 species of $\text{Xe}_2\text{F}_{11}^+$, are not equivalent. Curiously, the greatest cis angle, of each XeF_5 equatorial set, is that furthest from the bridging F atom (F7). It may be that the close approach of the bridging F(7) atom (which presumably has appreciable F^- 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 $\text{Xe}_2\text{F}_{11}^+$. These deflections would be towards the bisectors of the $F(3)\text{-Xe}(1)\text{-}F(3')$ and the $F(5)\text{-Xe}(2)\text{-}F(5')$ angles. Such deflection of the electron pairs could also account for the lengthening of the $\text{Xe}(1)\text{-}F(3)$ and $\text{Xe}(2)\text{-}F(5)$ interatomic distances and the shortening of the $\text{Xe}(1)\text{-}F(2)$ and $\text{Xe}(2)\text{-}F(6)$ distances. In XeF_5^+ the Xe-F equatorial distances⁸ are $\sim 1.84 \text{ \AA}$.

As may be seen from the Raman data given in the Table, the complex $4\text{XeF}_6 \cdot \text{PdF}_4$ (ref. 11) contains essentially the same cation as $\text{Xe}_2\text{F}_{11}^+ \text{AuF}_6^-$ and may, therefore, be confidently formulated as $(\text{Xe}_2\text{F}_{11}^+)_2 \text{PdF}_6^{2-}$. The F bridging of two XeF_5 groups in the $\text{Xe}_2\text{F}_{11}^+$ cation appears to be characterized by a 'bridge stretch' at $\sim 360 \text{ cm}^{-1}$; but, in keeping with the observed structure, the complex cation otherwise behaves vibrationally, like two weakly coupled XeF_5^+ species..

It seems probable that all XeF_6 complexes with fluoride ion acceptors will prove to be either XeF_5^+ or $\text{Xe}_2\text{F}_{11}^+$ salts. In particular, the $2\text{XeF}_6 \cdot \text{MF}_5$ and $4\text{XeF}_6 \cdot \text{MF}_4$ complexes reported by Cady and his coworkers^{4,6} are very probably $\text{Xe}_2\text{F}_{11}^+$ salts.

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TABLE

Raman Spectra of $\text{Xe}_2\text{F}_{11}^+$ Salts and Related Species (shifts in cm^{-1})

$\text{IF}_5^{(a)}$	$(\text{NO}^+)_2\text{PdF}_6^{2-}$	$(\text{XeF}_5^+)_2\text{PdF}_6^{2-}$	$(\text{Xe}_2\text{F}_{11}^+)_2\text{PdF}_6^{2-}$	$(\text{Xe}_2\text{F}_{11}^+)\text{AuF}_6^-$	$\text{Cs}^+\text{AuF}_6^-$
710($\underline{\nu}_1$) vs	653 s		668 w 651 vs	661 s	
631($\underline{\nu}_7$) sh	634 vw		630 m	640 w	
614($\underline{\nu}_2$) vs		616 vw 606 w	615 w 610 m 606 w	626 w 600 s	
602($\underline{\nu}_4$) sh		590 ms	591 s 583 m	595 vs 590 vs	595($\underline{\nu}_1$) vs
	573($\underline{\nu}_1$) s	558 ms	568 s		
	554($\underline{\nu}_2$) ms	535 s	546 w		
					530($\underline{\nu}_2$) vw
370($\underline{\nu}_8$) w		425 vw 396 vw	412 vw 396 vw	400 w	
			375 w	356 w	
318($\underline{\nu}_3$) m	309 w		296 w (b)	290 w	
274($\underline{\nu}_6$) w	269 w		270 w (b)	---	
	243($\underline{\nu}_5$) ms	245 w	245 w (b)		
					221 m 224($\underline{\nu}_5$) s

(a) L. E. Alexander and I. R. Beattie, J. Chem. Soc. (A),
1971, 3091.

(To set alongside figure)

Anion

F9-Au-F9'	179.1(3)°
F8	90.4(4)
F8-Au-F11	91.6(6)
12	88.0(5)
F10-Au-F11	89.2(5)
F12	91.2(6)

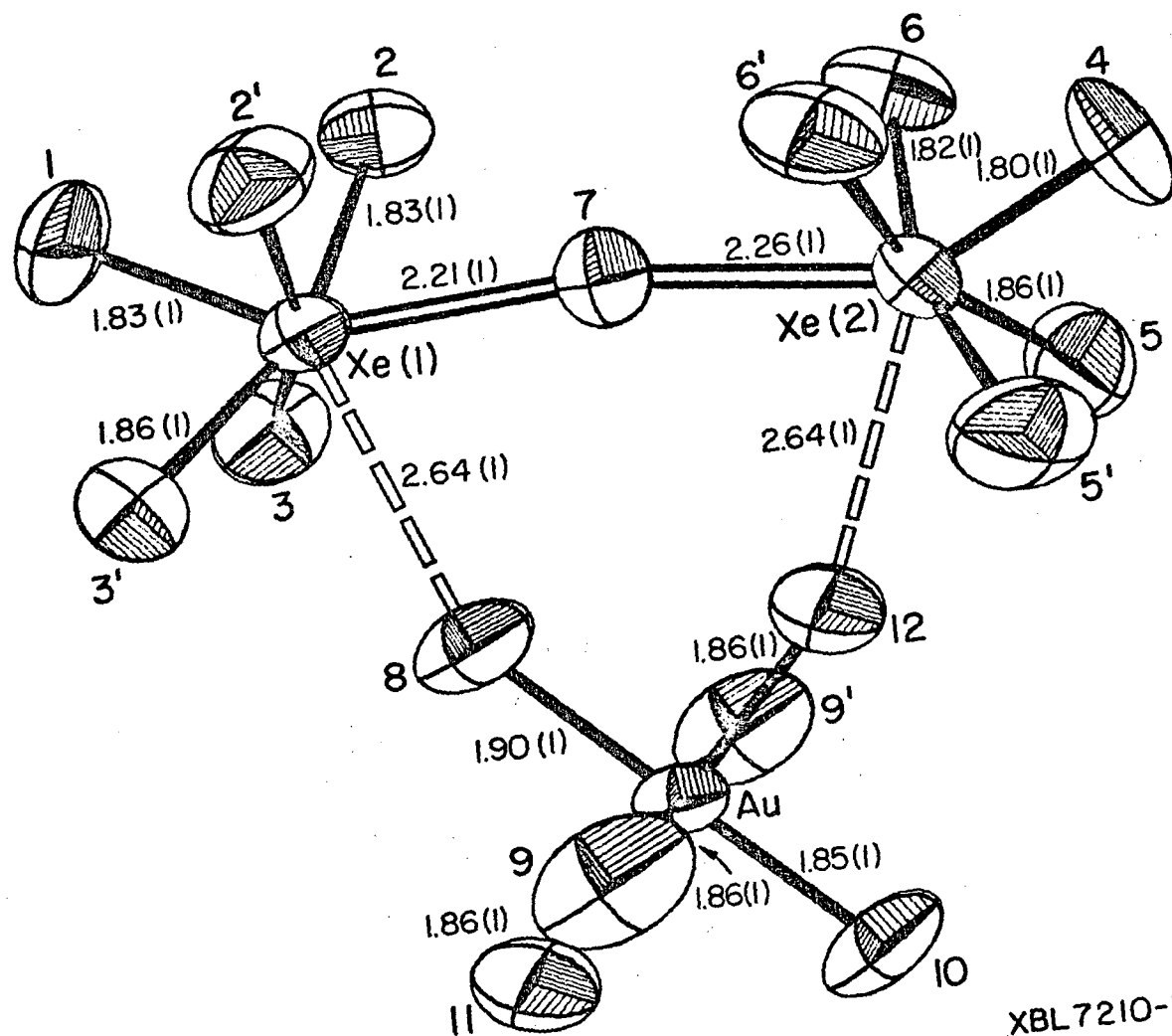
Cation

F1-Xe1-F2	79.6(4)°	F4-Xe2-F6	79.4(4)°
F3	79.0(4)	F5	81.1(5)
F2-Xe1-F2	86.8(3)	F6-Xe2-F6	88.6(3)
F3	87.1(4)	F5	87.4(6)
F3-Xe1-F3	91.1(3)	F5-Xe2-F5	89.9(3)
Xe2-F7-Xe1	169.2(2)		

Interionic Distances and Angles

Xe1-F8	2.64(1) Å	F1-Xe1-F7	147.6(6)°	F4-Xe2-F7	146.3(7)°
F9	3.27(1)	F8	136.3(6)	F12	139.8(7)
Xe2-F12	2.64(1)	F9	132.2(3)	F9	135.9(2)
F9	3.52(1)				

Figure Legend: Figure The Structural unit of $\text{Xe}_2\text{F}_{11}^+\text{AuF}_6^-$ (estimated standard deviations in parentheses)



XBL7210-7119

Fig. 1.

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