Submitted to
Chemical Communications

RECEIVED
LAWRENCE
RADIATION LABORATORY

DEC 14 1972

LIBRARY AND
DOCUMENTS SECTION

LBL-1189
Preprint

THE CRYSTAL STRUCTURE OF $Xe_2F_{11}^+AuF_6^-$ AND THE RAMAN SPECTRUM OF $Xe_2F_{11}^+$

Kevin Leary, Allan Zalkin and Neil Bartlett

October 1972

Prepared for the U.S. Atomic Energy
Commission under Contract W-7405-ENG-48

For Reference

Not to be taken from this room

LBL-1189

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

0 0 0 0 3 8 0 0 0 1 1

LBL-1189

THE CRYSTAL STRUCTURE OF $Xe_2F_{11}^+AuF_6^-$ AND THE RAMAN SPECTRUM OF $Xe_2F_{11}^+$

by

Kevin Leary, Allan Zalkin and Neil Bartlett

Inorganic Materials Research Division, Lawrence Berkeley Laboratory and
Department of Chemistry; University of California
Berkeley, California 94720

Summary: Two novel ions are described by the crystal structure of $Xe_2F_{11}^+AuF_6^-$. 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 laboratories[1] 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 $Xe_2F_{11}^+AuF_6^-$ salt.

Crystal data: $F_{17}AuXe_2$, M = 782.5, orthorhombic, a = 9.115(6), b = 8.542(25), c = 15.726(20) Å, V = 1224 Å^3, 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 Kα 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 $\underline{t}_{2g}^{6}$ configuration of Au(V) and is as anticipated from the vibrational spectroscopic[1] and Mössbauer studies[2]. 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 reported[3] for the anion in $XeF_5^+PtF_6^-$.

Although proof[3] that $XeF_6 \cdot PtF_5$ was the salt $XeF_5^+PtF_6^-$, suggested that $2XeF_6 \cdot PtF_5$ was probably $Xe_2F_{11}^+PtF_6^-$, efforts to obtain suitable single crystal crystals of this and related compounds[4,5,6] had failed hitherto[7]. 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 (~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[8,9,10]. Furthermore, the approach of the angle Xe(1)-F(7)-Xe(2) [169.2(2)°] to linearity, indicates that the bridge bond may be close to the ionic form $XeF_5^+F^-XeF_5^+$.

Although each XeF_5 group in the complex cation departs significantly from the ideal $\underline{C}_{4\underline{v}}$ symmetry of the XeF_5^+ cation[8], each is still

characterized by F_{axial}-Xe-$F_{equatorial}$ angles of ~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. 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 $Xe_2F_{11}^+$. These deflections would be towards the bisectors of the F(3)-Xe(1)-F(3') and the F(5)-Xe(2)-F(5') angles. Such deflection of the electron pairs could also account for the lengthening of the Xe(1)-F(3) and Xe(2)-F(5) interatomic distances and the shortening of the Xe(1)-F(2) and Xe(2)-F(6) distances. In XeF_5^+ the Xe-F equatorial distances[8] are ~ 1.84 Å

As may be seen from the Raman data given in the Table, the complex $4XeF_6 \cdot PdF_4$ (ref. 11) contains essentially the same cation as $Xe_2F_{11}^+AuF_6^-$ and may, therefore, be confidently formulated as $(Xe_2F_{11}^+)_2PdF_6^{2-}$. The F bridging of two XeF_5 groups in the $Xe_2F_{11}^+$ cation appears to be characterized by a 'bridge stretch' at ~ 360 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 $Xe_2F_{11}^+$ salts. In particular, the $2XeF_6 \cdot MF_5$ and $4XeF_6 \cdot MF_4$ complexes reported by Cady and his coworkers[4,6] are very probably $Xe_2F_{11}^+$ salts.

ACKNOWLEDGMENT

This work was supported by the U.S. Atomic Energy Commission.

REFERENCES

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, F. Einstein, D. Steward, and J. Trotter, Chem. Comm. 1966, 550; and J. Chem. Soc.(A), 1967, 478.
4. G. L. Gard, and G. H. Cady, Inorg. Chem. 1964, 3, 1945.
5. N. Bartlett, and F. O. Sladky, J. Amer. Chem. Soc., 1968, 90, 5316.
6. K. E. Pullen, and G. H. Cady, Inorg. Chem., 1966, 5, 2077; 1967, 6, 1300 and 2267.
7. N. Bartlett, and M. Wechsberg, Z. anorg. u. allgem. Chem., 1971, 385, 5.
8. N. Bartlett, K. Leary, D. Templeton, and A. Zalkin,"The Crystal Structure of $(XeF_5^+)_2PdF_6^{2-}$", to be published.
9. 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 to Inorg. Chem.
10. N. Bartlett, B. DeBoer, F. Hollander, F. O. Sladky, D. Templeton, and A. Zalkin, "The Crystal Structures of $Xe_2F_3^+AsF_6^-$ and $XeF_5^+AdF_6^-$, to be published.
11. K. Leary and N. Bartlett, to be published.

TABLE

Raman Spectra of $Xe_2F_{11}^+$ Salts and Related Species (shifts in cm^{-1})

IF_5 [a]	$(NO^+)_2PdF_6^{2-}$	$(XeF_5^+)_2PdF_6^{2-}$	$(Xe_2F_{11}^+)_2PdF_6^{2-}$	$(Xe_2F_{11}^+)AuF_6^-$	$Cs^+AuF_6^-$
710(ν_1) vs		653 s	668 w 651 vs	661 s	
631(ν_7) sh		634 vw	630 m	640 w	
614(ν_2) vs		616 vw 606 w	615 w 610 m 606 w	626 w 600 s	
602(ν_4) sh		590 ms	591 s 583 m	595 vs 590 vs	595(ν_1) vs
	573(ν_1) s	558 ms	568 s		
	554(ν_2) ms	535 s	546 w		
					530(ν_2) vw
370(ν_8) w		425 vw 396 vw	412 vw 396 vw	400 w	
			375 w	356 w	
318(ν_3) m		309 w	296 w (b)	290 w	
274(ν_6) w		269 w	270 w (b)	---	
	243(ν_5) ms	245 w	245 w (b)		
				221 m	224(ν_5) s

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

(To set alongside figure)

Anion		Cation			
F9-Au-F9'	179.1(3)°	F1-Xe1-F2	79.6(4)°	F4-Xe2-F6	79.4(4)°
F8	90.4(4)	F3	79.0(4)	F5	81.1(5)
F8-Au-F11	91.6(6)	F2-Xe1-F2	86.8(3)	F6-Xe2-F6	88.6(3)
12	88.0(5)	F3	87.1(4)	F5	87.4(6)
F10-Au-F11	89.2(5)	F3-Xe1-F3	91.1(3)	F5-Xe2-F5	89.9(3)
F12	91.2(6)	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 $Xe_2F_{11}^+AuF_6^-$ (estimated standard deviations in parentheses)

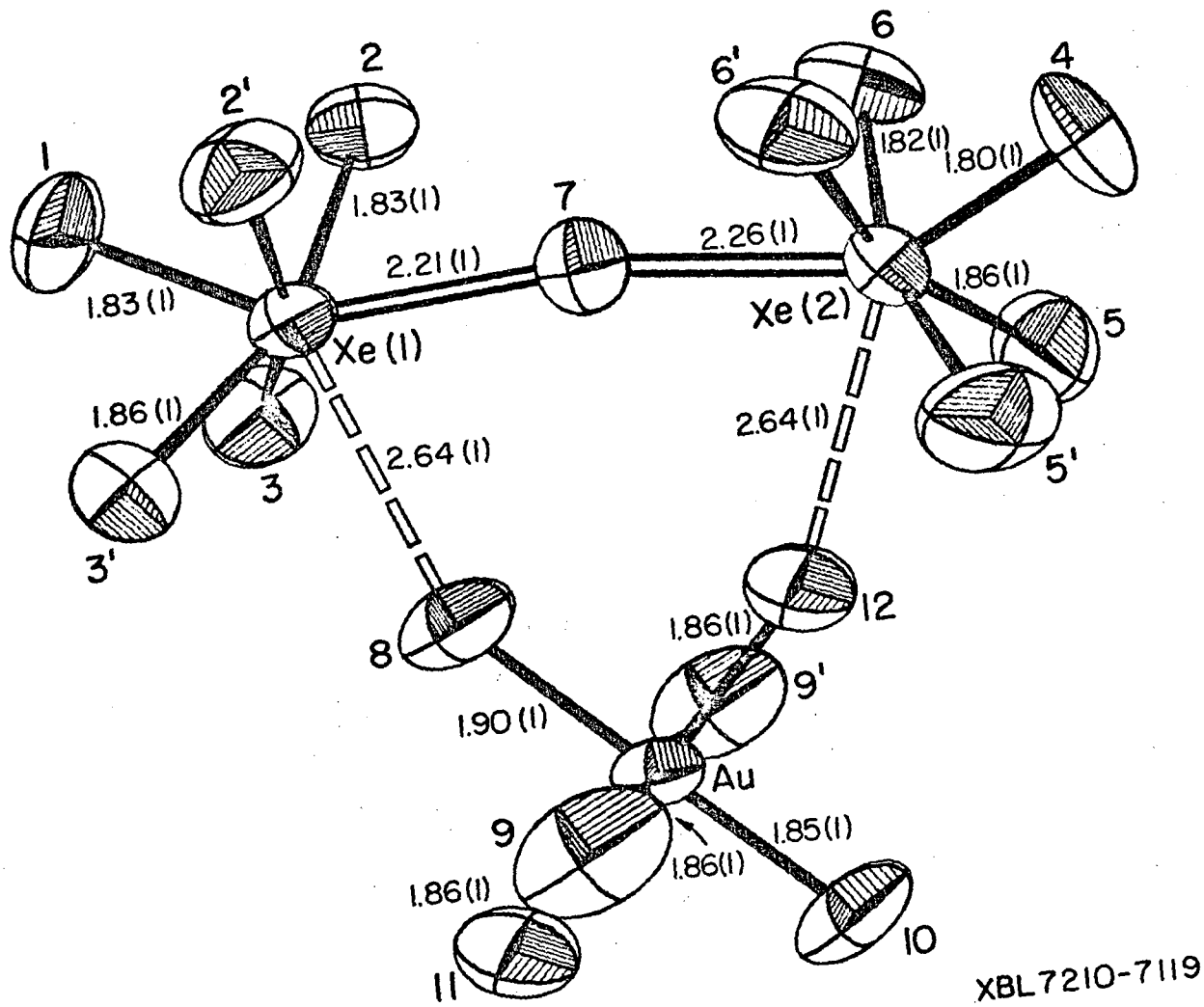
1
2
2'
1.83(1)
1.83(1)
2.21(1)
7
2.26(1)
6'
6
1.82(1)
1.80(1)
4
1.86(1)
5
5'
Xe(1)
Xe(2)
1.86(1)
3
3'
2.64(1)
2.64(1)
8
12
1.86(1)
9'
1.90(1)
Au
9
1.85(1)
1.86(1)
1.86(1)
10
11
XBL7210-7119

Fig. 1.

LEGAL NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

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