The Preparation, Crystal Structure, and Magnetic Properties of Pentafluoroxenonyl Hexafluoroplatinate(V), $[XeF_5]^+[PtF_6]^-$

By NEIL BARTLETT*, FRED EINSTEIN, D. F. STEWART*, and JAMES TROTTER
(*Dept. of Chemistry, The University of British Columbia, Vancouver* 8, *B.C., Canada*)

THE reaction of xenon with platinum hexafluoride[1] yields at least two distinct quinquevalent platinum products, $XePtF_6$ and $Xe(PtF_6)_2$. A third compound $XePt_2F_{10}$ which is diamagnetic, is produced by heating the former. During continuing investigations of the reaction between xenon, fluorine, and platinum pentafluoride, at least two different compounds have been detected. The better characterized compound is produced when 1 : 1 molar ratios of xenon and platinum pentafluoride are employed in admixture with 80 p.s.i. fluorine gas at 180—220°. The yellow needle-shaped crystals, m.p. ~100°, have an empirical composition $F_{11}PtXe$. The colour, magnetic properties, and infrared spectrum of the solid indicate that it contains quinquevalent platinum. Analytical data suggest that a second compound, formed when the Xe : PtF_5 molar ratio exceeds one, may have the composition $F_{17}PtXe_2$. A single-crystal *X*-ray structure determination of $F_{11}PtXe$ has disclosed a molecular geometry consistent with an ionic formulation $[XeF_5]^+[PtF_6]^-$.

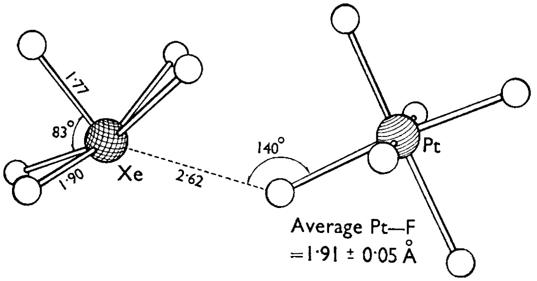
---

* Present address: The Frick Chemical Laboratories, the University of Princeton, Princeton, N.J., U.S.A.

The yellow solid resembles nitrosyl hexafluoroplatinate(V), $NO^+[PtF_6]^-$, in appearance,[2] and shows a similar intense absorption in the infrared at ~640—650 cm.$^{-1}$, attributable to the octahedral ν_3 vibrational mode of PtF_6^-. The magnetic susceptibility of the compound obeys the Curie–Weiss Law in the range 77—298°K with θ = 35°. As indicated in Table 1 this behaviour is intermediate between that observed[2,3] for the quinquevalent platinum compounds $NO^+[PtF_6]^-$ and Pt_4F_{20}.

Crystals of the compound of empirical formula $F_{11}PtXe$ are orthorhombic with unit-cell dimensions: a = 8·16, b = 16·81, c = 5·73 Å, V = 785·4 Å^3. The unit cell volume is consistent with Z = 4, since with 44 fluorine atoms in the unit cell[5] the volume per fluorine atom has its usual value of ~18 Å^3. Successful refinement of the structure is proceeding in space group *Pmnb* (No. 62). Three-dimensional intensity data were collected with Mo-K_α radiation on a G.E. spectrogoniometer equipped with a scintillation counter. For the subsequent structure analysis 565 observed reflexions were used. The platinum and xenon positions were determined from a three-dimensional Patterson map, and the fluorine atom positions from subsequent electron-density maps. Block diagonal least-squares refinement has led to an R-value of 0·15. Further refinements which take account of imaginary terms in the anomalous dispersion corrections are in progress.

The geometric arrangement of the atoms is represented in the Figure. Each platinum atom has six close fluorine atom neighbours in an approximately octahedral arrangement; the six Pt–F distances are in the range 1·87—1·99, with a mean bond length of 1·91 ± 0·05 Å, and F–M–F angles for adjacent fluorine atoms in the group are ~90°. Each xenon atom has five close fluorine atom neighbours in a square- pyramidal arrangement; the xenon atom is slightly below (~0·2 Å) the base of the pyramid, and the Xe–F distances are 1·89 (2 ×), 1·91 (2 ×), 1·77 Å. One fluorine atom of the PtF_6^- group is sufficiently close to the xenon atom, 2·62 Å, to form a weak bridge bond, and the direction of approach of this fluorine suggests steric activity of the xenon nonbonding electron pair. However, the main features of the crystal structure can be accounted for simply in terms of the ionic formulation $[XeF_5]^+[PtF_6]^-$. $[IF_6]^+[AsF_6]^-$ has demonstrated[6] the fluoride ion donor ability of IF_7 and this capacity is also implied for XeF_6 by the formulation $[XeF_5]^+[PtF_6]^-$.



FIGURE

The geometry of the XeF_5^+ ion is of special interest. The dimensions are compared with those of related pseudo-octahedral molecules in Table 2. It is a characteristic of each of these species that the M–Y distance is shorter than the M–X.

Of the two conventional bonding theories, the valence shell electron pair repulsion theory, which has been applied to similar species,[7] can account for the shorter Xe–F (apical) bond and for the F(apical)–Xe–F angles of less than 90°. The steric activity of the nonbonding electron pair causes repulsion and lengthening of the adjacent Xe–F bonds. The simple molecular-orbital treatment[8] could explain the bond-length differences, but not the angular variations.

TABLE 1.

A comparison of magnetic data for $NO^+[PtF_6]^-$, $[XeF_5]^+[PtF_6]^-$, *and* Pt_4F_{20}.

($10^6\chi_A$ in c.g.s. units)

Temp.	80	150	220	290°K	μ_{eff}(B.M.)
$NOPtF_6$	3356	2074	1458	1176	1·74
XeF_5PtF_6	4255	2625	1901	1488	1·97
Pt_4F_{20}	4739	2882	2075	1616	2·05

† Recent work in these laboratories[3] has shown that the "pentafluoride" is isostructural with its ruthenium analogue.[4] In this structure the metal atoms are only approximately octahedrally co-ordinated by fluorine atoms, two of the atoms having a bridging role of the tetramer, the other four being uniquely associated with a ruthenium atom. On the other hand PtF_6^- in the nitrosyl salt is probably close to octahedral.[2] The difference in magnetic properties may well be a consequence of the differences in shape of the PtF_6 species.

TABLE 2.

The geometry of XeF_5^+ *and related* MYX_4 *molecules*

Molecule	M–Y (Å)	M–X (Å)	∠YMX	Reference
$XeOF_4$	1·71	1·90	91·9	9, 10
XeF_5	1·77	1·90	83	Present work
IF_5	1·75	1·86	—	10
BrF_5	1·68	1·79	80—86·5	11

It is of interest that a compound of composition $F_{17}PtXe_2$ is indicated. Since platinum in a fluorine ligand environment is unwilling to adopt higher co-ordination than six,[12] this compound presumably involves fluorine bridging between xenon species.

(*Received, July* 14*th*, 1966; *Com.* 498.)

---

[1] (a) N. Bartlett, *Proc. Chem. Soc.*, 1962, 218; (b) N. Bartlett and N. K. Jha in "Noble Gas Compounds" H. H. Hyman ed., The University of Chicago Press, Chicago and London 1963, pp. 23—30.
[2] N. Bartlett and S. P. Beaton, *Chem. Comm.*, 1966, 157.
[3] M. Akhtar and N. Bartlett, unpublished observations.
[4] J. H. Holloway, R. D. Peacock, and R. H. W. Small, *J. Chem. Soc.*, 1964, 644.
[5] W. H. Zachariason, *Acta Cryst.*, 1949, **2**, 390.
[6] F. Seel and O. Detmer, *Z. anorg. Chem.*, 1959, **301**, 8; and N. Bartlett and S. P. Beaton, unpublished observations.
[7] R. J. Gillespie. *J. Chem. Soc.*, 1963, 4672.
[8] R. E. Rundle, *Rec. Chem. Progr.*, 1962, **23**, 195.
[9] J. Martins and E. B. Wilson, Jr., *J. Chem. Phys.*, 1964, **41**, 570.
[10] G. M. Begun, W. H. Fletcher, and D. F. Smith, *J. Chem. Phys.*, 1965, **42**, 2236.
[11] R. D. Burbank and F. N. Bensey, Jr., *J. Chem. Phys.*, 1957, **27**, 981.
[12] N. Bartlett, S. P. Beaton, and N. K. Jha, *Chem. Comm.*, 1966, 168.