

Scientific paper

Reactions of Xenon with Iridium- and Osmiumhexafluoride

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Dedicated to Professor Boris Žemva

Abstract

Xenon and Iridiumhexafluoride react at temperatures above room temperature forming $\text{XeF}^+\text{IrF}_6^-$. In presence of SbF_5 $\text{FXe}^+\text{IrSbF}_{11}^-$ is formed. Xenon and Osmiumhexafluoride form in solution a blue charge transfer complex that cannot be isolated as a solid.

Keywords: Xenon oxidation, iridium hexafluoride, osmium hexafluoride, fluoro xenon hexafluoroiridate crystal structure

1. Introduction

The reaction between Xenon and PtF_6 is of historical importance since it marked the beginning of noble gas chemistry.¹ Ironically it is not even now clear what the mustard colored amorphous, paramagnetic powder, »XePtF₆«, is.² After warming to room temperature the material converts into $\text{XeF}^+\text{PtF}_6^-$ or $\text{XeF}^+\text{Pt}_2\text{F}_{11}^-$.²

In the beginning of noble gas chemistry it has been shown that some other metal hexafluoride promote a similar redox reaction with xenon, namely RuF_6 ³ and RhF_6 ,⁴ whereas other do not, e.g. IrF_6 , OsF_6 , ReF_6 , WF_6 , and MoF_6 . It is striking that the deeply colored hexafluorides PtF_6 , RhF_6 , RuF_6 have an electron affinity high enough to oxidize xenon, while lightly colored (yellow, orange) IrF_6 , OsF_6 , ReF_6 , TcF_6 or colorless WF_6 and MoF_6 have a too low electron affinity. The absorptions in the visible region are assigned to fluorine to metal charge transfer bands⁵ and therefore reflect the extreme electron affinity of the Pt, Ru, and Rh centers in the hexafluorides.

But the actual electron affinities of these metal hexafluorides are till under discussion. N. Bartlett has proposed a qualitative sequence: $\text{WF}_6 < \text{ReF}_6 < \text{OsF}_6 < \text{IrF}_6 < \text{PtF}_6$.⁵ Classical theory would clearly rank OsF_6 (d^2) higher in electron affinity than IrF_6 (d^3). This sequence can be exchanged if spin orbit coupling is taken into ac-

count.⁷ Precise experimental data for the electron affinities are not available and seem very difficult to be obtained, at least with a certain minimum accuracy.

Qualitatively it is obvious that IrF_6 is a stronger oxidator than OsF_6 . The former can oxidize Cl_2 to $\text{Cl}_4^+\text{IrF}_6^-$, while OsF_6 cannot do the same under similar conditions.⁸ IrF_6 also fluorinates NO up to NOF_3 , while OsF_6 gives only NOF .⁶

2. Results and Discussion

Xenon and OsF_6 or IrF_6 , if condensed into a quartz tube⁹ and held at -78°C give an intense blue solution. If these samples are warmed to room temperature a slow reaction sets in. In case of Xe/IrF_6 yellow crystals are formed. No reaction is observed in the Xe/OsF_6 samples.

The blue color is certainly due to a charge transfer absorption of a Xe/MF_6 complex which exists in solution, but cannot be crystallized. Similar charge transfer colors have been observed in the Cl_2/OsF_6 , Cl_2/IrF_6 , and $\text{Xe}_2^+/\text{Xe}/\text{SbF}_5$ mixtures.⁹

The identity of the crystalline material is $\text{XeF}^+\text{IrF}_6^-$, as is established by a single crystal structure determination, see figure 1 and table 1.

The crystal structure reveals that there are three different $\text{XeF}^+\text{IrF}_6^-$ unit in the asymmetric unit. But with one

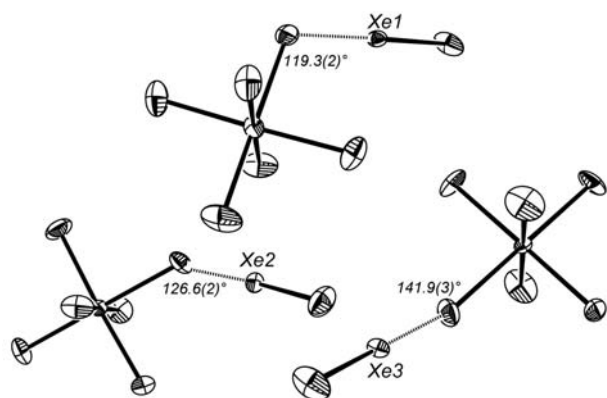


Figure 1. $\text{XeF}^+\text{IrF}_6^-$, Ortep representation, 50% probability ellipsoids. There are three crystallographically independent, but chemically quite similar units in the asymmetric unit.

exception their bond lengths and angles are so close that they can be discussed altogether, see Table 1.

The ionic formulation $\text{XeF}^+\text{IrF}_6^-$ should be extended by calling this compound an ion pair with a directed attraction of the bridging fluorine atom between the iridium and the xenon atom, giving an almost linear fluorine environment around the xenon atom. This is a well known behaviour of Xe(II), e.g. observed in $\text{XeF}^+\text{Sb}_2\text{F}_{11}^-$ for the first time,¹⁰ and in many cases later on. The three crystallographic different

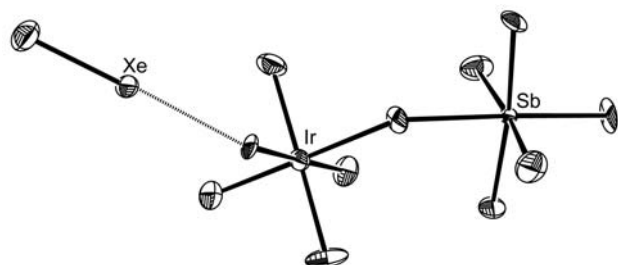


Figure 2. $\text{FXe}^+\text{IrSbF}_{11}^-$, Ortep representation, 50% probability ellipsoids. The overall structure is very similar to $\text{FXe}^+\text{Sb}_2\text{F}_{11}^-$ and other salts of that stoichiometry. To our knowledge it is the first time that a mixed anion ABF_{11}^- is identified.

Table 1. Important bond lengths (pm) and angles ($^\circ$) of $\text{FXe}^+\text{IrF}_6^-$ and $\text{FXe}^+\text{IrSbF}_{11}^-$. The three values for $\text{FXe}^+\text{IrF}_6^-$ correspond to the three crystallographic different molecules in the asymmetric unit.

	$\text{FXe}^+\text{IrF}_6^-$	$\text{FXe}^+\text{IrSbF}_{11}^-$
XeF	185.4(5), 186.7(5), 185.4(4)	187.9(10)
$\text{Xe}\cdots\text{F}_{\text{br}}^{\text{a}}$	227.2(4), 222.0(4), 224.5(5)	228.8(8)
$\text{Ir}-\text{F}_{\text{br}}^{\text{a}}$	195.6(5), 196.1(4), 195.9(5)	197.3(9)
$\text{Ir}-\text{F}_{\text{br}}^{\text{b}}$	185.4(5), 186.9(9), 186.3(5)	202.0(9) ^c
$\text{Ir}-\text{F}$	185.4–187.3(5), 185.8(5)–187.1(5), 185.7–186.1(5)	180.8–186.4(10)
Sb-F		183.5–185.6(10), 201.8(8) ^c
$\text{F}-\text{Xe}\cdots\text{F}_{\text{br}}$	177.9(2), 177.4(2), 179.3(2)	178.1(4)
$\text{Xe}\cdots\text{F}-\text{Ir}$	119.3, 126, 141.9	122.0(4)

^a F_{br} : bridging fluorine atom between Ir and Xe ^b F_{ax} : fluorine atom opposite to the bridging fluorine atom
^c bridging fluorine atom between Ir and Sb

ion pairs $\text{FXe}^+\text{IrF}_6^-$ differ essentially only in the angle of the bridging fluorine atom, with values of 119.3, 126, and 141.9. In compounds of a similar composition $\text{FXe}^+\text{AF}_6^-$ A=As, Sb, Bi, and Ru this angle at the bridging fluorine atom varies between 133.6(2) $^\circ$ (A=As and 156.1(4) $^\circ$ A=Bi).^{11–14}

The reaction between Xe and IrF_6 can be speeded up dramatically if it is performed in anhydrous HF and in presence of SbF_5 . The reaction sets in at temperatures below 20 $^\circ\text{C}$ and is completed quickly at this temperature. No blue charge transfer complex is observed as an intermediate. The outcome is the compound $\text{FXe}^+\text{IrSbF}_{11}^-$, see figure 2 and tables 1 and 2.

Table 2. Crystallographic Data

	$\text{FXe}^+\text{IrF}_6^-$	$\text{FXe}^+\text{IrSbF}_{11}^-$
a (pm)	794.9(2)	589.8(1)
b (pm)	1085.8(3)	2091.1(1)
c (pm)	2132.0(6)	787,9(1)
β ($^\circ$)	91.637(7)	90.02(2)
V ($\text{pm}^3 \cdot 10^6$)	1839.4	971.7
lattice	monoclinic	monoclinic
space group	$\text{P2}_1/\text{c}$	C_c
size (mm)	$0.05 \times 0.05 \times 0.04$	$0.1 \times 0.03 \times 0.003$
color	yellow	yellow
ρ_{calcd}	4.945	4.602
μ (mm^{-1})	27.27	20.04
reflexions		
total	21942	6566
unique	5478	3192
R_{int}	0.044	0.088
$2\theta_{\text{max}}$ ($^\circ$)	62.28	65.11
parameters	245	140
R_1	0.0323	0.0571
wR_2	0.0619	0.1617
Goof	1.127	1.053

3. Experimental Section

3. 1. Preparation of $\text{FXe}^+\text{IrF}_6^-$

A quartz tube is connected to a metal vacuum line and cooled to -196 $^\circ\text{C}$. 300 mg (0.98 mmol) IrF_6 and 1 ml

xenon are condensed into it. The tube is sealed and warmed to room temperature.

Caution: high pressure! A dark blue, almost black solution is formed. The tube is further warmed to 45 °C, and then cooled to –196 °C and connected again to the metal vacuum line. By slow warming to room temperature the volatiles, mostly excess xenon, are pumped off. A yellow microcrystalline solid remains. 200 mg of it are filled into a PFA tube, and 600 mg anhydrous HF are condensed on it. Recrystallisation by cooling from 80 °C to room temperature bring out large, cubic shaped, yellow crystals.

3. 2. Attempted Reaction Between Xenon and OsF₆

The same procedure as described above is tried with xenon and OsF₆. Also a dark blue–black solution is formed. After evaporation no solid remains. If the OsF₆ solution in xenon is cooled to –78 °C, yellow OsF₆ crystallizes out, and the blue color of the charge transfer complex disappears.

3. 3. Preparation of Xe⁺IrSbF₁₁[–]

1.2 g (5.5 mmol) SbF₅ are given into a PFA tube, and the tube is connected to a metal vacuum line. 680 mg anhydrous HF are condensed into it, the sample is warmed to room temperature and well mixed. At –196 °C 1.06 g (3.5 mol) IrF₆ are condensed in, warmed to room temperature, mixed, a yellow solution is formed, and cooled again to –196 °C, when 1.5 g (11 mol) xenon are condensed in. The tube is sealed and warmed slowly to room temperature. The orange solution is cooled slowly to –60 °C, yellow crystals of FXe⁺IrSbF₁₁[–] are formed. The crystal structure suffers from racemic and a non-merohedral twinning, resulting only in moderate crystallographic characteristics.

Crystals are selected and mounted with help of a special device¹⁶ on a Bruker CCD Smart diffractometer (MoK α irradiation, ω -scan in 0.3° steps, 2400 frames). Absorption correction equilibration of symmetry selected reflections. Structure solution and refinement by Shelx programs.¹⁷ Further details of the crystal structure determinations may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (FAX +49-7247-808-666; E-Mail: crysdata@fiz-karlsruhe.de, <http://www.fiz-karlsruhe.de/request>) for deposited data.html on quoting the depository numbers CSD 424640 (FXe⁺IrF₆[–]) and 424641 (FXe⁺IrSbF₁₁[–]).

4. Conclusion

While the quantitative difference in oxidation potential and/or electron affinity between OsF₆ and IrF₆ is still

unclear, it is obvious that IrF₆ has considerable higher values than OsF₆. The difference in electron affinity as suggested by N. Bartlett, namely 0.5–1.0 eV may be too high, but the recently calculated value of this difference, 0.07 eV⁷ should be regarded as a lower limit, since converted into a chemical reaction enthalpy under otherwise identical conditions comes out only at 1.6 kcal/Mol. The assumption of a kinetic difference of the oxidation reaction of IrF₆ and OsF₆ with xenon has been disapproved with our result.

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Povzetek

$\text{XeF}^+\text{IrF}_6^-$ je produkt reakcije med ksenonom in iridijevim heksafluoridom pri temperaturah do 45 °C. V prisotnosti SbF_5 nastane $\text{FXe}^+\text{IrSbF}_{11}^-$. Pri reakciji med ksenonom in osmijevim heksafluoridom v raztopini opazimo modro obarvan kompleks, ki ga ni mogoče izolirati kot trdno snov.