

## On the synthesis of Xenon (VI) fluoroargentate (III)

by

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**ABSTRACT.** — The reaction between silver difluoride and an excess of xenon hexafluoride and krypton difluoride in anhydrous hydrogen fluoride yields a light yellow diamagnetic solid, xenon (VI) fluoroargentate(III). On the basis of vibrational data this compound could be formulated as a  $\text{XeF}_5^+$  salt with four coordinated silver. Xenon(VI) fluoroargentate (III) is thermally stable in a dynamic vacuum up to 70°C where it begins to lose  $\text{XeF}_6$ , yielding  $\text{AgF}_3$ .

**RÉSUMÉ.** — La réaction entre le difluorure d'argent et un excès d'hexafluorure de xénon et de difluorure de krypton donne un solide jaune diamagnétique : le fluoroargentate (III) de xénon (VI). D'après les spectres de vibration, ce composé peut se formuler comme un sel de  $\text{XeF}_5^+$  avec de l'argent à coordination IV. Le fluoroargentate (III) de xénon (VI) est thermiquement stable sous vide dynamique jusqu'à 70°C où il commence à perdre  $\text{XeF}_6$  avec résidu de  $\text{AgF}_3$ .

### INTRODUCTION

The existence of  $\text{AgF}_3$  [1], Ag(III) complex fluorides [2], mixed Ag(III) and Ag(V) complex fluorides [3], taken together with  $\text{XeF}_5^+$  and  $\text{Xe}_2\text{F}_{11}^+$  salts of palladium (IV) [4] and gold (V) [5], suggests that xenon (VI) fluoroargentate (III) should exist.

Previously, we had found  $\text{AgF}_2$  to be a very good catalyst in the formation of xenon fluorides from the elements (6), but there was no evident reaction product between  $\text{AgF}_2$  and xenon hexafluoride up to 120°C. Our approach to the synthesis of xenon (VI) fluoroargentate (III) was to use krypton difluoride as a strong fluorinating agent in combination with xenon hexafluoride as a moderately good fluoride-ion donor. The atomization energy of  $\text{KrF}_2$  ( $\Delta H_{at} = 96 \text{ kJ/mole}$ ) is smaller than the dissociation energy of elemental fluorine ( $\Delta H_{diss.} = 155 \text{ kJ/mole}$ ) thus indicating that krypton difluoride is closest in activity to atomic fluorine. Anhydrous hydrogen fluoride was used as a solvent and heat transfer medium. Using

this method xenon (VI) fluoronickelates (IV) were isolated [7]. This paper describes the preparation and some of the properties of xenon (VI) fluoroargentate (III).

## EXPERIMENTAL

### 1. General apparatus and preparation

Reactions were carried out in Teflon-FEP reaction vessels (18 mm o.d.) equipped with Teflon valves, or in argon arc welded nickel pressure and weighing vessels (100 ml) equipped with Teflon packed nickel valves. The compounds used or prepared in this work are decomposed by water and many are exceedingly strong oxidizers. All handling of solid materials was, therefore, carried out in the dry atmosphere of a dry box. Volatiles were transferred using an all nickel vacuum system.

In a typical experiment,  $\text{AgF}_2$  (5 mmoles) was weighed into a Teflon-FEP reaction vessel. Then a few ml of anhydrous HF were distilled and condensed onto the  $\text{AgF}_2$ . Krypton difluoride and xenon hexafluoride were added by sublimation to  $-196^\circ\text{C}$ . The Teflon-FEP reaction vessel was connected with the expansion vessel for removal of krypton and fluorine generated by the reaction and/or krypton difluoride decomposition. The reaction vessel was then slowly warmed up to room temperature. After the reaction was completed (several days), the volatiles were pumped off at room temperature and the products were isolated and characterized. The stoichiometry of the reaction was followed by mass balance throughout the experiment with an accuracy of  $\pm 5$  mg.

### 2. Routine characterization of materials

**Raman spectroscopy.** — Raman spectra were obtained using a Spex 1401 double monochromator, and a detection system that utilized photon counting techniques was used in conjunction with a variety of laser lines (Coherent Radiation) (principally 488.0, 514.5 and 647.1 nm). Powdered samples were loaded into 1 mm i.d. quartz capillaries in the dry-box, sealed temporarily with a plug of Kel-F grease, and the tube drawn and sealed in a small flame outside the dry-box.

**Infrared spectroscopy.** — Infrared spectra were obtained on a Zeiss UR-20 spectrometer over the range  $400\text{--}5000\text{ cm}^{-1}$ . A 10 cm path length nickel cell with AgCl windows (2 mm thick) was used for gases. Spectra of solids were obtained by dusting samples onto silver chloride plates sandwiched in a leak-tight brass holder.

**X-ray powder photography.** — X-ray powder diffraction patterns of solid samples were obtained with an ENRAF apparatus (Delft, Holland), using graphite monochromatized  $\text{CuK}_\alpha$  radiation. Finely powdered sample was sealed into 0.5 mm quartz capillaries as described under Raman spectroscopy.

**Thermal analysis.** — Thermal decomposition of the sample (100 mg) was performed on a Mettler TA 1 thermoanalyzer referenced by  $\alpha\text{-Al}_2\text{O}_3$ . The operating conditions were: heating rate of the furnace,  $4^\circ\text{C}/\text{min}$ ; flow of dry argon, 5 l/h; DTG range, 10 mg/min; and DTA range 100  $\mu\text{V}$ .

**Magnetic susceptibility measurements.** — Magnetic susceptibility was measured using the Faraday method on a modified Newport Instrument magnetic balance. The powdered sample was packed into a thin walled, screw capped Kel-F container (4 mm o.d., 4 mm height) in a dry box.

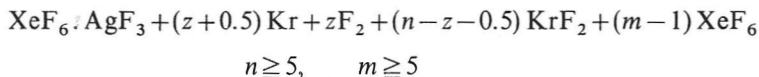
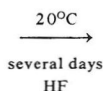
*Chemical analysis.* — Silver was determined both gravimetrically and by the atomic absorption method. Total fluoride ion was determined by the direct method using an ion-selective electrode. Xenon was determined both gravimetrically and volumetrically after a weighed sample had been allowed to react with mercury at 400°C in a nickel container.

### 3. Reagents

Silver difluoride was used as supplied, 99.5% pure by Fluka (Switzerland). Krypton difluoride was prepared by irradiation of a liquefied mixture of fluorine and krypton with near UV light at -196°C[8]. Xenon hexafluoride was prepared by the reaction between xenon and fluorine in the presence of nickel difluoride as a catalyst at 120°C[9]. Fluorine was prepared and purified in this laboratory as described elsewhere[10]. Its purity was  $99 \pm 0.5$  vol.%. Additional purification was performed by a photochemical method[11]. The purity of the fluorine so obtained was better than 99.9%. Xenon (99.99%) and krypton (99.99%) were used as supplied by Messer Griesheim (Austria). Commercial anhydrous hydrogen fluoride was purified by a modified method as described elsewhere [12]. Before use this HF was treated with krypton difluoride.  $\text{KAgF}_4$  was synthesized from  $\text{AgNO}_3$  and  $\text{KNO}_3$  under a pressure of 20 atm of elemental fluorine at 200°C.

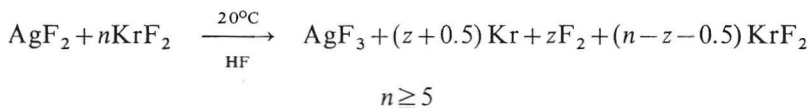
## RESULTS AND DISCUSSION

The reaction between silver difluoride, excess of krypton difluoride and xenon hexafluoride at room temperature in anhydrous hydrogen fluoride as solvent yields a light yellow solid  $\text{XeF}_6 \cdot \text{AgF}_3$ .

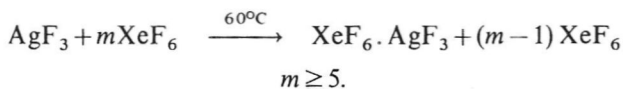


$z$  — part of  $\text{KrF}_2$  which thermally decomposes to the elements.

This approach is generally useful in cases where the higher metal fluoride is not stable, the high oxidation state being stabilized in the anion of the  $\text{XeF}_5^+$  salt. But in the case of silver, the parent fluoride  $\text{AgF}_3$  is thermodynamically stable at the reaction temperatures used, therefore the synthesis of  $\text{XeF}_6 \cdot \text{AgF}_3$  could occur in two steps:



$z$  — as stated in the above reaction



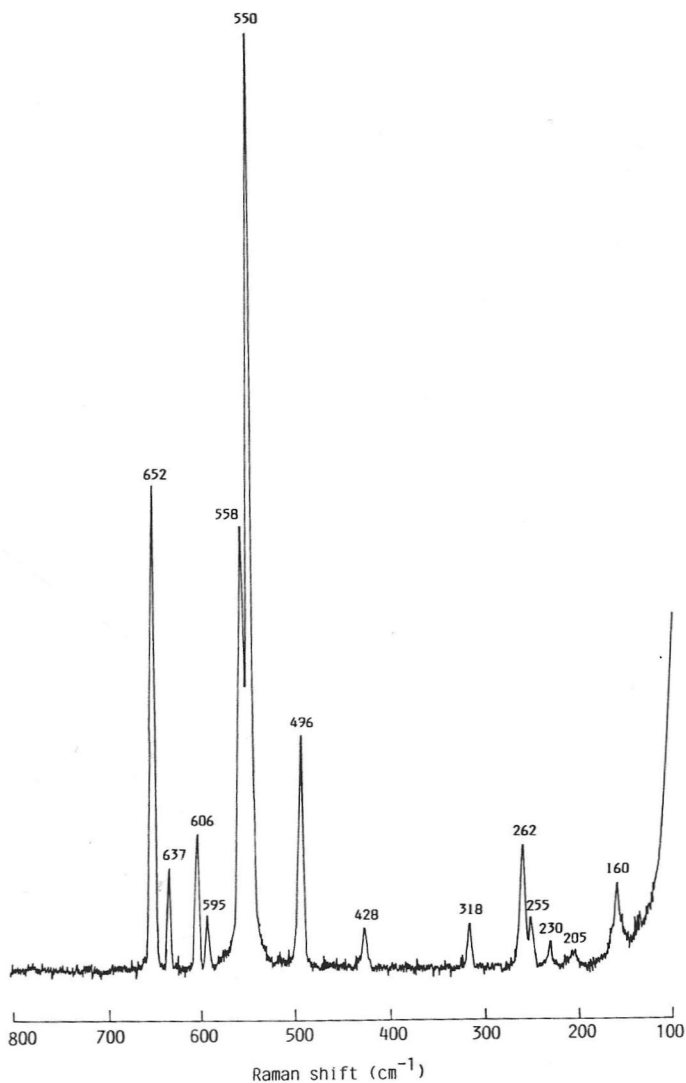
$\text{XeF}_6 \cdot \text{AgF}_3$  has negligible vapour pressure at room temperature (Analysis: Calcd.: for  $\text{XeF}_6 \cdot \text{AgF}_3$ : Ag, 26.30; Xe, 32.01; F, 41.69. Found: Ag, 26.2; Xe, 31.9; F, 41.0). It is stable in thoroughly dried nickel, Teflon, FEP or glass vessels. It is extremely sensitive to traces of moisture which rapidly turns it brown.

$\text{XeF}_6 \cdot \text{AgF}_3$  is stable in a dynamic vacuum up to  $70^\circ\text{C}$ , where it begins to lose  $\text{XeF}_6$  as was shown by IR spectroscopy. The final product of thermal decomposition at this temperature is  $\text{AgF}_3$  as was shown by X-ray powder diffraction patterns. The  $d$ -values of  $\text{AgF}_3$  thus obtained are practically identical with the Bougon  $d$ -values for  $\text{AgF}_3$  [13]. Silver trifluoride decomposes further to  $\text{AgF}_2$  and fluorine below  $200^\circ\text{C}$ . The difluoride decomposes, close to  $600^\circ\text{C}$ , to fluorine and  $\text{AgF}$ , shown by the X-ray powder diffraction patterns. From the DTA curves it is evident that the decomposition of xenon (VI) fluoroargentate (III) into  $\text{AgF}_3$  and  $\text{XeF}_6$  is an endothermic process.

The vibrational spectra of  $\text{XeF}_6 \cdot \text{AgF}_3$  are given in Table I and in Figure. All nine Raman lines attributable to fundamentals of  $\text{XeF}_5^+$  were observed and assigned by comparison with the spectra of related molecules. The strong band at  $\text{ca. } 652\text{ cm}^{-1}$  is assigned with confidence to the  $\nu_1$  stretching fundamental.  $\nu_7$ , the degenerate stretching mode of the basal  $\text{XeF}_4$  unit, should generate a strong infrared absorption, and is assigned at  $\text{ca. } 637\text{ cm}^{-1}$ , since the infrared spectrum of  $\text{XeF}_5^+\text{AgF}_4^-$  has its strongest absorption at this frequency. The fundamental  $\nu_4$  is not allowed in the infrared, and by analogy with other  $\text{MX}_5\text{C}_{4v}$  species, should give only a very weak Raman line.  $\nu_4$  is assigned at  $\text{ca. } 606\text{ cm}^{-1}$ . An unexplained feature in the Raman spectrum of  $\text{XeF}_5^+\text{AgF}_4^-$  is the low intensity of  $\nu_2$  which is usually one of the strongest Raman bands. The Raman bands of the compound  $\text{KAgF}_4$  provided for the assignment of the anionic part of the  $\text{XeF}_5^+\text{AgF}_4^-$ .

The vibrational data provide clear support for the formulation of xenon(VI) fluoroargentate (III) as a  $\text{XeF}_5^+$  salt. Comparison of the spectrum of  $\text{XeF}_5^+\text{AgF}_4^-$  with published Raman spectra of salts of the  $\text{XeF}_5^+$  ion with monomeric anions [14, 15] and polymeric anions [16, 17] indicate that the  $\text{AgF}_4^-$  is a monomeric anionic species.

The X-ray powder diffraction patterns indicates a low symmetry of the lattice and were not indexed.



The Raman spectrum of  $\text{XeF}_5\text{AgF}_4$  at  $-196^\circ\text{C}$ .

Magnetic susceptibility measurements of  $\text{XeF}_6 \cdot \text{AgF}_3$  show that the compound is diamagnetic. According to Hoppe [18], silver (III) complexes which are yellow and diamagnetic are square planar with four coordinated silver, while six coordinated complexes are paramagnetic and red. The observed diamagnetism and the close correspondence between the anionic

TABLE 1

*Vibrational spectra (cm<sup>-1</sup>) of XeF<sub>6</sub>·AgF<sub>3</sub> and KAgF<sub>4</sub>.*

IR	XeF <sub>6</sub> ·AgF <sub>3</sub>	KAgF <sub>4</sub>	Assignment	
	R	R	XeF <sub>5</sub> <sup>+</sup>	AgF <sub>4</sub> <sup>-</sup>
665 (sh)	652 (52) 637 (11)	556 (100) 552 (96)	v <sub>1</sub>	
640 (vs) }				
625 (sh) }			v <sub>7</sub>	
590 (sh)	606 (14) 595 (6)		v <sub>4</sub> v <sub>2</sub>	
560 (vs, br)	558 (47)			v <sub>1</sub>
520 (sh)	550 (100)			
423 (m)	496 (25) 428 (4) 318 (5) 262 (13) 255 (6) 230 (3) 205 (2) 160 (8)	506 (32)    241 (42)  159 (6)	v <sub>8</sub> v <sub>3</sub> v <sub>6</sub>  v <sub>5</sub> v <sub>9</sub>	v <sub>4</sub>    v <sub>3</sub>

vibrational features of XeF<sub>5</sub><sup>+</sup>AgF<sub>4</sub><sup>-</sup> and KAgF<sub>4</sub> (Table I) indicate that the anion is at least approximately square planar (D<sub>4h</sub> symmetry). Since XeF<sub>5</sub><sup>+</sup> commonly bridges to four anionic fluorine ligands to generate a total Xenon coordination which has been described (19,20) as a capped Archimedian antiprism arrangement, it is anticipated that the same sort of arrangement may occur in XeF<sub>5</sub><sup>+</sup>AgF<sub>4</sub><sup>-</sup>. It is anticipated that the structural arrangement will maximize the separation of the "non-bonding" d<sub>z</sub><sup>2</sup> pair of electrons of the Ag(III) and the sterically active "non-bonding" valence electron pair of the Xe(VI).

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