ON THE SYNTHESIS OF XENON(VI) FLUOROBISMUTHATE(V)

B. DRUŽINA and B. ŽEMVA

'Jožef Stefan' Institute, 'Edvard Kardelj' University of Ljubljana, 61000 Ljubljana (Yugoslavia)

SUMMARY

The reaction between bismuth pentafluoride and excess liquid xenon hexafluoride yields a white diamagnetic solid $XeF_6 \cdot BiF_5$. On the basis of its Raman and infrared spectra the 1:1 compound could be formulated as $XeF_5^+ BiF_6^-$. The strong fluorine-bridge interaction between cation and anion distorts the anion from O_h symmetry.

INTRODUCTION

The system bismuth pentafluoride - noble gas fluorides has been extensively investigated in the past [1]. The adducts $2XeF_2 \cdot BiF_5$, $XeF_2 \cdot BiF_5$, $XeF_2 \cdot 2BiF_5$, $XeF_4 \cdot BiF_5$, $XeF_4 \cdot 2BiF_5$ and $KrF_2 \cdot BiF_5$ have been prepared and characterized by low temperature Raman spectroscopy [1], and the crystal structure of $XeF_3^+ \cdot BiF_6^-$ has been determined [2]. Taking into account the existence of xenon(II), xenon(IV) and even krypton(II) fluorobismuthates(V), and the much better fluoride-ion donor ability of XeF_6 in comparison to XeF_2, and particularly XeF_4 and KrF_2, it is surprising that xenon(VI) fluorobismuthates(V) have not been described previously. The compound $Xe_2F_{11}^+ BiF_6^-$ has been mentioned, however, in the context of a Mössbauer study of xenon compounds [3]. Therefore to settle the question of whether $XeF_6 \cdot BiF_5$ exists or not, the system bismuth pentafluoride - xenon hexafluoride was investigated. The compound $XeF_6 \cdot BiF_5$ was isolated and is the subject of this paper.

RESULTS AND DISCUSSION

To favour the formation of xenon hexafluoride rich complexes, we began by treating bismuth pentafluoride with a large excess of liquid xenon hexa-fluoride at 60°C because the reaction did not proceed at room temperature.

$$BiF_5 + nXeF_6 \xrightarrow[\text{several hours}]{60^{\circ}C} XeF_6 \cdot BiF_5 + (n-1)XeF_6$$
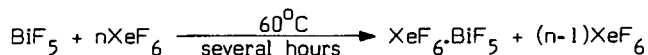
$n > 5$

Removal of the excess of xenon hexafluoride at room temperature yielded the 1:1 compound. From the curve of weight loss versus time of pumping (Fig. 1), the existence of $Xe_2F_{11}{}^{+}BiF_6{}^{-}$ was not evident. The slope of the curve changes at the composition $4XeF_6 \cdot 3BiF_5$ and finally levelled at the composition 1:1. The 1:1 compound is a white diamagnetic solid with a negligible vapour pressure at room temperature. It is very sensitive to traces of moisture which quickly turn it brown. $XeF_6 \cdot BiF_5$ starts to loose XeF_6 in a dynamic vacuum above 50°C. Above 200°C bismuth pentafluoride begins to de-compose to BiF_3 and fluorine. The end product of thermal decomposition of $XeF_6 \cdot BiF_5$ above 250°C was shown by X-ray powder diffraction patterns to be BiF_3.

The vibrational spectra of $XeF_6 \cdot BiF_5$ are given in Table 1. The $XeF_5{}^{+}$ cation of C_{4v} symmetry has the vibrational representation $3a_1 + 2b_1 + b_2 + 3e$; all modes are Raman active, but only $3a_1 + 3e$ are infrared active. Nine Raman lines attributed to the fundamentals of $XeF_5{}^{+}$ were observed and assigned on the basis of their relative intensities and by comparison with the spectra of related molecules. The strong lines at cca. 660 cm^{-1} and cca. 598 cm^{-1} are ν_1 and ν_2, the a_1 stretching fundamentals. The deformations ν_3, ν_6, ν_8 and ν_9 are assigned in the same order as in other $XeF_5{}^{+}$ salts [4,5] . The Raman line at cca. 355 cm^{-1} is ν_3 (a_1). The splitting of the cca. 400 cm^{-1} line in several $XeF_5{}^{+}$ salts suggests that it is indeed ν_8 (e). ν_7 (e), the de-generate stretching mode of the basal XeF_4 unit, should generate a strong infrared absorption, and it is assigned at 650 cm^{-1} since the infrared spectrum of $XeF_6 \cdot BiF_5$ has its strongest absorption at this frequency. The assignment of the two b_1 fundamentals ν_4 and ν_5 and the b_2 fundamental ν_6 was based on their infrared inactivity and the weakness of their Raman lines, which are also weak in analogous MX_5 C_{4v} species.
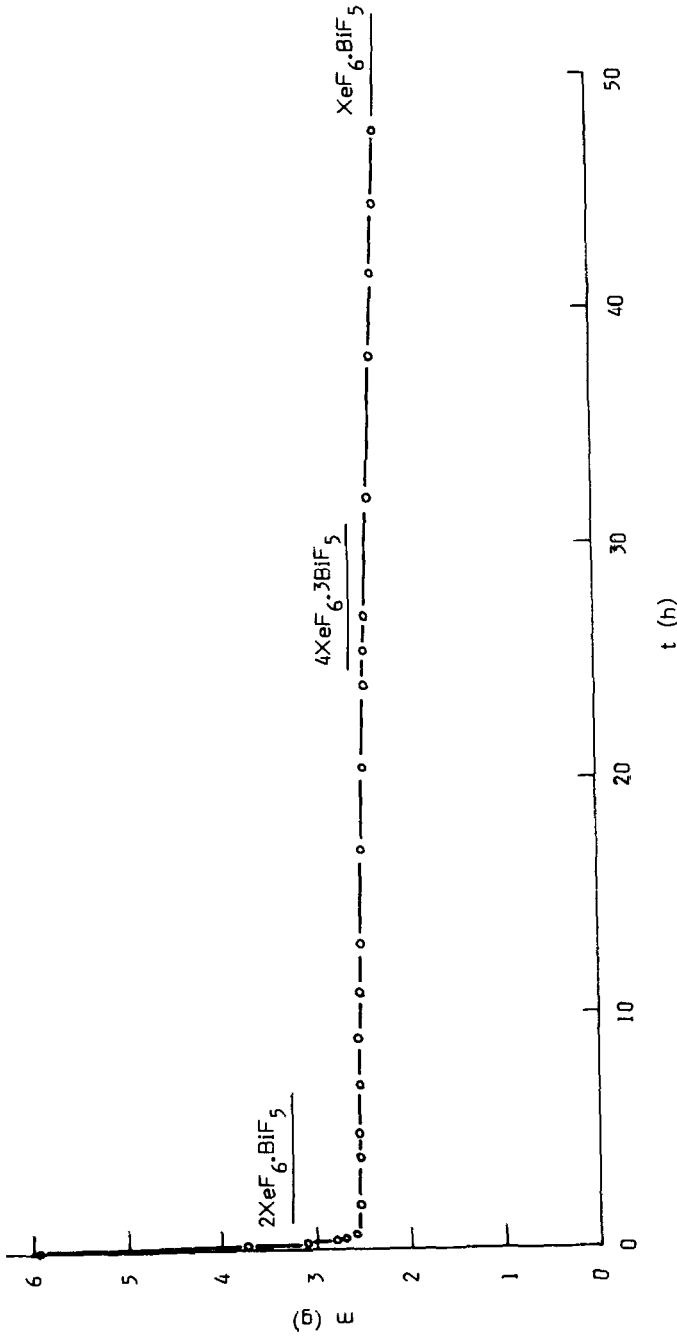
Fig. 1. Dependence of the total weight of the sample of the time of pumping off in the course of $XeF_6 \cdot BiF_5$ preparation.

TABLE 1

Raman and infrared frequencies (cm^{-1}) and assignments for $\left[XeF_5^{+}\right]\left[BiF_6^{-}\right]$

| $XeF_5^{+}BiF_6^{-}$ | | Assignment | |
IR	R	XeF_5^{+}	BiF_6^{-}
	660 (100)	$\nu_1(a_1)$	
650 (vs)	650 (25)	$\nu_7(e)$	
	635 (4)	$\nu_4(b_1)$	
	628 (2)		
605 (w)	598 (34)	$\nu_2(a_1)$	
590 (s)	587 (27)		$\nu_8(e)$
	585 (28)		
570 (vs)	568 (55)		$\nu_1(a_1)$
	543 (<1)		$\nu_2(a_1)$
508 (w)	510 (10)		$\nu_5(b_1)$
	472 (<1)		$\nu_4(a_1)$
	415 (1)	$\nu_8(e)$	
	395 (1)		
	355 (3)	$\nu_3(a_1)$	
	291 (3)	$\nu_6(b_2)$	
	242 (4)	$\nu_5(b_1)$	
	235 (3)		$\nu_9(e)$
	218 (1)	$\nu_9(e)$	$\nu_{11}(e)$
	200 (1)		
	182 (<1)		$\nu_{10}(e)+\nu_6(b_1)$
	165 (3)		
	155 (2)		
	120 (2)		$\nu_3(a_1)$

The other Raman bands and infrared lines could be attributed to the BiF_6^{-} anion. If the compound $XeF_6 \cdot BiF_5$ resembles $XeF_5^{+}SbF_6^{-}$, which is isostructural with some $XeF_5^{+}MF_6^{-}$ salts (M = Nb [6], Ru [7], Pt [8] etc.), the XeF_5^{+} species would be coordinated to four anion F ligands. This means that each anion would be coordinated to four cations. If the salt resembles $XeF_5^{+}AsF_6^{-}$

[9] or the isostructural $XeF_5^+AuF_6^-$ [10] , the cation would be three coordinated and three ligands of each anion would be involved in bridging to the cations. Thus the anion would not have O_h symmetry in either circumstance. The multiple Raman and infrared bands assigned to the BiF_6^- ion (Table 1) could be explained on the basis of solid state effects or as arising from the C_{4v} distortion of the octahedral anion by the fluorine bridge (13 bands in Raman are observed instead of just 3 Raman active bands of an isolated MF_6^- ion of O_h symmetry [11]). In view of the previous structural reasoning, we consider the distortion of the BiF_6^- to be the main cause of the observed splittings. Tentative assignment was made (Table 1) by using the correlation between O_h and C_{4v} symmetry [14] and by making comparison with the spectra of similarly distorted BiF_6^- in $XeF^+BiF_6^-$ and $KrF^+BiF_6^-$ [1]. Splitting of some modes of e symmetry (ν_8, ν_{10} and ν_{11}) and weak appearance in i.r. of ν_5 (b_1) mode which is in C_{4v} symmetry infrared inactive are most probably caused by solid state effects. It is difficult to choose between ν_6 (b_1) and ν_{10} (e) modes in making assignment of the Raman bands at 155, 165 and 182 cm^{-1}. ν_6 (b_1) and ν_{10}(e) modes in C_{4v} symmetry originated both from ν_6 (t_{2u}) vibration of undistorted MF_6^- (O_h) [14].

EXPERIMENTAL

General apparatus and techniques

The product was synthesized in an argon-arc welded nickel pressure and weighing vessel, equipped with Teflon packed nickel valve. The volume of the reaction vessel was about $10^{-4}m^3$. Transfer of all materials was carried out either in the atmosphere of a dry box, or by distillation under vacuum in well dried apparatus.

Raman spectra were recorded using a Spex 1401 double monochromator instrument. As exciting radiation, the 514.5 nm line of an Ar^+ laser (Coherent Radiation) was used. Powdered samples were loaded into quartz capillaries in a dry box and temporarily plugged with Kel-F grease. They were sealed with a small flame outside the dry box. Spectra were recorded at -196^oC by placing the sample tube inside a partly unsilvered glass Dewar filled with liquid nitrogen.

Infrared spectra were recorded using a Zeiss UR-20 spectrometer. Spectra were obtained by dusting samples onto silver chloride plates which were later sandwiched in a leak-tight brass holder.

X-ray powder photographs were obtained by the Debye-Scherrer method on an ENRAF apparatus (Delft, Holland) using graphite monochromator CuK_α radiation. Finely powdered samples were sealed in 0.5 mm thin-walled quartz capillaries.

The magnetic susceptibility was measured using the Faraday method on a modified Newport Instrument magnetic balance. The magnetic field was calibrated by mercury(2+) thiocyanatocobaltate(II). The powdered sample was packed into a thin-walled, screw capped Kel-F container (4 mm o.d., 4 mm height).

Reagents

Bismuth pentafluoride was prepared by the fluorination of bismuth trifluoride with elemental fluorine under pressure at $550^\circ C$ [12].

Xenon hexafluoride was prepared by the reaction between xenon and fluorine at $250^\circ C$ in the presence of NiF_2 as a catalyst [13]. Its purity was checked by recording infrared spectra of the vapour.

TABLE 2

Mass analysis of xenon(VI) fluorobismuthates(V)

Reaction	Product	Starting amount of BiF_5(g)	Mass of the product		Difference (%)
			Calcd.(g)	Found(g)	
$BiF_5 + nXeF_6 \xrightarrow{60^\circ C} XeF_6 \cdot BiF_5$		4.0594	7.3351	7.3621	0.367
$BiF_5 + nXeF_6 \xrightarrow{60^\circ C} XeF_6 \cdot BiF_5$		1.2420	2.2442	2.2612	0.752
$BiF_5 + nXeF_6 \xrightarrow{60^\circ C} XeF_6 \cdot BiF_5$		1.0849	1.9604	1.9562	0.215
$BiF_5 + nXeF_6 \xrightarrow{60^\circ C} XeF_6 \cdot BiF_5$		2.1606	3.9041	3.9261	0.560
$BiF_5 + nXeF_6 \xrightarrow{60^\circ C} XeF_6 \cdot BiF_5$		2.5354	4.5814	4.5692	0.267

Preparation

The compound $XeF_6 \cdot BiF_5$ was prepared by the reaction between bismuth pentafluoride and excess liquid xenon hexafluoride at $60^\circ C$. Bismuth pentafluoride was prepared directly in the reaction vessel or was weighed in the reaction vessel in a dry box. Xenon hexafluoride was added by sublimation. The reaction vessel was thermostatted at $60^\circ C$ for several hours. After reaction ceased, the excess of xenon hexafluoride was pumped away at room temperature. The stoichiometry of the reactions was followed by weighing the reactants and products with an accuracy of $\pm$ 1 mg throughout the experiments (Table 2).

The compound $XeF_6 \cdot BiF_5$ was chemically analysed: calcd. for $XeF_6 \cdot BiF_5$ % F, 38.05; % Bi, 38.05; % Xe, 23.90; found: % F, 38.3; % Bi, 38.0; % Xe, 23.2.

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