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ON THE SYNTHESIS OF XENON(II) FLUOROSTANNATES(IV)

B. DRUŽINA and B. ŽEMVA

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

SUMMARY

The reaction between tin difluoride and an excess of xenon difluoride at 140°C yields two new xenon(II) fluorostannates(IV): $3XeF_2.4SnF_4$ and $XeF_2.2SnF_4$. The 3:4 compound can be written as a molecular adduct of XeF_2 and the 1:2 compound. On the basis of vibrational spectra, the 1:2 compound can be formulated as a XeF^+ salt with a polymeric anion.

INTRODUCTION

The system xenon hexafluoride - tin fluorides has been extensively studied [1,2], which is not the case for the analogous system with xenon difluoride. It is known that SnF_4 forms addition compounds with electron donors, and therefore it was expected that XeF_2 would also form adducts with SnF_4. So far, only the reaction between $SnCl_4$ and XeF_2 has been reported [3] and the adduct $2XeF_2.SnF_4$ was claimed on the basis of an infrared spectrum only. To obtain more data, the system XeF_2 - SnF_4 has been thoroughly investigated.

RESULTS AND DISCUSSION

To favour the formation of xenon difluoride rich complexes, we set out by treating tin difluoride with a large excess of liquid xenon difluoride. Xenon difluoride oxidized the Sn(II) forming xenon(II) fluorostannate(IV).

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$$2SnF_2 + nXeF_2 \xrightarrow{140^0C} XeF_2.2SnF_4 + 2Xe + (n-3)XeF_2$$

$n > 20$

The same compound could also be prepared using hydrazinium(2+) tetrafluorostannate(II) as starting material:

$$2N_2H_6SnF_4 + nXeF_2 \xrightarrow{60^0C} XeF_2.2SnF_4 + 2N_2 + 12HF + 6Xe + (n-7)XeF_2$$

$n > 20$

The analogous reaction with ammonium trifluorostannate(II) proceeds at 50^0C with only the formation of ammonium pentafluorostannate(IV) [4] .

$$NH_4SnF_3 + nXeF_2 \xrightarrow{50^0C} NH_4SnF_5 + Xe + (n-1)XeF_2$$

$n > 20$

A melt of XeF_2 at 130^0C had to be used in order to prepare xenon(II) fluorostannate(IV).

During the preparation of $XeF_2.2SnF_4$, the weight of the mixture in the reaction vessel was followed during the course of pumping off the volatiles. It was found that there is a change in the slope of the curve corresponding to the composition $3XeF_2.4SnF_4$. This compound is not stable at room temperature and loses XeF_2 under dynamic vacuum at the rate of about 4 mole % per hour. The 3:4 compound can be isolated at 0^0C.

It is interesting that the existence of the compound $2XeF_2.SnF_4$ [3] was not noticed even when very carefully recording the course of pumping off the volatiles at 0^0C. It is possible that the compound claimed to be $2XeF_2.SnF_4$ was only $XeF_2.2SnF_4$ with some impurities. In favour of this conclusion are the following facts: the published infrared spectrum of the compound reported to be $2XeF_2.SnF_4$ is practically identical with the infrared spectrum of our 1:2 compound, and the colour of the 2:1 compound is lemon yellow, whereas pure xenon(II) and xenon(VI) fluorostannates are all white solid materials [2] .

$3XeF_2.4SnF_4$ is a white diamagnetic solid with a negligible vapour pressure at 0^0C. It loses XeF_2 slowly in dynamic vacuum at room temperature approaching the 1:2 composition, $XeF_2.2SnF_4$, which is also a white diamagnetic solid with a negligible vapour pressure at room temperature.

Thermal decomposition of both xenon(II) fluorostannates(IV) is very simple. $3XeF_2.4SnF_4$ starts to lose XeF_2 even below room temperature, while $XeF_2.2SnF_4$ starts to lose XeF_2 at about 50°C. In both cases the final product at decomposition temperatures lower than 300°C is SnF_4.

TABLE 1

Vibrational spectra (cm^{-1}) of $3XeF_2.4SnF_4$ and $XeF_2.2SnF_4$

$3XeF_2.4SnF_4$		$XeF_2.2SnF_4$		Tentative assignments
IR	R	IR	R	
675 (m)		670 (m)		
625 (m)		627 (m)		ν (Xe-F)
	619 (38)		619 (43)	
	594 (66)	595 (sh)	594(100)	ν (Sn-F)
582 (s)	588(100)	585 (s)	580 (25)	
	574 (sh)			
550 (sh)		550 (vs)		
530 (vs)				ν XeF_2
	509 (34)			
475 (s)		475 (s)		ν(Sn-F)
420 (sh)		420 (sh)		
	309 (2)			ν (Xe····F)
	283 (2)		284 (2)	
	160 (12)		150 (18)	δ(F-Xe····F)

Vibrational spectra of $3XeF_2.4SnF_4$ and $XeF_2.2SnF_4$ are shown in Table 1. The Raman and infrared spectra of both compounds are very similar except for the Raman band at 509 cm^{-1} and the infrared absorption at 530 cm^{-1} in the 3:4 compound. This latter compound could be written as $XeF_2(XeF_2.2SnF_4)_2$ which is a molecular adduct of XeF_2 and the 1:2 compound. This formulation explains the similarity of the two vibrational spectra and the thermal instability of the 3:4 compound, which loses XeF_2 in dynamic vacuum below room temperature forming $XeF_2.2SnF_4$. The prominent Raman band at 509 cm^{-1} and the strong infrared band at 530 cm^{-1} are most probably the symmetric stretching vibration and the asymmetric stretching vibration of weakly associated molecular XeF_2 which in the free molecule is at 497 cm^{-1} and 547 cm^{-1} respectively.

Similar bands in the same region have been observed previously [5,6] and similarily attributed to 'weakly associated' molecular XeF_2. The same phenomenon has also been observed in related krypton difluoride adducts [7,8] .

Vibrational spectra of $3XeF_2.4SnF_4$ and $XeF_2.2SnF_4$ provide evidence of an XeF^+ species, which is characterized in the $XeF^+MF_6^-$ and $XeF^+M_2F_{11}^-$ salts by a band or pair of bands in the Raman spectrum in the 621-598 cm^{-1} region [9] , and in the infrared spectrum in the 626-600 cm^{-1} region [5] . The occurrence of a band at 619 cm^{-1} in both Raman spectra, and bands at 625 cm^{-1} and 627 cm^{-1} in the infrared spectra of the 3:4 and 1:2 compounds, respectively, suggests the presence of XeF^+ species.

It is very unlikely that the anion is $Sn_2F_9^-$, since octahedral coordination of Sn is anticipated, and face-sharing of two octahedra has never been confirmed for any polyfluoro metal species. There are two other possibilities: firstly that we have an infinite polymer as in noble metal pentafluoride or tetrafluoride structures [10] , or secondly that we have discrete species, the simplest of which we would expect to be $Sn_8F_{36}^{4-}$ [11] . Tin is considered to be octahedrally coordinated to the fluorine atoms (3 uniquely, 3 bridging). The same fluorine bridged polymeric anion was also proposed in the analogous compound between xenon hexafluoride and tin tetrafluoride $3XeF_6.4SnF_4$ [2] . The vibrational spectra of this compound do not show anion lines below 400 cm^{-1}, and therefore the bands appearing in this region in the vibrational spectra of $XeF_2.2SnF_4$ were assigned to stretching and bending modes of the xenon-fluorine bridge.

EXPERIMENTAL

General apparatus and techniques. The products were synthesized in argon arc welded nickel pressure and weighing vessels, equipped with Teflon-packed nickel valves. The volume of the reaction vessels was about 100 cm^3. The reaction vessels were hydrostatically tested up to 20 MPa. 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 monochromated 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.

Infrared spectra were recorded using a Zeiss UR-20 spectrometer. A 10 cm path length nickel cell with silver chloride windows was used for gas phase work. Spectra of solids were obtained by dusting samples onto silver chloride plates 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 monochromated CuK$_\alpha$ radiation. Finely powdered samples were sealed in 0.5 mm thin-walled quartz capillaries.

Thermal analyses were carried out on a Mettler TA-1 Thermoanalyzer under the following experimental conditions: low temperature furnace heating rate 4^{0}C/min; argon atmosphere with a flow rate 5 dm^3/h; Pt or alumina crucibles. The sample weight was 100 mg and the reference substance was α - Al_2O_3. Some thermal decompositions were also carried out in the nickel reaction vessel on several-gram quantities of the sample.

The magnetic susceptibility was measured using the Faraday method on a modified Newport Instrument magnetic balance. The magnetic field was calibrated using $HgCo(CNS)_4$. The powdered sample was packed into a thin-walled screw-capped Kel-F container (4 mm o.d., 4 mm height).

<u>Reagents.</u> Tin(II) fluoride, 99.99% was from Ventron Alfa Products (ultrapure). $N_2H_6SnF_4$ was prepared as described elsewhere [12] . Xenon difluoride was prepared by photosynthesis [13] .

<u>Preparation.</u> The compound $XeF_2.2SnF_4$ was prepared by reaction between SnF_2 and excess xenon difluoride at 140^{0}C. After the reaction ceased, the xenon formed was pumped off at -80^{0}C, while excess of xenon difluoride was removed at room temperature.

The compound $XeF_2.2SnF_4$ was also prepared by reaction between $N_2H_6SnF_4$ and excess xenon difluoride at 60^{0}C. After the reaction was complete, the reaction products, nitrogen, xenon, hydrogen fluoride and excess xenon difluoride, were pumped away at -196^0 C, -80^{0}C, -50^{0}C, and at room temperature, respectively.

$3XeF_2.4SnF_4$ was isolated by pumping off excess XeF_2 at 0^{0}C.

The stoichiometry of the reactions was also followed by weighing the reactants and products with an accuracy of ± 1 mg throughout the experiments (Table 2).

TABLE 2

Mass analysis of xenon(II) fluorostannates(IV)

Run	Mass of SnF_2 and $N_2H_6SnF_4$ (g)	Mass of the products Calcd. (g)	Mass of the products Found (g)	Difference (%)
$SnF_2+nXeF_2 \rightarrow XeF_2.2SnF_4$	0.8529	1.5196	1.5398	1.3
$SnF_2+nXeF_2 \rightarrow XeF_2.2SnF_4$	0.5223	0.9302	0.9370	0.7
$SnF_2+nXeF_2 \rightarrow XeF_2.2SnF_4$	0.5308	0.9489	0.9664	1.8
$SnF_2+nXeF_2 \rightarrow 3XeF_2.4SnF_4$	0.7089	1.4476	1.4632	1.1
$N_2H_6SnF_4+nXeF_2 \rightarrow XeF_2.2SnF_4$	0.5936	0.7263	0.7402	1.9

The xenon(II) fluorostannates(IV) were examined by X-ray powder photography, Raman and infrared spectroscopy, magnetic susceptibility measurements and were chemically analysed.

Calcd. for $XeF_2.2SnF_4$: F, 34.01%; Sn, 42.49%; Xe, 23.50%
Found F, 34.3 %; Sn, 41.9 %; Xe, 24.2 %

Calcd. for $3XeF_2.4SnF_4$: F, 32.69%; Sn, 36.51%; Xe, 30.80%
Found F, 32.2 %; Sn, 37.1 %; Xe, 30.0 %

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