Journal of Fluorine Chemistry, 46 (1990) 521–528

Received: April 13, 1989; accepted: June 29, 1989

PREPARATION AND CHARACTERIZATION OF HYDRAZINIUM(1+) AND (2+) HEXAFLUOROSTANNATES(IV) AND HYDRAZINIUM(2+) HEXAFLUOROSTANNATE(IV) DIFLUORIDE

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SUMMARY

Reaction between $N_2H_6F_2$ and $Sn(OH)_4$ in aqueous HF as solvent gave two new complexes, $N_2H_6SnF_6$ and $(N_2H_6)_2SnF_6.F_2$, depending on the initial molar ratio of the starting materials. In a laser beam $N_2H_6SnF_6$ is slowly destroyed and the product of decomposition was identified as a mixture of the $N_2H_5^+$ and NH_4^+ compounds. Thermal decomposition of $(N_2H_6)_2SnF_6.F_2$ in a vacuum system yields pure $(N_2H_5)_2SnF_6$. Hydrazinium(1+) and (2+) fluorostannate(IV) compounds were characterized by chemical analysis and vibrational spectra. An X-ray powder photograph of $N_2H_6SnF_6$ was indexed on the basis of a cubic cell with a=10.550(4) Å, V=1174(1) Å^3. The thermal behaviour of $(N_2H_6)_2SnF_6.F_2$ was additionally investigated using TG, DTG and DTA measurements.

INTRODUCTION

The hexafluorostannates of alkali metals, divalent metals, ammonium [1] and several heterocations have so far been described [2-5]. The crystal structures [6,7], vibrational spectra [4,8-11], Mössbauer spectra [4,12,13] and the ^{19}F nuclear magnetic resonance [11] of some complexes have been studied to provide information concerning the symmetry of the SnF_6^{2-} ion, cation - anion interactions, distortion of the anion and the bonding in the complexes. For $(N_2H_5)_2SnF_6$ its preparation and optical properties have been reported [2].

The present study is concerned with the synthesis of two new N_2H_6(2+) compounds, the vibrational spectra of $N_2H_6SnF_6$, $(N_2H_5)_2SnF_6$ and $(N_2H_6)_2SnF_6.F_2$ and the thermal analysis of the latter compound.

0022-1139/90/$3.50

RESULTS AND DISCUSSION

In the reaction between $N_2H_6F_2$ and $Sn(OH)_4$ in a 2:1 molar ratio, $(N_2H_6)_2SnF_6.F_2$ was crystallized from an aqueous HF solution. This type of compound is known for $(N_2H_6)_2TiF_6.F_2$ [14] and $(N_2H_6)_2GeF_6.F_2$ [15] ; the crystal structure of $(N_2H_6)_2TiF_6.F_2$ [14] consists of TiF_6^{2-} layers sandwiched between composite layers in which a F^- ion is surrounded by four $N_2H_6^{2+}$ units and vice versa. We assume a similar structure also for $(N_2H_6)_2SnF_6.F_2$.

$N_2H_6SnF_6$ was obtained when $N_2H_6F_2$ and $Sn(OH)_4$ in a 1:1 molar ratio dissolved in 40% HF; it was also prepared by the reaction of $N_2H_6F_2$ and SnF_4 in anhydrous hydrogen fluoride. Thermal decomposition of $(N_2H_6)_2SnF_6.F_2$ in a vacuum system at 80°C gave $(N_2H_5)_2SnF_6$. Hydrogen fluoride liberated during the heating of the solid was identified by its infrared spectrum. $(N_2H_5)_2SnF_6$ is also produced when $(N_2H_6)_2SnF_6.F_2$ is exposed to a laser beam for a long period.

The vibrational spectra of $N_2H_6SnF_6$, $(N_2H_6)_2SnF_6.F_2$ and $(N_2H_5)_2SnF_6$ are given in Table 1. The spectra of $N_2H_6SnF_6$ and $(N_2H_5)_2SnF_6$ show the greatest similarity with the alkali metal hexafluorostannates for the anionic part of the spectrum [4].

The Raman spectrum of $(N_2H_6)_2SnF_6.F_2$, has the ν_1 mode of the SnF_6^{2-} group split into two strong bands, a feature which was observed in the Raman spectrum of $(ClO_2)_2SnF_6$ [11]. The splitting can be attributed to solid state splitting, as was suggested for $(ClO_2)_2SnF_6$.

In a laser beam $N_2H_6SnF_6$ and $(N_2H_6)_2SnF_6.F_2$ decompose and changes can be observed in the regions of the cationic and anionic parts of the Raman spectra. In the Raman spectrum of $N_2H_6SnF_6$ the strongest band lies at 580 cm^{-1}, and after a while additional bands at 635 and 670 cm^{-1} appear. In the low frequency region a new band at 323 cm^{-1} is also observed. In the cationic part of the spectrum a new band at 978 cm^{-1} becomes the strongest, confirming the presence of the $N_2H_5^+$ ion. The bands appearing at 3050, 3140 and 3298 cm^{-1} can be assigned to the NH_4^+ ion [16]. The decomposition of $N_2H_6SnF_6$ is very complex: $N_2H_6^{2+}$ decomposes to the $N_2H_5^+$ and NH_4^+ ions, and besides the SnF_6^{2-} ion, the SnF_5^- ion or SnF_4 is present. Both have the Sn-F stretching vibration at 620 cm^{-1}; SnF_5^- at 622 cm^{-1} [3] and SnF_4 at 621 cm^{-1} [1]. The band observed at 635 cm^{-1} can, therefore, be attributed either to SnF_5^- or SnF_4. The thermal decomposition of $N_2H_6SnF_6$ has to be studied in detail to elucidate the mixture of compounds formed and the gases released in the process.

TABLE I

Vibrational spectra (cm^{-1}) of $N_2H_6SnF_6$, $(N_2H_6)_2SnF_6.F_2$ and $(N_2H_5)_2SnF_6$

$N_2H_6SnF_6$		$(N_2H_6)_2SnF_6.F_2$		$(N_2H_5)_2SnF_6$		Assignment
IR	R	IR	R	IR	R	
	167(10)					
	202(13)		205(15)			
250sh	265(34)		278(25)		252(28)	$\nu_5(SnF_6^{2-})$
281sh						
320vs			331(15)			
403w		400w		410w		
	418(4.0)		420(15.5)			
	461(13)	469m	460(17)	461sh	474(6.6)	$\nu_2(SnF_6^{2-})$
	505(7.5)					
538vs		545vs		542vs		$\nu_3(SnF_6^{2-})$
			588(100)	583sh	583(100)	$\nu_1(SnF_6^{2-})$
	602(100)		609(45)			
	670(5)					
		709w		713w		
920m		942m	981(10)		978(33)	$(N-N)_s$
	1041(70)		1043(18)			
			1050(15)			
			1059(32)			
		1078vs		1083s	1091(11.4)	$(NH_3^+)_r$
1101vs	1100(2)			1118s	1115(83)	
				1147sh		
		1223w				
1292w						
		1405w			1409(4.4)	$(NH_2)_r$
		1469w				
		1485w				
1500vs				1519m		$(NH_3^+)_d$
1570vs	1562(5)			1540w	1540(4.8)	
		1598w				
1622w		1610w			1617(6.1)	
	1648(7.5)			1632w	1643(7.0)	$(NH_2)_d$

The recording of the Raman spectrum of $(N_2H_6)_2SnF_6.F_2$ gives rise to significant changes in the region of the N-N stretching vibration: the $N_2H_6^{2+}$ ion is transformed to the $N_2H_5^+$ ion, the bands at 1043, 1050 and 1059 cm^{-1} slowly disappear and the band at 981 cm^{-1} becomes the strongest. In the region of the Sn-F stretching vibration only the band at 580 cm^{-1} is observed unchanged. $(N_2H_6)_2SnF_6.F_2$ decomposes to $(N_2H_5)_2SnF_6$ by proton transfer between

$N_2H_6^{2+}$ and F^-, producing $N_2H_5^+$ and liberating HF. The same feature was first observed for $(N_2H_6)_2TiF_6.F_2$ [17].

$N_2H_6SnF_6$ crystallizes in the cubic system. The results of indexation of the diffraction photograph are summarized in Table 2.

TABLE 2

X-ray powder diffraction data for $N_2H_6SnF_6$

h k l	$d_{calc.}$	$d_{obs.}$	I
2 0 0	5.27	5.27	s
2 2 0	3.73	3.72	s
2 2 2	3.04	3.04	w
2 3 1	2.820	2.822	vw
4 0 0	2.637	2.643	vw
4 1 1	2.487	2.484	vw
2 4 0	2.359	2.358	m
3 3 2	2.249	2.248	w
4 2 2	2.153	2.161	m
4 4 0	1.865	1.863	w
4 4 2	1.758	1.759	m
2 6 0	1.668	1.667	w
6 2 2	1.590	1.591	w

Indexed on the basis of a cubic cell with a=10.550(4) Å, V=1174(1) $Å^3$.

A thermal decomposition study of $(N_2H_6)_2SnF_6.F_2$ is illustrated in Figure 1. The compound $(N_2H_6)_2SnF_6.F_2$ starts to lose weight immediately after heating, and up to 155°C it loses 11.6% of its weight, corresponding to the formation of $(N_2H_5)_2SnF_6$. The first step is endothermic with a DTA peak at 112°C and a DTG minimum at 115°C. The next step is exothermic with a DTA peak and DTG minimum at 213°C. The cumulative weight loss up to 228°C is 22.2% and the intermediate is identified as $(NH_4)_2SnF_6$. The third endothermic step accompanied by a DTA peak at 317°C and DTG minimum at the same temperature occurs between 228 and 369°C. The sample loses 36.0% of its starting weight and the intermediate is identified as NH_4SnF_5. The weight loss is greater than that calculated for the formation of NH_4SnF_5 due to partial reduction of tin in the sample. Further decomposition is endothermic and composed of three steps with DTA peaks at 427, 470 and 565 °C and DTG minima at 425, 470 and 551°C. In the temperature range between 400 and 520°C decomposition of the sample and reduction of tin occur simultaneously, and only nonstoichiometric compounds can be obtained. The last step intermediate was isolated; the cumulative weight loss (64.9%) up to 740°C corresponds to the formation of metallic tin.

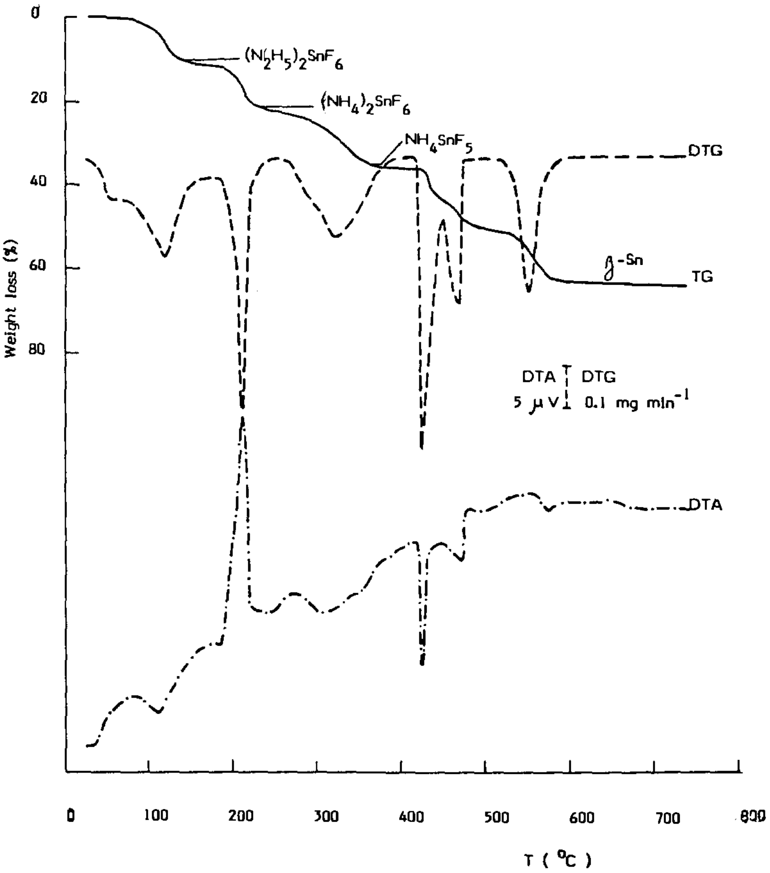

Fig. 1. TG, DTG and DTA curves of $(N_2H_6)_2SnF_6.F_2$.

The thermal decomposition of $(N_2H_6)_2SnF_6.F_2$ can be described by the equations:

$$(N_2H_6)_2SnF_6.F_2 \longrightarrow (N_2H_5)_2SnF_6 + 2\ HF \qquad (1)$$

$$(N_2H_5)_2SnF_6 \longrightarrow (NH_4)_2SnF_6 + N_2 + H_2 \qquad (2)$$

$$(NH_4)_2SnF_6 \longrightarrow NH_4SnF_5 + NH_3 + HF \qquad (3)$$

Intermediates $(N_2H_5)_2SnF_6$ were characterized by chemical analyses, vibrational spectra and their X-ray diffraction patterns. NH_4SnF_5 was characterized by chemical analysis of ammonium and by comparison with the X-ray diffraction photograph of NH_4SnF_5 isolated in the reaction between NH_4SnF_3 and XeF_2 [18]. The end product was identified on the basis of its X-ray diffraction patterns as β-Sn [19].

EXPERIMENTAL

Preparation of the samples

$N_2H_6SnF_6$ was prepared by dissolving $Sn(OH)_4$ in a 40% HF solution and adding $N_2H_6F_2$ in a 1:1 molar ratio. The crystals were obtained by slow evaporation of the solution. The reaction between $N_2H_6F_2$ and SnF_4 in anhydrous HF yielded the same compound.

$(N_2H_6)_2SnF_6.F_2$ was obtained when $Sn(OH)_4$ and $N_2H_6F_2$ were mixed in a 1:2 molar ratio in 40% HF.

$(N_2H_6)_2SnF_6.F_2$ was decomposed on a vacuum system at 80°C yielding $(N_2H_5)_2SnF_6$.

$(N_2H_5)_2SnF_6$ was isolated as the first step intermediate at 155°C when $(N_2H_6)_2SnF_6.F_2$ was decomposed using a Mettler TAII Thermoanalyzer.

Chemical analysis

Hydrazine was determined potentiometrically by potassium iodate titration [20], fluorine by the direct method using an ion-selective electrode [21] and ammonium by a Kjeldahl method [22].

$N_2H_6SnF_6$

Found: N_2H_4, 12.0; F, 42.3

Calcd.: N_2H_4, 12.01; F, 42.73

$(N_2H_5)_2SnF_6$

Found: N_2H_4, 21.1; F, 38.5

Calcd.: N_2H_4, 21.45; F, 38.15

NH_4SnF_5

Found: NH_4, 8.3; F, 40.9

Calcd.: NH_4, 7.79; F, 40.99

$(N_2H_6)_2SnF_6.F_2$

Found: N_2H_4, 18.6; F, 44.9

Calcd.: N_2H_4, 18.92; F, 44.86

$(NH_4)_2SnF_6$

Found: NH_4, 12.7; F, 41.7

Calcd.: NH_4, 13.42; F, 42.41

The infrared spectra of the solids pressed between CsBr discs were obtained using a Perkin-Elmer 521 spectrometer. The Raman spectra of the solid in a Pyrex tube were recorded on a Spex-1401 double monochromator and the excitation band was 514.5 nm of an Ar^+ laser, Coherent radiation model CR-3. For thermal analysis a Mettler TA1 Thermoanalyzer was employed. The sample was heated in a dry argon atmosphere at a flow rate of 5 lh^{-1}. α-Al_2O_3 was used as reference material. The heating rate of the furnace was 1^oC min^{-1}, the DTG range was 10 mg min^{-1} and the DTA range was 100 μV. The starting weight of the sample was 230-500 mg when intermediates were isolated.

X-ray powder diffraction data were obtained with a Debye-Scherrer type camera and CuK_α radiation. The diffraction photograph was indexed using the PARAM program of the X-ray 72 system [23].

ACKNOWLEDGEMENT

We thank Miss B. Sedej for chemical analysis. The work was financed by the Research Community of Slovenia.

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