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SYNTHESIS AND CHARACTERIZATION OF NEW HYDRAZINIUM(1+) FLUOROSTANNATES(II)

D. GANTAR, A. RAHTEN

Jožef Stefan Institute, E. Kardelj University, 61000 Ljubljana (Yugoslavia)

B. VOLAVŠEK

Visoka tehniška šola, The University, 62000 Maribor (Yugoslavia)

SUMMARY

Two new compounds, $N_2H_5SnF_3$ and $N_2H_5Sn_2F_5$, were obtained when the system $N_2H_5F-SnF_2-H_2O$ was investigated. The solids were characterized by chemical analysis, vibrational spectra and X-ray powder diffraction patterns. Thermal decomposition studies of the compounds showed that they decompose through intermediates, the corresponding ammonium fluorostannates(II), to tin(II) fluoride.

INTRODUCTION

The Lewis acid ability of tin(II) fluoride to form different types of complexes with suitable Lewis bases is well established.

Products containing the trifluorostannate ion, SnF_3^- , have been prepared by reactions of tin(II) fluoride with alkali metal fluorides, ammonium fluoride or non-transition metal(II) nitrates in aqueous hydrofluoric solution [1-5]. The existence of the SnF_3^- group was proved by vibrational analysis and X-ray diffraction studies.

When a 2:1 molar ratio of tin(II) fluoride to alkali fluoride was used, solids with composition MSn_2F_5 ($M = Na, K, Rb, Cs, NH_4$) were isolated and characterized [2, 6-8]. The formation of a polynuclear $Sn_2F_5^-$ ion was confirmed by various physicochemical studies.

Following our previous research on hydrazinium(1+) fluorometallates in aqueous solution [9], it seemed likely that new hydrazinium(1+) fluorostannates(II) could be prepared by reaction between hydrazinium(1+) fluoride and tin(II) fluoride.

RESULTS AND DISCUSSION

Colourless crystals of $N_2H_5SnF_3$ were obtained when tin(II) fluoride was dissolved in an aqueous solution of the stoichiometric amount of hydrazinium(1+) fluoride. When a 1:2 ratio of $N_2H_5F:SnF_2$ was used, $N_2H_5Sn_2F_5$ was prepared.

The SnF_3^- ion is pyramidal due to the presence of a sterically active non-bonding pair of electrons which makes it an excellent ligand. The $Sn_2F_5^-$ ions are formed in concentrated tin(II) solutions containing insufficient fluoride ions to complete the formation of SnF_3^- . In the crystal structure of $NaSn_2F_5$ [10] it was confirmed that two SnF_2 groups are linked by a bridging fluorine.

The vibrational spectra of $N_2H_5SnF_3$ and $N_2H_5Sn_2F_5$ are given, together with the assignments, in Table 1.

The anionic part of the infrared spectrum of $N_2H_5SnF_3$ is close to that of NH_4SnF_3 which was analysed on the basis of the C_{3v} symmetry of the SnF_3^- anion [11]. The Raman spectrum shows additional bands beside the bands which clearly originate from SnF_3^- . The frequencies ν_2 and ν_4 , which were previously calculated by Donaldson and coworkers [11] for SnX_3^- complexes, are in fact observed experimentally in the Raman spectrum of $N_2H_5SnF_3$. The splitting of ν_3 and ν_4 is probably caused either by site symmetry effects or by distortion of the SnF_3^- groups. Due to unassigned additional bands, which should be understood only as a consequence of the interaction between the anionic units, we ascribe this splitting mainly to the distortion of the anions.

In the cationic part of the vibrational spectra of $N_2H_5SnF_3$ and $N_2H_5Sn_2F_5$ all bands in the region from 950 to 1667 cm^{-1} are assigned to the $N_2H_5^+$ group [12].

The $Sn_2F_5^-$ ion has C_2 point symmetry and therefore fifteen vibrations of the molecule are expected, all infrared and Raman active. Assignment of the vibrational spectrum of $N_2H_5Sn_2F_5$ is consistent with normal coordinative analysis of the $Sn_2F_5^-$ complexes [13]. The symmetric stretching vibration in $Sn_2F_5^-$ is higher in $N_2H_5Sn_2F_5$ than in $NH_4Sn_2F_5$. This can be attributed to one Sn-F bond which is stronger than the others in the $Sn_2F_5^-$ complexes which were investigated by Donaldson *et al.* [13]. Distortion of the structure caused by the cation can be explained by the size of $N_2H_5^+$ in comparison to NH_4^+ .

TABLE 1

Vibrational spectra [cm^{-1}] of $\text{N}_2\text{H}_5\text{SnF}_3$ and $\text{N}_2\text{H}_5\text{Sn}_2\text{F}_5$

Assignment	$\text{N}_2\text{H}_5\text{SnF}_3$		$\text{N}_2\text{H}_5\text{Sn}_2\text{F}_5$		Assignment	
	R	IR	R	IR		
$\nu_4(\text{SnF}_3^-)$	108 (1.5)		130 (2.7)		}	$(\text{Sn-F}_t)_b$
	146 (2.8)					
	[154 (5.6)					
	[162 (2.5)					
$\nu_2(\text{SnF}_3^-)$	196 (2.8)		193 (2.7)		}	$(\text{Sn-F}_b)_s$
	228 (1.7)		230 (2.2)			
	254 (2.0)		253 (1.2)			
$\nu_3(\text{SnF}_3^-)$	352 (4.3)		338 (3.4)	319 m	}	$(\text{Sn-F}_t)_s$
	[408 (5.1)	415 s	375 (3.4)	342 m		
			399 (5.6)	375 m		
	[425 (4.4)		429 (10)	415 m		
			450 (7.5)			
$\nu_1(\text{SnF}_3^-)$	464 (8.2)	475 s		472 s		$(\text{Sn-F}_b)_s$
$(\nu_3+\nu_4)(\text{SnF}_3^-)$		547 s	581 (0.7)	545 s		$(\text{Sn-F}_t)_s$
	958 (10)	950 vs		945 s	}	$(\text{N-N})_s$
			1019 (5.9)	970 s		
				1004 s	}	$(\text{NH}_3^+)_b$
	1118 (2.5)	1085 vs		1082 vs		
		1107 vs	1145 (2.2)	1115 vs		
			1159 (1.6)		}	$(\text{NH}_2)_b$
	1508 (2.5)	1230 w		1260 w		
		1505 s		1505 m	}	$(\text{NH}_3^+)_d$
			1518 (1.1)			
		1606 s	1555 (1.7)		}	$(\text{NH}_2)_d$
	1650 (3.8)	1645 s	1667 (1.3)	1580 m		

The X-ray powder diffraction data for $\text{N}_2\text{H}_5\text{SnF}_3$ and $\text{N}_2\text{H}_5\text{Sn}_2\text{F}_5$ are given in Tables 2 and 3.

The X-ray powder photographs of $\text{N}_2\text{H}_5\text{SnF}_3$ and $\text{N}_2\text{H}_5\text{Sn}_2\text{F}_5$ were indexed on the basis of an orthorhombic cell; $\text{N}_2\text{H}_5\text{SnF}_3$, $a = 15.05(1)$, $b = 6.95(0)$, $c = 4.36(0)$ Å; $\text{N}_2\text{H}_5\text{Sn}_2\text{F}_5$, $a = 10.56(0)$, $b = 4.53(0)$, $c = 7.16(0)$ Å.

$\text{N}_2\text{H}_5\text{SnF}_3$ was indexed by comparison with isomorphous $\text{N}_2\text{H}_5\text{CdF}_3$ and $\text{N}_2\text{H}_5\text{MF}_3$ ($M = \text{Mg}, \text{Co}, \text{Cu}, \text{Zn}$) complexes [14, 15]. The cell parameters of this complex are also very close to those of monoclinic CsSnF_3 : $a = 14.283$, $b = 6.530$, $c = 4.855$ Å, $\beta = 90.998^\circ(5)$. The cell parameters of $\text{N}_2\text{H}_5\text{Sn}_2\text{F}_5$ are very close to those of monoclinic RbSn_2F_5 : $a = 10.124$, $b = 4.272$, $c = 7.401$ Å, $\beta = 90.07^\circ(8)$.

TABLE 2

X-ray powder diffraction data of $N_2H_5SnF_3$

h k l	d _{calc.}	d _{exp.}	I	h k l	d _{calc.}	d _{exp.}	I
0 1 0	6.95	6.94	w	0 3 1	2.05	2.05	w
2 1 0	5.11	5.18	s	1 3 1	2.03	2.02	w
0 0 1	4.36	4.36	m	3 1 2	1.922	1.937	w
1 0 1	4.19	4.14	w	4 0 2	1.886	1.884	w
2 0 1	3.77	3.81	m	0 2 2	1.847	1.850	w
0 1 1	3.69	3.66	m	2 2 2	1.794	1.794	w
0 2 0	3.48	3.51	s	-	-	1.751	w
1 2 0	3.39	3.37	m	4 2 2	1.658	1.660	vw
2 1 1	3.32	3.30	s	8 2 0	1.654	1.631	vw
3 1 1	2.97	3.01	m	4 4 0	1.577	1.572	vw
5 1 0	2.76	2.77	w	3 3 2	1.514	1.514	vw
1 2 1	2.67	2.68	w	1 0 3	1.447	1.441	vw
4 1 1	2.64	2.61	s	1 1 3	1.416	1.416	vw
6 0 0	2.51	2.50	w	3 1 3	1.369	1.365	vw
5 0 1	2.48	2.47	w	0 2 3	1.341	1.347	vw
6 1 0	2.36	2.36	vw				
1 3 0	2.29	2.28	vw				
3 3 0	2.10	2.13	vw				
2 0 2	2.09	2.09	vw				

TABLE 3

X-ray powder diffraction data of $N_2H_5Sn_2F_5$

h k l	d _{calc.}	d _{exp.}	I	h k l	d _{calc.}	d _{exp.}	I
1 1 0	4.16	4.09	m	3 2 1	1.840	1.831	w
1 1 1	3.60	3.58	s	2 2 2	1.799	1.796	m
0 0 2	3.58					1.739	vw
3 0 0	3.52	3.52	s	2 0 4	1.695	1.696	vw
1 0 2	3.39	3.40	w	4 1 3	1.649	1.649	w
		3.28	vw	6 1 1	1.600	1.602	w
2 1 1	3.10	3.03	s	4 2 2	1.550	1.551	vw
2 0 2	2.96	2.99	vw			1.520	w
1 1 2	2.71	2.72	w	3 2 3	1.489	1.486	w
2 1 2	2.48	2.46	m	1 3 1	1.463	1.463	w
1 0 3	2.33	2.33	w	1 3 2	1.382	1.380	vw
1 2 0	2.21	2.22	vw	1 1 5	1.354	1.353	w
0 2 1	2.16	2.16	w	2 1 5	1.322	1.321	w
1 1 3	2.07	2.06	m				
4 1 2	1.924	1.936	m				
1 2 2	1.883	1.892	w				

Thermal decomposition studies of the salts $N_2H_5SnF_3$ and $N_2H_5Sn_2F_5$ show that their decomposition occurs in two steps through the intermediate: NH_4SnF_3 and $NH_4Sn_2F_5$. In both cases the final product is tin(II) fluoride.

The thermal decomposition of $N_2H_5SnF_3$ (Fig. 1) begins at 41°C , and up to 206°C the sample loses 7.2 % of its initial weight, which coincides well with the formation of NH_4SnF_3 (calculated weight loss is 7.19 %). The intermediate was isolated and identified by chemical analysis.

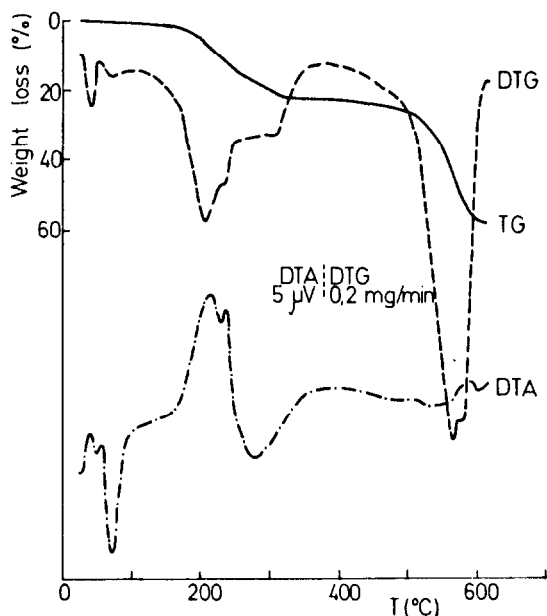


Fig. 1. TG, DTG and DTA curves of $N_2H_5SnF_3$

The first step is accompanied by an endothermic DTA peak at 65°C . The second step, which occurs immediately, is accompanied by exothermic DTA peaks at 213° and 234°C and the DTG minima at the same temperatures. Up to 350°C the cumulative weight loss is 24.3 %, which correlates well with the theoretical value for the production of tin(II) fluoride (24.94 %). At 560°C the thermal decomposition of tin(II) fluoride begins.

The decomposition of $N_2H_5Sn_2F_5$ (Fig. 2) begins at 40°C , and in the temperature range 40° to 203°C it loses 4.2 % of its initial weight, which agrees with the expected weight change (4.11 %) for the formation of $NH_4Sn_2F_5$, the intermediate, which was characterized by chemical analysis. The DTA curve exhibits two endothermic peaks at 48° and 74°C and a DTG minimum at 40°C . Further decomposition is exothermic with a DTA peak at 218°C , and the DTG minima at 208° and 222°C . Up to 345°C the sample loses 15.3 % of the starting weight, which is very close to the theoretical value (14.25 %) for the formation of tin(II) fluoride.

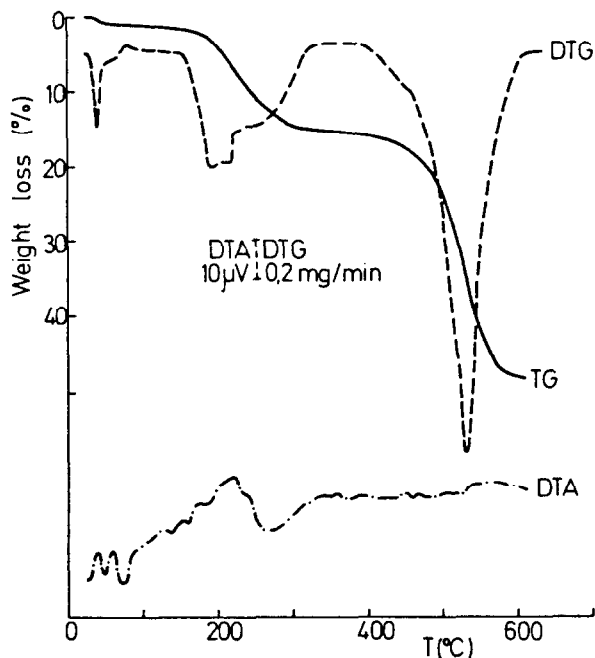
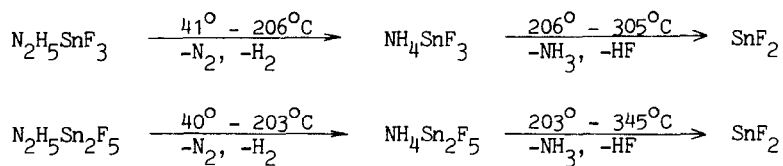


Fig. 2. TG, DTG and DTA curves of $N_2H_5Sn_2F_5$

The thermal decomposition of $N_2H_5SnF_3$ and $N_2H_5Sn_2F_5$ can be described as shown below:



EXPERIMENTAL

Materials

Hydrazinium(1+) fluoride was synthesized by heating anhydrous hydrazine and hydrazinium(2+) fluoride [16]. Hydrazinium(2+) fluoride was prepared by neutralization of hydrazinium hydrate with an aqueous solution of hydrogen fluoride [17].

Preparation of the samples

A stoichiometric quantity of tin(II) fluoride was dissolved in an aqueous solution of hydrazinium(1+) fluoride. After evaporation nearly to dryness, crystalline $N_2H_5SnF_3$ was obtained.

$N_2H_5Sn_2F_5$ was prepared by taking a 2:1 molar ratio of tin(II) fluoride and hydrazinium(1+) fluoride.

Characterization

Hydrazine was determined potentiometrically [18]. Tin was determined by a modified method of indirect complexometric titration [19,20]. Total fluoride ion (F_t) and free fluoride ion (F_f^-) were determined by the direct method, or after distillation, using an ion selective electrode [21,22].

Chemical analyses are summarized as follows:

$N_2H_5SnF_3$: Found: N_2H_4 , 15.8; Sn, 56.8; F_t , 27.3; Calc.: N_2H_4 , 15.84; Sn, 56.86; F_t , 27.30.

$N_2H_5Sn_2F_5$: Found: N_2H_4 , 9.1; Sn, 63.4; F_t , 26.4; F_f^- , 26.2; Calc.: N_2H_4 , 8.77; Sn, 64.96; F_t , 25.99.

NH_4SnF_3 : Found: NH_4^+ , 9.2; Calc.: NH_4^+ , 9.31.

$NH_4Sn_2F_5$: Found: NH_4^+ , 5.0; Calc.: NH_4^+ , 5.15.

Infrared spectra of the powdered solid pressed between CsBr discs were obtained using a Perkin-Elmer 521 spectrometer. The Raman spectra of the solids in a Pyrex tube were recorded using a Spex 1401 machine. As exciting radiation, the 514.5 nm line of an Ar^+ laser (Coherent Radiation) was used. X-ray powder diffraction data were obtained with a Debye-Scherrer type camera and $CuK\alpha$ radiation.

A Mettler TA 1 Thermoanalyzer was used for the thermal decomposition studies. In a run 100 mg of sample was used and this was referenced against a 100 mg sample of $\alpha-Al_2O_3$. The heating rate for the furnace was $4^\circ C\ min^{-1}$ and the decompositions were carried out in a dried argon atmosphere with a flow rate of $5\ l\ hr^{-1}$. The DTG range was $10\ mg\ min^{-1}$ and the DTA range was $100\ \mu V$.

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