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THERMAL ANALYSIS OF NEW HYDRAZINIUM(2+) HEXAFLUOROANTIMONATE

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Hydrazinium(2+) hexafluoroantimonate was prepared by the reaction of $N_2H_6F_2$ with an excess of SbF_5 in anhydrous HF as solvent. The compound was characterized by chemical analysis and vibrational spectra. The X-ray powder photograph was indexed on the basis of a monoclinic cell with $a = 8.22(2)$, $b = 10.04(3)$, $c = 9.51(2)$ Å, $\beta = 97.2(2)^\circ$ and $V = 780$ Å^3.

The thermal decomposition study of $N_2H_6(SbF_6)_2$ showed that it decomposed to gaseous components through an intermediate, a mixture of $N_2H_5SbF_6$ and NH_4SbF_6. In the DSC curve, a strong endothermic effect and medium exothermic and endothermic effects were observed in the range 25-600 °C.

Within the past five years, intensive research on hydrazinium compounds at the "Jozef Stefan" Institute has yielded more than twenty new $N_2H_5^+$ and $N_2H_6^{2+}$ fluorometalates, which have been characterized by chemical analysis, vibrational spectroscopy, in some cases X-ray diffraction analysis [1] and above all thermal analysis.

For group VA elements in the pentavalent state, $N_2H_6(PF_6)_2$, $N_2H_5PF_6$ [2], $N_2H_6(AsF_6)_2$ [3] and $N_2H_5AsF_6$ [2, 4] have been investigated so far. This study has recently been extended to the remaining hydrazinium hexafluorometalates of Sb and Bi; in the present work we report the synthesis and characterization of $N_2H_6(SbF_6)_2$.

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Experimental

Hydrazinium(2+) fluoride was loaded into a KelF reaction vessel and about 5 g of anhydrous HF and afterwards an excess of SbF_5 were distilled onto the solid by using a conventional vacuum line. After the reaction, volatiles were removed and the crystalline $N_2H_6(SbF_6)_2$ was isolated. The solid was dried to the constant weight in vacuo.

Chemical analysis of $N_2H_6(SbF_6)_2$:

found: N_2H_4, 6.2; calcd.: N_2H_4, 6.34.

found: F, 44.8; calcd.: F, 45.09.

For thermal analysis, a Mettler TA 1 thermoanalyzer was used. The decomposition was carried out in an argon atmosphere with a flow rate of 5 $l\ h^{-1}$. The heating rate of the furnace was 1 deg min^{-1}; the sample weight was 100 mg or 500 mg when the intermediates were isolated. The DTG range was 10 mg min^{-1} and the DTA range was 200 μV.

Heat flow as a function of temperature was determined with a differential scanning calorimeter (Mettler, DSC-20). DSC recording was made in a closed Al cell with a pin-hole in the cover and in a flowing argon atmosphere. The heating rate of the instrument was 4 deg min^{-1}. ΔH was determined by graphical integration using a Mettler TC 10A processor.

The Raman spectra of the solids in a Pyrex tube were obtained on a Spex 1401 spectrometer with Ar^+ (514.5 nm) excitation from a Coherent Radiation model CR-3 laser. For recording of the infrared spectra of the solids, taken as powders pressed between KBr or CsBr plates, a Perkin-Elmer 521 and a Perkin-Elmer FTIR 1710 spectrometer were used.

X-ray powder diffraction patterns were obtained with a Debye-Scherrer-type camera and CuK_α radiation. The diffraction photograph of $N_2H_6(SbF_6)_2$ was indexed by using a Haendler program [5] on an IBM-1130 computer.

Hydrazine was determined potentiometrically [6], ammonium by a Kjeldahl method [7] and fluorine by a modified distillation method [8].

Results and discussion

$N_2H_6(SbF_6)_2$ is a colourless compound which hydrolyses in moist air. The *d*-spacings and intensities of an X-ray powder diffraction photograph of $N_2H_6(SbF_6)_2$ (Table 1) are related to those of $N_2H_6(AsF_6)_2$; both are indexed on the basis of a monoclinic cell.

Table 1 X-ray powder diffraction data for $N_2H_6(SbF_6)_2$

h	k	l	$d_{calc.}$	$d_{obs.}$	I
1	1	-1	5.51	5.55	w
0	2	0	5.02	5.03	w
0	0	2	4.72	4.75	w
0	2	1	4.43	4.45	w
0	1	2	4.27	4.25	m
2	0	0	4.08	4.09	m
1	2	-1	3.99	3.98	w
2	0	1	3.58	3.57	m
0	2	2	3.44	3.41	vw
1	1	-3	2.93	2.93	vw
0	2	3	2.67	2.68	vw
2	3	2	2.197	2.208	w
3	1	-3	2.148	2.147	w
3	3	-1	2.104	2.105	w
3	2	2	2.044	2.042	w
3	2	-4	1.781	1.780	vw
1	4	-4	1.652	1.649	vw
4	4	0	1.583	1.583	vw

$N_2H_6(SbF_6)_2$ was indexed on the basis of a monoclinic cell, with $a = 8.22(2)$ Å, $b = 10.04(3)$ Å, $c = 9.51(2)$ Å, $\beta = 97.2(2)°$ and $V = 780$ Å^3.

The vibrational spectrum of $N_2H_6(SbF_6)_2$ and its assignments are given in Table 2.

In the Raman spectrum of $N_2H_6(SbF_6)_2$ the most intense line, which corresponds to ν_1 (SbF_6^-), is observed at 666 cm^{-1}; the other two Raman active modes, ν_2 and ν_5, are split. The bands attributed to the $N_2H_6^{2+}$ cation appear at 1038 and 1604 cm^{-1}. In the infrared spectrum, the strongest absorption is observed at 663 cm^{-1} (ν_3); there are also three very weak absorptions at 554, 452 and 709 cm^{-1}, of which the last two can be attributed to traces of SbF_5 [9]. All absorptions between 800 and 1600 cm^{-1} are assigned to the cationic part of the molecule [10].

The thermal stability of hydrazinium(2+) hexafluorometalates reflects the increasing Lewis acidity from PF_5 to SbF_5 . $N_2H_6(PF_6)_2$ loses PF_5 slowly even at room temperature, while $N_2H_6(AsF_6)_2$ begins to decompose at 68° and $N_2H_6(SbF_6)_2$ at 158°.

Table 2 Vibrational spectra (cm^{-1}) of $N_2H_6(SbF_6)_2$ and $KSbF_6$ (11)

$N_2H_6(SbF_6)_2$		$KSbF_6$		Assignment
IR	R	IR	R	
		270		$\nu_4(SbF_6^-)$
	279(7)			
	293(23)		298	$\nu_5(SbF_6^-)$
452 w				
554 w				
	570(10)			$\nu_2(SbF_6^-)$
	581(8)		583	
663 vs		655		$\nu_3(SbF_6^-)$
	666(100)		664	$\nu_1(SbF_6^-)$
709 vw	706(2)			
831 w				
	1038(15)			$(N\text{-}N)_s$
1056 m				
1072 m				$(NH_3^+)_b$
1117 w				
1515 m				
1546 m				$(NH_3^+)_d$
1621 w	1604(3)			

The thermal decomposition study of $N_2H_6(SbF_6)_2$ (Fig. 1) shows that the decomposition occurs in two steps. The first step actually consists of two processes, which is confirmed by the DTA curve. Up to 245°, the sample loses 48.0% of its starting weight. This step is accompanied by the DTG minimum at 240°, the endothermic DTA peaks at 230 and 236° and an exothermic DTA peak at 241°. The exothermic DTA peak during the decomposition of hydrazinium compounds invariably accompanies the formation of ammonium compounds, e.g. $NH_4^+Sb_6^-$. The intermediate was isolated and identified by chemical analysis and its infrared spectrum.

In the next step, which occurs immediately and is finished at 400°, the DTG curve exhibits minima at 263, 304 and 348°. The DTA curve gives an endothermic peak at 263°. In the second step, the intermediate decomposes to the volatile components.

The intermediate isolated at 245 or 248° was a paste-like material, unstable in moist air. Chemical analysis of the intermediate gave 7.2% N_2H_4 and 2.8% NH_4. For $N_2H_5SbF_6$, the calculated value of N_2H_4 is 11.92%. All attempts to isolate pure $N_2H_5SbF_6$ (without ammonium complex) failed.

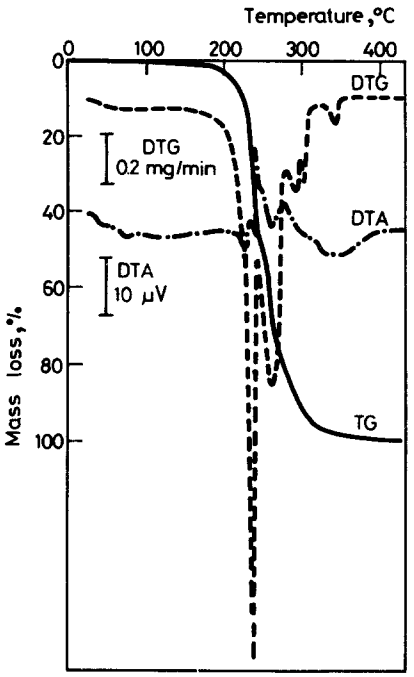

Fig. 1 TG, DTA and DTG curves of $N_2H_6(SbF_6)_2$

The decomposition of $N_2H_6(SbF_6)_2$ to $N_2H_5SbF_6$ is so rapidly followed by further decomposition to NH_4SbF_6 that the salts could not be separated. On the basis of chemical analysis, it is calculated that the intermediate contains approximately 60% $N_2H_5SbF_6$ and 40% NH_4SbF_6.

The Raman spectrum of this intermediate is of very poor quality; the strongest absorption in the infrared spectrum occurs at 666 cm^{-1}, which is attributed to ν_3 (SbF_6^-). Other absorptions, at 975, 1052, 1068, 1301 and 1621 cm^{-1}, are assigned to the $N_2H_5^+$ ion [10], and that at 1434 cm^{-1} to the NH_4^+ ion [12].

Comparison of the thermal properties of $N_2H_6(PF_6)_2$, $N_2H_6(AsF_6)_2$ and $N_2H_6(SbF_6)_2$ shows that, upon heating in an inert atmosphere, these materials behave completely differently: $N_2H_6(PF_6)_2$ decomposes through the isolable intermediates $N_2H_5PF_6$ and NH_4PF_6, $N_2H_6(AsF_6)_2$ decomposes directly to $N_2H_6F_2$ and AsF_5, and $N_2H_6(SbF_6)_2$ most resembles $N_2H_6(PF_6)_2$ in its thermal decomposition.

In the DSC curve for $N_2H_6(SbF_6)_2$, a strong endothermic effect at 140° and medium exothermic and endothermic effects at 225° and 255° are observed in the range 25-600°; ΔH for complete decomposition is endothermic (ΔH = 1440 J/g).

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Zusammenfassung – Mit der Reaktion von $N_2H_6F_2$ mit einem Überschuss von SbF_5 in wasserfreiem HF als Lösungsmittel wurde Hydrazinium(2+)hexafluoroantimonat hergestellt. Die Verbindung wurde durch Elemetaranalyse und Schwingungsspektren charakterisiert. Röntgendiffraktionsaufnahmen ergaben ausgehend von einer monoklinen Zelle $a = 8.22(2)$, $b = 10.04(3)$, $c = 9.51(2)$ Å, $\beta = 97.2°$ und $V = 780$ Å^3.

Die Untersuchung der thermischen Zersetzung von $N_2H_6(SbF_6)_2$ ergab, dass es sich diese Verbindung über eine Zwischenstufe, ein Gemisch aus $N_2H_5SbF_6$ und NH_4SbF_6, in gasförmige Komponenten zersetzt. In der DSC-Kurve können im Bereich 25-600°C ein starker endothermer sowie mittelstarke exotherme und endotherme Effekte beobachtet werden.