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THERMAL DECOMPOSITION OF $N_2H_6GeF_6 \cdot H_2O$, ISOLATION AND CHARACTERIZATION OF INTERMEDIATES

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ABSTRACT

The thermal behaviour of $N_2H_6GeF_6 \cdot H_2O$ was investigated by TG, DTG and DTA measurements. The decomposition proceeded in three steps, in which anhydrous $N_2H_6GeF_6$ and $N_2H_5GeF_5$ were isolated and characterized by chemical analysis and vibrational spectroscopy. The X-ray powder photographs of the intermediates were indexed, namely, for $N_2H_6GeF_6$ on the basis of a monoclinic cell with $a = 8.86(9)$, $b = 9.29(2)$, $c = 7.40(0)$ Å, $\beta = 85°$ and for $N_2H_5GeF_5$ on the basis of an orthorhombic cell with $a = 8.43(5)$, $b = 9.19(9)$, $c = 7.43(6)$ Å.

INTRODUCTION

Studies of hydrazinium(1 +) and (2 +) fluorometalates at the "Jožef Stefan" Institute, Ljubljana, have been carried out, and a series of new compounds have been prepared and characterized by different methods, in most cases also by thermal analysis [1–4]. Their thermal properties revealed that they decomposed either in a simple way (e.g., $N_2H_6FeF_5$, $N_2H_5CuF_3$) [1], or that their decompositions were very complex and distinct intermediates (hydrazinium, ammonium fluorometalates or adducts) were formed.

The present work on the decomposition of $N_2H_6GeF_6 \cdot H_2O$ was undertaken to examine its thermal behaviour and to characterize its intermediates.

As the crystal structure of the starting material was known [5], it was interesting to investigate the change in the structure of intermediates isolated during the heating process.

EXPERIMENTAL

$N_2H_6GeF_6 \cdot H_2O$ was prepared by reaction between solutions of $N_2H_6F_2$ and fluorogermanic acid. The purity was checked by chemical analysis

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($N_2H_6GeF_6 \cdot H_2O$; found: N_2H_4, 13.5; Ge, 30.5; F, 47.3%; calc.: N_2H_4, 13.43; Ge, 30.42; F, 47.76%).

A Mettler thermoanalyser was used for the thermal decomposition study in which a 100-mg sample was referenced against 100 mg of α-Al_2O_3. Platinum crucibles (1 ml) were used and the heating rate of the furnace was 2°C min^{-1}. The experiment was carried out in a dry argon atmosphere with a flow rate of 5 l h^{-1}. The DTG range was 10 mg min^{-1} and the DTA range was 200 μV. When intermediates were isolated, the starting weight of the sample was 500 mg. The first intermediate was isolated at 122°C and the second at 244°C. Both intermediates were also isolated in a vacuum system. Approximately 1 g of $N_2H_6GeF_6 \cdot H_2O$ was weighed in a nickel can, evacuated and then warmed up to 70°C to isolate the first intermediate, and to 170°C for the second. The gases released were collected in a Kell-F tube, cooled by liquid nitrogen. The mass balance was monitored carefully throughout the experiments.

The infrared spectra of the powdered solids pressed between CsBr plates were obtained on a Perkin-Elmer 521 spectrometer. The Raman spectra of the solids in a pyrex tube were recorded using a Spex 1401 machine, employing the 5145 Å line of an Ar^+ laser (coherent radiation) as the exciting radiation.

X-ray powder diffraction data were obtained with a Debye–Scherrer type camera and CuK_α radiation. The X-ray diffraction photographs were indexed using a Haendler program [6] on an IBM-1130 computer.

Hydrazine, ammonium ions and fluoride ions were determined by conventional analytical methods [7–9]. Germanium was determined by atomic absorption spectroscopy [10].

RESULTS AND DISCUSSION

Thermal decomposition of $N_2H_6GeF_6 \cdot H_2O$ begins at 48°C (Fig. 1) and its behaviour is given in Table 1. Up to 90°C the sample loses 7.6% of its starting weight, with an endothermic DTA peak at 81°C and a DTG minimum at 80°C. In the second step anhydrous $N_2H_6GeF_6$ decomposes further, with an endothermic DTA peak at 230°C and a DTG minimum at the same temperature. In the temperature interval from 90 to 240°C the sample loses 8.5% of its weight and the combined weight loss for the two steps amounts to 16.1% of the initial sample weight. With increasing temperature a further decomposition occurs and is accompanied by an endothermic DTA peak and a DTG minimum at 270°C. The intermediates, isolated at 278 and 298°C, are not homogeneous products and their chemical analysis confirms the presence of hydrazine and ammonium ion. Up to 400°C the overall weight loss is 99.0% and the last step is endothermic with DTA peaks at 335 and 349°C and DTG minima at 321, 335 and 345°C.

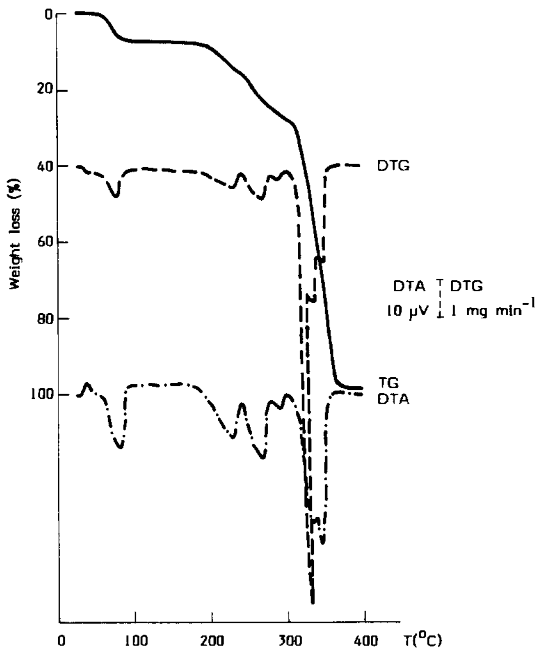

Fig. 1. TG, DTG and DTA curves of $N_2H_6GeF_6 \cdot H_2O$.

$N_2H_6GeF_6 \cdot H_2O$ decomposes according to the following equations

$$N_2H_6GeF_6 \cdot H_2O \rightarrow N_2H_6GeF_6 + H_2O \qquad (1)$$

$$N_2H_6GeF_6 \rightarrow N_2H_5GeF_5 + HF \qquad (2)$$

$$2\ N_2H_5GeF_5 \rightarrow 2\ GeF_4 + 2\ NH_3 + N_2 + H_2 + 2\ HF \qquad (3)$$

The intermediates, $N_2H_6GeF_6$ and $N_2H_5GeF_5$, isolated in thermal decomposition on the thermoanalyser, have the same X-ray powder photographs as the products prepared by decomposition in a vacuum system at 70 and

TABLE 1

Thermal behaviour of $N_2H_6GeF_6 \cdot H_2O$

Temperature range (°C)	Transformation	Weight loss (%)	
		Calc.	Found
48–90	Removal of water molecule and formation of $N_2H_6GeF_6$	7.55	7.6
90–240	Removal of HF and formation of $N_2H_5GeF_5$	8.38	8.5
240–400	Removal of gaseous products. No residue	84.07	82.9

TABLE 2

Chemical analysis of the intermediates

	Calc. (%)			Found (%)		
	N_2H_4	Ge	F	N_2H_4	Ge	F
$N_2H_6GeF_6$	14.51	32.90	51.66	14.1	–	50.7
$N_2H_5GeF_5$	15.97	36.18	47.34	15.9	35.5	46.9

170°C. Their chemical analysis is given in Table 2. The volatiles, released at 170°C, were collected and characterized by their infrared spectra. Only absorption attributable to the hydrogen fluoride molecule was observed.

TABLE 3

X-ray powder diffraction data[a] for $N_2H_6GeF_6$

h	k	l	d_{calc}	$d_{obs.}$	I	h	k	l	$d_{calc.}$	$d_{obs.}$	I
1	0	0	8.84	8.84	m	0	5	0	1.858	1.868	m
0	1	1	5.77	5.72	m	4	2	2	1.815	1.815	w
−1	0	1	5.43	5.37	m	1	5	−1	1.758	1.759	w
1	1	1	4.99	5.11	m	5	1	1	1.723	1.723	w
1	1	−1	4.69	4.86	s	1	2	4	1.707	1.704	w
0	2	0	4.64	4.64	s	2	5	1	1.681	1.682	w
2	0	0	4.42	4.47	w	0	5	2	1.659	1.661	w
1	2	0	4.11	4.31	s	4	2	3	1.612	1.615	m
2	1	0	3.99	4.00	m	4	4	1	1.585	1.585	w
0	2	1	3.93	3.87	s	3	5	1	1.551	1.552	m
0	0	2	3.69	3.71	s	5	1	−2	1.521	1.512	m
2	1	1	3.63	3.60	s	4	2	−3	1.492	1.495	m
1	0	2	3.51	3.51	w	6	0	0	1.472	1.472	w
1	0	−2	3.30	3.33	w	6	1	1	1.451	1.451	w
2	2	0	3.20	3.21	m	3	5	−2	1.425	1.423	m
2	2	−1	2.895	2.897	s	2	4	4	1.401	1.401	w
1	3	0	2.849	2.827	w	5	0	−3	1.378	1.378	w
3	1	1	2.800	2.733	s	3	6	1	1.357	1.356	m
1	3	−1	2.636	2.635	w	5	1	4	1.321	1.319	w
3	2	0	2.547	2.566	m	2	2	−5	1.308	1.308	w
2	2	2	2.496	2.501	w	3	5	−3	1.297	1.296	w
1	0	3	2.422	2.426	m	5	5	0	1.281	1.281	w
1	0	−3	2.316	2.315	s	6	2	3	1.265	1.265	w
2	0	3	2.232	2.235	w	3	3	5	1.250	1.250	w
1	2	3	2.148	2.151	m	4	6	−1	1.239	1.237	w
3	3	1	2.086	2.091	m	5	0	−4	1.223	1.223	w
0	4	2	1.965	1.967	m	6	3	3	1.210	1.210	w
1	4	2	1.937	1.935	w	5	5	−2	1.187	1.187	w
1	3	3	1.908	1.904	m	1	2	−6	1.164	1.164	w

[a] Indexed on the basis of a monoclinic cell with $a = 8.86(9)$, $b = 9.29(2)$, $c = 7.40(0)$ Å, $\beta = 85°$, $V = 607.5$ Å^3.

Volatiles were dissolved and chemical analysis of the aqueous solution confirmed that there was neither ammonium, hydrazinium nor germanium present.

The vibrational spectrum of the first stage intermediate, $N_2H_6GeF_6$, confirms the presence of $N_2H_6^{2+}$ and GeF_6^{2-}. In the Raman spectrum the band at 1043 cm^{-1} is assigned to the N–N vibration, which, for the $N_2H_6^{2+}$ ion, is inactive in the infrared spectrum. The bands observed in the region from 1050 to 1700 cm^{-1} in the infrared and in the Raman spectra attributed to the deformation and bending vibrations of the NH_2 and NH_3^+ groups are in accordance with the literature [11]. In the anionic part of the Raman spectrum, Raman active frequencies ν_5, ν_2 and ν_1 of the octahedral GeF_6^{2-} ion are observed at 342, 488, 617 and 630 cm^{-1}. In the infrared spectrum, absorptions at 348 (ν_4), 615 and 580 cm^{-1} (ν_3) are observed. The splitting of the strongest symmetric stretching mode ν_1 and the antisymmetric F–Ge–F stretching mode ν_3 can be explained by correlation field effects.

The vibrational spectrum of the second intermediate, $N_2H_5GeF_5$, differs markedly from that of $N_2H_6GeF_6$. In the anionic part of the spectrum the strongest band is shifted to higher frequency (639 cm^{-1} in the Raman, 638 cm^{-1} in the infrared) and additional bands can also be observed (304, 328, 360, 456 and 572 cm^{-1} in the Raman; 408, 462, 568, 670 and 720 cm^{-1} in

TABLE 4

X-ray powder diffraction data[a] for $N_2H_5GeF_5$

h	k	l	$d_{calc.}$	$d_{obs.}$	I	h	k	l	d_{calc}	$d_{obs.}$	I
1	0	1	5.57	5.40	w	4	1	2	1.799	1.801	w
1	1	1	4.77	4.88	s	2	4	2	1.774	1.774	w
0	2	0	4.60	4.60	w	0	2	4	1.723	1.721	s
1	2	0	4.04	4.01	s	0	4	3	1.686	1.686	w
0	1	2	3.44	3.44	s	5	1	1	1.619	1.622	s
1	1	2	3.19	3.23	w	4	3	2	1.574	1.576	m
0	3	0	3.06	3.06	w	3	5	0	1.539	1.543	w
0	2	2	2.891	2.909	w	3	5	1	1.507	1.505	w
2	1	2	2.669	2.658	w	1	6	1	1.478	1.479	w
3	0	1	2.630	2.598	s	2	6	0	1.441	1.438	m
3	2	0	2.399	2.414	w	2	0	5	1.403	1.404	w
2	3	1	2.352	2.349	s	3	3	4	1.383	1.382	w
3	2	1	2.283	2.290	w	3	6	0	1.346	1.350	m
3	0	2	2.242	2.232	w	6	2	1	1.323	1.323	m
3	1	2	2.179	2.175	w	4	5	2	1.299	1.296	w
1	2	3	2.112	2.118	w	3	6	2	1.265	1.265	w
2	3	2	2.063	2.066	s	5	1	4	1.238	1.237	m
4	1	1	1.981	1.988	s	6	3	2	1.209	1.209	w
2	4	1	1.949	1.949	w	5	5	2	1.179	1.180	m
1	2	4	1.905	1.907	w	0	7	3	1.161	1.163	w
3	0	3	1.859	1.860	w	7	2	1	1.152	1.152	w

[a] Indexed on the basis of an orthorhombic cell with $a = 8.43(5)$, $b = 9.19(9)$, $c = 7.43(6)$ A, $V = 577.0$ Å^3.

the infrared). These bands in the 300–720 cm^{-1} region are assigned to the GeF_5^- group, which was previously investigated by several authors [12–14].

The cationic part of the spectrum is identified as the $N_2H_5^+$ ion. The N–N stretching vibration appears with high intensity both in the Raman (1038 cm^{-1}) and in the infrared (1032 cm^{-1}). This vibration is shifted to higher frequencies in comparison with the other known $N_2H_5^+$ fluorocomplexes [11]. This shift has been explained by coordination of $N_2H_5^+$ to the metal [15,16]. Other bands observed in the 1050–1700 cm^{-1} region in the Raman and in the infrared spectra are attributable to deformation and rocking vibrations of the N–H bonds in $N_2H_5^+$.

The X-ray powder diffraction data for $N_2H_6GeF_6$ and $N_2H_5GeF_5$ are given in Tables 3 and 4. The X-ray powder data of $N_2H_6GeF_6$ were indexed on the basis of a monoclinic cell with $a = 8.86(9)$, $b = 9.29(2)$, $c = 7.40(0)$ Å, $\beta = 85°$, $V = 607.5$ Å^3. The X-ray powder diffraction data of $N_2H_5GeF_5$ were indexed on the basis of an orthorhombic cell with $a = 8.43(5)$, $b = 9.19(9)$, $c = 7.43(6)$ Å, $V = 577.0$ Å^3.

A comparison with the cell parameters of the orthorhombic $N_2H_6GeF_6 \cdot H_2O$ [5] ($a = 8.869(1)$, $b = 9.292(1)$, $c = 7.400(1)$ Å, $V = 609.8$ Å^3) shows that the structures are closely related. The structure of $N_2H_6GeF_6$ can be described as a monoclinal distorted structure of $N_2H_6GeF_6 \cdot H_2O$.

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