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SYNTHESIS AND CHARACTERIZATION OF $(N_2H_5)_2SiF_6$ AND THERMAL ANALYSIS OF $(N_2H_5)_2SiF_6$ AND $N_2H_6SiF_6$

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ABSTRACT

A new complex, hydrazinium(1 +) hexafluorosilicate was prepared and characterized by chemical analysis, vibrational spectroscopy and X-ray powder photography. It is isostructural with $(N_2H_5)_2GeF_6$; the crystals are monoclinic with unit-cell dimensions $a = 5.96(2)$, $b = 5.19(1)$, $c = 10.99(5)$ Å and $\beta = 100.1(3)°$. TG, DTG and DTA techniques were used to study its thermal decomposition and also the decomposition of the known compound $N_2H_6SiF_6$. Their thermal behaviour was compared with that of the corresponding hydrazinium hexafluorogermanates, $(N_2H_5)_2GeF_6$ and $N_2H_6GeF_6$; the latter was formed as the first step intermediate in the thermal decomposition of $N_2H_6GeF_6 \cdot H_2O$.

Both hydrazinium hexafluorosilicates decomposed in two steps through the intermediate $(NH_4)_2SiF_6$.

INTRODUCTION

Hydrazinium(2+) hexafluorosilicate was isolated as early as 1910 [1], and the authors reported that heating in vacuo yielded silicon tetrafluoride and hydrazinium difluoride. In the eighties the crystal structure of $N_2H_6SiF_6$ was determined by two different groups [2,3]. In the present work the synthesis of $(N_2H_5)_2SiF_6$ and its identification are described. Further, the thermal decompositions of $N_2H_6SiF_6$ and $(N_2H_5)_2SiF_6$ were studied, showing that in the first step both decompositions occurred by mechanisms different from that of the corresponding germanium compounds.

EXPERIMENTAL

$N_2H_6SiF_6$ was produced by adding $N_2H_6F_2$ to a solution of H_2SiF_6 (30%). Colourless crystals were obtained by evaporation at room temperature. An aqueous solution of $N_2H_6SiF_6$ and diluted hydrazinium hydrate were mixed (pH = 5) and yielded colourless crystals of $(N_2H_5)_2SiF_6$. Their chemical analysis is summarized below.

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$N_2H_6SiF_6$
Found: N_2H_4, 18.2; F, 64.7.
Calcd.: N_2H_4, 18.19; F, 64.72.

$(N_2H_5)_2SiF_6$
Found: N_2H_4, 30.5; F, 54, 7.
Calcd.: N_2H_4, 30.79; F, 54.75.

Thermal analyses were carried out by use of a Mettler TA 1 thermoanalyser. Samples of 100 mg were used for TG and the heating rate was 1°C min^{-1}. The reference sample was α-Al_2O_3. The decompositions took place 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 100 or 200 μV. When intermediates were isolated, the starting weight of the sample was 100–200 mg. When the decomposition was studied in a vacuum system, approximately 1 g of sample was weighed in a nickel reaction vessel, evacuated and warmed up. The gases released were collected in an infrared cell, cooled by liquid nitrogen. The gases were identified by their infrared spectra. The mass balance was monitored throughout the experiment.

The Raman spectra of the starting materials and the intermediates in a Pyrex tube were recorded on a Spex 1401 instrument with the 5145 Å line of an argon laser (Coherent Radiation) as the exciting radiation. For infrared spectra the powdered solids were pressed between CsBr plates and a Perkin-Elmer 521 spectrometer was used.

X-ray powder diffraction photography was performed with a Debye–Scherrer type camera using CuK_α radiation. The cell dimensions were refined from 20 reflexions using a Param of the X-ray 76 system [4] on a DEC 10 computer. In chemical analyses, hydrazine, ammonium ions and fluoride ions were determined by conventional analytical methods [5–7].

RESULTS AND DISCUSSION

The vibrational spectra of $N_2H_6SiF_6$, $(N_2H_5)_2SiF_6$ and the intermediate $(NH_4)_2SiF_6$ and their assignments are given in Table 1. The spectrum of $(NH_4)_2SiF_6$ is in agreement with previous studies [8]. An isolated octahedral SiF_6^{2-} ion (O_h point-group) has six fundamental vibrational frequencies: ν_1, ν_2 and ν_5 are Raman active, ν_3 and ν_4 are infrared active and ν_6 is inactive.

The strongest band (ν_1) in the Raman spectra is shifted to a higher frequency for $N_2H_5^+$ and $N_2H_6^{2+}$ compounds. For these compounds the Raman active modes ν_1 and ν_5 are also observed in the infrared spectra. This can be understood as a consequence of the slight distortion of the structure caused by the size of the $N_2H_5^+$ and $N_2H_6^{2+}$ ions in comparison to NH_4^+.

TABLE 1

Vibrational spectra (cm^{-1}) of $N_2H_6SiF_6$, $(N_2H_5)_2SiF_6$ and $(NH_4)_2SiF_6$

$N_2H_6SiF_6$		$(N_2H_5)_2SiF_6$		$(NH_4)_2SiF_6$		Assignment
IR	R	IR	R	IR	R	
					182 (47)	
		348m				
400W			402 (11.8)		402(61.8)	$\nu_5(SiF_6^{2-})$
	410 (21.4)	419m	413 (13.6)			
462m		464s			467 (6.6)	$\nu_2(SiF_6^{2-})$
476m				472s		$\nu_4(SiF_6^{2-})$
488sh	480 (7.7)		487 (5.2)			
		638vs				ν_1 (SiF_6^{2-})
665sh	671 (59.2)		654 (100)		642 (100)	
710vs		708vs		708vs		$\nu_3(SiF_6^{2-})$
		961vs	981 (60)			$(N{-}N)_s$
	1050 (100)					
1065s		1072s				$(NH_3^+)_r$
1084sh		1095s				
			1118 (55)			
1140m		1225w	1258 (2.6)			
1290w						
	1380 (4.1)		1399 (7.4)			
				1418vs	1424 (20)	$\nu_4(NH_4^+)$
			1492 (3.5)			$(NH_3^+)_d$
1505w						
1540w	1537 (16.3)	1532s	1557 (5.7)			
1557m	1597 (14.8)	1598s	1570 (3.5)			
	1612 (5.1)		1618 (8.8)			
		1639m	1639 (7)			
			1650 (17)			$(NH_2^+)_d$
				3287m	3231 (59.2)	$\nu_3(NH_4^+)$

TABLE 2

X-ray powder diffraction data for $(N_2H_5)_2SiF_6$

h	k	l	$d_{calc.}$	$d_{obs.}$	I	h	k	l	$d_{calc.}$	$d_{obs.}$	I
1	0	−1	5.59	5.64	s	0	1	3	2.934	2.921	w
0	0	2	5.41	5.36	s	1	0	3	2.857	2.857	w
1	0	1	4.82	4.87	vs	0	2	0	2.596	2.614	w
0	1	1	4.68	4.65	vs	2	1	0	2.554	2.553	w
1	1	0	3.89	3.91	m	2	1	−2	2.460	2.464	s
1	1	−1	3.80	3.78	w	0	1	4	2.400	2.401	s
1	1	1	3.53	3.54	w	1	2	0	2.374	2.356	vw
1	0	−3	3.35	3.36	s	2	1	2	2.184	2.183	m
1	1	2	2.997	2.994	m	1	2	2	2.119	2.123	m

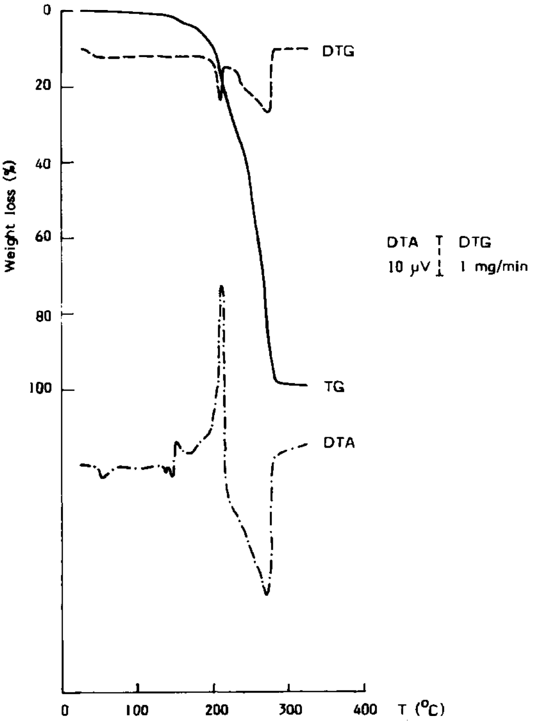

Fig. 1. TG, DTG and DTA curves of $(N_2H_5)_2SiF_6$.

The cationic parts of the molecules are assigned according to ref. 9 for $N_2H_5^+$ and $N_2H_6^{2+}$ and to ref. 10 for NH_4^+.

X-ray diffraction patterns of $(N_2H_5)_2SiF_6$ are given in Table 2. From inspection of the powder diffraction patterns of $(N_2H_5)_2SiF_6$ and $(N_2H_5)_2GeF_6$ isomorphism of the two compounds was deduced [11].

$(N_2H_5)_2SiF_6$ is monoclinic with the unit-cell dimensions $a = 5.96(2)$, $b = 5.19(1)$, $c = 10.99(5)$ Å and $\beta = 100.1(3)°$; the calculated density (g cm^{-3}) is 2.066 and that measured is 2.001.

Thermal decomposition of $(N_2H_5)_2SiF_6$ begins at 30°C (Fig. 1) and its behaviour is summarized in Table 3. Up to 160°C the sample loses 3.2% of

TABLE 3

Thermal behaviour of $(N_2H_5)_2SiF_6$

Temp. range (°C)	Transformation	Weight loss (%)	
		Calc.	Found
25–218	Removal of gaseous components SiF_4, HF, N_2, H_2 and formation of $(NH_4)_2SiF_6$	22.98	23.5
218–325	Removal of gaseous SiF_4, N_2, H_2, HF; no residue	77.02	75.2

its weight due to initial decomposition which is endothermic with a DTA peak at 146 °C. Further decomposition is exothermic with a DTA peak at 208°C and a DTG minimum at the same temperature. Between 30 and 218°C the sample loses 23.5% of its weight. The intermediate was isolated at 218°C. In the next step between 218 and 325°C the intermediate decomposes completely to gaseous components. This step is endothermic with a DTA peak and a DTG minimum at 270°C. Experimental cumulative weight loss is 98.7%. The thermal decomposition of $(N_2H_5)_2SiF_6$ is described in terms of the following equations:

$$10(N_2H_5)_2SiF_6 \rightarrow 9(NH_4)_2SiF_6 + SiF_4 + 11N_2 + HF + 13H_2 \quad (1)$$

$$(NH_4)_2SiF_4 \rightarrow SiF_4 + 2HF + N_2 + 3H_2 \quad (2)$$

In comparison to $(N_2H_5)_2GeF_6$ [12], the thermal decomposition of $(N_2H_5)_2SiF_6$ is more complex: both $N_2H_5^+$ fluorometalates give corresponding NH_4^+ fluorometalates as intermediates, but $(N_2H_5)_2SiF_6$ emits silicon tetrafluoride and hydrogen fluoride as well as N_2 and H_2. This is confirmed by the thermal decomposition of $(N_2H_5)_2SiF_6$ in a vacuum system. The

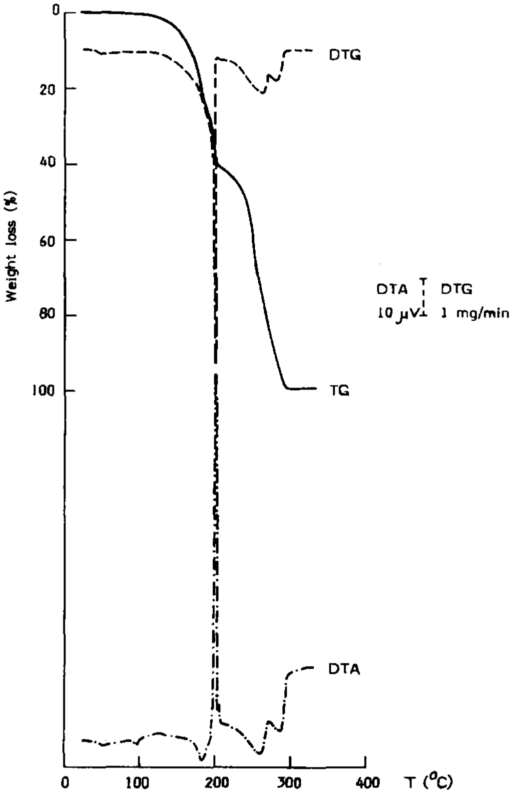

Fig. 2. TG, DTG and DTA curves of $N_2H_6SiF_6$.

TABLE 4

Thermal behaviour of $N_2H_6SiF_6$

Temp. range (°C)	Transformation	Weight loss (%)	
		Calc.	Found
25–202	Formation of $(NH_4)_2SiF_6$ and removal of SiF_4, HF, N_2 and H_2	42.58	40.5
202–330	Removal of gaseous SiF_4, HF, N_2 and H_2; no residue	57.42	58.5

gases released were collected in an infrared cell and the infrared spectrum clearly showed absorption frequencies attributable to SiF_4 and HF.

The difference in thermal behaviour of $(N_2H_5)_2SiF_6$ and $(N_2H_5)_2GeF_6$ is a consequence of the lower thermal stability of the former.

The thermal decomposition of $N_2H_6SiF_6$ is described in Fig. 2 and Table 4. It starts at 44°C. Up to 202°C the sample loses 40.5% of its starting weight. The decomposition is accompanied by a weak endothermic DTA peak at 97°C, a strong exothermic DTA peak at 199°C, and a DTG minimum at 199°C. The intermediate was isolated at 218°C. The next step is endothermic, with DTA peaks at 258 and 287°C, and DTG minima at 264 and 281°C. Between 44 and 330°C the overall weight loss is 99.0%.

The thermal decomposition of $N_2H_6SiF_6$ can be described in terms of the following equations:

$$2N_2H_6SiF_6 \rightarrow (NH_4)_2SiF_6 + SiF_4 + 2HF + N_2 + H_2 \tag{3}$$

$$(NH_4)_2SiF_6 \rightarrow SiF_4 + 2HF + N_2 + 3H_2 \tag{4}$$

The first step of the thermal decomposition of $N_2H_6SiF_6$ was also observed in a vacuum system, and the SiF_4 and HF released were qualitatively determined from their infrared spectra.

Decomposition of $N_2H_6GeF_6$, which is the first intermediate of the thermal decomposition of $N_2H_6GeF_6 \cdot H_2O$ [13], occurs through $N_2H_5GeF_5$ liberating HF, whereas $N_2H_6SiF_6$ releases HF and SiF_4 at the same time and $(NH_4)_2SiF_6$ is formed as an intermediate. It is clear that the mechanism of $N_2H_6SiF_6$ decomposition is completely different: during the heating process $N_2H_6^{2+}$ groups are transformed to NH_4^+ and half of the SiF_6^{2-} anions decomposes and gaseous SiF_4 is released.

The intermediate $(NH_4)_2SiF_6$ was characterized by chemical analysis (found: NH_4, 20.0 for $(NH_4)_2SiF_6$ isolated by thermal analysis of $N_2H_6SiF_6$; found: NH_4, 20.1; F, 63.7 isolated by thermal analysis of $(N_2H_5)_2SiF_6$; calcd. for $(NH_4)_2SiF_6$: NH_4, 20.25; F, 63.98).

Further decomposition of $(NH_4)_2SiF_6$ occurs in the same way as that of $(NH_4)_2GeF_6$.

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