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Hydroxylammonium fluorogermanates

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Abstract

A new hydroxylammonium compound $(NH_3OH)_2GeF_6$, has been synthesized by the addition of solid NH_3OHF to a solution of GeO_2 dissolved in 20% HF. The compound was characterized by chemical analysis and X-ray powder diffraction, the thermal decomposition was studied by thermal analysis and mass spectrometry. $(NH_3OH)_2GeF_6$ crystallizes monoclinic. Two endothermic and two exothermic peaks have been observed on the DSC curve, the decomposition product at 500 °C is GeO_2.

Keywords: Hydroxylammonium fluorogermanates; Mass spectroscopy; Thermal analysis; X-ray powder diffraction

1. Introduction

Hydroxylamine, NH_2OH, may be thought of as derived from ammonia by replacement of hydrogen atom by the –OH group. The first hydroxylammonium fluorometallates were reported in 1908 [1]. Only five compounds were reported up to 1990.

In the past decade, we systematically synthesized hydroxylammonium fluorometallates of the 4th group of transition elements: Ti, Zr, Hf, which have the diverse structural chemistry and also of 13th main group Al, Ga and In [2–7]. In a series of experiments, we isolated the hydroxylammonium fluorosilicates [8] which belong to group 14.

Fluorogermanates of ammonium and hydrazinium are well-known and there are several papers reporting their synthesis, structure and thermal behaviour [9–12]. On the other hand, there are only a few reports about hydroxylammonium fluorometallates. Because they are analogous with ammonium and hydrazinium compounds, we decided to study the synthesis of hydroxylammonium fluorogermanate and investigate the product by modern methods.

By using solid NH_3OHF instead of the aqueous solution of NH_2OH used in previous reports, a new compound with the formula $(NH_3OH)_2GeF_6$ was obtained, but no single crystals, suitable for structure determination, could be isolated, due to difficult experimental conditions.

Hydroxylamine is an intermediate of the nitrogen cycle, produced by encimatic oxidation of ammonia to nitrites and/or nitrates and the product of anaerobic oxidation is N_2O [13], a known pollutant of lakes and rivers [14], so special emphasis was placed on measuring hydroxylamine, a potential precursor to nitrous oxide in aquatic systems. Therefore, it is very important to stabilize hydroxylamine in hydroxylamonium compounds to prevent its oxidation to N_2O.

The aim of the paper is to study the thermal properties of some hydroxylammonium fluorometallates and so deepen the basic knowledge of the chemistry of hydroxylamine.

2. Experimental

$(NH_3OH)_2GeF_6$ has been synthesized by the addition of solid NH_3OHF to a solution of GeO_2 dissolved in hot HF (20%).

Hydroxylamine was isolated in ethanolic solution by the reaction of solid hydroxylammonium chloride with sodium ethylate [15]. By adding HF, white crystals of NH_3OHF were obtained [16] and the product was used for further synthesis. Initially, 1.80 g (34 mmol) of solid NH_3OHF were dissolved in solution of 1.78 g (17 mmol) GeO_2, dissolved in 20.4 g (204 mmol) of 20% HF in a platinum beaker. The same experiment was carried out, using various amounts of

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NH_3OHF. After a few days of evaporation at room temperature, colourless crystals were obtained. The product was filtered, dried and characterized by chemical, thermal and X-ray analysis. The yields of the synthesis were 95–98%.

Hydroxylamine was determined by titration with $KMnO_4$ [17] and fluorine by direct calibration with a combination fluoride electrode [18]. Germanium was determined by the combination of ICP–MS method.

Thermal analysis (TG and DSC) was carried out on TA-4000 System/Mettler in a nitrogen stream with a heating rate of 10 K/min, using platinum (TG) and gold crucibles (DSC). The thermal behaviour was checked visually in a glass capillary.

Thermal decomposition was also studied by combination of Knudsen effusion and mass spectrometry. For this, a few milligrams of the sample was heated in a Knudsen cell having orifice diameter of 3 mm, located near the ion source of the mass spectrometer. The molecules of the sample pass through the ion source and the intensity of the ions is finally measured versus the mass-to-charge ratio.

In the method which was used, some milligrams of the sample was heated at a heating rate of 10 K/min, and the mass spectrum was recorded every 20 K.

X-ray powder diffraction data was collected with an AXS-Bruker/Siemens/D5005 diffractometer using Cu Kα radiation at 293(1) K. The samples were finely ground, placed on a Si—single crystal holder and measured in the range $5^\circ < 2\Theta < 65^\circ$. The measuring times were from 47 to 52 h with a step of 0.010 and a scanning speed of 1 s per step. The values for divergence and antiscattering slit were fixed at 0.2 mm. The measurements were corrected for the sample height and the Kα2 radiation was stripped off. The X-ray diffraction pattern has been indexed with the help of the automatic indexing program TREOR [19] and ITO [20]. For determination of the end product, the Search/Match [21] program was used.

3. Results and discussion

By using solid NH_3OHF instead of solution of NH_2OH, a new compound with the formula $(NH_3OH)_2GeF_6$ was obtained. Changing the molar ratio of the reactants yielded identical products. Chemical analysis of a typical product was: 25.9% NH_3OH^+ (calc. 26.7%), 28.9% Ge (calc. 28.5%) and 43.1% F (calc. 44.8%). Chemical analyses of the other samples differ from the values less then ±1 percentage points.

The synthesized compound was characterized using X-ray powder diffraction analysis. Indexing of X-ray powder diffraction data for $(NH_3OH)_2GeF_6$ gave the best matching (FOM) in the monoclinic system with unit cell parameters: $a = 12.108(6)$ Å, $b = 5.865(3)$ Å and $c = 5.853(3)$ Å; $\alpha = \gamma = 90.00(0)^\circ$, $\beta = 98.82(8)^\circ$ and $V = 410.76$ Å^3.

Thermal decomposition of $(NH_3OH)_2GeF_6$ (Fig. 1) starts at 25.0 °C. Up to 144.0 °C the sample loses 9.4% (calc. 10.4%) of its starting weight, which corresponds to 4 moles of HF in the first step. Endothermic DSC peak at 77.1 °C represents the melting point of the compound, which was confirmed visually with glass capillary.

In the second temperature interval between 144 and 270 °C the sample loses 35.5% of its weight due to removal of gaseous products and is accompanied by an exothermic DSC peak at 224.1 °C and a DTG maximum at 239.7 °C. Ammonium hexafluorgermanate was found as intermediate at 230 °C, which is confirmed with powder diffraction analysis. With increasing temperature, a further decomposition occurs between 270.0 and 314.3 °C with additional weight loss of 10.6% and is accompanied by an exothermic DSC peak at 283.6 °C. In the last step, in the temperature interval from 314.3 to 408.0 °C the sample loses 29.1% of its weight and is accompanied by an endothermic DSC peak at 322.6 °C. The DSC peaks are in good agreement with the maximum on the TG curve.

The fourth step is probably accompanied with hydrolysis of the intermediate GeF_4, which is formed during thermal decomposition.

Up to 500 °C, the overall weight loss is 86.3% (calc. 86.3%) and the decomposition product is GeO_2, which is confirmed with powder diffraction analysis (Fig. 2).

In order to identify the individual decomposition products, Knudsen cell mass spectrometry (KCMS) was applied. Mass spectra obtained at 200 °C can be seen in Fig. 3.

At 200 °C, several peaks which can be attributed to HF, NH_2OH and GeF_4 can be observed. From a series of such measurements, we constructed the Fig. 4, which represents intensities of various ionic species versus temperature.

According to the spectra, the decomposition of $(NH_3OH)_2GeF_6$ is accompanied with the gaseous products in two stages. In the first stage (170 °C), the peaks which can be contributed to NH_2OH, HF and GeF_4 are observed.

In the second stage (220 °C), several other peaks are abundant like NH_3 and N_2. NH_3 is the decomposition product of NH_4F. The decomposition equation is:

$$3(NH_3OH)_2GeF_6 \rightarrow (NH_4)_2GeF_6 + 4HF + 2N_2 + 6H_2O + 2GeF_4 \quad (1)$$

followed by:

$$(NH_4)_2GeF_6 \rightarrow GeF_4 + 2HF + 2NH_3 \quad (2)$$

Simultaneous production of H_2O and GeF_4 results in hydrolysis [22] of the intermediate GeF_4, according to reaction 3, forming the final product of decomposition, GeO_2.

$$3GeF_4 + 2H_2O \rightarrow GeO_2 + 2H_2GeF_6 \uparrow \quad (3)$$

The results indicate that there are some similarities, compared to the thermal decomposition of hydroxylammonium fluorometallates of group 4 [2–4,7]. $(NH_3OH)_2GeF_6$ decomposes at similar temperatures and shows similar endothermic and exothermic peaks than hydroxylammonium compounds of titanium, zirconium and hafnium.

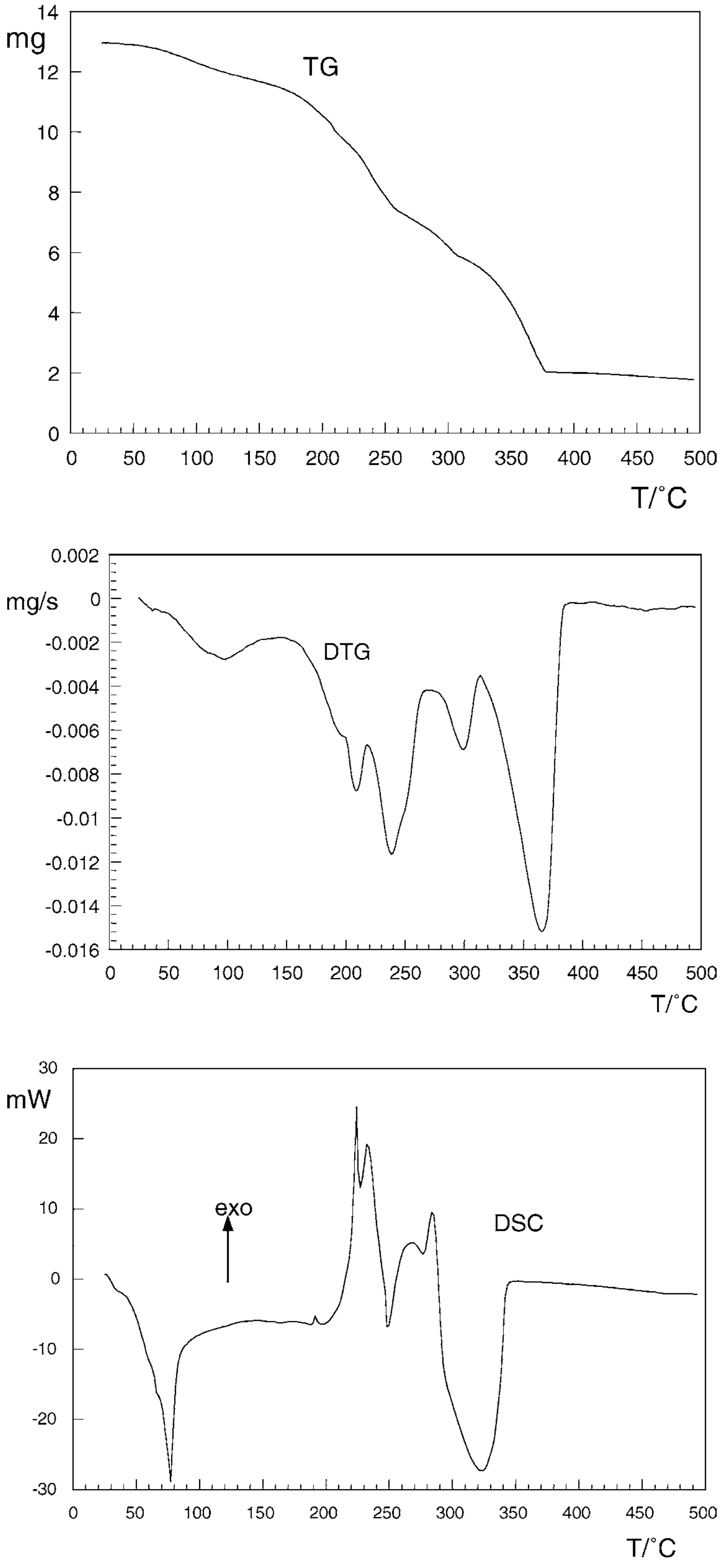

Fig. 1. Thermal analysis of $(NH_3OH)_2GeF_6$ (TG: thermogravimetry, DTG: derivative thermogravimetry and DSC: differential scanning calorimetry).

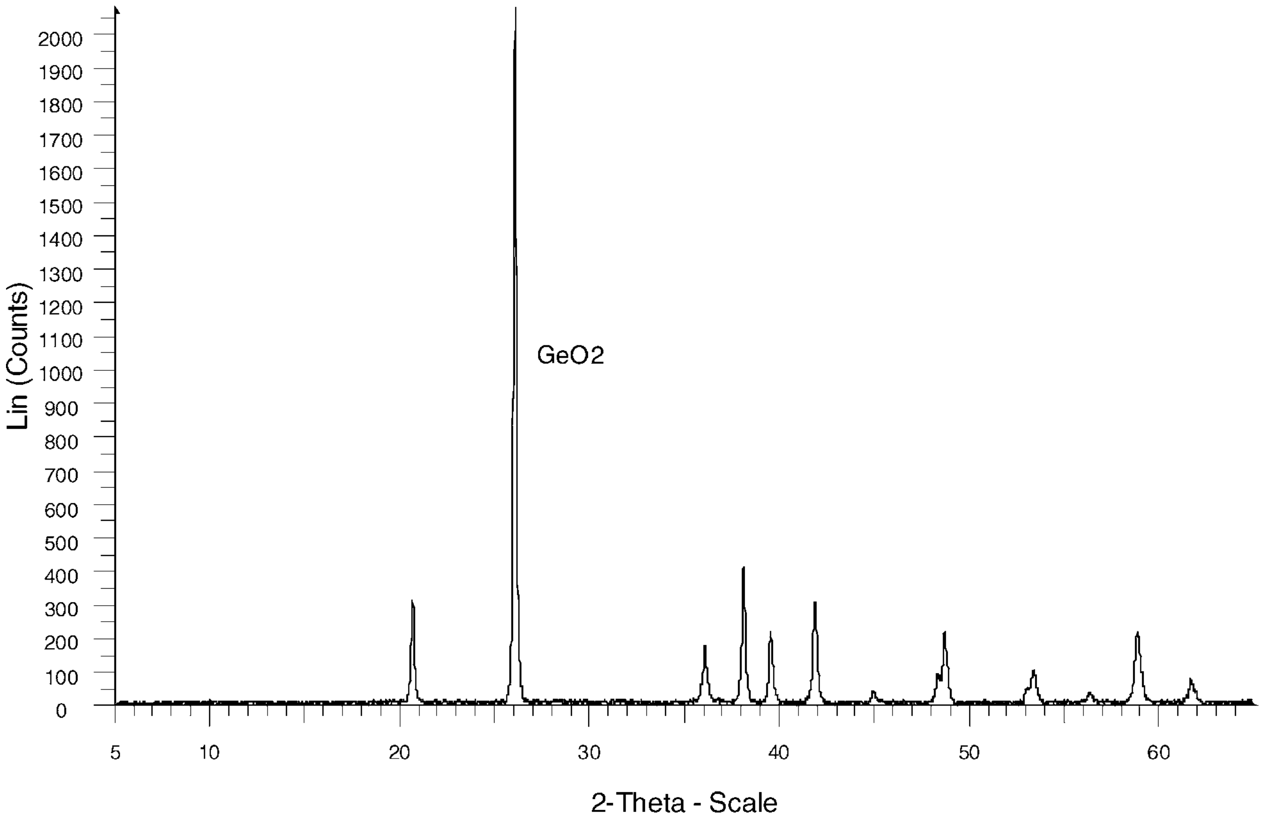

Fig. 2. Powder diffraction analysis of the decomposition product GeO_2.

Endothermic peak is accompanied with melting point and decomposition begins bellow this temperature. By heating the hydroxylammonium fluorometallates of Ti, Zr and Hf, disproportionation of hydroxylamine to NH_3 and N_2 was observed in the first step. Ammonium fluorometallates were found as intermediates and their crystallization results in exothermic DSC peaks, between 200 and 250 °C. The end products of these fluorometallates are TiO_2, ZrF_4 and ZrO_xF_y ($x = 1.3$–2.714, $y = 1.4$–2.714) and HfF_4. [7]. The decomposition product of $(NH_3OH)_2GeF_6$ is GeO_2, which is confirmed with X-ray powder diffraction.

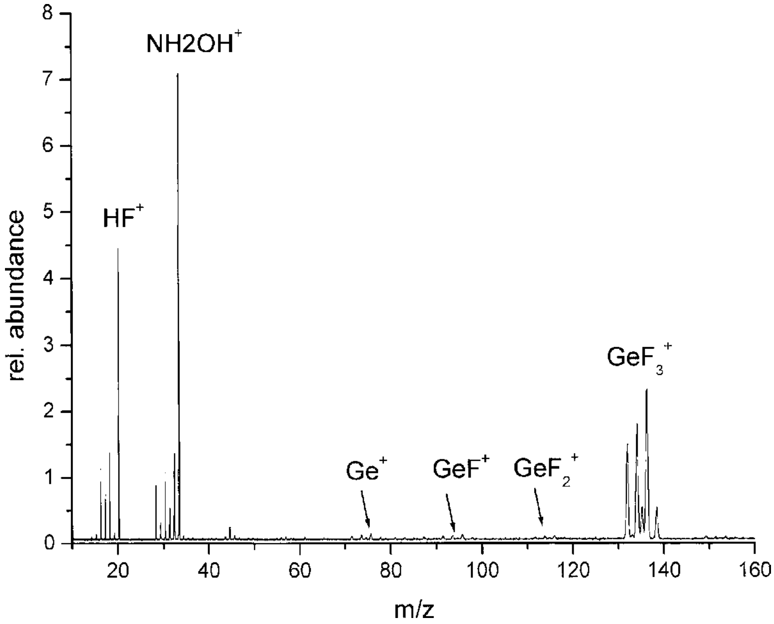

Fig. 3. Mass spectra of gaseous molecular species leaving the surface of $(NH_3OH)_2GeF_6$ at 200 °C.

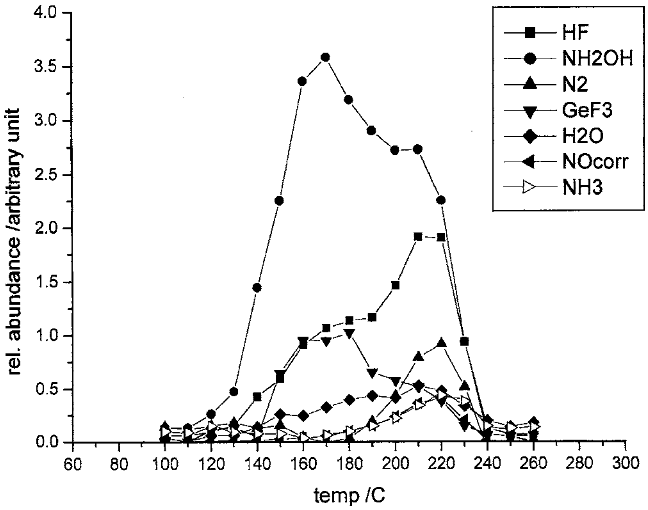

Fig. 4. Intensities of various ionic species vs. temperature.

$(NH_3OH)_2SiF_6$ [8], decomposes at lower temperatures than hydroxylammonium fluorometallates of Ti, Zr, Hf and Ge. All the DSC peaks are endothermic with one decomposition step. Up to 265 °C the decomposition nearly 100%, which is due to sublimation of SiF_4 product.

The differences are the result of weaker hydrogen bonds at $(NH_3OH)_2SiF_6$. The temperature, needed for the cleavage of the hydrogen bonds in $(NH_3OH)_2SiF_6$ is lower than the temperature, needed for the disproportionation of the hydroxylamine to ammonium as at $(NH_3OH)_2GeF_6$.

Acknowledgements

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