SYNTHESIS AND STRUCTURE OF HYDROXYLAMMONIUM FLUOROSILICATES†

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Abstract

A new hydroxylammonium compound with the formula $(NH_3OH)_2SiF_6$ has been synthesized by reaction of solid NH_3OHF and H_2SiF_6. By recrystallization from aqueous HF, single-crystals of $(NH_3OH)_2SiF_6{\cdot}2H_2O$ were isolated. Both compounds were characterized by elemental analysis and thermal analysis, the structure of $(NH_3OH)_2SiF_6{\cdot}2H_2O$ has been determined by single crystal x-ray analysis. The compound crystallizes monoclinic with cell parameters: a = 10.772(5) Å, b = 7.336(6) Å, c = 10.447(3) Å, β = 102.09(3)°.

Introduction

Fluorosilicates of ammonium and hydrazinium are well known and there are several papers reporting their synthesis and structure.[1-6] On the other hand, there are only a few reports about hydroxylammonium fluorometallates. The first hydroxylammonium fluorosilicate with the formula "$(NH_3O)_2{\cdot}H_2SiF_6 + 2H_2O$" was reported in 1908,[7] but the compound was characterized only by the chemical analysis and the fluorine ion was determined indirectly. Several hydroxylammonium fluorometallates of main group III and side group IV metals were synthesized in the last decade[8-12] whereas no recent reports about silicone compounds could be found in literature. So we decided to study reactions in the systems NH_2OH - H_2SiF_6 and NH_3OHF - H_2SiF_6 and to investigate the product by modern methods. By using solid NH_3OHF instead of the aqueous solution of NH_2OH, used in the original work, a new compound with the formula $(NH_3OH)_2SiF_6$ was obtained,[13] but no single-crystals, suitable for structure determination, could be isolated. In this paper we report the

synthesis and structure of the compound with the formula $(NH_3OH)_2SiF_6 \cdot 2H_2O$, obtained by recristallization of $(NH_3OH)_2SiF_6$ from aqueous solution.

Results and discussion

Chemical analysis of $(NH_3OH)_2SiF_6$ gave the following results: 31.9% NH_3OH^+ (calc. 32.4%), 13.4% Si (calc. 13.4%) and 54.2% F^- (calc. 54.2%). The compound was characterized using X-ray powder diffraction analysis. Indexing of X-ray powder diffraction data for $(NH_3OH)_2SiF_6$ gave the best matching (FOM) in the triclinic system with unit cell parameters: a = 6.167(10) Å, b = 10.386(20) Å, c = 6.054(11) Å; α = 98.58(11)°, β = 108.56(11)°, γ = 97.27(13)^0, V = 357.22 Å^3.

$(NH_3OH)_2SiF_6 \cdot 2H_2O$ has also been identified by elemental analysis: 27.4% NH_3OH^+ (calc. 27.6%), 11.3% Si (calc. 11.4%) and 46.1% F^- (calc. 46.3%). The compound crystallizes monoclinic, *I 2/a*, with four formula units in the unit cell. The stereoscopic picture is shown in Fig. 1.

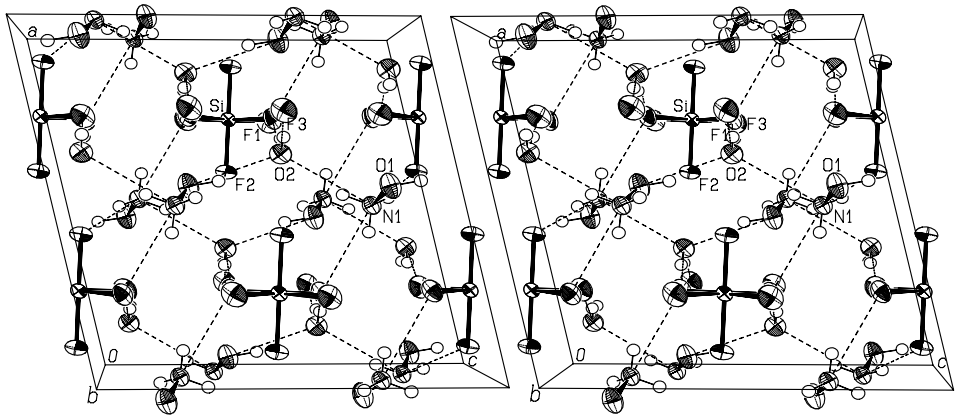

Figure 1. Stereoscopic picture of the $(NH_3OH)_2SiF_6 \cdot 2H_2O$ unit cell

The structure consists of isolated SiF_6^{2-} octahedra, which are connected with hydrogen bridges with NH_3OH^+ ions and H_2O molecules. The atomic coordinates and equivalent displacement parameters are given in Table 1, some selected bond lengths and angles can be found in Table 2.

Table 1. Fractional coordinates and Equivalent Displacement Parameters ($Å^2$) for $(NH_3OH)_2SiF_6 \cdot 2H_2O$. $^*U = U_{eq} = 1/3\ \Sigma_i \Sigma j U_{ij} a_i^* a_j^* a_i a_j$

	x/a	y/b	z/c	U_{eq}
Si	3/4	0.13605(4)	1/2	* 0.01463(9)
F(1)	0.74629(7)	-0.02392(9)	0.61412(7)	* 0.03432(19)
F(2)	0.59069(5)	0.13435(9)	0.45962(6)	* 0.02772(17)
F(3)	0.74587(6)	0.29835(8)	0.61299(6)	* 0.02769(16)
O(1)	0.54483(9)	0.84021(10)	0.84156(8)	* 0.03118(22)
O(2)	0.63563(7)	0.64076(10)	0.59620(7)	* 0.02724(19)
N(1)	0.49066(7)	0.67277(10)	0.79569(7)	* 0.02207(19)
H(1)	0.5210(21)	0.649(3)	0.7297(23)	0.036(4)
H(2)	0.4154(23)	0.683(3)	0.7713(22)	0.038(4)
H(3)	0.5122(23)	0.592(4)	0.8494(25)	0.043(5)
H(4)	0.5588(24)	0.831(4)	0.921(3)	0.047(5)
H(21)	0.6817(24)	0.553(4)	0.6101(24)	0.045(5)
H(22)	0.6812(25)	0.725(4)	0.6098(24)	0.047(5)

The bond lengths and angles for the SiF_6^{2-} octahedra are in good agreement with literature data[1, 3, 5] for similar fluorosilicates, where bond lengths from 1.668 Å to 1.688 Å and angles from 89.08° to 90.92° are reported. The O-N lengths are also in good agreement with values, reported in papers[8-12] for other fluorometallates of hydroxylammine.

The hydrogen bonds (N-H···F and O-H···F) in the structure of $(NH_3OH)_2SiF_6 \cdot 2H_2O$ (described in Table 3) are rather long, compared to most of the reported hydroxylammonium fluorometallates, where bond lengths N-H···F varied from 2.666 Å to 2.738 Å and the reported O-H···F lengths were in the range 2.503 Å – 2.661 Å. The only known hydroxylammonium fluorometallate with similar hydrogen bond lengths is the hexafluorotitanate-dihydrate,[10] $(NH_3OH)_2TiF_6 \cdot 2H_2O$, with N-H···F lengths 2.856 Å – 2.903 Å and O-H···F lengths 2.755 Å – 2.758 Å.

Table 2. Bond lengths (Å) and angles (°) of $(NH_3OH)_2SiF_6{\cdot}2H_2O$

Si - F(1)	1.6793(10)	N(1) - H(1)	0.840(25)
Si - F(2)	1.6793(9)	N(1) - H(2)	0.801(24)
Si - F(3)	1.6837(10)	N(1) - H(3)	0.817(25)
O(1) - N(1)	1.4006(14)	O(2) - H(21)	0.808(25)
O(1) - H(4)	0.82(3)	O(2) - H(22)	0.78(3)
F(1) - Si - F(2)	89.89(4)	H(4) - O(1) - N(1)	104.3(19)
F(1) - Si - F(3)	89.34(6)	H(1) - N(1) - O(1)	104.7(15)
F(2) - Si - F(3)	90.32(3)	H(2) - N(1) - O(1)	110.2(17)
		H(3) - N(1) - O(1)	111.4(17)
		H(21) - O(2) - H(22)	105(3)

Table 3. Hydrogen bond lengths (Å) and angles (°)

A-H···B	Distance A-H	Distance B-H	Distance A-B	Angle A-H···B	Symmetry operation of B
N(1)-H(1)···O(2)	0.840(25)	2.048(25)	2.8637(14)	163.5(20)	x, y, z
N(1)-H(2)···F(3)	0.801(24)	2.196(21)	2.9211(13)	150.7(23)	-½+x, 1-y, z
N(1)-H(3)···F(2)	0.817(25)	2.093(25)	2.8978(17)	168.0(25)	x, ½-y, ½+ z
O(1)-H(4)···O(2)	0.82(3)	1.855(25)	2.6387(13)	161(3)	x, 3/2-y, ½+z
O(2)-H(21)···F(3)	0.808(25)	1.99(3)	2.7683(21)	162(3)	x, y, z
O(2)-H(22)···F(1)	0.78(3)	1.97(3)	2.7228(21)	162(3)	x, 1+y, z

Thermal behavior of both compounds showed similar results. $(NH_3OH)_2SiF_6$ and $(NH_3OH)_2SiF_6{\cdot}2H_2O$ are thermally stable up to 70 °C. The decomposition of $(NH_3OH)_2SiF_6$ starts at 75 °C, becomes significant above 125 ^{0}C, reaches the peak temperature at 231.3 °C and is finished at 265 °C. In the case of $(NH_3OH)_2SiF_6{\cdot}2H_2O$, the corresponding temperatures are lower: decomposition starts at 70 °C, becomes faster at 120 °C, the peak temperature is 228.7 °C and the decomposition is finished at 260 °C.[13] The measured mass loss is 100% for both compounds. During the thermal analysis of $(NH_3OH)_2SiF_6{\cdot}2H_2O$, only one decomposition step could be observed. Even by lowering the heating rate down to 1K/min, no separated decomposition peaks could be observed. According to the results, only the total decomposition equation can be assumed:

$$(NH_3OH)_2SiF_6{\cdot}2H_2O \rightarrow 2NH_2OH + 2HF + SiF_4 + 2H_2O$$

The results show some significant differences, compared to the thermal decomposition of hydroxylammonium fluorometallates of side group 4.[8-10] Hydroxylammonium fluorosilicates decompose at lower temperatures than hydroxylammonium compounds of zirconium and hafnium, a fact, that can be explained with weaker hydrogen bonds (O-H ··· F and N-H ··· F) in silicone compounds. Hydroxylammine decomposes to NH_3 and N_2 at elevated temperatures and ammonium fluorometallates were always found as intermediates in the thermal decomposition of hydroxylammonium fluorotitanates, -zirconates and hafnates. In the case of hydroxylammonium fluorosilicates, the hydrogen bonds cleave at low temperatures

Table 4. Crystal data, data collection and refinement summary

$(NH_3OH)_2SiF_6 \cdot 2H_2O$	$Z = 4$
$M_r = 246.18$	$D_x = 2.026$ Mg m^{-3}
Monoclinic, *I 2/a*, No.: 15	Mo $K\alpha$ radiation
$a = 10.772(5)$ Å	Cell parameters from 25 reflections
$b = 7.336(6)$ Å	$\theta = 8.59\text{-}15.25°$
$c = 10.447(3)$ Å	$\mu = 0.3943$ mm^{-1}
$\beta = 102.09(3)°$	$T = 293(1)$ K
$V = 807.2(8)$ Å^3	Irregular form colorless
$F_{(000)} = 503.92$	0.46 x 0.57 x 0.84 mm
Enraf-Nonius CAD4 diffractometer	$R_{int} = 0.027$
$\omega\text{-}2\theta$ scan	θ range = 3.38 – 29.97°
No absorption correction	$h = -15 \rightarrow 15$
9515 measured reflections	$k = -10 \rightarrow 10$
2533 unique reflections	$l = -14 \rightarrow 14$
1127 reflections with $I > 2.5\sigma(I)$	
Refinement on F	Empirical weighting scheme
R (on F_{obs}) = 0.025	Zachariasen's extinct. coeff. =$3.8 \cdot 10^3$
wR (on F_{obs}) = 0.028	$(\Delta/\sigma)_{max} = 0.00068$
$S = 0.973$	$(\Delta/\sigma)_{ave} = 0.00011$
85 parameters	$\Delta\rho_{max} = 0.30$ eÅ^{-3}
H-atoms refined with isotropic displacement parameters	$\Delta\rho_{min} = -0.36$ eÅ^{-3}

(even below 80 °C), which are insufficient for disproportionation of hydroxylammine. Mass spectrometry of $(NH_3OH)_2SiF_6$ confirmed[13] the presence of NH_2OH as a decomposition product at 80 °C.

Conclusions

The use solid NH_3OHF as a source of hydroxylammine has led to sucessful synthesis of two hydroxylammonium compounds. The new compound with the formula $(NH_3OH)_2SiF_6$ has been characterized by elemental analysis, thermal analysis, mass spectra and X-ray powder diffraction.[13] The second compound, $(NH_3OH)_2SiF_6 \cdot 2H_2O$, mentioned in the early work by Ebler and Schott,[7] was prepared by a new method. Besides the characterization by elemental and thermal analysis, the structure has been determined by single crystal x-ray analysis. The compound crystallizes monoclinic with cell parameters: a = 10.772(5) Å, b = 7.336(6) Å, c = 10.447(3) Å, β = 102.09(3)°.

Experimental

Synthesis. In the first step, hydroxylammine was isolated in ethanolic solution by the reaction of solid hydroxylammonium chloride with sodium ethylate[14]. Crystals of NH_3OHF were obtained by adding 40% HF dropwise to the ethanolic solution at 0 °C.[15] Various amounts of NH_3OHF were dissolved in the H_2SiF_6 solution in a platinum beaker. Evaporation at room temperature yielded colourless crystals. The product with the formula $(NH_3OH)_2SiF_6$ was filtered, dried and characterized by chemical and thermal analysis and X-ray powder diffraction,[12] but the crystals were of poor quality and a determination of the structure was impossible. In an attempt to solve this problem, the product was dissolved again in 40% HF and recrystallized by slow evaporation of the solvent, introducing some crystals of the primary product as crystallization seeds. After some days, colourless crystals of $(NH_3OH)_2SiF_6 \cdot 2H_2O$ were obtained and characterized by chemical and thermal analysis, the structure was determined by single-crystal X-ray analysis.

Methods. Hydroxylammonium was determined by titration with $KMnO_4$[16] and fluorine by direct calibration with a combination fluoride electrode[17]. Silicon was

determined by gravimetric methods[7]. Thermal analysis (TG and DSC) was carried out for both compounds in a nitrogen stream with a heating rate of 10 K/min, using platinum (TG) and gold crucibles (DSC).

X-ray powder diffraction data was collected with an AXS-Bruker/Siemens/D5005 diffractometer using CuK_α radiation at 293(1) K. The samples were finely ground, placed on a silicone single-crystal holder and measured from 47 to 52 hours in the range $5^0 < 2\Theta < 65°$ with a step of 0.01° and a scanning speed of 1 s/step. The values for divergence and antiscattering slit were fixed at 0.2 mm. The measurements were corrected for the sample height and the $K_{\alpha 2}$ radiation was stripped off. The X- ray diffraction pattern was indexed with the help of the automatic indexing program TREOR[18] and ITO[19].

X-ray structure analysis. Diffraction data for $(NH_3OH)_2SiF_6{\cdot}2H_2O$ were collected on an Enraf Nonius CAD-4 diffractometer at room temperature with MoK_α radiation and graphite monochromator. The structure was solved by direct methods using SIR92 program.[20] A full-matrix least-squares refinement on F was employed with anisotropic displacement parameters for all non-hydrogen atoms and isotropic for hydrogen atoms, using the weighting function: $w = 9.5 \times W_f \times W_s$, where W_f ($|F_o| < 2.9$) = ($|F_o|/2.9$), W_f ($|F_o| > 19.0$) = $(19.0/|F_o|)^{1.5}$, W_f ($2.9 \leq |F_o| \leq 19.0$) = 1 and W_s ($\sin\theta < 0.6$) = $(\sin\theta/0.6)^3$, W_s ($\sin\theta > 0.7$) = $(0.7/\sin\theta)^4$, W_s ($0.6 \leq \sin\theta \leq 0.7$) = 1. Xtal 3.4 system[21] of programs was used for the correlation and reduction of data, structure refinement and interpretation.Graphics were produced using ORTEPII program[22]. Further details of crystal data, data collection and refinement can be found in Table 4. Detailed crystallographic data have been deposited with the Fachinformationszentrum Karlsruhe (FIZ), D-76344 Eggenstein-Leopoldshafen, with the deposition number CSD 412185.

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Povzetek

Z reakcijo med trdnim NH_3OHF in raztopino H_2SiF_6 smo sintetizirali novo spojino hidroksilamina s formulo $(NH_3OH)_2SiF_6$. Pri rekristalizaciji te spojine iz vodne raztopine HF smo izločili monokristale s sestavo $(NH_3OH)_2SiF_6{\cdot}2H_2O$. Obe spojini smo karakterizirali s kemijsko in termično analizo, strukturo $(NH_3OH)_2SiF_6{\cdot}2H_2O$ smo določili z rentgensko strukturno analiza na osnovi monokristala. Spojina kristalizira monoklinsko s parametri osnovne celice: a = 10.772(5) Å, b = 7.336(6) Å, c = 10.447(3) Å, β = 102.09(3)°.