



Synthesis, crystal structure, and properties of sodium heptafluorodiantimonate(III) hydrate ($\text{NaSb}_2\text{F}_7 \cdot \text{H}_2\text{O}$)

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ABSTRACT

A new compound $\text{NaSb}_2\text{F}_7 \cdot \text{H}_2\text{O}$ (I) has been synthesized from aqueous solutions of NaSCN and SbF_3 (components molar ratio 0.5:1) and investigated by means of the methods of chemical, X-ray structural, and thermal analysis and IR, $^{121,123}\text{Sb}$ NQR, and ^1H , ^{19}F NMR spectroscopy. The structure of I is composed of Na^+ cations, H_2O molecules, and asymmetric dimeric $[\text{Sb}_2\text{F}_7]^-$ complex anions. The anions are composed of two trigonal $[\text{SbEF}_4]$ bipyramids, in which E is a lone electron pair of antimony(III) atoms linked through the bridge fluorine atom. Complex anions in the structure are linked through secondary $\text{Sb} \cdots \text{F}$ bonds (2.628–3.344 Å), $\text{Na} \cdots \text{F}$ bonds (2.270–2.387 Å), and $\text{O} \cdots \text{H} \cdots \text{F}$ hydrogen bonds (2.727–2.837 Å) into a framework. In the temperature range 90–150 K, the compound I manifests piezoelectric properties in the radio-frequency field. The complex fluoride sublattice remains rigid in the temperature range 150–343 K in accordance with the ^{19}F NMR data. Upon recrystallization from water and heating in the temperature range 343–423 K, the substance under study decomposes with the formation of stable complexes $\text{NaSb}_3\text{F}_{10}$ and NaSbF_4 known from the literature.

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1. Introduction

The present work is devoted to the synthesis of a new complex sodium fluorodiantimonate(III), $\text{NaSb}_2\text{F}_7 \cdot \text{H}_2\text{O}$ (I), and studies of its crystal structure and physical–chemical properties by means of the methods of chemical, X-ray structural, and thermal analysis and IR, $^{121,123}\text{Sb}$ NQR (77–298 K), and ^1H , ^{19}F NMR (150–350 K) spectroscopy.

2. Results and discussion

2.1. Synthesis

Interaction of aqueous solutions of fluorides of alkali metals ($M = \text{Na}, \text{K}, \text{Rb}, \text{Cs}$) and ammonium with antimony trifluoride yields crystalline complex compounds of antimony(III), whose composition depends on the ratio of initial components and the nature of a cation [1]. The F:Sb ratio in complexes varies in the range 3.25–5. Four compounds were synthesized with the Na^+ cation and their crystal structures were determined: $\text{NaSb}_3\text{F}_{10}$ [2], $\text{Na}_3\text{Sb}_5\text{F}_{18}$ [3], NaSbF_4 [4], and Na_2SbF_5 [5]. It was also reported on the synthesis of

such complexes as $\text{NaSb}_4\text{F}_{13}$, NaSb_2F_7 , and $\text{Na}_3\text{Sb}_4\text{F}_{15}$ [6], but these data had not been corroborated by structural studies. Although the crystal structure of the compound $\text{NaSb}_2(\text{OH})\text{F}_6 \cdot \text{H}_2\text{O}$ obtained from the aqueous solution of NaSCN and SbF_3 was described in [7], the presence of a hydroxo group having the role of a bridge in the dimer raised some doubts. That is why more detailed studies of the components interaction in the system $\text{NaSCN} \text{--} \text{SbF}_3 \text{--} \text{H}_2\text{O}$ in the molar ratio range 0.25–1:1 were performed, and three compounds were obtained. At the molar ratio of initial substances 0.25:1, a fluoride complex $\text{NaSb}_3\text{F}_{10}$ of the known crystal structure [2] crystallizes from the solution. The increase of the $\text{NaSCN} : \text{SbF}_3$ ratio up to 0.5:1 results in the formation of colorless large crystals of the composition $\text{NaSb}_2\text{F}_7 \cdot \text{H}_2\text{O}$. From the solution containing sodium thiocyanate and antimony trifluoride at the equimolar ratio, one obtained a fine-crystal colorless antimony(III) compound of the composition $\text{Na}_2\text{Sb}_5\text{F}_9\text{O}_3(\text{NCS})_2$, whose structure is described in [8]. No other compounds of different compositions were revealed in the system $\text{NaSCN} \text{--} \text{SbF}_3 \text{--} \text{H}_2\text{O}$. Therefore, sodium heptafluorodiantimonate(III) could be synthesized, but, unlike the compounds MSb_2F_7 with other cations ($M = \text{K}, \text{Rb}, \text{Cs}, \text{NH}_4, \text{Tl}$), this complex is formed as a crystal hydrate from an aqueous solution containing, aside from SbF_3 , sodium thiocyanate rather than sodium fluoride. The compound I is unstable and, according to the X-ray phase analysis data, decomposes with the formation of more stable complexes $\text{NaSb}_3\text{F}_{10}$ [2] and NaSbF_4 [4].

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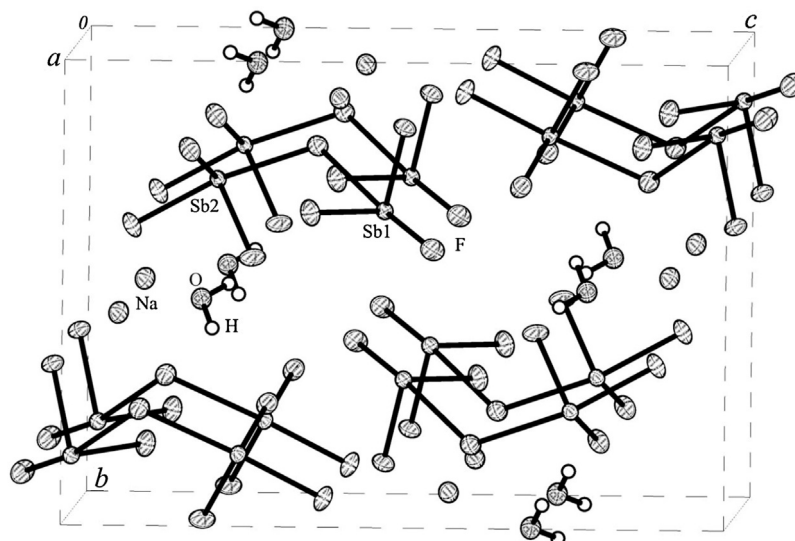


Fig. 1. Crystal structure of sodium heptafluorodiantimonate(III) hydrate ($\text{NaSb}_2\text{F}_7 \cdot \text{H}_2\text{O}$).

2.2. Crystal structure

The crystal structure of I (Fig. 1) was determined at reduced temperature (173 K) and large angle recording range ($\theta = 2.62\text{--}47.67^\circ$). The obtained number of independent reflections (6388) was far higher than earlier (1914) [7], whereas the *R*-factor became equal to 0.0211, as compared to 0.065 (Tables 1–3). The crystals of I have a monoclinic syngony: $a = 5.3590(1)$, $b = 9.5432(2)$, $c = 13.4775(3)$ Å, $\beta = 95.993(1)^\circ$, $Z = 4$, space group $P2_1/c$. The structure is composed of Na^+ cations, H_2O molecules, and asymmetric dimeric complex anions $[\text{Sb}_2\text{F}_7]^-$. The anions are formed from two trigonal bipyramids $[\text{SbEF}_4]$, in which E is a lone electron pair of antimony(III) atoms linked through the bridge fluorine atom (Fig. 2). Complex anions in the structure are linked through secondary $\text{Sb} \cdots \text{F}$ bonds (2.628–3.344 Å), $\text{Na} \cdots \text{F}$ bonds (2.270–2.387 Å), and $\text{O} \cdots \text{H} \cdots \text{F}$ hydrogen bonds (2.727–2.837 Å) into a framework. The bridge bond $\text{Sb} \cdots \text{F} \cdots \text{Sb}$ is asymmetric, while geometrical parameters of Sb(1) and Sb(2) atoms polyhedra are noticeably different. The crystal structure of I is similar to that of RbSb_2F_7 [9]: the latter contains two nonequivalent antimony

Table 1
Crystal data and structure refinement.

Empirical formula	$\text{H}_2\text{F}_7\text{NaOSb}_2$
Formula weight	417.51
Temperature (K)	173(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
<i>a</i> (Å)	5.3590(1)
<i>b</i> (Å)	9.5432(2)
<i>c</i> (Å)	13.4775(3)
β ($^\circ$)	95.993(1) $^\circ$
Volume (Å ³)	685.50(2)
<i>Z</i>	4
Density (calculated) (Mg/M ³)	4.045
Absorption coefficient (mm ⁻¹)	8.023
<i>F</i> (000)	744
Crystal size (mm)	0.25 × 0.25 × 0.25
θ range for data collection	2.62–47.67 $^\circ$
Reflections collected	22,281
Independent reflections	6388 [<i>R</i> (int) = 0.0295]
Data/restraints/parameters	6388/0/103
Goodness-of-fit on <i>F</i> ²	1.103
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	0.0211
<i>R</i> indices (all data)	0.0221

polyhedra SbEF_4 . The comparative analysis of the antimony polyhedra in MSb_2F_7 complexes are presented in Table 4. It shows that the both polyhedra in $\text{NaSb}_2\text{F}_7 \cdot \text{H}_2\text{O}$ structure is the most distorted.

Two H atoms of the water molecule forming three nonequivalent H-bonds were determined from the electronic density difference (Table 3). One of the bonds is stronger ($\text{OH}(1) \cdots \text{F}(6)$), whereas two others (with F(1) and F(5) atoms) are weaker and similar to each other. No electron density peaks, which can be assigned to the hydrogen atom, were present in the bridge atom surrounding. The replacement of the bridge F atom by the O atom results in the *R* increase from 0.0211 up to 0.0224. Therefore, the

Table 2
Selected bond lengths (Å) and angles ($^\circ$).

Sb(1)–F(1)	1.923(1)	Sb(2)–F(5)	1.931(1)
Sb(1)–F(2)	1.940(1)	Sb(2)–F(6)	1.968(1)
Sb(1)–F(3)	2.022(1)	Sb(2)–F(7)	1.986(1)
Sb(1)–F(4)	2.237(1)	Sb(2)–F(4)	2.323(1)
Sb(1)–F(3) ⁱ	2.715(1)	Sb(2)–O	2.628(1)
Sb(1)–F(6) ⁱⁱ	2.848(1)	Sb(2)–F(3) ⁱⁱⁱ	2.982(1)
Sb(1)–F(5)	3.118(1)	Sb(2)–F(1) ^{iv}	3.133(1)
Sb(1)–F(7) ⁱⁱ	3.344(1)	Sb(2)–F(5) ^v	3.325(1)
F(1)–F(2)	2.605(2)	F(4)–F(6)	2.740(2)
F(1)–F(3)	2.627(2)	F(4)–F(5)	2.630(2)
F(1)–F(4)	2.738(2)	F(5)–F(6)	2.716(2)
F(2)–F(3)	2.646(2)	F(6)–F(7)	2.538(2)
F(2)–F(4)	2.727(2)	F(5)–F(7)	2.629(2)
F(1)–Sb(1)–F(2)	84.83(5)	F(4)–Sb(2)–F(6)	78.90(4)
F(1)–Sb(1)–F(3)	83.43(5)	F(4)–Sb(2)–F(5)	75.75(4)
F(1)–Sb(1)–F(4)	81.92(5)	F(5)–Sb(2)–F(6)	88.32(5)
F(2)–Sb(1)–F(3)	83.80(5)	F(6)–Sb(2)–F(7)	79.87(5)
F(2)–Sb(1)–F(4)	81.19(4)	F(5)–Sb(2)–F(7)	84.32(5)
F(3)–Sb(1)–F(4)	159.86(5)	F(4)–Sb(2)–F(7)	151.14(4)

Symmetry codes: (i) $-x+2, -y+1, -z+1$; (ii) $x, -y+1/2, z+1/2$; (iii) $x-1, -y+1/2, z-1/2$; (iv) $x-1, y, z$; (v) $-x+1, y-1/2, -z+1/2$.

Table 3
Hydrogen bonding geometry (Å, $^\circ$).

D–H \cdots A	D–H	H \cdots A	D \cdots A	D–H \cdots A
O–H(1) \cdots F(6) ⁱ	0.76	2.00	2.727(2)	159
O–H(2) \cdots F(1) ⁱⁱ	0.74	2.22	2.819(2)	139
O–H(2) \cdots F(5) ⁱⁱ	0.74	2.24	2.837(2)	138

Symmetry codes: (i) $-x+1, y+1/2, -z+1/2$; (ii) $x-1, y, z$.

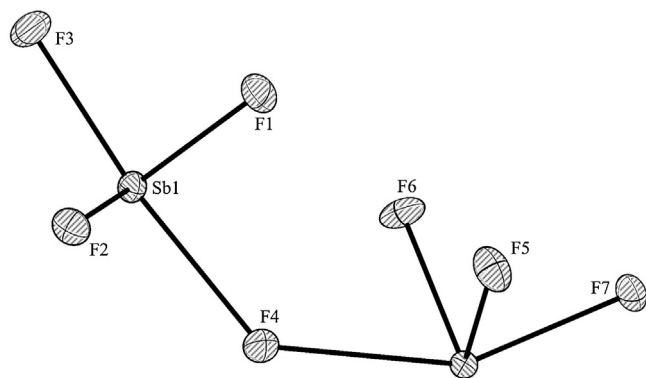


Fig. 2. Structure of the dimeric complex $[\text{Sb}_2\text{F}_7]$ in the structure of I.

dimeric complex anion has the composition $[\text{Sb}_2\text{F}_7]^-$ (Fig. 2) rather than $[\text{Sb}_2(\text{OH})\text{F}_6]^-$, as was reported earlier [7].

2.3. Thermogravimetry results

The thermal behavior of I was investigated in the temperature range 343–423 K: it was established that the compound decomposed in two stages. The first decomposition stage accompanied by a weight loss of 1.75% proceeds in the temperature range 343–388 K. The second stage proceeds in the temperature range 388–423 K with a weight loss of 2.25%. Total substance weight loss is equal to 4% that corresponds to the calculated water content in I. One should mention that at approximately the same weight losses

at both first and second stages the heat absorption at the first stage is significantly larger than at the second one (i.e., the weight loss does not correlate to the heat absorption). The latter must be concerned with the incongruent melting (melting with decomposition) of the compound I upon heating, since the substance residue after heating up to 150 °C is not a loose powder and has a milky shade. The final product of the $\text{NaSb}_2\text{F}_7 \cdot \text{H}_2\text{O}$ decomposition at 423 K is, according to the X-ray phase analysis data, a mixture of compounds ($\text{NaSb}_3\text{F}_{10}$ and NaSbF_4), just like upon recrystallization of I from water.

2.4. IR spectroscopy

The IR absorption spectrum of I is shown in Fig. 3a. A complicated system of bands in the range 400–575 cm^{-1} was assigned to valence vibrations of Sb–F bonds, just like in earlier studied complex fluoroantimonates(III) [12]. The most probably, the absorption bands at 642–709 cm^{-1} are related to libration vibrations of water molecules producing Sb–F...HO hydrogen bonds that correlates with the crystal structure (Fig. 1 and Table 2). The absorption bands at 3520 and 3420 cm^{-1} are related to valet vibrations and those at 1620 cm^{-1} to deformation vibrations of water molecules with inequivalent OH bonds (Table 3).

The IR spectra related to the products of the compound I decomposition upon heating up to 150 °C and recrystallization (Fig. 3b) do not contain water molecules vibrations and are characterized by the presence of absorption bands of main phases of NaSbF_4 and $\text{NaSb}_3\text{F}_{10}$ in accordance with the X-ray phase analysis data.

Table 4
Polyhedron type, bond lengths and valent angles in fluoride complex compounds MSb_2F_7 (M – Na, K, Rb, Cs) at 298 K.

Cation	Polyhedron type	Bond lengths (Å)		Valent angles (°)		References
		$F_{\text{акс}}$	$F_{\text{экр}}$	$F_{\text{акс}}\text{Sb} F_{\text{акс}}$	$F_{\text{экр}}\text{Sb} F_{\text{экр}}$	
$\text{Na}^+ (\times \text{H}_2\text{O})$	Sb(1)EF ₄	2.022; 2.237	1.923; 1.940	159.85	84.33	The present work
	Sb(2)EF ₄	1.986; 2.323	1.931; 1.968	151.14	78.90	
Rb^+	Sb(1)EF ₄	1.99; 2.33	1.93; 1.96	156.4	85.3	[9]
	Sb(2)EF ₄	2.03; 2.12	1.91; 1.93	156.1	85.1	
K^+	Sb(1)EF ₅	1.93	1.93; 1.96; 2.41; 2.57	75.3; 84.3; 88.4; 81.2	$(81.4; 82.3) \times 2$	[10]
	Sb(2)EF ₄	2.05; 2.08	1.91; 1.93	155.2	90.4	
Cs^+	SbEF ₄	1.98; 2.24	1.94×2	151.6	90.5	[11]

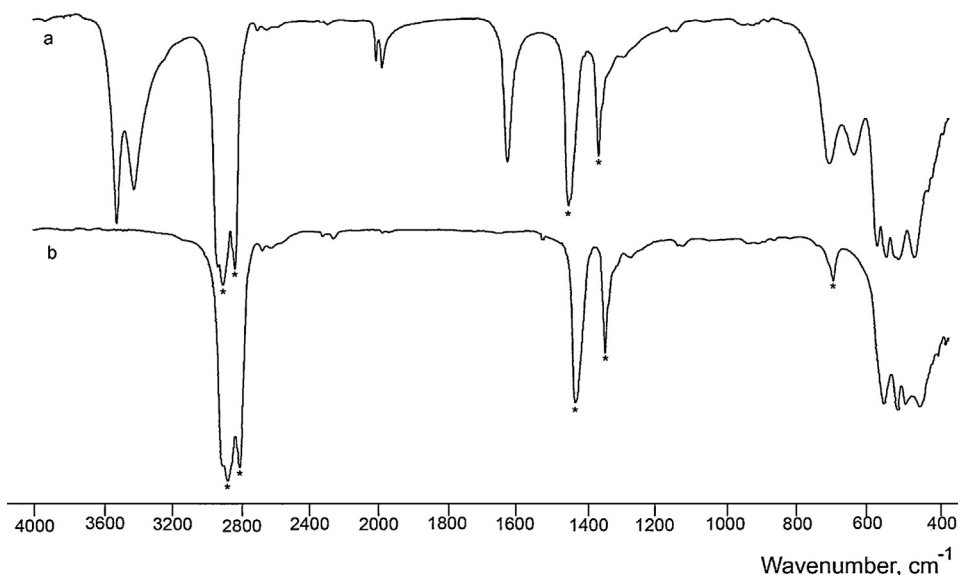


Fig. 3. IR absorption spectra of sodium heptafluorodiantimonate(III) hydrate: a – initial $\text{NaSb}_2\text{F}_7 \cdot \text{H}_2\text{O}$; b – sample after recrystallization.

2.5. NQR spectroscopy results

In the $^{121,123}\text{Sb}$ NQR spectrum of the compound I (Table 5) at 77 K we observed ten signals assigned to two nonequivalent positions of antimony atoms in the elementary unit, which is in agreement with the crystal structure. The assignment of NQR frequencies for sodium heptafluorodiantimonate(III), whose structure contains two different antimony polyhedra, was conducted using the correlation of the values of the parameter of asymmetry (η) of the electric field gradient to angle and structural distortions of antimony polyhedra (Table 2).

The doublet $^{121,123}\text{Sb}$ NQR spectra at 77 K are characteristic for most of the known heptafluorodiantimonates(III) with K^+ , Rb^+ , NH_4^+ , CN_3H_6^+ , CN_4H_7^+ , $[(\text{C}_2\text{H}_5)_2\text{NH}_2]^+$, $\text{C}_{10}\text{H}_9\text{N}_2^+$, and $\text{C}_2\text{N}_3\text{H}_4^+$ cations, except the compounds with Cs^+ (antimony atoms occupy equivalent positions in the elementary unit) and Ti^+ (six nonequivalent positions of antimony atoms) cations [1,13]. The values of the asymmetry parameter (η) of the electric field gradient of Sb atoms of the above group compounds are in the range 4.9–12.2% depending on the cation nature. The shifts in the quadrupole coupling constant (QCC, $e^2\text{Qq}/h$) of antimony atoms relatively to those in SbF_3 [1] are equal to 2.5–5.3% and have opposite signs: QCC of one antimony atom in MSb_2F_7 increases relatively to that of antimony atoms in SbF_3 that corresponds to the increase of the p_z -orbital occupancy, whereas for another antimony atom QCC decreases due to the increase of the p_x - and p_y -orbitals occupancies.

During the studies of the temperature dependence of the $^{121,123}\text{Sb}$ NQR spectrum of the compound I, one established the emergence of noises (on an oscilloscope upon feeding radio-frequency pulses) observed in the range 90–150 K characteristic for substances with piezoelectric properties. Possibly, the emergence of noises in the radio-frequency field is related to the presence of a second-order phase transition in I. The piezoelectric phase was also revealed earlier in CsSb_2F_7 in the temperature range 220–270 K [13]. Along with the complex I temperature increase, the intensity of $^{121,123}\text{Sb}$ NQR signals gradually decreases and, further, the signals are not registered above 240 K.

2.6. NMR spectroscopy results

The ^1H NMR spectra of the sample $\text{NaSb}_2\text{F}_7\cdot\text{H}_2\text{O}$ in the temperature range 200–300 K consist of a Pake doublet and a narrow band (Fig. 4). The component parameters were determined using the spectrum computer simulation. The Pake doublet splitting 2α was equal to 54 kHz, the parameter of isotropic broadening was $\beta = 20$ kHz, the narrow component had a Lorentz shape of a resonance line half-width of 1.3 kHz. The ratio between the doublet and the narrow component is 70:30 at 300 K. The parameters of the Pake doublet correspond to those of the resonance line of crystallization water molecules, whereas a significant isotropic line broadening is caused by dipole-dipole interactions with fluorine atoms. Registration of a narrow component in the ^1H NMR spectrum at 300 K (taking into account the XRD, IR, and ^{19}F NMR data) is, most probably, caused by the

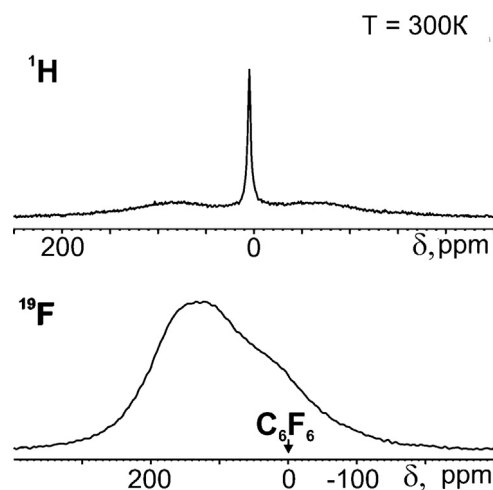


Fig. 4. ^1H , ^{19}F NMR spectra of sodium heptafluorodiantimonate(III) hydrate ($\text{NaSb}_2\text{F}_7\cdot\text{H}_2\text{O}$).

presence of high-mobility “free” water molecules in the sample: they are located in its crystal voids.

The ^{19}F NMR spectrum of the sample of $\text{NaSb}_2\text{F}_7\cdot\text{H}_2\text{O}$ in the temperature range 150–320 K consists of a broad line ($\Delta H \approx 60$ kHz – Fig. 4), whose asymmetry results from the structural nonequivalence of fluorine atoms in the crystal lattice and the chemical shift anisotropy. The line shape can be described by an axial-symmetrical tensor with the parameters $\sigma_{\parallel} \approx -40$ ppm and $\sigma_{\perp} \approx 200$ ppm. The chemical shifts (CS) of the ^{19}F NMR signal of the compound studied were measured relative to C_6F_6 standard because of CFCl_3 absence. The simple recalculation shows that the CS(C_6F_6) equals –167 ppm provided the CS(CFCl_3) is 0 and then 200 ppm tensor values equals $\rightarrow 33$ ppm and those of –40 ppm is –207 ppm. A significant line width and the observed shape of the sample ^{19}F NMR spectrum indicate to the absence of local motions with frequencies above 10^4 Hz in the fluoride sublattice below 330 K. Unlike earlier studied MSb_2F_7 ($\text{M} = \text{K}, \text{Rb}, \text{Cs}$) [13], in which the probability of the transition of fluorine containing groups in the temperature range 150–450 K from a rigid lattice to diffusion increases with the increase of the alkali cation, in the compound $\text{NaSb}_2\text{F}_7\cdot\text{H}_2\text{O}$ ionic motions in the fluoride sublattice are absent until the beginning of its decomposition at 343 K.

3. Experimental

3.1. Synthesis

The compound $\text{NaSb}_2\text{F}_7\cdot\text{H}_2\text{O}$ was obtained by interaction of NaSCN (chemical pure grade) and SbF_3 (chemical pure grade) in an aqueous solution at a molar component ratio of 0.5:1. A sample of antimony trifluoride was dissolved in distilled water in a platinum cup and added with pre-dissolved sodium thiocyanate. The obtained solution was evaporated down to 1/3 of the initial volume and left for slow crystallization at room temperature. The

Table 5
The parameters of the NQR spectrum $^{121,123}\text{Sb}$ at 77 K for $\text{NaSb}_2\text{F}_7\cdot\text{H}_2\text{O}$.

Atom	ΔR^a (Å)	The transition frequency (MHz)					η (%)	$e^2\text{Qq}/h$ (MHz)	
		^{121}Sb		^{123}Sb				^{121}Sb	^{123}Sb
		$1/2 \leftrightarrow 3/2$	$3/2 \leftrightarrow 5/2$	$1/2 \leftrightarrow 3/2$	$3/2 \leftrightarrow 5/2$	$5/2 \leftrightarrow 7/2$			
Sb_1	0.45	79.45	157.63	48.95	95.39	143.49	7.9	526.1	670.1
Sb_2	0.39	83.91	166.90	51.35	100.91	151.66	6.5	556.8	708.1

^a The value of ΔR – equal to the difference between the longest and shortest distance Sb–F in a polyhedron is defined according to Table 2.

formed crystals were separated from the stock solution by filtering on a water-jet pump, washed with acetone, and dried in air until a constant weight. The individuality of the obtained substance was established by the methods of chemical and X-ray phase analysis and IR spectroscopy in accordance with standard techniques. The determined values (wt.%): Sb – 58.2, F – 31.0, Na – 5.5; H₂O – 4.0. The calculated values for NaSb₂F₇·H₂O: Sb – 58.32; F – 31.85, Na – 5.51; H₂O – 4.31.

3.2. X-ray study

The X-ray images of the compounds under study were recorded on a Bruker D8 ADVANCE X-ray diffractometer in the Cu K α -radiation. Identification of the obtained X-ray images was performed using the EVA program with the PDF-2 powder database.

The X-ray image for the spherical single crystal of I was obtained at 173 K on a KAPPA APEX II CCD diffractometer (Mo K α -radiation, graphite monochromator). The data gathering was carried out through a combination of φ - and ω -scans from the hemisphere of the reciprocal space; the crystal-detector distance was equal to 45 mm. The X-rays absorption in the sample was taken into account from equivalent reflections. The structure was determined by a direct method and corrected using the least-square method in the anisotropic approximation of non-hydrogen atoms. Hydrogen atoms were reliably localized on the electron density difference and were not corrected.

Gathering and editing of the data and corrections of the elementary unit parameters were performed on the Apex II software pack [14]. All the calculations on the structure determination and correction were performed on the SHELXTL/PC programs [15]. The crystallography data and correction details are presented in Table 1, the main geometrical parameters are given in Tables 2 and 3. The CIF-file containing the complete information on the structure under study was deposited in the ICSD database 426002 and can be freely obtained on a request at the Internet-site: www.ccdc.cam.ac.uk/data_request/cif.

3.3. Thermogravimetry analysis

The differential thermal analysis of the compound NaSb₂F₇·H₂O was carried out in air on a Q-1000 MOM derivatograph (Hungary) at a sample heating rate of 5°/min. The sample weight was 200 mg. Annealed Al₂O₃ was used as a standard sample.

3.4. IR spectroscopy

The samples IR absorption spectra were recorded in the range 400–4000 cm⁻¹ using a Shimadzu FTIR Prestige-21 Fourier spectrometer (Japan) at room temperature. Prior to recording the samples were ground in an agate mortar until finely dispersed state and mixed with Vaseline oil until the formation of a suspension that was then deposited on a KBr substrate.

3.5. NQR spectroscopy

^{121,123}Sb NQR spectra of the compound I were obtained on an ISSH-1-13 pulse radio-spectrometer (Russia) with a temperature add-on in the temperature range 77–298 K. The temperature measurement accuracy was ± 0.3 K, the NQR frequency accuracy was ± 0.01 MHz. The values of the quadrupole coupling constant (QCC) e^2Qq/h and the asymmetry parameter (η) of the Sb atoms electric field gradient tensor were calculated from experimental NQR frequencies in accordance with [1,13]. The accuracies of QCC and η determination were equal to ± 0.1 MHz and $\leq \pm 0.1\%$, respectively.

3.6. NMR measurements

The ¹⁹F, ¹H NMR spectra of the solid NaSb₂F₇·H₂O were registered at a multinuclear digital Bruker AV-300 spectrometer at Larmor frequencies $\nu_L = 282.404$ MHz (for ¹⁹F nuclei) and $\nu_L = 300.13$ MHz (for ¹H nuclei) in the temperature range 150–350 K.

A sample of I was placed into a closed ampoule without air access. The accuracy of temperature maintenance was ± 2 K. The parameters of the axial-symmetrical tensor were determined on an original program using the formulas provided in [16]. The line width ΔH (at the semi-height – in kHz), chemical shifts δ (in ppm), and integral intensities of ¹⁹F and ¹H NMR spectra components were measured with a maximal error of 3%. The chemical shifts of ¹⁹F and ¹H NMR signals were measured relatively to the C₆F₆ standard (C₆F₆ chemical shift – 589 ppm relatively to gaseous F₂, $\delta(F_2) = 0$ ppm) and tetramethylsilane Si(CH₃)₄.

4. Conclusions

The complex compound NaSb₂F₇·H₂O was obtained from an aqueous solution containing NaSCN and SbF₃ at the components molar ratio 0.5:1, and its crystal structure has been determined. The structure is composed of Na⁺ cations, H₂O molecules, and asymmetric dimeric complex anions [Sb₂F₇]⁻. The anions are formed from two trigonal bipyramids [SbEF₄] with a free lone electron pair E, linked through the bridged fluorine atom.

Upon recrystallization from water and heating in the temperature range 343–423 K, the compound under study decomposes with the formation of more stable complexes NaSb₃F₁₀ and NaSbF₄, which was corroborated by the methods of X-ray phase analysis and IR spectroscopy.

Analysis of ^{121,123}Sb NQR spectra of the compound NaSb₂F₇·H₂O in the temperature range 77–240 K indicates to the presence of two types of antimony atoms in the [Sb₂F₇]⁻ anion and the absence of first-order phase transitions in the structure. Registration of piezoelectric noises in the radio-frequency field in the temperature range 90–150 K is caused by the existence of the piezoelectric phase, whose emergence is probably related to the second-order phase transition. According to the ¹H, ¹⁹F NMR data, there are no motions with frequencies above 10⁴ Hz in the fluoride sublattice of the compound NaSb₂F₇·H₂O in the studied temperature range 150–343 K.

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