

## Synthesis and Crystal Structure of New Sodium Oxothiocyanofluoroantimonate(III) $\text{Na}_2\text{Sb}_5\text{F}_9\text{O}_3(\text{NCS})_2$

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**Abstract**— $\text{Na}_2\text{Sb}_5\text{F}_9\text{O}_3(\text{NCS})_2$ , a new complex, has been synthesized from  $\text{NaSCN}$  and  $\text{SbF}_3$  aqueous solutions and studied by chemical, X-ray diffraction, and thermal analyses and IR,  $^{121,123}\text{Sb}$  NQR, and  $^{19}\text{F}$  NMR spectroscopy. Its layered structure (triclinic symmetry system,  $a = 6.9998(1)$  Å,  $b = 9.4180(1)$  Å,  $c = 13.1094(2)$  Å,  $\alpha = 74.815(1)^\circ$ ,  $\beta = 78.188(1)^\circ$ ,  $\gamma = 82.779(1)^\circ$ ,  $Z = 2$ , space group  $P1$ ) is built of  $\text{Na}^+$  cations and  $[\text{Sb}_{10}\text{F}_{18}\text{O}_6(\text{NCS})_4]^{4-}$  decanuclear complex anions that consist of two  $[\text{Sb}_5\text{F}_9\text{O}_3(\text{NCS})_2]^{2-}$  pentanuclear complex anions linked by two weak Sb–F ionic bonds (2.529(2) Å). Decanuclear complex anions are linked into layers by secondary Sb···F bonds and Na–F bonds. Van der Waals interactions link these layers into a framework. The complex is stable up to 200°C.

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Antimony(III) heteroligand complexes with alkali cations and diverse, in particular, oxofluoride complexes, are of interest due to the essential physicochemical properties (optical, electrical, electrochemical) discovered in some compounds of this class [1, 2]. Antimony(III) thiocyanofluoride complexes have been synthesized earlier on the basis of antimony fluoride by solid-phase synthesis [3, 4], but their compositions and structures have not been established. This study deals with the synthesis and characterization of  $\text{Na}_2\text{Sb}_5\text{F}_9\text{O}_3(\text{NCS})_2$ , a new mixed-ligand sodium oxothiocyanofluoroantimonate(III) complex.

### EXPERIMENTAL

**Synthesis and elemental analysis of complex I.** Antimony trifluoride and sodium thiocyanate (rhodanite) of pure grade served as initial reagents for the synthesis of complex I. Weighed portions of the initial reagents taken in the molar ratio 1 : 1 were separately dissolved in water ( $\text{SbF}_3$  was dissolved in a platinum cap under heating). The solution obtained by pouring them together was allowed to stand at room temperature, and a white precipitate settled from it in several minutes. The precipitate was separated from the mother solution by filtering under vacuum, washed with acetone, and dried in air to a constant weight. The identity of the synthesized complex was established by chemical, X-ray diffraction, and IR spectroscopic analyses. Since  $\text{SCN}^-$  ions hamper the direct titration of  $\text{Sb}^{3+}$  ions, the content of this element was determined as follows: a weighed portion of the complex was dissolved in water, thereupon an ammonia

solution was added until the complete precipitation of  $\text{Sb}^{3+}$ , and the precipitate was separated from the solution, washed on a vacuum filter with water, transferred into a flask, and dissolved in hydrochloric acid for bromatometric titration. The fluorine was determined by its distillation in the form of  $\text{H}_2\text{SiF}_6$  and subsequent titration with thorium nitrate, and the sodium was established by atomic absorption using standard techniques.

For  $\text{Na}_2\text{Sb}_5\text{F}_9\text{O}_3(\text{NCS})_2$  anal. calcd. (%): Sb, 61.50; F, 17.28; Na, 4.65.

Found (%): Sb, 59.6; F, 17.5; Na, 5.0.

**Thermal stability** of the complex was studied on a Paulik-Paulik-Erdey derivatograph in an air flow at a heating rate of 10 K/min. Alumina calcinated up to 1000°C was used as a reference.

**X-ray diffraction patterns** of the complex were taken on a Bruker D8 ADVANCE X-ray diffractometer in  $\text{CuK}_\alpha$  radiation. The obtained X-ray diffraction patterns were identified using the EVA software with the PDF-2 powder database.

**X-ray diffraction analysis** was performed on a KAPPA APEXII CCD diffractometer ( $\text{MoK}_\alpha$  radiation, graphite monochromator) at 173 K. Colorless transparent crystals of complex I are shaped as thin plates. The collection of data was performed using the combination of  $\varphi$ - and  $\omega$  scans over a hemisphere in reciprocal space at a crystal–detector distance of 45 mm. The absorption of X-rays in a sample was taken into account via equivalent reflection intensities. The structure was solved by direct methods and refined by least-squares in the anisotropic approxima-

tion. The collection and edition of data and the refinement of unit cell parameters were performed by the Apex2 software [5]. All structure solution and refinement calculations were performed by the SHELXTL/PC software [6]. Crystallographic data and refinement details are given in the table. The CIF file containing full information on the studied structure was deposited with the Inorganic Crystal Structure Database (ICSD) (no. 424972), from which it can easily be downloaded by request from the website [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

**IR absorption spectra** were recorded in the region of 400–4000  $\text{cm}^{-1}$  using a Shimadzu FTIR Prestige-21 Fourier-transform infrared spectrophotometer.

$^{121,123}\text{Sb}$  **NQR spectra** were taken on an ISSh-1-13 pulsed radiospectrometer at 77 K.

$^{19}\text{F}$  **NMR spectra** were recorded on a Bruker AV-300 multinuclear digital spectrometer within a temperature range of 300–460 K. The temperature adjustment accuracy was  $\pm 2$  K. The root-mean-square width (second moments  $S_2$ ) of NMR spectra (in  $\text{Gs}^2$ ) was calculated by the original software using the formulas [7]. The calculation error for  $S_2$  did not exceed 10%. The full width at half maximum  $\Delta H$  (kHz), the chemical shift (CS,  $\delta$ , ppm), and the integral intensity of  $^{19}\text{F}$  NMR spectrum components were measured with an accuracy of up to 3%. The chemical shift of a  $^{19}\text{F}$  NMR signal was determined with respect to the  $\text{C}_6\text{F}_6$  reference sample.

## RESULTS AND DISCUSSION

The reaction between  $\text{NaSCN}$  and  $\text{SbF}_3$  aqueous solutions is accompanied by the formation of three antimony(III) complexes, whose compositions depend on the ratio of the initial reagents. The  $\text{NaSbF}_{10}$  fluoride complex, whose crystal structure is known, crystallizes from a solution at a molar ratio of 0.25 : 1 [8]. An increase in the  $\text{NaSCN} : \text{SbF}_3$  ratio up to 0.5 : 1 leads to the formation of colorless coarse crystals, whose composition corresponds to the formula  $\text{NaSb}_2\text{F}_6(\text{OH}) \cdot \text{H}_2\text{O}$  [9] (however, the recently performed refinement of its crystal structure showed that this complex has the composition  $\text{NaSb}_2\text{F}_7 \cdot \text{H}_2\text{O}$ ). The fine-crystalline colorless antimony(III) oxothiocyanofluoride complex, whose composition was determined as  $\text{NaSb}_2\text{F}_4\text{O}(\text{SCN})$  from elemental analysis [10], settles from an equimolar solution of sodium thiocyanate and antimony trifluoride. The single crystals synthesized in our work made it possible to revise the composition of this complex, whose formula is  $\text{Na}_2\text{Sb}_5\text{F}_9\text{O}_3(\text{NCS})_2$  (**I**). No complexes of other compositions have been found in the  $\text{NaSCN}-\text{SbF}_3-\text{H}_2\text{O}$  system.

As-synthesized complex **I** is stable within a range from room temperature to 200°C. An increase in temperature to 250°C induces the decomposition of this complex with a weight loss of 4.4%. According to X-ray diffraction data, solid decomposition products

Crystallographic data, parameters of X-ray diffraction experiments, and refinement details for the structure of  $\text{Na}_2\text{Sb}_5\text{F}_9\text{O}_3(\text{NCS})_2$

Parameter	Value
Empirical formula	$\text{C}_2\text{F}_9\text{N}_2\text{Na}_2\text{O}_3\text{S}_2\text{Sb}_5$
FW	989.89
$T$ , K	173(2)
Radiation ( $\lambda$ , Å)	$\text{MoK}_\alpha$ (0.71073 Å)
Symmetry system	Triclinic
Space group	$P\bar{1}$
$a$ , Å	6.9998(1)
$b$ , Å	9.4180(1)
$c$ , Å	13.1094(2)
$\alpha$ , deg	74.815(1)
$\beta$ , deg	78.188(1)
$\gamma$ , deg	82.779(1)
$V$ , Å <sup>3</sup>	814.01(2)
$Z$	2
$\rho_{\text{calcd}}$ , g/cm <sup>3</sup>	4.039
$\mu$ , mm <sup>-1</sup>	8.604
$F(000)$	880
Crystal size (mm)	$0.08 \times 0.08 \times 0.03$
$\theta$ scan range, deg	1.64–31.33
Reflection index ranges	$-10 \leq h \leq 10$ , $-13 \leq k \leq 13$ , $-19 \leq l \leq 18$
Measured reflections	19476
Independent reflections	5330 ( $R_{\text{int}} = 0.0314$ )
Reflections with $I > 2\sigma(I)$	4517
Refinement variables	227
$R$ factors for $I > 2\sigma(I)$	$R_1 = 0.0215$ , $wR_2 = 0.0421$
$R$ factors for all reflections	$R_1 = 0.0311$ , $wR_2 = 0.0445$
GOOF	0.950
Residual electron density (min/max), e/Å <sup>3</sup>	-0.994/1.309

contain antimony(III) sulfide  $\text{Sb}_2\text{S}_3$ . Being further heated in air,  $\text{Sb}_2\text{S}_3$  slowly oxidizes to  $\text{Sb}_2\text{O}_3$ , thus causing additional gradual weight loss of 8.5% at 300°C. The final decomposition products at temperatures above 600°C have not been identified.

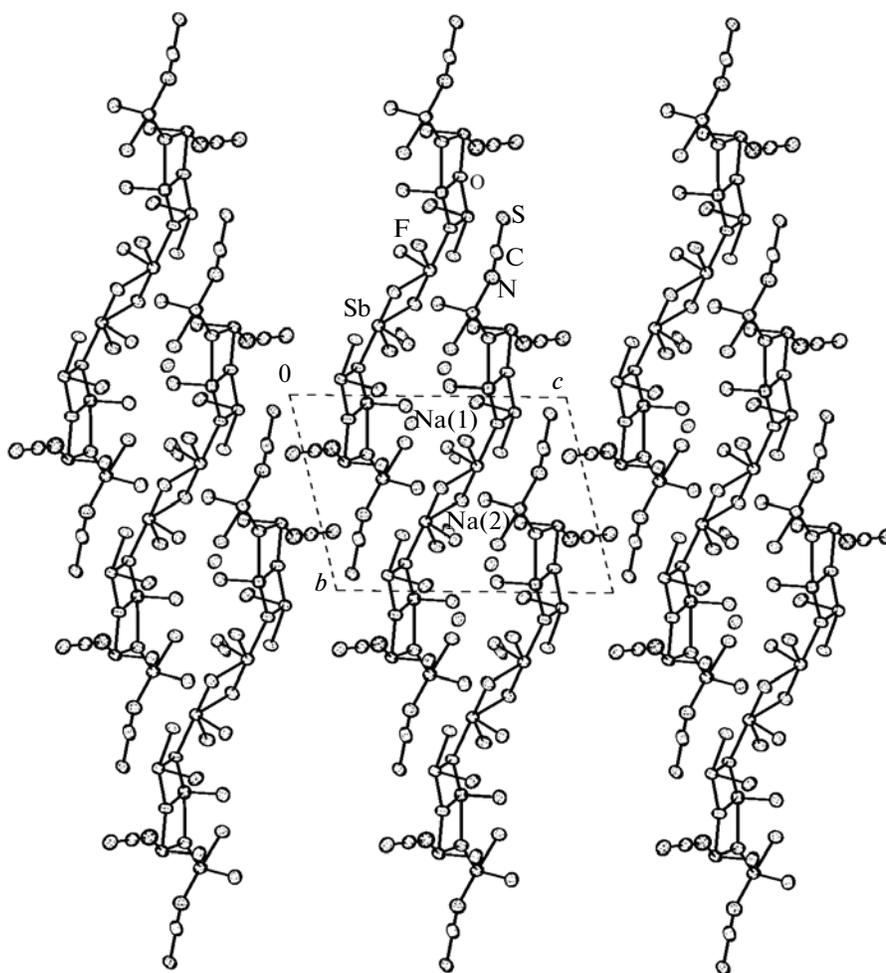


Fig. 1. Projection of the crystal structure of complex I along the  $a$  axis.

The crystal structure of complex I (Fig. 1) is built of  $[\text{Sb}_{10}\text{F}_{18}\text{O}_6(\text{NCS})_4]^{4-}$  discrete decanuclear complex anions and  $\text{Na}^+$  cations. Sb–F secondary bonds (2.747(2)–2.989(2) Å) and Na–F ionic bonds (2.24–2.50 Å) link anions in the structure into layers parallel to the (0 1 9) plane. The layers are linked into a framework only by van der Waals Sb–S interactions (3.507 and 3.641 Å).

In its turn, the  $[\text{Sb}_{10}\text{F}_{18}\text{O}_6(\text{NCS})_4]^{4-}$  symmetric complex anion (Fig. 2) consists of two  $[\text{Sb}_5\text{F}_9\text{O}_3(\text{NCS})_2]^{2-}$  pentanuclear complex anions linked by two weak Sb–F ionic bonds (2.529(2) Å). The  $[\text{Sb}_5\text{F}_9\text{O}_3(\text{NCS})_2]^{2-}$  anion is built of four  $\text{SbEX}_4$   $\psi$ -trigonal bipyramids (E is the lone pair), such as Sb(2)EO<sub>2</sub>F<sub>2</sub>, Sb(3)EO<sub>3</sub>F, Sb(4)EO<sub>2</sub>FN, and Sb(5)EOF<sub>2</sub>N, and one Sb(1)EOF<sub>4</sub>  $\psi$ -tetragonal bipyramid. All the oxygen atoms in this complex, as well as the oxygen atoms in the structure of  $\alpha$ -Sb<sub>3</sub>O<sub>2</sub>F<sub>5</sub> and  $\beta$ -Sb<sub>3</sub>O<sub>2</sub>F<sub>5</sub> [11], are triple bridges and represent both equatorial and axial vertices in polyhedra. The fluorine atoms are terminal except for the F(3) atom.

The two NCS thiocyanate groups in the structure are terminal in  $\text{SbEX}_4$  polyhedra and have nearly linear configurations (176° and 179°). The C–N bonds (1.166(5) and 1.170(4) Å) and C–S bonds (1.624(3) and 1.638(4) Å) are double.

The IR absorption spectra of NaSCN and complex I are shown in Fig. 3. In contrast to the IR spectrum of sodium thiocyanate [12], the C–N bond absorption band is split into two components in the region of 2000–2100  $\text{cm}^{-1}$ , thus indicating the formation of coordination bonds between SCN groups and antimony atoms. The bands in the region of 400–650  $\text{cm}^{-1}$  belong to the stretching vibrations of Sb–F bonds (by analogy with the earlier studied antimony(III) fluoride complexes in, e.g., [13]), the vibrations of Sb–O–Sb bonds [14], and the bending vibrations of the C–S bonds of NCS groups [12].

The  $^{121,123}\text{Sb}$  NQR spectrum of complex I at 77 K has been found to contain eight weak intensity signals with maxima at 76.35, 78.33, 80.18, 83.46, 85.19, 85.66, 98.98, and 103.27 MHz. The first five signals are likely to belong to the  $\pm(1/2 \leftrightarrow 3/2)$  transition

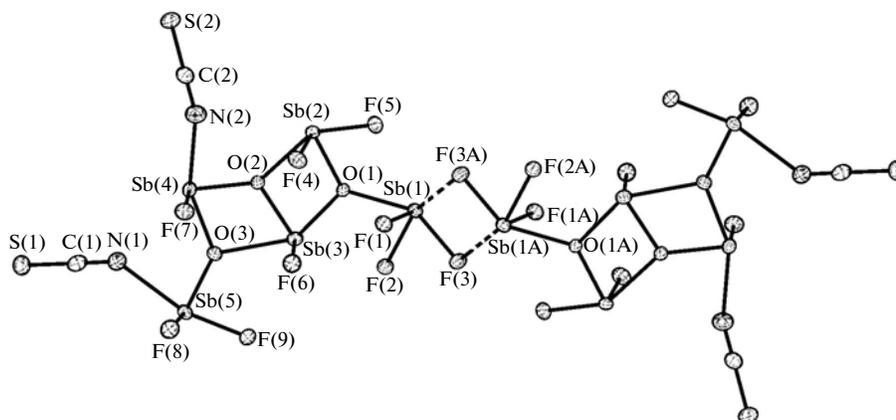


Fig. 2. Structure of  $[\text{Sb}_{10}\text{F}_{18}\text{O}_6(\text{NCS})_4]^{4-}$  decanuclear anion.

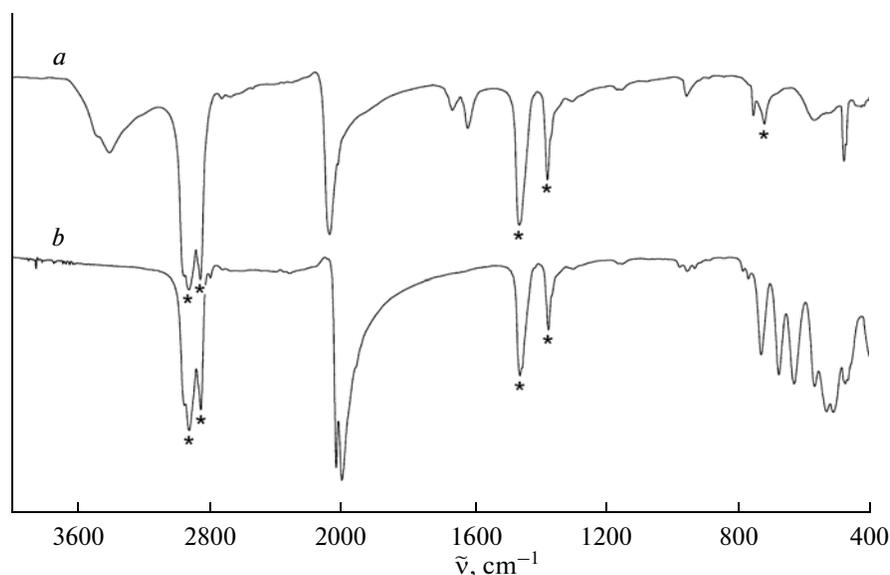


Fig. 3. IR spectra of (a) sodium thiocyanate and (b) complex I.

of five nonequivalent  $^{121}\text{Sb}$  atoms according to the solved structure of the complex, and the other signals are produced by the  $\pm(3/2 \leftrightarrow 5/2)$  transition of  $^{123}\text{Sb}$  atoms similarly to the NQR spectra of the antimony(III) fluoride complexes with monovalent cations [15]. However, the found frequencies do not allow us to determine the quadrupole coupling constants and asymmetry parameters for the antimony atoms in this complex.

The  $^{19}\text{F}$  NMR spectrum of the  $\text{Na}_2\text{Sb}_5\text{F}_9\text{O}_3(\text{NCS})_2$  complex in the temperature region of 250–340 K consists of an asymmetric structureless line with a width of  $\approx 40$  kHz (Fig. 4) and a second moment of  $\approx 35$   $\text{Gs}^2$ . According to X-ray diffraction data, the observed asymmetry of the spectrum may be related to the presence of different fluoride ions in the lattice and the anisotropy of chemical shifts. The recorded param-

eters of the NMR spectrum at these temperatures indicate the absence of any ion motions with frequencies above  $10^4$  Hz in the fluorine sublattice (a “rigid” lattice in the NMR terms [16]). An increase in temperature up to 350 K leads to the transformation of the NMR spectrum with its partial narrowing and the appearance of a new “narrow” component with  $\text{CS} \approx 98$  ppm. In the absence of phase transitions, similar transformations of  $^{19}\text{F}$  NMR spectra are generally produced by local ion motions with frequencies above  $10^4$  Hz in the fluoride sublattice [16]. The number of highly mobile fluoride ions, which the narrow component in the  $^{19}\text{F}$  NMR spectrum corresponds to, increases with increasing temperature, and the observed character of the NMR spectrum remains unchanged up to 460 K (Fig. 4). From the ratio of integral intensities of the NMR spectrum components, it follows that the num-

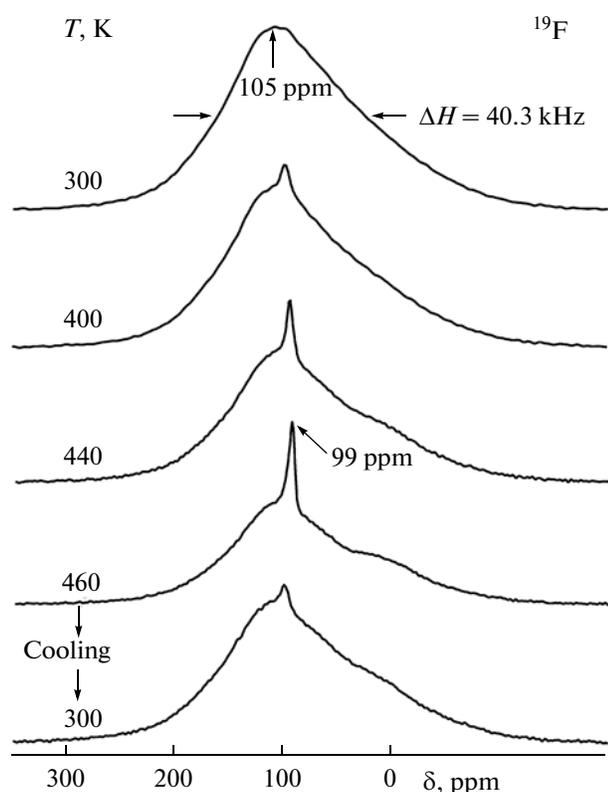


Fig. 4. Transformation of the  $^{19}\text{F}$  NMR spectra of complex I with temperature.

ber of highly mobile fluoride ions at this temperature is  $\approx 10\%$ . Taking into account the width ( $\Delta H \approx 2$  kHz) and second moment ( $S_2 \leq 0.1$  Gs $^2$ ) of the narrow component, it may be suggested that this line corresponds to local motions in the lattice of the studied complex, namely, the diffusion of fluoride ions [16]. This suggestion may also be confirmed by the chemical shift of the narrow component, which is typical for, e.g., the line that is present in the  $^{19}\text{F}$  NMR spectra of  $\text{K}_{1-x}\text{Cs}_x\text{SbF}_4$  ( $0 \leq x \leq 0.5$ ) complexes ( $0 \leq x \leq 0.5$ ) and belongs to fluoride ions participating in diffusion [17]. From the ratio of integral intensities of the components in the NMR spectrum (Fig. 4) it can be seen that a rigid lattice dominates at high temperatures and, consequently, this complex should not be expected to have high ionic conductivity. The  $^{19}\text{F}$  NMR spectrum cannot completely restore after the cooling of complex I (Fig. 4), thus seemingly indicating that this complex begins to decompose.

In summary, sodium oxothiocyanoantimonate(III)  $\text{Na}_2\text{Sb}_3\text{F}_9\text{O}_3(\text{NCS})_2$ , a new mixed ligand

complex, has been synthesized from aqueous solutions of the initial reagents (sodium thiocyanate and antimony trifluoride). Its crystal structure containing five non-equivalent antimony(III) polyhedra linked into the  $[\text{Sb}_{10}\text{F}_{18}\text{O}_6(\text{NCS})_4]^{4-}$  decanuclear complex anion has been solved. The IR absorption spectra of this complex in the region of  $400\text{--}4000$   $\text{cm}^{-1}$ , the spectrum of  $^{121,123}\text{Sb}$  NQR frequencies at 77 K, and the  $^{19}\text{F}$  NMR spectra in the temperature region of  $250\text{--}460$  K have been considered. It has been established that the crystal lattice of the complex is stable within a temperature range of  $250\text{--}473$  K ( $23\text{--}200^\circ\text{C}$ ), and there are no ion motions with frequencies above  $10^4$  Hz.

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