



# Synthesis, crystal structure and ion mobility in the complex fluorides of antimony (III) with the lithium cation



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## ABSTRACT

Two compounds  $\text{LiSb}_2\text{F}_7$  (I) and  $\text{LiSbF}_4$  (II) were synthesized from aqueous solutions of  $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$  and  $\text{Sb}_2\text{O}_3$  in the presence of HF and studied by the X-ray diffraction, IR and  $^7\text{Li}$ ,  $^{19}\text{F}$  NMR spectroscopy. The first obtained lithium heptafluorodiantimonate(III)  $\text{LiSb}_2\text{F}_7$  belongs to the orthorhombic system, the space group Pnma. The unit cell contains four formula units consisting of  $\text{Sb}_2\text{F}_7$  groups. The structure is formed by  $\text{Li}^+$  cations and dimeric  $[\text{Sb}_2\text{F}_7]^-$  complex anions.

The crystal structure of lithium tetrafluorodiantimonate(III)  $\text{LiSbF}_4$  is a new structural type in the group of tetrafluoroantimonates(III) with alkali metal cations. The main structural units of  $\text{LiSbF}_4$  are  $\text{SbF}_3\text{E}$  groups linked through the bridge fluorine atoms into a three-dimensional framework and the cations  $\text{Li}^+$ . The compound crystal belongs to the cubic system, space group  $\text{P}2_13$ , and contains three formula units per the unit cell. It was found that in the temperature range 150–420 K in the compound II structure there is a lithium cation transition from a rigid lattice to diffusion, while in the fluoride subsystem there are no ion motions with frequencies above  $10^4$  Hz in the entire temperature range (150–450 K).

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## 1. Introduction

There are not many published data concerning the fluoride complex compounds of antimony(III) with lithium cation, contrary to fluorodiantimonate(III) with cations of other alkali metals [1]. Thus, by the solid-phase interaction of  $\text{LiF}$  and  $\text{SbF}_3$  the compound  $\text{Li}_3\text{Sb}_2\text{F}_9$  was obtained [2], and from the aqueous solutions– $\text{LiSbF}_4$ , having piezoelectric properties [3], which structures were not defined. The lithium fluoride is poorly soluble in water, so, as a rule, from the system  $\text{LiF}-\text{SbF}_3-\text{H}_2\text{O}$  one obtains a crystalline product of hydrolysis of antimony trifluoride  $\text{Sb}_3\text{O}_2\text{F}_5$ , which structure is described in [4].

In this work the interaction of  $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$  and  $\text{Sb}_2\text{O}_3$  was studied at various molar ratios in the system  $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}-\text{Sb}_2\text{O}_3-\text{HF}-\text{H}_2\text{O}$ . Two crystalline compounds of antimony(III)  $\text{LiSb}_2\text{F}_7$  and  $\text{LiSbF}_4$  were obtained, the structure and physical chemical properties were studied by the X-ray diffraction, IR and  $^7\text{Li}$ ,  $^{19}\text{F}$  NMR spectroscopy.

## 2. Results and discussion

### 2.1. Crystal structure of $\text{LiSb}_2\text{F}_7$

The first synthesized lithium heptafluorodiantimonate(III)  $\text{LiSb}_2\text{F}_7$  belongs to the orthorhombic system, the space group Pnma. The unit cell of the compound contains four formula units consisting of  $\text{Sb}_2\text{F}_7$  groups. The structure is formed by  $\text{Li}^+$  cations and dimeric  $[\text{Sb}_2\text{F}_7]^-$  complex anions (Fig. 1). The symmetrical dimeric  $[\text{Sb}_2\text{F}_7]^-$  complex anion (Fig. 2) is built from two trigonal  $[\text{SbEF}_4]$  bipyramids (the antimony atoms occupy equivalent positions) linked by the common axial vertex – the bridging atom F(4).

Two fluorine atoms F(1), F(2) and a lone pair of 5s-electrons of antimony E are located in the equatorial plane of the bipyramid. Fluorine atoms forming the trigonal  $[\text{SbEF}_4]$  bipyramid are located at a short distance from Sb atom (1.925–2.315 Å) and form its first coordination sphere (Table 1), according to [5]. Three more fluorine atoms of the neighboring dimers (Sb–F 2.723, 2.773, and 3.069 Å) are located in the second coordination sphere within a sum of the van der Waals radii (3.55 Å). Due to these additional weak bonds  $\text{Sb}\cdots\text{F}$  and ionic bonds  $\text{Li}-\text{F}$  the dimers are linked into a three-dimensional framework in the structure. The complex  $\text{CsSb}_2\text{F}_7$  has a similar structure. The coordination polyhedron of  $\text{Li}^+$  cation in I is

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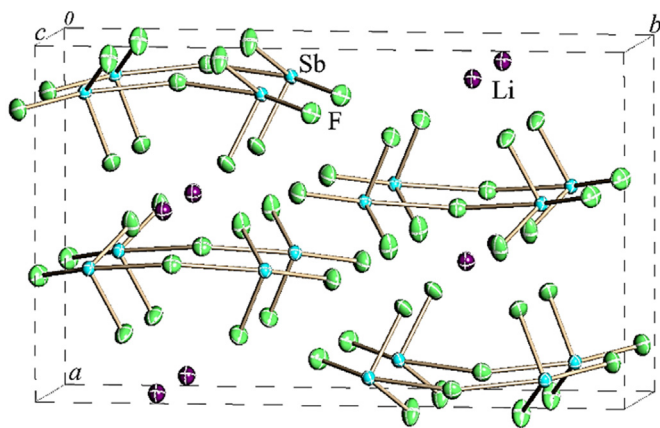


Fig. 1. Crystal structure of  $\text{LiSb}_2\text{F}_7$ .

a tetragonal  $\text{LiF}_5$  pyramid ( $\text{Li}-\text{F}$ ,  $2 \times 1.928(4)$ ,  $2 \times 1.987(4)$  and  $1.948(6)$  Å).

The present work has completed the structure definition in a series of  $\text{MSb}_2\text{F}_7$  compounds where  $M = \text{Li}$ ,  $\text{Na}$  [6],  $\text{K}$  [7],  $\text{Rb}$  [8],  $\text{Cs}$  [9]. In  $\text{KSb}_2\text{F}_7$  structure the coordination  $\text{SbF}_4\text{E}$ ,  $\text{SbF}_5\text{E}$  polyhedra of antimony atoms form polymer chains through two common vertices ( $\text{Sb}-\text{F}$ , 2.41 and 2.57 Å). Table 1 shows for comparison the structural parameters of  $\text{Sb}_2\text{F}_7$  groups in the compounds  $\text{MSb}_2\text{F}_7$  ( $M = \text{Li}$ ,  $\text{Na}$ ,  $\text{Rb}$ ,  $\text{Cs}$ ) in which  $\text{Sb}$  polyhedra are similar to those in I.

## 2.2. Crystal structure of $\text{LiSbF}_4$

The crystals of  $\text{LiSbF}_4$  belong to the cubic system, the space group  $\text{P2}_13$  and contain three formula units per the unit cell. All antimony atoms in the cell are equivalent as in the complexes  $\text{MSbF}_4$  ( $M = \text{Na}$ ,  $\text{Rb}$ ) [10,11]. The main structural units of  $\text{LiSbF}_4$  are  $\text{SbF}_3\text{E}$  groups linked through the triple fluorine bridges into the three-dimensional framework and  $\text{Li}^+$  cations (Fig. 3). The antimony atom environment in the complex compound II (Fig. 4) includes three fluorine atoms of  $\text{SbF}_3$  groups at distances  $\text{Sb}-\text{F}$   $1.954(1) \times 3$  (Table 2) which differ slightly from the bond lengths  $\text{Sb}-\text{F}$  in the crystal structure  $\text{SbF}_3$  ( $\text{Sb}-\text{F}$  1.900(2), 1.900(2), and 1.937(2) Å [12]). The angles  $\text{F}-\text{Sb}-\text{F}$  are also similar to those in lithium tetrafluoroantimonate(III) (Table 2) and in  $\text{SbF}_3$  structure.

Besides three atoms  $\text{F}(1)$ , located at short distances, the coordination of  $\text{Sb}$  atom includes more three fluorine atoms  $\text{F}(2)$  with the bond  $\text{Sb}-\text{F}$  lengths of 2.574 Å, which complement the antimony coordination up to a distorted octahedron  $[\text{SbF}_6]$  (Fig. 4).

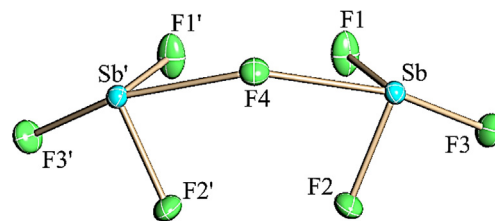


Fig. 2. Structure of the dimeric  $[\text{Sb}_2\text{F}_7]^{2-}$  complex anion in the structure of  $\text{LiSb}_2\text{F}_7$ .

The symmetrical fluorine bridges  $\text{F}(2)$  are triple bridges, and they link the nearest  $\text{SbF}_3$  groups into trimers – the anion  $[\text{Sb}_3\text{F}_{12}]^{3-}$  complexes with distances  $\text{Sb}\cdots\text{Sb}$  of 4.265 Å (Fig. 5).

The trimers are linked together through the triple bridging atoms  $\text{F}(2)$  into the anion  $[\text{SbF}_4]_n^{n-}$  framework (Fig. 3).  $\text{Li}^+$  cations are located within the framework, and they link additionally  $\text{SbF}_3$  groups with each other. The coordination polyhedron of lithium atom is a regular  $\text{LiF}_4$  tetrahedron (Table 2).

The crystal structure II is a new structure type in the group of tetrafluoroantimonates(III) with alkali metal cations  $\text{MSbF}_4$  ( $M = \text{Li}$ ,  $\text{Na}$ ,  $\text{K}$ ,  $\text{Rb}$ ,  $\text{Cs}$ ). In  $\text{NaSbF}_4$  structure [10] the coordination polyhedra of antimony(III) within the first coordination sphere are trigonal  $\text{SbEF}_4$  pyramids which are linked into the polymer layers through the secondary  $\text{Sb}\cdots\text{F}$  bonds (2.66(1) and 2.864(8) Å).  $\text{KSbF}_4$  structure [13] consists of antimony coordination polyhedra which are tetragonal  $\text{SbF}_5\text{E}$  pyramids linked into  $[\text{Sb}_4\text{F}_{16}]^{4-}$  tetramer through the fluorine bridge bonds (2.21(1) Å). The tetramers are joined into columns by the secondary  $\text{Sb}\cdots\text{F}$  bonds (2.94(1) and 2.99(2) Å). In  $\text{RbSbF}_4$  structure [11] the antimony(III) coordination polyhedra are tetragonal  $\text{SbEF}_5$  pyramids linked into the polymer chain through the fluorine bridge bonds (2.249 Å). The chains are linked together in layers through the secondary  $\text{Sb}\cdots\text{F}$  bonds (3.146 Å).  $\text{CsSbF}_4$  structure [14] is built from the antimony(III) coordination polyhedra which are tetragonal  $\text{Sb}(1)\text{F}_5\text{E}$ ,  $\text{Sb}(2)\text{F}_5\text{E}$  pyramids linked through the fluorine bridge bonds (2.24(2) and 2.29(2) Å) into the infinite polymer chains.

## 2.3. IR spectroscopy

IR spectra of  $\text{LiSbF}_4$  and  $\text{LiSb}_2\text{F}_7$  compounds are shown in Fig. 6. In the IR spectrum of lithium tetrafluoroantimonate(III) there are two intense bands with the frequencies  $\nu_s \sim 596$  and  $\nu_{as} \sim 515 \text{ cm}^{-1}$  (Fig. 6a) which belong to the symmetric and asymmetric stretching vibrations of terminal fluorine atoms in the structure II. The bands at  $\nu_s \sim 594$  and  $\nu_{as} \sim 505 \text{ cm}^{-1}$  in the IR

Table 1  
Some bond lengths (Å) and angles ( $^\circ$ ) of  $\text{MSb}_2\text{F}_7$ .

Bond, Å	$\text{LiSb}_2\text{F}_7$ (I)	$\text{NaSb}_2\text{F}_7 \cdot \text{H}_2\text{O}$ [6] <sup>a</sup>	$\text{RbSb}_2\text{F}_7$ [8] <sup>a</sup>	$\text{CsSb}_2\text{F}_7$ [9]
$\text{Sb1}(\text{Sb2})-\text{Feq}$	1.925(1)	1.923(1) 1.931(1)	1.994(1) 1.921(1)	1.936(2)
$\text{Sb1}(\text{Sb2})-\text{Fax}$	1.940(1)	1.940(1) 1.968(1)	1.963(1) 1.934(2)	1.942(2)
$\text{Sb1}(\text{Sb2})-\text{Fm}$	2.013(1)	2.022(1) 1.986(1)	1.931(2) 2.109(1)	1.975(2)
$\text{Sb1}(\text{Sb2})-\text{F}^{\text{i}}$	2.315(1)	2.237(1) 2.323(1)	2.336(1) 2.036(1)	2.240(1)
$\text{Sb1}(\text{Sb2})-\text{F}^{\text{ii}}$	2.723(1)	2.715(1) 2.628(1)	2.684(2) 2.654(2)	2.774(2)
$\text{Sb1}(\text{Sb2})-\text{F}^{\text{iii}}$	2.773(1)	2.848(1) 2.982(1)	2.699(2) 2.913(2)	2.893(2)
$\text{Sb1}(\text{Sb2})-\text{F}^{\text{iv}}$	3.069(1)	3.118(1) 3.133(1)	3.220(2) 3.119(2)	3.124(2)
Angle ( $^\circ$ )				
$\text{Feq}-\text{Sb1}(\text{Sb2})-\text{Feq}$	89.61(6)	84.83(5) 88.32(5)	84.7(5) 85.2(6)	90.53(9)
$\text{Fax}-\text{Sb1}(\text{Sb2})-\text{Feq}$	79.25(6)	81.92(5) 75.75(4)	73.1(5) 79.1(6)	76.43(8)
$\text{Fax}-\text{Sb1}(\text{Sb2})-\text{Fax}$	79.82(5)	81.19(4) 78.90(4)	77.1(6) 82.9(5)	77.31(8)
$\text{Fax}-\text{Sb1}(\text{Sb2})-\text{Fm}$	82.33(6)	83.43(5) 79.87(5)	82.9(5) 81.6(5)	81.42(8)
$\text{Fax}-\text{Sb1}(\text{Sb2})-\text{F}^{\text{i}}$	84.53(5)	83.80(5) 84.32(5)	85.3(6) 81.6(6)	85.49(9)
$\text{Fax}-\text{Sb1}(\text{Sb2})-\text{F}^{\text{ii}}$	155.81(6)	159.80(5) 51.14(4)	151.6(6) 156.1(6)	151.64(7)
$\text{Sb}-\text{Fm}-\text{Sb}'$	139.75(9)	124.57(5)	119.4(5)	125.3(1)

Symmetry codes for I: (i)  $-x+3/2, -y+1, -z+1/2$ ; (ii)  $-x+1, -y+1, -z$ ; (iii)  $x-1/2, y, -z+1/2$ .

<sup>a</sup> The distances  $\text{Sb}(1)-\text{Fm}$  and  $\text{Sb}(2)-\text{Fm}$  are shown in the non-symmetric dimers.

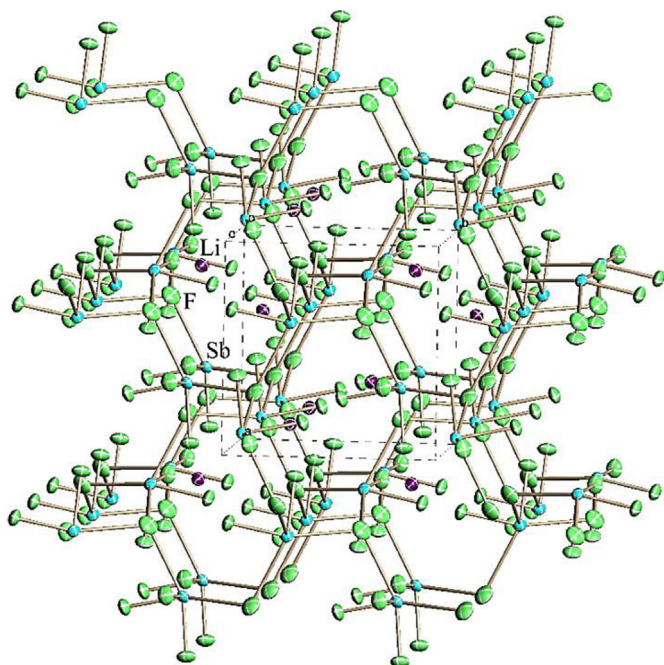


Fig. 3. Crystal structure LiSbF<sub>4</sub>.

spectrum of lithium heptafluorodiantimonate(III) are also attributed to the stretching vibrations of Sb–F bonds (Fig. 6b).

#### 2.4. NMR spectroscopy results

The compound II was studied by the <sup>7</sup>Li, <sup>19</sup>F NMR. The temperature dependence of <sup>7</sup>Li NMR spectrum shape is shown in Fig. 7. <sup>7</sup>Li NMR spectra (the nuclear spin I is equal to 3/2) of this compound at temperatures below 250 K consist of a single line, the shape of which is described by a superposition of the Gaussian and Lorentzian functions.

The absence in NMR spectra the clearly defined satellites may indicate a wide distribution in size and in symmetry of the EFG tensor (electric field gradient) in the positions of lithium ions in this compound crystal lattice. The relatively large line width (~24 kHz) indicates rigidity (in the NMR terms [15]) of the lithium cation positions of in the structure II. An appearance in the <sup>7</sup>Li NMR spectra the narrow component, belonging to highly mobile ions in the lithium sublattice of LiSbF<sub>4</sub> compound, is

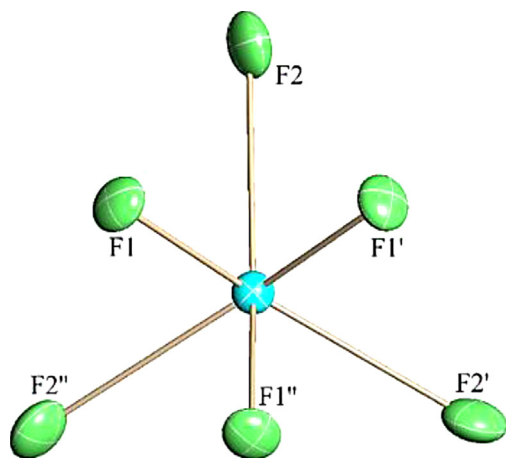


Fig. 4. SbF<sub>6</sub> polyhedron in the structure II.

**Table 2**  
Some bond lengths (Å) and angles (°) in II.

Bond	d, Å	Angle	ω (°)
Sb–F(1)	1.954(1) × 3	F(1)–Sb–F(1')	84.68(8) × 3
Sb–F(2)	2.574(1) × 3	F(2)–Sb–F(2')	115.29(1) × 3
Sb...F(1)	3.320(2) × 3	F(1)–Sb–F(2)	75.47(7) × 3
F(1)–F(1')	2.632(3) × 3	F(1)–Sb–F(2')	76.65(6) × 3
F(2)–F(2')	4.349(3) × 3	F(1)–Li–F(1')	109.8(2) × 3
F(1)–F(2)	2.814(2) × 3	F(1)–Li–F(2)	109.1(2) × 3
F(1)–F(2')	2.850(2) × 3		
Li–F(1)	1.845(2) × 3		
Li–F(2)	1.861(7)		

observed above 370 K. This component intensity grows with temperature increasing, and at the experiment maximum temperature (420 K) its share (according to the computer simulations) is not less than 40% of the total area of the <sup>7</sup>Li NMR spectrum of LiSbF<sub>4</sub> compound (Fig. 7). An exact estimation of this component size is difficult due to a wide base of the NMR resonance line (Fig. 7). Given temperature dependence of the narrow component area, it can be assumed that at a temperature increase (above 420 K) the amount of lithium ions participating in diffusion will grow.

<sup>19</sup>F NMR spectra of LiSbF<sub>4</sub> compound at different temperatures are shown in Fig. 7. In the temperature range from 150 to 450 K the spectra consist of a relatively broad asymmetric line, a shape of which does not virtually change in this temperature range. The line width with temperature increasing 150 → 200 K decreases from 50.6 to 45.8 kHz, and then it does not vary up to 320 K. Given the line shape, the second moment value (55 ± 5 G<sup>2</sup> at 150 K), and its width, one can conclude on the absence of ion motions in the fluoride sublattice with frequencies higher than 10<sup>4</sup> Hz (rigid lattice).

With temperature increasing, a further reduction in the line width is observed (up to 35.7 kHz at 450 K), that can be associated with an appearance of diffusion processes of lithium cations resulting in a partial averaging of dipole–dipole F–Li interactions which contribute to the line width through fluorine. Above 410 K a “narrow” line of low intensity with the chemical shift of 84 ppm appears in the NMR spectrum (Fig. 7). Computer modeling of the NMR spectrum at 470 K shows that this component area does not exceed 2.5% of the total spectrum area. Therefore, it can be concluded that in the studied temperature range (150–470 K) the ion mobility is virtually absent in the fluoride sublattice of LiSbF<sub>4</sub> compound. It should be noted that in the DSC curve any endo-effects were not registered in the temperature range of 300–520 K,

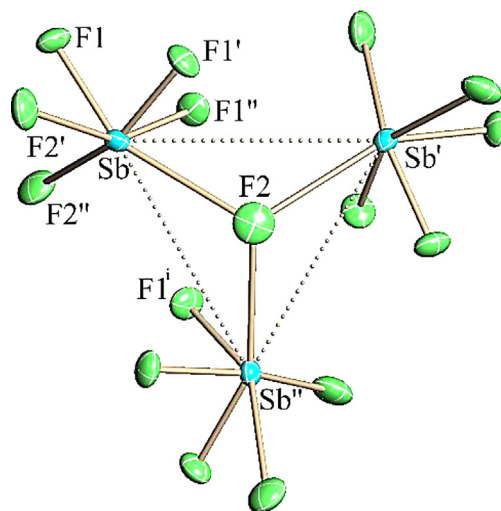


Fig. 5. Fragment structure II.

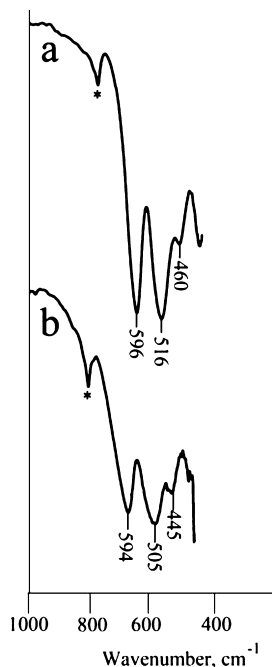


Fig. 6. IR spectra of: (a)  $\text{LiSbF}_4$ ; (b)  $\text{LiSb}_2\text{F}_7$ . \* – Vaseline.

and the temperature maximum, at which  $\text{LiSbF}_4$  sample melts, is 528 K.

A comparison of  $^{19}\text{F}$  NMR data on ion mobility in  $\text{LiSbF}_4$  sample and in the tetrafluoroantimonates(III) with alkali cations (Na, K, Rb, Cs) [16,17] shows that the nature of ion motions in the fluoride sublattice in these compounds is different. In the compound II the ion motions with frequencies above  $10^4$  Hz in the fluoride subsystem are virtually absent in the range of 150–490 K, but in the compounds with other alkali cations they are represented by reorientations of complex anions as well as by a diffusion of fluoride ions. At this, the fluoride ion diffusion is a dominant type of ion mobility in these compounds above 490 K, that provides a high ionic (superionic) conductivity of the tetrafluoroantimonates(III) of sodium, potassium, rubidium, and cesium ( $\sim 10^{-4}$ – $10^{-2}$  S/cm at 490–505 K) [16,17]. Nevertheless, given ion diffusion in the lithium sublattice,  $\text{LiSbF}_4$  compound can also be an ionic conductor.

### 3. Experimental

#### 3.1. Synthesis

$\text{LiSbF}_4$  and  $\text{LiSb}_2\text{F}_7$  compounds were synthesized from the aqueous solution of  $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$  and  $\text{Sb}_2\text{O}_3$  at molar ratios of the components of 0.25–0.5:1 in the presence of hydrofluoric acid. At the molar ratio of 0.25:1, lithium heptafluorodiantimonate(III)

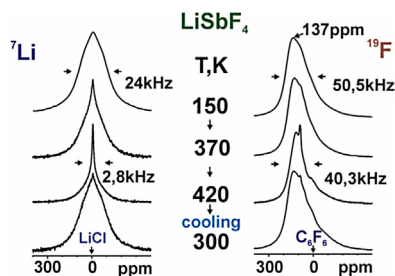


Fig. 7.  $^7\text{Li}$ ,  $^{19}\text{F}$  NMR spectra of lithium tetrafluoroantimonate(III)  $\text{LiSbF}_4$ .

$\text{LiSb}_2\text{F}_7$  (I) crystallizes from the solution. An increase of the ratio of  $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}:\text{Sb}_2\text{O}_3$  up to 1:1 leads to a formation of colorless crystals of lithium tetrafluoroantimonate(III)  $\text{LiSbF}_4$  (II). Single crystals of the synthesized compounds for the X-ray diffraction study were grown by a slow crystallization of the substance aqueous solution at room temperature. According to the DSC study,  $\text{LiSbF}_4$  melting temperature is equal to 528 K.

#### 3.2. X-ray study

The X-ray diffraction experiment was carried out at 296 K on a BRUKER KAPPA APEXII CCD diffractometer (Mo  $K_\alpha$ -radiation, graphite monochromator,  $0.3^\circ$   $\omega$ -scanning with the exposure time of 20 s per a frame). Absorption of X-rays in the sample was accounted using the equivalent reflections. The crystal structures were determined by the direct method and refined by the least squares method in the anisotropic approximation.

Collecting and editing of the experimental data, a refinement of the unit cell parameters were done with the software package Apex II [18]. All calculations to identify and clarify the structures were done with the programs SHELXTL/PC [19]. The crystallographic data and details of refinement are shown in Table 3. CIF-files containing the complete data on the studied structures have been deposited in the inorganic structure database ICSD numbered 428176, 428177, where from they can be freely obtained on a request at the website: <http://www.fiz-karlsruhe.de/icsd.html>

#### 3.3. IR spectroscopy

IR spectra of the samples were recorded in the range of 400–4000  $\text{cm}^{-1}$  using a Fourier spectrometer Shimadzu FTIR Prestige-21 (Japan) at room temperature. The samples were ground in an agate mortar to a finely divided state and mixed with vaseline oil to form a suspension which was applied onto a substrate of KBr.

#### 3.4. NMR measurements

$^{19}\text{F}$ ,  $^7\text{Li}$  NMR spectra were recorded on a multinuclear digital Bruker AV-300 spectrometer at Larmor frequencies 282.404 and

Table 3

Crystal data, experimental and refinement details for the structures I and II.

Formula	$\text{LiSb}_2\text{F}_7$ (I)	$\text{LiSbF}_4$ (II)
Formula weight	191.72	244.70
Temperature (K)	296(2)	296(2)
Wavelength (Å)	$\text{MoK}_\alpha$ (0.71073)	$\text{MoK}_\alpha$ (0.71073)
Crystal system	Orthorhombic	Cubic
Space group	Pnma	P2 <sub>1</sub> 3
a (Å)	8.717(1)	6.8999(3)
b (Å)	14.527(2)	
c (Å)	4.7551(6)	
V, Å <sup>3</sup>	602.1(1)	328.49(2)
Z	4	3
Density (calculated) (Mg/m <sup>3</sup> )	4.230	3.711
Absorption coefficient (mm <sup>-1</sup> )	9.037	6.279
F(000)	672	333
Crystal size (mm)	0.12 × 0.12 × 0.12	0.18 × 0.15 × 0.05
$\theta$ range for data collection	2.80–34.14	4.18–68.42
Reflections collected	7767	14365
Independent reflections	1204 [R(int)=0.0222]	2042 [R(int)=0.0293]
Data/restraints/parameters	1204/0/50	2042/0/20
Goodness-of-fit on $F^2$	1.106	1.101
Final R indices [I > 2 $\sigma$ (I)]	0.0191	0.0254
R indices (all data)	0.0195	0.0305

116.65 MHz, respectively, in the temperature range 150–420 (450) K with an accuracy of 2 K. RMS width calculations (or the second moments  $S_2$ , in  $G^2$ ) of NMR spectra were carried out by the original program with the use of formulae given in [20]. The linewidth  $\Delta H$  (in kHz), chemical shifts (CS,  $\delta$  in ppm) and integral intensities of  $^{19}\text{F}$  NMR spectrum components were measured with an error not more than 2%. The chemical shifts NMR of  $^{19}\text{F}$  and  $^7\text{Li}$  NMR signals were measured relative to  $\text{C}_6\text{F}_6$  and the aqueous solution of  $\text{LiCl}$ , respectively.  $\text{C}_6\text{F}_6$  chemical shift is equal to  $-589$  ppm relative to the gaseous  $\text{F}_2$  [ $\delta(\text{F}_2) = 0$  ppm] and  $-167$  ppm relative to  $\text{CFCl}_3$  [20]. Simulations of the experimental  $^{19}\text{F}$  and  $^7\text{Li}$  NMR spectra were carried out by the original program with an error not more than 5%.

#### 4. Conclusions

Two crystalline compounds of antimony(III)  $\text{LiSb}_2\text{F}_7$  and  $\text{LiSbF}_4$  were obtained. The lithium heptafluorodiantimonate(III) was first synthesized. The basic structural units of  $\text{LiSb}_2\text{F}_7$  compound are dimeric  $[\text{Sb}_2\text{F}_7]$  complex anions and  $\text{Li}^+$  cations. The anions are formed by two trigonal  $[\text{SbEF}_4]$  bipyramids with a lone electron pair E, linked through the bridging fluorine atom, similarly to the structures  $\text{RbSb}_2\text{F}_7$ ,  $\text{CsSb}_2\text{F}_7$ ,  $\text{NaSb}_2\text{F}_7 \cdot \text{H}_2\text{O}$ .

$\text{LiSbF}_4$  complex compound represents a new structural type and completes the crystal structure definition in a number of tetrafluoroantimonates(III)  $\text{MSbF}_4$  with alkali metal cations ( $M = \text{Li}, \text{Na}, \text{K}, \text{Rb}, \text{Cs}$ ). The structure II was formed from  $\text{SbF}_3\text{E}$  groups linked through the triple symmetrical fluoride bridges into the three-dimensional framework.

The ion mobility in  $\text{LiSbF}_4$  complex compound was studied by  $^7\text{Li}$ ,  $^{19}\text{F}$  NMR. It was found the presence of ion diffusion in the lithium sublattice and its absence in the fluoride subsystem that makes it possible to consider lithium tetrafluoroantimonate(III) as a promising cation conductor.

#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jfluchem.2014.09.027>.

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