121,123Sb and 209Bi Nuclear Quadrupole Resonance Study of Complex Compounds of Antimony(III) and Bismuth(III) in the Temperature Range 77–400 K*

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A large number of solid fluoride and heteroligand acidocomplex compounds of antimony(III) and bismuth(III) with single and mixed cations has been prepared from aqueous solutions. Their crystal structures and 121,123Sb and 209Bi NQR spectra have been investigated in a wide temperature range.

Preface

The present paper complex compounds of Sb(III) and Bi(III) are studied by the 121,123Sb and 209Bi NQR spectroscopy.

All the crystal line substances dealt with in this work were prepared from aqueous solutions. Some complexes of Sb(III) and Bi(III) have analogs among complexes of trivalent aluminium, gallium, indium, and thallium, whose NQR spectra were reported and discussed by Deeg and Weiss [1, 2], Ramakrishnan and co-authors [3], Chihara and Nakamura [4], Guibé and Jugie [5], and Semin with co-authors [6].

The NQR spectra of 121•123Sb and 209Bi were measured with an ISSh-1-13 pulse NQR spectrometer equipped with a temperature accessory. The first work on NQR study of antimony(III) complexes was carried out with the help of Dr. Kravchenko [7], some successive works on temperature dependences of NQR spectra were carried out jointly with Professor G. K. Semin’s Laboratory at the Institute of Organoelement Compounds, Russian Academy of Sciences. The calculations of temperature parameters of some NQR spectra were performed by Professor R. Sh. Lotfullin. X-ray analysis and another physical methods were used to study the complexes obtained along with the NQR method.

Results and Discussion

I. Antimony Trifluoride, SbF3

Each antimony atom in the crystal structure of SbF3 is bound to three fluorine atoms (Fig. 1), and the SbF3 groups form a three-dimensional network through fluoride bonds [8]. The coordination polyhedron of antimony is a distorted SbF6 octahedron, where E indicates a lone electron-pair. The complete 121,123Sb NQR spectrum at 77 K was reported in [7, 9]. The study of the temperature dependence of the NQR parameters for SbF3 [10] showed the following:

1) both 121Sb and 123Sb NQR spectra are singlet, the signals are observed in the range 77–350 K;
2) a phase transition resulting in the piezoelectric phase occurs in the range 190–215 K;
3) the temperature dependence of 121Sb NQR spectral parameters in SbF3 is explained on the basis of Bayer’s

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theory and described by the formula [11]:

$$v_{\exp} = v_{\text{Bayer}} + \sum_{n=0}^{6} B_n T^n.$$  \hspace{1cm} (1)

4) unlike SbCl$_3$ [12], the asymmetry parameter varies in the range $4.3 - 5.6\%$ and increases nonlinearly as the temperature increases;

5) a zero-magnetic-field splitting of line corresponding to the $(1/2 \leftrightarrow 3/2)$ transition in the range $92 - 275$ K is observed.

II. Homoligand Fluoride Complexes of Antimony(III)

The NQR spectra of antimony(III) fluoride complexes with monovalent MSb$_4$F$_{13}$, MSb$_3$F$_{10}$, MSb$_2$F$_7$, M$_3$Sb$_4$F$_{15}$, MSbF$_4$, and M$_2$SbF$_5$ cations are studied.

Complexes MSb$_4$F$_{13}$

The MSb$_4$F$_{13}$ complexes (M = K, Rb, Cs, and NH$_4$) are isostructural at room temperature. The structure of the complex KSb$_4$F$_{13}$ [13] contains [Sb$_4$F$_{13}$]$^-$ anions built of four SbF$_3$ molecules shifted to a thirteenth fluorine atom by weaker “secondary” bonds. The investigation of the $^{121,123}$Sb NQR spectra of MSb$_4$F$_{13}$ complexes has shown that

1) NQR signals can be observed only at low temperatures;

2) complexes with M=K and Rb [14] exhibit singlet, while those with M=Cs and NH$_4$ [7] exhibit doublet NQR spectra at 77 K;

3) the temperature coefficients of the NQR frequencies for RbSb$_4$F$_{13}$ are negative [14] like those for SbF$_3$, but their values differ from one another in the range 77–270 K (Fig. 2);

4) the complex RbSb$_4$F$_{13}$ exhibits piezoelectric properties.

Complexes MSb$_3$F$_{10}$

Only complex NaSb$_3$F$_{10}$ was studied. Earlier, it was erroneously described as NaSb$_2$F$_7$. The structure of NaSb$_3$F$_{10}$ and its NQR spectrum at 77 K were investigated in [15] and [7], respectively.

Complexes MSb$_2$F$_7$

A group of heptafluoroantimonates MSb$_2$F$_7$ (M=K, Rb, Cs, Tl, NH$_4$, Et$_2$NH$_2$, CN$_3$H$_6$, CN$_4$H$_7$, C$_2$N$_3$H$_4$, Nic, and Gly) has been investigated. The crystal structures of KSB$_2$F$_7$ [16], CsSb$_2$F$_7$ [17], and (C$_2$N$_3$H$_4$)Sb$_2$F$_7$ [14] are known. All the antimonates(III), except CsSb$_2$F$_7$, have

![Fig. 2. Temperature dependence of the $^{123}$Sb NQR frequencies in RbSb$_4$F$_{13}$: 1 $v_1$=$\pm$(1/2 $\leftrightarrow$ 3/2); 2 $v_2$=$\pm$(3/2 $\leftrightarrow$ 5/2).](image)
Fig. 3. Temperature dependence of the quadrupole coupling constants $e^2Qq$ (1 and 2 for Sb, and Sb$_2$) and asymmetry parameters $\eta$ (3 and 4 for Sb, and Sb$_2$) for the antimony atoms $^{123}$Sb in K$_2$Sb$_2$F$_7$.

multiplet $^{121,123}$Sb NQR spectra at 77 K [7, 18–23], similarly to analogous gallium compounds [1]. TlSb$_2$F$_7$ [18] has the most complicated NQR spectrum corresponding to six nonequivalent sites of the antimony atoms in the crystal lattice. The temperature variations of the NQR parameters for MSb$_2$F$_7$ (M = K, Tl, and CN$_3$H$_6$) are studied [14]. Their NQR spectra are characterized by fading the signals in the range 220–290 K (Figs. 3–5). A superionic phase transition occurs in TlSb$_2$F$_7$ at 240 K [24].

Complexes M$_3$Sb$_4$F$_{15}$

The study of the crystal structure of M$_3$Sb$_4$F$_{15}$ complexes (M = K and Cs) is now in progress. K$_3$Sb$_4$F$_{15}$ exhibits piezoelectric properties. The complexes have multiplet spectra at 77 K [14].

Complexes MSbF$_4$

Tetrafluoroantimonates MSbF$_4$ (M = Na, K, Rb, Cs, Tl, NH$_4$, Pr$_2$NH$_2$, Et$_2$NH$_2$, Et$_4$N, CN$_3$H$_6$, CN$_4$H$_7$, Nic,
and Gly) are not isostructural. The crystal structures were determined for NaSbF$_4$ [25], K$_2$SbF$_4$ [26], TlSbF$_4$ [27], CN$_3$H$_6$SbF$_4$ [28], CsSbF$_4$ [27a], and NH$_4$SbF$_4$ [27]. The NQR spectra of MSbF$_4$ at 77 K have different multiplicity depending on the character of the cation [7, 18–23].

KSbF$_4$, containing the [Sb$_4$F$_{16}$]$^{4-}$ anion in its structure, has the most complicated quadruplet spectrum. The temperature dependence of the NQR spectra for MSbF$_4$ (M = Na, K, Tl, NH$_4$, and CN$_3$H$_6$) was studied [29–31]. The temperature range in which the signals are observed depends on the cation. A phase transition in K$_2$SbF$_4$ at 190 K was found from its NQR spectrum. The asymmetry parameter $\eta$ for MSbF$_4$ (M = NH$_4$ and CN$_3$H$_6$) increases with temperature; this may be due to the presence of hydrogen bonds in these complexes. Superionic phase transitions in complexes MSbF$_4$ (M = K and CN$_3$H$_6$) were also observed at 483 and 253 K [29, 32].

Complexes M$_2$SbF$_5$

Pentafluoroantimonates M$_2$SbF$_5$ (M = Na, K, Rb, Cs, Tl, NH$_4$, Et$_2$NH$_3$, Et$_4$N, Bu$_3$N, CN$_3$H$_6$, and CN$_4$H$_7$) are the most investigated group among fluoride complexes of antimony(III). Some of them form the isostructural series. The structures of the following pentafluoroantimonates(III) are known: Na$_2$SbF$_5$ [33], K$_2$SbF$_5$ [34, 35] and (NH$_4$)$_2$SbF$_5$ [36, 37]. The [SbF$_5$]$^{2-}$ anion in M$_2$SbF$_5$ was shown to have a distorted octahedral SbF$_5$ configuration with the lone pair in one of its vertices.

All pentafluoroantimonates(III), except (CN$_4$H$_7$)$_2$SbF$_5$, have singlet $^{121,123}$Sb NQR spectra at 77 K [7, 18–20]. Their NQR parameters depend on the cation. The temperature dependence of NQR parameters for all (even isostructural) complexes are different, and their specific features depend on the character on the cation [31, 38–41]. A change in the multiplicity of the NQR spectrum was found in K$_2$SbF$_5$, and the transition from the paraelectric phase to the commensurate one was shown to pass via incommensurate and then commensurate-modulated phases. The NQR frequencies in (NH$_4$)$_2$SbF$_5$ increase anomalously with temperature. This complex was also studied by Nakamura [38].

A nonlinear change of the asymmetry parameter $\eta$ is observed for the remaining M$_2$SbF$_5$ (M = Na, Rb, Cs, Tl, and CN$_3$H$_6$) complexes. The complexes M$_2$SbF$_5$
Fig. 5. Temperature dependence of the quadrupole coupling constants $e^2Qq$ (1 and 2 for Sb$_2$ and Sb$_1$) and asymmetry parameters $\eta$ (3 and 4 for Sb$_1$ and Sb$_2$) for the antimony atoms $^{121,123}$Sb in CN$_3$H$_6$SbF$_7$.

(M=Na, K, Rb, Cs, and NH$_4$) were also shown to be ionic conductors, while (NH$_4$)$_2$SbF$_5$ is a superionic conductor [42]. Moreover, Na$_2$SbF$_5$ exhibits piezoelectric properties.

III. Fluorocomplexes of Antimony(III) with Mixed Cations

Two types of antimony(III) fluorocomplexes with mixed cations, $\text{M}_2\cdot\text{M}'\text{SbF}_5$ and $\text{M}_1\cdot\text{M}'\text{SbF}_4$ (M, M'=Na, K, Rb, Cs, and NH$_4$), were prepared.

Pentafluoride Complexes $\text{M}_{2-x}\cdot\text{M}'\text{SbF}_5$.

The individual complexes NaM'SbF$_5\cdot$1.5 H$_2$O (M'= K and Rb) are isostructural only at room temperature, and the solid solutions of composition $\text{M}_2\cdot\text{M}'\text{SbF}_5$ (M= K, Rb, and Cs; M'= Rb and NH$_4$), isostructural to $\text{M}_2\text{SbF}_5$, contain a complex [SbF$_5$]$^{2-}$ anion [43]. The $^{121,123}$Sb NQR spectra of these substances have the following peculiarities:

1) unlike $\text{M}_2\text{SbF}_5$, the singlet spectra of all pentafluoroantimonates with mixed cations are observed only at low temperatures;
2) a second-order phase transition occurs for the complexes NaM’SbF₅ • 1.5 H₂O in the range 160–180 K;
3) the complete NQR spectrum for the solid solutions of composition M₂₋ₓM’SbF₅ is observed in a narrow temperature range (77–120 K);
4) a sharp decrease in the integrated intensities of the signals and the line broadening from 180 to 1400 kHz are observed at x > 0.25; no NQR signals for the substances with M’ = NH₄ are observed even at 77 K;
5) the [SbF₅]²⁻ polyhedra show an increase in the symmetry of the electric field gradient on the antimony atom.

Tetrafluoride Complexes Mₓ₋ₓM’SbF₄

The solid solutions of composition MM’SbF₄ (M = K and Cs; M’ = Cs and NH₄) and a new complex NaCs₃SbF₁₆ • H₂O were prepared by the reaction of tetrafluoroantimonates MSbF₄ and M’SbF₄ [14]. A preliminary investigation shows that NaCs₃SbF₁₆ • H₂O probably has the [SbF₁₆]⁴⁻ anion, as KSBF₄. This new complex has a multiplet NQR spectrum corresponding to four nonequivalent positions of the antimony atoms in the unit cell, and the complex [SbF₁₆]⁴⁻ anion exists in the temperature range 77–295 K. The NQR spectra of the solid solutions of composition Mₓ₋ₓM’SbF₄ either have very broad lines at 77 K (Figure 6) or are not detected at all (Figure 7).

IV. Fluorocomplexes of Antimony with Mixed Ligands

A large number of heteroligand complexes of antimony(III) was synthesized. Their compositions belong to six types: M₄SbxF₁₃₋ₓYₓ, M₃SbxF₁₀₋ₓYₓ, MSbxF₇₋ₓYₓ, MSbF₄₋ₓYₓ, M₂SbF₅₋ₓYₓ, and M₃SbF₆₋ₓYₓ.

Complexes M₄SbxF₁₃₋ₓYₓ

Our attempts to obtain fluoride analogs of such composition from aqueous solutions failed. Only the complex M₄SbxF₁₃₋ₓYₓ (M = K; Y = Cl, x = 6), erroneously
described as K₃Sb₂Cl₄F₅, was studied [44]. The study of the structure of K₂Sb₂F₇Cl₈ is now in progress. This compound exhibits piezoelectric properties. Its NQR spectrum, measured at 77 K, has a multiplet pattern that shows that the antimony atoms occupy three nonequivalent sites [14].

**Nonaligand Complexes M₃Sb₂F₀₋ₓYₓ**

Five complexes of this composition, belonging to the groups nitrate-fluorides and sulphate-fluorides, were studied. Among complexes M₃Sb₂F₀, the crystal structure of [Co(NH₃)₆]Sb₂F₀ has been determined. It contains [Sb₂F₀]⁻ anions which consist of distorted octahedral SbF₃ polyhedra [45]. The structure of K₃Sb₂F₇(NO₃)₂ was found to contain the dimeric [Sb₂F₇]²⁻ anions consisting of distorted trigonal SbF₃ bipyramids [46]. The structure of CsSb₂F₆(NO₃)₃ is built of zigzag-like [Sb₂F₆(NO₃)₃]₃⁻ ribbons consisting of SbF₃ octahedra [47]. The NQR spectra of these complexes are singlet [48] and have lower frequencies in the octahedral polyhedra.

Complexes M₆Sb₂F₁₂(SO₄)₃ (M = Rb, Cs, and NH₄) are isostructural [49]. Compounds with Rb and NH₄ cations are piezoelectric, while the ammonium compound has anomalous dielectric properties in the temperature range from 240 to 260 K. The structure of (NH₄)₆Sb₂F₁₂(SO₄)₃ has six nonequivalent sites of the antimony atoms that belong to the octahedra of two different types: SbF₂O₂ and SbF₃O₃ [50]. The NQR spectra studied by us [51] and Chihara [52] at 77 K have a complicated multiplet structure corresponding to four nonequivalent sites of the antimony atoms and weak broad lines.

**Heptaligand Complexes MSb₂F₇₋ₓYₓ**

The NQR spectra of two complexes with mixed ligands, NaSb₂F₀(OH) · H₂O [53] and RbSb₂F₅C₂O₄ [54], were investigated. The structure of NaSb₂F₀(OH) · H₂O contains dimeric [Sb₂F₀(OH)]⁻ anions consisting of two SbF₃ groups linked via a bridge hydroxyl group. The structure of [Sb₂F₀(OH)]⁻ is similar to that of CsSb₂F₇. However, unlike the singlet spectrum of CsSb₂F₇, the heptaligand complex has a doublet NQR spectrum.

The anionic [Sb₂F₆C₂O₄]⁻ layers consisting of two different antimony polyhedra, the pentagonal Sb₁EF₂O₂ bipyramids and the trigonal Sb₂EF₂O₂ bipyramids, form the basis for the structure of complex RbSb₂F₅C₂O₄, which has doublet NQR spectra at 77 K and 298 K. The asymmetry parameters differ considerably from one another.

**Tetraligand Complexes MSbF₄₋ₓYₓ**

Tetrafluoroantimonates(III) with mixed ligands are the largest group of complexes studied by the NQR method. They can be divided into the following series:

1. complexes MSbF₃Y (Y = Cl [7, 55], Br [56, 57], NO₃ [31, 48], H₂PO₄ [58], and NCS [19]);
2. complexes MSbF₂Y₂ (Y = SO₄ [19], SeO₄ [59], C₂O₄ [14], and C₆H₆O₇ [19]);
3. complexes MSbFY₃ (Y = PO₄ [58]).

As a rule, these complexes have singlet NQR spectra. Their parameters, as well as their temperature dependence, depend on the type of the complex and the nature of the cation. The asymmetry parameters η of the antimony atoms in complexes MSbF₄₋ₓYₓ have higher values than those in SbF₃. The NQR spectrum of CsSbF₃Cl has been analysed in more detail in at 77–330 K [60]. The layers of isolated [Sb₂F₁₂Cl₄]⁺ anions form the basis for the structure of the complex [61]. The coordination polyhedron of antimony is a distorted SbF₃Cl₂ octahedron. The temperature dependence of the experimental values of QCC is described by the formula:

\[
\left( e^2 Q q_{zz} \right)_{\text{exp}} = \left( e^2 Q q_{zz} \right)_{\text{Bayer}} + \sum_{n=0}^{3} B_n T^n,
\]

where \( B_0 = 27.913 \times 10^{-2} \), \( B_1 = 43.413 \times 10^{-4} \), \( B_2 = -13.349 \times 10^{-5} \), and \( B_3 = -23.253 \times 10^{-9} \).

The temperature dependence of the asymmetry parameter η is not described by the Bayer’s theory. We assume that the redistribution of the electron density between the electric field gradient (EFG) components \( e^2 Q q_{xx} \) and \( e^2 Q q_{yy} \) at the ²¹Sb nucleus, resulting in a change in the asymmetry parameter, is due to the volume effect in CsSbF₃Cl crystal.

**Pentaligand Complexes M₂SbF₅₋ₓYₓ**

The ²¹,²³Sb NQR spectra of the following compounds were studied:

1. complex K₄Sb₂F₄(NO₃)₃ [48];
2. complexes Rb₂SbF₅(NO₃)₂ [48] and M₂SbF₅Y₂ (Y = SO₄ [9, 41, 51], SeO₄ [59] and C₂O₄ [9]);
3. complexes M₂SbF₅Cl₃ [62].

They have different multiplicities depending on the type of the complex and the cation nature.
Hexaligand Complexes $M_2SbF_6-xY_x$

The NQR spectra of hexafluoride complexes of such composition are unknown. Among mixed hexafluoro-
ligand complexes, the compounds $M_2SbF_5(NO_3)_3$ ($M = $ Rb and NH$_4$) with singlet spectra at 77 K [48] and
$Cs_2SbF_5(C_2O_4)_2 \cdot 3H_2O$ were studied. No NQR signals
were detected in the last complex [14].

V. Adducts $SbF_3L_n$

The acceptor properties of the $SbX_3$ halides ($X = $ Cl, Br, and I), which are typical Lewis acids, are well known
[1–3]. The Lewis acid properties of $Sb$(III) halides in-
crease in the sequence $SbCl_3 > SbBr_3 > SbI_3$, but the avail-
able data are too scarce to place $SbF_3$ in this series [63].

We have synthesized and investigated by the NQR
$^{121,123}Sb$ method three groups of new adducts of $SbF_3$
with the oxygen-containing donor ligands (dimethylsul-
phoxide (DMSO) [64], dimethylformamide (DMF) [19],
and glycine (Gly) [22]) and with the nitrogen-containing
donor ligands (nicotinic amide (Nic) [21]). Specific fea-
tures of their spectra follow:

The 2:1 Adducts, $2SbF_3L$ ($L = $ DMSO and Gly)

Such type of complexes of $SbF_3$ with an organic li-
gand were prepared for the first time. They have double-
let NQR spectra. The transition frequencies and asym-
metry parameters for the $Sb(1)$ and $Sb(2)$ atoms are higher than those in $SbF_3$. The adduct with DMSO exhibits piezoelectric properties.

The 1:1 Adducts, $SbF_3L$ ($L = $ DMSO, DMF, and Gly).

The structure of $SbF_3 \cdot $ Gly consists of molecular com-
plexes $[SbF_3('NH_2CH_2COO')]$ linked via hydrogen bonds in a three-dimensional framework. The $^{121,123}Sb$
NQR spectra of the $SbF_3$ adducts are singlet. The fre-
cuencies in the adducts with DMSO and DMF are close to
those for $SbF_3$, but the asymmetry parameters are higher.

The 1:2 Adducts, $SbF_3L_2$ ($L = $ DMSO and Nic)

The NQR spectrum of $SbF_3 \cdot $ 2 DMSO has not been de-
tected. The complex $SbF_3 \cdot $ 2 Nic has a singlet NQR spec-
trum with lower transition frequencies and smaller asym-
metry parameter than those in $SbF_3$.

VI. Oxofluoride Compounds of $Sb$(III)

Previously, two modifications of antimony oxofluo-
ride $SbOF$ were obtained by hydrolysis of $SbF_3$ [65].

Their NQR spectra are unknown up to date. We have al-
so synthesized the $SbOF \cdot $ Gly adduct but failed to detect
the NQR signals in this compound even at 77 K [22]. We
have prepared another oxofluoride, $Sb_2O_2F_5$ [66], and some complexes of the $Sb_2OF_4 \cdot $ 2 Urea [67] and $Sb_2OF_4 \cdot $ MX

types ($M = $ K, Rb, and Cs; $X = $ Cl, Br, and I [68]).

Oxofluoride $Sb_2O_2F_5$

The structure of $Sb_2O_2F_5$ crystals consists of the poly-
meric layers ($Sb_3O_2F_5$)$_n$ of four different polyhedra with
mixed ligands $SbEX_4$. The NQR spectrum of this anti-
mony(III) oxofluoride at 77 K has a complicated multi-
plet structure of 20 lines (Table 1). Moreover, a zero-
magnetic-field splitting of line corresponding to the
$(1/2 \leftrightarrow 3/2)$ transition similar to that for $SbF_3$ [14] is ob-
erved (Figure 8).

Adduct $Sb_2OF_4 \cdot $ 2(NH$_2$)$_2$CO

We investigated the structure of $Sb_2O_2F_5 \cdot $ 2 Urea [67]
simultaneously and independently of Bourgault and co-
workers [69] and showed that it consists of the dimeric
molecular complexes $[[SbF_2CO(NH_2)$_2$]_2O]$ with two nonequivalent antimony atoms. This compound has a doublet NQR spectrum in the range 77–365 K. The tem-
perature coefficients of the asymmetry parameters are positive [31].

<table>
<thead>
<tr>
<th>Compound</th>
<th>$T$, K</th>
<th>$\eta$, %</th>
<th>$e^2Qq$ MHz</th>
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<td>536.7</td>
<td>[7, 9]</td>
</tr>
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<td>298</td>
<td>5.2</td>
<td>527.1</td>
<td>[10]</td>
</tr>
<tr>
<td>$Sb_3O_2F_5$</td>
<td>77</td>
<td>7.7</td>
<td>499.5</td>
<td>[14]</td>
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<tr>
<td></td>
<td></td>
<td>23.8</td>
<td>499.6</td>
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<td>36.0</td>
<td>659.2</td>
<td></td>
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<td></td>
<td></td>
<td>36.7</td>
<td>754.2</td>
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<tr>
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<td>485.4</td>
<td>[70]</td>
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<td>433.6</td>
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<td></td>
<td>298</td>
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<td>signals were not observed</td>
<td></td>
</tr>
<tr>
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<td>11.8</td>
<td>482.7</td>
<td>[70]</td>
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<tr>
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<td>19.3</td>
<td>542.2</td>
<td>[59]</td>
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<td>298</td>
<td>20.3</td>
<td>524.5</td>
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<td>12.7</td>
<td>384.7</td>
<td>[76]</td>
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Fig. 8. Fragments of the $^{123}$Sb NQR spectrum for Sb$_3$O$_3$F$_5$ (77 K). The projection of the structure of Sb$_2$O$_3$F$_5$ along the axis c.

Complexes Sb$_2$OF$_4$ · MX

Oxofluoride complexes Sb$_2$OF$_4$ · MX (M = K, Rb, Cs, and NH$_4$; X = Cl, Br, and I) have not been adequately studied. No NQR signals were observed in these compounds. Since they are often formed as mixtures with heptafluoroantimonates MSb$_2$F$_7$ whose signals are well detected, the MSb$_2$F$_6$Cl composition was erroneously ascribed to these complexes [7].

VII. The Products of Fluorine Substitution in SbF$_3$

Two compounds were synthesized: SbF(SeO$_4$) · H$_2$O and SbF(OH)(HSO$_4$) [70]. A distorted SbEF$_5$ octahedron is the coordination polyhedron of antimony in the structure of antimony(III) selenate-fluoride. The $^{121,123}$Sb NQR spectrum of SbF(SeO$_4$) · H$_2$O is a multiplet at 77 K but it has not been observed at room temperature, which likely indicates a phase transition in this compound (Table 1). According to the NQR spectrum of SbF(OH)(HSO$_4$) measured at 77 K, the antimony atoms in this compound are equivalent, and their asymmetry parameter $\eta$ is larger than that in selenatofluoroantimonate(III).

VIII. Halogen-Containing Complexes of Bismuth(III)

The NQR $^{209}$Bi spectra of complex halogen-containing compounds of bismuth(III) are less investigated than the antimony(III) complexes. This is likely due to the fact that many halogen-containing bismuth(III) complexes have a regular octahedral surrounding in their structures. We have studied the $^{209}$Bi NQR spectra of the following compounds: nonaligand dibismuthate, tetraligand and pentaligand bismuthates.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$T$, K</th>
<th>$\eta$, %</th>
<th>$\delta^2 Q q$ MHz</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi$_2$(SO$_4$)$_3$ · 3H$_2$O</td>
<td>77</td>
<td>28.0</td>
<td>446.8</td>
<td>[71]</td>
</tr>
<tr>
<td></td>
<td>298</td>
<td>25.0</td>
<td>437.5</td>
<td></td>
</tr>
<tr>
<td>MBi(SO$_4$)$_2$</td>
<td>77</td>
<td></td>
<td></td>
<td>[14]</td>
</tr>
<tr>
<td>(M-K, Rb, NH$_4$)</td>
<td>298</td>
<td>signals were not observed</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rb$_3$Bi$_2$Cl$_3$(SO$_4$)$_2$ · 3 H$_2$O</td>
<td>77</td>
<td>62.3</td>
<td>377.7</td>
<td>[71]</td>
</tr>
<tr>
<td></td>
<td>69.8</td>
<td>405.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>KBiCl$_2$SO$_4$</td>
<td>77</td>
<td>77.1</td>
<td>464.8</td>
<td>[71]</td>
</tr>
<tr>
<td></td>
<td>298</td>
<td>81.0</td>
<td>438.1</td>
<td></td>
</tr>
<tr>
<td>NH$_4$BiCl$_2$SO$_4$</td>
<td>77</td>
<td>84.0</td>
<td>469.9</td>
<td>[71]</td>
</tr>
<tr>
<td></td>
<td>298</td>
<td>84.5</td>
<td>442.6</td>
<td></td>
</tr>
<tr>
<td>MBiCl$_2$SO$_4$</td>
<td>77</td>
<td></td>
<td></td>
<td>[14]</td>
</tr>
<tr>
<td>(M-Rb, CN$_3$H$_6$)</td>
<td>298</td>
<td>signals were not observed</td>
<td></td>
<td></td>
</tr>
<tr>
<td>K$_2$BiF$_5$</td>
<td>77</td>
<td>40.7</td>
<td>144.9</td>
<td>[14]</td>
</tr>
<tr>
<td>BiHedta</td>
<td>77</td>
<td>39.0</td>
<td>261.1</td>
<td>[76]</td>
</tr>
</tbody>
</table>

Nonaligand Complexes M$_3$Bi$_2$Cl$_{9-x}$Y$_x$

Several chloronitrate and chlorosulphate nonaligand bismuth(III) complexes were studied. Some of them are
piezoelectrics. NQR spectra for most compounds are not detected. A doublet NQR spectrum [71] was observed for Rb$_3$Bi$_2$Cl$_5$(SO$_4$)$_2$·3H$_2$O, whose structure contains two nonequivalent sites of bismuth atoms [72] with high asymmetry parameters (Table 2).

**Tetraligand Complexes MBiCl$_4$·xY**

We synthesized chloronitrate and chlorosulphate bismuth(III) complexes of composition MBiCl$_3$NO$_3$ (M = K and CN$_3$H$_6$) and MBiCl$_2$SO$_4$ (M = K, Rb, NH$_4$, and CN$_3$H$_6$), respectively [14, 71, 73]. The latter form an isostructural series. Some of these complexes are piezoelectric. The bismuth polyhedron in MBiCl$_2$SO$_4$ [74] can be described as a distorted [BiECl$_2$O$_3$]$^-$ octahedron similar to the [SbEF$_2$O$_3$]$^-$ anions in MSbF$_2$SO$_4$ compounds [75]. No NQR signals were detected in the compounds (CN$_3$H$_6$) BiCl$_3$NO$_3$ and MBiCl$_2$SO$_4$ (M = Rb and CN$_3$H$_6$); the remaining complexes have singlet spectra observed only at low temperatures and high values of the asymmetry parameters compared to complex tetrafluoroantimonates(III) (Table 2).

**Pentafluorobismuthate K$_2$BiF$_5$**

This complex was prepared from a solution in our laboratory [14]. The $^{209}$Bi NQR spectrum of potassium pentafluorobismuthate(III) is a singlet at 77 K and near room temperature, as for K$_2$SbF$_5$ (Figure 9). Unlike the antimony complex K$_2$SbF$_5$, it has no phase transitions with change of multiplicity in the range 77–270 K. The asymmetry parameter of bismuth atoms in K$_2$BiF$_5$ is larger by almost an order of magnitude than that for the antimony atoms in K$_2$SbF$_5$ [40]. It should be noted that the asymmetry parameters of bismuth atoms are, as a rule, much larger than those in similar antimony(III) compounds, which was also confirmed in our studies of the $^{121,123}$Sb and $^{209}$Bi NQR spectra of ethylenediaminetetraacetates [76].

**Conclusions**

The investigation of complex compounds of antimony(III) and bismuth(III) by NQR spectroscopy on the $^{121,123}$Sb and $^{209}$Bi nuclei allowed us to obtain information on the structure and properties of these compounds in the temperature range from 77 to about 400 K and to show that many compounds, first of all complex fluorides of antimony(III), have special physical properties related to phase transitions.

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