^{209}Bi NQR study of bismuth(III) complexes

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Potassium pentafluorobismuthate(III), nitrate-chloride Bi^{III} complexes $MBiCl_3NO_3$ ($M = K, (NH_2)_2CNH_2$), sulfate-chloride Bi^{III} complexes $MBiCl_2SO_4$ ($M = K, Rb, NH_4, (NH_2)_2CNH_2$), and Bi^{III} complexonates with the anions of ethylenediaminetetraacetic acid $M[Bi(edta)]_2 \cdot nH_2O$ (M = Mg, Ca, Ni, Cd) and nitrilotriacetic acid $Bi(nta) \cdot 2H_2O$, and $Bi(nta) \cdot 3thio \cdot H_2O$ (thio is thiourea) were studied by ^{209}Bi NQR spectroscopy. A second-order phase transition was observed in K_2BiF_5 at 100 K. The compounds $Bi(nta) \cdot 2H_2O$, $(NH_2)_2CNH_2BiCl_3NO_3$, and $MBiCl_2SO_4$ (M = K, NH_4) are piezoelectrics.

Key words: ^{209}Bi NQR spectra; bismuth(III), complexes, complexonates, potassium pentafluorobismuthate(III), nitrate-chloride and sulfate-chloride bismuth(III) compounds.

The method of nuclear quadrupole resonance (NQR), highly accurate and highly sensitive to changes in the electric field gradient (EFG) in molecules, is used to obtain information on the nature of complexes containing atoms of the elements with quadrupole nuclei. Among such elements is bismuth, which has the only natural isotope ^{209}Bi with the nuclear spin $I = 9/2$.[1] Four signals can be observed in the ^{209}Bi NQR spectrum for crystallographically (structurally) equivalent bismuth atoms when exciting the transitions between the five degenerate energy levels: $\pm[(1/2 \rightleftharpoons 3/2), (3/2 \rightleftharpoons 5/2), (5/2 \rightleftharpoons 7/2)$, and $(7/2 \rightleftharpoons 9/2)]$. The values of the frequencies ν_1—ν_4 of NQR signals are dependent on the mutual orientation of the asymmetrically distributed charge of the Bi atomic nucleus, the electrons of the atomic core, and the charges induced by other atoms in the molecule. The main parameters obtained from experimentally measured frequencies of the NQR spectra are the quadrupole coupling constant (QCC) e^2Qq_{zz} (e is the charge of the electron, eQ is the electric quadrupole moment of the nucleus, and eq_{zz} is the maximum diagonal component of the EFG tensor at the nuclear site) and the EFG asymmetry parameter (η); the methods for calculation of these parameters have been reported previously.[1]

In this work, the following bismuth(III) complexes were studied by ^{209}Bi NQR spectroscopy: K_2BiF_5; $MBiCl_3NO_3$ ($M = K, (NH_2)_2CNH_2$); $MBiCl_2SO_4$ ($M = K, Rb, NH_4, (NH_2)_2CNH_2$); $M[Bi(edta)]_2 \cdot nH_2O$ (M = Mg, Ca, Ni, Cd; $(edta)^{4-}$ is the anion of ethylenediaminetetraacetic acid H_4edta); $Bi(nta) \cdot 2H_2O$ ($(nta)^{3-}$ is the anion of nitrilotriacetic acid H_3nta); and $Bi(nta) \cdot 3thio \cdot H_2O$ (thio is thiourea).

Experimental

The procedures for the synthesis of the compounds studied were described previously.[2–6] The ^{209}Bi NQR spectra of polycrystalline specimens were recorded on an ISSh-1-13 NQR spectrometer equipped with a temperature control accessory analogous to that described in the literature.[7] The positions of the maxima of the ^{209}Bi NQR spectral lines were measured with an accuracy of 5 kHz, and the accuracy of temperature measurements was 0.5 K.

Results and Discussion

Potassium pentafluorobismuthate(III). The quadruplet ^{209}Bi NQR spectrum of potassium pentafluorobismuthate(III) (Table 1) is observed in the temperature range 77—270 K and corresponds to crystallographically equivalent Bi atoms. The relative intensities of the NQR signals gradually decrease as temperature increases and at $T > 270$ K the spectrum is not observed. In the antimony compound K_2SbF_5 of the same type the ^{121,123}Sb NQR signals fade at $T > 350$ K.[8] The large EFG asymmetry parameter at the nuclei of bismuth atoms in K_2BiF_5 at 77 K (40.7%), which far exceeds the η value for the antimony atoms in K_2SbF_5 (8.8%), indicates considerable distortion of the electron density distribution around the ^{209}Bi nucleus as compared with that around the Sb^{III} nuclei in K_2SbF_5.

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Table 1. ^{209}Bi NQR spectral parameters of bismuth(III) compounds at 77 K

Compound	Transition frequency, ν/MHz				η	e^2Qq_{zz}
	±(1/2 ⇌ 3/2)	±(3/2 ⇌ 5/2)	±(5/2 ⇌ 7/2)	±(7/2 ⇌ 9/2)	(%)	/MHz
K_2BiF_5 [a]	11.69	11.16	17.52	23.84	40.7	144.9
$BiCl_3$ [b]	33.72	25.90	37.90	52.70	58.3	325.5
$KBiCl_3NO_3$	22.30	20.50	32.01	43.66	41.1	266.0
$KBiCl_2SO_4$ [c,d]	58.35	41.01	51.68	74.08	77.1	464.8
$NH_4BiCl_2SO_4$ [c,d]	63.05	43.18	51.16	74.01	84.0	469.9
$Mg[Bi(edta)]_2 \cdot 8H_2O$	26.87	24.19	37.69	51.46	44.0	314.3
$Ca[Bi(edta)]_2 \cdot 9H_2O$	27.79	25.58	39.96	54.50	43.0	332.0
$Ni[Bi(edta)]_2 \cdot 9H_2O$	27.24	25.32	39.59	53.96	42.4	328.6
$Bi(nta) \cdot 2H_2O$ [c]	23.93	27.23	42.94	57.91	31.4	350.2
$Bi(nta) \cdot 3thio \cdot H_2O$	27.03		47.62			

[a] ^{209}Bi NQR spectrum at 270 K: 11.85, 10.23, 15.76, and 21.61 MHz; e^2Qq_{zz} = 132.1 MHz; and η = 47.5%.

[b] Data taken from Ref. 14.

[c] Piezoelectric noises are detected.

[d] Data taken from Ref. 4.

The temperature dependences of the ^{209}Bi NQR spectral parameters (the frequencies of the lines ν_3 and ν_4, and the QCC values; curves *1—3*, respectively) for K_2BiF_5 in the temperature range 77—270 K are shown in Fig. 1. Their behavior is in agreement with the Bayer—Kushida theory,[9] according to which the EFG temperature dependence is due to a change in the mutual orientation of the EFG tensor and the nuclear quadrupole moment tensor caused by libration thermal molecular vibrations including reorientational motions.

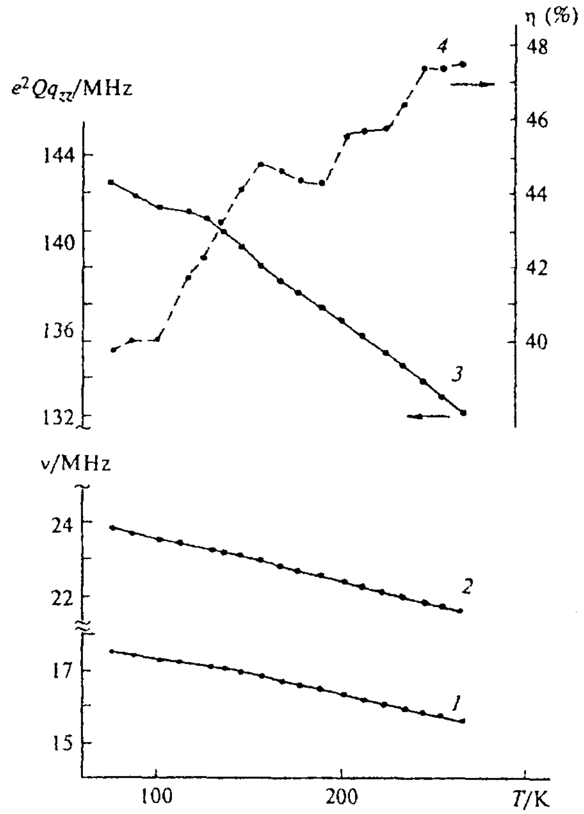

Fig. 1. Temperature dependence of ^{209}Bi NQR spectral parameters in K_2BiF_5: *1, 2*, frequencies of transitions ν_3 = ±(5/2 ⇌ 7/2) and ν_4 = ±(7/2 ⇌ 9/2), respectively; *3*, e^2Qq_{zz}; and *4*, EFG asymmetry parameter (η).

In contrast to K_2SbF_5,[8] no phase transitions with changes in the multiplicity of the NQR spectrum are observed for K_2BiF_5. However, the temperature coefficient $\partial(e^2Qq_{zz})/\partial T$ changes from $-6.2 \cdot 10^{-2}$ to $-7.2 \cdot 10^{-2}$ MHz deg^{-1} in the region 110 K, which indicates a second-order phase transition in the K_2BiF_5 structure. The temperature dependence of the EFG asymmetry parameter at the bismuth nuclei in K_2BiF_5 (see Fig. 1, curve *4*) in the range 77—270 K differs from the Bayer-type dependence in that the coefficient $\partial\eta/\partial T$ is positive ($4.1 \cdot 10^{-2}$ deg^{-1}). This points to the fact that the EFG symmetry at the nuclei of Bi atoms in K_2BiF_5 decreases as temperature increases. In this case the parameter η changes non-monotonically, which is likely due to the reorientation vibrations of the molecule. The positive temperature coefficient $\partial\eta/\partial T$ makes it possible to conclude that the crystal structure of K_2BiF_5 is more rigid and stable to temperature in the range 77—270 K than the structure of K_2SbF_5 (phase transitions in the latter compound have been studied in detail, see Refs. 8 and 10). The temperature coefficient $\partial\eta/\partial T$ for the antimony atoms in K_2SbF_5 is $1 \cdot 10^{-2}$ deg^{-1}.

Nitrate-chloride bismuth(III) complexes $MBiCl_3NO_3$ (M = K, $(NH_2)_2CNH_2$). The crystal structure of compound $KBiCl_3NO_3$ is formed of K^+ cations and $BiCl_3$ groups that weakly interact with NO_3^- anions.[11] The geometry of $BiCl_3$ fragments in $KBiCl_3NO_3$ differs slightly from that in the $BiCl_3$ crystal.[12] Like analogous AX_3 groups of p-elements of Group V of the Periodic system in the low-valence state, the $BiCl_3$ fragments have a typical pyramidal structure with the stereochemically active lone electron pair (E) of the Bi^{3+} cation; this pair completes the trigonal $BiCl_3$ pyramid to the $BiCl_3E$ tetrahedron. The antimony(III) compound $KSbF_3NO_3$ has a similar structure.[13]

Like the spectrum of the initial bismuth trichloride,[14] the ^{209}Bi NQR spectrum of $KBiCl_3NO_3$ (see Table 1) corresponds to crystallographically equivalent bismuth atoms. The ^{209}Bi e^2Qq_{zz} and h values for $KBiCl_3NO_3$ are 17 and 30% lower than those for $BiCl_3$, respectively, which indicates the marked distinction in the electron environment of Bi atoms in the molecules of these compounds. The formation of the complex $KBiCl_3NO_3$ results in appreciable decrease of the EFG at the nuclei of Bi atoms compared to $BiCl_3$. Unlike the NQR spectrum of $BiCl_3$, the spectrum of $KBiCl_3NO_3$ is not observed at room temperature.

The compound $(NH_2)_2CNH_2BiCl_3NO_3$ is piezoelectric, as indicated by characteristic noises in the frequency range 20—50 MHz on cooling the specimen. The noises disappear at 77 K; however, no ^{209}Bi NQR signals of this compound are observed.

Sulfate-chloride Bi^{III} complexes $MBiCl_2SO_4$ ($M = K, Rb, NH_4, (NH_2)_2CNH_2$). Such complexes form an isostructural series. Previously,[15] the crystal structure of $KBiCl_2SO_4$ has been studied. As in the case of $RbSbF_2SO_4$,[16] the nearest environment of the Bi atom in the structure of $KBiCl_2SO_4$ consists of two Cl atoms. The $BiCl_2$ fragments are linked to the SO_4 tetrahedra. The coordination polyhedron of the Bi atom in the $MBiCl_2SO_4$ structure and the structural motif of the compound can be represented respectively as a distorted $BiECl_2O_3$ octahedron and double chains of $BiECl_2O_3$ octahedra and SO_4 tetrahedra sharing common vertices. In the $RbSbF_2SO_4$ structure, the zigzag-like $(SO_4—SbF_2)_n^{n-}$ chains are bound into sheets by longer Sb...O bonds.

The ^{209}Bi NQR spectra of compounds $MBiCl_2SO_4$ ($M = K, NH_4$) at 77 and 298 K have been studied previously[4] and are in agreement with the data of X-ray study.[16] The ^{209}Bi QCC and η values in these compounds are larger than those in $BiCl_3$, analogously to changes in the corresponding ^{121,123}Sb parameters in $RbSbF_2SO_4$ compared to those in SbF_3.[17] The shifts of the EFG asymmetry parameters at the nuclei of bismuth atoms in $MBiCl_2SO_4$ ($M = K, NH_4$) and at the nuclei of antimony atoms in $RbSbF_2SO_4$ are of the same order of magnitude (24, 30, and 22%, respectively). This indicates a lowering of the symmetry of the electron environment of the nuclei of Bi and Sb atoms in the $MAHal_2SO_4$ ($A = Bi, Sb$) complexes compared to initial trihalides. Another picture is observed when analyzing the shifts of the QCC of Bi atoms in $MBiCl_2SO_4$ with respect to $BiCl_3$ (30%) compared to the shifts of the QCC of Sb atoms in $RbSbF_2SO_4$ with respect to SbF_3 (0.97%).

Attempts at recording the ^{209}Bi NQR spectra of compounds $MBiCl_2SO_4$ ($M = Rb, (NH_2)_2CNH_2$) failed.

Bismuth(III) complexonates. The quadruplet ^{209}Bi NQR spectra of bismuth(III) ethylenediaminetetraacetates $M[Bi(edta)]_2 \cdot nH_2O$ with Mg^{2+}, Ca^{2+}, and Ni^{2+} cations recorded at 77 K (see Table 1) correspond to crystallographically equivalent Bi atoms. Bismuth(III) complexonates with univalent cations have similar spectra;[18] however, these groups of compounds differ in the symmetry of the local fields on bismuth atoms: the shifts in the ^{209}Bi e^2Qq_{zz} and η in compounds with divalent cations (see Table 1) with respect to Bi(Hedta)[18] are, on the average, 19 and 9%, whereas those in compounds with univalent cations are 4 and 22%, respectively. In all the complexonates studied, the EFG asymmetry parameters at the nuclei of bismuth atoms are rather large ($\eta > 40\%$) and far exceed the corresponding values for Sb atoms in the antimony(III) compounds of the same type due to the highly asymmetric electron density distribution in the Bi atom.

No NQR signals were found for the bismuth complexonate $Cd[Bi(edta)]_2 \cdot 8H_2O$.

At 77 K, the compound $Bi(nta) \cdot 2H_2O$ is piezoelectric and is characterized by the ^{209}Bi NQR spectrum corresponding to crystallographically equivalent bismuth atoms (see Table 1), analogously to the compound $Bi(Hedta) \cdot 2H_2O$.[18] The bismuth QCC value for $Bi(nta) \cdot 2H_2O$ is 30% larger than for $Bi(Hedta) \cdot 2H_2O$. Comparison of the values of the EFG asymmetry parameters for these compounds shows that the electron environment of bismuth atoms in $Bi(nta) \cdot 2H_2O$ is more symmetric.

Two weak ^{209}Bi NQR signals at 23.03 and 47.62 MHz were found for compound $Bi(nta) \cdot 3thio \cdot H_2O$; however, it is impossible to calculate the QCC and η values for bismuth unambiguously using only two frequency values.

We also studied the compounds BiF_3, $Bi(OH)_3$, $Bi(NO_3)_3 \cdot 5H_2O$, $K_2BiCl_5 \cdot 2H_2O$, $K_3Bi_2Cl_9 \cdot 2KNO_3$, $K_3Bi_2Cl_5(SO_4)_2 \cdot 3H_2O$, $K_3BiCl_6 \cdot 2KCl \cdot KH_3F_4$, $(NH_4)_3BiCl_6 \cdot NH_4Cl \cdot 2NH_4HF_2$, $MBi(SO_4)_2$ ($M = K, Rb, NH_4$), $K_3Bi(SO_4)_3$ and $K_2Bi(SO_4)_2(SeO_4)_{0.5} \cdot H_2O$; however, no ^{209}Bi NQR signals were observed.

In conclusion, we will point out two peculiarities revealed when studying the ^{209}Bi NQR spectra of the above bismuth(III) complexes. First, the values of EFG asymmetry parameters at the nuclei of Bi atoms lie in the range 21—84% and are much larger than the η values for Sb in the antimony(III) compounds of the same type. This is primarily due to the larger size of the electron core of the Bi atom, to the availability of free low-energy 5f- and 6d-orbitals, which increases the capability for the d- and f-electrons of atoms belonging to the same group of the Periodic system to participate in bond hybridization when moving from top to bottom of the Periodic Table, and to the increase in the number of σ-bonds formed by the central atom in the compounds.[19]

Second, the ^{209}Bi NQR signals for bismuth(III) compounds are often not observed even at 77 K. The absence of NQR signals can be due to several reasons, the main ones of which are the spherical electron density distribution around the quadrupole nucleus and the high concentrations of defects in the crystal and paramagnetic impurities in the substance.[1] For bismuth(III) compounds, this is first of all associated with the fact that the coordination number 6 is characteristic of Bi(III) rather than antimony(III) compounds,[20] with the formation of a regular octahedral configuration and, as a result, with the zero EFG at the nuclei of Bi atoms.

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