Nuclear Quadrupole Resonance in Chloro- and Bromoantimonate(III) Complexes*

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^{35}Cl, ^{81}Br, and ^{121}Sb NQR spectra were observed in complexes of the type $R_xSb_yX_z$ with anion stoichiometries $SbCl_4^-$, $SbCl_6^{3-}$, $SbBr_4^-$, $SbBr_5^{2-}$, $SbBr_6^{3-}$, and $Sb_2Br_9^{3-}$. Several complexes show widely spaced halogen resonance lines and unusual temperature dependences of the NQR frequencies. These findings are accounted for in terms of a three-center four-electron bond of the X-Sb-X group and cation-anion interaction.

Introduction

A wide range of solid complexes are formed by treating antimony trihalides with amine hydrohalides [1, 2]. These complexes are expressed by the general formula $R_xSb_yX_z$, in which R and X represent an amine and a halogen atom, respectively, the anions having the stoichiometries SbX_4^-, SbX_5^{2-}, SbX_6^{3-}, and $Sb_2X_9^{3-}$. The stoichiometry obtained seems to depend on the experimental conditions such as the concentration of reactants and the solvents [3]. The molecular structures of the complexes are affected by many factors, e.g., the halogen atoms, the cation dimensions, and the hydrogen bonding abilities of the cations [4]. Although various anion stoichiometries are considered as mentioned above, the anion structures in the crystals show that the antimony(III) atom tends to attain six-coordination, either by association between anions or by stereochemically active s-electron pairs.

In hexahalogenoantimonate(III) complexes, the anion has seven electron pairs and the nonbonding electron pair plays an important stereochemical role; if the lone pair electrons are stereochemically active, the structure of the anion is significantly distorted [5].

In the present work we selected a wide variety of chloro- and bromoantimonate(III) complexes to investigate the effect of cation substitution on the anion and the lone pair effect, i.e. bond character and structure of anion, using NQR spectroscopy. Our preliminary results have been communicated [6, 7] and we now report further details.

Experimental

The complexes were prepared by the method described in [2], in which antimony trihalide was allowed to react with amine halide in a concentrated hydrohalogenic acid. The antimony trihalide solution was prepared by dissolving antimony trioxide in an excess of hot hydrohalogenic acid, and the amine hydrohalide by adding an excess of hydrohalogenic acid to the amine. All the complexes gave satisfactory analysis for C, H, and N as listed in Table 1.

The NQR spectrometers used were superregenerative oscillators with Zeeman modulation. The resonance lines were observed on a recorder. The NQR frequencies were measured by use of a signal generator and a frequency counter with an estimated accuracy of ± 0.002 MHz for ^{35}Cl and ^{121}Sb and ± 0.02 MHz for ^{81}Br.

Results and Discussion

SbX_4^- (X = Cl, Br)

The crystal structures of $(C_5H_5NH)SbX_4$ (X = Cl, Br) have already been determined by X-ray analysis [8, 9]. The SbX_4^- ions form an infinite chain by halogen bridges. Each antimony atom is surrounded

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Table 1. Chemical analysis of antimony(III) halide complexes.

Compound	Found (%)			Calcd (%)		
	C	H	N	C	H	N
$(C_5H_5NH)SbCl_4$	16.56	1.76	4.04	17.47	1.76	4.08
$(CH_3NH_3)_3SbCl_6$	8.89	4.52	10.15	8.37	4.21	9.76
$(C_5H_5NH)SbBr_4$	11.66	1.16	2.77	11.51	1.16	2.68
$(n\text{-}C_3H_7NH_3)_2SbBr_5$	11.71	3.23	4.43	11.23	3.14	4.37
$(C_6H_5NH_3)_2SbBr_5$	20.41	2.25	3.91	20.32	2.37	3.95
$(4\text{-}CH_3C_5H_5NH)_2SbBr_5$	20.53	2.39	4.04	20.31	2.27	3.95
$[(CH_3)_2NH_2]_3SbBr_6$	9.94	3.21	5.76	9.75	3.27	5.68
$[(C_2H_5)_2NH_2]_3SbBr_6$	17.62	4.35	5.07	17.62	4.41	5.14
$[(C_3H_7)_2NH_2]_3SbBr_6$	23.33	5.26	4.46	23.81	5.33	4.63
$[(C_4H_9)_2NH_2]_3SbBr_6$	28.90	6.10	4.35	29.10	6.10	4.24
$(CH_3NH_3)_3Sb_2Br_9$	3.49	1.63	4.00	3.40	1.71	3.97

Table 2. ^{35}Cl, ^{81}Br, and ^{121}Sb NQR frequencies in $(C_5H_5NH)SbX_4$ (X = Cl, Br).

Compound	Nucleus	Frequency (MHz)	
		77 K	≈ 300 K
α-$(C_5H_5NH)SbCl_4$	^{35}Cl	19.844	18.972
	^{35}Cl	16.220	16.863
	^{35}Cl	14.351	12.815
	^{121}Sb	ν_1 43.91	42.67
	^{121}Sb	ν_2 82.83	71.92
β-$(C_5H_5NH)SbCl_4$	^{35}Cl	–	17.998
	^{35}Cl	–	6.232
	^{121}Sb	ν_1 –	38.69
	^{121}Sb	ν_2 –	68.90
$(C_5H_5NH)SbBr_4$	^{81}Br	130.58	121.76
	^{81}Br	116.70	
	^{81}Br	85.85	49.28
	^{81}Br	36.52	
	^{121}Sb	ν_1 36.43	34.10
	^{121}Sb	ν_2 55.10	49.12

by a distorted octahedron formed by four bridging and two terminal halogen atoms. Since the antimony atom is on a two-fold axis, two crystallographically nonequivalent halogen atoms are present in the anion.

Table 2 lists the ^{35}Cl, ^{81}Br, and ^{121}Sb NQR frequencies observed at 77 K and about 300 K. The chloride gives two crystal forms at room temperature; the α-form is a low-temperature stable phase and the β-form is a high-temperature stable one. The bromide and the β-form of the chloride yielded two halogen lines and one $^{121}Sb(1/2-3/2)$ resonance line at room temperature. The two halogen resonance lines are widely spaced. These results are consistent with those of the X-ray analysis [8, 9]; the higher resonance line is assigned to the terminal halogen and the lower line, to the bridging halogen.

The α-form yielded three ^{35}Cl lines and one $^{121}Sb(1/2-3/2)$ line at 77 K. Although one more ^{35}Cl resonance line, which is expected to appear near 5 MHz, could not be observed due to low sensitivity of the oscillator in this frequency region, the spectra are similar to those of the bromide at 77 K.

The splitting of the ^{81}Br resonance lines is quite large, especially for the bridging bromine atoms, and it reaches about 50 MHz for the bridging atoms and about 14 MHz for the terminal ones at 77 K. Therefore it is reasonable to ascribe the splitting to a change in bond nature; below the phase transition point described later, the two-fold symmetry axis disappeared and the anion has the form of $SbBr_3 \cdot Br^-$ rather than $SbBr_4^-$.

$SbBr_5^{2-}$

Table 3 lists the ^{81}Br and ^{121}Sb NQR frequencies at 77 K and about 300 K. The $SbBr_5^{2-}$ ions yielded three or five ^{81}Br resonance lines depending on their shape. The crystal structures of the complexes have not been reported as yet. However, those of the chlorides are available [4, 10–12] and give valuable information about the structure of the bromide. The chlorides form linear chains of $SbCl_5^{2-}$ by chlorine bridges. The antimony atom is surrounded by six chlorine atoms; five chlorine atoms are strictly bonded to the antimony atom and the sixth completes the distorted octahedral coordination through weak interaction. In $(NH_4)_2SbCl_5$ the anion contains three crystallographically nonequivalent chlorine

Table 3. ^{81}Br and ^{121}Sb NQR frequencies in $SbBr_5^{2-}$ ions.

Compound	Nucleus	Frequency (MHz)	
		77 K	≈ 300 K
$(n\text{-}C_3H_7NH_3)_2SbBr_5$	^{81}Br	83.22	–
	^{81}Br	74.31	–
	^{81}Br	53.22	–
	^{121}Sb	ν_1 23.056	–
	^{121}Sb	ν_2 31.957	–
$(C_6H_5NH_3)_2SbBr_5$	^{81}Br	120.76	117.71
	^{81}Br	86.61	86.70
	^{81}Br	80.27	73.98
	^{81}Br	63.82	68.28
	^{81}Br	49.50	48.36
	^{121}Sb	ν_1 16.263	16.259
	^{121}Sb	ν_2 29.331	–
$(4\text{-}CH_3C_5H_5NH)_2SbBr_5$	^{81}Br	111.30	110.70
	^{81}Br	91.84	90.40
	^{81}Br	74.23	73.33
	^{81}Br	61.28	59.77
	^{81}Br	37.65	36.11

atoms because of the presence of a mirror plane [10], while in $(C_5H_5NH_3)_2SbCl_5$ the anion contains five nonequivalent ones because of the lack of symmetry [11]. Judging from the ^{81}Br NQR spectra, $(n\text{-}C_3H_7NH_3)_2SbBr_5$ has the anion structure found for $(NH_4)_2SbCl_5$, and $(C_6H_5NH_3)_2SbBr_5$ and $(4\text{-}CH_3C_5H_5NH)_2SbBr_5$ have the anion one found for $(C_5H_5NH_3)_2SbCl_5$. The ^{81}Br resonance lines of the $SbBr_5^{2-}$ ions are widely spread in a similar manner as those of the $SbBr_4^-$ ions. The lower resonance lines below 70 MHz are assigned to the bridging bromine atoms. In the $SbCl_5^{2-}$ ions, two Sb–Cl bond lengths, trans to each other, are correlated: the short one is trans to the long one [4, 10–12]. This correlation is also found in the ^{81}Br resonance frequencies because the resonance frequency is related with the bond length.

SbX_6^{3-} (X = Cl, Br)

Table 4 lists the ^{35}Cl, ^{81}Br, and ^{121}Sb NQR frequencies for the SbX_6^{3-} ions at 77 K and about 300 K. The observed NQR spectra for the chloride are not complete because the resonance lines are distributed over a wide frequency range. The observed ^{81}Br NQR spectra of the bromide are classified into two types as seen from Table 4; the spectra consist of (1) only one ^{81}Br resonance line and (2) widely spacd two ^{81}Br resonance lines with the same intensity.

According to the X-ray crystal analysis [7, 13], these complexes contain discrete SbX_6^{3-} ions. The anion is a regular octahedron in $[(n\text{-}C_3H_7)_2NH_2]_3SbBr_6$ but a distorted one with a three-fold axis in $[(C_2H_5)_2NH_2]_3SbBr_6$. These shapes of the anions can explain the results of the NQR measurements in Table 4.

Important features in the spectra of these bromides are that the average resonance frequencies are almost equal except for $[(CH_3)_2NH_2]_3SbBr_6$ which yielded a slightly larger frequency, and that the ^{81}Br resonance lines are widely spaced. It is also worth noting that one of the two ^{81}Br lines has an extremely low frequency. In general, a low resonance frequency is observed for a bridging bromine atom, e.g. in the $SbBr_4^-$ and $SbBr_5^{2-}$ ions as tabulated in Tables 2 and 3. In $[(C_2H_5)_2NH_2]_3SbBr_6$, half the bromine atoms have two short Br ... N contacts which are formed by hydrogen bonds [7]. If lone pair electrons of the bromine atom take part in the bond formation, the lower resonance line can be interpreted in terms of hydrogen bond. The other bromine atoms give the higher ^{81}Br resonance line, and the average resonance frequency of the two lines in this complex is almost equal to the resonance frequency in the others which yield only one ^{81}Br line. This means that the more one of the two resonance lines decreases in frequency, the more the other one increases; this finding suggests that three-center four-electron bonds participate in the bonds of this complex.

Table 4. ^{81}Br and ^{121}Sb NQR frequencies in $SbBr_6^{3-}$ ions.

Compound	Nucleus	Frequency (MHz)	
		77 K	≈ 300 K
$(CH_3NH_3)_3SbCl_6$	^{35}Cl	15.498	15.30
	^{35}Cl	15.094	14.40
	^{35}Cl		10.57
	^{35}Cl		7.95
	^{121}Sb	ν_1 18.390	15.11
	^{121}Sb	ν_2 36.166	29.35
$[(CH_3)_2NH_2]_3SbBr_6$	^{81}Br	146.47	147.23
	^{81}Br	23.03	22.66
$[(C_2H_5)_2NH_2]_3SbBr_6$	^{81}Br	103.39	105.25
	^{81}Br	32.57	30.97
	^{121}Sb	ν_1 13.13	15.27
	^{121}Sb	ν_2 26.27	30.55
$[(C_3H_7)_2NH_2]_3SbBr_6$	^{81}Br	65.38	65.13
$[(C_4H_9)_2NH_2]_3SbBr_6$	^{81}Br	62.49	59.05

Table 5. ^{121}Sb NQR parameters in antimony(III) halide complexes at 77 K.

Compound	Frequency (MHz)	η	e^2Qq/h (MHz)
α-$(C_5H_5NH)SbCl_4$	ν_1 43.91 ν_2 82.83	0.218	278.70
$(C_5H_5NH)SbBr_4$	ν_1 36.43 ν_2 55.10	0.522	192.55
$(n\text{-}C_3H_7NH_3)_2SbBr_5$	ν_1 23.056 ν_2 31.957	0.622	113.48
$(C_6H_5NH_3)_2SbBr_5$	ν_1 16.263 ν_2 29.331	0.295	99.41
$[(C_2H_5)_2NH_2]_3SbBr_6$	ν_1 13.13 ν_2 26.27	0	87.53

The ^{121}Sb(1/2-3/2) resonance line was observed only for $[(C_2H_5)_2NH_2]_3SbBr_6$. The asymmetry parameters and the quadrupole coupling constants are listed in Table 5. An increase in the number of halogen atoms around the antimony atom tends to decrease the ^{121}Sb quadrupole coupling constant. This decrease reflects access of the shape of the anion to a regular octahedron.

We can not generally observe the NQR line of the central atom in a regular octahedron and in a distorted octahedron with a three-fold symmetry axis because its electric field gradient is zero [14]. In $[(C_2H_5)_2NH_2]_3SbBr_6$, the anion is a distorted octahedron with a three-fold axis and has seven electron pairs. The contribution of the cation and the other anions to its EFG can be ignored because the antimony atom is centered in the anion. If a nonbonding pair of the seven electron pairs has only 5s character, the EFG is zero. However, if the nonbonding electrons have p-character, this gives rise to an imbalance in the electron density around the antimony atom and results in a NQR line. If the nonbonding electrons are on the three-fold symmetry axis, the quadrupole coupling constant is given by

$$e^2Qq_{zz}/h = N_z e^2Qq_0/h\,,$$

where N_z is the p-electron population and e^2Qq_0/h is 2000 MHz [15]. The value of N_z obtained from the observed e^2Qq_{zz}/h is 0.044. This value is the minimum value of the p-character because the p-electrons in the nonbonding pair will distribute in the other directions.

$Sb_2Br_9^{3-}$

For $(CH_3NH_3)_3Sb_2Br_9$, two ^{81}Br resonance lines were observed at 64.91 MHz and 101.71 MHz at room temperature although three lines were reported by Brill et al. [16]. The crystal structure of this complex has not been reported as yet but a discrete $Sb_2Br_9^{3-}$ unit is found in $(C_5H_5NH)_5$–$Sb_2Br_9(Br)_2$ [17]. The anion has two distorted $SbBr_6$ octahedra sharing a face, and therefore it has three bridging and six terminal bromine atoms. This shape of the anion is consistent with our NQR results.

Temperature Dependence of Resonance Lines

Figure 1 shows the temperature dependence of ^{81}Br and ^{121}Sb resonance lines in $(C_5H_5NH)SbBr_4$. As the temperature was lowered from 350 K, the higher ^{81}Br and ^{121}Sb resonance lines increased gradually in frequency but the lower ^{81}Br resonance line changed scarcely its frequency. Near 290 K, the lower line disappeared. At about 253 K, the higher line has a discontinuous point on the frequency vs. temperature curve and the ^{121}Sb resonance lines

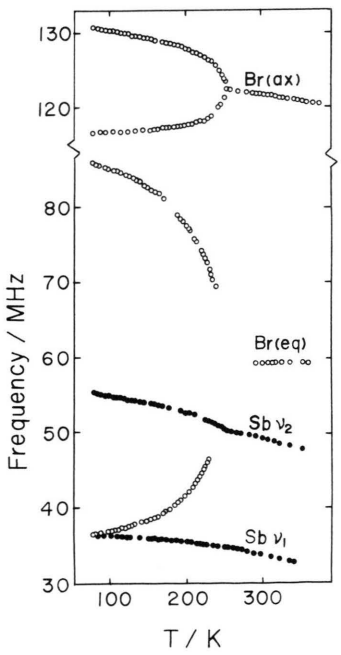

Fig. 1. Temperature dependence of the ^{79}Br and ^{121}Sb resonance lines in $(C_5H_5NH)SbBr_4$.

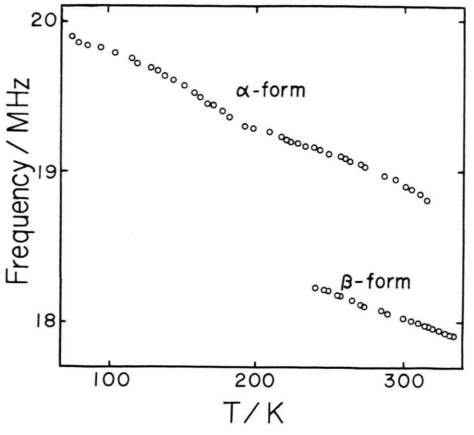

Fig. 2. Temperature dependence of the highest ^{81}Br resonance line in $(C_5H_5NH)SbCl_4$.

showed only a dip or a change in slope of the curve. At nthe lower temperature each ^{81}Br resonance line split into two lines, indicating that a two-fold axis, which is present in $SbBr_4^-$ at room temperature, disappears below the transition point. The splitting of the ^{81}Br resonance lines became progressively greater with temperature. These large splittings suggest not only a reduction in the symmetry but also a large change in the Sb−Br bond character.

Figure 2 shows the temperature dependence of the highest ^{81}Br resonance line in $(C_5H_5NH)SbCl_4$. As the temperature was lowered, the resonance line of the β-form increased in frequency and decreased in intensity. The resonance line disappeared at about 140 K with further decreasing temperature.

On the other hand, the resonance line of the α-form decreased in frequency and intensity with increase in temperature. At 190 K, the resonance line had a small dip which disappeared at 316 K. Measurements of thermal differential analysis were carried out. With increasing temperature, the β-form gave an endothermic anomaly at 236 K while the α-form gave two endothermic anomalies at 194 K and 316 K and an exothermic one at 333 K. These temperatures are in good agreement with those from the NQR measurements. Therefore, the disappearance of the resonance line and the dip on the curve are attributed to these phase transitions.

Figure 3 illustrates the temperature dependence of the ^{81}Br resonance lines in $(C_5H_5NH_3)_2SbBr_5$. The highest resonance line decreased monotonously in frequency with increase in temperature because this line arises from the terminal bromine atom located at the vertex of a square pyramidal $SbBr_5^{2-}$ ion. The other four resonance lines due to the bromine atoms in the basal plane of the square pyramid show a characteristic temperature dependence; the frequency changes of the four resonance lines with temperature are symmetric about the line at 72 MHz. The two resonance lines which are assigned to the two bromine atoms trans to each other show the opposite temperature dependence. This indicates that two Sb−Br bonds trans to each other are strongly correlated, suggesting that these bonds are formed by a three-center four-electron bond.

Figure 4 illustrates the temperature dependence of the ^{81}Br resonance lines in $[n\text{-}C_3H_7NH_3]_2SbBr_5$. As the temperature was raised, the highest resonance line increased in frequency but the other lines decreased slightly. The lowest line arises from the bridging atom located at the vertex of the square pyramidal $SbBr_5^{2-}$ ion while the higher two re-

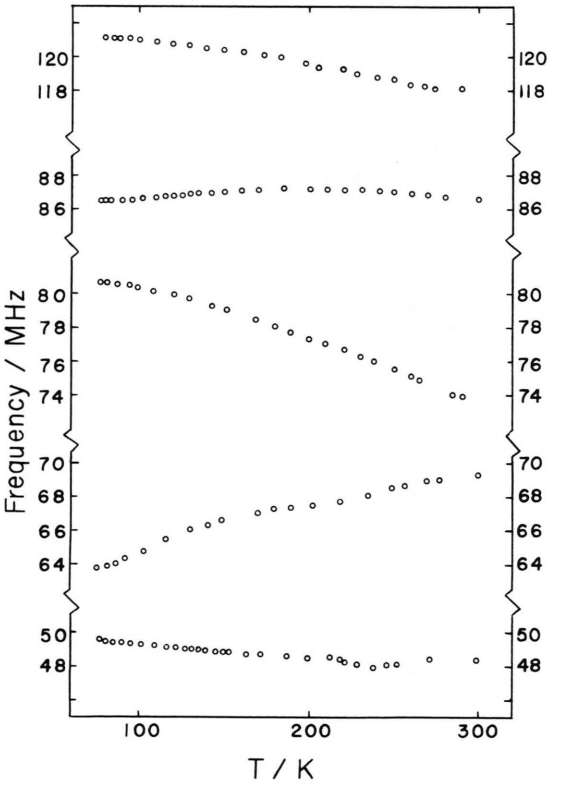

Fig. 3. Temperature dependence of the ^{81}Br resonance lines in $(C_5H_5NH_3)_2SbBr_5$.

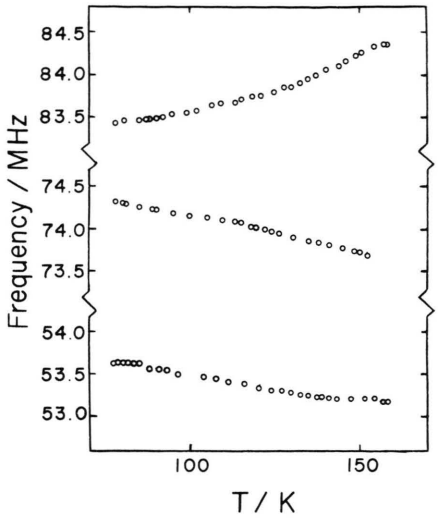

Fig. 4. Temperature dependence of the ^{81}Br resonance lines in $(n\text{-}C_3H_7NH_3)_2SbBr_5$.

sonance lines arises from the bromine atoms in the basal plane. The frequency changes of the higher two lines with temperature are also symmetric, suggesting the presence of a three-center four-electron bond. All the resonance lines disappeared at about 160 K. Our differential thermal analysis measurements showed an endothermic anomaly at 170 K. Therefore the disappearance of the resonance lines seems to be caused by this phase transition. Even when the temperature was further raised up to room temperature, no resonance lines could be observed.

Figures 5 and 6 illustrate the temperature dependence of the ^{79}Br and ^{121}Sb resonance lines in $[(C_2H_5)_2NH_2]_3SbBr_6$. As the temperature was raised, the higher ^{79}Br resonance line increased in frequency while the lower one decreased. The higher line decreased in intensity with an increase in temperature and disappeared at about 120 K. However, this line appeared again at about 170 K. With a further increase in temperature, the line increased in frequency and intensity but decreased in frequency through a peak at about 270 K. The temperature dependence of the ^{121}Sb resonance line bears a strong resemblance to that of the ^{79}Br resonance line in Figure 5. Since the Sb–Br bonds in the $SbBr_6^{3-}$ ion are formed by the three-center four-electron bond as mentioned above, the temperature dependences of the ^{79}Br resonance lines are nearly symmetric about the line of about 81 MHz. As the temperature is raised, the enhanced thermal motions will partially break the longer Sb–Br bond; the anion is described as $SbBr_3 \cdot (Br^-)_3$. Therefore the bromine atom in the longer Sb–Br bond is closer to that in $(C_2H_5)_2NH_2Br$ and the other bromine atom approaches to that in $SbBr_3$. Thus, the resonance frequency of the former decreases and that of the latter increases with increasing temperature.

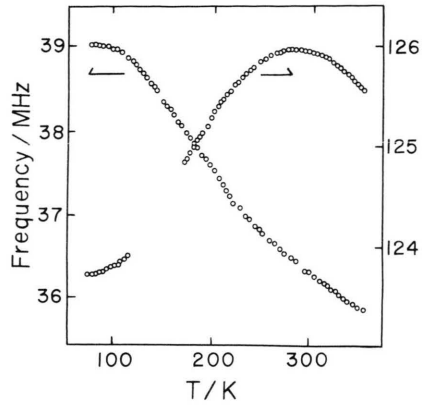

Fig. 5. Temperature dependence of the ^{79}Br resonance lines in $[(C_2H_5)_2NH_2]_3SbBr_6$.

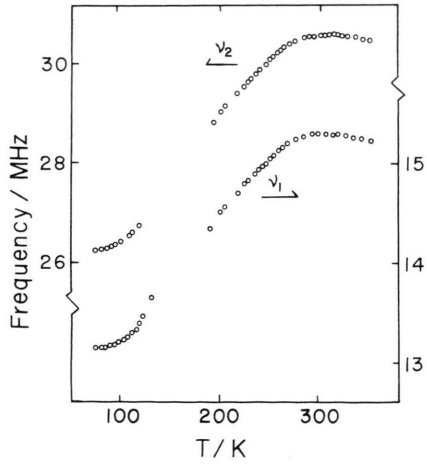

Fig. 6. Temperature dependence of the ^{121}Sb resonance lines in $[(C_2H_5)_2NH_2]_3SbBr_6$.

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