Structural and Motional Study of Pyridinium Tetrahalogenoantimonates(III) by Means of Nuclear Quadrupole Resonance Spectroscopy†

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The temperature dependences of ^{35}Cl and ^{81}Br nuclear quadrupole resonance (n.q.r.) frequencies, ^{35}Cl nuclear quadrupolar spin–lattice relaxation time T_1, and the ^{1}H n.m.r. second moment were observed for $[C_5H_5NH][SbCl_4]$, $[C_5H_5NH][SbBr_4]$, and their N-deuteriated analogues. The β phase of the chloride exhibited a second-order transition at 232 K similar to the phase transition of the bromide at 253 K. The phase transition points of the deuteriated compounds are lower by *ca.* 4 K for the chloride and *ca.* 5 K for the bromide. A minimum in ^{35}Cl T_1 was observed at about 125 K for the chloride and its deuteriated compound. This minimum is responsible for the reorientation of the pyridinium cation.

Antimony halides containing Sb^{III} or Sb^{V} form a variety of compounds with organic amines.[1] In particular, complex halides of Sb^{III} are stereochemically interesting because anions in the complexes have various compositions and structures. Pyridinium tetrahalogenoantimonates(III) $[C_5H_5NH][SbX_4]$ (X = Cl or Br) are isostrucutral and the SbX_4^- ions form an infinite chain through unsymmetrical halogen bridges between the SbX_6 groups, and the Sb atom is co-ordinated in a distorted octahedral manner by four bridging and two terminal halogen atoms.[2,3] We have reported briefly the existence of phase transitions, and the unusual temperature dependence of nuclear quadrupole resonance (n.q.r.) resonance lines.[4,5] However, the details of these anomalous behaviours remain equivocal.

In the present study, we examined complexes $[C_5H_5NH][SbX_4]$ (X = Cl or Br) and their deuteriated analogues $[C_5H_5ND][SbX_4]$ (X = Cl or Br) by means of n.q.r. and n.m.r. spectroscopy in order to discuss the effect of ionic motion on the phase transition and the unusual temperature dependence. The results are discussed in terms of known and likely structures of the complexes.

Experimental

The complexes were prepared by the method described by Porter and Jacobson.[6] Deuterium chloride (99% D, 35% in D_2O) and DBr (99.6% D, 45% in D_2O) were obtained from the MSD Isotopes Division of Merck Frosst Canada Inc.

N.q.r. spectra were recorded by super-regenerative spectrometers and a Matec pulse spectrometer. The n.q.r. frequency was measured by use of a signal generator and frequency counter with an estimated accuracy of ±0.005 MHz for ^{35}Cl, ±0.01 MHz for ^{121}Sb, and ±0.02 MHz for ^{81}Br. The spin–lattice relaxation times were measured by the 90°–90° or four-pulse method to within about 15%.[7] The desired sample temperature was achieved by adding liquid nitrogen to light petroleum contained in a Dewar vessel. A copper–constantan thermocouple was used to measure the temperature with a precision not worse than ±1 K. Second moments of ^{1}H n.m.r. spectra recorded at 60 MHz were evaluated at various temperatures using a JEOL-JNM-FW 60 spectrometer.

Differential thermal analysis (d.t.a.) experiments were carried out by use of a home-made apparatus.

Results and Discussion

Tables 1 and 2 list ^{35}Cl, ^{81}Br, and ^{121}Sb n.q.r. frequencies at 77 K and room temperature, although all the resonance lines in the deuteriated complexes were not detected because of low intensity. The n.q.r. frequencies of the deuteriated complexes are almost equal to those in the protonated ones, so that deuteriation cannot have a striking effect on the X atom. The chloride exists in two crystal forms at room temperature. The low-temperature phase (α) yielded four ^{35}Cl resonance lines and the high-temperature phase (β) two ^{35}Cl lines. The bromide yields four ^{81}Br resonance lines at lower temperature and two lines at room temperature. The resonance lines observed for the β phase in the chloride and for the bromide at room temperature are consistent with the spectra expected from *X*-ray diffraction.[2,3] The SbX_4^- anions in these complexes contain a two-fold symmetry axis but this symmetry disappears in the α

Table 1. Chlorine-35 and ^{81}Br n.q.r. frequencies of pyridinium tetrahalogenoantimonates(III)

	Frequency/MHz				
Compound	77		295 K		Assignment*
α-$[C_5H_5NH][SbCl_4]$	19.893	16.213	18.944	16.783	t
	14.387		12.940	5.38	b
α-$[C_5H_5ND][SbCl_4]$	19.916	16.207	18.927	16.810	t
	14.349		12.875		b
β-$[C_5H_5NH][SbCl_4]$			18.035		t
			8.707		b
β-$[C_5H_5ND][SbCl_4]$			18.007		t
			9.127		b
$[C_5H_5NH][SbBr_4]$	130.58	116.70	121.76		t
	85.85	36.52	59.28		b
$[C_5H_5ND][SbBr_4]$	130.62	116.84	121.9		t
	85.46	37.00	—		b

* t and b denote terminal and bridging atoms respectively.

Table 2. Antimony-121 n.q.r. frequencies of pyridinium tetrahalogenoantimonates(III)

		Frequency/MHz			
Compound	T/K	ν_1	ν_2	η^a	e^2Qq/h^b (MHz)
α-$[C_5H_5NH][SbCl_4]$	77	43.91	82.83	0.22	278.7
α-$[C_5H_5ND][SbCl_4]$	77	43.87	79.52	0.29	269.3
β-$[C_5H_5NH][SbCl_4]$	300	38.69	68.90	0.31	234.0
β-$[C_5H_5ND][SbCl_4]$	300	38.54	65.90	0.37	225.4
$[C_5H_5NH][SbBr_4]$	77	36.43	55.10	0.52	192.5
$[C_5H_5ND][SbBr_4]$	77	36.52	55.12	0.54	192.5

^{a} The asymmetry parameter of electric field gradient. ^{b} The quadrupole coupling constant.

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† *Non-S.I. unit employed:* G = 10^{-4} T.

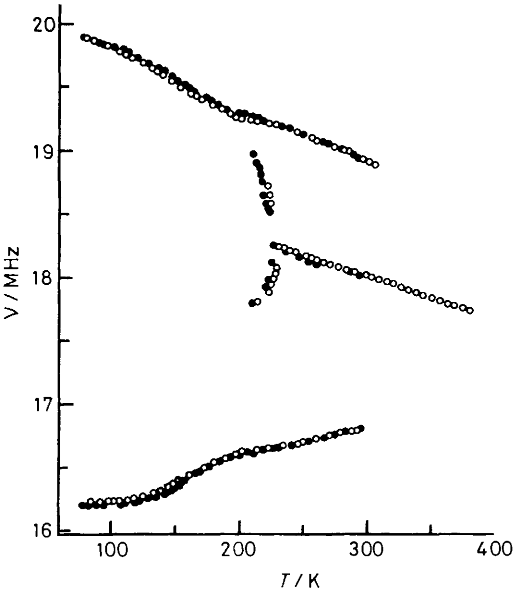

Figure 1. Temperature dependence of ^{35}Cl n.q.r. frequencies due to the terminal Cl atoms in $[C_5H_5NH][SbCl_4]$ (○) and $[C_5H_5ND][SbCl_4]$ (●)

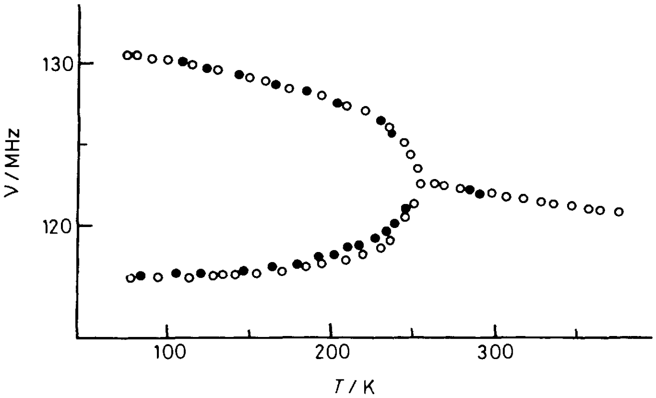

Figure 2. Temperature dependence of ^{81}Br n.q.r. frequencies due to the terminal Br atoms in $[C_5H_5NH][SbBr_4]$ (○) and $[C_5H_5ND][SbBr_4]$ (●)

phase of the chloride and the bromide at lower temperature. That is, two bridging and two terminal bromine atoms in the bromide are equivalent respectively at temperatures higher than 253 K but become inequivalent at lower temperatures, because one of the terminal atoms forms a hydrogen bond with the cation. This is also the case for the α and β phases in the chloride. The terminal Br–N distance in the bromide at room temperature is 3.44 Å,[3] which is comparable to the sum of the van der Waals radii,[8] indicating the formation of a hydrogen bond. In the chloride, although the nitrogen position is disordered, the distance from the terminal Cl atom to the nearest ring atom is 3.56 Å which is a little longer than the sum of the van der Waals radii,[2] indicating that the hydrogen bond is very weak at room temperature.

In order to examine the phase transition in the chloride, we observed the temperature dependence of the n.q.r. frequencies. Figure 1 shows the results for the terminal Cl atoms in the chloride. As the temperature rose from 77 K, the highest ^{35}Cl resonance line of the α phase decreased in frequency and the lower one increased. Both lines exhibited slope changes near 120 and 190 K. The former value is consistent with the temperature of the onset of the cationic reorientation which was deduced from the ^{1}H n.m.r. and ^{35}Cl spin–lattice relaxation time measurements as will be mentioned later. When the temperature reached about 316 K, the resonance lines disappeared, and with further increase in temperature the crystal transforms into the β phase. This phase transition is first order. Although the temperature of the β phase rose to 380 K, the resonance lines were observed without any abnormal behaviour. On the contrary, with decreasing temperature, the resonance line split into two at about 230 K, indicating the presence of a phase transition. However, with further decrease in temperature these lines disappeared at about 210 K and the solid transforms slowly to the α phase. It is worth noting that the temperature of splitting of the resonance line was about 4 K lower in the deuteriated complex than in the protonated one. This suggests that the hydrogen bonding due to the D atom is slightly weaker than that of H.

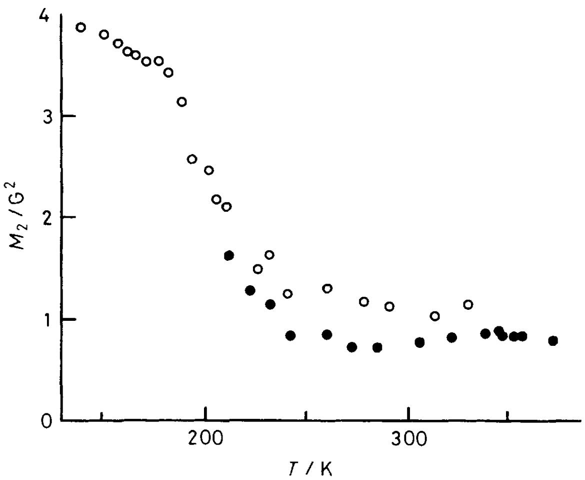

Figure 3. Temperature dependence of the ^{1}H n.m.r. second moment for $[C_5H_5NH][SbCl_4]$: α phase (○); β phase (●)

We recorded d.t.a. curves in order to confirm the phase transition in the β phase. When the sample was cooled from room temperature, an exothermic anomaly appeared at 232 K. When the sample was warmed from about 200 K, an endothermic one was observed at 231 K. From the shape of the curves and no thermal hysteresis, the β phase undergoes a second-order phase transition at 232 K. This transition point is in agreement with the temperature evaluated from the n.q.r. experiment.

Figure 2 shows the temperature dependence of ^{81}Br n.q.r. frequencies due to the terminal Br atoms in the bromide. When the temperature fell from room temperature, the resonance line split into two lines at 253 K in analogy with the resonance line of the β phase of the chloride shown in Figure 1. The temperature of splitting was 5 K lower for the deuteriated compound than for the protonated one. With further decrease in temperature to 77 K, the higher line increased its frequency and the lower one decreased. Both resonance lines had slope changes near 100 K although the changes in Figure 2 are not more obvious than those of the chloride in Figure 1. The change near 100 K is a result of the onset of the reorientation of the pyridinium cation. This is also supported by the temperature dependence of the second moment of the ^{1}H n.m.r. spectrum shown in Figure 4.

Next, the n.m.r. spectrum was examined in order to obtain information regarding the motions of the cation. Figure 4 shows the temperature dependence of the second moments of the ^{1}H n.m.r. spectrum of the chloride. The rapid decrease from 150 K

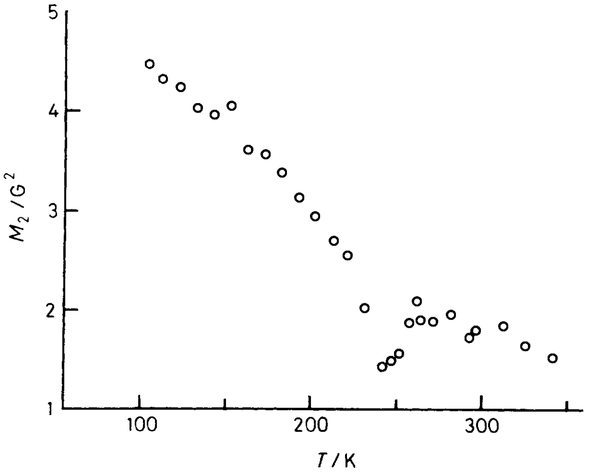

Figure 4. Temperature dependence of the ^{1}H n.m.r. second moment for $[C_5H_5NH][SbBr_4]$

is responsible for the reorientation of pyridinium ion about a quasi-six-fold axis. From 280 to 320 K the second moment was almost constant, 1.2 G^2, and this value indicates that the motion was still restricted. With further increase in temperature, the α phase transformed into the β phase at about 330 K. The latter yielded a small second moment of 0.8 G^2 in the range from 240 to 370 K, indicating free rotation of the cation. When the temperature fell, the solid transformed into the α phase at about 210 K, but at about 230 K where the n.q.r. line split into two lines no obvious change in the second moment was observed. This finding suggests that the phase transition at *ca.* 230 K is mainly determined by the anion.

Figure 4 shows the temperature dependence of the second moment of the ^{1}H n.m.r. spectrum of the bromide. The decrease from about 100 K is due to the reorientation of the pyridinium cation as well as of the chloride. A small dip near 240 K corresponds to the phase transition which was detected from the temperature dependence of the n.q.r. frequency.

Chlorine-35 spin–lattice relaxation times (T_1) were observed in order to examine the influence of the cationic motion on the n.q.r. The results are reproduced in Figure 5 for the highest ^{35}Cl resonance line due to the terminal Cl atom. The T_1 curve of the deuteriated complex is almost the same as that of the protonated one. For the β-phase, ^{35}Cl T_1 decreased rapidly with decreasing temperature, due to a phase transition, as is evident from the d.t.a. and the temperature dependence of the n.q.r. lines in Figure 1. The α phase showed a single T_1 minimum at about 125 K. The decrease in T_1 may be caused by a large fluctuation in the electric field gradient tensor components induced by motions in the neighbourhood of the Cl nucleus considered. The parameter T_1 is given by[9] equation (1) where ω_Q is the

$$1/T_1 = (1/12)(eQ/h)^2[4\langle V_{\pm 1}(0)V_{\pm 1}{}^*(0)\rangle + \langle V_{\pm 2}(0)V_{\pm 2}{}^*(0)\rangle]^2(\tau_C/1 + \omega_Q{}^2\tau_C{}^2) \quad (1)$$

angular resonance frequency, τ_C, the correlation time, eQ is the nuclear quadrupole moment, and h is Planck's constant. $V_{\pm 1} = V_{xy} \pm V_{yz}$ and $V_{\pm 2} = (\frac{1}{2})(V_{xx}-V_{yy}) \pm i\,V_{xy}$, in which V_{ij} denote the spatial derivatives at the nucleus of the electric field due to the surrounding charges. By assuming that $\omega_Q{}^2\tau_C{}^2 \gg 1$ and $\tau_C = \tau_0 \exp(E_a/RT)$ and using the relations $e^2Qq = 2h\omega_Q$ and $(eq')^2 = 4\langle V_{\pm 1}(0)V_{\pm 1}{}^*(0)\rangle + \langle V_{\pm 2}(0)V_{\pm 2}{}^*(0)\rangle$, we can rewrite equation (1) in the form (2). By fitting equation (2) to the

$$1/T_1 = (1/3\tau_0)(q'/q)^2\exp(E_a/RT) \quad (2)$$

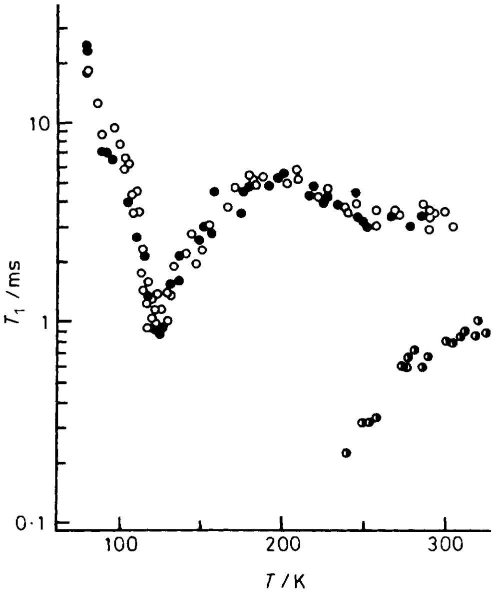

Figure 5. Temperature dependence of ^{35}Cl spin–lattice relaxation times for the highest resonance line of α-$[C_5H_5NH][SbCl_4]$ (○), α-$[C_5H_5ND][SbCl_4]$ (●), and β-$[C_5H_5NH][SbCl_4]$ (◑)

experimental T_1 values on the low-temperature side of the T_1 minimum, the activation energies derived are 11.0 ± 0.5 kJ mol^{-1} for $[C_5H_5NH][SbCl_4]$ and 9.4 ± 0.2 kJ mol^{-1} for $[C_5H_5ND][SbCl_4]$. These values are too small to be considered as resulting from the reorientation of the anion, because the SbX_4^- anions which form an infinite chain are expected to require a higher energy for initiating the reorientation. Therefore, the T_1 minimum is attributable to the modulation effect caused by the reorientation of the pyridinium cation.

The correlation time τ_0 at infinite temperature is given by[10] equation (3) where $T_{\text{min.}}$ is the temperature at which the T_1

$$\tau_0 = \exp(E_a/RT_{\text{min.}})/\omega_Q \quad (3)$$

minimum occurs. Using equations (2) and (3), we find $\tau_0 = 1.8 \times 10^{-13}$ s and $(q'/q) = 0.0058$ for $[C_5H_5NH][SbCl_4]$ and $\tau_0 = 8.6 \times 10^{-13}$ s and $(q'/q) = 0.0052$ for $[C_5H_5ND][SbCl_4]$. The values of (q'/q) are small compared to those of $(CH_3)_2CCl_2$.[9] This finding is consistent with the fact that the temperature dependence of the highest ^{35}Cl resonance line shows a slope change only near 100 K.

In conclusion, when the temperature is lowered, the high-temperature stable β phase of the chloride transforms into the low-temperature stable α phase *via* a metastable phase and the high-temperature phase of the bromide transforms directly into the low-temperature phase. These phase transitions were as a result of the motions of the pyridinium cation. At lower temperatures, one of two terminal halogen atoms in the SbX_4^- anion forms a hydrogen bond with NH in the cation. Then, this bond causes the terminal halogen atoms to be inequivalent and, therefore, the bridging halogen atoms *trans* to the terminal ones become inequivalent. As the temperature rises, the pyridinium cation begins to reorientate around the quasi-six-fold axis. This motion allows both terminal atoms to come close to equivalence and the α phase transforms into the β phase. The transition of the β-phase of the chloride to the metastable phase is due to the change in the cationic motion from free rotation to hindered rotation. This change causes the terminal atoms (and also the bridging atoms) to become inequivalent.

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