^{81}Br NQR and ^{1}H NMR of Ethylammonium Tetrabromomercurate (II) $(C_2H_5NH_3)_2HgBr_4$: Phase Transition and Molecular Motion

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Crystals of $(C_2H_5NH_3)_2HgBr_4$ were investigated by means of ^{81}Br NQR, T_1 of ^{1}H NMR, and DTA measurements. The crystals undergo phase transitions at T_{c1} = 342 K and T_{c2} = 96 K. In phase III ($T < T_{c2}$) sixteen ^{81}Br NQR lines, and in both phase II ($T_{c2} < T < T_{c1}$) and phase I ($T_{c1} < T$) four lines were observed. The DTA peak positions at the T_{c1} transition depend strongly on the thermal history. In the cooling runs from the melt the crystals exhibited a strange thermal behavior. The $\log T_1$ vs. T^{-1} curves of ^{1}H NMR (42.5 MHz), measured in $(C_2H_5ND_3)_2HgBr_4$ as well as $(C_2H_5NH_3)_2HgBr_4$, were characterized by V-shaped curves with a single minimum. They are explained by postulating C_3 reorientational motions of CH_3- and NH_3-groups with the experimentally same correlation time and activation enegy E_a. In Phase II, the E_a values were estimated as 13.9 kJmol^{-1} and 14.2 kJmol^{-1} for $(C_2H_5NH_3)_2HgBr_4$ and $(C_2H_5ND_3)_2HgBr_4$, respectively. The ^{2}H NMR spectra suggest that reorientation of the whole cations about the molecular axis is excited at high temperatures

Key words: $(C_2H_5NH_3)_2HgBr_4$; Phase Transition; Molecular Motion; NQR; NMR.

1. Introduction

The formation of a wide variety of halogenomercurates(II), such as $RHgX_3$, R_2HgX_4, and RHg_2X_5 (R = alkylammonium; X = Cl, Br, I) is well known [1, 2]. For many of these compounds structural phase transitions associated with cationic motions are expected. However, relatively few compounds of this kind have been investigated for the existence of phase transitions [3 - 12]. Nuclear quadrupole resonance (NQR) spectroscopy is a very sensitive method for the investigation of electronic states around the relevant nucleus, and hence phase transitions. Previously we have applied the halogen NQR to the compounds $(CH_3NH_3)_2HgX_4$ (X = Br, I) [13] and $[(CH_3)_4N]_2HgX_4$ (X = Cl, Br, I) [12]. In addition to an already-known phase transition in $[(CH_3)_4N]_2HgCl_4$ [7] it was found that $[(CH_3)_4N]_2HgX_4$ (X = Br, I) compounds also undergo phase transitions which are characteristically found in the β-K_2SO_4 structure. In the $(CH_3NH_3)_2HgX_4$ compounds no phase transition was deduced in the observed temperature range of 77 to ca. 380 K, but the NQR frequency (ν) vs. temperature (T) curves are very unusual. The ν vs. T curves of $[(CH_3)_4N]_2HgX_4$ are rather monotonous compared to those of $(CH_3NH_3)_2HgX_4$. The unusual ν vs. T dependence in the former compounds may be associated with the motion of the $CH_3NH_3^+$ ion which has a non-spherical charge distribution and also takes part in the N-H···X hydrogen bonds. In contrast, the $(CH_3)_4N^+$ ion has an almost spherical charge distribution and the C-H···X hydrogen bonding interaction may be neglected. It seems interesting to investigate the NQR ν vs. T curves and phase transitions in the other compounds with different cations. As an extension of the R_2HgBr_4 compounds, we have investi-

gated the phase transitions and the molecular motions in $(C_2H_5NH_3)_2HgBr_4$ by means of ^{81}Br NQR, ^{1}H and ^{2}H NMR, and DTA.

2. Experimental

Crystals of $(C_2H_5NH_3)_2HgBr_4$ were obtained by concentrating a methyl alcohol solution containing $HgBr_2$ and $C_2H_5NH_3Br$ in the molar ratio 1:2. The $C_2H_5NH_3Br$ crystals were obtained by adding hydrobromic acid to an aqueous solution of $C_2H_5NH_2$. The crystals were colorless deliquescent plates. The C, H, and N analyses were consistent with the chemical formula; found/calc.; weight %: C: 7.84/7.85; H: 2.46/2.63; N: 4.43/4.57 for $(C_2H_5NH_3)_2HgBr_4$. The partially deuterated compound $(C_2H_5ND_3)_2HgBr_4$ was prepared for the ^{2}H NMR as well as ^{1}H NMR measurements. The deuterated compound was obtained by mixing $C_2H_5ND_3Br$ and $HgBr_2$ in CH_3OD in a similar manner as the protonated analog. The $C_2H_5ND_3Br$ crystals were prepared by repeated recrystallizations of $C_2H_5NH_3Br$ from D_2O.

The DTA measurements were carried out by using a homemade DTA apparatus.

The NQR spectra were obtained by using a super-regenerative spectrometer and a Matec pulsed spectrometer. The signals of the former spectrometer were recorded on a recorder through a lock-in amplifier with Zeeman modulation. The accuracy of the frequency measurements is estimated to be within $\pm$ 0.02 MHz.

Spin-lattice relaxation times T_1 of ^{1}H NMR were measured by the inversion recovery method on a standard pulsed NMR spectrometer. As the magnetization recovery after the 180° pulse was slightly non-exponential at most temperatures, a longer component of T_1 was determined. The ^{2}H NMR powder spectra were recorded at 41.6 MHz (6.37 T). The measurements were carried out by means of a homemade spectrometer using a solid echo technique, followed by a Fourier transformation of the echo signal. The typical pulse length was 3 μs for an 8 mm diameter of sample tube.

3. Results and Discussion

3.1. ^{81}Br NQR and Phase Transitions

The ν vs. T curves of ^{81}Br NQR lines measured between 77 K and the melting point (378 K) are shown in Figure 1. The melting point was deduced from the DTA measurement. The ^{81}Br NQR frequencies at representative temperatures are listed in Table 1. The assignment to this nucleus was confirmed by the observation of the corresponding resonance

Table 1. ^{81}Br NQR frequencies (ν/MHz) of $(C_2H_5NH_3)_2HgBr_4$.

Phase III (77 K)				Phase II (280 K)	Phase I (360 K)
98.30	92.92	86.26	73.83	88.20	86.65
95.46	92.10	84.26	72.43	87.58	83.31
94.34	91.74	83.43	72.26	83.28	79.30
93.48	91.42	81.31	69.90	70.35	71.10

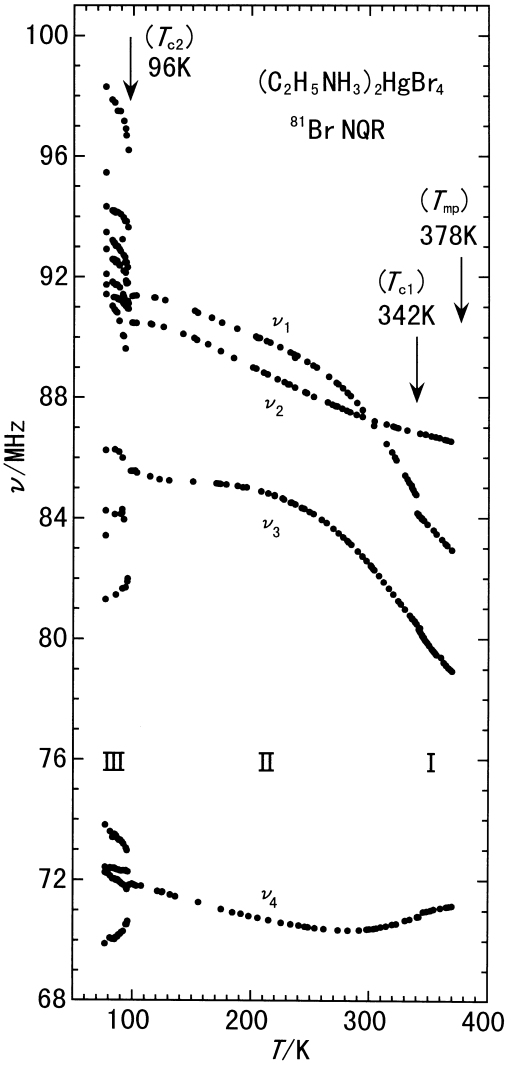

Fig. 1. Temperature dependence of ^{81}Br NQR frequencies of $(C_2H_5NH_3)_2HgBr_4$.

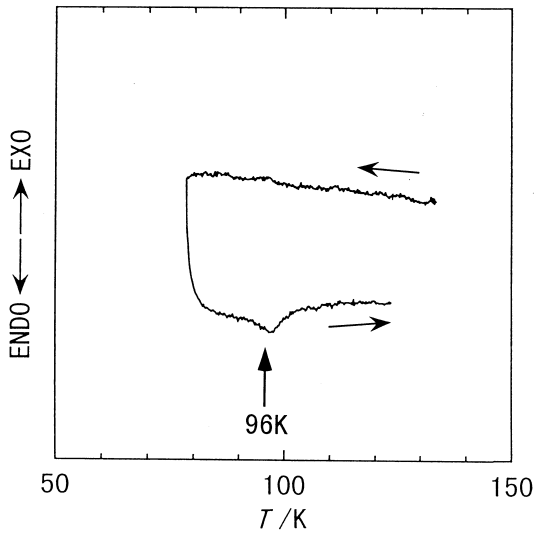

Fig. 2. A representative DTA curve for the T_{c2} = 96 K transition in $(C_2H_5NH_3)_2HgBr_4$.

lines for the ^{79}Br ones. These curves indicate the occurrence of two phase transitions at T_{c1} = 342 K and T_{c2} = 96 K in the measured range. Phase I (342 < T/K < 378) and phase II (96 < T/K < 342) are characterized by four lines with nearly the same intensities. By considering the low symmetry of the $C_2H_5NH_3^+$ ion it is difficult to imagine the existence of a high-symmetrical $HgBr_4^-$ tetrahedron in the crystal, and hence the four lines may be safely assigned to the respective non-equivalent Br atoms in a distorted anion. In accord with this expectation, the number of non-equivalent Br atoms in a $HgBr_4^-$ ion are three in $[(CH_3)_4N]_2HgBr_4$ [14] and four in both $(CH_3NH_3)_2HgBr_4$ [15] and $[(CH_3)_2NH_2]_2HgBr_4$ [16] at their room temperature structures.

On the other hand it was observed that sixteen lines exist in phase III (T/K < 96). Though the ν vs. T curves of these lines look complicated, a closer look shows that each line of phase II splits into four below T_{c2}. This indicates that four crystallographically equivalent $HgBr_4^-$ tetrahedra in phase II (and phase I) become nonequivalent in phase III, i. e., the unit cell of phase III has four-fold dimensions of that of phase II. The splitting of each line of phase II to four lines of phase III seems to occur discontinuously at T_{c2}, implying that the phase transition is a first-order one.

At the T_{c1} transition only a slight change is reflected on each line of both phase I and phase II. The largest frequency change is followed on the line

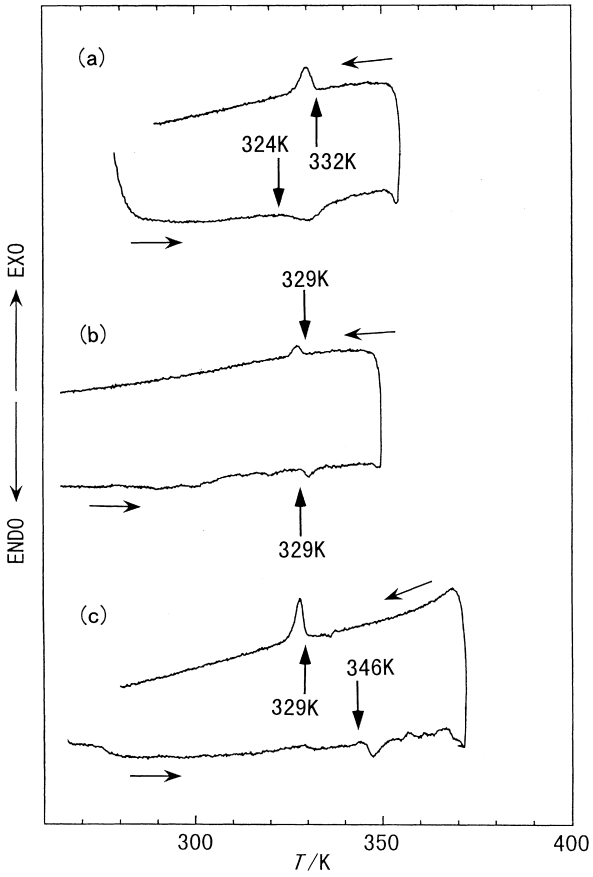

Fig. 3. Representative DTA curves for the T_{c1} = 342 K transition in the crystals of $(C_2H_5NH_3)_2HgBr_4$ which had not experienced melting. (a): a freshly prepared sample which had not experienced the T_{c1} transition; (b) and (c): the samples which had experienced the T_{c1} transition.

ν_1 (see Fig. 1), which jumps down ca. 500 kHz from phase II to phase I. The frequency discrepancy seen in each ν_3 and ν_4 between both phases are ca. 100 kHz. On the other hand, ν_2 follows only a slight change, less than ca. 50 kHz. For younger samples the ν vs. T curves showed that the transition temperature becomes by a few degrees higher than T_{c1}. The T_{c1} transition has a first-order nature. Each line in phase I was observable till ca. 7 K below the melting point T_{mp} = 378 K.

3.2. DTA Measurements and Thermal Behaviors

Figure 2 shows a representative DTA curve for the T_{c2} = 96 K transition. Though a hardly observable anomaly appeared in the cooling process, a small one

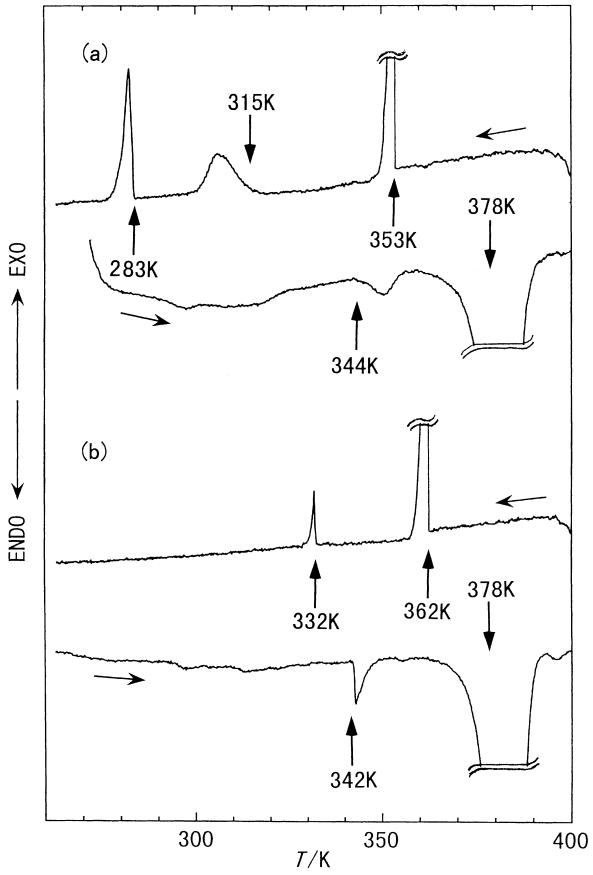

Fig. 4. Representative DTA curves for the T_{c1} = 342 K transition in the crystals of $(C_2H_5NH_3)_2HgBr_4$ which had experienced melting. (a) a sample which had not experienced melting; (b) a sample which had experienced melting.

was recognized at 96 K in the heating process. The DTA curves for the T_{c1} transition are shown in Figs. 3 and 4. It was found that the observed anomalies corresponding to the transitions were very dependent on the thermal process. Figure 3(a) shows an example for the run of a freshly prepared sample which had not experienced the T_{c1} transition. On heating a rather broad endothermic peak appeared at 324 K, while a relatively sharp exothermic one appeared at 332 K in cooling process. When the same process was repeated for the above sample, the peak positions changed strongly, depending on each heating or cooling run, as shown in the examples of Fig. 3 (b) and (c). On the other hand, Fig. 4 shows the examples of the process via melting. When the sample which had not experienced melting was heated, it showed a large melting peak at 378 K after the T_{c1} transition peak. On the contrary, the cooling process was characterized by three exothermic peaks, as shown in Fig. 4 (a), of which two were sharp and one was rather broad, indicating the complexity of the cooling process of this sample, exhibiting supercooling both on the T_{c1} transition and on the solidification. Interestingly, the sample experiencing the process of melting-solidifying several times showed two peaks instead of three in cooling process as shown in Figure 4 (b). Further, it was found that the peaks at 332 and 342 K corresponding to the T_{c1} transition were sharpened. The latter temperature coincides with the T_{c1} obtained from the NQR ν vs. T curves. It is worth to note the fact that the sample from the melt gives NQR signals just after solidification, whereas many similar compounds need a long time to recover the signals (e.g. a few months for $CH_3NH_3HgBr_3$) probably owing to a cation disorder remaining in the crystal.

3.3. ^{1}H T_1, ^{2}H NMR Line-shape, and Molecular Motions of Cations

The temperature dependence of ^{1}H T_1 measured at 42.5 MHz for $(C_2H_5NH_3)_2HgBr_4$ as well as $(C_2H_5ND_3)_2HgBr_4$ is shown in Figure 5. No change or anomaly was observed near T_{c1} and T_{c2} on the ^{1}H T_1 vs. $1/T$ curve of $(C_2H_5NH_3)_2HgBr_4$. One usually expects to observe two T_1 minima for the $C_2H_5NH_3^+$ ions in solids, the one at lower temperature of being ascribed to the C_3 reorientation of the CH_3-group, and a higher-temperature one to the C_3 reorientation of the NH_3- group because of possible H-bonds of the NH_3-group [17]. As seen in Fig. 5, however, the T_1-T curves are characterized by only a single minimum of 51 ms at ca. 165 K for the $C_2H_5NH_3^+$ ions in $(C_2H_5NH_3)_2HgBr_4$ and 80 ms at almost the same temperature for the C_2H_5-groups in $(C_2H_5ND_3)_2HgBr_4$, respectively. This observation indicates that both the CH_3- and NH_3-groups reorient with almost the same correlation times τ and activation energy E_a. Therefore we analyzed the T_1-T curve by assuming a single minimum and by using the BPP-type equation for T_1:

$$T_1^{-1} = C[\tau/(1+\omega^2\tau^2) + 4\tau/(1+4\omega^2\tau^2)], \quad (1)$$

where ω is an angular resonance frequency. An Arrhenius equation for the correlation times is assumed:

$$\tau = \tau_0 \exp(E_a/RT). \quad (2)$$

By the least-squares calculations of (1) and (2) for

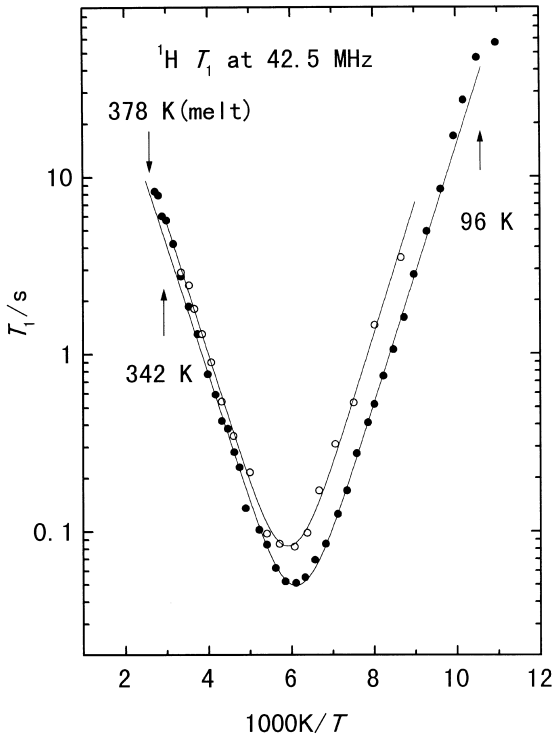

Fig. 5. Temperature dependence of ^{1}H T_1 at 42.5 MHz in $(C_2H_5NH_3)_2HgBr_4$ (●) and $(C_2H_5ND_3)_2HgBr_4$ (○). The solid lines show best-fitted curves to (1) and (2).

Table 2. Motional parameters obtained from ^{1}H NMR T_1 for $(C_2H_5NH_3)_2HgBr_4$ and $(C_2H_5ND_3)_2HgBr_4$.

Compound	C/s^{-2}	τ_0/s	E_a/kJ mol^{-1}
$(C_2H_5NH_3)_2HgBr_4$	3.79×10^9	8.3×10^{-14}	13.9
$(C_2H_5ND_3)_2HgBr_4$	2.26×10^9	9.4×10^{-14}	14.2

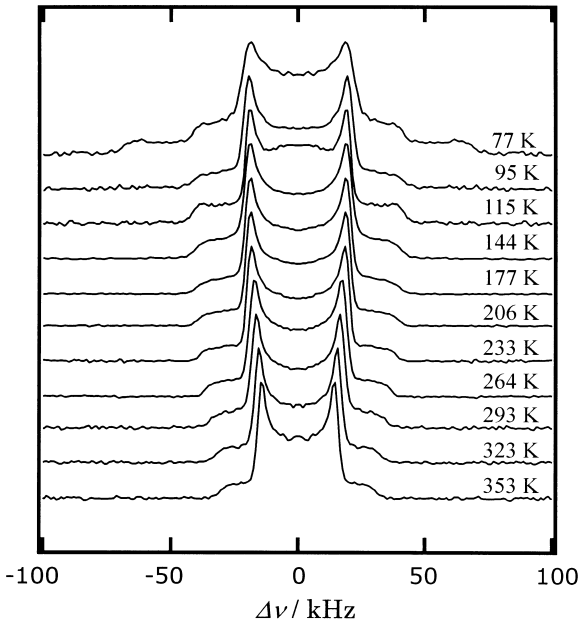

Fig. 6. ^{2}H NMR spectra of polycrystalline $(C_2H_5NH_3)_2HgBr_4$ at various temperatures.

T_1 in $(C_2H_5NH_3)_2HgBr_4$ and $(C_2H_5ND_3)_2HgBr_4$, the motional constant C, the correlation time at infinite temperature τ_0, and E_a were determined. Table 2 shows these motional parameters thus obtained. The E_a values for both compounds are experimentally the same, as expected, and slightly larger than 12.5 and 9.1 kJ/mol for the internal rotation barrier heights for the CH_3- and NH_3-groups in the $C_2H_5NH_3^+$ ion, which are estimated from *ab initio* MO calculations [17], indicating that the N-H···Br hydrogen bonds are weak.

The temperature dependence of the ^{2}H line-shape for $(C_2H_5ND_3)_2HgBr_4$ is shown in Figure 6. At 77 K, the line-shape is a superposition of two Pake spectra. The quadrupole splitting values of the narrower and wider bands are 39 and 130 kHz, respectively, when measured between the maximum intensities. These values are assigned to the C_3 reorienting and static ND_3-groups [18], if there exist two kinds of crystallographically nonequivalent cations in LTP. On heating the sample, the wider band disappeared till 95 K while the narrower splitting is almost unchanged up to 200 K. Above this temperature the splitting gradually decreased to 29.3 kHz at 353 K. This additional averaging suggests that reorientation of the whole ions about the molecular axis is excited at high temperatures. The unusual changes on the d ν/d T of the NQR $\nu(T)$ curves, begining from ca. 200 K on heating, may be connected with this motion of the cations.

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