81Br NQR and 1H NMR of Ethylammonium Tetrabromomercurate (II) 
(C₂H₅NH₃)₂HgBr₄: Phase Transition and Molecular Motion

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Crystals of (C₂H₅NH₃)₂HgBr₄ were investigated by means of 81Br NQR, T1 of 1HN M R , and DTA measurements. The crystals undergo phase transitions at Tc₁ = 342 K and Tc₂ = 96 K. In phase III (T < Tc₂) sixteen 81Br NQR lines, and in both phase II (Tc₂ < T < Tc₁) and phase I (Tc₁ < T) four lines were observed. The DTA peak positions at the Tc₁ transition depend strongly on the thermal history. In the cooling runs from the melt the crystals exhibited a strange thermal behavior. The log T1 vs. T−1 curves of 1H NMR (42.5 MHz), measured in (C₂H₅ND₃)₂HgBr₄ as well as (C₂H₅NH₃)₂HgBr₄, were characterized by V-shaped curves with a single minimum. They are explained by postulating C₃ reorientational motions of CH₃- and NH₃-groups with the experimentally same correlation time and activation energy Eₐ. In Phase II, the Eₐ values were estimated as 13.9 kJmol⁻¹ and 14.2 kJmol⁻¹ for (C₂H₅NH₃)₂HgBr₄ and (C₂H₅ND₃)₂HgBr₄, respectively. The 2H NMR spectra suggest that reorientation of the whole cations about the molecular axis is excited at high temperatures

Key words: (C₂H₅NH₃)₂HgBr₄; Phase Transition; Molecular Motion; NQR; NMR.

1. Introduction

The formation of a wide variety of halogenomercurates(II), such as RHgX₃, R₂HgX₄, and RHg₂X₅ (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 (CH₃NH₃)₂HgX₄ (X = Br, I) [13] and [(CH₃)₂N]₂HgX₄ (X = Cl, Br, I) [12]. In addition to an already-known phase transition in [(CH₃)₂N]₂HgCl₄ [7] it was found that [(CH₃)₂N]₂HgX₄ (X = Br, I) compounds also undergo phase transitions which are characteristically found in the β-K₂SO₄ structure. In the (CH₃NH₃)₂HgX₄ 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 [(CH₃)₂N]₂HgX₄ are rather monotonous compared to those of (CH₃NH₃)₂HgX₄. The unusual ν vs. T dependence in the former compounds may be associated with the motion of the CH₃NH₃⁺ ion which has a non-spherical charge distribution and also takes part in the N-H...X hydrogen bonds. In contrast, the (CH₃)₃N⁺ 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 R₂HgBr₄ compounds, we have investi-
gated the phase transitions and the molecular motions in \((C_2H_5NH_3)_2HgBr_4\) by means of \(^{81}\text{Br} \)NQR, \(^1\text{H}\) and \(^2\text{H}\) 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 \(C_2H_5NH_3\). 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 \(^2\text{H}\) NMR as well as \(^1\text{H}\) 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 \(C_2H_5ND_3\)Br 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 ±0.02 MHz.

Spin-lattice relaxation times \(T_1\) of \(^1\text{H}\) 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 \(^2\text{H}\) 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. \(^{81}\text{Br} \)NQR and Phase Transitions

The \(v\) vs. \(T\) curves of \(^{81}\text{Br} \)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 \(^{81}\text{Br} \)NQR frequencies at representative temperatures are listed in Table 1. The assignment to this nucleus was confirmed by the observation of the corresponding resonance
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$_2$H$_5$NH$_3^+$ 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$_3$)$_4$N]$_2$HgBr$_4$ [14] and four in both (CH$_3$NH$_3$)$_2$HgBr$_4$ [15] and [(CH$_3$)$_2$NH$_2$]$_2$HgBr$_4$ [16] at their room temperature structures.

On the other hand it was observed that sixteen lines exist in phase III (7/K $< 96$). Though the $\nu$ 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 occurs 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 $\nu_3$ (see Fig. 1), which jumps down ca. 500 kHz from phase II to phase I. The frequency discrepancy seen in each $\nu_2$ and $\nu_4$ between both phases are ca. 100 kHz. On the other hand, $\nu_2$ follows only a slight change, less than ca. 50 kHz. For younger samples the $\nu$ 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

![Figure 2](image)

**Fig. 2.** A representative DTA curve for the $T_{c2} = 96$ K transition in (C$_2$H$_5$NH$_3$)$_2$HgBr$_4$.

![Figure 3](image)

**Fig. 3.** Representative DTA curves for the $T_{c1} = 342$ K transition in the crystals of (C$_2$H$_5$NH$_3$)$_2$HgBr$_4$ 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.
Fig. 4. Representative DTA curves for the \( T_{c1} \) transition in the crystals of \((\text{C}_2\text{H}_5\text{NH}_3)_2\text{HgBr}_4\) 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 \( T \) 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 \( \text{CH}_3\text{NH}_3\text{HgBr}_3 \)) probably owing to a cation disorder remaining in the crystal.

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

The temperature dependence of \( 1\text{H} T_1 \) measured at 42.5 MHz for \((\text{C}_2\text{H}_5\text{NH}_3)_2\text{HgBr}_4 \) as well as \((\text{C}_2\text{H}_5\text{ND}_3)_2\text{HgBr}_4 \) is shown in Figure 5. No change or anomaly was observed near \( T_{c1} \) and \( T_{c2} \) on the \( 1\text{H} T_1 \) vs. \( 1/T \) curve of \((\text{C}_2\text{H}_5\text{NH}_3)_2\text{HgBr}_4 \). One usually expects to observe two \( T_1 \) minima for the \( \text{C}_2\text{H}_5\text{NH}_3^+ \) ions in solids, the one at lower temperature of being ascribed to the \( C_3 \) reorientation of the \text{CH}_3-group, and a higher-temperature one to the \( C_3 \) reorientation of the \text{NH}_3-group because of possible H-bonds of the \text{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 \( \text{C}_2\text{H}_5\text{NH}_3^+ \) ions in \((\text{C}_2\text{H}_5\text{NH}_3)_2\text{HgBr}_4 \) and 80 ms at almost the same temperature for the \( \text{C}_2\text{H}_5 \)-groups in \((\text{C}_2\text{H}_5\text{ND}_3)_2\text{HgBr}_4 \), respectively. This observation indicates that both the \text{CH}_3- and \text{NH}_3-groups reorient with almost the same correlation times \( \tau \) 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 \( T_1 \):

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

where \( \omega \) is an angular resonance frequency. An Arrhenius equation for the correlation times is assumed:

\[
\tau = \tau_0 \exp(E_a/RT).
\]

By the least-squares calculations of (1) and (2) for
$T_1$ in (C$_2$H$_5$NH$_3$)$_2$HgBr$_4$ and (C$_2$H$_5$ND$_3$)$_2$HgBr$_4$, the motional constant $C$, the correlation time at infinite temperature $\tau_0$, 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$_2$H$_5$NH$_3^+$ 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$_2$H$_5$ND$_3$)$_2$HgBr$_4$ 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 $\Delta \nu / dT$ of the NQR $\nu(T)$ curves, begining from ca. 200 K on heating, may be connected with this motion of the cations.

Table 2. Motional parameters obtained from $^1$H NMR $T_1$ for (C$_2$H$_5$NH$_3$)$_2$HgBr$_4$ and (C$_2$H$_5$ND$_3$)$_2$HgBr$_4$.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$C$/s$^{-2}$</th>
<th>$\tau_0$/s</th>
<th>$E_a$/kJ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(C$_2$H$_5$NH$_3$)$_2$HgBr$_4$</td>
<td>$3.79 \times 10^9$</td>
<td>$8.3 \times 10^{14}$</td>
<td>13.9</td>
</tr>
<tr>
<td>(C$_2$H$_5$ND$_3$)$_2$HgBr$_4$</td>
<td>$2.26 \times 10^9$</td>
<td>$9.4 \times 10^{14}$</td>
<td>14.2</td>
</tr>
</tbody>
</table>

Fig. 6. $^2$H NMR spectra of polycrystalline (C$_2$H$_5$NH$_3$)$_2$-HgBr$_4$ at various temperatures.