Self-Diffusion and Reorientation of Methylammonium Ions in \((\text{CH}_3\text{NH}_3)_2\text{ZnCl}_4\) Crystals as Studied by \(^1\text{H}-\text{NMR}

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Differential thermal analysis, differential scanning calorimetry, and measurements of the \(^1\text{H}\) spin-lattice relaxation times and second moments of \(^1\text{H}-\text{NMR}\) absorptions were performed on methylammonium tetrachlorozincate (II) crystals over a wide temperature range. A solid-solid phase transition was located at 477 K. From the \(^1\text{H}-\text{NMR}\) experiments it was found that the cations undergo overall reorientation as well as three dimensional translational self-diffusion in the high-temperature phase. In the low-temperature phase, a 120° reorientational motion of the CH\(_3\) and NH\(_3\) groups of the cation about its C—N bond axis was detected. The parameters for the motional modes of the cations in the crystal were evaluated from the analysis of the \(^1\text{H}-\text{NMR}\) experimental results.

1. Introduction

Metal complexes having the formula of \((\text{CH}_3\text{NH}_3)_2\text{MCl}_4\) can be classified into two groups from the crystal structure point of view. One group (\(\text{M} = \text{Cd}, \text{Mn}, \text{Fe}, \text{and Cu}\)) has a perovskite-type layer structure consisting of cationic layers and layers of corner-sharing chlorine octahedra with a divalent metal ion at the center \([1, 2]\). The other group, to which \((\text{CH}_3\text{NH}_3)_2\text{ZnCl}_4\) belongs, has a crystal structure similar to \(\beta\)-\(\text{K}_2\text{SO}_4\), containing discernible tetrahedral \([\text{MCl}_4]^{2-}\) complex anions \([3, 4]\). The complexes of the former type have been extensively investigated concerning characteristic phase transitions between which interesting phases are known to exist \([5-7]\). In the latter complexes, the change in the arrangement of the isolated cation or anion occurring at phase transitions has been investigated in detail on the \(\text{Zn(II)}\) and \(\text{Hg(II)}\) complexes \([8, 9]\).

\((\text{CH}_3\text{NH}_3)_2\text{ZnCl}_4\) forms monoclinic crystals at room temperature, belonging to the space group \(\text{P2}_1/\alpha\) with \(a = 10.873, b = 12.655, c = 7.648 \text{ Å}, \beta = 96.71^\circ\), and \(Z = 4\) \([3, 8]\). Pérez-Mato et al. reported the existence of two phase transitions in the crystal at 426 and 483 K from the study of thermal expansion, and calorimetric, dielectric, and optical experiments \([8]\). To clarify the ionic dynamics of methylammonium cations in the crystal, and also to obtain information about the mechanism of phase transition, we have carried out measurements of the 2nd moment \((M_2)\) of \(^1\text{H}-\text{NMR}\) absorptions, \(^1\text{H}\) spin-lattice relaxation time \((T_1)\), differential thermal analysis (DTA), and differential scanning calorimetry (DSC), over a wide range of temperature.

2. Experiments

\((\text{CH}_3\text{NH}_3)_2\text{ZnCl}_4\) was prepared by mixing aqueous solutions of \(\text{CH}_3\text{NH}_3\text{Cl}\) and \(\text{ZnCl}_2\). The colorless polycrystals obtained were purified by repeated recrystallization from methanol. A partially deuterated analog \((\text{CH}_3\text{ND}_3)_2\text{ZnCl}_4\) was prepared from the above sample by three times crystallization in heavy water. The samples were identified by taking X-ray powder patterns at room temperature and also usual elementary analysis. All diffraction lines recorded conformed with the reported crystal-structure data of the room-temperature phase \([3, 8]\). Anal. Caled. for \((\text{CH}_3\text{NH}_3)_2\text{ZnCl}_4\): C, 8.85%; H 4.42%; N, 10.32%;
Zn, 24.1%. Found: C, 8.83%; H, 4.21%; N, 10.24%; Zn, 24.1%.

The crystals were dried in a vacuum desiccator over P₂O₅ and NaOH, pulverized, put in glass ampoules in a dry bag and dried under high vacuum at room temperature for 24 h and additionally at 60 °C for 24 h to remove a trace of water and volatile impurities. Finally, the ampoules were sealed after putting in a small amount of dry nitrogen for better heat-exchange.

A homemade apparatus similar to that reported previously [10] was employed for the DTA. DSC was carried out with a Du Pont 9900 Thermal Analyzer. The wide-line ¹H NMR measurements were performed at 40 MHz by means of a JNM-MW-40S spectrometer from JEOL Co. and ¹H T₁ was determined at a Larmor frequency of 20 MHz using a homemade pulsed NMR spectrometer already described [11].

The measurements of ¹H T₁ at 32 MHz were performed with a pulsed ¹H-NMR spectrometer newly constructed by combining a gated amplifier Model 525, a preamplifier Model 254, and a receiver Model 625 from Matec Co., together with a pulse programmer, which was built by referring to the circuit diagram reported [12]. The sample temperatures were maintained with a gas-flow system similar to that already reported [11]. A conventional 180°-τ-90° pulse sequence was employed for the determination of ¹H T₁. The accuracy of the temperatures was estimated to be within ±1 K.

3. Results and Discussion

On heating, in the DTA, the sample with a rate of ca. 2 K min⁻¹, two large endothermic heat anomalies appeared at 477 and 552 K. These anomalies were attributed to a solid-solid phase transition and fusion. The corresponding entropy changes ΔSₛ and ΔSₕ, determined from the area of the transition peaks observed on the DSC curve, are 20 and 36 J K⁻¹ mol⁻¹, respectively. The transition temperature Tₓ of 477 K can be identified with that of 483 K reported by Perez-Mato et al. [8] if one takes into account the following difference in the data analysis. In the present study, the starting point of the anomaly in the DTA curve was assigned to Tₓ while Perez-Mato et al. assigned it to the peak temperature in the DSC experiments. When the sample was kept above ca. 490 K for a long time, it gradually decomposed and changed in color to brown.

No heat anomaly was found around 426 K in the present DTA and DSC experiments although the existence of a phase transition was reported [8]. No evidence for the occurrence of a phase transition around that temperature could be obtained also from the ¹H-NMR experiments. Therefore, we designate two solid phases existing above and below 477 K as high- and room-temperature phases, respectively, in the present investigation.

The temperature dependence of M₂ between 77 and 490 K is shown in Figure 1. An almost constant M₂ of (8.5 ± 0.5) G² was obtained below ca. 250 K. Comparing this value with the theoretical ones calculated for methylammonium halides [13–16], we concluded that both the CH₃ and NH₃ groups in the cation reorient by 120° about its C–N bond axis (abbreviated C₃ reorientation) more frequently than with 105° Hz even around 77 K. Above ca. 250 K, M₂ decreased gradually to (5 ± 1) G² around 470 K. At Tₓ, M₂ decreased suddenly to values less than 0.2 G². These extremely small values clearly indicate, in the high temperature phase, the onset of three dimensional self-diffusion and overall reorientation of the cation around its center of gravity.

The temperature dependences of ¹H T₁ for (CH₃NH₃)₂ZnCl₄ and (CH₃ND₃)₂ZnCl₄ are shown in Figure 2. ¹H T₁ values of (CH₃NH₃)₂ZnCl₄ observed at the Larmor frequencies of 20 and 32 MHz in the temperature ranges of 55–405 K and 294–507 K, respectively, are shown in the figure. For (CH₃ND₃)₂ZnCl₄, ¹H T₁ was determined at 20 MHz in the temperature range 58–213 K.

The log Tₓ vs. T⁻¹ plots in the room-temperature phase of (CH₃NH₃)₂ZnCl₄ and (CH₃ND₃)₂ZnCl₄ yielded the minimum Tₓ values of 21 and 33 ms, respectively, at almost the same temperature around
114 K as can be seen in Figure 2. Both complexes yielded a maximum $T_1$ at ca. 77 K. Referring to the foregoing discussion of $M_2$, the temperature dependence of $^1H$ $T_1$ in the room-temperature phase, especially below ca. 250 K, can be explained in terms of the $C_3$ reorientation of CH$_3$ and/or NH$_3$ groups in the crystal. The reorientation of either the CH$_3$ or the NH$_3$ group gives rise to $^1H$ $T_1$ expressed by [17, 18]

$$T_1^{-1} = \frac{2}{3} \gamma^2 A M_2 \left\{(\tau/(1 + \omega^2 \tau^2)) + 4 \tau/(1 + 4 \omega^2 \tau^2)\right\} \tag{1}$$

where $\gamma$, $A M_2$, $\tau$, and $\omega$ denote the gyromagnetic ratio of a proton, the reduction value of $M_2$ due to the onset of the reorientation of the CH$_3$ or NH$_3$ group, the correlation time of the reorientational motion, and the resonance angular frequency, respectively.

The $T_1$ minimum observed for (CH$_3$ND$_3$)$_2$ZnCl$_4$ at ca. 114 K can be assigned to the CH$_3$ $C_3$ reorientation. However, the minimum value of 33 ms is about twice as large as that of 14 ~ 15 ms observed for this motion of the CH$_3$ND$_3^+$ cation in some crystals and also calculated for the same [19, 20]. It is reported [3] that there exist two kinds of crystallographically nonequivalent cations in the room-temperature phase of (CH$_3$NH)$_3$ZnCl$_4$, and the cations of one kind form N–H…Cl type H-bonds having a H…Cl distance much shorter than that formed by the cations belonging to the other kind [3, 8]. Consequently, the $T_1$ minimum of (CH$_3$ND$_3$)$_2$ZnCl$_4$ appearing at ca. 114 K can be attributed to the CH$_3$ $C_3$ reorientation in the cations of the former kind. The other $T_1$ minimum of (CH$_3$ND$_3$)$_2$ZnCl$_4$ expected to exist below 50 K from the log $T_1$ vs. $T^{-1}$ plots in Fig. 2 is assignable to the same motion of the cations of the latter kind.

When two kinds of CH$_3$ groups exist in the crystal, $^1H$ $T_1$ for (CH$_3$ND$_3$)$_2$ZnCl$_4$ is written as

$$T_1^{-1} = \left\{\frac{2}{3} \gamma^2 A M_2 \left\{(\tau/(1 + \omega^2 \tau^2)) + 4 \tau/(1 + 4 \omega^2 \tau^2)\right\} + \frac{2}{3} \gamma^2 A M_2 \left\{(\tau///(1 + \omega^2 \tau^2)) + 4 \tau//(1 + 4 \omega^2 \tau^2)\right\}\right\} \tag{2}$$

where subscripts I and II denote the two kinds of CH$_3$ groups giving the $T_1$ minimum at high and low temperatures, respectively. Here, $\tau//_{II}$ is considered to be much shorter than $\tau//_I$, and the following relation must be satisfied:

$$\omega \tau//_{II} \ll 1. \tag{3}$$

Accordingly, (2) can be rewritten as

$$T_1^{-1} = \left\{\frac{2}{3} \gamma^2 A M_2 \left\{(\tau_I/(1 + \omega^2 \tau_I^2)) + 4 \tau_I/(1 + 4 \omega^2 \tau_I^2)\right\} + \frac{10}{3} \gamma^2 A M_2 \tau_{II}\right\} \tag{4}$$

Assuming an Arrhenius relationship for the activation energy $E_{ai}(i = I, II)$ for the motion under consideration, $\tau_i (i = I, II)$ can be written as

$$\tau_i = \tau_{0i} \exp(E_{ai}/RT), \tag{5}$$

where $\tau_{0i}$ expresses the correlation time for each CH$_3$ group at infinite temperature.

Fig. 2. Temperature dependences of $^1H$ $T_1$ observed at 20(●) and 32(○) MHz for (CH$_3$NH)$_3$ZnCl$_4$, and at 20(●) MHz for (CH$_3$ND)$_3$ZnCl$_4$. Solid lines indicate the sum of two independent BPP type $T_1$ curves attributable to two kinds of crystallographically nonequivalent cations. Inset: $2 \leq kK/T \leq 3.3$. 
The $^1$H $T_1$ data observed for $(\text{CH}_3\text{ND}_3)_2\text{ZnCl}_4$ were fitted to (4) and (5) using the least-squares method. The adjustable parameters $E_a$, $\tau_0$, and $\Delta M_2$ were employed in the fitting calculation; the most probable values obtained are listed in Table 1. The theoretical $T_1$ curve calculated for $(\text{CH}_3\text{ND}_3)_2\text{ZnCl}_4$ by use of the above parameters is given by a solid line in Figure 2.

By comparing the $T_1$ data observed for $(\text{CH}_3\text{NH}_3)_2\text{ZnCl}_4$ with those of $(\text{CH}_3\text{ND}_3)_2\text{ZnCl}_4$, and also considering the foregoing $M_2$ results, the deep $T_1$ minimum in the room temperature phase of the former complex can be attributed to the reorientation of the CH$_3$ and NH$_3^+$ groups simultaneously excited in the cation. Because there are two kinds of crystallographically nonequivalent cations in the crystal, the $^1$H $T_1$ decrease with decreasing temperature below 70 K is considered as arising from the same motions as described above for the remaining cations in the crystal. Hereafter, we denote the two kinds of cations as the cations I and II, and let the cation I be more tightly bound in the crystal than II. The motion responsible for the $T_1$ decrease below 70 K is assignable to the “correlated reorientation” of II, which is defined as the C$_3$ reorientation of the cation as a whole with keeping its rigid structure [21]. This is because $E_{\text{all}}$ estimated for the motion from the gradient of the log $T_1$ vs. $T^{-1}$ curve was ca. 4 kJ mol$^{-1}$, being much lower than ca. 8 kJ mol$^{-1}$ estimated for the barrier to the intracationionic or internal rotation [21–23].

The fact that the $T_1$ minimum temperature is approximately the same for $(\text{CH}_3\text{NH}_3)_2\text{ZnCl}_4$ and $(\text{CH}_3\text{ND}_3)_2\text{ZnCl}_4$ implies that the CH$_3$ and NH$_3^+$ groups in the cation I have correlation times of the C$_3$ reorientation being the same or very close to each other. However, it is doubtful whether or not the cation I performs “correlated reorientation”, because a fairly large $E_{\text{all}}$ of ca. 10 kJ mol$^{-1}$ was evaluated from the gradient of the log $T_1$ vs. $T^{-1}$ curve at its high-temperature side.

Here, we assume the correlation times for the motion of the CH$_3$ and NH$_3^+$ groups in I are the same because it is difficult to separate the observed $T_1$ minimum into two minima. When one accepts this assumption, the $^1$H $T_1$ data for $(\text{CH}_3\text{NH}_3)_2\text{ZnCl}_4$ can be analyzed by using (4) and (5), where the subscripts I and II denote the cations I and II, respectively. A fitting calculation similar to that performed for $(\text{CH}_3\text{ND}_3)_2\text{ZnCl}_4$ was carried out, and the best-fitted curve calculated with the values of the adjustable parameters given in Table 1 is depicted in Fig. 2 by a solid line.

The $E_{\text{all}}$ value of 3.8 kJ mol$^{-1}$ evaluated from the $T_1$ curve of $(\text{CH}_3\text{NH}_3)_2\text{ZnCl}_4$ obtained in the low-temperature region agrees well with that of 3.7 kJ mol$^{-1}$ obtained for $(\text{CH}_3\text{ND}_3)_2\text{ZnCl}_4$. This confirms that the protonated cation II undergoes correlated reorientation below ca. 70 K. On the other hand, $E_{\text{al}} = 10.7$ kJ mol$^{-1}$ of $(\text{CH}_3\text{NH}_3)_2\text{ZnCl}_4$ is somewhat larger than 10.1 kJ mol$^{-1}$ evaluated for $(\text{CH}_3\text{ND}_3)_2\text{ZnCl}_4$, suggesting that the protonated cation II performs uncorrelated reorientation. The $E_{\text{al}}$ values of both cations are small as compared with the activation energies of 26.4 and 32.0 kJ mol$^{-1}$ reported for the C$_3$ reorientation of the NH$_3^+$ groups of CD$_3$NH$_3\text{Cl}$ in its β and γ phases, respectively [19].

Accordingly, the H-bonds of N—H⋯Cl type in the present complex can be concluded to be fairly weak. In particular, the interactions between the cation II and its surrounding anions are very weak, and II is considered to reorient very freely in the crystal. The $^1$H $T_1$ values of $(\text{CH}_3\text{NH}_3)_2\text{ZnCl}_4$ determined at 20 and 32 MHz above room temperature are given in Fig. 2 as an insert, which is enlarged on the $T^{-1}$ scale. $^1$H $T_1$ observed at 32 MHz gave a maximum at ca. 435 K. A slight discontinuity in $T_1$ was observed at 478 ± 1 K, which temperature agrees well with $T_e$ determined by DTA carried out in the present study. In the high-temperature phase, log $T_1$ decreased linearly and smoothly with increasing temperature. No remarkable change in the $^1$H $T_1$ curve was observed.

### Table 1. Motional parameters of methylammonium ions: activation energy $E_a$ for the motion, correlation time $\tau_0$ at the limit of infinite temperature, and the reduction of the $^1$H-NMR 2nd moment $\Delta M_2$ in $(\text{CH}_3\text{NH}_3)_2\text{ZnCl}_4$ and $(\text{CH}_3\text{ND}_3)_2\text{ZnCl}_4$ crystals.

<table>
<thead>
<tr>
<th>Chemical</th>
<th>$E_a$ kJ mol$^{-1}$</th>
<th>$\tau_0 \times 10^{13}$/s</th>
<th>$\Delta M_2/\text{G}^2$</th>
<th>Motion</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(\text{CH}_3\text{NH}_3)_2\text{ZnCl}_4$</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>room-temperature phase</td>
<td>10.7 ± 0.2</td>
<td>0.67 ± 0.05</td>
<td>9.2 ± 1.5</td>
<td>CH$_3$ and NH$_3^+$ reorient.</td>
</tr>
<tr>
<td>high-temperature phase</td>
<td>3.8 ± 0.2</td>
<td></td>
<td></td>
<td>CH$_3$ and NH$_3^+$ reorient.</td>
</tr>
<tr>
<td>$(\text{CH}_3\text{ND}_3)_2\text{ZnCl}_4$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>room-temperature phase</td>
<td>10.1 ± 0.2</td>
<td>1.0 ± 0.1</td>
<td>5.5 ± 0.2</td>
<td>CH$_3$ reorient.</td>
</tr>
<tr>
<td></td>
<td>3.7 ± 0.2</td>
<td></td>
<td></td>
<td>CH$_3$ reorient.</td>
</tr>
</tbody>
</table>
around 426 K, at which temperature the existence of a phase transition was reported in [8].

Taking into account that the $M_2$ values observed just below $T_n$ are ca. $5 \text{ G}^2$, the $T_1$ decrease with increasing temperature around 470 K in the room-temperature phase is probably due to the occurrence of a cationic motion other than the $C_3$ reorientation. In the high-temperature phase, the $T_1$ decrease with increasing temperature is attributable to cationic self-diffusion, because of $M_2$ being $< 0.2 \text{ G}^2$. The activation energy for self-diffusion of the cations is estimated to be $(26 \pm 4) \text{ kJ mol}^{-1}$ from the gradient of the log $T_1$ vs. $T^{-1}$ curve.

The estimated $E_2$ value for self-diffusion of the CH$_3$NH$_3^+$ cations in the complex crystal is much smaller than $E_2$ of 76 kJ mol$^{-1}$ for the same motion in the high-temperature phase of (CH$_3$NH$_3$)$_2$SO$_4$ as determined from $^1$H-NMR [24]. This large discrepancy seems to related to the difference in the ionic interactions. Weaker electrostatic interaction of H-bonding between NH$_3^+$ groups and the anions can be expected to exist in the present complex than in the sulfate. Also in the low-temperature phase the $E_2$ values for NH$_3^+$ $C_3$ reorientation are much smaller in the present complex than those $(16.4 \sim 29.1 \text{ kJ mol}^{-1})$ in the sulfate, although the $E_2$ values of the CH$_3$C$_3$ reorientation in these two salts are comparable $(7.6 \sim 13.5 \text{ kJ mol}^{-1})$ for the sulfate) in the low-temperature phases immediately below $T_n$.

The rapid self-diffusion and overall rotation of the cations in the high-temperature phase of (CH$_3$NH$_3$)$_2$-ZnCl$_4$ is analogous to that in the high-temperature phases of several methyl-substituted ammonium salts, (CH$_3$)$_n$NH$_4^+$-X ($n = 0, 1, 2, 3$; X = NO$_3^-$, ClO$_4^-$, I$^-$) and (CH$_3$NH$_3$)$_2$SO$_4$ [16, 23–30]. In some of these salts, it has been confirmed by NMR, X-ray and DSC measurements that these phases can be considered as ionic plastic phases similar to the plastic crystals of molecular compounds [16, 23–27]. For example, methylammonium nitrate was shown to form CsCl-type cubic crystals in this phase, and small $\Delta S_f (12 \text{ J K}^{-1} \text{ mol}^{-1})$ and large $\Delta S_m (28 \text{ J K}^{-1} \text{ mol}^{-1})$ were observed [26]. For (CH$_3$NH$_3$)$_2$ZnCl$_4$, however, $\Delta S_f (36 \text{ J K}^{-1} \text{ mol}^{-1})$ is much larger than $\Delta S_m (20 \text{ J K}^{-1} \text{ mol}^{-1})$. This is probably because the [ZnCl$_4$]$^{2-}$ ions are not free enough to reorient even in the high-temperature phase. Similar results, $\Delta S_f (43 \text{ J K}^{-1} \text{ mol}^{-1})$ and $\Delta S_m (26 \text{ J K}^{-1} \text{ mol}^{-1})$, were also observed for (CH$_3$NH$_3$)$_2$SO$_4$ in our preliminary DSC measurements. Thus there seem to exist remarkable differences in the plastic nature between methylammonium salts with divalent anions and those with monovalent anions.

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