Self-Diffusion and Reorientation of Methylammonium Ions in $(CH_3NH_3)_2ZnCl_4$ Crystals as Studied by ^{1}H-NMR

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Differential thermal analysis, differential scanning calorimetry, and measurements of the ^{1}H spin-lattice relaxation times and second moments of ^{1}H-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}H-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}H-NMR experimental results.

1. Introduction

Metal complexes having the formula of $(CH_3NH_3)_2$-MCl_4 can be classified into two groups from the crystal structure point of view. One group (M = Cd, Mn, Fe, 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 $(CH_3NH_3)_2ZnCl_4$ belongs, has a crystal structure similar to β-K_2SO_4, containing discernible tetrahedral $[MCl_4]^{2-}$ 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 Zn(II) and Hg(II) complexes [8, 9].

$(CH_3NH_3)_2ZnCl_4$ forms monoclinic crystals at room temperature, belonging to the space group $P2_1/a$ with $a = 10.873$, $b = 12.655$, $c = 7.648$ Å, $\beta = 96.71°$, 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}H-NMR absorptions, ^{1}H spin-lattice relaxation time (T_1), differential thermal analysis (DTA), and differential scanning calorimetry (DSC), over a wide range of temperature.

2. Experiments

$(CH_3NH_3)_2ZnCl_4$ was prepared by mixing aqueous solutions of CH_3NH_3Cl and $ZnCl_2$. The colorless polycrystals obtained were purified by repeated recrystallization from methanol. A partially deuterated analog $(CH_3ND_3)_2ZnCl_4$ 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. Calcd. for $(CH_3NH_3)_2ZnCl_4$: C, 8.85%; H 4.42%; N, 10.32%;

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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 P_2O_5 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 ^{1}H NMR measurements were performed at 40 MHz by means of a JNM-MW-40S spectrometer from JEOL Co. and ^{1}H T_1 was determined at a Larmor frequency of 20 MHz using a homemade pulsed NMR spectrometer already described [11].

The measurements of ^{1}H T_1 at 32 MHz were performed with a pulsed ^{1}H-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 programer, 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 ^{1}H T_1. 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 ΔS_{tr} and ΔS_f, 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 T_{tr} of 477 K can be identified with that of 483 K reported by Pérez-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 T_{tr} while Pérez-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.

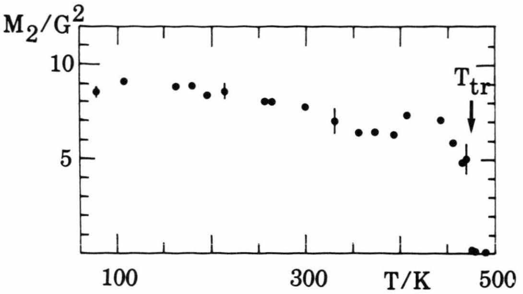

Fig. 1. ^{1}H NMR second moment (M_2) of $(CH_3NH_3)_2ZnCl_4$ vs. temperature. T_{tr} indicated by an arrow, is the phase transition temperature determined by DTA in the present study.

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 ^{1}H-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 M_2 between 77 and 490 K is shown in Figure 1. An almost constant M_2 of $(8.5 \pm 0.5)\,G^2$ was obtained below ca. 250 K. Comparing this value with the theoretical ones calculated for methylammonium halides [13–16], we concluded that both the CH_3 and NH_3^+ groups in the cation reorient by 120° about its C–N bond axis (abbreviated C_3 reorientation) more frequently than with 10^5 Hz even around 77 K. Above ca. 250 K, M_2 decreased gradually to $(5 \pm 1)\,G^2$ around 470 K. At T_{tr} M_2 decreased suddenly to values less than 0.2 G^2. 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 ^{1}H T_1 for $(CH_3NH_3)_2ZnCl_4$ and $(CH_3ND_3)_2ZnCl_4$ are shown in Figure 2. ^{1}H T_1 values of $(CH_3NH_3)_2ZnCl_4$ 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 $(CH_3ND_3)_2$-$ZnCl_4$, ^{1}H T_1 was determined at 20 MHz in the temperature range 58–213 K.

The $\log T_1$ vs. T^{-1} plots in the room-temperature phase of $(CH_3NH_3)_2ZnCl_4$ and $(CH_3ND_3)_2ZnCl_4$ yielded the minimum T_1 values of 21 and 33 ms, respectively, at almost the same temperature around

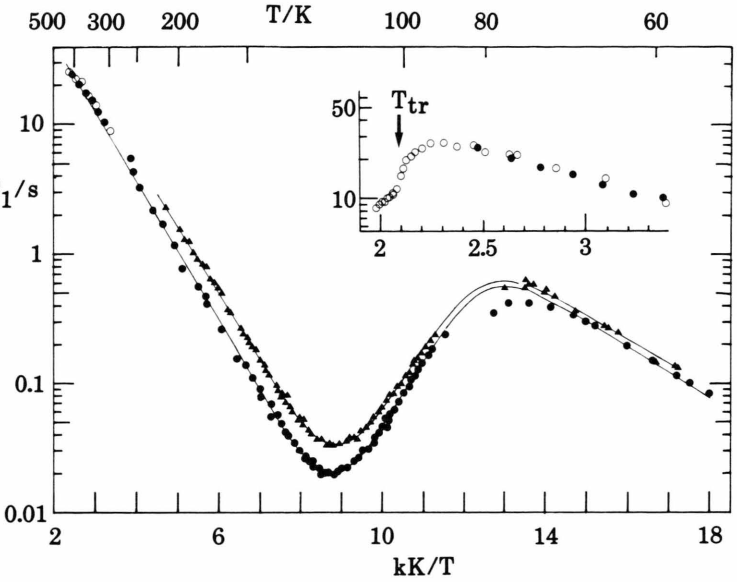

Fig. 2. Temperature dependences of ^{1}H T_1 observed at 20(●) and 32(○) MHz for $(CH_3NH_3)_2ZnCl_4$, and at 20(▲) MHz for $(CH_3ND_3)_2ZnCl_4$. Solid lines indicate the sum of two independent BPP type T_1 curves attributable to two kinds of crystallographically nonequivalent cations. Inset: $2 \leq kK/T \leq 3.3$.

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 ^{1}H 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 ^{1}H T_1 expressed by [17, 18]

$$T_1^{-1} = (2/3)\,\gamma^2\,\Delta M_2\{\tau/(1+\omega^2\tau^2) + 4\tau/(1+4\omega^2\tau^2)\} \tag{1}$$

where γ, ΔM_2, τ, and ω 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 $(CH_3ND_3)_2ZnCl_4$ 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 $CH_3ND_3^+$ 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 $(CH_3NH_3)_2ZnCl_4$, 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 $(CH_3ND_3)_2ZnCl_4$ 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 $(CH_3ND_3)_2ZnCl_4$ 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, ^{1}H T_1 for $(CH_3ND_3)_2ZnCl_4$ is written as

$$T_1^{-1} = (2/3)\,\gamma^2\,\Delta M_{2\mathrm{I}}\{\tau_\mathrm{I}/(1+\omega^2\tau_\mathrm{I}^2) + 4\tau_\mathrm{I}/(1+4\omega^2\tau_\mathrm{I}^2)\} + (2/3)\,\gamma^2\,\Delta M_{2\mathrm{II}}\{\tau_\mathrm{II}/(1+\omega^2\tau_\mathrm{II}^2) + 4\tau_\mathrm{II}/(1+4\omega^2\tau_\mathrm{II}^2)\}, \tag{2}$$

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, τ_II is considered to be much shorter than τ_I, and the following relation must be satisfied:

$$\omega\,\tau_\mathrm{II} \ll 1. \tag{3}$$

Accordingly, (2) can be rewritten as

$$T_1^{-1} = (2/3)\,\gamma^2\,\Delta M_{2\mathrm{I}}\{\tau_\mathrm{I}/(1+\omega^2\tau_\mathrm{I}^2) + 4\tau_\mathrm{I}/(1+4\omega^2\tau_\mathrm{I}^2)\} + (10/3)\,\gamma^2\,\Delta M_{2\mathrm{II}}\,\tau_\mathrm{II}. \tag{4}$$

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

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

where $\tau_{0\mathrm{i}}$ expresses the correlation time for each CH_3 group at infinite temperature.

The ^{1}H T_1 data observed for $(CH_3ND_3)_2ZnCl_4$ were fitted to (4) and (5) using the least-squares method. The adjustable parameters E_{ai}, τ_{0i}, and ΔM_{2i} were employed in the fitting calculation; the most probable values obtained are listed in Table 1. The theoretical T_1 curve calculated for $(CH_3ND_3)_2ZnCl_4$ by use of the above parameters is given by a solid line in Figure 2.

By comparing the T_1 data observed for $(CH_3NH_3)_2ZnCl_4$ with those of $(CH_3ND_3)_2ZnCl_4$, 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_{aII} 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 intracationic or internal rotation [21–23].

The fact that the T_1 minimum temperature is approximately the same for $(CH_3NH_3)_2ZnCl_4$ and $(CH_3ND_3)_2ZnCl_4$ 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_{aI} 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 $(CH_3NH_3)_2ZnCl_4$ 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 $(CH_3ND_3)_2ZnCl_4$ 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.

Table 1. Motional parameters of methylammonium ions; activation energy E_a for the motion, correlation time τ_0 at the limit of infinite temperature, and the reduction of the ^{1}H-NMR 2nd moment ΔM_2 in $(CH_3NH_3)_2ZnCl_4$ and $(CH_3ND_3)_2ZnCl_4$ crystals.

E_a/kJ mol^{-1}	$\tau_0 \times 10^{13}$/s	$\Delta M_2/G^2$	Motion
$(CH_3NH_3)_2ZnCl_4$			
room-temperature phase			
10.7 ± 0.2	0.67 ± 0.05	9.2 ± 1.5	CH_3 and NH_3^+ reorient.
3.8 ± 0.2			CH_3 and NH_3^+ reorient.
high-temperature phase			
26 ± 4			cationic self-diffusion
$(CH_3ND_3)_2ZnCl_4$			
room-temperature phase			
10.1 ± 0.2	1.0 ± 0.1	5.5 ± 0.2	CH_3 reorient.
3.7 ± 0.2			CH_3 reorient.

The E_{aII} value of 3.8 kJ mol^{-1} evaluated from the T_1 curve of $(CH_3NH_3)_2ZnCl_4$ obtained in the low-temperature region agrees well with that of 3.7 kJ mol^{-1} obtained for $(CH_3ND_3)_2ZnCl_4$. This confirms that the protonated cation II undergoes correlated reorientation below ca. 70 K. On the other hand, E_{aI} = 10.7 kJ mol^{-1} of $(CH_3NH_3)_2ZnCl_4$ is somewhat larger than 10.1 kJ mol^{-1} evaluated for $(CH_3ND_3)_2ZnCl_4$, suggesting that the protonated cation II performs uncorrelated reorientation. The E_{aI} 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_3NH_3Cl 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 $(CH_3NH_3)_2ZnCl_4$ 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_{tr} 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 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_{tr} are ca. 5 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 G^2. The activation energy for self-diffusion of the cations is estimated to be (26 ± 4) kJ mol^{-1} from the gradient of the $\log T_1$ vs. T^{-1} curve.

The estimated E_a value for self-diffusion of the $CH_3NH_3^+$ cations in the complex crystal is much smaller than E_a of 76 kJ mol^{-1} for the same motion in the high-temperature phase of $(CH_3NH_3)_2SO_4$ as determined from ^{1}H-NMR [24]. This large discrepancy seems to related to the difference in the interionic 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_a values for NH_3^+ C_3 reorientation are much smaller in the present complex than those ($16.4 \sim 29.1$ kJ mol^{-1}) in the sulfate, although the E_a values of the CH_3C_3 reorientation in these two salts are comparable ($7.6 \sim 13.5$ kJ mol^{-1} for the sulfate) in the low-temperature phases immediately below T_{tr}.

The rapid self-diffusion and overall rotation of the cations in the high-temperature phase of $(CH_3NH_3)_2ZnCl_4$ is analogous to that in the high-temperature phases of several methyl-substituted ammonium salts, $(CH_3)_nNH_{4-n}X$ ($n = 0, 1, 2, 3$: $X = NO_3, ClO_4, I$) and $(CH_3NH_3)_2SO_4$ [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 ΔS_f (12 J K^{-1} mol^{-1}) and large ΔS_{tr} (28 J K^{-1} mol^{-1}) were observed [26]. For $(CH_3NH_3)_2ZnCl_4$, however, ΔS_f(36 J K^{-1} mol^{-1}) is much larger than ΔS_{tr} (20 J K^{-1} 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, ΔS_f (43 J K^{-1} mol^{-1}) and ΔS_{tr} (26 J K^{-1} mol^{-1}), were also observed for $(CH_3NH_3)_2SO_4$ 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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