

# <sup>1</sup>H NMR Studies on the Cation Motions in Crystalline Cadmium Bromide Complexes [C(NH<sub>2</sub>)<sub>3</sub>]Cd<sub>2</sub>Br<sub>5</sub>, [(CH<sub>3</sub>)<sub>3</sub>NH]<sub>3</sub>Cd<sub>2</sub>Br<sub>7</sub>, and [*i*-C<sub>3</sub>H<sub>7</sub>NH<sub>3</sub>]CdBr<sub>3</sub>

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<sup>1</sup>H NMR  $T_1$  measurements of crystalline [C(NH<sub>2</sub>)<sub>3</sub>]Cd<sub>2</sub>Br<sub>5</sub> showed a single minimum due to the  $C_3$  reorientation of the planar [C(NH<sub>2</sub>)<sub>3</sub>]<sup>+</sup> ion with an activation energy ( $E_a$ ) of 35.8 kJ mol<sup>-1</sup>. In [(CH<sub>3</sub>)<sub>3</sub>NH]<sub>3</sub>Cd<sub>2</sub>Br<sub>7</sub> crystals, two  $T_1$  minima appeared which are assigned to the  $C_3$  reorientation of methyl groups in the [(CH<sub>3</sub>)<sub>3</sub>NH]<sup>+</sup> cation with  $E_a$  = 13.0 kJ mol<sup>-1</sup> and to the  $C_3$  reorientation of a whole cation around the molecular  $C_3$  axis with  $E_a$  = 28.9 kJ mol<sup>-1</sup>. In [*i*-C<sub>3</sub>H<sub>7</sub>NH<sub>3</sub>]CdBr<sub>3</sub> crystals, a very broad  $T_1$  minimum appeared near 160 K which is assigned to the  $C_3$  reorientations of two methyl groups with  $E_a$  = 11.3 kJ mol<sup>-1</sup> and of an NH<sub>3</sub> group with  $E_a$  = 13.3 kJ mol<sup>-1</sup> in the [*i*-C<sub>3</sub>H<sub>7</sub>NH<sub>3</sub>]<sup>+</sup> ion, and another minimum with  $E_a$  = 23.5 kJ mol<sup>-1</sup> near 300 K assigned to a higher order molecular motion of the cation.

**Key words:** <sup>1</sup>H NMR,  $T_1$ , DSC, Phase Transition, Cationic Motion

## Introduction

The crystal structures of [C(NH<sub>2</sub>)<sub>3</sub>]Cd<sub>2</sub>Br<sub>5</sub> (**1**), [(CH<sub>3</sub>)<sub>3</sub>NH]<sub>3</sub>Cd<sub>2</sub>Br<sub>7</sub> (**2**) and [*i*-C<sub>3</sub>H<sub>7</sub>NH<sub>3</sub>]CdBr<sub>3</sub> (**3**) have been determined [1, 2], and hydrogen bond networks were observed in each of them. The temperature dependence of <sup>81</sup>Br nuclear quadrupole resonance (NQR) frequencies and differential scanning calorimetry (DSC) measurements for **1** showed a first-order-like second-order phase transition at 283 K and a first-order phase transition at 535 K [1]. In **2** the disappearance of Br NQR frequencies was observed above 243 K, and a phase transition was detected at 436 K by differential thermal analysis (DTA). In **3** the <sup>81</sup>Br NQR lines disappeared above 193 K, and there was a thermal anomaly at 224 K in the DTA curve [2]. In these crystals the cationic motions seem to be involved in these phase transitions and also in the disappearance of NQR lines owing to fluctuations of the electric field gradients (EFG) at Br sites through changes in hydrogen bonds. In order to investigate the relation between the NQR results and the cation motion in these crystals, we undertook <sup>1</sup>H NMR experiments.

## Results and Discussion

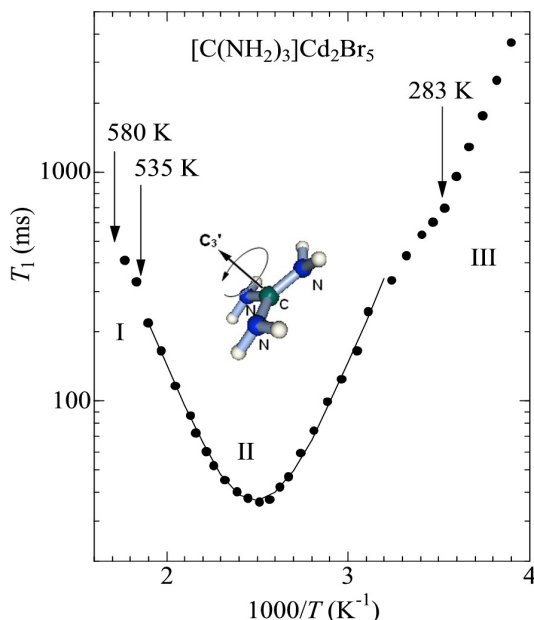
### [C(NH<sub>2</sub>)<sub>3</sub>]Cd<sub>2</sub>Br<sub>5</sub> (**1**)

The temperature dependence of the <sup>1</sup>H NMR (42.5 MHz) spin-lattice relaxation times ( $T_1$ ) at temperatures between 263 and 570 K below the temperature of decomposition at 580 K is shown in Fig. 1. Two phase transitions appear as deflection points of the log  $T_1$  vs.  $T^{-1}$  curve near 283 and 535 K. The phases are named as I, II and III in the order of decreasing temperature. Only one  $T_1$  minimum with 36 ms appears at 400 K in phase II. The planar [C(NH<sub>2</sub>)<sub>3</sub>]<sup>+</sup> ions usually undergo the  $C_3$  reorientation about the pseudo  $C_3$  axis perpendicular to a molecular plane in crystalline solids [3–6]. As the  $T_1$  minimum value of 36 ms is really comparable with those observed and calculated in [3–6], this  $T_1$  behavior is assignable to the cationic  $C_3$  reorientation, as shown by the inset of Fig. 1. The temperature dependence of  $T_1$  is analyzed by using the BPP-type equation and the Arrhenius relation for the correlation time  $\tau$  of the reorientation, respectively (Eqs. 1 and 2).

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

Table 1. Motional parameters in  $[\text{C}(\text{NH}_2)_3]\text{Cd}_2\text{Br}_5$  (**1**),  $[(\text{CH}_3)_3\text{NH}]\text{Cd}_2\text{Br}_7$  (**2**), and  $[i\text{-C}_3\text{H}_7\text{NH}_3]\text{CdBr}_3$  (**3**).

Compound	$C$ ( $10^9 \text{ s}^{-2}$ )	$\tau_0$ ( $10^{-14} \text{ s}$ )	$E_a$ ( $\text{kJ mol}^{-1}$ )	Assignment
<b>1</b>	5.11	5.06	35.8	cation $C_3$ rot.
<b>2</b>	7.07	37.2	13.05	3 $\text{CH}_3$ rot.
	2.97	0.653	28.88	cation $C_3$ rot.
<b>3</b>	4.06	34.5	11.35	2 $\text{CH}_3$ rot.
	3.16	28.4	13.62	$\text{NH}_3$ rot.
	1.30	21.9	23.53	cation $C_3$ rot. (?)

Fig. 1. Temperature dependence of  $^1\text{H}$  NMR  $T_1$  at 42.5 MHz of  $[\text{C}(\text{NH}_2)_3]\text{Cd}_2\text{Br}_5$  (**1**).

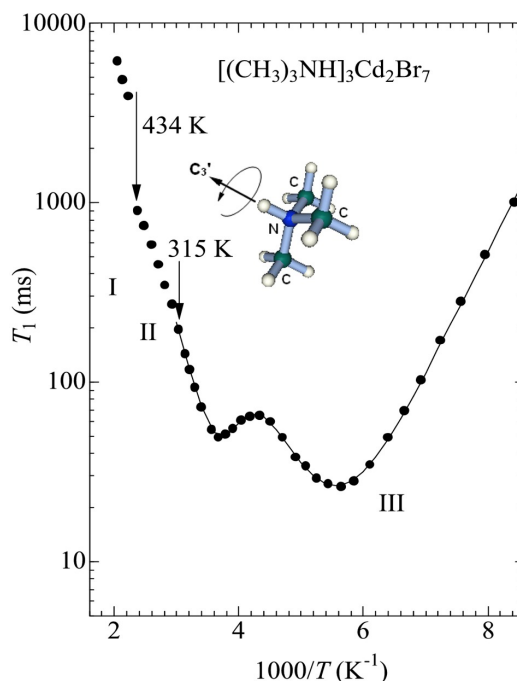
$$\tau = \tau_0 \exp(E_a/RT) \quad (2)$$

By least-squares calculations, the motional constant  $C$ , the correlation time at infinite temperature  $\tau_0$ , and the activation energy  $E_a$  were determined as given in Table 1. The  $E_a = 35.8 \text{ kJ mol}^{-1}$  value is similar to the value of  $36.6 \text{ kJ mol}^{-1}$  for  $[\text{C}(\text{NH}_2)_3]\text{AuBr}_4$  [4] and of  $35.0 \text{ kJ mol}^{-1}$  for  $[\text{C}(\text{NH}_2)_3]\text{HgBr}_3$  [5]. These values suggest that the  $[\text{C}(\text{NH}_2)_3]^+$  ions are rather loosely bound in the crystals [4], although hydrogen bonds are observed according to the X-ray structure analysis of **1** [1]. A first-order phase transition was observed at 535 K by DSC measurements [1]. During this transition II→I, there is no change of the free induction decay (FID) shape, and the  $\log T_1$  vs.  $T^{-1}$  curve is almost continuous. Therefore, only the cation  $C_3$  reorientation occurs also in phase I. The results of DSC measurements suggest that the transition II→III is nearly

first-order and of a displacive type because of small transition entropies [1]. The X-ray structure analysis of phase II at 301 K has shown large thermal parameters of N(2) atoms on the mirror plane in the  $[\text{C}(\text{NH}_2)_3]^+$  ions [1], and this phenomenon may give a small downward cusp of  $T_1$  during the transition II→III.

#### $[(\text{CH}_3)_3\text{NH}]\text{Cd}_2\text{Br}_7$ (**2**)

Fig. 2 shows the temperature dependence of  $^1\text{H}$  NMR  $T_1$  at temperatures between 113 and 476 K below the melting point of 494 K. Two phase transitions appear as a discontinuity and change in the tangent of the  $\log T_1$  vs.  $T^{-1}$  curve near 434 and 315 K, respectively. These phases are named as I, II and III from the high-temperature side. Two  $T_1$  minima, 26 ms at 175 K and 48 ms at 270 K, are observed. By considering the cation structure [2] and the comparable  $T_1$  minimum values observed for other hexahalogenometallates  $[(\text{CH}_3)_3\text{NH}]_2\text{MX}_6$  [7], the  $T_1$  minimum around 175 K is definitely assignable to the  $C_3$  reorientation of three  $\text{CH}_3$  groups with  $E_a = 13.0 \text{ kJ mol}^{-1}$  while the other  $T_1$  minimum around 270 K is assignable to the  $C_3$  reorientation of the whole cation of  $[(\text{CH}_3)_3\text{NH}]^+$  around the molecular  $C_3$  axis with  $E_a = 28.9 \text{ kJ mol}^{-1}$ , as shown by the inset of Fig. 2. During the transition

Fig. 2. Temperature dependence of  $^1\text{H}$  NMR  $T_1$  at 42.5 MHz of  $[(\text{CH}_3)_3\text{NH}]\text{Cd}_2\text{Br}_7$  (**2**).

of phase III→II at 315 K, the  $\log T_1$  vs.  $T^{-1}$  curve is continuous, and therefore the transition is of a second-order type. On the other hand, at the transition II→I at 434 K, the  $T_1$  value discontinuously jumps, and hence this phase transition is of first-order in accordance with the results of DSC measurements ( $T_{tr} = 436$  K,  $\Delta S_{tr} = 49.8$  J K<sup>-1</sup> mol<sup>-1</sup>,  $\Delta H_{tr} = 21.7$  kJ mol<sup>-1</sup>). This large value of  $\Delta S_{tr}$ , comparable with the entropy change of 94.9 J K<sup>-1</sup> mol<sup>-1</sup> observed at the melting point, suggests that phase I is highly disordered. In phase I the length of FID ( $T_2$ ) is larger than that in phase II, and hence a motion like an overall rotation of a whole cation should be excited. Phase I is easily supercooled and changes to a metastable room-temperature phase different from the stable room-temperature phase III. DSC measurements have shown that this metastable phase undergoes phase transitions at 325, 376, and 430 K, on heating. The <sup>81</sup>Br NQR lines disappear around 243 K [2], and this disappearance may be due to the fluctuation of the electric field gradients at Br sites caused by the C<sub>3</sub> reorientation of [(CH<sub>3</sub>)<sub>3</sub>NH]<sup>+</sup> ions about the molecular C<sub>3</sub> axis.

#### *[i-C<sub>3</sub>H<sub>7</sub>NH<sub>3</sub>]*CdBr<sub>3</sub>* (3)*

The temperature dependence of <sup>1</sup>H NMR  $T_1$  is given in Fig. 3, where  $T_1$  is measured between 105 and 434 K below the temperature of 459 K at which **3** melts accompanied by decomposition. The phase transition ap-

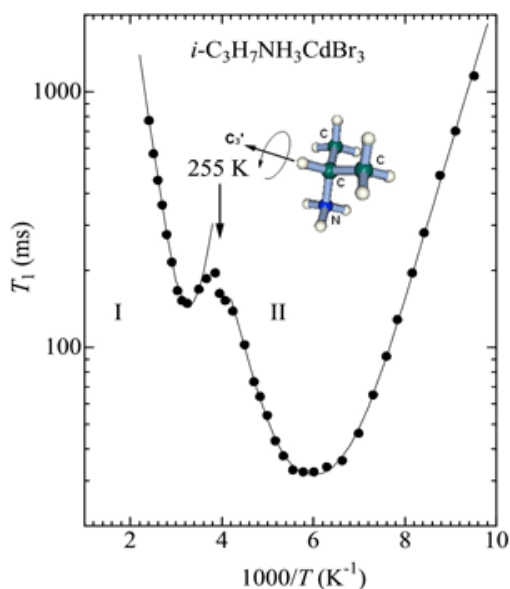


Fig. 3. Temperature dependence of <sup>1</sup>H NMR  $T_1$  at 42.5 MHz of *[i-C<sub>3</sub>H<sub>7</sub>NH<sub>3</sub>]*CdBr<sub>3</sub>* (**3**).*

pears as a discontinuity point of the  $\log T_1$  vs.  $T^{-1}$  curve around 255 K. These phases are named as I and II from the high-temperature side. A broad  $T_1$  minimum with *ca.* 32 ms appears over a wide temperature range of 155 to 180 K. This  $T_1$  minimum can be analyzed by postulating that  $T_1$  consists of two minima, the  $E_a$  values of which are 11.6 and 13.3 kJ mol<sup>-1</sup> for the low- and high-temperature minimum, respectively. However, taking into consideration that the molecular shape of the *[i-C<sub>3</sub>H<sub>7</sub>NH<sub>3</sub>]<sup>+</sup>* ion is similar to that of [(CH<sub>3</sub>)<sub>3</sub>NH]<sup>+</sup>, except for the substitution of one CH<sub>3</sub> with an NH<sub>3</sub> group, and that another  $T_1$  minimum observed in phase I is too long to be assigned to the reorientation of the NH<sub>3</sub> group, it is better to analyze the broad minimum in phase II as being composed of three inseparable minima due to the reorientations of two CH<sub>3</sub> groups and one NH<sub>3</sub> group [8]. This conclusion is supported by the fact that the  $T_1$  minimum value of *ca.* 32 ms is comparable with 26 ms observed for the reorientation of three CH<sub>3</sub> groups in the [(CH<sub>3</sub>)<sub>3</sub>NH]<sup>+</sup> ions of **2**. The  $E_a$  values of 11.6 and 13.3 kJ mol<sup>-1</sup> are assignable to the reorientation of two CH<sub>3</sub> groups and to the NH<sub>3</sub> reorientation, respectively. In phase I, a  $T_1$  minimum with 150 ms appears at 303 K. This  $T_1$  minimum with  $E_a = 23.5$  kJ mol<sup>-1</sup> is assignable to a higher order molecular motion such as a pseudo C<sub>3</sub> reorientation of a whole cation as shown in the inset in Fig. 3, like the tumbling of a whole *[i-C<sub>3</sub>H<sub>7</sub>NH<sub>3</sub>]<sup>+</sup>* cation observed in ref. [8]. In this case, unequal potential wells for the C<sub>3</sub> reorientation should be adopted to interpret the long  $T_1$  minimum compared with 48 ms for the [(CH<sub>3</sub>)<sub>3</sub>NH]<sup>+</sup> ion [9].

The DSC experiments have shown that a first-order phase transition occurs at 224 K, with  $\Delta S_{tr} = 1.6$  J K<sup>-1</sup> mol<sup>-1</sup> and  $\Delta H_{tr} = 0.36$  kJ mol<sup>-1</sup>. In addition, another first-order phase transition was detected at 379 K ( $\Delta S_{tr} = 7.7$  J K<sup>-1</sup> mol<sup>-1</sup>,  $\Delta H_{tr} = 2.9$  kJ mol<sup>-1</sup>, temperature hysteresis  $\Delta T = 10$  K), but there is no clear evidence in the  $\log T_1$  vs.  $1/T$  curve for this phase transition.

#### Experimental Section

Crystals for measurements were those made for the X-ray structure analysis [1, 2]. A standard pulsed NMR spectrometer was employed at 42.5 MHz. A conventional  $\pi$ - $\tau$ - $\pi/2$  pulse sequence (inversion recovery method) was applied for the measurements of <sup>1</sup>H NMR  $T_1$ . Sample temperatures were controlled by a gas-flow system. DSC measurements were carried out using a differential scanning calorimeter DSC 220 from Seiko Instruments Inc. as before [1].

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