# A Study of Complex Anionic Motions in $(Me_2NH_2)_2ZnCl_4$ Crystals by Means of Chlorine Nuclear Quadrupole Resonance Techniques *

Hiroshi Yamamoto, Atsushi Ishikawa, Tetsuo Asaji, and Daiyu Nakamura
Department of Chemistry, Faculty of Science, Nagoya University, Nagoya 464-01, Japan

Z. Naturforsch. **45a**, 464–466 (1990); received October 5, 1989

Three $^{35}$Cl NQR frequencies were observed for $(Me_2NH_2)_2ZnCl_4$ at room temperature, indicating the existence of three crystallographically nonequivalent chlorines in the crystal. With decreasing temperature, the frequency of the lines increased almost linearly and disappeared below ca. 220 K near the reported phase transition temperature (ca. 215 K) detected on cooling. The three NQR lines faded out above room temperature because of the occurrence of rapid anionic reorientational motions disclosed from measurements of the $^{35}$Cl NQR spin-lattice relaxation time.

## Introduction

Recently, a group of crystals expressed by $R_2MX_4$ where R, M, and X denote a monovalent cation, a divalent metal atom, and a halogen, respectively, have attracted much attention because of their interesting solid state properties including phase transitions [1]. Among those, some complexes having $(Me_2NH_2)^+$ cations are known to undergo phase transitions closely related to $N-H\cdots X$ type H-bonding, and also to exhibit ferroelectricity [2, 3]. The crystal of $(Me_2NH_2)_2ZnCl_4$ is known to undergo a phase transition at ca. 215 K when the temperature decreased [2]. To obtain information about the ionic dynamics and solid state properties in the high and low temperature phases, the present investigation of the temperature dependences of $^{35}$Cl NQR frequencies and of the $^{35}$Cl NQR spin-lattice relaxation time $T_{1Q}$ has been undertaken.

## Experimental

$^{35}$Cl NQR signals were searched by use of a superregenerative spectrometer [4] over a frequency range 8.2–10.5 MHz. For the determination of resonance frequencies and $T_{1Q}$, a homemade pulsed NQR spectrometer [5, 6] was employed. $T_{1Q}$ was determined using a $180°-\tau-90°-\tau_e-180°$ pulse sequence where the spacing time $\tau$ was varied and $\tau_e$ was fixed at ca. 100 μs throughout the measurements. The sample temperature was controlled by means of a temperature controller [5] and measured by using a copper vs. constantan thermocouple within an estimated accuracy of ±0.5 K. The experiments of DTA were carried out with a homemade apparatus already described [7].

$(Me_2NH_2)_2ZnCl_4$ crystals were prepared according to the method reported in [1]. Identification of the sample was performed by usual elementary analysis. Anal. Calc. for $[(CH_3)_2NH_2]_2ZnCl_4$: C, 16.1; H, 5.4; N, 9.4; Cl, 47.4%. Found: C, 16.1; H, 5.4; N, 9.3; Cl, 47.5%.

## Results and Discussion

Three $^{35}$Cl NQR frequencies, 9.794, 9.395, and 8.318 MHz, were observed for $(Me_2NH_2)_2ZnCl_4$ at room temperature using the superregenerative spectrometer. The lowest frequency ($\nu_3$) line was sharp and intense whereas the middle ($\nu_2$) and especially the highest frequency ($\nu_1$) lines were weak. It should be noted that the three lines were fairly strong when observation was made with the pulsed NQR spectrometer. The weak $\nu_1$ line could be observed up to 347 K whereas $\nu_2$ and $\nu_3$ faded out at ca. 340 and 328 K, respectively. The assignment of the above lines to $^{35}$Cl NQR ones was performed by observing the $^{37}$Cl NQR lines at the frequencies expected from the isotope ratio of chlorine quadrupole moments. The $^{35}$Cl NQR frequencies observed at several temperatures are listed in Table 1.

---

* Presented at the Xth International Symposium on Nuclear Quadrupole Resonance Spectroscopy, Takayama, Japan, August 22–26, 1989.

Reprint requests to Prof. D. Nakamura, Department of Chemistry, Faculty of Science, Nagoya University, Nagoya 464-01, Japan.

0932-0784 / 90 / 0300-0464 $ 01.30/0. – Please order a reprint rather than making your own copy.

Table 1. The $^{35}$Cl NQR frequencies $\nu_1$, $\nu_2$, and $\nu_3$ ($\pm 2$ kHz) determined for $(Me_2NH_2)_2ZnCl_4$ at several temperatures.

| $T$/K | $\nu_1$/MHz | $\nu_2$/MHz | $\nu_3$/MHz |
|---|---|---|---|
| 220 | – | 9.503 | 8.358 |
| 240 | 9.906 | 9.473 | 8.349 |
| 291 | 9.794 | 9.395 | 8.318 |
| 311 | 9.749 | 9.363 | 8.306 |
| 326 | 9.713 | 9.341 | 8.296 |
| 337 | 9.685 | 9.319 | – |
| 347 | 9.659 | – | – |

The temperature dependence of the $^{35}$Cl NQR frequencies and $^{35}$Cl $T_{1Q}$ were determined with decreasing temperature from ca. 330 K. The results are shown in Figs. 1 and 2. The NQR signals could be observed down to ca. 220 K with the pulsed spectrometer.

As already reported [2], this salt undergoes a phase transition at ca. 215 K with decreasing the temperature. This agrees with the present experimental fact that the three $^{35}$Cl NQR lines disappear around 220 K when the sample is cooled. To confirm the phase transition temperature $T_{tr}$ reported, DTA measurements were performed in the temperature range 150–370 K. The results are shown in Figure 3. When the temperature increased from ca. 150 K, an endothermic anomaly appeared at 270 K whereas an exothermic anomaly was detected at 215 K on the cooling run. Measurements were made repeatedly and almost the same results were obtained on every heating and cooling run although the $T_{tr}$'s observed on these runs changed within ±5 K. Accordingly, we concluded that the phase transition at ca. 270 K is a first order one accompanied by an unusually large hysteresis. The type of this phase transition is probably different from that of the usual incommensurate-normal one observed for $Rb_2ZnCl_4$ [8].

Recently, Vasil'ev et al. [9] have reported that the temperature dependence curve of the heat capacity of $(Me_2NH_2)_2ZnCl_4$ crystals yielded four anomalies at 201, 250, 272, and 310 K. In our DTA experiments, however, no heat anomaly could be observed except for the foregoing exo- and endothermic anomalies. The present temperature dependence curves of $^{35}$Cl NQR frequencies recorded on the heating run were smooth at 310 K.

If the crystal structure of the room temperature phase of the present salt is similar to that of $Cs_2CdBr_4$ [10], the three $^{35}$Cl NQR frequencies observed can be assigned to the three crystallographically nonequiva-

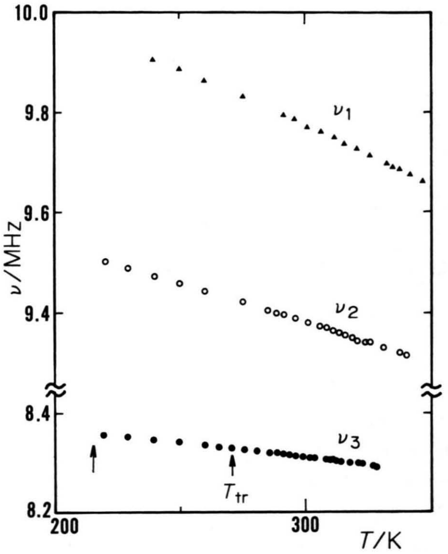

Fig. 1. Temperature dependences of $^{35}$Cl NQR frequencies observed for $(Me_2NH_2)_2ZnCl_4$. The three NQR lines are denoted as $\nu_1$, $\nu_2$, and $\nu_3$ in the order of decreasing frequency. Below room temperature, observation was made only with decreasing temperature. The arrows without and with $T_{tr}$ indicate the DTA phase transformation temperatures observed with decreasing and increasing temperature, respectively.

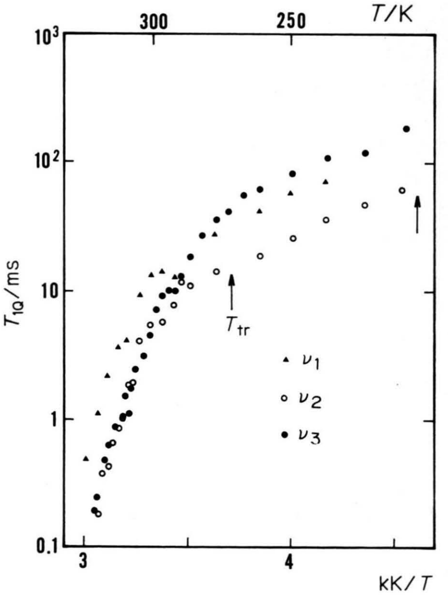

Fig. 2. Temperature dependences of the NQR spin-lattice relaxation time $T_{1Q}$ observed for $\nu_1$, $\nu_2$, and $\nu_3$ of $(Me_2NH_2)_2ZnCl_4$. The same symbols as those of Fig. 1 are used to discriminate $T_{1Q}$ data of the three NQR lines. Arrows have the same meaning as in Figure 1.

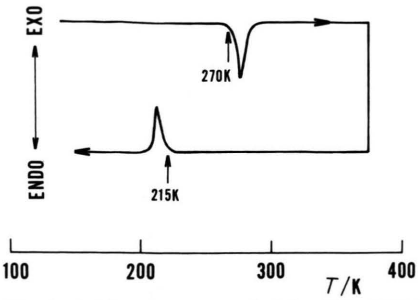

Fig. 3. DTA curves recorded for $(Me_2NH_2)_2ZnCl_4$.

lent chlorines in $[ZnCl_4]^{2-}$. In the $Cs_2CdBr_4$ crystal, one set of Br−Cd−Br atoms is located on a mirror plane and two bromines of the other set in each anion becomes crystallographically equivalent by the plane. Accordingly, there exist in the anion three crystallographically nonequivalent bromines with the ratio of 1:1:2. For the present complex, the lowest frequency line is considered as arising from the two crystallographically equivalent chlorines from its stronger intensity compared to the others. This assignment is the same as that made for the bromine NQR lines of $Cs_2CdBr_4$ [10].

In the temperature range where the $T_{1Q}$ measurements were performed, the $^{35}Cl$ spin-lattice relaxation for these lines can be interpreted by considering contributions from the lattice vibrations mainly at lower temperatures and the reorientations of the complex anions at higher temperatures [11, 12]. The $T_{1Q}$ data obtained above room temperature suggest that the complex anion reorients more frequently about its pseudo-$C_3$ axis along one of Zn−Cl bond axes than about the other axes, because $T_{1Q}$ of the $\nu_1$ line is appreciably longer than that of the others. From the gradient of the linear portion of log $T_{1Q}$ vs. $T^{-1}$ plots (Fig. 2) above ca. 300 K, the activation energy $E_a$ of the reorientation was estimated to be ca. $1.1 \times 10^2$ kJ mol$^{-1}$. To the best of our knowledge, no data have been reported so far for $E_a$ of the reorientation of tetrahedral complex anions in solids.

[1] F. Milia, Ferroelectrics **24,** 151 (1980).
[2] Z. A. Bobrova and V. M. Varikash, Dokl. Akad. Nauk BSSR **30,** 510 (1986).
[3] Z. A. Bobrova, V. M. Varikash, A. I. Baranov, and L. A. Shuvalov, Sov. Phys. Crystallogr. **32,** 148 (1987).
[4] D. Nakamura, Y. Kurita, K. Ito, and M. Kubo, J. Amer. Chem. Soc. **82,** 5783 (1960).
[5] K. Horiuchi, R. Ikeda, and D. Nakamura, Ber. Bunsenges. Phys. Chem. **91,** 1351 (1987).
[6] A. Ishikawa, K. Horiuchi, R. Ikeda, and D. Nakamura, J. Mol. Struct. **192,** 237 (1989).
[7] Y. Kume, R. Ikeda, and D. Nakamura, J. Magn. Reson. **33,** 331 (1979).
[8] F. Milia and V. Rutar, Phys. Rev. **B 23,** 6061 (1981).
[9] V. E. Vasil'ev, V. M. Rudyak, Z. A. Bobrova, and V. M. Varikash, Sov. Phys. Solid State **29,** 882 (1987).
[10] S. Plesko, R. Kind, and H. Arend, Ferroelectrics **26,** 703 (1980).
[11] H. Nakayama, N. Nakamura, and H. Chihara, Bull. Chem. Soc. Japan **60,** 99 (1987).
[12] K. R. Jeffrey and R. L. Armstrong, Phys. Rev. **174,** 359 (1968).