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The NQR and DTA Study of Phase and Polymorphic Transitions of Bromocadmate and Bromozincate Complexes

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Summary

The ^{81}Br NQR measurement showed that [*i*-$(CH_3)_2CHNH_3]_2CdBr_4$ (**1**) had two phases: the four ^{81}Br NQR lines of the high-temperature phase could be observed at temperatures between 77 and about 235 K when **1** was rapidly cooled. On the other hand, two ^{81}Br NQR lines of low-temperature phase could be observed at temperatures between 77 and 295 K after when **1** was kept at 77 K overnight. During the preparation of [*t*-$(CH_3)_3CNH_3]_2CdBr_4$ (**2**) two kind of crystals appeared: one (**2a**) showed the eight ^{81}Br NQR lines at temperatures between 77 and 320 K and another (**2b**) showed two additional NQR lines. The crystal **2b** is probably mixed crystal. Ten ^{81}Br NQR lines for $[H_2NNH_3]_4[H_3NNH_3][CdBr_5]_2$ (**3**) were observed at temperatures between 250 K and around 350 K. $[Mg(H_2O)_6]Zn_2Br_6$ (**4**) showed second-order phase transition at 290 K. In the low-temperature phase three ^{81}Br NQR lines was observed and two ^{81}Br NQR lines in high-temperature phase in accordance with the crystal structure at room temperature.

Key words: ^{81}Br NQR, DTA, Phase transition, Bromocadmate complex, Boromozincate complex

Introduction

Nuclear quadrupole resonance (NQR) is the sensitive method to detect the even slight change of the electric field gradient (EFG) around the relevant nuclei and therefore the suitable method for detection of phase transition and modification. The compounds of the A_2MX_4 family have been reported to show the interesting series of phase transitions. The Br NQR of title compounds are observed in this context.

The studies by means of X-ray diffraction and ^{79,81}Br NQR of bromocadmate anions $[CdBr_{2+n}]^{n-}$ show variety of polymer anionic structures and isolated $[CdBr_4]^{2-}$ tetrahedron [1-8]. The anion with composition of $[CdX_3]^-$ is apt to have the chain structure like [*t*-$(CH_3)_3NHCdBr_3]_2H_2O$ and [*i*-$(CH_3)_2CHNH_3]CdBr_3$ [9]. The condition for preparation of bromocadamte complexes of $[CdBr_4]^{2-}$ with same cations are also investigated in this study.

Experimental

Preparation of [*i*-$(CH_3)_2CHNH_3]_2CdBr_4$ (**1**) is as follows: 0.2 mol of *i*-propylamine and 0.1 mol of $CdCO_3$ were mixed in 48% HBr acid. The large excess of HBr acid was necessary. The water sol-

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vent was evaporated by P_2O_5 in a dessicator. The colorless, rectangle prism appeared from the solution. The crystal was hygroscopic. Elemental analysis (Obsd. % / Calcd. %): C(12.95/13.04), H (3.65/3.65), N(5.11/5.07).

$[t\text{-}(CH_3)_3CNH_3]_2CdBr_4$ (**2**) was prepared by mixing *t*-butylamine and $CdCO_3$ in 48 % HBr acid in molar ratio of 2:1. The large excess of HBr acid was necessary. The water solvent was evaporated by P_2O_5 in a dessicator. The colorless, prism-like crystals (**2a**) appeared from the solution. On the other hand, white rod-like crystals (**2b**) appeared from the hot saturated solution. Elemental analysis for **2a**, (Obsd. % / Calcd. %): C(16.46/16.55), H(4.16/4.16), N(4.80/4.82). The crystal was hygroscopic.

$[N_2H_5]_4[N_2H_6][CdBr_5]_2$ (**3**) appeared during preparation of $[N_2H_5]_3CdBr_5$: addition of 0.3 mol of N_2H_5Br, which was made by neutralizing (N_2H_4)-H_2O with 48 % HBr acid, to a water solution containing 0.1 mol of $CdBr_2$-$4H_2O$. In addition, excess 0.3 mol of HBr as 48 % HBr acid was added to this solution. The solvent was evaporated by heating the solution at about 70 ℃. When the hot saturated solution was cooled to room temperature, at first, colorless, needle-type crystals appeared from the solution. Then big colorless square crystals of $[N_2H_5]_2CdBr_4$-$4H_2O$ and **3** appeared from the rest of the solution. When **3** was kept in the rest of solution and it turned to be $[N_2H_5]_2CdBr_4$-$4H_2O$ in a few hours. Elemental analysis, (Obsd. %/Calcd. %): Cd (18.33/18.89), N (11.60/11.76), H (2.16/2.20), Br (67.60/67.13), suggests that the plausible composition is $(N_2H_5)_4(N_2H_6)[CdBr_5]_2$.

$[Mg(H_2O)_6]Zn_2Br_6$ (**4**) was prepared by solving Mg metal in 30 % HBr acid containing stoichiometric amount of $ZnBr_2$ [10].

The ^{79,81}Br NQR spectra were recorded by a home-made NQR spectrometer working in the super-regenerative mode. The sample temperature was measured with copper-constantan thermocouple, and the frequencies were determined by counting techniques. The observed ^{81}Br NQR frequencies at several temperatures are listed in Appendix I. DTA was measured by home-made apparatus.

Results and Discussion

*NQR and DTA measurement of $[i\text{-}(CH_3)_2CHNH_3]_2CdBr_4$ (**1**)*

The NQR measurement of **1** shows that there are two phases of this crystal. One phase is high-temperature phase (**1H**) and this phase is meta-stable at low temperatures. When sample was cooled at once down to 77 K, the four NQR lines were observed as seen in Fig. 1. The NQR frequencies of these four NQR lines varied with increasing temperature and they disappeared around 235 K. On the other hand, when a sample was kept at 77 K overnight or repeating the low-temperature measurement, only two NQR lines came to appear. It was low-temperature phase (**1L**) *i.e.*, a stable form at low temperatures. These two resonance lines could be observed between 77 K and 295K. Both NQR spectra of **1H** and **1L** are different from those of $[i\text{-}(CH_3)_2CHNH_3]CdBr_3$ [9]: this compound has the chain structure which consists of face-sharing $[CdBr_6]$ octahedra and therefore three bridging Br atoms show three ^{81}Br NQR lines at around 42 MHz which are lower than ^{81}Br NQR frequencies of **1H** and **1L**.

The result of DTA measurement of the newly prepared sample **1N** shows that phase transitions take place at 187 K and 290 K on cooling run and at 178 K and 289 K on heating run as shown in Fig. 2. The sample **1N** seems to be high-temperature form, although there is no indication of the phase transition in the curves of ν_H *vs.* T. The phase transition around 180 K seems to be

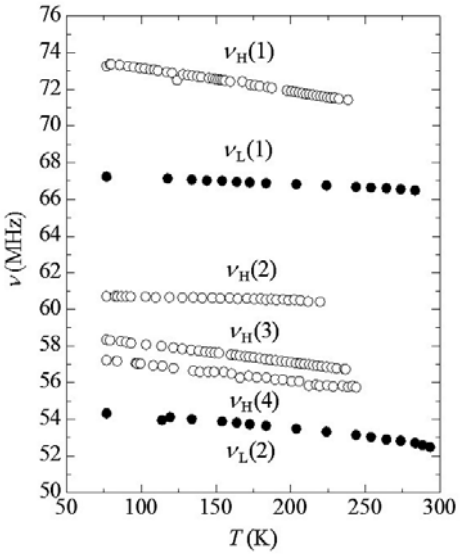

Fig. 1. The temperature dependece of ^{81}Br NQR frequencies of **1**. ν_H and ν_L indicate the frequencies of **1H** and those of **1L**, respectively.

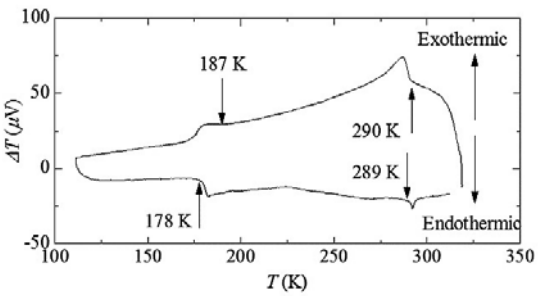

Fig. 2. DTA curve of **1N**. Upper curve is cooling run and lower curve is heating run.

the second-order type by taking the shape of the heat anomaly into consideration. Therefore, this phase transition may cause little displacement of ν_H *vs.* T curve around the transition point, *i.e.*, the continuous change of ν_H *vs.* T may be expected.

*NQR measurement of [t-$(CH_3)_3CNH_3]_2CdBr_4$ (**2**)*

For the sample **2a**, eight ^{81}Br NQR lines could be observed at temperatures between 77 K and 320 K as shown in Fig. 3. For the sample **2b**, two additional NQR lines accompanied with NQR lines

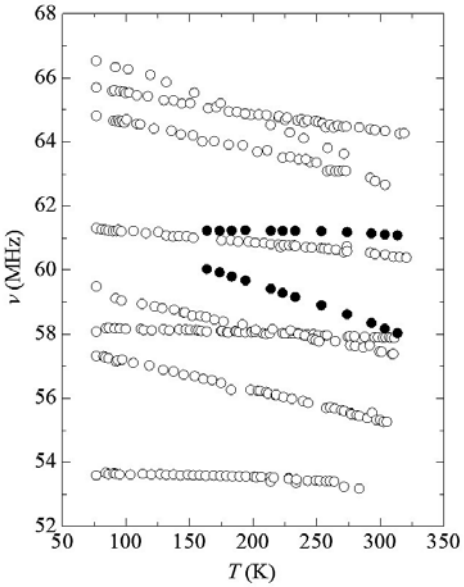

Fig. 3. The temperature dependence of ^{81}Br NQR frequencies for **2a** (white circle) and two extra lines of **2b** (black circle).

of **2a** could be observed at temperatures between 153 K and 323 K as shown in Fig. 3. The both NQR spectra of **2a** and **2b** are different from [*t*-$(CH_3)_3CNH_3CdBr_3]_2H_2O$ [10]: this compound has two kind of chains which consist of edge-sharing $[CdBr_5]$ square pyramids. Two Br atoms in apical position show two ^{81}Br NQR lines at around 75 MHz which is higher than other lines of bridging Br atoms at around 58 and 47 MHz. Once the sample **2b** experiences temperatures below 153 K, **2b** shows neither two extra NQR lines nor even the NQR lines for **2a** until when the crystal was kept for about one week at room temperatures. The crystal of **2b** may be the mixed crystal of two component: one is **2a** and another shows two extra NQR lines.

*NQR measurement of $(N_2H_5)_4(N_2H_6)[CdBr_5]_2$ (**3**)*

Ten NQR lines were observed at temperatures between 253 K and around 353 K as shown in Fig. 4 and could not be observed below 243 K. The composition of **3** is acceptable according to

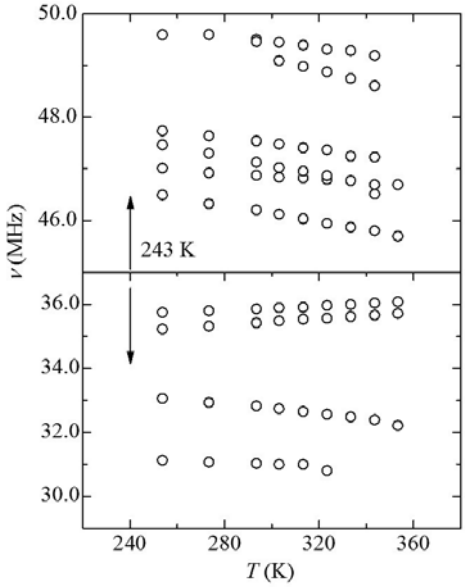

Fig. 4. Temperature dependence of ^{81}Br NQR frequencies for **3**.

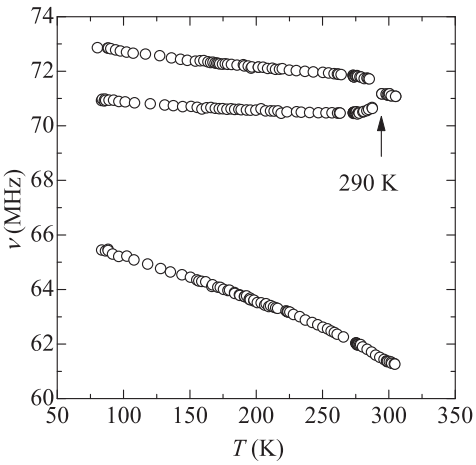

Fig. 5. The temperature dependence of ^{81}Br NQR frequencies of **4**.

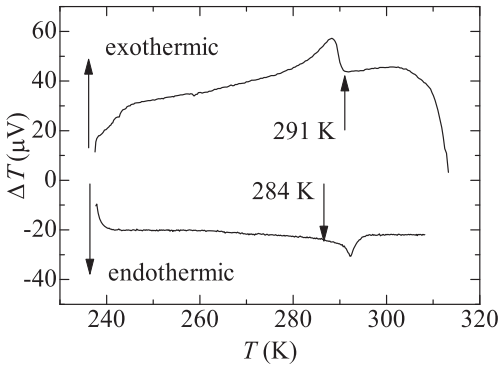

Fig. 6. DTA curve for **4**. Upper curve is cooling run and lower curve is heating run.

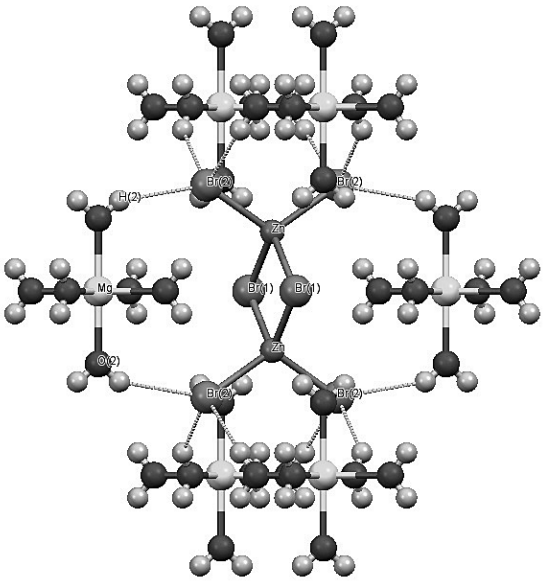

Fig. 7. Crystal structure of **4**. Hydrogen bonds are dotted line [11].

the results of NQR measurement: ten observed NQR lines, which consist of five pairs of NQR lines, indicate that ten nonequivalent Br atoms exist in the crystal of **3** and therefore two kinds of $[CdBr_5]$ unit may exist. This NQR spectra are different from $[N_2H_5]_3Cd_2Br_5$ and $[N_2H_5]_2CdBr_4$-$4H_2O$ [11]: the former has a chain structure which consist of *cis*-corner-sharing $[CdBr_6]$ octahedra and shows five ^{81}Br NQR lines at 28 MHz to 50 MHz. The structure of the latter is unknown and two NQR lines was observed at around 47 MHz.

*NQR and DTA measurement of $[Mg(H_2O)_6]Zn_2Br_6$ (**4**)*

The temperature dependence of ^{81}Br NQR frequencies for **4** is shown in Fig. 5 and shows that the phase transition occurs at 290 K. The lowest-frequency line does not show any change

at the transition point. This phase transition seems to be second-order type because the changes of ν *vs.* T at transition point are continuous, although the DTA curve shows the thermal hysteresis as shown in Fig. 6. In the high-temperature phase two NQR lines are observed in accordance with the result of X-ray structure determination [10]. The structure determined at room temperature is shown in Fig. 7. Two NQR lines has intensity ratio of 2:1 in the order of decreasing frequency. In the crystal there are two kind of Br atoms, bridging Br(1) and terminal Br (2). Terminal Br(2) atoms take part in hydrogen bond with water molecules coordinated to Mg^{2+} ions. Three NQR lines with intensity ratio of 1:1:1 are observed in the low-temperature phase. Below the transition point the motion of water molecules may terminate and then terminal Br(2) atoms are supposed to be divided into two groups. Therefore three NQR lines can be observed in the low-temperature phase. The phase transition cause little effect of EFG around bridging Br(1) atom because of the lack of hydrogen bond.

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Appendix

I. The ^{81}Br NQR frequencies of the title compounds at several temperatures.

Compound	ν (MHz) (T (K))	
1H	73.24(77)	71.62(220)
	58.34(77)	56.87(220)
	57.21(77)	55.81(220)
	60.69(77)	60.40(220)
1L	67.22(77)	66.53(273)
	54.30(77)	52.81(273)
2a	66.51(77)	-
	65.70(77)	64.39(296)
	64.80(77)	62.77(296)
	61.30(77)	60.48(296)
	59.47(77)	57.44(300)
	58.06(77)	57.88(296)
	57.31(77)	55.31(300)
	53.57(77)	53.16(283)
2b	61.22(164)	61.07(313)
	60.02(164)	58.02(313)
3	49.58(253)	49.18(343)
	49.45(293)	48.60(343)
	47.73(253)	47.22(343)
	47.45(253)	46.50(343)
	47.00(253)	46.69(353)
	46.49(253)	45.69(353)
	35.73(253)	36.07(353)
	35.21(253)	35.70(353)
	33.04(253)	32.19(353)
	31.11(253)	30.78(323)
4	72.85(77)	71.15(293)
	70.91(77)	-
	65.43(77)	61.50(293)