Isolated versus Condensed Anion Structure VI: X-ray Structure Analysis and ^{81}Br NQR of Guanidinium Pentabromodicadmate(II), $[C(NH_2)_3]Cd_2Br_5$, *tris*-Hydrazinium Pentabromocadmate(II), $[H_2NNH_3]_3CdBr_5$, and *bis*-Hydrazinium Tetrabromocadmate(II)-Tetra Hydrate, $[H_2NNH_3]_2CdBr_4$-$4H_2O$

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The structure of the condensed bromocadmate anions in $[C(NH_2)_3]Cd_2Br_5$ (**1**) and $[H_2NNH_3]_3CdBr_5$ (**2**) were studied at room temperature by X-ray diffraction. (**1**) crystallizes with double-chains bridged by Br atoms (orthorhombic, Pmmn, $Z = 2$, $a = 1394.0(5)$, $b = 394.5(1)$, $c = 1086.9(5)$ pm). This chain structure was not described previously. (**1**) shows three ^{81}Br NQR lines at temperatures between 77 and 323 K. Structural phase transitions take place at 283 K and at 535 K. (**2**) crystallizes with Br bridged zigzag-chains (monoclinic, $P2_1$, $Z = 2$, $a = 943.1(1)$, $b = 778.8(2)$, $c = 942.0(2)$ pm, $\beta = 102.10(2)°$) and shows a first-order phase transition around 304 K with a large thermal hysteresis. Below the transition point five ^{81}Br NQR lines are observed at temperatures between 122 and 304 K, and above the transition point four ^{81}Br NQR lines at temperatures between 288 and 353 K. Two ^{81}Br NQR lines are observed in $[H_2NNH_3]_2CdBr_4$-$4H_2O$ (**3**) at temperatures between 77 and around 320 K with positive temperature coefficients.

Key words: NQR; DSC; Crystal Structure; Phase Transition; Bromocadmate.

Introduction

In recent studies of complex salts with bromocadmate(II) anions by X-ray diffraction and ^{79,81}Br NQR, we found a variety of polymer anionic structure types [1 - 7] and an isolated $[CdBr_4]^{2-}$ tetrahedron [7 - 9]. In the previous papers of these series we showed that the $[CdBr_3]^-$ anion may easily adopt a chain structure [4, 6]. The chemical formula of the isolated complex anion is reported to be $[CdX_4]^{2-}$, $[CdX_6]^{4-}$ [1, 5], or $[CdX_5]^{3-}$ [10, 11]. In order to investigate whether Cd may form additional structure types we determined the structures of $[C(NH_2)_3]Cd_2Br_5$ (**1**) and $[H_2NNH_3]_3CdBr_5$ (**2**), and observed NQR of these two compounds and $[H_2NNH_3]_2CdBr_4$-$4H_2O$ (**3**).

Experimental

$[C(NH_2)_3]Cd_2Br_5$ (**1**) was prepared as follows: 0.05 mol of $[C(NH_2)_3]Br$ was added to a water solution with 0.1 mol of $CdBr_2$-$4H_2O$. The addition of a small excess hydrobromic acid was necessary to crystallize (**1**). The solvent was evaporated by keeping at about 70 °C. Colorless wool-like crystals appeared when the hot concentrated solution was cooled down to room temperature. Chemical analysis (observed / calculated weight %): Cd(32.95/32.85), N(5.72/6.14), H(0.80/0.88). $[H_2NNH_3]_3CdBr_5$ (**2**) was prepared as follows: 0.4 mol of $(N_2H_5)Br$ was added to a water solution with 0.1 mol of $CdBr_2$-$4H_2O$. A small amount of hydrobromic acid had to be added. The solvent was evaporated by heating at about 70 °C. Colorless nee-

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Table 1. Experimental conditions for the crystal structure determinations and crystallographic data of guanidinium pentabromodicadmate(II), $[C(NH_2)_3]Cd_2Br_5$ (**1**), and *tris*-hydrazinium pentabromocadmate(II), $[H_2NNH_3]_3CdBr_5$ (**2**). Diffractometer: Enraf Nonius CAD4, Wavelength: 71.093 pm (MoKα), Monochromator: graphite (002); Scan: $\omega/2\theta$. (**1**): $CH_6Br_5Cd_2N_3$ $M = 684.45$, (**2**): $Br_5CdH_{15}N_6$ $M = 611.09$.

	1	**2**
Crystal Size/(mm^3)	1.25×0.05×0.025	1.0×0.15×0.1
Temperature/K	301(2)	301(2)
Absorption Coeff./(mm^{-1})	20.26	16.35
θ-range for data collected	$1.87 \leq \theta/° \leq 29.97$	$2.21 \leq \theta/° \leq 30.03$
Index Ranges	$-19 \leq h \leq 19, -5 \leq k \leq 3, -15 \leq l \leq 0$	$-13 \leq h \leq 13, -10 \leq k \leq 0, -13 \leq l \leq 11$
Space Group	Pmmn	$P2_1$
Lattice Constants *a*/pm	1394.0(5)	943.1(1)
b/pm	394.5(1)	778.8(2)
c/pm	1086.9(5)	942.0(2)
α/°	90.00	90.00
β/°	90.00	102.10(2)
γ/°	90.00	90.00
$V \times 10^{-6}$/(pm^3)	597.7(4)	676.5(2)
Formula Units *Z*	2	2
ρ_{cal}/(Mg·m^{-3})	3.803	3.000
F(000)	608	530
Reflection Collected	2945	4139
Independent Reflections	1030 [*R*(int) = 0.0761]	2109 [*R*(int) = 0.0605]
Data ($I_0 > 2\sigma(I_0)$)	1030	2109
Restraints/Parameters	0/37	1/109
Goodness of Fit *S* on F^2(obs./all)	1.088/1.074	1.097/1.070
Final *R* ($I_0 > 4\sigma(I_0)$)	$R_1 = 0.0439$, $wR_2 = 0.1178$	$R_1 = 0.0516$, $wR_2 = 0.1376$
R (all data)	$R_1 = 0.0622$, $wR_2 = 0.1322$	$R_1 = 0.0939$, $wR_2 = 0.1661$
Largest Diff. (peak, hole) $\times 10^{-6}$/(e·pm^3)	1.835 and −1.710	1.515 and −2.015
Max. and Min. Trans.	0.5605 and 0.1422	0.2205 and 0.0732
Absolute Structure Flack Parameter		−0.07(4)
Point Positions	Cd, Br(2), Br(3), N(1) in 4f, Br(1) in 2a, N(2), C in 2b	All atoms in 2a

dles crystallized when the hot saturated solution was cooled down to room temperature. Chemical analysis: Cd(18.33/18.39), N(12.60/13.72), H(2.16/2.47), Br(66.60/65.38). $[H_2NNH_3]_2CdBr_4$-$4H_2O$ (**3**) was prepared as follows: a water solution of $(N_2H_5)Br$ was added to a solution of $CdBr_2$, which was prepared by adding $CdCO_3$ to hydrobromic acid, in a molar ratio of $(N_2H_5)Br$:$CdBr_2$ with 4:1, 3:1, or 2:1. When water was evaporated by P_2O_5 in a dessicator below 10 °C, colorless, big, and square crystals appeared from each solution. The colorless square crystals of (**3**) also appeared from the rest of the solution for preparing (**2**) when the solution was kept around 20 °C, or the needle crystals of $(N_2H_5)_3CdBr_5$ in this solution turned to (**3**) in a few hours. The composition of these crystals was the same as $(N_2H_5)_2CdBr_4$-$4H_2O$. Chemical analysis: Cd(19.57/19.71), N(9.74/9.82), H(2.53/3.18), Br(56.23/56.05), H_2O(12.66/12.63).

The crystal structure was determined using a four circle X-ray diffractometer, Enraf Nonius CAD4. From the measured intensities, corrected for Lorentz-polarization and absorption effects, the structures were solved by direct methods and Fourier syntheses, and refined by least-squares analysis with the programs given in [12]. The ^{79,81}Br NQR spectra were recorded by an NQR spectrometer working with the superregenerative mode. The sample temperature was measured with a copper-constantan thermocouple, and the frequencies were determined by counting techniques. DSC measurements were carried out above 130 K with a differential scanning calorimeter DSC220 from Seiko Instruments Inc. under the following conditions: sample weight *ca.* 10 mg, heating rate 2 - 10 K min^{-1} with flowing dry N_2 gas at 40 ml min^{-1}.

Result and Discussion

Crystal Structure

$[C(NH_2)_3]Cd_2Br_5$ (**1**)

Guanidinium pentabromodicadmate(II) (**1**) is orthorhombic with space group D_{2h}^{13}-Pmmn at 301 K; the lattice constants etc. are listed in Table 1. Table 2 lists the positional coordinates and equivalent isotropic thermal parameters U_{eq} [13]. Intramolecu-

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters U_{eq} (10^{-1} pm^2) for (**1**) and (**2**). U_{eq} is defined as one third of the trace of the U_{ij} tensor. The temperature factor T has the from $T = \exp\{-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)\}$. Anisotropic displacement parameters U_{ij} and atomic coordinates for hydrogen atoms are given in [13].

Atom	x	y	z	$U_{eq} \times 10^{-1}$/pm^2
$[C(NH_2)_3]Cd_2Br_5$ (**1**)				
Cd	4244(1)	2500	1418(1)	31(1)
Br(1)	2500	2500	2533(1)	32(1)
Br(2)	3851(1)	−2500	−269(1)	27(1)
Br(3)	4945(1)	−2500	2943(1)	30(1)
C	2500	−2500	5847(14)	86(10)
N(1)	3297(7)	−2500	5309(10)	85(5)
N(2)	2500	−2500	7040(13)	273(33)
$[H_2NNH_3]_3CdBr_5$ (**2**)				
Cd	1406(1)	9(4)	8594(1)	32(1)
Br(1)	1(7)	2527(6)	10005(7)	72(1)
Br(2)	−1081(2)	116(8)	6468(2)	82(1)
Br(3)	2655(4)	−2477(2)	7344(4)	63(1)
Br(4)	3532(2)	85(8)	11082(2)	83(1)
Br(5)	2634(5)	2584(2)	7368(4)	67(1)
N(1)	−1470(19)	5765(33)	5994(20)	82(6)
N(2)	−458(19)	5351(45)	6827(21)	98(11)
N(3)	3177(23)	5369(28)	10452(17)	85(8)
N(4)	4055(24)	5688(31)	11472(18)	87(7)
N(5)	4666(16)	5629(22)	5334(16)	52(3)
N(6)	5350(19)	5558(23)	4663(19)	64(4)

lar bond distances and angles are given in Table 3. In Fig. 1, the formula unit is drawn with the numbering of atoms and the thermal ellipsoids. Figure 2 shows the projection of the unit cell along [100] onto the *bc* plane. The anion consists of a complex double-chain structure which was determined for the first time as far as we know; Two chains, each built of Cd atoms with bridging Br(2) and Br(3) atoms, are connected by Cd-Br(1)-Cd bridges with the same Cd-Br(1) distances of 271.6 pm. Therefore, the Cd atom has five coordinated Br atoms with a square pyramidal configuration: 2×Br(2), 2×Br(3), and Br(1). A guanidinium ion has a planar molecular structure parallel to the *ac* plane; cations are connected to anions by hydrogen bonds, as shown in Fig. 2 and Table 3. The thermal displacement parameters of nitrogen atoms in the cations are fairly large, especially that of N(2). The averaged value of C-N bond distances in (**1**) is 126.7 pm and is somewhat short in comparison with those observed in $[C(NH_2)_3]CdBr_3$ (130.2 pm) and $[C(NH_2)_3]_4CdBr_6$ (131.0 pm) [3, 5].

Table 3. Bond distances (in pm) and bond angles (°) with hydrogen bond scheme. The hydrogen atoms have been determined in the least-squares refinements of the structures by fixing the bond lengths of N-H and bond angles in C-N-H.

$[C(NH_2)_3]Cd_2Br_5$ (**1**)

Connection	*d*/pm	Connection	Angle/°
Cd-Br(1)	271.6(1)	Br(1)-Cd-Br(2)	96.8(0)
Cd-Br(2)	274.8(1)	Br(1)-Cd-Br(3)	92.8(0)
Cd-Br(3)	275.6(1)	Br(2)-Cd-Br(3)	87.6(0)
C-N(1)	126(1)	Br(2)-Cd-Br(2)$^{\#1}$	91.7(0)
C-N(2)	130(2)	Br(2)-Cd-Br(3)$^{\#1}$	170.3(0)
		Br(3)-Cd-Br(3)$^{\#1}$	91.4(0)
		Cd-Br(1)-Cd$^{\#2}$	127.0(1)
		Cd-Br(2)-Cd$^{\#3}$	91.7(0)
		Cd-Br(3)-Cd$^{\#3}$	91.4(0)
		N(1)-C-N(1)$^{\#2}$	125(2)
		N(2)-C-N(1)$^{\#2}$	117.7(8)

Hydrogen bond scheme

N-H···X	*d*(H···X)/pm	*d*(N···X)/pm	∠(N-H···X)/°
N(1)-H(1A)···Br(1)	314.0	377.2	132.3
N(1)-H(1A)···Br(3)	283.9	344.8	129.3
N(1)-H(1B)···Br(3)$^{\#4}$	298.9	367.5	138.1
N(2)-H(2B)···Br(2)$^{\#5}$	274.2	347.9	144.6

Symmetry code: $^{\#1}$ $x, y+1, z$; $^{\#2}$ $-x+1/2, y, z$; $^{\#3}$ $x, y-1, z$; $^{\#4}$ $-x+1, -y, -z+1$; $^{\#5}$ $x, y, z+1$.

$[H_2NNH_3]_3CdBr_5$ (**2**)

Connection	*d*/pm	Connection	Angle/°
Cd-Br(1)	284.7(4)	Br(1)-Cd-Br(2)	84.8(2)
Cd-Br(2)	274.8(2)	Br(1)-Cd-Br(3)	176.9(1)
Cd-Br(3)	266.6(4)	Br(1)-Cd-Br(4)	85.1(2)
Cd-Br(4)	274.7(2)	Br(1)-Cd-Br(5)	88.4(1)
Cd-Br(5)	269.4(3)	Br(1)-Cd-Br(1)$^{\#1}$	86.7(0)
Cd-Br(1)$^{\#1}$	282.4(5)	Br(2)-Cd-Br(3)	95.1(1)
N(1)-N(2)	115(2)	Br(2)-Cd-Br(4)	168.6(1)
N(3)-N(4)	116(2)	Br(2)-Cd-Br(5)	92.5(1)
N(5)-N(6)	99(2)	Br(2)-Cd-Br(1)$^{\#1}$	87.0(2)
		Br(3)-Cd-Br(4)	94.7(1)
		Br(3)-Cd-Br(5)	94.7(1)
		Br(3)-Cd-Br(1)$^{\#1}$	90.2(1)
		Br(4)-Cd-Br(5)	92.7(1)
		Br(4)-Cd-Br(1)$^{\#1}$	86.9(2)
		Br(5)-Cd-Br(1)$^{\#1}$	175.1(1)
		Cd-Br(1)-Cd$^{\#2}$	179.6(2)

Symmetry code: $^{\#1}$ $-x, y-1/2, -z+2$; $^{\#2}$ $-x, y+1/2, -z+2$.

The shortening of the C-N distances is due to large thermal displacement parameters in C and N atoms. The planar $[C(NH_2)_3]^+$ ion often undergoes C_3 reorientation about the pseudo C_3-axis perpendicular to a molecular plane [14]. The large displacement param-

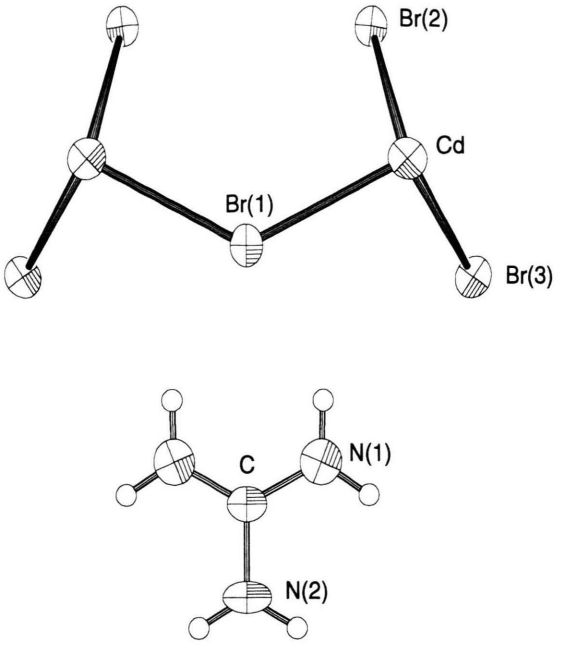

Fig. 1. The formula unit of guanidinium pentabromodicadmate(II) (**1**) with the numbering of atoms. Anions are shown as a part of bridged structures. The thermal ellipsoids (50% electrons as contour) are shown, too.

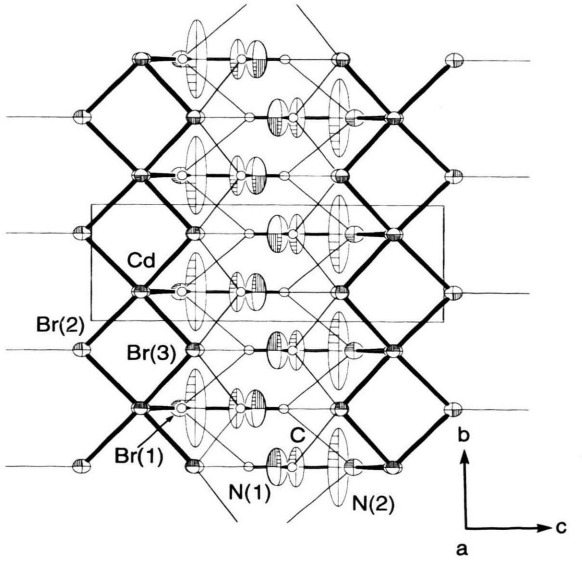

Fig. 2. The projection of the unit cell of (**1**) along [100] onto the *bc* plane. Hydrogen bonds are shown with thin lines.

eters U_{22}, which represent a motion perpendicular to the cationic plane, cannot, however, be explained by a C_3 reorientation. In fact, such a reorientation should enlarge the component parallel to that plane.

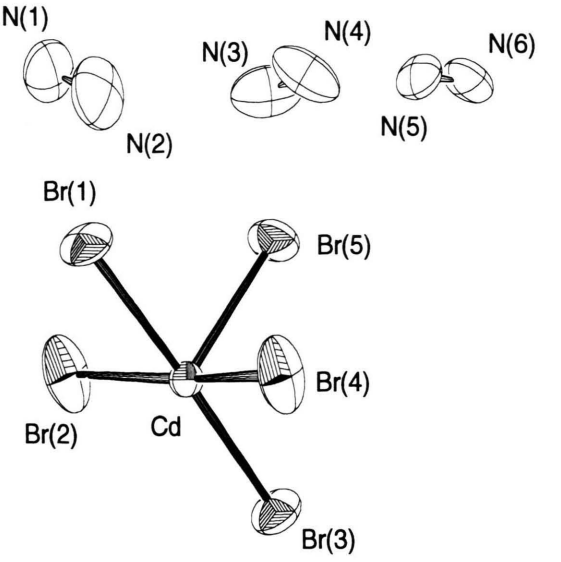

Fig. 3. The formula unit of *tris*-hydrazinium pentabromocadmate(II) (**2**) with the numbering of atoms. The thermal ellipsoids (50% electrons as counter) are shown, too.

$[H_2NNH_3]_3CdBr_5$ (**2**)

tris-Hydrazinium pentabromocadmate(II), (**2**) is monoclinic with space group C_2^2-$P2_1$ at 301 K; the lattice constants etc. are listed in Table 1. Table 2 lists the positional coordinates and equivalent isotropic thermal parameters U_{eq} [13]. Intramolecular bond distances and angles are given in Table 3. In Fig. 3, the formula unit is drawn with the numbering of atoms and the thermal ellipsoids. Figure 4 shows the projection of the unit cell onto the *ab* plane. The position of hydrogen atoms could not be determined. The anion has a zigzag chain structure of the Cd-Br(1)-Cd$^{\#}$ bridges with different Cd-Br(1) distances of 284.7 and 282.4 pm. In other words, the anion consists of $[CdBr_6]$ octahedra connected at the apices. The cations are located near to the *ac* plane. The structure of $[H_2NNH_3]_3CdCl_5$ is monoclinic with space group $C2_1/d$ not isomorphous with (**2**), while the anionic structure in the compound is similar to that in (**2**), i.e. $[CdCl_6]$ octahedra are connected at the apices [15]. The averaged N-N bond distance in (**2**) is 110 pm, which is considerably shorter than that reported for $[N_2HNH_3]_3CdCl_5$ (147.7 pm) [15] and $[H_2NNH_3]CdBr_3$ (143.4 pm) [3]. The temperature of

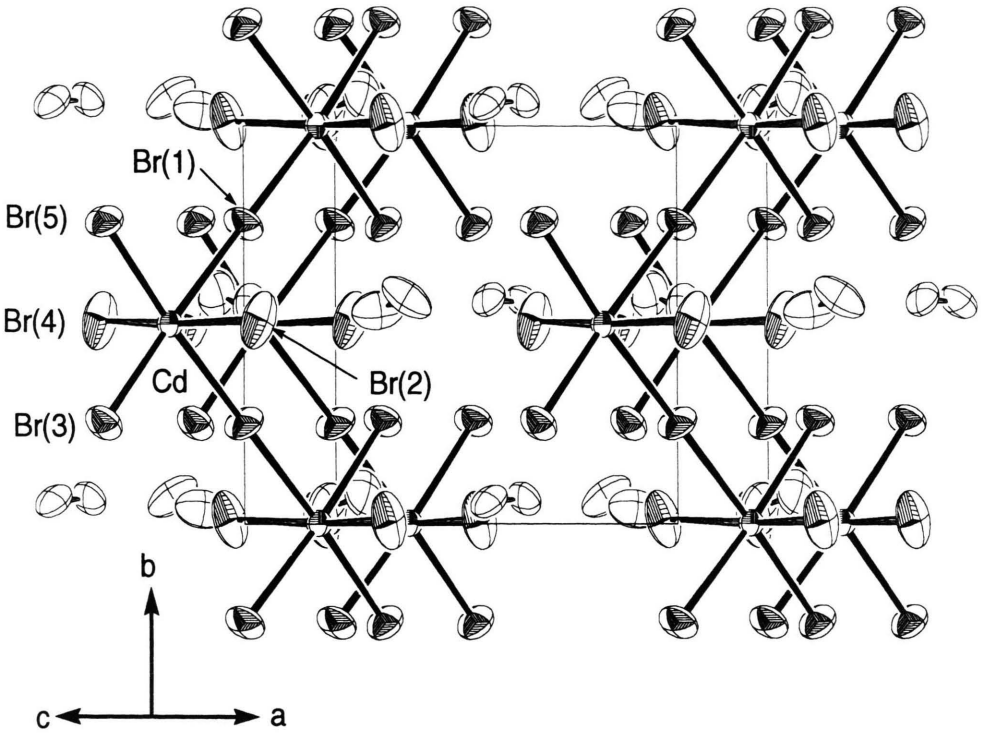

Fig. 4. The projection of the unit cell of (**2**) onto the *ab* plane.

301±2 K, where the X-ray measurement was carried out, is just below the transition point of 304 K. Hence the considerably short distances observed in N-N bonds may be influenced by the phase transition.

$[H_2NNH_3]_2CdBr_4\text{-}4H_2O$ (**3**)

Since (**3**) is air-sensitive and X-ray-sensitive, it was difficult to determine the structure. However, we can refer to the molecular and crystal structures of (**3**), based on the knowledge of Cd compounds accumulated in the previous works [1 - 9] and NQR results. First of all, the anion is considered to be an isolated tetrahedron. Secondly, the fact that two ^{81}Br NQR lines were observed suggests that the anion is located at a site with a symmetry of *mm*. Hence, the crystal seems to have two mirror planes.

Nuclear Quadrupole Resonance and Phase Transition

DSC measurements showed that $[C(NH_2)_3]Cd_2Br_5$ (**1**) undergoes a phase transition at 283 K. This phase transition seems to be nearly first-order based on the shape of a heat anomaly in the DSC measurement, although a thermal hysteresis was not observed. Moreover, it appears to be of a displacive type, because

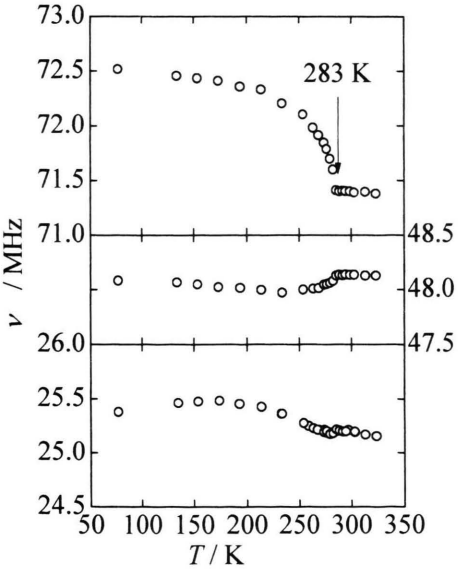

Fig. 5. The temperature dependence of ^{81}Br NQR frequencies in guanidinium pentabromodicadmate(II) (**1**).

Table 4. ^{81}Br NQR frequencies at several temperatures.

Compound	ν/MHz (T/K)	ν/MHz (T/K)
$[C(NH_2)_3]Cd_2Br_5$ (**1**)	25.38(77)	25.20(292)
	48.08(77)	48.13(292)
	72.52(77)	71.40(292)
$[H_2NNH_3]_3CdBr_5$ (**2**)	30.10(122)	36.97(343)
	30.28(122)	42.38(343)
	38.37(122)	43.18(343)
	41.21(122)	53.21(343)
	50.61(122)	
$[H_2NNH_3]_2CdBr_4$-$4H_2O$ (**3**)	46.45(77)	46.96(300)
	48.16(77)	49.04(300)

the observed transition entropy ΔS_{tr} is very small ($\Delta S_{tr} = 0.7$ J K^{-1} mol^{-1} and transition enthalpy ΔH_{tr} = 0.2 kJ mol^{-1}). Another first-order phase transition occurs at 535 K (ΔS_{tr} = 0.8 J K^{-1} mol^{-1}, ΔH_{tr} = 0.4 kJ mol^{-1}) and (**1**) decomposes around 580 K. The solid phases are named as I, II, III with decreasing temperature. Figure 5 shows the temperature dependence of ^{81}Br NQR frequencies in (**1**). The NQR frequencies at several temperatures are listed in Table 4. Three NQR lines were observed in both phases II and III, and the NQR frequencies-temperature curves changed almost continuously at 283 K. These NQR results suggest a transition at 283 K of second-order, which agrees with the absence of a hysteresis in the DSC measurements.

The temperature dependence of ^{81}Br NQR frequencies in $[H_2NNH_3]_3CdBr_5$ (**2**) is shown in Figure 6. NQR lines were not observed at 77 K, and on heating five NQR lines gradually appeared around 122 K, which can be followed up to 304 K. Four NQR lines appeared above this temperature and could be followed up to 353 K. On cooling the four lines were present down to 288 K. Therefore, a first-order phase transition with a large thermal hysteresis occurs around 304 K. On the other hand, DSC measurements showed that (**2**) undergoes a first-order and order-disorder type phase transition at 293 K (ΔS_{tr} = 6.8 J K^{-1} mol^{-1}, ΔH_{tr} = 2.0 kJ mol^{-1}, and temperature hysteresis ΔT = 3 K). The result is not in agreement with the result of NQR (T_{tr} = 304 K and ΔT = 16 K). This disagreement may be due to the difference of the rate of heating or cooling of the sample in NQR and DSC measurements. Another first-order phase transition was observed at 445 K (ΔT = 35 K) from DSC measurement. The peak of this phase transition overlapped with the peak of the melting (T_m = 452 K, ΔT_m = 40 K) and a fusion was followed by

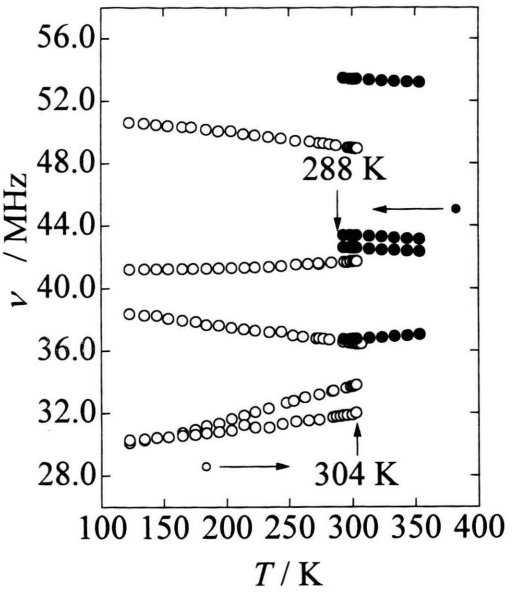

Fig. 6. The temperature dependence of ^{81}Br NQR frequencies in *tris*-hydrazinium pentabromocadmate(II) (**2**).

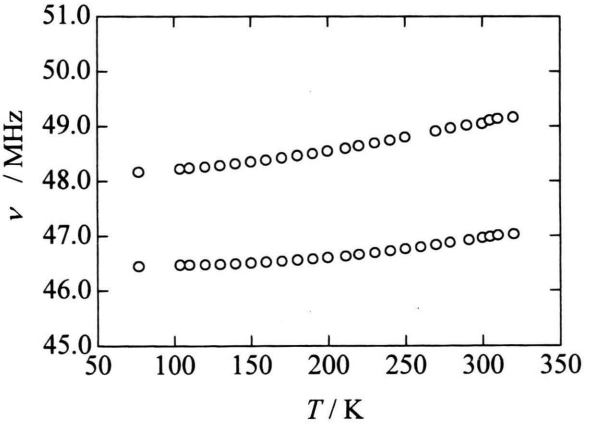

Fig. 7. The temperature dependence of ^{81}Br NQR frequencies in *bis*-hydrazinium tetrabromocadmate(II)-tetra hydrate (**3**).

decomposition. The sum of the transition enthalpies for the phase transition and the melting is ΔH_{tr} = 49.4 kJ mol^{-1} and the sum of the transition entropies $\Delta S_{tr} \approx 110$ J K^{-1} mol^{-1}, respectively. The peak of the phase transition is larger than that of the melting, and the transition enthalpy of the phase transition seems to be larger than that of the melting. The phase transition therefore must be of order-disorder type.

Based on the NQR results and the structure of the room-temperature phase, the structure of the high-

temperature phase may be assumed. In the room-temperature phase, hydrazinium ions, Br(2), Br(4), and Cd atoms are located nearly on the same plane parallel to the *ac* plane, as seen from Figure 4. Hence, in the high-temperature phase, this plane may become a mirror plane, leading to space group of $P2_1/m$. In this case, Br(3) and Br(5) in the room-temperature phase will be equivalent, resulting in four ^{81}Br NQR lines.

The temperature dependence of ^{81}Br NQR frequencies in $[H_2NNH_3]_2CdBr_4$-$4H_2O$ (**3**) is shown in Figure 7. Two NQR lines were observed at temperatures between 77 and around 320 K. TGA measurement shows that a dehydration starts around 320 K on heating. Hence, the disappearance of NQR lines around 320 K can be ascribed to a dehydration. As already pointed out above, the anion is considered to form an isolated tetrahedron. The ^{81}Br NQR frequencies observed are considerably lower than those in $CdBr_4$ complexes. This may be ascribed to hydrogen bonds between Br atoms and hydrazinium ions and/or water molecules [16]. Accordingly the positive temperature coefficients of NQR lines are probably due to a destruction of NH···Br and/or OH···Br hydrogen bonds.

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