NQR Study of Piperazinium Tetrahalogenometalates(II) $[C_4H_{12}N_2]MX_4$ (M = Zn, Cd, Hg; X = Br, I)

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The ^{81}Br and ^{127}I NQR (ν_1: $m = \pm 1/2 \leftrightarrow m = \pm 3/2$ transition) frequencies in the title compounds were measured as functions of temperature. Four NQR lines were observed for each bromide or iodide in the temperature range investigated. Piperazinium tetrabromocadmate(II) was obtained as a monohydrate (**1**) containing isolated $CdBr_4{}^{2-}$ anions, piperazinium dications, and water molecules (monoclinic, $P2_1/c$ at 293 K). The crystal structure of piperazinium tetraiodocadmate(II) (**2**) was found to consist of isolated $CdI_4{}^{2-}$ anions and dications (orthorhombic, $P2_12_12_1$ at 293 K). The structures of others seem to be similar to that of (**2**). The DSC measurement of (**1**) showed heat anomalies at ca. 363, 386 and 556 K, that of the anhydrous sample only at 556 K, which suggests that the former two heat anomalies are due to dehydration. All the other compounds exhibited also a phase transition around 550 K and decomposed above 600 K. Disappearance (or remarkable weakening in intensity) of the NQR lines was observed at 330 - 350 K in all compounds, indicating the pronounced excitation of librational motions of anions and/or cations. The NQR results indicate that the covalent character of M-X bond is in the order Zn-X < Cd-X $\ll$ Hg-X.

Key words: NQR; DSC; Piperazinium Tetrahalogenometallate(II); Bond Character; Phase Transition.

1. Introduction

We have studied the structures and phase transitions of cadmium(II) halide complexes for the last decade by means of nuclear quadrupole resonance (NQR) and X-ray crystal structure analysis [1 - 11].

In accordance with the expectation of successive phase transitions in A_2MX_4 and A'MX_4 type compounds we found such transitions in most of those (A = $[H_3N(CH_2)_2CH_3]^+$ and $[H_3N(CH_2)_3CH_3]^+$ and A' = $[H_3N(CH_2)_3NH_3]^{2+}$) [6 - 8, 11, 12]. It is interesting to inquire which combination of cation and anion results in crystals subjected to phase transitions. Phase transitions seem to be frequent in crystals in which cations and/or anions sustain rotational motions (such as reorientaion) as a whole or in the parts when the temperature is raised.

Piperazinium dication $[C_4H_{12}N_2]^{2+}$ has a non-planar structure. Further, it may take part in the hydrogen bonding N-H···X with anions through four N-H bonds per dication. It is therefore expected that the piperazinium dications in the crystals do not undergo rotational motions as a whole or in part at low temperatures. In a study of the structures and phase transitions of a series of A'CdX_4 compounds we prepared $[C_4H_{12}N_2]MX_4$ (M = Zn, Cd, Hg; X = Br, I). In the present work the halogen NQR and DSC measurements and part of the X-ray results on these compounds are described. The M-X bond character is also discussed on the basis of the NQR data. The tetrabromocadmate(II) was obtained as a monohydrate $[C_4H_{12}N_2]CdBr_4$-H_2O from a hydrobromic acid solution.

2. Experimental

Piperazinium halogenocadmate(II) was synthesized by mixing piperazine and cadmium(II) carbo-

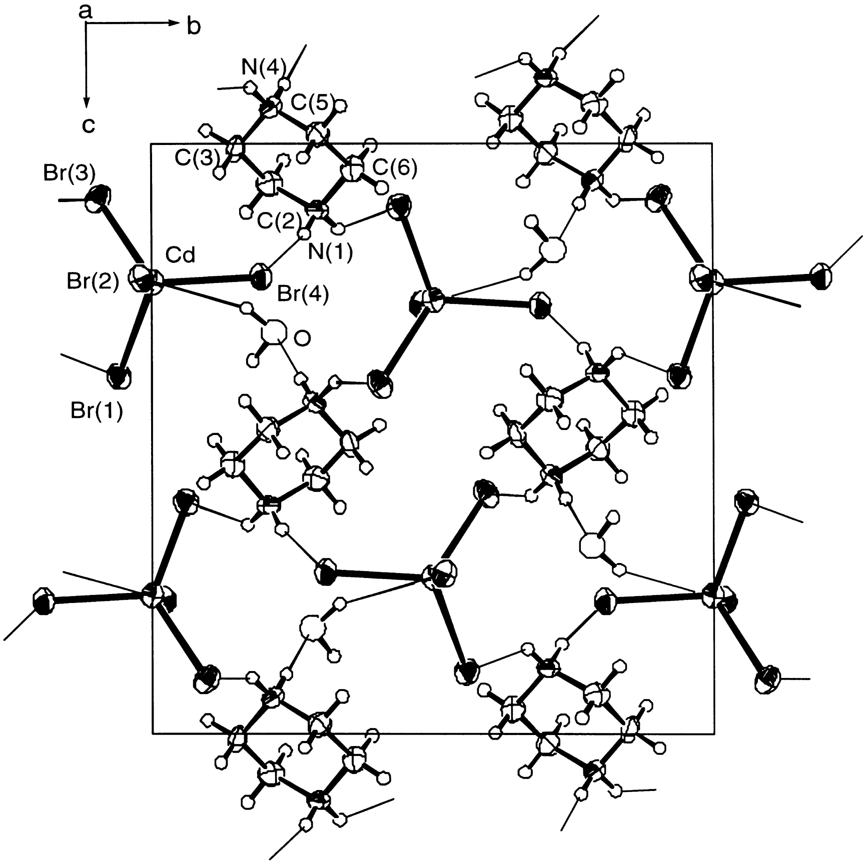

Fig. 1. The projection of the unit cell of $[C_4H_{12}N_2]CdBr_4$-H_2O (**1**) along [100] onto the *bc* plane. Hydrogen bonds are shown with thin lines.

Table 1. Chemical analysis (wt.%) of piperazinium complexes.

Compound	C Calcd.	C Obsd.	H Calcd.	H Obsd.	N Calcd.	N Obsd.
$[C_4H_{12}N_2]CdBr_4$-H_2O	8.92	8.98	2.62	2.63	5.20	5.24
$[C_4H_{12}N_2]CdI_4$	6.78	6.83	1.70	1.67	3.95	3.99
$[C_4H_{12}N_2]ZnBr_4$	10.15	10.02	2.55	2.55	5.92	5.83
$[C_4H_{12}N_2]ZnI_4$	7.26	7.28	1.82	1.85	4.23	4.23
$[C_4H_{12}N_2]HgBr_4$	7.90	7.89	1.99	1.85	4.60	4.63
$[C_4H_{12}N_2]HgI_4$	6.03	6.25	1.52	1.46	3.52	3.67

nate of the molar ratio 1:1 in concentrated hydrobromic acid or hydroiodic acid. Colorless prismatic crystals of $[C_4H_{12}N_2]CdBr_4$-H_2O precipitated from the mixture. $[C_4H_{12}N_2]CdI_4$ formed pale yellow rods. Piperazinium tetrahalogenozincate(II) and tetrahalogenomercurate(II) were prepared in a similar way using zinc(II) and mercury(II) bromide or iodide, respectively. $[C_4H_{12}N_2]ZnBr_4$ and $[C_4H_{12}N_2]HgBr_4$ crystallized as colorless rods, $[C_4H_{12}N_2]ZnI_4$ and $[C_4H_{12}N_2]HgI_4$ as pale yellow rods. The results of the chemical analyses are listed in Table 1.

The ^{81}Br and ^{127}I NQR signals were observed using a homemade super-regenerative type spectrometer, and the resonance frequencies were determined by a counting method. The structure of the piperazinium halogenocadmates will be reported elsewhere in detail [13]. The DSC measurements were carried out between ca. 130 and 590 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}.

3. Results and Discussion

$[C_4H_{12}N_2]CdBr_4$-H_2O (**1**) crystallizes with isolated $CdBr_4^{2-}$ anions, piperazinium (Pipz) dications, and water molecules (monoclinic, $P2_1/c$, $a = 698.7(1)$, b = 1348.6(3), c = 1432.4(3) pm, β = 92.97(3)°, Z = 4 at 293 K) as shown in Figure 1. The crystal of $[C_4H_{12}N_2]CdI_4$ (**2**) consists of isolated CdI_4^{2-} anions and Pipz dications (orthorhombic, $P2_12_12_1$, a = 903.2(5), b = 1226.3(6), c = 1307.9(7) pm, Z = 4 at

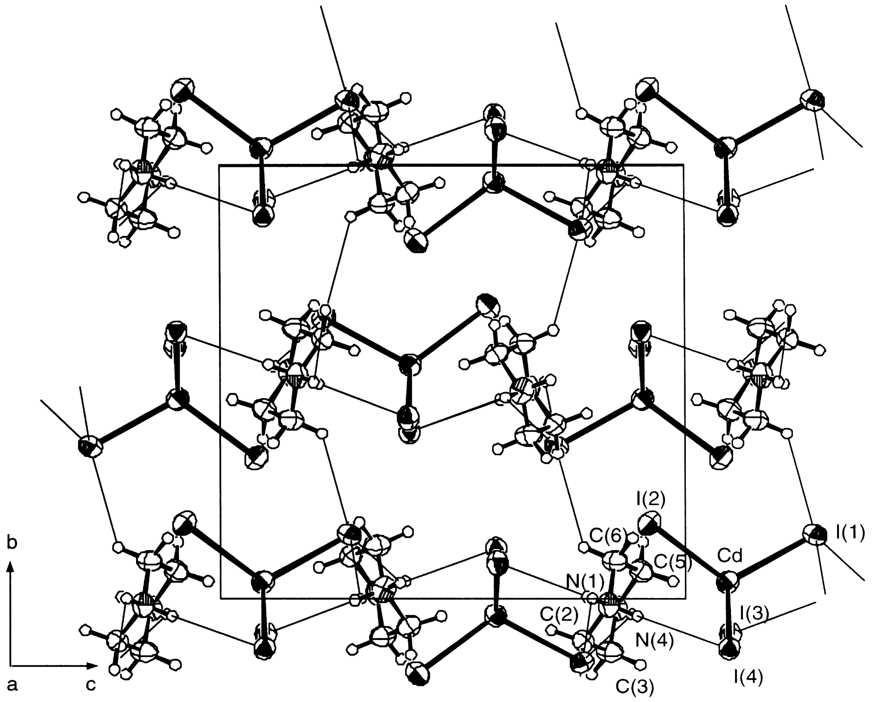

Fig. 2. The projection of the unit cell of $[C_4H_{12}N_2]CdI_4$ (**2**) along [100] onto the *bc* plane. Hydrogen bonds are shown with thin lines.

Table 2. ^{81}Br NQR frequencies and ^{127}I NQR frequencies of piperazinium complexes at several temperatures.

Compound	T / K		ν / MHz[a]			
$[C_4H_{12}N_2]ZnBr_4$	77		68.91	64.19	56.65	52.29
	275		67.80	62.63	55.54	51.30
$[C_4H_{12}N_2]CdBr_4$-H_2O	77		68.96	64.15	61.95	54.24
	275		67.34	63.49	60.09	53.65
$[C_4H_{12}N_2]HgBr_4$	77		100.46	94.12	80.26	67.53
	275		98.19	90.91	78.04	65.81
$[C_4H_{12}N_2]ZnI_4$	77	ν_1	88.60	84.51	83.81	72.87
	275	ν_1	87.14	82.56	81.10	71.13
	77	ν_2	173.77	158.43	137.48	112.70
	275	ν_2	171.18	154.47	135.09	111.75
$[C_4H_{12}N_2]CdI_4$	77	ν_1	90.74	84.75	83.97	74.40
	275	ν_1	88.70	82.63	81.17	72.62
	77	ν_2	177.99	160.96	141.33	113.88
	275	ν_2	174.62	156.23	138.31	112.38
$[C_4H_{12}N_2]HgI_4$	77	ν_1	122.52	115.56	98.39	97.58
	275	ν_1	120.02	112.51	95.65	94.23
	77	ν_2	225.24	191.01	150.57	139.78
	275	ν_2	n.o.	n.o.	147.52	137.36

[a] ν_1 and ν_2 are frequencies corresponding to the transitions of $m = \pm 1/2 \leftrightarrow \pm 3/2$ and $m = \pm 3/2 \leftrightarrow \pm 5/2$ for ^{127}I, respectively.

293 K) as shown in Figure 2. The crystal lattices of (**1**) and (**2**) are stabilized by the N-H···Br, O-H···Br, and N-H···O hydrogen bond networks and by the N-H···I networks, respectively. The structures of other compounds have not been determined yet, but they seem to be similar to that of (**2**) according to the DSC and NQR results described below.

Table 2 lists the NQR frequencies including the ^{127}I NQR frequencies (ν_2: $m = \pm 3/2 \leftrightarrow m = \pm 5/2$ transition) at 77 K and 275 K. The anhydrous sample of $[C_4H_{12}N_2]CdBr_4$-H_2O (**1**) showed no NQR signals, although we have tried to measure at several temperatures. All compounds listed in Table 2 give four resonance lines for each transition, indicating that the four halogen atoms of each anion are crystallographically nonequivalent in accordance with the structures shown in Figs. 1 and 2. The relatively large asymmetry parameter of the electric field gradients (EFG's) which could be expected for the iodine compounds suggest that the N-H···I hydrogen bonds are fairly strong. We did not calculate them in Table 2 because of the difficulty of paring up of ν_1 and ν_2 due to the proximity of the resonance lines. The temperature dependencies of the ^{81}Br NQR frequencies in the bromides are given in Fig. 3, and those of the ^{127}I NQR frequencies (ν_1: $m = \pm 1/2 \leftrightarrow m = \pm 3/2$ transition) in the iodides in Figure 4. All the frequencies in each compound decrease almost linearly with temperature without showing any signs of phase transition. Although the intensities of resonance lines of these compounds were quite large at low temperatures, they

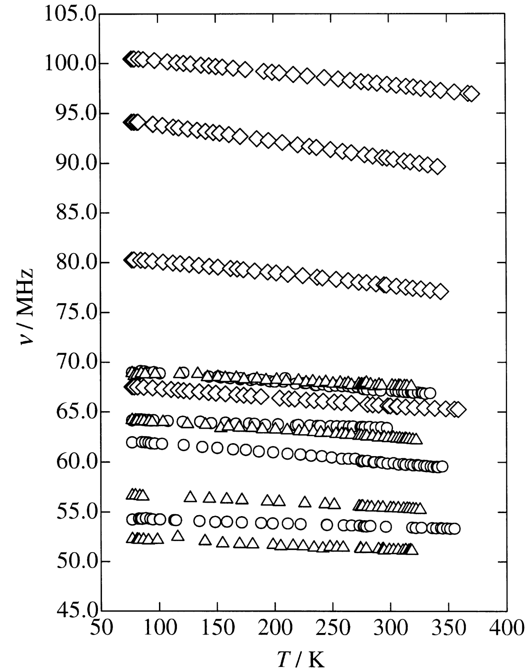

Fig. 3. The temperature dependence of ^{81}Br NQR frequencies. o: $[C_4H_{12}N_2]CdBr_4$-H_2O, △: $[C_4H_{12}N_2]ZnBr_4$, ◇: $[C_4H_{12}N_2]HgBr_4$.

decreased gradually with increasing temperature and diminished below the limit of observation around 330 - 350 K with the exceptions of $[C_4H_{12}N_2]HgBr_4$ and $[C_4H_{12}N_2]HgI_4$. In these two compounds the resonance lines were still observed above 350 K in spite of severe decrease in intensities. It should be noted that the highest-frequency lines of these two compounds were rather strong and sharp at high temperatures, whereas the other lines were almost vanishing. The disappearance and weakening of the NQR lines around 330 - 350 K in these compounds, except for $[C_4H_{12}N_2]CdBr_4$-H_2O (**1**), must be due to the librational motions of Pipz cations and/or MX_4^{2-} anions which fluctuate the EFG's at the halogen nuclei. The disappearance of the NQR lines in the case of (**1**) must be due to dehydration, as mentioned below.

All the compounds investigated decomposed at temperatures above 600 K. In the DSC measurement of $[C_4H_{12}N_2]CdBr_4$-H_2O (**1**) heat anomalies were found at ca. 363, 386, and 556 K. On the other hand, the anhydrous sample of (**1**), obtained by drying on silica gel, showed a heat anomaly only at 556 K. This indicates that the former two anomalies of (**1**) must be due to dehydration. All the other compounds showed a single heat anomaly corresponding to the 556 K transition of (**1**)3. The transition temperatures show slightly the anion dependence in a plot of the phase transition temperatures against the metals in MX_4 anions in (Fig. 5). These phase transitions seem to be first-order by considering the shape of a heat anomaly. In addition, they appear to be of the displacive type, because the observed transition entropies ΔS_{tr} are very small. The phase transitions in the anhydrous analogues seem to follow the same mechanism.

Although the A_2MX_4 or $A'MX_4$ type compounds are known to undergo successive phase transitions [6 - 8, 11, 12], these anhydrous Pipz complexes show only one phase transition at considerably high temperature. This reflects probably the lattice stability which depends on the strength of N-H···X hydrogen bonds. The average positive charge on hydrogen atoms in NH_2^+ groups in a Pipz dication is greater than in NH_3^+ groups in a propanediammonium (Pda) dication [14], which should lead to stronger N-H···X hydrogen bonds in Pipz complexes than in Pda ones. Therefore, the crystal lattice of Pipz tetrahalogenocadmate seems to be more stable than that of Pda

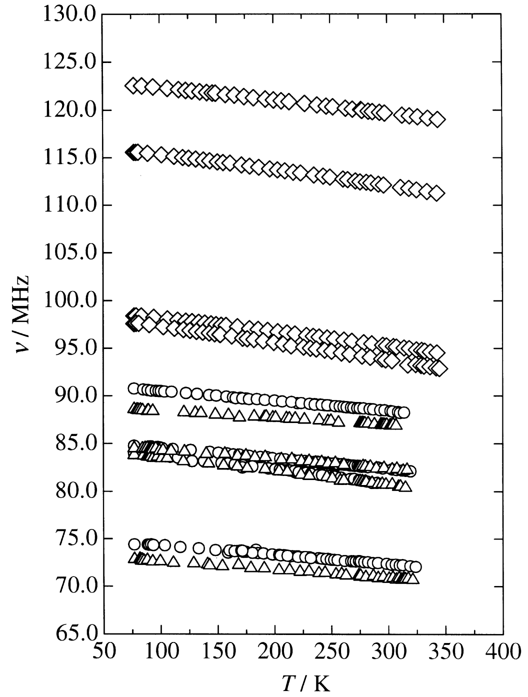

Fig. 4. The temperature dependence of $^{127}I(\nu_1)$ NQR frequencies. o: $[C_4H_{12}N_2]CdI_4$, △: $[C_4H_{12}N_2]ZnI_4$, ◇: $[C_4H_{12}N_2]HgI_4$.

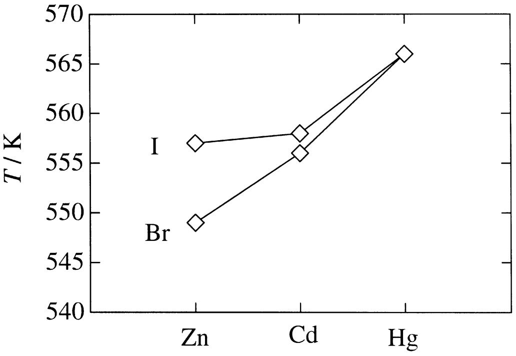

Fig. 5. Transition temperatures of anhydrous piperazinium complexes.

tetrahalogenocadmate, which must be experimentally observed as a difference in the decomposition temperatures or melting points, and as the existence or nonexistence of a phase transition. The decomposition temperature of Pda tetrabromocadmate(II) is 554 K, and its transition points are 328, 363, and 495 K [6]. Pda tetraiodocadmate(II) monohydrate decomposes at 351 K and undergoes a phase transition at 245 K [8]. The absence of a phase transition at low temperatures of these compounds seems to follow from the lack of any rotational freedom in Pipz dications.

The coincidence in the number and the resemblance in the temperature dependence among the NQR lines of the compounds studied indicate that these structures are similar to $[C_4H_{12}N_2]CdI_4$, and the structural difference between $[C_4H_{12}N_2]CdBr_4$-H_2O and $[C_4H_{12}N_2]CdBr_4$ may be small. Therefore we compare the bond character in M-X bonds with the different metal from the NQR frequencies. Figure 6 shows averaged NQR frequencies at 77 K for three metals. As usual, we expect that the higher the NQR frequencies are, the larger the covalent character is. Thus, the plot indicates that the covalent character is in the order Zn-X < Cd-X ≪ Hg-X. This is consistent with the expectation from the Hard and Soft Acid and Base theory [15]. According to this theory the order of softness as acids is $Zn^{2+} < Cd^{2+} \ll Hg^{2+}$ and the soft acids makes stronger bonds in the order of $Cl^- < Br^- < I^-$.

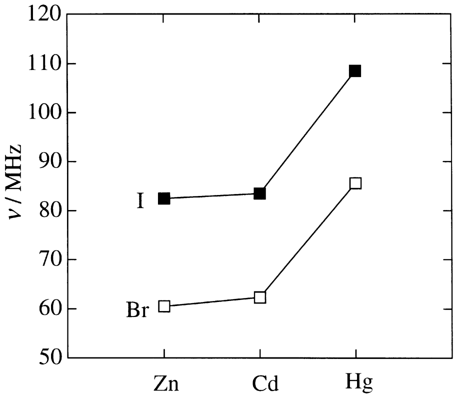

Fig. 6. Averaged NQR frequencies of piperazinium complexes. NQR frequencies (ν_1 for iodides) at 77 K.

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