Differential scanning calorimetry studies on structural phase transitions and molecular motions in $(CH_3NH_3)_2MBr_4$ and $[(CH_3)_2NH_2]_2MBr_4$ (M = Zn, Cd, and Hg)

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Abstract. Structural phase transitions and molecular motions in (CH$_3$NH$_3$)$_2$MBr$_4$ and in [(CH$_3$)$_2$NH$_2$]$_2$MBr$_4$ (M = Zn, Cd, and Hg) were investigated by differential scanning calorimetry (DSC) between about 130 K and the melting points. All of the compounds showed at least one structural phase transition over the temperature region investigated. The values of the transition entropies obtained suggest that these transitions are of the order–disorder type. N–H$\cdots$Br hydrogen bonds were found to play an important role in the stability of $P2_1/c$ room-temperature phases of the title compounds. In the highest-temperature solid phases of all title compounds, orientational orders of cations seem to be completely lost.

1. Introduction

In the last few years, the title compounds have been investigated by means of ^{81}Br nuclear quadrupole resonance (NQR) [1–5] and ^{1}H nuclear magnetic resonance (NMR) [2, 6, 7]. All six compounds are known to have the same crystal structure, monoclinic $P2_1/c$ or $P2_1/n$ [4, 8–12], which is a subgroup of orthorhombic $Pnma$. The A$_2$BX$_4$ family with the β-K$_2$SO$_4$ structure (space group: $Pnma$) have already been extensively investigated, and many compounds in this family have been reported to show successive phase transitions including a $Pmcn$–$P2_1/c$ transition, and to have incommensurate and/or ferroelectric phases [13]. However, no phase transitions have been detected for the title compounds except for (CH$_3$NH$_3$)$_2$ZnBr$_4$ [1, 6] and (CH$_3$NH$_3$)$_2$CdBr$_4$ [7]. The aim of this investigation is to study structural phase transitions in the title compounds by differential scanning calorimetry (DSC).

2. Experimental procedure

The samples used in the NQR measurements were employed in the present DSC study. A differential scanning calorimeter, DSC220, with a disk-station, SSC5200, from Seiko Instruments Incorporated was used for thermal measurements between about 130 K and the melting points. Samples of around 10 mg were employed and the heating and cooling rates were usually set at 10 and 5 K min^{-1}, respectively. The measurements were carried out under an atmosphere of dry N$_2$ gas with a flow rate of about 40 ml min^{-1} and repeated more than three times.

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Since detailed crystal data for $(CH_3NH_3)_2ZnBr_4$ are unavailable, its crystal structure was determined by a single-crystal x-ray diffraction method. A single crystal for the x-ray measurement was obtained by recrystallizing a polycrystalline sample from water. Crystal data and experimental conditions are listed in table 1. Data for structure determinations were collected on a Nonius CAD-4 diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å) at room temperature. The intensity data were corrected for both Lorentz-polarization and absorption effects. The structure was solved by direct methods and refined by full-matrix least-squares methods. Hydrogen atoms were not located and all atoms were refined with anisotropic thermal parameters. All of the calculations were performed on a VAX station 4000 with the MolEN program package [14].

Table 1. Crystal data, data collection, and structure refinement.

Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	7.971(1)
b/Å	13.148(3)
c/Å	11.250(1)
β/deg	96.37(1)
Volume of unit cell/Å^3	1171.8(3)
Formula unit per cell	4
D_x/g cm^{-3}	2.546
Linear absorption coefficient/mm^{-1}	31.218
Crystal size/mm^3	$0.50 \times 0.41 \times 0.28$
Number of reflections measured	2358
Number of independent reflections	2136
Number of reflections with $I \geqslant 3\sigma(I)$	957
Maximum value of θ/deg	25.3
R	0.077
wR	0.095
S	3.110
Number of parameters	83

3. Results and discussion

3.1. Crystal structures

The results of the crystal structure analysis are given in tables 2 and 3 and figure 1. Crystal data for the title compounds at room temperature are summarized in table 4 [4, 9–12]. We see that all complexes have the same crystal structure; the anion has an isolated tetrahedral structure and layers made up of cations and anions stack along the longest axis as can be seen from figure 1. However, NQR results for methylammonium compounds (abbreviated as MABr) are slightly different from those for dimethylammonium ones (abbreviated as DMABr) [1–5].

First of all, the distributions in NQR frequencies of DMABr are wider than those of MABr. All compounds gave four ^{81}Br NQR signals originating from four crystallographically independent bromine atoms belonging to the same anion. The frequency difference between the highest and lowest lines in each DMABr at 77 K is 1.5–2.5 times as large as that in the corresponding MABr. This can be ascribed to the fact that the deviation from a regular tetrahedron in MBr$_4$ anions is larger in DMABr, i.e., distributions in metal–bromine bond distances in DMABr are wider than those in MABr as can be seen from table 5.

Secondly, it can be pointed out that all of the lowest- and second-lowest-frequency lines in MABr show anomalous temperature dependences, i.e., little dependence on temperature

Table 2. Fractional atomic coordinates and equivalent isotropic displacement parameters (10^{-2} Å^2). U_{eq} is defined as one third of the trace of the orthogonalized U_{ij}-tensor; $U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \boldsymbol{a}_i \cdot \boldsymbol{a}_j$.

Atom	x	y	z	U_{eq}
Zn	0.2341(4)	−0.0651(2)	0.2712(3)	3.22(6)
Br1	0.2555(4)	0.1172(2)	0.2723(3)	5.55(7)
Br2	0.2014(4)	−0.1302(2)	0.0704(2)	4.95(6)
Br3	0.4914(3)	−0.1284(2)	0.3764(2)	4.50(6)
Br4	−0.0040(3)	−0.1165(2)	0.3688(3)	5.03(6)
N1	0.718(3)	0.098(2)	0.372(2)	5.9(6)
C1	0.741(4)	0.116(2)	0.252(2)	5.9(7)
N2	−0.203(2)	−0.203(2)	0.013(2)	5.1(5)
C2	−0.328(4)	−0.135(2)	0.064(2)	6.3(8)

Table 3. Bond distances (Å), angles (deg), and N$\cdots$Br distances (Å).

Bond distance		Bond angle		N$\cdots$Br distance	
Zn–Br1	2.404(4)	Br1–Zn–Br2	111.0(2)	N1$\cdots$Br3	3.48(2)
Zn–Br2	2.402(4)	Br1–Zn–Br3	106.7(2)	N1$\cdots$Br3	3.46(2)
Zn–Br3	2.400(4)	Br1–Zn–Br4	109.8(2)	N1$\cdots$Br4	3.59(2)
Zn–Br4	2.392(4)	Br2–Zn–Br3	109.7(2)	N1$\cdots$Br4	3.50(2)
		Br2–Zn–Br4	108.8(2)	N2$\cdots$Br1	3.39(2)
		Br3–Zn–Br4	110.8(2)	N2$\cdots$Br1	3.43(2)
N1–C1	1.41(3)			N2$\cdots$Br2	3.36(2)
N2–C2	1.51(4)			N2$\cdots$Br3	3.52(2)
				N2$\cdots$Br4	3.36(2)

Table 4. Crystal data for $(CH_3NH_3)_2MBr_4$ and $[(CH_3)_2NH_2]_2MBr_4$ (M = Zn, Cd, and Hg).

Compound	Space group	a/Å	b/Å	c/Å	β/deg	V/Å^3	Z	Reference
$(CH_3NH_3)_2ZnBr_4$	$P2_1/c$	7.971(1)	13.148(3)	11.250(1)	96.37(1)	1171.8	4	This work
$(CH_3NH_3)_2CdBr_4$	$P2_1/c$	8.123(1)	13.436(2)	11.419(1)	96.19(1)	1239.0	4	[9]
$(CH_3NH_3)_2HgBr_4$	$P2_1/c$	8.124(1)	13.431(4)	11.389(5)	96.14	1227.5	4	[10]
$[(CH_3)_2NH_2]_2ZnBr_4$	$P2_1/c$	8.706(3)	11.956(4)	16.289(5)	121.84(1)	1440.3	4	[4]
$[(CH_3)_2NH_2]_2CdBr_4$	$P2_1/n$	8.158(3)	11.632(4)	15.166(8)	94.82(5)	1434.1	4	[11]
$[(CH_3)_2NH_2]_2HgBr_4$	$P2_1/n$	8.209(3)	11.778(3)	15.269(8)	94.42(4)	1471.9	4	[12]

and a positive temperature coefficient, respectively, while all NQR signals for DMABr except for the lowest-frequency line in $[(CH_3)_2NH_2]_2ZnBr_4$ exhibit normal temperature variations. Such anomalies in the temperature variation of the NQR frequency are usually observed for a system where atoms containing resonant nuclei make hydrogen bonds [15–17]. In fact, table 5 indicates that there are weak N$\cdots$Br hydrogen bonds in the title compounds. Both NQR and x-ray results suggest that hydrogen bonds in MABr are stronger than those in DMABr.

3.2. $(CH_3NH_3)_2MBr_4$

DSC results for MABr are given in table 6. We carried out DSC measurements previously on $(n\text{-}C_nH_{2n+1}NH_3)_2ZnX_4$ (X = Cl and Br; n = 1–5) [18, 19], and some of these results are added to tables 6 and 7 for comparison. $(CH_3NH_3)_2ZnCl_4$ also forms monoclinic crystals with space group $P2_1/c$ at room temperature [20]. All compounds listed in table 6 undergo a
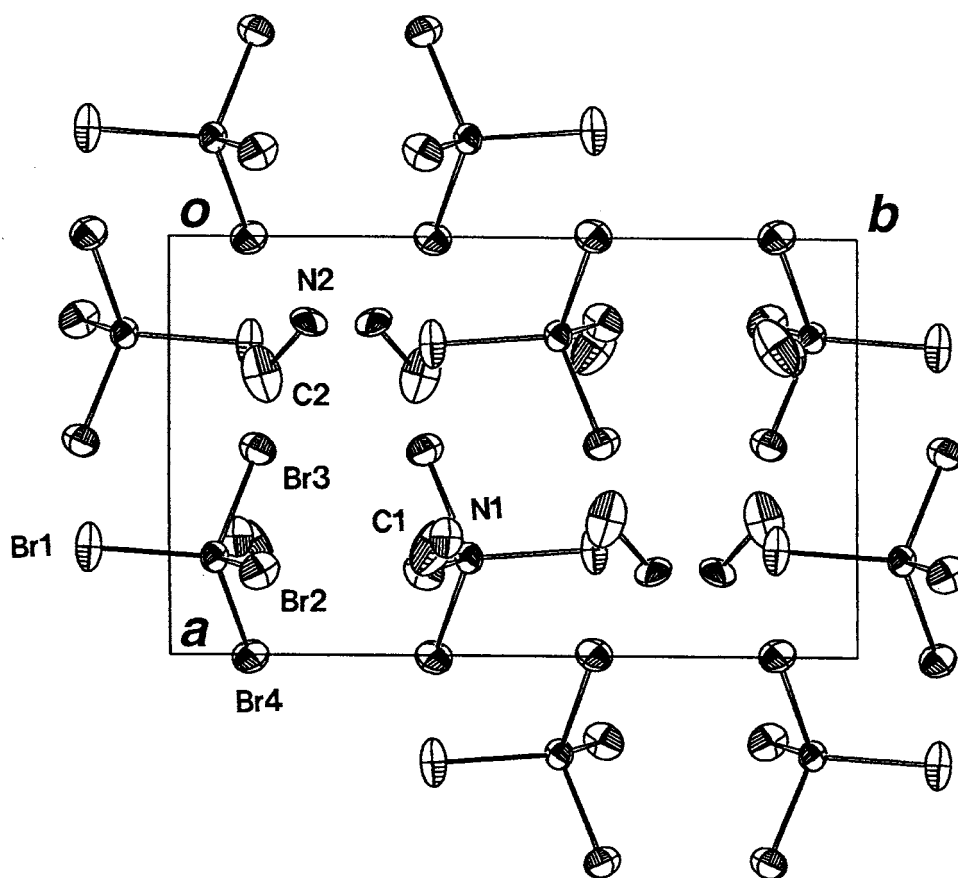
Figure 1. Projection of the unit cell onto the *ab*-plane drawn using ORTEP with 50%-probability-displacement ellipsoids.

single structural phase transition of first order between about 130 K and the melting points. We see that transition temperatures T_c and transition entropies ΔS in these phase transitions and melting entropies ΔS_m are similar to one another. The ΔS values observed suggest that all of these transitions are of the order–disorder type. ^{1}H NMR investigations on $(CH_3NH_3)_2ZnBr_4$ [6], $(CH_3NH_3)_2CdBr_4$ [7], and $(CH_3NH_3)_2ZnCl_4$ [21] revealed that in the high-temperature solid phases of these compounds, methylammonium cations perform overall reorientation around their centre of gravity. This means that orientational orders of cations are completely lost at the transitions, because it has been confirmed by x-ray measurements that the cations are ordered in the room-temperature phases [9, 10, 20]. Accordingly, these phase transitions are considered to be induced by disordering of methylammonium cations.

The fact that the ΔS_m values of $(CH_3NH_3)_2CdBr_4$ and $(CH_3NH_3)_2ZnCl_4$ are nearly the same and the above-mentioned ^{1}H NMR results for the two compounds and $(CH_3NH_3)_2ZnBr_4$ suggest that their high-temperature phases are in very analogous states. It is most likely that the crystal structures of these phases are quite similar or the same. Since the orientational order of the tetrahedral anions and the positional order of the cations and the anions are probably preserved in the high-temperature phase, the ΔS_m value of ≈ 27 J K^{-1} mol^{-1} is ascribable to losing these orders. In this case, a ΔS value of ≈ 18 J K^{-1} mol^{-1} is attributable to

Table 5. Metal–bromine distances and N···Br distances (less than 3.5 Å) in $(CH_3NH_3)_2MBr_4$ and $[(CH_3)_2NH_2]_2MBr_4$ (M = Zn, Cd, and Hg) [4, 9–12].

	Metal–bromine distance/Å			N···Br distance/Å		
	Zn–Br	Cd–Br	Hg–Br	Zn	Cd	Hg
MABr	2.392	2.575	2.591	3.36	3.37	3.38
	2.400	2.580	2.601	3.36	3.37	3.39
	2.402	2.582	2.602	3.39	3.38	3.41
	2.404	2.585	2.602	3.43	3.42	3.42
				3.46	3.42	3.44
				3.48	3.50	
				3.50		
DMABr	2.385	2.526	2.569	3.335	3.32	3.39
	2.388	2.543	2.588	3.368	3.37	3.41
	2.406	2.551	2.603	3.423	3.38	3.41
	2.434	2.576	2.650	3.455	3.46	3.48
					3.47	

Table 6. Transition temperatures T_c, orders of transitions, transition enthalpies ΔH, transition entropies ΔS, thermal hystereses ΔT, melting points T_m, melting enthalpies ΔH_m, melting entropies ΔS_m, and total entropy changes ΔS_t ($=\Delta S + \Delta S_m$) for $(CH_3NH_3)_2MBr_4$ (M = Zn, Cd, and Hg). Values for $(CH_3NH_3)_2ZnCl_4$ are given for comparison.

Compound	T_c (K)	Order	ΔH (kJ mol^{-1})	ΔS (J K^{-1} mol^{-1})	ΔT (K)	Reference
$(CH_3NH_3)_2ZnBr_4$	457 ± 1	1st	9.1 ± 0.5	20 ± 1	10 ± 2	[19]
$(CH_3NH_3)_2CdBr_4$	481 ± 1	1st	7.2 ± 0.4	15 ± 1	13 ± 1	This work
$(CH_3NH_3)_2HgBr_4$	451 ± 3	1st				This work
$(CH_3NH_3)_2ZnCl_4$	478 ± 1	1st	8.8 ± 0.5	18 ± 1	12 ± 2	[19]

Compound	T_m (K)	ΔH_m (kJ mol^{-1})	ΔS_m (J K^{-1} mol^{-1})	ΔT (K)	ΔS_t (J K^{-1} mol^{-1})	Reference
$(CH_3NH_3)_2ZnBr_4$	$569 \pm 1^*$					[19]
$(CH_3NH_3)_2CdBr_4$	488 ± 1	13.7 ± 0.7	28.0 ± 1.4	20 ± 1	43 ± 2.5	This work
$(CH_3NH_3)_2HgBr_4$	456 ± 3				48 ± 2.5	This work
$(CH_3NH_3)_2ZnCl_4$	552 ± 1	14 ± 1	26 ± 1.5		44 ± 2.5	[19]

* Decomposed.

losing the orientational order of methylammonium cations. These assignments agree with our evaluations for a contribution of each order to the entropy made in the previous paper [19]; from the analysis of thermal data on $(n\text{-}C_nH_{2n+1}NH_3)_2ZnCl_4$ ($n = 1$–18), we roughly estimated the entropy gains due to the melting of the positional order for the cation and the anion, ΔS_p, and of the orientational order for the anion, ΔS_{ao}, and the cation, ΔS_{co}, as 9, 17, and 18 J K^{-1} mol^{-1} ($n = 1$). In the present case, $\Delta S = \Delta S_{co}$ and $\Delta S_m = \Delta S_p + \Delta S_{ao}$. These estimated values are interpreted qualitatively as follows. Since a rigid methylammonium cation and MBr$_4$ anion have two and three degrees of freedom in rotation, respectively, hindered rotations of the cations about two axes and of the anions about three axes have contributions of $4R$ (~33 J K^{-1} mol^{-1}) and $3R$ (~25 J K^{-1} mol^{-1}) to the entropy, respectively. Values of 18 and 17 J K^{-1} mol^{-1} are smaller than $4R$ and $3R$, respectively. This is because ionic rotations in liquid (fused salt) are not completely free but fairly hindered. A small value of $\Delta S_p = 9$ J K^{-1} mol^{-1}, suggesting that the anions and the cations scarcely obtain translational degrees of freedom in a liquid state,

Table 7. Transition temperatures T_c, orders of transitions, transition enthalpies ΔH, transition entropies ΔS, thermal hystereses ΔT, melting points T_m, melting enthalpies ΔH_m, melting entropies ΔS_m, and total entropy changes ΔS_t ($=\Delta S + \Delta S_m$) for $[(CH_3)_2NH_2]_2MBr_4$ (M = Zn, Cd, and Hg). Values for $(C_2H_5NH_3)_2ZnCl_4$ are given for comparison [19].

Compound	T_c (K)	Order	ΔH (kJ mol^{-1})	ΔS (J K^{-1} mol^{-1})	ΔT (K)
$[(CH_3)_2NH_2]_2ZnBr_4$	401 ± 1	1st	8.9 ± 0.4	22 ± 1	2
	435 ± 1	1st	5.7 ± 0.3	13 ± 1	0.5
$[(CH_3)_2NH_2]_2CdBr_4$	380 ± 1	1st	10.5 ± 0.5	27.7 ± 1.4	1
	413 ± 1	1st	2.3 ± 0.1	5.6 ± 0.3	3
	426 ± 2	1st	1.7 ± 0.2	3.9 ± 0.4	1
$[(CH_3)_2NH_2]_2HgBr_4$	356 ± 1	1st	9.9 ± 0.5	28 ± 1.5	0
$(C_2H_5NH_3)_2ZnCl_4$	234 ± 1	1st	3.9 ± 0.2	17 ± 1	12 ± 2

Compound	T_m (K)	ΔH_m (kJ mol^{-1})	ΔS_m (J K^{-1} mol^{-1})	ΔT (K)	ΔS_t (J K^{-1} mol^{-1})
$[(CH_3)_2NH_2]_2ZnBr_4$	459 ± 1	11.2 ± 0.6	24.4 ± 1.2	22 ± 1	60 ± 3
$[(CH_3)_2NH_2]_2CdBr_4$	435 ± 2	8.4 ± 0.8	19 ± 2	35 ± 2	57 ± 4
$[(CH_3)_2NH_2]_2HgBr_4$	$\sim 405^*$				
$(C_2H_5NH_3)_2ZnCl_4$	457 ± 1	18 ± 1	40 ± 2		57 ± 3

* Decomposed.

is much smaller than $3R$, which is estimated from Richards' rule. This is probably because translational motions of molecular ions in a liquid state are highly restricted compared with the motions of atomic ions.

In $(CH_3NH_3)_2HgBr_4$, a transition takes place very close to the melting point; thus enthalpy changes at the transition and the melting could not be measured separately, although we scanned as slowly as possible. However, we could obtain the sum of ΔS and ΔS_m (here we call it a total entropy change ΔS_t), whose value of 48 J K^{-1} mol^{-1} is similar to ΔS_t for $(CH_3NH_3)_2CdBr_4$ and $(CH_3NH_3)_2ZnCl_4$. Probably $(CH_3NH_3)_2HgBr_4$ also belongs to this group, i.e., a phase transition at 451 K is caused by disordering of methylammonium cations and in the high-temperature phase cations perform overall reorientations.

3.3. $[(CH_3)_2NH_2]_2MBr_4$

The DSC results measured for DMABr are given in table 7, where thermal data on $(C_2H_5NH_3)_2ZnCl_4$ are added for comparison, because $C_2H_5NH_3^+$ has a molecular structure very similar to that of $(CH_3)_2NH_2^+$. DMABr showed some structural phase transitions between ≈ 130 K and the melting points. Like in MABr, all of these transitions are first order and of the order–disorder type. Thermal hysteresis in these transitions is however very small, unlike the case for those in MABr.

For $(C_2H_5NH_3)_2ZnCl_4$, we obtained $\Delta S_p = 9$ J K^{-1} mol^{-1}, $\Delta S_{ao} = 17$ J K^{-1} mol^{-1}, and $\Delta S_{co} = 31$ J K^{-1} mol^{-1} [19]. (Since a rigid ethylammonium ion has three degrees of freedom in rotation, ΔS_{co} for $C_2H_5NH_3$ is larger than that for CH_3NH_3.) Hence it is expected that about 57 J K^{-1} mol^{-1} will be observed for ΔS_t in DMABr, because rigid ethylammonium and dimethylammonium ions have the same degrees of freedom in rotation. In fact, $[(CH_3)_2NH_2]_2ZnBr_4$ and $[(CH_3)_2NH_2]_2CdBr_4$ showed almost the same ΔS_t values: 57 J K^{-1} mol^{-1}. This suggests that our estimation for the entropy gains due to the melting of ionic orders in crystal holds for DMABr. Since ΔS_t for $[(CH_3)_2NH_2]_2HgBr_4$ is supposed to have nearly the same values too, the hypothetical ΔS_m for $[(CH_3)_2NH_2]_2HgBr_4$ is estimated

to be ≈ 30 J K^{-1} mol^{-1}. In the case where the highest-temperature phases in DMABr are almost the same as the high-temperature phases in MABr, i.e., the cations have lost their orientational orders completely, ΔS_m for DMABr is expected to be nearly the same as ΔS_m for MABr (≈ 27 J K^{-1} mol^{-1}). ΔS_m values observed for $[(CH_3)_2NH_2]_2ZnBr_4$ and estimated hypothetically for $[(CH_3)_2NH_2]_2HgBr_4$ are close to that value; however, ΔS_m for $[(CH_3)_2NH_2]_2CdBr_4$ is smaller than that value. This is probably because the orientational order of the anions is partly lost in a phase transition. At least, the orientational order of dimethylammonium cations is thought to be wholly lost in the highest-temperature phases in DMABr.

A phase transition between *Pmcn* and $P2_1/c$ is frequently observed in the A_2BX_4 family. For example, the $[(CH_3)_4N]_2MBr_4$ (M = Zn, Cd, and Hg; abbreviated as TMABr) each undergo a single structural phase transition with such a symmetry change [22–26]. These transitions are of the order–disorder type but second order. Phase transitions in Zn and Cd compounds are well known to show anomalous ferroelasticity. The phase transitions in MABr and transitions of the $P2_1/c$ phase in DMABr, i.e., a 401 K transition in $[(CH_3)_2NH_2]_2ZnBr_4$, a 380 K one in $[(CH_3)_2NH_2]_2CdBr_4$, and a 356 K one in $[(CH_3)_2NH_2]_2HgBr_4$, are different from a *Pmcn*–$P2_1/c$ transition. However, we can see some relationship between transition temperatures T_c and unit-cell volumes V of $P2_1/c$ phases in MABr, DMABr, and TMABr. T_c for TMABr is lower than those for MABr and DMABr, i.e., 288 K (Zn), 272 K (Cd), and 272 K (Hg), and V for TMABr is larger than those for MABr and DMABr, i.e., 1865.9 Å^3 (Zn), 1916.3 Å^3 (Cd), and 1924.3 Å^3 (Hg, *Pnma* phase) [22–26]. That is, T_c separating $P2_1/c$ and the higher-temperature phase increases with decreasing V; in other words, the $P2_1/c$ phase becomes stable as V decreases, as can be seen from figure 2. This volume dependence of T_c is manifested in the pressure experiments, too. In measurements of the hydrostatic pressure effect on the phase transitions in $[(CH_3)_4N]_2MBr_4$ (M = Zn and Co), T_c increased with increasing pressure [27]. This suggests that some similarity exists among the transition mechanisms of the nine transitions. N–H$\cdots$Br hydrogen bonds seem to be important for the stability of the $P2_1/c$ phase, because as pointed out previously the hydrogen bonds in MABr are stronger than those in DMABr and there are no N–H$\cdots$Br hydrogen bonds in TMABr.
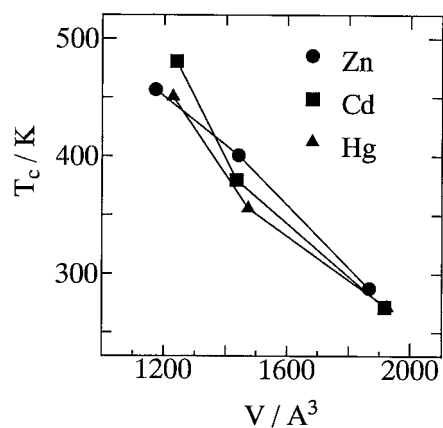

Figure 2. Unit-cell-volume dependences of transition temperatures separating the $P2_1/c$ and higher-temperature phases in $(CH_3NH_3)_2MBr_4$, in $[(CH_3)_2NH_2]_2MBr_4$, and in $[(CH_3)_4N]_2MBr_4$ (M = Zn, Cd, and Hg).

4. Conclusions

$(CH_3NH_3)_2MBr_4$ (M = Zn, Cd, and Hg) each undergo a single structural phase transition between ≈ 130 K and the melting points. These transitions are caused by disordering of

methylammonium cations, and in the high-temperature phases the cations perform overall reorientation around their centre of gravity.

$[(CH_3)_2NH_2]_2MBr_4$ (M = Zn, Cd, and Hg) show some structural phase transitions between ≈ 130 K and the melting points. It is inferred that these transitions are caused by disordering of dimethylammonium cations, and in the highest-temperature phases the orientational orders of the cations are entirely lost.

The estimation for the entropy gains due to the melting of ionic orders in crystal, which was made previously for (n-$C_nH_{2n+1}NH_3)_2ZnCl_4$ (n = 1–18), is found to be applicable to $(CH_3NH_3)_2MBr_4$ and $[(CH_3)_2NH_2]_2MBr_4$ (M = Zn, Cd, and Hg).

The transition temperature marking the separation between the $P2_1/c$ and higher-temperature phases increases with decreasing unit-cell volume of the $P2_1/c$ phase in $(CH_3NH_3)_2MBr_4$, $[(CH_3)_2NH_2]_2MBr_4$, and $[(CH_3)_4N]_2MBr_4$ (M = Zn, Cd, and Hg). N–H$\cdots$Br hydrogen bonds appear to play an important role in the stability of the $P2_1/c$ phase.

Acknowledgment

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