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Differential scanning calorimetry studies on structural phase transitions in $(C_nH_{2n+1}NH_3)_2ZnX_4$ crystals ($n = 1-5$, $X = Br$ or Cl)

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Abstract. The structural phase transitions in $(C_nH_{2n+1}NH_3)_2ZnX_4$ ($n = 1-5$, $X = Br$ or Cl) 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 range investigated. The results for the Cl compounds agreed well with the reported data obtained by DSC or adiabatic calorimetry measurements. The transition temperatures of the Br compounds are in good agreement with those determined by nuclear quadrupole resonance measurements. The values of the transition entropies obtained suggest that most of the phase transitions in the Br compounds are of the order–disorder type like those in the Cl analogues. The nature of the phase transitions in the Br compounds is discussed in comparison with that of those in the corresponding Cl compounds. The entropy changes due to the melting of orientational and positional orders in the alkylammonium and tetrachlorozincate ions are estimated.

1. Introduction

Bis-alkylammonium tetrahalozincates $(C_nH_{2n+1}NH_3)_2ZnX_4$ belong to the A_2MX_4 family with the β - K_2SO_4 structure (space group: $Pnma$). Although many compounds in this family have been extensively investigated already [1], the title compounds have not been studied in detail [2–12]. Tello and co-workers have systematically studied bis-alkylammonium tetrachlorozincates by optical, calorimetric and x-ray measurements [2, 4–9]. According to their investigations: $(CH_3NH_3)_2ZnCl_4$, $(n-C_3H_7NH_3)_2ZnCl_4$ and $(n-C_4H_9NH_3)_2ZnCl_4$ undergo ferroelastic phase transitions; and $(C_2H_5NH_3)_2ZnCl_4$ and $(n-C_5H_{11}NH_3)_2ZnCl_4$ exhibit ferroelastoelectric phase transitions.

In the A_2MX_4 family, Cl and Br compounds frequently show very different phase transitions or phase sequences to each other—for example, the compounds $[(CH_3)_4N]_2ZnCl_4$ and $[(CH_3)_4N]_2ZnBr_4$. We have recently examined the temperature dependence of ^{81}Br nuclear quadrupole resonance (NQR) frequencies in $(C_nH_{2n+1}NH_3)_2ZnBr_4$ ($n = 1-4$) between 77 K and the fade-out temperatures of the NQR signals and determined phase transition temperatures precisely [12]. All of these crystals showed at least one structural phase transition [12]. These results were, however, not sufficient for obtaining an understanding of the phase transitions. In the present investigation, we have carried out calorimetric measurements for the Br compounds as well as the Cl ones with $n = 1-5$

in order to confirm the results of the former experiments and to study further the phase transitions in the Br compounds.

Table 1. Transition temperatures T_c , orders of the transitions, transition enthalpies ΔH , transition entropies ΔS and thermal hysteresis ΔT_c for phase transitions in $(C_nH_{2n+1}NH_3)_2ZnCl_4$ ($n = 1-5$). The numbers in parentheses appear in the references cited.

n	T_c (K)		ΔH Order		ΔS (kJ mol ⁻¹)		ΔT_c (J K ⁻¹ mol ⁻¹)		ΔT_c (K)	Reference
1	478 ± 1	(483)	1st	(1st)	8.8 ± 0.5	(8.7)	18 ± 1	(18.1)	12 ± 2	(22) [2]
	—	(426)	—	(1st)	—	(0.29)	—	(0.68)	—	(11) [2]
2	234 ± 1	(234.3)	1st	(1st)	3.9 ± 0.2	(3.41)	17 ± 1	(15)	12 ± 2	[4]
3	310 ± 2	(310.2)	2nd	(2nd)	2.7 ± 0.3	(2.963)	9.2 ± 1	(10)		[5]
4	290 ± 2	(290.2)	2nd?	(2nd?)	5.8 ± 0.6	(7.73)	21 ± 2.5	(29.3)		[6]
5	350 ± 1	(349.05)	1st	(1st)	9.2 ± 0.5	(8.696)	26 ± 1.5	(24.4)	10 ± 2	[8]
	250 ± 1	(249.65)	1st	(1st)	3.5 ± 0.2	(3.584)	14 ± 1	(14.38)	7 ± 2	[7]
	149 ± 1	(147.95)	1st	(1st)	0.35 ± 0.1	(0.50)	2.3 ± 0.5	(3.3)		[8]
	143 ± 1	(141.5)	1st	(1st)	0.27 ± 0.1	(0.44)	1.9 ± 0.5	(3.1)		[8]

Table 2. Transition temperatures T_c , orders of the transitions, transition enthalpies ΔH , transition entropies ΔS and thermal hysteresis ΔT_c for phase transitions in $(C_nH_{2n+1}NH_3)_2ZnBr_4$ ($n = 1-5$). The reported values are given in parentheses.

n	T_c (K)		Order		ΔH (kJ mol ⁻¹)		ΔS (J K ⁻¹ mol ⁻¹)		ΔT_c (K)	Reference
1	457 ± 1	(456)	1st	(1st)	9.1 ± 0.5	20 ± 1	(19)	10 ± 2	[10]	
	—	(426)	—	(2nd)					[12]	
2	302 ± 1	(299.5)	1st	(1st)	6.9 ± 0.4	23 ± 1.5		33 ± 2	[12]	
3	347 ± 2		2nd		4.6 ± 0.5	14 ± 1.5				
	—	(298)	—	(2nd)					[12]	
	—	(130)	—	(2nd)					[12]	
	299 ± 2	(299)	2nd	(2nd)	3.5 ± 0.4	12 ± 1.5			[12]	
5	244 ± 1		1st		3.2 ± 0.2	13 ± 1		11 ± 2		

In this paper, we will abbreviate $(C_nH_{2n+1}NH_3)_2ZnCl_4$ ($(C_nH_{2n+1}NH_3)_2ZnBr_4$) as meCl (meBr), etCl (etBr), prCl (prBr), buCl (buBr) and peCl (peBr), respectively, in the order of increasing n .

2. Experimental details

The title compounds were made as described in the literature [12] by adding $ZnBr_2$ ($ZnCl_2$) and alkylamine solutions in a molar ration of 1:2 to a small excess of hydrobromic (hydrochloric) acid, and then by the slow evaporation of solvents in a desiccator over P_2O_5 . All of the reagents were obtained from Kanto Chemical Co. Since the crystals obtained are hygroscopic, they were pulverized and then dried over silica gel in a desiccator before the DSC measurements were performed.

A differential scanning calorimeter DSC220 with a disk-station SSC5200 from Seiko Instruments Inc. was used for the 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 N₂ gas with a flow rate of about 40 ml min⁻¹.

Table 3. Melting points T_m , melting enthalpies ΔH_m , melting entropies ΔS_m and total entropy changes $\Delta S_t (= \Delta S + \Delta S_m)$ in $(C_nH_{2n+1}NH_3)_2ZnCl_4$ ($n = 1-5, 10-15, 18$). The numbers in parentheses are from the references cited.

n	T_m (K)	ΔH_m (kJ mol ⁻¹)	ΔS_m (J K ⁻¹ mol ⁻¹)	ΔS_t (J K ⁻¹ mol ⁻¹)	Reference
1	552 ± 1 (552)	14 ± 1	26 ± 1.5 (36)	44 ± 2.5	[3]
2	457 ± 1	18 ± 1	40 ± 2	57 ± 3	
3	454 ± 1	21 ± 1.5	44 ± 2.5	53 ± 3.5	
4	436 ± 1	23 ± 1.5	54 ± 3	75 ± 5.5	
5	436 ± 1 (437)	14 ± 1 (6.8)	33 ± 2 (15.6)	77 ± 5.5 (61)	[8]
10			— (15)	— (112)	[9]
11			— (17)	— (148)	[9]
12			— (17)	— (150)	[9]
13			— (15)	— (172)	[9]
14			— (17)	— (178)	[9]
15			— (15)	— (189)	[9]
18			— (16)	— (240)	[9]

Table 4. Melting points T_m , melting enthalpies ΔH_m , melting entropies ΔS_m and total entropy changes $\Delta S_t (= \Delta S + \Delta S_m)$ for $(C_nH_{2n+1}NH_3)_2ZnBr_4$ ($n = 1-5$).

n	T_m (K)	ΔH_m (kJ mol ⁻¹)	ΔS_m (J K ⁻¹ mol ⁻¹)	ΔS_t (J K ⁻¹ mol ⁻¹)
1	569*			
2	477 ± 1	20 ± 1	41 ± 2.5	64 ± 4
3	472 ± 1	21 ± 1.5	45 ± 2.5	59 ± 4
4	470 ± 1	24 ± 1.5	51 ± 3	63 ± 4.5
5	440 ± 1	25 ± 1.5	56 ± 3	69 ± 4

* ΔH_m could not be determined because of the melting DSC peak being immediately followed by the decomposition.

3. Results

The DSC measurements were carried out for the title compounds, and heat anomalies due to structural phase transitions or the melting were observed. The results are listed in tables 1–4. The reported values are also listed in parentheses for comparison. The measurements were repeated 3–10 times and the averaged values are given in the tables. The order of transition was determined from the shape of the observed DSC peak and by measuring thermal hysteresis. We see from tables 1 and 2 that most of the phase transitions are accompanied by large entropy changes, more than 10 J K⁻¹ mol⁻¹, which suggests the order–disorder character of the transitions.

Table 1 shows that our results for the Cl complexes are in good agreement with the reported values determined by DSC or adiabatic calorimetry [2–8] except for the following. (1) We could not observe the heat anomaly due to the transition reported at 426 K in meCl. (2) The transition enthalpy ΔH -value observed for buCl was different from the reported

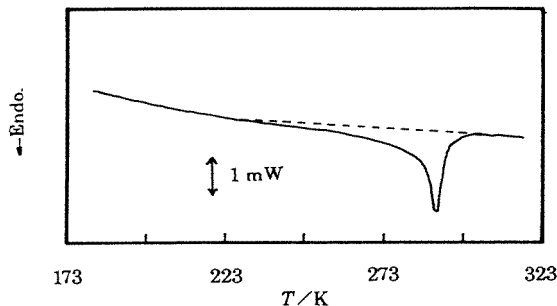


Figure 1. The DSC curve of $(n\text{-C}_4\text{H}_9\text{NH}_3)_2\text{ZnCl}_4$ recorded on heating. The broken line indicates the base-line for obtaining the enthalpy change.

value. This disagreement in ΔH seems to be ascribable to the difference in estimating the base-lines in the analysis of the DSC curves, because the observed DSC anomaly with a sharp peak and long tail depicted in figure 1 is quite similar to the specific-heat curve in [6].

Some of the phase transitions in the Br complexes found in the NQR measurements [12] were confirmed by the present experiments as seen from table 2. In our previous paper, it was inferred from the temperature variations of NQR frequencies that phase transitions are located at 426 K in meBr and at 298 K in prBr [12]. It was, however, difficult to definitely conclude so, because the NQR signals were very weak and faded out at around 430 K in meBr and 300 K in prBr. The present DSC measurements, however, gave no heat anomaly around 426 K in meBr and 298 K in prBr.

4. Discussion

The solid phases in the title compounds are summarized in figure 2 [2, 4, 5, 7, 13, 14]. Since many of the crystal structures of the Br salts have been unknown up to now, the natures of the phase transitions in the Br salts are discussed by referring to the corresponding transitions in the Cl salts.

4.1. $(\text{CH}_3\text{NH}_3)_2\text{ZnBr}_4$

The transition at 457 K in meBr is similar to that at 478 K in meCl because thermodynamic functions associated with these transitions have almost the same values, as seen from tables 1 and 2. According to the ^1H NMR investigations, the methylammonium cations in both compounds undergo overall reorientation around their centre of gravity as well as three-dimensional self-diffusion in the highest-temperature phase [3, 10]. Large transition entropies ΔS of about $20 \text{ J K}^{-1} \text{ mol}^{-1}$ observed in both compounds are, accordingly, attributed to the melting of orientational orders of the methylammonium ions.

In the previous paper [12], it was concluded that, in meBr, a phase transition is located at 426 K and is quite analogous to the transition at 426 K in meCl, which has been reported to be a ferroelastic phase transition [2]. In the present examination, however, no heat anomaly was observed at around 426 K in meBr. It may be no surprise that the 426 K transition in meBr is similar to that in meCl, because no heat anomaly was observed in meCl in the present experiment.

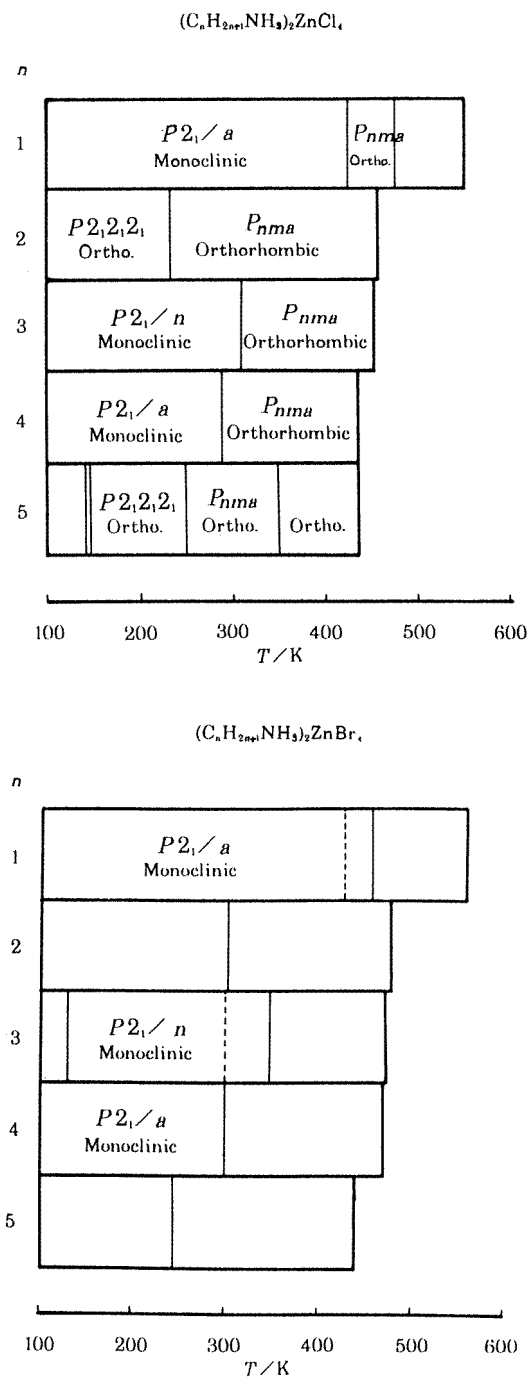


Figure 2. Solid phases and their crystal structures in $(C_nH_{2n+1}NH_3)_2ZnCl_4$ and $(C_nH_{2n+1}NH_3)_2ZnBr_4$ ($n = 1-5$). The vertical broken lines represent doubtful phase transitions (see the text). The unique axes of $P2_1/a$ and $P2_1/n$ are c - and a -axes, respectively.

4.2. $(C_2H_5NH_3)_2ZnBr_4$

We have observed four ^{81}Br NQR signals with an equal intensity below 299.5 K in etBr [12], and the low-temperature phase of etCl crystallizes in the $P2_12_12_1$ (D_2^4) structure [4], which contains four crystallographically non-equivalent chlorine atoms in a unit cell.

The fact that etCl and etBr have almost the same melting entropies ΔS_m , 40 and 41 $\text{J K}^{-1} \text{mol}^{-1}$, respectively, suggests that the solid phases just below the melting points of both compounds have similar degrees of order. This fact can be well understood if one assumes that they have similar crystal structures. Our ^1H NMR experiments on etBr revealed that above the transition temperature T_c , $\text{CH}_3\text{CH}_2\text{NH}_3^+$ chains have dynamically disordered orientations along their long axes, i.e., rotate along the axes [15]. From these results we can assume that the mirror plane is formed on the cations above T_c . This symmetry element is found in the reported structure $Pnma$ (D_{2h}^{16}) of the high-temperature phase of etCl. The transition at 302 K in etBr is therefore considered to be similar to that at 234 K of etCl, in which the structural change between $Pnma$ and $P2_12_12_1$ is observed [4]. On the other hand, there are some differences between these two transitions. The transition in etBr showed a considerable thermal hysteresis extending to 33 K compared with that of 12 K in etCl. Large values of ΔS of 17 and 23 $\text{J K}^{-1} \text{mol}^{-1}$ for etCl and etBr, respectively, are attributable to the melting of orientational orders around the long axes of the ethylammonium cations in both compounds. This numerical difference in ΔS , however, seems to be significant, and the high-temperature phase of etBr may be a conformational disordered state.

4.3. $(n\text{-}C_3H_7NH_3)_2ZnBr_4$

Although the value of ΔS of 9.2 $\text{J K}^{-1} \text{mol}^{-1}$ observed at the 310 K transition for prCl is obviously different from 14 $\text{J K}^{-1} \text{mol}^{-1}$ at the 347 K transition of in prBr, this difference is not that significant. This is because numerical values obtained in second-order transitions are much less accurate than those obtained in first-order ones owing to the ambiguity in estimating base-lines of DSC curves. It appears that the ΔS -values of 9.2 and 14 $\text{J K}^{-1} \text{mol}^{-1}$ are well explained by the order-disorder phase transition with a double-minimum potential for $n\text{-}C_3H_7NH_3^+$ ions, where ΔS is expected to amount to $R \ln 2 = 5.8 \text{ J K}^{-1} \text{mol}^{-1}$ per mole of propylammonium ions. According to the x-ray measurements on prCl, the propylammonium ions are disordered between two symmetric positions related by the mirror plane in the $Pnma$ phase [5].

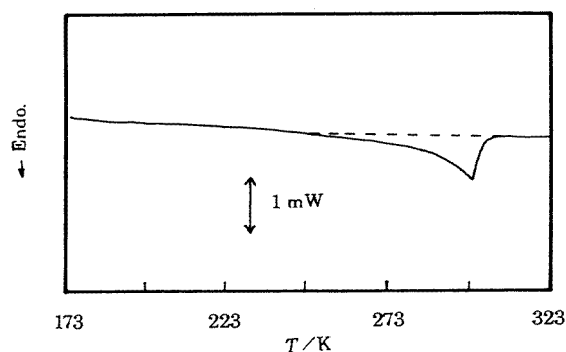


Figure 3. The DSC curve of $(n\text{-}C_4H_9NH_3)_2ZnBr_4$ recorded on heating. The broken line indicates the base-line for obtaining the enthalpy change.

The presence of the transition at 298 K in prBr could not be confirmed in the present study. In the ^{81}Br NQR measurements [12], four resonance signals were observed at room temperature. The number of the signals doubled below 130 K and became eleven at 77 K. There was no discontinuity in the temperature variations of the NQR frequencies at 130 K. From these results, it is certainly concluded that prBr undergoes a second-order phase transition at 130 K and that at least one phase transition occurs between 77 and 130 K. These transitions are considered to be not of the order–disorder type but of the displacive type. The corresponding phase transitions in prCl have not been reported so far and were not detected in the present investigation.

4.4. $(n\text{-}C_4H_9NH_3)_2ZnBr_4$

The transition at 299 K in buBr is also interpreted as an order–disorder transition for the $n\text{-}C_4H_9NH_3^+$ orientation in a double-minimum potential in view of the ΔS -value of $12\text{ J K}^{-1}\text{ mol}^{-1}$ that was obtained. Since the low-temperature phase is a $P2_1/a$ (C_{2h}^5) one [14], the high-temperature phase of buBr is probably a $Pnma$ one, like in prCl. This transition is different from that at 290 K in buCl, even if they have the same symmetry change. This is because the shapes of the DSC heat anomalies in these transitions are clearly different from each other as shown in figures 1 and 3, and also because their ΔS -values differ considerably. This difference between 21 and $12\text{ J K}^{-1}\text{ mol}^{-1}$ in buCl and buBr, respectively, suggests that buCl obtains more disorder at the transition than does buBr.

4.5. $(n\text{-}C_5H_{11}NH_3)_2ZnBr_4$

From the observed ΔS -values of 14 and $13\text{ J K}^{-1}\text{ mol}^{-1}$ for peCl and peBr, respectively, it follows that order–disorder phase transitions with a double-minimum potential for the pentylammonium orientation take place at 244 K in peBr and at 250 K in peCl; the latter has been reported to be the ferroelastoelectric phase transition [7]. The x-ray experiments on peCl also indicate that, in the $Pnma$ phase, the pentylammonium orientation is disordered between two symmetric sites related by the mirror plane [7]. These transitions are of the first-order type unlike those in prCl, prBr and buBr.

No heat anomaly corresponding to the transitions at 143, 149 and 350 K in peCl was observed in peBr in the present DSC measurements between 130 and 460 K. As shown in tables 3 and 4, the Cl and Br compounds with the same n ($=2\text{--}4$) have almost the same ΔS_m -values whereas ΔS_m for peBr is greater by $23\text{ J K}^{-1}\text{ mol}^{-1}$ than that for peCl. The transition at 350 K in peCl, reported as a conformational phase transition [8], has a ΔS of $26\text{ J K}^{-1}\text{ mol}^{-1}$, and hence this difference in ΔS_m is assignable to the lack of the corresponding transition in peBr.

4.6. Melting entropies ΔS_m and total entropy changes ΔS_t

The melting entropies ΔS_m in the Cl and Br complexes are listed in tables 3 and 4, respectively. The total entropy changes ΔS_t ($=\Delta S + \Delta S_m$) are given in the same tables. From the observed ΔS_m -values given in table 3, let us estimate the contributions from the orientational or positional orders of the alkylammonium and $[ZnCl_4]^{2-}$ ions to the entropy change. In the following discussion, we are interested only in the highest-temperature solid phase just below the melting point.

In peCl, the pentylammonium ions have dynamically disordered orientations along their long axes [16]. Since they do not perform overall reorientation around their centre of gravity,

which was observed in meCl, peCl has the residual orientational order of the cations. Let us denote the contribution from this residual order to the entropy as $\Delta S_{\text{co}}^{\text{R}}$ and suppose that the difference of ΔS_{m} between $26 \text{ J K}^{-1} \text{ mol}^{-1}$ (meCl) and $33 \text{ J K}^{-1} \text{ mol}^{-1}$ (peCl) is assigned to $\Delta S_{\text{co}}^{\text{R}}$.

We see from table 3 that the ΔS_{m} -values for $n \geq 10$ are nearly equal (the average value is $16 \text{ J K}^{-1} \text{ mol}^{-1}$). This suggests that these compounds have similar degrees of freedom in the highest-temperature phase and that their alkylammonium ions are in a quite analogous state of both static and dynamic nature. The ^1H NMR measurements on $(n\text{-C}_{12}\text{H}_{25}\text{NH}_3)_2\text{ZnCl}_4$ showed that the alkylammonium cations rotate along their long axes as observed in peCl [16], whereas the value of ΔS_{m} of $17 \text{ J K}^{-1} \text{ mol}^{-1}$ for $(n\text{-C}_{12}\text{H}_{25}\text{NH}_3)_2\text{ZnCl}_4$ differs considerably from that of $33 \text{ J K}^{-1} \text{ mol}^{-1}$ for peCl. From these results, it is inferred that in the compounds with $n \geq 10$, the anions lose their orientational orders before melting and that this causes the difference in ΔS_{m} -values. We can then assume that the compounds with $n \geq 10$ have only the residual orientational order of the cations and positional orders of the cations and anions. Let us represent the contribution from the orientational order of the anions and the positional order of both ions to the entropy as ΔS_{ao} and ΔS_{p} , respectively. Furthermore, $\Delta S_{\text{co}}^{\text{R}}$, ΔS_{ao} and ΔS_{p} are assumed to be equal for all $(\text{C}_n\text{H}_{2n+1}\text{NH}_3)_2\text{ZnCl}_4$ compounds. The foregoing discussion is summarized as follows:

$$\begin{aligned}\Delta S_{\text{m}}(\text{meCl}) &= \Delta S_{\text{ao}} + \Delta S_{\text{p}} \\ \Delta S_{\text{m}}(\text{peCl}) &= \Delta S_{\text{co}}^{\text{R}} + \Delta S_{\text{ao}} + \Delta S_{\text{p}} \\ \Delta S_{\text{m}}(n \geq 10) &= \Delta S_{\text{co}}^{\text{R}} + \Delta S_{\text{p}}.\end{aligned}$$

Putting $\Delta S_{\text{m}}(\text{meCl}) = 26 \text{ J K}^{-1} \text{ mol}^{-1}$, $\Delta S_{\text{m}}(\text{peCl}) = 33 \text{ J K}^{-1} \text{ mol}^{-1}$ and $\Delta S_{\text{m}}(n \geq 10) = 16 \text{ J K}^{-1} \text{ mol}^{-1}$ into the above equations, we obtain $\Delta S_{\text{co}}^{\text{R}} = 7 \text{ J K}^{-1} \text{ mol}^{-1}$, $\Delta S_{\text{ao}} = 17 \text{ J K}^{-1} \text{ mol}^{-1}$ and $\Delta S_{\text{p}} = 9 \text{ J K}^{-1} \text{ mol}^{-1}$.

Using these values, we can estimate ΔS_{co} , which is the contribution from the orientational orders of the alkylammonium cations to the entropy. Since $\Delta S_{\text{co}} = \Delta S_{\text{t}} - (\Delta S_{\text{ao}} + \Delta S_{\text{p}})$ and $\Delta S_{\text{ao}} + \Delta S_{\text{p}} = 26 \text{ J K}^{-1} \text{ mol}^{-1}$, $\Delta S_{\text{co}} = 18, 31, 27, 49$ and $51 \text{ J K}^{-1} \text{ mol}^{-1}$ with increasing n from 1 to 5 in $(\text{C}_n\text{H}_{2n+1}\text{NH}_3)_2\text{ZnCl}_4$. In this rough estimation, the entropy gain in the crystals below 130 K is not included; however, we may ignore it, because it seems to be negligible or very small compared with the entropy gain at higher temperatures.

From the above estimation, we see that ΔS -values of etCl, prCl and buCl are less than half of ΔS_{co} and these crystals obtain more than half of ΔS_{co} at the melting. The phase transitions in these crystals have quite different features from each other. These differences are ascribed to how the cations lose their orders at the transitions. On the other hand, the compounds with $n \geq 10$ obtain almost all of ΔS_{co} before their melting. It has been reported that these crystals show the following common phase sequence [9]: a phase transition with a very large ΔS occurs between about 350 and 380 K, where the crystals obtain ΔS_{co} , and the fusion takes place at almost the same temperature (436–438 K) with nearly the same ΔS_{m} .

5. Conclusions

(1) At the 457 K transition in meBr, the methylammonium cations lose all of their orientational order, while the ethylammonium ions in etBr show dynamically disordered orientations along their long axes and conformational disorder above 302 K. The transitions observed at 347 K in prBr, 299 K in buBr and 244 K in peBr are well explained by an order–disorder phase transition with a double-minimum potential for the alkylammonium

orientation. Here, the former two transitions are the second-order type whereas the last is of first-order type.

(2) The Cl and Br compounds having the same n undergo similar phase transitions to each other. This means that the alkylammonium cations play a central role in these transitions.

(3) The entropy gains due to the melting of the positional order for both ions and of the orientational order for the anion and the cation are evaluated for $(C_nH_{2n+1}NH_3)_2ZnCl_4$ ($n = 1-5$) as 9, 17 and 18, 31, 27, 49, 51 J K⁻¹ mol⁻¹ (with increasing n), respectively.

Acknowledgments

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