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Thermoanalytical and X-ray study of some alkylammonium tetrachlorozincates

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Abstract

DSC and X-ray studies on mono-, di-, tri- and tetraalkylammonium tetrachlorozincates (alkyl is ethyl, propyl, *n*-butyl or *sec*-butyl) were performed in the range 173–500 K. Transition temperatures, enthalpies, entropies, and also lattice parameters of the compounds are given.

Keywords: Alkylammonium tetrachlorozincates; DSC; Enthalpies of transition; Lattice constants

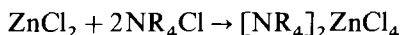
1. Introduction

Compounds of the type A_2BX_4 or ABX_3 (A, B is metal; X is halogen or oxygen) have attracted considerable attention because of their physical properties, including ferro-, piezo- or pyroelectricity, ferri-, antiferro- or piezomagnetism and non-linear optical effects, and their technical application for electro- or magneto-optical devices. Similar physical and structural properties are observed when metal A is substituted by an $[NR_4]^+$ ion (R is H, alkyl, or aryl) [1]. Because melting temperatures are much lower, measurements of their physical properties can be performed more easily. In addition, motions of the quarternary ammonium cation induce phase transitions, thus providing an interesting field for temperature-dependent thermoanalytical investigations. So far, these compounds have only been used as model substances for oxides and halides, although it might be possible that they will find technical applications because of their physical properties which are similar to those of the corresponding oxides or halides. Searching for new materials with electro-optic effects, we have synthesized compounds of the type $[NR_4]_2ZnCl_4$. This work describes a thermoanalytical and X-ray study on some of these compounds.

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2. Experimental

The synthesis of the compounds was performed by mixing hot saturated aqueous or ethanolic solutions of ZnCl_2 and the organoammonium halide in stoichiometric amounts, according to the reaction



The alkylammonium tetrachlorozincates precipitated when the solutions were slowly cooled. The products were then twice-recrystallized from the same solvent, suction-filtered, washed with diethylether, and dried. The tripropyl- and tributylammonium tetrachlorozincates were handled in a glove box, because they are hygroscopic. The alkylammonium chlorides were synthesized by adding gaseous HCl to solutions of the respective amines in ether.

The DSC experiments were carried out using a DSC 92 (Setaram) with a cooling device in the range 173–500 K. Typical sample sizes were 50 mg. All scans were performed with a heating rate of 5 K min^{-1} . An empty aluminum crucible served as a reference. Indium and 1,2-dichlorethan were used for temperature and enthalpy calibration. The accuracy in the transition temperatures is $\pm 2 \text{ K}$ and in the transition enthalpies, $\pm 5\%$.

X-ray diffraction data were collected with a Guinier-4-camera (Huber), with $\text{Cr K}\alpha_1$ radiation and $\alpha\text{-SiO}_2$ as reference. Temperature-dependent data were obtained with $\text{Cu K}\alpha_1$ radiation in a Guinier-Simon camera (Enraf-Nonius), operating between 123 and 573K with variable heating rates.

3. Results

The lattice parameters of some alkylammonium tetrachlorozincates are listed in Table 1. The structure of all the compounds consists of alternating layers of ZnCl_4^{2-} tetrahedra and alkyl ammonium cations. The layers are connected by N–H–Cl

Table 1
Lattice parameters of some alkylammonium tetrachlorozincates^a

	<i>a</i> /pm	<i>b</i> /pm	<i>c</i> /pm	$\beta/^\circ$	
$[(\text{C}_2\text{H}_5)_3\text{NH}_3]_2\text{ZnCl}_4$	1003.1	1756.3	739.3		Orthorh.
$[(\text{C}_2\text{H}_5)_4\text{N}]_2\text{ZnCl}_4$	902.59		1496.34		P4 ₂ /nmc
$[(\text{C}_3\text{H}_7)_3\text{NH}_3]_2\text{ZnCl}_4$	1021.9	736.32	2007.7	92.65(2)	P2 ₁ /n [6]
	2106.9	1022.3	735.7	107.46	
HT-phase	1024.3	738.3	2021.3		[6]
$[(\text{C}_3\text{H}_7)_2\text{NH}_2]_2\text{ZnCl}_4$	1383.4	1352.8	1212.1	109.91	P2 ₁ or P2 ₁ /n
$[(\text{C}_4\text{H}_9)_3\text{NH}_3]_2\text{ZnCl}_4$	1044.9	2219.1	739.5		Orthorh.
$[\text{sec}(\text{C}_4\text{H}_9)_3\text{NH}_3]_2\text{ZnCl}_4$	1214.5	1899.7	750.6		P2 ₁ 2 ₁ 2 ₁
$[(\text{CH}_3)_3(\text{C}_6\text{H}_5)_3\text{N}]_2\text{ZnCl}_4$	1555.4	955.6	3086.5	95.38	C2/c (<i>Z</i> = 8)

^a If not otherwise stated, data at 298 K.

hydrogen bridges. In all modifications, the ZnCl_4^{2-} tetrahedra are ordered and show only small deviations from the ideal tetrahedral geometry, due to hydrogen bonding to neighboring cation layers. All compounds of which the structure is known have four formula units in the elementary cell [1]. The ability to form suitable crystals for single-crystal structure determinations decreases with increasing length and number of chains of the alkylammonium cation.

The thermodynamic data of the phase transitions for the compounds $[(\text{C}_n\text{H}_{2n+1})_{4-m}\text{NH}_m]_2\text{ZnCl}_4$ ($n = 2-4$; $m = 0-3$) are given in Table 2. In contrast to the measurements of Zubillaga et al. [2], the DSC runs of $[(\text{C}_2\text{H}_5)\text{NH}_3]_2\text{ZnCl}_4$ (Fig. 1) revealed two phase transitions at 239 and 257 K instead of one at 234 K. Both effects could be reproduced in samples crystallized from different solvents, so that different solvation could be excluded. Temperature-dependent X-ray photographs between

Table 2
Phase transition temperatures, enthalpies and entropies of some alkylammonium tetrachlorozincates

Compound	T_{tr}/K	$\Delta_{tr}H/\text{kJ mol}^{-1}$	$\Delta_{tr}S/\text{J mol}^{-1} \text{K}^{-1}$
$[(\text{C}_2\text{H}_5)\text{NH}_3]_2\text{ZnCl}_4$	239/234 [2]	2.75	11.49
	257 {350} (s/1)	1.18	4.60
$[(\text{C}_2\text{H}_5)_2\text{NH}_2]_2\text{ZnCl}_4 \cdot 0.75\text{H}_2\text{O}$	297/298 [3]	1.35	4.53
	344/341 [3] (s/1)	17.58	51.10
$[(\text{C}_2\text{H}_5)_3\text{NH}]_2\text{ZnCl}_4$	313 (272) ^a	5.74	18.33
	338	11.01	32.56
	377 (369) ^a {473} (s/1)	1.46	3.88
$[(\text{C}_2\text{H}_5)_4\text{N}]_2\text{ZnCl}_4$	231/228 [5]	9.15/9.57 [5]	39.61/41.73 [5]
	{ > 573} [7] (s/1)	8.87 [7]	38.91 [7]
$[(\text{C}_3\text{H}_7)_2\text{NH}_2]_2\text{ZnCl}_4$	356 (s/1) 356 [4]	31.7 [4]	89.0 [4]
	372	3.85	10.34
$[(\text{C}_3\text{H}_7)_4\text{N}]_2\text{ZnCl}_4$	433	2.11	4.88
	462 (s/1)	20.99	45.44
	293/290 [8]	6.65 [8]	22.9 [8]
$[(\text{C}_4\text{H}_9)\text{NH}_3]_2\text{ZnCl}_4$ $[(\text{sec-C}_4\text{H}_9)\text{NH}_3]_2\text{ZnCl}_4$	327		
	408 (s/1)	18.10	55.35
$[(\text{C}_4\text{H}_9)_2\text{NH}_2]_2\text{ZnCl}_4$	224/222 [4]	2.99/3.06 [4]	13.3/13.8 [4]
	427 [4]	29.5 [4]	69.0 [4]
$[(\text{sec-C}_4\text{H}_9)_2\text{NH}_2]_2\text{ZnCl}_4$	343 (s/1)	22.29	65.00
	233	0.79	3.37
$[(\text{C}_4\text{H}_9)_3\text{NH}]_2\text{ZnCl}_4$	242	0.86	3.56
	355	8.12	22.87
	287	4.44	15.47
	325	2.65	8.13
$[(\text{C}_4\text{H}_9)_4\text{N}]_2\text{ZnCl}_4$	428	8.24	19.26
	483 (D)		
	256	0.49	1.91
$[(\text{C}_6\text{H}_5)(\text{CH}_3)_3\text{N}]_2\text{ZnCl}_4$	271	5.11	18.84

Key: 239/234: first value, this work; second, from literature; (s/1) solid–liquid transition; { } measurement of the solid–liquid transition with a melting point apparatus; (D) decomposition.

^a From X-ray cooling experiments.

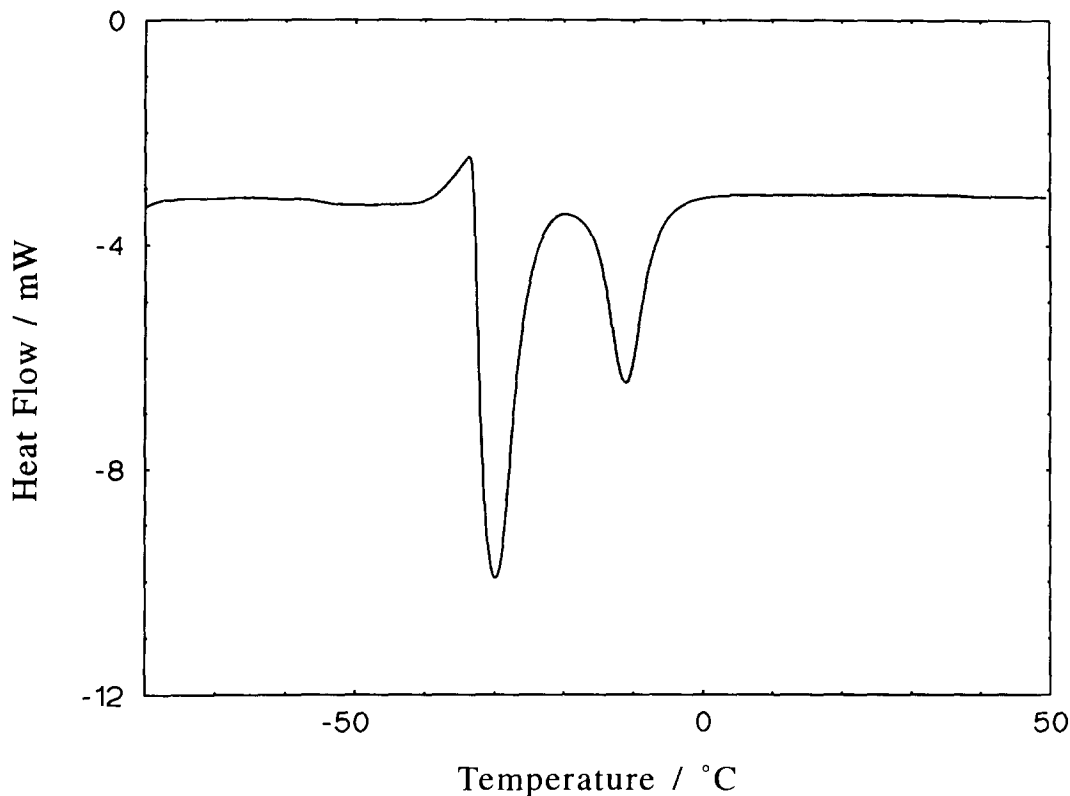


Fig. 1. DSC trace of $[(\text{C}_2\text{H}_5)\text{NH}_3]_2\text{ZnCl}_4$.

223 and 303 K did not indicate transitions; therefore we assume that these transitions are due to small changes in the position of the hydrogen atoms. Attempts to synthesize $[(\text{C}_2\text{H}_5)_2\text{NH}_2]_2\text{ZnCl}_4$ failed and always gave the hydrate $[(\text{C}_2\text{H}_5)_2\text{NH}_2]_2\text{ZnCl}_4 \cdot 0.75 \text{H}_2\text{O}$. In this case, our data agreed well with those given by Bloomquist and Willett [3] for the lattice parameters and van Oort et al. [4] for the thermal data. The X-ray reflections of $[(\text{C}_2\text{H}_5)_3\text{NH}]_2\text{ZnCl}_4$ could not be indexed and are given in Table 3. Calorimetric measurements with a heating rate of 5 K min^{-1} revealed three phase transitions (Table 2) which were also observed in the temperature-dependent X-ray measurements. The transition at 313 K had a thermal hysteresis and was lower (38 K) in cooling runs, which indicates a first-order transition. $[(\text{C}_2\text{H}_5)_4\text{N}]_2\text{ZnCl}_4$ was investigated by Landee and Westrum [5]. They measured the specific heat in an adiabatic calorimeter and found that the thermal effect at 228.9 K is bifurcated. An equilibration, necessary to observe this effect, needed several days. For this reason, a bifurcation was not observed in the dynamic DSC runs. $[(\text{C}_3\text{H}_7)\text{NH}_3]_2\text{ZnCl}_4$ has a second-order transition at 313 K [6] (Fig. 2). Phase transitions in $[(\text{C}_3\text{H}_7)\text{NH}_3]_2\text{ZnCl}_4$, $[(\text{C}_4\text{H}_9)\text{NH}_3]_2\text{ZnCl}_4$ and $[(\text{sec-C}_4\text{H}_9)\text{NH}_3]_2\text{ZnCl}_4$ are characterized by strong pre-

Table 3
X-ray reflections of alkylammonium tetrachlorozincates ($\lambda = 228.9750$ pm)

[(C ₂ H ₅) ₃ NH] ₂ ZnCl ₄		[(C ₃ H ₇) ₃ NH] ₂ ZnCl ₄		[(C ₃ H ₇) ₄ N] ₂ ZnCl ₄		[(C ₄ H ₉) ₂ NH ₂] ₂ ZnCl ₄		[(sec-C ₄ H ₉) ₂ NH ₂] ₂ ZnCl ₄	
d_{OBS}/pm	$2\theta_{\text{OBS}}/^\circ$	d_{OBS}/pm	$2\theta_{\text{OBS}}/^\circ$	d_{OBS}/pm	$2\theta_{\text{OBS}}/^\circ$	d_{OBS}/pm	$2\theta_{\text{OBS}}/^\circ$	d_{OBS}/pm	$2\theta_{\text{OBS}}/^\circ$
8.8309	14.81004	9.29546	14.14960	10.259	12.81	12.39295	10.60121	9.367	14.04
7.9618	17.80955	8.13052	16.18968	9.865	13.33	11.12084	11.81798	9.249	14.22
6.66230	19.79008	7.96599	16.52637	8.779	14.99	8.20499	16.04176	9.107	14.44
6.23361	21.16621	6.86154	19.20990	8.410	15.65	7.85927	16.75237	8.767	15.01
6.02568	21.90548	6.56294	20.09277	8.024	16.41	6.88778	19.13604	8.612	15.28
5.73224	23.04185	6.23246	21.17017	7.836	16.80	6.26369	21.06342	7.860	16.75
5.49058	24.07082	6.05211	21.80864	7.581	17.37	6.20272	21.27287	6.760	19.50
5.31521	24.87752	5.93154	22.25755	7.231	18.22	5.95984	22.15053	6.678	19.74
5.28545	25.01987	5.83220	22.64163	6.967	18.92	4.95589	26.71341	6.612	19.94
5.05577	26.17622	5.61506	23.52949	6.653	19.82	4.91536	26.93782	6.527	20.21
4.65643	28.46644	5.28783	25.00842	6.492	20.31	4.78970	27.65840	6.467	20.39
4.46269	29.73018	5.14454	25.71671	5.623	23.50	4.56796	29.02976	6.285	20.99
4.42059	30.01990	5.09934	25.94866	5.358	24.68	4.52011	29.34393	6.106	21.61
3.96321	33.58135	5.04833	26.21551	5.225	25.31	4.42458	29.99220	5.934	22.25
3.90264	34.11832	4.81035	27.53732	5.126	25.81	4.39531	30.19666	5.594	23.62
3.88197	34.30563	4.22393	31.45289	4.962	26.68	4.37134	30.36621	5.406	24.45
3.68228	36.22871	3.97797	33.45306	4.787	27.67	4.23796	31.34611	5.219	25.34
3.56813	37.43002	3.93299	33.84711	4.750	27.89	4.21378	31.53062	4.978	26.59
3.53652	37.77717	3.90368	34.10898	4.710	28.14	4.16058	31.94452	4.861	27.24
3.50197	38.16429	3.87755	34.34591	4.435	29.92	4.02876	33.01916	4.759	27.84
3.47657	38.45400	3.86070	34.50054			4.01109	33.16877		
3.44026	38.87608	3.84695	34.62774			3.93047	33.86940		
3.41308	39.19826	3.75351	35.51809			3.70874	35.96135		
3.38595	39.52543					3.62169	36.85647		
						3.44323	38.84120		
						3.23059	41.51160		

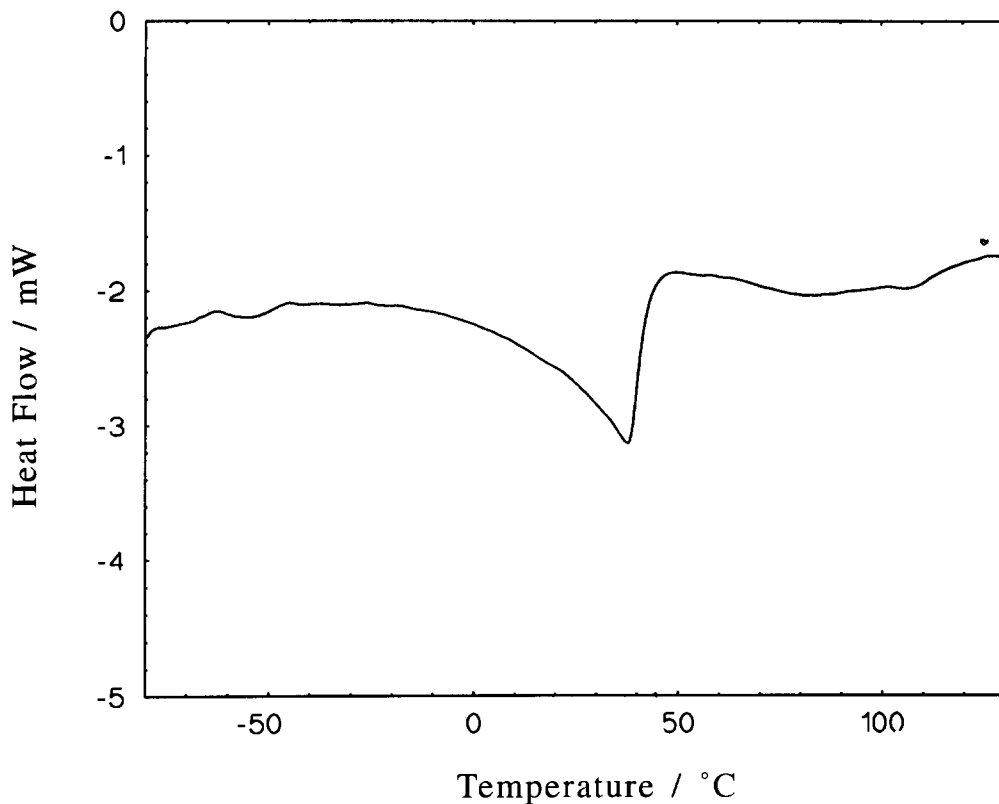


Fig. 2. DSC trace of $[(C_3H_7)NH_3]_2ZnCl_4$.

transition effects which indicate that they are of second-order. The assumption is confirmed by X-ray diffraction experiments (Fig. 3). In $[(C_3H_7)NH_3]_2ZnCl_4$, the (hkl) and (hke) reflections of the monoclinic low-temperature form merge gradually with increasing temperature to one in the orthorhombic high-temperature form. $[(C_3H_7)_2NH_2]_2ZnCl_4$ crystallizes in the monoclinic space group $P2_1$ or $P2_1/n$. It has no solid state transition above 143 K and melts at 356 K. $[(C_3H_7)_3NH]_2ZnCl_4$ behaves similarly and melts at 335 K. $[(C_3H_7)_4N]_2ZnCl_4$ melts after two transitions in the solid state at 462 K. The X-ray reflections of both latter compounds could not be indexed and are listed in Table 3.

Di-monobutylammonium tetrachlorozincate crystallizes in the orthorhombic system and has a phase transition at 290 K. The order of this transition is ambiguous: the DSC effects looked like those of second-order; however, the temperature-dependent X-ray photographs showed merging of some reflections, ending in a sudden change at the transition temperature. Di-*sec*-monobutylammonium tetrachlorozincate crystallizes in the space group $P2_12_12_1$. A second-order transition occurs at 327 K, with melting at 408 K.

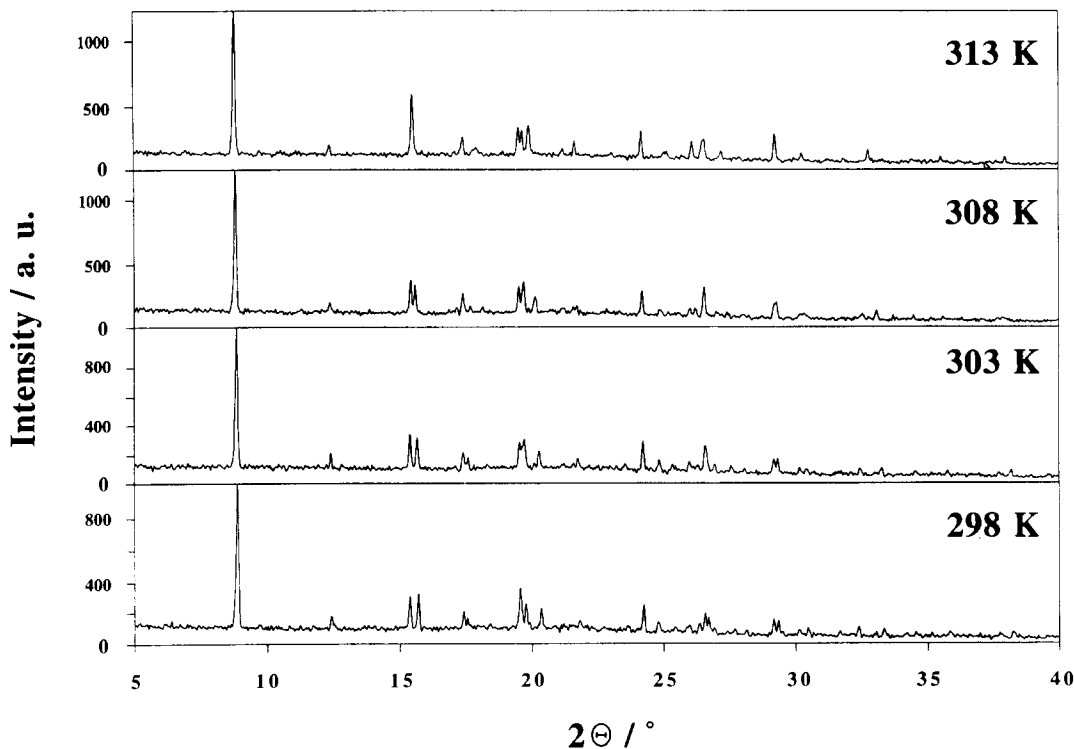


Fig. 3. X-ray powder diffraction patterns of $[(C_3H_7)NH_3]_2ZnCl_4$ at different temperatures.

X-ray reflections of the compounds $[(sec-C_4H_9)_nNH_{3-n}]_2ZnCl_4$ ($n = 1-2$) were generally so weak and diffuse that a determination of the lattice parameters was not possible. $[(sec-C_4H_9)_2NH_2]_2ZnCl_4$ has a bifurcated peak at the melting temperature, which could not be resolved properly; thus the melting enthalpy, given in Table 2, includes a solid state transition. Tributylammonium tetrachlorozincate has two transitions at 233 and 242 K with very small entropies. In the X-ray measurement, no phase transition could be observed. The DSC run of tetrabutylammonium tetrachlorozincate disclosed three phase transitions. Compared with the tributylammonium tetrachlorozincate, the transition entropies are much higher, which indicates a larger rearrangement of the alkyl chains during the transitions. The X-ray measurement in the range 173–373 K again failed to show these phase transitions.

We also investigated the phase transitions and structure of a compound which was obtained when a methyl group in tetramethylammonium tetrachlorozincate is substituted by an aryl group: trimethyl phenylammonium tetrachlorozincate [9] showed a solid–solid phase transition at 256 K in the DSC run. This transition had a very low transition entropy and is followed by a transition at 271 K. At room temperature the compound crystallizes in the space group (A2/n).

4. Discussion

Solid–solid phase transitions in these compounds may arise from order–disorder transitions or from conformational changes in the alkyl chain. The ZnCl_4^{2-} anions play a minor role in the transitions. They form the matrix for the movement of the alkyl groups. The DSC data normally show a sequence of effects which indicates the transition from order to disorder of the alkyl chains through a series of intermediate phases. The number and magnitude of the transformations are a function of the length and number of the alkyl chains. The order–disorder transition in monomethyl ammonium compounds stems from a fast precessional motion of the C–N bond axis [10]. In the simplest order–disorder transition of monoalkylammonium cations with longer chains, the chain changes from one conformation below T_{tr} to random distribution between two equivalent conformations above the transition temperature ($\Delta S = 1.0\text{--}5.0 \text{ J mol}^{-1} \text{ K}^{-1}$). A second class of transitions arises from cooperative changes within the conformation of the alkyl chains: it is assumed that at lower temperatures the chains contain trans or gauche conformations, so called “kinks”. Each kink involves four consecutive chain atoms, which can be arranged in different ways in the high-temperature form ($\Delta S = 0.9 (n-2)R$ per mole of chains, where R is the gas constant, and n the carbon chain length) [11–13]. The entropies of solid state transitions, listed in Table 2, reveal that for cations with two or more alkyl chains the entropies do not obey these patterns. The entropies of transition are generally lower, as expected for the second class, and higher, as would be expected for the first class of transitions.

Table 2 also reveals that the entropies of melting are generally large, compared with the transition entropies, which means that the cations of these salts are not in a completely disordered state in their high-temperature forms. In the series $[(\text{C}_n\text{H}_{2n+1})\text{NH}_3]_2\text{ZnCl}_4$, one crystallographic direction is mainly influenced by the length of the alkyl chain. This axis increases by approximately 230 pm per CH_2 -group.

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