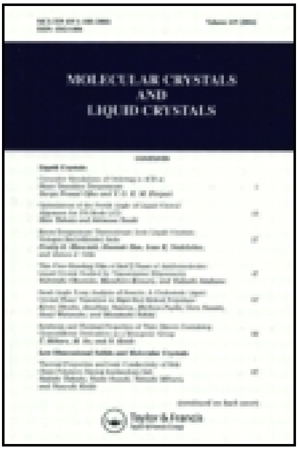

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Thermal Behavior and Liquid Crystalline Phases of a Series of Bis (n-Alkylammonium) Tetrabromozincates

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Thermal Behavior and Liquid Crystalline Phases of a Series of Bis (*n*-Alkylammonium) Tetrabromozincates

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The thermal behavior of compounds of the kind $(n\text{-}C_nH_{2n+1}NH_3)_2ZnBr_4$ with *n* between 10 and 16 has been investigated by means of DSC, IR and X-ray diffraction techniques. All the compounds show order-disorder phase transitions in the solid state, and melt around 430 K to smectic mesophases stable up to at least 550 K.

1 INTRODUCTION

In a recent paper,[1] we have presented the results of a study on the thermal behavior of the compound $(n\text{-}C_{15}H_{31}NH_3)_2ZnBr_4$. This compound, as evidenced by means of DSC and X-ray diffraction techniques, undergoes two high entropy solid-solid phase transitions at 332 and 393 K and melts at 429 K to a smectic mesophase stable up to at least 550 K.

The wide stability range of this liquid crystalline phase and its structural analogy with the disordered phases of some relevant biological systems such as, for example, the lipid bilayer membranes, make of interest a deeper investigation of the thermal behavior of this and of related systems. In this paper we wish to report on a series of compounds of the general formula $(n\text{-}C_nH_{2n+1}NH_3)_2ZnBr_4$ with *n* between 10 and 16.

2 EXPERIMENTAL

All the compounds were synthesized by solving the appropriate long chain *n*-alkylamines in glacial acetic acid, and adding concentrated HBr(aq) and—

subsequently—$ZnBr_2$ in stoichiometric amounts. After boiling for 5 minutes, the resulting solutions were allowed to cool slowly to room temperature, and the white crystalline precipitates filtered off, recrystallized twice from the same solvent and dried in vacuo.

The purity of the products has been checked by means of elemental analysis, IR and NMR techniques.

The DSC curves were registered between 270 and 550 K on a PERKIN-ELMER DSC-2 differential scanning calorimeter, at the scanning rate of 10 K min^{-1}, in N_2 atmosphere. Pure reference compounds were used to calibrate the temperature scale. The transition enthalpies were obtained using, as a reference standard, a sample of pure Indium ($\Delta H_m = 28.4\,J g^{-1}$). Optical observations were made with a LEITZ polarizing microscope, equipped with a variable temperature METTLER FP-5 microfurnace.

The X-ray powder diffraction measurements were performed on a PHILIPS PW-1011 diffractometer with proportional counter (Cukα radiation, Ni filter). Variable temperature X-ray photographs were taken by means of a flat camera at a fixed distance from the samples; these were mounted in glass capillaries placed in an oven constructed from an insulated Aluminum block, with a thermocouple placed next to the sample (temperature control ±1 K).

3 RESULTS

All the compounds investigated in this work undergo two sharp solid-solid phase transitions and melt to liquid crystalline phases stable—as evidenced by polarizing microscopy, DSC and X-ray diffraction techniques—up to at least 550 K (the highest temperature achievable by our variable temperature equipments).

Transition temperatures, enthalpies and entropies, as obtained by the DSC curves, are reported in Table I. The enthalpic and entropic values in the table are mean values of several measurements on independent samples; for each set of measurements, the standard deviation is of the order of 5%. Figure 1 shows typical DSC heating curves of some representative compounds.

As for other alkylammonium tetrahalogenometallates, the X-ray powder diffraction patterns of the compounds under study are indicative of a layered structure, in which ionic regions are sandwiched between hydrocarbon regions (see Discussion).

Table II reports the values of the "long spacings"—that is of the distances between two successive inorganic layers—obtained by X-ray diffraction on the room temperature crystalline modifications and on the mesophases for all the compounds under study. The X-ray photographs of these mesophases, with two or three reflection maxima which are successive orders corresponding to a unique interplanar distance for each system, are typical of smectic liquid crystalline phases.[2]

TABLE I

Transition temperatures, enthalpies and entropies for compounds of the general formula $(n\text{-}C_nH_{2n+1}NH_3)_2ZnBr_4$ with n between 10 and 16.

	HEATING			COOLING		
n	$T(K)$	ΔH(KJ/mol)	ΔS(J/K mol)	$T(K)$	ΔH(KJ/mol)	ΔS(J/K mol)
10	331	2.0	6.0	324	2.5	7.7
	403	22.6	56.1	394	21.8	55.3
	432[a]	9.1	21.1	425	8.2	19.3
11	298	11.7	39.3	289	10.8	37.4
	396	31.1	78.5	386	27.7	71.8
	433[a]	11.0	25.4	426	11.3	26.5
12	327	4.4	13.5	317	5.9	18.6
	397	31.3	78.8	389	33.2	85.3
	433[a]	12.0	27.7	427	10.1	23.6
13	317	10.2	32.2	310	10.4	33.5
	397	34.5	86.9	388	34.4	88.7
	431[a]	9.3	21.6	426	10.1	23.7
14	326	4.6	14.1	316	4.9	15.5
	399	37.1	93.0	389	40.3	103.6
	430[a]	8.5	19.8	424	8.8	20.7
15	332	13.1	39.5	321	12.6	39.2
	393	38.6	98.2	388	38.4	99.0
	429[a]	8.2	19.1	424	9.4	22.1
16	321	3.6	11.2	311	3.6	11.6
	393	51.1	130.0	381	49.8	130.7
	429[a]	9.7	22.6	424	10.0	23.6

[a] Melting.

4 DISCUSSION

In the last few years, the long chain n-alkylammonium tetrachlorometallates have been subjected to a detailed investigation, in order to understand their peculiar phase changes in the solid state.

For compounds of the kind $(n\text{-}C_nH_{2n+1}NH_3)_2MCl_4$ with $n \geq 9$ and M = Co, Zn, the room temperature crystal structure has been shown to consist of ionic

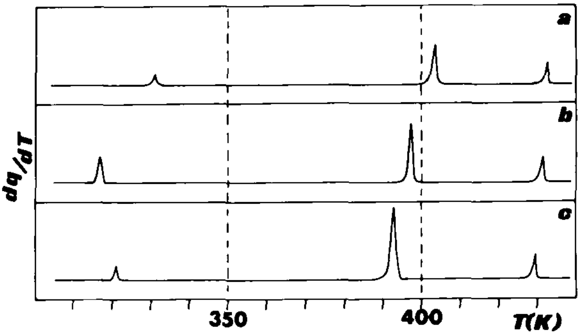

FIGURE 1 Typical DSC heating curves for some representative compounds of the general formula $(n\text{-}C_nH_{2n+1}NH_3)_2ZnBr_4$: (a) $n = 10$; (b) $n = 13$; (c) $n = 16$.

TABLE II

Long spacings of the room temperature crystalline forms, c and of the smectic mesophases, c_s for compounds of the general formula $(n\text{-}C_nH_{2n+1}NH_3)_2ZnBr_4$ vs. the number *n* of chain carbon atoms.

n	c(Å)	c_s(Å)
10	18.91	22.9
11	20.39	24.7
12	21.42	25.7
13	21.58	27.0
14	23.94	28.1
15	23.82	29.6
16	26.37	31.7

layers sandwiched each between two layers of paraffinic chains.[3-5] The ionic regions are built up of $ZnCl_4^{2-}$ tetrahedra in nearly hexagonal planar array, each $ZnCl_4^{2-}$ anion being surrounded by six $—NH_3^+$ groups. The alkyl chains in the hydrocarbon regions, mainly in the planar zig-zag conformation, are nearly perpendicular to the ionic layers and show a double layer packing, with intercalation of chains from adjacent layers (Figure 2).[5]

Due to the preferential orientation of the platelet-like crystals with their basal planes parallel to the surface of the sample holder, the outstanding feature in the X-ray reflection Geiger spectra of such compounds is a series of reflection maxima from lattice planes parallel to the ionic layers (OOl reflections).[6]

Similar series of reflections are observed in the room temperature X-ray powder diffraction patterns of the bromocomplexes investigated in this work, and the corresponding long spacings (Table II) are of the same order of magnitude than those found for the chlorocobaltates and zincates.[3,4] The layer struc-

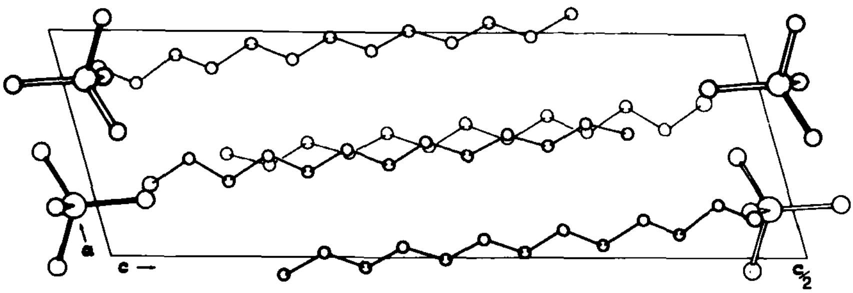

FIGURE 2 The structure of the long chain bis(*n*-alkylammonium) tetrahalogenozincates: $(n\text{-}C_{12}H_{25}NH_3)_2ZnCl_4$.[5]

ture seems therefore not much influenced by the substitution of bromine for chlorine.

The constant increment of 2.5 Å in the long spacings of successive even members of the homologous series is indicative of the substancial invariance of the crystal structure with varying chain length. Moreover, the value of this parameter, which corresponds to the distance between C_i and C_{i+2} atoms in the alkyl chains, shows that the alkylammonium ions are in the all-trans conformation—at least in their terminal hydrocarbon part—and nearly perpendicular to the ionic layers.

The strong but irregular odd-even effects and the non-linear trend in the long spacings for the odd members of the series may be taken as indicative of a different packing mode for the latter. A single crystal X-ray investigation is presently in progress in our laboratories in order to clarify this point.

From this peculiar structure, in which long linear hydrocarbon chains are linked at one end to a relatively high melting inorganic framework, originates the complex thermal behavior of the tetrabromozincates.

As already stated in the last section, all the compounds undergo two reversible high entropy solid-solid phase transitions, which seem to be of the same kind than those observed for a number of other long chain alkylammonium tetrahalogenometallates.[3,4,7] These transitions, as shown by means of X-ray diffraction,[6,8] IR,[6] NMR and NQR[8] techniques, arise from the "conformational melting" of the hydrocarbon regions, that change from an ordered planar zig-zag state into a "liquid-like" one, in which the chains gain a conformational freedom comparable with that of the *n*-paraffins in the melt. A possible theoretical model of such phase changes, in satisfactory agreement with the experimental structural and thermal transition parameters, has been recently proposed by Vacatello and Corradini.[9]

Variable temperature X-ray diffraction investigations[9-11] showed that the ionic regions in the structure of these systems remain nearly unaltered after the transition(s). In fact, the high temperature stable polymorphs are still crystalline solids, in which, nevertheless, the greatest part of the molar volume, that occupied by the paraffinic chains, is in a "liquid-like" state. This state, due to the tendency of the comformationally molten chains to maintain a layered organization and some reciprocal parallelism,[10,11] shows several structural analogies with a smectic mesophase of rodlike molecules.

The mean increment of the total molar solid-solid transition entropy for the addition of 1 C atom in the alkyl chains of the title compounds is of about 0.85 R (close to that observed for the tetrachlorometallates studied so far[9] and only slightly lower than the same parameter for the melting of linear hydrocarbons,[10,11]) and the value of the increase in the interlayer distances at the solid-solid transitions[1] compares well with that observed for the tetrachlorozincates and -cobaltates.[4] Thus, also for the long chain alkylammonium tetrabromozincates, the observed phase changes in the solid state can be interpreted on the ground of a "conformational melting" of the hydrocarbon regions of the structure.

The independence of the melting parameters on the chain length (Table I) agrees with such interpretation. In fact, in the hypothesis that the conformational and volumic contributions have been released to a great extent at the transitions in the solid state, the melting entropy of these compounds should consist of the positional and orientational terms only, that do not depend on the length of the alkyl chains. Indeed, the molar melting entropies of the systems under investigation are of the same order of magnitude than those of ionic compounds of the type A_2B without conformationally flexible bonds.[12]

This also indicates that the structure of the smectic mesophases of the long chain bis(*n*-alkylammonium) tetrabromozincates is not too much different from that of their highest temperature solid polimorphs. The interlayer distance shows at the melting point only a small increase, of the order of 20% the one observed at the solid-solid transitions.[1] Fusion for the title compounds is in practice a "bidimensional melting" of the inorganic regions, as evidenced by the absence of high angle reflection maxima in the X-ray diffraction patterns of the mesophases.

As a matter of fact, the most dramatic structural change is not the one to the liquid crystalline state, but that to the high temperature layered solid forms. Furthermore, once the existence of such forms has been verified, that of thermotropic mesophases (likely of smectic mesophases) at higher temperatures can be considered as quite expected.

In fact, it seems reasonable to suppose that the interactions allowing the stability of highly disordered solids of the kind previously described will be able to maintain some degree of order also in their melts.

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