Energetics of long alkyl chains embedded in a crystalline matrix: (n-C1 8H3 7NH3)2CdCl4

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Energetics of long alkyl chains embedded in a crystalline matrix: (n-$C_{18}H_{37}NH_3)_2CdCl_4$

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Heat capacity measurements of (n-$C_{18}H_{37}NH_3)_2CdCl_4$ from 10 to 370 K are reported. By analogy with homologs of shorter chain lengths, the heat capacity of a CH_2 unit as a function of temperature has been derived. In addition, four phase transitions in the title compound are reported: at 349.6 ± 0.1, 356.0 ± 01, 359.5 ± 0.3, and 365.6 ± 0.3 K, with transition entropies of 132 ± 1, 6.5 ± 0.3, 9.6 ± 0.3, and 95 ± 1 J K^{-1} mol^{-1}, respectively.

INTRODUCTION

The energetics and dynamics of long hydrocarbon chains have been studied in many materials, including paraffins, polymers, and liquid crystals. As well as for their intrinsic interest, these systems have also been studied more recently as biomembrane models.

A series of compounds of the general formula $(C_nH_{2n+1}NH_3)_2MX_4$, where M = Mn, Fe, Cu, Pd, Cd and X = Cl, Br, in which the alkyl chains are in well-characterized environments can also be used to model membrane bilayers. The general structure of these materials, as shown schematically in Fig. 1, is layers of corner-sharing MX_6^{2-} octahedra, with alkylammonium chains intercalated between the layers.[1,2] The chains between adjacent layers point in opposite directions, as in membrane bilayers, and the bilayers are bound to each other by weak van der Waals forces between the alkyl chains.

The alkylammonium groups (RNH_3^+) are directed at the cavities in the octahedral layer and attached to the metal halide layer by hydrogen bonds. For $n = 1$ (i.e., methyl derivatives) there are two possible orientations of this H bonding: 2 bonds to equatorial and 1 to axial halides, or 2 bonds to axial and 1 to equatorial halides.[3] Because these two hydrogen-bonding schemes give rise to different orientations of the alkyl chains, steric factors allow only the latter type (to 2 axial and 1 equatorial halide, the so-called monoclinic scheme) in most of the longer chain derivatives.[4] The orientation of the ammonium head group in this H-bonding scheme, as viewed down the c axis, is illustrated in Fig. 2 where, for clarity, only one carbon of the alkyl chain is illustrated.

The distance between the adjacent alkyl chains is dictated by the spacing between the cavities in the octahedral layer; the distance differs by about 0.2 Å in the a and b directions, and varies slightly with temperature and the metal but averages about 7.3 ± 0.3 Å for the chloride derivatives.[4–6] The direction of the packing arrangement of the alkyl chains is also metal dependent. For example, the low-temperature structure of $(C_{10}H_{21}NH_3)_2CdCl_4$, as shown in Fig. 3, has alkyl chains that make an angle with the c axis of + 40° or − 40° such that chains on opposite sides of the same $(MX_4)_m$ layer are oriented in opposite directions, forming a herringbone packing arrangement.[4] By contrast, in the corresponding Cu and Mn compounds, at low temperature all the alkyl chains are aligned in the same direction, making an angle of about 40° with c axis.[7]

In the compounds with alkyl chains that are more than a few carbons long, the low temperature structure is monoclinic. The distortion from orthorhombic is small ($\beta \sim 92°$) and comes about because of the puckering of the $(MX_4)_m$ layers,[8] as shown in Fig. 2 and 3. At higher temperatures, these compounds undergo one or more phase transitions to an orthorhombic phase. NMR studies have shown this phase to be of higher symmetry due to dynamic disorder in both the $(MX_4)_m$ layers and the alkyl chains; the latter is the primary contributor to the large entropy transition (s), since the chains "melt" such that the average orientation of the chain is parallel to the c axis.[4–6]

The purpose of this work is to report a study of the heat capacity of (n-$C_{18}H_{37}NH_3)_2CdCl_4$ from 10 to 370 K by adia-

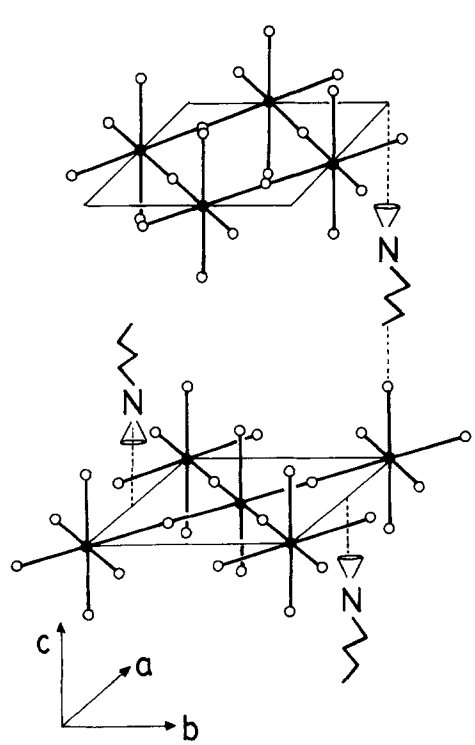

FIG. 1. A schematic illustration of the overall structure of compounds of the general formula $(RNH_3)_2MX_4$, as described in the text. The protons on the N are illustrated as cones to represent various H-bonding configurations.

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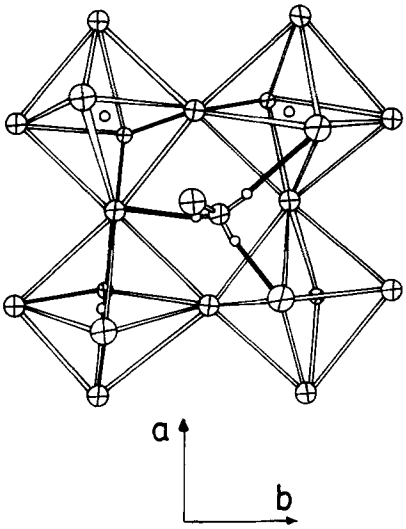

FIG. 2. The monoclinic H-bonding scheme (to 2 axial and 1 equatorial halide), as viewed looking down the c axis. For clarity, only one carbon of the alkyl chain is included.

batic calorimetry. Although no structural studies have been carried out on this compound, its low temperature structure could be expected to be similar to that of the analogous decyl compound. The present study has detected and characterized four phase transitions in $(n\text{-}C_{18}H_{37}NH_3)_2CdCl_4$. In addition, by comparison of the heat capacity of this compound with the analogous methyl, propyl, and heptyl compounds, the heat capacity of a CH_2 group imbedded in an alkyl chain has been derived.

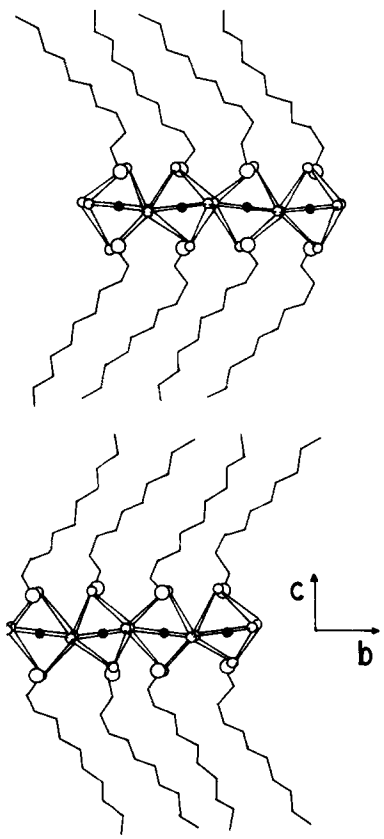

FIG. 3. The low temperature structure of $(n\text{-}C_{10}H_{21}NH_3)_2CdCl_4$, from Ref. 4.

EXPERIMENTAL

$(n\text{-}C_{18}H_{37}NH_3)_2CdCl_4$ was prepared[9] by the stoichiometric reaction of reagent grade n-octadecylamine (Aldrich Chemicals) with HCl and $CdCl_4{\cdot}2H_2O$ in ethanol at 90 °C. The product was filtered and twice recrystallized from absolute ethanol. Chemical analysis gave the following results (theoretical mass % in brackets): C, 55.3 (54.4); H, 10.9 (10.1); N, 3.59 (3.52); Cl, 17.94 (17.83).

The heat capacity of 6.548 g of $(n\text{-}C_{18}H_{37}NH_3)_2CdCl_4$ was measured from $T = 10$ to 370 K in a copper adiabatic calorimeter that was fitted with a calibrated Pt resistance thermometer. The calorimeter, which is described in more detail elsewhere,[10] had previously been found to give heat capacity values for NBS standard benzoic acid that were within 1% of the literature values[11] over the temperature range from 10 to 350 K.

RESULTS

The experimental values of the heat capacity of $(n\text{-}C_{18}H_{37}NH_3)_2CdCl_4$ over the temperature range from 10 to 370 K are listed in Table I and illustrated in Fig. 4.

Four phase transitions can be seen in the more detailed display of the results for 340 to 370 K (Fig. 5). The temperature of the transitions, as determined from the maxima in the heat capacity curves are listed in Table II.

In order to evaluate the transition enthalpies and entropies, an estimate of what the heat capacity would have been had the transitions not occurred is necessary. Such an estimate of C_p (baseline) has been made based on the heat capacity curve below and above the transitions; it is shown by the dashed line in Fig. 4.

The transition enthalpies and entropies can be evaluated in the usual way, i.e.,

$$\Delta H_{\text{trans}} = \int C_p(\text{expt})\,dT - \int C_p(\text{baseline})\,dT \qquad (1)$$

and

$$\Delta S_{\text{trans}} = \int \frac{C_p(\text{expt})}{T}\,dT - \int \frac{C_p(\text{baseline})}{T}\,dT\,, \qquad (2)$$

where $\int C_p(\text{expt})\,dT$ in the region of the heat capacity discontinuity is the molar enthalpy change to take the sample from just below to just above the discontinuity (the "long heat" method). Although the enthalpy and entropy changes associated with the sum of the four transitions can be accurately assessed, the transitions overlap and the partitioning of the entropy and enthalpy changes into each of the four transitions must necessarily be somewhat arbitrary. The divisions chosen are indicated by dashed lines in Figs. 5, and the corresponding enthalpies and entropies attributed to each of the transitions are given in Table II.

DISCUSSION

The heat capacity of a CH_2 unit

There has been considerable discussion in recent years concerning the constancy of the CH_2 increment and thermo-

TABLE I. The experimental values of the heat capacity of $(n\text{-}C_{18}H_{37}NH_3)_2CdCl_4$.

T/K	C_p/J K^{-1} mol^{-1}	T/K	C_p/J K^{-1} mol^{-1}	T/K	C_p/J K^{-1} mol^{-1}
10.20	11.17	244.04	930.1	351.41	3267.1
14.78	31.64	250.29	953.1	351.51	2940.0
19.51	56.91	259.39	992.1	352.43	2516.1
23.78	83.57	269.50	1041.7	352.66	2404.9
28.21	112.5	280.06	1083.1	353.68	2376.7
32.94	145.1	289.99	1145.7	353.90	2312.4
37.93	180.2	299.52	1217.7	354.63	2407.1
43.18	218.3	301.22	1238.7	354.70	2528.7
48.74	254.2	308.60	1309.4	355.22	2700.1
54.61	286.7	312.08	1324.8	355.26	2802.8
60.80	324.1	314.79	1388.9	355.58	3003.3
67.80	360.8	321.87	1454.7	355.83	3574.1
75.06	402.4	328.84	1533.7	356.40	3603.5
82.83	438.6	334.28	1631.2	356.73	3232.7
87.04	453.5	339.35	1883.6	356.95	2961.7
93.22	475.5	340.92	1987.8	357.70	3019.3
100.41	501.2	345.84	2530.3	358.77	3086.4
108.08	526.9	347.75	2957.3	359.66	4792.7
117.01	555.3	347.83	3049.7	360.68	3869.5
126.29	582.9	348.19	3546.3	361.65	3042.4
135.94	609.2	348.59	4264.1	362.67	3101.2
145.62	636.8	348.90	5500.6	363.51	4257.9
155.01	659.6	348.91	5862.8	364.20	6287.5
164.38	684.4	349.14	8345.7	364.81	8453.6
173.96	710.2	349.51	45051	365.27	1094.7
184.09	736.5	349.68	69006	365.61	1165.0
194.73	767.2	349.88	26804	366.00	7626.7
204.33	792.7	350.12	18652	366.82	2831.9
214.40	824.2	350.40	17017	368.07	1485.9
224.22	855.4	350.65	14226	368.09	1499.0
233.76	890.0	350.96	4080.7	370.96	1500.4

dynamic properties of consecutive members of homologous series.[12,13] The present availability[14–17] of heat capacity data for compounds of the general formula $(n\text{-}C_aH_{2a+1}NH_3)_2MCl_4$ for $a = 1, 3, 7, 18$ allows an opportunity to calculate the heat capacity of a CH_2 unit. This series is particularly useful for this calculation because alkyl chains in a given layer are known to be aligned in a parallel manner, thereby eliminating more complex chain–chain interactions.

The range of the heat capacity of a CH_2 unit as a function of temperature has been calculated from

$$C_p(CH_2) = \{C_p[(n\text{-}C_aH_{2a+1}NH_3)_2MCl_4] - C_p[(n\text{-}C_bH_{2b+1}NH_3)_2MCl_4]\}/[2(a-b)] \quad (3)$$

for the six pairs of compounds for which the heat capacity was known, namely $a, b = 1, 3, 7$ and M = Mn, Cd. This method of differences eliminates all contributions to the heat capacity other than that of the CH_2 unit. The range of the

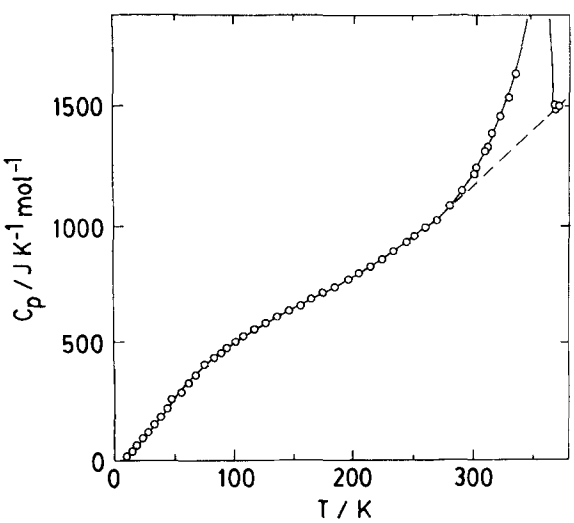

FIG. 4. The experimental values of the heat capacity of $(n\text{-}C_{18}H_{37}NH_3)_2CdCl_4$. The dashed line represents the baseline heat capacity.

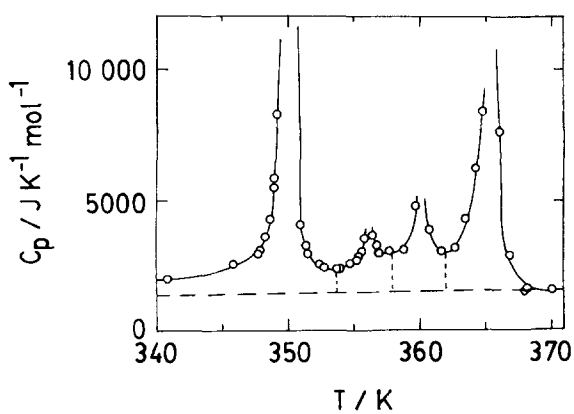

FIG. 5. The heat capacity of $(n\text{-}C_{18}H_{37}NH_3)_2CdCl_4$ in the region of the phase transitions. The divisions of the transitions for purposes of enthalpy and entropy evaluations are shown by the dashed lines.

TABLE II. The temperatures, enthalpies, and entropies of the solid–solid phase transitions in $(n\text{-}C_{18}H_{37}NH_3)_2CdCl_4$, as determined by adiabatic calorimetry.

T/K	ΔH_{trans}/J mol^{-1}	ΔS_{trans}/J K^{-1} mol^{-1}
349.6 ± 0.1	49 500 ± 500	132 ± 1
356.0 ± 0.1	2 300 ± 100	6.5 ± 0.3
359.5 ± 0.3	3 500 ± 100	9.6 ± 0.3
365.6 ± 0.3	34 300 ± 300	95 ± 1

heat capacity per CH_2 unit for the six pairs of compounds used is illustrated by the crosshatched area in Fig. 6, and amounts to about ± 5% in the temperature range shown. While some of the uncertainty may indicate subtle differences between members of the series, a large portion likely can be attributed to error involved in the estimation of the baseline (i.e., nontransition) heat capacity in the temperature region of the transitions. As a test of the validity of this evaluation of the heat capacity of a CH_2 increment, the heat capacity of $(n\text{-}C_{18}H_{37}NH_3)_2CdCl_4$ was calculated from $C_p[(CH_3NH_3)_2CdCl_4] + 34\ C_p(CH_2)$, and the agreement with experiment from 20 to 300 K was within 5%.

The heat capacity of a CH_2 increment in this series can be represented by

$$C_p(CH_2) = (-0.865 + 0.126T - 3.65\times10^{-4}T^2 + 9.05\times10^{-7}T^3)\ \text{J K}^{-1}\,\text{mol}^{-1}, \quad (4)$$

where T is the temperature in Kelvin. In light of the intrinsic interest in the dynamics of a CH_2 unit, some attempt has been made to compare various calculations of the heat capacity with the experimental values.

Pitzer's early discussion of the thermodynamic functions of long chain hydrocarbons,[18] while relatively simple, can account for many of the features of the heat capacity curve. According to this model, the contributions to the heat capacity of a CH_2 increment are additive, and include terms that express the degrees of freedom associated with the following modes: C–C stretching, C–C bending, C–H vibrations, "hindered rotation" of the CH_2 unit. The sum of the first three of these contributions has been assessed using 1D Einstein models and the frequencies suggested in Ref. 18, and is represented by the dotted line in Fig. 6. (It should be noted here that while Pitzer suggested the use of a Debye function to describe the C–C bending mode, this overestimates the low temperature heat capacity considerably. In any case, optic modes are more accurately represented by the Einstein function.[19])

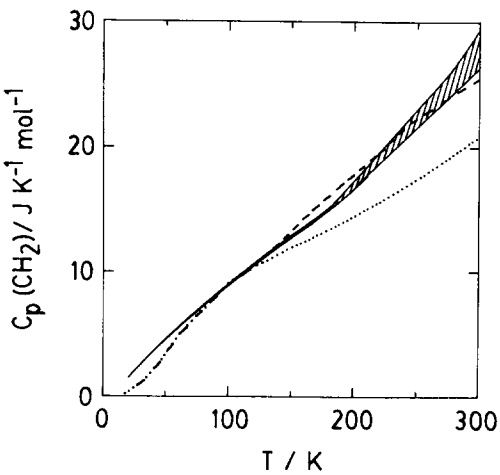

FIG. 6. The heat capacity of a CH_2 unit in an alkyl chain. The crosshatched area represents the range of experimental values, as described in the text. The dotted line is the calculation of the contribution due to C–C stretch, C–C bend, and C–H vibrations, as in Ref. 18. The dashed line is the sum of the latter contributions and a highly hindered Einstein vibrational contribution for CH_2 oscillations.

The difference between the dotted line and the experimental range of $C_p(CH_2)$ can be attributed to two possible sources. The first of these is that the measured values are C_p, whereas the calculations are for C_v. The usual relationship between C_p and C_v:

$$C_p - C_v = \alpha^2 BVT, \quad (5)$$

where α is the coefficient of thermal expansion, B is the bulk modulus, V is the molar volume, and T is the temperature, indicates an increasing difference between C_p and C_v with increasing temperature for most materials. However, due to the thermally activated population of "kink" orientations in alkyl chains and subsequent negative thermal expansion in paraffinic materials, the difference between C_p and C_v could be expected to be negligible in the present discussion.

The more likely source of the difference between the measured heat capacity and the values calculated according to the method described thus far, is the omission of a term to account for "hindered rotation" of the CH_2 unit with respect to the long axis of the alkyl chain. It seems likely in the case of $(n\text{-}C_{18}H_{37}NH_3)_2CdCl_4$ where there are no phase transitions below room temperature, that this sort of motion of the CH_2 unit is highly hindered; this is also likely the case for the other homologs below 300 K, based on the similarity of $C_p(CH_2)$. Before presenting a discussion of various models of this reorientation, it should be pointed out that hindered rotations of CH_2 units in alkyl chains cannot be represented as truly single-particle motions: in order to maintain the overall directionality of the alkyl chain, more than one CH_2 unit must rotate about the long axis. In a classical sense, the most likely of such interactions would involve two CH_2 units, in the formation of a kink along the chain. However, the number of two-carbon units in an alkyl ammonium chain is the same as the number of CH_2 units, i.e., $(n-1)$, where n is the number of carbons in the chain. In this sense the residual contribution to $C_p(CH_2)$ can equivalently be considered to arise from CH_2 motion or $(CH_2)_2$ motion.

Several types of models for barriers to rotation within the chain can be envisaged. The simplest of these, in which the barrier is very high relative to the available thermal energy such that the CH_2 unit oscillates with a characteristic frequency, actually gives the best fit to the experimental data in this case. The heavy dashed line in Fig. 6 illustrates the sum of the previously mentioned contributions (C–C stretch, C–C bend, C–H vibrations) and an Einstein vibrational contribution for CH_2 oscillations with frequency of 500 cm^{-1}. This frequency was chosen as it gave the best fit to the experimental data.

More complex barriers such as the threefold potential suggested by Pitzer[18]:

$$V = 15(1 - \cos\phi)\text{kJ mol}^{-1} \quad (6)$$

and the potential proposed for C_2H_4 rotation in polyethylene[20]:

$$V = [9.00(1 - \cos\phi) - 4.90(1 - \cos 2\phi) + 16.0(1 - \cos 3\phi)]\text{kJ mol}^{-1}, \quad (7)$$

where ϕ is the angle of displacement of the CH_2 or C_2H_4 unit from its equilibrium position as measured by the displacement from the long axis of the chain have been proposed. Although they give C_p values that are within 20% of the experimental values at room temperature, both greatly overestimate the contribution to C_p below 100 K where the experiment indicates a negligible contribution due to internal rotation. [Equations (6) and (7) give C_p contributions due to internal rotation of 8.6 and 5.4 J K^{-1} mol^{-1}, respectively, at 100 K.]

Although the overall fit of the calculated (dashed) curve to the experimental values of the heat capacity of a CH_2 unit is good above 80 K, it underestimates the heat capacity below 80 K. This fact indicates the existence of additional low frequency modes, probably in the interactions within the carbon skeleton of the chain. It is hoped that this presentation of the experimental heat capacity of a CH_2 unit and the simple model for its calculation will inspire further theoretical work in this area.

Phase transitions

In order to understand the processes responsible for the phase transitions in $(n\text{-}C_{18}H_{37}NH_3)_2CdCl_4$, it is instructive first to summarize what is known about the phase transitions in homologous compounds. Table III gives the transition temperatures and entropy changes for several members of the series.

In principle, there are two possible sources of structural phase transitions in these compounds: "melting" of the alkyl chains, and changes in the H-bond configurations. Since $(CH_3NH_3)_2CdCl_4$ does not have alkyl chains long enough to melt, it undergoes only H-bond related transitions.[15] As the chain is increased to *n*-propyl, there are contributions from both types of transitions, resulting in three low temperature phase transitions. The lowest of these has been associated primarily with H-bonding changes, while the upper transitions involve both H-bond disorder and alkyl chain motion.[16] The introduction of a carbon–carbon double bond to give $(CH_2{=}CHCH_2NH_3)_2CdCl_4$ moves the phase transitions to higher temperatures due to easier accommodation of the low-temperature H-bonding scheme as a consequence of the shortened chain.[21]

As mentioned in the Introduction, steric interactions allow only the monoclinic H-bonding configuration for much longer alkyl chains. For this reason, the transitions in the heptyl and longer compounds are dominated by the melting of the alkyl chains.[17] In contrast with the shorter chain homologs where the H-bonding controls the chain orientations, the transitions in the longer alkyl chain compounds can be described as "the tail wagging the dog."

TABLE III. Phase transitions in $(RNH_3)_2CdCl_4$.

R	T_{trans}/K	ΔS_{trans}/R	Reference
CH_3	164.2	1.30	15
	282	0.029	15
$n\text{-}C_3H_7$	105.5	1.68	16
	156.8	0.46	16
	178.7	0.74	16
$CH_2{=}CHCH_2$	206.9	2.51	22
	266.7	1.88	22
$n\text{-}C_7H_{15}$	250.0	8.59	17
	316.7	1.92	17
$n\text{-}C_8H_{17}$	267.7	6.5	5
	307.1	2.0	5
$n\text{-}C_{10}H_{21}$	303	1.80	4
	313	12.6	4
$n\text{-}C_{12}H_{25}$	334[a]	15.2	6
$n\text{-}C_{14}H_{29}$	345[a]	8.30	6
	347[a]	5.6	6
	351[a]	8.4	6
$n\text{-}C_{18}H_{37}$	349.6	15.9	present
	356.0	0.78	present
	359.5	1.15	present
	365.6	11.4	present

[a] Values for second and subsequent scans.

Based on the melting points of paraffins, one might expect the phase transitions in the long chain compounds to increase with chain length, and indeed this is the general trend. For the heptyl to dodecyl compounds, there are two phase transitions, one major and one minor. From an extensive study of the decyl cadmium compound, it has been proposed that a disordering of the chains between two equivalent positions gives rise to the minor transition while complete melting of the chains to give an average orientation parallel to the *c* axis is the driving force for the major transition, at least when the minor transition is at a temperature lower than the major transition.[4] In these cases, the minor transition includes only a very small volume change while the transition with the larger entropy change is coincident with a substantial ($\sim 10\%$) extension of the lattice parameter in the *c* direction. The postulated sources of the transitions imply that there is sufficient room between the chains to allow for twofold disorder, but not enough for full chain melting. Although alkyl chains are known to contract in length due to kink formation as they melt, in this case the chains reorient to become parallel to the *c* axis on average as they melt, and a net increase in the *c* axis spacing results.

The processes that give rise to transitions in the opposite order, i.e., with the major transition followed by the minor one, are less well understood. Although this transition sequence has been attributed to chain melting followed by a twofold positional disorder,[5] an investigation of the phase transitions in $(n\text{-}C_{14}H_{29}NH_3)_2CdCl_4$ has shown that the major transition includes more than one disordering process.[6] In fact, examination of Table III indicates a general trend to an increased number of phase transitions as the alkyl chain is lengthened. We will return to this point below.

Before proceeding with the discussion of the results for $(n\text{-}C_{18}H_{37}NH_3)_2CdCl_4$, it is instructive to summarize the influence of the metal on the structural phase transitions. As one might expect, the transitions in the very short alkyl chain members of the series are highly dependent on the metal cation due to its influence on the H-bond strength.[14–16] An investigation of the C_{14} compounds indicates a chain melting temperature that is metal independent, but a chain "flopping" (i.e., twofold disorder) temperature that is influenced by the metal.[6] The conclusion of that investigation was that the intralayer metal–metal distance in each case provides sufficient space for the complete disorder of the chains, but the cooperative flopping motion is highly dependent on the spacing between the chains.

In order to more fully discuss the source of the phase transitions in $(n\text{-}C_{18}H_{37}NH_3)_2CdCl_4$, it is important first to address the question of changes in H-bonding. A proton NMR study of the decyl homolog[4] revealed a large variation in the second moment of the proton absorption and a minimum in the spin-lattice relaxation time, T_1, at low temperatures, and these were ascribed to a broad H-bonding phase transition between 100 and 150 K, although T_1 minima have also been observed[22] in *n*-alkanes at ~ 150 K, and attributed to methyl group reorientations. The present work, which appears to be the first measurement of the heat capacity of very long chain compounds of the series, clearly shows no phase transitions below room temperature. Based on the NMR results one might expect to see a hump in the heat capacity curve similar to that observed[23] in NH_4BF_4 due to the gradual reorientation of the ammonium ion, but there is also no evidence for this. It seems quite clear, therefore, that there are no changes in the H-bonding configuration below room temperature.

By comparison with the transitions in homologous compounds, it can be shown that the alkyl chains in $(n\text{-}C_{18}H_{37}NH_3)_2CdCl_4$ are completely disordered above the highest transition temperature. In the decyl compound, where x-ray diffraction has shown the chains to be "molten" at high temperatures, an analysis of the total experimental phase transition entropy change gives each $R\text{–}CH_2\text{–}CH_2\text{–}R$ group a value of $\Delta S = 0.9$ R;[4] this can be understood in terms of maximum entropy change per two-carbon unit represented as dimers on a two-dimensional triangular lattice, $R \ln(2.3565) = 0.857$ R.[24] Based on this result, the total entropy change predicted for $(n\text{-}C_{18}H_{37}NH_3)_2CdCl_4$, based on complete disorder at high temperatures, would be 28.8 R, in good agreement with the experimental value of 29.2 R.

$(n\text{-}C_{18}H_{37}NH_3)_2CdCl_4$ also illustrates the trends of increased transition temperature and increased number of phase transitions with increased alkyl chain length. While the transition temperature reflects the increased thermal energy required to melt the chains, the increased number of transitions suggest a stepwise melting of the chains.

The entropy changes associated with each of the four transitions in $(n\text{-}C_{18}H_{37}NH_3)_2CdCl_4$ indicate the following transition sequence: major, minor, minor, major. This is in direct contrast with the (major, minor) or (minor, major) sequence observed in analogous compounds with shorter chain lengths, indicating an increased complexity of the melting process with increased chain length. In addition, in the shorter chain compounds the entropy changes for the minor transitions appear[4–6] as $\sim 2R \ln 2 (= 1.39$ R), more than is observed here (0.78 R, 1.15 R). The entropy values therefore suggest a complex multistep melting process; additional experiments will shed light on the microscopic mechanism involved in these phase transitions.

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