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# STUDIES OF SOLID–SOLID PHASE TRANSITIONS FOR $(n\text{-}C_{18}H_{37}NH_3)_2MCl_4$

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## ABSTRACT

Bis(*n*-octadecylammonium)tetrachlorometallates(II) (C18M, M ≡ Mn, Cu, Fe, Zn or Co), which are one kind of potential thermal storage material, were synthesized and, at the same time, chemical analysis was carried out and the crystal structure for C18M compounds were determined. The solid–solid phase transitions for C18M compounds were studied using DSC, IR, XRD and statistical thermodynamics. Two kinds of solid–solid transitions were observed by DSC, IR and XRD.The main transition is assumed to correspond to the order–disorder transition of the methylene groups, and the minor transition is believed to be the order–disorder transition of the rigid chains between two equivalent sites. The entropies of these phase transitions were calculated by means of statistical thermodynamics.

## INTRODUCTION

Compounds of the general formula $(n\text{-}C_nH_{2n+1}NH_3)_2MX_4$ (M ≡ Mn, Cu, Fe, Hg, Cd, Pd, Zn or Co; X ≡ Cl or Br; short notation C*n*M), have received attention in many areas of solid-state physics and chemistry [1–4]. Single crystal X-ray diffraction (XRD) studies [5,6] have revealed that these compounds are 'sandwich' systems, i.e. each inorganic layer is sandwiched between two hydrocarbon layers. For M ≡ Mn, Cu, Cd, Hg or Fe, the inorganic regions of the compounds consist of a nearly two-dimensional macroanion network made up of corner-sharing $MX_6$ octahedra; but for M ≡ Zn or Co, isolated $MX_4^{2-}$ tetrahedra are present. Owing to the large enthalpies of the solid–solid phase transitions, these chemicals ($n \geqslant 10$) are a kind of potential thermal energy storage material [7]. In this paper, a series of bis(*n*-octadecylammonium)tetrachlorometallates(II) (M ≡ Mn, Cu, Fe, Zn or Co; short notation C18M) were synthesized and identified. Their solid–solid phase transitions were studied using DSC, IR, XRD and statistical thermodynamics calculation.

## EXPERIMENTAL

Octadecylamine (98%, Koch–Light Labs., Ltd. Gt. Britain) was dissolved in warm absolute ethanol, to which excess HCl was added. The metal(II) chloride (AnalaR, First Reagent Manufactory of Shanghai) was dissolved in further warm absolute ethanol. The second solution was slowly added to the first one, and the mixture was boiled for 1 h. The products were recrystallized three times from absolute ethanol [8]. The C18M chemical analysis results are given in Table 1.

The solid–solid phase transition enthalpies of the C18M compounds were examined using a differential scanning calorimeter CDR-1, Shanghai Balance Instrument Factory, in the range 298–450 K at a scanning rate of 1 K $min^{-1}$. Indium (99.999%) was used as a calibration standard ($\Delta H = 28.5$ J $g^{-1}$).

IR spectra were taken using an FT/IR spectrometer 5DX, Nicolet, equipped with a variable-temperature controller on the sample vacuum cell. The powdered samples were mixed with KBr and pressed into pellets.

An X-ray powder diffraction camera D/Max-$\gamma\beta$, Rigaku Japan, was used for collection of the data, using Cu $K\alpha$ radiation (Ni filter) at a scanning rate of 0.25° $min^{-1}$.

## DIFFERENTIAL SCANNING CALORIMETRY (DSC)

Table 2 gives the solid–solid phase transition enthalpies and entropies of the C18M compounds in the range 350–390 K. Typical DSC curves of the C18M compounds show that there are two kinds of solid–solid phase transition, a main transition and a minor transition. The main transition is assumed to correspond to the order–disorder transition of the methylene groups, and the minor transition is believed to be the order–disorder transition of the rigid chains between two equivalent sites [2]. For C18M compounds where M ≡ Mn, Cu or Fe, and where the inorganic layer consists of a two-dimensional macroanion network, the main transition

TABLE 1

Chemical analysis (theoretical mass% in parentheses)

| | C (%) | H (%) | N (%) | Cl (%) | M (%) |
|---|---|---|---|---|---|
| $C18NH_2$ | 80.30 (80.22) | 14.59 (14.58) | 5.11 (5.20) | | |
| C18Mn | 58.30 (58.61) | 10.97 (10.93) | 3.81 (3.80) | 19.63 (19.22) | 7.50 (7.45) |
| C18Cu | 58.26 (57.93) | 10.62 (10.80) | 3.66 (3.75) | 19.01 (19.00) | 8.47 (8.51) |
| C18Fe | 58.45 (58.54) | 10.80 (10.92) | 3.69 (3.79) | 19.11 (19.20) | 7.60 (7.56) |
| C18Zn | 57.98 (57.78) | 10.99 (10.78) | 3.50 (3.74) | 18.81 (18.95) | 8.74 (8.74) |
| C18Co | 58.24 (58.29) | 11.10 (10.87) | 3.60 (3.77) | 18.91 (19.12) | 7.89 (7.94) |

TABLE 2

Solid–solid phase transition temperatures, enthalpies and entropies

| | $T$ (K) | $\Delta H$ (kJ mol$^{-1}$) | | | $\Delta S$ (J mol$^{-1}$ K$^{-1}$) | | |
|---|---|---|---|---|---|---|---|
| C18Mn | 353 | 61.38 | 70.05 | 84.83 | 173.80 | 197.94 | 237.13 |
| | 359 | 8.67 | | | 24.14 | | |
| | 377 | 14.78 | 14.78 | | 39.19 | 39.19 | |
| C18Cu | 355 | 13.00 | 70.37 | 85.42 | 36.83 | 196.25 | 236.45 |
| | 357 | 17.60 | | | 49.30 | | |
| | 360 | 24.30 | | | 67.50 | | |
| | 363 | 15.47 | | | 42.62 | | |
| | 374 | 15.05 | 15.05 | | 40.24 | 40.24 | |
| C18Fe | 351 | 16.09 | 64.75 | 81.55 | 45.84 | 183.33 | 227.89 |
| | 353 | 37.49 | | | 106.20 | | |
| | 357 | 11.17 | | | 31.29 | | |
| | 377 | 16.80 | 16.80 | | 44.56 | 44.56 | |
| C18Zn | 364 | 1.28 | 8.39 | 87.70 | 3.52 | 22.96 | 232.77 |
| | 366 | 7.11 | | | 19.43 | | |
| | 378 | 79.31 | 79.31 | | 209.82 | 209.82 | |
| C18Co | 365 | 4.38 | 14.46 | 88.43 | 12.00 | 39.47 | 237.25 |
| | 367 | 10.08 | | | 27.47 | | |
| | 374 | 73.97 | 73.97 | | 197.78 | 197.78 | |

occurs at about 353 K and the minor transition follows at about 375 K. On the contrary, for C18M compounds where M ≡ Zn or Co, and where the inorganic layer consists of $MX_4^{2-}$ tetrahedra, the minor transition occurs before the main transition.

## IR SPECTRA

Fig. 1, curves 1, shows the IR spectra of the powdered C18M samples at room temperature. These are characteristic of such compounds containing long straight-chain alkyl groups which are mainly in the *trans* configuration [9]. The absorption bands at about 725 cm$^{-1}$ and 1470 cm$^{-1}$, which are the methylene rocking and scissoring vibrations respectively, are each doublets owing to interactions between two non-equivalent chains in the crystallographic unit cell. The absorption peaks in the region 1050–1350 cm$^{-1}$, which are the methylene twisting and wagging vibrations, are split into several peaks because of interactions between methylene groups within the same chain.

The solid–solid phase transitions were followed by IR, and the curves obtained are shown in Fig. 1. Curves 2 (313 K), 3 (333 K) and 4 (343 K) in Fig. 1 are all the same as curves 1 (room temperature), showing that the long

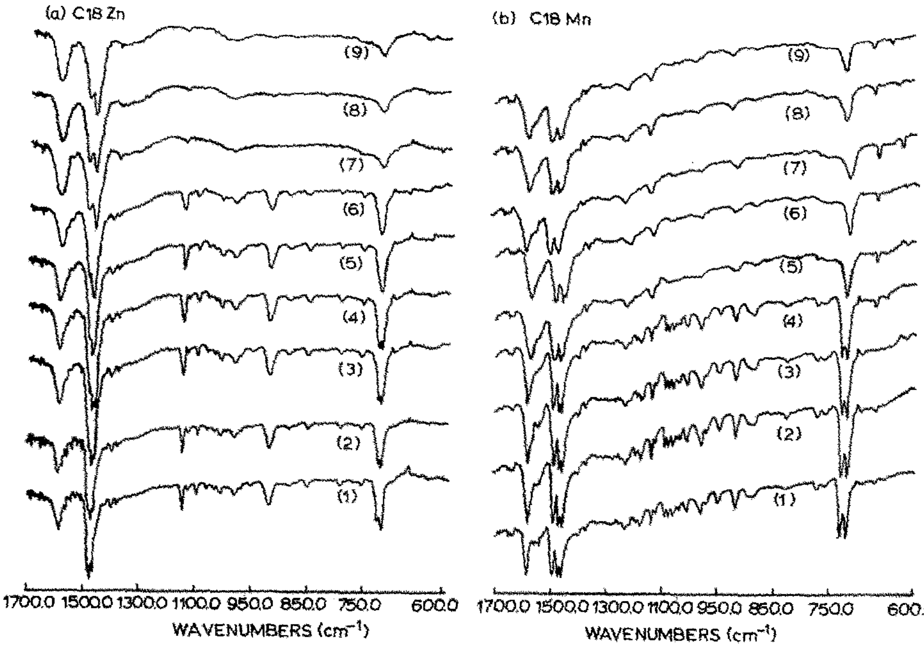

Fig. 1. IR spectra: a, C18Zn; b, C18Mn. (1) 298 K; (2) 313 K; (3) 333 K; (4) 343 K; (5) 353 K; (6) 363 K; (7) 378 K; (8) 393 K; (9) molten phase (for C18Zn, $T = 453$ K; for C18Mn, $T = 533$ K).

alkyl chains are conformationally ordered, mainly in a planar zig-zag arrangement, before their solid–solid phase transitions. In curve 5 (353 K) of Fig. 1a, the IR spectrum of C18Zn, it may be observed that the splitting of the 1470 cm$^{-1}$ and 725 cm$^{-1}$ bands disappears. This indicates that the interactions between adjacent chains no longer exist. Curve 6 (363 K) in Fig. 1a is similar to curve 5. Curve 7 (378 K) in Fig. 1a shows that the absorption peaks in the 1050–1350 cm$^{-1}$ region are unsplit and very broad; in other words, there are no interactions between methylene groups in the same chain. Curve 9 (molten state) in Fig. 1a is identical to the corresponding region of Curves 7 (378 K) and 8 (393 K), which are the IR spectra of the high temperature solid state. The variation in the IR spectra of C18Mn (Fig. 1b) within the solid–solid phase transitions is similar to that of C18Zn, except that in curve 5 (353 K) of Fig. 1b not only the bands at 1470 cm$^{-1}$ and 725 cm$^{-1}$ but also those in the 1050–1350 cm$^{-1}$ region are unsplit and very broad. This reveals the absence of interactions among the methylene groups.

## X-RAY POWDER DIFFRACTION

The C18M samples were studied using XRD. The $2\theta$ values, which had been corrected using an internal standard, silicon powder, were indexed. The

TABLE 3

X-ray crystallographic data

| Molecular formula | C18Mn | C18Zn |
|---|---|---|
| Molecular weight (a.m.u.) | 737.79 | 748.23 |
| Crystal system | Monoclinic | Monoclinic |
| Space group | $P_{2_1/c}$ | $P_{2_1/c}$ |
| No. of molecules per unit cell | 2 | 2 |
| Cell parameters | $a = 40.21 \pm 0.06$ Å | $a = 28.85 \pm 0.16$ Å |
|  | $b = 7.29 \pm 0.01$ Å | $b = 10.13 \pm 0.06$ Å |
|  | $c = 7.24 \pm 0.01$ Å | $c = 7.36 \pm 0.04$ Å |
|  | $\beta = 90.03 \pm 0.01°$ | $\beta = 90.28 \pm 0.01°$ |
| Cell volume (Å$^3$) | 2123.75 | 2150.28 |
| Density (calc., g cm$^{-3}$) | 1.154 | 1.155 |
| Density (expt., g cm$^{-3}$) | 1.172 | 1.175 |

TABLE 4

Interplanar spacings $d_{h00}$ at room temperature (RT) and high temperature (HT)

| Compound | $d_{h00}$ (Å) |  |
|---|---|---|
|  | RT | HT |
| C18Mn | 40.21 | 46.53 |
| C18Cu | 39.53 | 44.28 |
| C18Zn | 28.85 | 35.98 |
| C18Co | 28.80 | 35.39 |

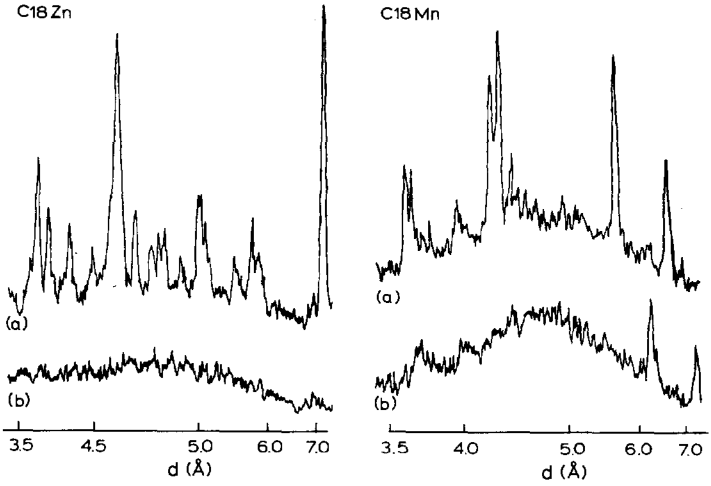

Fig. 2. X-ray transmission spectra: a, room temperature; b, high temperature ($T = 393$ K).

crystal data at room temperature, which were calculated from about forty high-angle reflections ($2\theta > 20°$), are given in Table 3.

Table 4 gives the interplanar spacings $d_{h00}$, which are parallel to the ionic layers (*h*00 reflections) and which are observed in the powder spectra of the C18M compounds before and after the solid–solid phase transitions. The interplanar spacings $d_{h00}$ increase at the transitions. In Fig. 2, several sharp diffraction peaks in the range 4.0–5.0 Å are found in the room-temperature spectra, while there is an amorphous halo at the high temperature. These phenomena correspond to crystalline and amorphous polyethylene respectively.

## STATISTICAL THERMODYNAMICS CALCULATION

In addition to observing the two transitions using DSC, IR and XRD, the two kinds of transition entropy of the compounds under study may be calculated by means of statistical thermodynamics as follows.

(a) The main transition in these systems is believed to be a conformational transition of the alkyl chains. The following assumptions may be made.

(1) The methylene groups in long straight-chain alkyl groups at room temperature exist mainly in the *trans* configuration (T) [5,6]:

N–C–C–C–C–C– ...
T $G^{\pm}$T T ... (where M ≡ Mn or Cu)
T T T T ... (where M ≡ Zn or Co)

(2) After the main transition, the internal rotation levels of the methylene groups in C*n*M compounds are excited, and three stable conformations of methylene exist: the *trans* (T), the *gauche* plus ($G^+$), and the *gauche* minus ($G^-$) conformations.

(3) The populations of species in various conformations of methylene have Boltzmann distributions.

(4) The entropy of the main transition is provided by the internal rotation entropy of methylene in C*n*M compounds. (The activation energy of the internal rotation is denoted by $E$.)

According to the four assumptions above, the entropy of the main transition may be obtained as follows

$$S/2R = (n-2)\ln(1 + 2\,e^{-E/RT}) + (E/RT); \qquad \text{where M} \equiv \text{Mn or Cu}$$

$$S/2R = (n-2)\ln(1 + 2\,e^{-E/RT}); \qquad \text{where M} \equiv \text{Zn or Co}$$

Using the thermodynamic data available on C*n*M compounds ($n = 10$–18, M ≡ Mn, Cu, Zn or Co), the activation energies of internal rotation of methylene in C*n*M compounds are obtained. These are in accordance with

TABLE 5

Calculated and experimental entropies of the main transition

| Compound | $n$ | $T$ (K) | $\Delta S_{\text{expt.}}$ (J mol$^{-1}$ K$^{-1}$) | $\Delta S_{\text{calc.}}$ (J mol$^{-1}$ K$^{-1}$) | Ref. |
|---|---|---|---|---|---|
| CnMn | 10 | 308 | 113 | 102 | 7 |
| | 11 | 316 | 120 | 114 | 7 |
| | 12 | 318 | 124 | 126 | 7 |
| | 13 | 331 | 132 | 139 | 7 |
| | 14 | 339 | 150 | 152 | 7 |
| | 15 | 340 | 180 | 164 | 7 |
| | 16 | 345 | 174 | 177 | 7 |
| | 17 | 349 | 183 | 190 | 7 |
| | 18 | 353 | 198 | 202 | [a] |
| | $E = 1872 \pm 35$ J mol$^{-1}$ | | | | |
| CnZn | 10 | 351 | 97 | 97 | 4 |
| | 11 | 354 | 104 | 110 | 4 |
| | 12 | 361 | 133 | 123 | 4 |
| | 13 | 363 | 131 | 136 | 4 |
| | 14 | 367 | 139 | 149 | 4 |
| | 15 | 370 | 150 | 162 | 4 |
| | 16 | 376 | 197 | 176 | 4 |
| | 18 | 378 | 210 | 201 | [a] |
| | $E = 1805 \pm 45$ (J mol$^{-1}$) | | | | |
| CnCu | 10 | 306 | 91 | 99 | 7 |
| | 11 | 313 | 124 | 111 | 7 |
| | 12 | 330 | 127 | 124 | 7 |
| | 13 | 333 | 145 | 136 | 7 |
| | 14 | 334 | 150 | 147 | 7 |
| | 15 | 343 | 157 | 160 | 7 |
| | 16 | 345 | 165 | 172 | 7 |
| | 17 | 352 | 179 | 185 | 7 |
| | 18 | 353 | 196 | 196 | [a] |
| | $E = 2023 \pm 39$ (J mol$^{-1}$) | | | | |
| CnCo | 10 | 355 | 104 | 98 | 7 |
| | 11 | 358 | 100 | 111 | 7 |
| | 12 | 363 | 124 | 124 | 7 |
| | 13 | 366 | 131 | 137 | 7 |
| | 14 | 370 | 159 | 150 | 7 |
| | 15 | 373 | 147 | 163 | 7 |
| | 16 | 378 | 207 | 176 | 7 |
| | 17 | 378 | 191 | 189 | 7 |
| | 18 | 374 | 198 | 200 | [a] |
| | $E = 1793 \pm 56$ (J mol$^{-1}$) | | | | |

[a] This work.

Flory's value for the enthalpy of a *gauche* bond relative to a *trans* bond, 2000 J mol$^{-1}$. A comparison between experimental entropies and calculated entropies is given in Table 5. The agreement between the calculated values and the experimental values is within experimental error.

(b) The minor transition is to be an order–disorder transition of the rigid alkylammonium chains. The entropy for a chain oscillating between two equivalent positions is $R$ ln 2, so that the entropy of the minor transition is postulated as

$$S = 2R \ln 2$$

However, the experimental values for C18M exceed those required for a simple two-fold disorder. This implies that additional degrees of freedom, probably motion of the metal halide framework, are involved.

## CONCLUSIONS

The solid–solid phase transitions of the C18M compounds in the range 350–390 K are of the order–disorder kind, mainly in the hydrocarbon structure. There are two kinds of solid–solid transitions: the main transition, which is assumed to correspond to the order–disorder transition of the methylene groups, and the minor transition, which is believed to be the order–disorder transition of the rigid chains between two equivalent sites. The metal ions and thin inorganic regions also have an influence on the solid–solid phase transitions of the C18M compounds. In the regions of these phase transitions the enthalpies and entropies are higher ($\Delta H = 80$–$90$ kJ mol$^{-1}$, $\Delta S = 220$–$240$ J mol$^{-1}$ K$^{-1}$), so that C18M compounds are potential thermal energy storage materials.

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