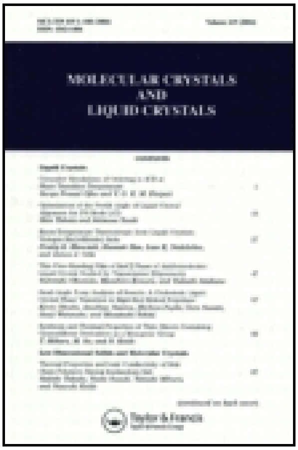

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Thermal Behaviour of Mercury(II) Carboxylates

Henry A. Ellis [a] [b]

[a] Department of Chemistry, University of the West Indies, Mona, Kingston 7, Jamaica

[b] Kent State University, Kent, Ohio, U.S.A.

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Thermal Behaviour of Mercury(II) Carboxylates

HENRY A. ELLIS†

Department of Chemistry, University of the West Indies, Mona, Kingston 7, Jamaica

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Data are presented on thermotropic phase transition temperatures and heats of phase changes for even-chain-length mercury(II) carboxylates from octanoate to octadecanoate inclusive. Phase structures are characterised by hot stage polarising light microscopy and x-ray diffractometry. Mesophases are not observed in the phase sequences, for octanoate to tetradecanoate, as suggested by Adeosun. Rather, these compounds exhibit simple melting and melt recrystallisation only. In contrast, a premelting transition is observed in each of mercury(II) hexadecanoate and octadecanoate, probably as a consequence of some modifications to the usual bilayer arrangement of molecules within the layers. For these, crystalline polymorphism is observed. The data are interpreted in terms of the disordering of hydrocarbon chains as the major process occurring up to and during melting.

INTRODUCTION

It is well known that a number of divalent metal carboxylates undergo numerous phase transitions on heating the solid to the isotropic liquid.[1,2] Some of these transitions play an important role in the rheology of these compounds.[3] X-ray studies by Spegt,[4] Luzzati and co-workers[5–7] on several divalent metal carboxylates have demonstrated that some of the observed phases were mesophases. Additionally, several structures were proposed for these consistent with the x-ray data. Nevertheless, Winsor[8] has questioned the reliance of the data on the assumption that the mesophases were quasi-crystalline and has suggested

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that the proposed structures be regarded with some caution. Thermotropic mesophases have been suggested in the phase sequence for even-chain-length mercury(II) carboxylates from octanoate to octadecanoate. For example, a low temperature smectic mesophase was suggested to form in the decanoate, tetradecanoate, hexadecanoate and octadecanoate though, surprisingly, not in the octanoate and dodecanoate.[2] Because of these discrepancies in the data, the thermal behaviour of these compounds have been reinvestigated here.

Transition temperatures and heats of phase transition (ΔH) were determined by differential scanning calorimetry (DSC). Phase structures were characterised by hot-stage polarising light microscopy and x-ray diffractometry.

EXPERIMENTAL

The preparation of mercury(II) carboxylates of general formula: $(CH_3(CH_2)_nCOO)_2Hg$ ($n = 6 \ldots 16$) has been described elsewhere.[2] The compounds were recrystallised at least three times from hot toluene and fused under vacuum to remove toluene and any traces of water. Analyses of the IR spectra of the compounds showed that they were free of water and excess of organic acid.

DSC

Approximately 4–10 mg of samples were sealed in standard aluminium crucibles of the Perkin-Elmer DSC-4-TADS system and scanned at 1K $\min^{-1}$ in both the heating and cooling cycles. Measurements were made at least in triplicate on fresh samples.

Microscopy

Phase structures were determined by a Leitz polarising light microscope fitted with a Mettler FP-2 heating stage (scan rate 2K $\min^{-1}$). Samples were examined sandwiched between microscope slides and coverslips. These were cleaned, prior to their use, by washing in acetone. They were then rubbed dry in one direction, parallel to the long axis of the slide, with soft tissue. The rubbed direction of the coverslip was always aligned with that of the slide.

X-ray diffractometry

X-ray diffraction photographs from samples sealed in glass capillaries (0.7 mm diameter) were recorded on flat polaroid film (type 57) at a sample to film distance of 80.03 mm. Each sample was irradiated for 1 hr with Ni-filtered Cu K_α radiation (λ = 1.5418Å). The temperature of the sample could be controlled by a heated copper block which acted, also, as a collimator for the x-ray beam.

RESULTS AND DISCUSSION

DSC curves for HgC_8 to HgC_{14} inclusive, show, for each compound, a single, well defined curve in both the heating and cooling cycles. On cooling each of these compounds, from the isotropic liquid, plate-like crystals first appeared which, on further cooling, slowly converted to a fine mosaic texture (Figure 1).

Considerable supercooling (ca. 5–7K) was observed on forming the crystalline phase. Transition temperatures obtained by DSC are summarised in Table I.

Whilst melting transition temperatures are in reasonable agreement with previously published values,[2] no evidence was found for the presence of a mesophase in any of the phase sequences, as suggested

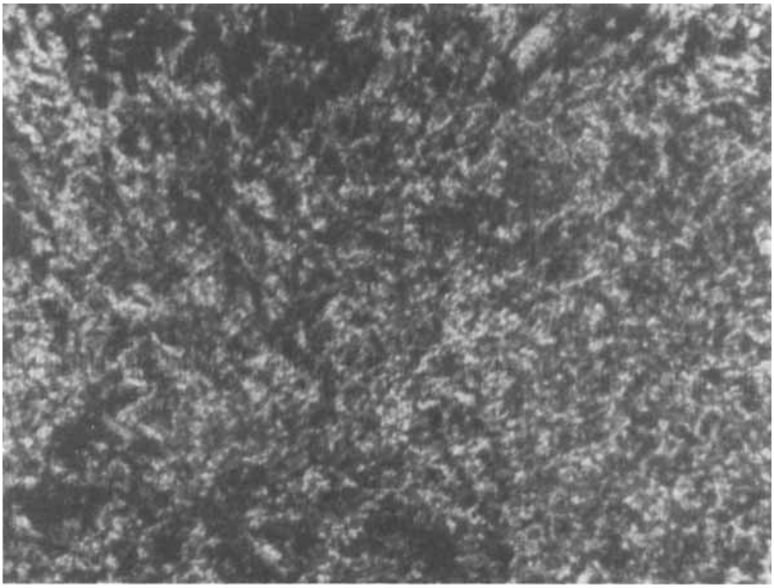

FIGURE 1 Texture of HgC_{14} crystalline phase at 388.3K.

TABLE I

Transition temperatures of Hg(II) carboxylates

N_c[a]	Crys ⟶ Liquid		Crys ⟵ Liquid
	T/K		T/K
8	386.7		380.0
10	389.9		384.6
12	395.0		388.0
14	400.3		395.1
	Crys ⟶ $Crys_1$		$Crys_1$ ⟶ Liquid
16	387.7		392.7
18	387.9		393.9
	Crys ⟵ $Crys_2$	$Crys_2$ ⟵ $Crys_1$	$Crys_1$ ⟵ Liquid
16	375.2		384.2(shoulder at 385.8)
18	372.0	384.0	388.8

[a] N_c ≡ carbon chain length; Crys ≡ Crystal.

by Adeosun. Both high and low temperature phases were characterised as crystal phases by their resistance to a sheer stress applied to the coverslip, their texture and x-ray diffraction pattern. For example, the x-ray pattern from HgC_{10} up to temperatures approaching melting always consisted of many sharp inner and outer reflections, typical of diffraction from an ordered crystalline structure.

An approximate molecular length for HgC_{10}, calculated from a model of the molecule with standard angles and bond lengths, is $l = 15Å$. This compared with a d spacing, calculated from the inner diffraction ring by $\lambda = 2d \sin\theta$ ($\lambda = 1.5418Å$), of 30.05Å at 297.1 and 370.5K, suggests a bilayer structure for these compounds with the molecules arranged orthogonally within the phases. Bilayer structures have been found for other divalent metal carboxylates.[9] It is unclear why low temperature mesophases were proposed for HgC_{10} and HgC_{14} though not HgC_8 and HgC_{12} in spite of their expected similarities in crystal structure. This inconsistency suggests that the low temperature transitions reported in HgC_{10} and HgC_{14} might arise from the presence of impurities in those compounds. In contrast these results were always reproducible and self-consistent.

A pre-melting transition was always observed whenever HgC_{16} and HgC_{18} were heated to the isotropic liquid (Table I). These transitions overlapped with the melting transition. Only in the case of HgC_{18} was the transition large enough to be isolated by slow cooling from the isotropic liquid. Similar pre-melting transitions have been reported for long chain monocarboxylic acids and have been ascribed to rocking motions involving methylene groups in the solid which tend to disorder the lattice in the temperature range close to the melting point.[10,11] As expected, the phenomenon disappeared with decreasing chain length. Clearly, these results in conjunction with the diffuse x-ray diffraction pattern observed for HgC_{16} at ambient temperatures, suggest that packing of the chains in the crystal structure might differ somewhat from the bilayer structure described hitherto. For example, a monolayer or some other structure is suggested for HgC_{16} where $\ell \simeq 22.7Å \simeq d$. Modifications in chain packing with increasing chain length are not unusual and have been reported in some copper(II) carboxylates.[12] Interestingly, in these long chain compounds, crystalline polymorphism was observed.

Melting enthalpies (ΔH) and entropies (ΔS) are given in Table II.

For HgC_8 to HgC_{14} inclusive, ΔS is a regular function of chain length (correlation coefficient of 0.99) and is described by the line: $\Delta S = -49.5 \pm 9 + 23.5 \pm 0.8\ N_c$. Unlike long-chain hydrocarbons, where ΔS increases by a factor close to R ln3 for each additional methylene group added to the chain,[13] the value here is much bigger. It could be as a consequence of a strong mercury-carboxylate bond confering some stiffness to the chains. However, the results suggest that the major process during melting is the disordering of hydrocarbon chains in the crystal lattice. In HgC_{16} and C_{18}, the melting process is somewhat different. In these, the following phase sequence

TABLE II

Thermodynamic data for phase changes

N_c	Crys ⟶ ΔH/kJmol^{-1}	Liquid ΔS/JK^{-1}mol^{-1}
8	54.58	141.14
10	71.35	183.05
12	91.10	229.41
14	113.03	282.34
	Crys ⟶ $\Sigma\Delta H$/kJmol^{-1}	Liquid
16	105.37	
18	117.52	

Error in values are within ±2%

is suggested:

$$\begin{tikzcd}
\mathrm{Crys} \arrow[rr] & & \mathrm{Crys}_1 \arrow[r, shift left] \arrow[dl] & \text{Isotropic Liquid} \arrow[l, shift left] \\
& \mathrm{Crys}_2 \arrow[ul] & &
\end{tikzcd}$$

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