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A comparison of thermal characteristics of Cu(II) carboxylates and their complexes with pyridine

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Abstract

TG and DTA measurements of $Cu_2(RCO_2)_4$ and $Cu_2(RCO_2)_4\,py_2$ ($R = CH_3(CH_2)_{n-2}$; $n = 7, 8, 9, 10, 12$) were done to compare their thermal behavior and establish the influence of pyridine in complexes on phase transition from solid state to liquid crystalline phase. Transitions from a crystalline to a liquid crystalline phase were observed for all $Cu_2(RCO_2)_4$ compounds, but only for pyridine complexes of Cu(II) nonanoate, decanoate and dodecanoate. The transition temperatures for pyridine complexes are lower than that for corresponding $Cu_2(RCO_2)_4$. Upon repeated heating just above the melting temperatures, $Cu_2(RCO_2)_4\,py_2$ complexes decompose to $Cu_2(RCO_2)_4$, which undergo the known crystalline to liquid crystalline phase transition at higher temperatures. © 1997 Elsevier Science B.V.

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1. Introduction

Previous studies of Cu(II) carboxylates showed that crystalline to liquid crystalline phase transitions occur in the temperature interval 373–393 K [1–4]. There has been some disagreement about the influence of hydrocarbon chain length on transition temperatures for these compounds. In the study of even chain length Cu(II) carboxylates from decanoate to octadecanoate, only in the cases of decanoate and octanoate, an intermediate phase was observed [1]. However, different results have been reported in other investigations of $Cu_2(RCO_2)_4$, where it was found that all compounds with an even number of carbon atoms in the 12–24 range transform to a thermotropic columnar mesophase at about 383–393 K [2,3]. A pre-peak, prior to the main peak of the crystalline to liquid crystalline phase transition, was observed in DTA curves of compounds with $n = 12$, 18 and 22. These pre-peaks were explained by a thermal history of samples. An extensive study of a homologous series of binuclear Cu(II) carboxylates ($n = 5, 6, 7, 8, 9, 11, 15$ and 24) showed that they also produce columnar mesophases around 373 K [4].

The structures of simple anhydrous Cu(II) carboxylates consist of centrosymmetric tetracarboxylate-bridged dimers as reported for Cu(II) octanoate [5] and Cu(II) decanoate [6]. In the case of Cu(II) acetate hydrate [7] the basic structure is similar with the

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additional water molecules coordinated to the apical positions. Water molecules in the structure of Cu(II) acetate hydrate are replaced by pyridine rings in the apical positions in the $Cu_2(C_7H_{15}COO)_4\,py_2$ [8]. The packing of the dimers in this pyridine complex does not involve any significant interdimer associations as typical for the simple Cu(II) carboxylates. Similar structures were proposed for the other $Cu_2(RCO_2)_4\,py_2$ ($R = CH_3(CH_2)_{n-2}$; $n =$ 7, 9, 10 and 12) complexes according to the vibrational and EPR spectra [9].

To the best of our knowledge, the influence of nitrogen donor ligands in Cu(II) carboxylate complexes on a crystalline to liquid crystalline phase transition, has not been reported in the literature yet. Therefore, we have compared DTA and TG curves and X-ray diffraction patterns of compounds, which are known to transform to a mesophase at elevated temperatures, $Cu_2(RCO_2)_4$, with $Cu_2(RCO_2)_4\,py_2$ ($R = CH_3(CH_2)_{n-2}$; $n = 7$, 8, 9, 10 and 12), which have not been investigated in this point of view yet. We tried to find out, if the stability and structural differences between $Cu_2(RCO_2)_4$ and corresponding pyridine complexes prevent formation of mesophase during heating in case of pyridine complexes and lead to direct melting.

2. Experimental

2.1. Materials

The studied $Cu_2(RCO_2)_4$ complexes were synthesized by the direct metathesis of the corresponding sodium soaps in slightly acidic aqueous solutions with the required amount of Cu(II) sulphate dissolved in water, as described by Mehrotra and Bohra [10].

The green Cu(II) carboxylate complexes with pyridine, $Cu_2(RCO_2)_4\,py_2$, were isolated from methanol/pyridine solutions, as already reported [9], and recrystallized from boiling methanol.

2.2. Physical measurements

Simultaneous TG and DTA measurements were made on a Mettler TA 2000 under a 99.999% pure argon with the flow rate of 35 ml/min. The reference material, Al_2O_3, was employed in all experiments. The first measurements for each compound were done at a heating rate of 2 K/min up to 673 K in order to determine the solid-mesophase and mesophase-isotropic liquid transition temperatures. The subsequent measurements were performed at a heating rate of 1 K/min, some of them with consequent cooling and repeated heating. In some cases, the sufficient cooling was achieved by submerging a sample in the liquid nitrogen.

The temperature calibration was done by melting of indium (429.6 K) and tin (504.9 K). Repeated measurements have shown uncertainties in the temperature range of ±1 K. The noise in DTA curve is negligible in the applied temperature range, it is less than 2% of observed peaks.

X-ray powder diffraction patterns of samples before and after thermal treatment were recorded on a Huber Guinier camera. Polycrystalline samples were sealed in capillary tubes, heated and observed under magnification, as typically in a melting-point determination apparatus and done by other groups [11].

3. Results and discussion

Representative DTA and TG curves of Cu(II) nonanoate and its complex with pyridine are shown in Fig. 1 and Cu(II) dodecanoate and its pyridine complex in Fig. 2, respectively.

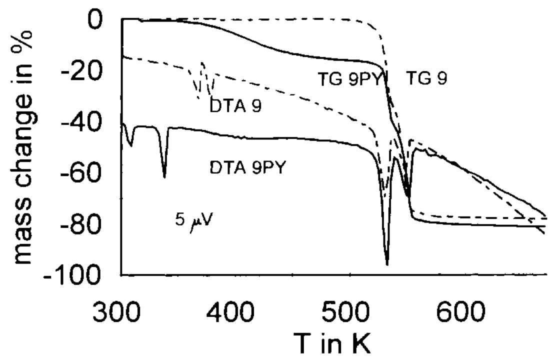

Fig. 1. DTA and TG curves of Cu(II) nonanoate (TG 9 and DTA 9) and its pyridine complex (TG 9PY and DTA 9PY).

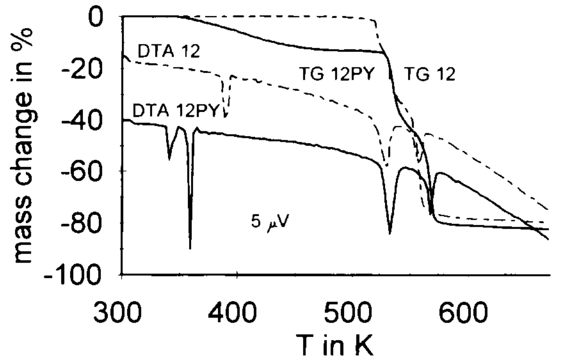

Fig. 2. DTA and TG curves of Cu(II) dodecanoate (TG 12 and DTA 12) and its pyridine complex (TG 12PY and DTA 12PY).

3.1. $Cu_2(RCO_2)_4$

DTA curves of all investigated $Cu_2(RCO_2)_4$ ($R = CH_3(CH_2)_{n-2}$; $n = 7$, 8, 9, 10 and 12) compounds show endothermic peaks due to a crystal to mesophase transition in the 361–483 K range. Temperatures of the phase transitions are listed in Table 1 and compared with the published data. In some cases ($n = 8$ and 9), where we observed two endothermic peaks in the region of the phase transition (Fig. 1), only the appearance of a single peak was reported [4]. On the other hand, we found a single peak for phase transition of dodecanoate (Fig. 2), but two peaks are mentioned in the literature [2].

In addition to the TG and DTA measurements, the samples, sealed in capillaries, were examined under a microscope during heating until 473 K. We observed only a change of transparency and no formation of free-flowing liquids during heating. A non-crystalline opaque material appeared after the samples were cooled down to the room temperature. Therefore, we believe that the peaks on DTA curves represent a crystal to mesophase transition and not melting. These results correspond well to the reported ones [2,12]. Transitions from a liquid crystalline phase into isotropic liquid occur above 523 K, but the melting points cannot be determined exactly, due to the thermal decomposition which begins at similar temperatures as melting.

Repeated heating up to 403 K with subsequent cooling was done for compounds with $n = 7$, 8 and 10. DTA curves obtained during heating were practically unchanged. The two endothermic peaks, at 366 and 375 K for octanoate and at 361 and 382 K for decanoate appeared again in DTA curves even after several heating–cooling cycles. We assume that these two peaks indicate formation of different mesophases, but we did not make any further attempts to clarify the origin of these peaks. The inverse transition from a mesophase to a crystalline phase occurs in all samples in one step at temperatures, which are, due to the slow nucleation, approximately 35 K lower than the transition temperatures on heating.

The transition temperatures for the first four investigated compounds ($n = 7$, 8, 9 and 10) decrease with an increasing number of carbon atoms in aliphatic chains and then increase for dodecanoate as already described previously (Table 1) [4]. The structure is mainly determined by the headgroups in the compounds with short paraffin chains, and in this case, an extension of chains lowers the thermal stability of the crystal and consequently the transition temperature. On the other hand, ordering of paraffin chains plays an important role in stabilizing the compounds which

Table 1

Temperatures of transition from a crystal to liquid crystalline phase for all investigated compounds and melting points of $Cu_2(RCO_2)_4\,py_2$, determined from DTA curves. The data for $Cu_2(RCO_2)_4$ are compared with the published ones

$Cu_2(RCO_2)_4$			$Cu_2(RCO_2)_4\,py_2$		
Number of C	T_{trans} per K (Measured, ±1K)	T_{trans} per K (Literature)	Number of C	T_{trans} per K (Measured, ±1 K)	T_{melt} per K (Measured, ±1 K)
7	370	365 [4]	7	—	325
8	366, 375	358 [4]	8	—	332
9	366, 377	372 [4]	9	308	336
10	361, 382	368, 380 [1]	10	329	347
12	380	363, 380 [2]	12	344	359

include twelve or more carbon atoms and the result is an increase in transition temperatures for compounds with $n \geq 12$.

3.2. $Cu_2(RCO_2)_4 py_2$

The compounds containing pyridine, $Cu_2(RCO_2)_4\,py_2$, are far less stable than $Cu_2(RCO_2)_4$. Endothermic peaks in the DTA curves of $Cu_2(RCO_2)_4\,py_2$ appear at lower temperatures, in the 308–359 K range. One peak was observed for heptanoate and octanoate complexes and two peaks for the other three compounds (Figs. 1 and 2). The samples were studied also under the microscope during heating from room temperature to melting points. The results led us to the conclusion that heptanoate and octanoate complexes with pyridine melt directly to an isotropic liquid. The other three studied pyridine complexes undergo a crystal to liquid crystalline phase transition indicated by the first endothermic peak at a lower temperature (Table 1) and then melt, as shown by the second, more intense peak in DTA curves (Figs. 1 and 2).

The compounds $Cu_2(RCO_2)_4\,py_2$ ($R = CH_3(CH_2)_{n-2}$; $n = 9$, 10 and 12) which transform to a liquid crystalline phase upon heating, were repeatedly heated to the temperatures just above transition temperatures and cooled subsequently. A transition to a liquid crystalline phase was observed only during the first heating cycle. Because of the temperature hysteresis, the liquid crystalline to crystalline phase transformation was not observed during cooling process. In an additional experiment, after transforming to a liquid crystalline phase, decanoate and dodecanoate were cooled in the liquid nitrogen and heated again. Upon repeated heating, an endothermic peak suggesting a crystal to liquid crystalline phase transition appeared again. However, in both cases, the peaks were shifted toward lower temperatures, 317 K.

A decomposition of $Cu_2(RCO_2)_4\,py_2$ compounds starts with an emission of pyridine in the same temperature region as melting. Mass loss in the 353–503 K temperature interval corresponds to the quantity of coordinated pyridine in $Cu_2(RCO_2)_4\,py_2$ compounds, as calculated from TG curves (Figs. 1 and 2). Repeated heating to the temperatures just above the melting temperatures and subsequent cooling to room temperature of all pyridine complexes resulted in the gradual emission of pyridine. After eight heating–cooling cycles, all compounds convert to the simple $Cu_2(RCO_2)_4$ complexes, showing a crystal to liquid crystalline phase transformation at about 373 K, characteristic for these compounds. The conversion from $Cu_2(RCO_2)_4\,py_2$ to $Cu_2(RCO_2)_4$ was confirmed also by X-ray powder diffraction analysis of the compounds prior to and after the thermal treatment. A comparison of TG and DTA curves of $Cu_2(RCO_2)_4\,py_2$ and $Cu_2(RCO_2)_4$ in the 503–673 K range also indicates the same way of decomposition of these compounds (Figs. 1 and 2). A mixture of Cu_2O and CuO remains as a final product at 673 K, as reported previously [13].

The lower thermal stability of $Cu_2(RCO_2)_4\,py_2$ than $Cu_2(RCO_2)_4$ could be explained by structural features. The packing of the octanoate dimers in the unit cell of $Cu_2(C_7H_{15}COO)_4\,py_2$ complex does not involve any significant inter-dimer associations. The distance of 3.45 Å, between two pyridine carbon atoms from neighboring molecules represents the closest interaction between discrete dimeric units. This distance is much longer than the closest interaction between neighboring molecules in $Cu_2(RCO_2)_4$, which is, for example, in Cu(II) propanoate 2.28 Å [14]. Therefore, we presume that the weaker inter-dimer interactions are the main reason for the significant lowering of transition temperatures and melting points in the pyridine complexes of Cu(II) carboxylates.

4. Conclusion

$Cu_2(RCO_2)_4\,py_2$ ($R = CH_3(CH_2)_{n-2}$; $n = 9$, 10 and 12) compounds undergo a crystal to liquid crystalline phase transition and melting at much lower temperatures than their $Cu_2(RCO_2)_4$ analogs. The transition temperature of nonanoate is, at 308 K, already at the detection limit of the applied method. The melting points of investigated pyridine complexes are only 15–30 K higher than temperatures of the transition to mesophase, while the melting points of $Cu_2(RCO_2)_4$ differ from transition temperatures for about 150 K. A decomposition of $Cu_2(RCO_2)_4\,py_2$, with an emission of pyridine, begins simultaneously with melting. $Cu_2(RCO_2)_4$ compounds were formed during repeated heating cycles of $Cu_2(RCO_2)_4\,py_2$ compounds just above the melting points.

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