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THERMAL CHARACTERISTICS OF Cu(II) CARBOXYLATES WITH FATTY ACID CHAINS AND THEIR PYRIDINE ADDUCTS

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Abstract

The compounds $Cu_2(RCO_2)_4$ and $Cu_2(RCO_2)_4py_2$ [R=$CH_3(CH_2)_{n-2}$; n=14, 16, 18; *py*=pyridine] were prepared, analysed and characterized by means of DSC calorimetry, thermogravimetry and infrared spectroscopy. Generally, the pyridine complexes are unstable, losing pyridine already at room temperature. Transition from a crystalline to a liquid crystalline phase after heating was observed for all $Cu_2(RCO_2)_4$ compounds but only for pyridine complex of Cu(II) tetradecanoate. However, the melting process was observed for all Cu(II) carboxylate complexes with pyridine. The lower thermal stability of pyridine complexes, than corresponding $Cu_2(RCO_2)_4$ compounds can be explained by structural features.

Keywords: Cu(II) carboxylates, DSC, infrared spectroscopy, thermogravimetry

Introduction

Divalent–metal salts of the higher fatty acids have many applications in industry: in the preparation of lubricating greases, as waterproofing agents, in colour printing and in dyeing and also as adhesive promoters in rubber technology. Besides their practical importance, these compounds exhibit very interesting thermochemical properties. It was found that all compounds with even number of carbon atoms (n) in the 12–24 range transform to a thermotropic columnar mesophase at about 110–120°C [1–3].

With only one exception [4], thermal characteristics of pyridine complexes of long chain Cu(II) carboxylates (n=6–22) have not been studied. The results of DSC calorimetry, thermogravimetry and vibrational spectroscopy have been used to study the influence of the length of aliphatic chains in the carboxylates studied on the:

a) occurrence of a crystalline to liquid–crystalline phase transition;

b) transition temperatures and enthalpic changes for this transition and the melting process;

c) release of pyridine from the studied $Cu_2(RCO_2)_4py_2$ complexes [R=$CH_3(CH_2)_{n-2}$, n=14, 16, 18].

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Experimental

Materials

The starting compounds $Cu_2(RCO_2)_4$, where *R* is $C_{13}H_{27}$, $C_{15}H_{31}$, $C_{17}H_{35}$, were prepared in the reaction between the aqueous solution of the sodium salt (pH 7) of fatty acid (0.02 mole) with the aqueous solution of Cu(II) sulphate (0.01 mole) dissolved in water, as described by Mehrotra and Bohra [5]. The fine compounds which precipitated were filtered off (cca 95% yield), washed with cold water and dried at room temperature. The crude products were purified by recrystallization from hot methanol with the yield of 80%.

The green pyridine complexes $Cu_2(RCO_2)_4py_2$ were prepared by the following procedure: 3 mmol $Cu_2(RCO_2)_4$ were dissolved in pyridine with hot methanol. After the solvent evaporated, needle-shaped green precipitates were obtained. The yields were 80%. The complexes were recrystallized from hot methanol with five drops pyridine added. The yields were 70%.

The contents of C, H and N were determined by elemental analysis and the content of Cu was established by complexometric titration. The analytical data of $Cu_2(RCO_2)_4$ and $Cu_2(RCO_2)_4py_2$ reported in Table 1.

Table 1 Analytical data for Cu(II) carboxylate complexes and their pyridine analogues

Conpound	Analysis: found (calc.)/%			
	Cu	C	H	N
$Cu_2(C_{13}H_{27}CO_2)_4$	12.3 (12.3)	63.7 (64.9)	10.2 (10.5)	–
$Cu_2(C_{15}H_{31}CO_2)_4$	11.2 (11.1)	67.2 (66.9)	11.1 (10.9)	–
$Cu_2(C_{17}H_{35}CO_2)_4$	10.3 (10.1)	68.9 (68.6)	11.4 (11.2)	–
$Cu_2(C_{13}H_{27}CO_2)_4(py)_2$	10.6 (10.6)	66.3 (66.4)	10.2 (10.0)	2.1 (2.3)
$Cu_2(C_{15}H_{31}CO_2)_4(py)_2$	9.9 (9.8)	67.9 (68.4)	10.0 (10.4)	2.1 (2.2)
$Cu_2(C_{17}H_{35}CO_2)_4(py)_2$	9.1 (9.0)	69.4 (69.4)	10.4 (10.7)	2.0 (2.0)

Physical measurements

Thermal decomposition of the complex, under dynamic conditions, was studied using Derivatograph, TA Instruments. The sample (17.0±0.1 mg) was heated at atmosphere of nitrogen, at a heating rate of 5°C min^{-1}, at temperature from 20 to 250°C.

The Perkin Elmer Differential Scanning Calorimeter DSC-7 was used for DSC studies with a sample mass cca. 5 mg, pure nitrogen and a scanning rate of 10°C min^{-1}. Calibration of the temperature and change of enthalpy axes were made with pure indium with the melting point of 156.6°C and $\Delta_f H$=28.47 J g^{-1}.

IR spectra were measured in KBr tablets in the region of 4000–200 cm^{-1} with the Philips PU 9800 FTIR spectrophotometer.

Results and discussion

The structures of simple anhydrous Cu(II) carboxylates consist of centrosymmetric tetracarboxylate-bridged dimers as reported for Cu(II) octanoate [6] and Cu(II) decanoate [7]. In the case of Cu(II) acetate hydrate [8], the structure is similar to the additional water molecules coordinated to the apical positions, water molecule in the structure of Cu(II) acetate hydrate is replaced by pyridine molecules in the apical positions in $Cu_2(C_7H_{15}COO)_4py_2$ [9]. TG and DTA measurements of $Cu_2(RCO_2)_4$ and $Cu_2(RCO_2)_4py_2$ (R=$CH_3(CH_2)_{n-2}$; n=7, 8, 9, 10, 12) showed [4] that transition from a crystalline to a liquid crystalline phase was observed for all $Cu_2(RCO_2)_4$ compounds, but only for pyridine of Cu(II) nonanoate, decanoate and dodecanoate. The transition temperatures for pyridine complexes are lower than for the corresponding $Cu_2(RCO_2)_4$. It was challenging, therefore, to make comparative measurements with carboxylate complexes with longer chain (n>12).

DSC curves of all the investigated $Cu_2(RCO_2)_4$ compounds show endothermic peaks due to a crystal to mesophase transition in the 109–117°C range. Temperatures of the phase transition are listed in Table 2 and compared with the published data (n<14). In all cases we observed one endothermic peak in the region of the phase transition (Fig. 1). On the other hand, two peaks for the phase transition of octanoate, nonanoate and decanoate are mentioned in literature [4]. In addition to DSC measurements, the samples

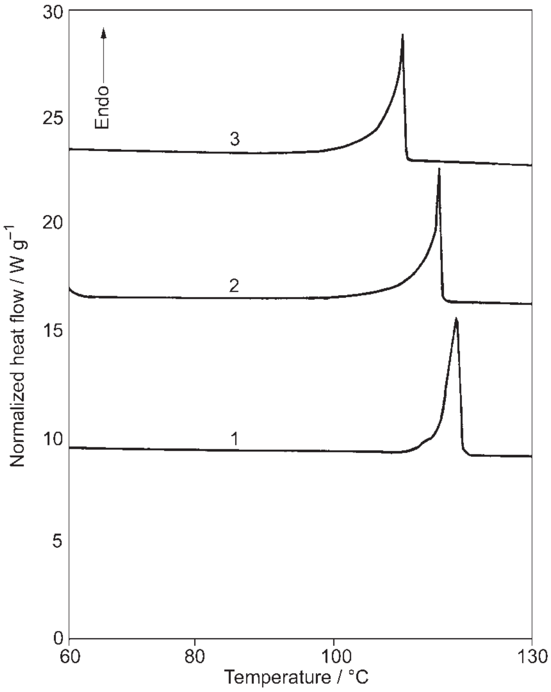

Fig. 1 DSC curves of 1 – $Cu_2(C_{13}H_{27}CO_2)_4(py)_2$, 2 – $Cu_2(C_{15}H_{31}CO_2)_4(py)_2$, 3 – $Cu_2(C_{17}H_{35}CO_2)_4(py)_2$

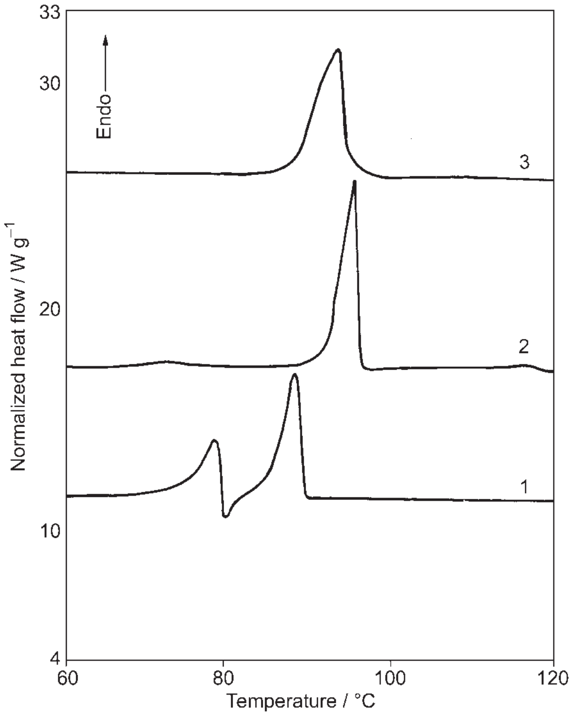

Fig. 2 TG curves of 1 – $Cu_2(C_{13}H_{27}CO_2)_4(py)_2$, 2 – $Cu_2(C_{15}H_{31}CO_2)_4(py)_2$, 3 – $Cu_2(C_{17}H_{35}CO_2)_4(py)_2$

were examined under a microscope during heating, up to 200°C. We observed only a change of transparency and no formation of free-flowing liquids during heating. The transition temperatures for the three investigated $Cu_2(RCO_2)_4$ compounds (n=14, 16, 18) decrease with an increasing number of carbon atoms (n) in aliphatic chains, but are higher than were observed for compounds with n<14. On the other hand, the corresponding enthalpic changes increase in the sequence: (according to n): 14<16<18. Thus, we assume, that extension of paraffin chains and their ordering influence the thermal stability of the studied compounds.

The compounds containing pyridine, $Cu_2(RCO_2)_4py_2$ are far less stable than $Cu_2(RCO_2)_4$. Endothermic peaks in the DSC curves of $Cu_2(RCO_2)_4py_2$ appear at lower temperatures, in the 79–95°C range. Two peaks were observed for the tetradecanoate complex and one peak for the other two complexes (Fig. 2, Table 2). The samples were studied also under the microscope during heating. The results led us to the conclusion that hexadecanoate and octadecanoate complexes with pyridine melt directly to an isotropic liquid. The other pyridine complex (n=14) undergoes a crystal to liquid crystalline phase transition indicated by the first endothermic peak at a lower temperature (Table 2) and then melt, as shown by the second, more intense peak in the DSC curve (Fig. 2). The enthalpic changes, $\Delta_{melt}H$, increase in the sequence (according to n): 14<16<18, but the melting points and melting enthalpies cannot be determined exactly, due to the thermal decomposition which begins at similar temperatures as melting, equally as was observed for pyridine complexes with $n<14$ [4]. A thermal decomposition of $Cu_2(RCO_2)_4py_2$ complexes starts with a liberation of pyridine in the same temperature region as melting. Mass loss in the 70–112°C temperature range approximately corresponds to the quantity of coordinated pyridine in $Cu_2(RCO_2)_4py_2$ compounds, as calculated from TG curves (Table 2).

Table 2 Temperatures of transition from a crystal to liquid crystalline phase (T_{trans}), melting points (T_{melt}) corresponding enthalpic changes (ΔH) and mass loss of py (Δm, found (calc.))

n	$Cu_2(RCO_2)_4$		$Cu_2(RCO_2)_4py_2$				
	T_{trans}/ ±1°C	$\Delta_{trans}H$/ ±0.5 kJ mol^{-1}	T_{trans}/°C	$\Delta_{trans}H$/ kJ mol^{-1}	T_{melt}/°C	$\Delta_{melt}H$/ kJ mol^{-1}	Δm/%
14	117.0	52.2	79.0	35.1	88.0	57.9	12.4 (13.2)
16	114.0	60.3	–	–	95.0	81.9	11.6 (12.2)
18	109.0	72.0	–	–	93.0	106.4	10.7 (11.1)

n – the number of carbon atoms in the corresponding fatty acid

The infrared spectra of these compounds (Table 3) are characteristic for dicopper tetracarboxylates with additional bands arising from pyridine ligand vibrations [9]. The bands at ~1585 and ~1423 cm^{-1} for $Cu_2(RCO_2)_4$, and at ~1613 and 1419 cm^{-1} for $Cu_2(RCO_2)_4py_2$ can be assigned to asymmetric, ν_{as}(C–O), and symmetric, ν_s(C–O) carboxylate vibrations [10]. The difference between ν_{as}(C–O) and is ν_s(C–O) correlated quite well with the nature of carboxylate coordination. The differences 162–198 cm^{-1} found for the studied compounds are characteristic for bridging bond carboxylate groups [11] and are in agreement for dicopper tetracarboxylate structures [12, 13].

Table 3 Selected IR absorption bands (in cm^{-1}) of copper(II) carboxylates and their pyridine complexes

Assignment	$Cu_2(RCO_2)_4$				$Cu_2(RCO_2)_4py_2$		
	14	16	18	12	14	16	18
ν_{as}(CO)	1585	1585	1586	1614	1613	1617 (1600)	1613
ν_s(CO)	1423	1423	1421	1420	1419	1419	1416
Δ	162	162	165	194	194	198	197
Py: δ(C–H)	–	–	–	1078	1077	1076	1077
	–	–	–	1037	1036	1037	1037
	–	–	–	1011	1011	1010	1011

n – the number of carbon atoms in the corresponding fatty acid

Δ – [ν_{as}(CO)–ν_s(CO)]

Conclusions

$Cu_2(RCO_2)_4py_2$ [R=$CH_3(CH_2)_{n-2}$, n=14, 16, 18] complexes undergo a crystal to liquid crystalline phase transition and melting at much lower temperatures than their $Cu_2(RCO_2)_4$ analogs. The lower thermal stability of $Cu_2(RCO_2)_4py_2$ than $Cu_2(RCO_2)_4$ could be explained by structural features. The weaker inter-dimer interactions are probably the main reason for significant lowering of thermal characteristics of pyridine compounds. An emission of pyridine after heating begins simultaneously with melting and enthalpic changes for these processes increase in the sequence (according to the number of carbon atoms): 14<16<18.

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