Spectral and thermal characteristics of copper(II) carboxylates with fatty acid chains and their benzothiazole adducts

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Abstract The carboxylato–Cu(II) complexes of type $[Cu_2(RCOO)_4]$ and their benzothiazole adducts $[Cu_2(RCOO)_4bt_2]$ (bt = benzothiazole, R = $CH_3(CH_2)_{n-2}$, n = 12, 14, 16, 18) form the main objectives of this study. The studied carboxylato–Cu(II) complexes are formed from dimeric units to polymeric chains (chromofor CuO_5). The structural changes are due to coordination of ligand (benzothiazole). The polymeric chains of carboxylato–Cu(II) complexes degraded to discrete centrosymetric tetracarboxylate-bridged dimmers (chromofor CuO_4N). These prepared compounds $[Cu_2(RCOO)_4]$ and $[Cu_2(RCOO)_4L_2]$ were submitted to measurements relating to spectral (IR, UV–Vis) and thermal properties (TG, DTA, DSC).

Keywords Carboxylato–Cu(II) complexes ·
Benzothiazole adducts · TG–DTA–DSC–IR–UV–Vis

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Introduction

The carboxylates of the higher fatty acids with the metal ions have many applications in different industrial spheres such as driers in paints and inks, the components of lubricating greases, stabilizers of plastics, catalysts, the additives at fuel, as well as the corrosion-preventive materials [1], promoters of rubber–steel cord adhesion [2–4], etc. Their benzothiazole adducts can be utilized as antibacterial composites [5], inhibitors of endopeptidases [6], and the fast accelerators of sulfur vulcanization [7–11], etc.

The preparation, structures, thermal, and spectral properties of many copper(II) carboxylates and their adducts especially with nitrogen donor ligands, have already been extensively studied [9–14]. The carboxylato–Cu(II) complexes with a long alkyl-hydrocarbon chain belong to compounds, which form monocrystals very unwillingly [15]. This fact has connection especially with their length of hydrocarbon chain and, therefore, the indirect methods were used especially for their study. Previous studies of Cu(II) carboxylates showed that crystalline-to-liquid phase transitions occur at 100–120 °C, and the transition to the isotropic liquid occurs above 200 °C. However, melting appears to be accompanied by the onset of thermal decomposition [16–20]. In some cases, they appear to be small pre-transitions prior to formation of the mesophase [17, 19]. Many studies supported the fact, that benzothiazole is a monodentate ligand, which is coordinated to central ion through a donor atom of nitrogen. Also, a general similarity between benzothiazole and pyridine complexes was found, where benzothiazole as well as pyridin are N-donors [21, 22]. However, there are some specific cases, in which benzothiazole has a function of a bridging ligand with a coordination through nitrogen and sulfur atom [23]. Thermal and spectral analyses are very

useful techniques for material's characterization, and therefore, many authors have used these techniques for the characterization of various materials [24–43].

Experimental

Preparation of carboxylato–Cu(II) of type [Cu₂(RCOO)₄]

The basic carboxylato–Cu(II) complexes with their general formula $[Cu_2(RCOO)_4]$, where R = $C_{11}H_{23}$, $C_{13}H_{27}$, $C_{15}H_{31}$, $C_{17}H_{35}$, were prepared by reacting [44] the aqueous solutions of sodium salts of correspondent carboxylic acids (0.02 mol) with an aqueous solution of copper sulfate (0.01 mol) according to following reaction schematics:

$$R\text{-}COOH + NaOH \rightarrow Na(R\text{-}COO) + H_2O$$

$$2R\text{-}COONa + Cu(SO_4) \rightarrow Cu(R\text{-}COO)_2 + Na_2SO_4$$
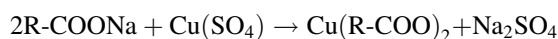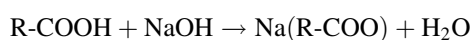
The obtained compounds were washed with hot distilled water and filtered at a reduced pressure and then were washed with hot ethanol again and dried at room temperature. Four carboxylato–Cu(II) complexes, tetrakis(μ-alkanoato-O,O')dicopper(II), (Table 1) of turquoise color were prepared by this method. The results of analyses are given in Table 1.

Table 1 Analytical data for selected carboxylato–Cu(II) complexes

Compound	CuC$_n$	Analyses Found (Calc.)/%		
		Cu	C	H
$[Cu_2(C_{11}H_{23}CO_2)_4]$	CuC$_{12}$	13.6 (13.75)	62.0 (62.37)	9.8 (10.08)
$[Cu_2(C_{13}H_{27}CO_2)_4]$	CuC$_{14}$	12.3 (12.26)	63.7 (64.89)	10.2 (10.50)
$[Cu_2(C_{15}H_{31}CO_2)_4]$	CuC$_{16}$	11.2 (11.06)	67.2 (66.91)	11.1 (10.88)
$[Cu_2(C_{17}H_{35}CO_2)_4]$	CuC$_{18}$	10.3 (10.08)	68.9 (68.58)	11.4 (11.19)

n the number of carbon atoms in chain

Preparation of carboxylato–Cu(II) complexes with benzothiazole of type $[Cu_2(RCOO)_4bt_2]$

Benzothiazole is a liquid ligand. The green solutions were prepared by dissolving a basic anhydrous carboxylato–Cu(II) complex in benzothiazole. The green microcrystal complexes of given compounds, which were stable in air, were obtained from these solutions after 10 days of waiting. These resulting complexes of given compound recrystallized after another 10 days in methanol–ethanol–acetone (1:1:1) solution again. The prepared four green crystal compounds, tetrakis(μ-alkanoato-O,O')-bis(benzothiazole)dicopper(II), with a general formula $[Cu_2(RCOO)_4bt_2]$, where R = $C_{11}H_{23}$, $C_{13}H_{27}$, $C_{15}H_{31}$, $C_{17}H_{35}$ and bt = benz-1,3-tiazol. The analytic data are given in Table 2.

Measurements

The infrared spectra were measured in KBr pellets in the region of 4000–500 cm^{-1} on a Philips PU 9800 FTIR spectrophotometer in the region of 500–200 cm^{-1}.

The electronic spectra were measured in Nujol suspension in the range of 200–1100 nm. A spectral photometer SPECORD 200 fy Analytik Jena was used for these measurements.

TG and DTA of the prepared complexes were studied on a derivatograph Universal V1.9D TA Instrument. The samples with a mass 5.0–17.0 ± 0.1 mg were measured in an atmosphere of nitrogen with a heating rate of 5 °C min^{-1} and a temperature range of 0–900 °C. The second instrument, which was used was a DERIVATO-GRAPH OD 102. The samples with a mass of 100 mg were measured statically in an atmosphere of air, with a heating rate of 5 °C min^{-1} and a temperature range of 20–500 °C.

DSC curves were scanned on a differential scanning calorimeter fy Perkin-Elmer DSC-7. The experimental conditions: mass of samples was 1.5–5 mg, and a scanning rate of 10 °C min^{-1} in nitrogen atmosphere. A calibration of the temperature was made using pure In and Zn and calibration of enthalpy using pure In with the melting point of 156.6 °C and $\Delta_f H = 28.47$ J g^{-1}.

Table 2 Analytical data for carboxylato–Cu(II) complexes with benzothiazole

Complex	(CuC$_n$bt)	Analyses Found (Calc.)/%				
		Cu	C	H	N	S
$[Cu_2(C_{11}H_{23}CO_2)_4(bt)_2]$	(CuC$_{12}$bt)	10.2 (10.23)	63.9 (63.79)	8.6 (8.27)	2.0 (2.25)	5.3 (5.16)
$[Cu_2(C_{13}H_{27}CO_2)_4(bt)_2]$	(CuC$_{14}$bt)	9.7 (9.73)	65.1 (64.43)	8.8 (9.10)	2.1 (2.14)	4.7 (4.91)
$[Cu_2(C_{15}H_{31}CO_2)_4(bt)_2]$	(CuC$_{16}$bt)	8.9 (8.96)	65.7 (66.02)	9.3 (9.51)	1.8 (1.97)	4.5 (4.52)
$[Cu_2(C_{17}H_{35}CO_2)_4(bt)_2]$	(CuC$_{18}$bt)	8.5 (8.30)	67.1 (67.46)	10.1 (9.86)	1.8 (1.83)	4.2 (4.19)

Thermal decomposition and phase changes were monitored using an optical microscopy Boëtius with a micro-heating table and a scanning equipment PHMK 05, Nagema. The temperature range was 40–360 °C. The reproducibility of measurement was ±0.2 °C.

Spectrometer AAS-3 (Carls-Zeis Jena) was used for determination of content of copper metal. The conditions of measurement: lamp 4.7 mA, carrier of air, fuel acetylene.

The contents of C, H, N, and S were determined using a CARLO ERBA instrument.

Results and discussion

IR spectra of carboxylato–Cu(II) of type [Cu₂(RCOO)₄]

The valence vibrations of functional groups and the plane deformation vibrations were mainly characterized from the IR spectra (Fig. 1). The process of study is mainly connected with the symmetric and asymmetric vibration of carboxylate groups, valence vibration of CH_3 and CH_2, valence vibration of Cu–O as well as plane deformation vibrations of CH_3, CH_2, and CO. The selected vibrations of carboxylato–Cu(II) complexes are summarized in Table 3. IR spectra of prepared carboxylato–Cu(II) complexes [45] can be used for identification of asymmetric valence vibration of carboxylate group in the range 1585–1586 cm^{-1} and symmetric valence vibration in the range 1421–1423 cm^{-1}. The carboxylate anions are coordinated at copper atoms through oxygen atom [46], and on the base of this fact, the mentioned valence vibrations of carboxylate group in free acids are situated in the range v_{asym}(COO): ∼1703–1712 cm^{-1} and v_{sym}(COO): ∼1411–1466 cm^{-1} [47]. On the basis of all these facts, a valence vibration of Cu–O, which is in the range 405–393 cm^{-1} can be
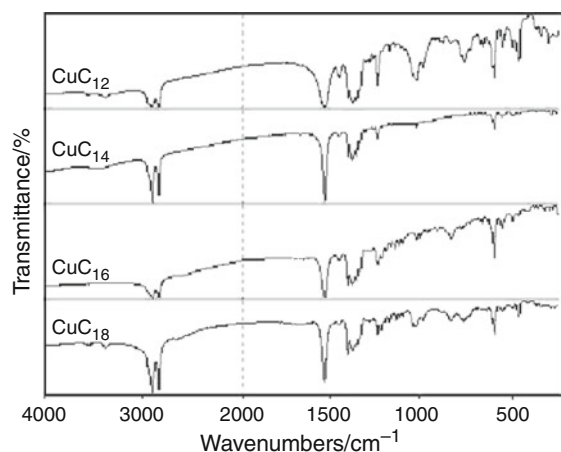

Fig. 1 IR spectra of carboxylato–Cu(II) complexes in the range 4000–500 cm^{-1}

Table 3 IR spectral data of carboxylato-Cu(II) complexes

IR vibrations/cm^{-1}	CuC_n			
	CuC_{12}	CuC_{14}	CuC_{16}	CuC_{18}
$v_{asym}(CH_3)$	2955	2954	2954	2954
$v_{asym}(CH_2)$	2915	2915	2915	2915
$v_{sym}(CH_3)$	2870	2872	2872	2873
$v_{sym}(CH_2)$	2848	2849	2849	2849
$\delta_{asym}(CH_3)$def	1468	1468	1468	1471
$\delta(CH_2)$wag	1317	1318	1319	1315
$\delta(CH_3)$def	1119	1118	1118	1128
$\rho(CH_2)$	721; 733	721	722	720
$\delta(COO)$	683	682	682	682
v(Cu–O)	405; 386	407; 388	393	385
$v_{asym}(COO^-)$	1585	1585	1585	1586
$v_{sym}(COO^-)$	1423	1423	1422	1421
$\Delta = v_{asym}(COO^-) - v_{sym}(COO^-)$	162	162	163	165

n the number of carbon atoms in hydrocarbon chain

confirmed too. The value $\Delta = v_{asym}(COO^-) - v_{sym}(COO^-)$ in the range 162–165 cm^{-1} can be understood as a bridging bond of carboxylate groups (Table 3) [21].

The intensity and the number of bands, which are assigned to plate deformation of groups CH_2 and CH_3 [17, 48] are changed together with a length of hydrocarbon chain (the number of carbon atoms in chain *n* = 12–18 in the range 1315–1118 cm^{-1}). The bands assigned to vibrations $\delta(CH_3)_{def}$ and $\rho(CH_2)$ depend on crystallographic system [49]. Spectra of these complexes are characteristic for dicopper tetracarboxylate complexes [17] of monohydrate copper acetate type.

IR spectra of carboxylato–Cu(II) complexes with benzothiazole of type [Cu₂(RCOO)₄bt₂]

The prepared complexes were studied using IR spectroscopy. The spectra of prepared complexes (Fig. 2) and the spectrum of free benzothiazole are quite complicated. Benzothiazole belongs to the group of 1,2 disubstituted benzenes and among heterocyclic ligands with six-sectional benzene circle and five-sectional circle of thiazole, which has two heteroatoms, nitrogen, and sulfur. IR spectra give us the information as to whether this molecule can be performed in prepared complexes as monodentate ligand, where nitrogen is donor atom, or this molecule can be performed as bidentate-bridging ligand, where nitrogen and sulfur are donor atoms.

The carboxylato–Cu(II) complexes with benzothiazole contain the carboxylate anion, which is bonded to copper ions as bidentate ligand in the above mentioned
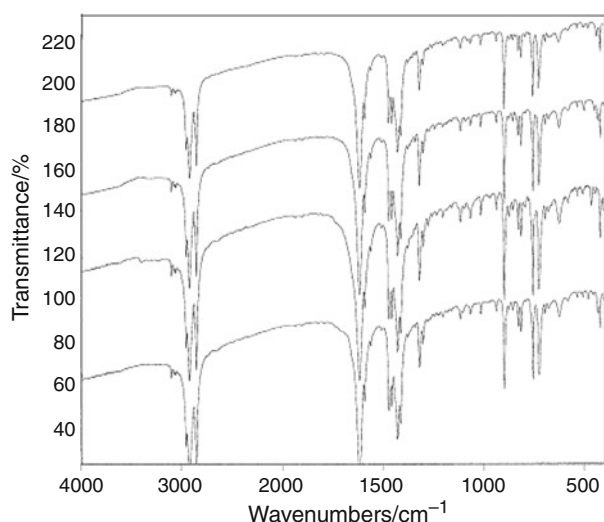
Fig. 2 IR spectra of carboxylato–Cu(II) complexes with benzothiazole in the range of 4000–500 cm^{-1}

carboxylates. The new prepared complexes contain functional groups N=C–S and COO^{-}, which have valence vibrations at the same regions, and it means that the exact assignment of bands is complicated. Despite the complication concerning the spectra, assignment of bands was done, where possible.

The valence vibrations of functional groups were mainly specified from the IR spectra. The closer specification is especially connected with study of symmetric and asymmetric vibration of carboxylate groups, valence vibration of group N=C–S, valence vibration of group C–S, and valence vibration C–H of aromatic system and aliphatic chains. There are also determined valence vibrations Cu–O and Cu–N, because these prepared complexes are supposed to

have the chromofor CuO$_4$N, where benzothiazole is bonded to central atom monodentately through nitrogen atom and it is similar to complexes which contain pyridine ligand [21]. The selected vibrations of prepared carboxylato–Cu(II) complexes with benzothiazole are summarized in Table 4.

The measured IR spectra of benzothiazole adducts of carboxylato–Cu(II) complexes are complicated, but it is possible to identify their bands, which correspond with characteristic groups. The bands in the range 1470–1080 cm^{-1} are assigned to vibrations of thiazole circle, and it is in accordance with literature [50]. Spectrum also involves bands in the region above 3000 cm^{-1}, and these bands belong to vibrations of C–H groups of aromatic circle and intensive bands of about 2850–2950 cm^{-1}, which may be assigned to valence vibrations C–H of alifatic hydrocarbon chains. The band about 667–679 cm^{-1} is concerned with the valence vibration C–S [50].

The intensive band at 1616 cm^{-1} and the weak band at 1592 cm^{-1} can be assigned to valence asymmetric vibration of carboxylate group [50, 51], and this vibration can partially include weak skeletal vibrations, which correspond to C–C valence vibration of benzene nucleus. The medium intensive split band of about 1428 and 1413 cm^{-1} of symmetric valence vibration of carboxylate group includes probably vibrations v(N=C–S). The values of valence vibrations v_{asym}(COO^{-}), v_{sym}(COO^{-}), and v(Cu–O), at about 373–393 cm^{-1} can be used for coming to a conclusion that carboxylate anions are coordinated to copper atom through oxygen atom. The calculated value Δ, which is in the range of 183–185 cm^{-1}, can be understood as bidentate-bridging coordination of carboxylate group to Cu(II) atom, and this fact corresponds with data in the literature [51].

Table 4 IR spectral data of carboxylato–Cu(II) complexes with benzothiazole

IR vibration/cm^{-1}	Ligand (bt)	Complex [CuC$_n$bt]			
	Benzothiazole	CuC$_{12}$bt	CuC$_{14}$bt	CuC$_{16}$bt	CuC$_{18}$bt
v(N=C–S)	1425	1413[b]	1413[b]	1413[b]	1413[b]
v(C=N)	1472; 1455	1472; 1456	1472; 1456	1472; 1456	1472; 1456
v(C–S)	667	677; 667	679, 667	679, 667	677
v(Cu–O)	–	393; 385; 373	390	378	391
v(Cu–N)	–	285	285sh; 267	317	299; 307
v_{asym}(COO)	–	1616s	1616s	1617s	1616s
		1592w	1592w	1591w	1592w
v_{sym}(COO)	–	1428m	1427m	1427m	1428m
		1413[b]	1413[b]	1413[b]	1413[b]
Δ[a]	–	183	184	185	183

sh shoulder, *s* strong, *m* medium, *w* weak

[a] v_{asym}(COO^{-}) − v_{sym}(COO^{-})

[b] Vibrations v(N=C–S) and v_{sym}(COO^{-})

On the basis of IR spectra and data from the literature, we can assume that all the new prepared substances are connected with occurrence of coordination of neutral ligand through nitrogen atom of thiazole group on the basis of mentioned vibration as well as other characteristic bands of benzothiazole of about 1070, 1015, 758, and 625 cm^{-1} [52] and valence vibration ν(Cu–N), which is about 267–317 cm^{-1}. The movement of valence vibration ν(N=C–S) is subject to the influence of coordination Cu(II) ion through nitrogen atom. This process is also concerned with the movement of electron density, and this fact means change of ν(N=C–S) vibration, on the basis of which, the absorption band gets into lower range [21].

Electronic spectra of carboxylato–Cu(II) complexes

All the prepared carboxylato–Cu(II) complexes have similar electron absorption spectra. Maxima of bands position for studied bands of carboxylato–Cu(II) complexes are mentioned in Table 5. The intensive absorption band range of about 672–677 nm is characteristic of carboxylato–Cu(II) complexes and is assigned to d–d transition of Cu(II) ion. This band moves to higher wave length with an increasing alkyl chain of carboxylic acid. This fact is concerned with weakening of bonds between donor oxygen atoms of relevant carboxylic groups, which are bonded directly to Cu(II) atom, in mentioned order [53].

Studied complexes show shoulders appearing in ultraviolet region with maxima at about 370 and 280 nm. The shoulder at higher wave lengths (362–373 nm) is characteristic of carboxylato–Cu(II) complexes with typical binuclear structure, in which two copper atoms are bonded by four three-atomic bridges (Cu–O–C–O–Cu) [51, 54]. This part of spectrum is the most interesting, and it may be characterized as spin–spin interaction of bridge system of monohydrate copper acetate type. Intensive absorbtion at wave length, which is shorter than 300 nm (275–284 nm), occurs in addition to transmission of charge from carboxylic group on Cu(II) atom.

Electronic spectra of carboxylato–Cu(II) complexes with benzthiazole

Electronic spectra of studied carboxylato–Cu(II) complexes with benzthiazole have a similar character (Table 5)

with expressive symmetric band with a maximum at about 700 nm, and the shoulders at about 380 and 280 nm. The band in visible region is typical for carboxylato–Cu(II) complexes, and it may be characterized as the band of d–d transitions of Cu(II) ion with a basic state, $d_{x^2-y^2}$. The shoulder with a maximum in the range 378–382 nm is characteristic, and it appears regularly in case of carboxylate–Cu(II) complexes with a composition, which is mentioned later. The shoulder with a maximum in the range 282–288 nm belongs to transmission of charge. Studied complexes can be assumed to have dimeric structure [Cu$_2$(RCOO)$_4$(bt)$_2$], in which two copper atoms are bonded by four carboxylate groups in structure syn–syn for the present creation of four three atom bridges in region of each copper atom. Each copper atom is surrounded by four oxygen atoms of corresponding RCOO$^-$ group, which form planar coordination around Cu(II) atoms (CuO$_4$). Monodentate ligands of benzothiazole are bonded through nitrogen atoms in axial position, and they create square–pyramidal coordination in the region of each Cu(II) atom with chromophore CuO$_4$N in the same way as it is in complexes with pyridine [16, 55, 56].

Thermal properties of carboxylato–Cu(II) complexes

Thermal properties of carboxylato–Cu(II) complexes are very important. They are especially important because of the phase transfer and their thermal stability. The transfer of solid phase to liquid-crystal mesophase was observed at all the studied anhydrous carboxylato–Cu(II) complexes. The thermal studies (TG, DTA) in the temperature range of 20–1000 °C reflects that mentioned complexes are changed into thermotropic column mesophase at about 108–117 °C [45]. Transfer of liquid-crystal phase to isotropic fluid occurs at about 220°C. This temperature is also connected with the thermal decomposition of given complexes, so it is not possible to determine the exact value for melting point in relation to studied compounds. The data of total mass loss, which were obtained from TG curves and a residue of mass after thermal processes of given complexes are mentioned in Table 6.

The thermal record (TG and DTA curves) for complex CuC$_{18}$ is presented in the Fig. 3. According to the TG curve of complex CuC$_{18}$, there is no change relating to mass loss

Table 5 Electronic spectral data of carboxylato–Cu(II) complexes and their benzothiazole adducts

Maxima of bands/nm	Carboxylato–Cu(II) complexes				Their benzothiazole adducts			
	CuC$_{12}$	CuC$_{14}$	CuC$_{16}$	CuC$_{18}$	CuC$_{12}$bt	CuC$_{14}$bt	CuC$_{16}$bt	CuC$_{18}$bt
Λ_1	280	282	283	275	288	282	287	287
Λ_2	370	373	370	362	378	380	378	382
Λ_3	672	675	677	677	700	698	698	697

Table 6 Total mass loss, residue, and final product of thermal decomposition of carboxylato–Cu(II) complexes

Complex	Total mass loss/%	Residue/%		
		Found/%	Calc./%	
			CuO	Cu
CuC$_{12}$	86.1	13.9	16.4	13.7
CuC$_{14}$	86.4	13.6	17.3	12.3
CuC$_{16}$	88.7	11.3	13.4	11.1
CuC$_{18}$	85.0	15.0	12.6	10.1
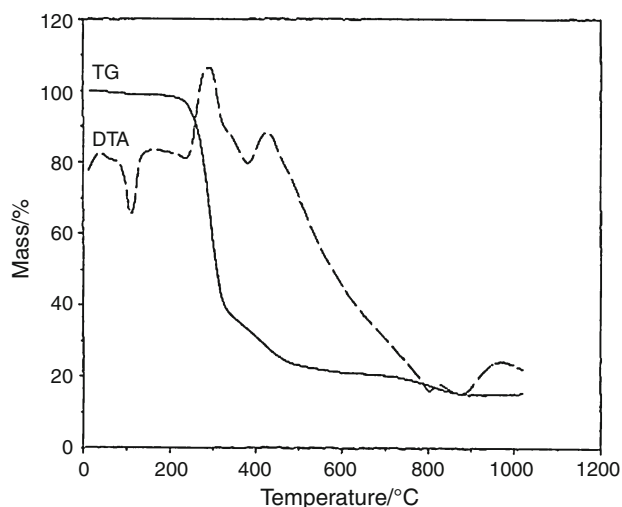
Fig. 3 TG and DTA curves of complex CuC$_{18}$

Table 7 Temperature of phase transfer from crystal to liquid-crystal mesophase from DTA and DSC, and change of enthalpy (ΔH) for CuC$_n$

| CuC$_n$	DTA (20–1000 °C)	DSC (50–200 °C)	
	T (± 1)/°C	T (± 1)/°C	ΔH (± 0.1)/kJ mol^{-1}
CuC$_{12}$	108	105	44.5
CuC$_{14}$	117	117	52.2
CuC$_{16}$	114	114	60.3
CuC$_{18}$	110	109	72.0

n number of carbon atoms in chain

up to 220 °C. However, the DTA curve reflects endothermic peak at 109.8 °C which corresponds to phase transfer from crystal to liquid-crystal phase (Fig. 3; Table 7). The TG curve also shows the intensive mass loss ($\sim 78\%$) from 220 to 430 °C. This temperature range is connected with the change of liquid-crystal phase into isotropic fluid, and there is also decomposition of the given complex. Within this temperature range, the change of mass is only about 7%, a final mass after its loss is 15%, and it corresponds to CuO.

The DSC measurements at 50–200 °C as well as measurements with TG and DTA [57] were made in nitrogen atmosphere. One endothermic effect on DSC curves for each of studied carboxylato-Cu(II) complex (Fig. 4) [13] at 105–117 °C (Table 7) has been observed. This endothermic effect can be assigned by coordinated phase transfer from solid state (crystal state), liquid-crystal state, or thermotropic column mesophase in thermal range [45].

Studied complexes were also investigated with help of optic microscope in the range of temperature from 50 to 200 °C during heating process. The changes of transparency as well as phase transfer between crystal and liquid-crystal phase were observed during the heating process, and the area was equivalent to endotherm on DSC curves. There was no state of isotropic fluid at this mentioned temperature range, which means that the observed changes are really the mesophase transfer from solid to liquid-crystal phase. The values of temperatures of this phase transfer and corresponding changes of enthalpy, as well as the values of temperatures of endothermic peaks from DTA curve are shown in Table 7. The changes of enthalpy (ΔH) assign linear dependency on of the number of carbon atoms in chain, and equivalent enthalpy changes increase in rank with increasing number of carbon atoms in chain [45]: $n = 12 < 14 < 16 < 18$, although transfer temperatures assign only weak dependence on length of aliphatic chain.
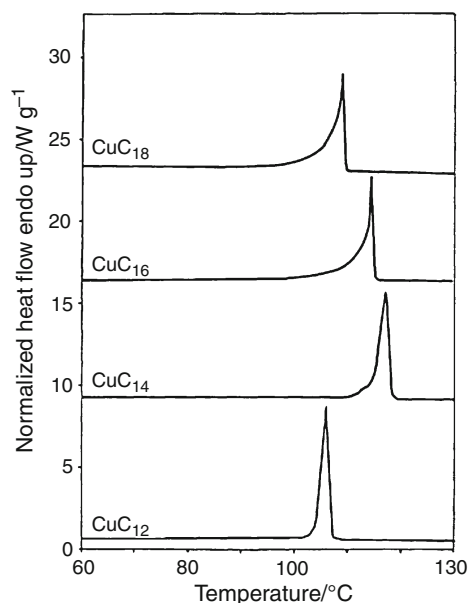
Fig. 4 DSC curves of CuC$_{12}$, CuC$_{14}$, CuC$_{16}$, and CuC$_{18}$ [17]

Thermal properties of carboxylato–Cu(II) complexes with benzothiazole

The thermal decomposition starts by a release of benzothiazole molecules at the same temperature range as melting. A mass loss in temperatures ranging from 80 to 220–230 °C corresponds to the mass of coordinate benzothiazole in the studied complexes as endorsed by the results from TG curves. The same thermal processes as in the case of corresponding carboxylato–Cu(II) complexes continue after loss of benzothiazole molecules. The transmission from a solid phase to a liquid-crystalline mesophase was observed for all the studied benzothiazole adducts of carboxylato–Cu(II) complexes. It was determined from thermal measurements (TG and DTA) in the temperature range of 20–1000 °C that the mentioned complexes are changed on thermotropic column mesophase in the temperature range of 56–72 °C. The transition from liquid-crystalline phase to isotropic liquid occurs at temperature range of 85–96 °C. The data of total mass loss, which were obtained from TG curves and a residue of mass after thermal processes of given complexes are shown in Table 8.

The thermal decomposition starts by a release of benzothiazole molecules: one-stage for $CuC_{12}bt$ and two-stage for $CuC_{16}bt$ and $CuC_{18}bt$ of complexes (Fig. 5). DSC records of benzothiazole adducts in the temperature range of 50–120 °C are given in Fig. 5. Two endothermic peaks were observed on DSC curves for all the prepared benzothiazole adducts of Cu(II) carboxylates. The complex $CuC_{12}bt$ has the first endotherm at ~ 57 °C with a shoulder at 56 °C and the second endotherm at ~ 85 °C. The complex $CuC_{14}bt$ has these endotherms: ~ 72 °C with a shoulder, at 70 °C, and at ~ 86 °C (Table 8). The first endothermic peaks are connected with a mesophase transition from a crystalline to liquid-crystalline phase, which was confirmed under optical microscope at temperature range of 50–200 °C and by TG and DTA measurements. Shoulders of the first endothermic peaks for complexes $CuC_{12}bt$, and $CuC_{14}bt$ show that a phase transition is a two-stage process. The second endothermic peaks corresponds to transition from a liquid-crystalline to isotropic liquid.

Two endotherms are observed at the complexes $CuC_{16}bt$ and $CuC_{18}bt$ too. The first endothermic peak, witch

Table 8 Total weight loss and residue of thermal decomposition of CuC_nbt and loss of bt

CuC_nbt	Δm loss of bt Found (Calc.)/%	Total Δm loss/%	Residue/% Found/%	Calc./% CuO	Cu
$CuC_{12}bt$	22.0 (21.8)	88.6	11.3	12.8	10.2
$CuC_{14}bt$	19.5 (20.7)	89.8	10.2	12.2	9.7
$CuC_{16}bt$	20.2 (19.1)	93.6	6.4	11.2	9.0
$CuC_{18}bt$	17.1 (17.7)	92.6	7.4	10.4	8.3

Fig. 5 DSC curves of $CuC_{12}bt$, $CuC_{14}bt$, $CuC_{16}bt$, and $CuC_{18}bt$

Table 9 Data T_{trs}, T_{fus}, from DSC and DTA curves and $\Delta_{trs}H$, $\Delta_{fus}H$ for complexes CuC_nbt

CuC_nbt	DTA (20–1000 °C)		DSC (50–200 °C)			
	T_{trs} (±1)/°C	T_{fus} (±1)/°C	T_{trs} (±1)/°C	$\Delta_{trs}H$ (±0.5)/kJ mol^{-1}	T_{fus} (±1)/°C	$\Delta_{fus}H$ (±0.5)/kJ mol^{-1}
$CuC_{12}bt$	56	89	56sh 57	7.7	85	45.0
$CuC_{14}bt$	72	88	70sh 72	9.2	86	58.6
$CuC_{16}bt$	61	91	61	2.9	83sh 88	61.0
$CuC_{18}bt$	67	96	68	1.1	90sh 93	92.5

n the number of carbon in chain, sh shoulder

corresponds to phase transition from solid phase to a liquid-crystalline mesophase occurs at 61 °C for CuC$_{16}$bt, and at 68 °C for CuC$_{18}$bt. The second endothermic peak has in both cases the shoulder at the lower temperature (Fig. 5). These temperatures are connected with a start of the thermal decomposition of the sudied complexes (Table 9).

Conclusions

This study of spectral and thermal properties is concerned with four prepared carboxylato–Cu(II) complexes (tetrakis(μ-alkanoato-O,O')dicopper(II) and four other complexes with benzotiazole (tetrakis(μ-alkanoato-O,O')-bis(benzothiazole)dicopper(II), with long alkyl-hydrocarbon chain with number of carbon atoms in chain, $n = 12, 14, 16$, and 18. The studied carboxylato–Cu(II) complexes are formed from dimeric units to polymeric chains (chromofor CuO$_5$). The structural changes are due to coordination of ligand (benzothiazole). The polymeric chains of carboxylato–Cu(II) complexes degraded to discrete centrosymetric tetracarboxylate-bridged dimmers (chromofor CuO$_4$N). From the IR spectra of the studied compounds, the calculated values of $\Delta(COO^-) = [v_{asym}\ (COO^-) - v_{sym}\ (COO^-)]$ were in the range 162–165 cm^{-1} for the carboxylato–Cu(II) complexes and in the range 183–185 cm^{-1} for the benzothiazole adducts. These values $\Delta(COO^-)$ correspond to the bridging bond carboxylic groups in a syn–syn configuration, and they are in agreement for dicopper tetracarboxylic structures. Splitting of $v_{sym}(COO^-)$ absorptions for benzothiazole adducts has been attributed to change coordination type from tridentate to bidentate bridging type of carboxylate groups. In UV–Vis spectra of the studied complexes, the band between 672 and 720 nm and broad shoulder between 355 and 381 nm were observed. The band is attributed as d–d transitions, and the shoulder is commonly attributed as characteristic for dimeric compounds. TG and DTA measurements of [Cu$_2$(RCOO)$_4$] and [Cu$_2$(RCOO)$_4$bt$_2$] showed that transition from a crystalline to a liquid crystalline phase was observed for all prepared compounds. The transition temperatures for benzothiazole complexes are somewhat lower than for the corresponding [Cu$_2$(RCOO)$_4$]. The complexes type [Cu$_2$(RCOO)$_4$bt$_2$] undergo a crystal to liquid crystalline phase transition and melting at much lower temperatures than their Cu$_2$(RCO$_2$)$_4$ analogues. The lower thermal stability of [Cu$_2$(RCOO)$_4$bt$_2$] than [Cu$_2$(RCOO)$_4$] could be explained by structural features. The weaker inter-dimer interactions are probably the main reason for significant decline in the thermal characteristics of benzothiazole compounds. An emission of benzothiazole after heating begins simultaneously with melting, and enthalpic changes for these processes increase in the sequence (according to the number of carbon atoms): 12 < 14 < 16 < 18.

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