# Synthesis, structure, and discotic mesomorphism of the new series of copper carboxylates

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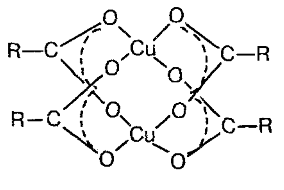
The synthesis, structure, and mesomorphism of a new series of copper carboxylates are described. The influence of periphery of the chelate node on the appearance of discophase is studied. A stacked hexagonal structure of copper erucate is proved. The effect of restructuring of the chelate node in this compound after its isothermic exposure, causing the loss of mesomorphism is revealed.

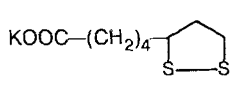
**Key words**: copper carboxylates, synthesis, structure, discotic mesomorphism, phase transition, textures.

Earlier[1] we studied the influence of conditions of synthesis on the structure, mesomorphism, and phase transitions of copper salts of saturated aliphatic carboxylic acids. It was found that all even members of this homologous series (from the tenth to the twenty-second) are discotic liquid crystals with the hexagonal packing of stacks in the supramolecular structure. All compounds of this series have a rather wide range of existence of discophase; however, they decompose upon transition into an isotropic liquid.

In order to study the effect of periphery of the chelate node of a carboxylate on the appearance of a discophase and its range of existence, and also to obtain mesophases with a lower clearing point, we carried out synthesis of a new series of copper carboxylates **1a—f**. For comparison with these compounds, potassium lipoate (**2**) was used. Compounds **1a,b,c,e** were obtained by fusing copper hydroxide with the corresponding acid,[1] while compounds **1d,f, 2** were obtained by the exchange reaction[2]. All of them are identified by means of elemental analysis (Table 1) and electronic and infrared spectroscopy (Tables 2 and 3). The data of elemental analysis are in a good agreement with the calculated data. In the electronic spectra of compounds **1a—d**, a long-wave absorption band (690 or 685 nm, Table 2) corresponding to the d—d* transition in the chelate node of the carboxylate is observed. In the IR spectra of complexes, the position of the band of asymmetric stretching vibrations of the carboxylic group indicates the formation of a bond between the metal and COO group[3]. In the spectra of complexes under investigation, there is no vibration frequency within the range from 1660—1690 cm$^{-1}$ that is characteristic of a protonated carboxylic group (Table 3). Upon substitution of hydrogen by copper in the carboxylic group the molecular symmetry changes; symmetric and asymmetric COO$^-$ vibrations appear within the ranges 1580 to 1586 and 1430 to 1460 cm$^{-1}$, respectively. The difference between the frequencies of the $\nu_{as}$ and $\nu_s$ vibrations of the COO group from 120 to 162 cm$^{-1}$ indicates bidentate cyclic or bidentate bridging coordination of the carboxylic group by the copper atom.



**1a—f**

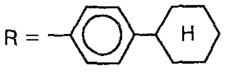


**2**

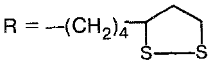
**a:** 

**d:** R = $-(CH_2)_{11}CH{=}CHC_8H_{17}$

**b :** R = $-(CH_2)_2-COOC_9H_{19}$

**e:** 

**c :** R = $-(CH_2)_2-COOC_{10}H_{21}$

**f:** 

## Experimental

Compounds **1a,b,c,e** were obtained by fusing 0.005 mol of copper hydroxide with 0.011 mol of the corresponding acid at 110 to 115 °C for 7 to 10 h. After cooling to *ca.* 20 °C, the melt was treated with tetrahydrofuran (analytical grade), and the carboxylate solution was passed through the column with silica gel L 40/100. THF was distilled off, and the residue was recrystallized to constant melting point from hexane, ethanol, or chloroform—heptane, depending on the solubility of the carboxylate.

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**Table 1.** Elemental analysis of compounds **1a—e, 2**

| Compound | Molecular formula | Molecular weight | Found/Calculated (%) | | | | |
|---|---|---|---|---|---|---|---|
| | | | C | H | Cu | K | S |
| **1a** | $C_{40}H_{44}O_8Cu$ | 778.94 | 61.88<br>61.59 | 5.00<br>5.69 | 16.00<br>16.30 | — | — |
| **1b** | $C_{52}H_{100}O_8Cu_2$ | 980.94 | 64.68<br>63.68 | 9.70<br>10.30 | 13.80<br>14.43 | — | — |
| **1c** | $C_{56}H_{100}O_8Cu_2$ | 1036.74 | 66.00<br>64.87 | 9.36<br>10.52 | 12.00<br>12.26 | — | — |
| **1d** | $C_{88}H_{164}O_8Cu_2$ | 1477.62 | 70.43<br>71.53 | 11.47<br>11.21 | 8.30<br>8.60 | — | — |
| **1e** | $C_{52}H_{56}O_8Cu_2$ | 935.18 | 65.61<br>66.78 | 7.06<br>6.02 | 13.00<br>13.54 | — | — |
| **1f** | $C_{16}H_{26}O_8S_4Cu_2$ | 601.52 | 33.42<br>31.94 | 4.16<br>4.37 | 20.45<br>21.12 | — | 20.20<br>21.28 |
| **2** | $C_8H_{13}S_2O_2K$ | 244.43 | 41.00<br>39.30 | 6.30<br>5.37 | — | 15.80<br>16.00 | 25.00<br>26.23 |

**Table 2.** Absorption bands in electronic spectra of compounds **1a—d**

| Compound | λ/nm; (logε), ethanol | | | |
|---|---|---|---|---|
| **1a** | 209 (4.92) | 217 | 255 (3.79) | 690 (2.27) |
| **1b** | 208 sh (3.51) | — | 244 (3.61) | 690 (2.27) |
| **1c** | 208 sh (3.51) | — | 244 (3.67) | 690 (2.31) |
| **1d** | 210 sh | — | 243 (3.95) | 685 (2.61) |

Copper lipoate (**1f**) and erucate (**1d**) were obtained through the exchange reaction by mixing 0.02 mol of potassium lipoate or erucate solution in aqueous ethanol with 0.01 mol of copper sulfate (chemically pure grade), which was preliminary purified from admixtures of iron salts. Yellow-green precipitates obtained were filtered off, washed with water and alcohol to remove starting reagents, and dried. Then copper erucate was recrystallized from toluene, and copper lipoate was used without further purification.

Potassium lipoate was obtained by mixing 2 g of lipoic acid (pharmacopoeic grade) in 50 mL of warm anhydrous alcohol with 14.5 mL of ether solution of potassium ethylate (stoichiometric amount) to the weak alkaline reaction. The solvents were distilled off *in vacuo*, the residue was treated with methanol, potassium lipoate was precipitated from the solution with diethyl ester to obtain a white substance soluble in alcohol.

Electronic spectra were recorded in ethanol using a Specord UV-VIS spectrophotometer; infrared spectra were recorded in KBr pellets or in Nujol using a Specord M-30 spectrometer. The elemental analysis was carried out using a PUMV apparatus. The temperatures of phase transitions were determined by polarization thermomicroscopy using an MIN-8 microscope and by differential thermal analysis (an F. Paulik — N. Paulik — Erdey derivatograph). X-ray diffraction studies were performed by the powder method in a passing beam using an IRIS apparatus (Cu-Kα radiation, Ni filter, flat film record).

**Table 3.** IR spectra ($\nu$/cm$^{-1}$) of compounds **1a—f** (KBr pellets, nujol)

| Compound | $\nu$(=C—H) | $\nu$(Ar) | $\nu_{as}$(—COO) | $\nu_s$(—COO) | $\delta_s$(Me) | $\delta_{ep}$(C—H) | $\rho$(—CH$_2$—) |
|---|---|---|---|---|---|---|---|
| **1a** | — | 1648<br>1560<br>1498<br>1440 | 1580 | 1460 | 1376 | 760 | 700 |
| **1c**[a] | — | — | 1596 | 1450 | 1376 | — | 720 |
| **1d** | 3050 | 1645[b] | 1588 | 1440 | 1375 | — | 720 |
| **1e**[a] | — | 1650<br>1550<br>1515 | 1592 | 1430 | — | — | — |
| **2**[a] | — | —<br>1620 | 1648 | 1430 | —<br>680 | 780 | 725 |

[a] In nujol. [b] $\nu$(C=C).

## Results and Discussion

To reveal the mesomorphic behavior of the synthesized compounds, we carried out thermomicroscopic (Table 4), derivatographic (Fig. 1), and X-ray diffraction (Table 5) studies. As shown by these investigations (Table 4), only two copper carboxylates (**1a** and **1d**) are mesomorphic. At 155 °C, compound **1a** turns into a very viscous birefringent liquid. The texture of flow is seen under a microscope with crossed polarizers, and the characteristic hatchure appears upon the shift deformation. Partial decomposition is observed upon heating the specimen above 200 °C. Complete destruction of the specimen takes place at 250 °C. For this reason, the derivatographic studies of phase transitions in the heating-cooling cycle were carried out only with heating below 200 °C (Fig. 1, *a*). The DTG and TG curves show that there is no change in the weight of the specimen up to 200 °C, *i.e.*, all changes in the DTA curve are associated with solid phase transitions. The significant asymmetry of the curve for the transition into mesophase indicates the possibility of an additional transition into mesophase, which is not identified texturally. According to the DTA data, the transition into mesophase is recorded at 149 °C, that is, by 6 °C lower than the value obtained from the thermomicroscopic studies. This fact is connected with the difficulty in recording of a phase transition by visual observation. The solid phase microstructure, which is visible under a microscope, also does not change above the transition point (similar to the case of copper carboxylates[1]). The pattern is noticeably brightened upon significant overheating, and the nongeometric texture is observed. The same change of color takes place right after the transition upon pressing on the cover glass. Pressing before the transition does not change the color.

**Table 4.** Phase transition temperatures of compounds **1a—e, 2**

| Compound | Phase state* | | | Transition temperature/°C | | | $T_{sd}^{**}$ |
|---|---|---|---|---|---|---|---|
| | SC | M | IL | SC→M | M→IL | SC→IL | °C |
| **1a** | + | + | + | 155 | 235 | | 270 |
| **1b** | + | — | + | | | 110 | 225 |
| **1c** | + | — | + | | | 111.5 | 233 |
| **1d** | + | + | + | 63 | 190 | | 215 |
| **1e** | + | — | — | | | | 355 |
| **1f** | + | — | — | | | | *** |
| **2** | + | — | — | | | | *** |

* SC is solid crystal phase; M is mesophase; IL is isotropic liquid.

** $T_{sd}$ is the starting decomposition temperature.

*** The substance melts with decomposition.

**Table 5.** Structural characteristics of substances under investigation

| Compound | Temperature of X-ray study /°C$^a$ | Periods of structure/Å$^b$ | |
|---|---|---|---|
| | | Large angles | Small angles |
| **1a** | 156 ($D_h$) | 5.1 | $a$ = 18.3$^c$ |
| **1c** | 100 (TK) | 4.1; 4.6 | 38.3 |
| | 16 (ИЖ) | 4.7 | 22.2 |
| **1d** | 18 (TK) | | 50.5$^d$ |
| | 60 (TK) | 4.34 | 51.6 |
| | 64 ($D_h$) | 4.6 | 24.8 |
| **1e** | 18 (TK) | 5—6 Diffuse halo | 24.4; 12.3 Pronounced reflections |

$^a$ SC is crystal phase; $D_h$ is stacked hexagonal phase; IL is isotropic liquid. $^b$ The strongest reflections. $^c$ $a$ is *ee*-period. $^d$ Six orders of reflection: the crystal structure is lamellar.

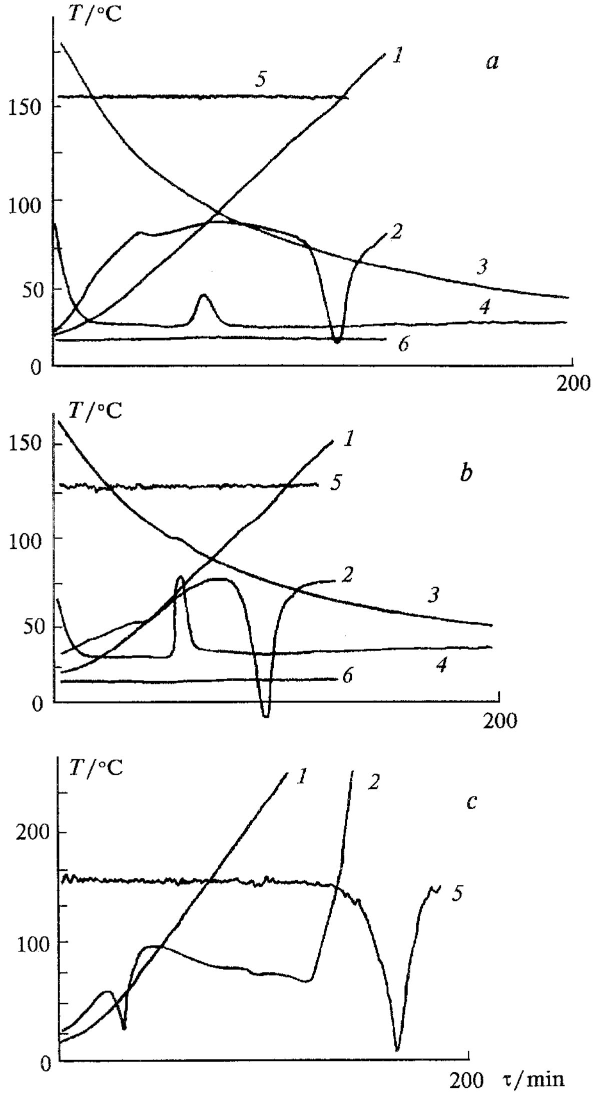

**Fig. 1.** Curves of thermal analysis of copper carboxylates **1a** (*a*), **1c** (*b*), and **1d** (*c*). *1*, curve of heating $T_h$; *2*, curve of differential thermal analysis, $DTA_h$, cycle of heating; *3*, curve of cooling, $T_c$; *4*, $DTA_c$ curve, cycle of cooling; *5*, DTG curve; *6*, curve of weight change $T_w$.

These changes can be accounted for by the significant viscosity of the mesophase. The most intense rings observed in the X-ray diffraction patterns are twinned. This fact may indicate the complex composition of the specimen **1a**, which we explain by the presence of *cis-* and *trans*-isomers of $\gamma$-phenylbutyrate. In the mesophase, we can see a very strong internal ring and two weaker rings corresponding in the first approximation to the hexagonal packing of stacks with the period of 18.3 Å, and also a sharp ring within the large angle range corresponding to the period of 5.1 Å. We preliminarily attributed the mesophase to the ordered stacked hexagonal phase $D_{h0}$ (Table 5). In fact, the hexagonal structure is deformed, and additional studies are necessary for its refinement.

The compound **1a** involves four phenyl radicals at the end of its hydrocarbon chain. As compared to aliphatic carboxylates,[1] such structure of this compound results in the increase of the temperature of transition into mesophase almost by 30 °C together with the increase of thermostability up to 270 °C. However, the shift of the phenyl radical to the central chelate node and the closure of the hydrocarbon tail into the cyclohexane ring (**1e**) does not favor the appearance of mesomorphism (Table 4). This fact seems to be accounted for by the increase in the molecular rigidity of the molecule as a whole. The introduction of polar groups like the ester group of succinate into the hydrocarbon tail near the chelate node (**1b, c**) also results in the loss of mesomorphism. According to the data of polarization thermomicroscopy and DTA (Table 4), copper monodecylsuccinate (**1c**) turns into green isotropic liquid already at 115 °C. The complete destruction of carboxylate is recorded at 233 °C (Table 4). The presence of a diffuse peak of phase transition in the DTA curve of compound **1c** within the range 40 to 60 °C (Fig. 1, *b*, curve *2*) seems to be connected with the transition of metastable solid phase into the stable phase.

We also carried out X-ray diffraction studies of compound **1c** at different temperatures. The strongest reflection in the solid crystal phase, which is connected with the periodic arrangement of copper atoms in the structure, corresponds to the period of 38 Å and equals 22 Å in the isotropic liquid. Within the assumption of bidentate bridging coordination of the carboxylic group by copper atom and *trans*-conformation of hydrocarbon tails, the building of molecular model of compound **1c** gives the molecular size of 44 and 35 Å, respectively. Thus, the period of 38 Å observed in the solid phase can be attributed to the lamellar packing of molecules with arrangement of one molecule along the thickness of layer. Upon transition into isotropic liquid, the molecule seems to fold up, and we observe the period of 22 Å which is significantly smaller than the length of molecule. Apparently, the degree of folding varies depending on the prehistory of the specimen, because the period of the structure is different in various experiments and corresponds either to 22 or 18 Å.

We should also note that the replacement of a phenyl ring at the end of hydrocarbon chain (**1a**) with a five-membered saturated heterocycle with two sulfur atom does not enable to obtain the mesomorphic state of copper lipoate (**1e**, Table 4).

Only lengthening of the hydrocarbon chain to 22 carbon atoms, introduction of a double bond into the middle of the chain, and removal of a phenyl radical (compare with compound **1a**) enabled us to significantly decrease the temperature of transition into mesophase and achieve the temperature of transition into the isotropic liquid without noticeable decomposition of the substance (compound **1d**, Fig. 1, *c*, curves *3* and *4*). The series of studies of freshly prepared compound **1d** showed that its transition into mesophase occurs at a temperature of 63 °C (Table 4), which is significantly lower than that of copper salts of saturated carboxylic acids. The transition into the isotropic liquid takes place at 190 °C. Upon cooling of the isotropic liquid, mesophase is formed with a flower texture, which is characteristic of discotic liquid crystals. For more distinct identification of mesophase, we obtained several series of X-ray diffraction patterns within the range 20 to 70 °C. A large number of orders of reflections (up to six) is observed in the crystal phase of compound **1d**, which indicates a layer structure. We should note the major period with a value of 50.5 Å. The period is increased up to 51.6 Å near the transition into mesophase. There is also a period with an average value of 4.34 Å. In the mesomorphic state, there are two remaining diffuse reflections corresponding to the periods of 24.8 and 4.6 Å at 64 °C. However, these two ring reflections do not form the combination characteristic of stacked hexagonal structure.

For interpretation of the X-ray diffraction patterns obtained, we carried out additional studies, namely, the thermal analysis of mixture of copper erucate (**1d**) and stearate accompanied in necessary cases by the X-ray diffraction studies (Fig. 2). As follows from Fig. 2, copper erucate and stearate form continuous solutions, *i.e.*, we observe the unlimited miscibility in the mesophase. The mixtures containing from 50 to 100 % of copper stearate have the additional region ($C_1$) between the solid crystal and liquid crystal phases. Thus, the unlimited miscibility of copper erucate and stearate in the mesophase suggests the conclusion of the similar supramolecular structures of these two compounds. Since we proved earlier[1] the stacked hexagonal supermolecular packing of copper stearate, the structure of copper erucate can also be referred to as stacked hexagonal. A study of mixtures of copper erucate and stearate revealed polymorphism of copper stearate in the solid phase. The range $C_1$ (Fig. 2) exists between 97 and 113 °C. One more feature of the phase diagrams of mixtures is the fact that the points of transition into mesophase and crystallization of copper stearate coincide, but crystallization of mixtures takes place at a higher temperature than melting, and the higher is the content of copper

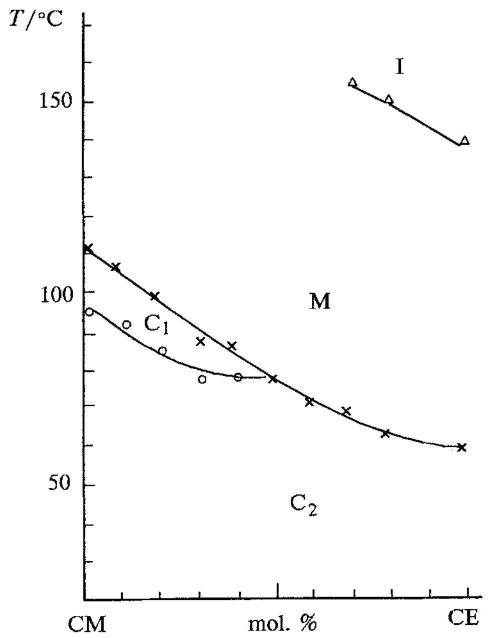

**Fig. 2.** Phase diagram of the mixture of copper erucate (CE) and stearate (CS) in the cycle of heating; I is isotropic phase, M is mesophase, and C is crystal phase.

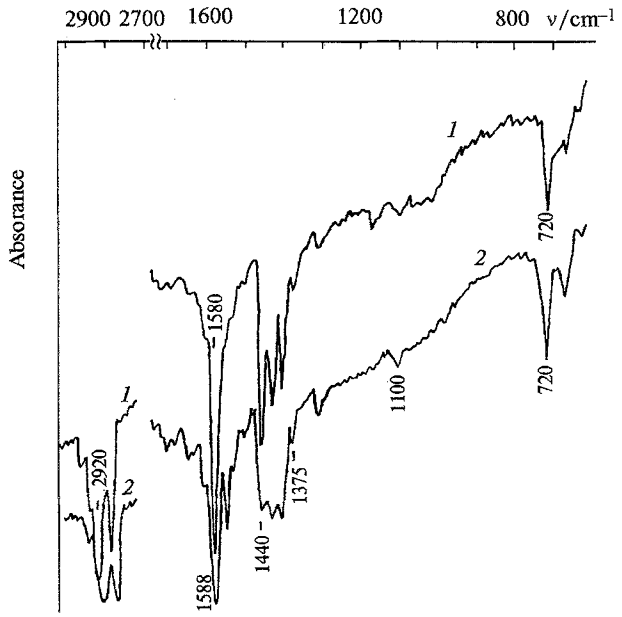

**Fig. 3.** IR spectra of copper erucate before (*1*) and after (*2*) isothermic exposure at 160 °C.

erucate in the mixture, the greater is the difference. This difference is 13 °C for the pure specimen of copper erucate. Such feature of the state diagrams of binary systems can be accounted for by the structural changes at the coordination node of a carboxylate. We made this conclusion on the basis of results of thermal analysis (Fig. 1, *c*) and spectral investigations in the IR region (Fig. 3) of the specimens of **1d** studied before and after the isothermic exposure at 160 °C for two hours.

Several processes are possible upon heating: thermodestruction, polymerization of the substance, *cis-trans*-isomerization in the side chain, and change at the coordination node of a carboxylate. Since thermodestruction takes place only at the temperature above 230 °C (Fig. 1, *c*), this fact cannot explain the change of crystallization temperature of **1d** after the isothermic exposure, in fact this temperature is increased almost by 13 °C. Polymerization and *cis-trans*-isomerization can be are also ruled out, since we do not observe any disappearance or decrease in intensity of the absorption band intensity of olefin bonds, or any appearance of absorption bands of the out-of-plane deformation vibrations of C—H bonds at the olefin groups that are characteristic of *trans*-configuration. The only changes observed in the IR spectra involve the change of absorption bands of stretching vibrations of carboxylate anions. A new band appears at 1560 $\text{cm}^{-1}$, while the band at 1440 $\text{cm}^{-1}$ corresponding to symmetric stretching vibrations of the C(O)O carboxylate group is shifted and broadened. Thus, we expect that the structure of coordination node is changed from bridging umbrella to bridging cyclic structure. Such structure of the coordination node implies denser packing and, hence, the higher temperature of crystallization (melting) of **1d**, which we observed, that results in the disappearance of mesomorphic properties of copper erucate after long isothermic exposure.

## References

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