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Discotic mesophase of copper(II) laurate

A. M. Godquin-Giroud, J. C. Marchon

Laboratoires de Chimie (*), Département de Recherche Fondamentale,
Centre d'Etudes Nucléaires de Grenoble, 85X, 38041 Grenoble Cedex, France

D. Guillon and A. Skoulios

Centre de Recherches sur les Macromolécules, C.N.R.S., 6, rue Boussingault,
67083 Strasbourg Cedex, France

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Résumé. — Le laurate cuivrique (dodécanoate cuivrique) donne une mésophase discotique aux températures supérieures à 107 °C, caractérisée par un réseau hexagonal de colonnes distantes d'environ 20 Å. Ces colonnes résultent de l'empilement de motifs élémentaires distants d'environ 4,7 Å. Le motif élémentaire est le complexe binucléaire $\text{Cu}_2(\text{C}_{11}\text{H}_{23}\text{CO}_2)_4$ qui constitue le premier mésogène discotique à quatre chaînes périphériques donnant une mésophase hexagonale thermotrope.

Abstract. — Copper(II) laurate (copper dodecanoate) shows a discotic mesophase at temperatures above 107 °C. This mesophase is characterized by a hexagonal columnar lattice with a repeat distance of about 20 Å. Each column is made of stacked units with a period of about 4.7 Å. The repeating unit in a column is the binuclear complex $\text{Cu}_2(\text{C}_{11}\text{H}_{23}\text{CO}_2)_4$ which is the first example of a discotic mesogen with only four peripheral chains showing a thermotropic hexagonal mesophase.

The higher homologues of copper(II) n-alkanoates aroused early interest for their peculiar magnetic properties [1]. Their unusually low magnetic moments were later shown to arise from exchange interaction between copper atoms within binuclear molecules [2-4] which are thought to be structurally similar to the well-known dimeric copper acetate [5] (Fig. 1). The dimeric structure is related to the syn-syn bridging arrangement of the carboxylate ion, in which two parallel sp^2 -hybrid orbitals from the oxygen atoms are used to bond two copper atoms approximately 2.2-2.6 Å apart.

Our interest in the thermotropic mesophases of transition metal complexes [6-8] prompted us to investigate selected physical properties of these compounds at temperatures above their melting points. In this Letter, we report on the discotic mesophase exhibited by copper (II) laurate above 107 °C. This compound was synthesized following the experimental method described by Martin and Waterman [3]. Recrystallization from heptane gave a pale blue powder in 97 % yield. (Found : C, 61.91 ; H, 9.91 ; Cu, 13.46. Calculated for $\text{Cu}_2(\text{C}_{11}\text{H}_{23}\text{CO}_2)_4$: C, 62.37 ; H, 10.03 ; Cu, 13.75).

(*) Laboratoire associé au C.N.R.S., n° 321.

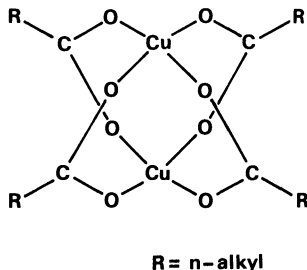


Fig. 1. — Molecular architecture of dimeric copper(II) alkanates.

Observation with a polarizing microscope showed that, on heating, the solid phase present at room temperature was transformed into a viscous birefringent dark blue liquid at about 107 °C. No specific textures characteristic of the usual mesomorphic phases could be detected to help identify the fluid anisotropic system ⁽¹⁾. This was apparently stable up to about 250 °C, where the product started to decompose. The same transition temperature at 107 °C was detected by differential scanning calorimetry; the corresponding enthalpy was found to be 17.1 kcal per mole of binuclear complex. On cooling (10 °C min⁻¹), the liquid crystalline phase remained stable down to 75 °C.

The X-ray diffraction patterns of the solid phase showed in the low-angle region at least three equidistant sharp Bragg reflections characteristic of a lamellar stacking of the molecules with a spacing of 32.5 Å. They also showed a large number of sharp reflections in the wide-angle region, denoting a well-developed three-dimensional crystalline order.

The X-ray patterns of the liquid crystal contained three sharp reflections in the low-angle region; the reciprocal Bragg spacings of these were in the ratio 1 : $\sqrt{3}$: $\sqrt{4}$, indicating a two-dimensional hexagonal lattice, with a spacing of about 20 Å. In the wide-angle region, they showed a rather narrow reflection emerging from a fairly diffuse band, both signals being located at 4.7 Å. Similar X-ray diagrams — in which, however, no narrow reflection could be detected in the wide-angle region — have been obtained with thermotropic mesophases of magnesium, cadmium, and calcium alkanates [9], and were later found with mesophases of flat disc-like molecules now known as discotic liquid crystals [10, 11]. In both cases, the structure corresponds to the stacking of molecules in columns, these being surrounded by aliphatic chains in a disordered state and arranged in a two-dimensional hexagonal lattice. In the latter case, the columns are made of the flat aromatic cores of the molecules, while they are formed by the polar metal dicarboxylate groups in the former. Clearly, the same columnar structure is present in copper laurate as well.

Using the X-ray patterns, the thickness of the lamellae for the crystal and the distance between the axes of neighbouring columns for the discotic liquid crystal were measured as a function of temperature (Fig. 2). It is of interest to note, first, that the transition temperature detected with X-rays is in perfect agreement with that determined by microscopy and differential scanning calorimetry; second, that the thermal evolution of the spacings in the crystal and in the discotic mesophase is reversible as a function of temperature; and third, that the thickness of the lamellae is nearly constant throughout the range of stability of the crystalline phase, while the distance between columns increases slightly with temperature for the discotic mesophase.

To characterize the stacking of the molecules within the columns, the distance between repeating units along the columns was calculated. This can be done in two ways. First, when a signal is present in the wide-angle region of the diffraction patterns, which can be attributed

⁽¹⁾ In our opinion the absence of well-developed textures is not meaningful; it is probably due to the fact that it is impossible, in a first stage, to get into the isotropic liquid without decomposition.

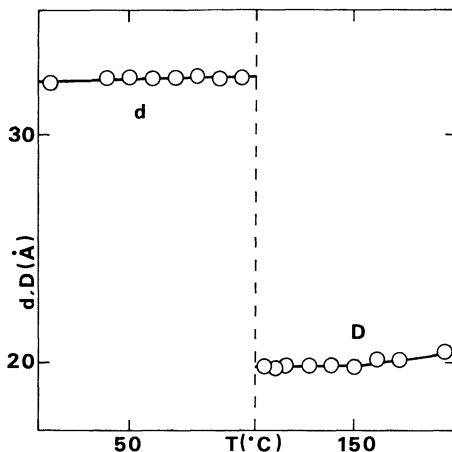


Fig. 2. — Thermal evolution of the thickness d of the lamellae for the crystal and the distance D between the axes of neighbouring columns for the discotic liquid crystal.

to a periodic structure along the columns, it is easy to calculate from its Bragg position the repeat distance of the diffracting elements. This is the case for the discotic mesophase of copper laurate, where a rather narrow reflection is observed at 4.7 \AA ⁽²⁾, distinct from the fairly diffuse band at about the same spacing which characterizes the disordered aliphatic chains. Second, when the molar volume V of the compound is known, it is possible to calculate the average repeat distance h of the molecules along the columns using the value of the distance D between the axes of neighbouring columns in the hexagonal lattice :

$$h = 2V/(\mathcal{N} \sqrt{3} D^2)$$

with \mathcal{N} , the Avogadro's number ($\mathcal{N} = 6.02 \times 10^{23}$). This was the case for Mg, Ca and Cd soaps where repeat distances of 1.47 \AA , 1.88 \AA and 1.28 \AA were respectively calculated [9]. Regarding copper laurate, the second way of calculating h cannot be used rigorously because to our knowledge, the molar volume of this compound has never been determined experimentally. However, taking into account the small size of the metal ions as compared to the overall size of an alkanolate complex, one can assume that the molar volume of binuclear copper laurate is not very different from twice that of, say, cadmium laurate, i.e. $V = 2 \times 475.5 \text{ cm}^3 \cdot \text{mole}^{-1}$ at $150 \text{ }^\circ\text{C}$ [9]. With this assumption, h of copper laurate is found equal to 4.6 \AA . The slight increase of D observed as a function of temperature does not affect at all the value of h , as it merely reflects the volume expansion of the material.

These values of h determined using the two above methods are in excellent agreement with each other. This is in favour of the assumption that the diffracting element within the columns is the same binuclear complex which is generally found with copper(II) alkanolates in the crystalline state. Further confirmation comes from the examination of C.P.K. molecular models. Constructed without copper ions (the size of which is expected to be rather small), these models show that the binuclear core of the complex is essentially flat with the aliphatic chains R pointing away from the Cu-Cu axis, as illustrated in figure 3; in addition, the dimensions of the complex are perfectly consistent with the observed period of 4.7 \AA . Thus it appears that copper laurate is the first example of a thermotropic hexagonal discotic mesogen containing only four peripheral chains. The currently accepted view is that six peripheral chains at least are required for a discoid molecule to exhibit a two-dimensional hexagonal lattice [10, 11].

⁽²⁾ It is important to note that, up to now, we have not been able to detect the harmonic reflection at $4.7/2 \text{ \AA}$ for instrumental reasons.

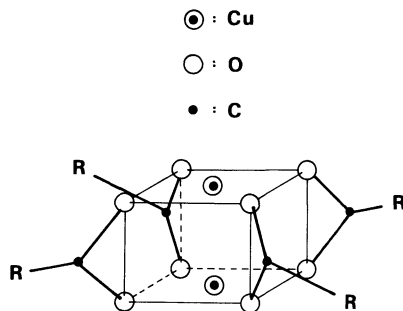


Fig. 3. — Molecular model of the binuclear copper(II) laurate : an average value of 2.20 Å was taken for the O-O distance in a carboxylic group, and a value of 1.99 Å for the shortest Cu-O distance [12].

To conclude this first study of the discotic mesophase of copper(II) laurate, it is useful to compare the structure described in this paper with that presented previously for other divalent metal soaps [9]. In all cases, the polar groups of the molecules do locate themselves within rods surrounded by the aliphatic chains, and the number of metal atoms per unit length (h^{-1}) do not depend significantly upon temperature. This invariance suggests that the polar groups are presumably locked in well defined positions. With the copper soap, the arrangement of the polar groups is related to the formation of the dimeric complex ; with the other soaps, it should in the same way be related to the specific geometrical features of the coordination of every metal atom. Unfortunately, with the information at our disposal presently, we are not in a position to offer any detail as for the geometry of the metal carboxylate complexes, nor to even tell if molecules form separate species, dimers, trimers or polymers.

Further experiments, such as direct molar volume measurements, or X-ray diffraction investigations on oriented samples, will be needed to get more precise information on the supramolecular structure within the columns. Much attention must be paid to carefully measure the profile and the intensity of the reflection at 4.7 Å and of its eventual harmonics, in order to specify the intermolecular and intramolecular copper-copper distances. Another point of interest is the geometry (linear or zig zag) of the copper atom chain. Finally, we note that the close proximity of the metal atoms in this system may give rise to peculiar magnetic and electron transport properties.

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