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Hexagonal columnar mesophase D_h in a new organometallic disk-like compound

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Résumé. — Un nouveau complexe de cuivre substitué par huit chaînes paraffiniques présente une mésophase thermotrope identifiée pour la première fois par miscibilité avec la mésophase colonnaire hexagonale D_h d'un discotique organique. Un effet d'orientation est obtenu à la transition I- D_h avec un fort champ magnétique, et dans le domaine mésomorphe le paramagnétisme du cuivre est compensé par la contribution diamagnétique. Des mesures de conductivité électrique apparente montrent une évolution thermique inhabituelle en phase mésomorphe.

Abstract. — A new copper complex substituted by eight paraffinic chains exhibits a thermotropic mesophase identified for the first time by miscibility with a hexagonal columnar mesophase D_h of an organic disk-like derivative. An orientational effect of a strong magnetic field at the isotropic- D_h transition is observed and in the mesomorphic range the paramagnetism of the copper atom is balanced by the diamagnetic component. Electrical conductivity measurements show an unusual behaviour in the mesomorphic domain.

1. Introduction.

A new class of mesogen formed by disk-like molecules was discovered some years ago [1]. Among the different organic compounds which have been found to exhibit columnar mesophases, very few contain metals. The only examples known are a lyotropic system formed by an aqueous solution of tetracarboxylated copper phthalocyanine [2] and an octasubstituted copper phthalocyanine which presents a thermotropic columnar mesophase [3]. Some of us previously reported [4] the synthesis and analytical characterization of a series of transition metal complexes, the bis (*p*-*n*-alkylbenzoyl) methanato copper (II) and suggested they could be mesomorphous. Nevertheless, these tetrasubstituted compounds did not show a two-dimensional columnar lattice.

Accounting for the empirical fact that at least six substituents are needed to get columnar mesophases [5], we report here the synthesis and some properties of a new copper complex substituted by eight paraffinic chains :

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— We give here evidence for the first time of the complete miscibility of the mesophase of an organometallic compound with a well known columnar mesophase of an organic mesogen. (Note that isomorphy between the mesophase of a transition metal complex, formed with rather elongated molecules, and the nematic or the smectic C phase of organic rod-compounds has been previously established by J. Billard and A. M. Giroud [6].)

— In addition, DSC analysis and a preliminary X-ray study have been performed.

— The orientational effect of a magnetic field at the isotropic-mesophase transition has also been investigated.

— Finally, the very first measurements of electrical conductivity in the isotropic and columnar phases are given.

2. Synthesis.

The organometallic derivative (1) is elaborated as follows : to a solution of bis (3, 4-nonyloxybenzoyl) methane (1 mM) dissolved in ethanol, we add a solution of copper chloride (CuCl_2 , 6 H_2O) (0.5 mM) dissolved in the same solvent.

The pH is adjusted at 7 to 8 with ammonia. After stirring 3 hours at room temperature, we filter and recrystallize the complex 1 from isopropanol and heptane.

The bis (3, 4-nonyloxybenzoyl) methane is obtained by reacting 3, 4-nonyloxybenzoic acid methyl ester with 3, 4-nonyloxyacetophenone in anhydrous dimethoxyethane with sodium hydride [7]. The diketone has a M. P. 80 °C. All compounds and complexes are characterized by the usual analytical methods and are in agreement with elemental analysis.

3. Microscopic observations, miscibility, DSC analysis and X-ray measurements.

The copper complex 1 has been first observed by means of polarizing microscopy : melting occurs at 102 °C giving a birefringent phase up to 112 °C where the compound transforms to the isotropic liquid. This last phase change corresponds to a weak transition enthalpy $\Delta H = 0.38 \text{ kcal mole}^{-1}$ compared to the melting enthalpy $\Delta H = 20.90 \text{ kcal mole}^{-1}$.

The characterization of this mesophase has been achieved by miscibility with a reference compound, the hexadecyl alkanoate of triphenylene (HATC10) which presents two well known columnar mesophases : an hexagonal columnar phase D_h and a rectangular one D_r [8]. Figure 1 shows the phase diagram obtained on heating a contact sample. Total miscibility is obvious for the mesophase of the organometallic compound and the hexagonal columnar phase of the ester of triphenylene taken as reference. To our knowledge no other isomorphy between the columnar D_h mesophase of a transition metal complex and of an organic compound has been obtained so far.

Remark : Although this miscibility diagram undoubtedly shows a two-dimensional hexagonal arrangement D_h of the columns, it does not give any quantitative information about the short-range stacking of the molecules inside the columns, since the « ordered » (D_{h_o}) and « disordered » (D_{h_d}) hexagonal columnar phases (of the same symmetry P6 2/m 2/m) cannot be distinguished by the contact method. Nevertheless for the copper complex, some arguments are in favour a « disordered » mesophase D_{h_d} : — first, some textural aspects (characteristic germination from

Fig. 1. — Binary diagram (T vs composition) between the transition metal complex and the hexadecylalkanoate of triphenylene (HATC10) taken as reference.

Fig. 2. — The same binary diagram (T vs composition) as figure 1, between the copper complex and the ester of triphenylene HATC10.

the isotropic phase and formation of fan shaped textures) — second, an $I \rightarrow D_h$ enthalpy ($0.38 \text{ kcal mole}^{-1}$) typical of an $I \rightarrow D_{hd}$ enthalpy and weaker than $I \rightarrow D_{ho}$ enthalpy ($\Delta H_{I \rightarrow D_{hd}} = 0.30 \text{ kcal mole}^{-1}$ (HATC10) and $\Delta H_{I \rightarrow D_{ho}} = 2.04 \text{ kcal mole}^{-1}$ (HETC5) [8]).

Small angle X-ray diffraction experiments performed on powdered samples (Guinier chamber) indicate one intense Bragg reflection indexed 10 in the hexagonal lattice which gives the distance between neighbouring columns $a = 29 \text{ \AA}$. Note that this value is clearly smaller than the molecular diameter obtained from an SASM model with stretched conformations of the aliphatic chains ($42 \text{ \AA}$).

Remark : Upon cooling, the hexagonal mesophase remains supercooled down to 95°C where a striated transient texture gives evidence for a phase transition. This metastable phase exists down to room temperature. Yet annealing around 90°C restores the crystalline state. The binary diagram established on cooling (Fig. 2) shows that this low temperature phase is not isomorphous with the rectangular columnar mesophase of the HATC10, but the texture is close to those of D_{hd} phases and in particular the domains of the hexagonal phase remain unchanged. Moreover, a strong transition enthalpy ($\Delta H_{D_h \rightarrow K_7} = 8 \text{ kcal mole}^{-1}$) and the occurrence of several intense Bragg reflections, in particular in the large angle domain, lead us to claim a tridimensional ordering.

4. Magnetic study.

Due to the presence of a bivalent copper atom, a paramagnetic contribution is expected in addition to the diamagnetism.

Magnetic susceptibility (χ) measurements in the bulk along the direction of the magnetic field (Faraday method [10]) are shown in figure 3.

A weak discontinuity of χ ($\delta\chi = 0.3 \times 10^{-8} \text{ cm}^3 \text{ g}^{-1}$) is observed at the $I \rightarrow D_h$ transition. This increase of the χ negative values probably corresponds to some orientational effect of the 15 kG magnetic field due to the diamagnetic anisotropy of the mesophase. This result has to be compared to the behaviour previously observed at the $I \rightarrow D_h$ transitions for the triphenylene series [11].

Fig. 3. — Thermal variations of the magnetic susceptibility χ measured in the bulk along the direction of the magnetic field.

We can note the sign change of the measured magnetic susceptibility in the mesomorphic range : on cooling the paramagnetism prevails and the decrease of the χ positive value at the D_h $\rightarrow$ K_r transition indicates that the magnetic field has no further orientating effect on the tridimensional structure.

5. Electric conductivity measurements.

A preliminary study of electric conductivity has been performed using the isotropic and D_h phases of the copper complex and of our reference disk-like compound HATC10. We stress that only an apparent conductivity σ_{app} in the D_h mesophase is determined since the orientation is not controlled in the cell.

The samples are introduced between the plates of a capacitor (100 μ mylar spacers) and the capacitance and the conductance are measured with a B224 Wayne Kerr bridge, at the frequency 1 600 Hz. Additional capacitances and electrode effects are ruled out by using a reference method and a double plate capacitor.

In figure 4, the thermal evolution of the apparent conductivity for the ester of triphenylene HATC10 is reported. A dielectric behaviour is observed : in the isotropic phase σ_{app} decreases as the temperature decreases. At the I $\rightarrow$ D_h transition σ_{app} drops and decreases in the mesomorphic range faster than in the isotropic phase. This thermal evolution is quite similar to that for rod-like systems near the I-N transition [12].

Figure 5 shows the temperature dependence of the apparent conductivity for the copper complex. In the isotropic phase σ_{app} decreases as the temperature decreases. But in contrast with the non-metallic compound, at the I $\rightarrow$ D_h transition the electrical conductivity slightly increases and then remains constant throughout the mesophase.

Thus it seems that the presence of a transition metal in a disk-like mesogen enhances the electric conductivity in the uniaxial columnar mesophase D_h. Taking into account the surrounding of each column by melted paraffinic chains, we suggest that some cooperative conductivity effects exist along the column. In order to specify the electric properties of the quasi uni-

Fig. 4. — Thermal evolution of the apparent electrical conductivity σ_{app} for the ester of triphenylene HATC10.

Fig. 5. — Temperature dependence of the apparent electrical conductivity σ_{app} for the copper complex.

dimensional liquid within the column, we plan to make measurements of the anisotropy of conductivity on oriented samples.

Finally, new syntheses are in progress to determine the influence of the metallic atom, and of the location and the length of the paraffinic chains on the mesomorphic state.

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