Liquid crystals complexed to copper (II) : an X-ray diffractometric study on monodomains of (DCBBA)\(_2\) -Cu and (HOBBA)\(_2\)-Cu

A.M. Levelut, M. Ghedini, R. Bartolino, F.P. Nicoletta, F. Rustichelli

To cite this version:

A.M. Levelut, M. Ghedini, R. Bartolino, F.P. Nicoletta, F. Rustichelli. Liquid crystals complexed to copper (II) : an X-ray diffractometric study on monodomains of (DCBBA)\(_2\) -Cu and (HOBBA)\(_2\)-Cu. Journal de Physique, 1989, 50 (2), pp.113-119. <10.1051/jphys:01989005002011300>. <jpa-00210906>

HAL Id: jpa-00210906
https://hal.archives-ouvertes.fr/jpa-00210906
Submitted on 1 Jan 1989

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
Short Communication

Liquid crystals complexed to copper (II) : an X-ray diffractometric study on monodomains of (DOBBA)$_2$–Cu and (HOBBA)$_2$–Cu

A.M. Levelut(1), M. Ghedini(2), R. Bartolino(3), F.P. Nicoletta(3) and F. Rustichelli(4)

(1) Laboratoire de Physique des Solides, Université de Paris-Sud, 91405 Orsay, France
(2) Università della Calabria Arcavacata di Rende, Department of Chemistry, 87036 Cosenza, Italy
(3) Università della Calabria Arcavacata di Rende, Department of Physics and GNSM (CNR)-CISM (MPI)-INFM unità di Cosenza, 87036 Cosenza, Italy
(4) Università di Ancona, Ist. di Fisica Medica, via Ranieri monti d’Ago, Ancona, Italy

(Reçu le 16 juin 1988, révisé le 24 octobre 1988, accepté le 7 novembre 1988)

Résumé. Une étude par diffraction des rayons X a été menée sur des monodomains de la phase smectique A de deux bases de Schiff complexées par du cuivre : les dérivés dodécyl oxo - et heptyloxy - de la série des Bis-[N-(phényl-butyl)(4n-alkyloxy)-2-salicylidène amino]-cuivre II respectivement (DOBBA)$_2$ Cu et (HOBBA)$_2$ Cu. Par refroidissement de ces monodomains nous obtenons une phase solide orientée sous forme de fibre qui a également été étudiée. Ces études mettent en évidence une organisation des molécules de la mésophase, liée au caractère spécifique des complexes ; nous confirmons le modèle proposé lors d'études préliminaires, où les chaînes paraffiniennes sont, soit imbriquées de couche à couche, soit partiellement fondues. En outre, l'existence de corrélations cuivre-cuivre montre que les molécules sont associées au moins par paire sinon en rubans de taille plus importante.

Abstract. We present the first experimental results of X-ray diffraction on monodomains of two Schiff bases complexed with copper : the (DOBBA)$_2$–Cu : Bis-[N-(phényl-4n-butyl)(4n-dodecyl oxo)-2-salicylideneamino]-Copper(II) and the (HOBBA)$_2$ –Cu : Bis-[N-(phényl-4n-butyl)(4n-heptyloxy)-2-salicylideneamino]-Copper(II), both in the smectic A phase and in a solid-like lower temperature phase. The results give new
insights into the structures of these peculiar liquid crystals: the proposed model of interdigitated layers or of partially melted chains is confirmed; moreover, a copper-copper correlation is found so that the molecules are coupled at least in pairs (or even possibly in larger ribbons) inside the smectic layers.

Stimulated by the constant growth of technological applications demanding new liquid-crystalline materials with peculiar properties, many investigations have been recently devoted to the preparation of new classes of mesogenic species containing transition metals [1-5].

In this field, we reported earlier on the synthesis and the mesomorphic properties of either Palladium (II) azo-complexes [6-8] or Copper (II salicylideneamino compounds [9] of general formulas depicted below:

![Chemical structure](image)

with \( R = C_m H_{2m+1} \) and \( R' = C_n H_{2n+1} \).

Remarkably, some of the uncomplexed Schiff bases give a nematic phase; the corresponding copper complexes show smectic phases only. Therefore, by the incorporation of a metal atom between two organic mesogenic ligands, more ordered mesophases appear. The resulting complexes, in comparison with the starting molecules, display a greater biaxiality. Therefore, the reported behavior can be tentatively ascribed to their molecular shape, which should discourage a highly symmetrical close packing arrangement. In order to gain more details on this point, we have performed a comparative X-ray investigation on unoriented polycrystalline samples of both the uncomplexed and complexed species [10]. Namely, the materials we considered were those having \( n = 4 \) and \( m = 7 \) or 12, thereafter reported as HOBBA, \((\text{HOBBA})_2-Cu\) and DOBBA and \((\text{DOBBA})_2-Cu\) respectively. The data obtained allowed the identification of the actual nature of the smectic mesophases displayed by the copper complexes (Sm.A) together with a qualitative picture of their packing. In particular, as far as DOBBA and \((\text{DOBBA})_2-Cu\) are concerned, the same layer thickness (30.8 Å) was observed, this in spite of their different molecular dimensions (e.g. the length of the fully extended DOBBA and \((\text{DOBBA})_2-Cu\) molecules are 30.8 and 42.4 Å respectively. Therefore, on the basis of this datum, the \((\text{DOBBA})_2-Cu\) packing mode can be visualised as the result of either partially melted aliphatic chains or of an inter-molecular interdigitated arrangement.

In the present letter, we report on the results of X-ray measurements carried on monodomains of \((\text{HOBBA})_2-Cu\) and \((\text{DOBBA})_2-Cu\) oriented by a magnetic field, performed with the aim of drawing quantitative data about the mutual order eventually displayed by the copper atoms. The latter compound has a wider temperature range in mesomorphic state, and we have mainly worked on it. The X-ray device has
already been described [11]. A monochromatic X-ray beam is issued from a double bent graphite monochromator. The sample, held in a Lindemann glass capillary of diameter 1.5 mm, is aligned by a magnetic field perpendicular to the X-ray beam and to the tube axis. The field can reach 1.7 T. The diffracted X-rays are collected on a cylindrical film (axis parallel to the magnetic field). The angle of diffraction is limited to 22° along the direction of the magnetic field and to 60° in the perpendicular direction. The samples are aligned at high temperatures and a typical diffraction pattern of the mesophase is shown in figure 1a. This pattern is characteristic of a Sm.A phase with Bragg spots aligned in a direction perpendicular to the field and with diffuse crescents at an angle of 20° in a direction parallel to the field. Below the temperature of the Sm.A phase, we obtain a fiber pattern of a crystalline phase, figure 1b. We will first discuss the conditions of alignment and thereafter comment on the diffraction pattern.

Fig. 1.— X-ray diffraction pattern of a monodomain of \((\text{DOBBA})_2\)–Cu in (a) the Sm.A phase and (b) in a solid phase. The arrows give the magnetic field direction.

The orientational order of the sample is conserved during any cycle of temperature unless we approach the clearing point by less than 5 K. This means that the viscosity of the mesophase increases with decreasing temperature and becomes very high at low temperatures. The diffraction pattern has a cylindrical symmetry around the tube axis direction; in other words, the director of the Sm.A phase is parallel to the sample holder axis and perpendicular to the field. We have therefore a single do-
main of Sm.A with the director perpendicular to the magnetic field. This unexpected symmetry cannot be explained by the influence of the magnetic field alone. If the anisotropy of the magnetic susceptibility is negative then the director can take any orientation perpendicular to the field. A single domain cannot be obtained without another interaction which must come from the geometry of the sample holder. Our experimental observation implies that the director is parallel to the wall of the Lindemann glass tube. It seems likely that our samples takes a planar orientation on a glass surface. Figure 2 shows how the association of the magnetic field and the wall interaction can induce a single domain of Sm.A phase; nevertheless, other observations are needed in order to check the magnetic and the anchoring properties of such molecules.

Fig. 2.— Sketch illustrating the constrains imposed by the walls of a circular tube and by a magnetic field \( H \), upon the director of a Sm.A phase. Point A is well inside the tube; B and C are close to the walls. Double arrows schematize the director in the figure plane and crosses characterize an orientation perpendicular to that plane. It is obvious that only a uniform orientation perpendicular to that plane satisfies to the boundary conditions everywhere.

Diffraction patterns are obtained under magnetic field (Fig. 1a), but X-ray experiments have also been performed on a Guinier camera, both on powder and oriented samples. In the latter case, we have not seen any diffracted intensity at angles higher than 22° in the equatorial plane. The diffraction pattern of the mesophase can be seen fully in figure 1a. As we have already pointed out, this pattern is characteristic of a Sm.A phase with a layer periodicity of 31 Å for \((DOBBA)_2 - Cu\) and 24.7 Å for \((HOBBA)_2 - Cu\). This periodicity is the same for the free ligand Sm.A phase (respectively DOBBA and HOBBA) and corresponds to the length of an extended free organic molecule. In fact, two kinds of differences appear between the pattern of a usual Sm.A phase and the pattern of figure 1a. Along the meridian axis, one sees at least two orders of reflection. For monolayered Sm.A phases of organic smectogen molecules similar to the ligands HOBBA or DOBBA, the average modulation of the electronic density is nearly sinusoidal and only one order reflection is seen [12]. We can assume that the contribution to the diffracted intensity issued for the organic ligands are more or less restricted to the first Bragg peak. Therefore, the high order reflections are mainly due to copper and the decrease of these intensities due to the static or dynamic disorder of the copper atoms. The corresponding Debye-Waller fac-
tor leads to a displacement standard-deviation of 4 Å in the direction of the director of the Sm.A phase.

On the equatorial plane, one sees a very weak diffuse crescent. The maximum of the intensity corresponds to a wave vector of \((2\pi/8.5) \, \text{Å}^{-1}\). The occurrence of diffraction issued from the harmonic wavelength \(\lambda/2\) has been ruled out by using suitable filters. The intensity profile of the diffracted intensity measure in the equatorial plane must contain mainly three terms which are related to the C-C, C-Cu and Cu-Cu correlation functions: the first two correlation functions are similar to the usual C-C correlation function in a liquid crystalline phase nematic or smectic A. Therefore, the intensity maximum at \(q = (2\pi/8.5) \, \text{Å}^{-1}\) must be related to the copper-copper interferences. Let us assume that the molecular section of the complex in the smectic plane is a rectangle of \(\sim (4 \times 9) \, \text{Å}^2\) labelled on its center by a copper atom. If such rectangles form an ideal isotropic liquid, the nearest neighbouring Cu-Cu distances will show a large distribution between 9 and 4 Å. Under such conditions, the diffracted intensity will be continuous between \(q = 2\pi/9 \, \text{Å}\) and \(2\pi/4 \, \text{Å}\). The existence of a weak peak at 8.5 Å gives some consistency to the existence of some kind of short range nematic ordering in the smectic layer: the largest edges (8;5) are locally parallel and pairs of complexes can be formed by fitting their narrowest faces (Fig. 3a). The existence of a more pronounced nematic ordering (concerning the cross section of the complexes) is questionable since the contribution of the Cu-Cu pair to the scattered intensity is weak. Further information can be derived from a very qualitative description of the molecular array in the low temperature phases.

![Diagram of molecular structure](image)

**Fig. 3a.—** Formation of a pair of complexes which promotes a Cu-Cu distance of about \(b = 8.5 \, \text{Å}\).

Oriented patterns of the low temperature phases are only obtained for DOBBA compounds: a fiber pattern with its axis of symmetry parallel to the tube axis is obtained. In fact, several phase transformations have been detected from optics and DTA measurements [6, 8]:

\[
\text{Solid} - \rightarrow 90 - \rightarrow \text{Sm.E} - \rightarrow 98 - \rightarrow \text{Sm.B} - \rightarrow 114 - \rightarrow \text{Sm.A} - \rightarrow 140 - \rightarrow \text{isotropic}
\]

but they correspond to very slight modifications of the X-ray pattern and we will only discuss the structure of the phase that is stable between 98 °C and 114 °C.
Taking \( c \) parallel to the fiber axis, one can assign the various reflections, and by comparison with the powder pattern we can deduce that the lattice is orthorhombic with \( a = 20.3 \, \text{Å}, b = 8.60 \, \text{Å} \) and \( c = 30.22 \, \text{Å} \) at 100 °C. The unit cell volume contains four complexes with a specific mass of 1.13 g cm\(^{-1}\). In fact, no reflections lying out of the \((h 0 l)\) reciprocal planes are seen on the powder patterns and only weak \((h k 0)\) reflections \((k \neq 0)\) are seen on the fiber patterns; moreover, they are elongated along the \( c^* \) axis. It is clear that this phase cannot be a usual Sm.B phase. Nevertheless, some disorder is still present in the \((100)\) planes. Taking into account this disorder and the fact that \( b \) is comparable to the width of a complex, we can give a schematic image of the projection of the structure on a \((b, c)\) plane: molecules form ribbons parallel to the \( b \) axis, but different ribbons are not in phase in the \( c \) direction (see Fig. 3b). The transition towards the mesophase Sm.A implies a melting of the paraffinic chains and an orientational disordering of the molecules around their long axis. Moreover, the disordered state in the \((b, c)\) planes of the crystalline structure fits pretty well with the sketches which have been proposed in the preliminary studies of the Sm.A phase [10].

![Illustration of the disorder of the lamellar crystalline phase (at 100 °C) in a (100) plane. \( a = 20.03 \, \text{Å}, b = 8.60 \, \text{Å}, c = 30.22 \, \text{Å}.\)](image)

To conclude, the results we have obtained can be summarized as follows:

1) The diffraction pattern of the \((\text{DOBBA})_2\text{Cu}\) and of \((\text{HOBBA})_2\text{Cu}\) Sm.A mesophases, contrary to the Sm.A usually observed, shows second order reflections along the meridian axis of diffraction. These high order reflections are due to the labelling by copper atoms which are localised around the medium plane of the layer within ± 4 Å.

2) In the smectic layers, according to the measurements carried out along the axis
lying on the equatorial plane, a short range interaction between the metal centers appears; thus, the molecular packing can be described in terms of pairs of molecules in a side-by-side array.

3) The X-ray investigations performed on a lower temperature phase give confirmation of the qualitative models wherein the molecules have partially melted aliphatic chains or are interdigitated, as previously reported.

Finally, in order to elucidate better the actual molecular structure of these new mesophases, EXAFS, anomalous X-ray scattering and neutron scattering measurements are currently under way.

Acknowledgements.

The authors want to thank S. Armentano for the preparation of the compounds, G. Torquati for helpful discussions and A. Braslau for reading the English manuscript. One of us (F.R.) thanks the CNR for supporting this international cooperation.

References