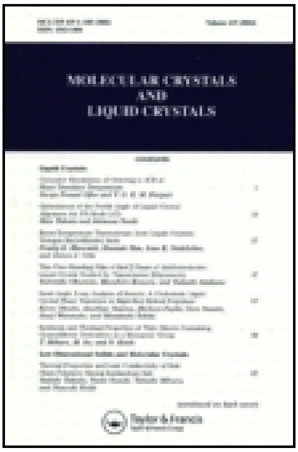

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Molecular Organization in Metallo-Organic Mesophases: Methods of Investigation and Specific Features

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MOLECULAR ORGANIZATION IN METALLO-ORGANIC MESOPHASES METHODS OF INVESTIGATION AND SPECIFIC FEATURES

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Abstract. During the last five years a lot of new metallo-organic mesogens have been synthesized. The molecular architecture is more or less modified by the metallic atom and therefore the molecular organization in the columnar, smectic or nematic mesophases containing metals is specific of this new kind of mesogens. We present a comparative study of various series of metallo-organic complexes. In these complexes one (or two) metallic atoms link two (or more) identical mesogenic ligands; the structural features of the mesophases depend on the nature of the metal bridge, and of the length and the nature of the ligand. It is also possible to compare, in their respective mesophases, the organization of the complex to that of ligand alone. The global molecular shape is derived from usual X-ray diffraction experiments. Taking into account some features of the diffraction pattern related to the metal atoms ordering, it is possible to describe the molecular environment. The short-range ordering depends of the nature of the complex. Moreover, there are specific methods of investigation of the metal environment: the comparison of variable wavelength X-ray scattering experiments and neutron scattering experiments might give access to the metal-metal pairs correlation function. At last, by X-ray spectroscopic methods (EXAFS and XANES), it is possible to investigate the close neighbouring of the metallic atom.

Keywords: metallo-organic mesophases, structure, x-ray diffraction

I. INTRODUCTION

Thermotropic liquid crystals are generally obtained with organic molecules of anisotropic shape. The introduction of a metallic atom on a mesogen can, if the mesogenic properties are preserved, supply a new kind of liquid crystals, the properties of which are related to the nature of the metal. The first known metallo-organic mesogens derive from lyotropic LC since dry salts of fatty acids form a great variety of thermotropic mesophases with several geometries (lamellar cylindrical)[1]. To our knowledge the first known rod-like transition metallomesogens were some mercury[2] and some ferrocene[3] derivatives. Contrariwise some disc-like molecules, the phthalocyanines[4] and porphyrins[5] octasubstituted with long paraffinic chains form columnar phases as well in their initial form as well when complexed by various metals. Cu complexes of fatty acids which are not at all of disc shape form also columnar mesophases.[6] Recently, the number of metallo-organic mesogens had increased drastically. Starting from simple organic mesogens a complexation, which generally links two identical ligands, induces new metallo-organic smectogenic and nematogenic compounds. Some series of such metallo-organic molecules have been studied using various methods of structural analysis. The number of these new compounds is now sufficient in order to give some basis to a comparative description of the molecular organization of the complexes in the mesophase.

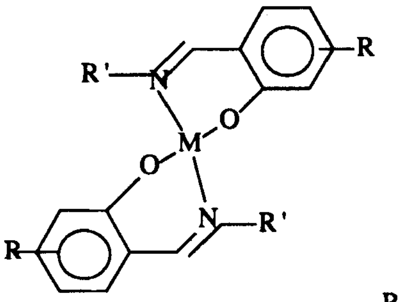
In this paper we will mainly focus our attention on nematic (N), smectic A (S_A) and smectic C (S_C) mesophases.

The first part describes the chemical architecture of the complexes, the geometry of the close neighbouring of the metal and the impact of these features upon the mesomorphism of the complexes.

In the second part, we give a description of the molecular organization in a direction parallel to the director while the third part describes the transverse ordering, finally, we give an insight over future experiments taking advantage of the X-ray or neutron scattering properties of the metal atoms.

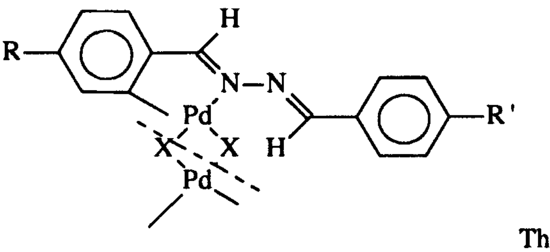
II. CHEMICAL ARCHITECTURE AND MESOMORPHISM

Among the great variety of new metallo-organic mesogens only very few of them have been studied by X-ray diffraction methods.Here we consider two classes of molecules. In the first one, two identical Schiff base ligands are complexes with one metallic atom. The general formula is:[7-9]



R and R' can be simple alkyl or alkoxy chains, or more complex groups with an aromatic part, M is a transition metal. The geometry of the close neighbouring of the metal is an important parameter. The two ligands cores of a complex are roughly parallel when the four oxygen and nitrogen atoms are in a planar square configuration while there are nearly perpendicular one to each other in case of a tetrahedral configuration. However, the flexibility and the size of the R' group have also to be considered. As an example, two homologous series with R = $C_nH_{2n+1}O$ ϕ COO- and R'=-ϕC_4H_9 present mesomorphic properties when complexed with Cu(II), and Pd(II) while no mesogen was detected in the same series complexed with Ni(II).[9] In order to explain such a difference, it was assumed that the configuration of the close neighbouring of the Ni (II) may be non- planar contrariwise to the case of Cu (II) and Pd(II). Another comparative study of complexes of Ni(II), $(VO)^{2+}$, Cu(II),Pd(II), with R = $C_{10}H_{2n+1}$-O-ϕ-COOR' = C_nH_{2n+1}- or CH_3ϕ-[10] correspond to a different conclusion since the four kinds of complexes present the same mesophases. However in this last case X-ray spectroscopic experiments performed at room temperature show that the Ni environment is planar square.[11]

The second class concerns binuclear complexes of Pd. The general formula is:[12,13]



The double Schiff base bridge can be replaced by a diazo bridge, X is an halogen or a carboxylato group $C_nH_{2n+1}COO$.

It is obvious that, due to the symmetrical configuration of the ligand core, the complex is generally a mixture of two isomers the composition of which can be characterized by spectroscopic methods.[14] In this kind of complexes, the long axes of the two ligands are parallel one to each other. However, the plane of each core including Pd can rotate around the X - X axis. When X is an halogen the dihedral angle between the two identical parts is 180° and the whole complex has a platelet shape whereas, when X is a carboxylato the dihedral angle is smaller and the complex has an open book shape.[14] The Pd-Pd distance will be dependent of the complex configuration and the different configurations can be checked using spectroscopic EXAFS methods.

In the case of $X = C_nH_{2n+1}COO$ it is expected that the aliphatic chains grafted at the center of complex units have an impact upon the mesomorphic properties and it was effectively shown that, complexes of intermediate chain length are only nematic on a very short temperature range, while with a short or a long chain, a SmC nematic polymorphism was observed . The first methylene groups points more or less perpendicularly to the axes of the book and therefore in a first step and increase of the number of CH_2 groups will destabilize the mesomorphic organization. In a second step due to the flexibility of the aliphatic chain, the end groups are parallel to the director and therefore the trend to nematic or smectic ordering is enhanced again.[14]This kind of behaviour have been also observed for simple organic mesogens,[15] moreover the longer the alkyl chains of the carboxylato groups are, the stronger is the aliphatic- aromatic segregation. In fact there is, in general, no direct experimental evidence of the conformation of the metal complex in the mesophase. However, the intermolecular ordering is also dependent of the shape of the complex and indirect information can be obtained from X-ray diffraction experiments.

Before giving the conclusions derived from these experiments, let us recall that the obtention of aligned samples, is a preliminary condition for a meaningful interpretation of the data. In many structural experiments these samples are obtained by the action of a magnetic field, nevertheless two kinds of difficulties can occur: Firstly, if the anisotropy of the magnetic susceptibility ($\chi_{//} - \chi_{\perp}$) is negative (which is the case for some copper derivatives[10,16]), one must apply the field in two perpendicular directions in order to have a unique director orientation perpendicular to the two field directions. Secondly, the viscosity of the smectic phases is higher than for similar mesophases of simple organic molecules and good alignements are obtained exclusively either in the nematic phase (if there is one) or just below the clearing point in the case of a smectogenic compound. Therefore the chemical stability of the complex must be still fair at the clearing temperature and in fact it is not the case for many complexes of $Pd_2X_2L_2$ where X is a halogen.[12,13] For these reasons the structural information upon the smectic phases of many Pd derivatives is rather poor.

III. MOLECULAR ORDER IN THE DIRECTOR DIRECTION

The different X-ray patterns (Fig. 1) of aligned samples are typical of the corresponding mesophases. In nematic phase, there is a first low angle diffuse arc indicative of local smectic ordering. If this arc is centered around the director direction (meridian) the fluctuations are of S_A type while approaching a S_C phase this arc splits into two spots located symmetrically on each side of the meridian. In both cases the component of the corresponding wave vector along the director measures the apparent length of the molecules. In S_A and S_C phases the diffuse spots become sharp corresponding to a long range periodicity. The wave vector length is inversely proportional to the layer thickness. For a S_A this is a measure of the apparent molecular length. In general in a S_C phase the degree of orientation is not sufficient to allow a good measure of the angle between the director and the layer normal (tilt angle). Therefore the apparent length and the tilt angle are measured in the nematic phase in the vicinity of the transition towards the SmC. The apparent molecular length is an important parameter in all mesophases since it can be related to the global shape of the molecules. The complex molecule has the shape of a H with four branches of inequal length which are symmetrical with respect to the metal center located on the horizontal bar of the H. Therefore the measured apparent molecular length has to be compared to two lengths: that of the ligand - i.e. one side of the H - in an extended conformation or in its own mesophase (if there is one), and that of the complex which is indeed roughly equal to twice the length of the largest branch of H. In fact, if the complex has a well defined H form, with sufficiently large branches, the

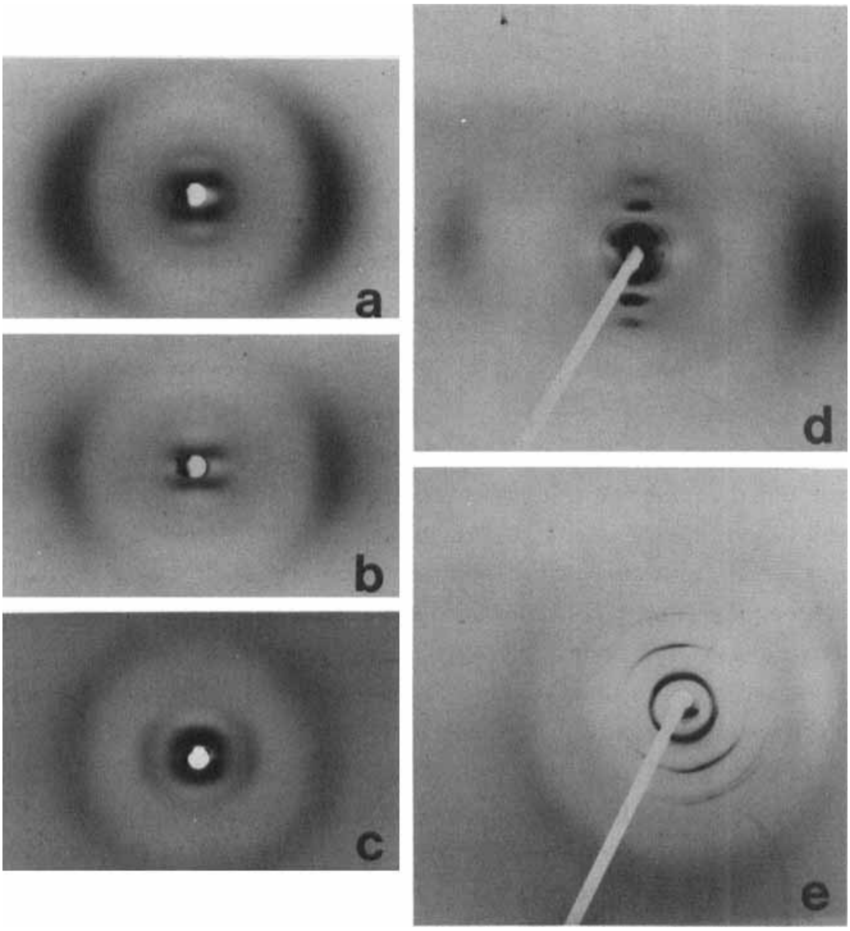


Fig. 1.

X-ray diffraction patterns of metallo-organic mesogens (the magnetic field is along the vertical direction)

a-c complexes $M L_2$ in the nematic phase

a) $L = C_{10}H_{21}O\text{-}\varphi\text{-}COO\text{-}\varphi(OH)\text{-}CH{=}N\text{-}C_5H_{11}$ $M = (VO)^{2+}$

b) L = " " " " " M = Pd(II)

c) $L = C_{10}H_{21}O\text{-}\varphi\text{-}COO\text{-}\varphi(OH)\text{-}CH{=}N\text{-}\varphi\text{-}CH_3$ M = Ni(II)

d) complex $Pd_2Cl_2\ (CH_3\text{-}\varphi\text{-}N = N - \varphi\text{-}OC_{12}H_{25})_2$ in the S_A phase

e) complex $(C_8H_{17}NH_2)_2Ag^+BF_4^-$ in the S_A phase apparent length in the mesophase of the complex is comparable to that of the ligand, that corresponds to an imbrication of paraffinic chains at the interface between two layers (Fig.2a).The complexation induces an increase of the mean chain area and, an additional contraction of the layer thickness comes from the molten state of the chain, consequently, the apparent length is generally slightly smaller than in the ligand mesophase (Fig. 3). Moreover, this length varies slightly with the complexing unit.

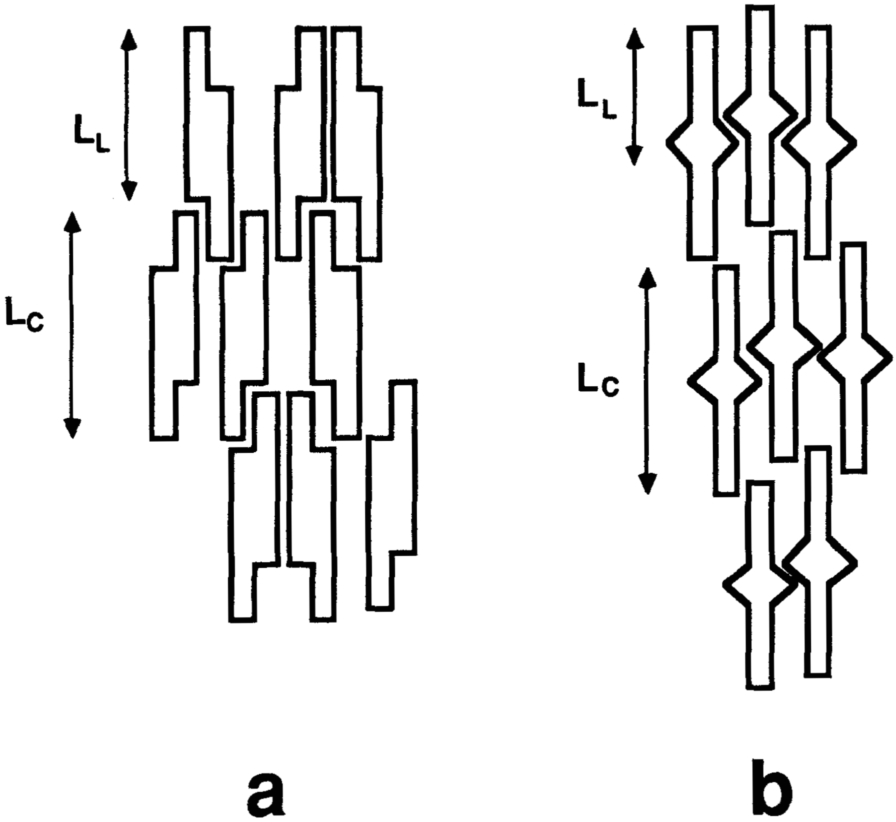


Fig. 2 –Schematic representation of the molecular stacking along the director a) large ligands, b) short ligands. L_L and L_C are respectively the lengths of the ligand and of the complex in a fully extended conformation

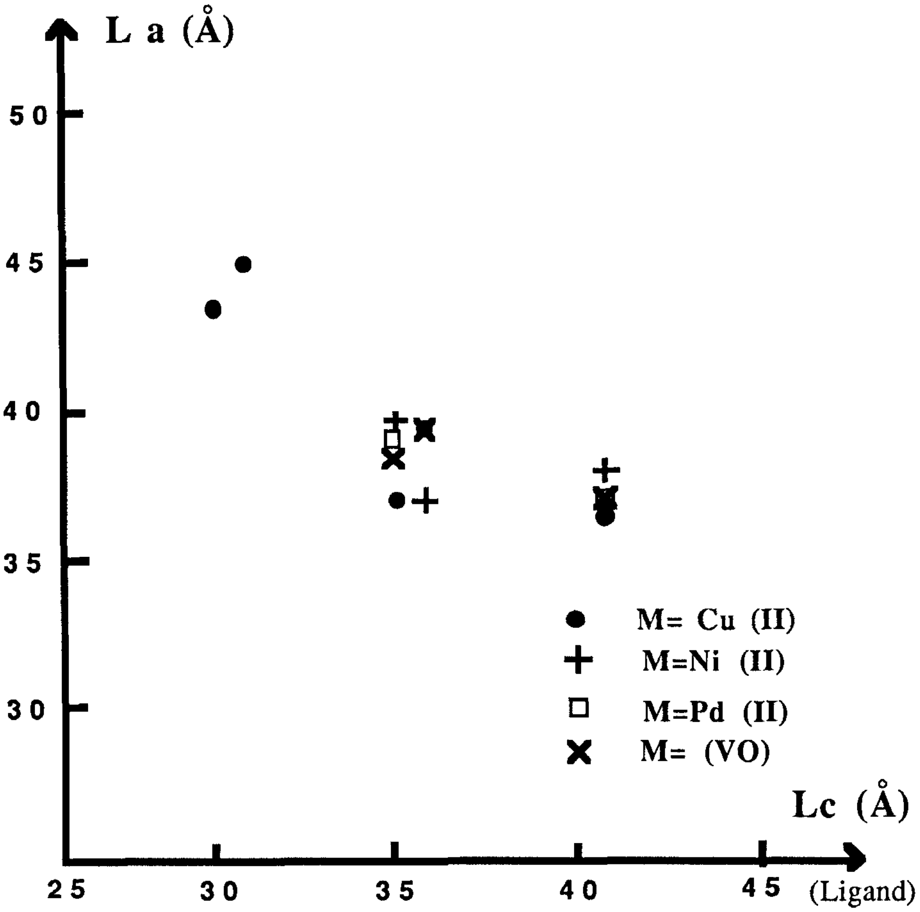


Fig. 3 – Variation of the apparent length La,of ML_2 complexes with the ligand length Lc,measured on models in an extended conformation. The complex calculated length is equal to 53Å for all the compounds.

This is well illustrated in the case of Pd complexes where X is a carboxylato. In Table I, we see that the the apparent length of the complex in the mesophase increases as the length of the carboxylato group is increasing.[17] When two of the four branches of H are very short, the global shape of the complex is close to that of a rod (Fig. 2b) and the apparent length is nearly equal to the complex length (Fig.3). In fact, the metal which links two ligands has a pairing effect similar to the pairing effect induced by dipolar interaction in smectogenic organic molecules with a strong longitudinal dipole. In both cases, the apparent length is comprised between one and twice the ligand length. However the dipolar pairing is flexible, inducing a continuous or discontinuous temperature dependence of the layer thickness, while in metallomesogens the two ligands are tight rigid .The role of the metal bridge is not obvious (Fig 3,4). In fact we see on Fig.4 that the behaviour of CuL'_2[18] and $Pd_2Cl_2L_2$[19] complexes with very similar organic moieties,but with metal bridges of different sizes are however similar. Contrariwise, (see Table I), the increase of the length of the carboxylato group fixed on this bridge seems to reduce the mean chain area (21 $Å^2$ for the longest bridge), as far as we can give a good estimation of it .

Table I

Structural features (in Å) of the mesophases of some $Pd\ X_2L_2$ derivatives with

$L = C_{10}H_{21}0\text{-}\Phi\text{-}CH = N\text{-}N = CH\text{-}\Phi\text{-}0C_{10}H_{21}$

L_a is the apparent length, and d_1 and d_2 are related to the wave vectors q_1 and q_2 for the two equatorial halos by the relation $q = 2\pi/d$. The mean molecular area $A(Å^2)$ corresponds to the area in a plane perpendicular to the director. The values here reported are deduced from roughly estimated densities ρ (gcm^{-3}) reported in the last column.

X	mesophase	L_a	d_1	d_2	A	ρ
B_2	S_A	32.5	8	4.4	53.0	1.3
C_2H_5COO	S_C	34.5	8.6	4.2	55.2	1.1
C_3H_7COO	N	34.5	8.6	4.2	55.9	1.1
$C_{15}H_{31}COO$	N	37	8.6	4.5	64.2	1

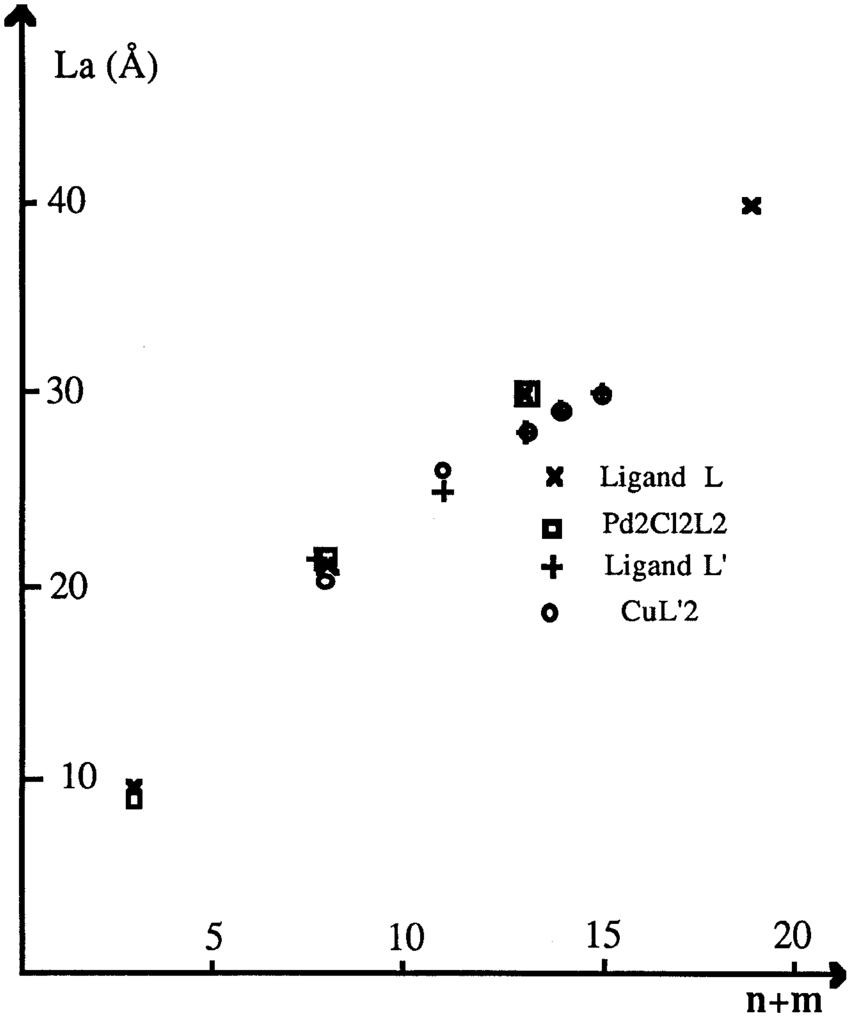


FIG.4. Apparent length La, of the complexes and of the ligands versus the total chain length of the ligands m+n.

a) $Pd_2Cl_2L_2$ and $L = C_nH_{2n+1}$-Φ-N = N-Φ-O C_mH_{2m+1} (nematic)

b) Cu L'2 and L' = $C_nH_{2n+1}O$ -Φ(OH)-CH = N-Φ-C_mH_{2m+1} (Smectic A)

Another point can be underlined about the longitudinal organization. For usual S_A and S_C phases one generally sees only one order of reflection on the layer planes. The higher orders being of very weak intensity. The electronic density profile along the normal to the layer is thus nearly sinusoidal-like. The origin of such a smooth profile can be found in the thermal fluctuations of conformation and position. The contrast which is mainly due to the difference between the electronic density of the aromatic moiety and that of the paraffinic ends is smeared out by fluctuations of large amplitudes (of the order of the core length). For organo-metallic smectic phases we observed generally at least three orders of reflection on the layer plane. Moreover, the relative intensities of the reflections depend of the metals and the highest order are more intense with Pd(II) or Ag(I) complexes than with Cu(II), Ni(II) or $(VO)^{2+}$ complexes. It is clear that the metal atom gives a peak in the electronic density profile the amplitude of which is dependent of the nature of the atom. Nevertheless, the fluctuations of the metallic atom position limit the number of observed Bragg reflections. A localization of the heavy atoms within a sublayer of one third of the total layer thickness seems to be consistent with the experimental observations but, in fact, a contribution due to H form of the complex cannot be excluded. In order to have a better estimation of the different terms, it will be necessary to vary the contrast between the organic part and the ligand part. The possibilities of contrast variation methods will be developped in the discussion following the next part in which we consider the local ordering in a plane perpendicular to the director.

IV.THE MOLECULAR ORGANIZATION IN A PLANE PERPENDICULAR TO THE DIRECTOR

The complexation by a metal is obviously active on the molecular organization in a plane perpendicular to the direction (equatorial plane) since the organic cores are rigidly linked two by two. If we do not take into account the orientational fluctuations of the director, a single complex has, in a plane perpendicular to the director (equatorial plane), a rectangular section of approximatively 10 x 5 Å size. The center of the rectangle is labelled by the metal. At a first glance, we can classify the diffraction patterns (see Fig 1) into two classes. In the first one, the diffracted intensity shows only one maximum in the equatorial plane for a wave vector $\sim(2\pi/4.5)$ $Å^{-1}$(Fig.1a,b). In the second class (fig. 1c) a second diffuse arc of weaker intensity appears for a wavevector of the order of $(2\pi/9)$ $Å^{-1}$. The position of this second maximum is slightly dependent of the compound and the wave vector varies between (2π/9.5) and (2π/8) Å^{-1}. The interpretation of this second arc is rather clear since the interferences come from pairs of atoms at a distance large compare to the ligand diameter. This maximum is mainly due to metal-metal pairs and the presence of the inner arc shows that large intermetallic distances are favoured.[16] The rectangular section of the complexes form a nematic-like ordering with formation of a side-by-side array (Fig. 5a). Moreover, EXAFS experiments, performed on the S_A phase of a Cu complex[20] -which exhibits a diffraction pattern of the second kind- have put in evidence Cu-Cu pairs at a distance of 3.8Å. This very short distance corresponds to a in-plane close packing of Cu atoms in a direction perpendicular to the ribbons formed by complexes aligned in a side-by-side array. Let us notice that the low symmetry properties of this local array do not extended over a large scale, the mesophase being globally uniaxial, moreover the diffraction pattern of the biaxial nematic phase of a Cu complex is different since the two characteristic distances in the equatorial plane are 24 and 47 Å.[21]

For binuclear Pd derivatives, the diffraction pattern is somewhat more complex since maxima in the diffuse scattering intensity appear in the range of (2π/9)Å^{-1} both in equatorial and meridian direction. This diffuse scattering ring takes generally an elliptic shape[17] but in the case of some S_A phases the ring is condensed into four spots localized out of the meridian and joined two by two by arcs centered on the equatorial plane (Fig 1d). A complex organization of the Pd_2X_2 bridges appears in which neighbouring bridges are located on each side of the median plane of the layer, at a distance of about 5Å of this plane. This kind of array exists as well for book-like structures as for planar ones.

The first kind of X-ray pattern (Fig.1a,b) which, at a first glance, shows no noticeable differences with that of usual organic LC is encountered in mononuclear complexes of Cu(II), Ni(II) or $(VO)^{2+}$ which present only a N-S_C polymorphism, without any S_A fluctuations. The organization of the rectangular sections of the complexes is more disordered than that previously described: neighbouring complexes are not parallel and the interferences coming from metal-metal pairs contribute to a background of wave vectors shorter than 2π/4.5 Å without any defined structure. In fact, in both cases every progress in the knowledge of the local ordering needs contrast variation experiments in order to make a distinction between the three basic contributions - metal - metal, metal-organic and organic-organic - to the pair correlation function. Another important point which can be clarified by the same kind of technics is the impact of the complexation upon the orientational order. Up to now, we have discussed the local order of rigid complexes. Let us remark that the S_A mesophase has been detected in salts of flexible complexes of Ag(I).[22] The X-ray pattern of the S_A phase (Fig. 1e) reveals a layer structure with an in-plane square local ordering of the Ag atoms and of the chain since two diffuse arcs at 6.3 and 4.5 Å are seen (Fig.5c). This structure is the fluid equivalent of the square $L\delta$ phase of some phosphatidylcholines lyotropic mesophases.

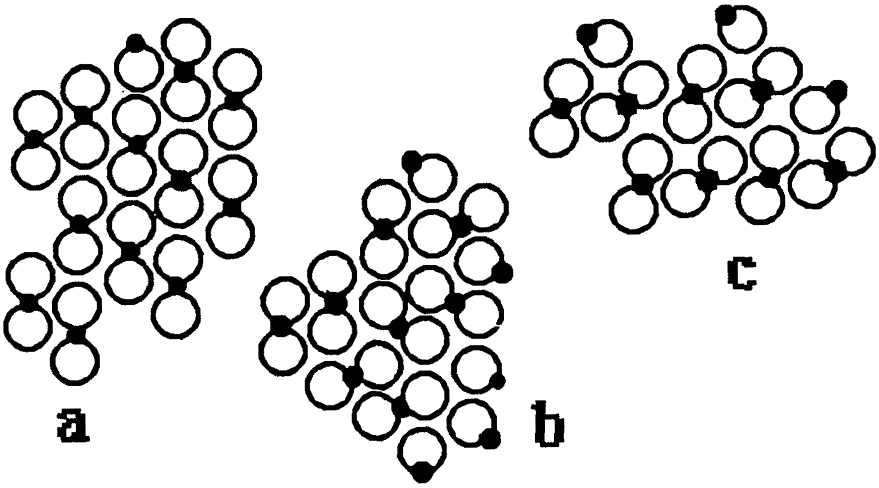


Fig. 5- Schematic representation of the different local molecular arrays in a plane perpendicular to the director. The open circles represent the organic ligands and the black points the metal atoms. a) a side-by-side array; b) an orientationnally disorderd array; c) a square array observed in ionic compounds.

V. CONCLUSION

The complexation of organic molecules with metals offers a large variety of mesogenic units. Some of these units keep the global shape of an organic mesogen.

Columnar mesophases are obtained with complexes of phthalocyanines[4] substituted by eight chains; simple aliphatic carboxylate forms columnar chains when four of them are associated to two copper atoms.[6]The association of two rigid rod-like units by a metal center keeps or even enhanced the mesogenic potentiality of the ligands. However, a specific ordering is developped taking into account the global shape of the complex and the short range metal-metal interactions. Up to now, this ordering has been only studied on a very qualitative point of view. As pointed out above it is possible to use contrast variation methods which will provide a better insight of the particularity of the metal ordering in the mesophase. The scattering amplitude of any radiation is dependent of the nature of the atom. With X-ray, this amplitude is, far from any absorption edge, proportional to the number of electrons of each atom. The absorption measures the imaginary part of a dielectric constant while the amplitude of diffraction (atomic scattering factor) is the real component of this dielectric constant of the wavelength. These two components are linked by a Kramers-Krönig relation, therefore,near an absorption edge, the imaginary part increases quickly with the wavelength and in the same range the atomic scattering factor changes (of about 30% maximum). K absorption edges of the first transition line elements are in the range of 2 - 1.3Å which is easily obtained with X-ray synchrotron sources. For elements such as Pd or Ag, the absorption edges are close to 0.5Å and can be still accessible. Successive diffraction profiles obtained for wavelengths near the K absorption edge of Cu with a Cu complex have been obtained at L.U.R.E.[23]. These preliminary experiments show clearly measurable changes in the diffraction patterns. The difference between two curves takes into account only interferences between a copper center and the whole environment. Such experiments would also provide interesting information on the orientational order of Cu-Cu pairs.

Another method uses isotopic substitution with neutrons: since the neutrons are scattered mainly by the nuclei, the scattered length depends on the isotope used in the experiment. If the classical H-D substitution implies the synthesis of new organic molecules and is at all not easy, the use of metallic compounds of suitable isotopic composition could be very simple. As an example when the scattering length of two isotopes have opposite signs, it is possible to have a non-scattering isotopic mixture. The nickel is known to give a zero scattering isotopic mixture, therefore the scattering properties of the ligands in the complex can be explored alone and compared to the non complexed ligands in the same mesophase; translational and orientational order of the organic part of a Ni complex can be analysed in an experiment of this kind.

At last, spectroscopic EXAFS method gives the close neighbouring of the metal atom within a range of 2 - 4Å. Therefore, this can bring new insights upon mesophase organization.

Acknowledgements

This work stems from a collaboration with colleagues of Zaragoza (Spain) and Cosenza (Italy). I thank the members of these two groups for the fruitful exchanges and discussions that we had together. A special thank is due to Dr. Joaquim Barbera who took an active part to the work performed at Orsay with enthusiasm and brightness. Finally, despite their preliminary aspect I am sure that experiments performed at L.U.R.E. will be decisive for the orientation of the structural work on metallo-mesogens in the near future. I acknowledge E. Dartyge, G. Tourillon, the EXAFS team, and C. Williams for introducing me to the synchrotron experiments.

REFERENCES

1. V. Luzzati, Biological Membranes edited by D. Chapman (Academic Press) London p.71 (1968)
2. D. Demus, H. Demus, H. Zarchke, Flüssigekristalle in Tabellen, Ed. VEB Deutsche Verlag für crundstoffe industrie (Leipzig), p. 273 (1974)
3. J. Malthête, J. Billard, Mol. Cryst. Liq. Cryst. Lett. 34, 117 (1976)
4. K. Ohta, L. Jacquemin, C. Sirlin, L. Bosio, J. Simon, New J. Chem. 12, 751 (1988)
5. P. Doppelt, S. Huille, New J. Chem., 14, 607 (1990)
6. A.M. Giroud Godquin, J.C. Marchon, D. Guillon, A. Skoulios, J. Physique Lett., 45, 681 (1984)
7. M. Ghedini, S. Armentano, R. Bartolino, G. Torquati, F. Rutichelli, Solid State Commun., 64, 1191 (1987)
8. M. Marcos, P. Romero, J.L. Serrano, J. Barbera, A.M. Levelut, Liq. Crystals, 7, 251 (1990)
9. E. Bui, J.P. Bayle, F. Perez, L. Liébert, J. Courtieu, Liq. Crystals, 8, 513 (1990) and E. Bui - Thèse de l'Université d'Orsay (1990)
10. J. Barbera, A.M. Levelut, M. Marcos, P. Romero, J.L. Serrano, Liquid Cryst. in press
11. XANES results obtained at L.U.R.E. (unpublished)
12. J. Barbera, P. Espinet, E. Lalinde, M. Marcos, J.L. Serrano, Liquid Crystals, 2, 833 (1987)

13. M. Ghedini, S. Armentato, R. Bartolino, F. Rustichelli, G. Torquati, N. Kirov, M. Petrov, Mol. Cryst. Liq. Cryst., 151, 75 (1987)
14. P. Espinet, E. Lalinde, M. Marcos, J. Perez, J.L. Serrano, Organometallics, 9, 555 (1990)
15. W. Weissflog, A. Wieglelben, D. Demus, Mater. chem. Phys. 12, 461 (1985) and W. Weissflog, D. Demus, Mol. Cryst. Liq. Cryst. 129 235 (1985)
16. A.M. Levelut, M. Ghedini, R. Bartolino, F.P. Nicoletta, F. Rustichelli, J. de Phys. France, 50, 113 (1989)
17. P. Espinet, J. Perez, H. Marcos, M.B. Bos, J.L. Serrano, J. Barbera, A.M. Levelut, Organo metallics, 9, 2029 (1990)
18. G. Torquati, O. Francescangeli, M. Ghedini, S. Armentano, F.P. Nicoletta, R. Bartolino, Nuovo Cimento, 12 D (1363 (1990)
19. M. Ghedini, Mol. Cryst. Liq. Cryst. this Vol
20. G. Albertini, A. Guido, G. Mancini, S. Stizza, M. Ghedini, R. Bartolino, Europhysics Letters, 12, 629 (1990)
21. S. Chandrasekhar, V.N. Raja, B.K. Sadashiva, Mol. Cryst. Liq. Cryst. Lett. 7 65 (1990)
22. J. Barbera, J.L. Serrano, A.C. Albeniz, P. Espinet, M.C. Lequerica, J. Lopez Marcos, A.M. Levelut, L. Liébert, in preparation
23. Preliminary anomalous scattering experiments performed at L.U.R.E.