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New Liquid Crystalline Compounds Containing Transition Metals

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Abstract A survey on the syntheses and mesomorphic properties of some organometallic or coordination transition metal complexes is reported. In particular, this review is dealing with palladium (II) complexed with three different classes of azobenzene ligands namely p-alkoxy(or p-alkyl) p'-ester azobenzenes,p-alkoxy-p'-alkylazobenzenes and p-alkoxy-phenil azo benzenes. A preliminar account on the synthesis, characterization and structural properties of a series of smectic copper (II). Schiff bases coordination compounds, together with a simple molecular model, is also presented.

Introduction

The synthesis of new liquid-crystalline compounds incorporating transition metals is constantly in progress and an increasing number of reports on such a subject is now appearing in the literature (1,4). In this field, with the aim of investigate on materials having anisotropic electric and magnetic properties few years ago we undertook an expletive study on the palladium (II) organometallic complexes arising from the reactions between the palladium salt K_2PdCl_4 and mesomorphic p-alkoxy (p-alkyl) p'-ester azobenzenes. Stimulated by the first encouraging result we obtained, subsequently we have extended such investigations to other classes of azoderivatives as well as to the coordination compounds formed from Schiff bases and first raw transition metals.

In this paper we briefly review the early studies carried on the palladated liquid crystals and report on both a new class of palladium containing p-alkoxy p'-alkylazobenzenes and on some preliminary results concerning the physical properties of a smetic bis-(salicydencaminato) copper (II) complex.

1. Palladium (II) organometallic complexes

1a) p-Alkoxy (or p-alkyl)-p'-esterozobenzene complexes.

Potassium tetrachloropalladate and the above mentioned liquid crystals, organic in nature, in the reaction conditions described by Sickman and Cope (5) give rise to the dinuclear cyclopalladated complexes of general formula depicted in Figure 1 (6).

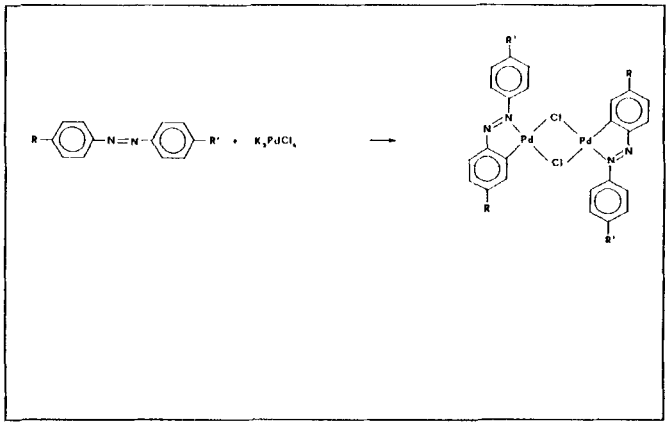


FIG.1 Schematic picture of the reaction of the Alkoxy(or Alkyl)-esterazobenzenes free ligands(on the left) with Potassium tetracloropalladate, leading to the complexes on the right side.

The synthetised compounds display mesophases in the region of 200°C, some 100°C higher than those for the related free ligands, as shown in table I, when the transition temperatures of both the uncomplexed azocompounds and of their organometallic derivatives are reported for comparison purpose.

Unfortunally, the palladated liquid crystals display mesophases at temperatures

TABLE I

Are reported the transition temperatures of the free ligands of fig 1 and of the corresponding complexes; the used free ligands contain the following R-R' chains: #1) R = C_2H_5O, R' = C_4H_9COO; #2) R = C_2H_5, R' = $C_5H_{11}COO$; #3) R = C_2H_5O, R' = $C_6H_{13}COO$; #4) R = C_2H_5O, R' = $CH_2=CH(CH_2)_8COO$

K = solid, N = nematic, Sa = smectic A, Sb = smectic B, Se = smectic E, I = isotropic

	FREE LIGAND	PALLADIUM-COMPLEX
#1	K----78 N----126 I	K----212 N----215 I
#2	K----73 N----127 I	K---------210 N----225 I 140 200 Sb 190---SA
#3	K----59 N----112 I	K----190 N----205 I
#4	K----64 N----107 I	K----165 N____185 I

close to the decomposition temperatures, therefore, a reproducible extensive physical characterisation was prevented.

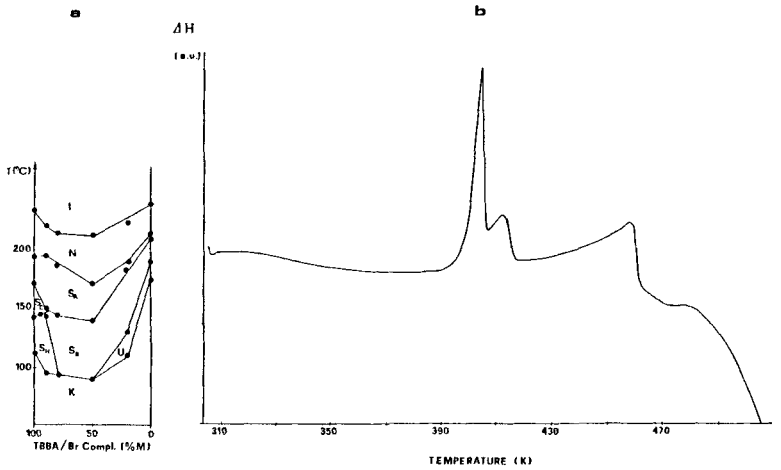


FIG.2 Examples of characterization of mesophases of palladate complexes: a) miscibilitydiagram of the bromine compound(see table II)with TBBA,andb)Latent heat of the Pyridyne compound(see table II)

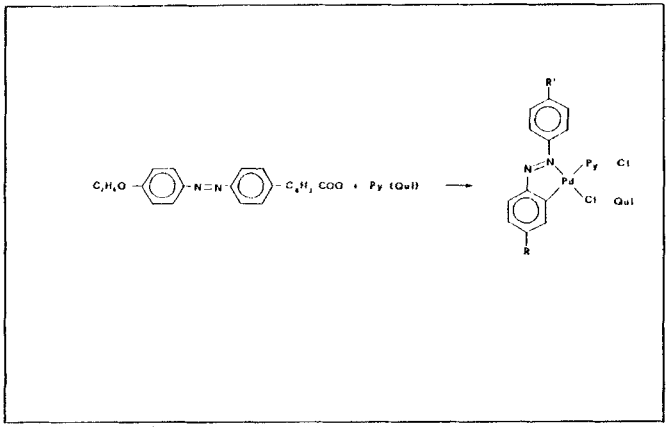


FIG.3 Sketch of the same reaction of fig.1but with a Pyridine(or Quinoline bridge splitting induced.

In order to investigate on the role played by nature of the metal-halo bridge, the p-ethoxy-p'-heptanoateazobene derivative, third compound in table I, was methatised

TABLE II

Transition temperatures of the complexes obtained from the third ligand of table I when the clorines are substituted by iodines or bromines or (partially) by a quinoline (Qui)or pyridine(Py) R=C2H5O

Cl	K-----190 N-----205 I
Br	K----175 K'----210 Se----215 N----250 I 190 205 Sb
I	K----220 Se----225 N----230 I
Py	K----180 SB----198 N----235 I
Qui	K----136 Se----151 N----180 I

with lithium bromide or iodide.

The result we obtained shows that the whole series of dinuclear complexes retain a nematic phase, at temperatures increasing in the order Cl<Br<I (see table II)(7). In particular, the nature of the different mesophases displayed by the bromine compounds was confirmed by miscibility experiments using as reference compound TBBA (terephthal-bis-(4-n-buthylaniline)), Figure 2 a(7).

Furthemore, the breaking of the halogen bridge was performed with neutral molecoles such as pyridine or quinoline. The new monometallic liquid crystals, in which a layered smectic phase is present(see table II) exhibit transition temperatures decreasing as larger is the added nitrogen containing ligand (7). A thermal analysis diagram for the pyridine bridge splitting product is shown in 2b.

1b) p-Alkoxy-p'-alkylazobenzene complexes.

A further class of liquid crystals we tested in palladation reactions, was the p-alkoxy-p'-alkylazobenzenes.Such ligands, reacted with (bis-benzonitrile) palladium

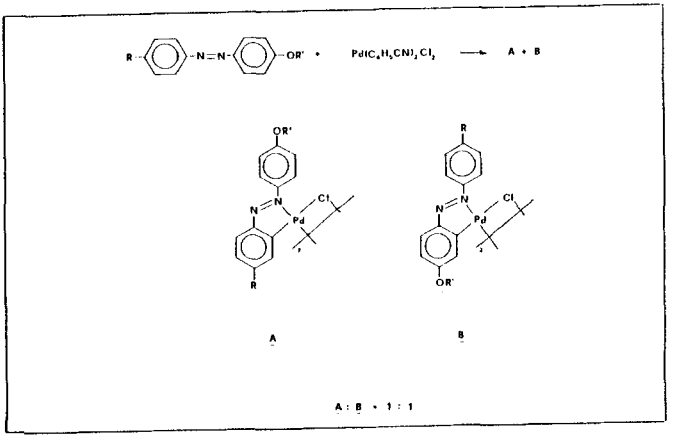


FIG.4 Sketch of the reaction to induce Palladated complexes from Alkoxy-alkylazo Benzenes and Benzonitril Palladium.The final complexes are the two isomers indicated on the lower part as A and B.Their relative weight is 1:1 as shown by NMR measurements.

(II) chloride, afford to binuclear compounds wherein the metallation occurs statistically on both the benzene rings (8). These products, actually 1:1 isomeric mixtures of the A and B frames (Figure4), about the mesomorphic properties (see table III), they display the following features:

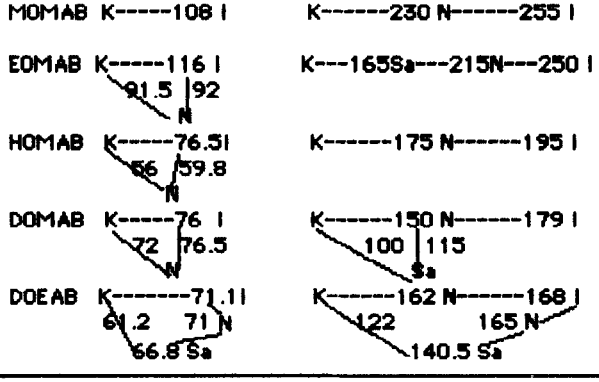
i) with respect to the nometallated ligand the nematic phase is usually stable over a larger temperature range(seetableIII).

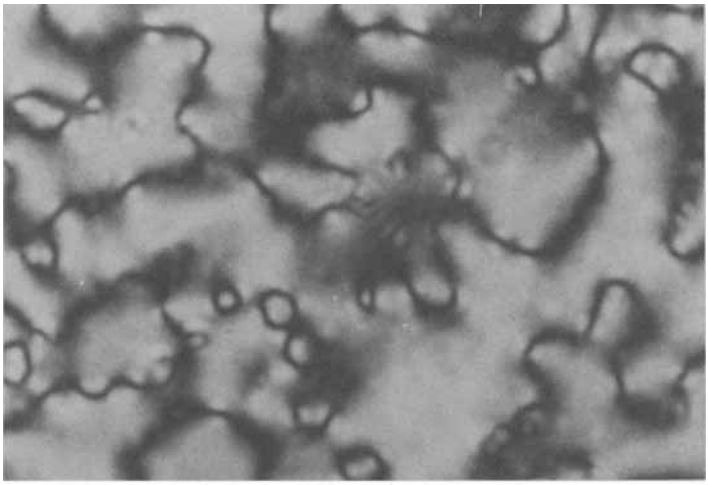
ii) as for the similar complexes of the paragraph 1a- the incorporation of the Pd-Cl moiety increases the transition temperatures of c.a. 100°C

iii) are thermally much more stable than those of the paragraph 1a.

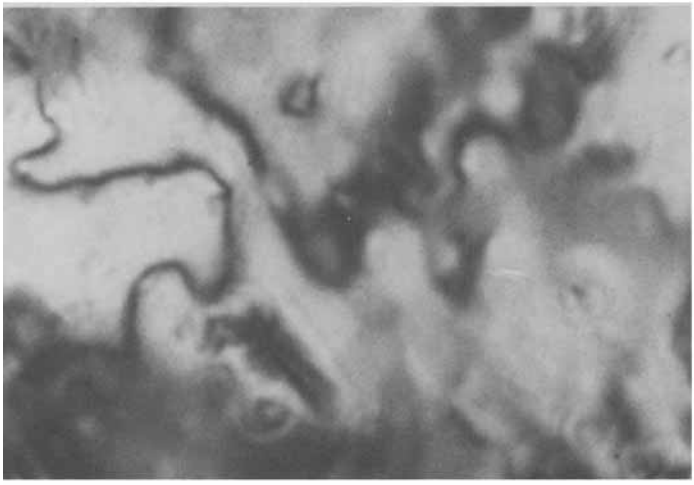
TABLE III

Temperature transition for the free ligands and the palladium complexes of fig.4.The different ligands we used:MOMAB (R=CH3,R'=CH2) .EOMAB (R=CH3,R'=C2H5) .HOMAB(R=CH3,R'=C3H7).DOMAB(R=CH3,R'=C12H25) and DOEAB (R=C2H5,R'=C12H25)

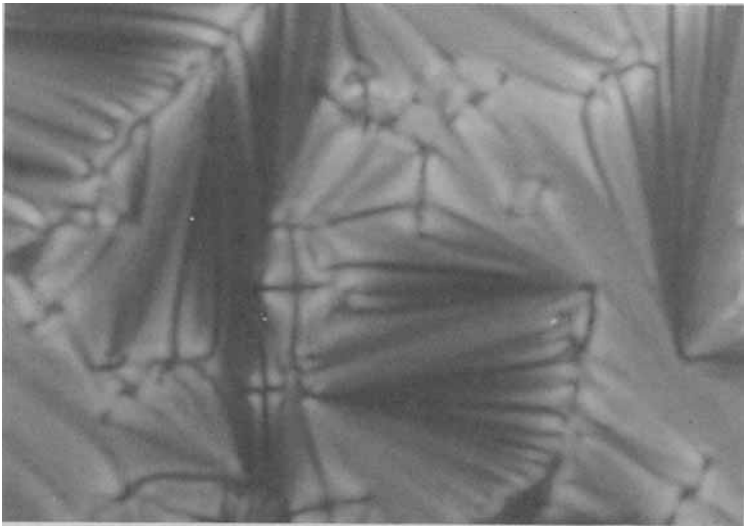




5A



5B



5C

Fig.5:Typicall textures of Palladated compounds:a) free ligand DOMAB in nematic phase,b)the corresponding metal complex in nematic phase,and c)in the smectic a phase (magnification 750 x). See Color Plates I, II, and III.

c) p-Alkoxyphenylazobenze complexes.

The complexes described (paragraphes1a and 1b) contained liquid crystals as ligands while the p-alkoxyphenylazobenes lack thermotropic properties.

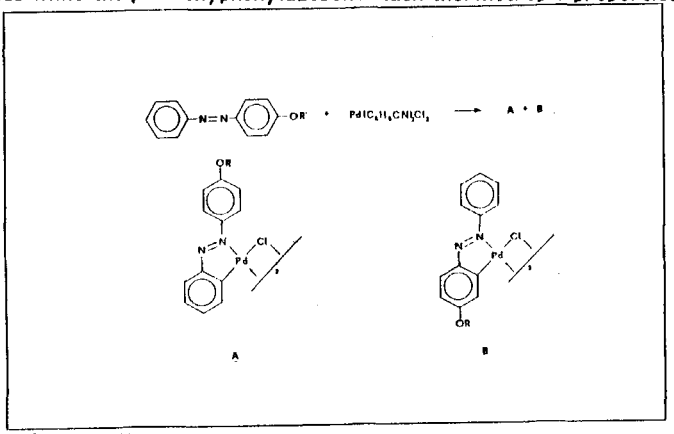


FIG.6 Shows the reaction between alkoxyphenyl azobenzenes (not liquid crystals)and benzonitrile palladium,to give the isomers A and B.The actual ratio A/B depends on the chains lenght as shown in the 3th column of table IV.

TABLE IV

Are reported the melting points for the free ligands and the transition temperatures for the palladium complexes of fig.6.The used ligands are: HOAB (R=C3H7); dOAB (R=C10H21); DOAB (R=C12H25); TDOAB (R=C14H29).In the third column is reported for each complex the ratio between the two isomers A and B.

NAME	FREE LIGAND	PALLADIUM COMPLEX	A/B
HOAB	K----70 I	K----------185 I	99
dOAB	K----63 I	153 I -- 118N -- 115Se--80 K	2.0
DOAB	K----69 I	150 I -- 136N -- 118Se--115 K	1.2
TDOAB	K----75 I	170 I --- 103N --- 98 K	1.7

Their palladium (II)reaction products, as Fig.6 shows actually isomeric mixtures containing metallated both the p-alkoxyphenilazo on the benzene ring (9,10), display smeetic or nematic mesophases, but on cooling only, seeTable IV.

Remarkably, in these compounds, the termal mesomorphism is induced by metal complexation, therefore we suggest that such a feature can be attributed to the new molecular geometry created by the metal-halo bridge.

2. Copper (II) coordination compounds.

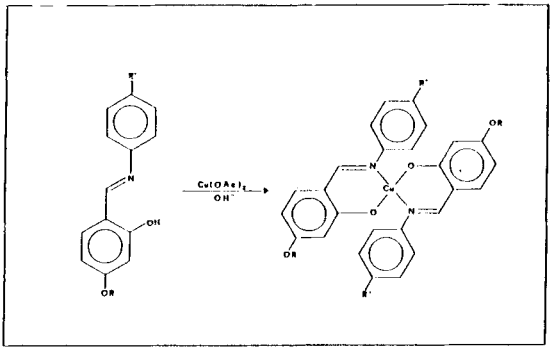


FIG.7 Shows the complexation of several alkybenzene-alkoxy salicylideneamine with copper acetate.

The azobenzene ligands undergoes cyclometallation reaction, so that the syntesis of organometallic complexes is severely restricted to a few transition metals (11). On the other hand, ligands such as Schiff bases derived from salicylaldheyde are known to be both much more versatile toward the formation of many metal (II) coordination compounds (12) and liquid crystalline materials (13). In this light we have therefore extended our investigations to N-4'-n-alkylbenzene(4-n-alkoxy) 2-salicylideneamine mesogenic species .

These ligands, reacted with copper (II) acetate in alkaline media, afford to the mesomorphic complexes. (Fig.7 and Table V).

The synthesis and characterization of other new materials containing different transition metals are currently under way.

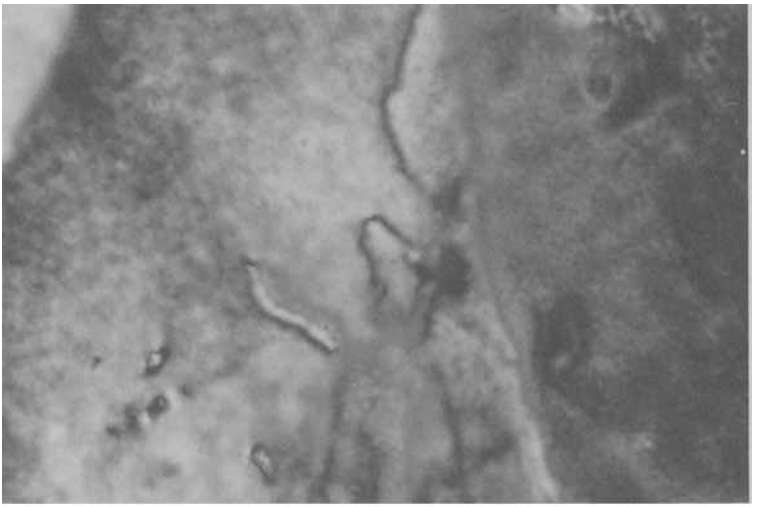
TABLE V

The transition temperatures of the free ligands and of the complexes of Fig.7. The free ligands we used are:
HOMBA (R=CH3,R'=C7H15);
HOEBA (R=C2H5,R'=C7H15); HOPBA (R=C3H7,R'=C7H15);
HOBBA (R=C4H9,R'=C7H15); DOMBA (R=CH3,R'=C12H25);
DOEBA (R=C2H5,R'=C12H25); DOPBA (R=C3H7,R'=C12H25);
DOBBA (R=C4H9,R'=C12H25).

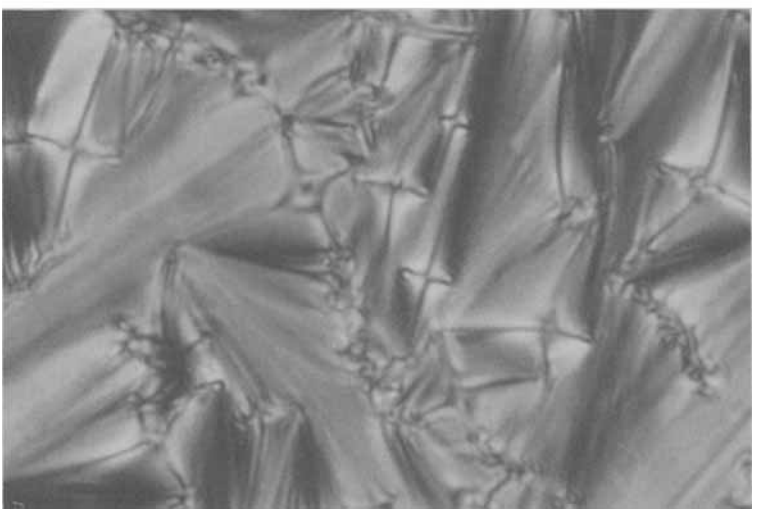
NAME	FREE LIGANDS	Cu-COMPLEXES
HOMBA		K-------145 I
HOEBA		K-------140 I
HOPBA		K-------131 I
HOBBA	K---60Sa---90 I	K-70.6Se-120Sb-147Sa-149 I
DOMBA	K---------- 72 I 39 72 N	K-------- 120 I 50 108 Sa
DOEBA	K-----49N--- 72 I 44 49 Sa	K---- 89Sb----94Sa----128 I
DOPBA	K—52Se—75N--89 I	K---- 99Sb----113Sa----149 I
DOBBA	K-46.5Sc-60.5Sa'-70Sa-86 I	K--89Se--97.5Sb--113Sa--140 I

2a) Copper complexes: preliminary properties

In order to give a partial account of the structure and the properties of the copper complexes we resticted ourself on the HOBBA-Cu and DOBBA-Cu compound, and mainly on this last one we performed the following experiment:a) optical observation of the textures, b) D.S.C., c) near and far infrared spectroscopies, d) X-ray power diffractometry, and e) bulk conductivity.



8A



8B

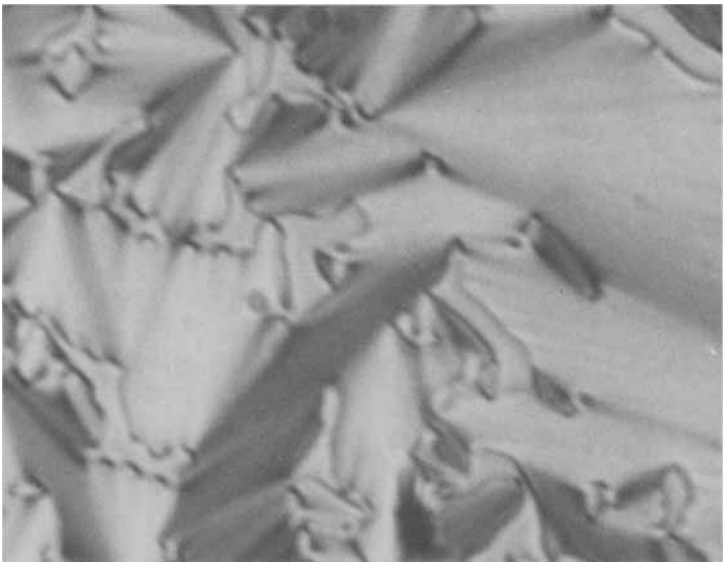


Fig.8 We present some typical textures for the DOBBA compound in the nematic phase (a)and of the complexes DOBBA-Cu(b) and HOBBA-Cu(c) in the smectic a phases. See Color Plates IV, V, and VI.

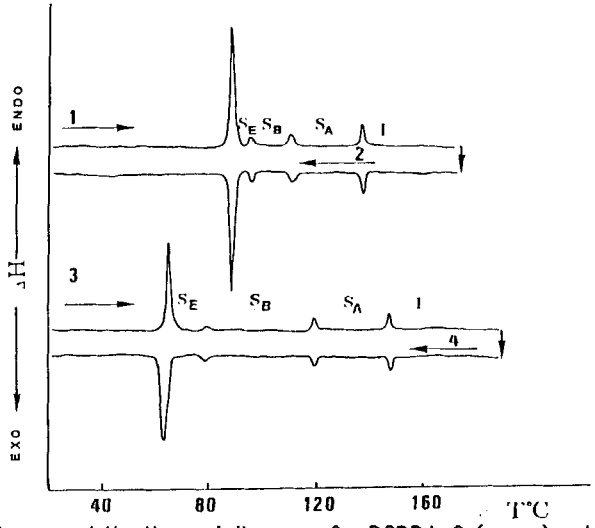


Fig.9 We present the thermal diagrams for DOBBA-Cu(upper) and HOBBA-Cu(lower)both on heating and cooling

a) The optical observations are made with a polarized hortopian Leitz microscope: the textures of the complexed mesophases are very similar to those of the free ligands, the number of defects seems to be smaller and the fluidity the systems also. We show some examples of textures on fig.8 The Se, and SA phases are observed on heating and cooling for both mesogens; the SA phase is macroscopically uniaxial. SB is the normal type and the SE is also pseudouniaxial.

b) In fig. 9 we display the D.S.C. obtained for HOBBA-Cu and DOBBA-Cu. The enthalpies of the phase transitions upon cooling coincide with those on heating in the limit of the experimental errors: such values are reported on Tab.VI. We want only put into evidence that the in this case the increase of the transition temperatures from the free ligands to the complexed systems is much smaller in this case in comparison to the azocompound cases, moreover there is an evident increase in the number of more ordered mesophases.

TABLE VI

Are reported the Hentalpies at the phase transitions of HOBBA-Cu and DOBBA-Cu

PHASE TRANSITIONS	H (KCal mol-1)
I - Sa	5.2
Sa- Sb	1.9
HOBBA Cu	
Sb- Se	0.41
Se- K	4.2
I - Sa	1.75
Sa- Sb	1.33
DOBBA Cu	
Sb- Se	0.43
Se- K	4.48

c) In fig.10 the I.R. spectra for DOBBA and DOBBA-Cu are reported as an example as recordered with a perkin-elmer 180 I.R.-spectrophotometer in the range 500-50cm^{-1} with a resolution of about 2cm^{-1}. The strong and well pronounced peak at 280cm^{-1} appearing for DOBBA-Cu is attributed to the Cu— O stretch vibration. Furthemore the results with the near I.R. show peak at 888cm^{-1} and 1172cm^{-1} would indicate some vibrations of the benzenic ring outside the layer. These considerations and some preliminary measurements of the biaxial order parameter $\langle D^2_{02} \rangle$ (~ 0,05) (16) would suggest a locally biaxial structure for these complexes.

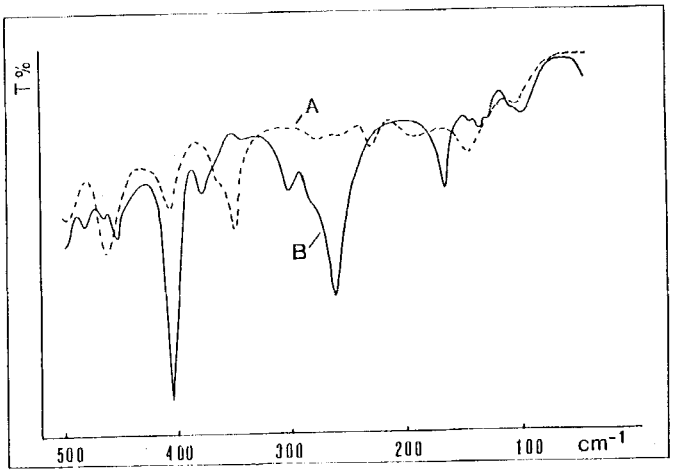


Fig.10 Are shown the far infrared spectra of DOBBA (A) and DOBBA-Cu(B)

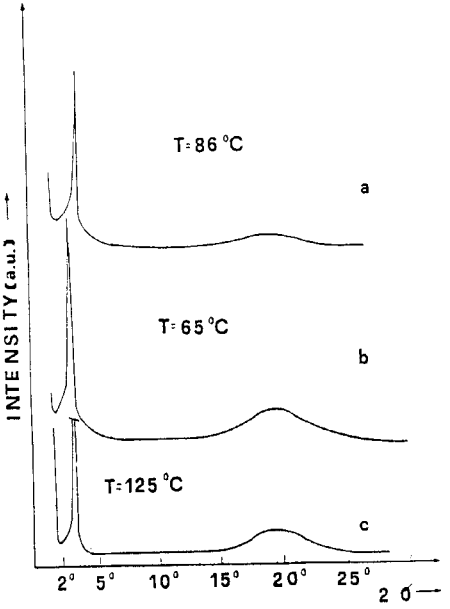


Fig.11 Typical powder X-Rays diffractograms for HOBBA-Cu(a),DOBBA(b)and DOBBA-Cu(c)

d) The X-rays powder spectra (see fig.11) made with a conventional X-rays diffractometer with Cu cathode, show that the complexed compounds in the SA phases have a layer thickness very close to the layer thickness of the corresponding free ligands. But in the latter case the found layer thickness correspond to that of an usual smectic a phase where the molecules are fully elongated (31Å), and in the complexed material the found value is much smaller(31Å) than the theoretical we can calculate when the chains are all elongated(42 ÅX15). It means that the Sa phase of the complexes should be interdigitated:i.e. or the longer chains are partially superimposed or the chains are mostly melted (see fig.12).

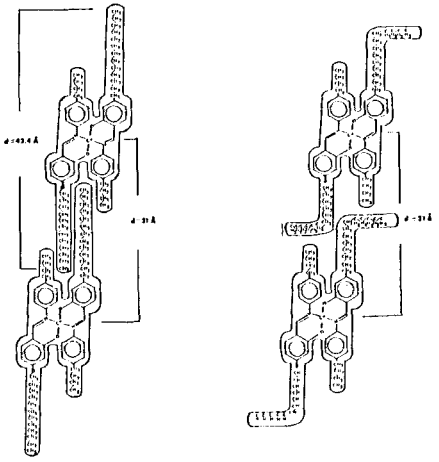


Fig.12 Two possible sketchs of the proposed interdigitation:a)with elongated chains,and b)with melted chains.

TABLE VII	
We report the bulk conductivity of unoriented samples	
COMPOUND	BULK CONDUCTIVITY(-1Cm-1)
HOBBA	10-7
HOBBA-Cu	10-5
DOBBA	10-7
DOBBA-Cu	6x10-6

e) Finally we report an indication of the bulk conductivities performed on unoriented samples with a wayne-kerr bridge at 10K H2. From table VII we can observe how the conductivity is increased of about two order of magnitudewhen the copper is complexed.

Conclusions

We presented the synthesis and the characterization of 21 mesogenic ligands (azobenzenes and schiffbases) and of the 28 metallorganic compounds that we obtained after complexation (with palladium in the former case and with copper in the latter). A general trend of these procedures is that the mesogenic character of the materials is preserved but the transition temperatures are increased, so that some of the obtained compounds can be unstable.

A second feature is that the complexed compound many times presents a more rich mesomorphism: mainly more ordered mesophases are induced. In the case of the azobenzenes monosubstituted the palladium complexes show mesophases,instead the free ligands do nt.

The priliminary results on the Shiff base complexes show that the layered mesophases should be interdigitated .This last class of compounds can be interesting also because could allow to complex other different metals.

Systematic measurements (X-rays and EXAFS) are now under way to well establish the structure as well EPR measurements to evaluate the paramagnetic character of these compounds. Finally experiments have begun to evaluate optical, electrical, magnetic, and electricooptical properties also for the applicative purposes.

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