Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

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To cite this Article Alonso, P. J. , Marcos, M. , Martínez, J. I. , Orera, V. M. , Sanjuán, M. L. and Serrano, J. L.(1993) 'Persistence of short range order in the fluid phases of a mesogen copper complex studied by EPR', Liquid Crystals, 13: 4, 585 — 596

To link to this Article: DOI: 10.1080/02678299308026330

URL: http://dx.doi.org/10.1080/02678299308026330

Liquid Crystals, 1993, Vol. 13, No. 4, 585–596

Persistence of short range order in the fluid phases of a mesogen copper complex studied by EPR

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(*Received 15 July 1992; accepted 21 December 1992*)

The synthesis and thermal characterization of a new copper complex, bis[*N*-(4-*n*-pentoxyphenyl)-4-*n*-decyloxysalicylaldiminate] Cu(II), having mesomorphic properties is given. The EPR spectrum of this material has been measured for its different phases as a function of temperature. The results are compared with those for two other Cu(II) compounds, bis[4-*n*-decyloxysalicylate] Cu[II) and bis[*N*-(*n*-pentyl)-4-*n*-decyloxysalicylaldiminate] Cu(II) which have a related molecular structure, but are not mesomorphic. The influence on the spectra of exchange interactions in all the phases, as well as the molecular motion in the fluid phases is discussed, and it is concluded that the exchange interactions are not destroyed by the molecular motion. These facts suggest that molecular motion in the high temperature phases takes places whilst keeping a short range order, resulting in a locally correlated motion.

1. Introduction

In recent years the synthesis and characterization of metallo-organic mesogens have received much attention because of either a basic desire to understand their different mesophase orderings or the potential of the materials for applications associated with their electronic, optical and magnetic properties, which are strongly influenced by the metal. The existence of directed valences associated with the metal imposes some structural conditions upon the molecular geometry. Moreover, the deformable d-electron orbitals favour an increased electronic polarizability of the molecule. So it is possible to obtain mesomorphic compounds from non-mesogenic organic ligands, as well as to modify the transition temperatures in such a way that the mesophase ranges become wider. In any case, the contribution of the metal to the properties of the materials makes these metallo-organic mesogens objects of interest. A comprehensive review [1] on this topic has been recently published.

Among metallo-organic mesogenic compounds, Cu(II) complexes have been the object of special interest [2–8]. In such cases, electron paramagnetic resonance (EPR) spectroscopy is a very useful tool for studying these kinds of material, since the spectrum of Cu(II) is observed without difficulty up to temperatures well above room temperature (RT). In this way, the spectra also provide information about the different mesophases. It is interesting to point out that contrary to other liquid crystal studies in which a spin probe is added to the diamagnetic organic compound, here the paramagnetic entity is a part of the liquid crystal molecule and all perturbations due to foreign probes are avoided.

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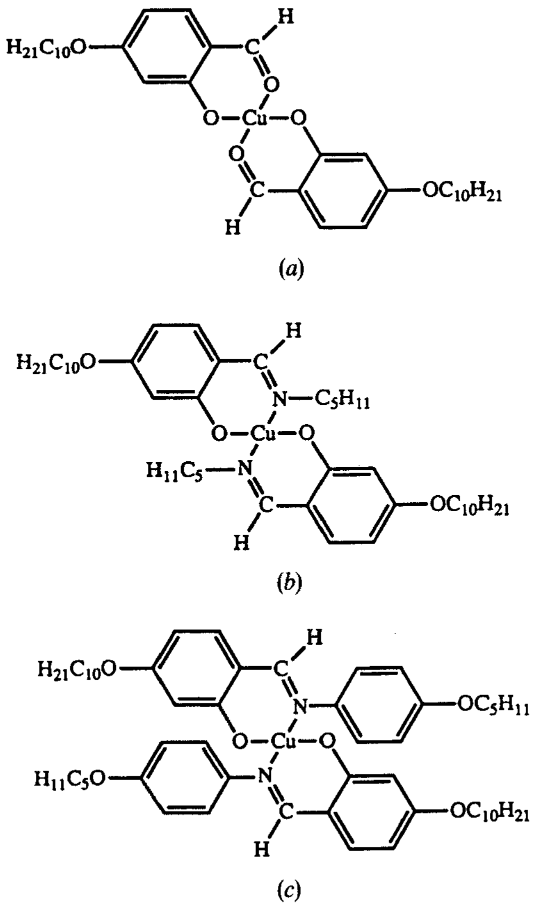
It is known that copper compounds tend to give exchange interactions between molecules leading to the formation of pairs [9, 10], trimers [11] and even long range coupled systems. Although the exchange constants have low values (typically of about 1 K or less), the spin correlation due to the exchange interaction induces modifications in the magnetic resonance spectra of these types of copper compound, and in some cases it is possible to obtain information on the magnetic interactions in the high temperature (not magnetically ordered) phases by studying the EPR spectra. Besides this, in the fluid phases (liquid crystalline and isotropic liquid phases) dynamical effects associated with the molecular motion can also be present. EPR spectroscopy is a suitable tool to identify and study these phenomena. The simultaneous presence of both effects, motion and exchange, could take place in the fluid phases, and then its influence on the EPR spectrum could give information about the structure of the high temperature mesophases.

We wish to note that recent papers by Ghedini *et al.* [12, 13], which report some X-ray diffraction and EXAFS measurements for the smectic phases of some Cu-metallo-mesogens, point out that rotation of the molecules is not free in these phases, in such a way that molecular correlations within the smectic layers appear. Besides, from QENS measurements [14], they suggest the existence of intramolecular hindered rotations in the mesophases.

In the present paper, we give an analysis of some EPR measurements for a new metallo-mesogens derived from a Schiffs base, bis[*N*-(4-*n*-pentoxyphenyl)-4-*n*-decyloxysalicylaldiminate Cu(II) (hereafter called CuLC), in the temperature range between room temperature (RT) and just above its clearing point (160°C). The EPR spectra of two related compounds: bis[4-*n*-decyloxysalicylate Cu(II) (CuS1) and bis[*N*-(*n*-pentyl)-4-*n*-decyloxysalicylaldiminate] Cu(II) (CuS2) which do not form mesophases are also presented and compared with CuLC in order to understand the influence of the local molecular environment and the mesophase structure on the EPR spectrum. The molecular formulae of these compounds are given in figure 1. The first coordination shell is shown by a planar square, bonded to rather long chains, so that these molecules can be considered as being rod-like. The existence of two flexible chains at both sides of the molecule in the case of CuCL is particularly important and plays an important role in the behaviour of this material in the fluid phases. In fact the shape of the molecule has to be considered more as an orthorhombic prism than as a cylindrical rod. In figure 2 we show a sketch of the environment of the Cu(II) in our compounds, together with an indication of the axes chosen for the following description. A detailed analysis of the EPR spectra measured for the different phases as a function of temperature as well as for RT frozen samples is presented. It is concluded that the exchange interaction plays an important role in the fluid phases and that a short range order of the molecules occurs even in the low viscosity phases.

2. Experimental

The complexes were prepared according to a procedure described in [15] by reaction of 4-decyloxy-2-hydroxybenzaldehyde with copper(II) acetate to obtain bis[4-*n*-decyloxysalicylate] Cu(II) (CuS1) which was then treated with an appropriate amine (*n*-pentylamine or 4-*n*-pentoxyaniline) to give bis[*N*-(*n*-pentyl)-4-*n*-decyloxysalicylaldiminate] Cu(II) (CuS2) or bis[*N*-(4-*n*-pentoxyphenyl)-4-*n*-decyloxysalicylaldiminate] Cu(II), respectively. Their purity was checked by microanalysis which agreed with the expected L_2Cu stoichiometry. Complex CuS1 ($C_{34}H_{50}O_6Cu$): calculated C, 66·07 per cent; H, 8·10 per cent; found C, 66·51 per cent;



(a)

(b)

(c)

Figure 1. Structures for the compounds studied. (a) bis[4-n-decyloxysalicylate] Cu(II) (CuS1), (b) bis[N-(n-pentyl)-4-n-decyloxysalicylaldiminate] Cu(II) (CuS2), (c) bis[N-(4-n-pentoxyphenyl)-4-n-decyloxy salicylaldiminate] Cu(II) (CuLC).

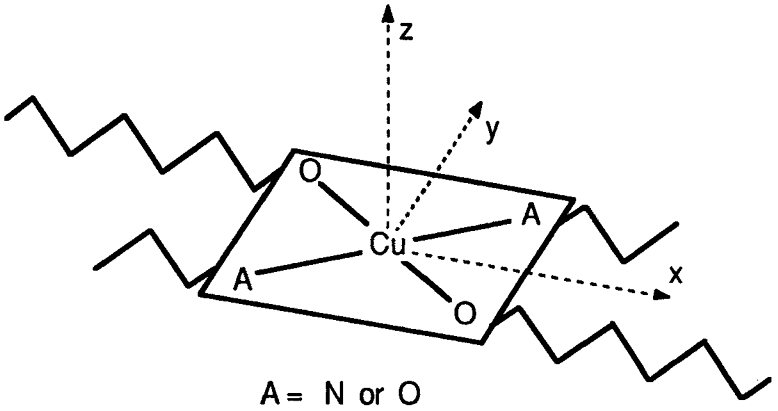


Figure 2. Sketch of the environment of the magnetic ion Cu(II). The axes used in the description given in the text are also shown.

H, 9·05 per cent. Complex CuS2 ($C_{44}N_2H_{72}O_4Cu$): calculated C, 69·89 per cent; H, 9·53 per cent; N, 3·71 per cent; found C, 70·28 per cent; H, 10·02 per cent; N, 3·78 per cent. Complex CuLC ($C_{56}N_2H_{80}O_6Cu$): calculated C, 71·53 per cent; H, 8·52 per cent; N, 2·98 per cent; found C, 71·30 per cent; H, 9·05 per cent; N, 2·90 per cent.

Differential scanning calorimetry (DSC) measurements were carried out with a Perkin–Elmer DSC-2 calorimeter using a $10°C\,min^{-1}$ heating or cooling rate. The phase behaviour was examined, using polarized light, and an optical microscope equipped with a Mettler FP 82 hot stage and a Mettler FP 80 microprocessor.

X-band EPR measurements were taken with an E-112 Varian spectrometer. We used the variable temperature accessory E-265 from Varian for measurements above room temperature (RT). Powder samples were put into quartz tubes and the temperature was monitored using a copper–constantan thermocouple attached to the tube. The error in temperature was estimated to be lower than 0·5°C and the stability was better than 0·1°C. Liquid nitrogen temperature (LNT) measurements were made by placing the quartz sample tube into an immersion quartz dewar filled with liquid nitrogen. Q-band measurements were done at RT using an ESP300 Bruker spectrometer.

Sometimes we shall refer here to measurements for frozen samples. We observed that these compounds could easily retain the molecular structures of the fluid phases when the sample was cooled down fast enough into the solid phase. Normally, putting the sample into liquid nitrogen after it has been heated up to the fluid phase was the way to achieve freezing, but even switching off the heater and cooling down the sample in a RT nitrogen flow gave good results. In frozen samples, polarized light microscopic textures were preserved, but the EPR spectra showed changes; we shall explain them in the following sections. The stable solid structure could be recovered by heating up the sample to a solid–solid transition temperature occurring below the first fluid transition.

3. Experimental results

The different phases and the transition temperatures for the three compounds are shown in table 1. They correspond to second DSC heating scans; that is the sample was previously heated up above the melting point and cooled down to RT. The reason is that sometimes the synthesis procedures impose a solid structure different from the stable one. The differences in the isotropization points of the compounds have a simple qualitative explanation following standard topological ideas [16]. Rod shape tends to favour molecular packing and this raises the melting point (CuS1). On the contrary, addition of a lateral chain (CuS2) produces a spatial impediment to packing and a decrease in the melting point is then observed. In CuLC the lateral chain effect is weakened, since the form of the molecules is rather like that of two rod-like entities linked by the central metal. Besides that the two additional aromatic rings cause an enhancement of the molecular electronic polarizability and the intermolecular interaction changes in such a way that it enables the appearance of mesophases.

The X-band EPR spectrum of a polycrystalline CuS1 sample measured at RT is displayed in figure 3. It shows two features: one at low field ($g \approx 2·28$) having a parallel character and the other one at about $g \approx 2·06$ with a perpendicular character. The RT polycrystalline spectra of CuS2 and CuLC given in figures 4 (*a*) and 5 (*a*), respectively, look like that of CuS1 with some minor differences. The lines of the CuS2 signal are narrower and in this case a splitting in the perpendicular feature is clearly observed, which reveals an orthorhombic symmetry of the paramagnetic entity. It is noteworthy that in all cases no evidence for hyperfine (HF) structure has been found. RT Q-band

Table 1. Phases and transition temperatures of the Cu complexes. C, solid crystal; N, nematic; S_C, smectic C; S_A, smectic A; and I, isotropic liquid.

CuS1	$C \xrightarrow{170^\circ C} I$†
CuS2	$$\begin{tikzcd} C \arrow[rr, "90^\circ C"] & & I \arrow[dl, "78^\circ C"] \\ & C^{*} \arrow[ul, "73^\circ C"] & \end{tikzcd}$$
CuLC	$$\begin{tikzcd} C \arrow[rr, "125^\circ C"] & & S_C \arrow[dl, "105^\circ C"] \arrow[r, shift left, "130^\circ C‡"] & S_A \arrow[l, shift left] \arrow[r, shift left, "162^\circ C"] & I \arrow[l, shift left] \\ & C^{*} \arrow[ul, "100^\circ C§"] & & & \end{tikzcd}$$

† Decomposed.
‡ Optical microscope data.
§ EPR data.

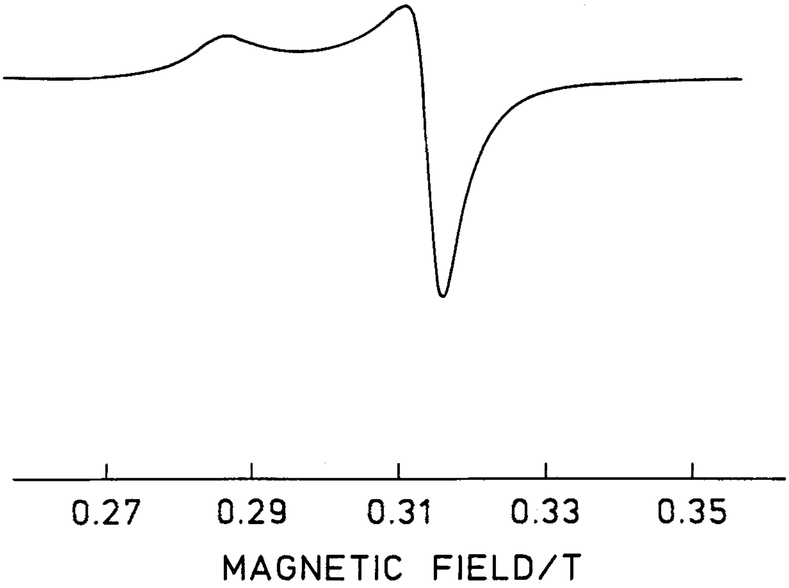


Figure 3. Room temperature X-band EPR spectrum of a bis[4-*n*-decyloxysalicylate] (Cu(II) (CuS1) powder sample.

spectra have also been taken and the results are similar to those obtained for X-band spectra except for a better resolution in the perpendicular components. In figure 6 (*a*) we show the RT Q-band spectrum of the CuLC compound, where an orthorhombic symmetry is clearly shown.

Evolution of the X-band spectra with temperature has also been measured. For all the compounds, the spectra measured at LNT coincide with those just described for RT. On the other hand, above RT, some modifications are found in the EPR signals for

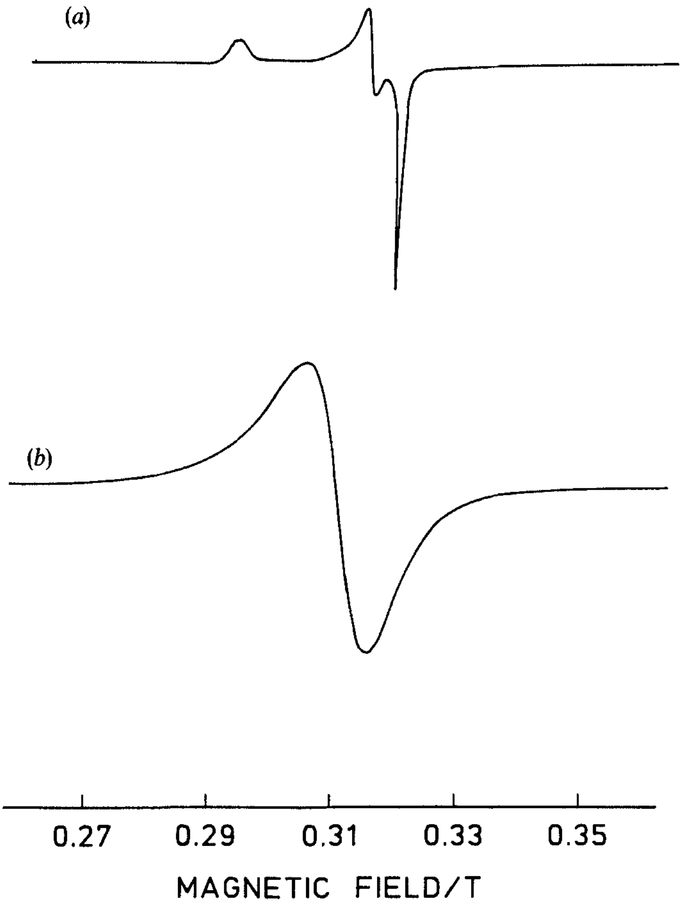


Figure 4. X-band EPR spectra of a bis[*N*-(*n*-pentyl)-4-*n*-decyloxysalicylaldiminate] (Cu(II) (CuS2) powder sample measured for the solid phase (*a*) and for the isotropic phase (*b*).

all our compounds. In the case of the CuS1 and CuS2 samples, no changes are observed for temperatures below the melting point. At higher temperatures, the spectra consist of a broad single band. In the case of CuS2, this appears at $g \approx 2{\cdot}11$ and has been plotted in figure 4 (*b*). A similar trace (at $g \approx 2{\cdot}14$) is observed in the case of CuS1 but it is difficult to measure with enough reliability, because this compound decomposes at any temperatures in the isotropic liquid phase.

The EPR spectrum of CuLC does not change when measured at temperatures below the C–S_C transition (T_{CS_C}). The spectrum in the smectic phase (no differences have been found between the S_C and S_A phases), is given in figure 5 (*b*) while that measured for the isotropic phase is shown in figure 5 (*c*). This last spectrum consists of a broad line ($\Delta H_{pp} \approx 10\,mT$) corresponding to an isotropic signal at $g \approx 2{\cdot}11$. The smectic phase EPR trace (see figure 5 (*b*)) is very similar to that of the isotropic phase, but shows some asymmetry, being wider on the low field side. As in the RT spectra, no evidence for hyperfine structure has been found in all the high temperature spectra.

Finally, we represent in figure 5 (*d*) the RT X-band spectrum of a sample which has been frozen from the smectic phases. When this trace is compared with that given in figure 5 (*a*), we find that the perpendicular features appear roughly at the same field in

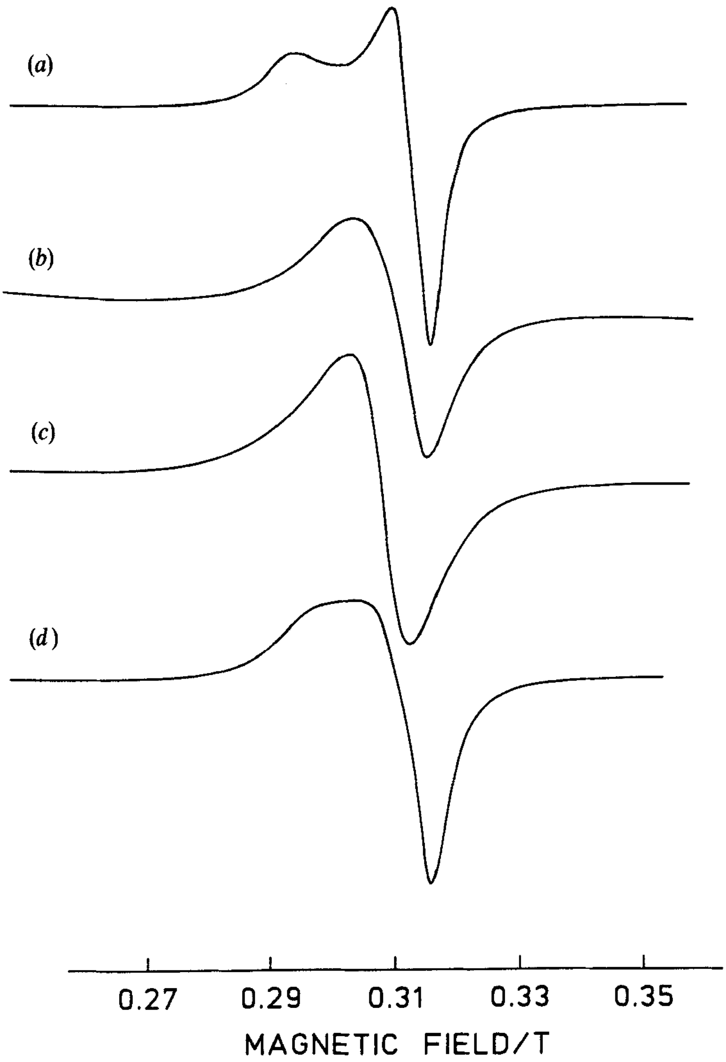


Figure 5. X-band EPR spectra of a bis[*N*-(4-*n*-pentoxyphenyl)-4-*n*-decyloxy salicylaldiminate] Cu(II) (CuLC) powder sample measured for the stable solid phase (*a*), the smectic phase (*b*), the isotropic phase (*c*) and a frozen solid obtained from the smectic phase as indicated in the text (*d*).

both spectra, but the parallel one is shifted toward high field in the frozen sample spectrum, which shows broader lines than for the stable solid. This behaviour is clearly observed in the Q-band spectra (see figure 6). The highest field feature (which will later be associated with g_x) does not shift, while the other two features (g_y and g_z) shift in such a way that the distance between them is lower for the frozen sample.

This suggests that some intermolecular interaction is taking place. In order to remove it and then get information about the molecular spectroscopic parameters, we have measured the EPR spectra of some solutions of our compounds (CuS1 in chloroform and CuS2 and CuLC in toluene) which have been frozen at LNT. The corresponding CuLC spectrum is shown in figure 7 (*a*) together with the LNT spectrum of a polycrystalline sample measured also at LNT (see figure 7 (*b*)). As can be seen, the

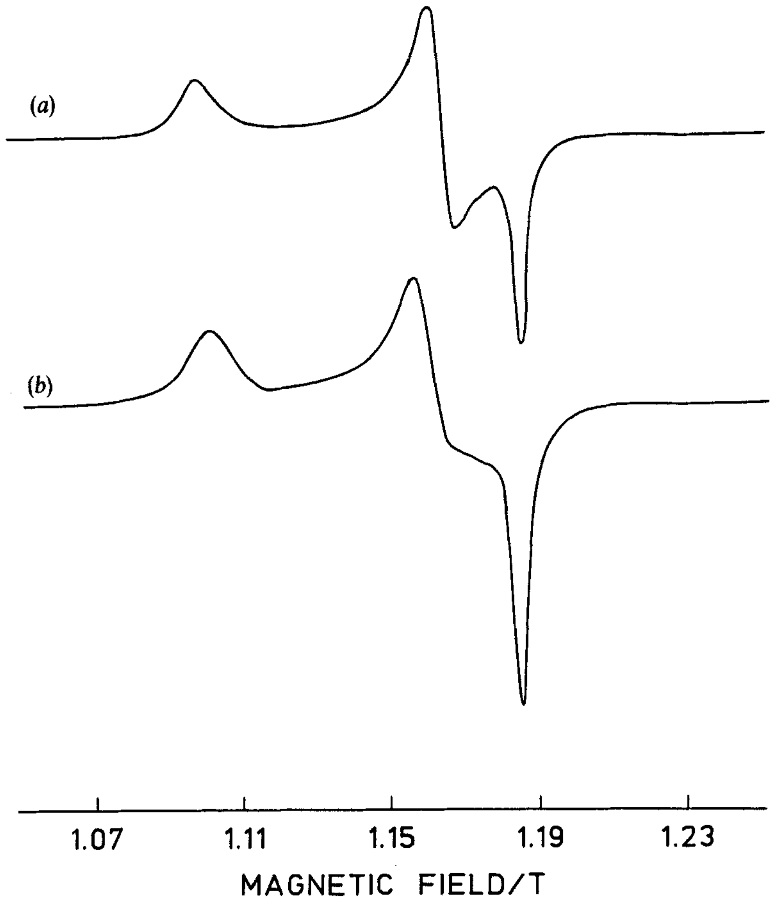


Figure 6. Room temperature Q-band EPR spectrum of a bis[*N*-(4-*n*-pentoxyphenyl)-4-*n*-decyloxy salicylaldiminate] Cu(II) (CuLC) powder sample measured for the RT stable phase (*a*) and the frozen smectic phase (*b*).

HF structure, at least in the parallel contribution, is clearly resolved in the solution spectrum, the splitting between two adjacent HF components being about 16 mT. On the other hand, it is noteworthy that the centre of this parallel contribution (g_z) appears at a lower field than for the polycrystalline CuCL spectra. The same behaviour is observed in the case of frozen solutions of CuS1 and CuS2 samples.

4. Discussion

All the above described EPR signals will be associated with Cu(II) (electronic configuration d^9): an $S=1/2$ system. Except for diluted samples, the spectra could be described as having only an electronic Zeeman contribution [17, 18]. By a direct inspection of our spectra for the solid stable phases and comparing these traces with that of an $S=1/2$ powder system [17], we obtained for the principal g factors the values collected in table 2. As observed, the g-tensor is essentially axial. These g values are close to those typical of divalent copper with its unpaired electron in a $|x^2-y^2\rangle$ orbital [18] in which the charge points towards the four ligands in the plane. It is known that this configuration gives a high stability to these Cu(II) metallo-organic compounds. A

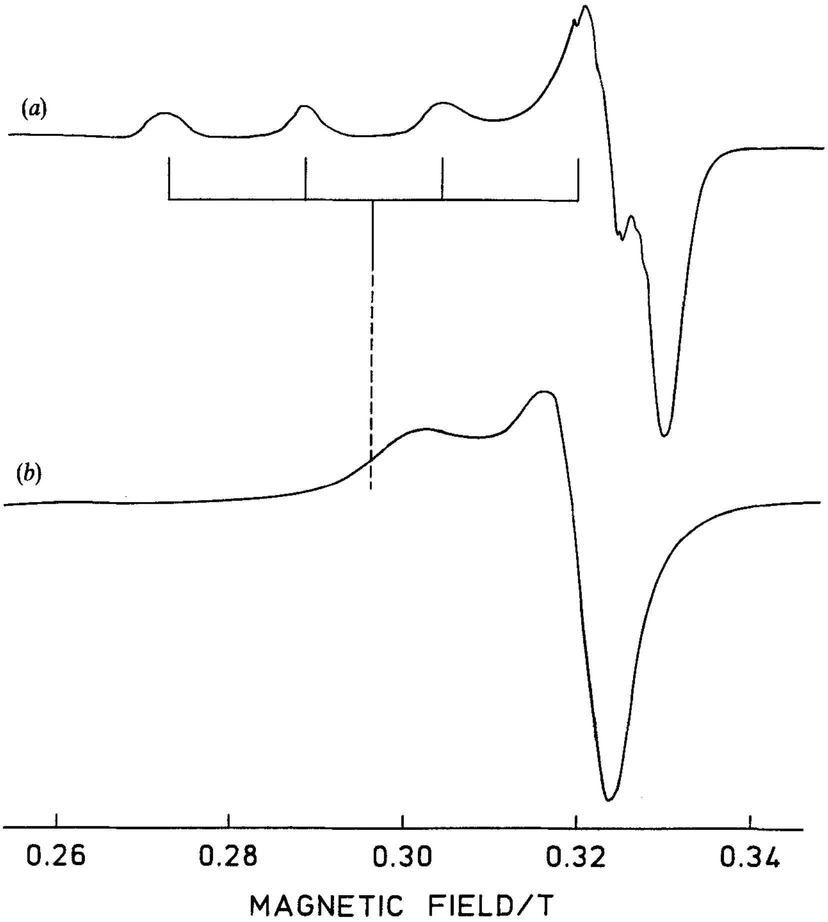


Figure 7. LNT X-band EPR spectra for a frozen solution of CuLC in toluene (*a*) and a polycrystalline CuLC sample (*b*).

sketch of the neighbourhood of Cu(II) in our compounds is given in figure 2 where, for further reference, we have indicated the choice of molecular axes.

Since copper has two isotopes with a nuclear moment $I = 3/2$: ^{63}Cu and ^{65}Cu (69·2 per cent and 30·8 per cent natural abundance) and very close nuclear g-factors, an HF contribution term has to be added to take into account the interaction of the unpaired electron with the nuclear spin; this can be taken as approximately axial, so it will be described by the two parameters $A_{\parallel}$ and $A_{\perp}$ [17, 18]. In our case the HF structure is only resolved in the parallel contribution of the spectrum of frozen diluted solutions (see figure 7 for the CuLC sample). The values obtained for the $A_{\parallel}$ coupling constant are typical for non-interacting Cu(II) systems where $A_{\parallel}$ ranges between 450 and 550 MHz. The perpendicular contribution is not clearly resolved in our case, but it is known that it is noticeably lower, so the isotropic contribution to the HF splitting would be at about 15 mT [18].

From the data of figures 3, 4, 5 and 6, it is concluded that in our compounds, (concentrated samples) the HF splitting, if any, is sensibly lower, by at least a factor of five, than in diluted samples. Besides that the formerly described molecular static model

Table 2. g-factors corresponding to the EPR signal of the different phases: C, stable solid; S, smectic; I, isotropic liquid; and FD frozen solution at LNT. The estimated error is about ±0·01. The parallel hyperfine coupling constants measured for the FD samples are also included.

	CuS1			CuS2			CuLC			
	C	I	FD	C	I	FD	C	S	I	FD
g_x	2·05		2·05	2·04			2·04			2·04
g_y	2·06		2·05	2·07			2·08			2·05
g_z	2·27		2·28	2·22		2·23	2·21			2·24
g_0	2·13	2·14	2·13	2·11	2·11		2·11	2·10	2·11	2·11
$A_{\|}$/MHz			495			530				485

g_0 in the C phase and in FD samples has been calculated as $(g_x+g_y+g_z)/3$.

for paramagnetic Cu(II) entities is not enough to describe the EPR spectra observed for the fluid phases, so we have to complete our former spin-hamiltonian description in order to understand all our experimental data.

Firstly there is the long range dipolar interaction which plays an important role particularly in concentrated systems. It accounts for the spreading out of the local magnetic field at the different paramagnetic sites due to the dipolar interaction and results in line broadening. The *n*th moment of the lines can be calculated using the well-known van Vleck method [19].

Furthermore, two dynamical [20] contributions must be taken into account: (i) The possibility of motion of the paramagnetic molecules in the fluid phases and (ii) the exchange interactions among the magnetic entities. The reason for introducing motional effects is obvious and the exchange processes will account for the collapse of the HF structure observed for concentrated samples as opposed to the diluted ones.

The bases of the theory for systems with exchange interactions and motion effects are well established. A summary is given by Abragam [21] and Carrington and McLachlan [22]. For systems with extreme exchange, a collapse of the HF splitting to zero and a narrowing of the signal (exchange narrowing) occurs. Changes in the principal values of the g-tensor are not observed if the molecules involved keep their principal g-factor axes parallel, but if that is not the case, an averaging of the g-tensor takes place. On the other hand, if we are dealing with a motion, besides a narrowing effect, an averaging of the g- and HF tensors to their isotropic values can be observed. In order to distinguish between motional and exchange effects, we have to focus attention on the existence of HF collapse and eventually on g-factor averaging effects.

The EPR spectra of our samples do not change between RT and LNT, so in solid phases there is a lack of mobility and only exchange effects have to be taken into account. For example, in the concentrated samples, the exchange is responsible for the collapse of the HF structure which is otherwise clearly resolved in the spectra of diluted samples. In those cases, we can assume that we are dealing with a case in the exchange narrowing limit. The comparison between the spectra corresponding to the stable solid and frozen smectic samples of CuLC with those shown in figure 7, is of particular interest. There the data relating to the g-factor indicate that a partial averaging of the g-tensor, generating a shift in the parallel features, takes place in the CuLC stable solid phase, because the g-tensors of interacting molecules are not coaxial. A comparison of the spectra of stable solid and frozen smectic samples shows that this effect is more pronounced in the frozen smectic phases. That is easy to understand as a consequence of the freedom of rotation about the long axis of the molecule in the mesophase [23] which results in a distribution of orientations of the z and y axes (see figure 2) when the mesophases is frozen. This distribution of orientations produced a short range ordering which induces the shift of the g_z and g_y lines and explains the increase in the width of these lines observed in figures 5 and 6.

With regard to the spectra for the fluid phases, the g-factor averaging, generating an isotropic signal, indicates that motion effects are important. An interesting question has to be discussed: as far as the exchange interaction works in the frozen smectic phase, that is in the topological structure of the smectic phase without motion, does it also occur in the fluid smectic phase? Physically exchange is produced through overlap of the electron orbitals of Cu(II) in adjacent molecules. If motion is fast enough, the overlap would be removed, but if the exchange frequency $\omega_e = J/h$ (J being the exchange constant) is higher than the inverse of the correlation time of the motion, the exchange effect remains. On the other hand, there are some movements that preserve the overlap of the electron wave functions. One of them is rotation of the whole molecule around its long axis. As we have said, this type of motion will produce a partial averaging of the g-tensor. Taking into account that these rotational frequencies are about 10^9 Hz (see [23]), we will be dealing in the smectic phase with a system having axial symmetry and effective g-factors, $g_\perp \approx 2{\cdot}14$ and $g_\parallel \approx 2{\cdot}08$. The existence of other restricted molecular motions, like shaking or lurching, will enhance the averaging of the g-tensor without a significant loss of the exchange interaction.

If the exchange induced correlation in the smectic phase were broken by the motion, the HF interaction would be averaged to its isotropic contribution. An analysis of our data (see figure 5 (*b*)) indicates an upper limit for the effective HF constant in the smectic phase of about 80 MHz, which is sensibly lower than the values expected for the isotropic HF constant of Cu(II) (see above). This suggests that the exchange also plays an important role in the fluid smectic phase. Furthermore, the fact that in the frozen samples only a partial g-factor averaging takes place indicates that some kind of short range order of the molecules within the smectic layer occurs even in the fluid phase. Then the molecular rotations would be correlated in order to preserve this short range molecular order in the frozen phase. This kind of correlation in the rotational motion is favoured by the form of the molecules and so it can be thought that rotation around the long axis of a molecule forces rotation of nearest neighbours to occur. In the case of the isotropic liquid phase, similar effects can also occur, but may be obscured due to the width of the observed lines (see figures 4 (*b*) and 5 (*c*)).

Finally we want to comment on the EPR results recently presented by Ghedini *et al.* [7] on some mesomorphic copper compounds derived from Schiff's bases. These authors also find some resonance lines close to the isotropic g-factor instead of the typical g_z value either in the solid or in the smectic phase. In so far as these EPR spectra do not show any resolved HF structure, their results can be interpreted in the same way as ours. This is in contrast to the interpretation given by these authors [7] on the basis of the existence of some motions even in the RT solid phases.

5. Summary

The EPR spectra of a new copper metallo-mesogen have been measured for its different phases as a function of temperature. These have been compared with those of two other Cu(II) compounds which have a related molecular structure, but do not form mesophases. An analysis of the exchange effects on the EPR spectrum for all the phases, as well as the motional averaging in the fluid phases, has been performed. A comparison of these spectra with those obtained for a frozen smectic phase allows us to conclude that exchange narrowing also occurs in the liquid crystalline state (S_C and S_A phases), together with motional effects associated with restricted motions of the molecules. These facts suggest that the molecular motion in the high temperature phases takes place whilst keeping some short range order and resulting in locally correlated motion.

This work has been sponsored by CICYT, Spain, under contract MAT90–0748 and MAT90—0813. Thanks are given to Professor T. Rojo of the Universidad del Pais Vasco, Spain, for the Q-band spectrometer facilities.

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