Magnetic exchange effects in nematogenic Schiff's base Cu(II) complexes. An EPR study

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Two new nematogens, copper complexes derived from Schiff's bases, bis(N-n-pentyl-4-[(4'-decyloxy)benzoyloxy]salicylaldiminate) copper(II) (labelled as Cu5) and bis(N-(4"-n-pentoxyphenyl)-4-[(4'-decyloxy)benzoyloxy]salicylaldiminate) copper(II) (CuO5) have been studied by electron paramagnetic resonance spectroscopy at different temperatures in their different mesophases. Both compounds show a nematic phase and CuO5 also presents a smectic C mesophase at lower temperatures. The copper coordination geometry in frozen solutions in toluene and in concentrated samples is square planar, while in solutions in their analogous zinc complexes, a twist of the N–Cu–O coordination planes is found. In the stable solid phases, the spectra reveal the existence of intermolecular magnetic exchange coupling. The fluid phases of Cu5 can be frozen forming different structures that depend on the freezing process rate. In Cu5 the exchange interaction is strongly reduced in the nematic phase because of the loss of positional correlation of the molecules. The EPR spectra indicate differences in the local arrangement of this mesophase compared to the nematic phases of cylindrically symmetric molecules.

1. Introduction

Mesogenic metal complexes derived from Schiff's bases are an interesting family of compounds. They show mesomorphic behaviour at relatively low temperatures and display a variety of molecular shapes. In recent years, some physical studies have revealed the structural peculiarities of their mesophases. For example, X-ray diffraction and EXAFS investigation of copper complexes derived from 4-hydroxysalicylaldimine pointed towards the existence of an unusual local order of the short axes of these molecules in their calamitic mesophases [1–5]. When the compounds contain a paramagnetic metal, such as divalent copper or oxovanadium, electronic paramagnetic resonance (EPR) spectroscopy is a suitable technique for obtaining information about structural and dynamical aspects of their liquid crystalline states [6–13].

We have studied elsewhere some smectogenic copper complexes of this family [12, 13]. We have found that the combination of the anisotropic molecular motion and the magnetic exchange coupling modifies the EPR spectrum from that of the isolated molecules. This gives us information about the axial correlation in the smectic phases. Our results allowed us to conclude that in the mesophase there exists (at least at medium range) a spatial

correlation of molecular short axes in the copper complexes associated with a brick-shape far removed from cylindrical symmetry [12].

We also studied by EPR the molecular motion of a smectogenic oxovanadium complex in its mesophases and in the mesophases of its palladium counterpart [14]. In the fluid phases, the EPR spectra show a partial averaging of the spin Hamiltonian anisotropy that was attributed to molecular tumbling. We developed a diffusional model in order to relate the changes in the measured spectra with that molecular motion and with the ordering of the brick-shaped molecules in the mesophase. We find a high local order of the molecular short axes quantitatively comparable to the director order.

In this paper we extend this work to two new mesogenic copper complexes derived from 4-hydroxysalicylaldimine and showing a nematic phase. The compounds are bis(N-n-pentyl-4-[(4'-decyloxy)benzoyloxy]salicylaldiminate) copper(II) (hereafter Cu5) and bis(N-(4"-n-pentoxyphenyl)-4-[(4'-decyloxy)benzoyloxy]salicylaldiminate) copper(II) (hereafter CuO5). Their corresponding formulae, phases and transition temperatures are presented in figure 1. Their synthesis has been reported elsewhere [15, 16]. The brick-like shape typical of this kind of complex, a consequence of their three markedly different molecular dimensions (typically

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$4 \times 9 \times 40$ Å), is preserved in both compounds although it is more evident in CuO5.

Interestingly, both compounds are nematogenic. Other compounds bearing different structures of the imine ligands are only smectogenic [12, 13]. Two factors could explain this behaviour. Firstly, these compounds have a more elongated structure than the bis[*N*-(4'-alkoxyphenyl)-4-alkoxysalicylaldiminate] copper(II) complexes, and secondly, the benzoyloxy groups introduced in the 4-position of the salicylic ring allow us to extend the conjugation of the central core. Then the polarization cloud spreads out and a mesophase without correlation of the positions of the molecular centres can occur.

In the smectogenic copper complexes previously studied [12], exchange and motional effects on the EPR spectrum were observed. In the present case, the nematic structure can also modify the magnetic exchange interaction, since the spin coupling between molecules depends dramatically on their relative orientation and separation. The disposition of the brick-like molecules in the calamitic nematic phase can also affect the motional modes and local order as in smectic liquid crystals.

In order to get information about these questions, we have carried out the study by EPR spectroscopy of the two new nematogenic compounds, Cu5 and CuO5. We will characterize the isolated molecules and present EPR spectra of the compounds in their different phases. Our results will be related to the structure and dynamics of the liquid crystal phases using our previous knowledge of such systems.

2. Experimental

X-band EPR measurements (microwave frequency about 9·5 GHz) were taken either with E-112 Varian or ESP380 Bruker spectrometers. For measurements above room temperature (RT), the variable temperature accessories E-265 from Varian and ER4111VT from Bruker were used. Powder samples were introduced 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. Measurements at liquid nitrogen temperature (LNT) were taken by putting the quartz tube into a quartz dewar vessel filled with liquid nitrogen. Q-band EPR measurements (microwave frequency about 34 GHz) were taken with an ESP380 Bruker spectrometer and are limited to temperatures below RT.

To characterize the isolated molecules, two kinds of low concentration solutions of the compounds were examined. Solutions in toluene were frozen at LNT and measurements made at this temperature. Solutions in the analogous zinc complexes were prepared by heating a mixture of the
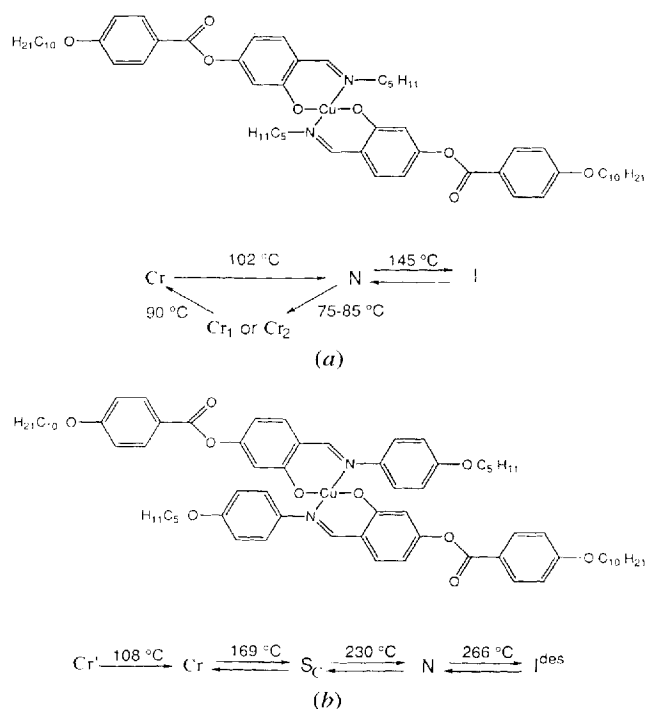

Figure 1. Molecular formulae and phase transition temperatures of (*a*) bis(*N*-*n*-pentyl-4-[(4'-decyloxy)benzoyloxy] salicylaldiminate)Cu(II), (Cu5) and (*b*) bis(*N*-(4"-*n*-pentoxyphenyl)-4-[(4'-decyloxy)benzoyloxy]salicylaldiminate)Cu(II), (CuO5). Cr, Cr₁, Cr₂, Cr', solid phases. Cr₁, Cr₂, two different frozen solid phases are obtained by cooling the nematic phase of Cu5 depending on the cooling rate. N, Nematic phase; S_C, Smectic C phase; I, isotropic liquid; des, an irreversible change of the CuO5 sample occurs in the isotropic state.

zinc and copper compounds up to the zinc complex melting point (below that of the melting point of the respective Cu complex) and cooling it down to RT.

3. Results

3.1. *Diluted samples*

The X-band EPR spectra of low concentrations, frozen solutions of Cu5 and CuO5 in toluene measured at LNT are given in figure 2 (traces (*a*)). In both cases, an ensemble of three equally spaced peaks in the low magnetic field region (between 270 mT and 300 mT) and a signal with some structure in the high field region (320 mT) can be seen. For Cu5, the low field peaks are at slightly lower fields than for CuO5. These spectra are typical of polycrystalline samples of copper complexes and can be interpreted using a spin Hamiltonian with two terms, the electronic Zeeman term and that accounting for the hyperfine interaction with the copper nucleus.

$$\mathcal{H} = \mu_B \mathbf{B} \cdot \mathbf{g} \cdot \mathbf{S} + \mathbf{I} \cdot \mathbf{A} \cdot \mathbf{S} \qquad (1)$$

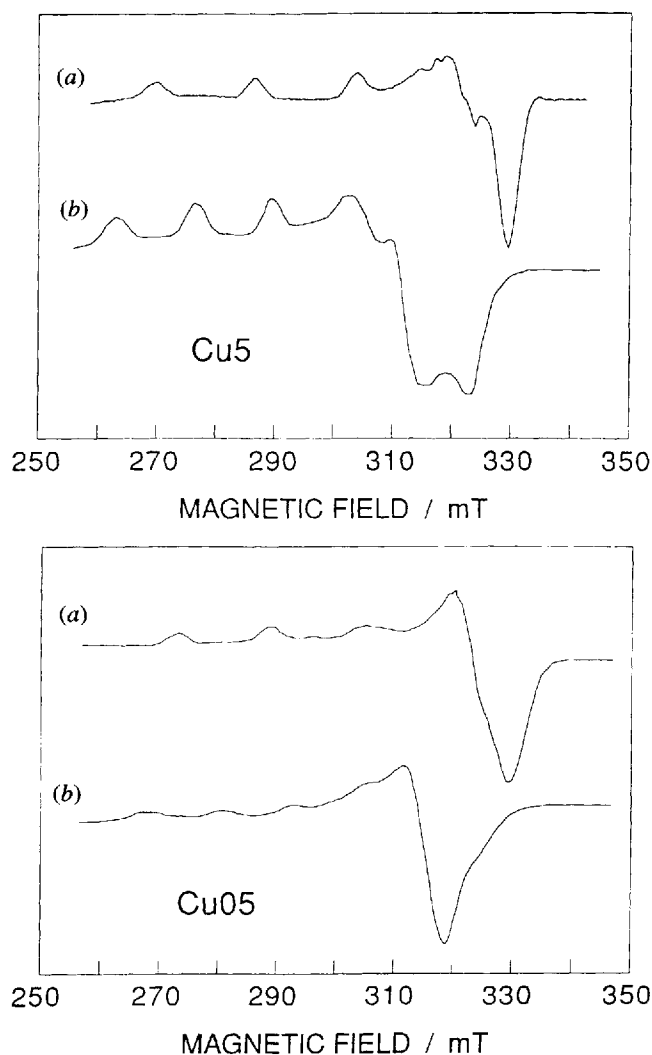where μ_B represents the Bohr magneton, **B** the magnetic

Figure 2. EPR spectrum of low concentration solutions Cu5 (upper) and CuO5 (lower): (*a*) frozen solution in toluene measured in LNT; (*b*) Solution in the analogous zinc complex measured at RT.

flux density, **g** the Zeeman coupling-tensor, **S** the electronic spin, **I** the nuclear spin and **A** the hyperfine interaction tensor.

Cu^{2+} is a $3d^9$ ion with a ground electronic term ^2D. In copper complexes derived from Schiff's bases, the metal is generally placed in an almost square planar environment [6–8, 10, 12, 13]. Such a situation leads to a non-degenerate orbital ground state $|x^2 - y^2>$ for copper forming a σ bond with ligands resulting in an effective electronic spin $S = 1/2$ [16–18]. Besides, copper has two natural isotopes (^{63}Cu and ^{65}Cu with 69·2 and 30·8 per cent natural abundance, respectively), both with a nuclear spin $I = 3/2$ and similar nuclear g factors, $g_n(^{63}Cu)/g_n(^{65}Cu) = 0.95$. If the EPR signals are broad enough, the hyperfine lines for the two isotopes overlap and the

spectrum resembles that of a single $S = 1/2$, $I = 3/2$ system. Because of the symmetry of the complex, the coupling tensors **g** and **A** are nearly axial. It has to be noted that the direction of the molecular long axis is contained in the copper coordination plane, whereas the principal axis of the spin Hamiltonian tensors with non-degenerate eigenvalues (the so-called *parallel values*) is perpendicular to that plane. The relation between molecular (X_M, Y_M, Z_M) and spin Hamiltonian (x, y, z) frames is shown in figure 3. It is worth remembering that only the orientational order of the molecular long axis is preserved in a calamitic uniaxial mesophase.

The measured spectra correspond to the following description. The low field peaks can be associated to the *parallel* (not degenerated) principal values of the spin Hamiltonian given by equation (1). If the higher field peak of this set is hidden in the signal at 320 mT, the ensemble of four equally spaced peaks can be associated to a hyperfine interaction with a $I = 3/2$ nucleus. The high field signal accounts for the *perpendicular* (degenerated) principal values of the axial spin Hamiltonian tensors. The perpendicular hyperfine splitting is not resolved. The values of the spin Hamiltonian parameters for the two compounds are presented in the table; they are very similar to those obtained for other copper (II) complexes in a square planar environment [17–19] and for copper metallomesogens derived from Schiff's bases [6–8, 12, 13]. This confirms the square planar environment suggested for the copper ions in that case.
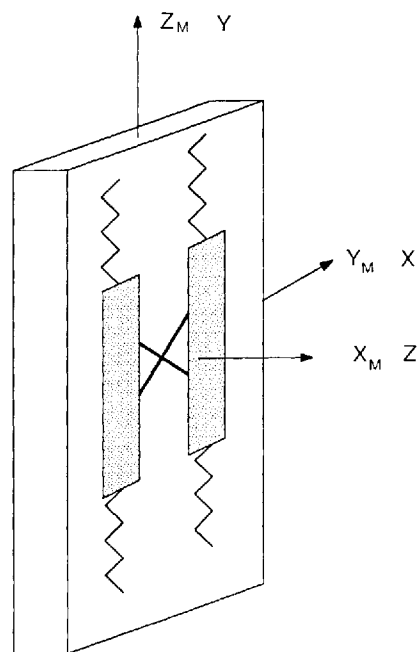

Figure 3. Schematic representation of the complexes showing the relation between the molecular (X_M, Y_M, Z_M) and the spin Hamiltonian (x, y, z) frames.

Table. g values and hyperfine coupling constants (in MHz) for the different samples. The estimated accuracy is 0·01 for the g values and 5 MHz for the hyperfine coupling constants. Blanks account for parameters that cannot be determined due to the sample orientation in the measuring magnetic field, while hyphens mean values too small to be resolved in the spectra.

	Cu5				CuO5			
	$g_\parallel$	$g_\perp$	$A_\parallel$	$A_\perp$	$g_\parallel$	$g_\perp$	$A_\parallel$	$A_\perp$
FTD	2·23	2·05	540	<50	2·24	2·06	500	<30
ZD	2·28	2·05	425	<60	2·27	2·06	395	<50
Solid phase†	2·23	2·05	480	<60	2·19	2·06 / 2·09	—	—
Nematic	2·21		500			2·06	—	—

FTD Frozen toluene solution. ZD Solution in the corresponding analogous zinc complex. † In the CuO5 complex the two smallest principal g values are considered that correspond to the perpendicular g axes.

There is a slight difference between the parameters obtained for Cu5 and CuO5 that can be attributed to a change in the electron density on the Cu nucleus due to the different substituent on the nitrogen atoms. In fact, an increase in the bond covalency causes a decrease in the values $g_\parallel$ and in the difference $(g_\parallel - g_\perp)$, as well as an increase in the $A_\parallel$ and in the difference $(A_\parallel - A_\perp)$ [18]. Our results point to a greater bond covalency in Schiff's base complexes with N-aliphatic substitution than in those with N-aromatic substitution.

Sometimes a similar diamagnetic complex is used as solvent. In order to compare the results for two kinds of solutions, we have measured the EPR spectra of Cu5 and CuO5 diluted, at low concentration, in the analogous diamagnetic zinc complexes Zn5 and ZnO5. The spectra are shown in figure 2 (traces (b)). No changes are observed when the temperature is lowered from RT to LNT. Both spectra can be interpreted as a copper powder spectrum with the spin Hamiltonian given by equation (1). However, some changes with respect to the frozen toluene solutions appear. The peaks of the parallel feature are shifted to lower fields and the hyperfine splittings decrease in such a way that the highest field peak is now well separated from the perpendicular signal. The corresponding values of the spin Hamiltonian parameters are also collected in the table. They are clearly different from the ones obtained with tolune solutions.

3.2. Concentrated samples

We have studied the EPR spectra of Cu5 and CuO5 as pure, concentrated samples at different temperatures through all the mesophase range(s). We shall describe the results for Cu5 and CuO5 separately.

3.2.1. Cu5 samples

This compound shows a nematic mesophase at relatively low temperatures (see figure 1). The X-band EPR spectrum of a concentrated (pure) powder sample of Cu5 at RT is shown in figure 4 (a). A high field signal at 320 mT and a single very broad shoulder in a low field region (about 280 mT) that is not well resolved can be observed. In the Q-band spectrum (see figure 5 (a)), the low field shoulder resolves as an ensemble of four equally spaced broad peaks. Therefore, these spectra can also be interpreted using the spin Hamiltonian (1) with the values for Zeeman and hyperfine parameters collected in the table. Comparing these results with those obtained for the Cu5 solutions, it is seen that the principal values of the **g** tensor are similar to those of the sample in toluene solution, but the $A_\parallel$ parameter is smaller.

The spectrum does not change when the temperature is increased below the melting point. In the nematic phase (see figure 4 (b)), the high field signal broadens and

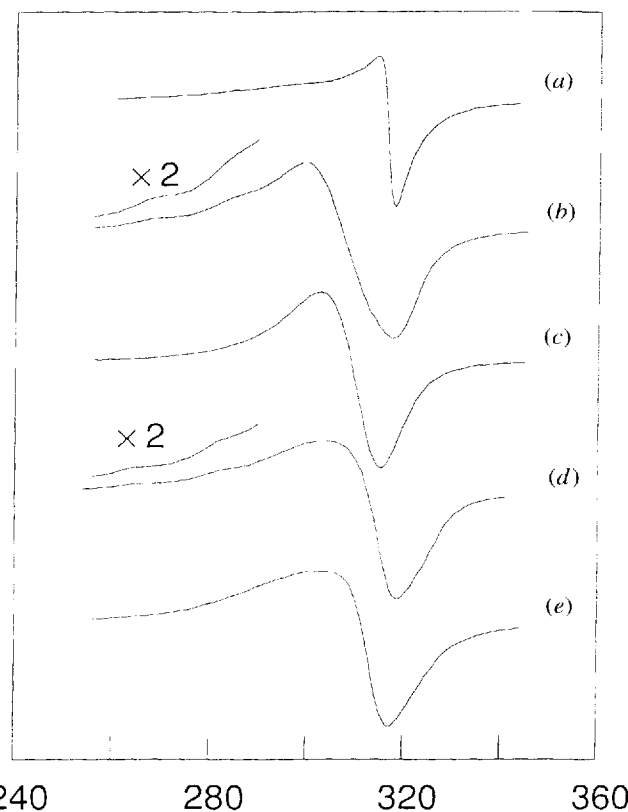240   280   320   360

Figure 4.   X-band EPR spectra of concentrated (pure) samples of Cu5 at different temperatures in different phases: (a) RT stable solid phase; (b) nematic phase at 125°C; (c) isotropic liquid phase at 160°C; (d) RT frozen solid phase obtained from the nematic by a quick cooling process; (e) RT frozen solid phase after cooling down the sample slowly.
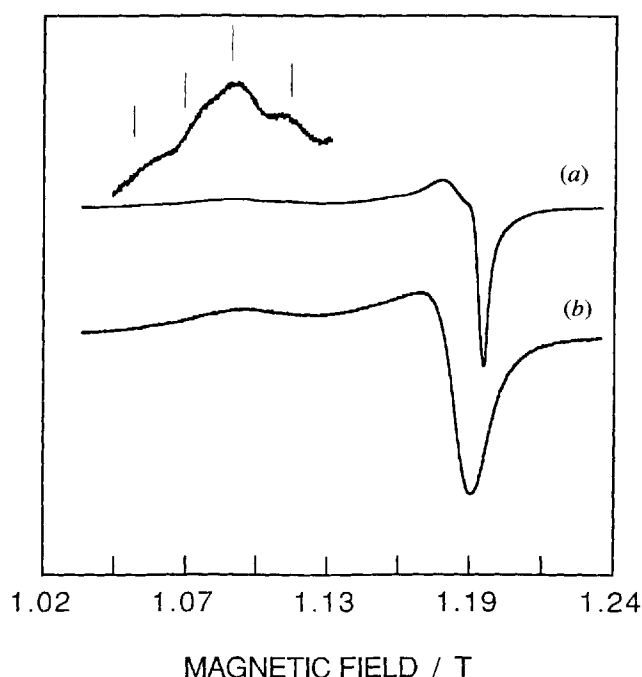
Figure 5. Q-band EPR spectra of Cu5 measured at RT: (*a*) stable solid phase; (*b*) frozen phase after a slow cooling process (this phase displays the X-band spectrum shown in figure 5 (*e*)).

superimposes on the parallel feature. At low temperature in the mesophase, the two low field, broad peaks of this feature are resolved. Although the signals are broad, the corresponding spin Hamiltonian parameters can be approximately determined (see the table). When the sample is heated up in the nematic phase, the low field peaks broaden and become unresolved. The spectrum in the isotropic liquid phase (see figure 4 (*c*)) shows a unique broad signal centred at about 315 mT.

It is worth noting that metallomesogenic complexes derived from Schiff's bases can generally be frozen by cooling them down from the fluid phases [12, 13]. Sometimes the sample preserves the mesophase structure in the frozen phase, but the molecular motion associated with the fluidity is quenched. In this aspect Cu5 shows a rich behaviour. Two different frozen phases appear depending on the cooling rate. When the freezing point is quickly passed, the EPR spectrum is quite similar to that obtained in the nematic phase (see figure 4 (*d*)), but when the transition to the frozen phase occurs move slowly, the measured EPR spectrum displays only a very broad asymmetric signal without any resolved low field peaks (see figure 4 (*e*)). In order to obtain more resolution in the *g* values, the Q-band spectrum in this last phase was measured (see figure 5 (*b*)). In this case the parallel and perpendicular features appear well resolved, and it has to be noted that they do not show any hyperfine structure.

The stable solid phase is recovered from the two frozen phases by heating the sample up to a solid–solid transition at about 80°C. After that, a spectrum similar to that found in untreated samples (see figures 4 (*a*) and 5 (*a*)) is obtained through the whole solid phase range.

3.2.2. *CuO5 samples*

This compound forms a smectic C phase and a nematic phase in a quite high temperature range. It suffers an irreversible change when it is heated above the clearing point. As in the case of the Cu5 compound, the phases and transition temperatures are shown in figure 1.

We study two different 'fresh' samples that we will label by their colour—green and brown. In spite of this initial difference, both types of sample have the same mesomorphic behaviour and as we will see later they become indistinguishable after a first heating cycle.

The green sample shows a RT EPR spectrum (see figure 6) very different from that obtained for Cu5 and CuO5 solutions. An approximately symmetric structure is displayed in a region between 250 mT and 400 mT. The parallel and perpendicular features typical of disordered samples of copper complexes cannot be identified, but some ensembles of seven equally spaced peaks and two broad bands are seen in the central part. Besides, a new feature appears in the field region between 100 mT and 200 mT. This whole spectrum is associated to the $S = 1$
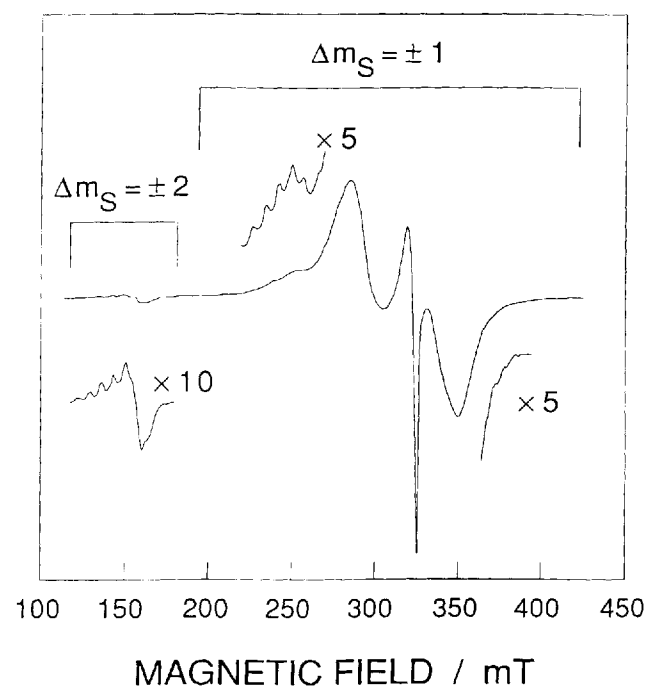

Figure 6. X-band EPR spectrum of the green sample of CuO5 measured at RT.

state of strongly coupled pairs of two equivalent Cu(II) and it is described using the following spin Hamiltonian:

$$\mathscr{H} = \mu_B\{g_\parallel B_z S_z + g_\perp(B_x S_x + B_y S_y)\}$$
$$+ \sum_{j=1}^{2} \{A_\parallel I_z^j S_z + A_\perp(I_x^j S_x + I_y^j S_y)\}$$
$$+ D\{S_z^2 - \tfrac{1}{3}S(S+1) + \eta(S_x^2 - S_y^2)\} \qquad (2)$$

with $I^j = 3/2$ and the following values for the spin Hamiltonian parameters: $g_\parallel = 2\cdot21$, $g_\perp = 2\cdot10$, $A_\parallel = 221$ MHz, $A_\perp < 25$ MHz, $D = 1625$ MHz and $\eta = E/D = 0\cdot04$. These pairs are probably due to an antiferromagnetic coupling of two Cu(II) as the singlet $S = 0$ in their ground state. The possible dimerization of the ground state of an 1-D Heisenberg antiferromagnet was proved by Pinpinelli [20] and this can explain the observed spectrum in this unstable phase.

The EPR spectrum of the brown sample displays three well-resolved features (see figure 7 (*a*)). A shoulder at about 295 mT, a broad signal centred at 305 mT and a narrow inverted peak at 315 mT. There is not any evidence of hyperfine structure. When this spectrum is measured at higher microwave frequency (Q-band), these three fea-
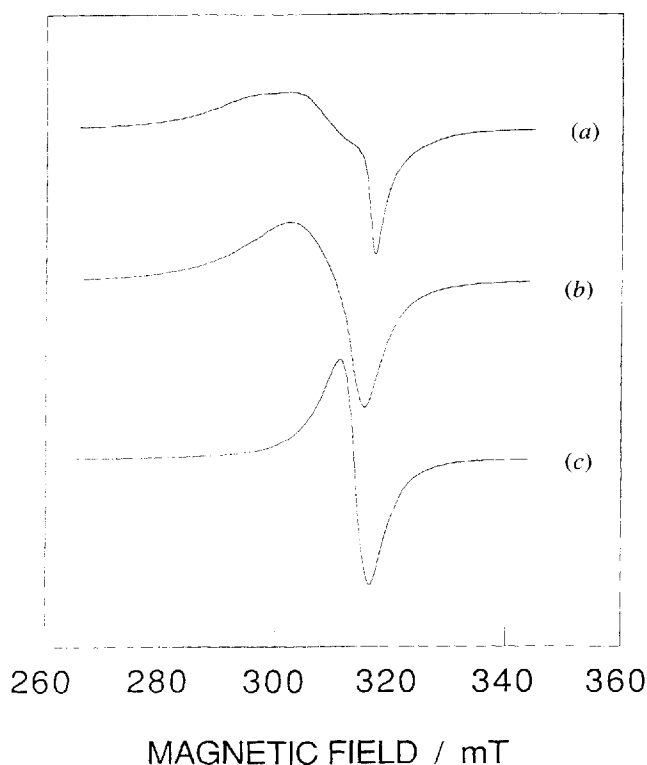
tures are clearly resolved (see figure 8). The anisotropy of the linewidth, as a consequence of the low dimensional intermolecular exchange coupling, is the reason for the anomalous shape of the central signal in the spectrum. Both the X- and Q-band spectra can be interpreted using a spin Hamiltonian with only a Zeeman term described by an orthorhombic **g** tensor.

$$\mathscr{H} = \mu_B\{g_x B_x S_x + g_y B_y S_y + g_z B_z S_z\} \qquad (3)$$

with the values shown in the table.

The spectrum of the brown sample does not change qualitatively when the sample is heated up in the solid phase. However, their features broaden in such a way that they are not well resolved at temperatures close to the melting point (169°C).

On the other hand when the green sample is heated up to about 110°C, a solid–solid transition takes place. Then the same spectra are displayed for the two types (green and brown) of sample at any temperature.

The compound forms a smectic C phase above the melting point. Within this mesophase, at temperatures below 210°C, the EPR spectrum consists of a unique asymmetric signal centred at 310 mT (see figure 7 (*b*)). It is similar to that found by other authors in mesogenic copper complexes derived from Schiff's bases [10, 12, 13]. Over 210°C (still in the S$_C$ phase), the sample becomes more fluid and the measuring magnetic field is able to orient the mesogenic domains with the director

260   280   300   320   340   360

MAGNETIC FIELD / mT

Figure 7.   X-band EPR spectra of concentrated (pure) CuO5 in different phases: (*a*) brown sample solid phase at RT; (*b*) low temperature (175–200°C) smectic phase; (*c*) oriented smectic phase (at 220°C). The same spectrum is observed over the whole N phase.

1.09   1.12   1.15   1.18   1.21   1.24
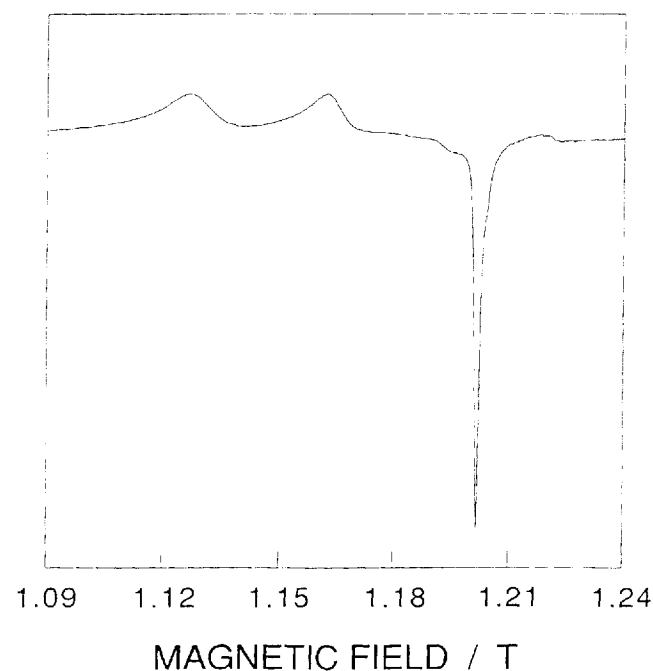
MAGNETIC FIELD / T

Figure 8.   Q-band EPR spectrum of a brown CuO5 sample measured at RT in the solid phase.

parallel to the magnetic field [21]. Then a symmetric signal at 315 mT (corresponding to the perpendicular signal of diluted CuO5 molecules, see figure 3) is displayed (see figure 7 (c)). The same spectrum is obtained for the nematic phase.

The EPR spectra found for the frozen phase obtained by cooling down from the mesophase depend on the rate of passing through the freezing point. Nonetheless, we do not observe several different phases, but a continued dependence of the linewidth on the freezing rate. The faster the cooling process, the broader the spectral features become. The slowest freezing processes produce a phase with an EPR spectrum very similar to that of the stable solid phase (see figure 7 (a)). Quicker cooling causes a broadening of the lines in such a way that the three features are not well resolved, as happen in the spectrum measured for the stable solid phase at high temperature.

4. Discussion

All the EPR spectra measured for diluted and concentrated Cu5 and CuO5 samples can be associated to Cu(II). In the first place, we will analyse the spin Hamiltonian parameters obtained for the isolated molecules dissolved in toluene, as well as in the analogous zinc complexes, and we will explain the dependence of their values on the solvent.

As we said above, there is no plausible explanation for a change in the covalency of a complex's bonds when the solvent is changed. We can associate the parameter variation to a change in the copper coordination geometry. It is well known that although the square planar coordination is the most frequent in this kind of copper complexes, such a geometry may vary easily because of structural conditions [22, 23]. Some authors have found by X-ray diffraction studies that similar copper complexes present distorted geometries involving a twist of the coordination plane (see figure 9), [7, 24, 25]. Furthermore, the zinc complex solvent has a nearly tetrahedral metal coordination geometry, corresponding to its closed shell electronic structure. When a square planar copper complex suffers such a distortion, its ground state can change from $|x^2 - y^2>$ one, but if this does not actually occur, the effect of the distortion on the spin Hamiltonian parameters is the same as that which we observe for the solutions in zinc complexes—an increase in the $g_\parallel$ value and in the difference $(g_\parallel - g_\perp)$ together with a decrease in the $A_\parallel$ coupling constant and in $(A_\parallel - A_\perp)$ difference [22]. Therefore we suggest that solutions in toluene leave the copper complexes in their more stable square planar coordination, and that the zinc complexes we have used as solvent induce a tetrahedral distortion in the solute copper molecules. Therefore we will use the spectroscopic parameters from the samples in toluene solution for further discussion.
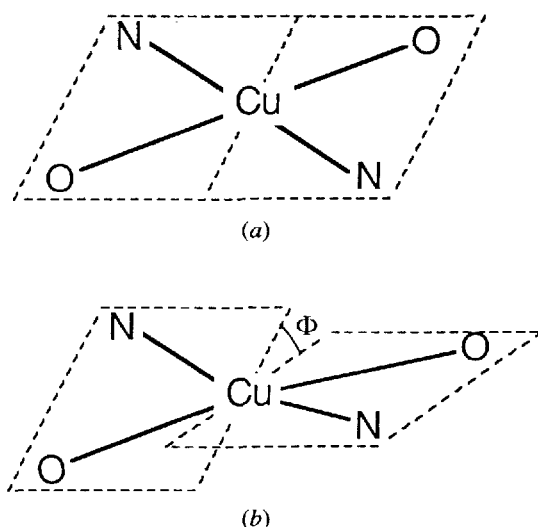

Figure 9. Sketch of the suggested distortion of the coordination geometry of our complexes. The square planar geometry (a) suffers a distortion in such a way that the two nitrogen–copper–oxygen planes make an angle Φ (b). If $\Phi = 90$ degrees, the coordination is tetrahedral.

Now we have to identify the coordination geometry of the molecules in the concentrated (pure) samples. We said above that motion and magnetic exchange can vary the EPR spectra and consequently the spin Hamiltonian parameters we obtain. Motion causes a temporal averaging of both **g** and hyperfine tensors and exchange is responsible for the collapse of the hyperfine splitting, together with a spatial averaging of the **g** tensor. However, the trace of the **g** tensor remains unchanged by those averaging processes. Then we can recognize the presence of molecules with distorted coordination geometries in a concentrated sample by a change in the **g** tensor trace. All the spin Hamiltonian parameters obtained in the different phases give a trace of the Zeeman tensor **g** similar to that obtained from toluene solutions. This indicates that square planar coordination occurs in both concentrated compounds.

Then we interpret the changes in the spectra of concentrated samples that mainly relate to the collapse of the hyperfine splitting and to the variations of the principal g values. In mesogenic copper complexes, this has been related to the magnetic exchange interactions and the structure and motion of the phases [6, 8–10, 12]. In order to have a complete picture of the phenomenology that can be found in exchanged mesogenic systems, we shall begin this discussion by giving an overview of the properties of such systems.

The exchange interaction consists in a coupling between the effective spins of two paramagnetic entities because of an overlapping of the electronic orbitals. In a

first approximation, it can be modelled by a Heisenberg–Dirac–Van Vleck exchange Hamiltonian $\mathcal{H}_{ex}$

$$\mathcal{H}_{ex} = \mathbf{S}_1 \cdot \mathbf{J}_{12} \cdot \mathbf{S}_2 \approx J_{12}\mathbf{S}_1 \cdot \mathbf{S}_2, \qquad (4)$$

1 and 2 being the two interacting paramagnetic species whose spins are $\mathbf{S}_1$ and $\mathbf{S}_2$. Although the exchange interaction generally couples nearest neighbour spins, each of them can interact with several others, allowing the indirect coupling of a great number of spins in the sample.

The exchange Hamiltonian has to be included in the complete spin Hamiltonian that then result as

$$\mathcal{H} = \mu_B \mathbf{B} \sum_i \mathbf{g}_i \cdot \mathbf{S}_i + \sum_i \mathbf{I}_i \cdot \mathbf{A}_i \cdot \mathbf{S}_i + \sum_{i>j} J_{ij}\mathbf{S}_i \cdot \mathbf{S}_j. \qquad (5)$$

If the exchange contribution is weak compared to the spin Hamiltonian anisotropy, it can be considered as a perturbation causing second order shifts and broadening of the EPR spectral signals. On the other hand, when the exchange coupling is strong with respect to the anisotropy (which is compatible with exchange energies smaller than 1 K), its effect on the EPR spectrum is more significant. For analysing this, we can separate the spin Hamiltonian into three parts, $\mathcal{H}_1$, $\mathcal{H}_a$, and $\mathcal{H}_{ex}$ given by

$$\mathcal{H}_{ex} = \sum_{i>j} J_{ij}\mathbf{S}_i \cdot \mathbf{S}_j,$$

$$\mathcal{H}_1 = \mu_B \mathbf{B} \left(\frac{1}{N}\sum_i^N \mathbf{g}_i\right) \cdot \left(\sum_i^N \mathbf{S}_i\right)$$

$$+ \left(\frac{1}{N}\sum_i^N \mathbf{I}_i \cdot \mathbf{A}_i\right) \cdot \left(\sum_i^N \mathbf{S}_i\right), \qquad (6)$$

$$\mathcal{H}_a = \mathcal{H} - \mathcal{H}_x - \mathcal{H}_{ex}.$$

$\mathcal{H}_a$ does not commute with $\mathcal{H}_{ex}$, so the exchange term causes a temporal evolution upon it. Since $\mathcal{H}_{ex}$ is strong, the temporal average of $\mathcal{H}_a$ vanishes and its contribution to the spectrum is unimportant. In such a way, $\mathcal{H}_1$ is the effective spin Hamiltonian that describes the spectrum. The effective $\mathbf{g}$ tensor accounting for the Zeeman interaction is the tensorial average of those of the species involved in the long range exchange interaction, and the hyperfine interaction collapses to zero because the contribution of many nuclei with small hyperfine parameters does not induce splitting, but only an additional broadening of the spectral lines [26].

An alternative physical view of the effect of strong exchange may be given: the coupling of the spins produces a real exchange of their location during the EPR interaction, so the interacting spin 'spends a part of its time' in each paramagnetic entity. This *dynamical* point of view [27] allows us to understand the effect of long range exchange. The spin diffusion is responsible for the spatial averaging of the gyromagnetic tensors. Besides, all the nuclei are 'visited', but for a short time, so the hyperfine splitting collapses.

Then the effective spin Hamiltonian becomes

$$\mathcal{H}_{eff} = \mu_B \mathbf{B} \cdot \langle \mathbf{g} \rangle \cdot \mathbf{S}_T \quad \text{with} \quad \mathbf{S}_T = \sum_i^N \mathbf{S}_i \qquad (7)$$

where $\langle \ldots \rangle$ indicates an average in the exchange path. The collapse of the hyperfine splitting is a specific property of long range exchange coupled systems. It allows one to distinguish exchange effects from motional ones, where the $\mathbf{g}$ tensor is also averaged, but the hyperfine splitting reaches a value corresponding to the isotropic part of the hyperfine coupling tensor.

In conclusion, the effects of exchange interaction on the spectra of our copper complexes are the following: if the coupling is weak compared to the spin Hamiltonian anisotropy, the spectral lines broaden and shift because of a partial averaging of the spin Hamiltonian tensors. If the exchange interaction is strong, the hyperfine splitting collapses to zero and the measured $\mathbf{g}$ tensor parameters corresponds to a tensorial average of the individual $\mathbf{g}$ tensors along the exchange path. From that we have information about the spatial correlation of the molecular frames in the phase.

With these ideas in mind, we can discuss our experimental results in concentrated samples using the spin Hamiltonian (1) and by considering the exchange coupling effect. In the fluid phases, additional effects due to molecular motion take place. It is worth noting that motion and exchange can simultaneously affect the EPR spectrum. Rapid enough tumbling modes are able to average the exchange constant J that depends on distance and relative orientation of the interacting paramagnetic systems. The averaged value of J indicates the effective strength of the exchange interaction [28]. As we pointed out elsewhere, some dynamical modes favour the preservation of exchange in fluid phases [12]. The presence of these restricted modes is related to additional local order in mesophases. On this basis, we have presented in a previous paper an EPR study of a smectogenic copper complex [12]. In the following we shall pay attention to the relation of exchange with the loss of positional correlation in nematic mesophases.

Firstly we consider the solid phase spectra. In both compounds, there exists a stable, solid phase. Sometimes it can be reached after a solid–solid transition and over the whole solid state temperature range it shows the same EPR spectrum, except for a linewidth change. The spectra for Cu5 practically give the same value for the Zeeman parameters as the isolated molecule in dilute toluene solution, but a smaller parallel hyperfine splitting. This may be due to a long range, weak exchange coupling. In CuO5, the EPR spectrum in the solid phase does not show any hyperfine splitting, whereas the parallel and perpendicular principal values of the $\mathbf{g}$ tensor are partially averaged, while the other perpendicular value remains
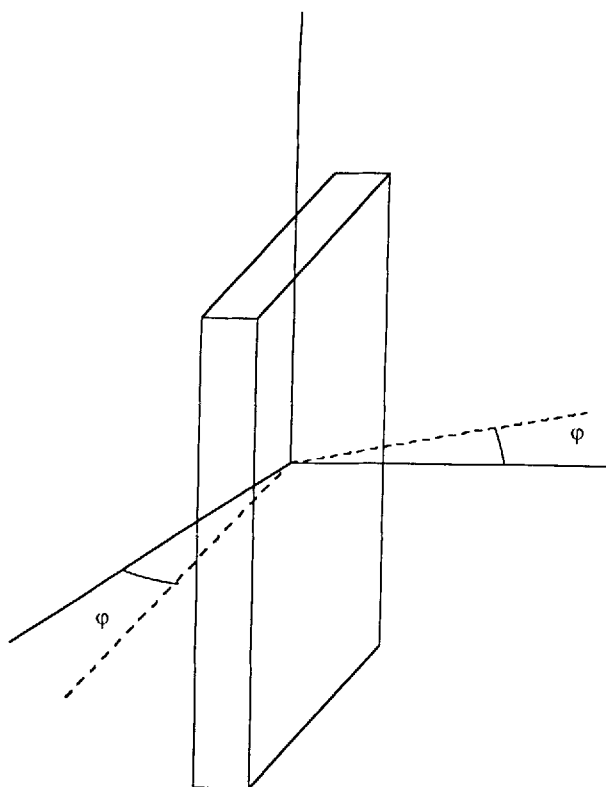
Figure 10. Decorrelation of the molecular short axes in the pre-smectic solid phase.

unchanged. These facts indicate that a strong exchange interaction takes place and that one of the principal axes contained in the copper coordination plane lies parallel for all the molecules. On the other hand, the two other principal axes are not parallel in the solid. This can be due to a book-like molecular packing or be a consequence of a decorrelation of the molecular short axes. Both cases are compatible with a pre-smectic structure in the solid phase of CuO5.

In the first case, a book-like molecular packing structure compatible with a perfect crystal order, we can obtain the angle $2\varphi_o$ made by two adjacent molecule from

$$\sin \varphi_0 = \left[\frac{g_\parallel^{isolated} - g_\parallel^{measured}}{g_\parallel^{isolated} - g_\perp^{isolated}} \right]^{1/2} \qquad (8)$$

and from the table we estimate $\varphi_o \approx 30$ degrees.

The decorrelation of the molecular short axes in the solid phases of similar complexes has been described by other authors [7]. We can also get information about the spatial decorrelation of the molecule axis in the phase. One of the perpendicular principal axes rests nearly parallel in the domain, since its corresponding parameter preserves the value of the isolated molecule (2·06). The other two principal g values change because of the decorrelation of the corresponding molecular axes along the exchange path that can be characterized by an angle φ. As can be seen in

figure 10, the orientation of the molecular short axes is rotated from a common reference frame for the whole domain around the long axis by and angle φ. An estimation of this decorrelation can be made assuming that in the domain the molecular rotation is uniformly distributed in the interval $(- \varphi_o, \varphi_o)$. The value of φ_o in the solid phase can be determined from the parameters of the isolated molecules and those of the concentrated samples [14]

$$\frac{g_\parallel^{measured} - g_\parallel^{isolated}}{g_\parallel^{isolated} - g_\perp^{isolated}} = - \varphi_0 + \tfrac{1}{2} \sin(\varphi_0) \qquad (9)$$

giving in our case $\varphi_o \approx 45$ degrees and indicating that the situation is far away from one of complete decorrelation of the two short axes.

Besides the stable solid, other non-fluid phases, recognized by their EPR spectra, appear after synthesizing (the green sample phase of CuO5) or by freezing the mesophase below a particular temperature. We have already discussed the spectrum of the green sample of CuO5 in the former section. Since this phase is unstable, its existence is anecdotal, but provides proof of the great variety of structures that we can find in this kind of compounds.

Two phases can appear by freezing Cu5. The one obtained by a quick cooling process shows an EPR spectrum (see figure 4 (d)) with spin Hamiltonian parameters which correspond to a copper complex without any evidence of exchange coupling. The spectrum is very similar to that observed for the nematic phase. When the cooling process takes place more slowly, the RT EPR spectrum shows broad features. The parallel hyperfine splitting is collapsed, as the Q-band spectrum (see figure 5 (b)) shows, which indicates a long range exchange interaction. Although the spins coupling is not strong enough to narrow the spectral lines, it is higher than in the stable solid phase. All these results lead us to suggest that in the quick cooling process, a freezing in of the nematic molecular structure occurs. A slower process allows the molecules to arrange themselves in another molecular disposition, probably in a pre-smectic structure.

The solidification process in CuO5 does not produce a new phase and only gives the stable solid which has a pre-smectic structure.

Finally we go on to comment on the spectra observed in the mesophase. In the nematic phase of Cu5, the exchange interaction is hardly reduced as the EPR spectrum (see figure 4 (b)) shows. The slight changes in the values of the $g_\parallel$ and $A_\parallel$ parameters relative to those of the isolated molecule are caused by molecular motion. Unfortunately, the broadening of signals does not allow a good determination of these values, so a quantitative study of the motional modes is not possible. Nonetheless, it is worth noting that the parallel g value in this phase is not far from the static one. It is not compatible with the

classical picture of molecules in a calamitic mesophase rapidly spinning around their long axes, where a complete averaging of the spin Hamiltonian principal values of the two short axes should take place. As in similar smecto-genic compounds [12–14], the peculiar shape of the molecules imposes a change in the molecular surroundings that affects the local structure of the liquid crystal.

A typical *smectic phase* spectrum is observed when CuO5 is examined at low temperatures within the smectic phase (see figure 7 (*b*)). It is due to the combined effects of motion and exchange. Apparently, a partial average of the principal *g* values of the two short axes, jointly with collapse of the hyperfine splitting occurs. It is similar to the behaviour observed in the brown sample solid phase of the same compound. The effect of motion causes an additional broadening of the signals that prevents the resolution of spectral features. It has been pointed out elsewhere that this spectrum is compatible with some local order of the molecular short axes in the smectic phase [12]. In the nematic phase, the sample is oriented and we cannot know the strength of the exchange coupling, because the perpendicular feature of the copper complex does not have a resolved hyperfine splitting in any case.

5. Summary

We have investigated the evolution of the EPR spectra of two mesogenic copper complexes, bis(*N*-*n*-pentyl-4-[(4'-decyloxy)benxoyloxy]salicylaldiminate) copper(II) (Cu5) and bis(*N*-(4''-*n*-pentoxyphenyl)-4-[(4'-decy-loxy)benzoyloxy]salicylaldiminate) copper(II) (CuO5), as a function of temperature. The characterization of the isolated molecule has been achieved using frozen solutions in toluene. The coordination geometry has been identified as nearly square planar. A distortion of this geometry consisting in a twist of the nitrogen–copper–oxygen coordination planes has been found when copper compounds are dissolved in the analogous zinc complexes. The geometry is concentrated samples is also square planar.

In the stable solid phases, the spectra of both compounds are different from those of the isolated molecules because of magnetic exchange coupling effects. CuO5 has an unstable phase whose EPR spectrum reveals that strongly exchange-coupled pairs are formed. The fluid phases of Cu5 can be frozen forming different structures that depend on the freezing process rate.

CuO5 displays an EPR spectrum in the smectic phase at low temperature similar to that found in other smectogenic copper complexes derived from Schiff's bases. When the temperature increases, the sample orients with the domain director parallel to the measuring magnetic field. On the other hand if Cu5 is in the nematic phase, the exchange interaction is strongly reduced because of the loss of positional correlation of the

molecules. The EPR spectrum indicates differences in the local molecular arrangement in this mesophase compared to that in the nematic phase of cylindrically symmetric molecules.

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