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J. I. Martínez[a]; D. W. Bruce[b]; D. J. Price[b]; P. J. Alonso[a]
[a] Instituto de Ciencias de Materiales de Aragón, Consejo Superior de Investigaciones Científicas-U. de Zaragoza, Zaragoza, Spain [b] Centre for Molecular Materials and Department of Chemistry, The University of Sheffield, Sheffield, England

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Mesophase order of a new smectic paramagnetic copper complex detected by EPR

by J. I. MARTÍNEZ†, D. W. BRUCE‡§, D. J. PRICE‡ and P. J. ALONSO*†
† Instituto de Ciencias de Materiales de Aragón,
Consejo Superior de Investigaciones Científicas-U. de Zaragoza,
Pza. S. Francisco s/n. 50009 Zaragoza, Spain
‡ Centre for Molecular Materials and Department of Chemistry,
The University of Sheffield, Sheffield S3 7HF, England

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Electron paramagnetic resonance measurements of a new copper dithiocarbamate complex having liquid crystal properties are presented. Spectra have been measured using a frozen toluene solution at liquid nitrogen temperature as well as concentrated samples at different temperatures covering the solid and smectic phases range. The existence of a long range intermolecular exchange interaction at all the temperatures is established by the collapse of the hyperfine structure in the spectra of the condensed samples. The comparison of the principal effective g-values in the solid phase with those of the isolated molecule obtained from the toluene solution spectra indicates that in the solid, the molecules pack keeping their molecular axes parallel. The drastic changes observed in the spectra when the sample reaches the smectic phase are interpreted as a consequence of the structure of this mesophase and on the basis of the calamitic shape of the molecules. This led us to obtain the temperature dependence of the Saupe order parameter in the smectic phase from the thermal evolution of the spectra directly, without using any foreign probe. This also contrasts with the behaviour observed in others copper metallomesogens derived from Schiffs bases whose molecules depart significantly from cylindrical shape.

1. Introduction

Electron paramagnetic resonance (EPR) spectroscopy has been widely used as a tool for studying conventional organic liquid crystal (LC) [1, 2]. Since these materials are diamagnetic, paramagnetic probes had to be dissolved in them and their spectra measured as a function of temperature in the different phases to provide information about the molecular order and the mesophase structure. In this approach, it is assumed that the dynamics of the foreign paramagnetic entity are driven by the host material. The appearance in the last decades of paramagnetic liquid crystals (PLC) opens new possibilities of obtaining structural information about the mesophase directly from the constituent molecules by using EPR spectroscopy, overcoming the weakness of the technique derived from the use of an external paramagnetic probe dissolved in diamagnetic mesogens.

A variety of PLCs has been studied by EPR. One of the main groups consists of mononuclear copper (II) complexes [3–6]. The reasons for that are the abundance of copper-containing metallomesogens and the simplicity of analysing their EPR spectra that can be readily measured above room temperature (RT) for the mesophases. As in the case of conventional organic LCs, information about the local molecular order in the mesophase can be reached from the variations that motional relaxation induces in the EPR spectrum of the paramagnetic entity. On the other hand, additional information can be obtained in the case of PLCs as a consequence of the higher concentration of the magnetic entity. Therefore, the mesogenic copper complexes often show intermolecular magnetic exchange interactions. Although in these compounds the energy of such a coupling is very small compared to the thermal energy of the mesophase, the exchange interaction provides other relaxation mechanisms that significantly affect the EPR spectrum. These interactions do not occur in diamagnetic liquid crystals with diluted paramagnetic probes.

The new possibilities for EPR on copper metallomesogens coupled by exchange are now being developed. Some mesogenic copper compounds (for example complexes derived from Schiffs bases and β-diketones) show the peculiarity that, although their mesophases are described conventionally as those of calamitic molecules, their molecular shape can deviate from cylindrical

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* Author for correspondence.

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symmetry [4–7]. The analysis of their EPR spectra has revealed their special local arrangement in the mesophase. However, mesophases of copper complexes with a true calamitic molecular shape have not been studied until now by EPR spectroscopy. Complexes derived from 2,5-salicylaldehyde have a suitable shape, but their mesophases generally appear at very high temperatures, and then present problems concerning chemical stability and display very broad EPR spectral features that are not well resolved [8].

This paper is devoted to the analysis of EPR spectra of a new smectogenic copper complex derived from thiocarbamate ligands. The formula of the compound (hereafter named S6) is presented in figure 1. Its mesophases and transition temperatures are given in the table. The S6 molecule clearly has a calamitic shape. Its EPR spectrum in the mesophases can be easily measured and interpreted. The appearance of the magnetic exchange coupling in the mesophase will allow us to obtain information about the global mesophase order in a different way from the case of systems without any exchange coupling.

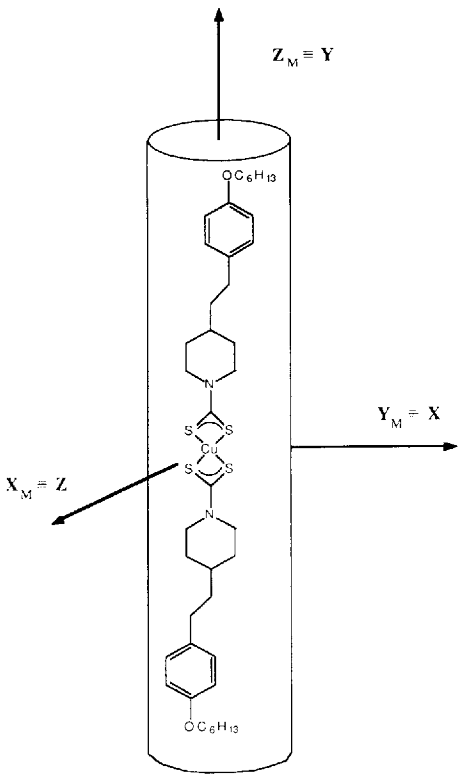


Figure 1. Molecular formula of S6. A scheme for the molecular (X_M, Y_M, Z_M) and magnetic (X, Y, Z) (spin-hamiltonian) axes is also included.

Table. Phases and transition temperatures (°C) for the S6 compound.

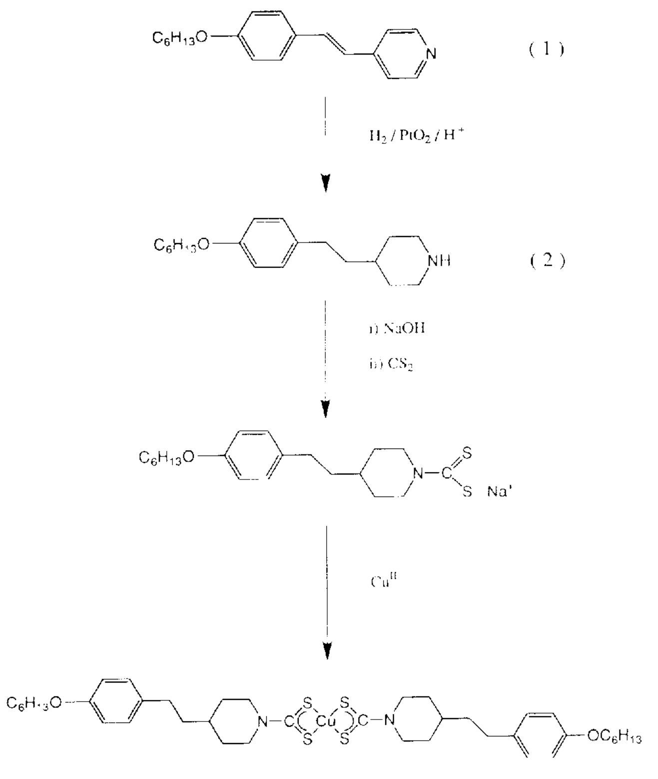
$$\begin{tikzcd}
Cr \arrow[r, "145"] & Cr' \arrow[r, "216"] & S_C \arrow[r, "248"] \arrow[dl, "201"] & I \\
 & S_B & &
\end{tikzcd}$$

Cr, Cr′: solid phases; S_C: smectic C phase; S_B: smectic B phase; I: Isotropic liquid.

2. Experimental

X-band EPR measurements were recorded using ESP380E Bruker and E112 Varian spectrometers. The variable temperature accessory ER4111VT from Bruker was used for measurements above RT. Powder samples were put into quartz tubes (707-SQ from Wilmad) and the temperature was monitored using a copper–constant 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. A glassy frozen solution of S6 in toluene was also analysed at liquid nitrogen temperature (LNT) by placing the quartz tube in an immersion quartz dewar filled with liquid nitrogen.

The complexes were prepared [9] as shown in the scheme. 4-Hexyloxystilbazole (**1**) was partially hydrogenated over PtO_2 to give the piperidine (**2**), from which the dithiocarbamate and its copper complex were readily



(S6)

Scheme.

obtained. Other mesomorphic dithiocarbamate complexes have been described by Hoshino-Miyajima [10].

3. Results

In order to characterize the isolated molecule, we have measured the EPR spectrum of a low concentration solution of S6 in toluene at liquid nitrogen temperature. In such a sample, the copper complexes are oriented randomly in all the possible orientations with respect to the d.c. magnetic field. The X-band spectrum shown in figure 2 is obtained. It shows three doublets at about 295, 310 and 340 mT. Besides, four equally spaced signals with some poorly resolved structure appear in the field region between 315 mT and 335 mT. Assuming that there is another doublet which remains unresolved in this central region, the former spectrum can be described as a combination of four equally spaced double peaks (doublets) and four equally spaced signals. We have marked the main spectral features with vertical lines in figure 2. This spectrum is similar to that found for other copper complexes with the same metal environment [11, 12]. In these complexes, the copper ion bonds with the four sulphurs of the ligands with a coordination geometry that is nearly square planar. In the ground electronic state, an unpaired electron is placed in a copper $d_{x^2-y^2}$ orbital that forms a σ bond with the sulphurs. The system is paramagnetic with an effective spin $S = 1/2$. Besides, copper has two natural isotopes both with nuclear spin $I = 3/2$ (^{63}Cu and ^{65}Cu, 69·2 per cent and 30·8 per cent natural abundance, respectively) and very similar nuclear giromagnetic factors ($g_n(^{63}\mathrm{Cu})/g_n(^{65}\mathrm{Cu}) = 0{\cdot}95$). For interpreting the spectra, a spin-hamiltonian including two terms, the electronic Zeeman interaction and the hyperfine coupling with the copper nucleus, is proposed:

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

with μ_B being the Bohr magneton $\mathbf{B}$ the magnetic field, $\tilde{\mathbf{g}}$ the Zeeman coupling (giromagnetic) tensor and $\tilde{\mathbf{A}}$ the hyperfine interaction tensor. Because of the symmetry of the coordination geometry, both $\tilde{\mathbf{g}}$ and $\tilde{\mathbf{A}}$ tensors are practically axial and are described by two principal values ($g_\parallel$ and $g_\perp$) and ($A_\parallel$ and $A_\perp$)) respectively. In figure 1 we show a sketch of the S6 molecule, together the molecular axes (x_M, y_M, z_M), z_M standing for the long axis. The *perpendicular* and *parallel* principal axes of the molecular spin hamiltonian tensors are also indicated. It has to be noted that the axis corresponding to the parallel principal values is perpendicular to the coordination plane of the complex, whereas the long molecular axis (whose mean orientation defines the mesophase director) relates to one of the two perpendicular axes. In our case we obtain

$$g_\parallel = 2{\cdot}085 \pm 0{\cdot}005 \qquad A_\parallel = 490 \pm 5\,\mathrm{MHz}$$

$$g_\perp = 2{\cdot}016 \pm 0{\cdot}005 \qquad A_\perp = 120 \pm 5\,\mathrm{MHz}.$$

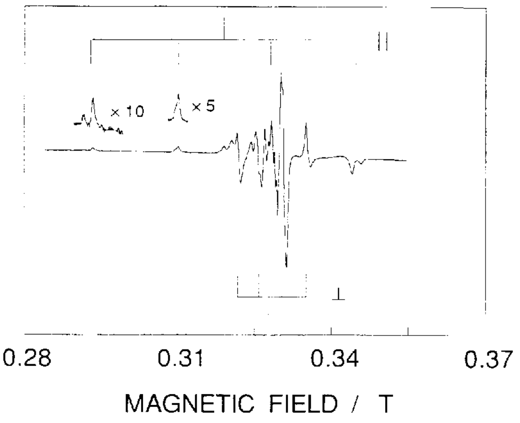


Figure 2. X-band EPR spectrum of S6 dissolved in toluene at liquid nitrogen temperature. The main features of the spectrum are marked with vertical lines.

These figures agree with those reported for Cu(II) in similar complexes [11, 12]. The doublet structure in the parallel signal (see figure 2) is associated with the existence of the two copper isotopes with very similar hyperfine coupling constants. The values for the hyperfine parameters given above are mean values of those of the two isotopes.

The EPR spectra measured for concentrated S6 samples are very different from that observed for the toluene solution. At RT, a spectrum with only one peak and one signal (see figure 3 (*a*)) is displayed. It is worthy of note that the signal peak of this spectrum is placed in the centre of the four doublets (317 mT) of the toluene solution spectrum, whereas the single signal occupies also the centre of the corresponding four signals (325 mT). The spectrum can be described using a simple spin-hamiltonian that includes only an electronic Zeeman term having orthorhombic symmetry. The principal g-values obtained from the RT spectrum are $g_x = 2{\cdot}03 \pm 0{\cdot}01$, $g_y = 2{\cdot}02 \pm 0{\cdot}01$ and $g_z = 2{\cdot}09 \pm 0{\cdot}01$.

Therefore the **g**-tensor turns out to be practically axial and its principal values are in agreement with those found for the isolated molecule in a toluene solution, despite the fact that the differences between g_x and g_y are not resolved in this last spectrum. No hyperfine structure is observed in the case of a concentrated S6 sample at RT.

When the EPR spectrum is measured at higher temperatures in the solid phase, it remains unchanged until 160°C. At this temperature some new peaks appear at fields in between those corresponding to the main features of the RT spectrum. Since these signals are not observed in the mesophase and are likely to be due to a molecular rearrangement in the Cr′ solid phase, we will not discuss these further.

Above the melting point, a completely different

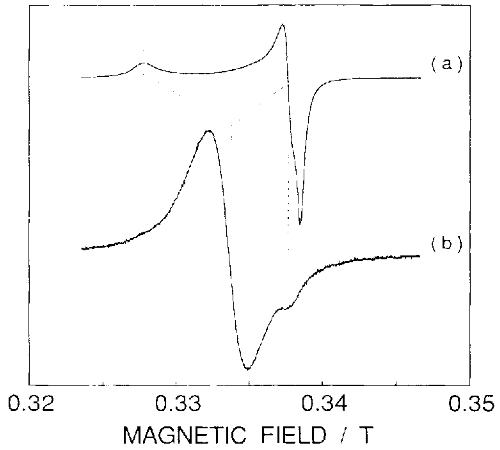


Figure 3. X-band EPR spectra of S6 concentrated sample: (*a*) solid phase at room temperature, (*b*) smectic phase at 210°C.

spectrum is obtained. It consists in a broad signal centred at 333 mT, together with a shoulder at 338 mT (see figure 3 (*b*)). As in the case of the RT spectrum, no hyperfine structure is observed and the EPR spectrum can be described with a spin-hamiltonian including only an electronic Zeeman term having an axial symmetry. The principal g-values are $g'_\parallel = 2{\cdot}03 \pm 0{\cdot}01$ and $g'_\perp = 2{\cdot}05 \pm 0{\cdot}01$. In this case, $g'_\parallel < g'_\perp$ in contrast to the situation at low temperature, where $g_\parallel > g_\perp$, but the trace of the **g**-tensor remains unchanged. It is also worthy of mention that the high field shoulder moves to higher fields when the temperature increases in the mesophase. In order to get a wider temperature range of measurement, data were obtained during both cooling and heating processes.

4. Discussion

When the RT spectrum of concentrated samples (see figure 3 (*a*)) is compared with that of isolated molecules (see figure 2), some drastic changes are observed. Whereas the principal g-values coincide, the hyperfine structure in the concentrated S6 samples vanishes. A collapse of the hyperfine structure is also observed in the spectra measured for the smectic phase.

The collapse of the hyperfine structure is typical of paramagnetic systems coupled by long range magnetic exchange interactions. Firstly we will indicate the effects of long range magnetic exchange [13–15]. The exchange interaction consists in a weak bond that couples the effective spins of two different species. To a first approximation, it can be modelled by a Heisenberg–Dirac–Van Vleck hamiltonian, $\mathcal{H}_{\text{ex}}$:

$$\mathcal{H}_{\text{ex}} = J\mathbf{S}_i\mathbf{S}_j \tag{2}$$

where J is the exchange coupling parameter. Generally this interaction takes place between nearby paramagnetic entities. The paramagnetic species can form pairs, trimers or other groups of a few molecules coupled by exchange. In such systems, the EPR spectrum is modified by the magnetic coupling. However, facts we found about our EPR spectrum of the concentrated sample, mainly the collapse to zero of the hyperfine splitting, are related to long range exchange coupling. In spite of the fact that there is exchange coupling only between nearby molecules, a particular molecule can interact with several others; the molecules involved in the coupling can form a long range domain. In the following, we will refer to long range coupled systems. Then the spin-hamiltonian has to include all the interacting spins and it is given by the summation of equation (1) over all the coupled spins. Assuming localized spin and then neglecting hyperfine interactions with other nuclei in sites different from that of the spin, we obtain

$$\mathcal{H} = \mu_{\text{B}} \sum_i (\mathbf{S}_i\tilde{\mathbf{g}}_i)\mathbf{B} + \sum_i (\mathbf{S}_i\tilde{\mathbf{A}}_i\mathbf{I}_i). \tag{3}$$

The exchange interaction produces a temporal evolution in the spin-hamiltonian since the exchange term (2) does not commutate with the complete spin-hamiltonian (3)

$$\frac{\partial \mathcal{H}}{\partial t} = -i[\mathcal{H}, \mathcal{H}_{\text{ex}}]. \tag{4}$$

We can separate the spin-hamiltonian of an exchange coupled system into two parts, the one $\mathcal{H}_{\text{I}}$ being time independent (that is, commutating with the $\mathcal{H}_{\text{ex}}$ term)

$$\mathcal{H}_{\text{I}} = \mu_{\text{B}}\left(\sum_i^N \mathbf{S}_i\right)\left(\frac{1}{N}\sum_i^N \tilde{\mathbf{g}}_i\right)\mathbf{B} + \left(\sum_i^N \mathbf{S}_i\right)\left(\sum_i^N \frac{1}{N}\tilde{\mathbf{A}}_i\mathbf{I}_i\right) \tag{5}$$

where N is the number of molecules coupled in an exchange domain, and the other $\mathcal{H}_{\text{a}} = \mathcal{H} - \mathcal{H}_{\text{I}}$, which time average vanishes, $\langle \mathcal{H}_{\text{a}} \rangle_{\text{time}} = 0$.

When the exchange interaction is weak compared with the spin-hamiltonian anisotropy, the $\mathcal{H}_{\text{ex}}$ perturbation has only minor broadening and shift effects on the EPR spectrum. On the contrary, a strong exchange term causes an average of the $\mathcal{H}_{\text{a}}$ part and completely modifies the spectrum. Then the $\mathcal{H}_{\text{I}}$ part becomes the effective spin-hamiltonian. The effective **g**-tensor tends to be an average of those of the individual molecules, and the hyperfine splitting collapses to zero because many nuclei interacting with very small hyperfine parameters do not produce a splitting—only an additional broadening.

When exchange takes place in fluid phases, the effects of motion also have to be considered. Motion also causes temporal variation of some parts of the spin-hamiltonian and then an additional averaging process. Moreover, a temporal average of the exchange term occurs because of tumbling. If this average leaves a strong exchange term in comparison with the spin-hamiltonian anisotropy, both motion and exchange effects are superimposed on the EPR spectrum [6, 16].

Taking into account these basic ideas, we go on to discuss the EPR spectra in the different phases of S6. Let us start with that measured for the solid phase (see figure 3 (*a*)). The collapse to zero of the hyperfine splitting is a characteristic property of long range exchange coupled systems. The EPR spectrum in such a system with a strong, long range exchange interaction gives information about the spatial averaging of the individual **g**-tensors. It is related to the spatial correlation of the molecular frame and then with the phase order. It is important to note that the exchange domain and the phase domain do not have to coincide, and the order detected by exchange does not immediately imply global phase order. Nevertheless, the information about this topic that we obtain from EPR in exchange coupled systems does not involve the individual molecules (as in the case of anisotropic motion effects), but a long range domain in the sample.

As we have said above, the principal values of the **g**-tensor obtained in the RT solid phase of S6 are the same as those we have obtained for the isolated molecules. That indicates that there exists a perfect spatial correlation of the molecular frame in the exchange domain. The three principal axes of the molecules are parallel in the domain.

Now we are mainly interested in the information that we obtain from the spectrum measured for the smectic phase. In this phase, the EPR spectrum also corresponds to an axial $S = 1/2$ paramagnetic entity, but the principal g-values ($g'_{\parallel} = 2{\cdot}03 \pm 0{\cdot}01$ and $g'_{\perp} = 2{\cdot}05 \pm 0{\cdot}01$) are markedly different from those measured for the isolated molecule and in concentrated samples in the solid phase ($g_x = 2{\cdot}02 \pm 0{\cdot}01$, $g_y = 2{\cdot}03 \pm 0{\cdot}01$ and $g_z = 2{\cdot}09 \pm 0{\cdot}01$), but in all cases the **g**-tensor trace is the same. The classical smectic arrangement of molecules in the domain can explain these features. One of the two perpendicular principal axes remains nearly parallel in all the molecules of the domain. It corresponds to the molecular long axis that is ordered in the mesophase (see figure 1), and to it is assigned the principal value of the averaged **g**-tensor obtained from the high field peak ($g'_{\parallel} = g_y$). The two other molecular short axes are completely uncorrelated, and so their principal values are completely averaged by exchange, giving $g'_{\perp} = (g_x + g_z)/2$. That leads to two degenerate principal values for the averaged **g**-tensor that are actually obtained from the low field spectral signal (see figure 3 (*b*)).

Moreover, the spatial correlation of the molecular long axis is not perfect, so the high field peak of the spectra is shifted from the position of the $g_{\perp} \approx g_x \approx g_y$ parameter of the isolated molecule. The shift, depending on the temperature, is related to Saupe's order parameter, S [17].

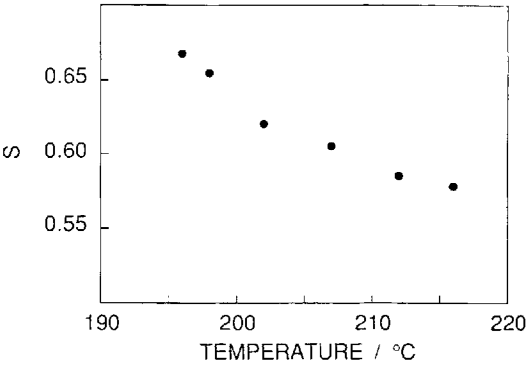


Figure 4. Thermal evolution of the Saupe order parameter obtained from EPR data for the smectic phases of S6. The data have been taken on cooling down the sample.

$$S = 1 - 3\left(\frac{g'_{\parallel} - g_{\perp}}{g_{\parallel} - g_{\perp}}\right). \tag{6}$$

Thus, we can directly obtain the Saupe parameter from the EPR spectrum without using an external probe (that can be differently ordered from the bulk molecules). Our results for the thermal evolution of the order parameter are presented in figure 4. The exchange interaction produces a spatial average, so the order information is not local as in systems with only motional effects. As far as we know, this is the first example reported concerning estimation of Saupe's parameter for a calamitic mesogen using the information about spatial correlation that is given by exchange coupled systems.

5. Summary

The EPR spectrum of a copper dithiocarbamate having liquid crystal properties has been measured at different temperatures in the solid phase as well as in the smectic range. The collapse of the copper nucleus hyperfine structure in the concentrated sample, as compared with that found for the isolated molecules (measured using a frozen toluene solution) shows the existence of a long range exchange interaction between the mesogenic molecules in both phases.

The coincidence of the effective principal g-values for isolated molecules with those obtained from the spectrum in the solid indicates that in this low temperature phase, the molecules are ordered with their molecular axes parallel.

The changes observed when the sample reaches the smectic phase are interpreted as a consequence of the freedom of rotation around the long axis of the molecule in the mesophase. This is due to the calamitic shape of the S6 molecules and contrasts with the behaviour previously reported in the case of other copper metallomesogens whose molecules depart strongly from this cylindrical shape.

Taking advantage of these facts, we have been able to determine the temperature dependence of the Saupe order parameter in the smectic phase from the thermal evolution of the EPR spectrum.

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