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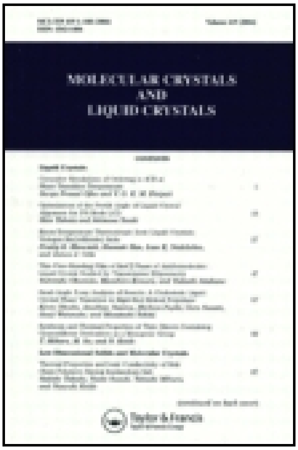

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EPR Studies on Copper and Cobalt Triazene-1-Oxide Complexes in a Frozen Nematic Medium

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EPR Studies on Copper and Cobalt Triazene-1-Oxide Complexes in a Frozen Nematic Medium

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EPR spectra of copper and cobalt complexes of certain triazene-1-oxide ligands have been measured in frozen nematic liquid crystal glasses in order to identify the principal directions of the magnetic interaction tensors. It is pointed out that the nature of solute alignment is primarily determined by its molecular shape and any chemical interaction between the metal complex and the functional groups of the solvent molecules. Once these factors are properly understood, oriented glass spectra can be used to identify the principal axes of the **g** and **A** tensors even for systems which deviate considerably from gross molecular planarity. The spin Hamiltonian parameters are discussed on the basis of the ligand field model. It is pointed out that all the cobalt complexes reported here have the unpaired electron in the d_{yz} orbital.

1 INTRODUCTION

Electron paramagnetic resonance (EPR) has been extensively used to probe the extent and nature of ordering in the nematic mesophase.[1,2] Most of these studies are done at room temperature where the paramagnetic solute molecules are rapidly tumbling. Such studies give valuable information about the order parameters for the liquid crystal. However, if the oriented nematic solution is frozen, EPR spectra with line shapes characteristic of glasses can be obtained.[3,4] Since the solute ordering is largely preserved in the frozen medium, such spectra can be used to identify the molecular magnetic tensor axes for the solute molecules. This method has obvious advantages over the usual single crystal method where one has to grow suitable single crystals of known crystal structure and measure spectra at a large number of orientations. However, caution must be exercised in interpreting the liquid crystal results because of the possible uncertainty in the relative orientations of the solute

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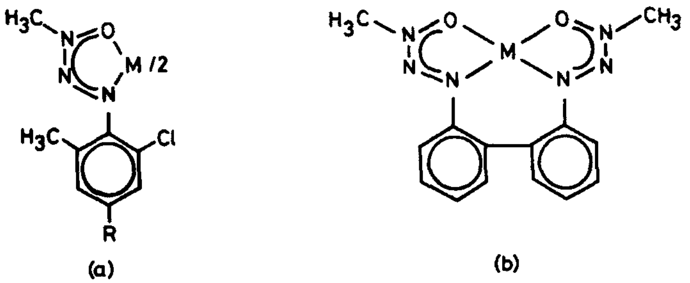

FIGURE 1 (a) R = H, *Bis*[1-methyl-3(2-chloro-6-methyl)phenyl triazene-1-oxidato] M (II) (MBPT): R = NO_2, *Bis*[1-methyl 3(2-chloro-4-nitro-6-methyl) phenyl triazene-1-oxidato] M(II) (MBPN): (b) 3,3′-(2,2′-biphenylene)*bis*(1-methyltriazene)1,1′-dioxidato M(II). M = Co, Cu.

molecules with respect to the director axis of the nematic solvent and also possible interaction of the solvent molecules with the paramagnetic solute. This point is illustrated in the present paper where we report the EPR results for copper(II) and cobalt(II) complexes of three types of triazene-l-oxide ligands, BPT, BPN and DPT (Figure 1). The BPT and DPT complexes of cobalt are found to take up essentially different types of stacking in the oriented nematic glass. In addition, in the case of the BPT ligand the copper and cobalt complexes are shown to take up different orientations in the nematic glass.

Low spin cobalt(II) complexes are of considerable interest because of the ability of some of these types of complexes to reversibly combine with molecular oxygen.[5] Many of these complexes exhibit an orthorhombic spin Hamiltonian.[6] Because of the possibility of a variety of electronic ground states for a low spin cobalt(II) complex, any discussion of the electronic structure would require a precise assignment of principal axes of the electronic Zeeman (g) and nuclear hyperfine (A) tensors. While in the case of CoBPT, this could be achieved by a detailed single crystal study,[7] no suitable single crystals containing CoDPT could be obtained. The present liquid crystal study was undertaken mainly to resolve this problem.

2 EXPERIMENTAL PROCEDURE

CoBPT, CoDPT, CuBPT and CuDPT were prepared using the methods found in the literature.[8] CoBPN was prepared by the same procedure, starting from 2-chloro-4-nitro-6-methylaniline. All complexes were recrystallised from benzene and dried in *vacu*, at 60°C.

All EPR spectra were measured on a Varian E–4 spectrometer fitted with a variable temperature accessory. *N*-(*p*-methoxybenzylidine)-*p*-butylaniline

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(MBBA) was used as the nematic solvent for all measurements. The sample of MBBA purchased from Vari–Light Corporation was used as such without further purification. It has a positive diamagnetic anisotropy and has a nematic range of 18–41°C. Solutions of paramagnetic complexes having concentrations of 3×10^{-3} M were prepared by heating the required amount of material with 0.3 ml of the solvent in an EPR tube to about 60°C on a water bath. In each case the isotropic solution was cooled to the nematic range and transferred to the variable temperature accessory where the temperature was maintained at 20°C. The magnetic field was switched on and maintained at 7000 G for 15–20 minutes. Keeping the magnetic field on, the temperature was rapidly lowered to −140°C. In all cases, very well aligned glasses were obtained. Care was taken to avoid slow cooling, which might lead to crystallisation of the solvent. As soon as the glass was obtained, the magnetic field was lowered and the spectrum recorded. This is referred to as the "in-plane" spectrum. Then the EPR tube was rotated by 90° about its own axis and the "out-of-plane" spectrum was recorded. In each case, the spectrum of the unoriented glass was also recorded for the purposes of comparison.

3 RESULTS AND DISCUSSION

Figure 2 shows the EPR spectra of CuDPT in the frozen unoriented glass as well as in oriented nematic glass. A similar spectrum was obtained for CuBPT. These spectra can be interpreted on the basis of an axially symmetric Hamiltonian (Eq. 1) including hyperfine interaction with the copper nucleus as well as the two coordinating nitrogen atoms of the ligand.

$$\mathscr{H} = \beta g_{\parallel} H_z S_z + \beta g_{\perp}(H_x S_x + H_y S_y) + A_{\parallel}{}^{\mathrm{Cu}}\mathrm{I}_z S_z + A_{\perp}{}^{\mathrm{Cu}}(I_x S_x + I_y S_y)$$
$$+ \sum_{i=1}^{2} [A_{\parallel}^{N(i)} I_z^{N(i)} S_z + A_{\perp}^{N(i)}(I_x^{N(i)} S_x + I_y^{N(i)} S_y)]$$

In the case of planar four—coordinate copper complexes the low field components certainly correspond to the "parallel" components (perpendicular to the coordination plane) of the **g** and **A** tensors, and their values obtained from the nematic glass spectra are essentially identical to the values measured in other glasses and polycrystalline media.[9] The interesting observation is that the "parallel" component is almost totally absent in the "in-plane" spectrum. The "parallel" component shows up after the rotation of the frozen glass ("out-of-plane" spectrum) with a concomitant reduction in the intensity in the "perpendicular" region. This clearly means that in the homogeneously aligned glass, both CuBPT and CuDPT solute molecules take up a preferred orientation with their symmetry axes (*z* axis) in a plane perpendicular to the magnetic field direction (the field direction must also correspond to the long

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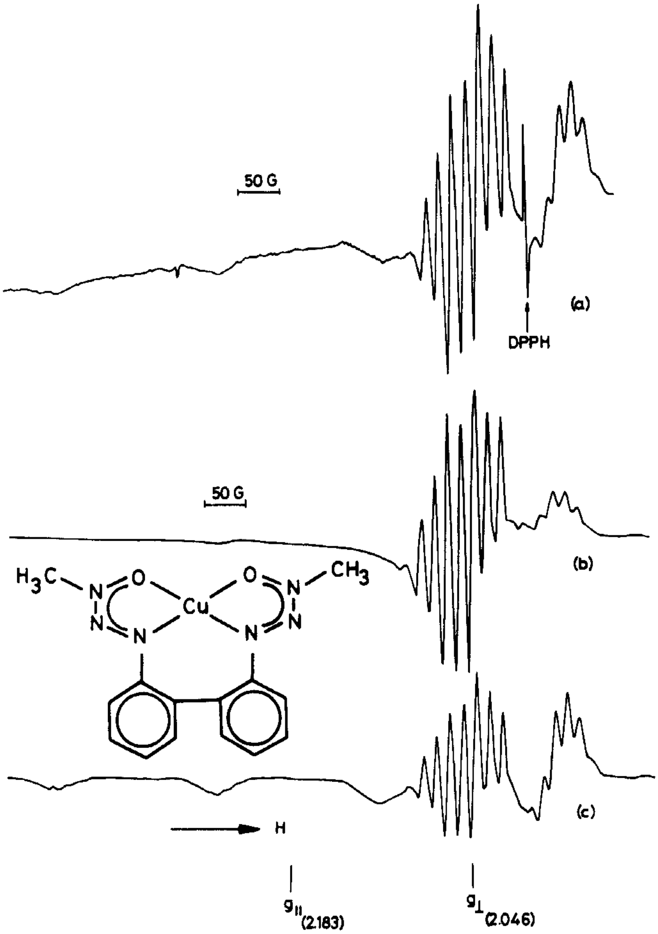

FIGURE 2 The X-band epr spectra of CuDPT at $-140°C$; (a) unoriented solution; (b) frozen nematic glass, no rotation (the-in-plane spectrum); (c) frozen nematic glass rotated by 90° (the-out-of-plane spectrum).

axis of the liquid crystal molecules, because MBBA has a positive diamagnetic anisotropy).

The spectra of the cobalt complexes shown in Figures 3 and 4 do not correspond to an axially symmetric case. The spectra of CoBPN are very similar to those of CoBPT and are hence not shown as a separate figure. They have to be understood on the basis of an orthorhombic spin Hamiltonian (Eq. 2) involving hyperfine interaction with only the cobalt ($I = \frac{7}{2}$) nucleus.

$$\mathcal{H} = \beta g_{zz} H_z S_z + \beta g_{xx} H_x S_x + \beta g_{yy} H_y S_y + A_{zz} I_z S_z + A_{xx} I_x S_x + A_{yy} I_y S_y \tag{2}$$

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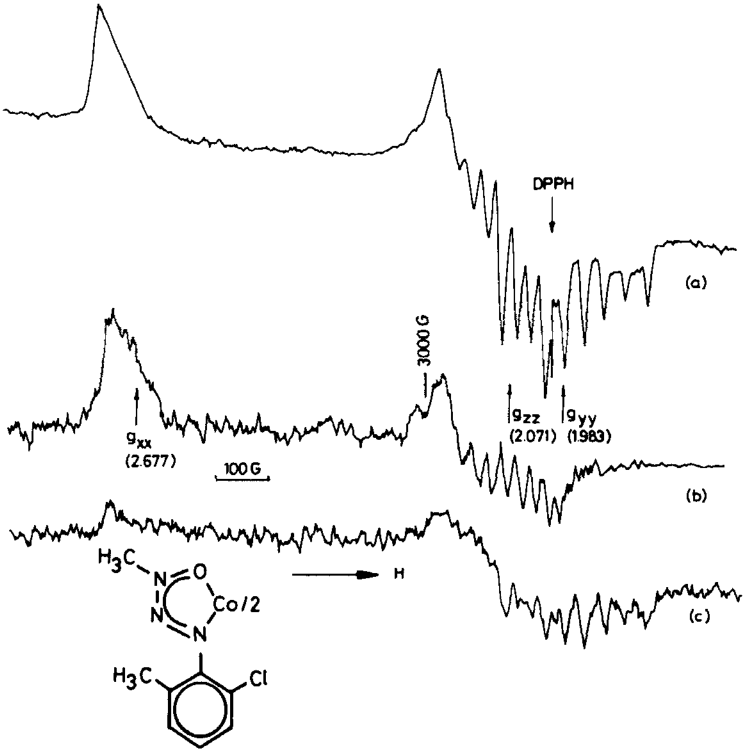

FIGURE 3 The X-band epr spectra of CoBPT at −140°C: (a) unoriented solution; (b) frozen nematic glass, no rotation (the-in-plane spectrum); (c) frozen nematic glass rotated by 90° (the-out-of-plane spectrum).

It can be seen that in all the three cases there is a pronounced decrease in the lowest field component in going from the "in-plane" spectrum to the "out-of-plane" spectrum. This indicates that the complex molecules tend to align with their molecular x axis (i.e. the direction corresponding to the maximum g value) nearly along the applied magnetic field. This direction is most likely to be the longest molecular direction as illustrated in Figure 5. If it is assumed that the alignment of CoBPT and CoBPN is same as that for CuBPT, it will appear that the highest field component in Figure 3 corresponds to the molecular z direction. However this assignment proved to be incorrect on the basis of single crystal studies of CoBPT doped in the isomorphous and isostructural NiBPT lattice[7] where it was found that the intermediate g value corresponds to g_{zz}. This anomaly can be explained on the basis of the actual molecular shape of the BPT complexes and their possible orientations in the liquid crystal. It is to be presumed that the two phenyl rings will play a greater role (due to their greater size and freedom of rotation) than the chelate ring

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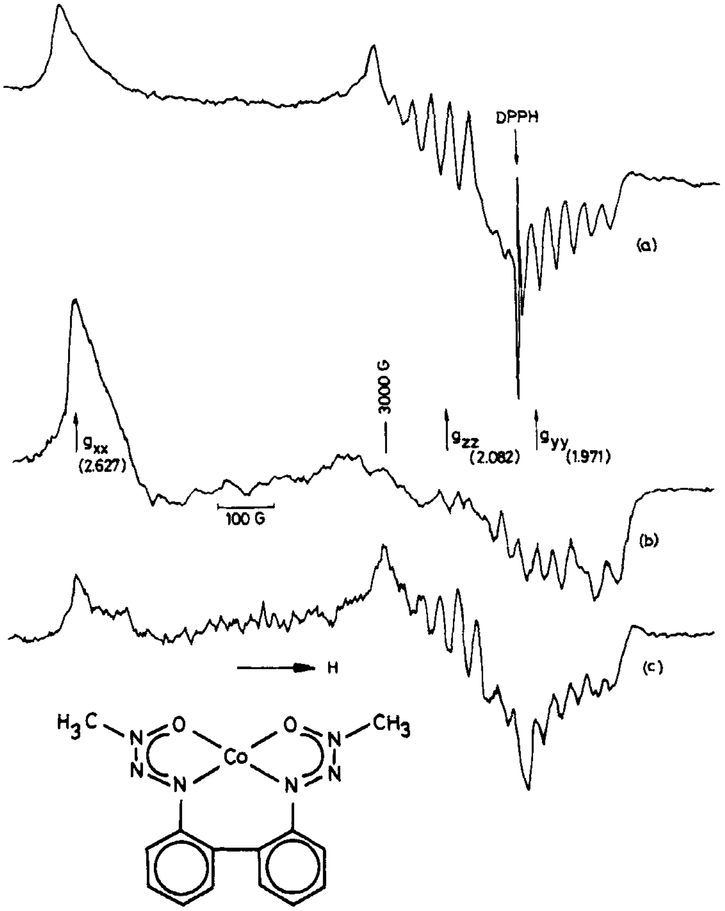

FIGURE 4 The X-band epr spectra of CoDPT at −140°C: (a) unoriented solution; (b) frozen nematic glass, no rotation (the-in-plane spectrum); (c) frozen nematic glass rotated by 90° (the-out-of-plane spectrum).

in determining the orientation of the complex molecule in the nematic solvent. A likely orientation is shown in Figure 5(a). For such an orientation the y and z components will be present in both the "in-plane" and "out-of-plane" spectrum to varying extents depending on the actual orientation of the chelate ring. Under such circumstances it will not be possible to unambiguously assign the molecular g_{zz} and g_{yy} values. The difference in alignment between CuBPT and CoBPT is probably due to a weak interaction of CoBPT with the liquid crystal molecules. Such an interaction is conceivable because cobalt complexes reported here have the unpaired electron in an out-of-plane π-oribtal (d_{yz}) while the copper complexes have a d_{xy} ground state.[7,9]

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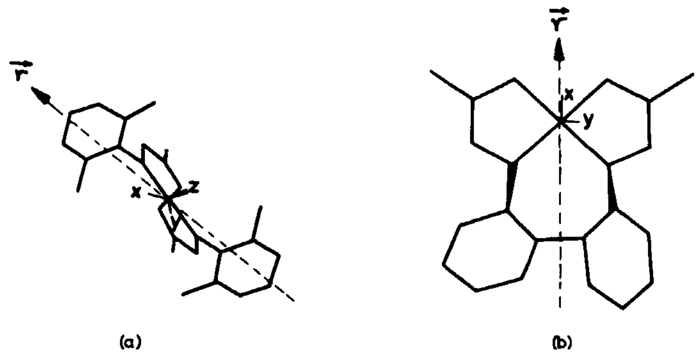

FIGURE 5 Proposed alignment direction (**r**) for (a) CoBPT and (b) CoDPT.

An examination of the spectra of CoBPN reveals that the parameters for CoBPT and CoBPN are nearly the same and are identical to the values obtained in the corresponding diamagnetic host lattice. Introduction of the electron withdrawing nitro-group will have an appreciable effect on the ligand field at the central metal ion, only if the phenyl rings are coplanar with triazene oxide rings. The absence of such an effect and the close similarity of the spectra with those obtained in the polycrystalline state indicates that, either there is considerable free rotation of the phenyl groups in the nematic solution, or the phenyl groups are tilted away from the chelate as suggested by the crystal structure on NiBPT.[10]

Perhaps the most important outcome of this work is the identification of the g_{zz} and A_{zz} values for CoDPT. Unlike in the case of CoBPT there is no ambiguity in alignment in this case because CoDPT as a whole is a rigid molecule and much more planar than CoBPT (see Figure 5(b)). The intermediate g value is readily identified as g_{zz} from the greatly enhanced intensity of the mid-field set of lines in the "out-of-plane" spectrum.

TABLE I

Spin Hamiltonian parameters for copper (II) and cobalt (II) complexes derived from nematic glass spectra[a]

	g_{xx}	$(g_\parallel)$	g_{yy}	g_{zz} $(g_\parallel)$	A_{xx}	$(A_\perp)$	A_{yy}	A_{zz} $(A_\parallel)$
Cu BPT		2.047		2.186		14		204 (^{63,65}Cu)
						14		13 (^{14}N)
Cu DPT		2.046		2.183		15		199 (^{63,65}Cu)
						15		14 (^{14}N)
Co BPT	2.677		1.983	2.071	[b]		34	27 (^{59}Co)
Co DPT	2.627		1.971	2.082	[b]		29	31 (^{59}Co)
Co BPN	2.682		1.972	2.074	[b]		34	27 (^{59}Co)

[a] Hyperfine coupling constants are in units of 10^{-4} cm^{-1}

[b] Not sufficiently resolved.

The spin Hamiltonian parameters obtained for the copper and cobalt complexes are given in Table I. The parameters reported for the copper complexes are essentially same as those obtained[9] in other frozen glass and polycrystalline media. The copper complexes certainly have a d_{xy} ground state (point group C_{2v} for Cu DPT and C_{2h} for Cu BPT). The molecular orbital coefficients obtained by second order perturbation treatment of the **g** and copper nuclear hyperfine tensors[11] indicate considerable delocalisation of the unpaired electron. A more convincing evidence of the extent of delocalisation is the observation of the hyperfine splitting from the two coordinated nitrogen atoms. The ^{14}N hyperfine splitting in this case is essentially isotropic with a value of nearly 0.0014 cm^{-1} which corresponds to about 25% spin transfer from the copper d_{xy} orbital to the sp^2 hybrid orbitals of the nitrogen atoms.

Unlike in the case of copper, the electronic ground states of low spin cobalt(II) complexes are extremely sensitive to the strength and symmetry of the ligand field. The most commonly observed ground state is d_{z^2} which in point group symmetry D_{2h} or less can participate in configuration interaction with $d_{x^2-y^2}$. The d_{yz} ground state has been proposed for four cobalt complexes.[7,13,14,15] Except in two cases,[7,14] this conclusion was not based on any unambiguous assignment of the magnetic tensor axes. This point has to be emphasized because unless definite assignments are made it may not be possible to fit the parameters either to a d_{yz} or d_{z^2} ground state using the equations derived based on a ligand field model.[12] Once the **g** tensor elements are assigned to the molecular axes, a distinction between the two ground states can be made based on the relative magnitudes of g_{yy} and g_{zz}. In all the cases reported here, we have $g_{zz} > g_{yy}$ which favours a d_{yz} ground state on the basis of the third order perturbation relations reported by McGarvey.[12]

In conclusion it can be stated that while nematic glass spectra can be used to identify the principal directions of magnetic tensors of paramagnetic transition metal complexes, one must be careful to recognise the possibility of more than one type of solute alignment. Chemical interaction between the functional groups of the solvent and the metal complex may also play a decisive role in determining solute ordering in the frozen glass.

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