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EPR Spectra of Alkoxy and Mixed Alkyl-Alkoxy Substituted Aryl β Diketonates of Discotic Copper Complexes 1: Computer Analysis to Identify the Quadrupole Forbidden Transitions

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The solid state Q band EPR spectra of the mixed octyl-octyloxy substituted aryl β diketonate of Cu-(II) resemble to a great extent the quadrupole-cum-hyperfine spectrum of C_8OCu. Since the spectra in both cases arise from overlapping lines, one could not assign the quadrupole forbidden lines directly from the spectra. Thus two very weak hyperfine quartets from $\Delta m = 0$ in the computed spectra, is not observed in the experimental spectra, which start with a single line from $\Delta m = \pm 1$, followed by the first quadrupolar forbidden doublet (not resolved) from $\Delta m = \pm 2$ with admixture from $\Delta m = \pm 1$. The situation is the same on the other side. Between the first doublet and the partially resolved middle doublet lies the strong hyperfine line from $\Delta m = 0$. So also is the case between the middle doublet and the third unresolved doublet. The middle doublet (partially resolved in C_8OCu but not resolved in the mixed complex) results from two very strong $\Delta m = \pm 2$ lines with an admixture of a very weak $\Delta m = \pm 1$ for each line. So the present work identifies all the quadrupolar forbidden transitions present. Since the dimer is the basic repeating unit in both systems, the resemblance in the spectra is not unexpected. The subtle differences viz., partial splitting of the middle doublet in C_8OCu and presence of shoulders in the outer doublets as against symmetric doublets in the mixed complex, possibly arise from its larger hyperfine (B) term. However the 'Q' parameter has the same value in both cases.

Keywords: EPR spectra; quadrupolar forbidden transitions; substituted aryl β diketonates of Cu-(II); computer analysis

1. INTRODUCTION

Quadrupole effects in the EPR spectra of Bis[1,3-di(*p-n*-octyloxyphenyl propane-1,3 dionate] Cu-(II) abbreviated as C_8OCu was first reported by Bose and Sadashiva [1] but no proper analysis of these forbidden transitions was given. In the present paper also, we report a somewhat similar quadrupole effect in the EPR spectra of the mixed alkyl-alkoxy Cu complex represented as $2C_8Cu - 2OC_8$ (Fig. 1). However, here we present a detailed analysis of the quadrupole forbidden transitions (q.f.t) in Cu complexes and then apply them to C_8OCu and mixed alkyl-alkoxy Cu complex.

EPR has been a late entrant in the field of liquid crystals, as most of them are diamagnetic. Only recently, with the advent of paramagnetic metallo-mesogenic liquid crystals, EPR is being applied increasingly. However, the field of discotic square-planar copper complexes with their strong asymmetry, has indicated the importance of quadrupole effects in such systems. Though in the history of EPR, quadrupole effects were discovered by Bleaney and co-workers [2–4] in early fifties in Cu complexes, it is not a common occurence. So a short discussion on quadrupole forbidden transitions will be in order.

2. THEORETICAL CONSIDERATIONS

The usual spin Hamiltonian for an axially symmetric d' system is given by

$$\mathcal{H} = \beta[g_\parallel H_z S_z + g_\perp (H_x S_x + H_y S_y)] + A S_z I_z + B(S_x I_x + S_y I_y) + Q[I_z^2 - I(I+1)/3] - g_n \beta_N \vec{H} \cdot \vec{I} \quad (1)$$

where the first term represents the electron Zeeman term, the terms containing A and B are the anisotropic electron-nuclear hyperfine interaction terms, the term in Q contains the quadrupole interaction, whereas the last one is the nuclear Zeeman term. S and I are the electron and nuclear spin vectors. g_n is the nuclear gyromagnetic ratio; β is the Bohr magneton; H is the applied magnetic field and g is the gyromagnetic ratio for the electron.

Figure 2 schematically illustrates the behaviour of the energy levels according to the spin Hamiltonian. In a strong external magnetic field, the electron spin doublet (d') splits up by an amount of $g\beta H$. Each electronic level is further split up into 4 equally spaced levels owing to interaction with the magnetic moment of Cu nucleus ($I = 3/2$). These hyperfine levels are displaced by the nuclear quadrupole interaction and by the direct effect of the external field of the nuclear magnetic moment. Normally, the allowed transitions are those in which the nuclear orientation does not change

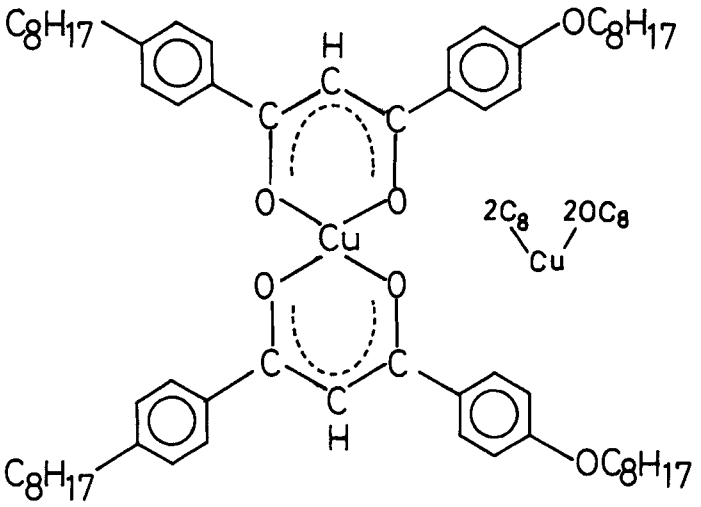

FIGURE 1 Structure of mixed alkyl-alkoxy Cu complex.

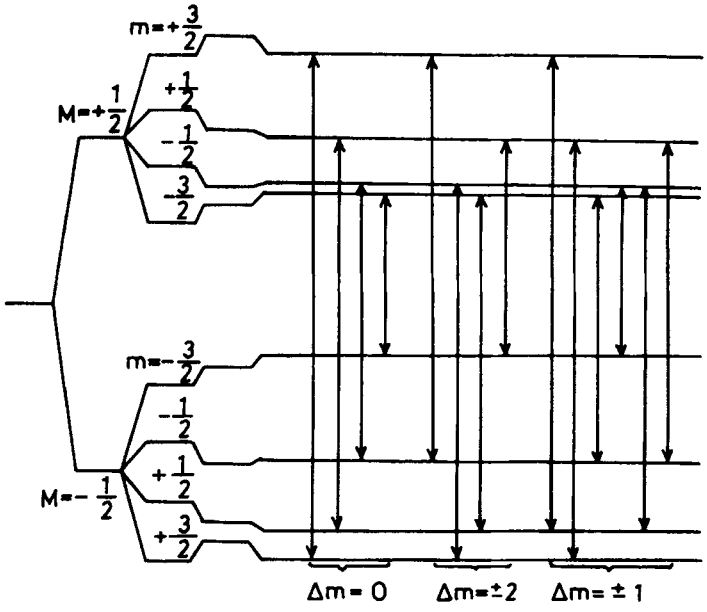

FIGURE 2 Schematic energy-level diagram for $S = 1/2$, $I = 3/2$ in a magnetic field.

($\Delta m = 0$), but if the quadrupole interaction is comparable with the magnetic interaction, transitions corresponding to $\Delta m = \pm 2$ are also possible. In addition, $\Delta m = \pm 1$ transitions become allowed, if the external magnetic field is not along the symmetry axis but makes an angle with it.

The physical reason for the occurence of such 'forbidden transitions' is that the quadrupole interaction tries to align the nucleus along the symmetry axis, whereas the magnetic field established by the electron tries to align the nucleus nearly at right angles to the symmetry axis. The selection rules are then broken down, since several nuclear states become admixed. Inspection of spin Hamiltonian $\mathscr{H}$ (eq. 1) shows that the reason for the breakdown lies in the off-diagonal terms, giving rise to the transitions for which $\Delta m = \pm 1$ and $\Delta m = \pm 2$. The transitions are shown in Table I.

Table I indicates that for $\begin{cases} \Delta m = \pm 1 & - \text{ There are in all 6 lines} - 3 \text{ doublets} \\ \Delta m = \pm 2 & - 4 \text{ lines} - 2 \text{ doublets} \\ \Delta m = \quad 0 & - 4 \text{ lines} - \text{hyperfine quartets.} \end{cases}$

The experimental spectrum may be the result of several overlapping lines and as such the origin of the lines cannot be readily predicted. So one has to go in for computer simulation based on the spin Hamiltonian (eq. 1), containing only the spin operators. To analyse the spectrum, it is necessary to determine the position and intensity of the component resonant lines. For the sake of simplicity, we have taken the systems as axially symmetric, neglecting small departure from such symmetry. The resulting 8×8 matrix obtained form eq. (1) was then diagonalized, using a standard subroutine. Then eigenvalues and eigenvectors were

TABLE I

Transition for different Δm values		
$\Delta m = 0$	$\Delta m = \pm 1$	$\Delta m = \pm 2$
$\frac{3}{2} \rightarrow \frac{3}{2}$	$\frac{3}{2} \rightarrow \frac{1}{2}$	$\frac{3}{2} \rightarrow -\frac{1}{2}$
	$\frac{1}{2} \rightarrow \frac{3}{2}$	
$\frac{1}{2} \rightarrow \frac{1}{2}$	$\frac{1}{2} \rightarrow -\frac{1}{2}$	$\frac{1}{2} \rightarrow -\frac{3}{2}$
	$-\frac{1}{2} \rightarrow \frac{1}{2}$	
$-\frac{1}{2} \rightarrow -\frac{1}{2}$	$-\frac{1}{2} \rightarrow -\frac{3}{2}$	$-\frac{1}{2} \rightarrow \frac{3}{2}$
$-\frac{3}{2} \rightarrow -\frac{3}{2}$	$-\frac{3}{2} \rightarrow -\frac{1}{2}$	$-\frac{3}{2} \rightarrow \frac{1}{2}$

calculated numerically with the help of a computer program. The former gave the position of the allowed and forbidden lines, while the latter gave their intensities. Of the spin Hamiltonian parameters, the values of $g_{\parallel}$, $g_{\perp}$, field position of DPPH are obtained from the experimental spectra. However, A, B and Q values are to be chosen in such a way, that the best fit to the experimental spectrum is obtained. Thus, one obtains the stick diagram for the different transitions and it can be seen from Figure 3 that the B and Q parameters have the greatest effect on the position and intensity of the lines.

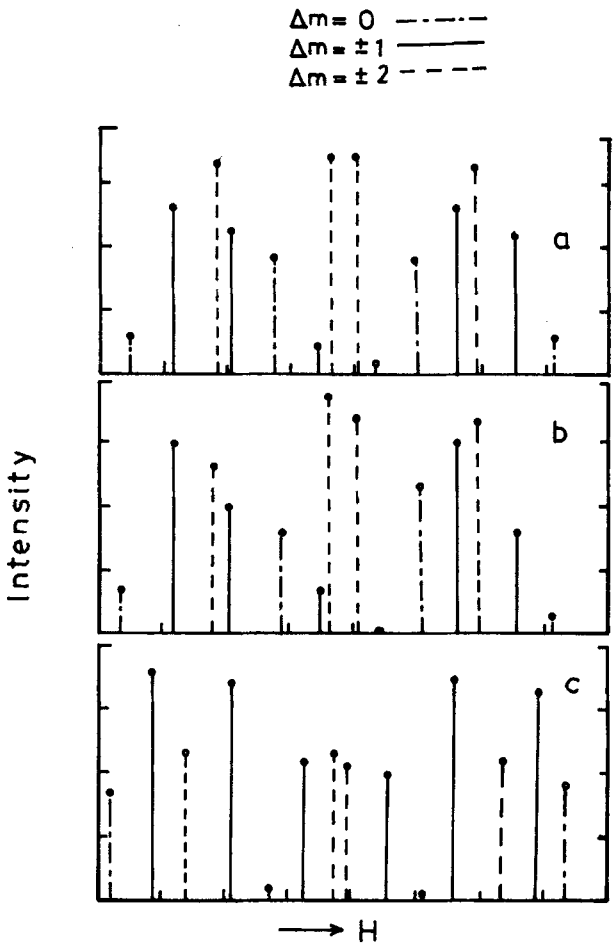

FIGURE 3 Effect of B and Q parameters on line intensities and positions. (a) B = −0.00052, Q = −0.00003. (b) B = −0.00052, Q = 0.00008. (c) B = −0.0008, Q = 0.00003.

In a single crystal, the resonance field or frequency depends on the orientation of the crystal with respect to the applied magnetic field. The powder spectrum, however, has to encompass all possible orientations of the paramagnetic entities. The number of ions for which H makes an angle between θ and $\theta + d\theta$ with the unique axis, is then proportional to $\sin\theta d\theta$. Thus for an ion with an anisotropic g factor with axial symmetry [5]

$$g^2 = g_{\parallel}^2 \cos^2\theta + g_{\perp}^2 \sin^2\theta$$

or

$$\cos\theta = \left(\frac{g^2 - g_{\perp}^2}{g_{\parallel}^2 - g_{\perp}^2}\right)^{1/2} = \left(\frac{H^{-2} - H_{\perp}^2}{H_{\parallel}^2 - H_{\perp}^2}\right)^{1/2}$$

where H, $H_{\parallel}$ and $H_{\perp}$ refer to fields at which the lines appropriate to values g, $g_{\parallel}$ and $g_{\perp}$ respectively would occur.
Differentiation gives

$$\sin\theta d\theta = \frac{H_{\perp}^2 H_{\parallel} dH}{H^2\{(H^2 - H_{\perp}^2)(H_{\parallel}^2 - H_{\perp}^2)\}^{1/2}}$$

Non-dimensional form of the powder intensity I can be expressed as

$$I \propto \frac{H_{\perp}^2(H^2 + H_{\parallel}^2)dH}{H_{\parallel}H^2\{(H^2 - H_{\perp}^2)(H_{\parallel}^2 - H_{\perp}^2)\}^{1/2}}$$

Giving the best apparent fit of the spin Hamiltonian parameters on the basis of Gaussian line shape, the field position and intensity of each transition has been generated numerically with the help of a computer program. The fitted values are the following:

(i) For C_8OCu
$g_{\parallel} = 2.55$, $g_{\perp} = 2.1$, $A = -.007$, $B = -.00052$,
position of DPPH = 12.27, $Q = .00003$.

(ii) For $2C_8Cu - 2OC_8$
$g_{\parallel} = 2.55$, $g_{\perp} = 2.1$, $A = -.007$, $B = -.00055$,
position of DPPH = 12.27, $Q = .00003$.

These individual lineshapes were then summed up to get a resultant spectrum. This computer synthesized spectrum has been used to analyse the experimental spectrum.

3. PRESENT WORK

The behaviour of pure alkyl and pure alkyloxy, substituted aryl β diketonates have been extensively investigated and the role of the substituent alkyl vs. alkoxy has been brought out in determining phase behaviour and other physical properties [6–12]. Sadashiva and Ramesh [13] and later Veena Prasad and Sadashiva [14] prepared some mixed alkyl-alkoxy substituted aryl β-diketonates, expecting them to have properties intermediate between pure tetra-*n*-alkyl and tetra-*n*-alkoxy substituted ones. This was, however, not the case. Some of the properties were similar to pure alkyl compounds, while others corresponded to alkoxy systems. Though $K \rightarrow M$ and $M \rightarrow I$ transitions were within 1–3°C of the corresponding C_nCu, they were freely missible only with C_nOCu. However, as in pure alkyl complexes, heat of $K \rightarrow M$ transition is higher than that of the $M \rightarrow I$ transition. The decrease in the temperature range of the mesophase with increasing chain length is also anomalous. Thus it is evident that the properties of the mixed alkyl-alkoxy compounds are not properly understood and needs further investigation.

The present work attempts to unravel the mystery of this system from EPR, which has been very successful in understanding the behaviour of the pure alkyl and alkoxy Cu-complexes. Figure 1 represents the compound $2C_8Cu2OC_8$. Crystallographic studies of the Cu complex of lower homologue (C_7H_{15}) [15] have demonstrated that identical chains have the same cis configuration and the experimental work would be interpreted on this basic assumption.

4. EXPERIMENTAL

Q band spectra of the mixed complex at room temperature is presented along with that for C_8OCu, which has been reported previously [1] but not computer analysed. Figure 4 gives the spectra for the two complexes, which involves the computer generated stick diagram and computed spectra with a suitable broadening and experimentally obtained spectrum.

The experimental spectrum for C_8OCu at $g_{\|}$ appears as three complex quadrupolar forbidden (strong doublets) among four lines, apparently the four quartets. But computed spectrum indicates otherwise. The two very weak outermost quartets from $\Delta m = 0$ in the computed spectrum, is not observed in the symmetric experimental spectrum, which starts with a comparatively strong single line ($\Delta m = \pm 1$) followed by the first quadrupolar

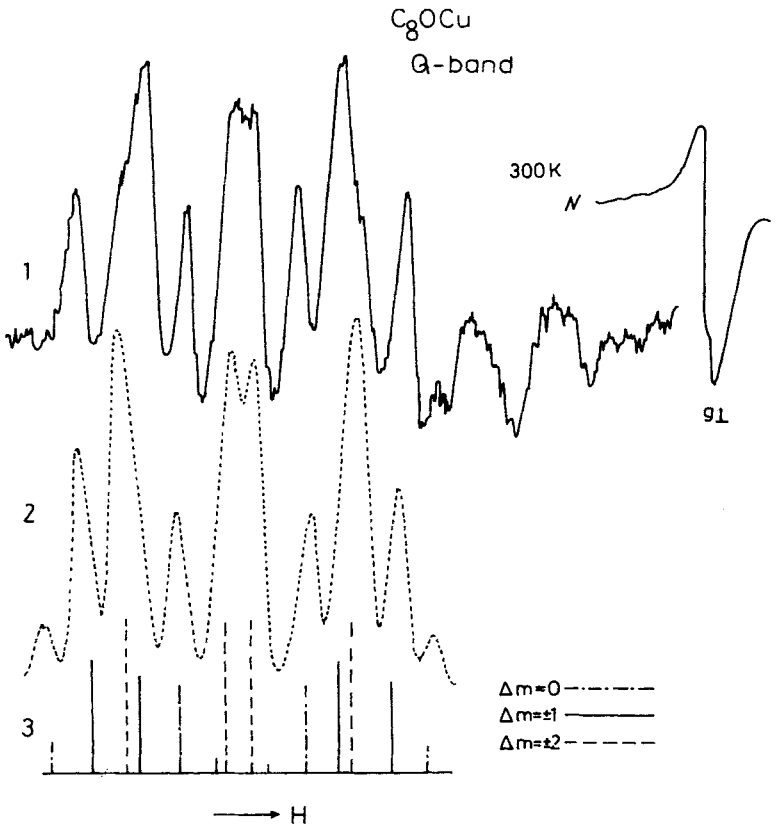

FIGURE 4(a) Composition of experimental spectra of C_8OCu with the computed one. 1. Experimental spectrum, 2. Computed Spectrum, 3. Stick diagram.

forbidden doublet (not resovled) from $\Delta m = \pm 2$ with admixture from $\Delta m = \pm 1$. The situation is the same on the other side. Between the first doublet and the partially resolved middle doublet lies the strong hyperfine line from $\Delta m = 0$. So also is the case between the middle doublet and the third unresolved doublet. The middle doublet results from two very strong $\Delta m = \pm 2$ lines forming a doublet with an admixture form a very weak $\Delta m = \pm 1$ for each line. So all the quadrupolar forbidden lines are accounted for, but all 4 $\Delta m = \pm 2$ lines are prominent, whereas for $\Delta m = \pm 1$ lines, only four are. Two broad lines are seen after this before $g_\perp$ but cannot be assigned.

The Q band spectrum of the mixed complex $2C_8Cu$–$2OC_8$ is very similar, though displays subtle differences. Thus none of the q.f.t (doublets) are resolved. However, though it is evident that they arise from overlapping

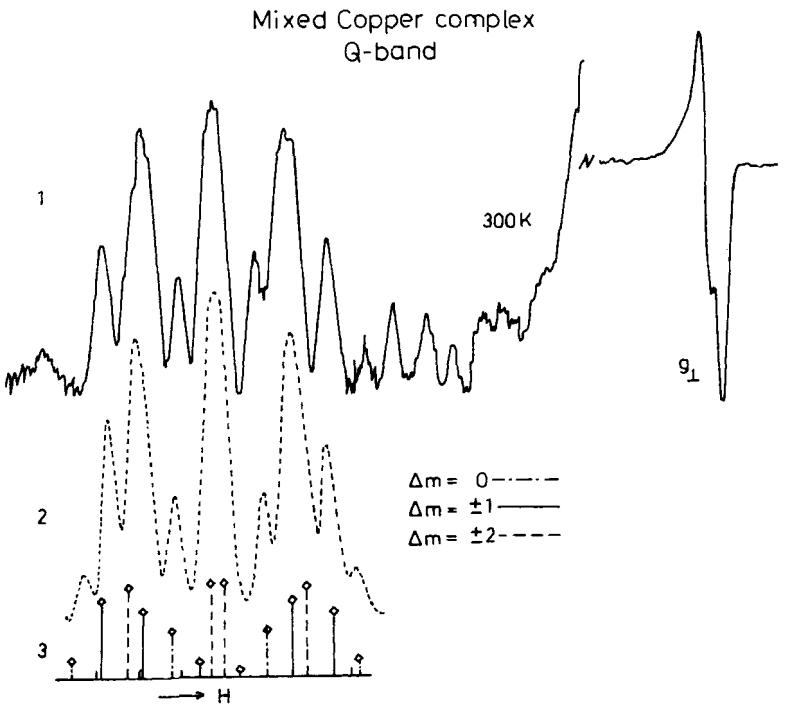

FIGURE 4(b) Comparison of experimental spectra of Mixed alkyl-alkoxy complex with the computed one, 1. Experimental Spectrum, 2. Computed Spectrum, 3. Stick Diagram.

lines, they are more symmetric. In C_8OCu, q.f.t lines (even the ones not resolved) display shoulders. Further, in the mixed complex after q.f.t in $g_\parallel(g_l)$ four weaker lines are observed before $g_\perp$, but again as in C_8OCu, cannot be assigned. The similarity in the EPR spectra between the two is not unexpected, as here also, the repeating unit in the unit cell is a molecular pair (Fig. 5). However, the structure of the dimer differs considerably from that of C_8OCu. Thus the Cu atom is displaced (0.027 Å) from the plane of the co-ordinating oxygen atoms. This is in striking contrast to the in-plane arrangement of the metal atom in pure alkyl/alkoxy Cu complexes. Moreover, due to the presence of bulkier alkoxy groups in the cis position (assumed on the basis of crystal structure studies of Usha and Vijayan [15] on the lower homologue $2C_7H_{15}Cu - 2OC_7H_{15}$), the molecule presents the appearance of a distorted rectangular disc. Further the difference in hyperfine interaction parameter (B) values of the compounds, as determined from the computed spectrum, appears to be responsible for the non-resolution and more symmetric appearance of the q.f.t in the mixed doublet. Thus the

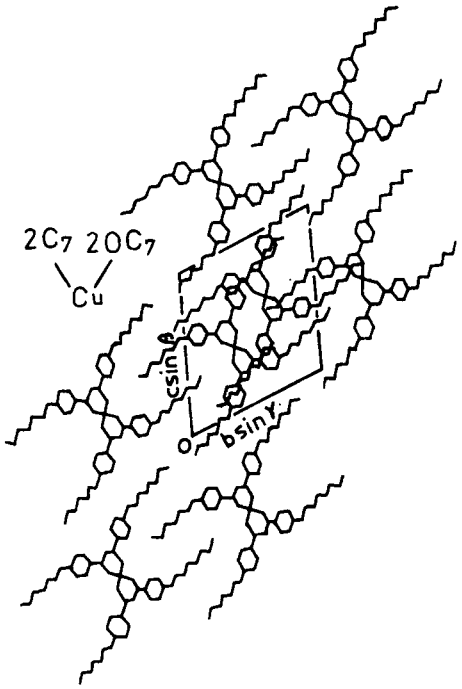

FIGURE 5 X-ray structure of $2C_7 - Cu - 2OC_7$.

present computer simulation studies clearly establish the presence of quadrupole forbidden transitions both $\Delta m = \pm 1$ and $\Delta m = \pm 2$ in the C_8OCu and the mixed complex.

Existence of Quadrupolar forbidden transitions is also corroborated from phase transition studies in the compounds.

5. PHASE TRANSITION STUDIES IN C_8OCu AND MIXED COMPLEX

5.1. High Temperature Studies

EPR studies of the phase transition of C_8OCu have been reported previously [1] in the Q band and it has been seen that q.f.t present in the crystal (K) phase, disappear in the mesophase but the hyperfine quartet remains. This is expected, as the field-gradient q will average out due to fluidity in the mesophase, but in the isotropic phase, hf structure tends to disappear but does not disappear completely, due to the persistence of short range order in these complex discotics.

In the mixed-alkoxy compound, EPR studies at X band indicate that on passing from the K to the mesophase, though there is considerable loss of intensity of the central and hyperfine lines, the fine structure including the quadrupolar forbidden lines persists (Fig. 6). Thus, a substantial number of dimers remain in an ordered state in this phase in the lower magnetic field (3000 Oe) of the X band. A great deal of energy is required to break up to dimer [10] and this is accomplished in the Q band in C_8OCu. However, in the isotropic phase, the fine structure tends to be smeared out – indicating loss of long range order but short-range order still persists. In C_8OCu [1], the high temperature phase transitions reported in X band are similar to that in the mixed alkyl/alkoxy complex (Fig. 6).

5.2. Low Temperature Studies

As pointed out, structurally the mixed complex presents a much more distorted configuration and in the dimer, the adjacent cores related to the centre of inversion are well separated (distinction from C_8OCu where there is a considerable overlap of the cores). However, the phenyl rings with the alkoxy chains partially overlap bringing out the important role of O atom (higher B). In addition, each dimer is surrounded by 4 others situated at $\pm b$ and $\pm c$ respectively and not 6 as in C_8OCu and C_nCu. Further, the crystal structure clearly indicates that the bulky alkoxy groups on one side prevents close packing and causes distortion and results in an EPR spectrum similar to the alkoxy compound. However, the less distorted centrosymmetric C_8OCu dimer undergoes a low temperature phase transition [1] at around 220°K, where the q.f.t disappears but the hyperfine quartets remain and there is a narrowing of the $g_\perp$ line. In the strongly distorted mixed complex, no further distortion can occur and the low temperature EPR spectra is the same as that of the room temperature spectrum, except intensification due to increase in susceptibility with decrease of temperature. Thus, an expected packing effect is seen to play a predominant role in structure-property relationship.

6. CONCLUSIONS

1. The presence of quadrupolar forbidden transitions in a Q band EPR spectra, both $\Delta m = \pm 1$ and $\Delta m = \pm 2$ have been established in C_8OCu and $2C_8Cu2OC_8$ from computer simulations.
2. The role of bulky alkoxy group in preventing close packing leading to lamellar crystal structures is indicated.

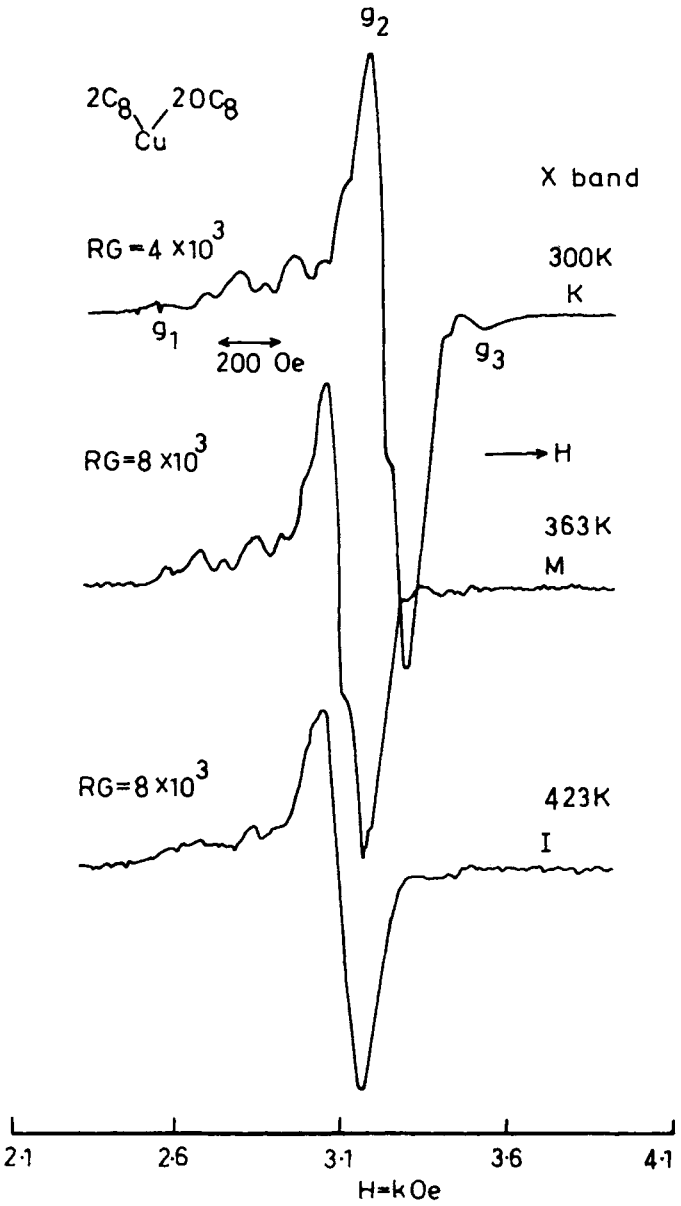

FIGURE 6 X-band EPR of the mixed complex at high temperatures.

3. Mixed alkyl/alkoxy Cu complex present a strongly distorted rectangular discotic, as distinct from C_8OCu a more symmetric discotic.
4. As one half of the mixed complex is alkyl substituted, whereas the other half alkoxy, its behaviour is determined by a competition between the two halves. The stronger contribution to the property investigated, is shown up experimentally.

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