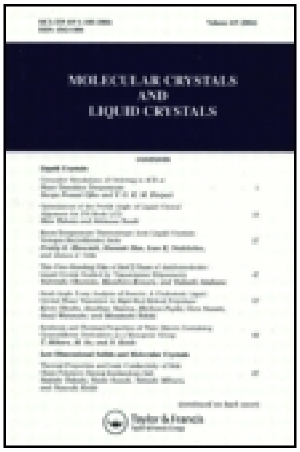

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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To cite this article: Monisha Bose, Chanchal K. Majumdar & B. K. Sadashiva (1997): EPR Studies of Alkyl Substituted Aryl β Diketonates of Discotic Copper Complexes 2: Concentrated Versus Dilute Systems, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 307:1, 57-68

To link to this article: http://dx.doi.org/10.1080/10587259708047086

Mol. Cryst. Liq. Cryst., 1997, Vol. 307, pp. 57–68
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EPR Studies of Alkyl Substituted Aryl *β* Diketonates of Discotic Copper Complexes 2: Concentrated Versus Dilute Systems

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(Received 15 October 1996)

Striking differences occur between alkyl and alkoxy substituted transition metal β diketonates. Thus pure C_8Cu exhibit polymorphic discotic phases, whereas C_8OCu shows a single mesophase. The length of the chain and the nature of the metal atom also play an important role. Thus $C_{10}Cu$ exhibits a single discotic phase, whereas $C_{10}Pd$ is a polymorphic discotic. Magnetic resonance studies indicate the presence of strong long-range antiferromagnetic exchange-interaction in C_nCu, as against no such interaction in C_8OCu. However, C_8Cu does not order antiferromagnetically, even at liquid He temperature. A comparative ^{1}H NMR study of diamagnetic $C_{10}Pd$ against C_8Cu reveals interesting features of the phase transitions. The highly asymmetric, strongly exchanged-narrowed EPR line ($g_\perp$) in C_nCu becomes somewhat wider in the mesophase (D_1), broadens significantly (decreases in intensity) in the D_2 phase and remains almost unchanged in the isotropic phase. However, in dilute systems viz., C_8Cu doped in C_8Pd and $C_{10}Cu$ doped in $C_{10}Pd$, the results are very different. The $g_\parallel$ line now splits up into a quartet ($I = 3/2$ for Cu), with the outer lines clearly exhibiting a doublet structure from the isotopes of Cu (viz., ^{63}Cu and ^{65}Cu in the ratio of their concentration of ~ 70:30). However, $g_\perp$ exhibits the quadrupole-split pattern, as in C_8OCu, with loss of axial symmetry. The frozen solution spectra of C_8Cu and $C_{10}Cu$ in $CHCl_3$ at 77 K are very similar to that in the doped solid. Thus, at the molecular level, there is virtually no difference between C_nCu and C_nOCu, due to the absence of the strong exchange-interaction. However, in the solid, the strong exchange-interaction in C_nCu modifies the packing situation, leading to different structures, columnar in C_nCu but lamellar in C_nOCu.

Keywords: EPR; discotic; copper complex

1. INTRODUCTION

The striking difference between the effect of alkyl substitution in the discogens bis[1, 3-di(*p*-*n*-alkylphenyl)propane-1, 3-dionato] Cu(II), as against alkoxy substitution has attracted attention in recent times [1–7]. The alkyl substituted compound (Fig. 1) abbreviated as C_nCu, exhibit the regular discotic columnar mesophase [1], while the alkoxy mesogens (C_nOCu) seem to exhibit a new lamellar (D_L) discotic phase [2, 3]. Further, C_8Cu exhibit two different discotic (D_1 and D_2) phases. Though the melting temperatures are not very different in C_8Cu and C_8OCu, the clearing temperatures are much higher for the latter (177°C), as compared to 141.6°, of the former. However, the chain length and nature of the metal atom are clearly deciding factors. Thus, $C_{10}Cu$ exhibits a single discotic phase [1], whereas $C_{10}Pd$ follows the pattern of C_8Cu. Further magnetic interactions [4] possibly account for increasing the range of mesophase in C_nCu, as compared to $C_{10}Pd$.

It has been pointed out that the basic difference between $C_8Cu(C_nCu)$ and $C_8OCu(C_nOCu)$ is structural [5–7]. In the latter, the repeating unit in the unit cell is a dimer [5], while in the former it is a monomer [7] with Cu at the inversion centre, as in $C_{10}Pd$ [6]. The bond in C_8OCu is pretty strong (high clearing temperature), pointing to a strong magnetic exchange-interaction within the dimer, in addition to weak Van der Waals and C—H...O hydrogen bonded effects. X-ray data indicate that the two molecules in the dimer are not on top of one another but are somewhat staggered. Thus the Cu atoms are distributed about the molecular axis in a

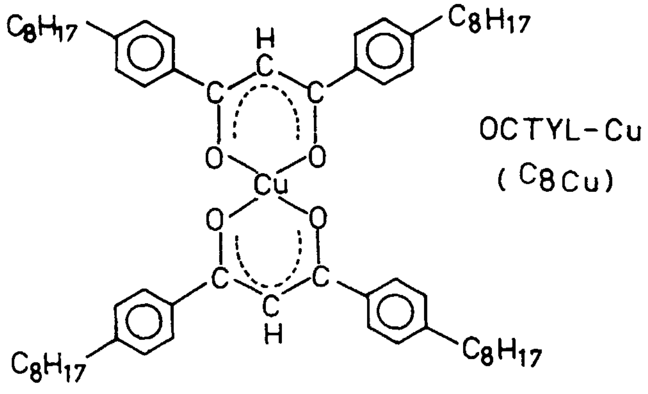

FIGURE 1 Structure of bis[1,3-di(*p*-*n*-octyl phenyl)propane-1,3 dionato] Cu(II).

zig-zag fashion, with zig-zig distances between 6.3 and 6.6 Å respectively, compared to a Cu–Cu distance of 5.82 Å in C_8Cu [7].

In the present work, magnetic resonance studies clearly bring out the role of magnetic interactions in the pure Cu complexes. Thus ^1H NMR studies of the diamagnetic $C_{10}Pd$, and magnetic C_8Cu, reported for the first time are very revealing. Earlier Eastman *et al.* [4] from angular dependence of EPR line-widths and line shapes in crystalline C_8Cu, had claimed that it is a spin 1/2 one dimensional Heisenberg antiferromagnet at room temperature, but gave no direct proof of magnetic ordering in this system. He used Bartkowski and Morosins [8] (B&M) ESR line shape theory, which was based on certain involved assumptions, to arrive at this conclusion. Be it noted, that B&M used their theory to show that their Cu complex was a one-dimensional exchange-coupled linear chain, but did not conclude of any antiferromagnetic order. Eastman's experiments and results and his contention of a strongly exchange coupled linear chain in C_8Cu are perfectly in order. But Eastman or for that matter, no other person has reported the straight-forward conclusive method of observing magnetic ordering viz., magnetic susceptibility studies on C_8Cu. So we decided to carry out susceptibility studies in the present work, in addition to EPR.

EPR studies of several C_nCu compounds exhibit strong magnetic exchange-narrowing effects, while for C_8OCu, no such effects were observed, instead complex hyperfine structure was recorded [10, 11]. In dilute systems viz., doped and frozen solution spectra, the situation changes dramatically. The single asymmetric line $g_\perp$ breaks up and a complex hyperfine split spectrum is observed, due to absence of the exchange effect. This, coupled with the absence of dipolar interaction, causes splitting of $g_\parallel$, leading to the normal Cu hyperfine quartet for $I = 3/2$, with hyperfine doublets from the ^{63}Cu and ^{65}Cu isotopes.

2. RESULTS AND DISCUSSIONS

2.1. Work in Concentrated Systems

2.1.1. Susceptibility Studies

Magnetization measurements of C_8Cu in Squid Magnetometer showed that the system did not order, even at liquid Helium temperature (Fig. 2). Thus Eastman *et al*'s contention that C_8Cu is a one dimensionally ordered antiferromagnet, even at room temperature is not correct. However, that there is a strong antiferromagnetic exchange-interaction in one dimension in C_8Cu/C_nCu is amply borne out in the present work.

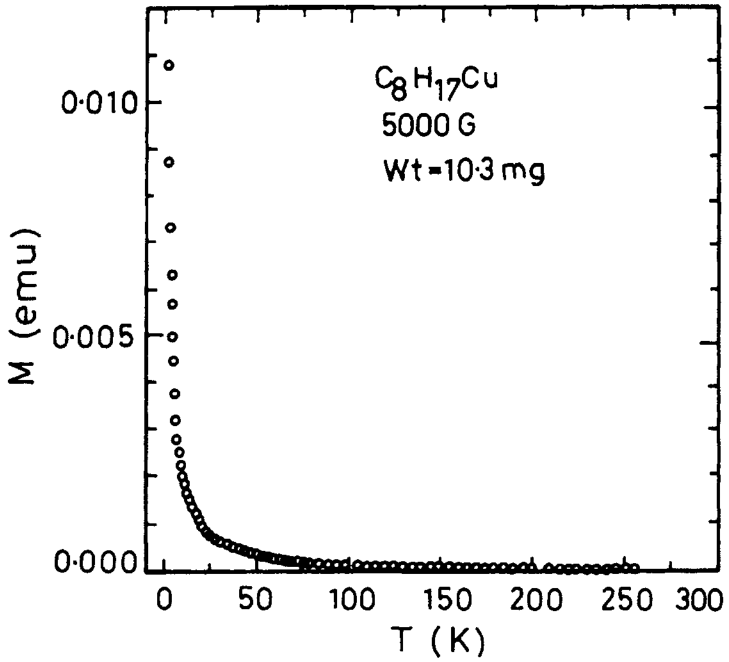

FIGURE 2 Magnetization measurement of C_8Cu in a Squid Magnetometer.

2.1.2. ^1H NMR Spectra

A comparison of C_8Cu with the analogous $C_{10}Pd$ (Fig. 3) is of interest. The ^1H spectrum of $C_{10}Cu$ has already been reported in our earlier paper [10]. In $C_{10}Pd$, there is no paramagnetic broadening effect. Thus the room temperature ^1H spectrum of $C_{10}Pd$ at 400 MHz, unlike that of the copper complexes studied viz., $C_{10}Cu$ and C_8OCu [10] and C_8Cu (present paper) is not a single wide line, but exhibits a comparative intense line from the alkyl group, peaked around 4 ppm and a weak broad line from the aromatic protons (~ 10.5 ppm) in the polycrystalline state. It was very surprising to find a single broad line (mixed gaussian-lorentzian) in the D_1 phase, indicating fluidity. Possibly, in the ordered crystalline columnar phase with interlocking alphatic tails [6], motional effects of the alkyl group are permitted, while in D_1, this motion is hindered, due to disordering. Just below the isotropic phase (D_2), the line narrows (clearly lorentzian) with the appearance of two shoulders. In the isotropic phase (I), the alkyl group itself splits up with the end CH_3 group, appearing as a kink and the end CH_2

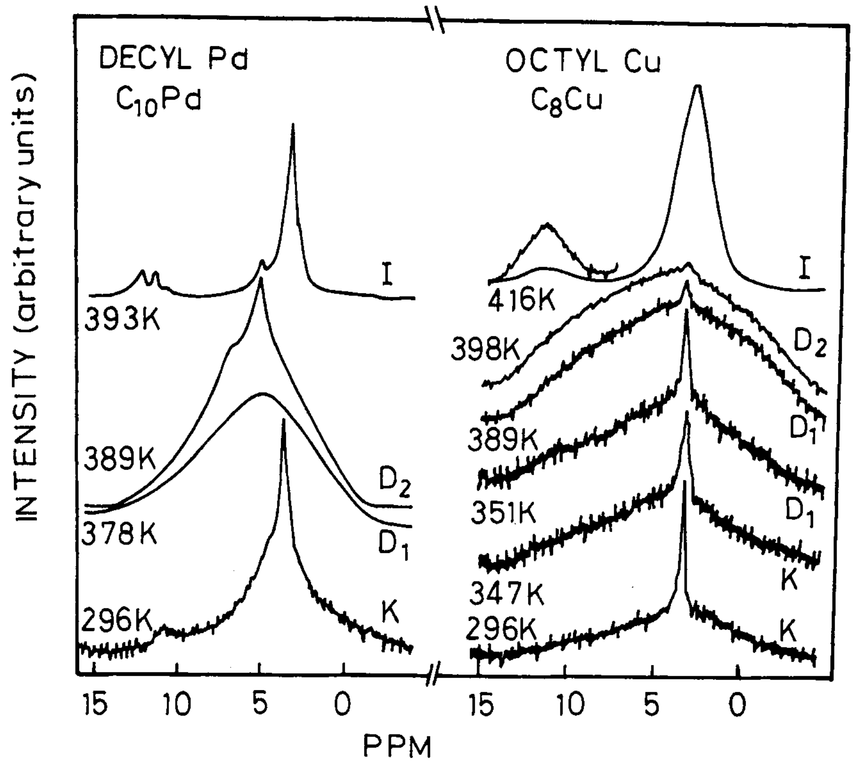

FIGURE 3 Phase Transitions from ^1H NMR spectra of diamagnetic Pd and paramagnetic Cu complexes at 400 MHz.

group attached to phenyl, clearly resolved, from the intense but comparatively wide peak of the remaining CH_2 groups. Contrary to the Cu complexes, the α and β protons of the phenyl group give separate peaks. The shoulder, just preceeding the aromatic protons, could be ascribed to the core CH group. This spectrum basically follows the $CHCl_3$ solution spectrum of $C_{10}Pd$.

However, in the K phase of magnetic C_8Cu, a single broad line with a sharp narrow peak at around 4 ppm, possibly from the CH_3 group of the alkyl chain is observed. Just after transition to the D_1 phase, the CH_3 peak decreases in intensity and the line is somewhat wider. At the upper limit of the D_1 phase, just below D_2, the line becomes very much wider, primarily due to disordering and the CH_3 peak is just visible. In the D_2 phase, the line further broadens and becomes virtually gaussian due to reduction in both motional and exchange effects. Finally, in the isotropic phase, the broad line splits up, gives a single intense sharp line from the alkyl group, clearly separated from the very weak broad line, arising from aromatic protons. Thus magnetic broadening effects in C_8Cu precludes splitting of the different types of ^1H as in $C_{10}Pd$.

2.1.3. EPR Spectra

X band studies at room temperature reveal strongly exchange-narrowed asymmetric central line $g_\perp$ along with a very weak g line, in both powdered $C_{10}Cu$ and C_8Cu. The lines with axial symmetry remain almost unchanged at 77 K, except for a slight increase in intensity. Thus C_nCu compounds do not exhibit any structural change at low temperatures, as in C_8OCu [11]. Thus for C_8Cu in X and Q bands, (Fig. 4) intensity of the asymmetric line in the mesophase diminishes only slighly, as exchange interaction is still significant [4] in the D_1 phase, but decreases sharply in the D_2 phase, due to disordering. This decrease in exchange-interaction, results in broad lines, which are less asymmetric. However, the line in the isotropic phase is not very different from D_2, indicating the presence of short-range magnetic order. The case of $C_{10}Cu$ in X and Q bands is very similar, inspite of the increase in the number of CH_2 groups. However, the linewidth of C_8Cu at 298 K is ~ 25 Oe, as compared ~ 30 Oe in $C_{10}Cu$, whereas, in the isotropic phase it is ~ 44 Oe in the former but 37.5 Oe in the latter. This points to a stronger exchange-interaction in C_8Cu in the K phase.

Finally, it may be pointed out that the isotropic phase in a discotic appears to be rather different from that in a rod-like nematic/smectic. In the latter class, the mobility, particularly the translational and rotational mobility is very much like that in a regular liquid. Our studies on the discotic over the years indicate that fluidity in the isotropic phase is not truly isotropic, because of their bulky nature (cores with long chains) and further supramolecular order giving rise to columnar, lamellar and other complex structures, wherein each column etc. are surrounded by 8, 6 or 4 other similar units. Thus, though the system becomes disordered, the presence of long chains which are often interleaved, does not allow completely non-interacting isolated molecules with full freedom of translational, rotational and vibrational degrees of motion. Thus in Chandrasekhar's discotic benzene-hexa-*n*-heptanoate, IR spectra of meso and isophases were identical, which led Sorai [10] to postulate that short range order effects in mesophase persists in the isotropic phase. In our case also, in mixed alkyl-alkoxy complex (see previous paper in this Journal), EPR of isotropic phase is not very different from that of the mesophase.

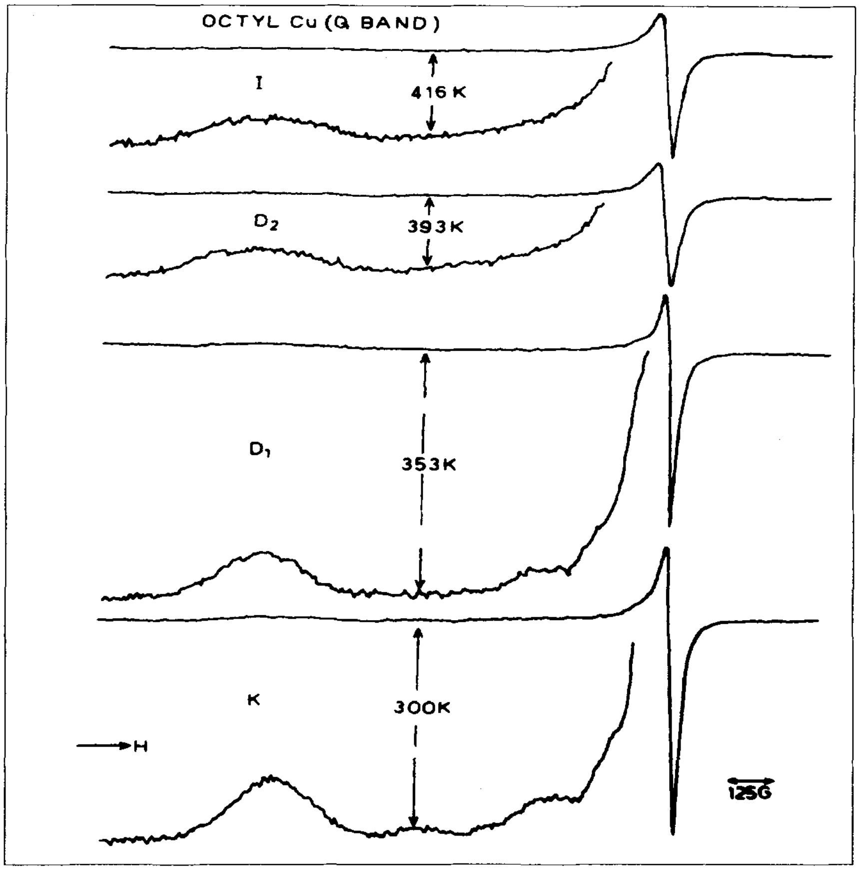

FIGURE 4 Q band EPR spectra of C_8Cu ($K \rightarrow M \rightarrow I$).

2.2. EPR Studies in Dilute Systems

2.2.1. Q Band Studies in Doped Solids at Room Temperature

Results in 5% doped C_8Cu and $C_{10}Cu$ in C_8Pd and $C_{10}Pd$ respectively are interesting (Fig. 5). As exchange and dipolar interactions are absent or drastically reduced, complex hyperfine structure appears in both. Further, Cu^{2+} in the doped solid loses its axial symmetry, having $g_1 \sim 2.258$, $g_2 \sim 2.138$ and $g_3 \sim 2.035$ values for C_8Cu, whereas the pure solid has $g_\perp \sim 2.234$ and $g_\perp \sim 2.042$ (Fig. 5). The corresponding values for $C_{10}Cu$ are $g_1 \sim 2.234$, $g_2 \sim 2.043$ and $g_3 \sim 2.038$, whereas $g_\parallel \sim 2.38$ and $g_\perp \sim 2.061$. Significantly, in place of the weak $g_\parallel$, the doped solids exhibit the normal hyperfine quartet

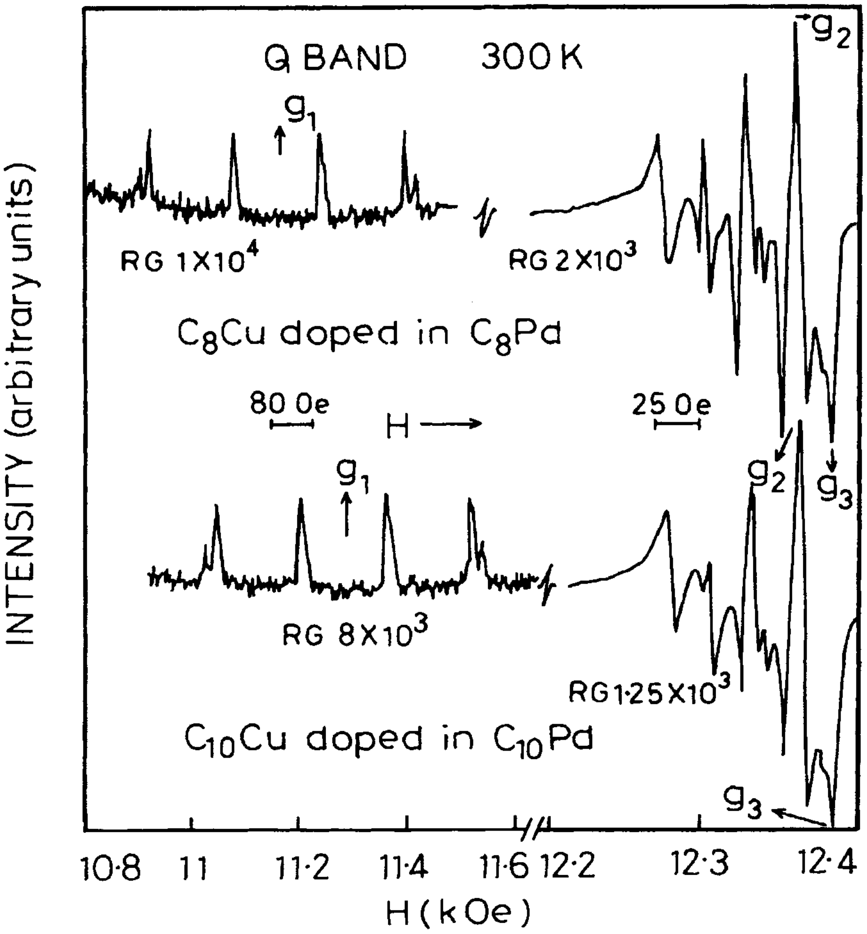

FIGURE 5 Q band EPR spectra of C_nCu doped in C_nPd at 300 K.

from Cu ($I = 3/2$). Each line of the quartet (specially the outermost ones), further splits up into a doublet (intensity ratio 2:1) due to the presence of ^{63}Cu and ^{65}Cu isotopes (ratio of their concentration ~ 70:30). The quartet separation was ~ 180 Oe, whereas the isotopic splitting was ~ 25–30 Oe.

The single asymmetric line ($g_\perp$) in the doped solids shows a complex hyperfine structure, somewhat akin to C_8OCu [11]. Thus the Cu ($I = (3/2)$) quartet, along with the quadrupolar forbidden doublets [12] are clearly observed. However, the quadrupolar transitions are weak, as compared to the hyperfine quartets (opposite in C_8OCu), which again are of unequal intensity. Further, the first two quadrupolar doublets are broad (not splitted) but the third is clearly splitted. The average separation of the quadrupolar lines are ~ 30 Oe. Finally, the loss of the axial symmetry in the doped solid, can be interpreted, as being due to the random distribution of the Cu^{2+} complex in the diamagnetic matrix, as compared to a columnar arrangement in the pure solid, wherein Cu^{2+} ions are situated on an inversion centre.

2.2.2. X Band Studies in Doped Chloroform Solution at 77 K

EPR spectrum of the frozen solution of C_8Cu in $CHCl_3$ is similar to that of the doped solid (Fig. 6). Thus $g_1 \sim (g_\parallel)$ 2.272 shows the hyperfine quartets with doublet splittings from the copper isotopes. The quartet separation was unchanged at ~180 Oe, as also the isotopic splitting at ~25 Oe. Interestingly, in between the quartets, it appears that weak quadrupolar forbidden transitions are present, unlike that in the doped solid. However, $g_2 \sim 2.061(g_\perp)$ gave a complex pattern wherein, the quartet and quadrupolar transitions, though discernable, are difficult to pinpoint with certainty and $g_3 \sim 1.933$ is clearly observed.

$C_{10}Cu$ gave a similar spectrum with $g_1 \sim 2.271$, quartet (180 Oe separation) and isotopic splitting of ~30 Oe, with indication of weak quadrupolar transitions in-between. However, the last line of the quartet is broad and rounded (doublet splitting not clear), unlike that in C_8Cu. g_2 and g_3 values are ~2.043 and ~2.038 respectively. g_2 as in C_8Cu, gave a complex h.f. structure, indicating presence of quadrupolar forbidden transitions.

Finally, the X band spectra of frozen chloroform solution of $C_{12}OCu$ is presented (Fig. 7). This is very similar to the frozen solution spectra of C_8Cu and $C_{10}Cu$. It shows a hyperfine quartet in $g_\parallel$ with indications of quadrupolar forbidden transition (qft) among the quartet and as in $C_{10}Cu$, the last line of the quartet is rounded and $g_\perp$ shows a complex structure from hyperfine and qft transitions. Thus the $C_{12}OCu$ spectra further corroborates that at the molecular level, the alkyl and the alkoxy complexes behave in the same fashion.

CONCLUSION

1. It has been shown that Eastman's contention of C_8Cu being a Heisenberg antiferromagnet at room temperature is not correct. Though C_nCu

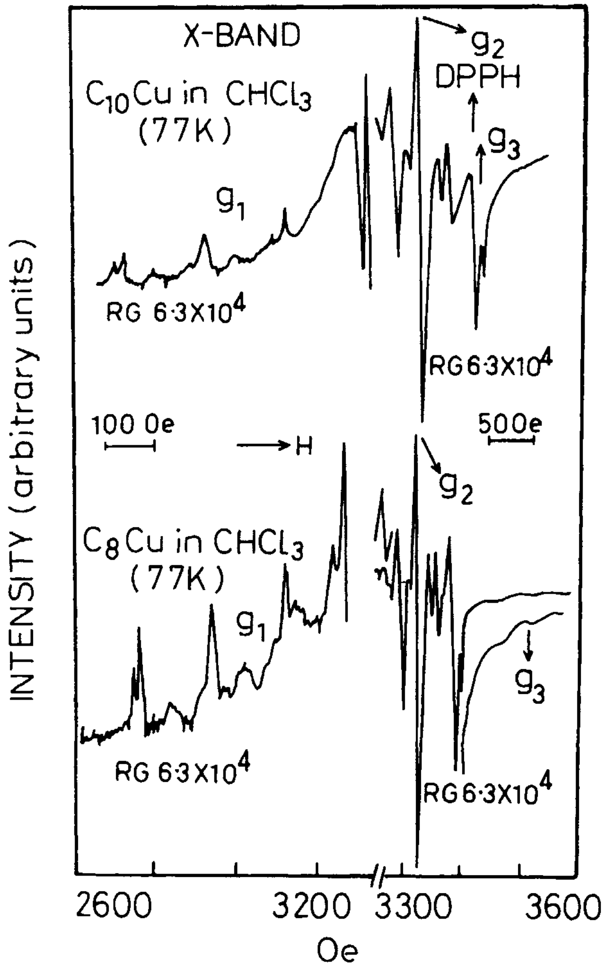

FIGURE 6 *X* band EPR spectra of frozen chloroform solution of C_nCu.

systems do not order, there is a strong antiferromagnetic exchange-interaction, within the columnar structure.

2. In concentrated C_nCu complexes, due to the presence of Cu at the inversion centre, close packing is possible, leading to a columnar structure with strong exchange-interaction, which however is absent in the lamellar alkoxy system, leading to a complex h.f. structure.
3. In dilute systems, due to absence of exchange-interaction and dipolar broadening, not only the hyperfine quartet from Cu($I = 3/2$ is observed in $g_{\parallel}(g_1)$, each line, particularly the outermost ones, shows hyperfine structure from the ^{63}Cu and ^{65}Cu isotopes (intensity ratio of $\sim 2{:}1$),

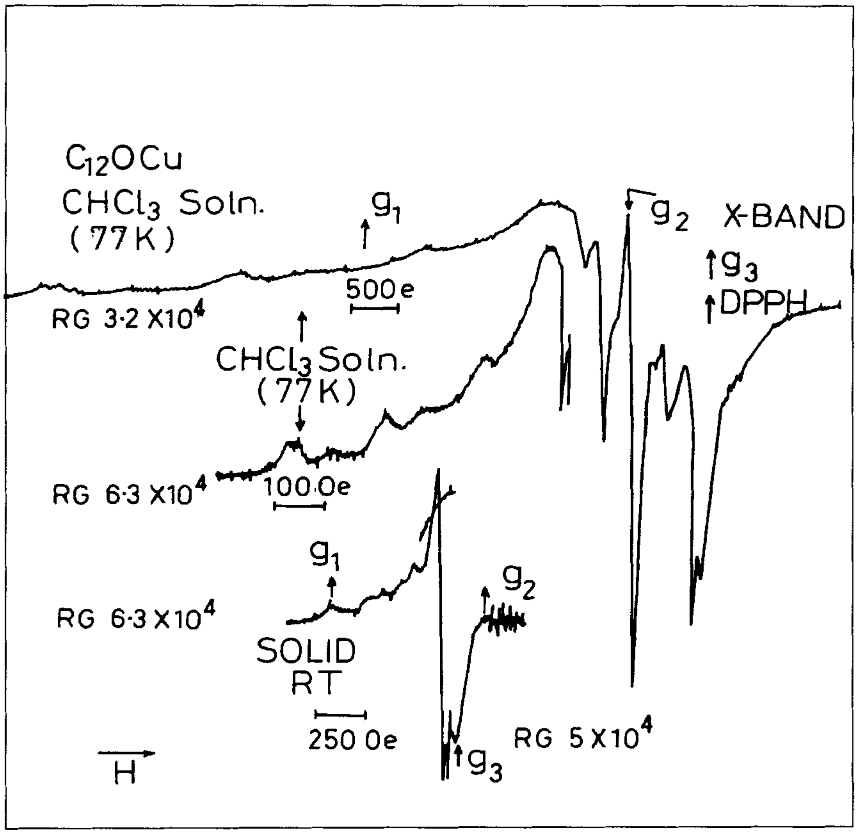

FIGURE 7 *X* band EPR spectrum of frozen chloroform solution of $C_{12}OCu$.

according to the isotopic abundance of ~ 70:30. Further $g_{\perp}(g_2)$ shows the hyperfine structure from quadrupolar forbidden transitions along with the hyperfine quartet from Cu and the system loses axial symmetry, as there is now a g_3 in C_8Cu and $C_{10}Cu$.

4. At the molecular level (dilute system), C_nCu and C_nOCu behave basically in the same fashion, due to absence of the strong exchange interaction. However in the crystalline state, packing effect decides the structure, columnar in C_nCu, lamellar in C_nOCu.

Acknowledgements

M. Bose and C. K. Majumdar are thankful to the Department of Science and Technology, Government of India for sanctioning the Project on

"Metallomesogens". The authors acknowledge the kind cooperation of Prof. S. Subramanian, RSIC, IIT (Madras) and Dr. M. D. Sastry of BARC, Bombay in the magnetic resonance work.

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