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E.S.R. of a one-dimensional Heisenberg antiferromagnet which undergoes a crystalline to discotic phase transition

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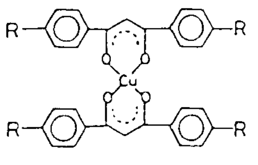
Single crystals and polycrystalline samples of the compounds bis(1,3-di(*p*-*n*-octylphenyl)propane-1,3-dionato)copper(II) [I], and bis(1,3-di(*p*-*n*-octyloxyphenyl)propane-1,3-dionato)copper(II) [II] have been studied by E.S.R. The E.S.R. spectra of single crystals of [I] at 298 K have the features associated with a spin 1/2 one-dimensional Heisenberg antiferromagnet while the spectra of single crystals of [II] do not. E.S.R. of single crystals of [I] and [II] provides a reliable means of detecting previously reported crystalline to discotic phase transitions. Single crystals of [I] heated beyond the temperature of the first discotic phase transition yield single line E.S.R. spectra which have an angular dependence and an asymmetric lineshape; these observations suggest that, in the discotic phase, exchange interactions are still significant and a degree of long range order is maintained.

1. Introduction

A number of organometallic compounds which undergo thermally induced transitions to one or more discotic phases have been synthesized [1–8]. Some of these compounds, such as the octakis((dodecyloxy)-methyl)metallophthalocyanines (M = Mn^{2+}, Cu^{2+}), bis(1,3-di(*p*-*n*-octylphenyl)propane-1,3-dionato)copper(II) [I], and bis(1,3-di(*p*-*n*-octyloxyphenyl)propane-1,3-dionato)copper(II) [II] contain paramagnetic metal ions at their centre. X-ray structure determinations for the metallophthalocyanines show the discotic phase to be columnar with the columns arranged hexagonally; the separation between columns is about 3 nm [2, 8]. Such a structure suggests, for the metallophthalocyanines containing a paramagnetic metal ion, a one-dimensional exchange coupled system in the discotic phase and; perhaps, the crystalline phase. Neither the crystalline nor the discotic phases of [I] and [II] have been studied by X-ray diffraction.

Studies of crystalline one-dimensional systems containing Cu^{+2} and Mn^{+2} have been reported; in particular, Bartkowski and Morosin have investigated the exchange coupled one-dimensional behaviour of bis(*N*-methylsalicylaldiminato)-copper(II) by X-ray diffraction and E.S.R. [9, 10]. This compound, which does not form a discotic phase, has the properties of a one-dimensional spin 1/2 Heisenberg antiferromagnet. The development and predictions of the E.S.R. theory for such one-dimensional systems are summarized in [10].

Here it is hypothesized that crystals of paramagnetic organometallics, which exhibit discotic phases, may exhibit the properties of one-dimensional exchange coupled systems either in the crystalline or in the discotic phase, and that the interaction between paramagnetic centres in such organometallics is altered by changes in molecular motion and spacing which occur during a discotic phase transition.



[I] ,[II]

[I]: R = C_8H_{17}

[II]: R = $C_8H_{17}O$

Figure 1. A representation of the molecular structures of bis(1,3-di(*p*-*n*-octylphenyl)propane-1,3-dionato)copper(II) [I], and bis(1,3-di(*p*-*n*-octyloxyphenyl)propane-1,3-dionato)-copper(II) [II].

As a consequence, the E.S.R. of organometallics, which exhibit discotic phases, should provide an important tool for the study of discotic phase transitions. E.S.R. of organometallics exhibiting one or more discotic phases has been confined to the investigation of metal free octakis((dodecyloxy)-methyl)phthalocyanine doped with octakis((dodecyloxy)-methyl)copper(II)phthalocyanine [11]. Samples containing the Cu^{2+} probe in concentrations above 4 per cent yield E.S.R. spectra which indicate the formation of dimers and substantial electron spin–spin interaction between the members of the dimer. These observations appear, however, to be of little value in studying the phase transition associated with the octakis((dodecyloxy)-methyl)phthalocyanine.

The purpose of this paper is to test the preceding hypothesis through E.S.R. studies of single crystals of [I] and [II]. The molecular structure of these compounds is given in figure 1.

2. Experimental

The syntheses of [I] and [II] were carried out essentially as described in the literature [6, 7, 12]. Single crystals of [I] and [II] were prepared by the following steps. (1) Dissolve the organometallic in warm acetone, add decolourizing charcoal, filter warm and allow filtrate to stand for 1 day. (2) Separate the crystals which form from the acetone by filtration. (3) Dissolve the crystals in a small volume of chloroform and allow acetone to diffuse into the chloroform solution over a 3- or 4-day period. This final step was carried out in a closed container held at a constant temperature. The crystals chosen for the E.S.R. experiments had thicknesses on the order of 1 μm and lengths of the order of 1 mm.

X-ray E.S.R. spectra were obtained using an IBM ER 200 D E.S.R. console and ER 041 MR microwave bridge. A Varian V-3900 12″ magnet system provided the magnetic field and temperature was controlled using a Bruker ER 4111 VT variable temperature controller. The phase transition temperatures for [I] and [II] were measured using a Nikon S-UK polarizing microscope and by E.S.R.

3. Results and discussion

The table lists the phase transition temperatures for the samples of [I] and [II] prepared in our laboratory. The values in this table were determined using a polarizing

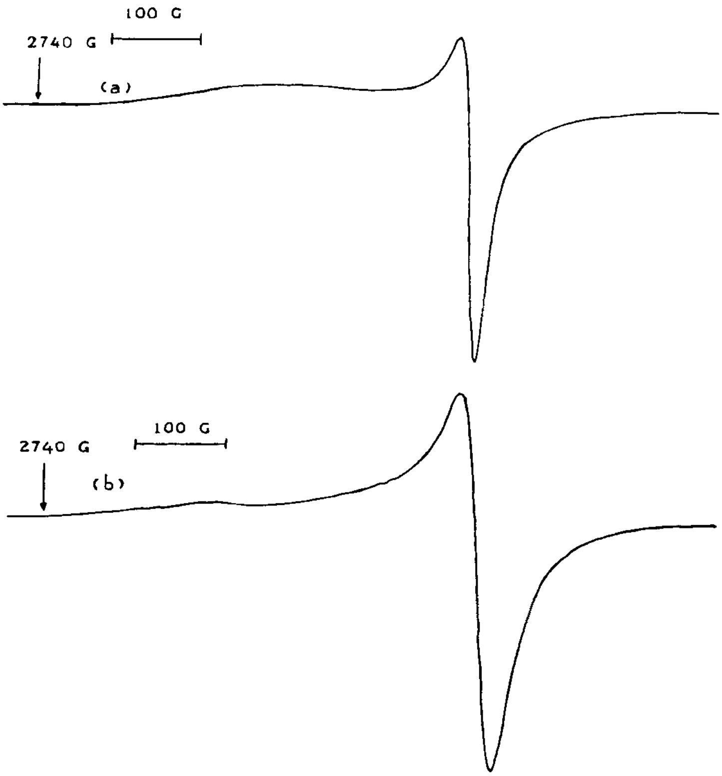


Figure 2. E.S.R. spectra of polycrystalline [I] at 298 K (*a*) and 357 K (*b*). (ν = 9·29 GHz.)

Phase transition temperatures of bis(1,3-di(*p*-*n*-octylphenyl)propane-1,3-dionato)copper(II) [I], and bis(1,3)-di(*p*-*n*-octyloxyphenyl)propane-1,3-dionato)copper(II) [II] as determined using a polarizing microscope and E.S.R.

Compound	T_t/K						
[I]	K	350	D_1	389	D_2	414	I.L.
[II]	K_1	294	K_2	358	D	448	I.L.

microscope. Attempts to use E.S.R. to measure phase transition temperatures initially focused on polycrystalline samples. Figure 2 shows the spectrum of [I] in the polycrystalline form and the spectrum after passing through the first discotic phase transition. The spectral changes observed seem, at first glance, relatively minor.

Single crystals of [I] mounted such that the angle (θ) between the *c* axis of the crystal and the applied field can be varied, produce a single line resonance whose lineshape and linewidth is dependent on θ. If [I] forms a one-dimensional Heisenberg antiferromagnet, it is expected, given the assumptions described in the literature, that the E.S.R. of a single crystal will exhibit a single line resonance with a linewidth which is proportional to $|3\cos^2(\theta) - 1|^{4/3}$ [10]. In addition, the lineshape for the resonance at $\theta = 54°$ should be lorentzian while the lineshape for the resonances at $\theta = 0°$ and 90° should have a lineshape corresponding to the Fourier transform of $\exp[-t^{3/2}]$ [10].

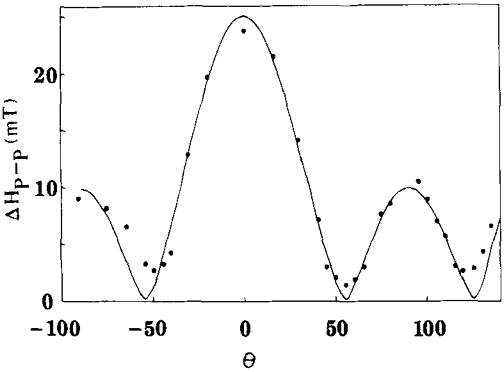


Figure 3. The first derivative linewidth determined for [I] at 298 K as a function of θ. The solid line represents the function $100|3\cos^2(\theta) - 1|^{4/3}$.

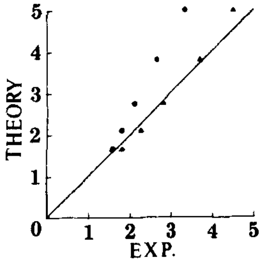


Figure 4. A comparison of the experimental lineshape for a single crystal of [I] at θ = 55° (▲) and 0° (●) with a lorentzian lineshape.

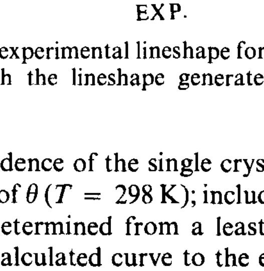


Figure 5. A comparison of the experimental lineshape for a single crystal of [I] at θ = 0° (■), 90° (▲) and 55° (●) with the lineshape generated from the Fourier transform of $\exp[-t^{3/2}]$.

Figure 3 shows the dependence of the single crystal peak to peak first derviative linewidth for [I] as a function of θ (T = 298 K); included in the figure is the theoretical curve $100|3\cos^2(\theta) - 1|^{4/3}$ determined from a least squares analysis of the experimental data. The fit of the calculated curve to the experimental data is good when compared with the examples of one dimensional systems given in [9, 10].

Figure 4 shows a comparison of the experimental lineshape for a single crystal of [I] at θ = 54° and θ = 0° with a lorentzian lineshape; while figure 5 shows a comparison of the experimental lineshape at θ = 0°, 90° and 54° with the lineshape expected from the Fourier transform of $\exp[-t^{3/2}]$. The details of this method of lineshape analysis have been described; deviations from the theoretical lineshape are

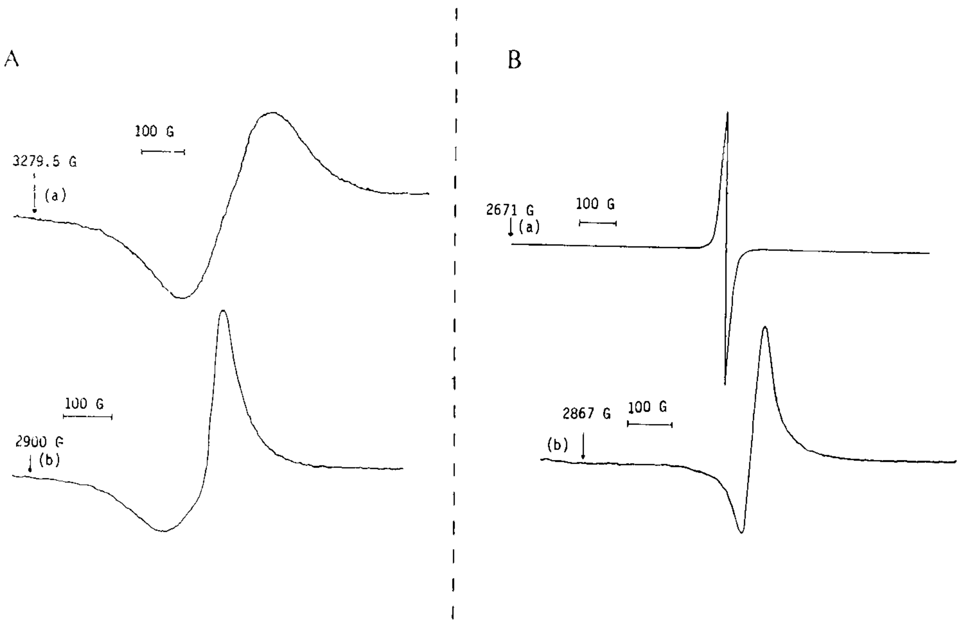


Figure 6. E.S.R. resonance of a single crystal of [I] under the conditions: $\theta = 0°$ (A) and $\theta = 55°$ (B); $T = 343\,K$ (*a*), $T = 356\,K$ (*b*). ($\nu = 9{\cdot}45\,GHz$.)

represented by the distance of the data points from the solid line [13]. The units on the axes represent multiples of the halfwidth of the first derivative line. The agreement between theory and experiment is excellent out to five first derivative halfwidths.

Following the resonance for [I] as a function of temperature provides several interesting observations. The linewidth for $\theta = 0°$ at $T = 298\,K$ is 24 mT and is 22 mT at $T = 340\,K$. The linewidth at $\theta = 54°$ does not change with temperature between 293 K and 349 K. Figure 6 shows the resonance of [I], at $\theta = 0°$ and 54°, below and above the crystalline-discotic phase transition temperature. The spectral changes exhibited in figure 6 occur within 1 K of the K to D_1 phase transition temperature determined using the polarizing microscope. The phase transition is not preceded by spectral changes other than those mentioned and the spectral effects of the phase transition occur immediately upon reaching the transition temperature. The discotic phase resonances in figure 6 show no change with time over a 4-hour period; thus, from the point of view of single crystal E.S.R. no 'slow' processes follow the phase transition. The spectral changes occurring at the D_1 to D_2 phase transition consist of a slight broadening (~ 10 per cent) of the resonances in figure 6 and a decrease in the spectral dependence on θ. These changes have not yet been extensively investigated.

Figure 6 shows that [I] in the discotic phase yields single line E.S.R. spectra which have an angular dependence and an asymmetric lineshape; these observations suggest that in the discotic phase exchange interactions are still significant and a degree of long range order is maintained.

Single crystals of [II] produced spectra which did not agree with the one-dimensional model. For example, the resonance at $\theta = 55°$ consists of approximately 18 lines separated by 4 mT and the resonance at $\theta = 0°$ consists of a single line having a gaussian lineshape. The resonance at $\theta = 55°$ changes at both the crystalline and discotic phase transition temperatures reported by Ohta *et al.* [7]. Single crystals of [II] in the discotic phase do not yield asymmetric single line spectra but rather spectra having resolvable splittings. Preliminary X-ray work on single crystals of [II] shows a 6 Å separation between Cu^{2+} ions [14]. A separation of this magnitude probably leads to weak exchange interactions between paramagnetic sites.

4. Conclusions

E.S.R. of single crystal samples provides clear evidence of crystalline to discotic phase transitons for compounds [I] and [II]. The E.S.R. spectra of single crystals of [I] have the dependence on θ and the lineshapes associated with a spin 1/2 one-dimensional Heisenberg antiferromagnet while the spectra from single crystals of [II] do not. These results suggest a columnar crystal structure for [I] with a linear arrangement of exchange coupled Cu^{2+} ions separated by an insulating hydrocarbon region of perhaps 2 to 3 nm and a more complicated structure for [II]. The spectral changes which occur at the K to D_1 phase transition of [I] are immediate and without any precursor. Spectral changes at the D_1 to D_2 phase transition of [I] are detectable but not dramatic. Experimentally observed lineshapes for [I] in the discotic phase indicate continued exchange interactions and a degree of long range order less than that observed in the crystalline phase.

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References

[1] Piechocki, C., Simon, J., Skoulios, A., Guillon, D., and Weber, P., 1982, *J. Am. chem. Soc.*, **104**, 5245.

[2] Guillon, D., Skoulios, A., Piechocki, C., Simon, J., and Weber, P., 1983, *Molec. Crystals liq. Crystals*, **100**, 275.

[3] Piechocki, C., and Simon, J., 1985, *J. chem. Soc. Chem. Commun.*, p. 259.

[4] Piechocki, C., and Simon, J., 1985, *Nouv. J. Chim.*, **9**, 159.

[5] Giroud-Godquin, A. M., and Billard, J., 1981, *Molec. Crystals liq. Crystals*, **66**, 147.

[6] Ohta, K., Ishii, A., Yamamoto, I., and Matsuzaki, K., 1984, *J. chem. Soc. Chem. Commun.*, p. 1099.

[7] Ohta, K., Ishii, A., Muroki, H., Yamamoto, I., and Matsuzaki, K., 1985, *Molec. Crystals liq. Crystals*, **116**, 299.

[8] Piechocki, C., 1982, Thesis, Strasbourg.

[9] Dietz, R. E., Merritt, F. R., Dingle, R., Hone, D., Silbernagel, B. G., and Richards, P. M., 1971, *Phys. Rev. Lett.*, **29**, 1186.

[10] Bartkowski, R. R., and Morosin, B., 1972, *Phys. Rev.* B, **6**, 4209.

[11] Andre, J., Bernard, M., Piechocki, C., and Simon, J., 1986, *J. phys. Chem.*, **90**, 1327.

[12] Horng, M-L., 1986, Thesis, University of Texas at El Paso.

[13] Eastman, M. P., Patterson, D. E., and Pannell, K. H., 1984, *Clays Clay Min.*, **32**, 327.

[14] Larson, E. M., Eastman, M. P., and Freiha, B. (unpublished results).