Columnar Liquid Crystals Derived from Long-Chain Carboxylates of Transition Metal Ions [and Discussion]

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Columnar liquid crystals derived from long-chain carboxylates of transition metal ions

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Copper^{II} complexes of the fatty acids exhibit a thermotropic liquid crystalline phase of the columnar type. X-ray diffraction studies of this mesophase indicate that the spine of a column is made of regularly stacked dicopper tetracarboxylate cores, which are surrounded by disordered, liquid-like alkyl chains. In turn, the column axes occupy the nodes of a two-dimensional hexagonal lattice.

Examination of the local environment of the copper atoms by Cu K_α EXAFS spectroscopy reveals insignificant changes in bond lengths within the binuclear core upon the transition from the lamellar crystalline phase to the columnar mesophase. However, a slight, but sharp, decrease of the magnetic moment of the dicopper unit is observed at the solid–mesophase transition temperature ($\Delta\mu_{\text{eff}} \approx -0.04\ \mu_B$). The columnar mesophase, and the crystalline phase alike, obey a Bleaney–Bowers relation. The singlet–triplet gap is higher in the former ($-2J = 310$–$330\ \text{cm}^{-1}$ against 290–300 cm^{-1}).

Dirhodium^{II,II} complexes of selected fatty acids were prepared, and their thermal behaviour was investigated. They exhibit the same thermotropic columnar mesophase as their Cu^{II} congeners, reflecting the presence of isostructural dimetallic cores in both series. The metal–metal single bond that is present in these dirhodium^{II,II} mesogens is Raman active ($\nu_{\text{Rh-Rh}} \approx 350\ \text{cm}^{-1}$); it is a potential probe of the change in molecular and supramolecular structures of this class of compounds at their phase transition.

Diruthenium^{II,II} complexes of fatty acids were obtained by Cr^{II} reduction of the mixed-valence chlorodiruthenium^{II,III} tetrabutyrate, followed by ligand exchange with the appropriate carboxylic acid. Magnetic susceptibility studies indicate that these diruthenium^{II,II} carboxylates have an $M_s = 0$ ground state and a thermally accessible $M_s = \pm 1$ excited state, suggesting a zero-field split ($D \approx 300\ \text{cm}^{-1}$) $\sigma^2\pi^4\delta^2(\delta^*\pi^*)^4$ configuration. The formation of a columnar liquid-crystalline phase is reflected by a sharp increase in the magnetic moment of these complexes at the phase transition ($\Delta\mu_{\text{eff}} \approx +0.15\ \mu_B$).

Introduction

There is considerable current interest in the design of metal-containing molecular materials with specific properties such as electrical conductivity or ferromagnetism (see, for example, Delhaes & Drillon 1987; Kahn 1987). Liquid-crystalline behaviour would be an added bonus to the desired properties, as it would possibly provide ease of processing and macroscopic orientation that would be useful for application in electronics. Since 1984, we have been studying the thermotropic liquid-crystalline properties of binuclear transition metal carboxylates (Godquin-Giroud *et al.* 1984). These complexes are generally easy to prepare from inexpensive starting compounds. They may contain unpaired d electrons that can bestow bulk properties such as magnetism or electron transport. They are therefore prospective candidates for use as molecular materials in electronics applications.

COPPER^{II} SOAPS

The liquid-crystalline phase obtained upon heating copper^{II} stearate (dicopper tetrakis(octadecanoate)) above 125 °C was first observed in 1964 (Grant 1964), but it was not until 1987 that this mesophase was thoroughly characterized and identified by us (Abied *et al.* 1987) as an hexagonal columnar mesophase (figure 1). We have now investigated a comprehensive series of binuclear Cu^{II} complexes with fatty acids having a number, n, of carbon atoms between 2 and 24. We have found that all members of the series with $4 \leqslant n \leqslant 24$ (butyrate to lignocerate) do exhibit a phase transition upon heating from a lamellar crystalline solid to an hexagonal liquid-crystalline phase.

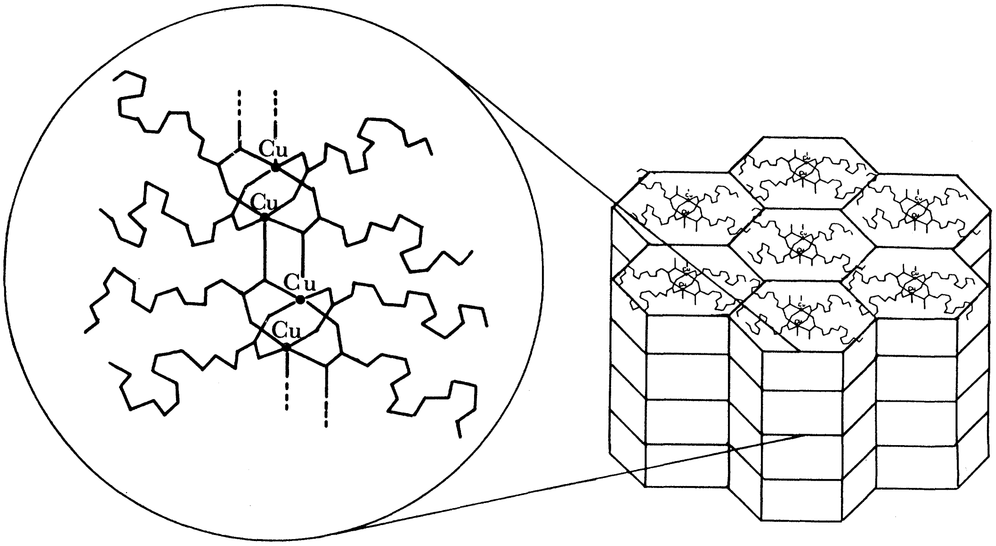

FIGURE 1. A schematic view of the columnar mesophase of a copper^{II} soap. Each column is made of stacked dicopper tetracarboxylate units. The polar inorganic cores are surrounded by disordered alkyl chains. The columns axes define a two-dimensional hexagonal lattice.

Copper-K edge EXAFS spectroscopy was used to probe the local environment of copper atoms in the crystalline and mesomorphic phases of a series of these copper soaps. Each copper atom in an anhydrous binuclear fatty acid complex is known from crystallographic data (Lomer & Perera 1974) to be surrounded by five oxygen atoms in a square-pyramidal environment at a mean distance of 2.01 Å†, by one 'proximal' copper atom, Cu$_p$, at 2.59 Å (the neighbouring copper within a dimer), and by one 'distal' copper atom, Cu$_d$, at 3.20 Å (the nearest copper in the neighbouring dimer). Our EXAFS data confirmed this view; furthermore, they indicated that a similar environment is retained in the columnar mesophase at temperatures close to 150 °C (Maldivi *et al.* 1989*a*). Pseudoradial distributions around copper in both phases of all the Cu^{II} soaps we have investigated are nearly identical. Table 1 shows a summary of interatomic distances measured by EXAFS in the binuclear cores of copper^{II} heptanoate and rhodium^{II}

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† $1\ \text{Å} = 1 \times 10^{-10}\ \text{m} = 10^{-1}\ \text{nm}$.

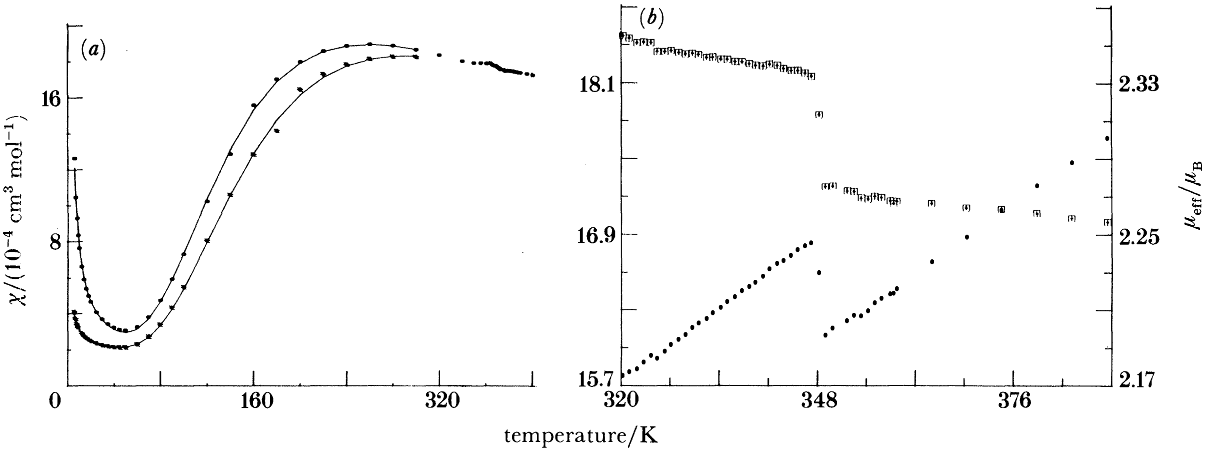

FIGURE 2. (*a*) Plot of the molar magnetic susceptibility of copper^{II} laurate against temperature: upper curve, crystalline and columnar phases; lower curve, quenched columnar phase. Experimental points and calculated Bleaney–Bowers best fit curves are shown. (*b*) Detailed plots of the molar magnetic susceptibility (squares) and of the magnetic moment per binuclear unit (dots) against temperature for $Cu_2[O_2CCH_2CH(C_9H_{19})_2]_4$ about the phase transition.

TABLE 1. ATOMIC SEPARATIONS DETERMINED BY EXAFS STUDIES OF DICOPPER^{II} AND DIRHODIUM^{II} HEPTANOATES IN A TEMPERATURE RANGE THAT INCLUDES THE SOLID–MESOPHASE TRANSITIONS

(All distances in ångströms.)

	$Cu_2(C_7)_4$			$Rh_2(C_7)_4$		
	20 °C	70 °C	120 °C	20 °C	70 °C	120 °C
M–O	2.01	2.01	2.01	2.03	2.06	2.03
$M–M_p$	2.59	2.58	2.59	2.38	2.38	2.37
$M–M_d$	3.19	3.19	3.19	3.16	3.12	3.16

heptanoate (see below) in a range of temperatures that encompasses their respective phase transitions; the changes in interatomic distances are insignificant. We therefore conclude that the interdimer copper–oxygen axial ligation, which prevails in the crystalline phase, is still present in the liquid-crystalline phase, and that it is probably a major factor of cohesion within the columns.

Magnetic susceptibility measurements indicated that, in addition to obeying the well-known Bleaney–Bowers relation (Jotham *et al.* 1972), anhydrous copper^{II} soaps exhibit a sharp drop of the susceptibility (figure 2) near the solid–mesophase transition temperature (Giroud-Godquin *et al.* 1985). This was assigned to a structural modification of the binuclear core at the phase transition. In the light of the EXAFS data summarized above, we can now conclude that this structural change most likely affects the bond angles rather than the bond distances of the binuclear copper cores. As a consequence of this core distortion at the phase transition, the singlet–triplet gap is higher in the columnar mesophase ($-2J = 310$–330 cm^{-1}) than in the crystalline phase ($-2J = 290$–300 cm^{-1}) (Giroud-Godquin *et al.* 1985).

RHODIUM^{II} SOAPS

We have also prepared fatty acid complexes of Rh^{II}. Rhodium^{II} acetate is binuclear and isostructural with copper^{II} acetate, and we thought that, presumably, its higher homologues

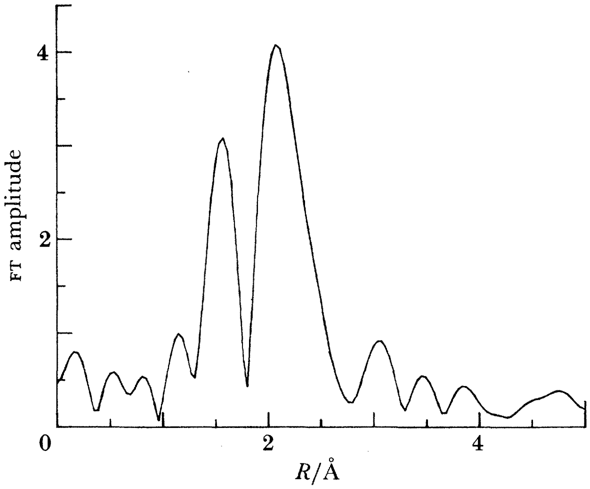

FIGURE 3. The pseudo-radial distribution around the rhodium atom in the columnar mesophase of dirhodium tetrakis(heptanoate) at 120 °C, as obtained from EXAFS measurements at the rhodium K edge. The highest peak is assigned to the 'proximal' rhodium atom and to the axial oxygen atom; that on the left to the four equatorial oxygen atoms, and that on the right to the 'distal' rhodium atom. The corresponding interatomic distances are reported in table 1.

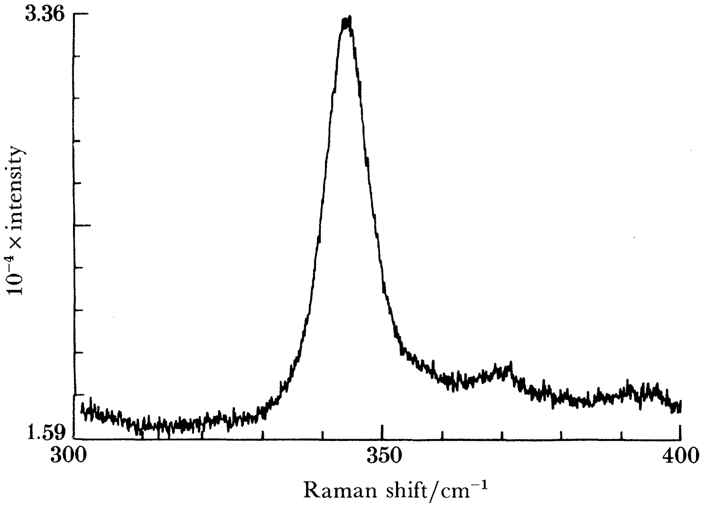

FIGURE 4. Raman spectrum of crystalline dirhodium tetrakis(heptanoate) at room temperature (Ar-ion laser, 514.5 nm; 30 mW; 4 scans). The peak at 344.7 cm^{-1} is assigned to the Rh–Rh stretching vibration.

would exhibit in the solid state the same pattern of interdimer metal–oxygen axial ligation that bestows on copper soaps their columnar structure. Indeed, all the Rh^{II} soaps that we have investigated do exhibit the same thermotropic columnar mesophase as their Cu^{II} congeners (Giroud-Godquin *et al.* 1986). These Rh^{II} compounds are the first examples of metal–metal bonded mesogens. EXAFS studies at the rhodium-K edge have revealed insignificant changes in interatomic distances within the binuclear rhodium core upon the solid–mesophase transition (see above, table 1). The pseudo-radial distribution around rhodium in the mesophase of rhodium^{II} heptanoate is shown in figure 3; it is nearly identical to that observed in the solid phase of the compound.

Magnetic susceptibility studies are useless for this class of diamagnetic mesogens, but Raman spectroscopy is a convenient probe of the Rh—Rh single bond in this series (Clark & Hempleman 1988). The stretching vibration of the latter is exquisitely sensitive to changes in axial ligation. We have found that Rh^{II} soaps are very good Raman scatterers even though the active dirhodium core is diluted in the alkyl chains. Figure 4 shows a Raman spectrum of $dirhodium^{II}$ tetrakis(heptanoate) at room temperature; we assign the band at *ca.* 350 cm^{-1} to the Rh—Rh stretching vibration, following the conclusions of a careful recent investigation (Clark & Hempleman 1988). Further work, currently under way, is focused on the change in Rh—Rh stretching frequency at the solid–mesophase transition, which would be related to a possible labilization of axial ligation (D. P. Strommen and co-workers, unpublished work).

RUTHENIUM^{II} SOAPS

The binuclear tetracarboxylates of Ru^{II} and their bis-solvent adducts has been isolated only recently, and their electronic structure and mode of bonding are still debated. (Lindsay *et al.* 1984, 1985, 1987). We have synthesized a series of unsolvated $diruthenium^{II,\,II}$ complexes with carboxylates of various alkyl chain lengths (Maldivi *et al.* 1989*b*). Our syntheses use an improved procedure that does not involve the so-called 'blue solution' of reduced ruthenium. Instead, $chromium^{II}$ reduction of the mixed-valence $chlorodiruthenium^{II,\,III}$ tetrabutyrate is used (Shehadeh *et al.* 1986), followed by ligand exchange of butyrate with the appropriate fatty acid under argon.

Magnetic suspectibility studies indicate that these compounds exhibit a low-temperature $M_s = 0$ state and a thermally accessible triplet state. Figure 5 shows the temperature dependence of the magnetic susceptibility and magnetic moment of $ruthenium^{II}$ palmitate. Computer simulation of the former was done with corrected (Telser *et al.* 1985) equations taken

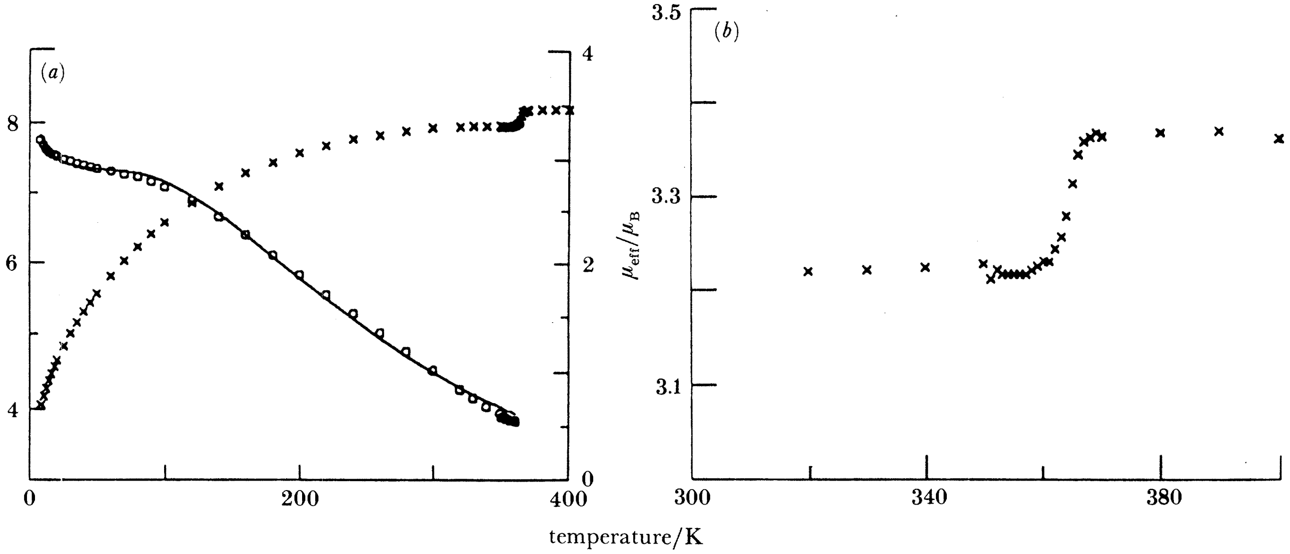

FIGURE 5. (*a*) Plots of the molar magnetic susceptibility (circles) and of the effective magnetic moment (crosses) per binuclear unit against temperature for $ruthenium^{II}$ palmitate. Experimental data have been corrected for diamagnetism of the metal and lignad atoms. The calculated susceptibility curve which is also shown was obtained by assuming an axial zero-field splitting within the diruthenium core in a D_{4h} $S = 1$ complex (Maldivi *et al.* 1989*b*). (*b*) Expanded scale plot of the effective magnetic moment against temperature for $ruthenium^{II}$ palmitate about the solid–liquid crystalline phase transition.

from O'Connor (1982) for a D_{4h} $S = 1$ complex, assuming an axial zero-field splitting within the diruthenium core (Telser & Drago 1984). The results of these calculations indicated an unusually large ($D \approx 300\ \mathrm{cm}^{-1}$) value of the zero-field splitting. The magnetic data obtained on ruthenium$^{\mathrm{II}}$ butyrate, laurate and palmitate (Maldivi *et al.* 1989*b*) can be rationalized by a simple molecular orbital scheme in which the three highest orbitals of the $\sigma\pi\delta\delta^*\pi^*$ manifold belong to the nearly degenerate π^*, δ^* set (Norman *et al.* 1979) and are occupied by four electrons (figure 6). These results, however, do not allow a choice to be made between the alternative $\pi^{*2}\delta^{*2}$ and $\pi^{*3}\delta^{*1}$ electronic structures. Whatever the configuration is, its degeneracy is removed by zero-field splitting to give rise to an $M_s = 0$ ground state and an $M_s = \pm 1$ excited state at $D \approx 300\ \mathrm{cm}^{-1}$ above the singlet state, as shown in figure 6.

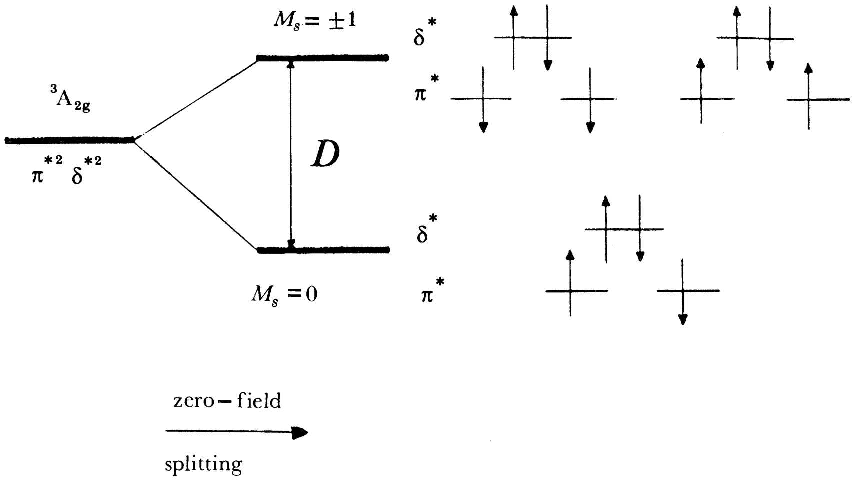

FIGURE 6. Electronic structure of the diruthenium core in unsolvated diruthenium$^{\mathrm{II,II}}$ tetracarboxylates in the $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*2}$ configuration.

A sharp increase in the magnetic moment of ruthenium$^{\mathrm{II}}$ palmitate is observed at *ca.* 370 K (figure 5). We relate this behaviour to a transition to a columnar mesophase, which we have been able to characterize by differential scanning calorimetry, and also by X-ray diffraction in the case of ruthenium$^{\mathrm{II}}$ laurate and pelargonate (Maldivi *et al.* 1989*b*).

These diruthenium$^{\mathrm{II,II}}$ tetracarboxylate complexes are exceedingly interesting mesogens as they exhibit both a double metal–metal bond (which one can dream of polymerizing) and two unpaired electrons at room temperature (which could be ordered in a one-dimensional ferromagnetic array within a column). Unfortunately, they are extremely oxygen sensitive, and therefore difficult to manipulate.

CONCLUSIONS

Our synthetic and physical studies on binuclear Cu$^{\mathrm{II}}$ and Ru$^{\mathrm{II}}$ have revealed a novel class of metallic mesogens which exhibit potential interest as models for molecular magnetic materials. The ability to process Cu$^{\mathrm{II}}$ soaps in highly oriented solid or liquid crystalline fibres by mere melt-spinning of their columnar mesophase, which we have demonstrated recently (Giroud-Godquin *et al.* 1989), gives further impetus to detailed investigation of the chemistry and solid state physics of these molecular materials.

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Discussion

P. Kathirgamanathan (*Cookson Group plc*, *Middlesex*, *U.K.*). Dr Marchon has discussed mainly dinuclear complexes; what about trinuclear and tetranuclear complexes? What is the effect of metal–metal bonding in molybdenum trimers?

J.-C. Marchon. We have not investigated yet any mesogenic complex with a nuclearity higher than 2, but we intended to. Indeed, we think that multinuclear metallic mesogens might exhibit a wealth of novel, fascinating physical properties, and deserve much synthetic efforts as well as detailed physicochemical investigation.

On the other hand, Dr Duncan Bruce told us recently that his group at the University of Sheffield has synthesized quadruply metal–metal bonded molybdenum$^{\mathrm{II}}$ alkylcarboxylates, but these apparently do not exhibit any liquid-crystalline behaviour. This has been related tentatively to the lack of interdimer bonding in this class of complexes.

H. J. Coles (*Liquid Crystal Group*, *Physics Department*, *The University*, *Manchester*, *U.K.*). Dr Marchon mentioned discontinuities in the paramagnetic susceptibilities as a function of temperature for Cu and Ru complexes. My first question is what technique was used to measure $\Delta\chi$? Secondly, across the discontinuities the density of the system did not change. This implies a second-order phase transition at which one would not expect to measure a heat of transition. Has he carried out DSC measurements on these materials and if so, are first-order phase transitions observed and are they weak or strong in comparison with more conventional low-molar-mass liquid crystals? The DSC data might give some indication of the possibility of ferromagnetic phenomena in these very interesting materials.

J.-C. MARCHON. The magnetic susceptibility measurements on the paramagnetic Cu^{II} and Ru^{II} soaps were performed between 6 K and 400 K with a SQUID susceptometer (SHE, model VTS 905) in a field of 0.5 T under helium. The results of these measurements are illustrated in figure 2*a* for copper^{II} dodecanoate, and in figure 5*a* for ruthenium^{II} palmitate. The discontinuity in the paramagnetic susceptibility is shown in detail in figure 2*b* for $Cu_2[O_2CCH_2CH(C_9H_{19})_2]_4$ and in figure 5*b* for ruthenium^{II} palmitate. Details can be found in our original publications (Giroud-Godquin *et al.* 1985; Maldivi *et al.* 1989*b*).

Contrary to Dr Cole's statement, the density (or molar volume) of these systems do change in the temperature domain where a discontinuity is observed in the paramagnetic susceptibility. The observed abrupt change in molar volume of Cu^{II} soaps has been studied in detail by dilatometry (Abied *et al.* 1988); it is characteristic of a first-order phase transition.

We have also carried out DSC measurements on these compounds. The observed molar enthalpy changes at the phase transition are similar to those obtained with more conventional liquid crystals. However, they are notably lower for Ru^{II} soaps (Maldivi *et al.* 1989*b*) than for Cu^{II} soaps (Abied *et al.* 1987). It seems difficult to extract from the overall enthalpy change a component that would be due to a possible transition from a paramagnetic to a ferromagnetic state.

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