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## Liquid Crystals

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**To cite this Article** Attard, G. S. and Cullum, P. R.(1990) 'Thermotropic mesomorphism in a branched chain copper(II) carboxylate and its pyrazine complex', *Liquid Crystals*, 8: 3, 299 – 309

**To link to this Article:** DOI: 10.1080/02678299008047349

**URL:** <http://dx.doi.org/10.1080/02678299008047349>

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## Thermotropic mesomorphism in a branched chain copper(II) carboxylate and its pyrazine complex

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(Received 8 November 1989; accepted 3 March 1990)

The thermotropic mesomorphism of tetrakis( $\mu$ -(2,2-(dioctyl(acetato))-*O,O'*)bis[copper(II)]) has been investigated by optical microscopy and X-ray diffraction. This compound was found to form a hexagonal discotic phase analogous to those reported for the copper(II) salts of *n*-alkanoic acids, but in contrast to these materials the mesophase of the branched chain compound was found to extend to below room temperature. Complexation of the copper(II) branched chain carboxylate with the difunctional ligands pyrazine and 4,4'-dipyridyl resulted in liquid-crystalline materials whose mesophase structure could not be established. The possibility of these complexes existing as polymeric/oligomeric entities is discussed.

### 1. Introduction

In recent years there has been a revival of interest in the thermotropic properties of divalent metal soaps of carboxylic acids [1-3]. Among these the soaps of certain transition metal ions, e.g. copper(II), are of particular interest because they promote the formation of discotic mesophases [4, 5]. This behaviour is a consequence of the disc-like shapes of the polar cores of the molecules which consist of two copper ions coordinated by four carboxylate groups as illustrated in figure 1. X-ray diffraction studies of the discotic mesophases of copper(II) salts of straight chain aliphatic carboxylates showed that these phases consist of columnar stacks of the dimers with the columns arranged on a hexagonal lattice [5-7]. Using the classification scheme adopted for more conventional thermotropic discotic mesophases these phases can be described as being of  $D_{ho}$  type [8]. EXAFS studies have revealed further details of the arrangement of the polar cores within a columnar stack [9]. It appears that there are weak bonds between the oxygen atoms of the carboxylate groups of one molecule and the free octahedral sites on the copper ions in neighbouring molecules resulting in a crankshaft appearance of the column (see figure 2). Dinuclear transition metal carboxylates exhibit anomalously low magnetic moments due to spin exchange between the unpaired electrons in each of the copper ions constituting the core [10-12]. It has been suggested that the combination of discotic mesomorphism and the electronic properties of the dinuclear cores could lead to interesting conductance effects [6].

With one exception, all studies reported to date have been concerned with salts prepared from straight chain carboxylic acids. It is, therefore, of interest to investigate how the thermotropic properties of materials prepared from branched chain acids differ from those of the straight chain analogues. In this paper we report the transitional behaviour of tetrakis( $\mu$ -(2,2-(dioctyl)acetato))-*O,O'*)bis[copper(II)] which is obtained from 2,2-(dioctyl)acetic acid.

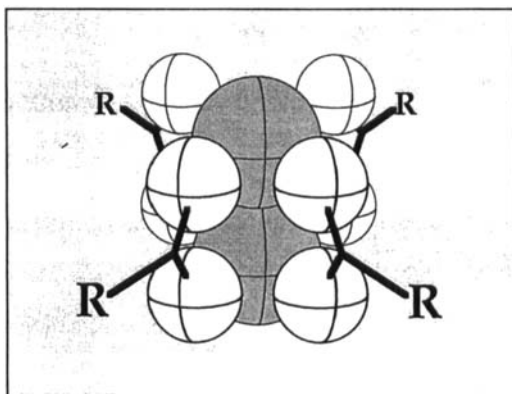


Figure 1. Schematic representation of the dinuclear disc-like polar core of copper(II) carboxylates. *R* can be an *n*-alkyl, a 4-alkylaryl or a branched alkyl substituent. The shaded spheres denote the copper ions.

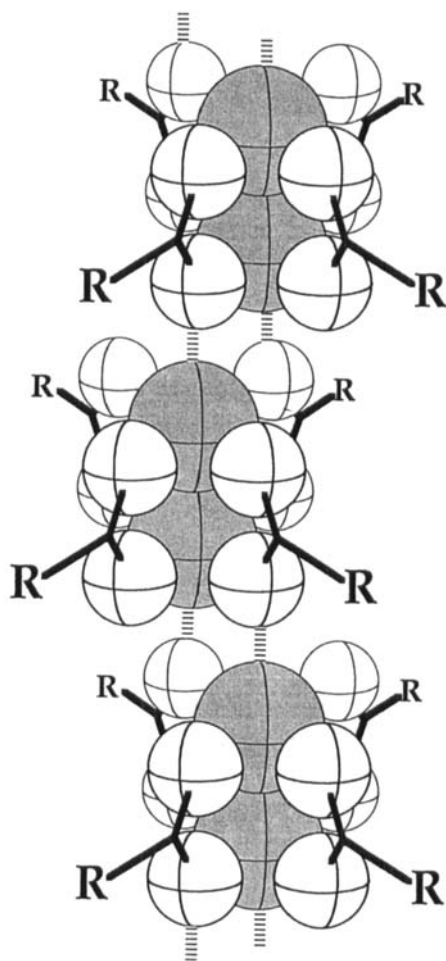


Figure 2. Schematic representation of the crankshaft arrangement of dinuclear cores postulated for the  $D_{h0}$  phases of copper(II) *n*-alkanoates. The specific chemical interactions which are believed to stabilize these phases further are indicated by the dashed lines.

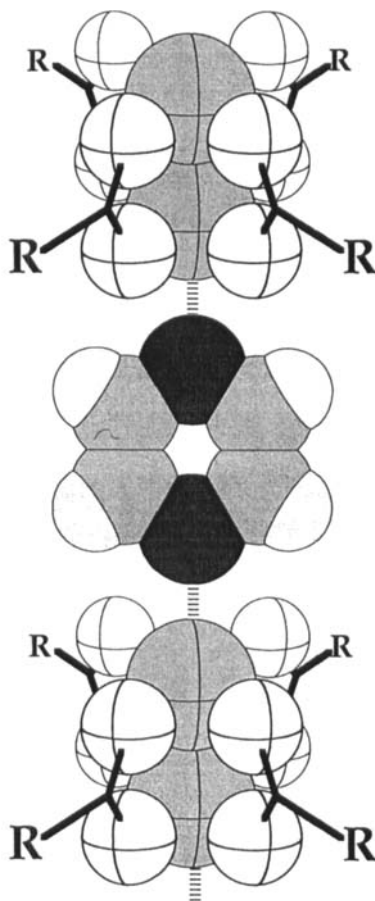


Figure 3. Schematic representation of a hypothetical stacked polymer obtained from copper(II) carboxylates with pyrazine as a bridging ligand.

It has been known for some time that the free octahedral sites in the copper carboxylates can form bonds with electron rich ligands such as ammonia or pyridine [10, 11]. Consequently we decided to investigate the possibility of preparing stacked polymeric species of the type shown schematically in figure 3 from the copper salts of both branched chain and straight chain carboxylic acids by the use of difunctional ligands such as pyrazine and 4,4'-dipyridyl. Such compounds would be analogous to the stacked metal containing macrocycles reported in the literature, and may hold the possibility of being one dimensional conductors due to the continuity of electronic structure along the stack [13–15].

## 2. Experimental

The copper(II) salts of the alkanolic acids were prepared by metathesis with copper(II) acetate in 70 per cent aqueous ethanol. The products, which ranged from pale blue to deep blue–green in colour ( $\lambda_{\max} \sim 667 \text{ nm}$ ;  $\text{CHCl}_3$  solution) were recrystallized twice from ethanol and dried in a vacuum oven overnight at  $80^\circ\text{C}$ . The purity of the materials was determined by IR spectroscopy (which revealed no traces of unreacted acid) and by elemental analysis. The complexes of the copper salts with pyrazine and 4,4'-dipyridyl were prepared by mixing stoichiometric quantities of the

ligand and the soap dissolved in minimum amounts of benzene and refluxing for about 2 hours. The complexes were obtained as pale green powders ( $\lambda_{\text{max}} \sim 678$  nm for the pyrazine complexes and  $\sim 699$  nm for the 4,4'-dipyridyl complexes;  $\text{CHCl}_3$  solution) which were stored in a desiccator. (Elemental analysis, pyrazine complex: (a) expected C = 68.6 per cent, H = 10.8 per cent, Cu = 10.1 per cent; (b) found C = 68.8 per cent, H = 10.9 per cent, Cu = 9.9 per cent). In order to assess the effect of deviations from the stoichiometric ratio on the structure of the material isolated from the reaction mixture a series of experiments were conducted in which the ratio of copper soap to the ligand was varied. From these studies it became apparent that the only effect of altering the ratio of the reagents was to lower the yield to the final product, which was identical in all cases as determined by melting point studies and UV-visible spectroscopy.

The transitional properties of the materials synthesized were investigated by means of an Olympus BHSP polarizing microscope equipped with a Linkam THM 600 hot stage. The sample temperature was regulated by means of a Linkam TMS 90 temperature control system. Heating/cooling rates of  $0.2 \text{ K min}^{-1}$  were used to locate the phase transitions accurately and to enable the mesophase textures to develop. Structural studies by X-ray diffraction were carried out on a Guinier camera equipped with crystal monochromator set to isolate the  $\text{CuK}_{\alpha 1}$  line ( $\lambda = 0.1405 \text{ nm}$ ).

### 3. Results and discussion

The development of the optical texture of the mesophase of tetrakis( $\mu$ -(2,2-(dioctyl)-acetato))- $O,O'$ bis[copper(II)] (denoted by  $[\text{C}_8]_2\text{C}_2\text{Cu}$ ) on cooling from the isotropic melt is illustrated by the sequence of photographs in figure 4. The liquid-crystalline phase grows as needles radiating from nucleation sites. By contrast the hexagonal discotic phases of the straight chain carboxylates tend to grow as platelets from the isotropic phase. A typical texture for the hexagonal discotic phase of copper(II) soaps of straight chain aliphatic acids is shown in figure 5 for comparison. It should be stressed that the anisotropic phase of the branched chain compound is highly viscous but does flow when pressure is applied to the material. No transitions are observed for this compound by differential scanning calorimetry, although at temperatures  $> 200^\circ\text{C}$  there is some evidence of material decomposition.

The texture of the liquid-crystalline phase of tetrakis( $\mu$ -(2,2-(dioctyl)acetato))- $O,O'$ bis[copper(II)]pyrazine (denoted by  $[\text{C}_8]_2\text{Cu.pyz}$ ) is shown in figure 6. The mesophase is viscous though easily deformable by pressure. At elevated temperatures ( $> 170^\circ\text{C}$ ) a band with a different birefringence to the bulk sample begins to develop at the edges of the sample, indicative of the loss of pyrazine into the atmosphere.

The transitional properties of the copper(II) salt of 2,2-(dioctyl)acetic acid and of its pyrazine and 4,4'-dipyridyl complexes as determined by optical microscopy are shown in table 1. The transition temperatures of copper(II)decanoate, copper(II)hexadecanoate, and their pyrazine and dipyridyl complexes are also listed for comparison.

The most striking feature to emerge from a comparison of the transitional properties of the branched chain compound with those of the straight chain analogues is that in the former material the liquid-crystalline phase appears to extend to below room temperature. Indeed, experiments in which the material was cooled to  $-20^\circ\text{C}$  failed to induce the formation of a crystalline phase. While it is possible that this effect is due to residual ionic impurities in our material we believe that it is likely that the branched alkyl chain promotes the formation of a glassy phase which effectively

prevents crystallization. It should be noted that a depression of the melting point in branched chain copper carboxylates has been observed for a compound similar to ours, namely  $[\text{C}_9]_2\text{C}_3\text{Cu}$ , which has a crystal to discotic transition at about  $75^\circ\text{C}$  [16] (compared with about  $108^\circ\text{C}$  for  $\text{C}_{12}\text{Cu}$ ). The liquid crystal to isotropic transition in both branched chain and straight chain carboxylates occurs at elevated temperatures and is accompanied by some degree of sample decomposition, although it should be noted that the branched chain compound is somewhat less labile at higher temperatures than the straight chain analogues. Thus, although there is some uncertainty in the location of the clearing temperature for the straight chain materials, the corresponding transition for the branched chain compound can be located with reasonable accuracy.

From a comparison of the optical textures shown in figures 4 and 5 it might be inferred that the mesophase of  $[\text{C}_8]_2\text{C}_2\text{Cu}$  is not of the  $D_{\text{ho}}$  type encountered for the straight chain materials. In order to investigate the ultrastructure of this mesophase we carried out X-ray diffraction experiments at different temperatures within the liquid-crystalline phase. Typical diffraction patterns exhibit four sharp low angle peaks which index as  $1:\sqrt{3}:\sqrt{4}:\sqrt{7}$  indicative of a two dimensional hexagonal lattice. The first order peak corresponds to a distance of  $18.6\text{ \AA}$  which gives a distance of  $21.5\text{ \AA}$  between nearest neighbours in the hexagonal lattice. The fairly diffuse peak observed at wide angle corresponds to a distance of  $4.6\text{ \AA}$ , characteristic of the packing of disordered aliphatic chains possibly modulated by the periodic stacking distance of the disc-like cores in the column. Accordingly we conclude that in spite of the unusual optical texture the mesophase of  $[\text{C}_8]_2\text{C}_2\text{Cu}$  is also of the  $D_{\text{ho}}$  type.

The intercolumnar distance of  $21.5\text{ \AA}$  measured from the X-ray diffraction data can be rationalized in several ways. First, however, it is worth recalling that in thermotropic smectic B materials composed of lath-like molecules the hexagonal packing distances revealed by X-ray diffraction are much smaller than the radius of rotation of the molecules about their long axes. This implies that molecular rotations in  $S_{\text{B}}$  phases are highly cooperative and involve a synchronized motion of all the molecules over semi-macroscopic distances. For the discotic straight chain copper carboxylates the hexagonal packing distance also appears to be smaller than the overall radius of the molecule as determined from space-filling models, even assuming that the alkyl chains are highly disordered. This may be explained by a degree of interdigitation of the alkyl chains of one molecule with those of another molecule in a neighbouring column. With branched chain compounds it becomes more difficult to obtain an estimate of the overall molecular diameter. This is because the alkyl chains in the two branches of each carboxylate group adopt a swallow-tail arrangement and the angle which defines the swallow tail may vary from about  $135^\circ$  to  $80^\circ$ . In addition gauche linkages along each branch may result in the molecules adopting a tuning fork arrangement. Estimates of the overall molecular diameters can thus vary over the range  $19\text{--}28\text{ \AA}$ . The intercolumnar distance obtained from our diffraction studies falls towards the lower end of this range of possible values. Accordingly it is possible that the existence of hexagonal packing induces the branched groups into a swallow tail arrangement with a wide angle between the branches. For this to be a realistic model the plane containing the two branches must lie at an angle with respect to the plane of the discotic core. Alternatively the swallow-tail angle may be intermediate in value and some degree of interdigitation exists between chains from neighbouring stacks.

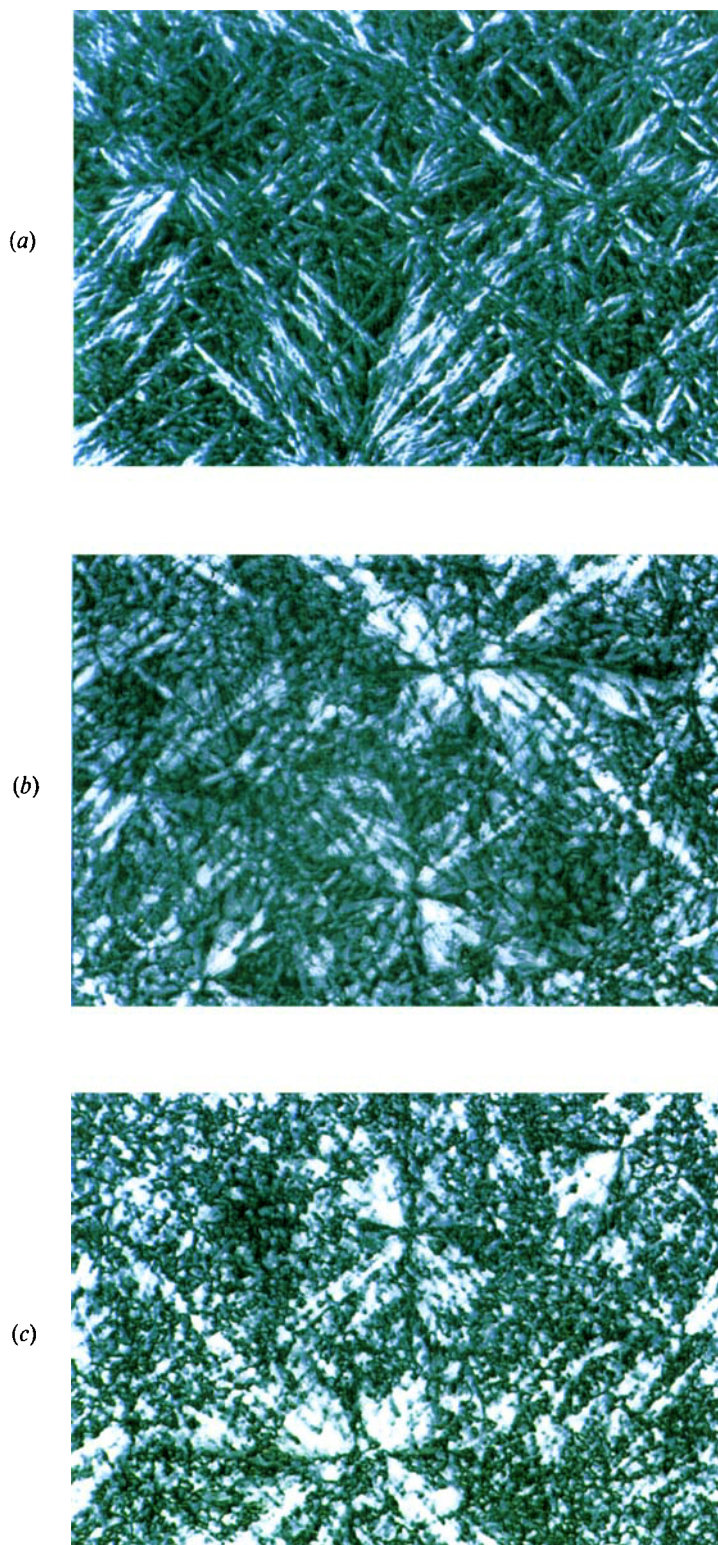


Figure 4. Development of the optical texture of the mesophase of  $[C_8]_2C_2Cu$  on cooling from the isotropic phase: (a)  $204.7^\circ C$ , (b)  $198^\circ C$ , (c)  $93.5^\circ C$ .



Figure 5. Optical texture of the mesophase of  $C_{25}Cu$  at  $177^{\circ}C$  which is typical of the textures observed for the discotic mesophases formed by copper(II) *n*-alkanoates.

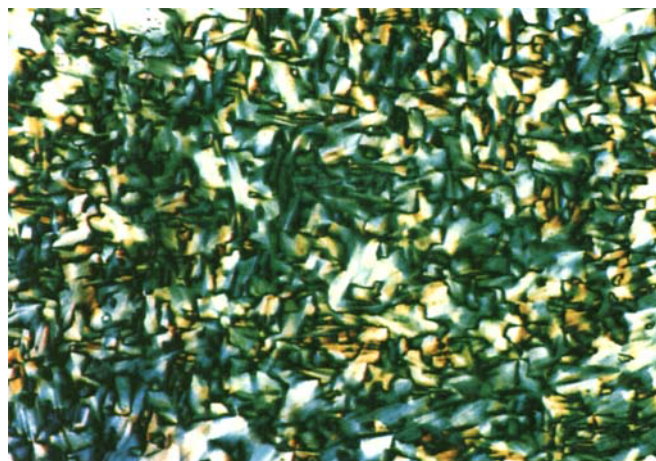


Figure 6. Optical texture of the pyrazine complex of the copper(II) carboxylate of  $[C_8]_2C_2Cu$  at  $185^{\circ}C$ .

The effect of complexation of the copper soaps with difunctional ligands is apparent from the transitional data presented in table 1. Upon complexation of the copper soaps of the straight chain acids with either pyrazine or 4,4'-dipyridyl the liquid-crystalline phase is lost. The pyrazine complexes of  $C_{10}Cu$  and  $C_{16}Cu$  (and other straight chain carboxylates) are crystalline solids that melt to an isotropic liquid at around  $152^{\circ}C$  irrespective of the length of the alkyl chain. Observations with the polarizing microscope at temperatures just above the clearing point reveal the formation of a birefringent phase at the edges of the preparation. This phase progressively grows towards the centre of the sample and has a texture identical to that of the uncomplexed soap. Heating a sample to  $154^{\circ}C$  without a coverslip results in a complete conversion to the birefringent material whose crystal to liquid crystal transition temperature corresponds to that of the uncomplexed salt. It would appear



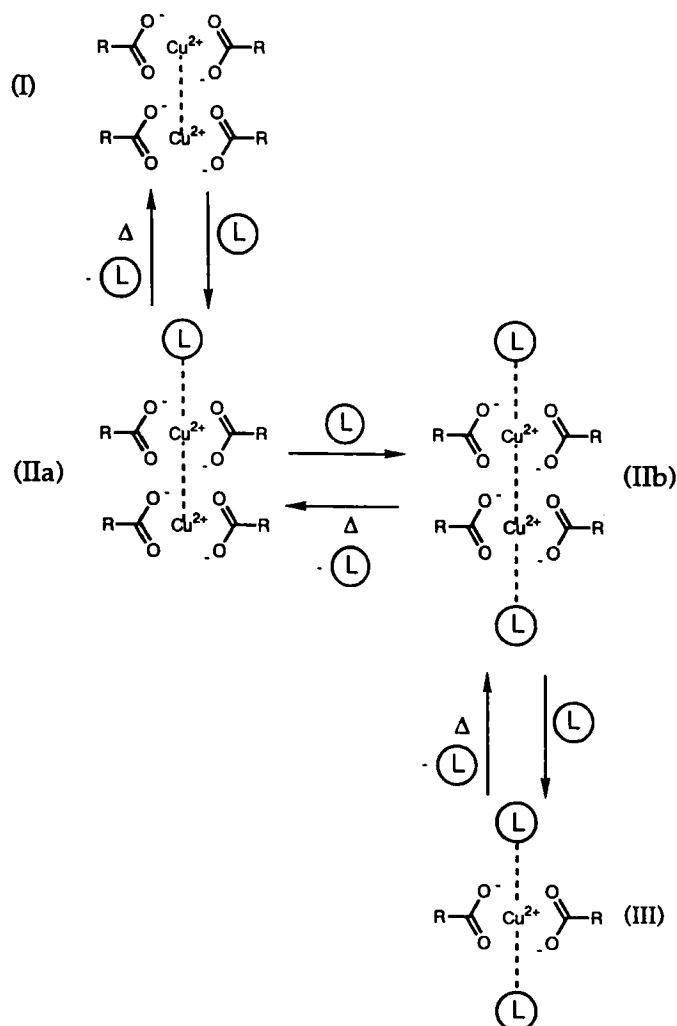
Table 1. Transitional properties of copper(II)carboxylates and related complexes. The (\*) denotes loss of pyrazine from the sample.

Compound	$T_{CD}/^{\circ}\text{C}$ († $T_{Cl}$ )	$T_{DI}/^{\circ}\text{C}$
$\text{C}_{10}\text{Cu}$	106.9	210 (dec.)
$\text{C}_{10}\text{Cu.pyz}$	153† (*)	-
$\text{C}_{10}\text{Cu.dipy}$	213† (dec)	-
$\text{C}_{16}\text{Cu}$	112	220 (dec.)
$\text{C}_{16}\text{Cu.pyz}$	152† (*)	-
$\text{C}_{16}\text{Cu.dipy}$	211† (dec)	-
$[\text{C}_8]_2\text{C}_2\text{Cu}$	-	214
$[\text{C}_8]_2\text{C}_2\text{Cu.pyz}$	-	206 (some dec.)
$[\text{C}_8]_2\text{C}_2\text{Cu.dipy}$	-	154

therefore that the thermal energy at approximately  $150^{\circ}\text{C}$  is comparable with the energy of the copper–nitrogen bond in a pyrazine liganded copper complex. Above this temperature pyrazine will be released into the material causing dissolution, hence the independence of the melting point from the length of the alkyl chain. Since the boiling point of pyrazine is about  $115^{\circ}\text{C}$  it will escape into the atmosphere, which for a covered sample can only occur at the edges, resulting in the appearance of the birefringent phase at the edges of covered preparations.

Complexes of copper(II) carboxylates and ammonia or pyridine have been studied and though not exhibiting thermotropic mesomorphism have similar thermal properties to the pyrazine and dipyriddy complexes we have studied. It has been shown that depending on the reaction conditions the various complexes shown in Scheme A can be formed. On heating in air to about  $95\text{--}100^{\circ}\text{C}$  compounds with structure (III) lose a ligand molecule to form compounds of structure (IIb) with a 1 : 1 metal to ligand stoichiometry. Further heating leads to the removal of the final ligands, possibly through an intermediate of type (IIa), to give the pure copper(II) carboxylates. The relatively low temperatures at which axial ligands can be lost in complexes of type (III) reflect the weak coordination of the axial ligands due to the Jahn–Teller effect. The different coordination geometries of complexes (II) and (III) are reflected by the relative magnitudes of their magnetic moments. At  $20^{\circ}\text{C}$  compounds consisting of isolated copper(II) ions (e.g.  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ) have magnetic moments of about  $1.9 \mu_B$ . By contrast dinuclear complexes (e.g. copper(II)laurate) have magnetic moments of about  $1.45 \mu_B$  indicative of spin coupling. The pyridine complex of copper(II)laurate with structure (IIb) has a magnetic moment of the order of  $1.4 \mu_B$  confirming the presence of the dinuclear species in the complex. On the other hand pyridine and ammonia complexes of copper(II)laurate with structure (III) have magnetic moments of approximately  $1.93 \mu_B$ , which is close to the value for copper(II)sulphate pentahydrate. It should be stressed that ammonia and pyridine complexes of copper(II)laurate of type (III) are thermally unstable, readily reverting to complexes with structure (IIb) upon moderate heating.

The 4,4'-dipyriddy complexes of the straight chain soaps melt to the isotropic liquid at about  $212^{\circ}\text{C}$ , accompanied by significant decomposition. It is, therefore, possible that this is not a true transition but is in fact induced by the presence of decomposition products. It is interesting to note that the copper–nitrogen bonds of the dipyriddy



complexes appear to be stronger than is the case for the copper–nitrogen bonds in the pyrazine complexes. 4,4'-dipyridyl melts at about 107°C and has a boiling point of 305°C. Accordingly, if the thermal energy at temperatures > 150°C exceeds the energy of the copper–nitrogen bond, free dipyridyl would be released into the material. It would be expected that the free dipyridyl would disrupt the structure of the meso-phase leading to a depression of the clearing point.

In contrast to the case of the straight chain salts, the pyrazine and dipyridyl complexes of the branched chain compound both exhibit liquid-crystalline phases. As with the parent soap the complexes could not be induced to crystallize even on cooling to  $-20^{\circ}\text{C}$ . The liquid crystal to isotropic transition for the branched chain pyrazine complex material is somewhat lower than is the case for the uncomplexed soap while the bipyridyl complex has a significantly lower clearing temperature.

The X-ray diffraction patterns obtained for the pyrazine complex of the branched chain soap are significantly different from those obtained for the uncomplexed material as illustrated in figure 7. For a diffraction measurement at  $95^{\circ}\text{C}$  there are two very sharp low angle reflections at  $19.8\text{ \AA}$  and  $15.0\text{ \AA}$ . The reflection at  $15\text{ \AA}$  is superposed on a diffuse band at about  $14.5\text{ \AA}$ . At wider angles there are two closely

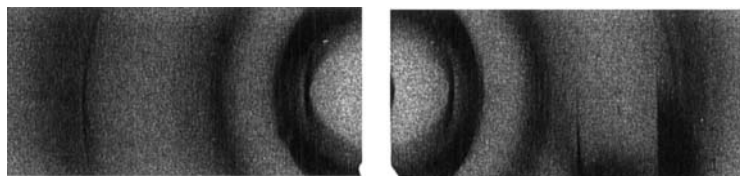


Figure 7. X-ray diffraction picture of  $[C_8]_2C_2Cu.pyz$  obtained at  $95^\circ C$ .

spaced sharp reflections at  $8.9 \text{ \AA}$  and  $9 \text{ \AA}$ , and a sharp reflection at  $4.95 \text{ \AA}$  followed by a series of diffuse reflections at about  $4.7 \text{ \AA}$ . We have not as yet been able to index these reflections to any specific lattice. It may be possible that the mesophase consists of two or more phases in equilibrium although from the optical studies this appears to be unlikely. The wide angle reflection at  $4.77 \text{ \AA}$  corresponds to the packing of disordered chains, the higher order reflections probably indicating the presence of well-defined stacking periodicity. From calculations on space-filling models the periodicity along a columnar stack due to the presence of pyrazine should be of the order of  $13\text{--}14.5 \text{ \AA}$ . Thus both the diffuse band centred at  $14.5 \text{ \AA}$  and the sharp reflection centred at  $15 \text{ \AA}$  could correspond to this distance.

Since the ligands used in our experiments are bifunctional it should be possible to form oligomeric or even polymeric species consisting of stacks of the dinuclear complexes with the pyrazine or the bipyridyl as bridging ligands (see figure 3). Pyrazine has been reported to form such structures with a number of transition metal complexes. However since the basicity of pyrazine is significantly lower than that of pyridine, which implies a weak Cu–N bond in the complex, the reverse dissociation reaction from high molecular weight species to lower molecular weight species may effectively limit the overall length of the molecules formed and could lead to an equilibrium mixture consisting of monomers, dimers, oligomers, and higher molecular weight polymers. There is also the possibility that the polymers/oligomers could consist of stacked mononuclear species (i.e. one half of the dimer). Such a structure would appear unlikely in view of the thermal instability of analogous compounds (e.g. dipyrindine copper(II)laurate). The magnetic moment data presented in table 2 further supports the view that the dinuclear species are present in the pyrazine and 4,4'-dipyridyl complexes; the magnetic moments of complexes derived from copper(II) *n*-alkanoates are also shown for comparison.

Table 2. Magnetic moments of tetrakis( $\mu$ -(2,2-(dioctyl)acetato))- $O,O'$ bis[copper(II)] and its complexes measured at  $20^\circ C$ . The (\*) denotes values for the solid state.

Compound	$\mu/\mu_B$
$[C_8]_2C_2Cu$	1.40
$[C_8]_2C_2Cu.pyz$	1.29
$[C_8]_2C_2Cu.dipy$	1.30
$C_{14}Cu$	1.45*
$C_{14}Cu.pyz$	1.28*
$C_{14}Cu.dipy$	1.32*
$C_{14}Cu.dioctylamine$	1.25*

The magnetic moment data do not rule out the possibility that the pyrazine and dipyridyl derivatives of the copper(II) carboxylates consist of a mixture of uncomplexed monomers and complexes consisting of two ligands per dinuclear species (e.g.  $[\text{C}_8]_2\text{C}_2\text{Cu.pyz}_2$ ; cf. structure (IIb) in Scheme A). However, since the measured magnetic moments of  $[\text{C}_8]_2\text{C}_2\text{Cu.pyz}$  and  $[\text{C}_8]_2\text{C}_2\text{Cu.dipy}$  are closer to the value of  $1.25 \mu_B$  found for  $\text{C}_{14}\text{Cu.dioctylamine}$  than the value for  $[\text{C}_8]_2\text{C}_2\text{Cu}$  it seems likely that uncomplexed monomers may only be present in low concentrations, if at all. It should also be noted that the kinetics of ligand exchange in copper(II) coordination complexes are extremely fast, and so it is probable that the oligomeric/polymeric species are dynamic rather than static entities.

Further studies to elucidate the structures of the mesophases formed by these complexes are in progress.

G.S.A. thanks Dr. R. H. Templer for obtaining the X-ray diffraction pictures, Dr. J. M. Seddon for the use of his X-ray equipment, and Mr. O. Howell for the gift of 2,2-(dioctyl)acetic acid. The award of an Advanced Fellowship to G.S.A. by the Science and Engineering Research Council is gratefully acknowledged.

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