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Liquid Crystals of Some Disk-like Copper β-diketonates

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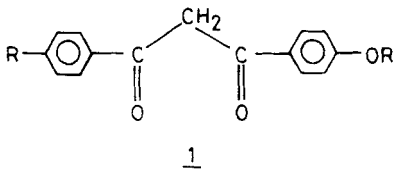
Three homologous copper β-diketonates have been prepared and their discogenic properties studied. The mesophases obtained from these are totally miscible with each other and are also with the mesophase exhibited by the known bis[1,3-di(p-n-octyloxyphenyl)propane-1,3-dionato] copper (II). However, the ligands from which these complexes are prepared are themselves not mesogenic.

Keywords: copper β-diketonates, ligand, miscibility

INTRODUCTION

Much progress has been made in the synthesis and characterisation of liquid crystals formed by disk-like molecules.[1–8] The first thermotropic organometallic disk-like mesogen, viz., bis[1,3-di(p-n-decylphenyl)propane-1,3-dionato] copper (II) was reported by Giroud-Godquin and Billard.[9] As a result of this quite a few metal β-diketonates have been prepared[10–12] and their mesomorphic behaviour examined. Some of the complexes containing unsymmetrical chains are not mesomorphic. In order to get a better understanding of the phase behaviour in these metal complexes, we have prepared three homologous copper β-diketonates (2) from the corresponding ligands (1) and report here their properties.

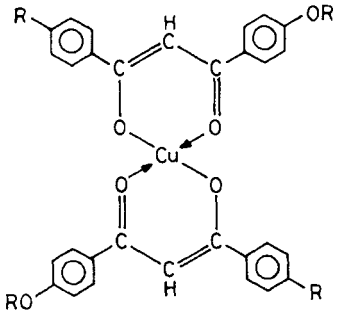


1

a : R = n-C_8H_{17}

b : R = n-C_9H_{19}

c : R = n-$C_{10}H_{21}$



2

EXPERIMENTAL

The compounds were prepared following standard procedures described in the literature.[9-12] The transition temperatures of these compounds were determined with a polarizing microscope equipped with a heating stage and a controller (Mettler FP52 and FP5) and from thermograms recorded on a differential scanning calorimeter (Perkin-Elmer, Model DSC-2). The enthalpies of transitions were also calculated from these thermograms. The purity of the ligands was checked by thin layer chromatography, spectral data and microanalytical data, and the corresponding copper complexes were checked by the latter two methods. The infrared and electronic absorption spectra were recorded on a Shimadzu IR-435 and a Hitachi U-3200 spectrophotometers respectively. Typical values for 2a are as follows.

IR ν_{max}^{Nujol} 1588 cm^{-1} and 1608 cm^{-1}

UV-VIS $\lambda_{max}^{CHCl_3}$ (ε) 381(36,000) 359(62,000) 303(29,000) 276(25,000) and 238(19,000)

Analysis	Found, %	Calculated, %
2a	C,75.08; H,8.96	C,75.19; H,8.69
2b	C,76.04; H,9.28	C,75.75; H,8.99
2c	C,76.05; H,9.58	C,76.25; H,9.26

RESULTS

The three ligands 1-(p-n-alkylphenyl)3-(p-n-alkyloxyphenyl)propane-1,3-diones (1) do not show any classical mesophase. However, it is worth noting here that some of the symmetrical ligands reported by Giroud-Godquin and Billard[10] and Ohta et al.[12] do exhibit mesophases and these have been identified to be smectic E through miscibility studies. The complexes 2a–c were obtained as green needle-like crystals. The transition temperatures and the enthalpies of transition of these are shown in Table I. On heating, between a glass slide and a cover slip, all the three compounds melt to a highly viscous, birefringent phase, the texture of which is not quite clear. Upon slow cooling of the isotropic liquid, small areas of brightly coloured domains appear which coalesce to form larger domains as the temperature is lowered. Crystallisation takes place on further cooling below the melting point and is characterised by a 'cracked' texture.

Each of the three complexes 2a–c, exhibited two sharp endothermic transitions on heating. The heat of the crystal-mesophase transition is higher as compared to the mesophase-isotropic transition. The melting point increases as the chain length is increased from octyl to decyl. However, the mesophase range decreases from about 67° for 2a to 39° for 2c. Structure 2 has two alkyl chains and two alkyloxy chains. Similar copper β-diketonates containing all four alkyl chains[9,12] and all four alkyloxy chains[12,13] are known. Hence structure 2 can be assumed to be intermediate between these three systems. One would expect the mesophase-isotropic transition temperature also to be in-

TABLE I

Transition temperatures and heats of transition of bis[1-(p-n-alkyl-phenyl)3-(p-n-alkyloxyphenyl)propane-1,3-dionato]copper(II)[a]

No.	n-Alkyl	K		D		I	ΔT
2a	n-C_8H_{17}	·	76.7 7.44	·	143.8 4.38	·	67.1
2b	n-C_9H_{19}	·	80.9 9.1	·	136.0 6.84	·	55.5
2c	n-$C_{10}H_{21}$	·	91.5 11.12	·	130.5 6.24	·	39.0

[a]The transition temperatures are given in degrees celsius and the corresponding heats of transition are given immediately below in kilocalories per mole. K: crystal, D: discotic liquid crystal, I: isotropic liquid. The melting points of the ligands 1a, b and c are 74.8, 75.5, and 77.7°C respectively.

TABLE II

Mesophase-isotropic transition temperatures of some copper β-diketonates

No.	Chain length	All four alkyl chains	Two alkyl and two alkyloxy chains	All four alkyloxy chains
1	n-C_8H_{17}	141.6[a]	143.8	177.0[a*]
2	n-C_9H_{19}	137.0[b]	136.0	171.8[c]
3	n-$C_{10}H_{21}$	128.5[d]	130.5	166.0[c]

[a]See reference 12
[a*]The temperature reported in reference 12 is 173.3°C
[b]See reference 14
[c]Our own data
[d]See reference 9.

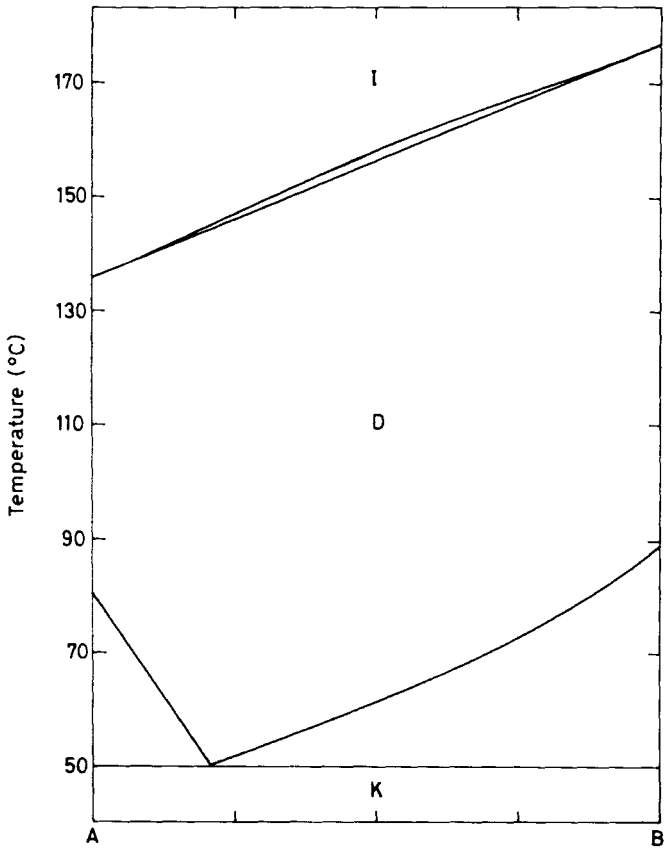


FIGURE 1 Binary phase diagram of a mixture of A: Bis[1-(p-n-nonyloxy-phenyl)3-(p-n-nonylphenyl)propane-1,3-dionato]copper(II); B: Bis[1,3-di(p-n-octyloxyphenyl-propane-1,3-dionato]copper(II).

termediate for compounds with similar chain length in these systems. However, this is not the case; Table II shows this temperature of a few representative compounds, belonging to these three different systems. It is interesting to note from the table that this temperature for 2a, 2b and 2c is within a couple of degrees of compounds containing all four alkyl chains. This is in contrast to the difference of about 35° observed for compounds containing all four alkyloxy chains.

The mesophases of 2a and 2b, and 2a and 2c are totally miscible with one another and hence they are all of the same kind. This mesophase was identified to be a discotic phase and also proved to be of the same kind as the one exhibited by bis[1,3-di(p-n-octyloxyphenyl)propane-1,3-dionato] copper (II),[12] through miscibility studies. However, Giroud-Godquin et al.[11] have reported that the bis[1,3-di(p-n-alkylphenyl(propane-1,3-dionato] copper (II) does not show a two-dimensional columnar lattice. The binary phase diagram is shown in Figure 1. As can be seen, the eutectic point is obtained when 80 mole per cent of 2b is present in the mixture and that the two phases are continuously miscible. It is proposed to examine the structure of the mesophase exhibited by these compounds by physical methods.

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