

Discotic Liquid Crystals of Organocopper Complexes: the Substituent Effects

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It was found that the bis(β -diketonato)copper(II) complexes (**2a,b**) have discotic mesophases: (**2a**), D₁: 76.1—117.2 °C, D₂: 117.2—141.6 °C and (**2b**), D: 82.5—173.3 °C, and that the corresponding β -diketone ligands (**1a,b**) have classical mesophases: (**1a**), smectic: 28.5—60.7 °C and (**1b**), smectic: 72.3—83.6 °C.

Recently, transition metal complexes of organic ligands with long alkyl chains have been synthesized for various purposes and as far as we know five properties of these complexes have been reported: (1) good solubility in alkanes,^{1,2} (2) micelle formation,³ (3) unusual thermochromism,² (4) double melting behaviour,⁴ and (5) mesomorphism.^{5–7} In focusing our interest on the fourth and fifth properties, two new disk-like complexes, bis[1,3-di(*p*-*n*-octylphenyl)propane-1,3-dionato]-

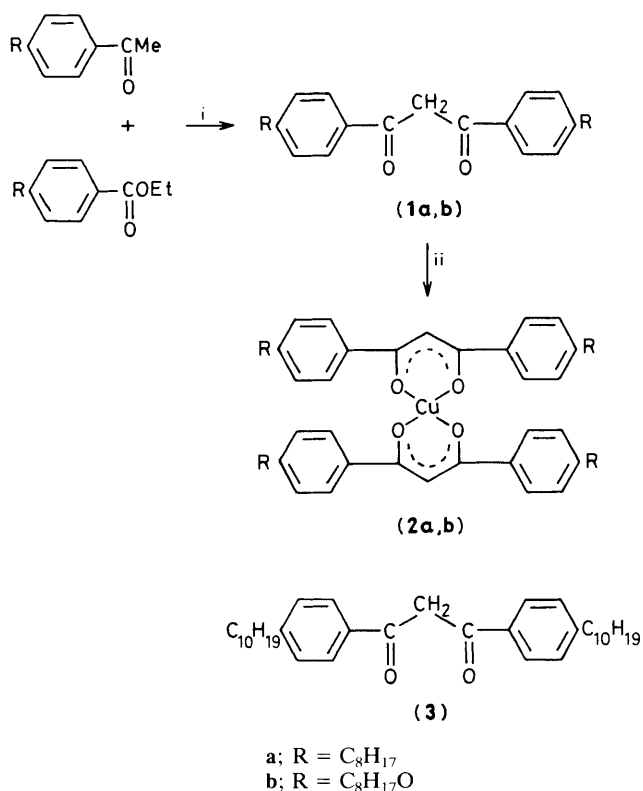
copper(II) (**2a**) and bis[1,3-di(*p*-*n*-octyloxyphenyl)propane-1,3-dionato]copper(II) (**2b**) were synthesized as shown in Scheme 1. It was found that each complex exhibits discotic mesomorphism, and that each of the corresponding β -diketone ligands exhibits classical mesomorphism. In Table 1 are summarized the phase transitions for the octyl ligand (**1a**), the octyloxy ligand (**1b**), (**2a**), and (**2b**).

Ligand (**1a**) showed two endothermic transitions at 28.5 °C

Table 1. Phase^a transition temperatures (T_t) and enthalpies (ΔH_t) of the β -diketone ligands (**1a,b**) and their corresponding copper(II) complexes (**2a,b**).

Compound		$\frac{T_t(^\circ\text{C})}{\Delta H_t(\text{kcal/mol})}$				Temperature range of L.C.		
(1a)	K	$\frac{28.5}{0.38}$	S	$\frac{60.7}{8.15}$	I.L.	32.2		
(1b)	K	$\frac{72.3}{2.91}$	S	$\frac{83.6}{12.06}$	I.L.	11.3		
(2a)	K	$\frac{76.1}{26.8}$	D ₁	$\frac{117.2}{0.76}$	D ₂	$\frac{141.6}{8.60}$	I.L.	65.5
(2b)	K ₁	$\frac{21.8}{0.79}$	K ₂	$\frac{82.5}{2.89}$	D	$\frac{173.3}{16.6}$	I.L.	91.8

^a Phase nomenclature: K = crystal, S = smectic liquid crystal (L.C.), D = discotic L.C., I.L. = isotropic liquid.



Scheme 1. i, NaH; ii, CuCl₂·2H₂O, KOH-EtOH.

($\Delta H = 0.38$ kcal/mol[†]) and 60.7 °C ($\Delta H = 8.15$ kcal/mol). Between 28.5 and 60.7 °C there is a smectic phase similar to that of 1,3-di(*p*-n-decylphenyl)propane-1,3-dione (**3**) synthesized for the first time by Giroud-Godquin *et al.*⁷ Ligand (**1b**) also has two endothermic transitions at 72.3 °C ($\Delta H = 2.91$ kcal/mol) and 83.6 °C ($\Delta H = 12.06$ kcal/mol). The phase between 72.3 and 83.6 °C is of the same nature as the smectic phase of (**3**).

Complex (**2a**) exhibited three endothermic transitions at 76.1 °C ($\Delta H = 26.8$ kcal/mol), 117.2 °C ($\Delta H = 0.76$ kcal/mol), and 141.6 °C ($\Delta H = 8.60$ kcal/mol). The phase between 76.1 and 117.2 °C (D₁) and the phase between 117.2 and 141.6 °C (D₂) were established as discotic mesophases by miscibility tests using the differential scanning calorimeter and by observation of the phases using a polarizing microscope. Through constructing the binary phase diagram between (**3**)-Cu^{II} and (**2a**) (Figure 1) by the miscibility test, it was found that the D₂ phase of (**2a**) is totally miscible in the discotic mesophase of the (**3**)-Cu^{II} complex synthesized by Giroud-Godquin *et al.*⁷ (the first transition metal complex discogen) and that a eutectic point exists in 17 wt% of (**3**)-Cu^{II} at 67 °C. The texture of the D₂ phase is a little different to that of the D₁ phase. The 'finger print texture'⁸ of the D₁ phase turned to the 'wrinkled' finger print texture of the D₂ phase when it was heated to over 117.2 °C. This slight texture difference seems to correspond to the small molar enthalpy change at 117.2 °C.

It was also found (Figure 2) that the D₁ phase of (**2a**) is totally miscible in the phase between 82.5 and 173.3 °C of (**2b**) described below, and that a eutectic point exists at 82 wt% of (**2b**) and at 62 °C. If the D₁ phase of (**2a**) and the phase of (**2b**) between 82.5 and 173.3 °C were not discotic mesophases but

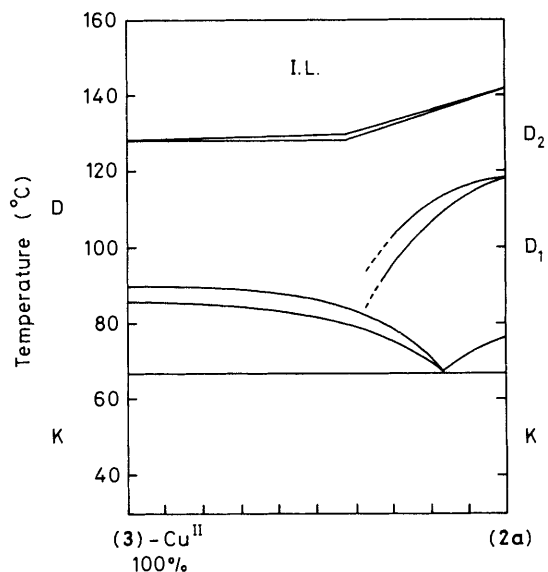


Figure 1. Miscibility diagram for the complexes (**3**)-Cu^{II} and (**2a**).

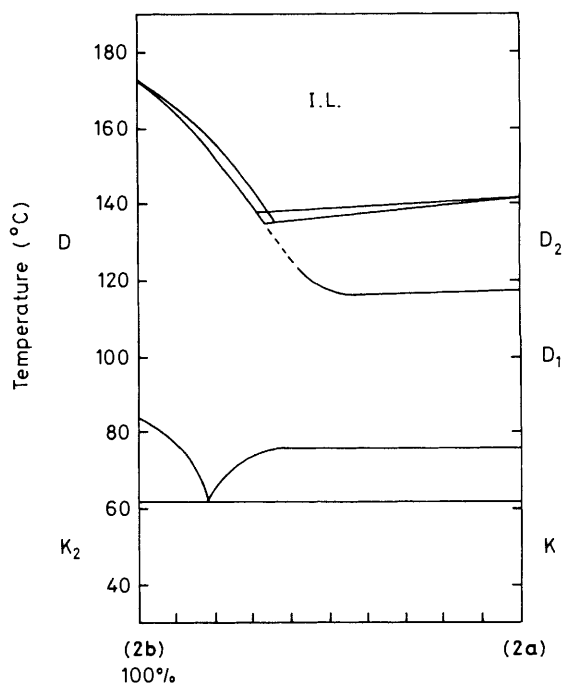


Figure 2. Miscibility diagram for the complexes (**2a**) and (**2b**).

crystals, such a eutectic point could not be observed. For the reasons mentioned above, therefore, it was concluded that the D₁ and D₂ phases of (**2a**) are both discotic mesophases. This is the first example of discotic mesogen polymorphism in transition metal complexes.

Complex (**2b**) showed three endothermic transitions at 21.8 °C ($\Delta H = 0.79$ kcal/mol), 82.5 °C ($\Delta H = 2.89$ kcal/mol), and 173.3 °C ($\Delta H = 16.6$ kcal/mol). The phase between 82.5 °C (fusion) and 173.3 °C (clarification) exhibits discotic mesomorphism. The enthalpy of clarification is higher than that of fusion. This rare situation was first observed for the organic discogens reported by Fugnitto *et al.*⁹ Recently, similar behaviour in organotransition metal complex discogens was reported for the first time (compound 4C in ref. 10). (**2b**) synthesized by us is another example of such behaviour in organotransition metal complex discogens.

[†] 1 kcal = 4.18 kJ.

The clarification and fusion temperatures of (**1b**) are higher than those of (**1a**), and those of (**2b**) are higher than those of (**2a**). The effect of changing octyl groups to octyloxy groups in the complexes has the same effect on the clarification and fusion temperatures as it does on those in the corresponding ligands. On the other hand, the temperature range of mesophase for (**1b**) is narrower than that of (**1a**) while the range of mesophase for (**2b**) is wider than that of (**2a**). Therefore for the temperature range of mesophase, the substituent change from octyl to octyloxy in the complexes has an opposite effect to that in the corresponding ligands. So far as we know, it is the first example of such substituent effects in mesomorphism.

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