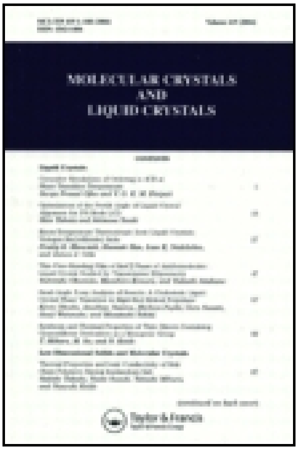

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Discotic Liquid Crystals of Transition Metal Complexes, 1: Bis[1,3-di(p-n-octylphenyl)propane-1,3-dionato]copper(II) and Bis[1,3-di(p-n-octyloxyphenyl)propane-1,3-dionato]copper(II)

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Discotic Liquid Crystals of Transition Metal Complexes, 1: Bis[1,3-di(p-n-octylphenyl)propane-1,3-dionato]copper(II) and Bis[1,3-di(p-n-octyloxyphenyl)propane-1,3-dionato]copper(II)

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It was found that the bis β-diketonato copper (II) complexes IIa, IIb have discotic mesophases; IIa(D_1:76.1 – 117.2°C, D_2:117.2 – 141.6°C), IIb(D: 82.5 – 173.3°C), and that the corresponding β-diketone ligands Ia, Ib have classical mesophases; Ia (Smectic: 28.5 – 60.7°C), Ib(Smectic: 72.3 – 83.6°C). IIa has two discotic mesophases, which is the first example exhibiting discotic mesogen polymorphism. The temperature range of mesophase for β-diketone ligand with octyloxy chains Ib is narrower than that of the ligand with octyl chains Ia, and on the contrary the range of the Cu(II) complex with octyloxy chains IIb is wider than that of the Cu(II) complex with octyl chains IIa. It is the first example of such substituent effect in mesomorphism.

INTRODUCTION

Recently, organic transition metal complexes substituted with long alkyl chains have been synthesized for various purposes, and up to the present, five properties of these complexes have been reported, so far as we know: (1) good solubility in alkane[1,2] (2) micelle formation,[3] (3) unusual thermochromism,[2] (4) double melting behavior,[4] and (5) mesomorphism.[5,6,7] So, focusing our interest on the fourth and the fifth properties above-mentioned, have been synthesized two new disk-like complexes: bis[1,3-di(p-n-octylphenyl)propane-1,3-

dionato]copper(II) (IIa) and bis[1,3-di(p-n-octyloxyphenyl)propane-1,3-dionato]copper(II) (IIb). It was found that each complex synthesized exhibits discotic mesomorphism, and that each of the corresponding β-diketone ligands also exhibits classical mesomorphism. The Cu(II) complex with octyl groups (IIa) has two discotic mesophases, which is the first example exhibiting discotic mesogen polymorphism in transition metal complexes. The temperature range of mesophase for the β-diketone ligand with octyloxy chains (Ib) is narrower than that of the ligand with octyl chains (Ia), and on the contrary the range of the Cu(II) complex with octyloxy chains (IIb) is wider than that of the Cu(II) complex with octyl chains (IIa). So far as we know, it is the first example of such substituent effect in mesomorphism.

EXPERIMENTAL

Synthesis

Syntheses of the present β-diketone ligands and the corresponding copper(II) complexes were carried out according to the scheme illustrated in Figure 1. The β-diketone ligands, Ia(abbreviated as Octyl-Ligand) and Ib(Octyloxy-Ligand) were prepared by the method of Koppecky et al.[8] These ligands and the copper(II) complexes, IIa(Octyl-Cu(II)) and IIb(Octyloxy-Cu(II)), were synthesized by the following detailed procedures.

Ia: Octyl-Ligand

A mixture of 6.0g (24 mmol) of ethyl p-n-octylbenzoate and 5.7g (24 mmol) of p-n-octylacetophenone in dimethoxyethane was refluxed for 2 hours in the presence of 2.0g of 60% sodium hydride (49 mmol) and then stirred overnight. Small portion of water was added very carefully to the resulting yellow stew, and then hydrochrolic acid solution was added to it. This product was extracted with ether. Evaporation gave 10.6g (99%) of crude Octyl-Ligand, which was purified by recrystallization from ethanol to slightly yellow plate-like crystals. Anal. Found (Calcd. for $C_{31}H_{44}O_2$):C 82.98%(82.98), H 9.54%(9.89). MS(m/e):448(M^+). I.R.(KBr disk) νcm^{-1} = 1612($\nu_{c=o}$), 1594($\nu_{c=c}$) ^1H – NMR($CDCl_3$,TMS): δ_{ppm} = 4.5(s, 0.08H, keto CH_2), 6.8(s, 0.96H, enol = CH), 17.0(s, 0.96H, enol OH; keto: enol = 0.04:0.96).

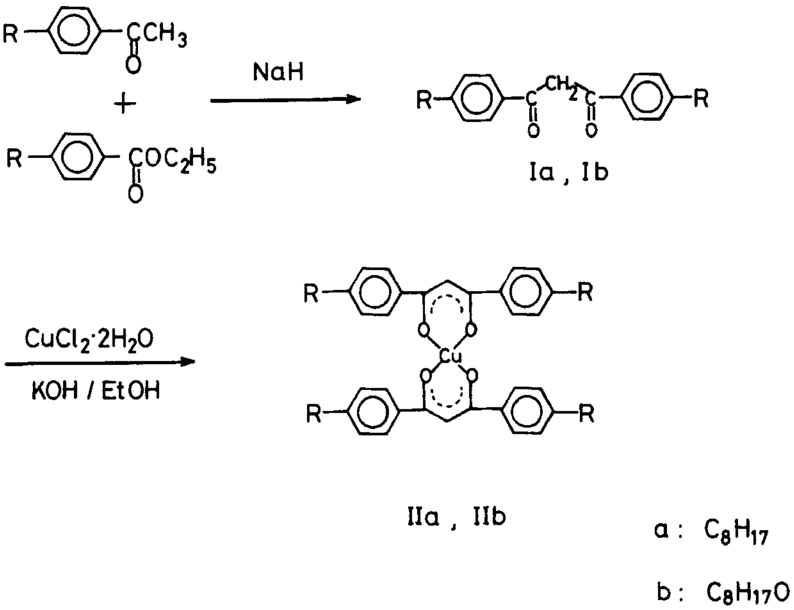

FIGURE 1 Synthetic scheme for the β-diketone ligands Ia, Ib and the corresponding copper (II) complexes IIa, IIb:
Ia = 1,3-di(p-n-octylphenyl)propane-1,3-dione; Octyl-Ligand,
Ib = 1,3-di(p-n-octyloxyphenyl)propane-1,3-dione; Octyloxy-Ligand,
IIa = bis[1,3-di(p-n-octylpheny)propane-1,3-dionato]copper(II); Octyl-Cu(II),
IIb = bis[1,3-di(p-n-octyloxypheny)propane-1,3-dionato]copper(II); Octyloxy-Cu(II).

Ib: Octyloxy-Ligand

The compound was synthesized and purified in the same manner as Octyl-Ligand. Anal. Found (Calcd . for $C_{31}H_{44}O_4$):C 77.55%(77.46), H 9.00%(9.23). MS(m/e):480(M$^+$). I.R.(KBr disk) νcm^{-1} = 1606($\nu_{c=o}$), 1588($\nu_{c=c}$) ^{1}H-NMR(CDCl$_3$,TMS)δ_{ppm} = 4.6(s, 0.15H keto CH$_2$) 6.7(s, 0.92H, enol = CH), 17.1(s, 0.92H, enol OH; keto: enol = 0.08 = 0.92).

IIa: Octyl-Cu(II)

An ethanolic solution of 3.6(8.0 mmol) of Octyl-Ligand was mixed with an equal mole of potassium hydroxide and then an ethanolic solution of 0.7g(4mmol) of cupric chloride. This mixed solution was stirred for 3 hours. The precipitate was collected and recrystallized from acetone to give green needle-like crystals. Anal. Found(Calcd. for $C_{62}H_{86}O_4Cu$):C 77.40%(77.66), H 8.70%(9.04). I.R.(KBr disk)

νcm^{-1} = 1612($\nu_{c=o}$), 1588 ($\nu_{c=c}$). Solid reflection electronic spectra λ_{max}(nm) = 542, 624.

IIb: Octyloxy-Cu(II)

The complex was obtained and purified in the same manner as Octyl-Cu(II). Anal. Found (Calcd. for $C_{62}H_{86}O_8Cu$):C 72.93%(72.80) H 8.35%(8.48). I.R.(KBr disk) νcm^{-1} = 1604($\nu_{c=o}$), 1588($\nu_{c=c}$). Solid reflection electronic spectra λ_{max}(nm) = 542, 607.

MEASUREMENTS

Phase transformation behavior of these compounds synthesized was observed with a polarizing microscope equipped with a heating plate controlled by a thermoregulator, Mettler FP 80 and 82, and measured with differential scanning calorimeters, Rigaku Denki Thermoflex TG-DSC and Rigaku Denki Thermoflex DSC-10A. Using these differential scanning calorimeters, the misciblity tests were carried out between Octyl-Cu(II) and Octyloxy-Cu(II), and between Octyl-Cu(II) and Decyl-Cu(II).[7] Since these mesophases are very viscous fluids, the mixing of them was made both in the states of isotropic liquid of the two complexes; the samples measured here were prepared by heating at 180°C for 15 min. followed by slow cooling to room temperature.

RESULTS AND DISCUSSION

In Table 1 are summarized the phase transitions for Octyl-Ligand (Ia), Octyloxy-Ligand(Ib), Octyl-Cu(II), and Octyloxy-Cu(II).

Mesophases of Octyl-Ligand and Octyloxy-Ligand

Octyl-Ligand presented two endothermic transitions at 28.5°C (ΔH = 0.38 kcal/mol) and 60.7°C (ΔH = 8.15 kcal/mol). The phase between 28.5°C and 60.7°C has the same mesomorphic texture as Decyl-Ligand (1,3-(p-n-decylpheny)propane-1,3-dione) synthesized by Giroud-Godquin et al. for the first time.[7]

Octyloxy-Ligand presented also two endothermic transitions 72.3°C (ΔH = 2.91 kcal/mol) and 83.6°C (ΔH = 12.06 kcal/mol). Under observation with a polarizing microscope, the phase between 72.3°C and 83.6°C exhibits also the same mesomorphic texture as Decyl-

TABLE 1

Phase transition temperatures (T_t) and enthalpies (ΔH_t) of the β-diketone ligands and the corresponding copper (II) complexes

Compound	$\xrightarrow[\Delta Ht\text{(kcal/mol)}]{T_t(^\circ\text{C})}$	Temperature range of L.C.
Ia	$\text{K} \xrightarrow[0.38]{28.5} \text{S} \xrightarrow[8.15]{60.7} \text{I.L.}$	32.2
Ib	$\text{K} \xrightarrow[2.91]{72.3} \text{S} \xrightarrow[12.06]{83.6} \text{I.L.}$	11.3
IIa	$\text{K} \xrightarrow[26.8]{76.1} \text{D}_1 \xrightarrow[0.76]{117.2} \text{D}_2 \xrightarrow[8.60]{141.6} \text{I.L.}$	65.5
IIb	$\text{K}_1 \xrightarrow[0.79]{21.8} \text{K}_2 \xrightarrow[2.89]{82.5} \text{D} \xrightarrow[16.6]{173.3} \text{I.L.}$	91.8

1) Compound
Ia: Octyl-Ligand, Ib: Octyloxy-Ligand, IIa: Octyl-Cu(II), IIb: Octyloxy-Cu(II).
2) Phase nomenclature
K: Crystal, S: Smectic liquid crystal, D: Discotic liquid crystal, I.L.: Isotropic liquid.

Ligand. Recently, this mesophase of Decyl-Ligand has been 'tentatively' identified as smectic E by Giroud-Godquin et al.[9]

Discotic mesophases of Octyl-Cu(II) and Octyloxy-Cu(II)

Octyl-Cu(II) presented three endothermic transitions at 76.1°C (ΔH = 26.8 kcal/mol), 117.2°C (ΔH = 0.76 kcal/mol), and 141.6°C (ΔH = 8.60 kcal/mol). The phase between 76.1°C and 117.2°C (D_1) and the phase between 117.2°C and 141.6°C (D_2) are both discotic mesophases of this complex, which was established by the miscibility tests using differential scanning calorimeter and by the observation of these mesomorphic textures using a polarizing microscope. As the results of constructing the binary phase diagram between Decyl-Cu(II) and Octyl-Cu(II) by the miscibility test, it was found that the D_2 phase of this Octyl-Cu(II) is totally miscible in the discotic mesophase of Decyl-Cu(II) synthesized by Giroud-Godquin et al. as the first transition metal complex discogen,[7] and that a eutectic point exists in 17 wt% of Decyl-Cu(II) at 67°C, as illustrated in Figure 2. The texture of the D_2 phase is only slightly different from that of the D_1 phase. The "finger prints texture"[10] appeared in the D_1 phase, which turned to "wrinkled" finger prints texture in the D_2 phase when it was heated up over 117.2°C. This slight texture difference seems to correspond

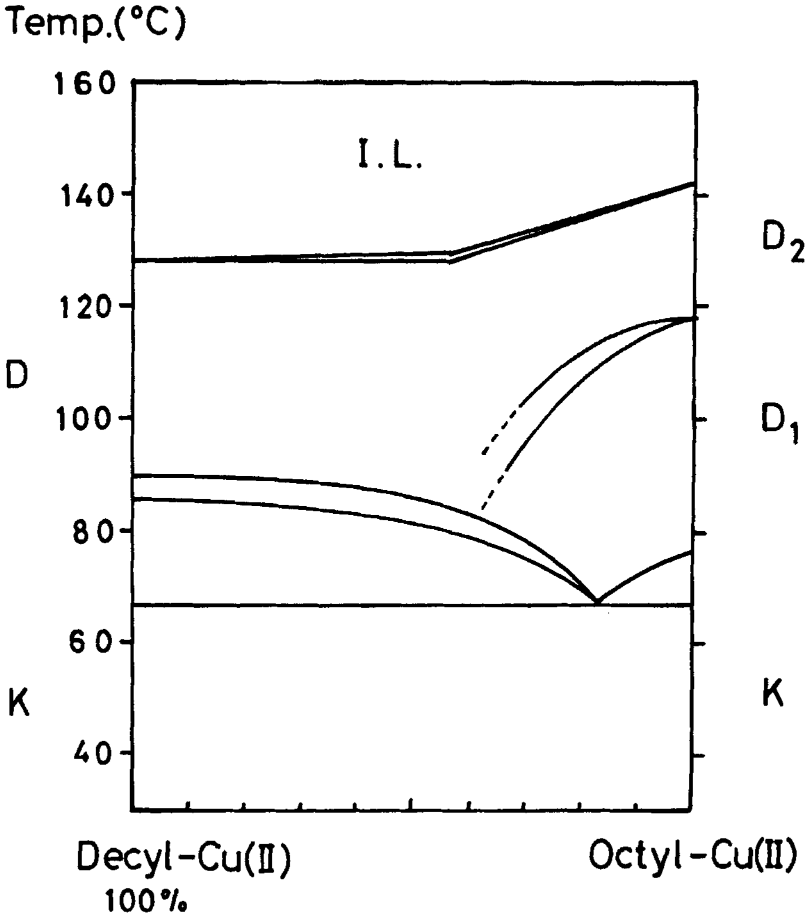

FIGURE 2 Miscibility diagram of Decyl-Cu(II) and Octyl-Cu(II).

to the small molar enthalpy change at 117.2°C. On the other hand, it was also found that the D_1 phase is totally miscible in the phase between 82.5°C and 173.3°C of Octyloxy-Cu(II), and that a eutectic point exists in 82 wt% of Octyloxy-Cu(II) at 62°C as illustrated in Figure 3. If this D_1 phase of Octyl-Cu(II) and the phase of Octyloxy-Cu(II) between 82.5°C and 173.3°C were not discotic mesophases but crystals, such a eutectic point could not be observed. For these reasons above-mentioned, therefore, it was concluded that the D_1 and D_2 phases of Octyl-Cu(II) are both discotic mesophases. This is the first example exhibiting discotic mesogen polymorphism in transition metal complexes.

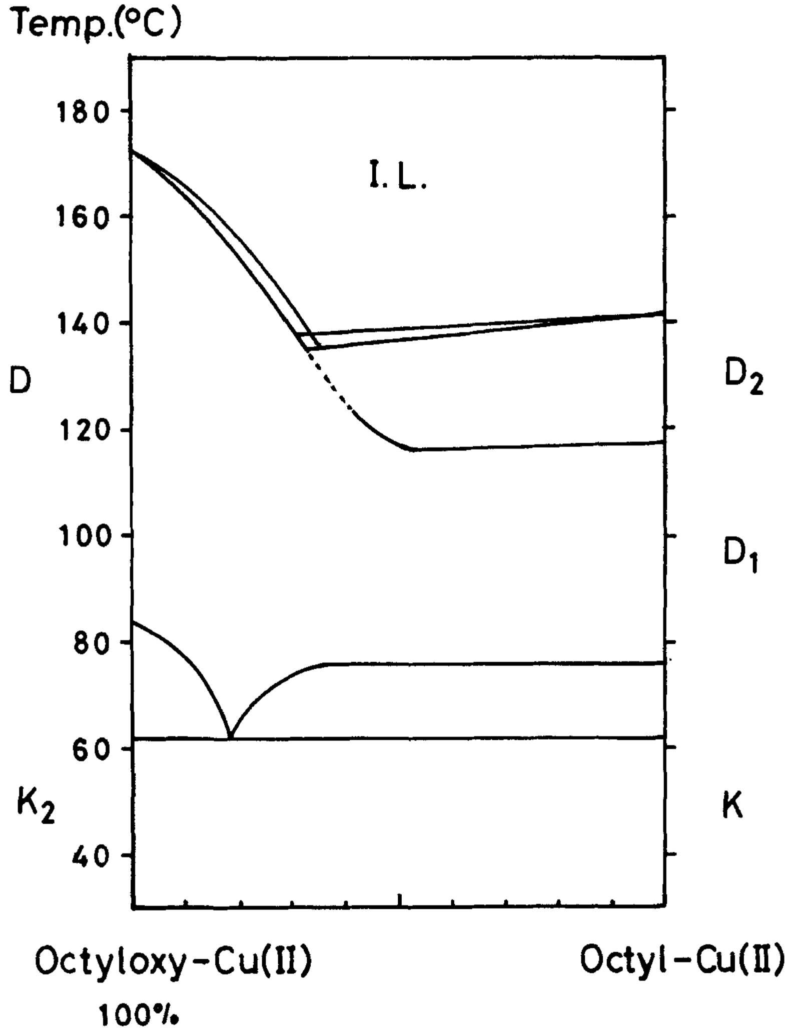

FIGURE 3 Miscibility diagram of Octyloxy-Cu(II) and Octyl-Cu(II).

Octyloxy-Cu(II) presented three endothermic transitions at 21.8°C (ΔH = 0.79 kcal/mol), 82.5°C (ΔH = 2.89 Kcal/mol), and 173.3°C (ΔH = 16.6 kcal/mol). The enthalpy of clarification is higher than that of fusion. This rare situation was first observed for organic discogens reported by Fugnitto et al.[11] Recently, the first same case in organic transition metal discogens was reported for compound 4C in the reference (9). Octyloxy-Cu(II) synthesized by us is another example for such situation in organic transition metal discogens.

Substituent effects on the temperature range of mesophases of the ligands and the corresponding complexes

The temperature range of mesophase of the β-diketone ligand with octyloxy chains (Ib) is narrower than that of the ligand with octyl chains (Ia), and on the contrary the range of the Cu(II) complex with octyloxy chains (IIb) is wider than that of the Cu(II) complex with octyl chains (IIa). It is obvious that the substituent effect on the temperature range of mesophase with changing from octyl groups to octyloxy groups in the complexes is quite opposite to that of the corresponding ligands. So far as we know, it is the first example of such substituent effect in mesomorphism.

CONCLUSION

Two new disk-like complexes, bis[1,3-di(p-n-octylphenyl)-propane-1,3-dionato]copper(II) and bis[1,3-di(p-n-octyloxyphenyl)-propane-1,3-dionato]copper(II), have been synthesized. It was found that each complex synthesized exhibits discotic mesomorphism, and that each of the corresponding β-diketone ligands also exhibits classical mesomorphism. Octyl-Cu(II) is the first transition metal complex exhibiting discotic mesogen polymorphism. It was also found that, concerning with the temperature range of mesophase, the substituent effect with changing from octyl groups to octyloxy groups in the complexes is quite opposite to that of the corresponding ligands. It is the first example of such substituent effects in mesomorphism.

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