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Discotic Liquid Crystals of Transition Metal Complexes, 2: The Effect of Alkyl Chain Length on Discotic Mesomorphism in Bis[1,3-di(*p*-*n*-alkylphenyl)propane-1,3-dionato]copper(II)

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A Series of disk-like complexes, bis[1,3-di(*p*-*n*-alkylphenyl)propane-1,3-dionato]copper(II) (*n*-alkyl: R=C_nH_{2n+1} n=0—12; C_n—Cu(II)), have been synthesized in focusing our interest on the effect of the alkyl chain length for the discotic mesomorphism. It was found that each of the copper(II) complexes substituted by R=C_4H_9—$C_{12}H_{25}$(C_4—Cu(II) – C_{12}—Cu(II)) is a discogen, and that each of the complexes from C_7—Cu(II) to C_9—Cu(II) has plural discotic mesophases. C_9—Cu(II) has three discotic mesophases which is the first example in transition metal complexes. Each of the complexes, C_n—Cu(II) (n=5—7,9—11), has two solid polymorphs with different m.p.s in monotropic relationship. Each of the ligands substituted by R=C_7H_{15} – $C_{12}H_{25}$(C_7—Ligand – C_{12}—Ligand) is a smectogen. It became to be clear that the discotic mesogen complexes can be obtained even when the non-mesomorphic ligands(n=4—6) are used.

Keywords: discotic mesophase, bis(β-diketonato)copper(II) complexes, alkyl chain length effect

I. INTRODUCTION

Only a few organic transition metal complexes exhibit discotic mesomorphism. The only complexes known to date are tetrasubstituted[1,2]

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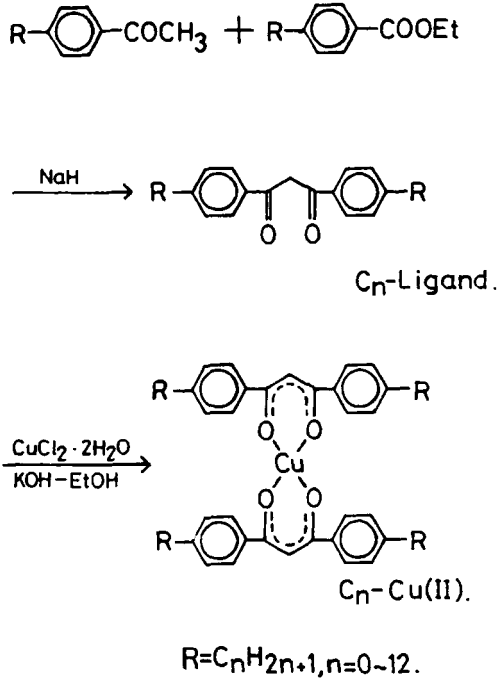
or octasubstituted β-diketonato copper(II) complexes,[3] an octasubstituted copper phthalocyanine,[4] and copper(II) laurate.[5] However, systematic investigations on the effect of the alkyl chain length for the discotic mesomorphism have never been performed in organic transition metal complexes. So, in focusing our interest on the effect of the alkyl chain length, a series of disk-like complexes, bis[1,3-di(*p*-*n*-alkylphenyl)propane-1,3-dionato]copper(II) (C_n-Cu(II) in Scheme 1) have been synthesized. It was found that each of the complexes substituted by R=C_4H_9 – $C_{12}H_{25}$ is discogen, and that each of the complexes substituted by R=C_7H_{15} – C_9H_{19} has plural discotic mesophases. Furthermore, it was also found for the first time in transition metal complexes that three discotic mesophases exist in the complex substituted by R=C_9H_{19}. So, we wish to report here the first examples of the effect of alkyl chain length on discotic mesomorphism in transition metal complexes.

II. EXPERIMENTAL



SCHEME 1 Synthetic route for the β-diketone ligands, C_n-Ligand, and the corresponding copper(II) complexes, C_n-Cu(II).

Synthesis

The synthetic route of the present complex is shown in Scheme 1. The detailed procedures were almost the same as the case of octyl substituent described in the previous paper.[2] Table 1 lists the yields and elemental analysis data for the β-diketone ligands; 1,3-di(*p*-*n*-alkylphenyl)propane-1,3-dione (alkyl: R=C_nH_{2n+1} n=0—12; abbreviated as C_n-Ligand). In Table 2 are summarized the elemental analysis data, recrystallization solvents, and the crystalline shapes for the corresponding copper(II) complexes; bis[1,3-di(*p*-*n*-alkylphenyl)propane-1,3-dionato]copper(II) (abbreviated as C_n-Cu(II)).

Measurements

Phase transformation behaviors of these compounds synthesized here were observed by a polarizing microscope equipped with a heating

TABLE I

Elemental analysis data and yields for the ligands, C_n-Ligand

C_n-Ligand	Elemental analysis Found(Calcd.) %		Yield(%)
n	H	C	
0	5.37 (5.39)	80.57 (80.34)	a
1	6.70 (6.39)	80.79 (80.93)	99
2	7.29 (7.19)	81.40 (81.40)	95
3	7.77 (7.84)	81.50 (81.78)	92
4	8.19 (8.39)	82.06 (82.10)	87
5	8.82 (8.85)	82.22 (82.37)	88
6	8.89 (9.24)	82.91 (82.61)	91
7	9.40 (9.59)	83.09 (82.81)	95
8	9.84 (9.89)	82.86 (82.98)	93
9	10.01(10.15)	83.28 (83.14)	97
10	10.28(10.38)	83.54 (83.28)	95
11	10.28(10.59)	83.49 (83.40)	96
12	10.82(10.78)	83.45 (83.51)	90

[a]Purchase.

TABLE II

Elemental analysis data, recrystallization solvents, and the crystalline shapes obtained from recrystallization for the complexes, C_n-Cu(II)

n	Elemental analysis Found(Calcd.)% H	C	Recrystallization solvent	Crystalline shape
0	4.39(4.35)	70.85(70.65)	Ethyl acetate	Rod
1	5.36(5.34)	72.16(72.13)	Ethyl acetate	Needle
2	6.34(6.16)	73.42(73.35)	Ethyl acetate	Needle(K_1)
3	6.82(6.84)	74.52(74.36)	Ethyl acetate	Parallerogram(K_1)
4	7.33(7.41)	75.26(75.22)	Ethyl acetate	Rod(K_1)
5	7.91(7.91)	75.81(75.96)	Ethyl acetate	Needle(K_2)
6	8.21(8.33)	76.71(76.60)	Ethyl acetate	Needle(K_1)
7	8.55(8.71)	77.28(77.16)	n-Hexane	Needle(K_2)
8	8.82(9.04)	77.44(77.66)	n-Hexane	Needle
9	9.29(9.34)	77.99(78.10)	n-Hexane	Needle(K_1)
10	9.28(9.60)	78.67(78.49)	n-Hexane	Needle(K_2)
11	9.51(9.84)	78.70(78.85)	n-Hexane	Needle(K_1)+Rod(K_2)
12	9.68(10.05)	79.21(79.17)	n-Hexane	Needle

plate controlled by a thermoregulator, Mettler FP80 and FP82, and measured with differential scanning calorimeters, Mettler FP85, Rigaku Denki Thermoflex TG-DSC, and Rigaku Denki Thermoflex DSC-10A. To distinguish between the solid polymorphs in the complexes, X-ray diffraction powder patterns were also measured with Cu-K_α radiation, using a Rigaku Geigerflex.

III. RESULTS AND DISCUSSION

1. Classic mesomorphism of β-diketone ligands

It was found that each of the ligands substituted by R=C_7H_{15} – $C_{12}H_{25}$ (C_7-Ligand – C_{12}-Ligand) is a smectogen, and that C_{10}-Ligand and C_{11}-Ligand have two smectic phases, respectively. In Table 3 the phase transition temperature(T_i) and their enthalpy changes (ΔH_i) of the β-diketone ligands are summarized. The ligands marked by "*a*"

TABLE III

Phase transition temperatures (T_t) and enthalpy changes (ΔH_t) of the ligands, C_n-Ligand

n	T_t / ΔH_t (kcal/mol)	
0	K —76.5→ I.L. (7.05)	
1	K —126.8→ I.L. (8.22)	
2	K —37.2→ I.L. (8.12)	
3	K —50.3→ I.L. (5.28)	
4	K —47.4→ I.L. (6.35)	
5	K —45.5→ I.L. (6.78)	
6	K —48.8→ I.L. (7.05)	
7	K —57.7→ I.L. (8.17); I.L. —ca.51→ S	a
8	K —28.5→ S (0.38) —60.7→ I.L. (8.15)	b
9	K —41.7→ S (0.89) —65.4→ I.L. (9.10)	a*
10	K —41.1→ S_1 (7.95) —50.7→ S_2 (0.52) —66.6→ I.L. (9.62)	a
11	K —44.3→ S_1 (7.13) —50.4→ S_2 (0.25) —68.0→ I.L. (10.77)	
12	Pl. —61.9→ S —67.8→ I.L. (12.49); Sph. —59.7→ Nd. —63.5→ S	a*

Phase nomenclature: K = crystal, Pl. = plate-like crystal, Sph. = spherulite, Nd. = needle-like crystal, S = smectic liquid crystal, and I.L. = isotropic liquid.

*See Reference 1.

[b]See Reference 2.

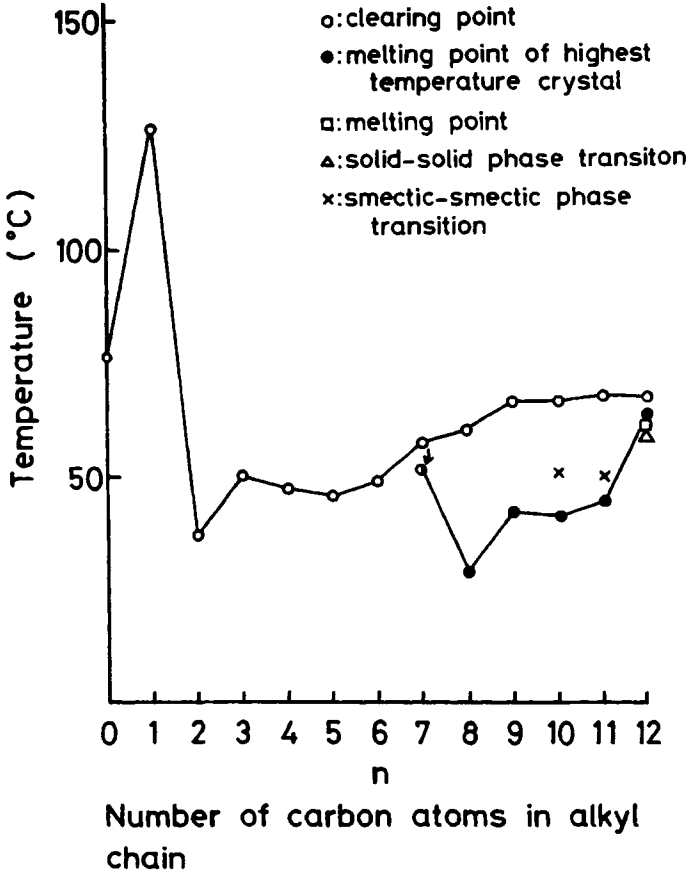


FIGURE 1 Phase transition temperatures vs. number of carbon atoms in alkyl chain for the β-diketone ligands, C_n-Ligand.

in this table, C_7-, C_9-, C_{10}-, and C_{12}-Ligand, were synthesized for the first time by A. M. Giroud-Godquin et al.,[1] and the ligand marked by "*b*", C_8-Ligand, was reported by us previously.[2] The results of the ligand marked by "*a**", C_9- and C_{12}-Ligand, are different from the results reported by A. M. Giroud-Godquin et al.[1]

Giroud-Godquin et al. have not reported the existence of smectic phase in C_9-Ligand. However, we confirmed by the microscopic observations and the measurements of DSC that C_9-Ligand has a smectic phase between 41.7°C and 65.4°C. They have not also reported the existence of plate-like crystals and needle-like crystals in C_{12}-Ligand. C_{12}-Ligand was recrystallized from ethanol to give a mixture of plate-

like crystals and needle-like crystals (relatively small portion). When the mixture of them is heated up, the plate-like crystals transform into a smectic phase at 61.9°C and then the needle-like crystals are turned into the same smectic phase at 63.5°C. On further heating, the smectic phase transforms into isotropic liquid at 67.8°C. When the isotropic liquid was cooled *rapidly* into room temperature, spherulites could be obtained. A solid-solid phase transition from the spherulites to the needle-like crystals was observed at 59.7°C. On the other hand, when the isotropic liquid was cooled *slowly*, the plate-like crystals could be obtained via the smectic phase. Thus, three kinds of crystalline phases in C_{12}-Ligand were confirmed by such microscopic observation and DSC measurements. However, all of the cases of the cooling gave a mixture of plate-like, needle-like, and spherulite-like crystals. So, we could not determine each of the correct enthalpy changes for the transformations of these crystals.

All transition temperatures of these β-diketone ligands are plotted against the number of carbon atoms in alkyl chain in Figure 1. Interestingly, the even-odd effect in the clearing points of the ligands could not be observed. As mentioned below, the even-odd effect of the corresponding copper(II) complexes also could not be observed.

2. Discotic mesomorphism of bis(β-diketonato)copper(II) complexes

It was found that each of the copper(II) complexes substituted by $R{=}C_4H_9$ – $C_{12}H_{25}$ is a discogen, and that furthermore each of the complexes substituted by $R{=}C_7H_{15}$ – C_9H_{19} has plural discotic mesophases. Phase transition temperatures (T_t) and the enthalpy changes (ΔH_t) of the complexes, C_n-Cu(II), were summarized in Table 4. In this table, the complexes marked by "*a*", C_{10}-Cu(II) and C_{12}-Cu(II), were synthesized for the first time by A. M. Giroud-Godquin et al.[1] The complex marked by "*b*", C_8-Cu(II), was previously reported by us.[2] All transition temperatures of these copper(II) complexes are plotted against the number of carbon atoms in alkyl chain in Figure 2.

2-1. Monotropic relationship between the two solid polymorphs. It was confirmed by microscopic observation, DSC and X-ray measurements that C_{10}-Cu(II) has two crystalline phases with different m.p.s, 86.0°C and 91.3°C. The higher m.p. of this complex has not reported by A. M. Giroud-Godquin et al.[2] The C_{10}-Cu(II) complex was recrystallized from *n*-hexane to give green needle-like crystals (K_2 in Table 4). When the needle-like crystals are heated on a hot plate equipped with polarizing microscope, these crystals melt

TABLE IV

Phase transition temperatures (T_t) and enthalpy changes (ΔH_t) of the complexes, C_n-Cu(II)

n	T_t(°C) / ΔH_t(kcal/mol)	
0	$K \xrightarrow[10.40]{317} ? \xrightarrow[1.69]{342} ?$ (decomp.)	c
1	$K \xrightarrow[13.06]{295.5}$ I.L.(decomp.)	
2	$K_1 \xrightarrow{171.6} K_2 \xrightarrow{275.2}$ I.L.(decomp.); $K_1 \xrightarrow{273.1}$ I.L.(decomp.)	
3	$K_1 \xrightarrow[1.10]{186.0} K_2 \xrightarrow[11.16]{226.3}$ I.L.	
4	$K_1 \xrightarrow[9.32]{68.7} K_2 \xrightarrow[8.29]{180.1}$ I.L.; D ca.162	
5	$K_1 \xrightarrow[3.95]{106.3} D \xrightarrow[5.91]{162.2}$ I.L.; $K_2 \xrightarrow[0.46]{115.0} D$	
6	$K_1 \xrightarrow[13.40]{79.3} D \xrightarrow[6.33]{154.0}$ I.L.; $K_2 \xrightarrow[5.55]{91.8} D$	
7	$K_2 \xrightarrow[13.71]{76.2} D_1 \xrightarrow[0.84]{94.6} D_2 \xrightarrow[6.92]{150.0}$ I.L.; $K_1 \xrightarrow{53.9} D_1$	
8	$K \xrightarrow[26.80]{76.1} D_1 \xrightarrow[0.76]{117.2} D_2 \xrightarrow[8.60]{141.6}$ I.L.	b
9	$K_1 \xrightarrow[21.66]{68.0} D_1 \xrightarrow[1.20]{99.8} D_2 \xrightarrow[0.49]{111.1} D_3 \xrightarrow[7.47]{137.0}$ I.L.; $K_2 \xrightarrow[2.39]{82.6} D_1$	

TABLE IV

(continued)

n	$\xrightarrow[\Delta H_t(\text{kcal/mol})]{T_t(^\circ\text{C})}$	
10	$K_2 \xrightarrow[29.50]{91.3} D \xrightarrow[7.71]{130.1} \text{I.L.}$; $K_1 \xrightarrow[21.67]{86.0} D$	a*
11	$K_1 \xrightarrow[8.54]{84.2} D \xrightarrow{125.3} \text{I.L.}$; $K_2 \xrightarrow{96.6} D$	
12	$K \xrightarrow[34.76]{98.9} D \xrightarrow[7.35]{119.8} \text{I.L.}$	a

Phase nomenclature: K = crystal, D = discotic liquid crystal, I.L. = isotropic liquid.
[a]See main text and Reference 1.
[b]See main text and Reference 2.
[c]Microscopic observation over 300°C could not be carried out by the instrumental limits. Only DSC measurements were used for the complex. So, the phase between 317° and 342°C and the phase over 342°C couldnot be determined.

into discotic mesophase at 91.3°C(ΔH_t = 29.50 kcal/mol from DSC). On further heating, the *D* phase transformed into isotropic liquid at 130.1°C of the clearing point (ΔH_t = 7.71 kcal/mol). When the isotropic liquid over the clearing point is *rapidly* cooled into room temperature, it converts another crystalline phase K_1 via the *D* phase. When the K_1 crystals are heated from room temperature, the K_1 crystals melt into the same *D* phase at 86.0°C(ΔH_t = 21.67 kcal/mol) without being accompanied by a solid-solid($K_1 \rightarrow K_2$) phase transition; on further heating it transforms into isotropic liquid at the same clearing point, 130.1°C. On the other hand, when the isotropic liquid over the clearing point is cooled *slowly*, it converts to the original crystal K_2. To confirm these melting behaviors much more, the DSC measurements were carried out for two cases: one of them is a case of a mixture of large portion of K_1 and small portion of K_2 prepared by appropriately rapid cooling of the isotropic liquid(case 1: $K_1 >> K_2$); the other is a case of mixture of small portion of K_1 and large portion of K_2 prepared by appropriately slow cooling of the isotropic

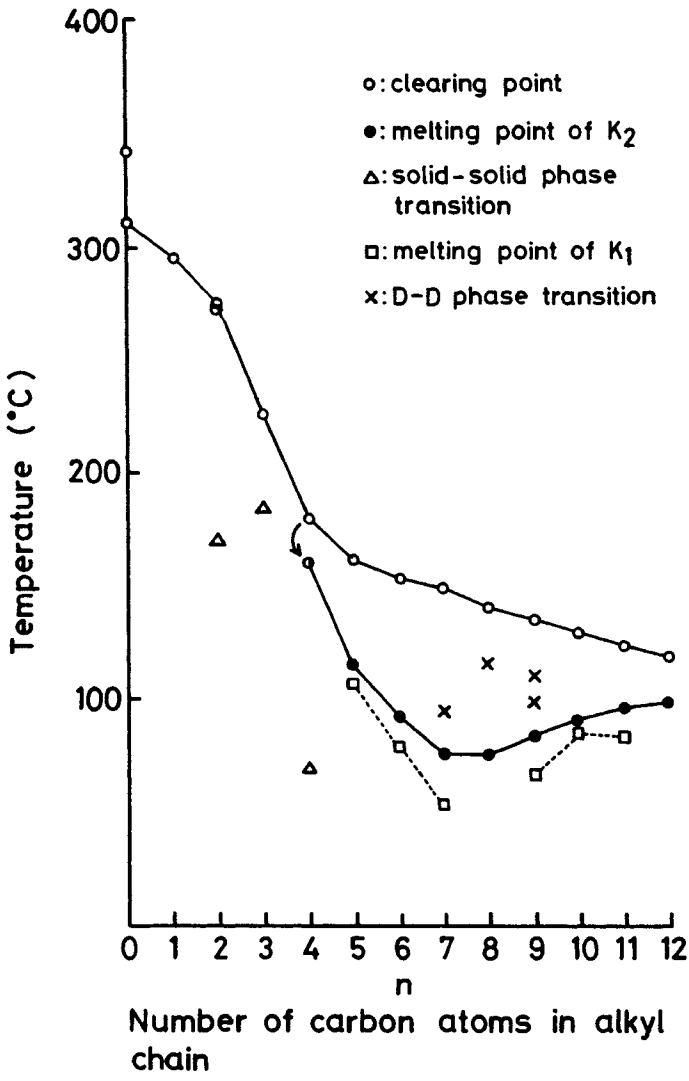


FIGURE 2 Phase transition temperatures vs. number of carbon atoms in alkyl chain for the copper(II) complexes, C_n-Cu(II).

liquid(case 2: $K_1 << K_2$). In Figure 3 the upper thermogram shows the case 1($K_1 >> K_2$). The lower one shows the case 2($K_1 << K_2$). It is clear from the thermograms that two different m.p.s exist for the C_{10}-Cu(II) complex, and that, in other words, the complex has two solid polymorphs. To distinguish between these two solid poly-

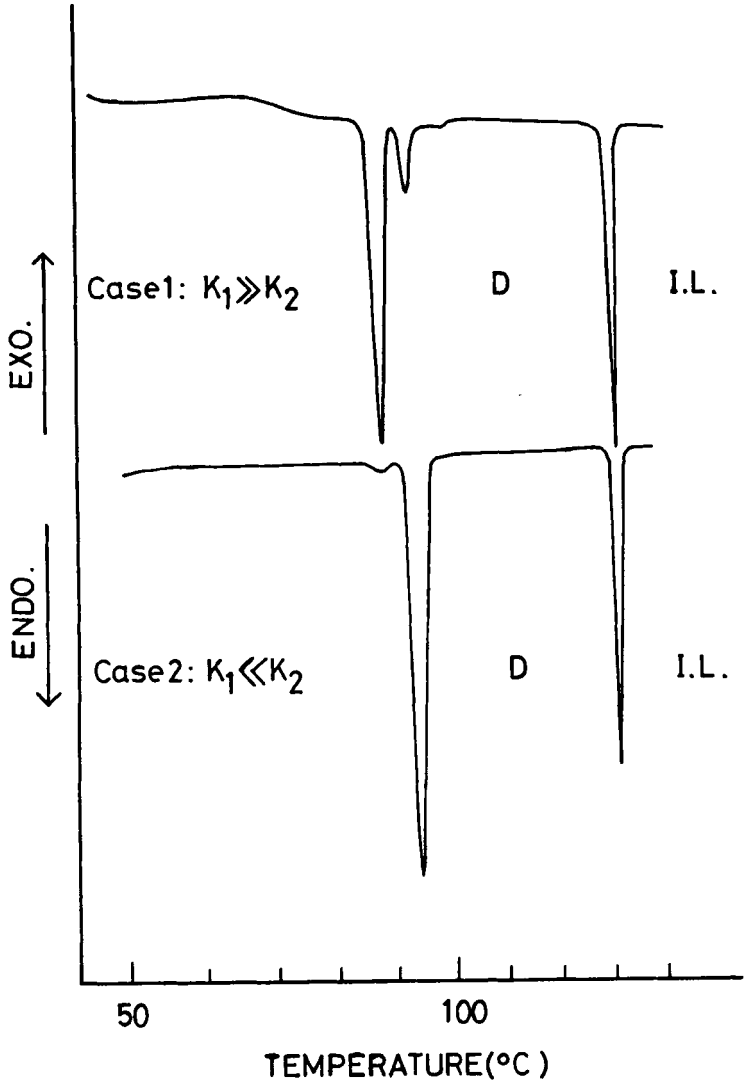


FIGURE 3 DSC thermograms of C_{10}-Cu(II) for the two cases: case 1 = a mixture of large portion of K_1 crystal and small portion of K_2 crystal, case 2 = a mixture of small portion of K_1 crystal and large portion of K_2 crystal. Heating rate = 10°C/min.

morphs, K_1 and K_2, X-ray diffraction powder patterns were observed for both of the crystals at room temperature. The diffraction data obtained are clearly different from each other. In Table 5 are summarized the four strongest lines in each of the solid polymorphs. Relationship between the two solid polymorphs of the complex is

TABLE V

X-Ray diffraction data with relative intensities (I/I_1) for the four strongest lines in each solid polymorph of C_{10}-Cu(II)complex

K_1	dA	4.55	16.07	10.53	4.15
	I/I_1	100	69	58	22
K_2	dA	13.60	3.68	9.31	4.42
	I/I_1	100	94	41	32

monotropic because solid-solid phase transition from K_1 to K_2 could not be observed.[6] Such monotropic relationship between K_1 and K_2 solid polymorphs in other complexes could be observed also in C_5-, C_6-, C_7-, C_9-, and C_{11}-Cu(II). The monotropic relationship between K_1 and K_2 solid polymorphs in C_{11}-Cu(II) complex makes it very difficult to obtain the crystalographically pure K_1 and K_2 solid polymorphs respectively. C_{11}-Cu(II) was recrystallized from *n*-hexane to give always a mixture of needle-like crystals(K_1) and rod-like crystals(K_2) as shown in Table 2. Even by the heat treatment as same as the case in C_{10}-Cu(II), we could not obtain the crystalographically pure solid polymorphs in C_{11}-Cu(II). So, each of the enthalpy changes in m.p.s of pure K_1 and K_2 in C_{11}-Cu(II) could not be obtained as summarized in Table 4. Because of the same reason the enthalpy change at melting of K_1 in C_7-Cu(II) could not also be determined. For C_8-Cu(II) complex only one crystalline phase was obtained in spite of any heat treatments.

Thus, the monotropic relationship between the lower melting solid(K_1) and the higher melting solid(K_2) can be observed for n=5—7 and n=9—11 in the C_n-Cu(II) complexes.

2-2. Discotic mesogen polymorphism of the transition metal complexes. In the previous paper we reported that C_8-Cu(II) has two discotic mesophases, and that the complex is the first example of discotic mesogen polymorphism in transition metal complexes.[2] We wish to report here other two examples exhibiting discotic mesogen polymorphism: C_7-Cu(II) has two discotic mesophases and especially, C_9-Cu(II) has three discotic mesophases, which is the first example in transition metal complexes.

C_7-Cu(II) complex showed three endothermic peaks at 76.2°C(ΔH_t

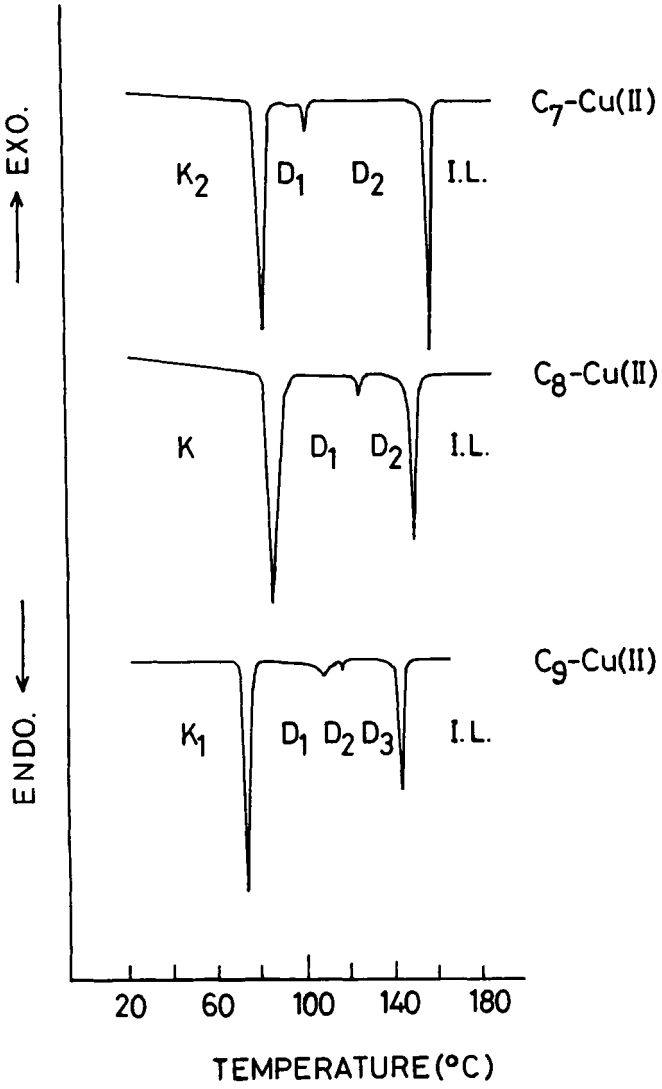


FIGURE 4 DSC thermograms of C_7-, C_8-, and C_9-Cu(II), which are exhibiting discotic mesogen polymorphism. Heating rates = 10°C/min.

= 13.71 kcal/mol), 84.6°C(ΔH_t = 0.84 kcal/mol), and 150.0°C(ΔH_t = 6.92 kcal/mol), as illustrated in Figure 4. The texture of the phase between 76.2°C and 94.6°C(D_1) is the same as the D_1 phase of C_8-Cu(II) between 76.1°C and 117.2°C reported previously.[2] Furthermore, the texture of the phase between 94.6°C and 150.0°C(D_2) is

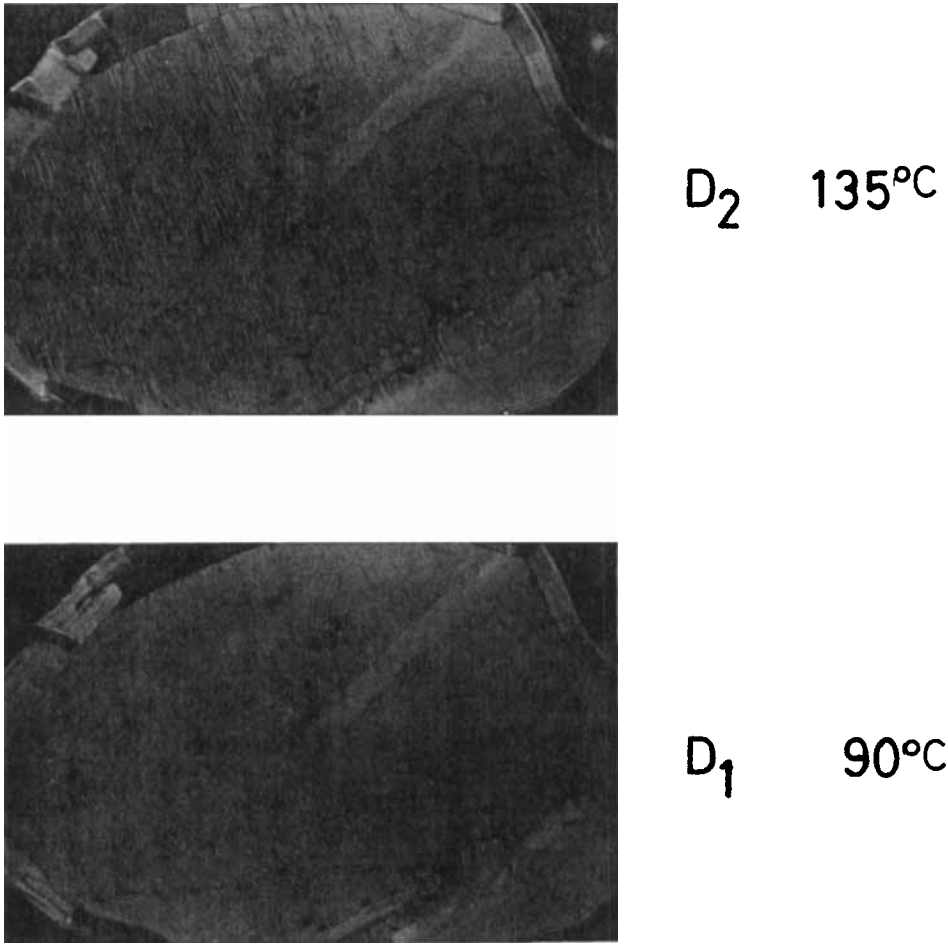


FIGURE 5 Microphotographs of two discotic mesophases in C_8-Cu(II): D_1 phase at 90°C and D_2 phase at 135°C.

also the same as the D_2 phase of C_8-Cu(II) between 117.2°C and 141.6°C. So, in Figure 5 are shown microphotographs of the textures of the D_1 and D_2 phases in C_8-Cu(II). The D_1 phase gave plane texture surrounded by lustrous ring for almost cases.[7] When it was heated over 117.2°C, the phase texture turned to the "wrinkled" texture of the D_2 phase.

C_9-Cu(II) complex showed four endothermic peaks at 68.0°C(ΔH_t = 21.66 kcal/mol), 99.8°C(ΔH_t = 1.20 kcal/mol), 111.1°C(ΔH_t =

0.49 kcal/mol), and 137.0°C(ΔH_t = 7.47 kcal/mol), as illustrated in Figure 4. The texture of the phase between 68.0°C and 99.8°C appeared as the spiral texture as shown in the bottom microphotograph of Figure 6. When it was heated over 99.8°C, the spiral texture was destroyed and mosaic texture surrounded by lustrous ring of the D_2 phase appeared. On further heating over 111.1°C, the lustrous ring began to be distorted and the mosaic texture became to wrinkle as the top microphotograph of Figure 6. The wrinkled texture of the D_3 phase disappeared at 137.0°C of the clearing point. Thus, C_9-Cu(II) complex has three discotic mesophases for the first time in transition metal complexes.

2-3. No even-odd effect in clearing points. Generally, a plot of the clearing points against the number of carbon atoms in alkyl chains shows an even-odd effect for long alkyl chain compounds. However, the even-odd effect in the clearing points of the present complexes could not be observed as illustrated in Figure 2. U. T. Mueller-Westerhoff et al.[8] reported for the first time in classic mesomorphism of transition metal complexes that bis(styryldithiolato)nickel and bis(styryldithiolato) platinium complexes do not exhibit the even-odd effect in the clearing points. Therefore, the unusual behavior at the clearing points of the present complexes is another example in mesomorphism of transition metal complexes.

3. Can one obtain the mesomorphic complex even when a non-mesomorphic ligand is used?

To date very few investigations on the effect on complexing for mesomorphic properties have been done. M. Ghedini et al. reported the synthesis and characterization of palladium(II) complexes with liquid crystal azobenzene.[9] They pointed out that the complexing dramatically reduces the temperature range in which the compounds exist in an ordered liquid crystal structure. On the other hand, we reported in the previous papers[2] that the temperature range of discotic mesophases of the β-diketonato copper(II) complexes are wider than that of the ligands. Although Ghedini et al. and we observed the opposite tendency for the temperature range of mesophases between the complexes and the ligands, both of them used the mesomorphic ligands for complexing. Hereupon, considering to get a mesomorphic complex, the following basic question must be raised: can one obtain the mesomorphic complex even when a non-mesomorphic ligand is used?

With respect to this question, a series of the present ligands and

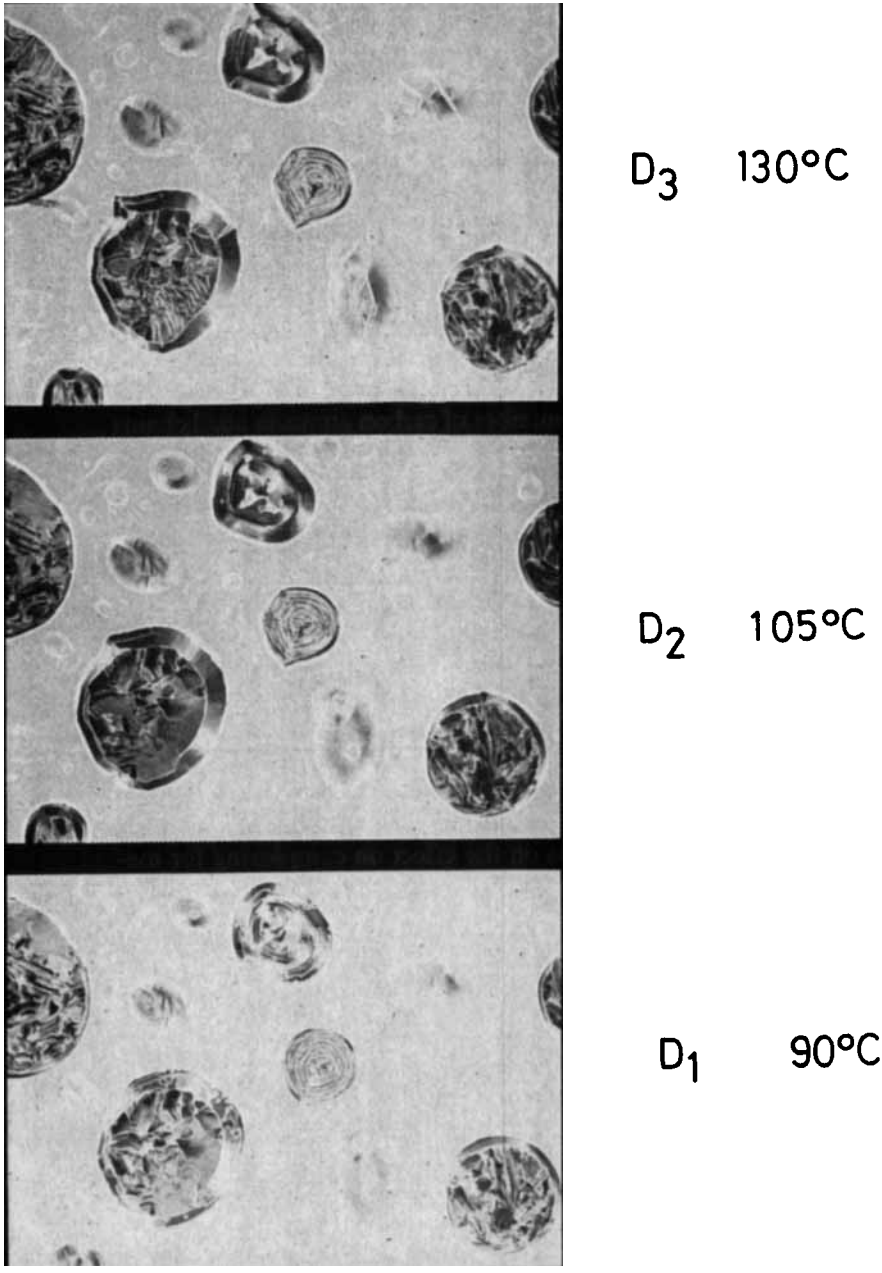


FIGURE 6 Microphotographs of three discotic mesophases in C_9-Cu(II): D_1 phase at 90°C, D_2 phase at 105°C, and D_3 phase at 130°C.

complexes, C_n-Ligand and C_n-Cu(II), were investigated. As the results, it has appeared that the smallest number of carbon atoms in the alkyl chains exhibiting mesomorphism is seven for the ligands and four for the Cu(II) complexes.[10] In other words, one can obtain the mesomorphic Cu(II) complexes even when the non-mesomorphic ligands(n=4—6) are used. Therefore, one need not to use always a mesomorphic ligand with a view to obtaining a mesomorphic complex. Such examples in this paper must contribute to a new field of liquid crystal chemistry of organic transition metal complexes.

IV. CONCLUSION

A Series of disk-like complexes, bis[1,3-di(*p-n*-alkylphenyl)propane-1,3-dionato]copper(II) (*n*-alkyl: R=C_nH_{2n+1} n=0—12; C_n-Cu(II)), have been synthesized in focusing our interest on the effect of the alkyl chain length for the discotic mesomorphism. It was found that each of the copper(II) complexes substituted by R=C_4H_9-$C_{12}H_{25}$ (C_4-Cu(II) – C_{12}-Cu(II)) is a discogen, and that each of the complexes from C_7-Cu(II) to C_9-Cu(II) has plural discotic mesophases. C_9-Cu(II) has three discotic mesophases which is the first example in transition metal complexes. Each of the complexes, C_n-Cu(II) (n=5—7,9—11), has two solid polymorphs with different m.p.s in monotropic relationship. Each of the ligands substituted by R=C_7H_{15} – $C_{12}H_{25}$(C_7-Ligand – C_{12}-Ligand) is a smectogen. It became to be clear that the discotic mesogen complexes can be obtained even when the non-mesomorphic ligands(n=4—6) are used.

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7. Occasionally, the texture resembled to "finger print" could be observed.

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10. See Tables 3 and 4 in this paper.