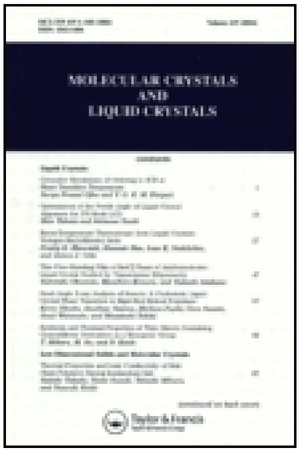

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Discotic Liquid Crystals of Transition Metal Complexes, 3: the First-Established Discotic Lamellar Phase in Bis[1,3- di(p-n-alkoxyphenyl)propane-1,3-dionato]copper(II)

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Discotic Liquid Crystals of Transition Metal Complexes, 3: the First-Established Discotic Lamellar Phase in Bis[1,3-di(*p-n*-alkoxyphenyl)propane-1,3-dionato]copper(II)

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A new series of disk-like complexes, bis[1,3-di(*p-n*-alkoxyphenyl)propane-1,3-dionato]copper(II) (abbreviated as C_nO-Cu, $n = 1-12$), has been synthesized. It was found that each of the complexes from C_3O-Cu to $C_{12}O$-Cu is a discogen, and that each of them has only one discotic mesophase. C_3O-Cu is the first compound substituted by the shortest side chains in the discogen, so far as we know. The mesomorphic textures could be observed as mosaic textures for C_3O-Cu ~ C_5O-Cu and as big broken fan-like textures for C_6O-Cu ~ $C_{12}O$-Cu. The eutectic point calculated from Le Chatelier-Schröder relations agrees well with the found eutectic point in the binary phase diagram between C_8O-Cu and C_8-Cu. This is the first example of such agreement in the discogens of the organic transition metal complexes. It has been established for the first time from X-ray diffraction measurements that each of the discotic mesophases in the complexes from C_6O-Cu to $C_{12}O$-Cu is a discotic lamellar phase. It becomes clear that this discotic mesophase is truly a new discotic lamellar phase (D_L) different from the mesophase in C_{10}-Cu, and that the D_L phase has a structure in which the molecules tilt to the layers.

Keywords: discotic liquid crystal, transition metal complex, bis(β-diketonato)copper(II), discotic lamellar phase

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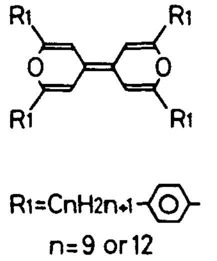
INTRODUCTION

At present, mesophases of disk-like molecules are divided into two classes: the columnar phase (D_{ho}, D_{hd}, $D_{rd(P2^1/a)}$, $D_{rd(P2/a)}$, $D_{rd(C2/m)}$, and $D_{ob,d}$) and the discotic nematic phase (N_D).[1,2] However, in this classification, thermotropic mesophases of the four long chains substituted bipiran-4-ylidenes **1**[3] and bis(β-diketonato)-copper(II) **2**[4] are not included, because the structures of the mesophases have not yet been resolved.[2,5] A. M. Levelut deduced from experiments with X-ray diffraction for the complex **2** (abbreviated as C_{10}-Cu) that it forms a lamellar phase having a thickness of 29Å, although the precise structure could not be determined.[6] From microscopic observation of defects in the mesomorphic texture of C_{10}-Cu, J. Billard suggested that this mesophase is "both a columnar and layered discophase."[7] He also reported that a stepped-drop texture (the same as the smectic A phase) could be observed. We previously synthesized two copper complexes similar to complex **2**, C_8-Cu (substituted by R_2 = *n*-octylphenyl) and C_8O-Cu (substituted by R_2 = *n*-octyloxyphenyl). Miscibility tests between C_8-Cu and C_{10}-Cu or C_8O-Cu revealed that each of these mesophases is surely a discotic mesophase but not crystal.[8] Furthermore, the following relations were found:



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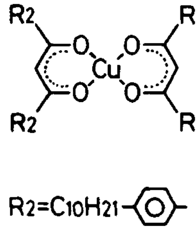


2

$$D \text{ phase in } C_{10}\text{-Cu} = D_2 \text{ phase in } C_8\text{-Cu} \qquad (1)$$

$$D \text{ phase in } C_8\text{O-Cu} = D_1 \text{ phase in } C_8\text{-Cu} \qquad (2)$$

In the previous paper,[9] we reported that a series of disk-like complexes, bis[1,3-di(*p-n-alkyl*phenyl)propane-1,3-dionato]copper(II) (abbreviated as C_n-Cu, n = 1 ~ 12), were synthesized for the first systematic investigations on the effect of the alkyl chain length for the discotic mesomorphism. It was found that each of the complexes from C_4-Cu to C_{12}-Cu is a discogen, and that each of the complexes, C_7-Cu and C_8-Cu, has two discotic mesophases and C_9-Cu has three discotic mesophases.

In the present paper, a new series of disk-like complexes, bis[1,3-di(*p-n-alkoxy*phenyl)propane-1,3-dionato]copper(II) (abbreviated as C_nO-Cu, $n = 1 \sim 12$), has been synthesized also for the purpose of investigating the effect of the alkoxy chain length for the discotic mesomorphism. As a result, it was found that each of the complexes from C_3O-Cu to $C_{12}O$-Cu is a discogen, and that each of them has only one discotic mesophase in contrast to the C_n-Cu complexes. C_3O-Cu is the first compound substituted by the shortest side chains in the discogens, so far as we know. Furthermore, each of the complexes from C_6O-Cu to $C_{12}O$-Cu could easily afford a supercooled discophase at room temperature. When X-ray diffraction experiments were carried out on the supercooled discophases at room temperature, each of them gave three or four narrow lines for low Bragg angles; their spacings are exactly in the ratios 1 : 1/2 : 1/3 : (1/4), characteristic of a lamellar phase. This means that each of the discophases in the complexes from C_6O-Cu to $C_{12}O$-Cu is a lamellar phase. It is the first time that the lamellar phase has been established in the mesophases of disk-like molecules. So, we propose that these lamellar phases are termed "discotic lamellar phase: D_L."

Hereupon, the following basic question must be raised: are these discotic lamellar phases of C_6O-Cu $\sim$ $C_{12}O$-Cu the same as the "both a columnar and layered discophase" of the C_{10}-Cu deduced and suggested by Levelut and Billard?[6,7] From the relations (1) and (2) mentioned above, the followng relation (3) can be derived easily:

$$D \text{ phase in } C_{10}\text{-Cu} \neq D \text{ phase in } C_8O\text{-Cu} \qquad (3)$$

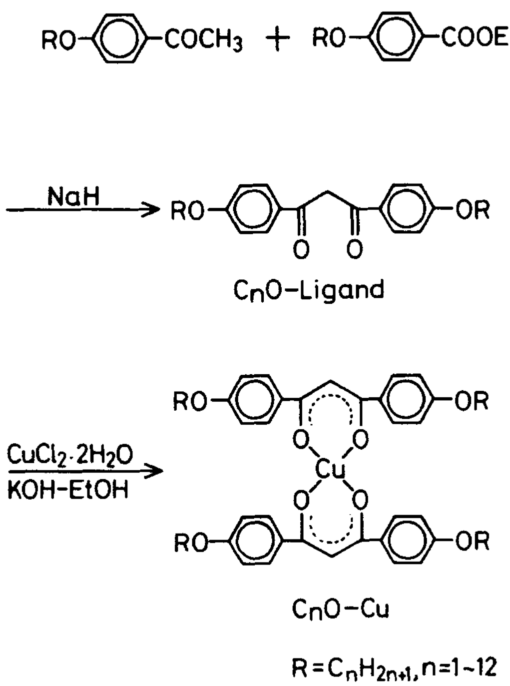
Therefore, the D phase in C_8O-Cu is truly another new discotic lamellar phase. S. Chandrasekhar predicted theoretically the existence of columnar smectic phases from MacMillan's mean field model.[10] Therefore, the discophase of the C_nO-Cu complexes ($n = 6$–12) may be such examples of the discotic smectic phase.

In this paper, we wish to report the synthesis and the new discotic mesomorphism of a series of the C_nO-Cu complexes.

EXPERIMENTAL

Synthesis

The synthetic route of the present bis(β-diketonato)-copper(II) complexes is shown in Scheme 1. The detailed procedures were almost



SCHEME 1 Synthetic route for the bis(β-diketonato)-copper(II) complexes, C_nO-Cu.

the same as the case of the octyloxy substituent described in the previous paper.[8] Elemental analysis data etc. for these corresponding ligands exhibiting both multiple melting behavior and smectic mesomorphism were already reported in the previous paper.[11] Table I lists elemental analysis data, recrystallization solvents, and the crystalline shapes obtained from recrystallization for the complexes; bis[1,3-(di-*p*-*n*-alkoxyphenyl)propane-1,3-dionato]copper(II) (alkoxy: RO = $C_nH_{2n+1}O$, n = 1–12; abbreviated as C_nO-Cu).

Measurements

The phase transformation behaviors of these complexes synthesized here were observed by a polarizing microscope equipped with a heating plate controlled by a thermoregulator, Mettler FP 80 and FP 82, and measured with a differential scanning calorimeter, Rigaku Denki Thermoflex TG-DSC. To distinguish between the solid polymorphs and the supercooled discotic liquid crystals in the complexes, X-ray diffraction powder patterns were also measured with Cu-K_α radiation,

TABLE I

Elemental analysis data, recrystallization solvents, and the crystalline shapes obtained from recrystallization for the complexes, C_nO-Cu

n	Elemental analysis Found(Calcd.) % C	H	Recrystallization solvent	Crystalline shape
1	64.57(64.81)	5.02(4.80)	Ethyl acetate	Rod
2	66.67(66.51)	5.71(5.58)	Ethyl acetate	Rod
3	67.71(67.95)	6.20(6.25)	Ethyl acetate	Needle(K_1)
4	69.22(69.19)	6.82(6.82)	Ethyl acetate	Needld(K_2)
5	70.23(70.27)	7.40(7.31)	Ethyl acetate	Needle(K_2)
6	71.23(71.22)	7.95(7.75)	n-Hexane	Rod(K_2)
7	71.76(72.06)	8.10(8.13)	n-Hexane	Rod(K_2)
8	73.29(72.80)	8.58(8.48)	n-Hexane	Rod(K_3)
9	73.46(73.47)	8.82(8.78)	n-Hexane	Plate(K_3)
10	73.88(74.07)	9.09(9.06)	n-Hexane	Plate
11	74.59(74.61)	9.38(9.31)	n-Hexane	Plate
12	75.26(75.11)	9.67(9.54)	n-Hexane	Needle

using a Rigaku Geigerflex. Each sample of the supercooled discophases from C_6O-Cu to $C_{12}O$-Cu (for X-ray diffraction measurements) could be prepared easily in the same manner, i.e., by rapidly cooling an isotropic liquid on a plate glass heated over the clearing point of the complex down to room temperature.

RESULTS AND DISCUSSION

1. Discotic mesomorphism of Bis(β-diketonato)copper(II) complexes, C_nO-Cu

It was found that each of the copper(II) complexes, C_3O-Cu ~ $C_{12}O$-Cu, is a discogen, and that each of these discogen complexes has only one discotic mesophase in contrast to the C_n-Cu complexes reported previously.[9] The phase transition temperatures (T_t) and the enthalpy changes (ΔH_t) of the present complexes, C_nO-Cu, were summarized in Table II. All transition temperatures of these complexes are plotted against the number of carbon atoms in the alkoxy chain in Figure 1.

TABLE II

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

n	$\xrightarrow[\Delta H_t(\text{kcal/mol})]{T_t(^{\circ}\text{C})}$	
1	$K \xrightarrow[5.8]{289.4}$ I.L.(decomp.)	
2	$K \xrightarrow[14.0]{241.9}$ I.L.	
3	$K_1 \xrightarrow[4.0]{153.1} K_2 \xrightarrow[1.5]{185.4} D \xrightarrow[12.3]{214.0}$ I.L.	
4	$K_2 \xrightarrow[5.6]{181.1} D \xrightarrow[13.9]{210.8}$ I.L. $K_1 \xrightarrow[6.6]{173.3} D$	
5	$K_2 \xrightarrow[5.2]{171.3} D \xrightarrow[20.3]{211.6}$ I.L. $K_1 \xrightarrow[5.4]{148.2} D$	
6	$K_2 \xrightarrow[3.2]{152.9} D \xrightarrow[15.3]{182.4}$ I.L. $K_1 \xrightarrow[1.0]{125.7} D$	
7	$K_2 \xrightarrow[12.8]{111.2} D \xrightarrow[12.1]{180.8}$ I.L. $K_1 \xrightarrow[3.9]{93.9} D$	
8	$K_3 \xrightarrow[14.0]{93.1} D \xrightarrow[16.6]{173.3}$ I.L. $K_1 \xrightarrow[0.79]{21.8} K_2 \xrightarrow[2.89]{82.5} D$	a

TABLE II *Continued*

n	$\xrightarrow[\Delta H_t(\text{kcal/mol})]{T_t(^\circ C)}$
9	$K_3 \xrightarrow[25.9]{94.5} D \xrightarrow[14.9]{170.7} \text{I.L.}$ $K_1 \xrightarrow[3.1]{55.6} K_2 \xrightarrow[0.5]{84.2} D$
10	$K \xrightarrow[10.9]{81.9} D \xrightarrow[15.1]{166.6} \text{I.L.}$
11	$K \xrightarrow[26.8]{87.6} D \xrightarrow[14.8]{161.2} \text{I.L.}$
12	$K \xrightarrow[29.4]{74.3} D \xrightarrow[12.4]{154.1} \text{I.L.}$

Phase nomenclatures: K = crystal, D = discotic liquid crystal, I.L. = isotropic liquid.

[a] See main text and Ref. 8.

1.1. Discotic mesomorphism of C_3O-Cu. C_3O-Cu is the first compound substituted by the shortest lateral chains in the discogens, so far as we know.

C_3O-Cu presented three endothermic transitions at 153.1°C (ΔH_t = 4.0 kcal/mol), 185.4°C (ΔH_t = 1.5 kcal/mol), and 214.0°C (ΔH_t = 12.3 kcal/mol). The phase between 185.4°C and 214.0°C is a discotic mesophase of this complex. The texture of the phase is a mosaic texture as shown in the top photomicrograph in Figure 2. The texture change from the K_2 crystal to the discotic mesophase could be observed clearly even in the heating stage. This mosaic texture of C_3O-Cu is very similar to the mosaic texture of the $D_{rd(C2/m)}$ phase in HBT(2*d*, *n* = 6: 2,3,6,7,10,11-*h*exa(*p*-*n*-hexyloxy)*b*enzoyloxy-*t*riphenylene) reported by C. Destrade et al.[12] The same mosaic texture could be observed also for C_4O-Cu and C_5O-Cu.

1.2. Discotic mesomorphism of C_8O-Cu. Different from these mosaic textures of C_3O-Cu ~ C_5O-Cu, big broken fan-like textures could be observed for the other complexes from C_6O-Cu to $C_{12}O$-Cu. The big broken fan-like texture of C_8O-Cu is shown in the upper photomicrograph of Figure 3. The texture seems to resemble the broken fan-shaped texture of smectic C.[13] As mentioned below, the

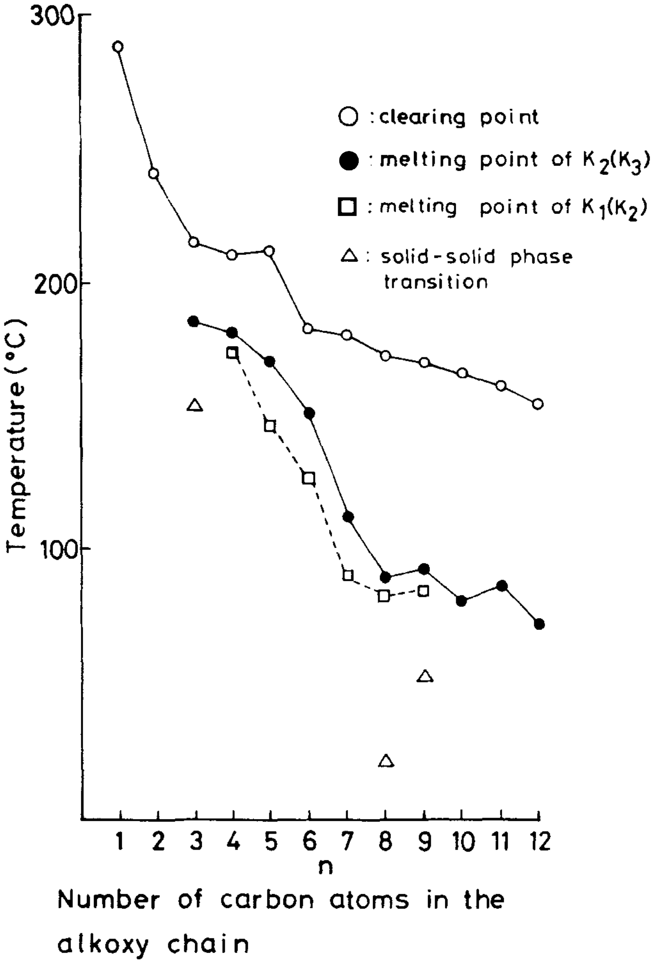


FIGURE 1 Phase transition temperatures vs. number of carbon atoms in the alkoxy chain for the bis(β-diketonato)-copper(II) complexes, C_nO-Cu.

discophase in C_8O-Cu is truly a new discotic lamellar phase established by X-ray diffraction experiments. Although two crystalline phases, K_1 and K_2, were reported in the previous papers,[8] one more crystalline phase K_3 was found by further investigation and is reported in this paper. The K_3 crystals could be obtained only from recrystallization from *n*-hexane. It gave the upper DSC thermogram in Figure 4. When the K_3 crystals were heated up from room temperature, these crystals melted into discotic mesophases at 93.1°C (ΔH_f = 14.0 kcal/mol) of the m.p. of the K_3 phase: on further heating,

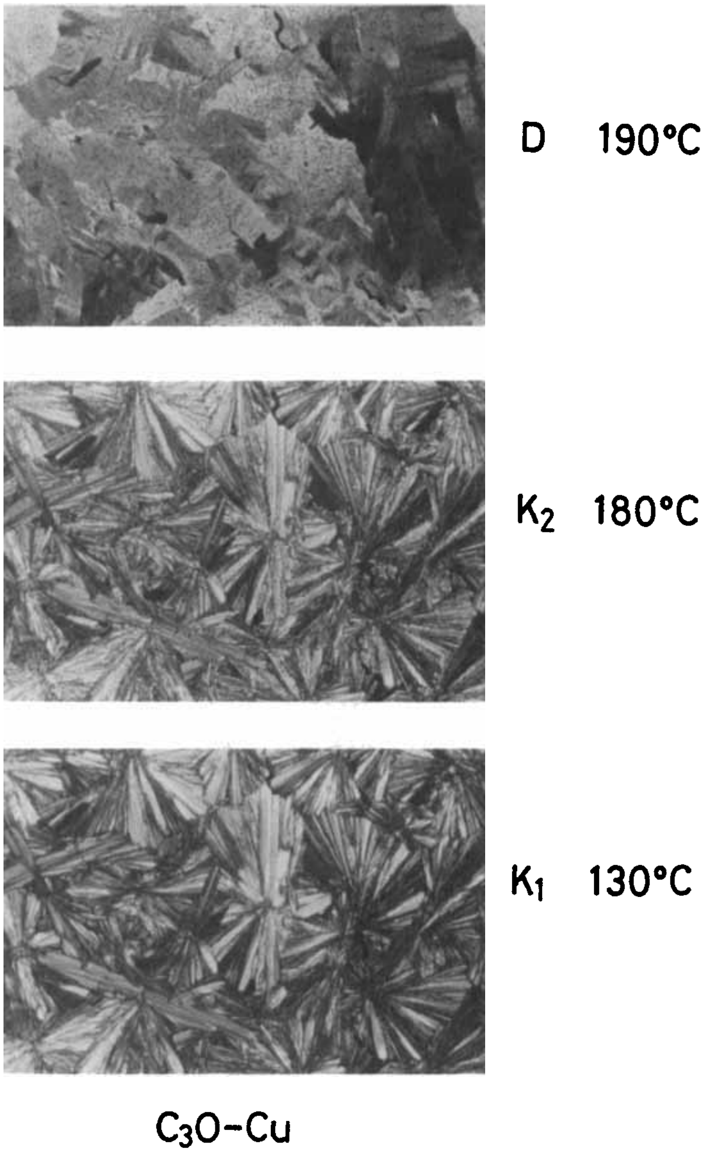


FIGURE 2 Photomicrographs of the state changes of C_3O-Cu complex in the heating stage.

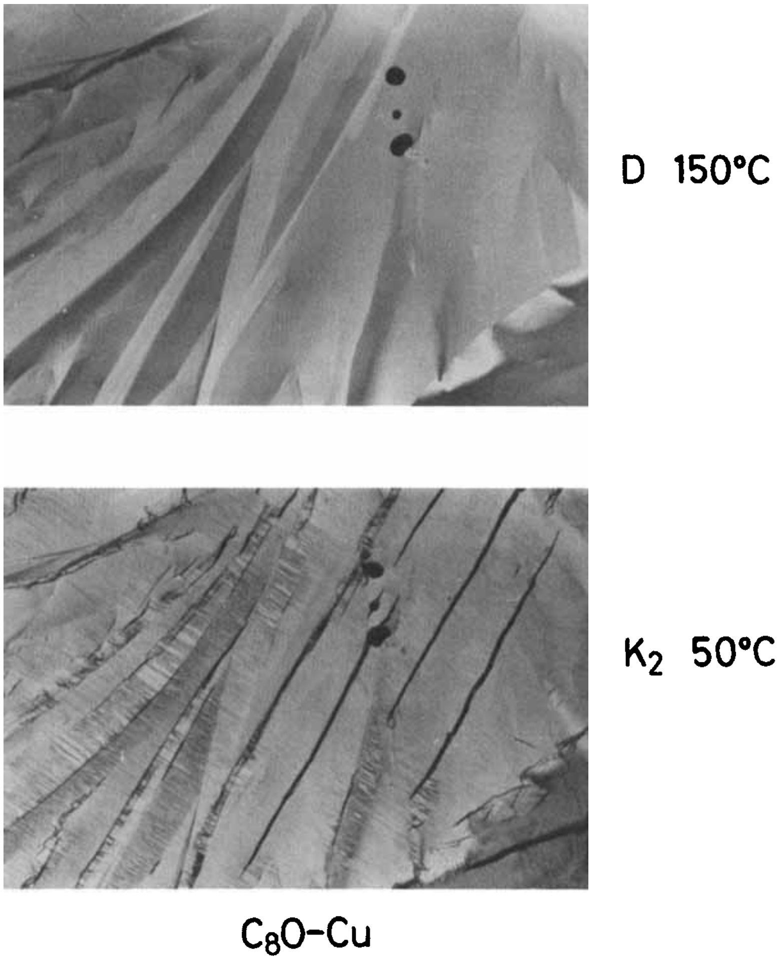


FIGURE 3 Photomicrographs of the state changes of C_8O-Cu complex in the cooling stage.

the discotic mesophases transformed into an isotropic liquid at 173.3°C (ΔH_t = 16.6 kcal/mol) of the clearing point. When the isotropic liquid was cooled slowly to room temperature, it turned into K_1 crystals. These K_1 crystals gave the lower DSC thermogram in Figure 4. The thermal behavior of these K_1 crystals has already been reported in the previous paper.[8] The K_3 crystal mentioned above could not be obtained by any thermal treatments.

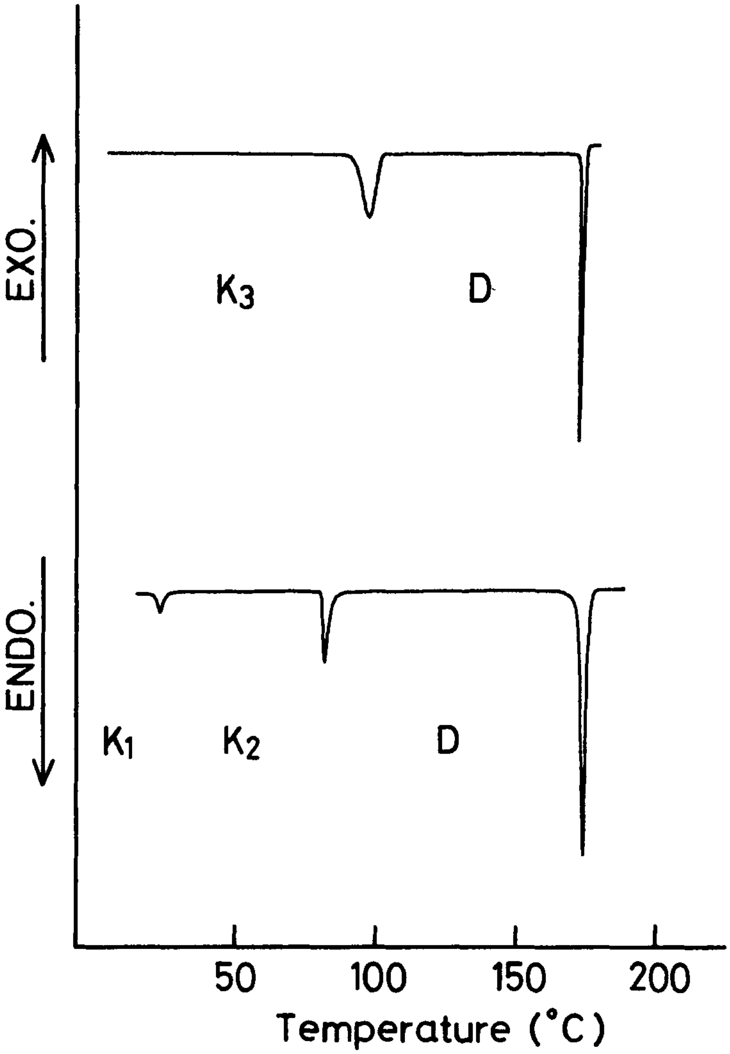


FIGURE 4 DSC thermograms of K_1 and K_3 of the C_8O-Cu complex. Both heating rates are 10°C/min.

In the previous papers,[8] we reported that the binary phase diagram between C_8O-Cu and C_8-Cu was constructed by a miscibility test, and that the discotic phase of C_8O-Cu was totally miscible in the D_1 phase of C_8-Cu. The eutectic point exists in 82 wt% of C_8O-Cu at 62°C. We tried here to calculate the eutectic point from the Le Chatelier-Schröder relations[14] using a microcomputer. The calculated value was

79.6 wt% of C_8O-Cu at 62.7°C.[15] As shown in Figure 5, fairly good agreement between the calculated and found values can be observed. This is the first example of such agreement in the discogens of the organic transition metal complexes.[16]

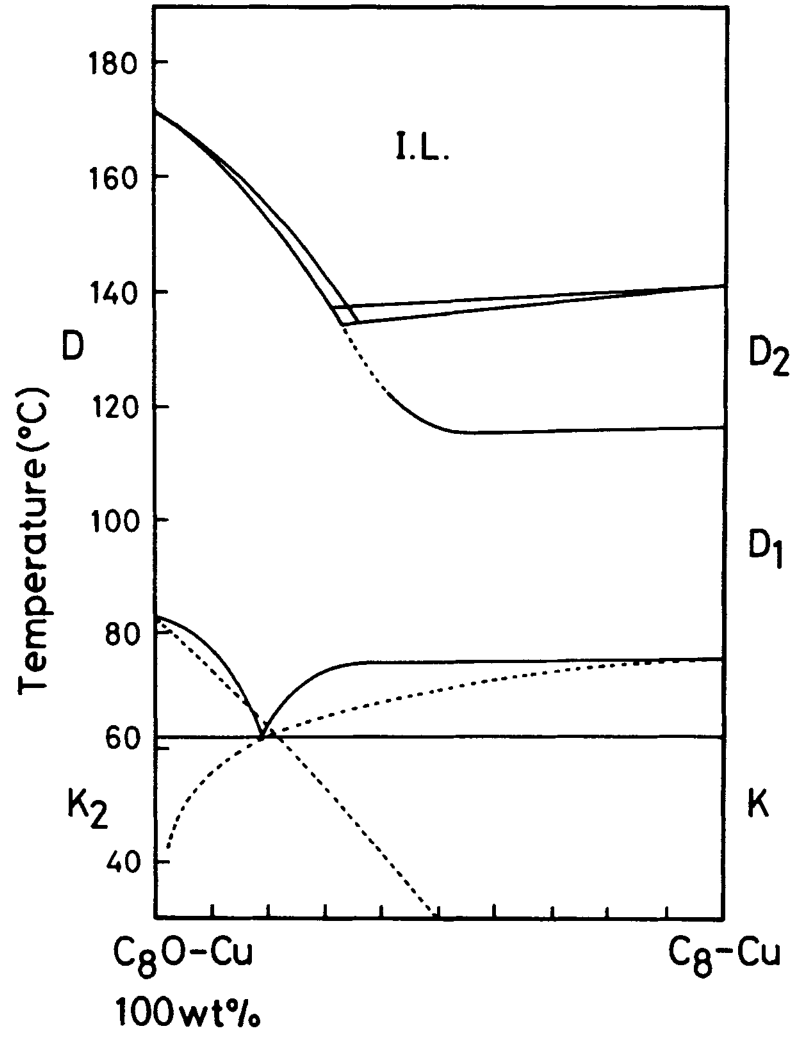


FIGURE 5 Miscibility diagram of C_8O-Cu and C_8-Cu.[8] In this figure the dashed lines correspond to the calculated values from the Le Chatelier-Schröder relations.[14,15]

2. Discotic lamellar phase of C_nO-Cu (n = 6–12)

2.1. The first-established discotic lamellar phases: D_L. Each of the complexes from C_6O-Cu to $C_{12}O$-Cu could easily afford a supercooled discophase at room temperature, when the isotropic liquid heated over the clearing point was cooled rapidly down to room temperature.

Figure 6 shows a DSC thermogram of supercooled discophase of $C_{11}O$-Cu. When the crystals of $C_{11}O$-Cu were heated from room temperature, they gave the upper thermogram in Figure 6. However, when the sample in the DSC cell, which had been heated over the

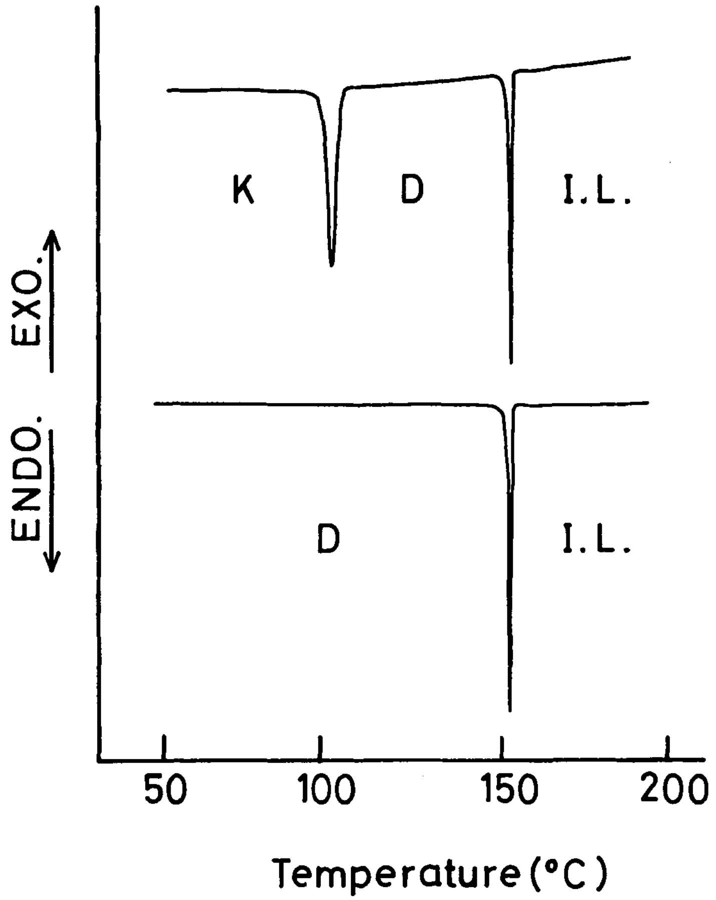


FIGURE 6 DSC thermograms of K and supercooled D phases of the $C_{11}O$-Cu complex.

clearing point of the $C_{11}O$-Cu, was taken out from the DSC apparatus and quickly put onto a stainless steel plate at room temperature, the sample gave the lower thermogram in Figure 6. Only one endothermic peak corresponding to the clearing point was observed. It is obvious from these thermograms that the supercooled discophase of the complex can be obtained at room temperature by such manners mentioned above. So, we thought here that if such a supercooled discophase of the present complex was prepared for X-ray diffraction measurement, the structure of the discophase could be observed easily at room temperature by using an ordinary X-ray apparatus. The sample of the supercooled discophase of $C_{11}O$-Cu could also be prepared easily on a plate glass for X-ray diffraction measurement at room temperature. When a portion of the sample for X-ray diffraction was measured by the DSC, the same thermogram as the lower one in Figure 6 was obtained. Therefore, the supercooled discophase of $C_{11}O$-Cu could be obtained surely even on the plate glass. Using this sample, an X-ray diffraction experiment was carried out on the supercooled discophase at room temperature. For low Bragg angles, four narrow lines were obtained. Their spacings are exactly in the ratios $1:1/2:1/3:1/4$, which is characteristic of a lamellar phase.

The other supercooled discophases of the C_nO-Cu complexes could be obtained at room temperature for $n = 6$–10, and $n = 12$. As shown in Figure 7, each X-ray diffraction pattern of the supercooled discophases gives three or four lines for low Bragg angles. As listed in Table III, their spacings for each of the complexes were also exactly in the ratios $1:1/2:1/3:(1/4)$. This means that each discophase of the complexes from C_6O-Cu to $C_{12}O$-Cu is a lamellar phase. It is the first time that the lamellar phases in the mesophases of disk-like molecules were established. So, we propose here that these lamellar phases are termed "discotic lamellar phase: D_L." If these lamellar phases were termed "discotic smectic phase: S_D" like "discotic nematic phase: N_D," they would be confused with the smectic D phase.

Hereupon, the following basic question must be raised: are these discotic lamellar phases the same as a "both columnar and layered discophase" of the C_{10}-Cu which was deduced and suggested by A. M. Levelut[6] and J. Billard?[7] Considering from the relations (1) and (2) obtained from the miscibility diagrams in the previous papers,[8] one more relation (3) can be derived easily:

$$D \text{ phase in } C_{10}\text{-Cu} \quad = D_2 \text{ phase in } C_8\text{-Cu} \quad = (D_{L2}) \qquad (1)$$

$$D \text{ phase in } C_8O\text{-Cu} \quad = D_1 \text{ phase in } C_8\text{-Cu} \quad = (D_{L1}) \qquad (2)$$

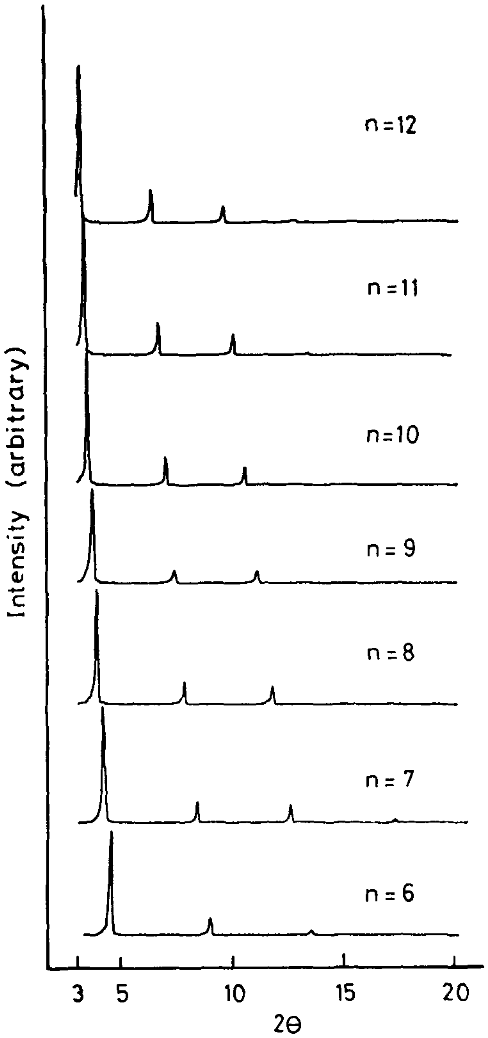


FIGURE 7 X-ray diffraction patterns of the supercooled D phases of the complexes, C_nO-Cu (n = 6–12).

$$D \text{ phase in } C_{10}\text{-Cu}(D_{L2}) \neq D \text{ phase in } C_8O\text{-Cu} = (D_{L1}) \quad (3)$$

Therefore, the D phase in C_8O-Cu is truly another new discotic lamellar phase (D_{L1}).

Each of the discophases of the complexes from C_6O-Cu to $C_{12}O$-Cu is thought to be the same discotic lamellar phase as that of C_8O-Cu(D_{L1}),

TABLE III

Observed spacings dÅ and calculated spacings using relation d_1 × Ratio for the C_nO-Cu complexes (n = 6–12)

n		d_1	d_2	d_3	d_4
	dÅ	19.81	9.87	6.56	
6	d_1 x Ratio[a]	19.81	9.91	6.60	
	I/I_1[b]	100	16	4	
	dÅ	21.45	10.61	7.05	5.14
7	d_1 x Ratio	21.45	10.73	7.15	5.36
	I/I_1	100	18	15	3
	dÅ	23.01	11.39	7.56	5.20
8	d_1 x Ratio	23.01	11.51	7.67	5.75
	I/I_1	100	19	16	1
	dÅ	23.94	12.01	7.99	
9	d_1 x Ratio	23.94	11.97	7.98	
	I/I_1	100	14	12	
	dÅ	25.46	12.65	8.42	
10	d_1 x Ratio	25.46	12.73	8.49	
	I/I_1	100	21	14	
	dÅ	26.53	13.25	8.85	6.62
11	d_1 x Ratio	26.53	13.27	8.84	6.63
	I/I_1	100	18	15	1
	dÅ	27.87	13.85	9.24	6.96
12	d_1 x Ratio	27.87	13.94	9.29	6.97
	I/I_1	100	21	11	1

[a] Ratio = 1, 1/2, 1/3, and 1/4 for d_1, d_2, d_3, and d_4, respectively.

[b] I/I_1 = relative intensity.

since all of the mesomorphic textures show the same as that of the C_8O-Cu—a big broken fan-like texture. However, each texture of the complexes from C_3O-Cu to C_5O-Cu is a mosaic texture different from that of the C_8O-Cu. Since each of the complexes, C_3O-Cu ~ C_5O-Cu, could not afford the supercooled discophase at room temperature, the structures could not be determined. Nevertheless, the

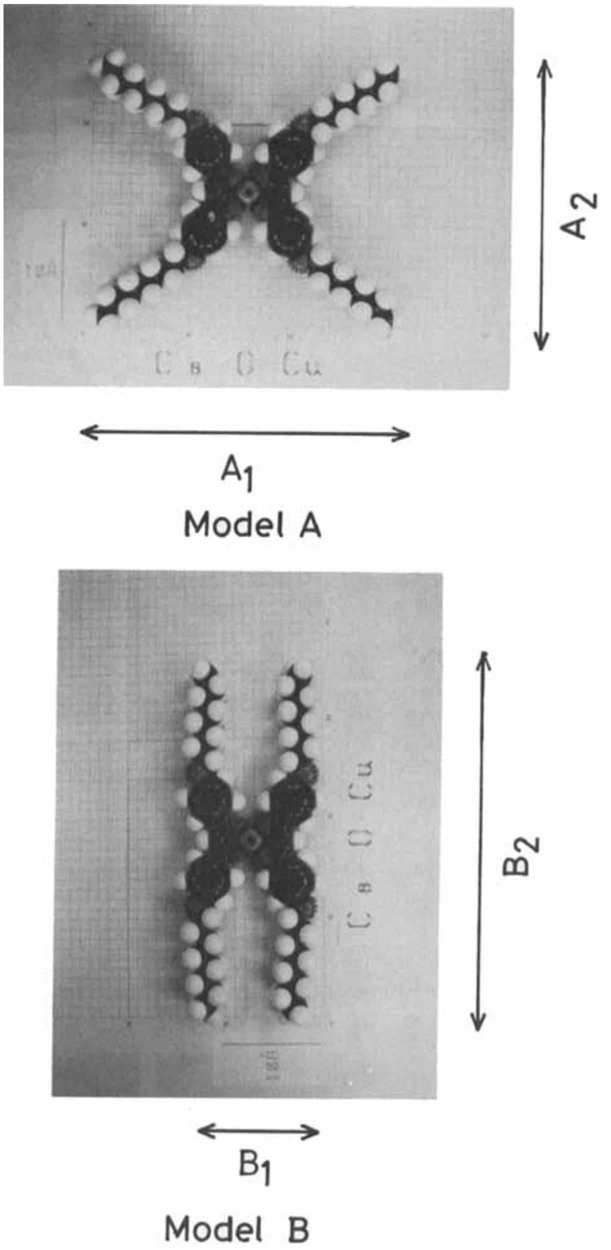


FIGURE 8 C.P.K. molecular models of C_8O-Cu.

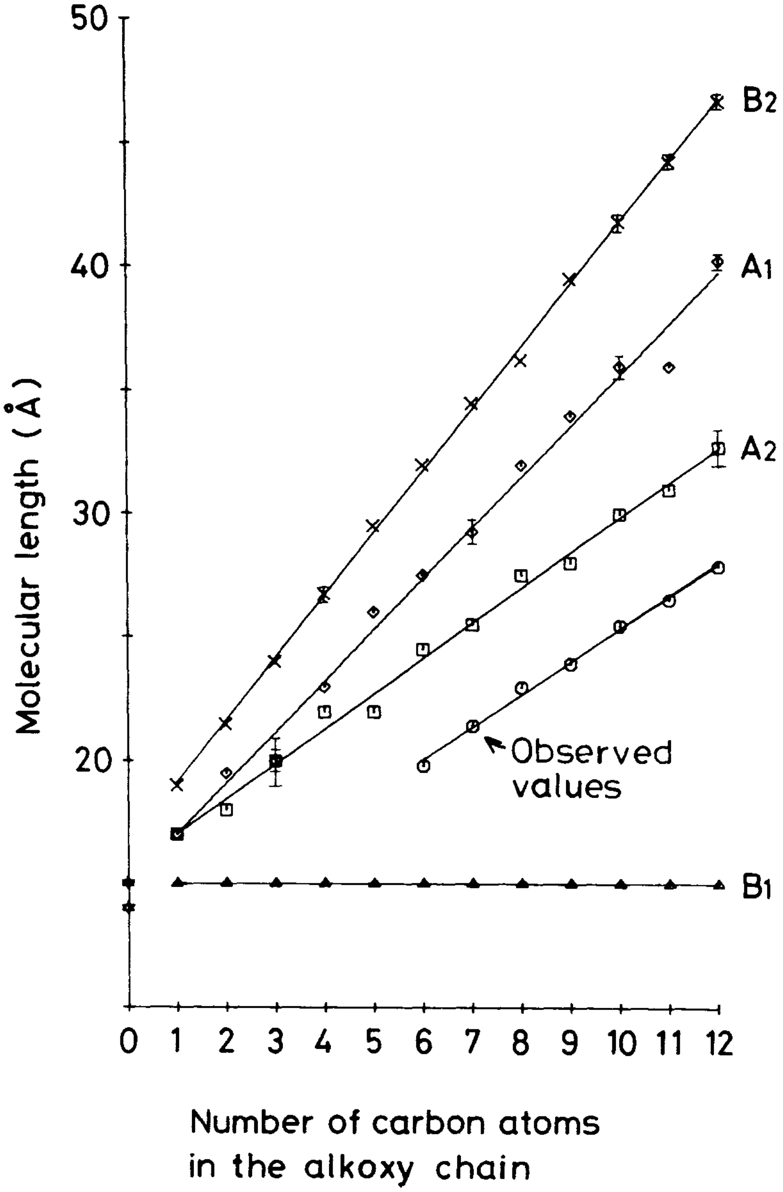


FIGURE 9 Molecular lengths of the C_nO-Cu complexes measured from their C.P.K. models vs. number of carbon atoms in the alkoxy chain. In this figure the values plotted with a circle are the observed spacings for d_1 in Table III.

discophases of the complexes at least from C_6O-Cu to $C_{12}O$-Cu were established to be new discotic lamellar phases.

2.2. Tilt angles of the molecules to the layers in D_L phases. C.P.K. molecular models of the C_nO-Cu complexes were constructed for determining the tilt angles of the molecules to the layers in the D_L phases. As shown in Figure 8, two different molecular models, Model A and Model B, were obtained. The difference between Model A and Model B exists at the positions of the lateral alkoxy chains. Each of the molecular lengths for these two models was measured with an error of 0.5 angstrom. Lengths, A_1, A_2, B_1, and B_2, are indicated in Figure 8. These measured lengths are plotted against the number of carbon atoms in the alkoxy chain in Figure 9. In this figure the values plotted with a circle are the observed spacings d_1 in Table III. Since d_1 is thought to be a distance between the layers in the D_L phase, the tilt angle θ of the molecules (molecular length l) to the layer can be derived from the equation: $\theta = \arcsin(d_1/l)$. This situation is illustrated in Figure 10. The tilt angles are summarized in Table IV. It is obvious from this table that each of the calculated tilt angles is almost constant, even for increasing the molecular lengths: θ = ca. 45 for A_1, ca. 32 for A_2, and ca. 52 for B_1. This means that the molecules from C_6O-Cu to $C_{12}O$-Cu tilt to the layers with a certain constant angle, irrespective of their molecular sizes.

Thus, it becomes clear that the D_L phase in C_nO-Cu complexes (n = 6–12) has a structure in which the molecules tilt to the layers.

2.3. Miscibility tests between D_L phase and smectic C phase. The smectic C phase has the same "tilt and layer structure" as the present

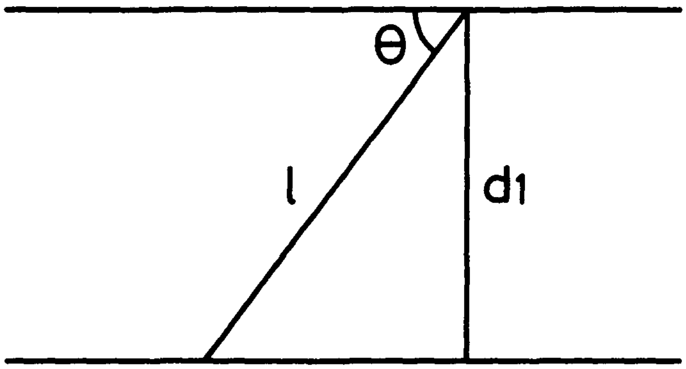


FIGURE 10 Tilt angle θ of the molecules to the layers. d_1 and l are the lamellar spacing and molecular length, respectively.

TABLE IV

Tilt angle of the molecules to the layers

n	Observed Spacing d_1(Å)[a]	Molecular length[l(Å)] determined by molecular model(C.P.K. model)[b]; l	Tilt angle(deg) $\Theta=\arccos(d_1/l)$
6	19.81	$A_1=27.5$	44
		$A_2=24.5$	36
		$B_1=15.0$	-[c]
		$B_2=32.0$	52
7	21.45	$A_1=29.0-29.5$	42-43
		$A_2=25.5$	33
		$B_1=15.0$	-
		$B_2=34.5$	52
8	23.01	$A_1=32.0$	44
		$A_2=27.5$	33
		$B_1=15.0$	-
		$B_2=36.0-36.5$	50-51
9	23.94	$A_1=34.0$	45
		$A_2=28.0$	31
		$B_1=15.0$	-
		$B_2=39.5$	53
10	25.46	$A_1=35.5-36.5$	44-46
		$A_2=30.0$	32
		$B_1=15.0$	-
		$B_2=41.5-42.0$	52-53
11	26.53	$A_1=36.0$	43
		$A_2=31.0$	31
		$B_1=15.0$	-
		$B_2=44.0-44.5$	53
12	27.87	$A_1=40.0-40.5$	46-47
		$A_2=32.0-33.5$	29-34
		$B_1=15.0$	-
		$B_2=46.5-47.0$	53-54

[a] d_1 is the same as d_1 in Table III.
[b] Each of the molecular lengths was determined with an error of 0.5 angstrom.
[c] θ for B_2 cannot be determined because B_2 is always shorter than d_1.

D_L phase. So, miscibility tests were carried out between a standard material of the smectic C phase, 4,4'-di-*n*-dodecyloxyazobenzene,[17] and the C_nO-Cu complex (n = 8 or 12). We found that each of the D_L phases of C_8O-Cu and $C_{12}O$-Cu is immiscible to the smectic C phase. Therefore, the D_L phase is thought to be a new discotic lamellar phase which is different from the classic smectic C phase.

IV. CONCLUSION

A new series of disk-like complexes, bis[1,3-di(*p*-*n*-alkoxyphenyl)propane-1,3-dionato]copper(II) (abbreviated as C_nO-Cu, n = 1–12), has been synthesized. It was found that each of the complexes from C_3O-Cu to $C_{12}O$-Cu is a discogen, and that each of them has only one discotic mesophase. C_3O-Cu is the first compound substituted by the shortest side chains in the discogen, so far as we know. The mesomorphic textures could be observed as mosaic textures for C_3O-Cu ~ C_5O-Cu and as big broken fan-like textures for C_6O-Cu ~ $C_{12}O$-Cu. The eutectic point calculated from the Le Chatelier-Schröder relations agrees well with the found eutectic point in the binary phase diagram between C_8O-Cu and C_8-Cu. This is the first example of such agreement in the discogens of the organic transition metal complexes. It has been established for the first time from X-ray diffraction measurements that each of the discotic mesophases in the complexes from C_6O-Cu to $C_{12}O$-Cu is a discotic lamellar phase. It becomes clear that this discotic mesophase is truly a new discotic lamellar phase (D_L), different from the mesophase in C_{10}-Cu, and that the D_L phase has a structure in which the molecules tilt to the layers.

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12. See Figure 6 in Ref. 2.

13. See Figure 10 in the following: H. Sackmann and D. Demus, *Mol. Cryst. Liq. Cryst.*, **21**, 239 (1973).
14. E. C.-H. Hsu and J. F. Johnson, *ibid.*, **20**, 177 (1973): Le Chatelier-Schröder relations:

$$\ln X_1 = \Delta H_{f1}/R(1/T_1 - 1/T)$$

$$\ln(1 - X_1) = \Delta H_{f2}/R(1/T_2 - 1/T)$$

15. This calculation was carried out using the following values:

$$\Delta H_{f1} = 28.6 \text{ kcal/mol}, \ T_1 = 76.1°\text{C for } C_8\text{-Cu}$$

$$\Delta H_{f2} = 2.89 \text{ kcal/mol}, \ T_2 = 82.5°\text{C for } C_8O\text{-Cu}$$

16. See the examples of the organic discogens in the following paper: P. Le Barny, J. Billard and J.-C. Dubois, *Liq. Cryst. Ordered Fluid*, **4**, 57 (1984).
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