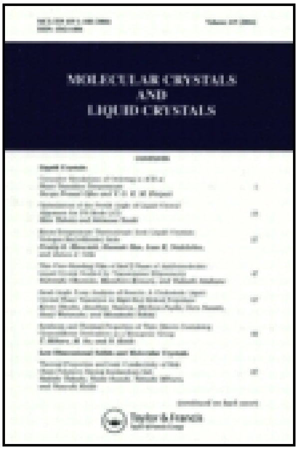


Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Discotic Liquid Crystals of Transition Metal Complexes, 5: Double Melting Behavior and Double Clearing Behavior of Discogens

Kazuchika Ohta [a] , Hiroshi Ema [a] , Hiromitsu Muroki [a] , Iwao Yamamoto [a] & Kei Matsuzaki [a]

[a] Department of Functional Polymer Science, Faculty of Textile Science & Technology, Shinshu University, Ueda, 386, Japan

Version of record first published: 28 Mar 2007.

Mol. Cryst. Liq. Cryst., 1987, Vol. 147, pp. 61–78
Photocopying permitted by license only

Printed in the United States of America

Discotic Liquid Crystals of Transition Metal Complexes, 5: Double Melting Behavior and Double Clearing Behavior of Discogens

KAZUCHIKA OHTA, HIROSHI EMA, HIROMITSU MUROKI, IWAO YAMAMOTO and KEI MATSUZAKI

Department of Functional Polymer Science, Faculty of Textile Science & Technology, Shinshu University, Ueda, 386, Japan

(*Received August 29, 1986; in final form December 16, 1986*)

Two new octa-substituted disk-like bis(β-diketonato)copper(II) complexes, $8C_8$—Cu and $8C_8O$—Cu, have been synthesized. The same type of octa-substituted copper complexes, $8C_9O$—Cu, which was synthesized for the first time by A. M. Giroud-Godquin *et al.*, has also been prepared. The thermal behavior of these three complexes was investigated by means of microscopic observations and DSC measurements. It was found that the $8C_8$—Cu exhibits not a discotic mesomorphism but a *usual* double melting behavior via the isotropic liquid, and that the $8C_9O$—Cu exhibits an *unusual* double melting behavior via the discophase which had not been reported by A. M. Giroud-Godquin *et al.* Furthermore, it was found that the $8C_8O$—Cu exhibits a new thermal phenomenon of "double clearing behavior" which is originated from a superheating of the transition from the crystalline phase to the discotic phase. Such double clearing behavior of the $8C_8O$—Cu is the first example in the mesomorphic compounds, so far as we know.

Keywords: discotic liquid crystal, transition metal complex, Bis(β-diketone)copper(II), double melting behavior, double clearing behavior

I. INTRODUCTION

In the previous papers[1,2] we suggested that the double melting behavior[3] of long chain substituted compounds is a thermal behavior close to mesomorphism.

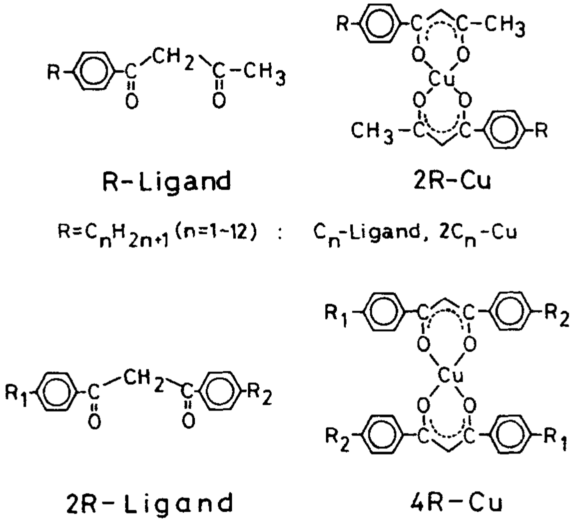
As summarized in Table I, the long chain substituted β-diketones and their corresponding copper(II) complexes exhibit so-called "multiple melting behavior"[3] and/or mesomorphism depending upon the number of the lateral long chains, the kinds of the chains, and the length of the chains. The di-substituted "crank-like" copper(II) complexes, 2R—Cu ($R{=}C_nH_{2n+1}$, n = 1–12), were synthesized in an attempt to obtain new *classic* (rod-like) mesomorphic compounds containing a transition metal.[4] Although each of the complexes does not have a classic mesophase, it exhibits multiple melting behavior: double melting for $n = 0-5,8,12$; triple melting for $n = 7, 9–11$. The tetra-substituted disk-like copper(II) complexes, 4R—Cu ($R_1{=}R_2{=}C_8H_{17}S$; $R_1{=}C_8H_{17}S$, $R_2{=}C_8H_{17}SO_2$; $R_1{=}R_2{=}C_nH_{2n+1}$ (n = 1–12); $R_1{=}R_2{=}C_nH_{2n+1}O$ (n = 1–12)), were synthesized in attempts to get new *discotic* mesomorphic compounds containing a transition metal.[1,5,6,7,8,9] The copper(II) complexes substituted by electron-withdrawing groups, $4C_8(S,S)$—Cu and $4C_8(S,SO_2)$—Cu, exhibit double melting behavior.[1] On the other hand, the copper(II) complexes substituted by electron-donating groups, $4C_n$—Cu (n = 4–12) and $4C_nO$—Cu (n = 3–12), exhibit discotic mesomorphism: both $4C_7$—Cu and $4C_8$—Cu have two discotic mesophases; $4C_9$—Cu has three discotic mesophases;[6] each of the $4C_nO$—Cu ($n = 3-12$) complexes has only one discophase and the discophase has been established to be a new discotic lamella phase (D_L) for $4C_6O$—Cu ~ $4C_{12}O$—Cu. Therefore, it is obvious from Table I that the thermal behaviors of the long-chain-substituted copper(II) complexes are strongly controlled by the number of the lateral long chains, the kinds of the chains, and the length of the chains.

So, in focusing our further interest on the substituent effect, two new octa-substituted disk-like complexes, bis[1,3-bis(m,p-di-n-octylphenyl)propane-1,3-dionato]copper(II) ($8C_8$—Cu) and bis[1,3-bis(m,p-di-n-octyloxyphenyl)propane-1,3-dionato]copper(II) ($8C_8O$—Cu), have been synthesized. The same type of octa-substituted copper(II) complex, bis[1,3-bis(m,p-di-n-nonyloxyphenyl)-propane-1,3-dionato]copper(II) ($8C_9O$—Cu), was synthesized for the first time by A. M. Godquin-Giroud *et al.*[10] These three copper(II) complexes, $8C_8$—Cu, $8C_8O$—Cu, and $8C_9O$—Cu, were investigated here precisely for their thermal behaviors. It was found that the $8C_8$—Cu exhibits a "usual" double melting behavior via an isotropic liquid, and that the $8C_9O$—Cu exhibits an "unusual" double melting behavior via a discotic mesophase which had not been reported by A. M. Godquin-Giroud *et al.*[10,11] Furthermore, it was found for the first

TABLE I

Melting behavior and mesomorphism of the long-chain-substituted β-diketones and their corresponding copper(II) complexes.

R-Ligand	Ref.	2R-Ligand	Ref.	4R-Ligand	Ref.
*$R{=}C_nH_{2n+1}$ ($n=0-12$) single melting	**4**	*$R_1{=}R_2{=}C_8H_{17}S$ double melting	**1**	*$R{=}C_8H_{17}$ liquid	this work
		*$R_1{=}C_8H_{17}S, R_2{=}C_8H_{17}SO_2$ double melting	**1**	*$R{=}C_8H_{17}O, C_9H_{19}O$ single melting	**10** + this work
		*$R_1{=}R_2{=}C_nH_{2n+1}$ ($n=0-12$) single melting ($n=0-6$) smectic ($n=7-12$)	**6,8,9**	*$R{=}C_7H_{15}O, C_{11}H_{23}O$ single melting	**11**
		*$R_1{=}R_2{=}C_nH_{2n+1}O$ ($n=1-12$) triple melting ($n=1$) double melting ($n=2-7$) smectic ($n=8-12$)	**2**		
2R—Cu	**Ref.**	**4R—Cu**	**Ref.**	**8R—Cu**	**Ref.**
*$R{=}C_nH_{2n+1}$ ($n=0-12$) double melting ($n=0-5$, 8, 12) triple melting ($n=7$, 9–11)	**4**	*$R_1{=}R_2{=}C_8H_{17}S$ double melting	**1**	*$R{=}C_8H_{17}$ double melting	this work
		*$R_1{=}C_8H_{17}S, R_2{=}C_8H_{17}SO_2$ double melting	**1**	*$R{=}C_9H_{19}O$ unusual double melting discotic, D_h	**10** + this work
		*$R_1{=}R_2{=}C_nH_{2n+1}$ ($n=1-12$) discotic ($n=4-12$)	**6, 8, 9**	*$R{=}C_8H_{17}O$ double clearing discotic	this work
		*$R_1{=}R_2{=}C_nH_{2n+1}O$ ($n=1-12$) discotic ($n=3-12$) discotic lamella phase, D_L ($n=6-12$)	**7**	*$R{=}C_7H_{15}O, C_{11}H_{23}O$ discotic, D_h	**11**



Formula Long-chain-substituted β-diketone ligands and their copper(II) complexes.
R_1=R_2=C_nH_{2n+1} (n = 1–12): $2C_n$-Ligand, $4C_n$—Cu;
R_1=R_2=$C_nH_{2n+1}O$ (n = 1–12): $2C_nO$-Ligand, $4C_nO$—Cu;
R_1=R_2=$C_8H_{17}S$: $2C_8S$-Ligand, $4C_8S$—Cu;
R_1=$C_8H_{17}S$, R_2=$C_8H_{17}SO_2$: $2C_8(S,SO_2)$-Ligand, $4C_8(S,SO_2)$—Cu

time that the $8C_8O$—Cu exhibits a new thermal phenomenon of "double clearing behavior."

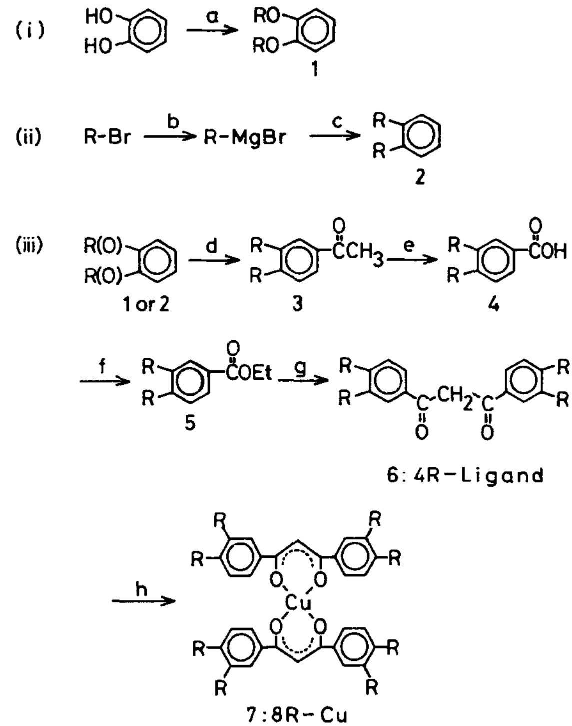
So, we wish to report in this paper the thermal behavior of these three octa-substituted copper(II) complexes.

II. EXPERIMENTAL

Synthesis

The synthetic route of the present complexes is shown in Scheme 1. The detailed procedures for the β-diketones **6** and their corresponding copper(II) complexes **7** are as follows:

*1,3-Bis(m,p-di-n-octyloxyphenyl)propane-1,3-dione (abbreviated as $4C_8O$-Ligand, **6** $R = C_8H_{17}O$)* A mixture of 7.0g (18mmol) of 3,4-di-n-octyloxyacetophenone and 7.5g (18 mmol) of ethyl 3,4-di-n-octyloxybenzoate in dimethoxyethane was refluxed for 12 hours in the presence of 0.6g of 60% sodium hydride (22mmol). Small portions of ethanol and than water were added very carefully to the resulting orange stew. After acidifying the basic stew with dilute hydrochloric



	6	7
$R=C_8H_{17}$	$4C_8$-Ligand	$8C_8$-Cu
$R=C_9H_{19}O$	$4C_9O$-Ligand	$8C_9O$-Cu
$R=C_8H_{17}O$	$4C_8O$-Ligand	$8C_8O$-Cu

Scheme 1.[a] Synthesis of the octa-substituted bis(β-diketonato)copper(II) complexes (8R—Cu) and their corresponding ligands (4R-Ligand).

[a]Reagents and conditions: (a) KOH/EtOH, RBr, reflux under N_2 gas, 6h (b) Mg/THF, r.t., 5h; (c) 1) $NiCl_2(Ph_2PCH_2CH_2PPh_2)_2$, 2) o-dichlorobenzene, reflux 10h; (d) CH_3COCl, $AlCl_3/CH_2Cl_2$, $-60°C$, 6h; (e) 10% aq. NaOCl/dioxane, 60°C, 6h; (f) EtOH, concentrated H_2SO_4, reflux, 5h; (g) compound 3 in this scheme, NaH/dimethoxyethane, reflux, 12h; (h) KOH/EtOH, $CuCl_2 \cdot 2H_2O$/EtOH, stir, 1h.

acid, the product was extracted with ether. Evaporation gave a crude $4C_8O$-Ligand, which was recrystallized from ethanol to give slightly yellow crystals (11.3g). Yield 85.2%, m.p. = 79.5–79.7°C, I.R. (KBr disk, cm^{-1}): 1460–1600 (β-diketone), ^{1}H-NMR ($CDCl_3$,TMS): δ_{ppm} = 0.9 (t,12H,CH_3), 1.3 (*m*,48H,—$(CH_2)_6$—), 4.0 (t, 8H,—OCH_2—), 4.5 (s, keto CH_2), 6.7 (*s*, enol =CH), 6.8–7.5 (m, 6H, aromatic), 17.2 (s, enol OH).[12] Anal. Found (Calcd. for $C_{47}H_{76}O_6$): C 76.78% (76.58), H 10.44% (10.39). MS(m/e): 736 (M^+).

1,3-Bis(m,p-di-n-nonyloxyphenyl)propane-1,3-dione(abbreviated as $4C_9O$-Ligand, 6 R=$C_9H_{19}O$) This compound was obtained in the same manner as $4C_8O$-Ligand mentioned above. Yield 84%, m.p. = 79.5–80.3°C,[13] I.R. (KBr disk, cm^{-1}): 1460–1600 (β-diketone), ^{1}H-NMR ($CDCl_3$, TMS): δ_{ppm} = 0.9 (t, 12H, CH_3), 1.3 (m, 56H,—$(CH_2)_7$—), 4.0 (t, 8H, —OCH_2—), 4.5 (s, keto =CH), 6.7 (s, enol =CH), 6.8–7.5 (m, 6H, aromatic), 17.1 (s, enol OH).[12] Anal. Found (Calcd. for $C_{51}H_{84}O_6$): C 77.18% (77.22), H 10.64% (10.67). MS(m/e): 792 (M^+).

1,3-Bis(m,p-n-octylphenyl)propane-1,3-dione (abbreviated as $4C_8$-Ligand, 6 R=C_8H_{17}) This compound was obtained as a slightly orange liquid. Yield 70.5%, I.R. (liquid film, cm^{-1}): 1470–1610 (β-diketone), ^{1}H-NMR ($CDCl_3$, TMS): δ_{ppm} = 0.9 (*t*, 12H, —CH_3), 1.3 (m, 48H, —$(CH_2)_6$—), 2.7 (t, 8H, —CH_2—), 4.6 (s, keto CH_2), 6.8 (s, enol =CH), 7.1–7.7 (m, 6H, aromatic), 17.1 (s, enol OH).[12] Anal. Found (Calcd. for $C_{47}H_{76}O_2$): C 83.63% (83.87), H 11.40% (11.38).

Bis[1,3-bis(m,p-di-n-octyloxyphenyl)propane-1,3-dionato]copper(II) (abbreviated as $8C_8O$—Cu, 7 R=$C_8H_{17}O$) To a solution of potassium hydroxide (0.30g, 4.0mmol) in ethanol (50ml) were added 2.0g (3.3mmol) of $4C_8O$-Ligand and then an ethanolic solution of 0.30g (1.7mmol) of cupric chloride. This mixture solution was stirred for 1 hour. The precipitate was collected and washed with hot water and ethanol. It was recrystallized from ethyl acetate to give pale green cotton-like crystals (0.92g) in 36% yield. Anal. Found (Calcd. for $C_{94}H_{150}O_{12}Cu$): C 73.67% (73.52), H 9.93% (9.85).

Bis[1,3-bis(m,p-di-n-nonyloxyphenyl)propane-1,3-dionato]copper(II) (abbreviated as $8C_9O$—Cu, 7 R=$C_9H_{19}O$) This complex was obtained and purified in the same manner as $8C_8O$—Cu. Yield 40%. Pale green cotton-like crystals. Anal. Found (Calcd. for $C_{102}H_{166}O_{12}Cu$): C 74.22% (74.34), H 10.05% (10.15).

Bis[1,3-bis(m,p-di-octylphenyl)propane-1,3-dionato]-copper(II) (abbreviated as $8C_8$—Cu, 7 R=C_8H_{17}) This complex was obtained as green wedge-shaped crystals. Yield 29.9%. Anal. Found (Calcd. for $C_{94}H_{150}O_4Cu$): C 80.29% (80.20), H 10.76% (10.74).

Measurements

The phase transformation behavior of these compounds was observed with a polarizing microscope equipped with a heating plate controlled by a thermoregulator, Mettler FP80 and 82, and measured with differential scanning calorimeters, 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

In Table II the phase transitions for the octa-substituted bis(β-diketonato)copper(II) complexes, $8C_8$—Cu, $8C_9O$—Cu, and $8C_8O$—Cu, are summarized. The detailed thermal behavior of these octa-substituted complexes is as follows:

1. *Usual double melting behavior of the $8C_8$—Cu*

Usual double melting behavior means a thermal behavior of melting twice *via an isotropic liquid* on one heating stage for a non-mesomorphic compound. The present complex, $8C_8$—Cu, exhibits the *usual* double melting behavior via an isotropic liquid as follows:

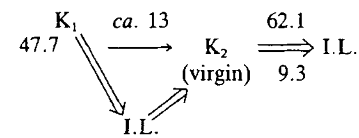
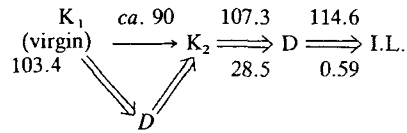
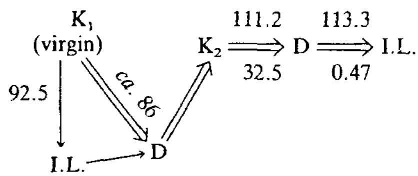
The complex $8C_8$—Cu was recrystallized from ethyl acetate to give wedge-shaped crystals (K_2 phase in Table II). When this virgin crystal (K_2) is heated up from room temperature on a heating plate equipped with a polarizing microscope, the crystal melts into an isotropic liquid (I.L.) at 62.1°C of the m.p. of K_2. By rapid cooling of the isotropic liquid over the m.p. of K_2 to room temperature, another crystalline phase K_1 (stripe-like crystal) could be obtained. When the K_1 crystal is heated up from room temperature, it transforms partially into the K_2 phase very slowly from room temperature and the remained *K_1 crystal melts into I.L. at 47.7°C* of the m.p. of K_1 crystal. The I.L. resolidifies into the K_2 crystals (wedge-shaped) and on further heating, the *K_2 crystal melts into the I.L. at 62.1°C* of the m.p. of the K_2 phase. Thus, the double melting behavior of the $8C_8$—Cu could be observed by a polarizing microscope.

This double melting behavior was also confirmed by DSC measurements, as shown in Figure 1. Typical DSC thermograms of the double melting behavior[14] of the K_1 crystal could be obtained at the heating rate of ≦20°C/min. Peak I (*ca.* 13°C), denoted in Figure 1, corresponds to the solid-solid phase transition from K_1 to K_2. The precise temperature of the solid-solid phase transition could not, however, be determined by microscopic observations, because the solid-solid phase transition is very slow and because the superheating

TABLE II

Sequence of the state changes, phase transition temperatures (T_t), and enthalpy changes (ΔH_t) for the octasubstituted bis(β-diketonato)copper(II) complexes ($8C_8$—Cu, $8C_9O$—Cu, and $8C_8O$—Cu).

$\Longrightarrow$ Main route $\longrightarrow$ Sub route

Compound	Phase[a] $\xrightarrow[\Delta H_t \text{ (kcal/mol)}]{T_t(°C)}$ Phase
$8C_8$—Cu	: Usual double melting
	
$8C_9O$—Cu[b]	: Unusual double melting
	
$8C_8O$—Cu:	: Double clearing[c]
	

[a]Phase nomenclature: K = crystal, D = discotic liquid crystal, I.L. = isotropic liquid.
[b]Although this complex was reported for the first time by A. M. Giroud-Godquin *et al.*, such unusual double melting behavior was not reported by them. See Ref. 10.
[c]A new definition we propose in this paper. See main text.

of K_1 crystals occurs easily. Although the superheating of K_1 crystals originates such double melting behavior, at the same time this makes it difficult to detect the precise temperature of the solid-solid phase transition from K_1 to K_2. Peak II and peak IV correspond to the melting of K_1 crystals and the melting of K_2 crystals, respectively. Exothermic peak III, between peak II and peak IV, corresponds to the recrystallization from the melt of K_1 crystals to K_2 crystals. The

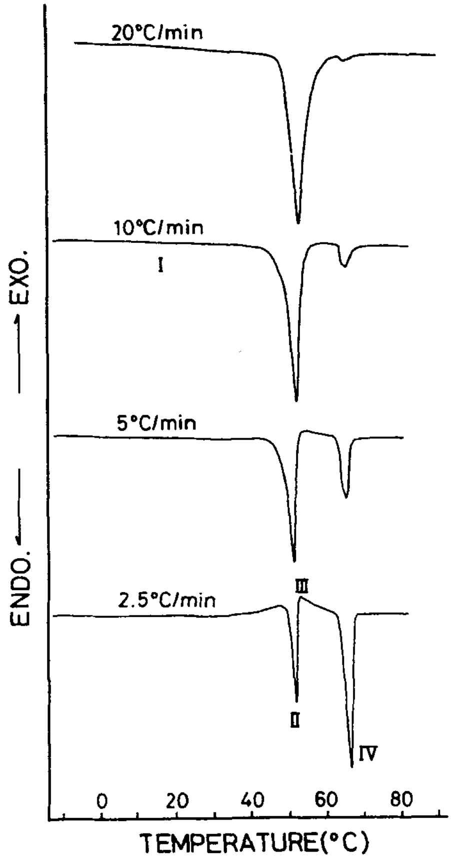


FIGURE 1 DSC thermograms of K_1 of $8C_8$—Cu for different heating rates. Peaks denoted with I, II, III and IV in this figure are explained in the main text.

ratio of peak IV (due to the melting of the K_2 phase) to peak II (due to the melting of the K_1 phase) increases with a slower heating rate. This fact means that K_1 crystals transform largely into K_2 crystals by the solid-solid phase transitions from K_1 to K_2, corresponding to peak I with a slower heating rate. This is a characteristic of double melting behavior.[15]

It is very interesting with regard to the effect of the number of the lateral chains on mesomorphism that although the present octa-substituted complex $8C_8$—Cu exhibits not discotic mesomorphism but such double melting behavior, the tetra-substituted complex, $4C_8$—Cu, reported previously, shows discotic mesomorphism.[5]

2. *Unusual double melting behavior of the 8C$_9$O—Cu*

Discotic mesomorphism of the 8C$_9$O—Cu has already been reported by A. M. Giroud-Godquin *et al.*[10] However, we found that the 8C$_9$O—Cu exhibits *unusual* double melting behavior *via the discotic mesophase* which had not been reported by A. M. Giroud-Godquin.[10,11] The sequence of the state changes for the complex 8C$_9$O—Cu is summarized in Table II.

The virgin crystals obtained by recrystallization from ethyl acetate are pale green cotton-like crystals (K$_1$ phase). X-ray diffraction powder patterns of the K$_1$ crystal are clearly different from those of the K$_2$ crystal, as summarized in Table III. When these virgin crystals (K$_1$) are heated on a heating plate equipped with a polarizing microscope from room temperature, it transforms in a very small portion into the K$_2$ phase slowly, and the remained K$_1$ crystals *melt into a discotic mesophase at 103.4°C* of the m.p. of the K$_1$ phase. The discophase exhibits fluidity and fan-shaped texture. By holding the temperature at 103.4°C, needle-like crystals (K$_2$ phase) are recrystallized slowly from the discophase. On further heating, the K$_2$ crystals *melt into the discophase at 107.3°C* of the m.p. of the K$_2$ phase. The discophase also exhibits fluidity and the same fan-shaped texture mentioned above. The discophase has been established as a hexagonal

TABLE III

X-Ray diffraction data with relative intensities (I/I_1) for the four strongest lines in each solid polymorph of 8R—Cu complexes.

8C$_8$—Cu	K$_1$	dÅ	unmeasurable[a]			
		I/I$_1$				
	K$_2$	dÅ	21.68	4.27	6.04	3.82
		I/I$_1$	100	22	8	8
8C$_9$O—Cu	K$_1$	dÅ	27.92	14.10	4.42	17.51
		I/I$_1$	100	15	13	11
	K$_2$	dÅ	24.55	20.54	4.39	4.01
		I/I$_1$	100	25	17	14
8C$_8$O—Cu	K$_1$	dÅ	26.74	18.13	6.74	13.54
		I/I$_1$	100	33	16	15
	K$_2$	dÅ	25.11	19.76	4.31	10.72
		I/I$_1$	100	21	7	7

[a]The pure solid polymorph of K$_1$ could not be obtained at room temperature because of the low temperature solid-solid phase transition at *ca.* 13°C. All attempts gave the mixture of K$_1$ and K$_2$ by any thermal treatments at room temperature (25°C).

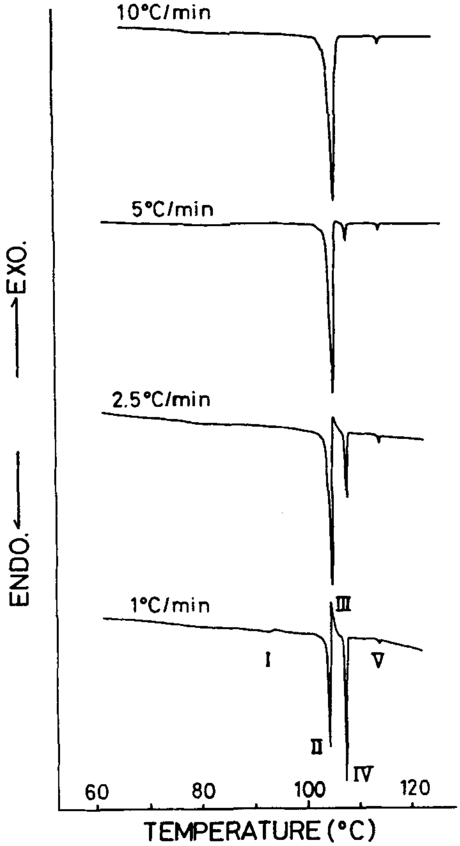


FIGURE 2 DSC thermograms of K_1 of $8C_9O$—Cu for different heating rates. Peaks denoted with I, II, III, IV and V in this figure are explained in the main text.

columnar phase D_h by A. M. Giroud-Godquin *et al.*[10,11] On further heating, the D_h phase clears into the isotropic liquid at 114.6°C.

Thus, unusual double melting behavior via the discophase of the $8C_9O$—Cu could be observed by means of the polarizing microscope. The unique double melting behavior was also confirmed by DSC measurements, as shown in Figure 2. Very typical DSC thermograms of the double melting behavior[14,15] of the K_1 crystal could be obtained at the heating rate of $\leqq$5°C/min. In this figure, the ratio of peak IV (due to the melting of the K_2 phase) to peak II (due to the melting of the K_1 phase) increases with a slower heating rate, which is the same case for the $8C_8$—Cu mentioned above. This is a characteristic of double melting behavior. Thus, the $8C_9O$—Cu exhibits *unusual* double melting behavior via the discophase.

3. *Double clearing behavior of the $8C_8O$—Cu*

W. C. McCrone expressed in his review of solid polymorphism,[16] "One significant way in which mesomorphs differ from crystals and resemble liquids lies in the fact, whereas a solid-solid transformation may be superheated, the 'transition' from a crystalline phase to a mesomorph behaves like a melting point in that superheating does not occur." However, we found for the $8C_8O$—Cu that a transition from the crystalline phase K_1 to the discophase D is superheated to show a new thermal behavior of *double clearing*.

A sequence of state changes for the $8C_8O$—Cu is shown by photomicrographs in Figure 3.

Photo No. 1: virgin cotton-like crystals (K_1 phase) of the $8C_8O$—Cu were set between the cross nicols on a hot plate at room temperature.

Photo No. 2: when the sample in Photo No. 1 was heated up to 90.0°C, a phase transition (K_1 to D) was observed. By pressing the cover glass of another sample of the present complex at 86.0°C, a fairly good fluidity with birefringence could be observed, as shown in Figure 4-a.

Photo No. 3: when the sample in Photo No. 2 was heated up to 108.9°C, it could be observed that the sample *cleared into an isotropic liquid*. See Figure 4-b in more detail.

Photo No. 4: by holding the temperature of the sample in Photo No. 3 for 1 hour, small needle-like crystals (K_2) were formed from the isotropic liquid at 108.9°C. See Figure 4-b in more detail.

Photo No. 5: when the sample in Photo No. 4 was heated up and the temperature was held at 112.4°C, the K_2 crystals started to melt into the discophase at 111.2°C and a mesomorphic texture appeared in this photo.[17]

Photo No. 6: when the sample in Photo No. 5 was heated up to 113.3°C, *the discophase cleared again into the isotropic liquid*. (See Figure 5 for the discotic textures obtained from the isotropic liquid in the cooling stage.)

Thus, the double clearing behavior could be observed by a polarizing microscope.

This double clearing behavior of the $8C_8O$—Cu was also confirmed by DSC measurements, as shown in Figure 6. Peak I (at *ca*. 86°C) and peak II (at 92.5°C), denoted in this figure, correspond to the melting from K_1 crystals to the D phase and the clearing from K_1

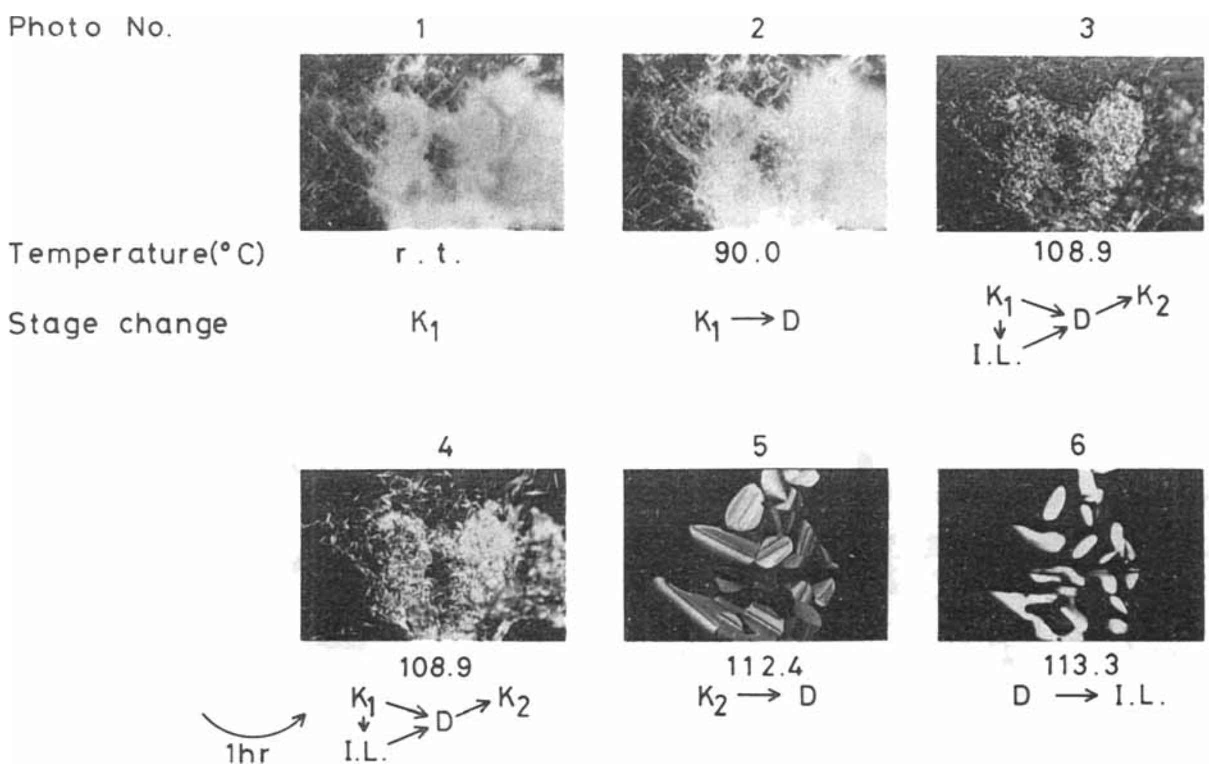


FIGURE 3 Photomicrographs of the double clearing behavior of $8C_8O$—Cu.

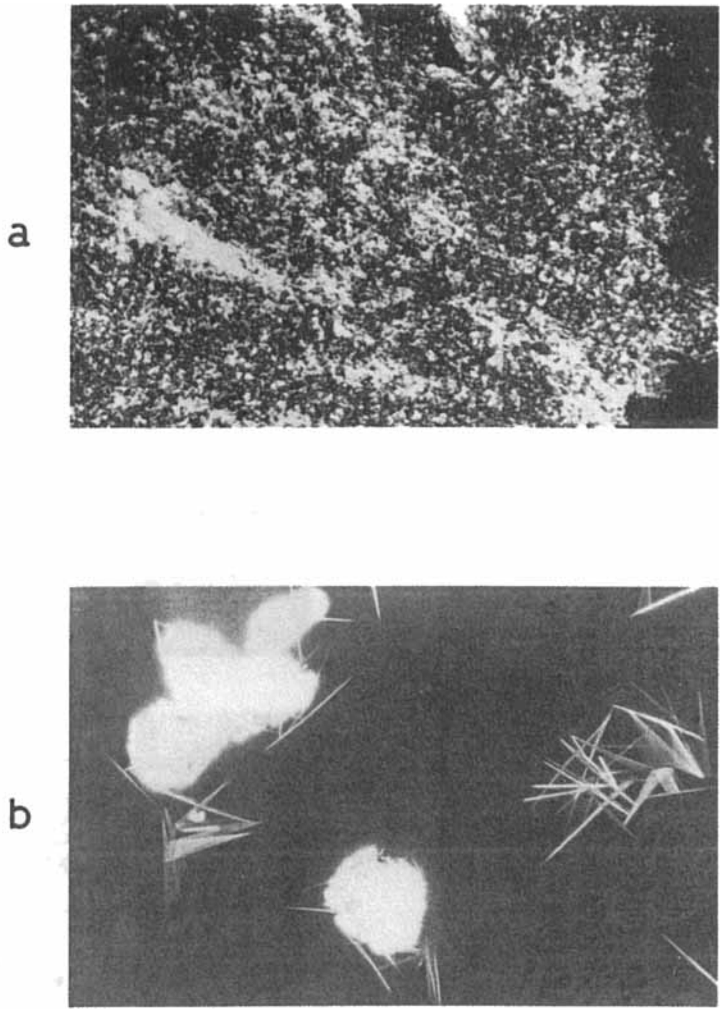
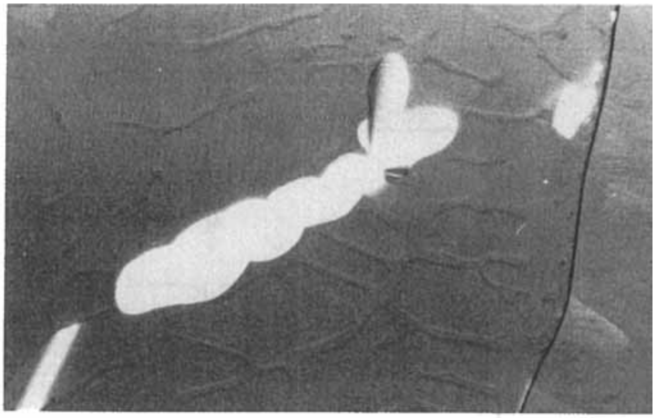


FIGURE 4 Photomicrographs of $8C_8O$—Cu.
(a) when the virgin crystals of the $8C_8O$—Cu were heated up to 86°C and the cover glass was pressed, it showed fluidity with birefringence. (b) when the virgin crystals (K_1 phase) of the $8C_8O$—Cu at room temperature were set on a hot plate at 110.0°C, they melted into the D phase and cleared into isotropic liquid and then the D phase and the I.L. were recrystallized slowly into needle-like crystals (K_2 phase).

crystals to the I.L., respectively. Exothermic peak III corresponds to the recrystallization from the D phase and from the I.L. to K_2 crystals. Peak IV (at 111.2°C) and peak V (at 113.3°C) correspond to the melting from K_2 crystals to the D phase and the clearing from the D a



b

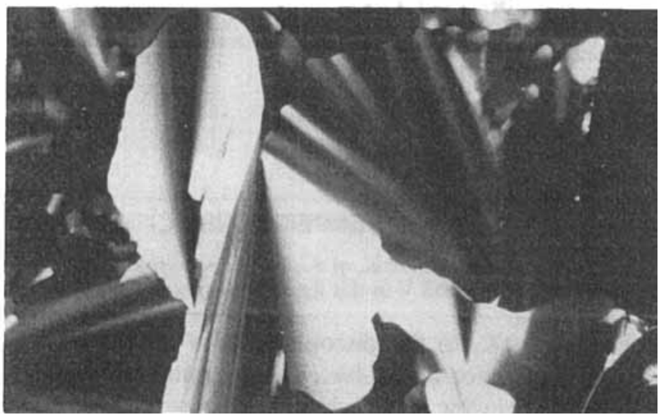


FIGURE 5 Optical textures of the mesophase of $8C_8O$—Cu at 111.2°C (a) and 110.0°C (b) on cooling from the isotropic liquid.

phase to the I.L., respectively. It is noteworthy that no weight losses were observed by thermogravimetric measurements for all transitions, and that the ratio of peak II (due to the clearing from the K_1 to the I.L.) to peak I (due to the melting from the K_1 to the D phase) increases with a rapider heating rate. These facts mean that since the superheating of the melting from the K_1 phase to the D phase occurs largely due to a rapider heating rate, the clearing from K_1 phase to the I.L. can be observed much clearly for a rapider heating rate.

Thus, we found for the $8C_8O$—Cu that the transition from the

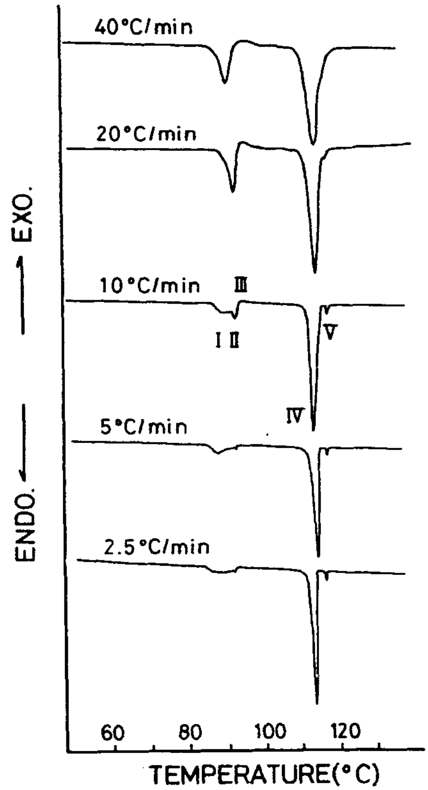


FIGURE 6 DSC thermograms of K_1 of $8C_8O$—Cu for different heating rates. Peaks denoted with I, II, III, IV and V in this figure are explained in the main text.

crystalline phase K_1 to the discophase D is superheated to show a new thermal behavior of *double clearing*, although W. C. McCrone expressed in his review that such a superheating of a transition from a crystalline phase to a mesophase does not occur.[16] Such *double clearing behavior* of the $8C_8O$—Cu is the first example for mesomorphic compounds, so far as we know.

4. *New definition of clearing*

Hereupon, we needed to modify the definition of "clearing." Conventionally, "clearing" is termed a transition *only from a liquid crystalline phase to an isotropic liquid phase* for a mesomorphic compound, as summarized in Table IV. However, when the definition is applied strictly to the thermal behavior of the present complex $8C_8O$—Cu, the transition *from the* K_1 crystal to the I.L. at 92.5°C

TABLE IV

Conventional and new definitions of melting and clearing

Phase[a] transition	Conventional definition	New definition
Melting	(i) Transition from K to I.L. for a non-mesomorphic compound (ii) Transition from K to L.C. for a mesomorphic compound	same
Clearing	Transition *only from L.C.* to I.L. for a mesomorphic compound	Transition *from L.C. and/or K* to I.L. for a mesomorphic compound

[a]Phase nomenclature: K = crystal, L.C. = liquid crystal, I.L. = isotropic liquid

in this mesomorphic compound cannot conventionally be termed "clearing." If the transition at 92.5°C is termed melting, it becomes confusing that both the transition from K_1 to D at 86.0°C and the transition from K_1 to I.L. at 92.5°C are termed as the same "melting." So, we propose here a new definition for "clearing," by which clearing is a transition *from a liquid crystalline phase and/or a crystalline phase* to an isotropic liquid phase for a mesomorphic compound. Using this definition of clearing, the transition from K_1 to D at 86.0°C is "melting," and, on the other hand, the transition from K_1 to I.L. at 92.5°C becomes "clearing." Therefore, we term here the unique thermal behavior of the $8C_8O$—Cu a "double clearing behavior."

IV. CONCLUSION

Two new octa-substituted disk-like bis(β-diketonato)copper(II) complexes, $8C_8$—Cu and $8C_8O$—Cu, have been synthesized. The same type of octa-substituted copper complexes, $8C_9O$—Cu, which was synthesized for the first time by A. M. Giroud-Godquin *et al.*, has also been prepared. The thermal behavior of these three complexes was investigated by means of microscopic observations and DSC measurements. It was found that the $8C_8$—Cu exhibits not a discotic mesomorphism but a *usual* double melting behavior via the isotropic liquid, and that the $8C_9O$—Cu exhibits an *unusual* double melting behavior via the discophase which had not been reported by A. M. Giroud-Godquin *et al.* Furthermore, it was found that the $8C_8O$—Cu exhibits a new thermal phenomenon of "double clearing behavior" which is originated from a superheating of the transition from the crystalline phase to the discotic phase. Such double clearing behavior of the $8C_8O$—Cu is the first example in the mesomorphic compounds, so far as we know.

References

1. K. Ohta, H. Muroki, K. Hatada, I. Yamamoto and K. Matsuzaki, *Mol. Cryst. Liq. Cryst.*, **130**, 249 (1985).
2. K. Ohta, H. Muroki, K. Hatada, A. Takagi, H. Ema, I. Yamamoto and K. Matsuzaki, *Mol. Cryst. Liq. Cryst.*, in press.
3. The multiple melting behavior of glycerides is well known: D. Chapman, *Chem. Rev.*, **62**, 433 (1962).
4. K. Ohta, M. Yokoyama, S. Kusabayashi and H. Mikawa, *J. Chem. Soc., Chem. Commun.*, 392, (1980); K. Ohta, M. Yokoyama, S. Kusabayashi and H. Mikawa, *Mol. Cryst. Liq. Cryst.*, **69**, 131 (1981); K. Ohta, G.-J. Jiang, M. Yokoyama, S. Kusabayashi and H. Mikawa, *Mol. Cryst. Liq. Cryst.*, **66**, 283 (1981); K. Ohta, M. Yokoyama and H. Mikawa, *Mol. Cryst. Liq. Cryst.*, **73**, 205 (1981).
5. K. Ohta, A. Ishii, I. Yamamoto and K. Matsuzaki, *J. Chem. Soc., Chem. Commun.*, 1099, (1984); K. Ohta, A. Ishii, H. Muroki, I. Yamamoto and K. Matsuzaki, *Mol. Cryst. Liq. Cryst.*, **116**, 299 (1985).
6. K. Ohta, H. Muroki, A. Takagi, I. Yamamoto and K. Matsuzaki, *Mol. Cryst. Liq. Cryst.*, **135**, 247 (1986).
7. K. Ohta, H. Muroki, A. Takagi, K. Hatada, H. Ema, I. Yamamoto and K. Matsuzaki, *Mol. Cryst. Liq. Cryst.*, in press.
8. A. M. Giroud-Godquin and J. Billard, *Mol. Cryst. Liq. Cryst.*, **66**, 147 (1981).
9. A. M. Giroud-Godquin and J. Billard, *Mol. Cryst. Liq. Cryst.*, **97**, 287 (1983).
10. A. M. Giroud-Godquin, G. Sigaud, M. F. Achard and F. Hardouin, *J. Physique Lett.*, **45**, L-387 (1984).
11. A. M. Giroud-Godquin, M. M. Gauthier, G. Sigaud, F. Hardouin and M. F. Achard, *Mol. Cryst. Liq. Cryst.*, **132**, 35 (1986).
12. The ratio of the keto form to the enol form could not be determined because the integral signal of the keto form was too small to detect.
13. The m.p. was reported as 80°C in Ref. 10 and 81°C in Ref. 11.
14. See Figure 7 in Ref. 3.
15. See Figures 2–4 in Ref. 1 and Figure 4 in Ref. 2.
16. W. C. McCrone, Chap. 8 in "Physics and Chemistry of the Organic Solid State," D. Fox, M. M. Labes and A. Weissberger, ed., Interscience Publishers, John Wiley & Sons, Inc., New York, 1965, p. 758.
17. This mesomorphic texture seems to be the same as the D_{ho} phase of C_8HET: See Figure 2(b) of the following paper: C. Destrade, N. H. Tinh, J. Malthete and A. M. Levelut, *J. Physique*, **44**, 597 (1983).