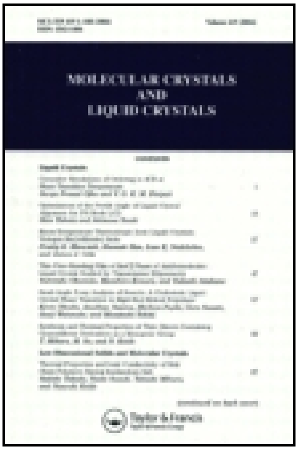

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Double Melting Behavior of Disk-like Complexes Substituted by Long Chains, 1: the Substituent Effect

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Double Melting Behavior of Disk-like Complexes Substituted by Long Chains, 1 : the Substituent Effect

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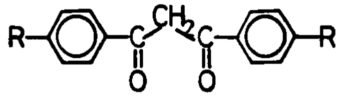
The bis (β-diketonato) copper (II) complexes, 2c and 2d, exhibit double melting behavior; 2c (m.p. of K_1:122.4 – 122.8°C, m.p. of K_2:135.2 – 135.6°C), 2d (m.p. of K_1:168.8 – 169.2°C, m.p. of K_2:208.3 – 208.6°C). The corresponding β-diketone ligands, 1c and 1d, also exhibit double melting behavior; 1c (m.p. of K_1:83.4 – 83.9°C, m.p. of K_1:84.9 – 85.4°C), 1d (m.p. of K_1:103.5 – 103.6°C, m.p. of K_2:108.1 – 108.2°C). 2c and 2d are the first examples exhibiting double melting behavior in the disk-like transition metal complexes substituted by long chains. Because the previously reported complexes (2a and 2b) exhibit discotic mesomorphism, the double melting behavior of 2c and 2d is thought of as thermal behavior close to mesomorphism. The chief determining factors which lead to either mesomorphism or double melting behavior are the substituent effect and the effect of central metal.

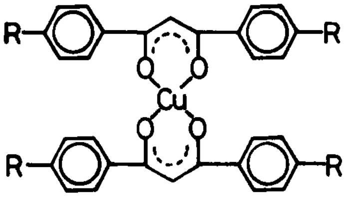
INTRODUCTION

Organic transition metal complexes substituted by long alkyl chains have been synthesized for various purposes. To date, five properties of these complexes have been reported. : (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] In focusing our interest on the fourth and fifth properties, two new disk-like complexes, bis[1,3-di(p-n-octylthiophenyl)propane-1,3-dionato] copper (II) (2c) and bis[1-(p-n-octylthiophenyl),3-(p-n-octylsulfonylphenyl)propane-1,3-dionato]copper(II) (2d), have been synthesized. It was found that each of the complexes (2c and 2d) exhibits double

a : $R = C_8H_{17}$
b : $R = C_8H_{17}O$



(1a , 1b)



(2a , 2b)

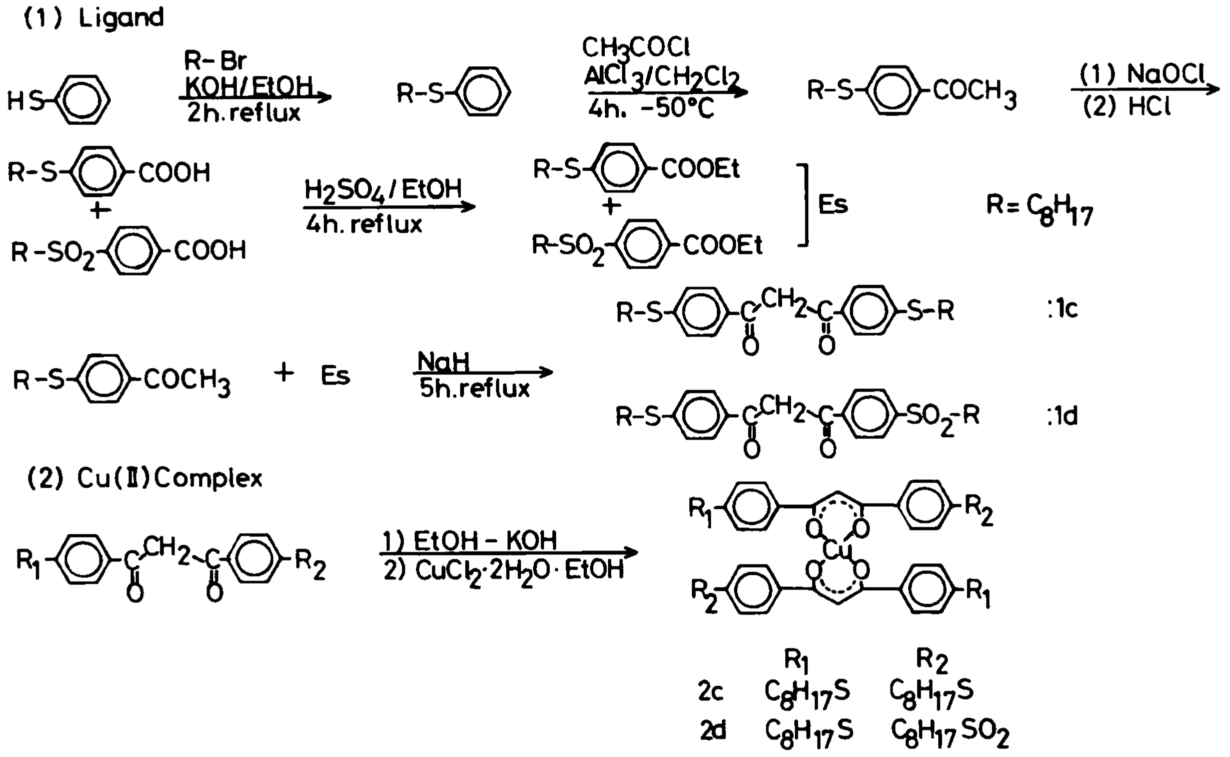
melting behavior, and that each of their corresponding β-diketone ligands (1c and 1d) also exhibits double melting behavior. 2c and 2d are the first examples exhibiting double melting behavior in the disk-like transition metal complexes substituted by long chains. On the other hand, in the previous paper[7] we reported that two related disk-like complexes, 2a and 2b, exhibit discotic mesomorphism, and that each of their corresponding β-diketone ligands (1a and 1b) also exhibit classical mesomorphism. Interestingly, the molecular structures of these complexes (2a and 2b) are very similar to the present complexes (2c and 2d): all these complexes (2a,2b,2c, and 2d) have the same disk-like core complex parts with slightly different side chains. Comparing these complexes, it is obvious that the double melting behavior is related to the mesomorphism of this type of complexes. The investigation on the double melting behavior of 2c and 2d serves to elucidate the problem of the relationship between mesomorphic property and its molecular structure. We wish to report here the double melting behaviors of 2c,2d, and 1c,1d, and we would like to point out the two determining factors of these thermal behaviors.

EXPERIMENTAL

Synthesis

Syntheses of the present β-diketone ligands and their corresponding copper (II) complexes were carried out according to the route illustrated in Scheme I. The β-diketone ligands, 1c and 1d, were prepared by the method of Kopecky et al.[8]

The first target molecule was ligand 1c, but a mixture of 1c(5%)



Scheme I Synthetic route for the β-diketone ligands (1c, d) and their corresponding copper (II) complexes (2c, d).

and 1d(95%) was obtained unexpectedly. The mass spectroscopy revealed that partial oxidation of octylthio groups to octylsulfonyl groups occurred in the carboxylation by sodium hypochlorite solution. The separation of them was carried out by column chromatography.

p-n-Octylthioacetophenone

p-n-Octylthioacetophenone was synthesized by alkylation of thiophenol with n-octylbromide in ethanolic solution of potassium hydroxide, followed by Friedel-Crafts acylation in the manner of Ref. 4. Overall yield was ca. 90%, based on thiophenol. The products were recrystallized from n-hexane to give white plate-like crystals; m.p.: 51–52°C, I.R.: 1660 cm^{-1} ($\nu_{c=o}$, KBr disk), N.M.R. δ_{ppm}($CDCl_3$, TMS): 2.5 (3H, s, $COCH_3$).

p-n-Octylthiobenzoic acid and p-n-octylsulfonylbenzoic acid

A solution of p-n-octylthioacetophenone (15.0 g, 57 mmol) in dioxane (150 ml) was poured into 255 ml of 10% sodium hypochlorite solution (342 mmol) in an ice bath and then heated up to 70°C, and stirred for 7 hours. After cooling to room temperature, 36 g of sodium bisulfite was added to the solution, which was kept vigorously stirring for 1 hour. After acidifying the basic solution with concentrated hydrochloric acid, the product was extracted with chloroform. Evaporation gave 19.7 g of a crude mixture of p-n-octylthiobenzoic acid and p-n-octylsulfonylbenzoic acid. This mixture product was recrystallized from benzene to give white plate-like crystals; I.R.: 2650, 2490 cm^{-1} (COOH). MS (m/e): 266 (M^+ of p-n-octylthiobenzoic acid), 298 (M^+ of p-n-octylsulfonylbenzoic acid).

Ethyl p-n-octylthiobenzoate and ethyl p-n-octylsulfonylbenzoate

To a stirred solution of the mixture obtained above (10g) in ethanol (200ml) was added dropwise 25 ml of concentrated sulfuric acid. After refluxing for 4 hours and then cooling to room temperature, the products was extracted with 1:1 (v/v) ether-ethyl acetate. Evaporation gave 9.6 g of a crude mixture of ethyl p-n-octylthiobenzoate and ethyl p–n–octylsulfonylbenzoate. I.R.: 1710 cm^{-1} (ester).

Ligands: 1c and 1d

A solution of the mixture of esters obtained above (9.0g) in dry dimethoxyethane (120 ml) was added dropwise to 4.9 g of 60% sodium hydride which had been washed several times with dry n-hexane.

Then a solution of p-n-octylthioacetophenone in dry dimethoxyethane (120 ml) was added dropwise and the solution was refluxed for 5 hours. After cooling to room temperature, a small portion of water was added very carefully to the resulting yellow stew, and then the solution was acidified with concentrated hydrochloric acid. This product was extracted with dichloromethane. Evaporation gave 14.7 g of a crude mixture of 1,3-di(p-n-octylthiophenyl)propane-1,3-dione (1c) and 1-(p-n-octylthiophenyl),3-(p-n-octylsulfonylphenyl)propane-1,3-dione (1d).

Separation and purification of 1c and 1d

The product mixture obtained above (14.7 g) was recrystallized from 1:10 (v/v) EtOH-acetone to give 6.9 g of yellow powder, which was chromatographed on a silica gel column, eluting with dichloromethane, to give 0.2 g of 1c (5% relative yield, Rf = 0.92) and 5.5 g of 1d (95%, Rf = 0.56). Each of them was further purified by recrystallization from acetone to afford the samples for elemental analysis and differential scanning calorimetry measurements.

1c; Anal. Found (Calcd. for $C_{31}H_{44}O_2S_2$):C 72.39% (72.61), H 8.43% (8.65). MS(m/e): 512 (M^+) I.R. (KBr disk, cm^{-1}): 1595 ($\nu_{c=o}$). ^{1}H-NMR ($CDCl_3$, TMS): δ_{ppm} = 4.5 (s, 0.07H, keto CH_2), 6.8 (s, 0.96H, enol =CH), 17.0 (s, 0.96H, enol OH); keto:enol = 0.04:0.96.

1d; Anal. Found (Calcd, for $C_{31}H_{44}O_4S_2$): C 68.30% (68.34), H 7.86% (8.14). MS (m/e): 544 (M^+) I.R. (KBr disk, cm^{-1}): 1145 (ν_{so_2}), 1598 ($\nu_{c=o}$). ^{1}H-NMR ($CDCl_3$, TMS): δ_{ppm} = 6.8 (s, 1.00H, enol =CH), 16.8 (s, 1.00H, enol OH); keto:enol = 0.00:1.00.

Copper (II) complexes; 2c and 2d

These complexes were obtained in the manner previously reported.[7] The purification was carried out by recrystallization from dioxane for 2c and from acetone for 2d.

2c; Anal. Found (Calcd. for $C_{62}H_{86}O_4S_4Cu$): C 68.34% (68.50), H 7.84% (7.97). I.R. (KBr disk, cm^{-1}): 1596 ($\nu_{c=o}$). Solid reflection spectrum λ_{max}(nm): 595, 635.

2d; Anal. Found (Calcd. for $C_{62}H_{86}O_8S_4Cu$): C 64.28% (64.58), H 7.51% (7.69). I.R. (KBr disk, cm^{-1}): 1586 ($\nu_{c=o}$). Slid reflection spectrum λ_{max}(nm): 542, 640.

Measurements

Phase transformation behavior of these compounds 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, Mettler FP 85 and Rigaku Denki Thermoflex TG-DSC.

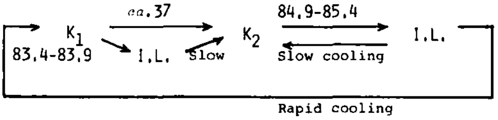
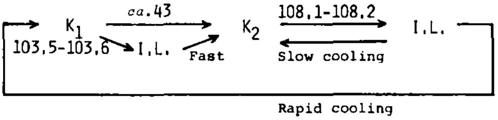
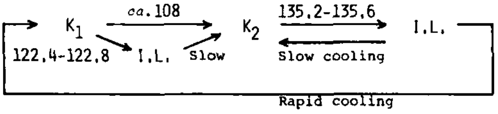
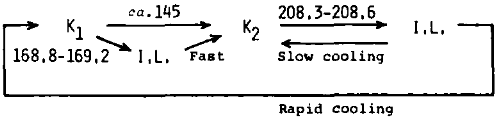
RESULTS AND DISCUSSION

(1) PHASE TRANSITIONS OF LIGANDS (1c and 1d) AND THEIR COMPLEXES (2c and 2d)

In Table I the phase transitions for the ligands (1c and 1d) and the corresponding copper (II) complexes (2c and 2d) are summarized. Each of the compounds has two solid polymorphs, K_1 (crystal of low m.p.) and K_2 (crystal of high m.p.), and each metastable polymorph K_1 exhibits so-called "double melting behavior".[9] All K_1 phases of these compounds observed here were prepared by the same manner, i.e., by rapid cooling an isotropic liquid heated over the m.p. of K_2

TABLE I

Phase[a] transition temperatures (T_t) and enthalpy changes of K_2 phases (ΔH_2) for the β-diketone ligands (1c,d) and their corresponding cooper (II) complexes (2c,d)

Compound	T_t(°C) →	ΔH_2(kcal/mol)
1c		12.9
1d		9.35
2c		18.9
2d		11.6

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

phase down to room temperature. The detailed double melting behaviors of these K_1 phases are described in the following.

Double melting behavior of K_1 phase of 1c

Photomicrographs in Figure 1 show a sequence of the state changes of 1c.

Film No. 29: a K_2 crystal was crystallized from the isotropic liquid at 83.9°C.

Film No. 30: the sample in Film No. 29 was rapidly cooled down to room temperature to give K_1 crystals surrounding the K_2 crystal.

Film No. 32: when the sample in Film No. 30 of room temperature was put on the hot plate of 83.9°C, only the K_1 crystals were melting.

Film No. 33: by holding the temperature of the sample at 83.9°C for 1.5 hour, many parallelogram-like crystals of the K_2 phase were formed from the isotropic liquid at 83.9°C.

Film No. 36: when the sample in Film No. 33 was heated up to 84.9°C, the K_2 crystals were melting.

Thus, the double melting behavior of the K_1 crystals of 1c could be observed by polarizing microscope, while DSC measurements did not give any typical thermograms of the double melting behavior[10] even at a slow heating rate (1°C/min.), because the m.p. of K_1 (83.4 – 83.9°C) is very close to the m.p. of K_2 (84.9 – 85.4°C), and because the isotropic liquid between the m.p.s of K_1 and K_2 phases transforms very slowly to the K_2 crystals even at the presence of K_2 crystal seeds. On the other hand, since the solid-solid phase transition from K_1 to K_2 is relatively fast, each of the DSC mesurements gave a single melting thermogram corresponding to the melting of K_2 phase for any heating rates (1 – 80°C/min.). The melting enthalpy change of K_2 (ΔH_2) only could be determined (12.9 kcal/mol).

Double melting behavior of K_1 phase of 1d.

Since the isotropic liquid between the m.p.s. of K_1 and K_2 phases of ld transforms fast even at the absence of K_2 crystal seeds, and since the m.p. of K_1 (103.5 – 103.6°C) is comparatively far from the m.p. of K_2 (108.1 – 108.2°C), the typical DSC thermograms of double melting behavior[10] of the K_1 crystal could be obtained for the heating rate of $\geqq$10°C/min. as shown in Figure 2. 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. Using a K_1 crystal (spherulite)

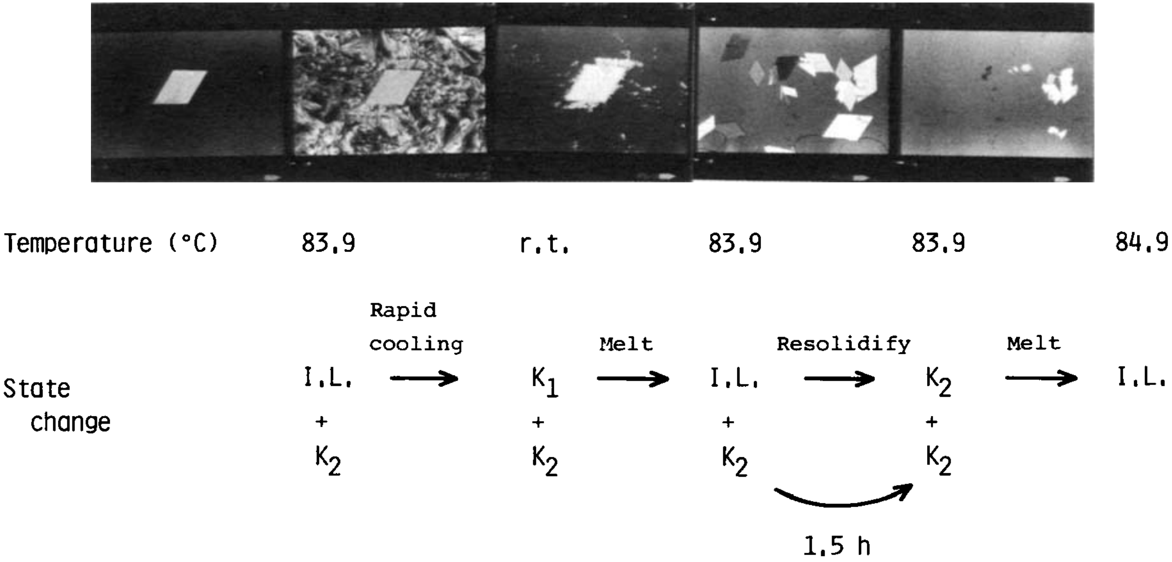


FIGURE 1 Photomicrographs of the double melting behavior of 1c.

surrounding K_2 crystals (plate-like) prepared between two slide glasses and holding the temperature of this sample for >1 hours at various temperatures on a heating plate, the solid-solid phase transition from K_1 to K_2 was observed under the polarizing microscope. By such observations described above, it became apparent that the phase transition from K_1 to K_2 begins at ca. 43°C.

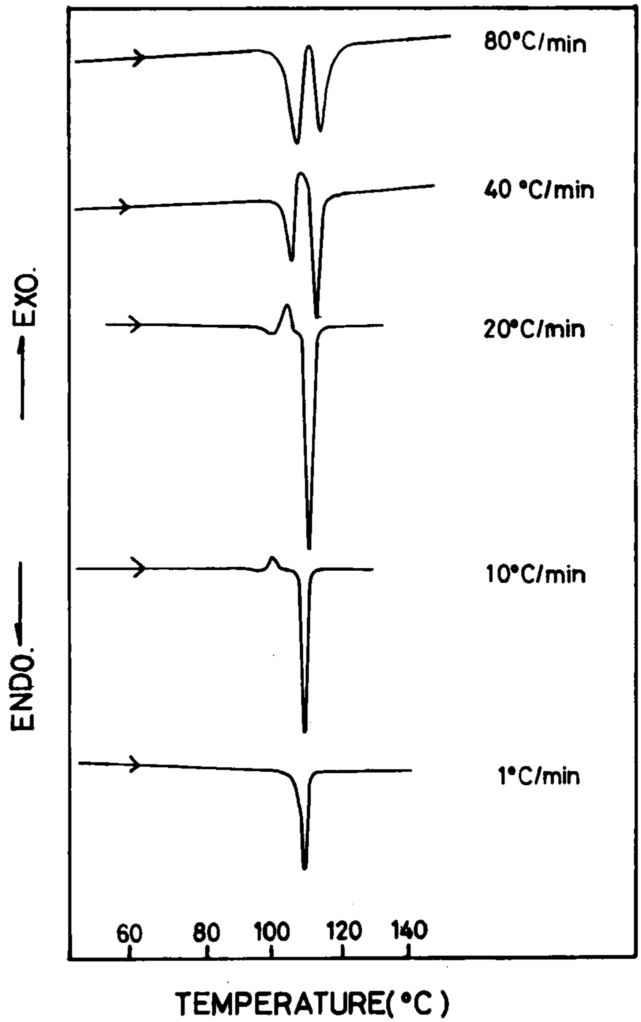


FIGURE 2 DSC thermograms of K_1 of 1d for different heating rates.

Double melting behavior of K_1 phase of 2c.

When the K_1 phase (plate-like crystal) was heated up from the room temperature, the solid-solid transformation from K_1 to K_2 phase (parallelogram-like crystal) could be observed at ca. 108°C under the microscope. As shown in Figure 3, peak I (108°C) of the DSC thermogram corresponds to the solid-solid phase transition. Peak II (123°C) shows the melting of K_1 crystals left over from the solid-solid phase transition. However, since the resolidification of this melt is very slow, no exothermic peak could be observed between peak II (123°C) and III (135°C). For ≤10°C/min. of heating rates, peak III due to the

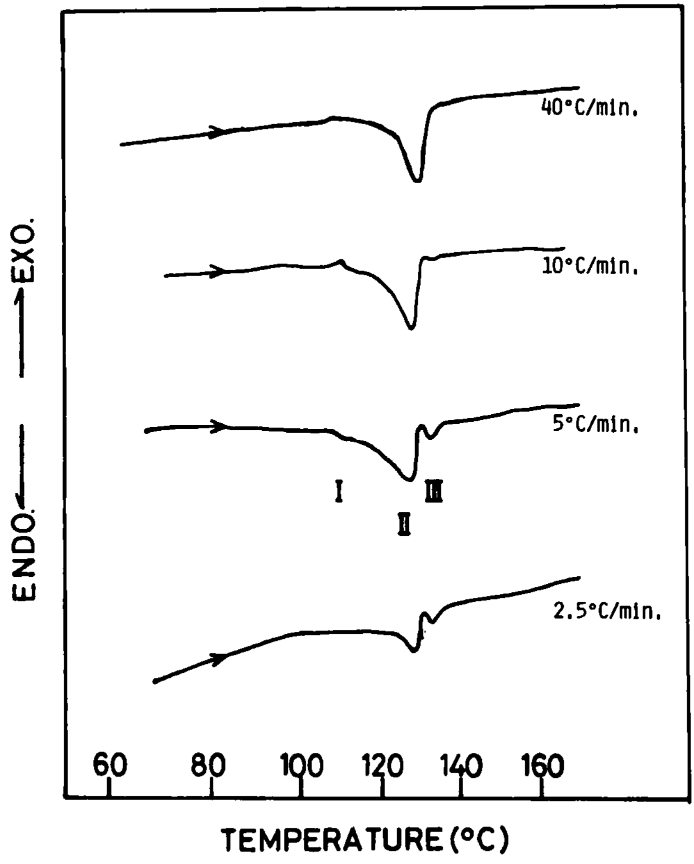


FIGURE 3 DSC thermograms of K_1 of 2c for different heating rates. Peaks denoted with I, II, and III in this figure are explained in the main text.

melting of K_2 phase could be detected by the DSC measurements. Thus, the double melting behavior of the K_1 phase of 2c could be observed only at slow heating rates.

Double melting behavior of K_1 phase of 2d

As shown in Figure 4, for all of the heating rates (2.5–80°C/min.) the double melting behavior of the K_1 phase of 2d could be observed.

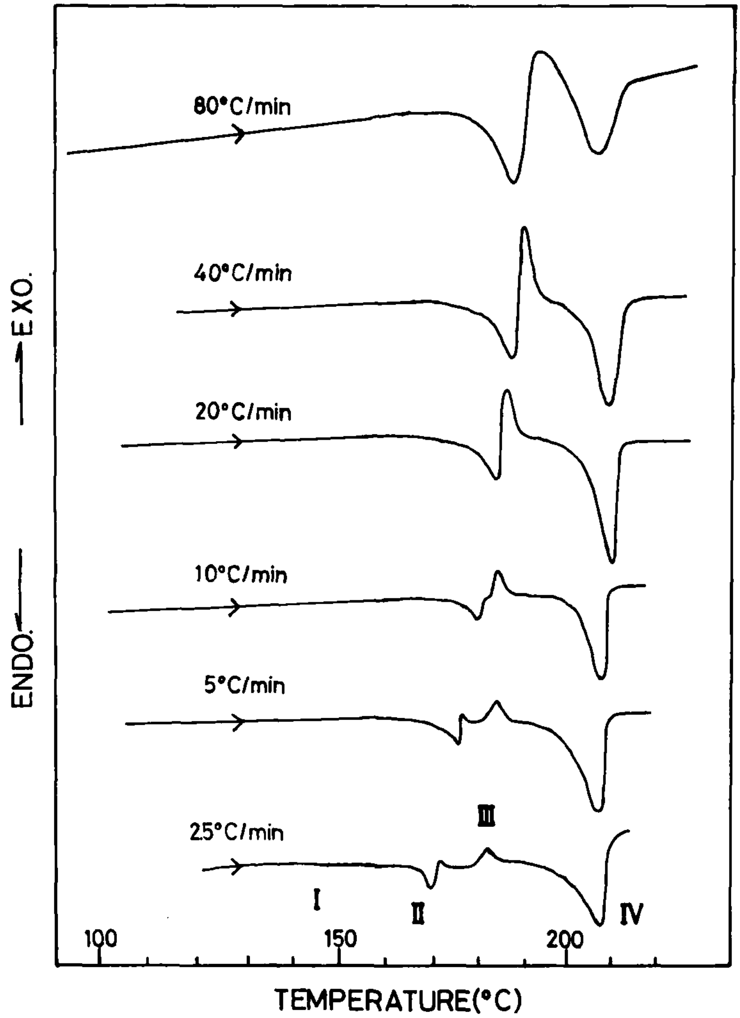


FIGURE 4 DSC thermograms of K_1 of 2d for different heating rates. Peaks denoted with I, II, III, and IV in this figure are explained in the main text.

However, the ratio of peak IV (208°C, due to the melting of K_2 phase, parallelogram-like crystal) to peak II (169°C, due to the melting of K_1 phase, plate-like crystal) increases the slower the heating rate. Furthermore, the temperature difference between the exothermic peak III (ca. 185°C, due to resolidification of the isotropic liquid into the K_2 crystals) and peak II becomes larger *the slower the heating rate* (<10°C/min). The opposite situation was reported[11] for (R)-stearin: the temperature difference between the $\alpha \rightarrow$liquid and liquid$\rightarrow \beta$ transformations was larger *for higher heating rates*. The origin of this effect was ascribed to the monotropic relationship[12] between the α- and β-crystals. On the contrary, the K_1 and K_2 crystals of the present complex 2d are in enantiotropic relationship[12] because of the existence of the solid-solid phase transition from K_1 to K_2 corresponding to the peak I(ca. 145°C). Nevertheless, the temperature interval between peaks II and III of this complex becomes larger for slower heating rates. It appears that superheating of K_1 crystal at higher heating rates causes higher apparent m.p. of K_1 than its inherent m.p., so that peak II becomes closer to the peak III. We were able to observe this effect even in the enantiotropic relationship.

2. DETERMINING FACTORS OF THE THERMAL BEHAVIORS

Comparing the β-diketone ligands (1a, 1b, 1c, and 1d) with each other, the ligands substituted by octyl or octyloxy groups (1a and 1b) show the classical mesomorphism and, on the other hand, the ligands substituted by octylthio and/or octylsulfonyl groups (1c and 1d) show the double melting behavior. Furthermore, the complexes substituted by octyl or octyloxy groups (2a and 2b) show discotic mesomorphism. On the other hand, the present complexes substituted by octylthio and/or octylsulfonyl groups (2c and 2d) show the double melting behavior. Therefore, concerning the thermal behavior of these ligands and their complexes, the following basic questions must be raised:
(i) What is relationship between the double melting behavior and the mesomorphism?
(ii) Can one obtain always the mesomorphic complex when a mesomorphic ligand is used? Can one obtain always the double melting complex when a double melting ligand is used?

For the first question, we could propose three stages of thermal behavior for long chain substituted compounds as shown in Table II. *Stage 1:* When the high temperature solid phase (K_2 polymorph) is highly stable and the low temperature solid phase (K_1 polymorph) is

TABLE II

Three stages of thermal behavior for long chain substituted compounds.

Stage	Type of melting behavior	Stability of solid phase[a] K_1	K_2	Appearance of phase[a]
Stage 1	single melting	unstable	highly stable	metastable solid phase transforms to K_2 phase or tends to disappear
Stage 2	double melting	stable	stable	metastable solid phase comes to appear
Stage 3	mesomorphic transition	highly stable	unstable	unstable K_2 phase becomes a stable mesophase

[a] Phase nonmenclature: K_1 = solid phase of low m.p. (metastable phase), K_2 = solid phase of high m.p.

unstable, the metastable phase (K_1 polymorph) completely transforms to K_2 phase or tends to disappear, and only single melting behavior is exhibited.

Stage 2: When both the high temperature solid phase (K_2 polymorph) and the low temperature solid phase (K_2 polymorph) are stable, the metastable phase (K_1 polymorph) comes to appear, and double melting behavior is inclined to occur.

Stage 3: When the high temperature solid phase (K_2 polymorph) is unstable and the low temperature solid phase (K_1 polymorph) is highly stable, the unstable K_2 solid polymorph becomes a stable mesophase (liquid crystalline phase), and mesomorphic transition can be observed.

Thus, at present we think that the double melting behavior of long chain substituted compounds is a thermal behavior close to the mesomorphism. The driving force of such stability of the solid phases is now under investigation from the viewpoint of electron-withdrawing abilities of the long chain substituents. It becomes clear that electron-withdrawing substituents give the ligands and complexes a tendency to exhibit such double melting behavior, and that electron-donating substituents give them a tendency to exhibit the mesomorphism. The details will be reported elsewhere.

For the second question mentioned above, examples of the thermal behavior of long chain ligands and their complexes are summarized in Table III. It is obvious from Table III that one can not always obtain the mesomorphic complex when a mesomorphic ligand is used, and that one can not always obtain the double melting complex when

TABLE III

Relationships between the thermal behavior of ligands and their complexes.

	Ligand		Complex	
Example No.	Thermal behavior[a]	Example of compound	Thermal behavior[a]	Example of compound
1	stage 3	1a,1b	stage 3	2a,2b
2	stage 2	1c,1d	stage 2	2c,2d
3	stage 1	n-OBA[b]	stage 2	$(\text{n-OBA})_2$ Cu(II)[b]
4	stage 3	1a	stage 2	Ni(II) complex of 1a[c]

[a] Table II in this paper.

[b] See Ref. 4. n-OBA: 1-(p-n-octylphenyl)butane-1,3-dione, $(\text{n-OBA})_2$Cu(II): bis[1-(p-n-octylphenyl)butane-1,3-dionato]copper(II).

[c] See Ref. 13.

a double melting ligand is used. However, from Table III two chief determining factors of these thermal behaviors can be extracted. Comparing example No. 1 with No. 2, the determining factor of the mesomorphism is thought to be 'substituent effect.' On the other hand, comparing example No. 1 with No. 4,[13] the factor is thought to be 'effect of central metal.' This is the first time that the determining factors of mesomorphism and double melting behavior in the transition metal complexes are pointed out. The two factors seem to be significant for the molecular design of complexes to have desirable mesomorphic properties.

CONCLUSION

Two new disk-like complexes, bis[1,3-di(p-n-octylthiophenyl)-propane-1,3-dionato]copper (II) (2c) and bis [1-(p-n-octylthiophenyl),3-(p-n-octylsulfonylphenyl)propane-1,3-dionato]copper (II) (2d), were synthesized. It was found that each of the complexes synthesized here exhibits double melting behavior, and that each of their corresponding β-diketone ligand (1c and 1d) also exhibits double melting behavior. 2c and 2d are the first examples exhibiting double melting behavior in the disk-like transition metal complexes substituted by long chains, so far as we know. Comparing these complexes reported here with the previously reported complexes (2a and 2b) exhibiting discotic mesomorphism, the double melting behavior of 2c and 2d is thought as a thermal behavior close to the mesomorphism. The chief factors determining the choice between mesomorphism and double melting behavior are the substituent effect and the effect of the central metal.

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13. Ni (II) complex of la will be reported elsewhere. The reddish brown complex exhibits double melting behavior: m.p.s. = 86 and 103°C.