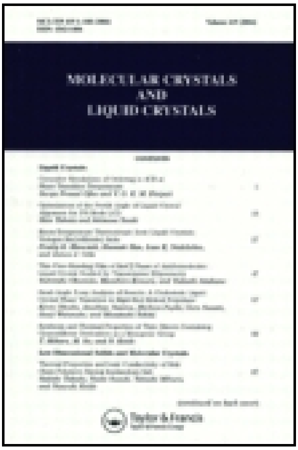

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Square-Planar trans-Bis-(1-p-n-octylphenylbutane-1,3-dionato) copper (II), a New Compound Exhibiting Three Kinds of 'Double Melting' Behaviour

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Square-Planar *trans*-Bis-(1-*p*-n-octylphenylbutane-1,3-dionato)copper (II), a New Compound Exhibiting Three Kinds of 'Double Melting' Behaviour

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The new compound, bis-(1-*p*-n-octylphenylbutane-1,3-dionato) copper(II) has four polymorphs, C^1 (m.p. 96°C), C^a (99°C), C^m (108°C), and C^h (109°C), all having the same square-planar trans structure. C^1, C^a, and C^m exhibit 'double melting' behaviour, *i.e.*, they melt at their m.p.s, resolidify into C^h, which on further heating melts again at its m.p. Double melting of C^1 was observed only on very rapid heating, while that of C^a and C^m only on slow heating. Slow solid–solid phase transition from C^1 to C^h was observed at *ca.* 50°C. Each polymorph could be obtained as a stable form at room temperature and gave a quite different X-ray diffraction powder pattern. The interrelationships of the four forms have been clarified by differential scanning calorimetric and microscopic measurements. When the melt of the complex is rapidly cooled, it converts into a glassy state, which is stable at room temperature. The glass transition temperature T_g and the crystallizing temperature T_c are very close to each other at 52.5°C and 58.0°C, respectively.

I INTRODUCTION

Some organic transition metal complexes are suggested to be useful for colour imaging devices[1,2,3] or for the electrical conversion of solar energy,[4,5] etc. For some uses, the complexes have the problem of thermal instability due to polymerization[6] or decomposition near their m.p.,[7,9] and the problem of low solubility especially in alkanes for some other uses.[8] Recently, several kinds of organic transition metal complexes with long *n*-alkyl chains have been synthesized. They exhibit interesting properties of (1) good solubility in alkane,[8] (2) mesomorphism,[9,10] (3) unusual thermochromism,[8] and (4) micell formation.[4,5] The first property is desirable as additives for gasoline, oil, and polymer etc. The second and third properties have the possibility of finding application in imaging devices. Memming *et al.* used the complexes with the fourth property as a converter of light energy into electrical currents with the SnO_2 electrodes on which the complexes were spread as a monolayer.[5]

The title complex was synthesized in an attempt to find a new mesomorphic compound containing transition metal. This complex was synthesized in very good yield and showed good thermal stability. Until it decomposes at 221.5°C, neither sublimation nor volatilization occurs. Although this complex does not have a mesomorphic state, it exists in four polymorphs[11]: C^l (*c*rystal of *l*ow m.p., 96°C), C^a (*c*rystal from *a*cetonitrile solution, m.p. 99°C), C^m (*c*rystal of *m*edium m.p., 108°C), and C^h (*c*rystal of *h*igh m.p., 109°C), all being stable at room temperature. Interestingly, C^l, C^a, and C^m exhibit the so-called double melting behaviour.[12] As to be reported elsewhere, spectroscopic evidence concludes no changes in co-ordination form of square-planar trans structure in each transition. So far as we know, this is the first compound of the ML_2 type (M = transition metal, L = ligand) with a long alkyl chain which has three double melting forms.

The purpose of the present paper is to describe the preparation of this complex, its polymorphic properties, and the interrelationships of them.

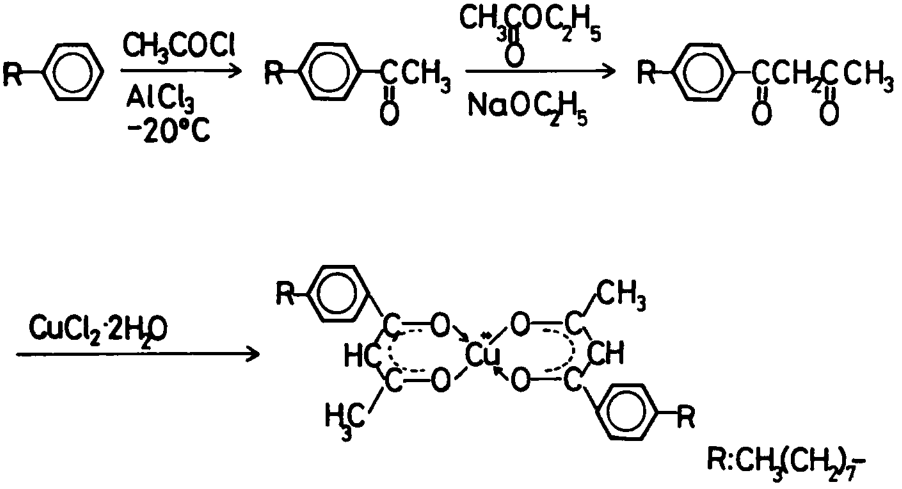
II EXPERIMENTAL

Synthesis of square-planar trans-bis-(1-*p*-n-octylphenylbutane-1,3-dionato)copper(II)

The starting material, *p*-n-octylacetophenone, was prepared as reported by Giroud *et al.*[9] The ligand, 1-*p*-n-octylphenylbutane-1,3-dione, was synthesized by the method of Beyer *et al.*[13] Its copper(II) complex was obtained according to the method reported by Hon *et al.*[14] The detailed procedures are as follows.

p-n-Octylacetophenone

By the acetylation of n-octylbenzene (0.35 mole) with acetyl chloride (0.70 mole) at −20°C in dichloromethane (*ca.* 350 ml) in the presence of aluminium chloride (0.70 mole) for 5 hours, *p*-n-octylacetophenone (colourless oil) was obtained in ca. 100% yield. The product was pure enough for further reactions.



1-*p*-n-Octylphenylbutane-1,3-dione (ligand)

A mixture of 51.2g (0.75 mole) of alcohol free sodium ethoxide and 66.3g (0.75 mole) of ethyl acetate was poured into 88.1g (0.38 mole) of *p*-n-octylacetophenone in an ice bath and was stirred at about 70°C for 8 hours. After one day, the product was collected and shaken with an aqueous solution of acetic acid and ether, and then washed well with water. Evaporation gave 84.0g (80.7%) of crude 1-*p*-n-octylphenyl butane-1,3-dione, which was purified by distillation to a colourless oil (b.p. = 146.0°C at 0.023 mmHg, m.p. = 39.0–41.0°C). In the i.r. spectrum of this compound, very strong absorption due to the β-diketone structure appeared at the region of 1600 cm^{-1}. Anal. Found (Calcd. for $C_{18}H_{26}O_2$): C 78.59% (78.70), H 9.69 (9.55).

Bis-(1-*p*-n-octylphenylbutane-1,3-dionato)copper(II)

The complex was precipitated from an aqueous solution of 17.0g (0.10 mole) of cupric chloride mixed with an ethanol solution of 13.7g (0.05 mole) of 1-*p*-n-octylphenylbutane-1,3-dione in the presence of an excess of ammonium hydroxide. The gray-green precipitate was washed with water and a small portion of ethanol and air dried. The powder was recrystallized from ethanol or acetone to give 14.9g (97.9%) of green long thin crystals of the complex. Anal. Found (Calcd. for $C_{36}H_{50}O_4Cu$): C 70.94% (70.85), H 8.27 (8.26). Electronic spectrum λ_{max} (in n-hexane): 264 (ε 39000), 293 (26000), 324 (51000), 549 (40.1), and 662 (48.0) nm.

Preparation of four polymorphic forms

C^1 form This polymorph was obtained as green long thin crystals by crystallization at 5°C from a solution of methanol, ethanol, acetone, or n-hexane; *i.e.* from the solvents of lower polarity than methanol. C^1, however, was also obtained from much polar solvents such as acetonitrile or N,N-dimethylformamide by crystallizing quickly at −15°C. Thus, the crystal growth of C^1 form seems to be dependent on the solvent polarity and the crystallizing temperature. It may be considered that the entropy difference between liquid and C^1 is much smaller than other polymorphic forms.

C^a form Evaporation of the acetonitrile solution kept a 30–32°C for about one month gave C^a form as green hair-like crystals. The C^a crystals thus obtained were crystallographically pure without contamination of other forms. When the temperature was kept below 20°C, however, the C^1 form was obtained. When the acetonitrile was rapidly evaporated by an evaporator at 30–32°C, only the C^1 form was produced. Slow evaporation of an acetone solution for about two weeks, only the C^1 form was obtained. Thus, the crystallization of C^a form was strongly dependent on the polarity and the evaporation rate of the solvent. Inclusion of solvent of acetonitrile in C^a crystal is ruled out, because, in the thermogravimetric measurement, no weight loss was observed up to the decomposition temperature of 221.5°C, and also because, when C^a form was heated up to 145°C and then slowly cooled to room temperature, C^m form was obtained without any weight loss.

C^m form This crystal form cannot be obtained by crystallization from solutions. The C^m crystal was obtained, when the melt of the complex at the temperature higher than the m.p. of C^h (109.3°C) was slowly cooled. However, when the melt was cooled very rapidly by cold water or liquid nitrogen, a glass was obtained. Pure C^m was obtained as green lustrous small spherulites when the melt was cooled down to the temperature between the m.p.s. of C^m and C^a (*ca.* 100°C) and the temperature was kept for about 10 min. Above 106.0°C, pure C^m was not easily obtained, but a large spherulite of C^m grew when a seed crystal was added to the melt.

C^h form This polymorph was obtained by slow crystallization at room temperature from the solvent of higher polarity than acetonitrile. This crystallization of C^h requires one day from acetonitrile and two weeks from N,N-dimethylformamide. C^h could be also obtained by the solid–solid phase transition of C^1 at about 50°C in the presence or absence of solvent. With the phase transition in the presence of solvent, namely solution phase transformation,[16] C^h was obtained when C^1 was added more than its solubility

limit into acetonitrile and stirred at 50°C for 20 min. With this procedure the transformation was complete. In the absence of solvent, the solid–solid phase transition was effected by gradual heating of C^l crystals at room temperature up to 106.0°C for 4 hours. However, when C^l crystals at room temperature were suddenly brought into contact with a bath at 106.0°C, a mixture of crystals of C^h and C^m was obtained (Route 4 in Figure 4). Although C^h can be obtained by these methods, the former method of solution phase transformation is much more convenient to obtain a large amount of pure C^h.

Measurements

Phase transition behaviour of this complex was observed with a polarizing microscope equipped with a heating plate controlled by a thermoregulator, Mettler FP5. Thermograms were obtained with a differential scanning calorimeter and with a thermogravimeter (Rigaku DSC–TG 8085 or Daini–Seikosha DSC SSC 560). X-Ray diffraction powder patterns of all polymorphs were measured with Cu-Kα radiation, using a Rigaku X-ray diffractometer.

III RESULTS AND DISCUSSION

Figure 1 shows the X-ray diffraction powder patterns of four polymorphs. As shown in the figure, each polymorph shows several characteristic peaks, as denoted with l, m, h, and a in the figure.

Thermogravimetric measurements revealed that the interconversion among these four crystal forms are not accompanied by decomposition of the complex, since no weight change was observed in each polymorph up to the decomposition temperature of 221.5°C.

The origin of the transformation among these four crystal forms in this type of complex was at first presumed to be due to a change of the co-ordination structures. However, each polymorph exhibited the same electronic spectrum, indicating the square-planar form in the co-ordination, and exhibited almost the same infrared and far-infrared spectra except for the absorption band attributed to the methylene rocking mode of n-alkyl chain.

Thus, it is suggested that the origin of the present polymorphism is due to neither the decomposition nor the co-ordination change, but due to the change in the packing of n-alkyl chain just as in the case of the well-known tristearine.[12] Actually, these four polymorphs showed different splitting intensities of the methylene rocking absorption bands, around 720 cm^{-1} from singlet to doublet. So far as we know, such a polymorphism is the first case in the organic transition metal complexes. The *trans*-type co-ordination

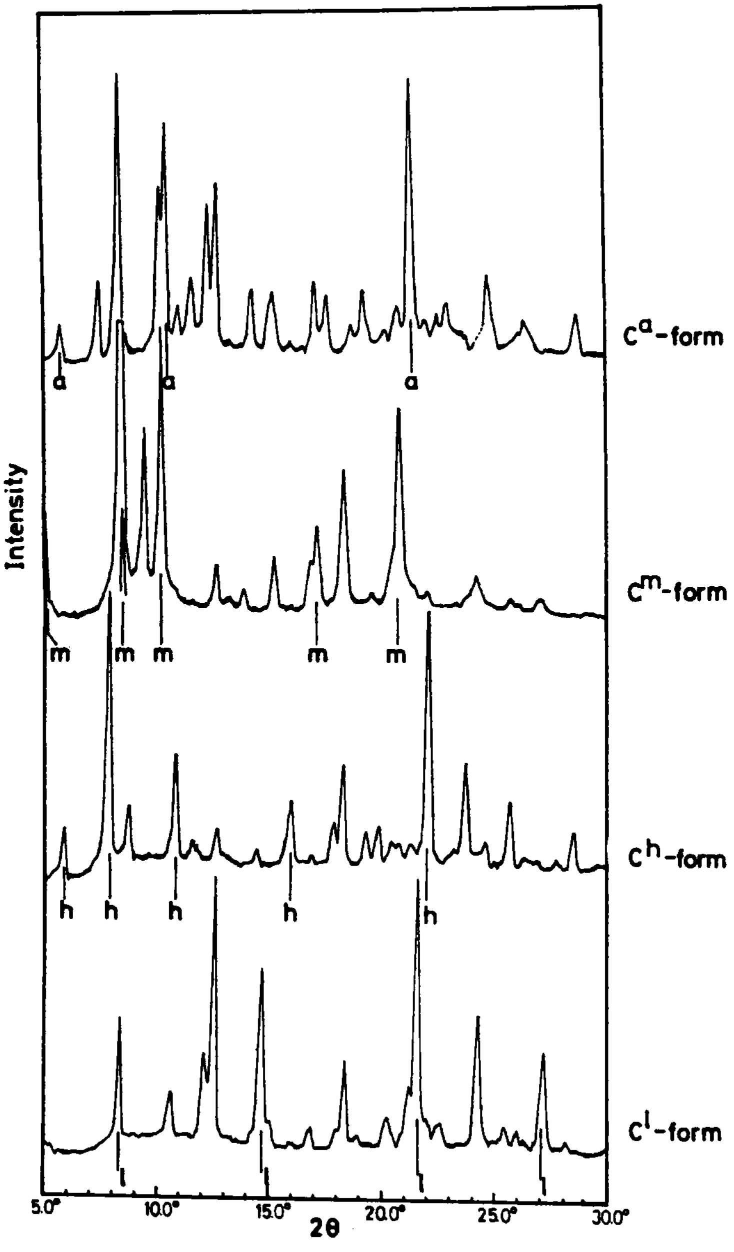


FIGURE 1 X-Ray diffraction powder patterns of four polymorphs of the title complex. Peaks denoted with l, a, m, and h in this figure are clearly distinguishable from each other.

of the present complex was concluded by confirming the existence of the 'mutual exclusion' rule in the far-infrared and Raman spectra, which is consistent with the *trans* *co*-ordination. The detailed discussion on the spectroscopic studies will be reported elsewhere.[15]

In Figure 2 are summarized the phase transitions of the present complex. The large arrows in the figure indicate the main route of heating for each polymorph. Among four polymorphs, C^1, C^a, and C^m exhibit "double melting" behaviour.

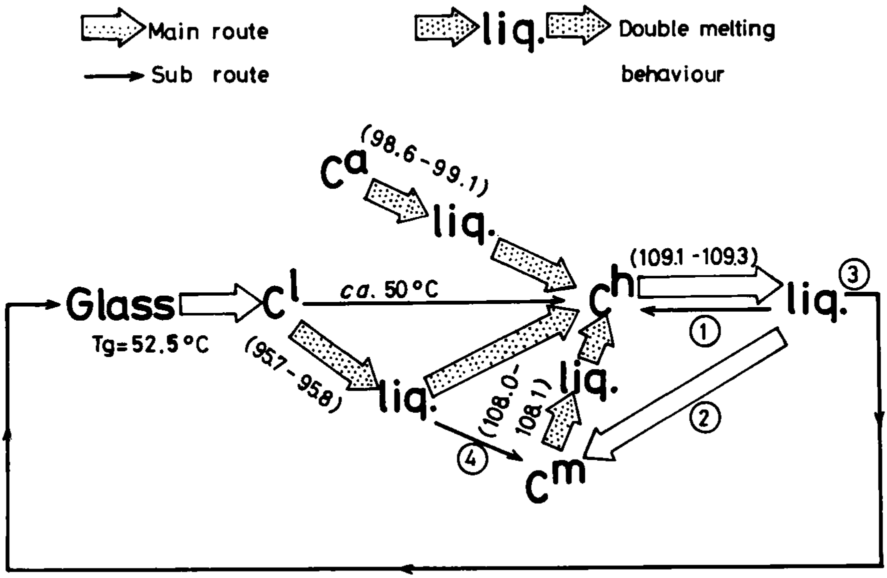


FIGURE 2 The sequence of changes of state for the title complex: (1) very slow cooling; (2) slow cooling; (3) rapid cooling; (4) see main text. Numbers in parentheses are m.p.s in °C.

When C^1 crystal was heated rapidly up to some temperature below the m.p. of C^1, a solid mixture of C^1 and C^h was obtained because of a relatively slow solid–solid phase transition from C^1 to C^h at *ca.* 50°C. The C^1 crystals in the mixture melted at the m.p. of C^1, 95.7–95.8°C, and then the melt resolidified completely in the C^h form because of the presence of seeds crystals of C^h formed by the solid–solid phase transition; on further heating, the C^h crystal melted finally at the m.p. of C^h, 109.1–109.3°C. In Figure 3(A) are shown in thermograms of C^1 crystal with various heating rates. In the case of higher heating rates, two endothermic peaks due to the meltings of C^1 and C^h were clearly observed. On very slow heating of C^1 crystal, however, only a single m.p. of C^h was observed, as a result of the complete solid–solid phase

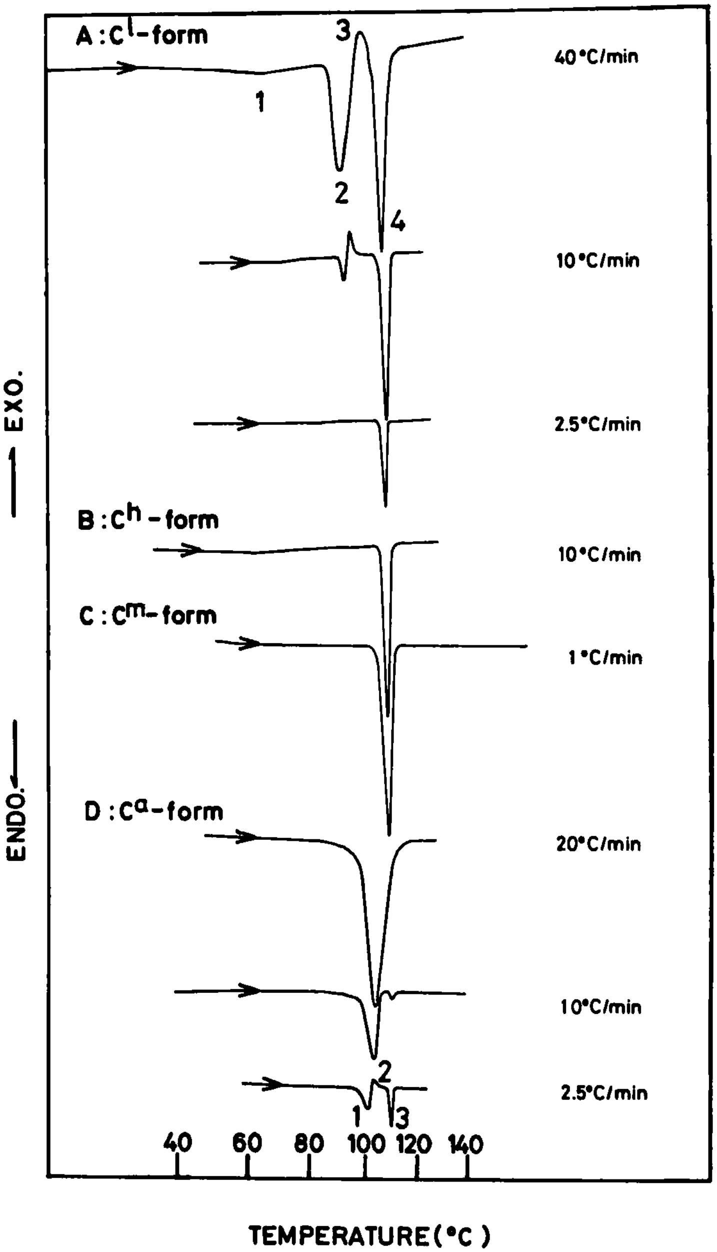


FIGURE 3 D.S.C. thermograms of four polymorphs for different heating rates. Peaks denoted with 1, 2, 3, and 4 in this figure (A and D) are explained in the main text.

transition. Thus, C^1 crystal exhibited the double melting behaviour only on rapid heating ($>10°C/min$).

In contrast to the case of C^1, C^a exhibited double melting behaviour only on slow heating ($<10°C/min$). No solid–solid phase transition was observed even when the C^a crystal was heated slowly from room temperature. As shown in Figure 3(D), when C^a crystal was heated slowly, it melted completely at its m.p. of 98.6–99.1°C; the melt then resolidified rather slowly into the C^h form, and, on further heating, it melted again at the m.p. of C^h, 109.1–109.3°C.

C^m also exhibited double melting behavior only on very slow heating without a solid–solid phase transition. At the heating rate of $<0.1°C/min$. C^m melted at its m.p., 108.0–108.1°C, and the resolidified as C^h. C^m gave a single melting thermogram observed by the D.S.C. apparatus even at the slowest heating rate of 1°C/min, as shown in Figure 3(C). However, as shown in Figure 4, careful observation with photomicrographs indicates that the double melting of C^m does exist only on very slow heating of $<0.1°C/min$. The C^h crystal form of the highest m.p. has, of course, only a single m.p.

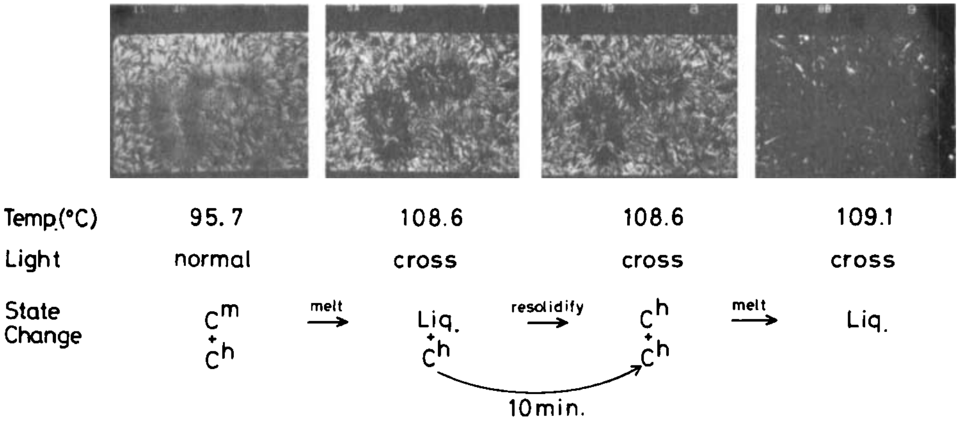


FIGURE 4 Photomicrographs of the double melting behaviour of spherulites of C^m surrounded by C^h.

As shown in Figure 2, there exist three choices of routes of different cooling rates. When the melt was kept just below the m.p. of C^h for a long time, the melt solidified into C^h form. With usual slow cooling rate, however, C^m form was obtained. On rapid cooling by cold water or liquid nitrogen a stable glass was obtained.

One of the reasons why the melt crystallized into C^m instead of C^h might be that the entropy change ΔS_m between C^m and liquid is smaller than the ΔS_m between C^h and liquid.

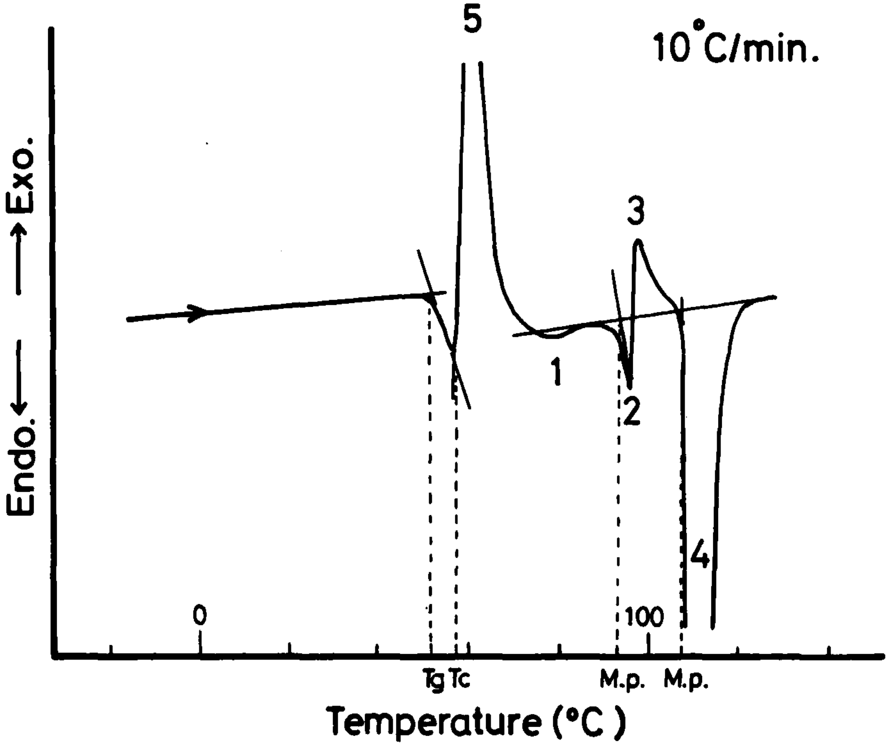


FIGURE 5 D.S.C. thermogram of glassy state of the title complex. The heating rate was 10°C/min. Peaks denoted with 1, 2, 3, and 4 in this figure correspond to the peaks denoted with 1, 2, 3, and 4 in Figure 3(A). Peak 5 is an exothermic peak of crystallization of supercooled liquid. T_g, T_c, and M.p. in this figure mean glass transition temperature, crystallization temperature, and melting point, respectively.

Figure 5 shows the thermogram for the glass between −16 and 130°C. When the glass was heated, a glass transition temperature T_g and a crystallizing temperature T_c were observed at 52.5°C and 58.0°C respectively.

The very complicated phase transitions of the title complex can be understood schematically as follows with free energy versus temperature (F–T) diagram shown in Figure 6. When the C^1 crystal, for example, is heated very rapidly, having not enough time for an appreciable solid–solid phase transition at 50°C to occur, it is superheated up to along the C^1 curve to its m.p., 96°C. Since the melt thus obtained is less stable than the C^h solid of this temperature, it resolidifies immediately into C^h form, and, on further heating along the C^h curve, the second melting occurs again at the m.p. of C^h, 109°C. Double melting behaviour of C^a and C^m crystals can be understood in the same way.

TABLE I

The melting point, the enthalpy change of melting (ΔH_m), and the entropy change of melting (ΔS_m) for each polymorph

Polymorph	M.p. (°C)	ΔH_m (kJ mol^{-1})	ΔS_m (JK^{-1} mol^{-1})
C^h	109.1–109.3	43.4 ± 0.2	113 ± 1
C^m	108.0–108.1	41.4 ± 0.2	108 ± 1
C^a	98.6–99.1	54.6 ± 0.5	146 ± 2
C^l	95.7–95.8	Unmeasurable	

It should be noted that T_g and T_c are very close. This property might have the possibility of being used as a potential image-forming material. Actually, as to be reported elsewhere, the glass sandwiched in two thin films of polyethylene terephtalates was sharply brought into local crystallization by N_2 laser pulse. The crystallized portion was stable for a long time and was clearly distinguishable in the light transmission from the glassy portion. The slide projection of this film gave a good contrast on a screen. By an appropriate heat treatment, the crystallized portion turned back again to the transparent

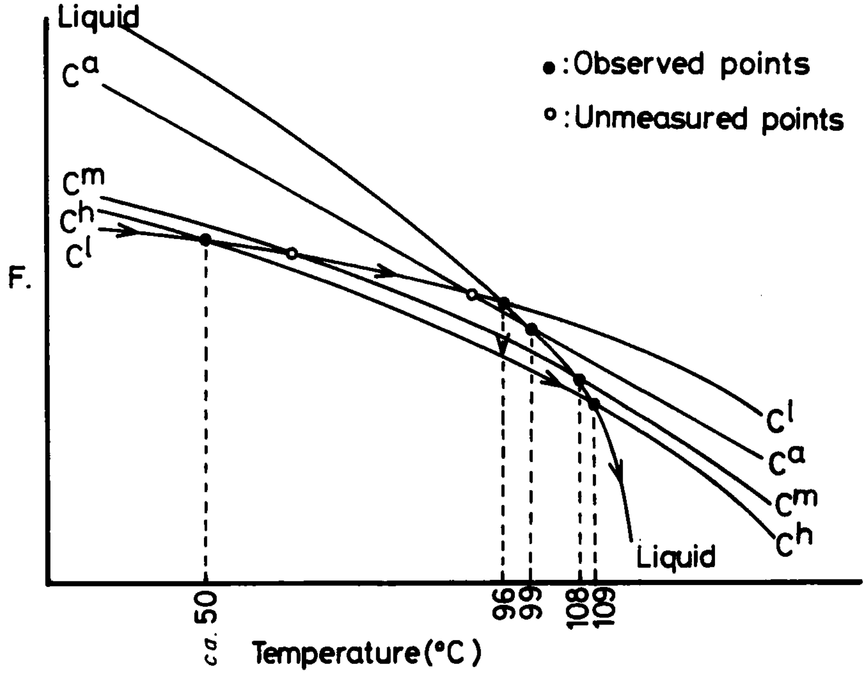


FIGURE 6 A free energy versus temperature (F–T) diagram for four polymorphs in the title complex. Except for the filled points the curves are schematic.

glassy state. Thus, this complex has a possibility to be used as an erasable imaging material.

As a natural extension of this work, the investigation of the properties of similar complexes with n-alkyl groups of different length are now in progress, and it has already been confirmed that most of the complexes also have several polymorphs and interesting phase transitions.

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