Studies on Syntheses and Properties of Organic Transition Metal Complexes with Long Alkyl Chains

（長鎖アルキル基を付与した有機遷移金属錯体の合成と物性に関する研究）

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KAZUCHIKA OHTA

PREFACE

This thesis was performed under the guidance by Professor Hiroshi Mikawa at Faculty of Engineering, Osaka University.

I would like to express my sincere thanks to Professor Hiroshi Mikawa for his invaluable guidance and constant encouragement throughout this work.

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It is a real pleasure to express my gratitude to Dr. Masamichi Kobayashi of Faculty of Science, Osaka University for measurement of Raman spectra of my samples in Chapter II, and to Mr. Guang-Jie Jiang (Kōketzu Kō in Japanese) for assistance with experiments in Chapter III.

The author wishes to thank all the members of Mikawa laboratory for their friendship.

Suita, Osaka
December, 1980

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LIST OF PAPERS

The contents of this thesis are composed of the following papers.

(1) Square-planar trans-Bis-(1-p-n-octylphenylbutane-1,3-dionato)copper(II), a New Compound exhibiting Three Kinds of 'Double Melting' Behaviour
K. Ohta, M. Yokoyama, S. Kusabayashi, and H. Mikawa
J. Chem. Soc., Chem. Commun., 392 (1980).

(2) Square-planar trans-Bis-(1-p-n-octylphenylbutane-1,3-dionato)copper(II), a New Compound exhibiting Three Kinds of 'Double Melting' Behaviour
K. Ohta, M. Yokoyama, S. Kusabayashi, and H. Mikawa
Mol. Cryst. Liq. Cryst., in press.

(3) Multiple Melting Behaviour in Square-planar trans-Bis-(1-p-n-alkylphenylbutane-1,3-dionato)copper(II)——The Effect of Alkyl Chain Length——
K. Ohta, G. Jiang, M. Yokoyama, S. Kusabayashi, and H. Mikawa
Mol. Cryst. Liq. Cryst., in press.

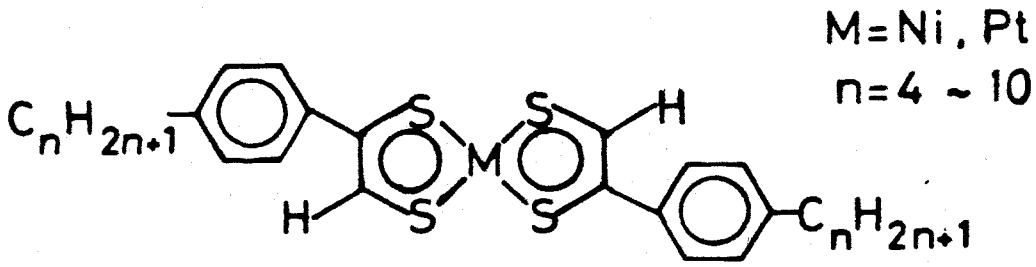
(4) Spectroscopic Studies on Polymorphism in Bis-(1-p-n-octylphenylbutane-1,3-dionato)copper(II)
K. Ohta, M. Yokoyama, and H. Mikawa
Mol. cryst. Liq. Cryst., in contribution.

CONTENTS

GENERAL INTRODUCTION

Recently, organic transition metal complexes with long alkyl chains have been synthesized for various purposes. These complexes are expected to have a posibility to resolve energy problem[1,2] and a posibility to be used as a new electronic or imaging material.[3,4,5] When long alkyl chains are substituted to core complexes, they exhibit interesting properties of (1) good solubility in alkane,[6] (2) mesomorphism,[7,8] (3) unusual thermochromism[6] and (4) micell formation.[1,2] 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.[2]

While, in this work, the author found solid polymorphism with multiple melting behaviour[9] as the fifth property in bis-(1-p-n-alkylphenylbutane-1,3-dionato)copper(II). The molecular structure of this complex is square-planar at its core complex part and rod-like for its whole structure. As summarized above as the second property, Mueller-Westerhoff et al. have reported that p-n-alkyl-substituted styryl-dithiolato Ni complexes and the Pt complexes show smectic and nematic, depending on the length of the p-n alkyl chains.[7] The molecular structure of those



Mueller-Westerhoff et al., Mol. Cryst. Liq. Cryst. Lett., 56, 249 (1980).

complexes are very similar to the author's complexes, because those are square-planar at their core complex parts and rod-like for their whole structures. Therefore, the mesomorphism and the solid polymorphism of these type of complexes would make a new field in the transition metal complex chemistry.

This thesis consists of three chapters. Chapter I describes the preparation of square-planar trans-bis-(1-p-n-octylphenylbutane-1,3-dionato)copper(II), its polymorphic properties, and the interrelationships. In Chapter II, spectroscopic studies on polymorphism in bis-(1-p-n-octylphenylbutane-1,3-dionato)copper(II) are described. Chapter III deals with the synthesis of bis-(1-p-n-alkylphenylbutane-1,3-dionato)copper(II) having different n-alkyl chains, and with the effect of alkyl chain length to the solid polymorphism and the multiple melting behaviour.

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CHAPTER I

SQUARE-PLANAR trans-BIS-(1-p-n-OCTYLPHENYLBUTANE-1,3-DIONATO)-COPPER(II), A NEW COMPOUND EXHIBITING THREE KINDS OF 'DOUBLE MELTING' BEHAVIOUR

I-1 INTRODUCTION

The title complex was synthesized in an attempt to find a new mesomorphic compound containing a transition metal. This complex was synthesized in very good thermal stability. Until it decomposes at 221.5°C, neither sublimation nor volatilization occurs. Although this complex does not have a mesomorphic sate, it exists in four polymorphs; C^l(crystal of low m.p., 96°C), C^a (crystallized from acetonitrile solution, m.p., 99°C), C^m(crystal of medium m. p., 108°C), and C^h (crystal of high 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.[1] As to be described in Chapter II, spectroscopic evidence concludes no changes in coordination form of square-planar trans structure in each transition. So far as the auther knows, this is the first compound of the ML_2(M = transition metal, L = ligand) with a long alkyl chain which has three double melting forms.

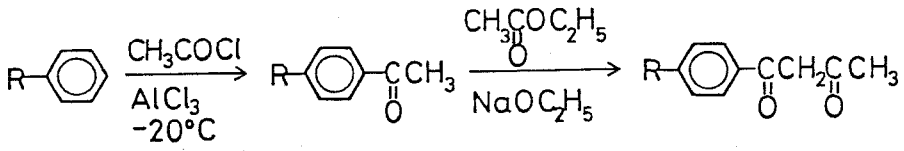
The purpose of the present chapter is to describe the

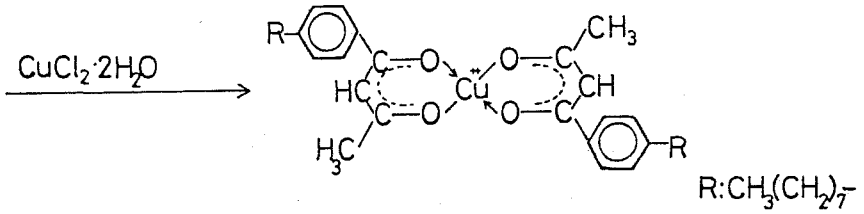
preparation of this complex, its polymorphic properties, and the interrelationships of them.

I-2 EXPERIMENTAL

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

The starting material, p-n-octylacetophenone, was prepared as reported by Giroud et al.[2] The ligand, 1-p-n-octylphenyl-butane-1,3-dione, was synthesized by the method of Beyer et al.[3] Its copper(II) complex was obtained according to the method reported by Hon et al.[4]





p-n-Octylacetophenone

By the acetylation of n-octylbenzene (0.35 mole) with acetyl chloride (0.75 mole) at -20°C in dichlorometane (ca. 350 ml) in the presence of aluminium chloride (0.70 mole) for 5 hours, p-n-

octlacetophenone (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 51.2 g (0.75 mole) of alcohol fre sodium etoxide and66.3 g (0.75 mole) of ethyl acetate was poured into 88.1 g (0.38 mole) of p-n-octlacetophenone in an ice bath and stirred at about 70°C for 8 hours. After one day, the product was collected and shaken with an aqueous soluton of acetic acid and ether, and then washed well with water. Evapolatin gave 84.0 g (80.7%) of crude 1-p-n-octenylbutane-1,3-dione, which was purified by distillaton to a colourless oil (b.p.=39.0-41.0°C). In the i.r. spectrum of this compound, very strong absorption due to the β-diketne structure appeared at te region of 1600 cm^{-1}. Anal. Found(Calcd. for $C_{18}H_{26}O_2$): C 78.59%(78.79), H 9.69(9.55).

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

The complex was precipitated from an aqueous solution of 17.0 g (0.10 mole) of cupric chloride mixed with an ethanol solution of 13.7 g (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 14.9 g (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 at 30-32°C for about one month gave C^a form as green hair-like crystals. The C^a crystals thus obtained were crystalographically 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 acertone 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. Including of solvent of acetonitrile in C^a crystal is ruled out, because, in

the themogravimetric measurement, no weight loss was observed up to 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 required from acetonitrile and two weeks from N,N-dimethylformamide. C^h could be also obtained by the solid-solid phase transition of C^l at about 50°C in the presence or absence of solvent. With the phase transition in the presence of solvent, namely solution phase transformation,[5] C^h was obtained when C^l 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 abcense 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 crystal 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 Fig. 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 scannining calorimeter and with a thermogravimeter (Rigaku DSC-TG 8085 or Daini-Seikosha DSC SSC 560). X-Ray diffraction powder patterns of all polymorphs were meadured with Cu-K_α radiation, using a Rigaku X-ray diffractometer.

I-3 RESULTS AND DISCUSSION

Figure 1 shows the x-ray diffraction powder patterns of four polymorphs. As shown in the figure, each polymorph shows

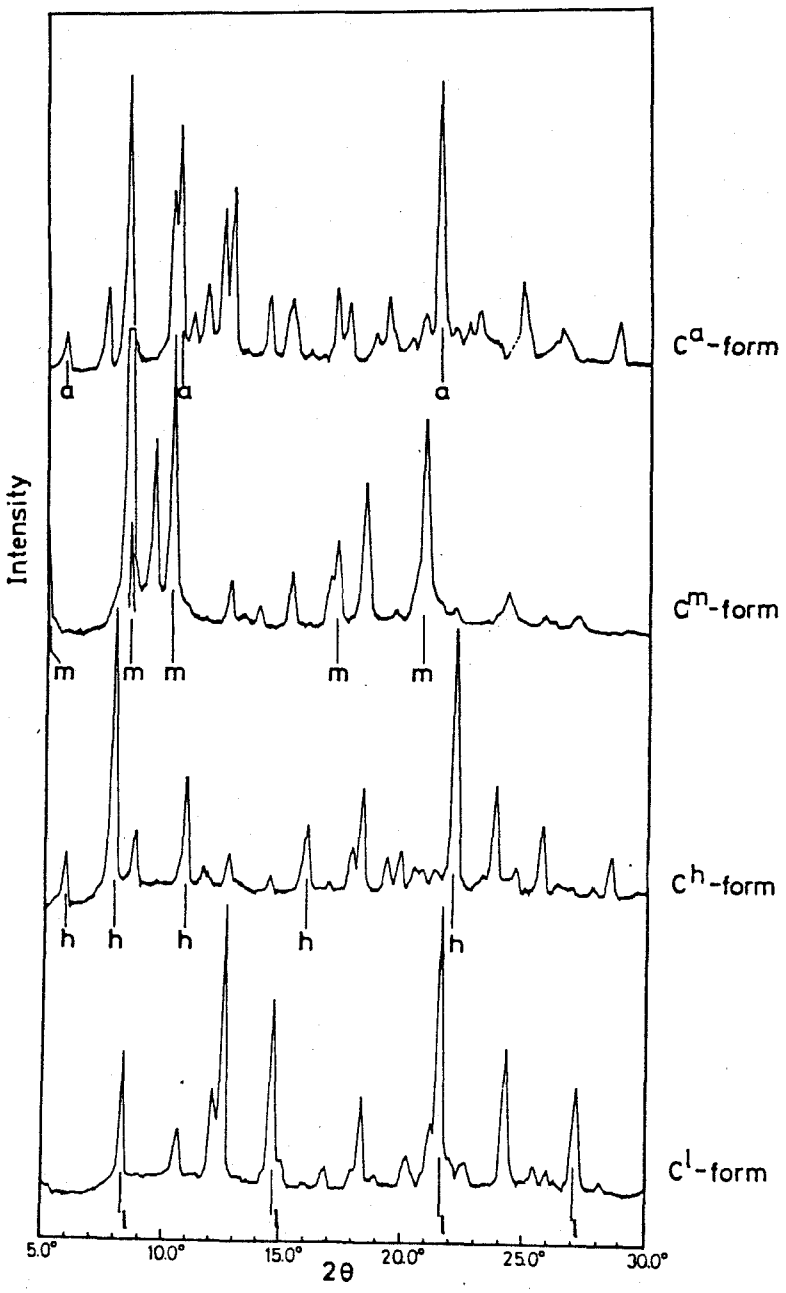


Fig. 1 X-Ray diffraction powder patterns of four polymorphs of the title complex. Peaks denoted with l, a, m, and h in this figure are clearly distinguishable from each other.

Table 1 X-Ray diffraction data with relative intensities (I) for the strongest lines in each polymorph.

C^h	d/Å	11.05	4.00	8.04	3.74
	I_o	100	89	43	38
C^m	d/Å	10.28	8.51	4.25	9.72
	I_o	100	51	37	34
C^a	d/Å	10.51	4.13	8.27	6.86
	I_o	100	98	91	61
C^l	d/Å	4.10	6.97	5.99	3.66
	I	100	100	68	51

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 due to a change of the coordination structures. However, each polymorph exhibited the same electronic spectrum, indicating the square-planar form in the coordination, and exhibited almost the same infrared and far-infrared spectra except for 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 coordination change, but due to the change in the packing of n-alkyl chain

just as in the case of the well-known tristearine.[1] Actually, these four polymorphs showed different splitting intensities of the methylene rocking absorption bands, around 720 cm from singlet to doublet. So far as the author knows, such a polymorphism is the first case in the organic transition metal complexes. The trans-type coordination 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 coordination. The detailed discussion on the spectroscopic studies will be described in Chapter II.

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

When C^l crystal was heated rapidly up to some temperature below the m.p. of C^l, a solid mixture of C^l and C^h was obtained because of a relatively slow solid-solid phase transition from C^l to C^h at ca. 50°C. The C^l crystals in the mixture melted at the m.p. of C^l, 95.7-95.8°C, and then the melt resolidified completely in the C^h form because of the presence of seed 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 the thermograms of C^l crystal with various heating rates. In the case of higher rates, two endothermic peaks due to the meltings of C^l and C^h were

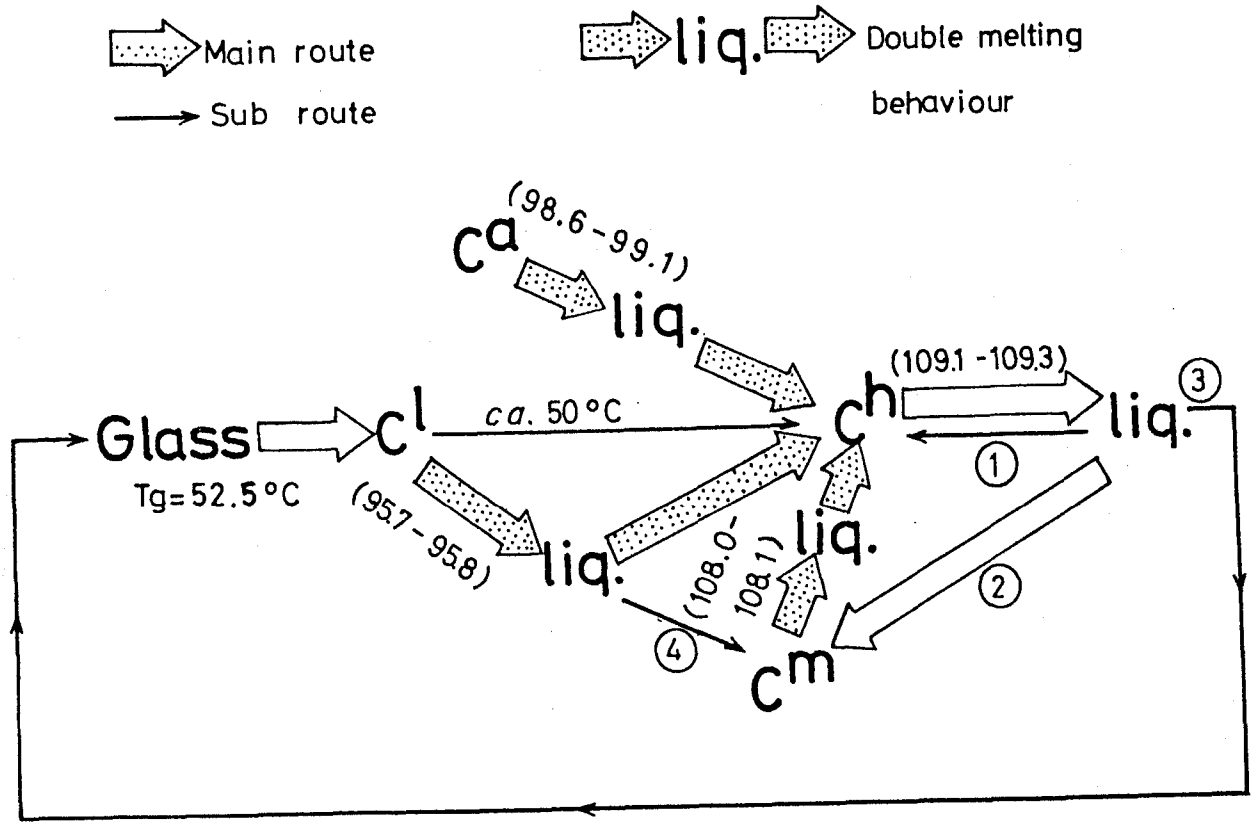


Fig. 2 The sequence of changes of state for the title complex: (1) very slow cooling; (2) slow cooling; (3) rapid cooling; (4) see main text. Numbers in parentheses are m.p.s in °C.

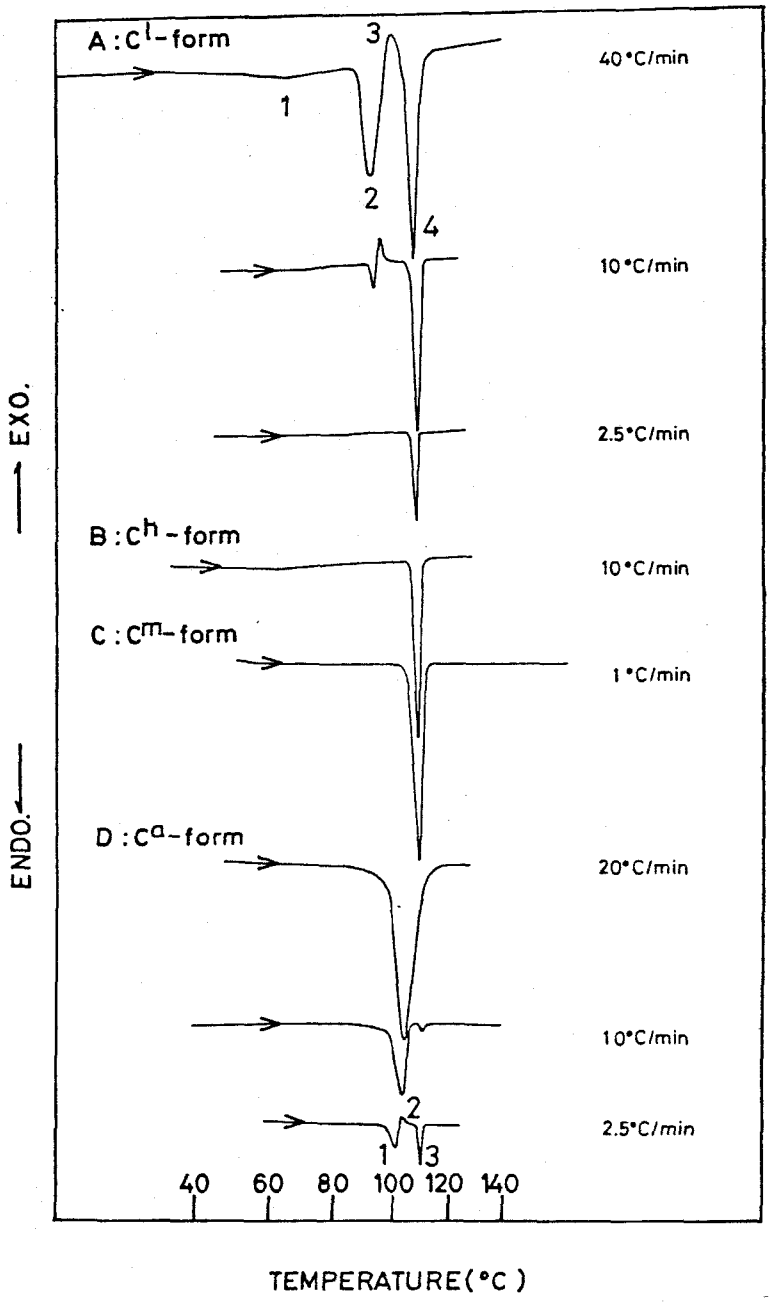


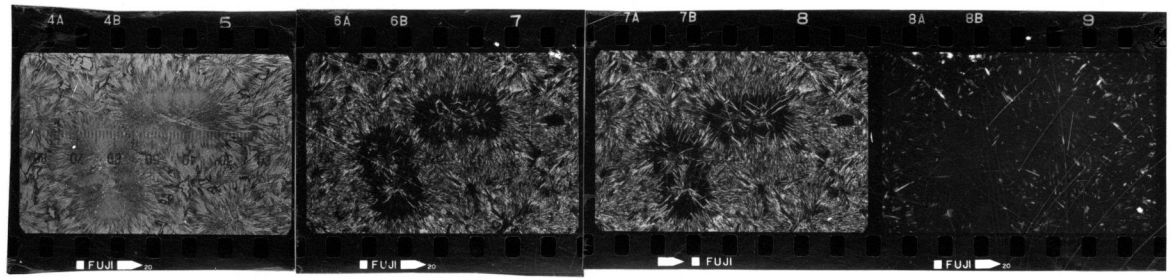
Fig. 3 D. S. C. thermograms of four polymorphs for different heating rates. Peaks denoted with 1, 2, 3, and 4 in this figure (A and D) are explained in the main text.

clearly observed. On very slow heating of C^l crystal, however, only single m.p. of C^h was observed, as a result of the complete solid-solid phase transition. Thus, C^l crystal exhibitied the double melting behaviour only on rapid heating (>10°C/min.).

In contrast to the case of C^l, 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 behaviour only on very slow heating without a solid-solid phase transition. As 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 dose 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.

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.



Temp.(°C)	95.7	108.6	108.6	109.1
Light	normal	cross	cross	cross
State Change	$C^m + C^h$	melt → $Liq. + C^h$	resolidify → $C^h + C^h$	melt → Liq.

10min.

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

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 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 Fig. 6. When the C^l crystal, for example, is heated very rapidly, having not enough time for as appreciable solid-solid phase transition at 50°C to occur, it is superheated up to along the C^h 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 socond 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.

It should be noted that T_g and T_c are very close. This property might be have the possibility of being used as a potential image-forming material. Actually, the glass sandwiched in two thin films of polyethylene terephtalates was

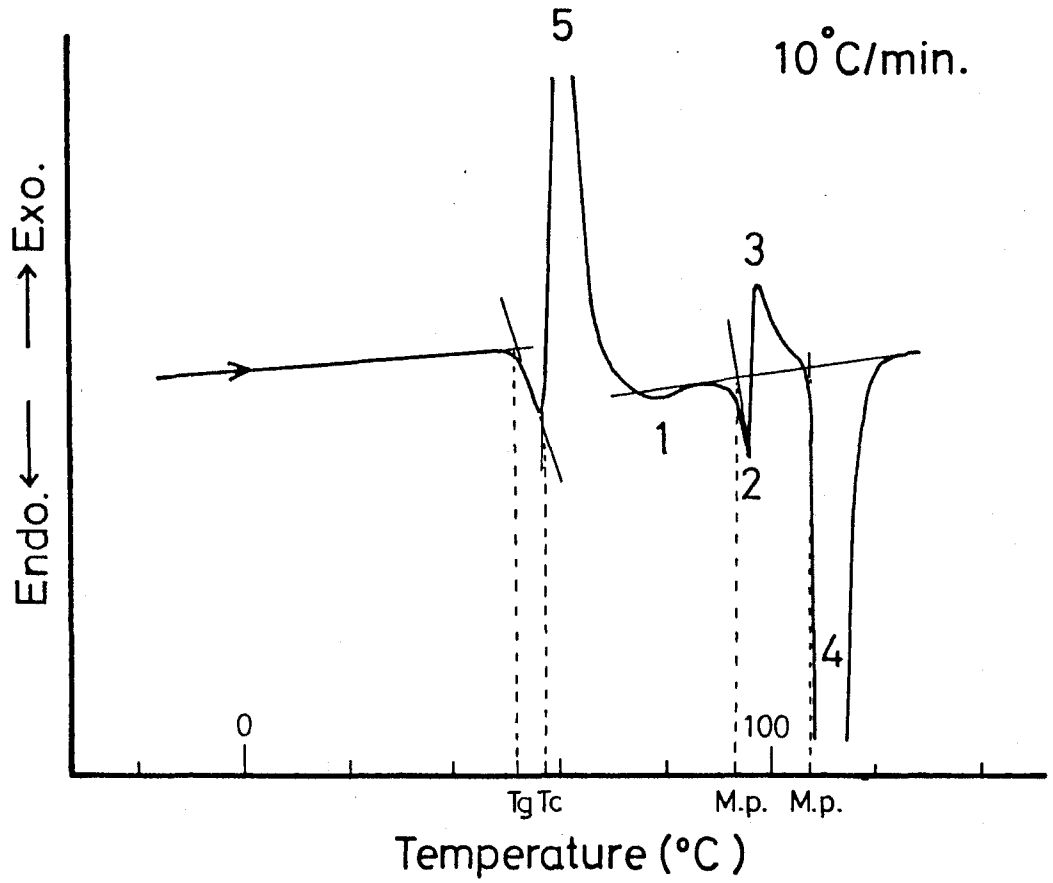


Fig. 5 D. S. C. thermogram of glassy state of the title complex. The heating rate was 10°C/min. Peaks denoted with 1, 2, 3, and 4 in this figure correspond to the peaks denoted with 1, 2, 3, and 4 in Fig. 3(A). Peak 5 is an exothermic peak of crystallization of supercooled liquid. T_g, T_c, and M.p.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

Table 2 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	

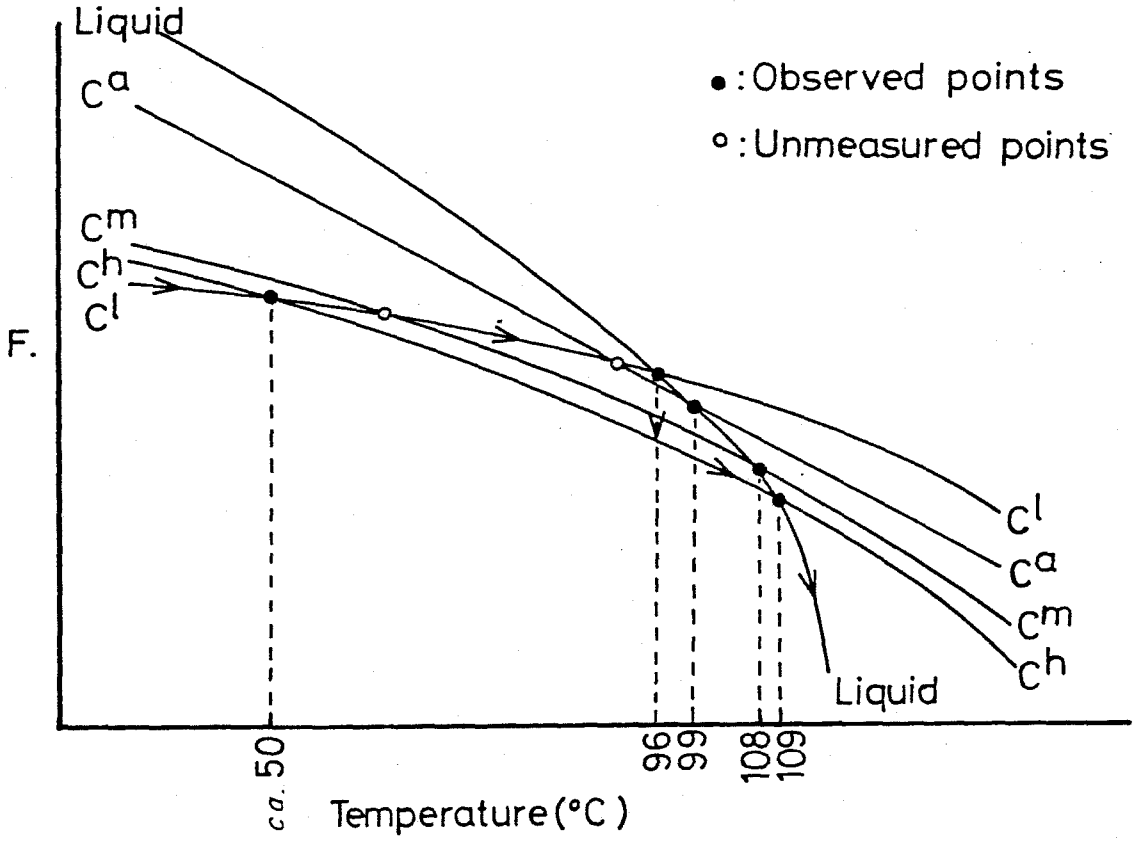


Fig. 6 A free energy versus temperature (F-T) diagram for polymorphs in the title complex. Except for the filled points the curves are schematic.

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 cryatallized portion turned back again to the transparent glassy state. Thus, this complex has a possibility to be used as an erasable imaging material.

The photocrystallization might be caused by two reasons. First of them, as mentioned abouve, T_g and T_c of this complex are very close. Second of them, as shown in Fig. 7, this complex strongly absorbs the light of 324 nm (ε= 51000 in n-hexane), which wavelength is very near to that of N_2 laser light, 337 nm. These properties are thought to be suitable such a photocrystallization.

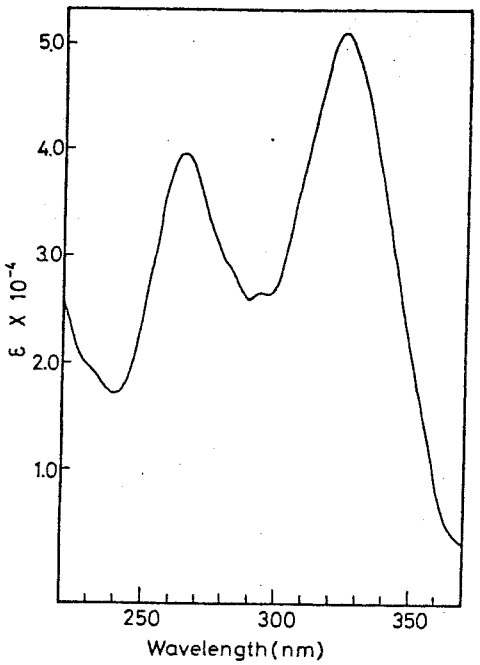


Fig. 7 The ultra violet absorption spectrum of the title complex.

I-4 SUMMARY

The new compound, bis-(1-p-n-octylphenylburtane-1,3-dionato)copper(II) has four polymorphs, C^l(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^l, C^a, and C^m exhibit "double melting" behaviour. Double melting of C^l 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^l to C^h was observed at ca. 50°C. 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. This property has a possibility to be used as an erasable imaging material.

I-5 REFERENCES

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CHAPTER II

SPECTROSCOPIC STUDIES ON POLYMORPHISM IN BIS-(1-p-n-OCTYLPHENYL-BUTANE-1,3-DIONATO)COPPER(II)

II-1 INTRODUCTION

In Chapter I, it has been described that the title complex, bis-(1-p-n-octylphenylbutane-1,3-dionato)coper(II), $(n\text{-OBA})_2Cu(II)$, shows four polymorphic forms with different melting points, C^l(m.p.=96°C), C^a(99°C), C^m(108°C), and C^h(109°C), and three of them exhibit "double melting" behaviour. It seems interesting to make clear whether the present polymorphism is caused by the change in the coordination structure or merely by the change in the molecular arrangement of each crystal.

Reacently, Bulkin et al. reported that the trans form of square-planar bis-(1-p-n-octyloxyphenylbutane-1,3-dionato)-palladium(II) might be a possible candidate for mesomorphic substance,[1] and that the trans form gave the quite different far-infrared and Raman spectra from the cis form.[2]
Mueller-Westerhoff et al. reported that p-n-alkyl substituted square-planar styryldithiolato Ni complexes and the Pt complexes show smectic and nematic, depending on the length of the p-n-alkyl chains.[3] In their report, however, they described that whether

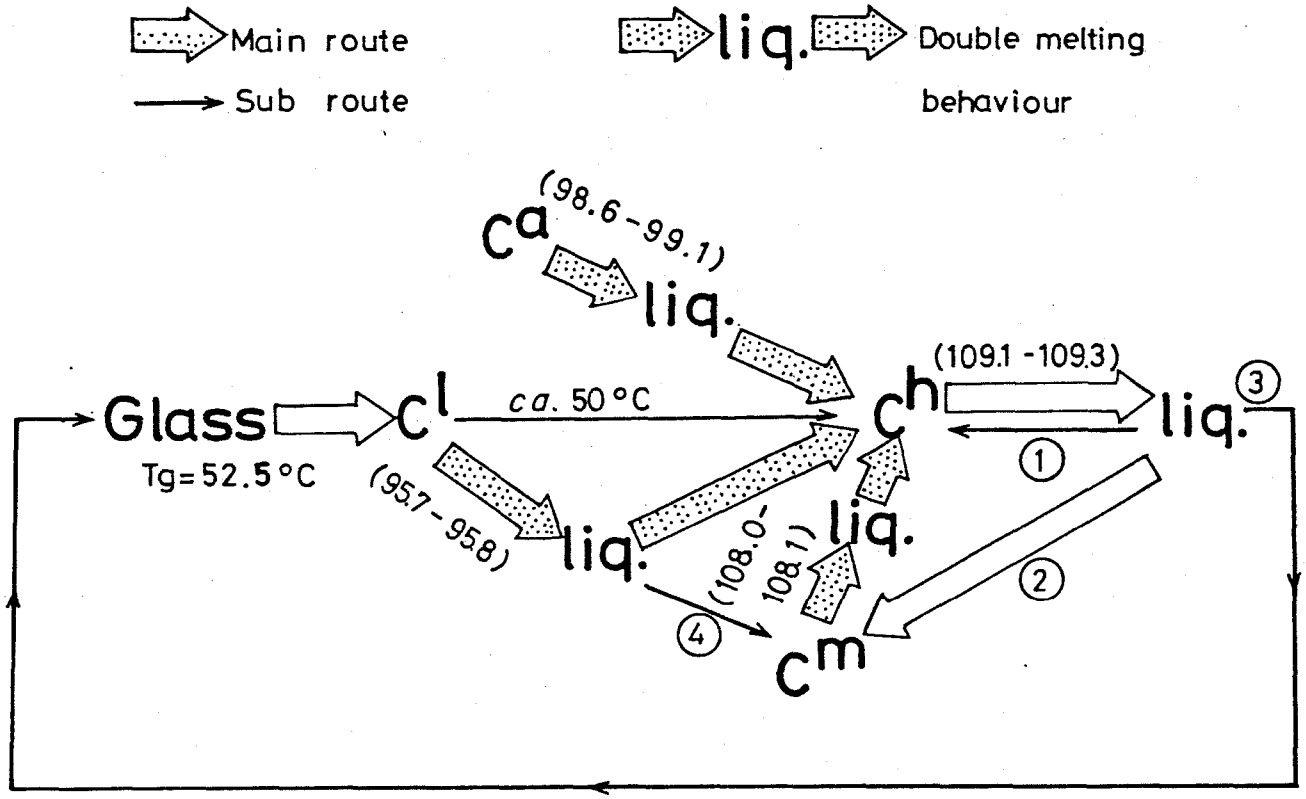
cis-trans isomerization causes such a mesomorphism was not clear at that time because of the difficulty in the isolation of cis- and trans-isomers. Thus, few structural studies are paied on the mesomorphism in such type of the transition metal complexes and the origin of such mesomorphism is remained unclear at present time. From this point of view, the structural studies on the polymorphism of our complex will provide some information concerning with the nature of the above-mentioned mesomorphism in the transition metal complexes, since the molecular structures of these complexes are very similar to our complex and polymorphism might be closely related to mesomorphism.

In this chapter, the author wishes to report structural studies on polymorphism of $(n\text{-OBA})_2Cu(II)$ by means of spectroscopic techniques. All four polymorphic forms of the present complex have the square-planar trans form in coordination structure. The main origin of this solid polymorphism is found to be due to the change in the n-octyl chain packing in each crystal.

II-2 EXPERIMENTAL

A. Materials The synthesis procedure of the title complex, $(n\text{-OBA})_2Cu(II)$, and the preparation of its four polymorphic forms were described in Chapter I. Each polymorphic form can be

obtained as a stable state at room temperature, and the phase transition diagram of these four forms are summarized in the following scheme.



Scheme The sequence of changes of state for bis-(1-p-n-octyl-phenylbutane-1,3-dionato)coper(II). Numbers in parentheses are m.p.s in °C. See the details of this scheme at Chapter I.

For comparison, bis(1-phenylbutane-1,3-dionato)copper(II), $(BA)_2Cu(II)$, was synthesized according to the method reported by Hon et al.,[4] and $(acac)_2Cu(II)$ was purchased from Wako Pure

Chemicals.

B. Measurements The infrared spectra were recorded on a Hitachi Parkin-Elmor 225 infrared spectrophotometer(4000 - 650 cm^{-1}). The far-infrared spectra were measured in Nujol mull method using Hitachi EPI-L (700 - 250 cm^{-1}) and/or Hitachi FIS-3 (400-30 cm^{-1}) far-infrared spectrophotometers. The Raman spectra were obtained by using a Japan Spectroscopic Company R750 triple monochromatic spectrophotometer irradiating with the 5145 Å line from an argon ion laser as the excitation light source. The visible electronic reflection spectra of the crystalline powders were measured by using a Hitachi 340 spectrophotometer.

II-3 RESULTS AND DISCUSSION

As mentioned in the introductory section, the present complex has four polymorphic forms having different melting points, C^l, C^a, C^m, and C^h. As a possibility for the origin of such polymorphism, a change in the coordination structure of the core complex as illustrated in Fig. 1 (A), might be easily inferred. Such a change in the coordination structure is expected to be reflected in the electronic spectra.

As described energy diagram in Fig. 2, the tetrahedral or

octahedral field around the copper(II) ion gave only single peak in the visible region due to the d-d electronic transition, while the square-planar field gave two peaks in the visible region ($d_{z^2} \rightarrow d_{x^2-y^2}$, $d_{xy} \rightarrow d_{x^2-y^2}$) and one peak in the ultra-violet region (d_{xy}, $d_{yz} \rightarrow d_{x^2-y^2}$). Thus, the electronic spectra reflect precisely such a change in the coordination structure.

A. Electronic Reflection Spectra As shown in Fig. 3, all the electronic reflection spectra of these four polymorphs of $(n\text{-OBA})_2Cu(II)$ gave two peaks in the d-d electronic transition region as same case as square-planar $(acac)_2Cu(II)$ and $(BA)_2Cu(II)$ which structures have been confiremed by X-ray analyses.[6] λ_{max}(nm): $(acac)_2Cu(II)$,561, 644; $(BA)_2Cu(II)$,576, 642; $(n\text{-OBA})_2Cu(II)$, 556(C^l), 558(C^m), 559(C^a), 555(C^h), ca. 650 (for all polymorphs). Furthermore, the benzene solution spectrum of $(n\text{-OBA})_2Cu(II)$ is same to that of square-planar $(BA)_2Cu(II)$. λ_{max}(nm) in benzene: $(BA)_2Cu(II)$, 545(ε = 51.8), 657(55.1); $(n\text{-OBA})_2Cu(II)$, 551(44.0), 656(49.9). In both cases of solid and solution, the $(n\text{-OBA})_2Cu(II)$ has the square-planar coordination structure, and no difference in coordination structure was found in each polymorph.

Thus, the tetrahedral or octahedral coordination structure was ruled out, since only single peak in this visible region due to the d-d electronic transition was expected if this type of complex is in such coordiantion forms.[7]

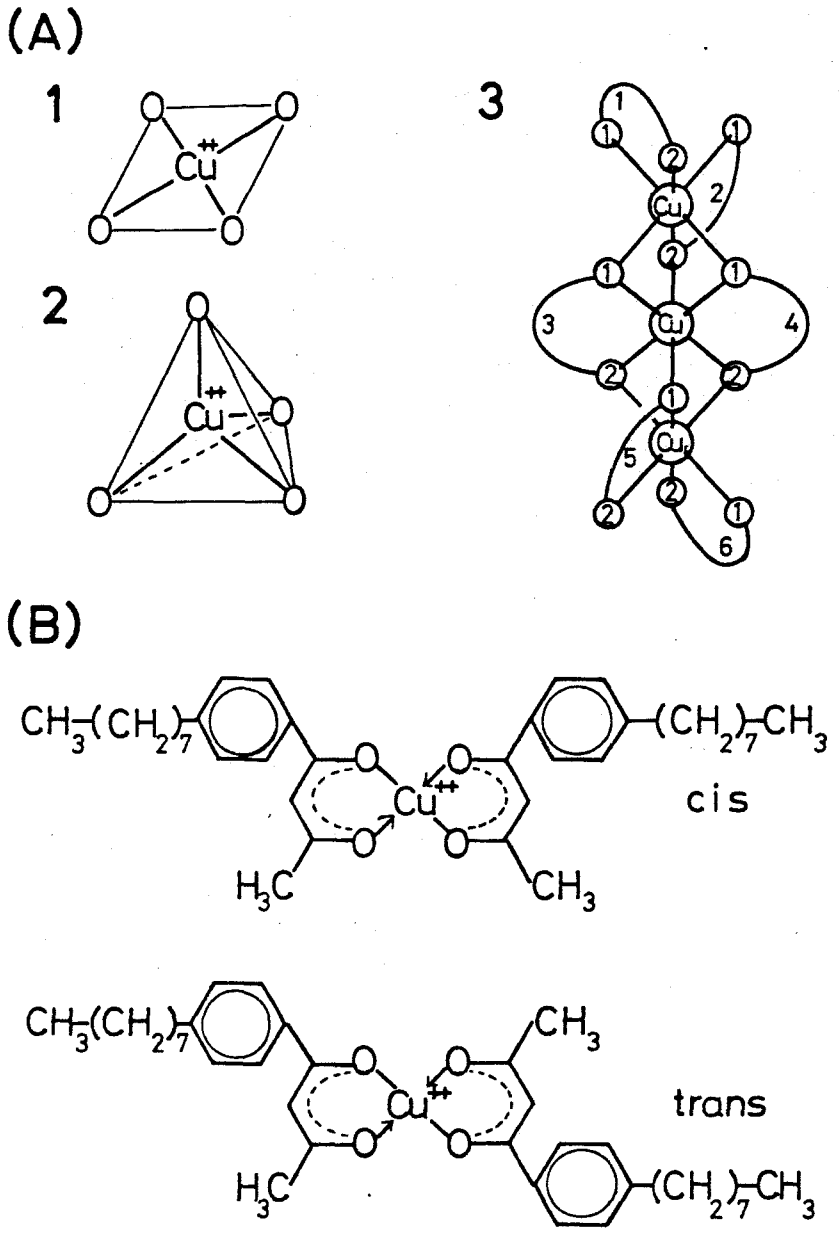


Fig. 1 Asumed origin of the solid polymorphism of bis-(1-p-n-octylphenylbutane-1,3-dionato)copper(II) (A): change in the coordination structure of the core complex part; 1:square-planar form, 2:teterahedral form, 3:octahedral form as reported in $[(acac)_2Ni(II)]_3$ by Bullen et al.,[5] (B):cis-trans isomerization maintaining square-planar form in the core complex part.

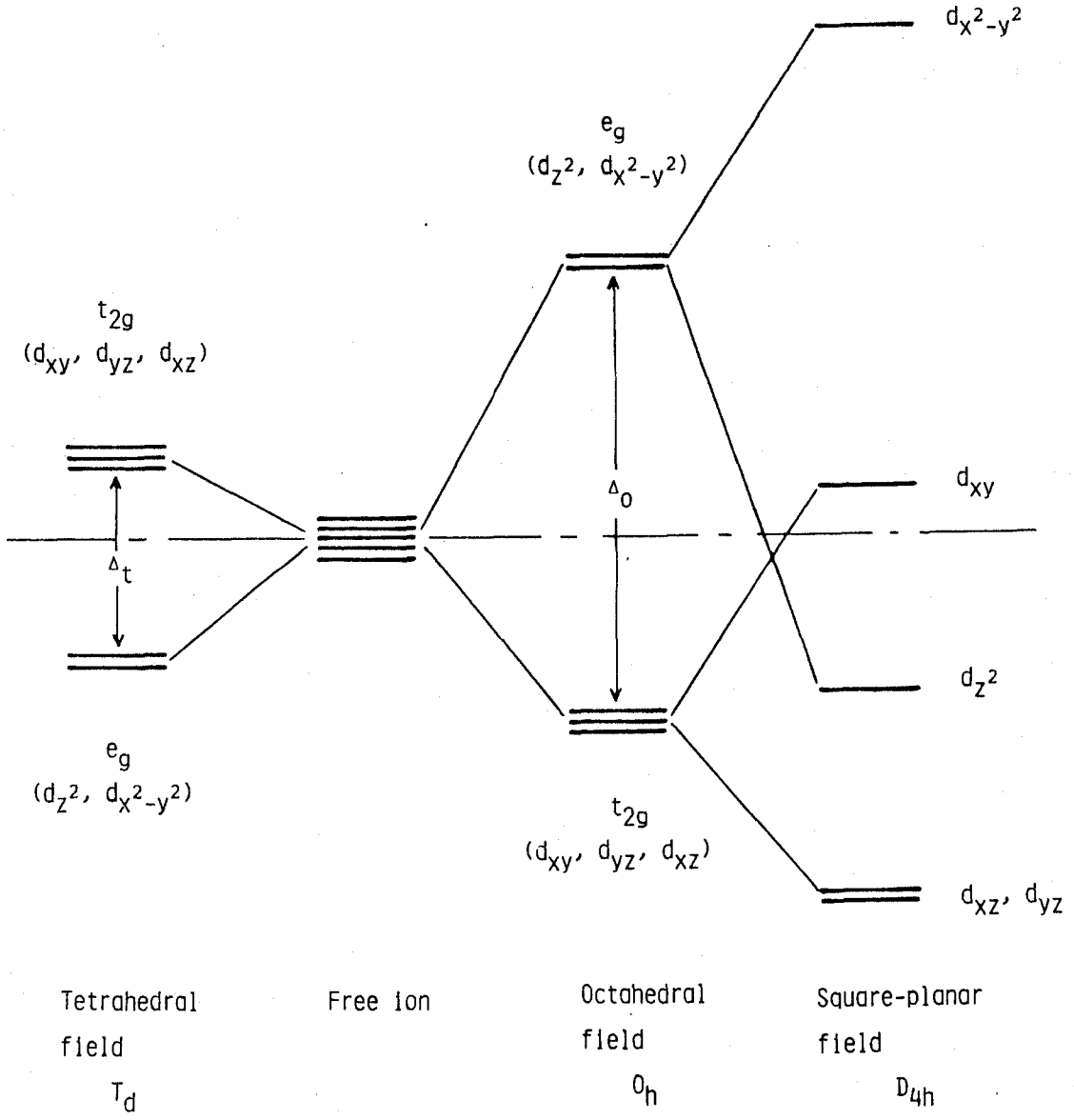


Fig. 2 Diagram showing the relative energies of orbitals resulting from the splitting of the set of *d* orbitals in tetrahedral, octahedral, and square-planar fields.

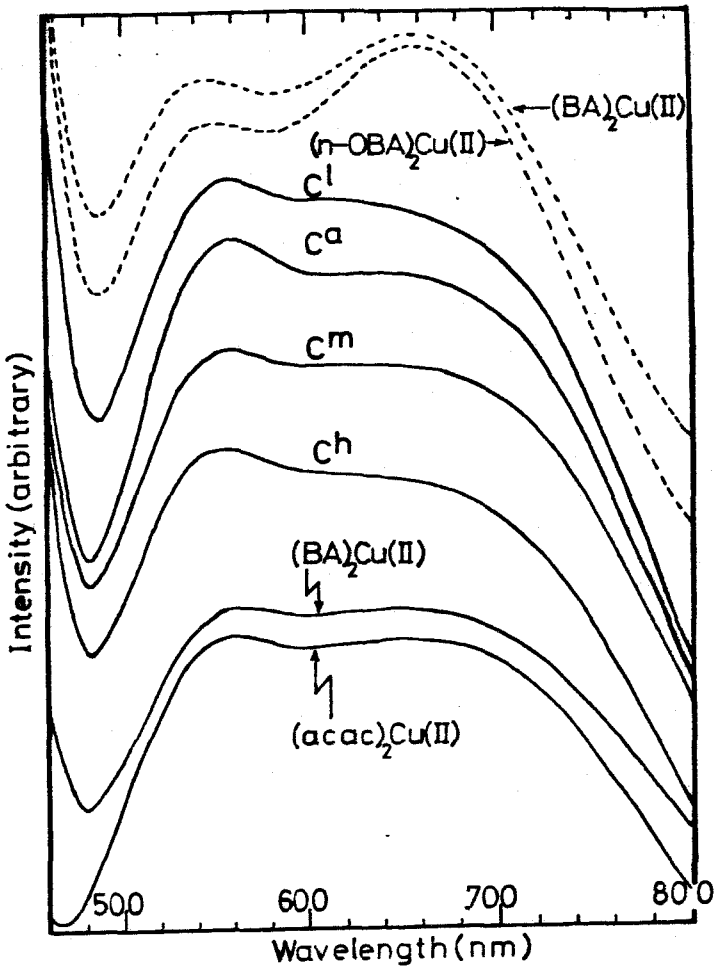


Fig. 3 Solid lines are electronic reflection spectra at the four polymorphs of $(n\text{-OBA})_2Cu(II)$, $(BA)_2Cu(II)$, and $(acac)_2Cu(II)$, respectively. Each spectrum was uncorrected into the absorption spectrum. Dashed lines are electronic absorption spectra of $(n\text{-OBA})_2Cu(II)$ and $(BA)_2Cu(II)$ in benzene solution. All scales are arbitrary.

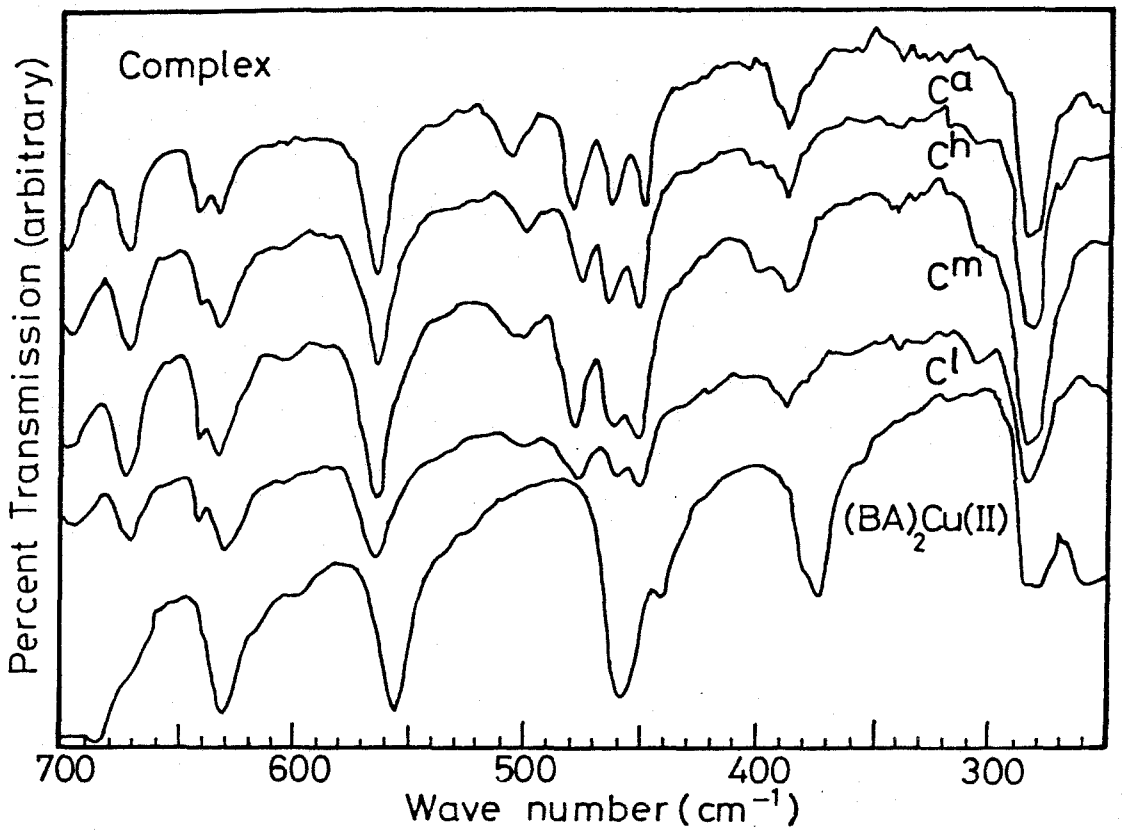


Fig. 4 Far-infrared spectra of the four polymorphism of $(n\text{-}OBA)_2Cu(II)$ and $(BA)_2Cu(II)$ in the region of 700-250 cm^{-1}, Nujol mull.

B. Far-infrared and Raman Spectra As the origin for the polymorphism of the present type of the square-planar transition metal complex, another possibility intuitively inferred is the cis-trans isomerization as illustrated in Fig. 1 (B). Such kinds of diferrence in the molecular structure will appear in their far-infrared spectra.

Figure 4 shows the far-infrared spectra of the four polymorphic forms. As can be seen clearly, each polymorph of $(n\text{-OBA})_2Cu(II)$ exhibited the same far-infrared spectrum in the frequency region asociated with the vibratrions invoving metal-oxygen streching and ligand skeltal deformation. Recently, Bulkin et al.[2] have reported that in the case of bis-(1-p-n-octyloxyphenylbutane-1,3-dionato)palladium(II) which has the square-planar coordination structure, the far-infrared spectra are quite different between cis- and trans-isomers. As the detailed analysis of the present spectra of this region will be presented later, no specstral difference in this region leads to the conclusion that such a cis-trans isomerization does not occur in the polymorphic transitions of the present complex at least, and therefore that each polymorph of the present $(n\text{-OBA})_2Cu(II)$ should be either isomeric form.

In order to asign the present complex to either cis or trans geometry, the group theoretical selection rule, so-called mutual exclusion rule, was examined for the infrared and Raman active vibrational modes. The cis and trans isomers in the square-planar structure have C_{2v} and C_{2h} molecular synmetry, respectively. Since the trans geometry belonging to C_{2h} synmetry has the center of synmetry, then the mutual exclusive selection rule can be expected to hold between infrared and Raman active modes. The correlation diagram and selection rules are gven in Table 1 for C_{2v}, C_{2h}, and D_{2h}. The last one

corresponding to the case of the square-planar symmetrical $(acac)_2Cu(II)$.

Table 1 Correlation table and selection rules

I. R.	Raman	C_{2v}	D_{2h}	C_{2h}	I. R.	Raman
M_x	α_{xx} , α_{yy} , α_{zz}	A_1	A_{1g}	A_g	forbidden	α_{xx} , α_{yy} , α_{zz} , α_{xy}
			B_{1g}			
M_y	α_{xy}	B_1	B_{2g}	B_g	forbidden	α_{zx} , α_{yz}
			B_{3g}			
forbidden	α_{yz}	A_2	A_{1u}	A_u	M_z	forbidden
			B_{1u}			
M_z	α_{zx}	B_2	B_{2u}	B_u	M_x , M_y	forbidden
			B_{3u}			

Each principal (z) axis is perpendicular to $-CuO_4-$ plane. M_x, M_y, and M_z: infrared active, α: Raman active.

In Fig. 5 is shown the far-infrared spectrum of $(n\text{-}OBA)_2Cu(II)$ in C^1 polymorphic form measured in Nujol mull. In the same figure is also shown the vibrational spectrum for $(BA)_2Cu(II)$, whose molecular structure has been determined as the square-planar trans form by X-ray analysis. If the present $(n\text{-}OBA)_2Cu(II)$ complex has the trans type of coordination, some similarity would be expected for these square-planar Cu(II) complexes. Actually, some strong bands in this region which should be assigned to the Cu - O vibratonal modes gave good correspondence for $(n\text{-}OBA)_2Cu(II)$ and $(BA)_2Cu(II)$. Figure 6(a)

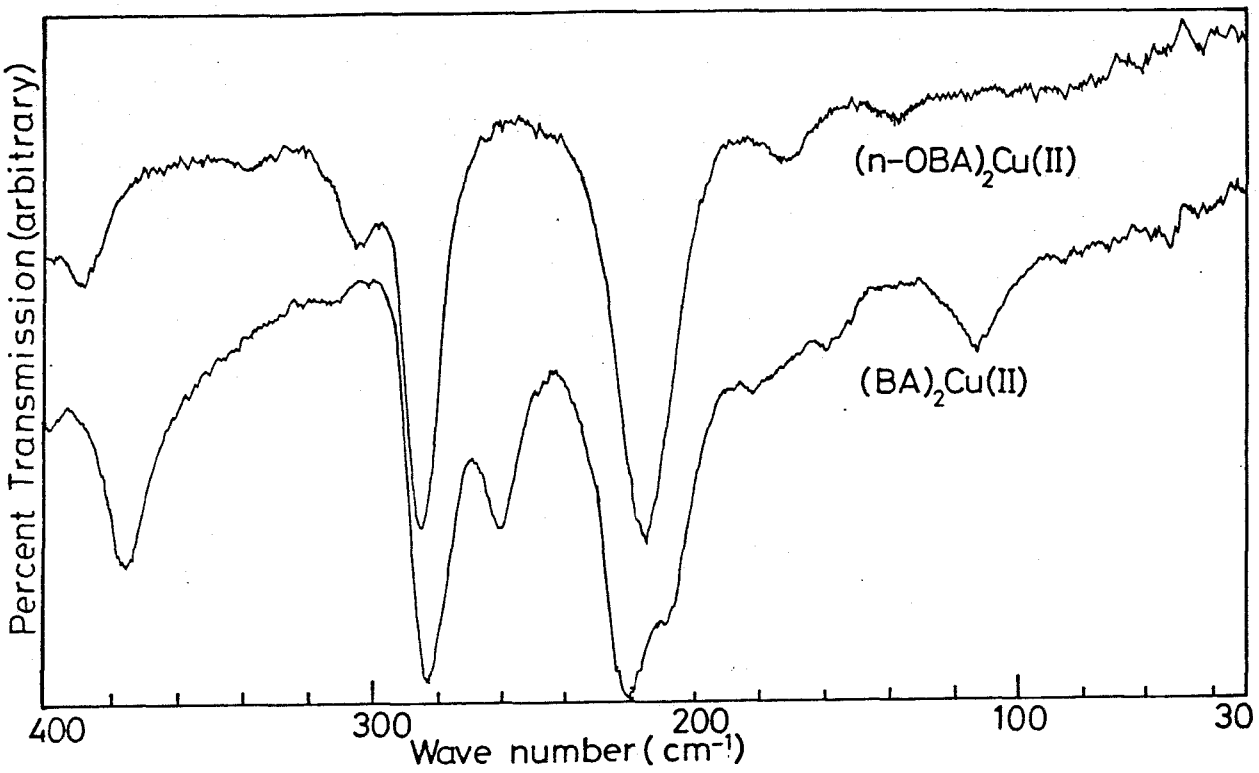


Fig. 5 Far-infrared spectra of $(n\text{-OBA})_2Cu(II)$ in C^1 polymorphic form and $(BA)_2Cu(II)$ in the region of 400-30 cm^{-1}, Nujol mull.

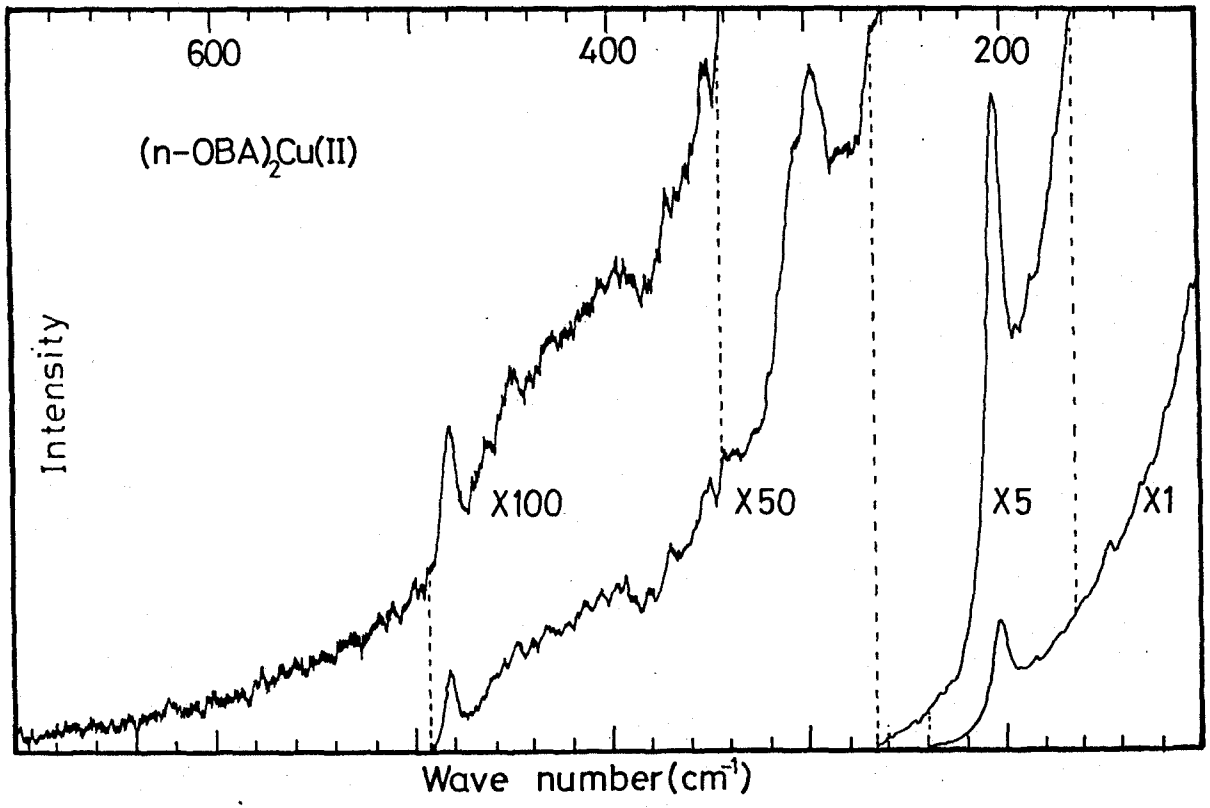


Fig. 6-(a) Low frequency Raman spectrum of $(n\text{-OBA})_2Cu(II)$ in C^1 polymorphic form, solid sample.

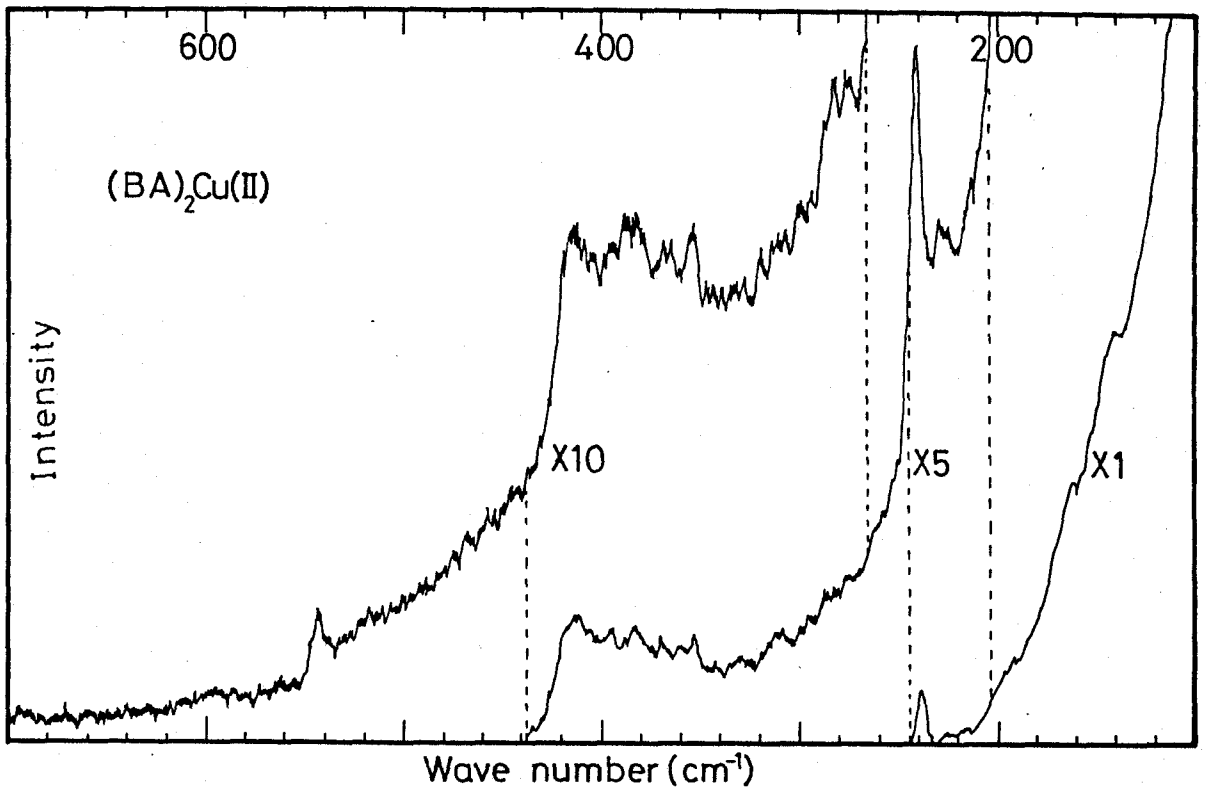


Fig. 6-(b) Low frequency Raman spectrum of $(BA)_2Cu(II)$, solid sample.

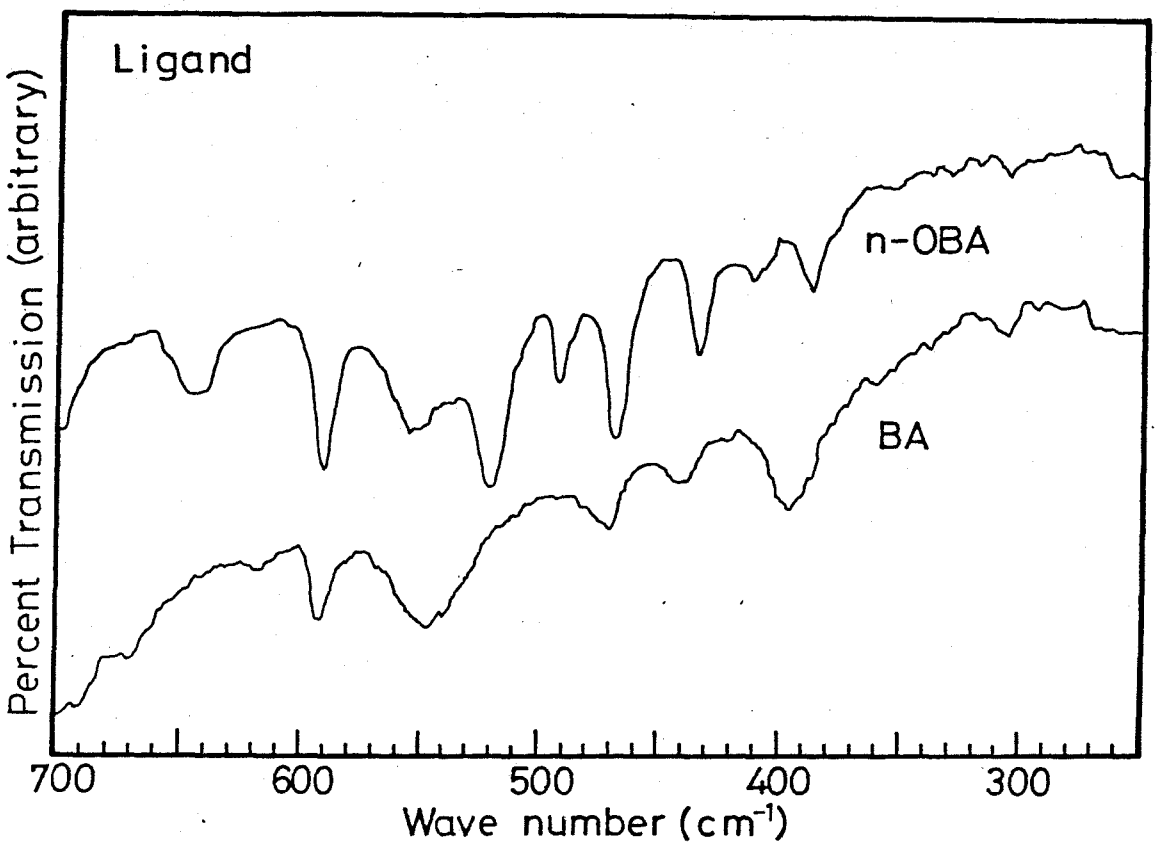


Fig. 7 Far-infrared spectra of 1-p-n-octylphenylbutane-1,3-dione, n-OBA, and 1-phenylbutane-1,3-dione, BA. Nujol mull.

Table 2 Vibrational spectra of $(n\text{-OBA})_2Cu(II)$[a] and $(BA)_2Cu(II)$[b].

$(n\text{-OBA})_2Cu(II)$[a]				$(BA)_2Cu(II)$[b]				Descriptions
Infrered		Raman		Infrared		Raman		
Freq. (cm^{-1})	Intens.[c]	Freq. (cm^{-1})	Intens.[c]	Freq. (cm^{-1})	Intens.[c]	Freq. (cm^{-1})	Intens.[c]	
		73	w	112	m			
138	w	146	w			140	w	
				160	w	162	w	
172	w	186	w	182	w			
				209	sh			
215	vs			220	vs			= Cu-O deformation [$(acac)_2Cu(II)$: 217 cm^{-1}][d]
						226	w	
		223	vs			241	vs	
				261	m	276	vw	
285	vs			283	vs			= Asymmetric Cu-O streching mode.[d]
		297	s					= Accordion mode of n-octyl chain.[e]
304	w							
				310	w	310	vw	
338	vw							
		350	w			353	m	
		372	w	375	m	383	m	
393	m							
397	w	397	w	399	vw			
						414	m	
		448	w	441	m			
450	m							= Local vibrational mode of ligand.[f]
461	m			458[g]	s			= Cu-O Streching.[d]
478	m							
		482	s			543	s	
500	w							
563	s			556	m			
602	w			599	w			
				614	w			
630	m			628	m			
638	m							
670	m			669	w			
691	m			684	s			
				694	s			
				709	s			

a $(n\text{-OBA})_2Cu(II)$= bis-(1-p-n-octylphenylbutane-1,3-dionato)copper(II). Infrared spectra of the four polymorphs of this complex were measured for the region of 700-250 cm^{-1}. As mentionted in the text, they are all the same. The infrared spectrum of the region 250-30 cm^{-1} and the Raman spectrum of 700-60 cm^{-1} region only for C^1 form are given here.

b $(BA)_2Cu(II)$=bis-(1-phenylbutane-1,3-dionato)copper(II).

c Relative intensity, vs: very strong; s: strong; m: medium; w: weak; vw: very weak; sh: shoulder.

d Referred to Ref. 9.

e Referred to Ref. 2.

f See Fig. 7 and 8.

g This band position is agreement with the result of Nakamoto, McCarthy, and Martell. See Ref. 8.

and 6(b) show the Raman spectra of the same frequency region for $(n\text{-OBA})_2Cu(II)$ and $(BA)_2Cu(II)$ complexes, respectively. The observed frequency, relative intensity, and tentative assignment are given in Table 2. In order to distinguish the local vibrational modes due to the ligand from those of Cu - O, the far-infrared spectra for BA and n-OBA ligands shown in Fig. 7 were also measured in Nujol mull.

It has been established from the far-infrared spectroscopic studies on various metal chelate compounds by Nakamoto et al.[8] that one of the M - O stretching modes appears in the 420 to 480 cm^{-1} region with the band shift to higher frequencies and increasing in intensity depending on the increasing stability of the metal chelates. In the case of $(BA)_2Cu(II)$, such a band appeared at 458 cm^{-1} with relatively strong intensity. In the case of $(n\text{-OBA})_2Cu(II)$, however, such a vibrational band appeared in almost same frequency region with reduced intensity and somewhat complicated feature. Since the far-infrared spectrum of n-OBA ligand shows distinct absorption bands in the same frequency regin as shown in Fig. 7, the lower frequency band of 450 cm^{-1} should be assigned to the local vibrational mode of the ligand part. The reduced intensity in 461 cm^{-1} of $(n\text{-OBA})_2Cu(II)$ seems to indicate the relatively weak interaction of metal - ligand in the present complex as compared with $(BA)_2Cu(II)$ and $(acac)_2Cu(II)$. The detailed assignments for the far-infrared spectrum of $(acac)_2Cu(II)$ complex based on the

normal coordinate treatments were made by Mikami et al.[9] They assigned the 291 cm^{-1} observed band to an asymmetric Cu - O stretching mode [$\nu 25$ (B_{2u}) in their notation]. In both $(BA)_2Cu(II)$ and $(n\text{-}OBA)_2Cu(II)$, the corresponding band was observed at 283 and 285 cm^{-1}, respectively, with strong intensity. Another far-infrared active band characteristic of the metal chelates associated with Cu - O deformation was observed at 220 cm^{-1} for $(BA)_2Cu(II)$ and 215 cm^{-1} for $(n\text{-}OBA)_2Cu(II)$, respectively, as shown in Fig. 5. These bands should correspond to the 217 cm^{-1} band observed in the case of $(acac)_2Cu(II)$, which is assigned to the out-of-plane $-CuO_4-$ deformatin $\nu 32$ belonging to B_{3u} symmetry species.

Thus, most of the characteristic far-infrared bands to be assigned to the vibrational modes in the central metal - oxygen coordinate part are identified by comparing with the far-infrared spectra of $(BA)_2Cu(II)$ and $(acac)_2Cu(II)$. These bands would be expected to reflect well the differece of cis-trans isomerization structure, C_{2h} (for trans-isomer) and C_{2v} (for cis-isomer). In Fig. 8 are compared schematically the observed far-infrared and Raman bands with rods propotioanal to the relative intensity. As can be seen clearly, no bands common to both the infrared and Raman spectra exist, and especially the bands due to the Cu - O vibrational modes mentioned above do not show the common bands for infrared and Raman spectra. This fact clearly indicates that the mutual exclusion rule is held in the

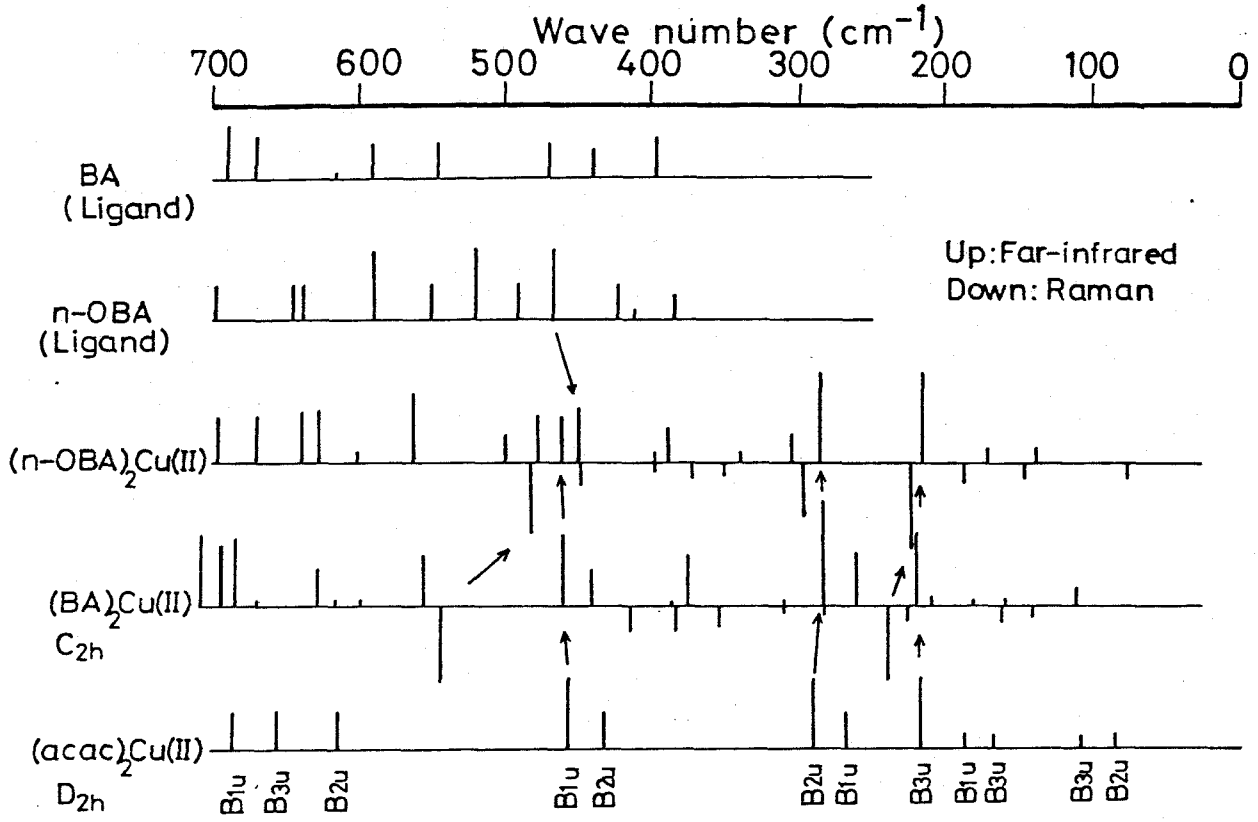


Fig. 8 Schematic comparison between the observed far-infrared and Raman bands with the rods propotional to the relative intensities, up:far-infrared, down:Raman. The only far-infrared bands of $(acac)_2Cu(II)$ and their assignments were referred to Ref. 9).

present $(n\text{-}OBA)_2Cu(II)$, i.e., the molecular strucure of the present complex has the trans type of coordination. In fact, in the case of $(BA)_2Cu(II)$ which was determined as the trans isomer by X-ray diffraction, same behaviour is recognized in both the infrared and Raman spectra.

It is conculuded, therefore, that each polymorph of

$(n\text{-OBA})_2Cu(II)$ has the same trans form of coordination, since each polymorph shows same far-infrared spectrum as shown in Fig. 4. It should be noted here that the intense Raman band of 297 cm^{-1} observed only in $(n\text{-OBA})_2Cu(II)$ will be assigned to the Raman active accordion mode of n-octyl chain. Bulkin et al. observed the same vibrational mode at 243 cm^{-1} in the Raman spectrum of the square-planar trans bis-(1-p-n-octyloxyphenyl-butane-1,3-dionato)Pd(II).[2)]

C. Infrared Spectra of Each Polymorph. As discussed above, each polymorph of $(n\text{-OBA})_2Cu(II)$ is decided to have the same square-planar trans type of coordination. However, there still remains the question what is the origin for this solid polymorphism. The answer has been found in the finger-pattern region of the infrared spectra.

In Fig. 9 are shown the infrared spectra (4000 - 650 cm^{-1}) of each polymorph. There can be seen the large difference in these ifrared spectra except for the frequency region of 850 - 700 cm^{-1}, as marked by stars. Figure 9 shows the expanded infrared spectra of the region interested. The distinct difference for each polymorph was found in the frequency region due to the CH_2 rocking mode of n-octyl chain. It is well-known that the CH_2 rocking mode of n-alkyl chain splits into doublet by the interaction of non-equivalent adjacent alkyl chain

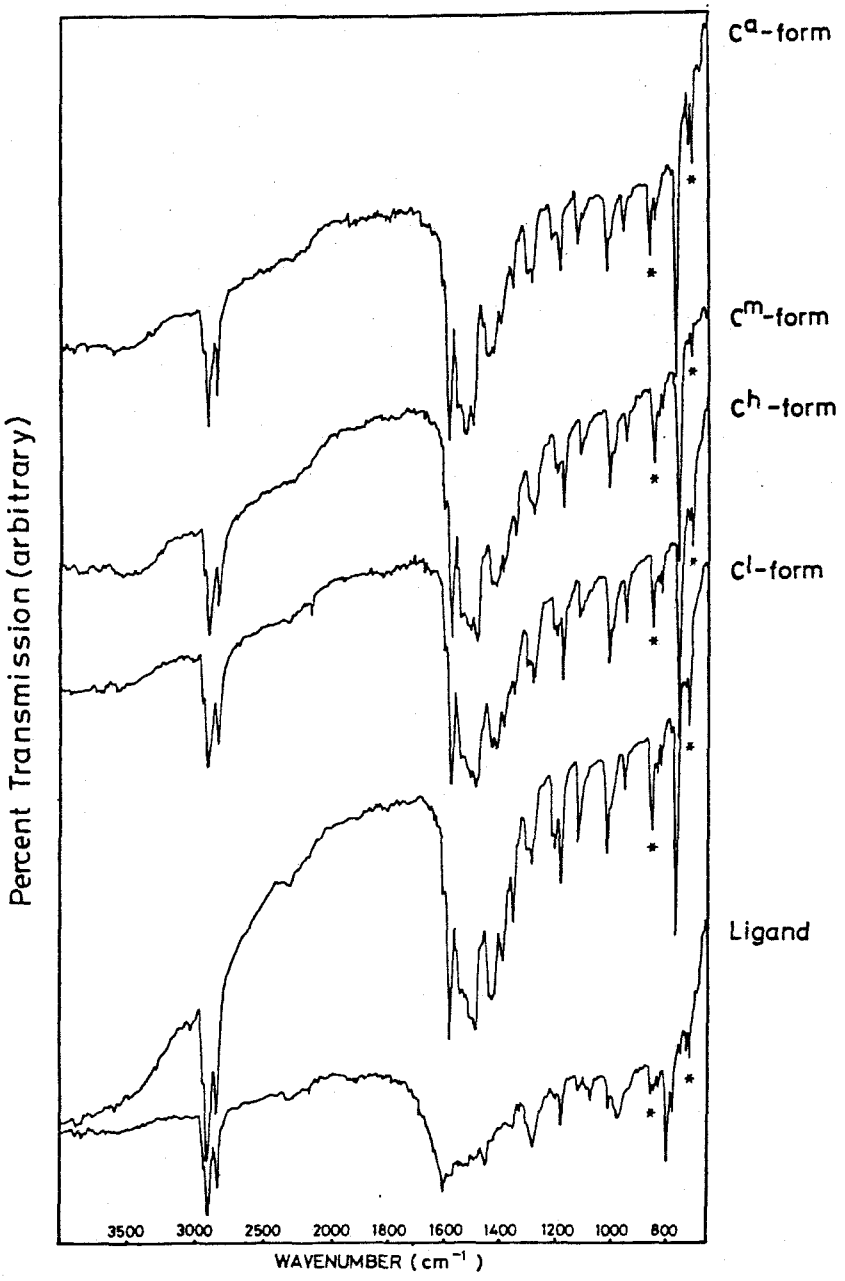


Fig. 9 Infrared spectra of the four polymorphs of $(n\text{-OBA})_2Cu(II)$ and the ligand, n-OBA, in the region of 4000-650 cm^{-1}, KBr disks.

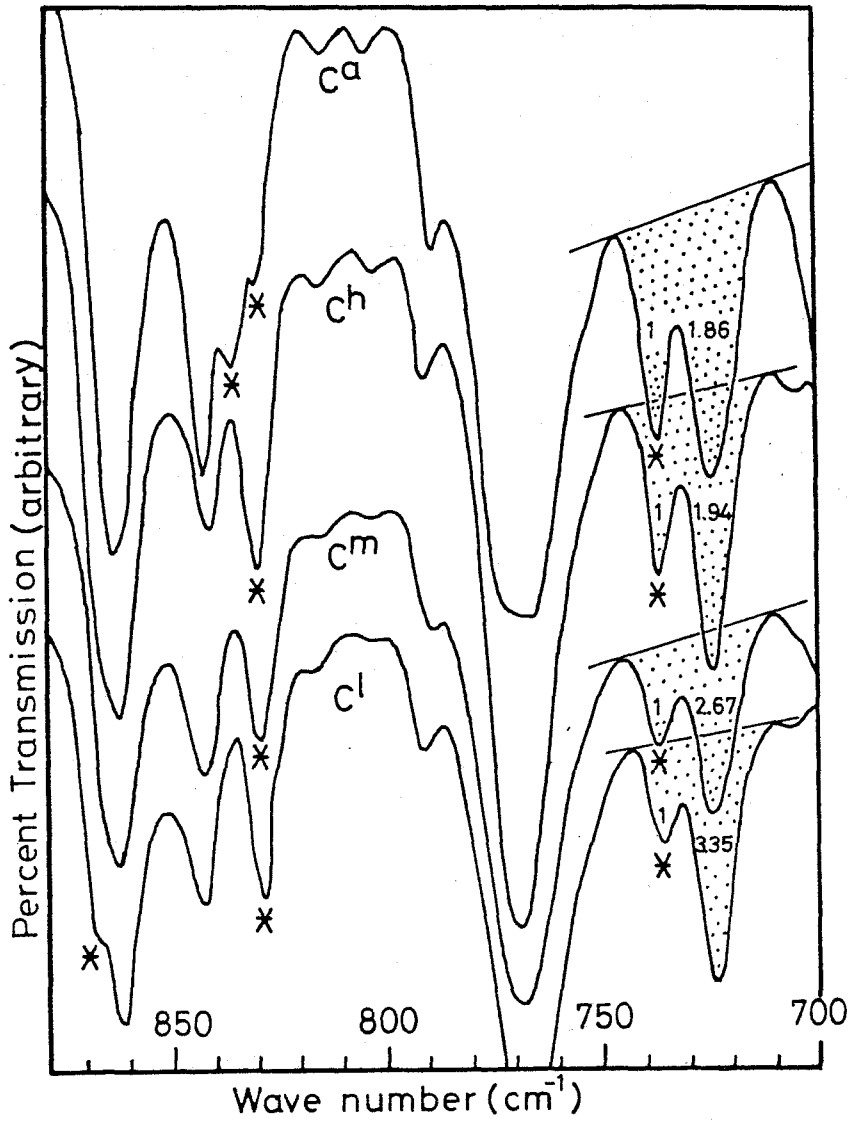


Fig. 10 The expanded infrared spectra of the four polymorphs of $(n\text{-OBA})_2Cu(II)$ in the region of 880-700 cm^{-1}, KBr disks. Numbers in this figure indicate relative intensity of ca. 726 cm^{-1} absorption bands against the intensity of ca. 736 cm^{-1} bands for each polymorph. The band indicated by star varied appreciably in the four polymorphs.

depending on the mutual orientation of the n-alkyl molecular plane.[10] In the $(n\text{-OBA})_2Cu(II)$, the CH_2 rocking mode was observed as a doublet of 726 and 736 cm^{-1} with different intensity ratio for each polymorph. This fact tells us that the orientation of the long n-octyl chains adjacent to each other is different in each polymorph. In Table 3 are summarized the relative intensity ratios F_{726}/F_{736} along with their melting points for each polymorph. Interestingly, the order of F_{726}/F_{736} is found to be strongly related the order of melting points for each polymorphic form except for the case of C^a form. Therefore, it indicates that the main origin of the present polymorphism seems to lie in the difference of the mutual orientation of the n-octyl chains adjacent to each other for C^l, C^m, and C^h forms at least, and that C^a form may have another origin of polymorphism. Actually, the C^a form gave the slightly different infrared spectrum near 830 cm^{-1} from other forms. Taking into account the fact that the preparation of

Table 3 Correlation between relative intensity ratios F_{726}/F_{736} and m.p.s (°C) for the four polymorphs of $(n\text{-OBA})_2Cu(II)$.

Polymorph	C^l		C^m		C^h		C^a	
F_{726}/F_{736}	3.35	>	2.26	>	1.94	>	1.86	→ Doublet
M.p. (°C)	96	<	108	<	109	,	99	

C^a form is very paticular from others as described in Chapter I, it is reasonably understood that the C^a form may have the different origin of polymorphism from other polymorph, although it is not clear at present time.

Thus, it is concluded that the main origin of the present polymorphism of $(n\text{-OBA})_2Cu(II)$ is condisered to be due to the difference in the packing of n-octyl chains. Similar type of polymorphism has been found in glycerides,[11] in which two polymorphs give the different infrared spectra in the 720 cm^{-1} region of the CH_2 rocking mode, singlet and doublet, respectively. So far as the auther knows, however, this type of polymorphism is the first case in the organic transition metal complexes.

II-4 SUMMARY

The origion of the solid polymorphism of $(n\text{-OBA})_2Cu(II)$ has been studied by means of the spectroscopic techniques. All of the present four polymorphs are found to be square-planar trans-isomers. The main origin of this solid polymorphism is due to neither coordination change nor cis-trans isomerization, but due to the difference in the packing of n-octyl chains.

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CHAPTER III

MULTIPLE MELTING BEHAVIOUR IN SQUARE-PLANAR trans-BIS-(1-p-n-ALKYLPHENYLBUTANE-1,3-DIONATO)COPPER(II)———THE EFFECT OF ALKYL CHAIN LENGTH———

III-1 INTRODUCTION

In Chapter I it has been described that trans-bis-(1-p-n-octylhpenylbutane-1,3-dionato)copper(II) exhibits the solid polymorphism and three kinds of double melting behaviour.

Recently, Mueller-Westerhoff et al.[1] have reported that p-n-alkyl-substituted square-planar styryl-dithiolato Ni complexes and the Pt complexes show smectic and nematic, depending on the length of the p-n-alkyl chains, while the Pd complexes have no mesomorphic properties at all. The molecular structure of those complexes are very similar to our complexes. The mesomorphism and the solid polymorphism of these type of complexes would make a new field in the transition metal complex chemistry.

In the present chapter, bis-(1-p-n-alkylphenylbutane-1,3-dionato)copper(II) having different n-alkyl chains have been synthesized. The author withes to describe the solid polymorphism and the multiple melting behaviour of these complexes.

III-2 EXPERIMENTAL

The synthetic scheme of the present complexes is shown in Fig. 1. The detailed procedures were almost the same as

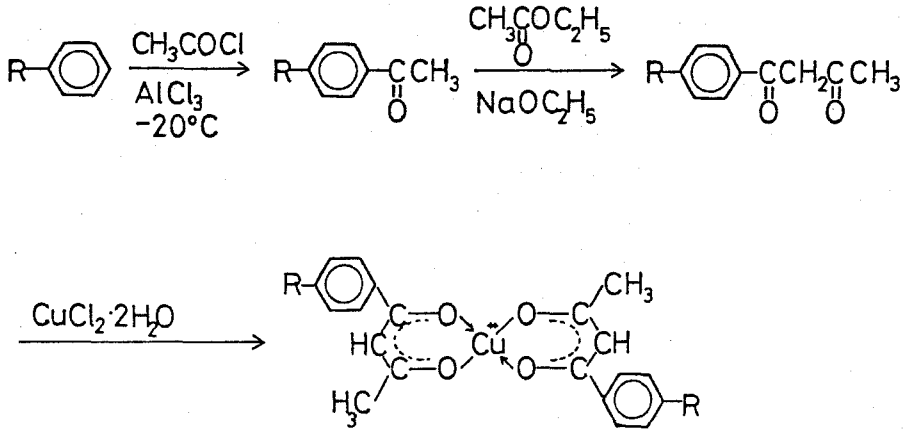

Fig. 1 Syntetic scheme for bis-(1-p-n-alkylphenylbutane-1,3-dionato)copper(II).

described for the case of octyl substituent in Chapter I. For each alkyl substituent the yields of the first step were ca. 100%. The ligands, 1-p-n-alkylphenylbutane-1,3-dione, were synthesized by the method reported by Beyer et al.[2] Table 1 are listed the yield, m.p.s, and elemental analysis data for these ligands. These compounds were purified by distilation under reduced pressure. The copper(II) complexes for each alkyl substituent were obtained according to the literature.[3] However, each having different n-alkyl group from ethyl to dodecyl is a new compound. The purification of these complexes were made by recrystallization

Table 1 Melting points, yield ,and elemental analysis data for the ligands : 1-p-n-alkylphenylbutane-1,3-dione.

Ligand	Yield (%)	Melting points (°C)	Elemental Analysis Found(Calcd) % H	C
R=H	Purchase	55-59		
R=CH_3	56	9.3	6.76(6.86)	74.98(74.96)
R=C_2H_5	83	0.7	7.37(7.42)	75.11(75.76)
R=C_3H_7	79	5.2	7.83(7.89)	76.22(76.44)
R=C_4H_9	78	27.2	8.12(8.31)	77.00(77.03)
R=C_5H_{10}	87	33.0-34.0	8.59(8.68)	77.48(77.55)
R=C_6H_{13}	77	35.5-37.1	9.02(9.00)	77.91(78.01)
R=C_7H_{15}	83	27.0-29.5	9.35(9.29)	78.48(78.42)
R=C_8H_{17}	81-87	39.0-41.0	9.69(9.55)	78.59(78.79)
R=C_9H_{19}	74	25.5-27.0	9.85(9.78)	79.12(79.12)
R=$C_{10}H_{21}$	72	41.8-43.0	10.07(10.00)	79.11(79.42)
R=$C_{11}H_{23}$	87	39.0-40.0	10.31(10.19)	79.84(79.70)
R=$C_{12}H_{25}$	98	52.0-54.0	10.39(10.37)	79.80(79.95)

Table 2 Elemental analysis data and recrystallization solvents for the complexes: square-planar trans-bis(1-p-n-alkylphenylbutane-1,3-dionato)copper(II)

Complexes	Elemental analysis Found (Calcd) % H	C	Recrystallization solvents	Crystalline shapes obtained from recrystallization
R=H	4.75 (4.70)	62.06 (62.25)	Acetone	-A mixture of striplike & needlelike
R=CH_3	5.40 (5.36)	63.82 (63.83)	Acetone	-Rodlike
R=C_2H_5	5.88 (5.93)	64.95 (65.22)	Acetone	-Plate
R=C_3H_7	6.59 (6.43)	66.29 (66.43)	Acetone	-A mixture of microcrystal & Plate
R=C_4H_9	6.88 (6.88)	67.14 (67.51)	Acetone	-A mixture of feathery & rodlike
R=C_5H_{11}	7.52 (7.28)	68.33 (68.48)	Ethanol	-Feathery
R=C_6H_{13}	7.74 (7.64)	69.10 (69.35)	Ethanol	-A mixture of feathery & plate
R=C_7H_{15}	7.99 (7.96)	69.96 (70.13)	Ethanol	-A mixture of feathery & needlelike
R=C_8H_{17}	8.27 (8.26)	70.94 (70.85)	Acetone	-Striplike
R=C_9H_{19}	8.57 (8.53)	71.45 (71.50)	Ethanol	-A mixture of striplike & feathery
R=$C_{10}H_{21}$	8.83 (8.77)	71.94 (72.09)	Ethanol	-A mixture of feathery & striplike
R=$C_{11}H_{23}$	9.13 (9.00)	72.57 (72.64)	Ethanol	-A mixture of striplike, feathery, & needlelike
R=$C_{12}H_{25}$	9.32 (9.21)	72.85 (73.14)	Acetone	-A mixture of feathery & striplike

from acetone or ethanol more than twice. The elemental analysis data, crystallization solvents, and the crystalline shapes obtained are summarized in Table 2. In some cases, a mixture of two crystal forms was obtained by crystallization from the solvents at room temperature. In the present work, each pure polymorph was not taken out for all complexes except for the case of n-octyl substituted complex, which was described in details in Chapter I.

The observation of all phase transitions of the present complexes was carried out by using a polarizing microscope equiped with a heating plate controlled by thermoregulator, FP5, whithin the accuracy of 0.1°C. A differential scanning calorimeter, Daini-Seikosha DSC SSC 560, was also used to establish the phase transitions.

III-3 RESULTS AND DISCUSSION

In Table 3 are given the m.p.s of each polymorph along with the respective crystalline shape. When n (the number of carbon atoms in the n-alkyl substituent)=0~2, each complex showed two polymorphs with different m.p.s, and when n=3~5 and 12, three polymorphs were recognized. Furthermore, four kinds of polymorphs were recognized when n=6~11. The observed number of m.p.s of these complexes is strongly related to the length of the

Table 3 Melting points and crystalline shapes of the polymorphs for p-n-alkyl derivatives of bis(1-phenybutane-1,3-dionato)copper(II).

Complexes	Melting points(°C)	Crystalline shapes	Complexes	Melting points(°C)	Crystalline shapes
R=H	Tm_1= 194.2-194.5	striplike	$R=C_8H_{17}$	Tm_1= 95.7- 95.8	striplike
	Tm_2= 197.9-198.2	needle		Tm_2= 98.6- 99.1	feathery
				Tm_3= 108.0-108.1	spherulite
$R=CH_3$	Tm_1= 224.5-226.2	rodlike		Tm_4= 109.1-109.3	rodlike
	Tm_2= 233.7-233.9	plate			
			$R=C_9H_{19}$	Tm_1= 102.0-102.5	striplike
$R=C_2H_5$	Tm_1= 188.0-188.5	spherulite		Tm_2= 115.3-116.3	feathery
	Tm_2= 210.8-211.3	plate		Tm_3= 120.0-120.4	needle
				Tm_4= 120.8-120.9	plate
	Tm_1= 168.6-168.8	microcrystal			
$R=C_3H_7$	Tm_2= 169.8-170.0	spherulite		Tm_1= 100.2-100.7	feathery
	Tm_3= 171.5-171.9	plate	$R=C_{10}H_{21}$	Tm_2= 102.3-102.5	striplike
				Tm_3= 102.7-102.8	plate
	Tm_1= 142.0-143.0	feathery		Tm_4= 107.0-107.4	needle
$R=C_4H_9$	Tm_2= 152.3-152.5	spherurite			
	Tm_3= 154.3-154.6	rodlike		Tm_1= 107.0-107.4	striplike
				Tm_2= 113.8-114.2	feathery
	Tm_1= 140.4-140.8	feathery	$R=C_{11}H_{23}$	Tm_3= 117.6-117.8	needle
$R=C_5H_{11}$	Tm_2= 146.1-146.4	spherulite		Tm_4= 118.6-118.8	plate
	Tm_3= 147.5-147.7	plate			
				Tm_1= 104.9-105.5	feathery
	Tm_1= 118.8-119.2	feathery	$R=C_{12}H_{25}$	Tm_2= 107.0-107.2	striplike
$R=C_6H_{13}$	Tm_2= 120.2-120.7	plate		Tm_3= 107.8-108.0	plate
	Tm_3= 125.3-125.5	spherulite			
	Tm_4= 126.3-126.5	needle			
	Tm_1= 125.2-125.5	feathery			
$R=C_7H_{15}$	Tm_2= 128.3-128.5	needle			
	Tm_3= 129.2-129.5	spherulite			
	Tm_4= 130.0-130.2	plate			

alkyl group. Although only a m.p. of 189-190°C had been reported in the core complex corresponding to the n=0 case by Ribeiro da Silva et al.,[4] it was found in the present work that this complex has two m.p.s at 194°C and 198°C, which could be confirmed by the microscope observation and the DSC measurement. When n=1, Lowe et al.[5] reported also only a m.p. of 228-229°C. However, the author found that the complex has two m.p.s at 225°C and 234°C by the precise microscope observation.

In Chapter II, the author described that the solid polymorphism is originated not from the change of coordination of ligands, i.e., cis or trans coordination, but mainly from the different packing of n-alkyl chains. However, the presently observed solid polymorphism in the core complex (n=0 case) and the complexes having relatively short alkyl chains indicates that another origin might be opperative in these complexes. Although the origin is not clear at the present stage, it sould be noted here that a possibility of the cis-trans coordination change would be excluded, because two polymorphic forms isolated in the case of the ethyl substituent gave the same far-infrared spectra. This indicates that the cis-trans coordination would not occur. The large difference was observed in the region from 750 to 850 cm^{-1} of their infrared spectra.

Figure 2 shows the sequence of the state changes for each complex from n=0∿to 12, which was comfirmed mainly by the microscopic observation. The complexes having the relatively

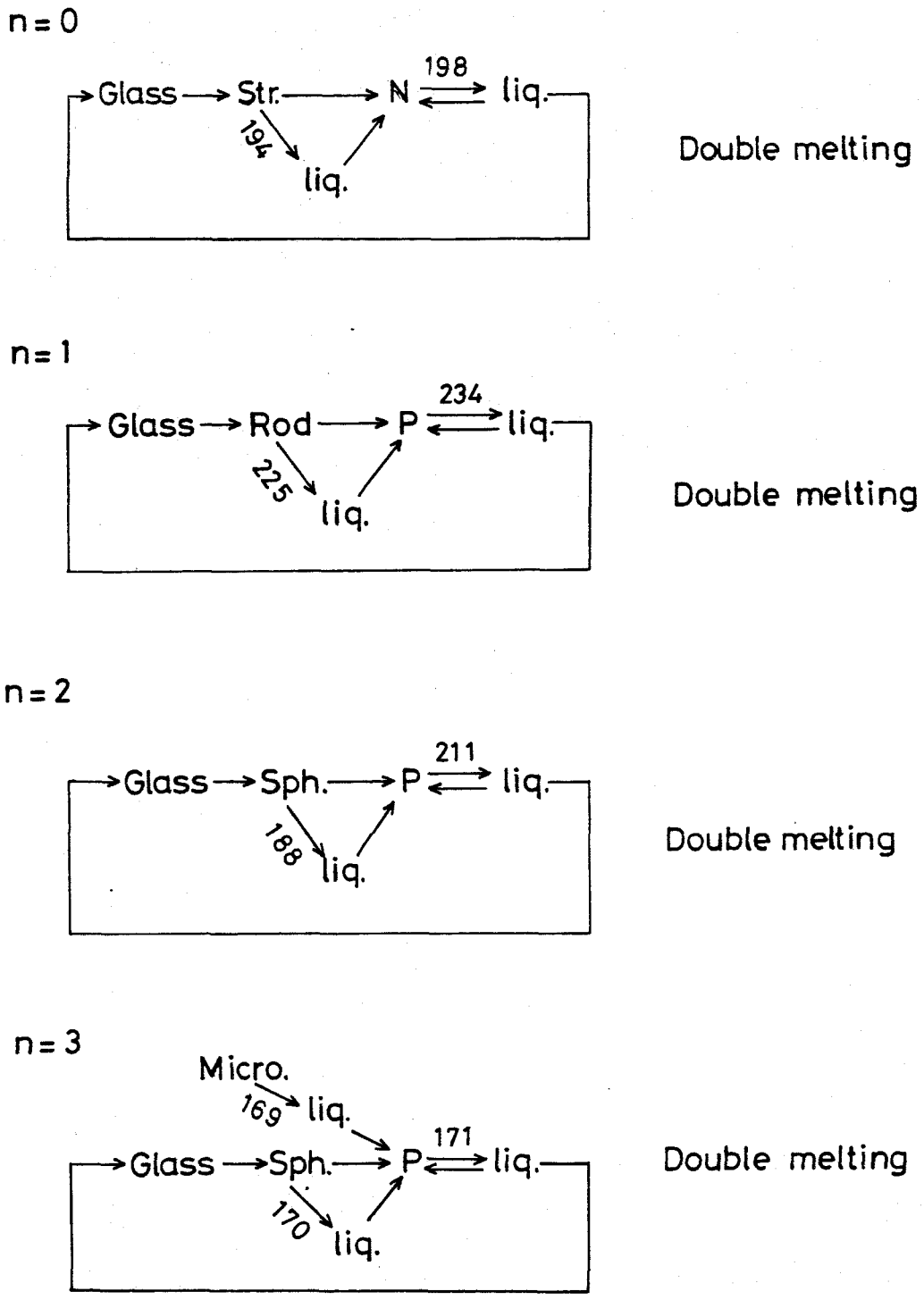

Fig. 2-1 The sequences of changes of state for bis-(1-p-n-alkylphenylbutane-1,3-dionato)copper(II). See the details at figure caption of Fig. 2-4.

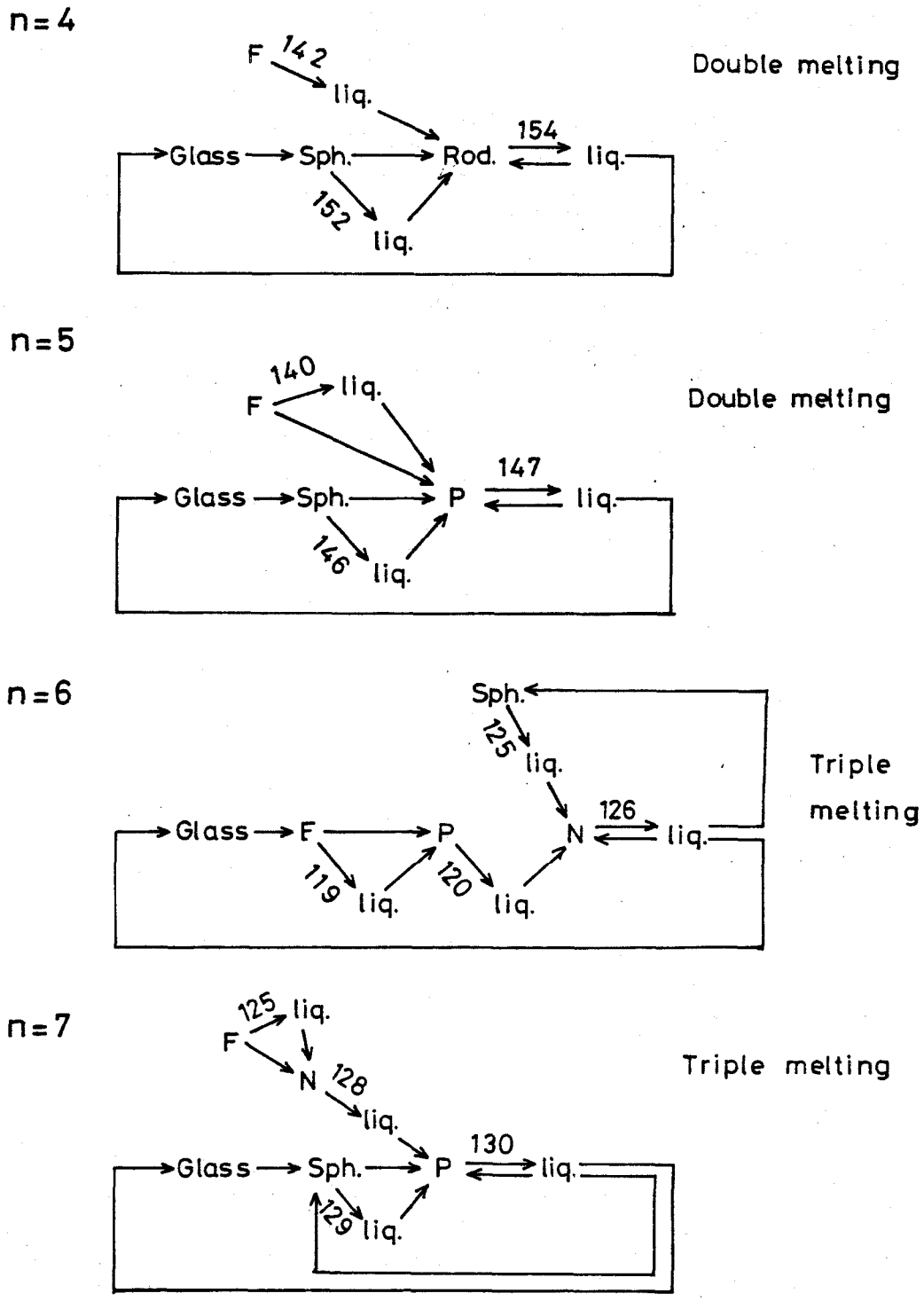

Fig. 2-2 The sequences of changes of state for bis-(1-p-n-alkylphenylbutane-1,3-dionato)copper(II). See the details at figure caption of Fig. 2-4.

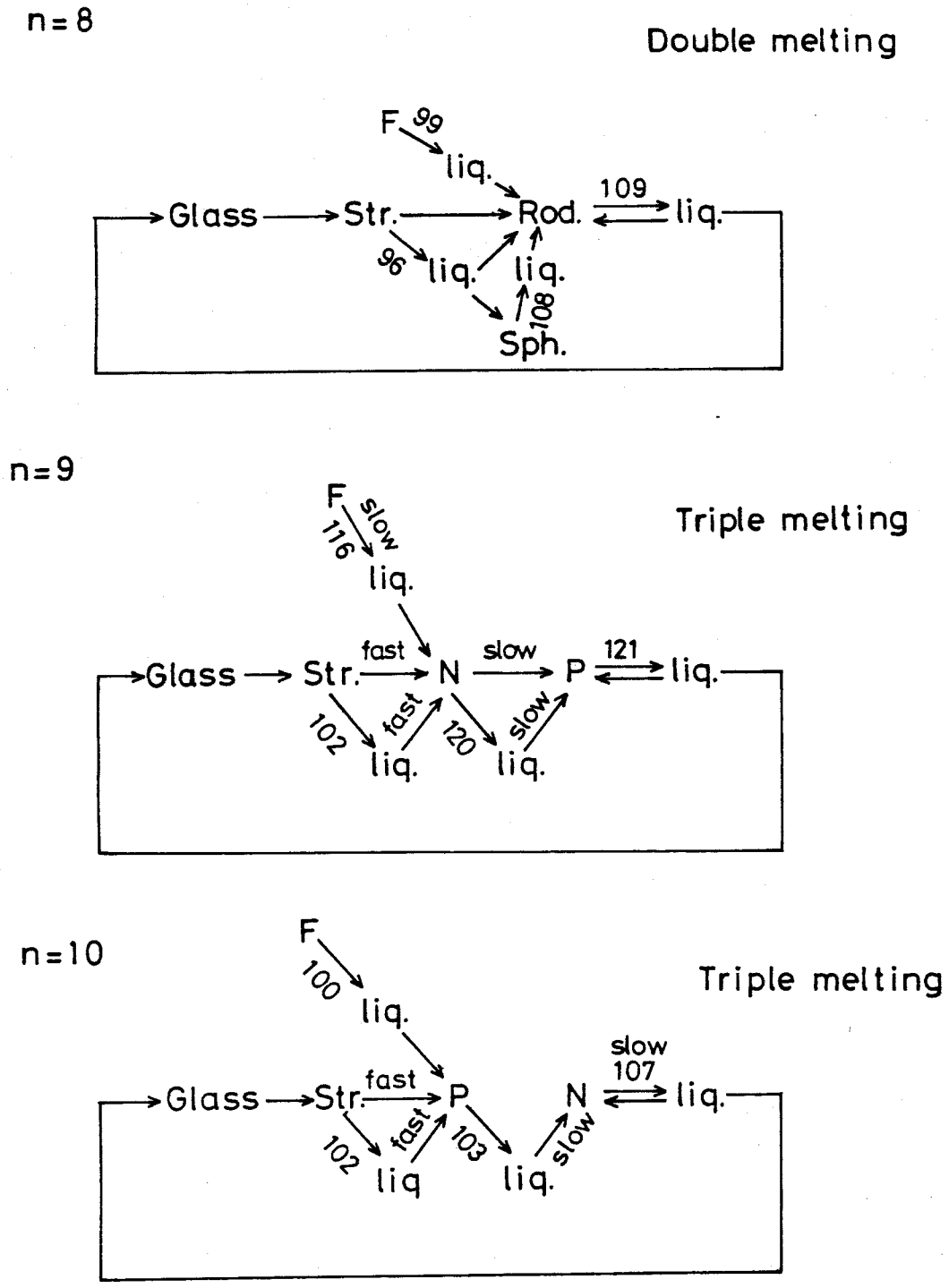

Fig. 2-3 The sequences of changes of state for bis-(1-p-n-alkylphenylbutane-1,3-dionato)copper(II). See the details at figure caption of Fig. 2-4.

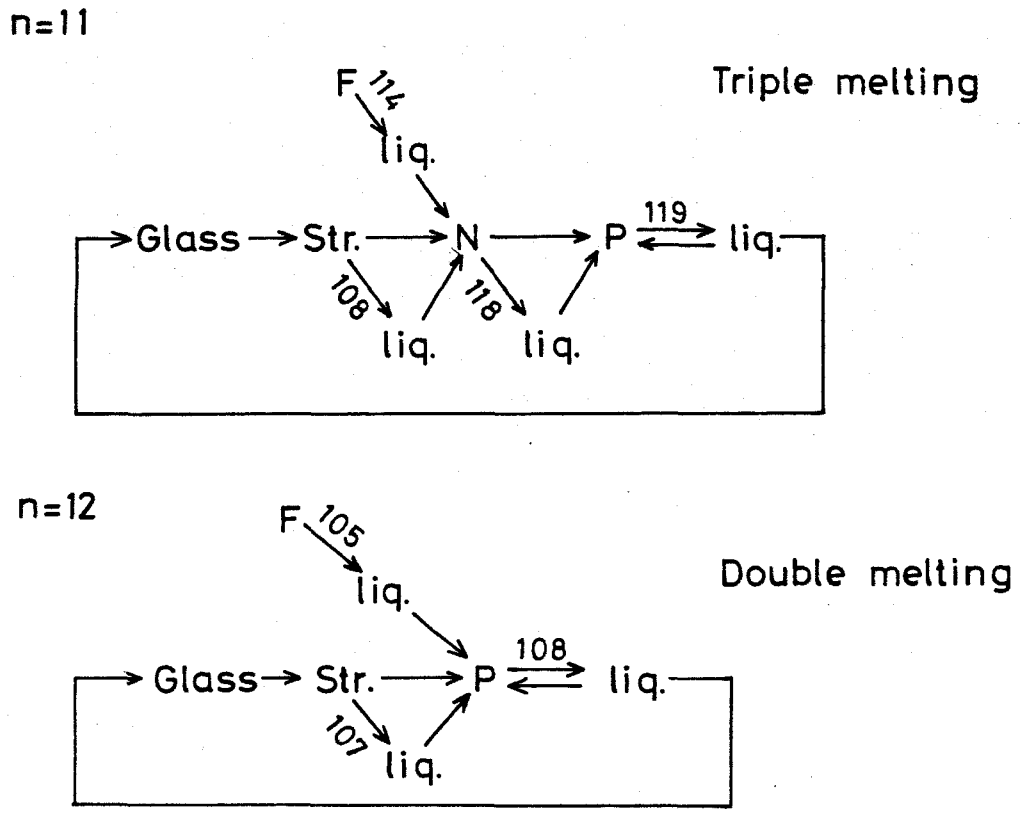

Fig. 2-4 The sequences of changes of state for bis-(1-p-n-alkyl-butane-1,3-dionato)copper(II). " n " is the number of carbon atomes in the n-alkyl group. Numbers in the figure are m.p.s. Nomenclature of crystalline shape is : Str.=striplike(long thin), N.=needle-like, Rod=rodlike, P=plate, Sph.=spherulite, F=feathery (hair-like), and Micro.=microcrystal.

long alkyl tails showed much more complicated state changes. When n=6∿11 except n=8, all complexes exhibited so-called triple melting behaviour, and other complexes also exhibited double melting behaviour. In the nonyl substituted complex, for example, when the strip-like(long thin) polymorphic form was heated from room temperature, it melted at 102°C except for a portion transformed by a solid-solid phase transition from the strip-like to the needle-like, and then the melt resolidified completely into the needle-like cryatal; on further heating, it melted at 120°C except for a portion transformed by a new slow solid-solid phase transiton from the needle-like to the plate-like crystal, and then the melt resolidified into the plate-like crystals of the most stable polymorphic form; on further heating, it melted completely at 121°C. Thus, the triple melting behaviour was observed on one heating stage.

As shown in Fig. 3, the even-odd effect in the melting points of the complexes was found when n=6∿12. Namely, the m.p.s of the complexes having odd number of carbon atoms in the n-alkyl group are higher than those of the even numbered complexes. On the contrary, the even-odd effect in the m.p.s of the respective ligands are opposite, as shown in Fig. 4. So far as the author knows, such a phenomenon seems to be the first example in the transition metal complexes.

Malikin suggested[6] about long-chain compound that the crystalline structure of odd menbers would be expected to be less

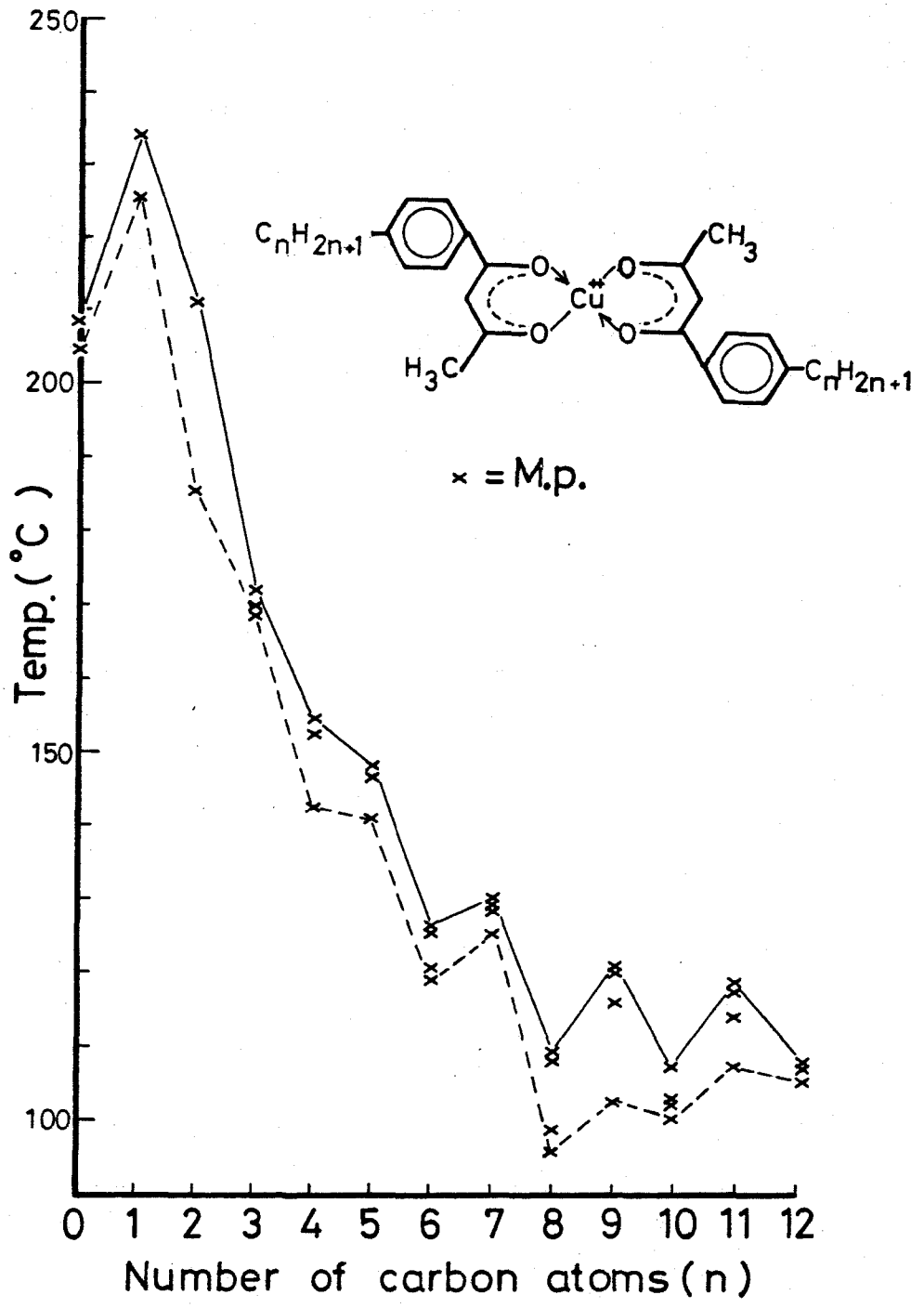

Fig. 3 Melting points versus chain length for the series of bis-(1-p-n-alkylphenylbutane-1,3-dionato)copper(II). See Table 3.

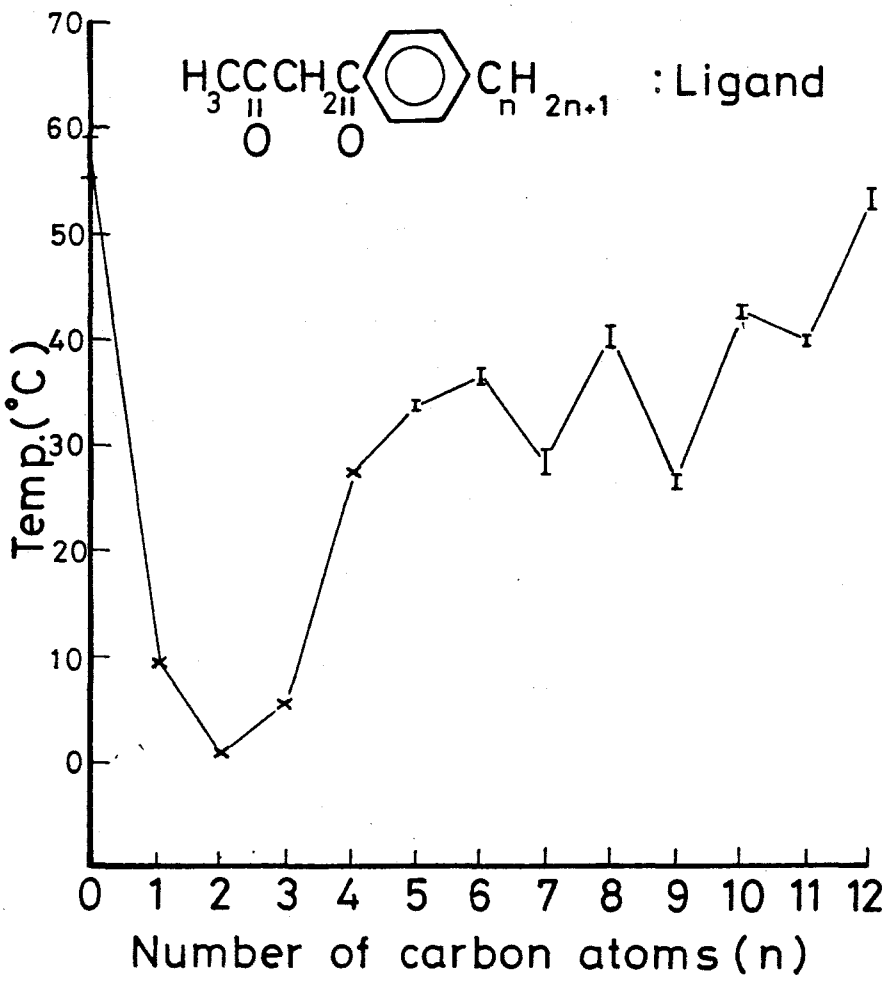

Fig. 4 Melting points versus chain length for the series of 1-p-n-alkylphenylbutane-1,3-dione (ligands). See Table 1.

stable, which is in agreement with their lower m.p.s. However, higher alkyl iodides with an odd carbon content melt at the higher temperature. He inferred in his paper that this was probably due to the large iodine atom having the same effect as an additional carbon atom, and thus giving an even chain the properties of an odd. Although his inferrence seems to be

useful, this could not be appricated with ease to the author's complexes because of the great difference of these molecular structures. Further investigation is required for this problem.

III-4 SUMMARY

Square-planar trans-bis-(1-p-n-alkylphenylbutane-1,3-dionato)copper(II) exhibit the multiple melting behaviour and the opposite even-odd effect in their m.p.s between the ligands and the corresponding complexes.

III-5 REFERENCES

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CONCLUSION

This study was undertaken to synthesize square-planar trans-bis-(1-p-n-alkylphenylbutane-1,3-dionato)copper(II) having the property of 'solid polymorphism with multiple melting behaviour'. The results of the present work are summarized as follows.

(1) The new compound, bis(1-p-n-octylphenylbutane-1,3-dionato)-copper(II) has four polymorphs, C^l(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^l, C^a, and C^m exhibit 'double meltg' behaviour. Double melting of C^l was observed only on rapid heating, while that of C^a and C^m only on slow heating. Slow solid-solid phase transition from C^l to C^h was observed at ca. 50°C. 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. This property has a possibiliry to be used as an erasable imaging material.

(2) The origin of solid polymorphism of bis-(1-p-n-octylphenyl-butane-1,3-dionato)copper(II) has been elucidated of spectroscopic techniques. All these four polymorphic forms were found to have the square-planar trans coordination. No changes were observed in the coordination structure of the

complex core part. From the detailed observation of the infrared absorption spectra it was revealed that the polymorphism in the present complex originates from the difference of the packing of n-octyl chains. The spliting intensity in the methylene rocking mode of n-octyl chain was found to be strongly related to the multiple melting points of these polymorphic forms.

(3) Square-planar trans-bis-(1-p-n-alkylphenylbutane-1,3-dionato)-copper(II) complexes having different n-alkyl groups from methyl to dodecyl have synthesized. All these complexes exhibit solid polymorphism. The number of polymorphs depends on the length of the alkyl chain: two for n(the number of carbon atoms)=0∿2, three for n=3∿5 and 12, and four for n=6∿11, respectively. Each polymorphic form except those with the highest m.p.s exhibit multiple melting behaviour+ double melting for n=0∿5, 8, and 12, and triple melting for n=6∿11 except . The m.p.s of the complexes with alkyl groups of odd carbon atoms are higher than those with even atoms, while the respective ligand solids show the opposite even-odd effect in their m.p.s.