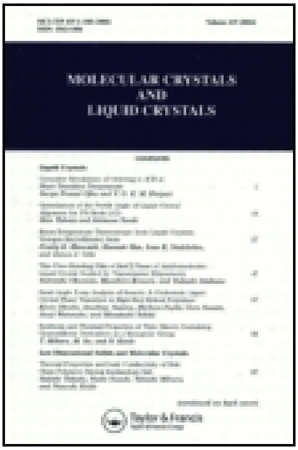

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Spectroscopic Studies on Polymorphism in Bis-(1-p-n-Octylphenylbutane-1, 3-dionato)-copper(II)

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Spectroscopic Studies on Polymorphism in Bis-(1-*p*-*n*-octylphenylbutane-1,3-dionato)-copper(II)

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The title transition metal complex shows four solid polymorphic forms having different melting points. The origin of solid polymorphism of the present complex has been elucidated by means 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 this polymorphism originates from the difference of the packing of *n*-octyl chains. The splitting intensity in the methylene rocking mode of *n*-octyl chain was found to be strongly related to the melting points of these polymorphic forms.

I INTRODUCTION

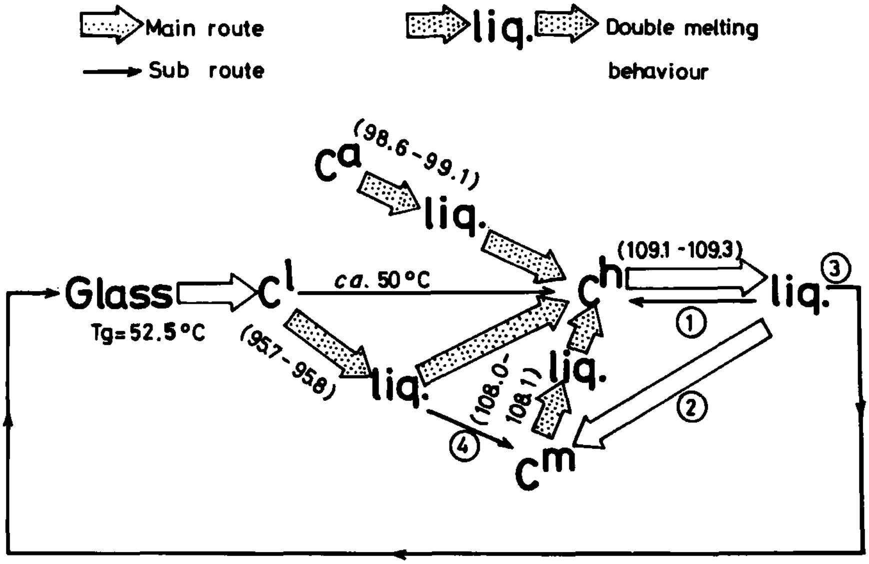
In a previous paper,[1] it has been reported that the title complex, bis-(1-*p*-*n*-octylphenylbutane-1,3-dionato)copper(II), (n-OBA)$_2$Cu(II), shows four polymorphic forms with different melting points, C^l (m.p. = 96°C), C^a (99°C), C^m (108°C), and C^h (109°C), and three of them exhibit "double melting" behavior. 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.

Recently, Bulkin *et al.* reported that the trans form of square-planar bis-(1-*p*-*n*-octyloxyphenylbutane-1,3-dionato)palladium(II) is a possible candidate for mesogenic substance,[2] and that the trans form gave the far-infrared and Raman spectra quite different from the cis form.[3] 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 *n*-alkyl chains.[4] 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 paid on the mesomorphism in such type of the transition metal complexes and the origin of such mesomorphism is remained unclear at present time. All the molecular structures of the above-mentioned complexes are, however, square-planar at their complex core parts and lod-like for their whole structures, whose features are very similar to our complex. 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 such our polymorphism might be closely related to the mesomorphism.

In the present paper, we wish to report structural studies on polymorphism of (n-OBA)$_2$Cu(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 EXPERIMENTAL

A. *Materials* The synthesis procedure of the title complex, (n-OBA)$_2$Cu(II), and the preparation of its four polymorphic forms were described in a pre-



SCHEME The sequence of changes of state for bis-(1-p-n-octylphenylbutane-1,3-dionato)-copper(II). Numbers in parentheses are m.p.s in °C. See the details of this scheme at Ref. 1.

vious paper.[1] 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 scheme.

For comparison, bis-(1-phenylbutane-1,3-dionato)copper(II), $(BA)_2Cu(II)$, was synthesized according to the method reported by Hon *et al.*,[5] and $(acac)_2$-Cu(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.

III RESULTS AND DISCUSSION

As mentioned in the introductory section, the present complex has four polymorphic forms having different melting points, C^1, 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 Figure 1 (A), might be easily inferred. Such a change in the coordination structure is expected to be reflected in the electronic spectra.

A. *Electronic Reflection Spectra* As shown in Figure 2, 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 $(acac)_2$-Cu(II) and $(BA)_2Cu(II)$, whose structures have been confirmed by X-ray analyses.[7] λ_{max} (nm): $(acac)_2Cu(II)$, 561, 644; $(BA)_2Cu(II)$, 576, 642; $(n\text{-}OBA)_2Cu(II)$, 556 (C^1), 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 the same to that of square-planar $(BA)_2Cu(II)$. λ_{max} (nm) in benzene: $(BA)_2Cu(II)$, 545 ($\epsilon = 51.8$), 657 (55.1); $(n\text{-}OBA)_2Cu(II)$, 551 (44.0), 656 (49.9). In the 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 such coordination forms.[8]

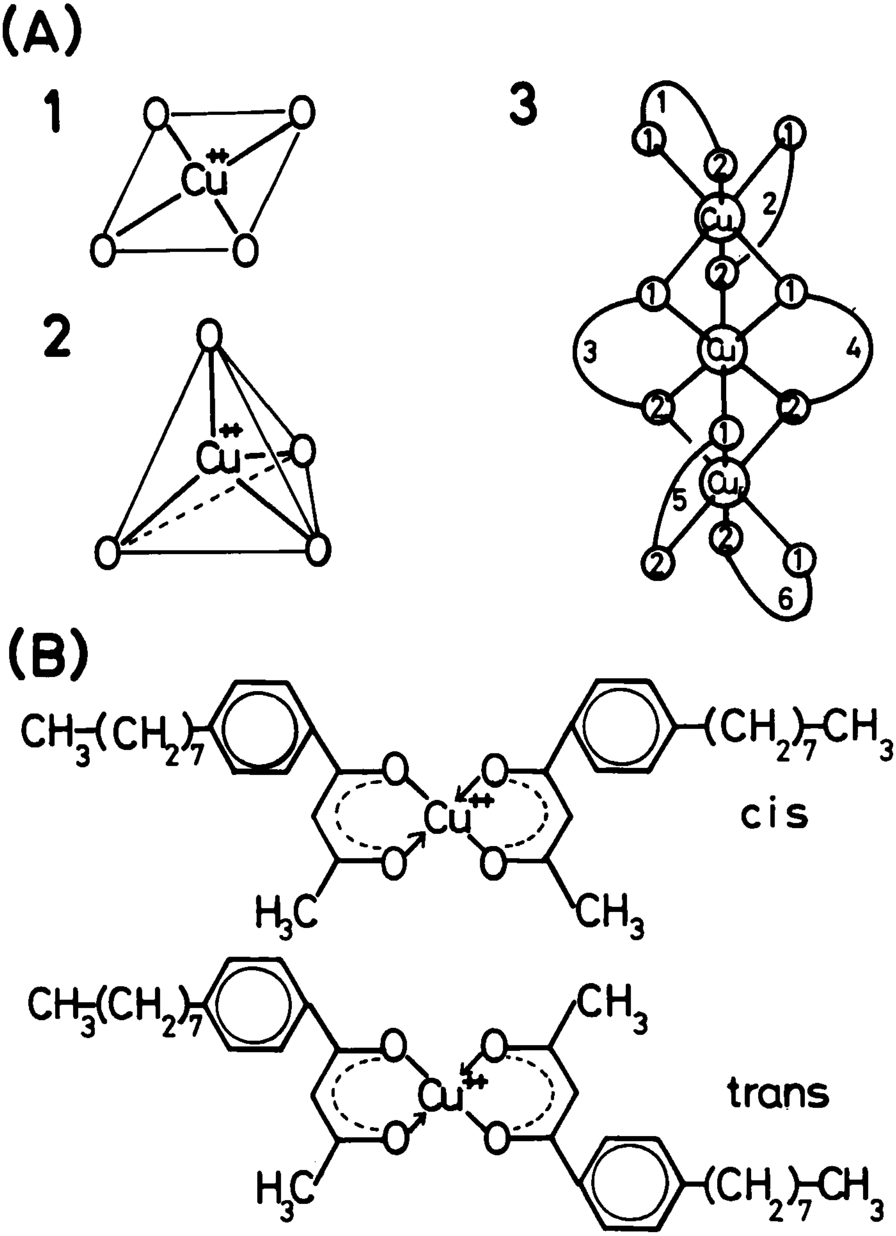


FIGURE 1 Assumed origin of the solid polymorphism of bis-(1-*p*-*n*-octylphenylbutane-1,3-dionato)copper(II)—(A): change in the coordination structure of the core complex part; 1: square-planar form, 2: tetrahedral form, 3: octahedral form as reported in $[(acac)_2Ni(II)]_3$ by Bullen, Mason, and Pauling,[6] (B): *cis-trans* isomerization maintaining square-planar form in the core complex part.

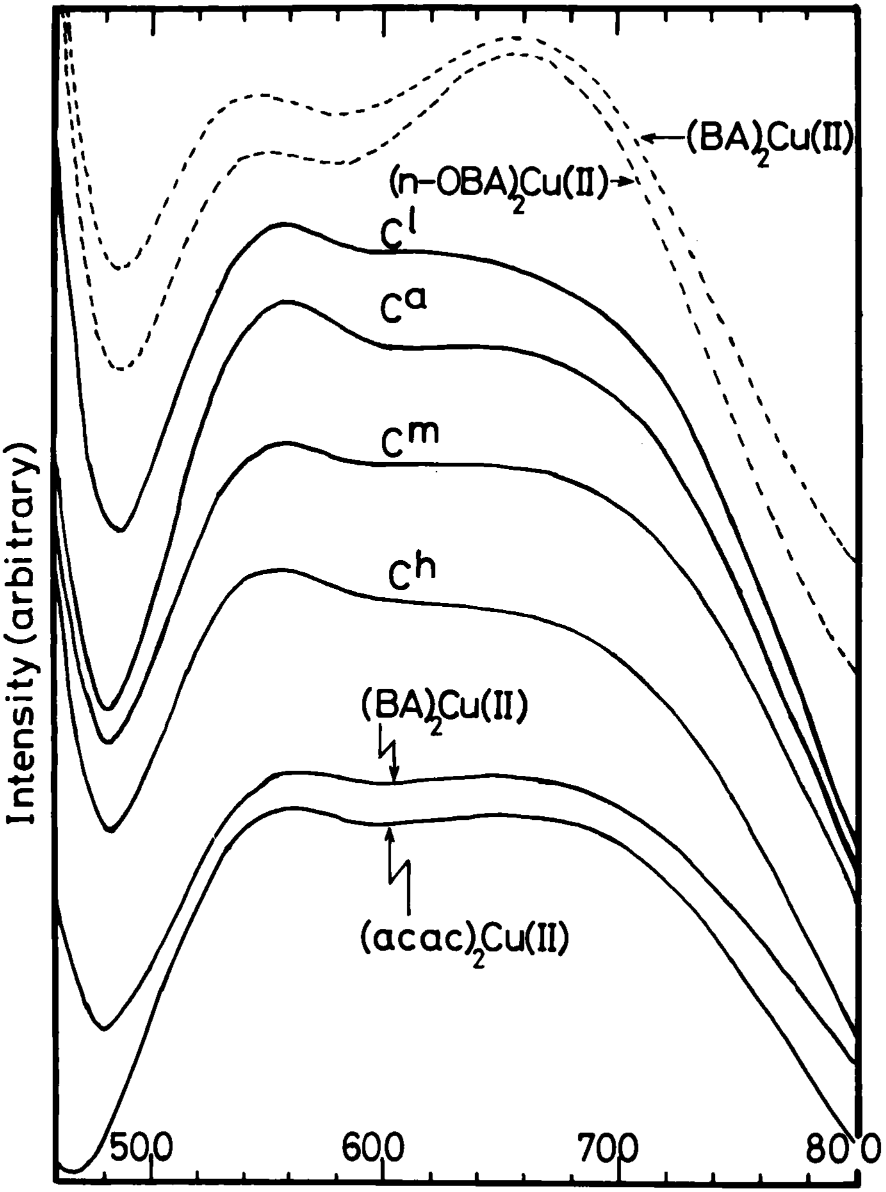


FIGURE 2 Solid lines are electronic reflection spectra of the four polymorphs of $(n\text{-OBA})_2$-Cu(II), $(BA)_2$Cu(II), and $(acac)_2$Cu(II), respectively. Each spectrum was uncorrected into the absorption spectrum. Dashed lines are electronic absorption spectra of $(n\text{-OBA})_2$Cu(II) and $(BA)_2$Cu(II) in benzene solution. All scales are arbitrary.

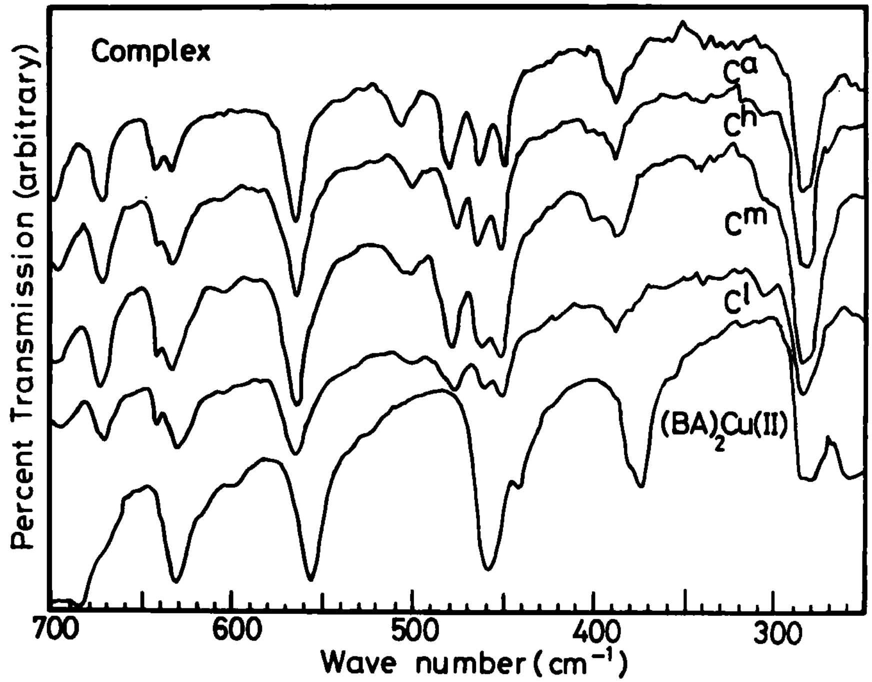


FIGURE 3 Far-infrared spectra of the four polymorphs of (n-OBA)$_2$Cu(II) and (BA)$_2$Cu(II) in the region of 700–250 cm^{-1}, Nujol mull.

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 Figure 1 (B). Such kinds of difference in the molecular structure will appear in their far-infrared spectra.

Figure 3 shows the far-infrared spectra of the four polymorphic forms. As can be seen clearly, each polymorph of (n-OBA)$_2$Cu(II) exhibited the same far-infrared spectrum in the frequency region associated with the vibrations involving metal-oxygen stretching and ligand skeletal deformation. Recently, Bulkin *et al.*[3] 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 spectral 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-OBA)$_2$Cu(II) should be either isomeric form.

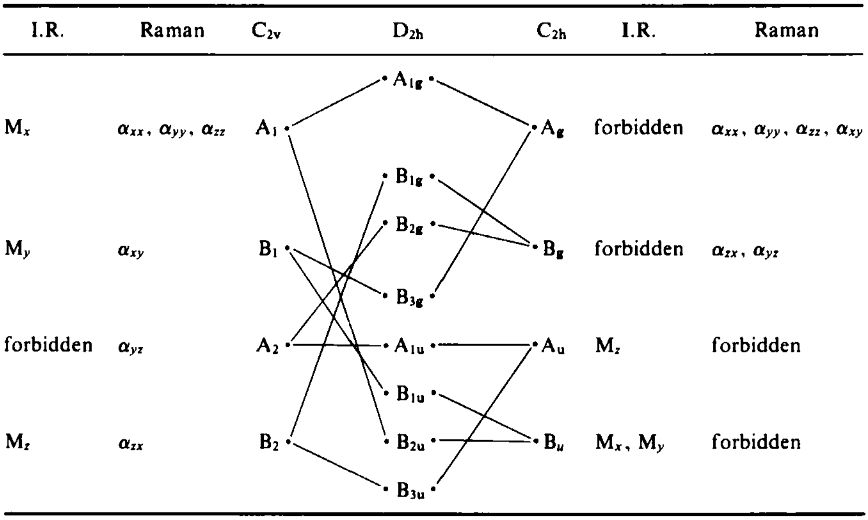
In order to assign the present complex to either *cis* or *trans* geometry, the group theoretical selection rule, so-called mutual exclusion rule, was examined for the infrared and Raman active vibrational modes. The *cis* and *trans* isomers in the square-planar structure have C_{2v} and C_{2h} molecular symmetry, respectively. Since the *trans* geometry belonging to C_{2h} symmetry has the center of symmetry, then the mutual exclusive selection rule can be expected to hold between infrared and Raman active modes. The correlation diagram and selection rules are given in Table I for C_{2v}, C_{2h}, and D_{2h}. The last one corresponding to the case of the square-planar symmetrical $(acac)_2Cu(II)$.

In Figure 4 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.[5] 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 vibrational modes gave good correspondence for $(n\text{-}OBA)_2Cu(II)$ and $(BA)_2Cu(II)$. Figures 5(a) and 5(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 II. 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 Figure 6 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.*[9] that one of the M—O stretching modes appeared in the 420–480 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 respectively strong intensity. In the case of $(n\text{-}OBA)_2$-Cu(II), however, such a vibrational band appeared in almost same frequency region with reduced intensity and somewhat complicated feature. Sine the far-infrared spectrum of *n*-OBA ligand shows distinct absorption bands in the same frequency region as shown in Figure 6, 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.*[10] 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 infrared ac-

TABLE I

Correlation table and selection rules



I.R.	Raman	C_{2v}	D_{2h}	C_{2h}	I.R.	Raman
			A_{1g}			
M_x	α_{xx}, α_{yy}, α_{zz}	A_1		A_g	forbidden	α_{xx}, α_{yy}, α_{zz}, α_{xy}
			B_{1g}			
			B_{2g}			
M_y	α_{xy}	B_1		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.

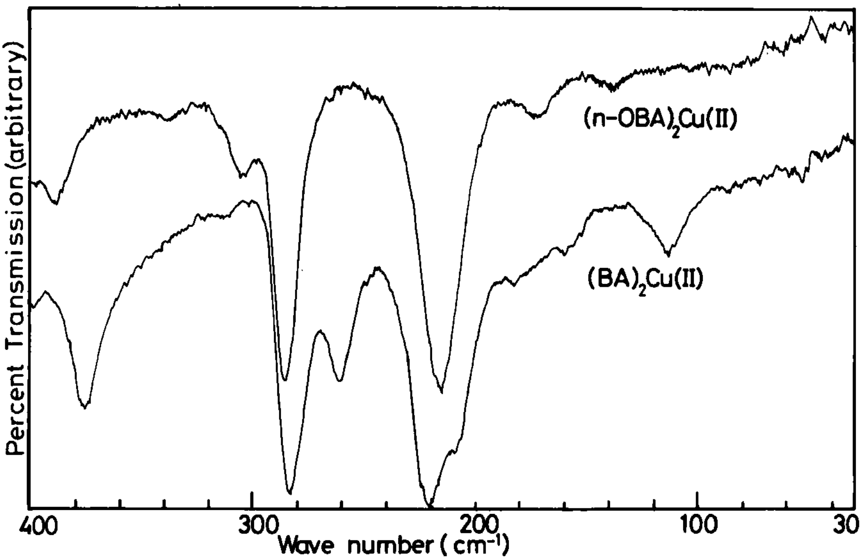


FIGURE 4 Far-infrared spectra of (n-OBA)$_2$Cu(II) in C^1 polymophic form and (BA)$_2$Cu(II) in the region of 400–30 cm^{-1}, Nujol mull.

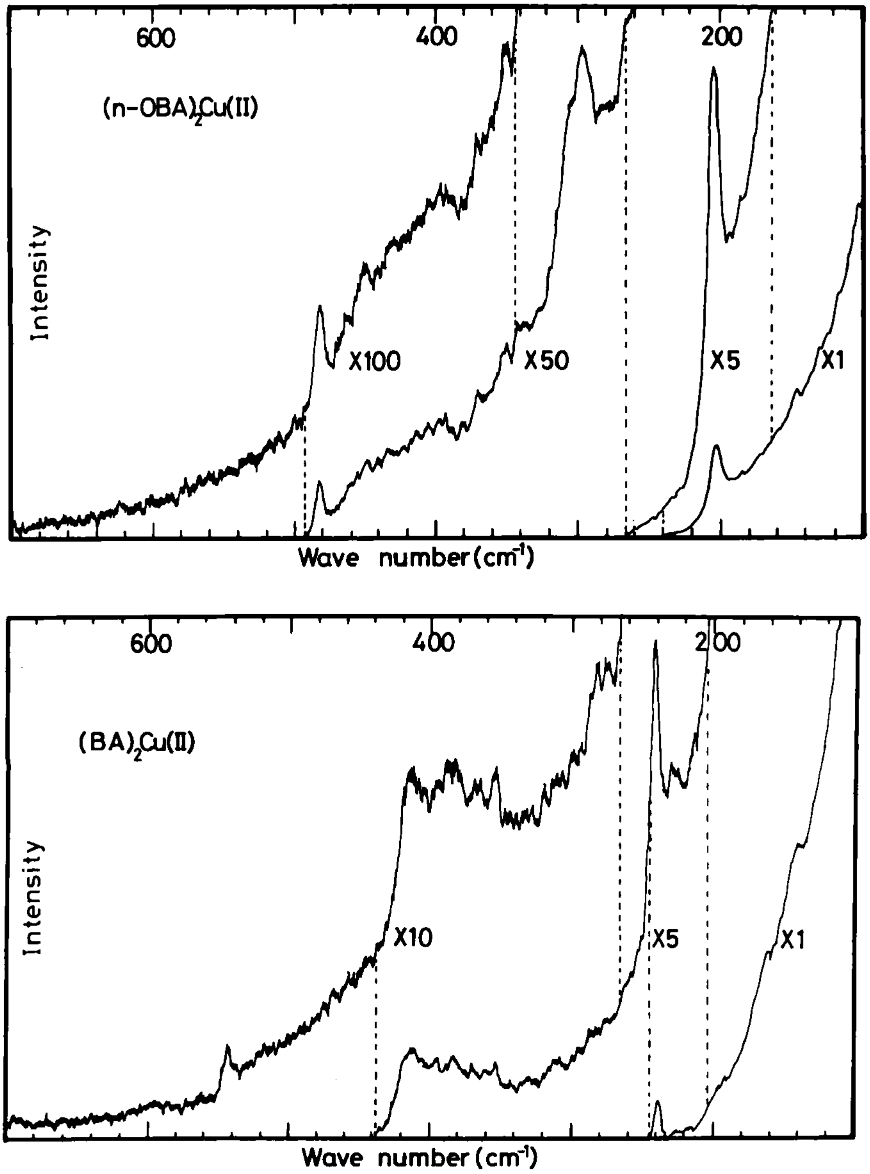


FIGURE 5 Low frequency Raman spectra of (a): (n-OBA)$_2$Cu(II) in C^1 polymorphic form and (b): (BA)$_2$Cu(II), solid samples.

tive band characteristic of the metal chelates associated with Cu—O deformation was observed at 220 cm^{-1} for (BA)$_2$Cu(II) and 215 cm^{-1} for (n-OBA)$_2$Cu(II), respectively, as shown in Figure 4. These bands should

TABLE II

Vibrational spectra of (n-OBA)$_2$Cu(II)[a] and (BA)$_2$Cu(II)[b]

(n-OBA)$_2$Cu(II)[a]				(BA)$_2$Cu(II)[b]				
Infrared		Raman		Infrared		Raman		
Freq. (cm^{-1})	Intens.[c]	Freq. (cm^{-1})	Intens.[c]	Freq. (cm^{-1})	Intens.[c]	Freq. (cm^{-1})	Intens.[c]	Descriptions
		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)$_2$Cu(II): 217 cm^{-1}][d]
						226	w	
		223	vs			241	vs	
				261	m	276	vw	
285	vs	297	s	283	vs			= Asymmetric Cu—O stretching mode.[d]
304	w							= Accordion mode of n-octyl chain.[e]
				310	w	310	vw	
338	vw							
		350	w			353	m	
		372	w	375	m	383	m	
383	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 Stretching.[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			

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[a] (n-OBA)$_2$Cu(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 mentioned 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)$_2$Cu(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. 10.

[e] Referred to Ref. 3.

[f] See Figures 6 and 7.

[g] This band position is agreement with the result of Nakamoto, McCarthy, and Martell. See Ref. 9.

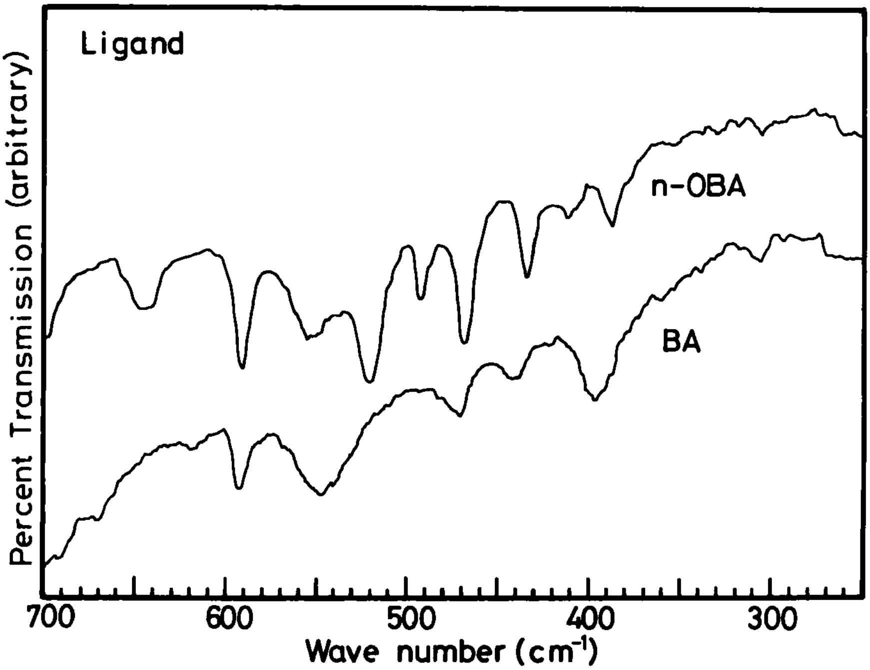

FIGURE 6 Far-infrared spectra of 1-*p*-*n*-octylphenylbutane-1,3-dione, *n*-OBA, and 1-phenylbutane-1,3-dione, BA, Nujol mull.

correspond to the 217 cm^{-1} band observed in the case of (acac)$_2$Cu(II), which is assigned to the out-of-plane —CuO$_4$—deformation ν_{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)$_2$Cu(II) and (acac)$_2$Cu(II). These bands would be expected to reflect well the difference of *cis-trans* isomerization structure, C$_{2h}$ (for *trans*-isomer) and C$_{2v}$ (for *cis*-isomer). In Figure 7 are compared schematically the observed far-infrared and Raman bands with rods proportional to the relative intensities. 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 present (*n*-OBA)$_2$Cu(II), *i.e.*, the molecular structure of the present complex has the *trans* type of coordination. In fact, in the case of (BA)$_2$Cu(II) which was determined as the *trans*-isomer by X-ray diffraction, some behavior is recognized in both the infrared and Raman spectra.

It is concluded, therefore, that each polymorph of $(n\text{-OBA})_2\text{Cu(II)}$ has the same *trans* form of coordination, since each polymorph shows the same far-infrared spectrum as shown in Figure 3. It should be noted here that the intense Raman band of 297 cm^{-1} observed only in $(n\text{-OBA})_2\text{Cu(II)}$ 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*-octyloxyphenylbutane-1,3-dionato)Pd(II).[3]

C. *Infrared Spectra of Each Polymorph.* As discussed above, each polymorph of $(n\text{-OBA})_2\text{Cu(II)}$ 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 the Figure 8 are shown the infrared spectra (4000–650 cm^{-1}) of each polymorph. There can be seen the large difference in these 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 on a variety of long chain compounds that the solid polymorphism with multiple melting behavior originates from the difference of the alkyl chain packing which is elucidated by the infrared spectra as singlet and doublet of the CH_2 rocking mode around 720 cm^{-1}, *i.e.* singlet for the parallel planes of the alkyl chains and doublet with equal intensities for the perpendicular planes of them.[11] These alkyl chain packing were revealed also by X-ray analysis.[12] Concerning about the doublet intensities, when the alkyl chain plane is rotated for the neighboring chain planes in various angles from the parallel to the perpendicular situation, the CH_2 rocking doublet is varied with various intensities from the singlet-like doublet to the just doublet; which can be proved easily by composition of the dipole moment vectors of CH_2 rocking. In the $(n\text{-OBA})_2\text{Cu(II)}$, 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 neighboring to each other is different in each polymorphic crystal. In Table III 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 polymorph 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 neighboring to each other for C^1, C^m, and C^h forms at least, and that C^a form may have another origin of the 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 C^a

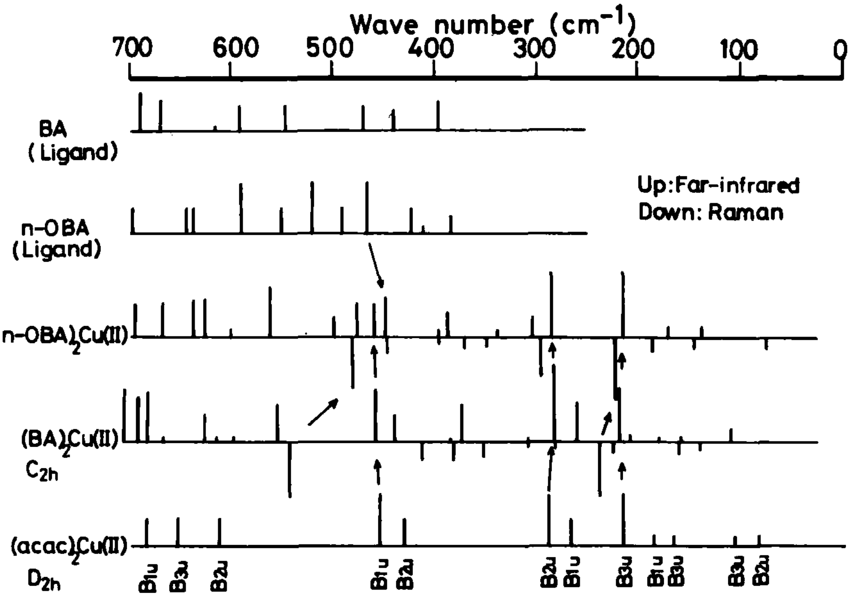

FIGURE 7 Schematic comparison between the observed far-infrared and Raman bands with the rods proportional to the relative intensities, up: far-infrared, down: Raman. The only far-infrared bands of (acac)$_2$Cu(II) and their assignments were referred to Ref. 10.

TABLE III

Correlation between relative intensity ratios F_{726}/F_{736} and m.p.s (°C) for the four polymorphs of (n-OBA)$_2$Cu(II)

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

form is very particular from others as reported in a previous paper; it is reasonably understood that the C^s form may have the different origin of polymorphism from other polymorphs, although it is not clear at the present time.

Thus, it is concluded that the main origin of the present polymorphism of (n-OBA)$_2$Cu(II) is considered to be due to the difference in the packing of n-octyl chains. Similar type of polymorphism has been found in glycerides,[13] 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 we know, however, this type of polymorphism is the first case in the organic transition metal complexes.

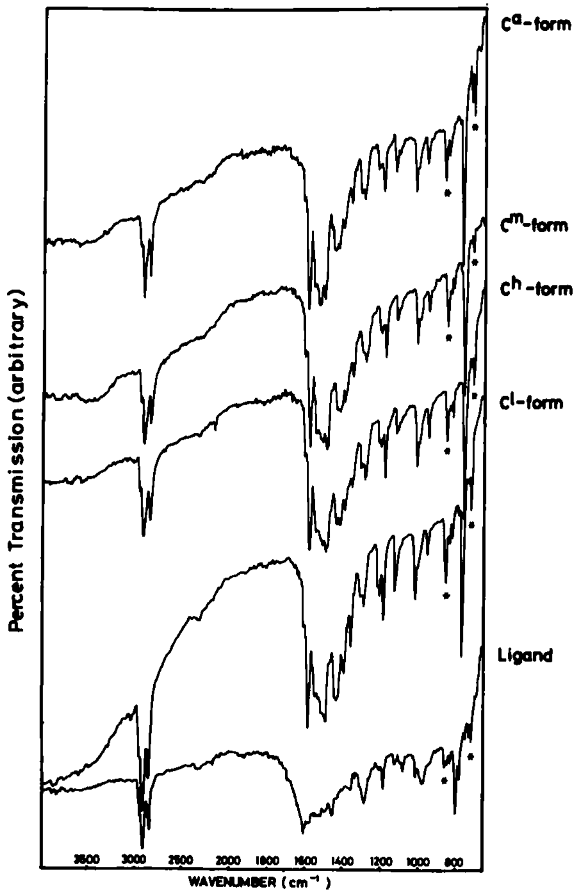

FIGURE 8 Infrared spectra of the four polymorphs of $(n\text{-OBA})_2\text{Cu(II)}$ and the ligand, *n*-OBA, in the region of 4000–650 cm^{-1}, KBr disks.

IV SUMMARY

The origin of the solid polymorphism of $(n\text{-OBA})_2\text{Cu(II)}$ has been studied by means of the spectroscopic techniques. All 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.

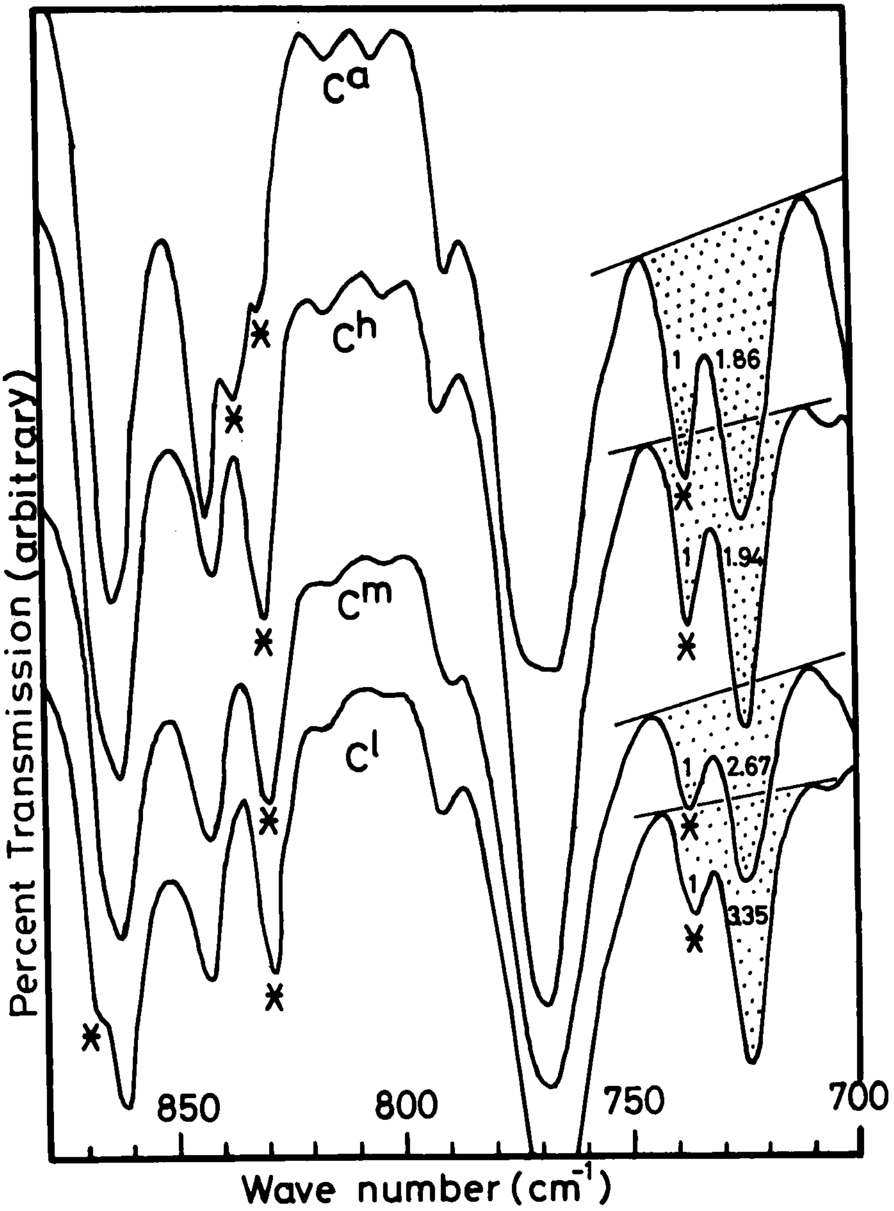

FIGURE 9 The expanded infrared spectra of the four polymorphs of (n-OBA)$_2$Cu(II) in the region of 880–700 cm^{-1}, KBr disks. Each intensity of ca. 726 and 736 cm^{-1} absorption band was measured as an area of the product of half value width and maximum highness from each base line illustrated in this figure. Numbers in this figure indicate relative intensities of ca. 726 cm^{-1} band when the intensity of 736 cm^{-1} band of each polymorph is set one. The band indicated by star varied appreciably in the four polymorphs.

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