December, 1993] *Bull. Chem. Soc. Jpn.*, ***66***, *3559—3564(1993)*

Discotic Liquid Crystals of Transition Metal Complexes. XVII. The Mechanism of "Mesomorphic Thermochromism" in Bis(octasubstituted diphenylglyoximato)palladium(II) Complexes Established by Their Temperature-Dependent Electronic Spectra[1)]

Kazuchika OHTA,* Mitsuo MORIYA, Mayumi IKEJIMA, Hiroshi HASEBE,
Tetsuya FUJIMOTO, and Iwao YAMAMOTO
Department of Functional Polymer Science, Faculty of Textile Science & Technology, Shinshu University, Ueda, 386

(Received April 16, 1993)

The bands in the electronic spectra of the $[Pd\{(C_{12}O)_4dpg\}_2]$ and $[Pd\{(C_6)_4dpg\}_2]$ complexes were assigned by using the results of temperature-dependent electronic spectral measurements. The temperature-dependent electronic spectra of "cast samples" of the complexes showed that two characteristic bands shift to higher energy (blue shift) with increasing temperature. The band which is located at a longer wavelength was assigned to the $4d_{z^2}$–$5p_z$ transition (d–p band), and that located at a shorter wavelength to the metal-to-ligand charge-transfer transition (MLCT band). The absorption intensities of both bands strongly depend on the sample film preparation manners and temperatures. From these facts, the mechanism of this unique "mesomorphic thermochromism" has been established.

In a previous study[1)] we introduced eight alkoxy-chains into the core bis[diphenylglyoximato]palladium(II) complex (abbreviated as $[Pd(dpg)_2]$; Fig. 1) in order to obtain the bis[1,2-bis(3,4-dialkoxyphenyl)ethanedione dioximato]palladium(II) complexes (abbreviated as $[Pd\{(C_nO)_4dpg\}_2]$; n=1—12; Fig. 1), and reported the discotic columnar mesomorphism and "mesomorphic thermochromism". In this study, the mechanism of this unique "mesomorphic thremochromism" was analyzed based on the temperature-dependent electronic spectra of the $[Pd\{(C_{12}O)_4dpg\}_2]$ complex. For a comparison, we also introduced eight alkyl-chains into the core $[Pd(dpg)_2]$ complex in order to obtain the bis[1,2-bis(3,4-dihexylphenyl)ethanedione dioximato]palladium(II) complex (abbreviated as $[Pd\{(C_6)_4dpg\}_2]$; Fig. 1); we also measured the temperature-dependent electronic spectra for the "mesomorphic thermochromism". For both compounds, the band located at a longer wavelength was assigned to the $4d_{z^2}$–$5p_z$ transition (d–p band), and the band located at a shorter wavelength was ascribed to the metal-to-ligand charge-transfer transition (MLCT band). It was found that the two characteristic bands shifted to higher energy (blue shift) with increasing temperature. Furthermore, the absorption intensities of the d–p and MLCT bands strongly depended on the sample film preparation procedures and temperatures. Based on these facts, the mechanism of this unique "mesomorphic thermochromism" is discussed.

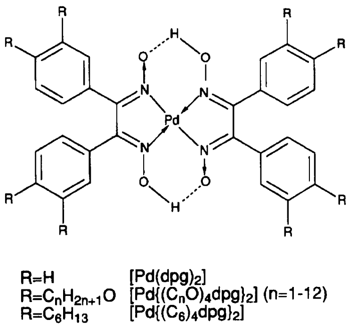
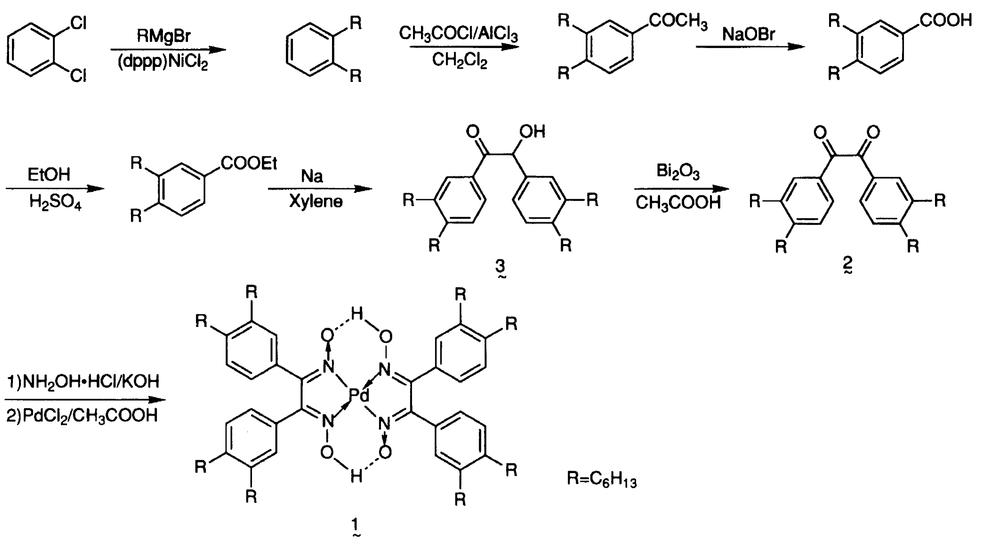


Fig. 1. Formula of the bis(octasubstituted diphenylglyoximato)palladium(II) complexes, abbreviated as $[Pd(dpg)_2]$, $[Pd\{(C_nO)_4dpg\}_2]$ (n=1—12), and $[Pd\{(C_6)_4dpg\}_2]$.

Experimental

Synthesis. The synthetic route of the $[Pd\{(C_6)_4dpg\}_2]$ complex (**1**) is shown in Scheme 1. The precursor benzoin (**3**) was synthesized following our previous method.[2)] Diketone 3,3′,4,4′-tetrahexylbenzil (**2**) was obtained by the same method as that of long-alkoxy-chain-substituted α-diketone derivatives reported in a previous paper.[3)] The $[Pd\{(C_6)_4dpg\}_2]$ complex was prepared by the following procedure.

Bis[1,2-bis(3,4-di-*n*-hexylphenyl)ethanedione dioximato]palladium(II) Complex (1), $[Pd\{(C_6)_4dpg\}_2]$: To 175 ml of ethanol were added hydroxylamine hydrochloride (7.12 g, 102 mmol) and potassium hydroxide (85% purity, 7.12 g, 102 mmol). The mixture was vigorously stirred for 30 min, and the precipitate was filtered off. To the filtrate was added 3,3′,4,4′-tetrahexylbenzil (**2**) (0.95 g, 1.73 mmol). Under a nitrogen atmosphere the mixture was refluxed with stirring for 6 h. To the hot reaction mixture was added palladium(II) chloride (0.13 g, 0.73 mmol) in 5 ml of ethanol. After neutralization with acetic acid, a yellow precipitate was separated out from the reaction mixture. The entire mixture was cooled to room temperature, and the yellow precipitate was collected on filter paper. The yellow solid was extracted with chloroform. Evaporation of the solvent gave the target complex (**1**) as orange crystals. The purification was carried out by column chromatography (silica gel, carbon tetrachloride : benzene=1 : 1 (v/v), R_f=0.66) and then by recrystallization from acetone to afford 0.18 g (17%) of orange crystals. Anal. Found: C, 72.86; H, 9.53, N, 4.32%. Calcd for $C_{76}H_{118}O_4N_4Pd$: C, 72.55; H, 9.45; N, 4.32%. ^{1}H NMR ($CDCl_3$) δ=0.78 (24H, t, J=5 Hz, $-CH_3$), 1.18 (64H, m), 2.27 (8H, t, J=8 Hz, Ph–C$\underline{H}_2$–),



Scheme 1. Synthetic route of the [Pd{$(C_6)_4$dpg}$_2$] complex, **1**.

2.40 (8H, t, $J=8$ Hz, Ph-C$\underline{H}_2$-), and 6.62—7.07 (12H, m, phenyl); IR (KBr) 2930 (alkyl), 2850 (alkyl), and 1600 cm^{-1} (aromatic).

Measurements. The product synthesized here was confirmed by elemental analysis. The phase transition behavior of the complex was measured with a Rigaku Thermoflex TG-DSC differential scanning calorimeter. A temperature-dependent X-ray diffraction measurement of the mesophase was performed using laboratory-made instruments.[4,5] Temperature-dependent electronic spectra were recorded by a previously reported technique.[5] Thin films of the complex for the spectral measurements were prepared by casting from a chloroform solution (abbreviated as "cast sample") and by cooling the isotropic liquid to room temperature (abbreviated as "cooled sample").

Results and Discussion

Discotic Mesomorphism of the [Pd{$(C_6)_4$-dpg}$_2$] Complex. Table 1 summarizes the phase transition behavior of the [Pd{$(C_6)_4$dpg}$_2$] complex. This complex has a discotic hexagonal disordered columnar (D_{hd}) mesophase in the 123 to 146 °C temperature range. This mesophase is the same as those of the previous [Pd{$(C_nO)_4$dpg}$_2$] ($n=2$—12) complexes.[1] The mesophase was identified by an X-ray diffraction measurement at 130 °C (Fig. 2). The five narrow peaks located at the lower angle region of the pattern could be assigned to reflections from a two-dimensional hexagonal lattice (Table 2).

Table 1. Phase Transition Temperatures (T) and Enthalpy Changes (ΔH) of the [Pd{$(C_6)_4$dpg}$_2$] Complex

Phase $\xrightarrow[{[\Delta H(\mathrm{kJ\,mol^{-1}})]}]{T(^\circ\mathrm{C})}$ Phase$^{a)}$
$\mathrm{K} \underset{[41.3]}{\overset{123}{\rightleftharpoons}} \mathrm{D_{hd}} \underset{[14.1]}{\overset{146}{\rightleftharpoons}} \mathrm{I.L.}$

a) Phase notation: K=crystal, D_{hd}=hexagonal disordered columnar mesophase, and I.L.=isotropic liquid.

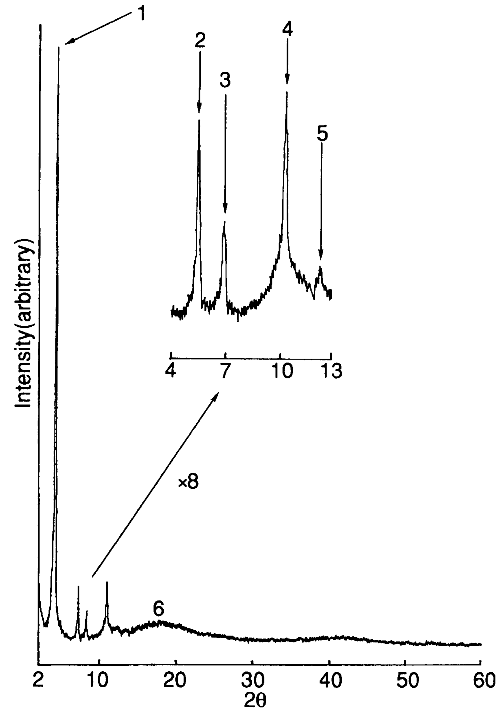


Fig. 2. X-Ray diffraction pattern of the [Pd{$(C_6)_4$-dpg}$_2$] complex at 130 °C. See Table 2.

Spectroscopic Properties of Bis(octasubstituted diphenylglyoximato)palladium(II) Complexes. In a previous paper[1] we reported that the [Pd{$(C_nO)_4$dpg}$_2$] complexes exhibit solvatochromism. It was found that the hexane solutions of these complexes are light orange, whereas the chloroform solutions are yellow. The concentrations of these solutions were almost the same. The color changes of the solutions were characterized by their electronic spectra. We have investigated whether or not the present

Table 2. X-Ray Diffraction Data of the $[Pd\{(C_6)_4dpg\}_2]$ Complex at 130 °C

Peak	Spacing (Å)		Miller	Lattice
No.	d_{obsd}	d_{calcd}	indices	constant (Å)
1	21.9	21.3	(100)	
2	12.3	12.3	(110)	
3	10.6	10.7	(200)	a=24.6
4	8.04	8.06	(210)	
5	7.10	7.11	(300)	
6	ca. 4.7	—	Melting of alkyl chains	

$[Pd\{(C_6)_4dpg\}_2]$ complex exhibits solvatochromism. The electronic spectra of chloroform and hexane solutions of the $[Pd\{(C_6)_4dpg\}_2]$ complex are shown in Fig. 3(b) and (c), respectively. In Fig. 3(a) the electronic spectrum of the "cast sample" of this complex is also shown at room temperature. As can be seen in this figure, the spectral shape of the chloroform solution (b) is almost the same as that of the hexane solution (c). These solutions are yellow. It is noteworthy that the $[Pd\{(C_6)_4dpg\}_2]$ complex does not exhibit solvatochromism.

Shirotani et al.[6] measured and assigned the electronic spectrum of a thin film of the unsubstituted core $[Pd(dpg)_2]$ complex. The spectrum is nearly the same as that of the "cast sample" of the $[Pd\{(C_6)_4dpg\}_2]$ complex [Fig. 3(a)]. The bands at 436, 347, and 280 nm of the thin film of the core $[Pd(dpg)_2]$ complex were assigned to the $4d_{z^2}$–$5p_z$ transition of Pd^{2+}, the metal-to-ligand charge-transfer transition, and the π–π^* transition in the ligand, respectively. As can be seen in Fig. 3(a), the electronic spectrum of the "cast sample" of the $[Pd\{(C_6)_4dpg\}_2]$ complex has four bands: 447 nm (A band), 359 nm (B band), 315 nm (C band), and 273 nm (D band). They could be assigned by comparing the electronic spectrum with that of the core $[Pd(dpg)_2]$ complex. The A, B, and D bands could be assigned to the $4d_{z^2}$–$5p_z$ transition (d–p band), the metal-to-ligand charge-transfer transition (MLCT band), and the π–π^* transition in the ligand, respectively. The C band could not be assigned. In addition, Shirotani et al. have also reported the electronic spectrum of the $[Ni(dpg)_2]$ complex in a chloroform solution.[7] This spectrum has three bands: 410 nm (the MLCT band), 360 nm (the MLCT band), and 275 nm (the π–π^* transition in the ligand). On the other hand, the electronic spectrum of the present $[Pd\{(C_6)_4dpg\}_2]$ complex in a chloroform solution [Fig. 3(b)] has two bands at 350 and 275 nm. When the spectrum was compared with that of the $[Ni(dpg)_2]$ complex in the chloroform solution, these two bands could be assigned to the MLCT band and the π–π^* transition in the ligand, respectively. It has been reported that the MLCT band of the thin film of the $[Ni(dpg)_2]$ complex is split into two bands,[7] and that the band of the thin film of the $[Pd(dpg)_2]$ complex is one degenerate band.[6] It was observed that the MLCT band of the present $[Pd\{(C_6)_4dpg\}_2]$ complex in a chloroform solution [Fig. 3(b)] is one degenerate band. The MLCT bands of the $[Pd(dpg)_2]$ and $[Pd\{(C_6)_4dpg\}_2]$ complexes tend to have one degenerate band. The d–p band (A band) in the "cast sample" of the $[Pd\{(C_6)_4dpg\}_2]$ complex disappears in both the chloroform solution and the hexane solution [Fig. 3(b) and (c)]. Since Shirotani et al.[7] reported a similar disappearance of the d–p band in the $[Ni(dpg)_2]$ complex, this is an additional support for our band assignment.

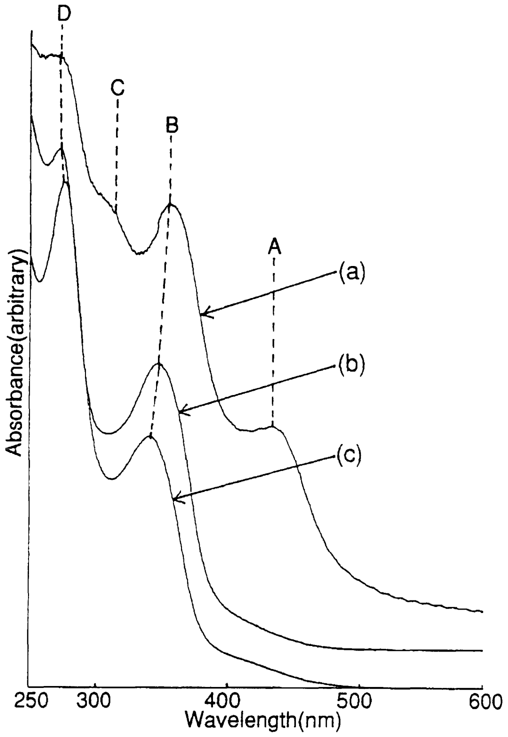


Fig. 3. Electronic spectra of the $[Pd\{(C_6)_4dpg\}_2]$ complex: (a) the film ("cast sample"), (b) the chloroform solution (c=4.60×10^{-5} mol dm^{-3}), and (c) the hexane solution (c=4.77×10^{-5} mol dm^{-3}). According to the assignment in the literatures, A band= $4d_{z^2}$–$5p_z$ transition (B_{1u}), B band=metal-to-ligand charge-transfer transition (MLCT: B_{2u} or B_{3u}), and D band=π–π^* transition in the ligand (B_{2u} or B_{3u}). The band C has not been reported.

In order to assign the electronic spectrum of the $[Pd\{(C_{12}O)_4dpg\}_2]$ complex, its electronic spectrum will be compared with that of the $[Pd\{(C_6)_4dpg\}_2]$ complex described above. Figures 4 and 5 show the electronic spectra of the $[Pd\{(C_6)_4dpg\}_2]$ and $[Pd\{(C_{12}O)_4dpg\}_2]$ complexes at various temperatures.

First of all, the temperature-dependent electronic spectra of the $[Pd\{(C_6)_4dpg\}_2]$ complex will be discussed, because the bands of the electronic spectrum at room temperature could be distinctly assigned, as mentioned hereinbefore. As can be seen in Fig. 4, the two characteristic bands of the A band (the d–p band) and the B band (the MLCT band) shift to a higher energy with increasing temperature. The energies of Peak

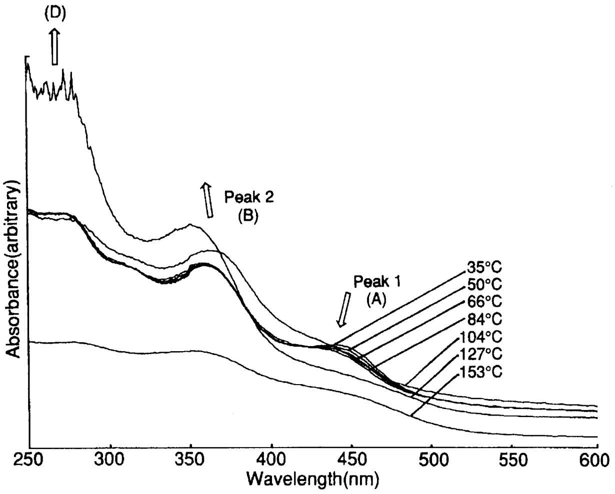


Fig. 4. Electronic spectra of the thin film of the $[Pd\{(C_6)_4dpg\}_2]$ complex at various temperatures. The thin film was prepared by casting (abbreviated as "cast sample").

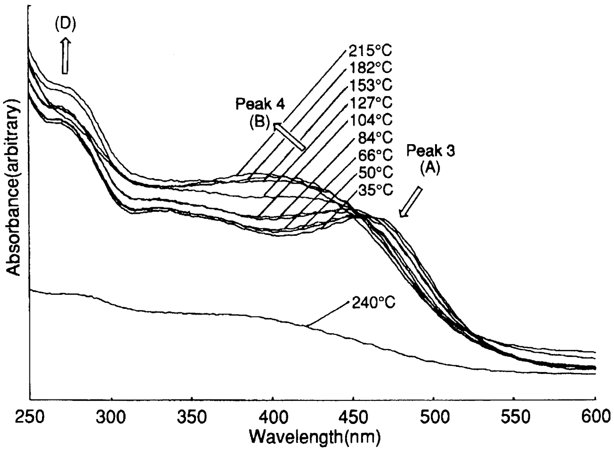


Fig. 5. Electronic spectra of the "cast sample" of the $[Pd\{(C_{12}O)_4dpg\}_2]$ complex at various temperatures.

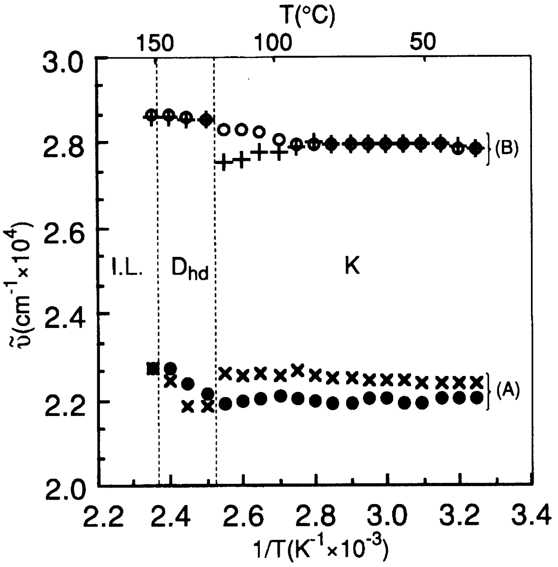


Fig. 6. Shift of peak energy vs. $1/T$ in the $[Pd\{(C_6)_4dpg\}_2]$ complex: × Peak 1, + Peak 2, ● Peak 5, and ○ Peak 6. See Figs. 4 and 9.

1 and 2 are plotted against the reciprocal of the temperature ($1/T$) in Fig. 6. The features from Figs. 4 and 6 can be summarized into the following: (i) Drastic shifts of Peak 1 and 2 occur at the crystal-liquid crystal phase transition (Fig. 6). (ii) Peak 1 (the A band) decreases in the absorption intensities with the blue shift when the temperature increases (Fig. 4). (iii) Peak 2 (the B band) increases in the absorption intensities with the blue shift when the temperature increases (Fig. 4). (iv) The D band tends to maintain a constant wavelength and to increase the intensities with increasing temperature (Fig. 4).

Next, the electronic spectra of the $[Pd\{(C_{12}O)_4dpg\}_2]$ complex is discussed. As can be seen in the electronic spectra given in Fig. 5, the band of 461 nm (Peak 3) at 35 °C decreases in absorption intensity with a blue shift when the temperature increases. A new band at around 400 nm (Peak 4) instead gradually appears and increases in absorption intensity with a blue shift. The energies of Peak 3 are plotted against the reciprocal of the temperature ($1/T$) in Fig. 7. The features from Figs. 5 and 7 can be summarized into the following: (i) Peak 3 decreases in absorption intensity with the blue shift when the temperature increases (Fig. 5). (ii) Peak 4 increases in absorption intensity with the blue shift when the temperature increases (Fig. 5). The critical change from Peak 3 to Peak 4 could not be determined from the successive spectra. (iii) A drastic shift of Peak 3 (or 4) occurs at around 120 °C (Fig. 7). It is not clear at present what causes this behavior. (iv) The band at around 275 nm tends to maintain a constant wavelength and to increase the intensities with increasing temper-

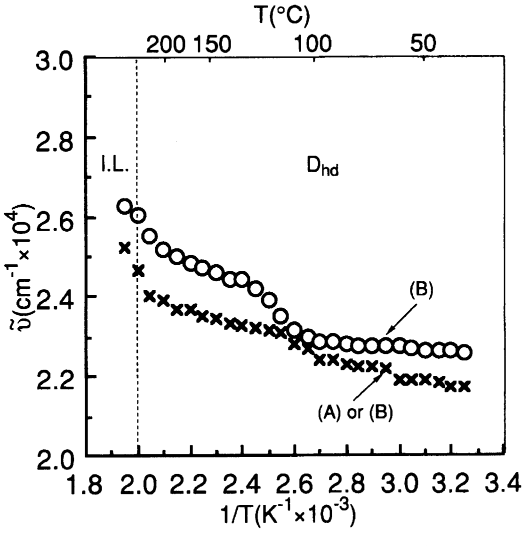


Fig. 7. Shift of peak energy vs. $1/T$ in the $[Pd\{(C_{12}O)_4dpg\}_2]$ complex: × Peak 3 or 4 and ○ Peak 7. See Figs. 5 and 10.

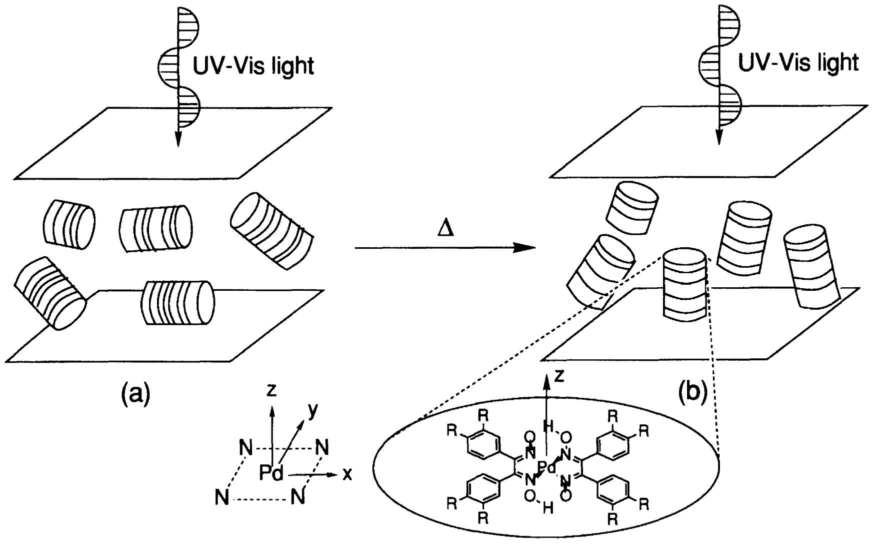


Fig. 8. Schematic models of columnar arrangements in the films of the Pd complexes for the electronic absorption spectra.

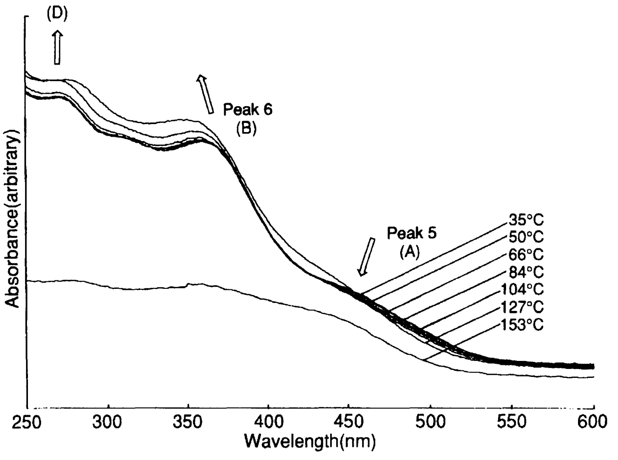


Fig. 9. Electronic spectra of a thin film of the $[Pd\{(C_6)_4dpg\}_2]$ complex at various temperatures. The thin film was prepared by cooling the isotropic liquid to room temperature (abbreviated as "cooled sample").

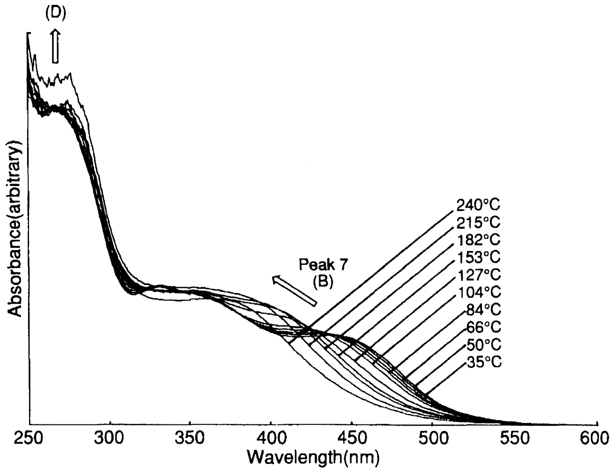


Fig. 10. Electronic spectra of a "cooled sample" of the $[Pd\{(C_{12}O)_4dpg\}_2]$ complex at various temperatures.

ature (Fig. 5).

Hence, these spectral results of the $[Pd\{(C_6)_4dpg\}_2]$ and $[Pd\{(C_{12}O)_4dpg\}_2]$ complexes could lead to the following conclusions. Since the behavior of Peak 4 is the same as that of the B band (Peak 2), it can be assigned to the metal-to-ligand charge-transfer transition; and since the behavior of Peak 3 is the same as that of the A band (Peak 1), it can be ascribed to the $4d_{z^2}$–$5p_z$ transition. The band at around 275 nm can be assigned to the π–π^* transition in the ligand (the D band).

It has been reported that the polarization of the transition of the d–p band (B_{1u}) is parallel to the z-axes of the complexes (i.e., also parallel to the columns formed by the complexes), and those for the MLCT band and the π–π^* transition (B_{2u} or B_{3u}) are perpendicular to the z-axes of the complexes (i.e., also perpendicular to the columns).[7,8] When the temperature increases, the d–p band decreases in absorption intensity, whereas the MLCT band and the π–π^* transition increase in intensity. This may mean that the columns gradually become arranged parallel to the direction of UV-vis light, as illustrated in Fig. 8. As can be seen in Fig. 8(a), the columns point perpendicular to the direction of UV-vis light at around room temperature. When the temperature increases, the z-axes of the columns begin to become parallel to the direction of the UV-vis light [Fig. 8-(b)]. This behavior is consistent with the results of the electronic spectral measurements described above.

In a previous paper[1] it was revealed that the blue shift of the d–p band in the $[Pd\{(C_{12}O)_4dpg\}_2]$ complex is attributable to an increase in the interdisk distance with increasing temperature. The d–p band of the $[Pd\{(C_6)_4dpg\}_2]$ complex also exhibits a blue shift in the liquid-crystalline state. Thus, this blue shift gen-

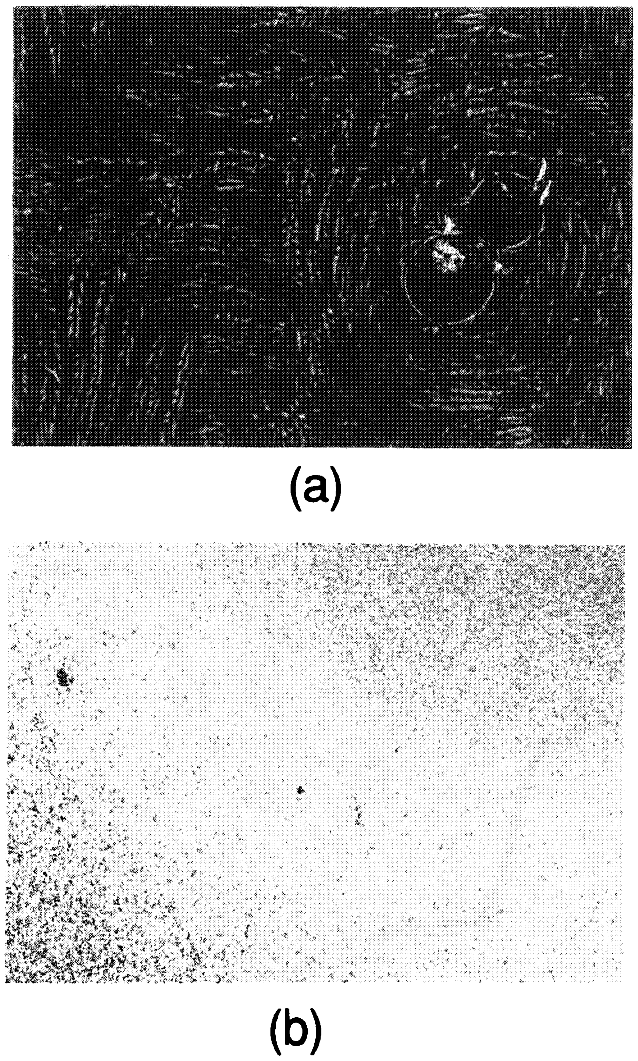


Fig. 11. Photomicrographs of $[Pd\{(C_{12}O)_4dpg\}_2]$ complex films between crossed polarizers: (a) the "cooled sample" at 35 °C and (b) the "cast sample" at 35 °C.

erates a "mesomorphic thermochromism" for both of the complexes. This phenomenon is also illustrated in Fig. 8(b) as an interdisk expansion.

Dependence of the Column Orientation on the Sample Preparation Manner. We noticed another interesting phenomenon, that the absorption intensities of the d–p and MLCT bands vary with the preparation procedures of the films. They were prepared by two different procedures: One was to prepare films by casting from the chloroform solution (abbreviated as "cast sample"); another one was to prepare them by cooling the isotropic liquid to room temperature (abbreviated as "cooled sample"). This phenomenon can be seen from a comparison of the spectra in Figs. 4 and 9 or Figs. 5 and 10. As can be seen from Figs. 4 and 9, the absorption intensities of the d–p bands (the A bands) observed in the "cast samples" are relatively stronger than those in the "cooled samples" at the same temperatures. As can be seen from Figs. 5 and 10, this d–p band of the $[Pd\{(C_{12}O)_4dpg\}_2]$ complex could not be observed for the "cooled sample". It is therefore apparent that the absorption intensity of the d–p band strongly depends on the sample-preparation procedure, and that more columns become arranged perpendicular to the direction of the UV-vis light in the "cast samples" than in the "cooled samples" at around room temperature.

This phenomenon could also be recognized by microscopic observations carried out for these samples between crossed polarizers. The "cooled samples" showed wide dark areas at 35 °C [Fig. 11(a)]; they also showed that the *z*-axes of the complexes in the columns point parallel to the direction of light. The "cast samples" at 35 °C are bright [Fig. 11(b)], in contrast to the "cooled sample" at the same temperature. This indicates that the *z*-axes of the columns point perpendicular to the direction of light in the "cast samples" more than in the "cooled samples".

References

1) Part XVI: K. Ohta, M. Moriyama, M. Ikejima, H. Hasebe, T. Fujimoto, and I. Yamamoto, *Bull. Chem. Soc. Jpn.*, **66**, 3553 (1993).

2) K. Ohta, H. Hasebe, H. Ema, M. Moriya, T. Fujimoto, and I. Yamamoto, *Mol. Cryst. Liq. Cryst.*, **208**, 21 (1991).

3) D. E. Ames, G. Hall, and B. T. Warren, *J. Chem. Soc. C*, **1968**, 2617.

4) H. Ema, Master Thesis, Shinshu University, Japan, Chap. 7, 1988.

5) H. Hasebe, Master Thesis, Shinshu University, Japan, Chap. 5, 1991.

6) I. Shirotani, K. Suzuki, and T. Yagi, *Proc. Jpn. Acad., Ser. B*, **68**, 57 (1992).

7) I. Shirotani, K. Suzuki, T. Suzuki, T. Yagi, and M. Tanaka, *Bull. Chem. Soc. Jpn.*, **65**, 1078 (1992).

8) Y. Ohashi, I. Hanazaki, and S. Nagakura, *Inorg. Chem.*, **9**, 2551 (1970).