Gels of Bis[1,2-bis(3,4-di-*n*-alkoxyphenyl)ethanedione dioximato]-palladium(II) Complexes

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(Received September 18, 1996)

Bis[1,2-bis(3,4-di-*n*-alkoxyphenyl)ethanedione dioximato]palladium(II) complexes (abbreviated as $[\mathrm{Pd}\{(\mathrm{C}_n\mathrm{O})_4\mathrm{dpg}\}_2]$; $n=7$—12) form gels in an over-concentrated *n*-hexane solution. We have developed a specific cell for X-ray diffraction in order to determine the gel structure. The gel has a two-dimensional hexagonal structure which is similar to the inverted hexagonal phase of lyotropic liquid crystals. The electronic spectra were measured for the gel and for a chloroform solution, which dose not form a gel. As a result, it has become apparent that a $4\mathrm{d}z^2$–$5\mathrm{p}z$ intermolecular charge-transfer transition between the neighboring palladium ions is the main driving force of the gel formation. The circular dichroism and magnetic circular dichroism of the gel suggested that this complex has a stack of left-handed helicity. The complex also has a thermotropic liquid-crystalline state, as previously reported. Hence, these three kinds of states are closely related to each other in terms of the formation of molecular aggregates.

We have reported in previous papers[1)] the synthesis, discotic columnar mesomorphism, and chromism of bis[1,2-bis-(3,4-di-*n*-alkoxyphenyl)ethanedione dioximato]palladium-(II) complexes, (abbreviated as $[\mathrm{Pd}\{(\mathrm{C}_n\mathrm{O})_4\mathrm{dpg}\}_2]$; $n=1$—12). In this paper, we wish to report on the structures and properties of the gels of the $[\mathrm{Pd}\{(\mathrm{C}_{12}\mathrm{O})_4\mathrm{dpg}\}_2]$ complex. The $[\mathrm{Pd}\{(\mathrm{C}_n\mathrm{O})_4\mathrm{dpg}\}_2]$ ($n=7$—12) complexes swelled and formed gels in an over-concentrated *n*-hexane solution. The gels of organic metal complexes having low molecular weights are particularly interesting, because they have rarely been reported.[2—4)] We also discuss the relationship between thermotropic liquid crystalline, lyotropic liquid crystalline, and gel states in this paper.

In general, if a very small amount of compounds is added into a pure solvent, each of the solute molecules is completely separated from the others. When the concentration is gradually increased, one molecule comes closer to another molecule to form a dimer. Upon further elevating the concentration, they stepwise form a trimer, tetramer, ···, oligomer, and finally multimer in this fluid solution. Eventually, the whole of the fluid solution comes to form a lyotropic liquid-crystalline state, or to solidify into a gel state in some cases. The gel states contain a large quantity of the solvent in the superstructure, and the system does not flow down, even when the bottle is turned upside-down. However, this gel state is far from a general rigid "solid state". Hence, it can be called a "soft state". When the concentration is infinitely elevated; in other words, when the system becomes a pure compound without a solvent, it shows a thermotropic liquid-crystalline state in some cases. This thermotropic liquid-crystalline phase may have a structure that is very close to that of the preceding gel state. A series of this molecular-assembling process in a solvent is very similar to the atomic-assembling process in vacuum to produce a hydrogen molecule from two hydrogen atoms, or a more complicated molecule from many heteroatoms. This atomic-assembling process can be well described by quantum chemistry. On the other hand, the chemistry which should precisely and generally describe the molecular-assembling process is still in its infancy. Hence, we believe that the present example of gel-forming liquid-crystalline complexes will contribute to this new field of chemistry.

Experimental

Material. The synthetic procedure for the $[\mathrm{Pd}\{(\mathrm{C}_{12}\mathrm{O})_4\mathrm{dpg}\}_2]$ complex has already been described in our previous papers.[1)] For the measurements, a complex which gave satisfactory elemental analysis data was used.

Measurements. The X-ray diffraction measurement of the gel was performed using a MAC Science M18XHF with Cu $K\alpha$ radiation (45 kV×400 mA). The electronic spectra were measured with a Hitachi 330 spectrophotometer. Spectrograde organic solvents were used. The number of the molecules in an aggregate was measured with a Korona 117 molecular-weight apparatus. In order to determine the structure of the gel by the X-ray diffraction technique, we have developed a specific sample cell. The schematic arrangement of the cell is illustrated in Fig. 1. A micro cover glass (18 mm×18 mm×0.15 mm) was etched by hydrofluoric acid to make a square hole (7 mm×7 mm). This micro cover glass was used as a spacer. The gel was placed into the hole of the spacer on another slip of micro cover glass (30 mm×30 mm×0.15 mm). It was covered by one more slip of micro cover glass (18 mm×18 mm×0.15 mm). These three slips of micro cover glass were adhered by gelatin.

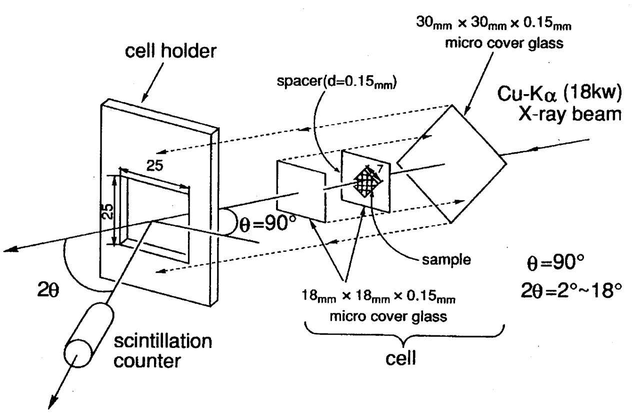

Fig. 1. Schematic arrangement of the cell for gel-forming materials for X-ray studies and the X-ray diffractometer system.

Table 1. Gelation of the $[\mathrm{Pd}\{(\mathrm{C_{12}O})_4\mathrm{dpg}\}_2]$ Complex in Various Solvents

Solvent	Dielectric constant	Gelation[a)]
Silicon oil	—	X (insoluble)
n-Pentane	1.84 (20 °C)	○
n-Hexane	1.89 (20 °C)	○
n-Heptane	1.92 (25 °C)	○
Petroleum ether	—	○
White gasoline	—	○
Diisocrotyl	—	○
Cyclohexane	2.05 (20 °C)	△
Benzene	2.28 (20 °C)	X (solune)
1-Hexanol	13.3 (25 °C)	X (insoluble)

a) ○: gelation at room tempreture, △: non-gelation at room temperature but gelation after solution with heating, and X: non-gelation.

This cell was mounted on a cell holder. An X-ray structural analysis of the gel was performed by the transmission method for a 2θ-angle of 2°—18° with the θ-angle being fixed at 90°. The circular dichromism (CD) and magnetic circular dichromism (MCD) were recorded with a JASCO J-700 spectrodichrometer in both the absence and presence of a magnetic field (1.2 T). For MCD, the spectra were recorded twice, once with a parallel field and then an anti-parallel field. Its magnitude was expressed in terms of the molar ellipticity per T, $[\theta]_\mathrm{M}/10^4\ \mathrm{deg\,mol^{-1}\,dm^{-3}\,cm^{-1}T^{-1}}$.

Results and Discussion

Characteristic Properties of Gels. We discovered the fact that $[\mathrm{Pd}\{(\mathrm{C}_n\mathrm{O})_4\mathrm{dpg}\}_2]$ ($n=7$—12) complexes form gels in an over-concentrated *n*-hexane solution. In general, gels can be obtained by cooling hot solutions. Nevertheless, the $[\mathrm{Pd}\{(\mathrm{C}_n\mathrm{O})_4\mathrm{dpg}\}_2]$ ($n=7$—12) complexes swell with a solvent to form a gel when the solvent is only poured on to them at room temperature. Needless to say, these complexes could also form gels by the general procedure mentioned above.

Hereupon, the minimum gel concentration in *n*-hexane was determined by using the $[\mathrm{Pd}\{(\mathrm{C_{12}O})_4\mathrm{dpg}\}_2]$ complex. The complex and *n*-hexane were placed into a sample bottle of 15 mm in diameter and then sealed with a resin stop cap. After the mixture in the sample bottle was heated to dissolve, it left standing in a bath at 20 °C, controlled by a thermostat for 10 min. When the sample bottle was taken out from the bath and was upset, the solution which did not drip was determined to be gel. As a result, the minimum gel concentration was $5.3\times10^{-3}\ \mathrm{mol\,dm^{-3}}$. Hanabusa et al.[5)] have reported the minimum gel concentrations of *N*-benzyloxycarbonyl-L-alanine 4-hexadecanoyl-2-nitrophenyl ester (abbreviated as L-alanine ester) in methanol and cyclohexane. In a comparison with their results, the minimum gel concentration of the present $[\mathrm{Pd}\{(\mathrm{C_{12}O})_4\mathrm{dpg}\}_2]$ complex in *n*-hexane is the value between that of the L-alanine ester in cyclohexane ($3.3\times10^{-3}\ \mathrm{mol\,dm^{-3}}$) and that of the L-alanine ester in methanol ($6.5\times10^{-3}\ \mathrm{mol\,dm^{-3}}$).

Table 1 summarizes the gelation of the $[\mathrm{Pd}\{(\mathrm{C_{12}O})_4\mathrm{dpg}\}_2]$ complex in various kinds of solvents. As Table 1 shows, gelation takes place in the solvents like a straight-chain hydrocarbon, except for cyclohexane, and the gels are observed at room temperature without heating. In the case of cyclohexane, the complex remains insoluble at room temperature, whereas the complex forms a gel upon cooling a hot solution after heating. Hence, the gelations tend to take place in solvents having structures and compositions which resemble the alkoxy chains in the $[\mathrm{Pd}\{(\mathrm{C_{12}O})_4\mathrm{dpg}\}_2]$ complex. In other words, solvents with a strong affinity for alkoxy chains are suitable for this gel formation.

Lyotropic Liquid Crystallinity of the $[\mathrm{Pd}\{(\mathrm{C_{12}O})_4\mathrm{dpg}\}_2]$ Complex in *n*-Hexane. Figure 2 shows a photomicrograph of the gel of the $[\mathrm{Pd}\{(\mathrm{C_{12}O})_4\mathrm{dpg}\}_2]$ complex. This texture was observed between crossed polarizers, and is quite similar to that of the lyotropic liquid-crystalline hexagonal phase of poly(γ-benzyl L-glutamate) (PBLG) in dioxane.[6)] Therefore, we supposed that the gel state of the present complex might be the same as the lyotropic liquid-crystalline state having a two-dimensional hexagonal structure. The relationship between the gel state and the lyotropic liquid-crystalline state will be discussed subsequently.

As Fig. 3 shows, the pattern gave four peaks which could be assigned to reflections from a two-dimensional hexago-

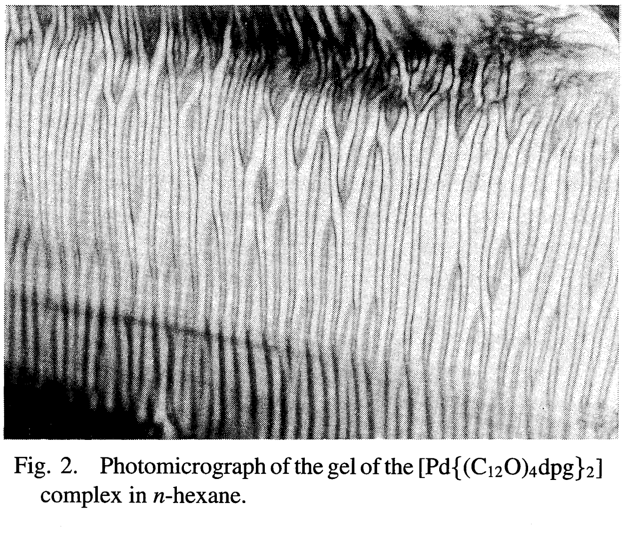

Fig. 2. Photomicrograph of the gel of the $[\mathrm{Pd}\{(\mathrm{C_{12}O})_4\mathrm{dpg}\}_2]$ complex in *n*-hexane.

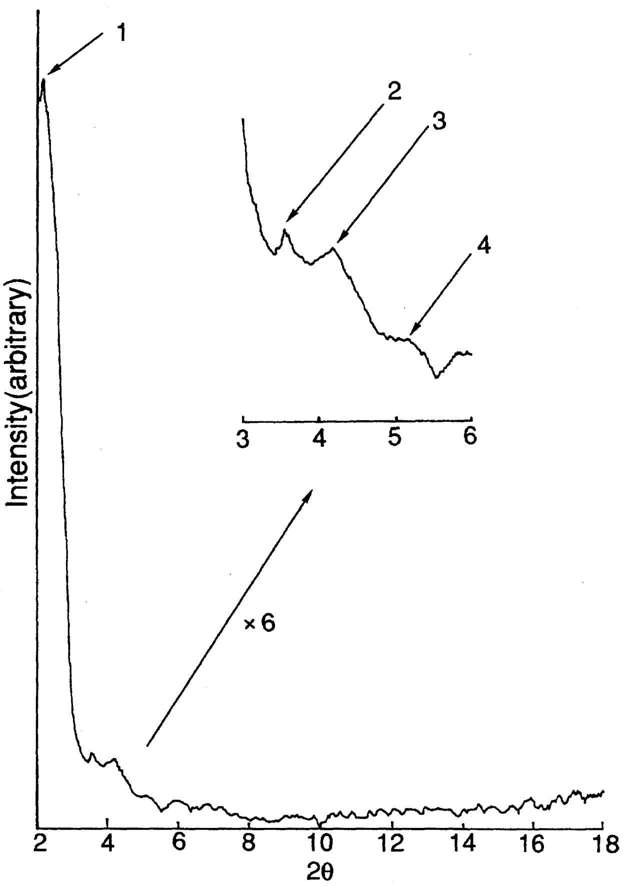

Fig. 3. X-Ray diffraction pattern of the $[\mathrm{Pd}\{(\mathrm{C_{12}O})_4\mathrm{dpg}\}_2]$ complex in the gel state (the Pd complex+n-hexane) at room temperature. See Table 2.

nal lattice (Table 2). According to our expectation based on the microscopic observation mentioned above, the gel has a two-dimensional hexagonal structure (HαII: $a = 49.9$ Å). Hence, this gel is neither amorphous nor crystalline, but exhibits lyotropic liquid crystallinity having a two-dimensional hexagonal structure.

Why Is This Gel Formed? Figure 4 shows the electronic absorption spectra of the chloroform solution (a), the n-hexane solution (b), and the gel (c) for the $[\mathrm{Pd}\{(\mathrm{C_{12}O})_4\mathrm{dpg}\}_2]$ complex, respectively. The concentration of the n-hexane solution (b: 3.9×10^{-5} mol dm^{-3}), which is lower than the minimum gel concentration (5.3×10^{-3} mol dm^{-3}), is the same as that of the chloroform solution (a: 3.9×10^{-5} mol dm^{-3}). As Fig. 4 shows, the spectral shape of the n-hexane solution (b) is quite similar to that of the gel (c). However, the shapes of these spectra (b, c) are quite different from that of the chloroform solution (a).

Table 2. X-Ray Diffraction Data of the $[\mathrm{Pd}\{(\mathrm{C_{12}O})_4\mathrm{dpg}\}_2]$ Complex in the Gel State (the Pd Complex+n-Hexane) at Room Temperature

Peak	Spacing(Å)		Miller	
no.	d_{obsd}	d_{calcd}	indices	
1	41.6	43.2	(100)	
2	24.9	24.9	(110)	H$_{\alpha\mathrm{II}}$ (= D_h)
3	21.2	21.6	(200)	$a = 49.9$ Å
4	17.1	16.3	(210)	

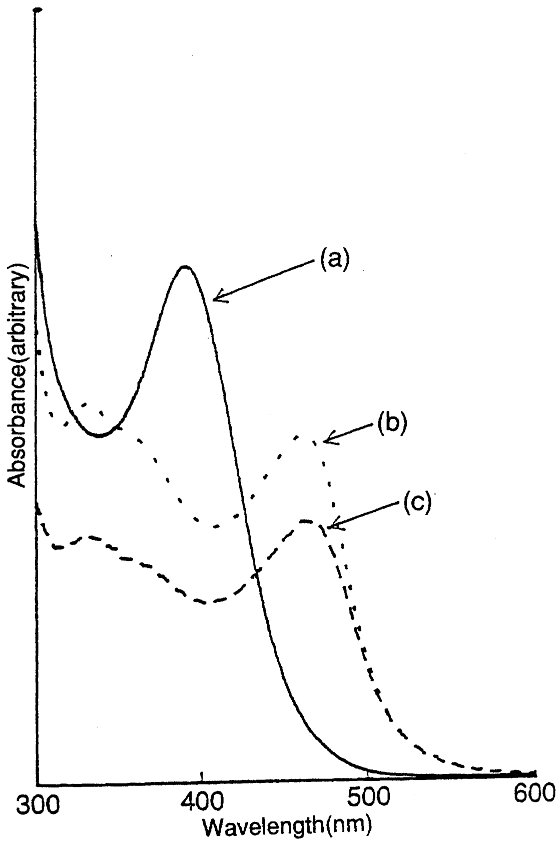

Fig. 4. Electronic spectra of the $[\mathrm{Pd}\{(\mathrm{C_{12}O})_4\mathrm{dpg}\}_2]$ complex: (a) the chloroform solution (3.9×10^{-5} mol dm^{-3}), (b) the n-hexane solution (3.9×10^{-5} mol dm^{-3}), and (c) the gel state (the Pd complex+n-hexane; 5.3×10^{-5} mol dm^{-3}).

In a previous paper,[1] we reported that a band at 390 nm of the chloroform solution can be assigned to the metal-to-ligand charge transfer transition, and that a band at 461 nm of the n-hexane solution can be attributed to the $4\mathrm{dz}^2$–$5\mathrm{pz}$ transition of Pd ion. Therefore, the band at 461 nm of the gel can be also regarded as the $4\mathrm{dz}^2$–$5\mathrm{pz}$ transition of the Pd ion. This transition, which could be observed both in the n-hexane solution and the gel, disappeared in the chloroform solution. Therefore, it can be expected that the molecules also aggregate in the n-hexane solution as well as in the gel, but do not aggregate in the chloroform solution.

To prove this idea of the number of the molecules in an aggregate in both the n-hexane solution and in the chloroform solution were measured of by means of vapor-pressure osmometry. The numbers are plotted against the concentration in Fig. 5. As the concentration of the n-hexane solution increases, the number of molecules in an aggregate becomes higher. When the highest concentration (1.05×10^{-3} mol dm^{-3}) is about 1/5 of the minimum gel concentration (5.3×10^{-3} mol dm^{-3}), the number of the molecules was 68. This figure shows an exponential increase in the number along with an increase in the concentration of the

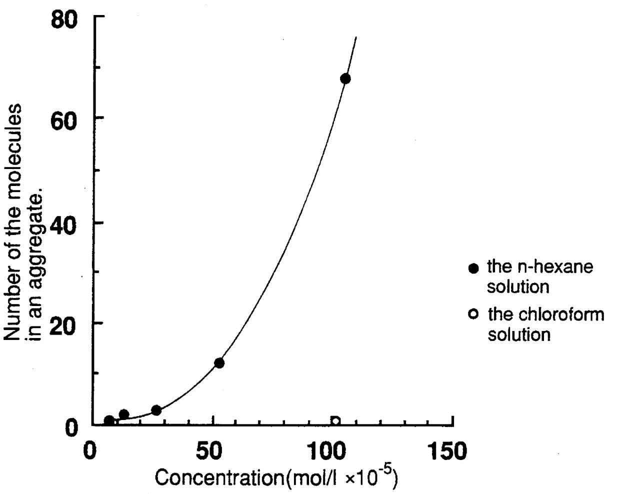

Fig. 5. Change in number of the molecules in an aggregate vs. the concentration of the $[Pd\{(C_{12}O)_4dpg\}_2]$ complex.

n-hexane solution. On the other hand, when the concentration of the chloroform solution was almost the same as the highest concentration of the *n*-hexane solution, the number of the molecules was 1. Hence, it is apparent that the complex aggregates in the *n*-hexane solution, whereas it does not associate in the chloroform solution. It has been reported that the band at 461 nm can be assigned to both an intramolecular transition and an intermolecular transition between neighboring palladium ions.[7] This transition, which could be observed both in the *n*-hexane solution and the gel, disappears in the chloroform solution. It can therefore be concluded from these facts that this transition should be an intermolecular transition between the neighboring palladium ions, and is a characteristic transition of the aggregates.[8] We thus revealed that the $4dz^2$–5pz transition located at 461 nm is the intermolecular CT transition. Hence, this transition can be regarded as the main driving force for aggregation and gel formation.

The pure $[Pd\{(C_{12}O)_4dpg\}_2]$ complex, which does not contain a solvent, has a two-dimensional hexagonal (Dhd) structure in the thermotropic liquid-crystalline state at room temperature (lattice constant: $a = 35.4$ Å), as illustrated in Fig. 6(a). When *n*-hexane is added to the pure complex, gelation takes place based on following three conditions: (i) the stacking columnar structure is maintained by the intermolecular $4dz^2$–5pz charge-transfer character between neighboring palladium ions, (ii) *n*-hexane has a strong affinity for the alkoxy-chains, and (iii) entangled flexible columns hold the solvent molecules of *n*-hexane. As shown in Fig. 6(b), bundles of the columns contain the solvents, which swell up until the lattice constant of the hexagonal structure becomes 49.9 Å.

The circular dichroism (CD) and magnetic circular dichroism (MCD) spectra were measured at room temperature in order to determine the structure of the gel in more detail. Figure 7, (a), (b), and (c) show the CD, MCD, and absorption spectra of the gel, respectively. The absorption peak at 461 nm [(c) in Fig. 7] was assigned to the $4dz^2$–5pz transition. Although the MCD spectrum [(b) in Fig. 7] shows a dispersion curve at a slightly shorter wavelength, perhaps this curve is a contribution of the Faraday B-term, since the band has been assigned to a $4dz^2$–5pz transition between nongenerate

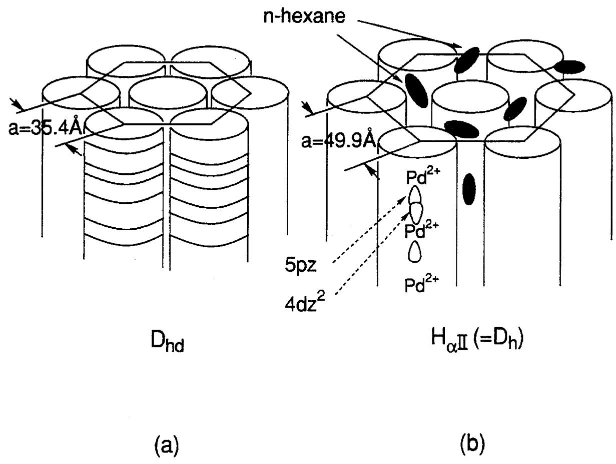

Fig. 6. Schematic models of the molecular arrangements for the $[Pd\{(C_{12}O)_4dpg\}_2]$ complex: (a) the thermotropic liquid crystalline state and (b) the gel state.

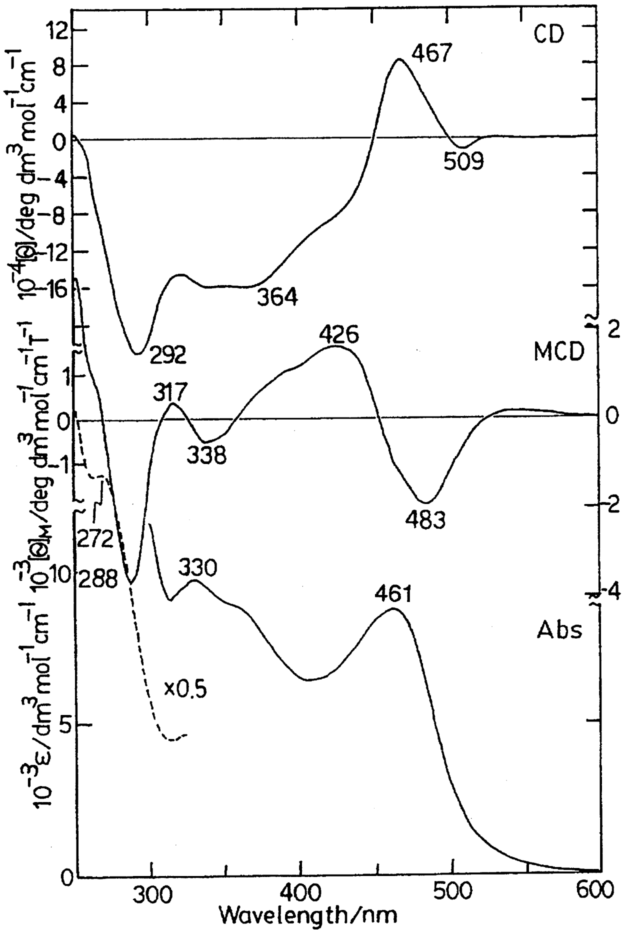

Fig. 7. Circular dichroism [CD; (a)], magnetic circular dichroism [MCD; (b)], and absorption [Abs; (c)] spectra of the $[Pd\{(C_{12}O)_4dpg\}_2]$ complex in *n*-hexane (gel state).

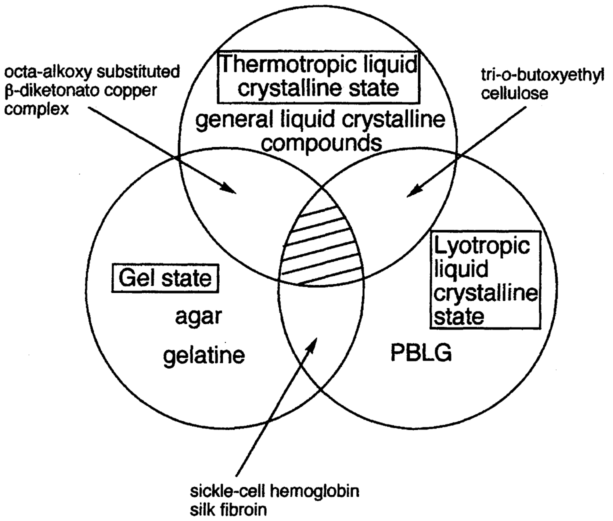

Fig. 8. Classification of molecular assemblies.

levels.1) The absorption corresponding to the MCD peak at 426 nm [(b) in Fig. 7] appears to be buried at around 400—440 nm. The transition corresponding to the absorption peak at 272 nm [(c) in Fig. 7] was attributed to the π–π^* transition in the ligand.1) If this is the case, the π^* orbital seems to be degenerate, since the Faraday A-term is seen to correspond to this band. In addition, since the π–π^* transition in the longest wavelength is generally that along the long axis of the chromophores,9) the CD pattern10) [(a) in Fig. 7] corresponding to this band suggests that this complex has a stack of left-handed helicity.

Classification of the Thermotropic Liquid Crystalline State, Lyotropic Liquid Crystalline State, and Gel State. Substances may be classified into three kinds of states, that is to say, thermotropic liquid-crystalline state, lyotropic liquid-crystalline state, and gel state. This classification is summarized in Fig. 8. It is defined that the thermotropic liquid-crystalline state and the lyotropic liquid-crystalline state are induced by heat and the solvent, respectively. Although it is also defined that the gel state is induced by swelling in the solvent without a gelling agent, it shows neither the thermotropic liquid-crystalline state nor the lyotropic liquid-crystalline state. For example, the thermotropic liquid-crystalline state, the lyotropic liquid-crystalline state, and the gel state can be observed in general liquid-crystalline compounds, poly-γ-benzil-L-glutamate (PBLG), and agar, respectively. On the other hand, it has been reported that tri-*o*-butoxyethyl cellulose11) is a compound which shows both the thermotropic liquid-crystalline state and the lyotropic liquid-crystalline state, and that sickle-cell hemoglobin and silk fibroin12—14) are substances which exhibit both the lyotropic liquid-crystalline state and the gel state. Giroud et al. reported that the octa-alkoxy substituted β-diketonato copper complex shows both the thermotropic liquid-crystalline state and the gel state.2)

Since the $[Pd\{(C_{12}O)_4dpg\}_2]$ complex has the characteristic of these three kinds of states, this complex belongs to the hatched part in Fig. 8. Such a unique compound has never been reported in low-molecular weight compounds, so far as we know.

Conclusion

Bis[1, 2-bis(3, 4-di-*n*-alkoxyphenyl)ethanedione dioximato]palladium(II) complexes (abbreviated as $[Pd\{(C_nO)_4dpg\}_2]$; $n = 7$—12) form gels in an over-concentrated *n*-hexane solution. In order to determine the structure of the gels, a specific sample cell was developed for X-ray diffraction studies. As a result, it was found that the gel of the $[Pd\{(C_{12}O)_4dpg\}_2]$ complex has a two-dimensional hexagonal structure which is similar to the inverted hexagonal phase of lyotropic liquid crystals. It was also revealed that the $4dz^2$–$5pz$ transition has an intermolecular charge-transfer character between the neighboring palladium ions, and that this charge transfer is the main driving force for gel formation. It has already been reported that the complex exhibits the thermotropic liquid-crystalline state. Hence, the complex can show three kinds of states: the thermotropic liquid-crystalline state, the lyotropic liquid-crystalline state, and the gel state. We proposed a classification of the molecular assemblies.

We would like to thank MAC Science Co., Ltd. for the X-ray measurement.

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