Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

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To cite this Article Hoshino, Naomi , Hasegawa, Hiroyuki and Matsunaga, Yoshio(1991) 'Mesomorphic properties of orthopalladated complexes of laterally substituted azobenzene derivatives, 2-alkoxycarbonyl-4-(4-ethoxyphenylazo)phenyl 4-methoxybenzoates', Liquid Crystals, 9: 2, 267 — 276
To link to this Article: DOI: 10.1080/02678299108035504
URL: http://dx.doi.org/10.1080/02678299108035504

Liquid Crystals, 1991, vol. 9, no. 2, 267–276

Mesomorphic properties of orthopalladated complexes of laterally substituted azobenzene derivatives, 2-alkoxycarbonyl-4-(4-ethoxyphenylazo)phenyl 4-methoxybenzoates

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(Received 5 June 1990; accepted 15 September 1990)

Homologous series of 2-alkoxycarbonyl-4-(4-ethoxyphenylazo)phenyl 4-methoxybenzoates (L) and their orthopalladated μ-chloro dimers ($Pd_2Cl_2L_2$) have been synthesized and their thermotropic phase transition behaviour has been characterized. The ligands, L, are three-ring nematogens with their central rings substituted in the 2-position by *n*-alkyl chains of varied length. The thermal stability of the nematic phases decreases rapidly with increasing side chain length and then levels off as the series is ascended. In every case the mesomorphic phase appears only over a small temperature range (less than 20°C). The orthopalladated species also proved to be nematogenic. Melting and clearing points rise on the average by 87°C and 126°C, respectively, and thus the temperature ranges of the nematic phases are enlarged considerably upon metallation. In relation to the observed stabilization of the nematic phases, particularly of higher homologues, a lath-like molecular structure, in which the side chains of the ligands fill up the clefts of the core part, has been deduced for a $Pd_2Cl_2L_2$ homologue from its solution ^{1}H-NMR spectrum.

1. Introduction

Metal-containing thermotropic liquid crystals (metallomesogens) have recently attracted much attention, due to the potential for a new area of materials chemistry, and many types of mesomorphic transition metal complexes are now known [1]. Among them is a class of orthopalladated dimeric species containing azobenzene and Schiff base derivatives, first reported by Ghedini and his co-workers [2].

Noting that the azo and azomethine linkages are often incorporated in liquid-crystalline compounds, the orthopalladation reaction could find its utility in preparation of new materials from a broader range of compounds without apparent chelating functionality. It is interesting, therefore, to assess the effect on the mesomorphism of structural change upon metallation. Mesomorphic behaviour could be promoted or even induced in favourable cases using organic ligands having molecular geometry unamenable to liquid-crystalline property.

Large lateral substituents on rod-like mesogens are one of such undesirable structural factors from a viewpoint of thermal stability of the mesophases. This paper reports synthesis and nematogenic properties of series of azobenzene derivatives, 2-alkoxycarbonyl-4-(4-ethoxyphenylazo)phenyl 4-methoxybenzoates (L), and their orthopalladated μ-chloro dimers ($Pd_2Cl_2L_2$). The ligand design is based on a view of

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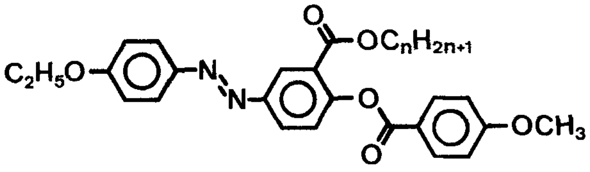
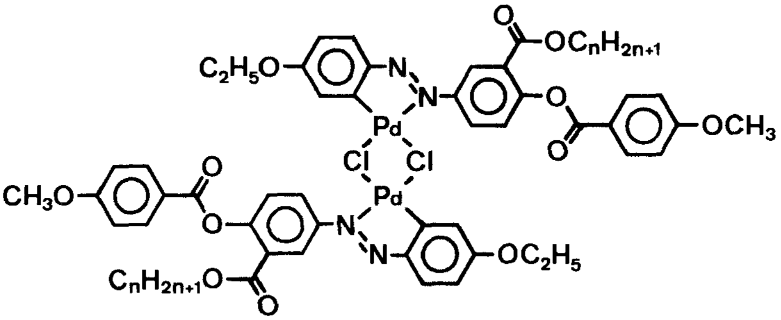
the 2-alkoxycarbonyl group as a large lateral group substituted in the rigid three-ring rod-like molecule, and this assignment of 'lateral' groups is carried over to the resulting metallated species. It is demonstrated that the unfavourable steric effect imposed by these lateral substituents can indeed be alleviated in the palladated complexes as shown by marked enhancement of the thermal stability of the nematic phases upon metallation.



L



$Pd_2Cl_2L_2$

2. Results and discussion

2.1. *Mesomorphic properties*

All of the compounds prepared in this study turned out to be nematogenic and their mesomorphic phase transitions were investigated by optical microscopic observation and differential scanning calorimetry. Table 1 summarizes the transition temperatures and enthalpies for the homologous series of L and $Pd_2Cl_2L_2$ determined by the latter means. Here C, N, and I denote crystalline [3], nematic, and isotropic liquid phases, respectively, and each homologue is designated by the number of carbon atoms in the lateral alkyl chain(s), n. The optical texture of the nematic phases is commonly of marble (and threaded) type, and the magnitude of isotropization enthalpies also supports the identification.

Figure 1 presents a graphic comparison of the phase behaviour of L and $Pd_2Cl_2L_2$. With regard to the thermal stability of the nematic phases of L, the clearing temperature, T_{NI}, decreases sharply at the beginning with increasing alkyl chain length but it tends to converge at large n. The melting curve shows a similar behaviour. The temperature ranges over which the nematic phases are stable are quite small (less than 20°C) for all of the homologues. It is, however, more than expected to observe enantiotropic mesophases considering the highly unfavourable molecular constitution of L.

Effects of lateral substitution of rod-like mesogens on the stability of mesophases have been the subject of numerous studies [4]. The results seem to indicate that liquid-crystalline property is allowed with only small substituents. For substituents of the size comparable to the rod-like moiety, however, Weissflog and Demus have shown that 1,4-bis(4-alkoxybenzoyloxy)-2-substituted-benzenes, three-ring diesters substituted on the central benzene ring as in L, do possess nematic phases but often as metastable states [4, 5]. They have also found the levelling-off curvature in the plot of T_{NI} versus the alkyl side chain length. Our system contains the azo linkage in the rigid core as well as the oxycarbonyl attachment of the lateral chain; both of these structural elements are apparently less damaging to the mesophase stability. It is likely, as they believe, that long chain lateral substituents tend to adopt a conformation more or less parallel to the molecular long axis and in this sense the molecules may be considered to be rod-like

Table 1. Mesomorphic transition temperatures (°C) and enthalpies (ΔH/kJ mol^{-1})† for L and $Pd_2Cl_2L_2$.

	L					$Pd_2Cl_2L_2$				
n	C‡		N		I	C§		N		I‖
1	●	149 (39)	●	194 (1·5)	●	●	265 —	●	275 —	●
2	●	154 (43)	●	162 (1·3)	●	●	249 (81)	●	277 —	●
3	●	122 (42)	●	132 (0·90)	●	●	212 (66)	●	268 —	●
4	●	111 (38)	●	122 (0·78)	●	●	211 (63)	●	266 —	●
5	●	109 (42)	●	113 (0·71)	●	●	193 (64)	●	259 —	●
6	●	92 (57)	●	105 (0·69)	●	●	200 (69)	●	255 —	●
7	●	89 (54)	●	97 (0·63)	●	●	177 (48)	●	246 —	●
8	●	78 (54)	●	97 (0·62)	●	●	159 (47)	●	245 (0·6)	●
9	●	76 (36)	●	95 (0·66)	●	●	170 (81)	●	236 (0·8)	●
10	●	72 (33)	●	94 (0·67)	●	●	169 (88)	●	231 (0·7)	●
12	●	73 (41)	●	89 (0·81)	●	●	148 (50)	●	218 (0·7)	●
14	●	74 (45)	●	85 (0·83)	●	●	145 (87)	●	203 (0·6)	●
16	●	73 (57)	●	83 (0·85)	●	●	134 (78)	●	192 (0·8)	●
18	●	75 (78)	●	81 (0·87)	●	●	135 (77)	●	183 (0·6)	●

† Values in parentheses.

‡ Stable form was obtained by annealing virgin crystals except for $n=3, 4, 5, 8$ and 12 homologues.

§ Stable form was obtained by annealing virgin powders. Homologues of $n=9$, 10, 14 and 16, in particular, contained mostly a metastable form in isolated samples.

‖ Onset of exothermic decomposition for $n=1$–7 homologues.

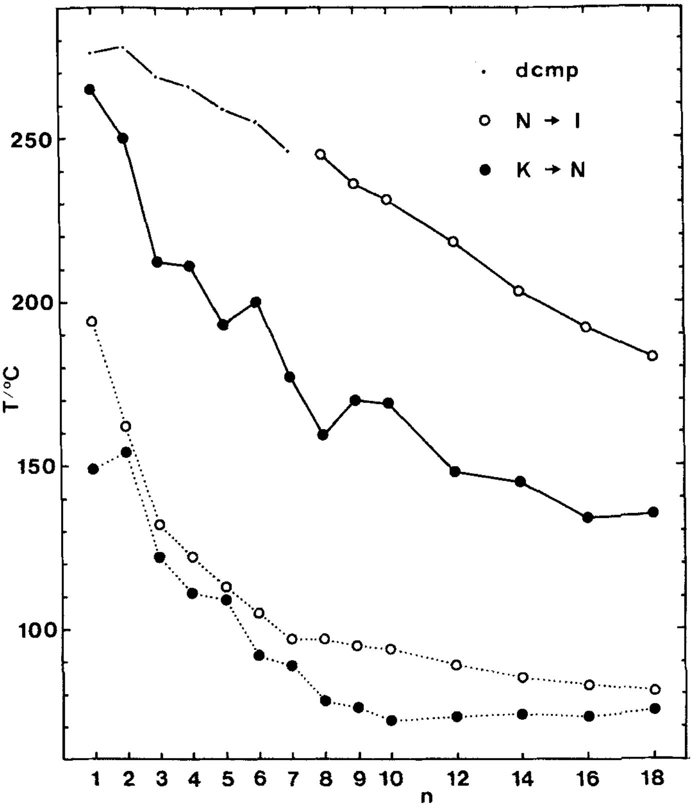


Figure 1. Plots of mesomorphic transition temperature versus alkyl substituent length (n) for L (dotted line) and $Pd_2Cl_2L_2$ (solid line).

with a still high length-to-breadth ratio, X, conforming to the molecular statistical theory [6]. This theory predicts a decrease of T_{NI} with decreasing X. It is then quite interesting to see what happens if two molecules of L are linked by the Pd_2Cl_2 unit.

Table 1 and figure 1 show that the change in molecular structure accompanying the metallation does not hamper the mesomorphic property and even enhances the nematic stability. Melting and clearing points are raised by more than 60°C and 102°C, respectively, and thus the temperature ranges of the enantiotropic nematic phases are considerably expanded on going from L to $Pd_2Cl_2L_2$ for all of the homologues except for $n = 1$. The values of N–I transition enthalpy suggest that the degree of order in each nematic phase of $Pd_2Cl_2L_2$ is no higher than that of the corresponding L, although there is a possibility that this is due to gradual thermal decomposition during a DSC heating scan. It is notable that the nematogenic property of L is retained throughout the series, but the clearing curve as a function of n now appears nearly linear for the metallated species. Considering the increment in molecular breadth by the Pd_2Cl_2 unit alone, the (further) widening effect of elongated lateral chains could be less drastic than in the case of L. But the difference in the T_{NI} versus n relationship suggests a situation for $Pd_2Cl_2L_2$ molecules in the mesophases quite unlike that of L, since the overall shape of the melting curve as a function of n is not altered as much.

2.2. *Molecular structure of $Pd_2Cl_2L_2$*

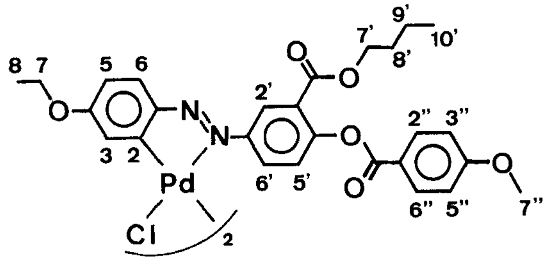
Since the nematic nature of the mesophases and the limitation in sample quantities hampered a detailed investigation within the mesophases, the molecular structure was analysed through ^{1}H-NMR measurements in solution. Table 2 summarizes the spectral data for L ($n=4$) and $Pd_2Cl_2L_2$ ($n=4$) in chloroform at room temperature, and the spectra within the aromatic region are compared in figure 2. The signal assignment as shown was assisted by selected decoupling for L ($n=4$) and reference to the literature on orthopalladated compounds [7]. The spectral pattern for L ($n=4$) indicates that the protons on both sides of outer *p*-phenylene groups are rendered nearly equivalent by rotation about the azo and ester linkages in L [8]. Metallation results in a centrosymmetric structure with the H^2 signal eliminated. Major spectral changes occur for the protons on the outer phenylazo group, whereas the benzoyl protons are affected only a little. The preferential palladation to this side of azobenzene moiety is probably due to its favourable electron density distribution (*p*-ethoxy substitution) and steric advantage (two *ortho* sites are equally open). Such ligand design is expected to yield a

Table 2. ^{1}H-NMR spectral data for L ($n=4$) and $Pd_2Cl_2L_2$ ($n=4$).†

	δ(*J*/Hz)			
Proton‡	L ($n=4$)		$Pd_2Cl_2L_2$ ($n=4$)	
10′	0·83t	(7·3)	0·79t	(7·3)
9′	1·32m		1·29m	
8	1·47t	(7·0)	1·44t	(7·0)
8′	1·50m		1·47m	
7″	3·91s		3·91s	
7	4·14q	(7·0)	4·16m	
7′	4·21t	(6·6)	§	
5	7·014d	(9·0)	6·72dd	(8·8, 2·6)
3	§		6·86s	
3″, 5″	7·006d	(9·0)	6·99d	(8·6)
5′	7·34d	(8·4)	7·32d	(8·4)
2	7·94d	(9·0)	—	
6	§		7·79d	(8·8)
6′	8·09dd	(8·4, 2·2)	8·06dd	(8·4, 2·6)
2″, 6″	8·20d	(9·0)	8·17d	(8·6)
2′	8·57d	(2·2)	8·45s	

† In $CDCl_3$ at room temperature. Chemical shifts are relative to internal TMS.

‡ Numbered according to the attached carbon atoms as shown below. Numbering scheme for the central ring is based on the chelate structure.



§ Equivalent to or inseparable from the proton(s) listed immediately above it.

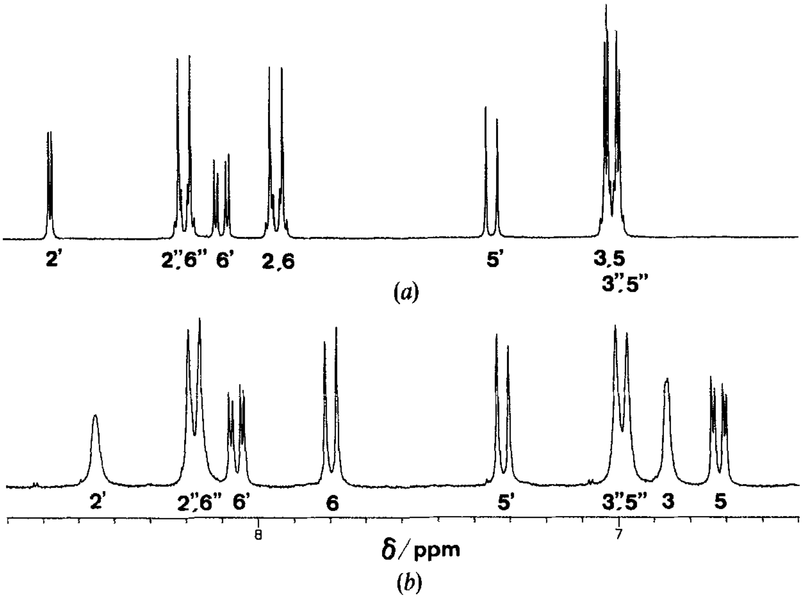


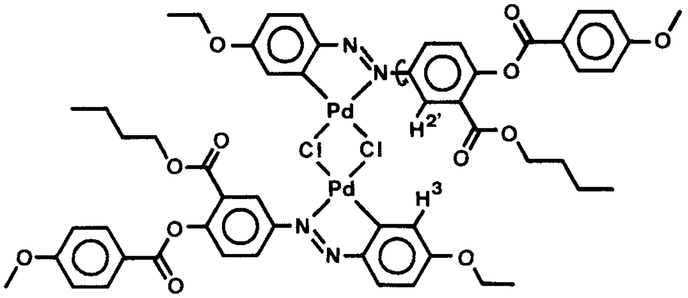
Figure 2. Aromatic region of ^{1}H-NMR spectra for (*a*) L ($n=4$) and (*b*) $Pd_2Cl_2L_2$ ($n=4$) in chloroform at room temperature. Solvent peaks are omitted for clarity. See table 2 for signal assignment.

more elongated molecule than one shaped like a fused twin [9]. It has also facilitated tremendously the isolation of a pure material instead of isomeric mixtures [2 (*a*), (*b*), 7 (*a*), (*b*)].

The magnitude of upfield shifts on going from L ($n=4$) to $Pd_2Cl_2L_2$ ($n=4$) is in the order of $H^5 > H^3 = H^6 \simeq H^{2'} >$ the rest. It should be noted that the change experienced by H^3, *ortho* to the palladium atom, is only half that of H^5 which is in the *para* position. In the case of orthopalladated μ-chloro and μ-bromo dimers of imine derivatives [7 (*c*)], the reported comparison of chemical shifts of H^3 and H^5 protons is qualitatively similar, but in reverse for μ-acetato and μ-thiocyanato species. Furthermore, a marked change by metallation is observed for $H^{2'}$, but not for $H^{6'}$.

Another feature to note is that an extensive broadening of signals from protons H^3 and $H^{2'}$ makes them appear as singlets in contrast to their *meta* counterparts, H^5 and $H^{6'}$, which display well-resolved spin–spin coupling. Such loss of resolution of *meta*-coupling from signals corresponding to H^3 in our $Pd_2Cl_2L_2$ ($n=4$) has been reported by other authors for similar μ-chloro dimers [7 (*a*)], but not for (η^5-cyclopentadienyl)palladium complexes [7 (*d*)] of azobenzene derivatives.

In order to clarify the source of this broadening effect the spectral change with temperature was examined. Figure 3 shows the result for the signals in question. The rest of the aromatic protons except for H^5 and $H^{6'}$ show additional tiny peaks with small upfield shifts at −50°C but they all coalesce below −25°C. The apparent order of recovering resolution and sharpness upon warming is $H^5 \rightarrow H^6 \rightarrow H^{6'} \rightarrow H^{5'} \rightarrow H^{2''}, H^{6''}, H^{3''}, H^{5''} \rightarrow H^3 \rightarrow H^{2'}$. The fluxional behaviour of the last two protons shown in figure 3 is perplexing since the coalesced peaks continue to shift towards downfield with temperature. The coincident coalescence around 0°C may be due to a common rate process, one of the possibilities for which is competitive interaction with bridging chlorine atoms. This model employs a molecular conformation in which the butoxycarbonyl substituents are oriented 'inward' so that the $H^{2'}$ protons face the chlorine atoms. It should be noted that such conformation would not provoke a severe steric crowding as illustrated by the CPK models presented in figure 4. Other processes which are accelerated at elevated temperatures, such as a rotational motion about N–$C^{1'}$ bond, would complicate the phenomenon; weakening of coordination bonds may lead to the downfield shift of coalesced peaks. But the resolution of $H^{2'}$–$H^{6'}$ coupling is only barely seen for the $H^{2'}$ signal even at 60°C and so the rotation does not seem to be rapid enough for the broadening effect on $H^{2'}$ to be fully eliminated at this temperature.



It is true that the solution NMR need not reflect the situation in mesophases, but the above results have a significant implication on the molecular structure and the thermal stability of the mesophases of higher homologues of $Pd_2Cl_2L_2$ in the present case. In their nematic phases, where the packing requirement could presumably be severer than in solution, the molecules may assume a lath-like shape as deduced above, in which the lateral substituents of L are accommodated in the molecular clefts formed by rigid three-ring parts and a Pd_2Cl_2 unit instead of extruding out sideways. This would contribute to the thermal stability of the nematic phases, which is much enhanced relative to L and decreases only gradually as the alkyl side chains are elongated. It is clear at least that the destabilizing effect of the longer chains in L can be effectively suppressed in $Pd_2Cl_2L_2$ in their mesophases. We would like to point out that vaulted structures of certain metal complexes may be exploited for such advantageous structural characteristics.

3. Experimental section

3.1. *Synthesis*

All of the homologues of L and $Pd_2Cl_2L_2$ were prepared in a similar manner, as described below.

Ligands. Azo coupling reaction between *p*-phenetidine and salicylic acid was carried out following the literature [10] and the product was subjected to acylation by *p*-methoxybenzoyl chloride by refluxing a benzene solution of the mixture also containing two equivalents of pyridine for 20 min. Rotary evaporation of the solution to dryness yielded crude 2-(4-methoxybenzoyloxy)-5-(4-ethoxyphenylazo)-benzoic acid, which was washed with dilute hydrochloric acid, water, ethanol, and then acetone, and recrystallized from 1,4-dioxane. Mp: 191°C. Yield for this step was between 61 and 74 per cent.

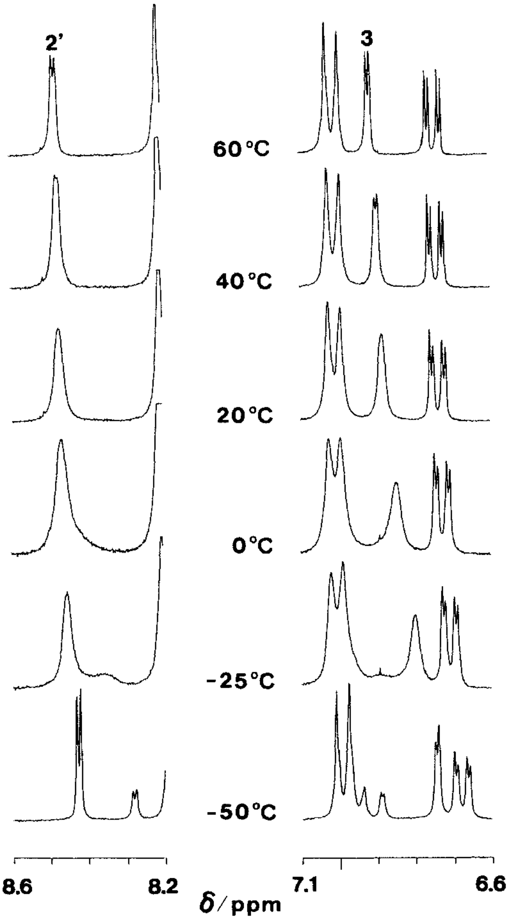


Figure 3. ^{1}H-NMR spectral changes with temperature in regions involving $H^{2'}$ and H^3 protons of $Pd_2Cl_2L_2$ ($n=4$) in chloroform.

Esterification with various *n*-alkanols was patterned after the method of Hassner and Alexanian [11], and purification was effected by silica gel chromatography, eluting the desired ester as the second moving orange band with a 2:1 benzene:*n*-hexane mixture containing small amounts of methanol. Homologues having longer alkyl chain substituents were more readily eluted. The isolated products were further recrystallized from methanol/benzene mixtures which yielded yellowish orange needle-like or fibrous crystals. Yields: 5–28 per cent. Anal. found (calcd) for $C_{37}H_{48}N_2O_6$ ($n=14$): C, 72·09 (72·05); H, 7·92 (7·84); N, 4·60 (4·54).

Orthopalladation. One mmole of $Na_2[PdCl_4]$ was allowed to react with an equimolar amount of a ligand homologue suspended in a 50 ml quantity of methanol at room temperature for several days. The resulting solid was isolated by filtration, washed extensively with methanol, and loaded on a column of silica gel [12]. After the unreacted ligand was run down with dichloromethane, up to 30 per cent of chloroform was mixed in, and this led to elution of a red band, leaving a small amount of violet species behind. Replacement of the solvent in the collected band by repeated rotary

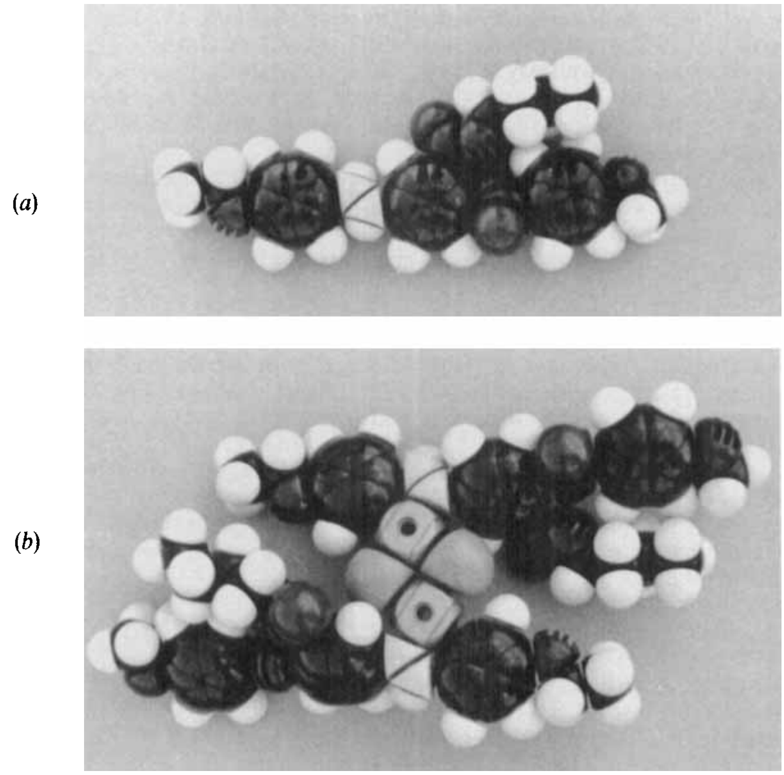


Figure 4. CPK models for (*a*) L ($n=4$) and (*b*) $Pd_2Cl_2L_2$ ($n=4$).

evaporation and addition of ethanol resulted in the formation of an orange powdery solid of the product. Attempted crystallization from various solvents was unsuccessful [3]. Yields: 38–79 per cent ($n \geqslant 2$). Anal. found (calcd) for $C_{54}H_{54}N_4O_{12}Pd_2Cl_2$ ($n=4$): C, 52·40 (52·53); H, 4·40 (4·41); N, 4·51 (4·54); Cl, 5·67 (5·74).

3.2. *Physical measurements*

Mesomorphic transition temperatures and enthalpy changes were determined using Rigaku Thermoflex, Rigaku TAS 100, and DuPont 9900 differential scanning calorimeters. Heating or cooling rate was $5\,K\,min^{-1}$. High resolution ^{1}H-NMR spectra were recorded on a JEOL JNM-270 spectrometer at the Centre of Instrumental Analyses, Hokkaido University, Japan.

This work was supported by a Grant-in-Aid for Scientific Research No. 63740328 from the Ministry of Education, Science and Culture of Japan, and in part by the IMS Joint Studies Program (1989). Helpful discussions on the NMR spectra by Drs. Kazunori Odashima and Seiichi Miyajima are gratefully acknowledged.

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