Supramolecular Helical Stacking of Metallomesogens Derived from Enantiopure and Racemic Polycatenar Oxazolines

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Abstract: The present report undertakes a challenge of general interest in supramolecular chemistry: the achievement of helical organizations with controlled structure. To achieve this target we considered the possibility of inducing supramolecular chirality using molecules that were designed to organize into columnar mesophases. The use of oxazoline-derived ligands and metal coordination served as tools to prepare molecules with a phasmidic-like structure, which show columnar organization in the liquid crystalline state. To ensure the formation of chiral mesophases, these complexes bear stereogenic centers in the rigid coordination environment of the metal. X-ray and circular dichroism experiments have revealed that chirality transfer does indeed take place from the chiral molecule to the columnar liquid crystal organization. This chiral columnar organization appears as a helix consisting of stacks of molecules that rotate with respect to one another along the column while maintaining their mean planes parallel to each other. In fact, it has been concluded that packing of these polycatenar molecules must be more efficient upon rotation of a molecule with respect to the adjacent one along the column. Furthermore, the same type of helical supraorganization has been found to be present in the mesophase of the racemic mixture and the mixture of diastereomers prepared from the racemic ligand. In this case, segregation of the optical isomers is proposed to occur to give rise to both types of helix (right-handed and left-handed).

Introduction

A major challenge in supramolecular chemistry is the design of simple molecular units that are capable of organizing into chiral architectures, the essence of which is helicity in different spatial manifestations. In this context, helical organizations have been described for supramolecular systems based on metal coordination,[1] H-bonding interactions,[2] and mesomorphic (thermotropic as well as lyotropic) systems.

These last systems have been found to be a versatile tool to obtain materials with controlled supramolecular chirality[3] that promotes the appearance of interesting properties for practical applications. Traditionally, SmC* and cholesteric mesophases have been the most widely investigated chiral organizations in liquid crystals. Thus, polar order (and, hence, electrooptical

ferro- and antiferroelectric switching and second-order optical properties)[4] in the former and the special optical features (i.e., selective reflection)[5] of the latter are the main consequences of the presence of chiral molecules in the SmC and the nematic phases, respectively.

Likewise, helical order is also possible in liquid crystals based on columnar organizations.[6] These are currently the target of studies by several authors, which range from a basic interest in the knowledge of the helical assembly and how to manipulate it[7] to the achievement of promising properties for practical applications such as nonlinear optical behavior (i.e., SHG)[8] or electrooptical switching.[9,10]

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Given the possibilities that metal coordination offers to molecular design, we have been using it as a means to achieve molecular shapes capable of organizing into chiral superstructures. Previous studies were based on discotic metal β-diketonates that showed a rectangular columnar mesophase whose helical structure was extensively studied, as well as its ferroelectric behavior.[11] The origin of the supramolecular chirality in these systems was the presence of stereogenic centers in the peripheral tails (derived from (S)-lactic acid) in the molecule.

Recently, we considered the possibility of inducing the transfer of chirality from the rigid part of the molecule to the supramolecular organization in the mesophase. Previous work carried out in our group on aryloxazolines derived from (S)-β-amino alcohols demonstrated the great potential of this type of compounds in the design of mesogenic structures that display chiral mesophases. For example, SmC* ferroelectric mesophases with high Ps values were obtained when the chiral oxazoline moiety was linked to the appropriate mesogenic core.[12] Further work was undertaken based on the ability of phenyloxazolines to coordinate to metals. Planar mesogenic complexes were obtained that induced broad cholesteric ranges when used as chiral dopants in nematic hosts.[13]

Studies have recently been expanded to encompass different mesogenic structures, such as elongated polycatenar molecules (phasmidic-like) that can give rise to columnar mesomorphism.[14] As a first attempt to obtain chiral columnar systems from aryloxazolines, chiral ligands were prepared derived from 3,4,5-trialkoxybenzoic acid. Complexation of these ligands with copper(II) or palladium(II) yielded planar phasmidic-like complexes that did not show mesomorphic behavior unless an electron acceptor such as TNF was added in certain proportions. These complexes were, however, shown to have high helical twisting powers in appropriate nematic hosts.[15]

On the basis of these results, and in order to achieve polycatenar metallomesogens that are able to induce helical columnar organizations, we have designed a new oxazoline-derived ligand with an extended aromatic core and six dodecyloxy terminal chains. Coordination to palladium(II) or copper(II) results in phasmidic-like planar complexes, i.e., Pd(S-C$_{12}$)$_2$ and Cu(S-C$_{12}$)$_2$ (Figure 1). X-ray studies of related chiral oxazoline complexes have demonstrated that upon complexation only the trans isomer is formed.[16] Hence, the molecule should have C$_2$
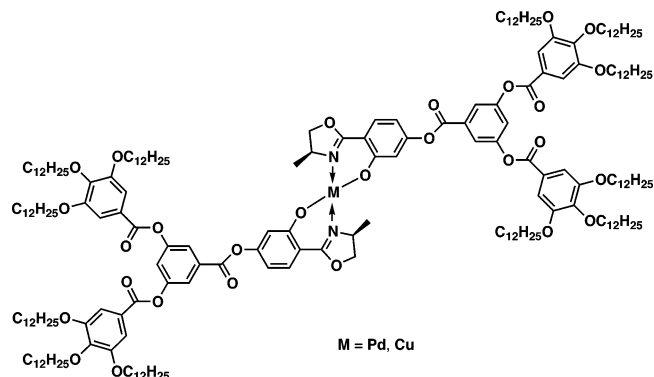

Figure 1. Chemical structure of the polycatenar palladium(II) (Pd(S-C$_{12}$)$_2$) and copper(II) (Cu(S-C$_{12}$)$_2$) oxazoline complexes.

symmetry, with its binary axis perpendicular to the coordination plane. This arrangement causes the two methyl groups in the stereogenic centers to lie on the same side of the molecular plane. Both complexes have been deeply investigated by X-ray diffraction and circular dichroism in order to elucidate the possible helical organization in the mesophase. Taking into account the geometry of the molecule and the strong influence of both stereogenic centers in the intermolecular interactions, we decided to go deeper into the study of supramolecular organization. Our aim was to assess the influence of both aspects on the supramolecular organization and also to answer an intriguing question: Does the helical organization maintain in the mesophase of the nonoptically active mixtures [Pd(S-C$_{12}$)$_2$ + Pd(R-C$_{12}$)$_2$ and Pd(RS-C$_{12}$)$_2$]? For this reason, we extended our investigation to the enantiomeric complex as well as to nonoptically active mixtures of complexes. Thus, the enantiomer Pd(R-C$_{12}$)$_2$, the racemic mixture, Pd(S-C$_{12}$)$_2$ + Pd(R-C$_{12}$)$_2$, and the palladium(II) complex of the racemic ligand (resulting in a diastereomeric mixture, Pd(RS-C$_{12}$)$_2$) were prepared. Palladium-(II) derivatives were chosen for this study according of preliminary results that indicated the possibility of producing well-aligned samples of the palladium(II) complex, Pd(S-C$_{12}$)$_2$. Furthermore, palladium(II) complexes yield higher diffraction intensities due to the presence of the heavier palladium atom.
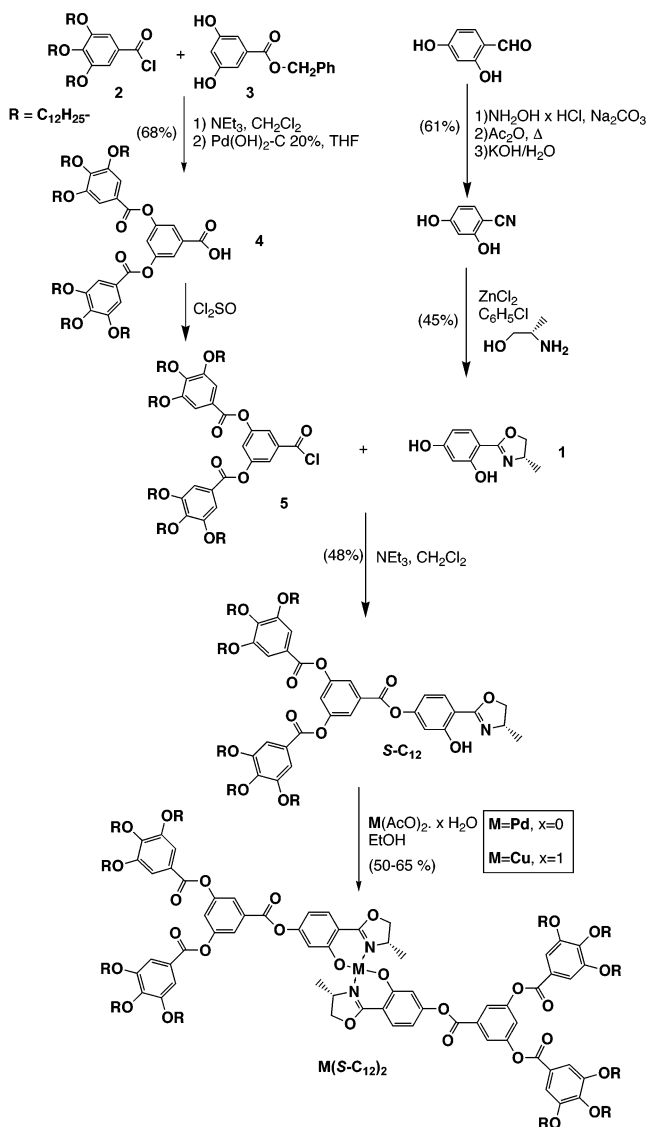
Results and Discussion

Synthesis.[17] The synthetic pathway for all the compounds is outlined in Scheme 1. The synthesis of the enantiomeric and racemic 4,5-dihydro-2-(2′,4′-dihydroxyphenyl)-4-methyloxazole (**1**) was carried out as reported previously.[12] The corresponding starting (S)-, (R)- and (RS)- amino alcohols were purchased from Aldrich. The 3,5-bis(3,4,5-tridodecyloxybenzoyloxy)benzoic acid (**4**) was prepared by esterification of benzyl 3,5-dihydroxybenzoate (**3**) with 2 equiv of 3,4,5-tridodecyloxybenzoyl chloride (**2**). The synthesis of **3** was carried out through a solid-state phase-transfer reaction between the potassium salt of 3,5-dihydroxybenzoic acid and benzylbromide, catalyzed by tetrabutylammonium chloride following the method described by Keller.[18]

Ligands and complexes were identified by ^{1}H NMR, ^{13}C NMR, FT-IR, and elemental analysis. The ^{1}H NMR spectra of both enantiomeric complexes show that only one isomer is

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Scheme 1. Synthetic Pathway for Ligands and Complexes

Table 1. Mesomorphic Behavior of Ligands and Complexes.

compound		t, °C (ΔH, kJ/mol)^a				
S-C$_{12}$	C	69.8 (109.3)	I			
R-C$_{12}$	C	63.7 (104.7)	I			
RS-C$_{12}$	C	66.0 (101.8)	I			
Cu(S-C$_{12}$)$_2$	C	−6.5 (43.9)	Col$_r$	97.2 (34.2)	I	
Pd(S-C$_{12}$)$_2$	C	1.7 (30.1)	Col$_r$	109.5 (53.2)	I	
Pd(R-C$_{12}$)$_2$	C	2.2 (28.8)	Col$_r$	110.2 (53.7)	I	
Pd(RS-C$_{12}$)$_2$	C	3.9 (25.0)	Col$_h$	110.6 (40.6)	I	
Pd(S-C$_{12}$)$_2$ + Pd(R-C$_{12}$)$_2$	C	2.7 (50.8)	Col$_h$	119.3 (50.7)	I	

well as the racemic mixture [Pd(S-C$_{12}$)$_2$ + Pd(R-C$_{12}$)$_2$] was studied by polarizing optical microscopy and DSC. Transition temperatures and their associated enthalpy changes are gathered in Table 1. The ligands do not show liquid crystalline properties in any case. However, all the pure complexes, as well as the mixtures of the palladium(II) complex isomers, display mesomorphic behavior at room temperature and over a wide temperature range. Thus, interactions between the aromatic cores of the complexes give rise to stacking and hence overcome the negative steric effect of the methyl groups in the stereogenic centers, both of which lie out of the planar core.[15]

Examination of the complexes by polarizing microscopy did not provide useful information about the type of mesophase shown by these complexes. When observed between crossed polarizers, the pure enantiomers appear black (homeotropic-like texture) on cooling from the clearing temperature (measured by DSC). In samples prepared without a cover glass, a gray texture appeared in both cases, but this was not representative of any particular liquid crystalline phase. Both the racemic mixture [Pd(S-C$_{12}$)$_2$ + Pd(R-C$_{12}$)$_2$] and the diastereomeric mixture [Pd(RS-C$_{12}$)$_2$] give rise to a gray texture on cooling, both with and without a cover glass. The columnar phases shown by the complexes are designated in Table 1 as rectangular [Cu(S-C$_{12}$)$_2$, Pd(S-C$_{12}$)$_2$, Pd(R-C$_{12}$)$_2$] or hexagonal [Pd(RS-C$_{12}$)$_2$, Pd(S-C$_{12}$)$_2$ + Pd(R-C$_{12}$)$_2$] according to X-ray powder diffraction analysis (see below).

Structure of the Columnar Mesophase. All the complexes were studied by X-ray diffraction with the aim of elucidating the type(s) of mesophase and determining the details of their structures. Most of the experiments were performed at room temperature; however, in the case of Pd(S-C$_{12}$)$_2$ high-temperature experiments were also carried out.

Likewise, the chirality of the supramolecular organization was studied at different temperatures by circular dichroism in order to corroborate the conclusions withdrawn from X-ray studies.

X-ray Diffraction Studies. In the cases of Pd(S-C$_{12}$)$_2$, its enantiomer Pd(R-C$_{12}$)$_2$, the racemic mixture [Pd(S-C$_{12}$)$_2$ + Pd(R-C$_{12}$)$_2$] and the diastereomeric mixture [Pd(RS-C$_{12}$)$_2$], we were able to obtain oriented X-ray patterns at room temperature. The samples were aligned by shearing with a metal or glass rod on the inner wall of the capillary when the sample was held at a temperature close to its clearing point. The use of this technique allowed us to obtain fiber patterns with the fiber axis parallel to the stretching direction. The patterns revealed that the columns are oriented parallel to the capillary axis and hence perpendicular to the X-ray beam.

(a) Mesophase Structure of the Pure Enantiomers. In the oriented patterns of pure enantiomer Pd(S-C$_{12}$)$_2$, or Pd(R-C$_{12}$)$_2$,[19] a set of spots is observed at low angles (Figure 2a), the intensity of which is maximum in the equator (plane perpendicular to
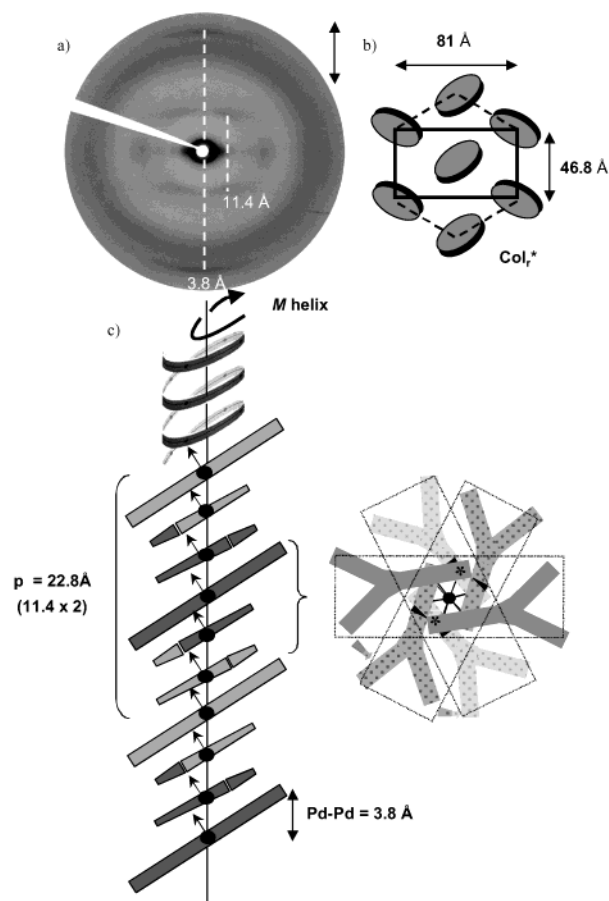
present in each case. It is expected that this is the trans isomer on the basis of reported X-ray diffraction studies.[16] The ^{1}H NMR spectrum of the complex prepared from the racemic ligand RS-C$_{12}$ shows different chemical shifts for some aromatic hydrogens. These hydrogens belong to the different diastereomers formed upon coordination of the racemic ligand RS-C$_{12}$ with palladium(II) (see Supporting Information). Analysis of the spectrum reveals a ratio of 0.25:0.25:0.5 of Pd(S-C$_{12}$)$_2$/Pd(R-C$_{12}$)$_2$/Pd(S-C$_{12}$)(R-C$_{12}$), respectively, within a diastereomeric mixture that, hereafter, will be referred to as Pd(RS-C$_{12}$)$_2$. This result indicates that the formation of Pd(RS-C$_{12}$)$_2$ is statistical, as expected from the same reactivity of both enantiomeric ligands against palladium(II). The racemic mixture Pd(S-C$_{12}$)$_2$ + Pd(R-C$_{12}$)$_2$ was prepared by dissolving equal amounts of the two enantiomeric complexes, Pd(S-C$_{12}$)$_2$ and Pd(R-C$_{12}$)$_2$, in methylene chloride and evaporating the solvent. Characterization of the copper(II) complex Cu(S-C$_{12}$)$_2$ was carried out by FT-IR and elemental analysis. NMR spectroscopy was not a suitable technique given the paramagnetic nature of the metal center.

Mesomorphic Behavior. The thermal and thermodynamic behavior of the ligands (S-C$_{12}$, R-C$_{12}$, RS-C$_{12}$) and their complexes [Cu(S-C$_{12}$)$_2$, Pd(S-C$_{12}$)$_2$, Pd(R-C$_{12}$)$_2$, Pd(RS-C$_{12}$)$_2$] as

Figure 2. Oriented X-ray pattern (a), rectangular lattice parameters (b), and proposed helical model (c) for the complex Pd(*S*-C$_{12}$)$_2$.

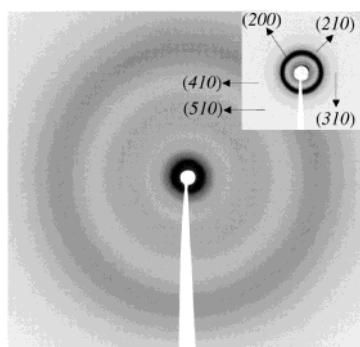**Figure 3.** Powder X-ray pattern of the Col$_r$ mesophase of Pd(*S*-C$_{12}$)$_2$ taken at room temperature. Inset: small-angle pattern with the proposed indexation (410 and 510 reflections are very weak)

the capillary axis). These maximums are related to a two-dimensional (2D) array of columns. This array is better characterized from the powder patterns (Figure 3), which provide more accurate spacings that can be indexed in a 2D rectangular lattice (*hk*0 spots, Table 2). The lattice constants of this rectangular lattice are $a = 81$ Å, $b = 46.8$ Å. The absence of mixed reflections (reflections with *h* or *k* and *l* simultaneously different from 0) confirms the mesomorphic nature of this structure and rules out a 3D organization.[20]

(19) In the following discussion, we will refer only to the *S*-enantiomer, Pd(*S*-C$_{12}$)$_2$, since X-ray results are identical and reveal equal parameters for both enantiomers.

(20) An X-ray pattern of Pd(*S*-C$_{12}$)$_2$ was taken at high temperature. The structure of the mesophase at 80 °C is the same as at room temperature, except for a slight increase in the lattice parameters.

Table 2. X-ray Results for the Mesophases of the Complexes*a*

compound	temp (°C)	meso-phase	h k l	d_{obs} (Å)	d_{calc} (Å)	lattice constants (Å)
Pd(*S*-C$_{12}$)$_2$*c*	25	Col$_r$	200, 110	41.0	40.5	$a = 81$
			210	30.1	30.6	$b = 46.8$
			310, 020	23.2	23.4	$c = 3.8$
			410	18.5	18.6	
			510, 420, 130	15.3	15.3	
			800, 440	10.2	10.1	
			930, 060	7.8	7.80	
				4.4*b*		
			001	3.8	3.8	
	80	Col$_r$	200, 110	41.9	41.0	$a = 82$
			210	30.4	31.0	$b = 47.3$
			310, 020	23.4	23.7	$c = 3.85$
			410	18.5	18.8	
			510, 420, 130	15.5	15.5	
			800, 440	10.4	10.2	
			930, 060	8.1	7.88	
				4.5*b*		
			001	3.85	3.85	
Pd(*RS*-C$_{12}$)$_2$*d*	25	Col$_h$	100	41.0	40.7	$a = 47$
			110	23.5	23.5	$c = 3.8$
			210	15.9	15.4	
			220	11.7	11.75	
			320	9.5	9.34	
			330	7.84	7.83	
			430	6.74	6.69	
			600	6.74	6.78	
				4.4*b*		
			001	3.8	3.8	
Cu(*S*-C$_{12}$)$_2$	25	Col$_r$	200, 110	41.5	41.5	$a = 83$
			210	31.9	31.4	$b = 47.9$
			310, 020	23.6	23.95	$c = 3.75$
			510, 420, 130	15.2	15.7	
			800, 440	10.6	10.4	
			930, 060	7.9	7.98	
				4.5*b*		
			001	3.75	3.75	

a The columns of the table show, respectively, the compound code, the temperature, the type of mesophase, the proposed indexation, the observed and calculated spacings, and the lattice constants. *b* Broad, diffuse maximum. *c* Data corresponding to Pd(*R*-C$_{12}$)$_2$ are identical to those of its enantiomer, Pd(*S*-C$_{12}$)$_2$. *d* Data corresponding to the racemic mixture [Pd(*R*-C$_{12}$)$_2$ + Pd(*S*-C$_{12}$)$_2$] are identical to those of the mixture of diastereomers, Pd(*RS*-C$_{12}$)$_2$.

At middle angles (Figure 2a), a pair of diffuse spots appears at both sides of the meridian (direction parallel to the column axis). This is indicative of a modulation of the electronic density and suggests the existence of a superlattice periodicity in the direction of the stacks of molecules. The periodicity of this modulation measured along the column axis is 11.4 Å. It is only possible to account for this modulation if we assume that the molecules adopt a helical stacking in the column.[21] The absence of scattering at the meridian itself is a consequence of the helical structure with its axis parallel to the column axis.

Another interesting point to be noted is a diffuse, nearly isotropic ring corresponding to a mean distance of 4.4 Å and, in the outermost part, a relatively sharp arc centered in the meridian at 3.8 Å. The diffuse ring is characteristic of the liquidlike order between the aliphatic chains, whereas the strong arc corresponds to the intracolumnar stacking distance (intermolecular Pd−Pd distance).

From density considerations it can be deduced that the 2D unit cell contains two columns, one located at the center and the other at the corner of the rectangle (Figure 2b). It is interesting to note that the lattice constants *a* and *b* are in the

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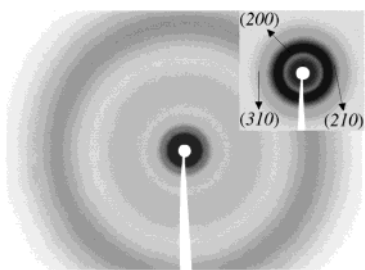
Figure 4. Powder X-ray pattern of the Col$_r$ mesophase of Cu(S-C$_{12}$)$_2$ taken at room temperature. Inset: small-angle pattern with the proposed indexation (the 210 reflection is partially overlapped with the intense 200 reflection)

ratio √3, which is characteristic of a hexagonal structure. However, the presence of the reflections indexed 210 and 410 is not consistent with a hexagonal symmetry. A hexagonal cell is equivalent to a C-centered orthorhombic cell with lattice constants a and b in the ratio √3. A C-centered orthorhombic symmetry implies that the molecule located at ($^1/_2$,$^1/_2$,0) has the same orientation as the molecule located at (0,0,0), and thus all the (hk0) reflections with an odd value for h + k should be systematically absent. This is not the case here, as revealed by the presence of the extra reflections.

Hence, it can be concluded that, although the column axes are located at the nodes of a hexagonal lattice, the molecules must be tilted and there is an alternation in the tilt direction. The resulting space group is P2$_1$, and the rectangular symmetry arises from a heringbone-like arrangement of the elliptical sections of the columns when viewed along the column axes (Figure 2b).[21b] The same kind of *pseudohexagonal* arrangement has been found in a number of nonchiral[22] and chiral[11a] columnar mesophases.

When we compare the periodicity of the helix, measured from the middle-angle scattering, and the stacking distance, measured from the meridional reflection, we find a ratio between the two periods of 11.4/3.8 = 3. This means that one helix period contains three stacked molecules. As this kind of complex has 2-fold symmetry, in fact three molecules make half a turn and thus the helical pitch is 11.4 × 2 = 22.8 Å (Figure 2c). All these data are consistent with a columnar structure in which the stacked molecular cores are tilted with respect to the column axis and parallel to each other; however, the molecules do rotate around the normal to their mean planes. Thus, two neighboring molecules are mutually rotated by an angle of 360°/6 = 60°. The fact that the 3.8-Å reflection is centered in the meridian suggests that the palladium atoms are located approximately on top of each other, meaning that they are arranged in a row along the column axis.

The X-ray pattern of the copper(II) complex [Cu(S-C$_{12}$)$_2$] has the same appearance, but in this case, good single domains could not be obtained. However, powder experiments performed at room temperature (Figure 4) led us to conclude that the mesophase of Cu(S-C$_{12}$)$_2$ is rectangular columnar with P2$_1$ symmetry and lattice constants a = 83 Å, b = 48 Å (Table 2). These constants are similar to those determined for Pd(S-C$_{12}$)$_2$ and the a/b ratio is still √3. As we were unable to obtain well-oriented patterns, we could not unambiguously establish that there is a helical stacking of the cores of the molecules. However, a diffuse maximum can be discerned at middle angles.
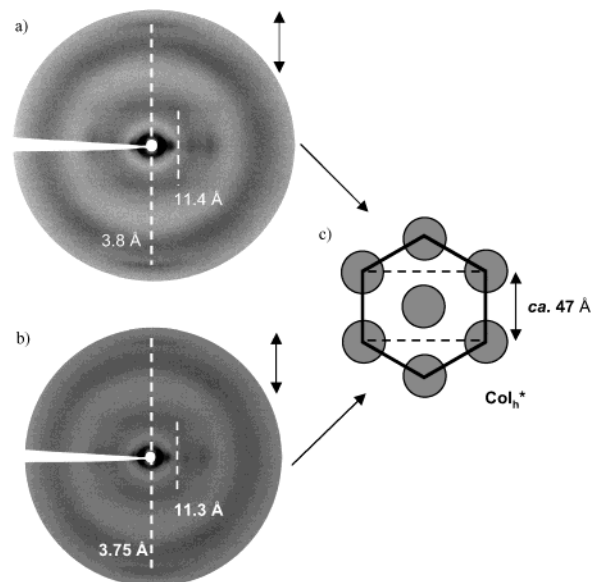
(22) Weber, P.; Guillon, D.; Skoulios, A. *Liq. Cryst.* **1991**, *9*, 369−382.

Figure 5. Oriented X-ray pattern for the racemic mixture Pd(S-C$_{12}$)$_2$ + Pd(R-C$_{12}$)$_2$ (a) and the mixture of diastereomers Pd(RS-C$_{12}$) (b), and hexagonal lattice parameter (c).

This halo is similar to that observed for Pd(S-C$_{12}$)$_2$, which appeared split in oriented patterns and was believed to be related to the helical organization. The distance between neighboring molecules in a stack is still defined and has a value similar to that found for the palladium(II) complexes.

(b) Mesophase Structure of Nonoptically Active Mixtures. It is interesting to compare the structure of the mesophases of the pure enantiomer Pd(S-C$_{12}$)$_2$ to that of its racemic mixture, Pd(S-C$_{12}$)$_2$ + Pd(R-C$_{12}$)$_2$, and that of its diastereomeric mixture, Pd(RS-C$_{12}$)$_2$. In the case of the mixtures (Figure 5), the columnar mesophase is hexagonal with a lattice constant a of ~47 Å (Figure 5c), as deduced from the powder experiments. The meridional region of the oriented patterns (Figure 5a and b) contains the same features as the pure enantiomer, which shows that the stacked molecules generate the same type of helical configuration. The measured pitch period and stacking distance have, within the experimental error, practically the same values as for Pd(S-C$_{12}$)$_2$. The middle-angle scattering is clearly visible in the original patterns. From these results, we propose a model in which segregation between optical isomers takes place and this would account for the subsistence of this modulation in the mixtures.[21b] However, it is difficult to assess whether segregation takes place to give different columns (each column containing only one optical isomer)[23] or within each column (segregated domains of each optical isomer along the column axis).

It is interesting to note that in the mixtures of optical isomers of [Pd(RS-C$_{12}$)$_2$ and Pd(R-C$_{12}$)$_2$ + Pd(S-C$_{12}$)$_2$] despite the fact that the symmetry of the mesophase is hexagonal rather than rectangular, the dimensions of the unit cell are practically equivalent to those of the pure S-enantiomer: A hexagonal lattice with a constant a = 47 Å is equivalent to a C-centered rectangular lattice with a = 81.4 Å, b = 47 Å (a/b = √3) and two molecules per unit cell. However, the difference between a rectangular lattice with a P2$_1$ symmetry and a hexagonal lattice

(23) Trzaska, S. T.; Hsu, H.-F.; Swager, T. M. *J. Am. Chem. Soc.* **1999**, *121*, 4518−4519.

is the fact that in the rectangular lattice the director (axis perpendicular to the molecular planes) has a fixed direction in each column and the mutual orientation of the directors of neighboring columns is defined by the symmetry of the lattice, in particular by the 2-fold screw axis. Due to the similarity of the measured lattice constants, the molecules of the isomer mixtures in the hexagonal columnar mesophase are also probably tilted, but a correlation does not exist between the tilt direction of different columns.[21b] A hexagonal symmetry therefore results, as confirmed by X-ray diffraction (all the observed reflections are consistent with a 2D hexagonal lattice). It can be concluded that the difference between the mesophases of the pure enantiomers and of the mixtures does not concern the organization within each column and is due only to modifications in the correlations between the columns.

Circular Dichroism Studies. Circular dichroism (CD) experiments were carried out in order to study the effect of the proposed helical organization on the optical activity of the materials. Experiments were performed for the corresponding isolated molecule, i.e., in hexane solution, and for thin films of neat samples prepared by sandwiching the material in question between two quartz plates. The sample thickness was not rigorously controlled, and therefore, ellipticity values are not significant for the spectra of neat samples. Experiments on the bulk material were performed at different relevant temperatures (according to the DSC trace) in order to establish whether the observed optical activity was dependent upon the organization within the mesophase. During the experimental procedure, and in order to avoid linear effects due to a possible anisotropy of the orientation in the mesophase, several CD spectra were recorded as the sample was rotated through successive 60° increments around the light beam, while maintaining a constant temperature. Each CD spectrum shown here is the averaged result of all the measured spectra for a given sample.

At first sight, the CD spectrum corresponding to the mesophase appears significantly different from those of the isolated molecule (solution) and the molecule in an isotropic environment (isotropic state) for both of the complexes studied, i.e., Pd(S-C$_{12}$)$_2$ (Figure 6) and Cu(S-C$_{12}$)$_2$ (Figure 7). In each case, the spectra taken from the isotropic melt and from the hexane solution exhibit Cotton effects at the same wavelength and with identical signs. These become negative exciton couplets when the spectra are registered at the temperature of the mesophase. Overlapping of CD signals at this wavelength region may be responsible for a slight shift of the deflection points of the exciton couplets with respect to the maxima of absorption in the UV spectra.

The stereogenic centers of the corresponding molecules are contained in the rigid coordination plane of the complex, and hence, a change in the chiral skeleton of the molecule would not be expected to account for the observed change in the CD spectra. Indeed, this change should arise from the modification of the chiral environment of the chromophores due to some sort of chiral supramolecular organization, i.e., a helical superstructure, as deduced from the X-ray experiments discussed above. Moreover, we can confirm the suggestion that the copper complex should adopt the same type of helical organization in the mesophase as the palladium analogue, as deduced from X-ray experiments, even in the absence of sufficient data from oriented X-ray patterns.
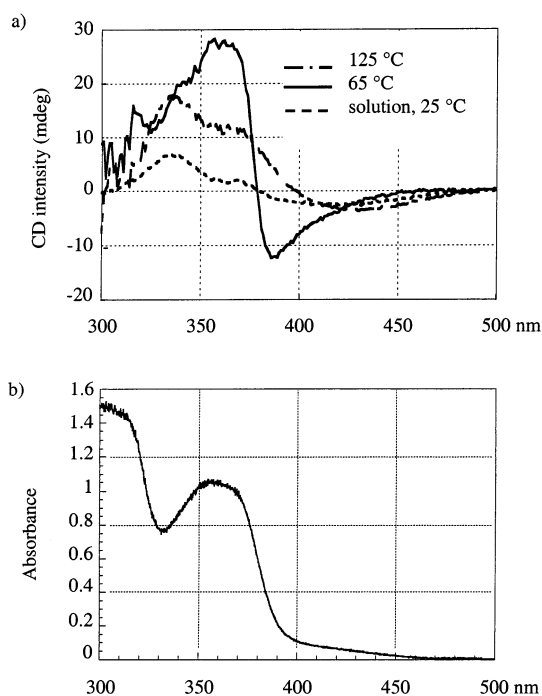

Figure 6. (a) CD spectral comparison of the complex Pd(S-C$_{12}$)$_2$ in the mesophase, in the isotropic liquid and in solution (10-mm cell, 1.07×10^{-5} M in hexanes). (b) Uv spectrum in the region under study of compound Pd(S-C$_{12}$)$_2$, in the mesophase.
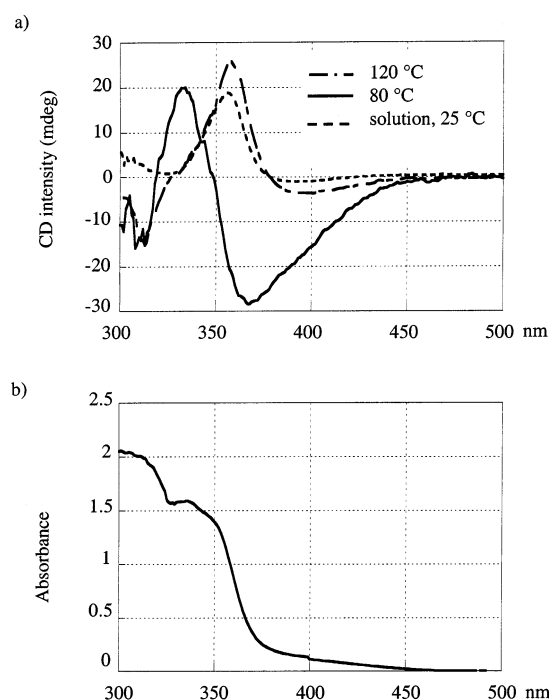

Figure 7. (a) CD spectral comparison of the complex Cu(S-C$_{12}$)$_2$ in the mesophase, in the isotropic liquid, and in solution (10-mm cell, 6×10^{-5} M in hexanes). (b) UV spectrum in the region under study of compound Cu(S-C$_{12}$)$_2$ in the mesophase.

As expected, the two enantiomers [Pd(S-C$_{12}$)$_2$ and Pd(R-C$_{12}$)$_2$] give rise to CD spectra of opposite sign (Figure 8). Moreover, the S-configuration of the stereogenic centers of complexes Pd-(S-C$_{12}$)$_2$ and Cu(S-C$_{12}$)$_2$ seems to bias their helixes toward a left-handed sense (M), as evidenced by the negative exciton CD couplets centered at 380 and 350 nm, respectively.[24] In contrast,
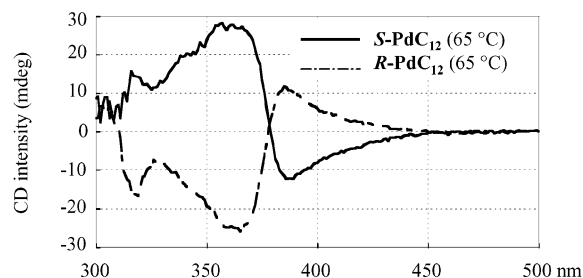
Figure 8. CD spectra of the pure enantiomers Pd(*S*-C$_{12}$)$_2$ and Pd(*R*-C$_{12}$)$_2$ showing opposite signs.

the CD spectrum taken in the mesophase of Pd(*R*-C$_{12}$)$_2$ shows a positive exciton CD couplet that corresponds to a right-handed helix (*P*).

Conclusion

The use of metal coordination has allowed the preparation of polycatenar oxazoline complexes that show columnar mesophases with a helical organization within the column. The diffraction patterns of enantiomerically pure Pd(*S*-C$_{12}$)$_2$ [and hence of Pd(*R*-C$_{12}$)$_2$], as well as of their racemic mixture Pd-(*S*-C$_{12}$)$_2$ + Pd(*R*-C$_{12}$)$_2$ and the mixture of diastereomers Pd-(*RS*-C$_{12}$)$_2$, are consistent with a structural model in which an assembly of helical columns adopts a 2D packing. One full helical turn occurs every six molecules: a rotation of 60° by each molecule, spaced 3.8 Å apart, produces a pitch of 22.8 Å. These results, in conjunction with CD experiments, reveal that chirality transfer takes place from the stereogenic centers in the rigid core to the supramolecular organization. The same conclusion can be extended to the oxazoline−copper(II) com-

plex, despite the fact that an oriented X-ray diffraction pattern could not be obtained.

Rotation of one molecule with respect to the adjacent one within the column is the method by which these molecules fill empty space, thus improving molecular packing within the mesophase. This process allows a better arrangement of the chains around the central core of the column and thus prevents the steric hindrance that could otherwise occur between the chains of neighboring molecules due to the difference in the preferred core−core (3.8 Å) and side-chain (4.4 Å) distances. This occurs in the chiral derivatives as well as in the nonoptically active mixtures. In the former, the rotation gives rise to a helix whose sense (right or left) is determined by the configuration of the corresponding stereogenic centers. In the nonoptically active mixtures, the helical organization deduced from X-ray diffraction is proposed to form through spatial segregation of the optical isomers, which organize themselves into both types of helix.

The work described here represents a significant example of a successful combination of coordination chemistry and liquid crystal self-organization processes to achieve and control supramolecular helical architectures.

Supporting Information Available: Additional information as noted in text. This material is available free of charge via the Internet at http://pubs.acs.org.

JA0294313

(24) Nakanishi, K.; Berova, N.; Woody, R. W. *Circular Dichroism: Principles and Applications*; VCH Publishers: New York, 1994.