

Helical supramolecular organizations from metal-organic liquid crystals

José Luis Serrano*, Teresa Sierra

Dpto. Química Orgánica, Facultad de Ciencias-I.C.M.A., Universidad de Zaragoza-C.S.I.C., Pedro Cerbuna 12, 50009 Zaragoza, Spain

Received 12 November 2002; accepted 14 March 2003

Contents

Abstract	73
1. Introduction	74
2. Mesogenic molecular structures	74
2.1 'Disk-like' square-planar complexes	75
2.2 'Propeller-like' octahedral complexes	76
2.3 Polycatenar elongated complexes	77
2.3.1 Polycatenar square-planar complexes	77
2.3.2 Polycatenar helicates	78
3. Helical structures	79
3.1 Azimuthal rotation of disk-like molecules	79
3.2 Interdigitated stacking of octahedral complexes	80
3.3 Staggered stacking of planar complexes	81
4. Concluding remarks	83
Acknowledgements	84
References	84

Abstract

The present paper is aimed at providing a survey of investigations undertaken regarding the preparation and characterization of helical supramolecular architectures using a strategy based on two concepts: coordination chemistry and mesomorphic behavior. Metal-coordination procedures have been used to design and synthesize molecular units capable of organizing into helical superstructures. In order to ensure this capability, the molecular building blocks have been complemented with a pro-mesogenic character, most commonly columnar, so that this type of mesophase is used as a template to build up helical supramolecular architectures with long-range orientational order and long-range positional order. For example, metal-containing liquid crystals have been described that organize into helical columnar mesophases whose structure has been fully investigated. To date, molecular units that display this organizational behavior have been found to be very different in shape, and hence the formation of helical structures has a different origin in each case. In this paper, three molecular structures are discussed (i.e. 'disk-like' molecules, 'propeller-like' molecules and polycatenar elongated molecules) that have been shown to give rise to helical organizations. Models have been proposed for the three systems described and in the present overview these have been classified as azimuthal rotation of planar disk-like complexes, interdigitated stacking of octahedral complexes and staggered stacking of polycatenar elongated planar complexes, respectively. Throughout this paper, emphasis is placed on studies carried out in the mesophase that have allowed authors to propose the corresponding models.

© 2003 Elsevier B.V. All rights reserved.

Keywords: Supramolecular organizations; Helical columnar mesophases; Circular dichroism; X-ray diffraction; Optical activity

* Corresponding author. Tel./fax: +34-976-761209.

E-mail address: joseluis@unizar.es (J.L. Serrano).

1. Introduction

Nowadays, helicity, an essential structural motif in biological systems, is the target of many researchers devoted to supramolecular chemistry and materials science. From an academic point of view, investigation into this subject is aimed at gaining an understanding of the factors involved in the formation of complex supramolecular architectures from simple molecular units designed to undergo processes such as self-assembly and self-organization [1]. Moreover, if these molecules are chiral, then chirality will often be transferred to the bulk material—thus providing chiral superstructures. In addition, a chiral helical organization gives the material special optical properties derived from the interaction of this organization with light (e.g. circularly polarized light). Furthermore, nonlinear optical (NLO) properties are also possible for materials with a helical orientation of chromophores. Indeed, a chiral helical supramolecular structure allows a non-centrosymmetric orientation of NLO-phores, and hence their coherent contribution to the 2nd order nonlinear response of the material [2].

The composition of molecular materials that present helical organizations range from synthetic macromolecules in which the helical stereostructure appears due to conformational preferences of the polymer chain [3], to supramolecular organizations driven by interactions other than covalent bonding. Thus, crystallization processes [4], metal-coordination [5], hydrogen bonding [6], mesomorphic behavior, or a combination of more than one of these characteristics, can act as driving-forces that give rise to molecular association with a helical packing.

Liquid crystals have demonstrated great potential in the design of functional supramolecular organizations on demand. Moreover, the molecular order and orientation achieved in the mesophase can often be maintained, by freezing, in the amorphous solid state. As far as helical assemblies are concerned, they have been found to be a versatile tool to achieve materials with controlled supramolecular helical organizations that promote the appearance of interesting properties for practical applications. The best known helical organization in liquid crystals corresponds to the cholesteric mesophase, whose special optical behavior (i.e. selective reflection) [7] is due to a helical orientation of the directors of the molecular components. The helical structure of the chiral SmC* phase, potentially ferroelectric, is also of practical importance [8]. Helical mesomorphic systems with higher complexity are represented by blue phases [9], in which more than one screw axis is present, and TGB phases, which appear as a competition between a cholesteric phase and the tendency to smectic arrangement [10]. Another approach to obtaining helical order involves taking advantage of the molecular stacking of

columnar liquid crystalline organizations to promote the formation of a helix within the column [11]. This strategy is the target of noteworthy studies by several authors, which range in scope from a basic interest in the knowledge of the helical assembly and how to manipulate it [12], to the achievement of promising properties for practical applications such as NLO behavior (i.e. SHG) [13] or electrooptical switching [14].

Regardless of the strategy employed, the resulting helical structure must somehow be encoded within the molecule itself and can affect molecular characteristics such as shape, topology and/or stereochemistry [15]. As a consequence, and in order to allow control of the helical organization, the design of the molecular building unit is of crucial importance. This situation has led chemists to think creatively about different synthetic strategies, as discussed above. Coordination chemistry has been employed as a useful tool to prepare metal-induced discrete aggregates, which organize themselves into mesophases. In this respect, research on metallo-mesogens has provided a number of molecular mesogenic structures capable of organizing into different mesomorphic organizations [16]. Not many metallomesogen structures have been conceived with the specific aim of self-assembly to form helical columnar superstructures. In this paper, we will explore the examples that have been reported on the construction of supramolecular organizations with a helical shape from polycatenar metallomesogens, with special emphasis placed on the strategies developed during the study of the mesophase structure that led the authors to propose a helical model. We would like to highlight the fact that, even though few structures have been reported to generate this type of mesophase, all of the compounds are very different in shape. This preliminary consideration accounts for the fact that a delicate balance between different parts of the molecule, i.e. rigid (aromatic) core, flexible paraffinic tails and the possible location of molecular chirality, is essential for discrete molecules to self-associate into the required liquid crystalline organization. On the basis of this consideration, we have organized this survey by taking into account the different molecular structures that can stack in the mesophase and, furthermore, can induce a helical arrangement biased towards a given sense according to the molecular chirality.

2. Mesogenic molecular structures

Metal-coordination of organic ligands offers the possibility of obtaining a wide variety of structures that can organize into columnar mesophases. Among these structures, which have been extensively reviewed [17], some have been demonstrated to organize into helical structures within the mesophase. The origin of

the helix can be very different, and more or less obvious, depending on the type of molecule. It may originate from the incorporation of stereogenic centers into the molecule as happens in discotic β -diketonates (Section 2.1) or from the shape of the molecule itself as demonstrated by octahedral β -diketones (Section 2.2). In this last case, both types of helix (right- and left-handed) are equally possible when non-optically active molecules are present in the mesomorphic organization. Then, the helical superstructure does not display optical activity. The origins of helicity in the mesophase of polycatenar oxazoline complexes (Section 2.3.1) is less clear, as far as the presence of stereogenic centers and/or the elongated shape of the molecule are concerned.

In all cases herein presented, the presence of stereogenic centers with the same chiral sense in the constituent molecules promotes chirality transfer from the molecule to the supramolecular architecture in the mesophase, and a formal optical activity due to the helical organization is observed (Section 3).

The present section presents the individual structures of the complexes that promote the appearance of columnar liquid crystalline mesophases with the potential for a helical structure within the column.

2.1. 'Disk-like' square-planar complexes

Disk-like metallomesogens can be readily prepared from bis(1,3-diphenyl-1,3-propanedionates) appropriately substituted with peripheral alkoxy tails and complexed to divalent transition metals. More specifically, metal β -diketonates of this type, surrounded by 10 peripheral tails, have shown a strong tendency to promote columnar mesomorphism [18]. X-ray diffraction studies carried out in our laboratory on copper(II) bis[1-(2,3-didecyloxyphenyl)-3-(2,3,4-tridecyloxyphenyl)-1,3-propanedionate] showed the existence of a hexagonal columnar mesophase that is stable from room temperature up to about 140 °C [19]. On the basis of these results, the next natural step was the introduction of chirality by means of stereogenic centers in the peripheral tails. Flexible chiral tails were prepared from L-(–)-lactic acid as the chiral starting material (Fig. 1) [20].

This work was undertaken in the context of our interest in ferroelectric liquid crystals. One particular aspect of our investigation into this area was concerned with ferroelectric metallomesogens based on chiral dimeric complexes that organized into calamitic mesophases [21]. The idea was to extend previous and novel studies on ferroelectric columnar liquid crystals based on organic chiral disk-like mesogens [22] to the field of metallomesogens. In these studies, requirements for the appearance of a macroscopic polarization were established. A tilted mesophase, such as the rectangular columnar phase, can undergo ferroelectric switching

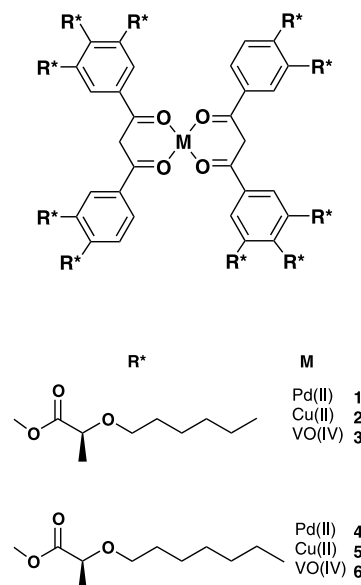


Fig. 1. General structure of the planar disk-like β -diketonate complexes described in Ref. [20].

when it is formed by chiral molecules. Chirality allows polar order perpendicular to the column axis arising from a tilt-induced molecular dipole moment within the columnar phase. Even though our initial interest was to demonstrate the possibility of ferroelectric behavior in columnar metallomesogens, we are always concerned with the study of the mesophase structure. In this case, the structural study was special since little was known about the nature of the chiral rectangular mesophase. The consequences of chirality on calamitic systems are well known. Formal chirality, i.e. helical organization, appears in tilted mesophases such as the SmC phase as well as in the nematic mesophase formed by chiral molecules. For this reason, along with the study of the ferroelectric behavior of the β -diketonates, whose electrooptic switching was demonstrated, much of our effort was devoted to the study of the structure of the switchable mesophase.

All six complexes synthesized show mesomorphic behavior at room temperature and the mesophase(s) are stable over a wide temperature range. The phase sequence and transition temperatures of these materials are given in Table 1. Melting or crystallization peaks were not observed for any of the compounds even down to –20 °C. This means that the materials maintain the

Table 1

Compound	Mesomorphic properties
1	$K < 20$ °C Col _r * 149 °C I
2	$K < 20$ °C Col _r * 130 °C I
3	$K < 20$ °C Col _r * 125 °C I
4	$K < 20$ °C Col _r * 147 °C I
5	$K < 20$ °C Col _r * 132 °C I
6	$K < 20$ °C Col _r * 122 °C I

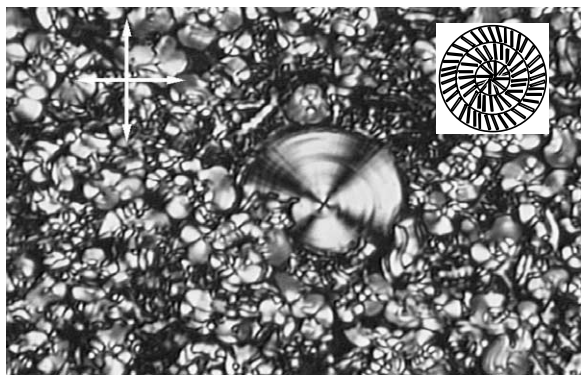


Fig. 2. Photomicrograph of the texture of the columnar mesophase of complex **6** at room temperature and cooled from the isotropic liquid. The texture shows a big Maltese cross inclined with respect to the cross polarizers (left-inset) indicating the presence of molecular tilt within the column, as represented in the scheme in the right-inset.

supramolecular organization of the mesophase well below room temperature. The mesomorphic state was studied by the techniques commonly used for liquid crystals, which include polarizing optical microscopy, differential scanning calorimetry and X-ray diffraction.

The most significant textures were observed in samples annealed at 100 °C for several hours. A flower-like texture with Maltese crosses often appears, which is characteristic of columnar mesophases. Moreover, the extinction brushes are inclined with respect to the direction of the crossed polarizers, indicating the presence of molecular tilt within the column (Fig. 2).

X-ray diffraction patterns (Fig. 3) confirm that all the compounds exhibit a columnar mesophase in which the columns are arranged in a two-dimensional rectangular lattice. The space group was found to be $P2_1$, which is characterized by a herringbone arrangement of the elliptical sections of the columns [23] (Fig. 3b).

2.2. 'Propeller-like' octahedral complexes

Non-mesogenic β -diketone ligands, similar to those described in the previous section, can also be used as building blocks for mesogenic complexes that show non-conventional columnar liquid crystal phases. Swager et al. found that trivalent transition metals, such as iron(III), manganese(III), cobalt(III) or chromium(III), coordinate to three β -diketone ligands (Fig. 4). These complexes were confirmed to have octahedral structures that can be accommodated within columns and display mesomorphic columnar behavior over wide temperature ranges [24]. A propeller-like molecular configuration, with all three ligands tilted in the same direction (Fig. 4b), favors interdigitation of the pendant aromatic rings, a situation that stabilizes the columnar ordering (Fig. 5). Tilting gives rise to two possible enantiomers (Δ and Λ) and it seems reasonable to expect their independent

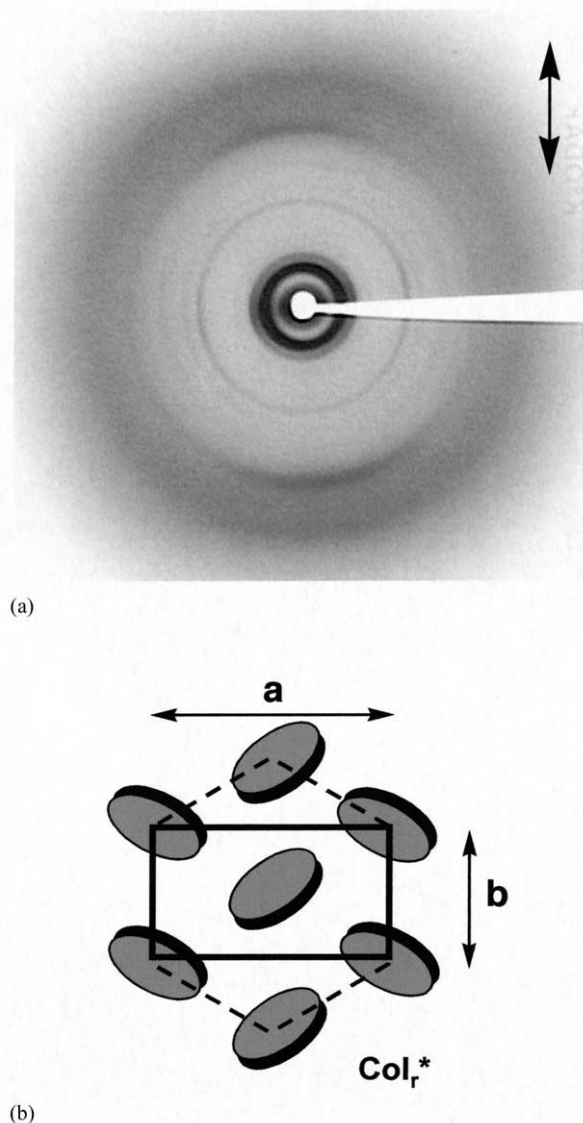


Fig. 3. (a) Oriented X-ray diffraction pattern of vanadium(IV) complex **6** at room temperature. (b) Schematic representation of the herringbone structure of the rectangular columnar mesophase with $p2gg$ symmetry. The 2D rectangular arrangement forms a pseudo-hexagonal lattice.

stacking into different columns with net chirality so that efficient packing occurs.

The mesomorphic behavior of the complexes synthesized is summarized in Table 2. The type of mesophase, as well as the lattice parameters, were established by powder X-ray diffraction. All of the compounds show hexagonal columnar mesophases below the clearing point. Achiral cobalt(III) (**9**) and chromium(III) (**10**) complexes show an additional rectangular columnar mesophase at low temperature, whereas achiral iron(III) (**7**) and manganese(III) (**8**) complexes show an additional hexagonal columnar mesophase. This different behavior seems to be related with the different fluxional nature of both pairs of complexes together to supramo-

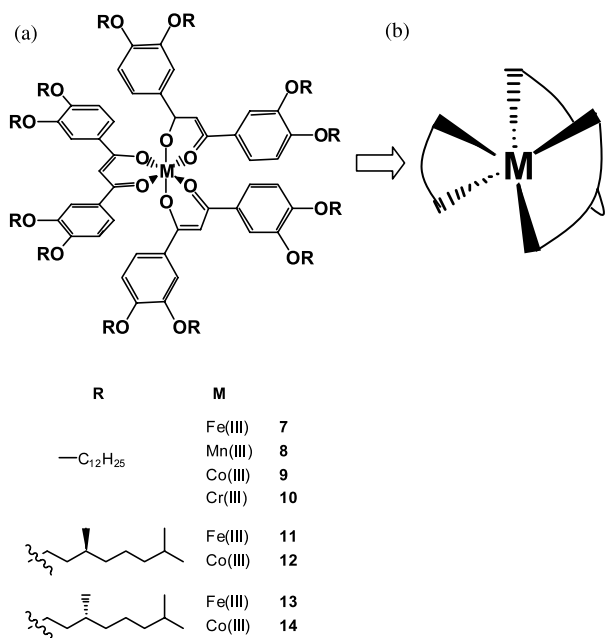


Fig. 4. (a) General structure of the octahedral β -diketonate complexes described in Ref. [24]. (b) Schematic representation of the shape of the octahedral complexes showing tilting of the ligands towards the same sense. This tilting provides the molecule a propeller-like shape.

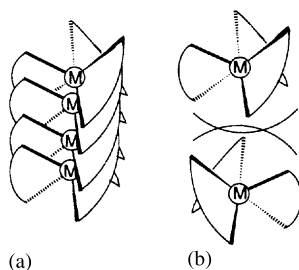


Fig. 5. (a) Interdigitated stacking of complexes with the same absolute configuration (all Δ) showing efficient packing within the column and a helical columnar structure. (b) Schematic representation of the mismatched structure occurring by stacking of complexes with different absolute configuration (Δ and Λ) (adapted from Ref. [24]).

Table 2

Compound	Mesomorphic properties
7	Col _h 91.1 °C Col _h 110.7 °C I
8	Col _h 62.1 °C Col _h 106.5 °C I
9	Col _r 61.4 °C Col _h 104.0 °C I
10	Col _r 64.6 °C Col _h 108.2 °C I
11	Col _h 83.8 °C I
12	Col _h 88.9 °C I
13	Col _h 81.0 °C I
14	Col _h 81.4 °C I

lecular symmetry of the columnar mesophase. Results indicate that hexagonal columnar mesomorphic behavior appears in fluxional iron(III) (7) and manganese(III) (8) complexes, whereas a lower symmetry rectan-

gular columnar mesophase occurs for cobalt(III) (9) and chromium(III) (10) complexes, whose higher rigidity must avoid interchange between the two possible enantiomers (Δ and Λ).

2.3. Polycatenar elongated complexes

2.3.1. Polycatenar square-planar complexes

A different concept for the formation of chiral molecular structures that self-assemble into helical supramolecular organizations has recently been proposed by our group. Studies were planned to encompass mesogenic structures based on elongated polycatenar molecules with low aspect ratios, which can give rise to columnar mesomorphic mesophases with the same symmetry as those displayed by disk-like mesogens [25].

2-(2-Hydroxyphenyl)oxazoline-derived compounds were suitable candidates for the design of organic ligands that are capable of incorporating chirality in a rigid environment in the final complex. The oxazoline ring is synthesized from the commercially available L- β -aminoalcohol by reaction with the corresponding 2,4-dihydroxybenzonitrile. Indeed, the resulting ligand has a stereogenic center in the ring and in the position α to one of the coordinating nitrogen atoms. As a consequence, complexation of these ligands to transition metals such as palladium(II) or copper(II) yields planar dimeric complexes with two stereogenic centers in the rigid coordination environment of the metal [26]. We prepared oxazoline ligands with an extended aromatic core and six alkoxy terminal chains in order to guarantee the appearance of mesomorphic behavior. The ligands were coordinated to palladium(II) and copper(II) (Fig. 6) [27]. Only the trans isomer of the dimeric complex is obtained [28]. Hence, the molecules should have C_2 symmetry with the binary axis perpendicular to the coordination plane, a situation that causes both methyl groups in the stereogenic centers to lie on the same side of the molecular plane.

Even though the ligands are not mesogenic in their own right, the copper(II) (16 and 18) and palladium(II) (15, 17, 19 and 20) complexes do show mesomorphic behavior at room temperature and over wide temperature ranges as deduced from differential scanning calorimetry and X-ray diffraction. Polarizing optical microscopy did not give useful information about the type of mesophase shown by these complexes. When a sandwich preparation between glass slides was observed with polarized light, the pure enantiomers appear black (homeotropic-like texture) on cooling from the clearing temperature (measured by DSC). When the samples were observed without a cover glass a gray texture appeared in both cases and this was not representative of any particular liquid crystalline phase. The thermal data for these materials are gathered in Table 3. The final identification of the mesophase was carried out by

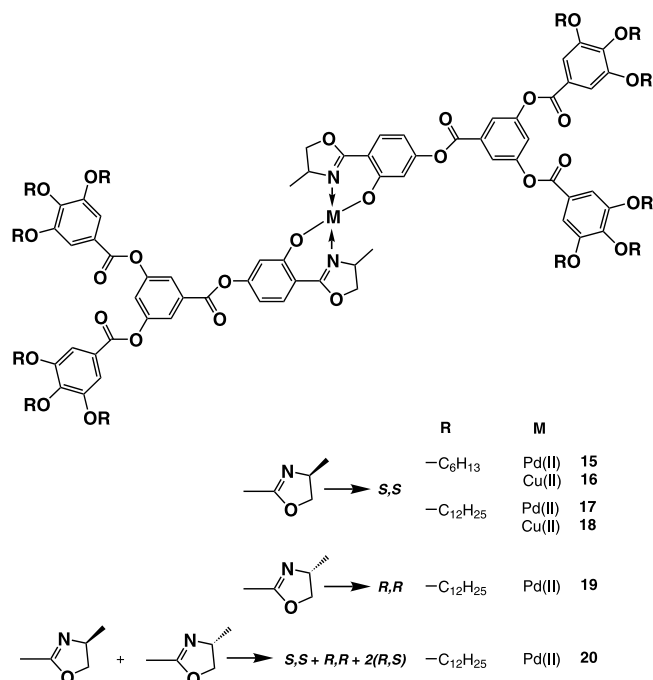


Fig. 6. General structure of the planar oxazoline complexes described in Ref. [27].

powder X-ray diffraction experiments. Rectangular columnar mesophases were confirmed for the longest-chain homologs (17, 18 and 19), whereas hexagonal columnar mesophases were identified for the shortest ones (15 and 16) and for the mixture of diastereomers (20) obtained from coordination of the racemic ligand to palladium(II). The rectangular arrangement corresponded to a $P2_1$ symmetry, with a herringbone-like organization when viewed along the column axes (see Fig. 3b).

2.3.2. Polycatenar helicates

We consider it appropriate to include liquid crystalline metallo-helicates within this section. The term helicate was first introduced by Lehn et al. [29] and refers to double-stranded supramolecular aggregates with a helical structure induced by metal-coordination. Since then, these structures have been thoroughly investigated [5c,5d]; as well as their use as templates

for topologically interesting molecules such as molecular knots described by Sauvage and coworkers [30].

Liquid crystalline metallo-helicates have been reported by Ziessel and coworkers [31]. Polycatenar elongated ligands derived from imino-pyridine or imino-bipyridine can coordinate to one or more cations such as copper(I), giving rise to tetrahedral ionic complexes. Some of these structures (Fig. 7) have shown a tendency to display columnar mesomorphism that has been characterized by DSC, optical microscopy and X-ray diffraction. Hexagonal columnar mesomorphism was found for species containing only one metal cation (Fig. 7a) and a rectangular columnar mesophase was identified for the bipyridine-derived complex with two metal cations (Fig. 7b). Despite the fact that these complexes have not yet been described as inducers of helical organizations within the mesophase, it is reasonable to believe that, in a similar way to the complexes described in Section 2.3.1, these complexes might organize to give a helix within the column as a means

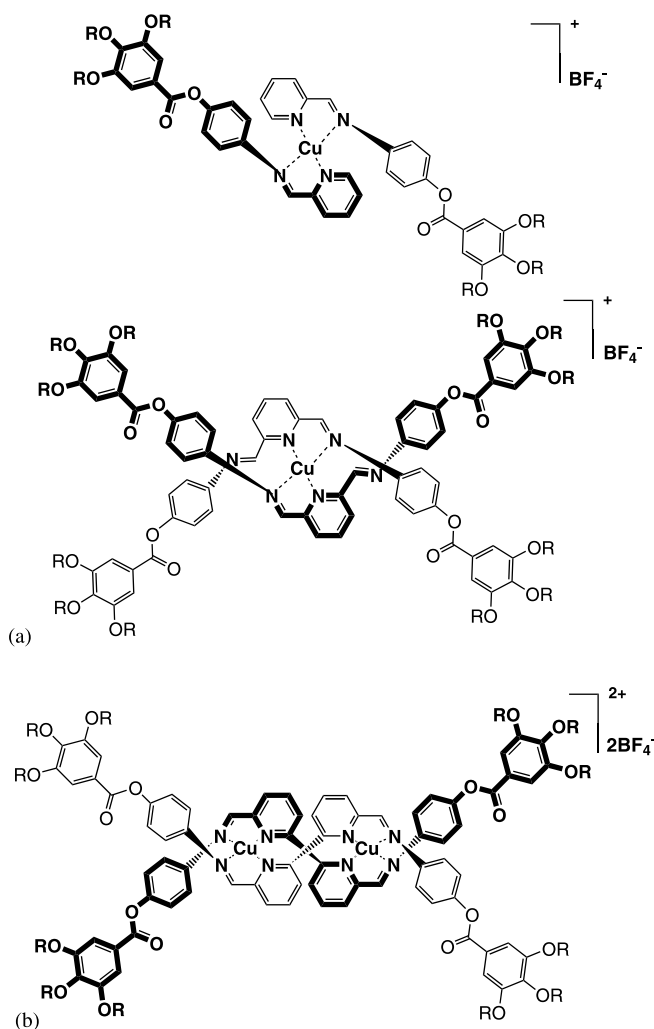


Fig. 7. Structure of representative examples of liquid crystalline helicates described in Ref. [32].

Table 3

Compound	Mesomorphic properties				
15	g	18.8 °C	Col _h	141.6 °C	I
16	g	21.4 °C	Col _h	140.9 °C	I
17	C	1.7 °C	Col _r	109.5 °C	I
18	C	−6.5 °C	Col _r	97.2 °C	I
19	C	2.2 °C	Col _r	110.2 °C	I
20	C	3.9 °C	Col _h	110.6 °C	I
17+19 [1:1]	C	2.7 °C	Col _h	119.3 °C	I

to efficiently pack in the mesophase. Moreover, it is also feasible that chiral organizations in the mesophase arising from the chirality inherent in the helical core may be obtained if one of the enantiomeric helicates could be isolated.

3. Helical structures

The complexes outlined above have been found to give rise to helical superstructures in the mesophase. The mechanisms by which these molecules can organize into helices must be very different if we take into account the structural characteristics of each individual molecule. For this reason, the current section is dedicated to describing the different helical structures in columnar mesophases according to three different types of molecule for which a reasonable model has been proposed. Each of the following sections consists of a reasoned presentation of the studies, carried out with different techniques, which led the respective authors to establish a helical model for the columnar mesophase.

In all of the helical supramolecular organizations presented here, the introduction of stereogenic centers influenced the helix towards a given sense, and hence to the appearance of optical activity. This optical activity has been measured and has been shown to be the result of the helical structure rather than just the response of the molecular chirality.

3.1. Azimuthal rotation of disk-like molecules

The first indication of a possible helical structure within the columns formed by planar β -diketonate complexes **1–6** was observed in the small-angle X-ray patterns at a diffraction angle of about 0.5° . This peak, which cannot be assigned to the rectangular lattice, is clearly seen in the power pattern from non-oriented samples and it could correspond to an intracolumnar periodic modulation resulting from a helical structure. In an attempt to confirm this possibility, we decided to use more specialized techniques such as circular dichroism (CD). CD spectra were recorded for three types of sample: (i) a dilute solution in THF; (ii) the neat compound freshly deposited on a quartz substrate as a thin film; and (iii) the annealed thin film (100°C for 24 h). All spectra were recorded at room temperature.

The absence of a signal in the solution sample and the appearance of strong signals in both preparations of the neat compound (Fig. 8a and b, corresponding to both oxovanadium(IV) complexes, **3** and **6**, respectively) provided a clear indication that the optical activity of the bulk material does not come from the presence of stereogenic centers in each peripheral tail, but from a chiral superstructure in the mesophase. The CD spectra of freshly prepared thin films show positive exciton

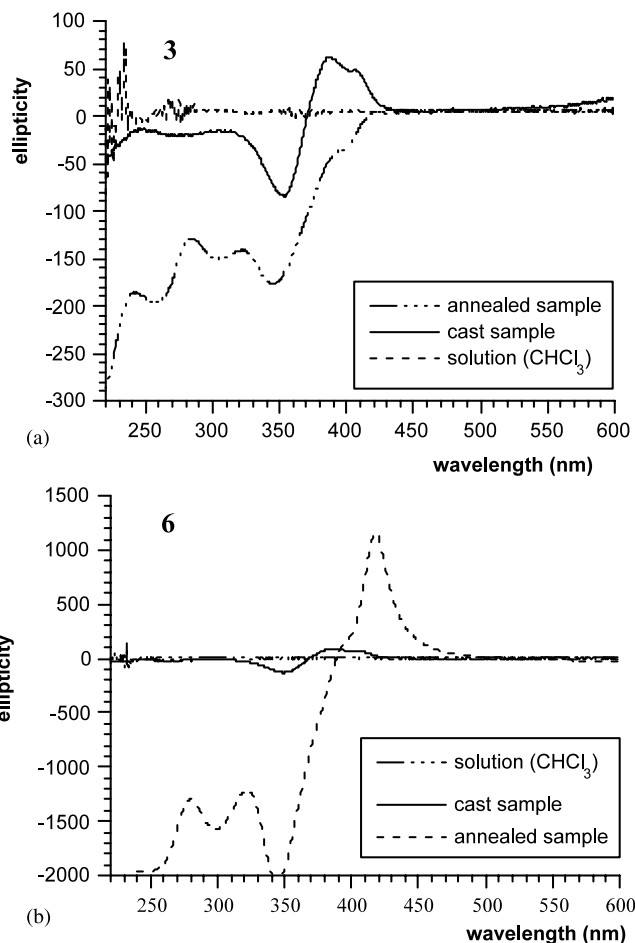


Fig. 8. CD spectra recorded for complexes **3** (a) and **6** (b) under three different conditions: solution in THF (0.1 g l^{-1}) and thin film deposited on a quartz substrate (cast sample and annealed sample, 100°C for 20 h).

splitting centered at the wavelength (ca. 365 nm) of the π – π^* transition associated with the β -diketone group. The exciton-coupling phenomenon is a consequence of through-space interaction between two chromophores that have an electric dipole moment allowed transition [32]. These dipoles cannot be parallel since the exciton effect is the result of a vectorial product. In the particular case described here, and given that the molecules are planar and stacked in columns, the exciton splitting can only be due to the intermolecular interaction of the electric dipole moment of the π – π^* transition being tilted with respect to the columnar axis and describing a helix along the column. We can therefore propose a helical arrangement within the column consisting of tilted molecules whose tilt direction rotates along the column axis (Fig. 9). Support for this model was provided by the results obtained from broadband dielectric spectroscopy performed at variable temperature. The mode appearing at low frequency—and only below the clearing point—corresponded to a collective mode and was assigned to azimuthal fluctua-

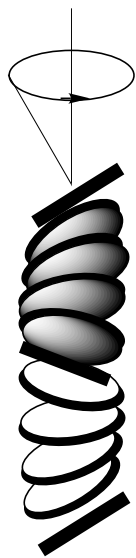


Fig. 9. Proposed helical arrangement for the disk-like β -diketonate complexes. A Minus helix is proposed that corresponds to the sign of the exciton splitting signal observed in circular dichroism.

tions of the molecular director as represented in Fig. 9 [33].

3.2. Interdigitated stacking of octahedral complexes

In this case, the structure of the molecule itself implies the possibility of the formation of a helix once molecules stack in the column. In fact, tilting of the ligands (Fig. 4) gives rise to the formation of two possible enantiomeric conformations with different chiral senses (Δ and Λ). The appearance of columnar mesophases led to the conclusion that efficient packing will only occur when nearest neighbors have the same absolute configuration about the transition metal (Fig. 5a). In this situation, one would expect a helical columnar structure. Moreover, a mismatch in the configuration of two neighbors would limit molecular stacking (Fig. 5b). Indeed, resolution of both enantiomers into microdomains

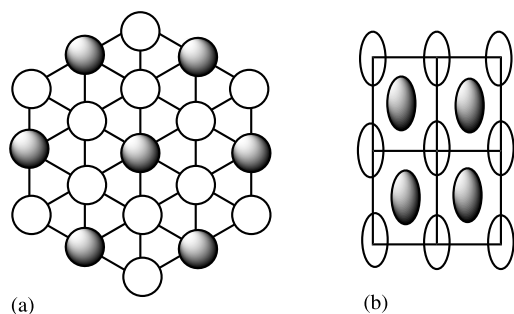


Fig. 10. Schematic representation of the model proposed for the 2D organization within the mesophases of octahedral complexes. Gray and white circles represent opposite absolute configuration of the complexes stacked within the column: (a) hexagonal lattice in which one chiral sense dominates; (b) rectangular lattice with equal amounts of each chirality (adapted from Ref. [24]).

with net chirality was proposed to take place within the mesophase (Fig. 10). Authors propose that, in order for this resolution to be effective, the supramolecular symmetry is essential and a hexagonal symmetry would facilitate it by means of a cooperative chiral state. This cooperative effect is strongly favored by fluxionality about the metallic center.

All the complexes show a high temperature hexagonal columnar mesophase. On cooling, an additional hexagonal columnar mesophase in Fe(III) (7) and Mn(III) (8) complexes, and a rectangular columnar mesophase in Co(III) (9) and Cr(III) (10) complexes are seen. This behavior at low temperature must be related to a stronger influence of chirality. It was proposed that enantiomer resolution into neighboring columns must exist in the rectangular columnar mesophase (Fig. 10b) of the most conformationally locked complexes, i.e. Co(III) (9) and Cr(III) (10), since this lattice can better accommodate two different neighboring columns (i.e. with different chirality). In contrast, chirality biasing towards one of the enantiomers can be expected in the hexagonal columnar mesophase (Fig. 10a) of the more fluxional complexes, i.e. Fe(III) (7) and Mn(III) (8), given that the hexagonal lattice promotes uniformity among all columns. In this situation, resolution of both enantiomers into microdomains can take place. In order to confirm this idea, CD experiments (Fig. 11) were carried out on complexes consisting of a mixture of diastereomers arising from complexation of ligands bearing chiral tails (11, 12, 13 and 14). Both complexes prepared showed almost the same mesomorphic behavior, which consisted of a hexagonal columnar phase. The first significant effect observed was that the

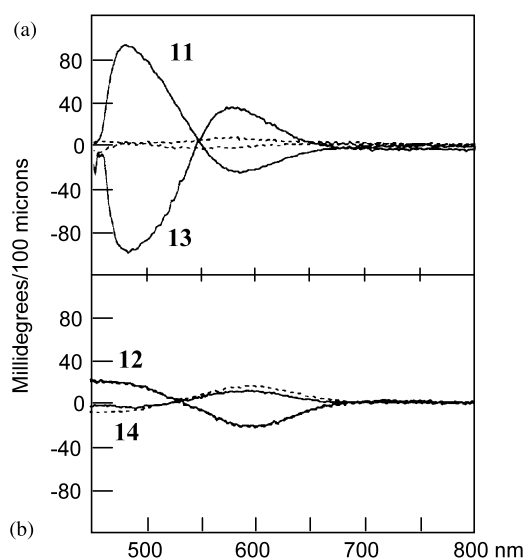


Fig. 11. CD spectra of chiral: (a) Fe(III) (11 and 13); and (b) Co(III) (12 and 14) in the hexagonal columnar mesophase at room temperature (solid line) and in the corresponding isotropic state at 105 °C (dashed line) (adapted from Ref. [24]).

rectangular columnar mesophase of locked Co(III) complexes disappears when chiral tails are incorporated. This situation may be due to the preferential formation of one of the diastereomers (Δ or Λ). However, the structures of the hexagonal mesophases were found to be different between Fe(III) (**11** and **13**) and Co(III) (**12** and **14**) according to the possible existence of formal optical activity. Despite the fact that optical activity was not observed in either the solution sample or the isotropic melt of the fluxional Fe(III) complexes **11** and **13**, a strong CD signal was observed for the neat sample in its mesomorphic state (Fig. 11a). Given that the stereogenic center is situated far away from the coordination site responsible for the chiral configuration of the complex, the explanation for the strong optical activity in the mesophase must be associated with a helical structure biased to one particular sense and due to the predominance of one of the configurational isomers (Δ or Λ). This prevalence must not occur in the hexagonally ordered mesophase of the locked Co(III) complexes (**12** and **15**) since no significant optical activity was measured under any conditions (Fig. 11b). In conclusion, when the possibility of interconversion between enantiomers exists due to the fluxionality about the metallic center [e.g. Fe(III) (**7**, **11** and **13**) and Mn(III) (**8**) complexes], the hexagonal columnar mesophase can display a cooperative effect in terms of inducing a given chiral state [12c].

Recently, the same authors have described the potential of chiral columnar phases to build up polymer networks with helical channels. In an attempt to develop this idea, reactive peripheral tails have been incorporated into the ligands so that polymer networks can be prepared by polymerization of fluxional Fe(III) complexes. Preliminary results concerning polymeric networks based on this idea have shown the presence of a hexagonal columnar mesophase [34].

3.3. Staggered stacking of planar complexes

In this particular case, X-ray diffraction studies (at room temperature and at 80 °C) proved conclusive in the elucidation of the supramolecular organization of the mesophase. In addition to maxima related to the stacking of molecules and a rectangular 2D arrangement of the columns, a maximum at middle angles was observed for both complexes suggesting the presence of some additional periodicity. Fortunately, aligned samples could be prepared for the palladium(II) complexes (**17** and **19**) and these yielded oriented X-ray patterns with split reflection maxima, which provided further clarification of the structure (Fig. 12).

At middle angle regions of the pattern shown in Fig. 12, 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 electron density, which

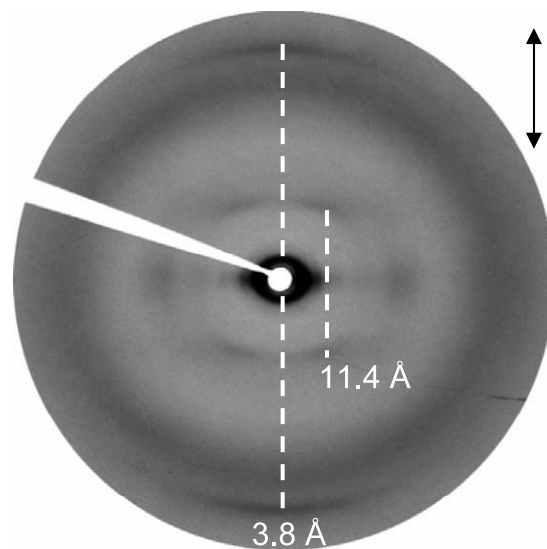


Fig. 12. Oriented X-ray pattern of oxazoline complex **17**, taken at room temperature.

could be related to the existence of a superlattice periodicity in the direction of the stacks of molecules. The periodicity of this modulation measured along the column axis was 11.4 Å. In accordance with previously reported studies [35], we assumed that a helical stacking of the molecules in the column could account for this modulation. The absence of scattering at the meridian itself was evidence that the helical structure developed parallel to the column axes, which were oriented perpendicular to the X-ray beam.

In addition, a diffuse, almost isotropic ring corresponding to a mean distance of 4.4 Å was observed in the pattern along with, in the outer-most part, a relatively sharp arc centered in the meridian at 3.8 Å. The diffuse ring is characteristic of the liquid-like order between the aliphatic chains, whereas the strong arc corresponds to the intracolumnar stacking distance (intermolecular Pd–Pd distance). This last maximum at 3.8 Å represents conclusive proof of a helical arrangement given the existence of a ratio $11.4/3.8 = 3$, which suggests a periodical distance corresponding to three stacked molecules. The pitch of the helix should then be $11.4 \times 2 = 22.8$ Å, since the complexes have twofold symmetry. On the basis of these measurements, we proposed a model (Fig. 13) in which the columnar structure of the mesophase consists of stacked molecular cores parallel to each other and tilted with respect to the column axis; however, the molecules rotate around the normal to their mean planes. Thus, two neighboring molecules are mutually rotated at an angle of $360^\circ/6 = 60^\circ$ yielding a staggered stacking of the elongated molecules along the column axis (Fig. 14). 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, so they are arranged in a

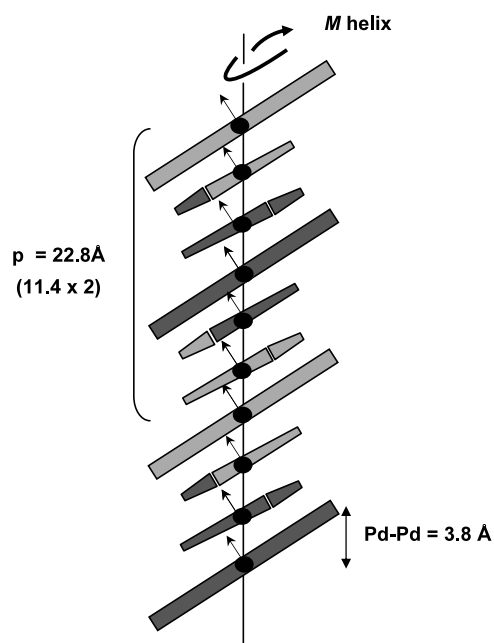


Fig. 13. Proposed helical model for the helical stacking of polycatenar oxazoline complexes within the rectangular columnar mesophase.

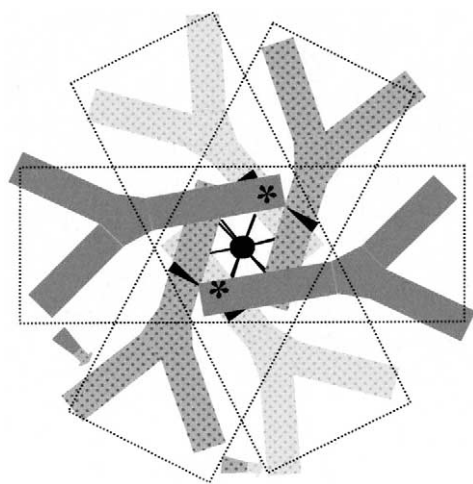


Fig. 14. Schematic representation of the staggered stacking of the oxazoline complexes viewed along the column axis.

row along the column axis. The persistence length of the helical order in the column could not be estimated due to the diffuse nature of the spots. However, for such a pitch to be visible by X-ray methods it is thought that it would persist over an extended length, i.e. several helical turns [36].

In order to gain a deeper insight into the influence of chirality on the mesophase structure, a racemate was prepared by mechanical mixing of equal amounts of the palladium complexes **17** and **19**, as well as the complex of the racemic ligand (**20**). The complex of the racemic ligand (**20**) is, in fact, a mixture of diastereomers depending upon the configuration of the stereogenic

centers in the ligands. Thus, *R*–*R*, *S*–*S* and *S*–*R* are formed in the ratio 0.25:0.25:0.50, as estimated by ¹H-NMR spectroscopy.

Both materials display a hexagonal columnar mesophase, as determined by X-ray diffraction. Moreover, oriented patterns (Fig. 15) were obtained that showed middle angle scattering, indicating that the stacked molecules generate the same type of helix as the pure enantiomers. The measured pitch period and stacking distance have, within experimental error, practically the same values as for **17**. Segregation between optical isomers was proposed as an explanation for the persistence of the helical modulation [35b]. It is possible that segregation takes place between columns, as proposed in Swager's model [24], or along the column. In any case, this is a question that is difficult to address. Middle angle maxima appear diffuse as long as the outer reflection is as strong and sharp as in the pure enantiomer. The helical order seems to be perturbed within an unperturbed molecular stacking compared to the pure enantiomers. It is possible that mixing the stereoisomers slightly perturbs the helical order, especially in the case of the diastereomeric mixture, which contains the meso diastereomer in addition to the two enantiomers.

A discrepancy between this model and the results showing a rectangular lattice for the pure enantiomer and a hexagonal lattice for the racemic and diastereomeric mixture can be ruled out. The dimensions measured for the unit cell are, within experimental error, the same for all the complexes. At this point, it should be taken into account that the difference between a rectangular lattice with a *P2*₁ symmetry and a hexagonal lattice concerns 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 director of neighboring columns is defined by the symmetry of the lattice, in particular by the twofold helical axis. Due to the similarity in 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 [35b]. Thus, hexagonal symmetry results, as demonstrated by X-ray diffraction (all the observed reflections are consistent with a 2D hexagonal lattice with *P6/mmm* symmetry). The conclusion is that the difference between the mesophases of the pure enantiomers and the mixtures does not concern the organization inside each column and modifies only the correlations between the columns.

Variable temperature CD experiments (Fig. 16) provide definitive support for the conclusions drawn from the X-ray measurements. In contrast with previous structures, oxazoline complexes have the stereogenic centers within the conjugated part of the ligand and this

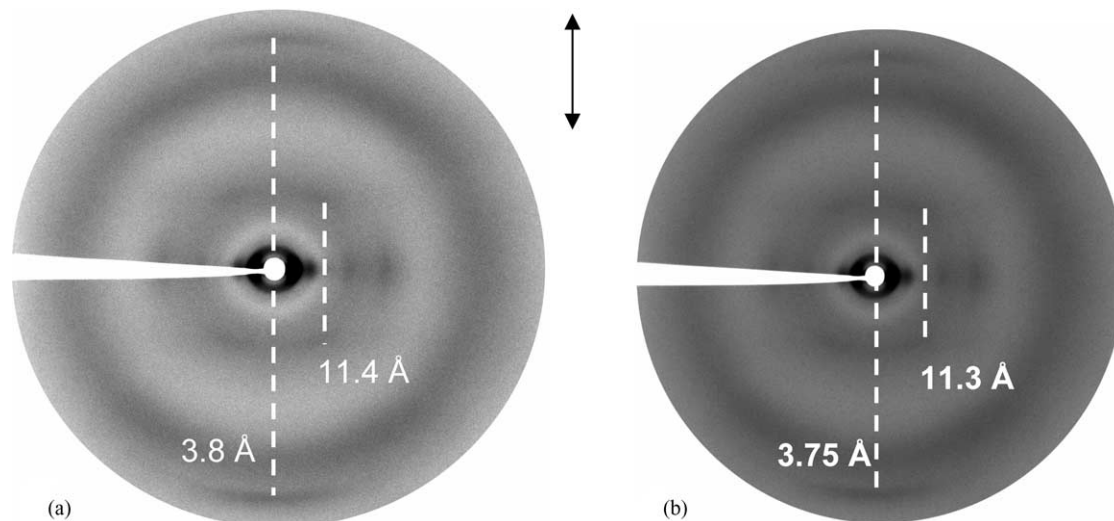


Fig. 15. X-ray diffraction pattern of non-optically active complexes: (a) **20** (complex obtained from the racemic ligand; and (b) prepared racemate, **17**+**19**.

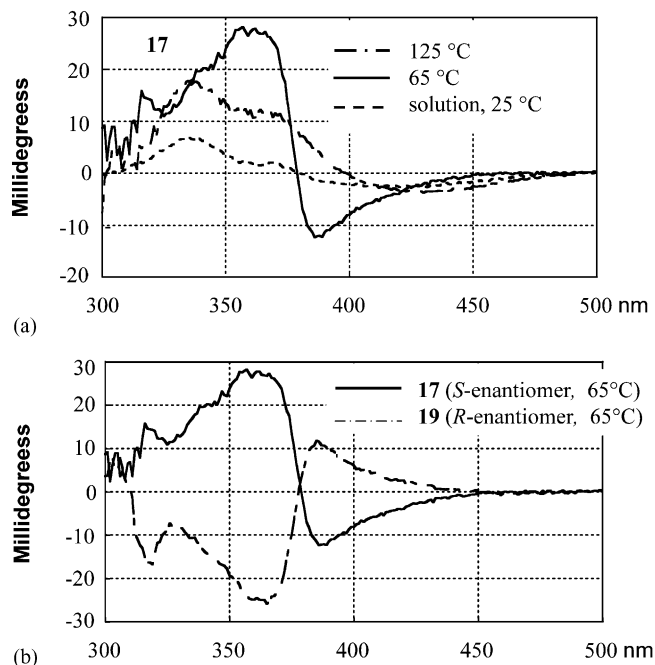


Fig. 16. (a) CD spectral comparison of the complex **17** in the mesophase (65 °C), in the isotropic liquid (125 °C) and in solution (10 mm cell, 1.07×10^{-5} M in hexanes). The positive sign of the exciton splitting corresponds to a right-handed helical arrangement of the electric transitions, and this leads to a 'minus' helix; (b) CD spectra of the pure enantiomers **17** and **19** showing opposite signs.

will influence the absorption of circularly polarized light of the isolated molecule. Indeed, a CD signal was observed for dilute solutions of both complexes **17** (Fig. 16a) and **18** [27] and these signals were the same as those obtained from the isotropic melt in each case. CD spectra of the mesophases appeared significantly

different. Exciton splitting can be observed in the spectrum at the wavelength of the Cotton effect in the spectra of the complex in an isotropic environment. An existing relationship between this new signal and a supramolecular helical structure was found in that the stereogenic centers responsible for the optical activity are in the rigid coordination plane of the complex. This means that a change in the skeleton of the complex itself is not a probable cause of the change in the CD spectrum. Indeed, a helical structure such as that proposed from X-ray diffraction studies could well explain the observed behavior to circularly polarized light. Moreover, the opposite sign of optical activity, corresponding to a *P* helix, was found for **19**—the enantiomer of complex **17** (Fig. 16b).

4. Concluding remarks

The aim of this review has been to highlight a fruitful combination of two strategies, i.e. coordination chemistry and liquid crystal self-organization processes, in order to achieve supramolecular helical architectures. The process is exemplified by three different types of metallomesogen that organize into helical columnar mesophases. It can be deduced that a considerable proportion of research undertaken on this subject is academic and results from the creative focus of chemists to build up aesthetic supramolecular architectures. However, if a functional supramolecular organization can be obtained with interesting properties (for example, the optical properties of a helical structure), then construction of advanced materials for new devices is envisaged to be a desirable consequence. Examples presented here demonstrate that a high level of structural supramolecular control can be attained for mole-

cular materials when they are designed to incorporate pro-mesogenic structures that enable liquid crystalline behavior to be achieved. Mesophases are thus used as templates for the desired level of organization, and the molecular unit must bear the required elements to promote the appropriate mesophase and thus give the desired properties. These elements are clearly related to molecular properties such as shape, topology, stereochemistry, etc. As far as these properties are concerned, metal-coordination has been shown to be a versatile tool to synthesize molecular building units that bring together all of these features: mesogenic character, molecular shape that itself promotes helical packing, molecular chirality, etc. If we consider these properties in terms of the structures presented here, it can be concluded that, together with the mesogenic character inherent in the three types of structure outlined, molecular chirality due to the presence of stereogenic centers is the main factor responsible for promoting the helical columnar organization of planar disk-like β -diketonates. On the other hand, molecular shape seems to have a strong influence on the appearance of a helical arrangement in octahedral β -diketonates and in planar elongated oxazoline complexes.

In summary, the introduction of stereogenic centers into the peripheral paraffinic tails of planar disk-like β -diketonates breaks the hexagonal symmetry present in the achiral analogues and leads to the appearance of a rectangular columnar mesophase with a helical arrangement within the column. In contrast, the propeller-like shape of octahedral β -diketonates leads to efficient packing that involves interdigitation of the tilted ligands within a column. This interdigitation gives rise to a helical arrangement within the column. Elongated planar oxazoline complexes organize into columnar mesophases in which molecules fill empty space by rotating with respect to their neighbors within the column. In these latter two cases, the crucial importance of molecular shape in the helical arrangement is evident in that the helix also appears (and in the last case has been directly observed by X-ray diffraction) in non-chiral and racemic mixtures that are not optically active. In all three cases, the presence of stereogenic centers in the molecule with a given chiral sense confers the material a formal optical activity derived from the helical organization.

Acknowledgements

The authors wish to acknowledge the CICYT (MAT2000-1293-C02-01) for financial support of part of the work presented in this review.

References

- [1] G.M. Whitesides, J.P. Mathias, C.T. Seto, *Science* 254 (1991) 1312.
- [2] M. Kauranen, T. Verbiest, C. Boutton, M.N. Teerenstra, K. Clays, A.J. Schouten, R.J.M. Nolte, A. Persoons, *Science* 270 (1995) 966.
- [3] T. Nakao, Y. Okamoto, *Chem. Rev.* 101 (2001) 4013.
- [4] T. Ezuhara, K. Endo, Y. Aoyama, *J. Am. Chem. Soc.* 121 (1999) 3279.
- [5] (a) C. Provent, A. Williams, in: J.P. Sauvage (Ed.), *Transitions Metals in Supramolecular Chemistry*, John Wiley and Sons Ltd, Chichester, 1999, p. 135 (Chapter 4);
(b) A. Williams, *Chem. Eur. J.* 3 (1997) 15;
(c) C. Piguet, G. Bernardelli, G. Hopfgartner, *Chem. Rev.* 97 (1997) 2005;
(d) M. Albrecht, *Chem. Rev.* 101 (2001) 3457.
- [6] (a) B.S.J. Geib, C. Vicent, E. Fan, A.D. Hamilton, *Angew. Chem. Int. Ed. Engl.* 32 (1993) 119;
(b) M.P. Lightfoot, F.S. Mair, R.G. Pritchard, J.E. Warren, *Chem. Commun.* (1999) 1945;
(c) S.L. Forman, J.C. Fetinger, S. Pieraccini, G. Gotarelli, J.T. Davis, *J. Am. Chem. Soc.* 122 (2000) 4060;
(d) H. Fenniri, P. Mathivanan, K.L. Vidale, D.M. Sherman, K. Hallenga, K.V. Wood, J.G. Stowell, *J. Am. Chem. Soc.* 123 (2001) 3854;
(e) P. Gandopadhyay, T.P. Radhakrishnan, *Angew. Chem. Int. Ed.* 40 (2001) 2451;
(f) T. Gulik-Krzywicki, C. Fouquey, J.-M. Lehn, *Proc. Natl. Acad. Sci. U.S.A.* 90 (1993) 163;
(g) S. Hanessian, A. Gromtsyan, M. Simard, S. Roelens, *J. Am. Chem. Soc.* 116 (1994) 4495;
(h) K. Hanabusa, M. Yamada, M. Kimura, H. Shirai, *Angew. Chem. Int. Ed. Engl.* 35 (1996) 1949.
- [7] N. Tamaoki, *Adv. Mater.* 13 (2001) 1135.
- [8] S.T. Lagerwall, *Ferroelectric and Antiferroelectric Liquid Crystals*, Wiley-VCH, Weinheim, 1999.
- [9] P.P. Crooker, in: H.S. Kitzerow, Ch. Bahr (Eds.), *Chirality in Liquid Crystals*, Springer, New York, 2001, p. 186 (Chapter 7).
- [10] H.S. Kitzerow, in: H.S. Kitzerow, Ch. Bahr (Eds.), *Chirality in Liquid Crystals*, Springer, New York, Chapter 10, 2001, p. 186.
- [11] (a) J. Malthête, J. Jacques, N.H. Tinh, Ch. Destrade, *Nature* 298 (1982) 46;
(b) M.M. Green, H. Ringsdorf, J. Wagner, R. Wüstefeld, *Angew. Chem. Int. Ed. Engl.* 29 (1990) 1478.
- [12] (a) C.F. van Nostrum, A.W. Bosman, G.H. Gelink, P.G. Schouten, J.M. Warman, A.J. Schouten, R.J.M. Nolte, *Chem. Eur. J.* 1 (1995) 171;
(b) H. Engelkamp, S. Middelbeek, R.J.M. Nolte, *Science* 284 (1999) 785;
(c) A.R.A. Palmans, J.A.J.M. Vekemans, E. Havinga, E.W. Meijer, *Angew. Chem. Int. Ed. Engl.* 36 (1997) 2648;
(d) C. Nuckolls, T.J.J. Katz, *J. Am. Chem. Soc.* 120 (1998) 9541;
(e) C. Nuckolls, T.J. Katz, T. Verbiest, S. van Elshocht, H.G. Kuball, S. Kiese-walter, A.J. Lovinger, A. Persoons, *J. Am. Chem. Soc.* 120 (1998) 856b;
(f) C. Nuckolls, T.J. Katz, G. Katz, P.J. Collings, L. Castellanos, *J. Am. Chem. Soc.* 121 (1999) 79.
- [13] (a) T. Verbiest, S. van Elshocht, M. Kauranen, L. Hellemans, J. Snauwaert, C. Nuckolls, T.J. Katz, A. Persoons, *Science* 281 (1998) 913;
(b) J.M. Fox, T.J. Katz, S. van Elshocht, T. Verbiest, M. Kauranen, A. Persoons, T. Thongpanchang, T. Krauss, L. Brus, *J. Am. Chem. Soc.* 121 (1999) 3453.
- [14] C. Nuckolls, R. Shao, W.G. Jang, N.A. Clark, D.M. Walba, T.J. Katz, *Chem. Mater.* 14 (2002) 773.

- [15] A.E. Rowan, R.J.M. Nolte, *Angew. Chem. Int. Ed. Engl.* 37 (1998) 63.
- [16] J.L. Serrano (Ed.), *Metallomesogens. Synthesis, Properties and Applications*, VCH, Weinheim, 1996.
- [17] J. Barberá, in: J.L. Serrano (Ed.), *Metallomesogens. Synthesis, Properties and Applications*, VCH, Weinheim, 1996 (Chapter 4).
- [18] (a) H. Zheng, C.K. Lai, T.M. Swager, *Chem. Mater.* 7 (1995) 2067;
(b) H. Zheng, P.J. Carroll, T.M. Swager, *Liq. Cryst.* 14 (1993) 1421.
- [19] M.M. Zurbano, Ph.D. Dissertation, University of Zaragoza, 1993, unpublished results.
- [20] (a) J. Barberá, R. Iglesias, J.L. Serrano, T. Sierra, M.R. de la Fuente, B. Palacios, M.A. Pérez-Jubindo, J.T. Vázquez, *J. Am. Chem. Soc.* 120 (1998) 2908;
(b) J.L. Serrano, T. Sierra, *Chem. Eur. J.* 6 (2000) 759.
- [21] (a) M. Marcos, J.L. Serrano, T. Sierra, M.J. Giménez, *Angew. Chem. Int. Ed. Engl.* 31 (1992) 1471;
(b) M. Marcos, J.L. Serrano, T. Sierra, M.J. Giménez, *Chem. Mater.* 5 (1993) 1332;
(c) R. Iglesias, M. Marcos, J.L. Serrano, T. Sierra, M.A. Pérez-Jubindo, *Chem. Mater.* 8 (1996) 2611;
(d) P. Espinet, J. Etxebarría, M. Marcos, J. Pérez, A. Remón, J.L. Serrano, *Angew. Chem. Int. Ed. Engl.* 28 (1989) 1065;
(e) M.J. Baena, J. Barberá, P. Espinet, A. Ezcurra, M.B. Ros, J.L. Serrano, *J. Am. Chem. Soc.* 116 (1994) 1899;
(f) M.J. Baena, P. Espinet, M.B. Ros, J.L. Serrano, A. Ezcurra, *Angew. Chem. Int. Ed. Engl.* 32 (1993) 1203;
(g) N. Thompson, J.L. Serrano, M.J. Baena, P. Espinet, *Chem. Eur. J.* 2 (1996) 214.
- [22] (a) H. Bock, W. Helfrich, *Liq. Cryst.* 12 (1992) 697;
(b) H. Bock, W. Helfrich, *Liq. Cryst.* 18 (1995) 387;
(c) H. Bock, W. Helfrich, *Liq. Cryst.* 18 (1995) 707;
(d) G. Heppke, D. Krücker, M. Müller, H. Bock, *Ferroelectrics* 179 (1996) 203;
(e) G. Scherowsky, X.H. Chen, *Liq. Cryst.* 17 (1994) 803;
(f) G. Scherowsky, X.H. Chen, *J. Mater. Chem.* 5 (1995) 417.
- [23] C.J. Tschierske, *Mater. Chem.* 11 (2001) 2647.
- [24] H. Zheng, T.M. Swager, *J. Am. Chem. Soc.* 116 (1994) 761.
- [25] H.T. Nguyen, Ch. Destrade, J. Malthête, *Adv. Mater.* 9 (1997) 375.
- [26] (a) M. Lehmann, M. Marcos, J.L. Serrano, T. Sierra, C. Bolm, K. Weickhardt, A. Magnus, G. Moll, *Chem. Mater.* 117 (2001) 8312;
(b) J. Barberá, M. Lehmann, J.L. Serrano, T. Sierra, R. Parker, *J. Mater. Chem.* 12 (2002) 1342.
- [27] J. Barberá, E. Caverio, M. Lehmann, J.L. Serrano, T. Sierra, J.T. Vázquez, *J. Am. Chem. Soc.* 125 (2003) 4527.
- [28] M. Gómez-Simón, S. Jansat, Muller Guillermo, D. Panyella, M. Font-Badía, X. Solans, *J. Chem. Soc. Dalton Trans.* (1997) 3755.
- [29] J.M. Lehn, A. Rigault, J. Siegel, J. Harrowfield, B. Chevrier, D. Moras, *Proc. Natl. Acad. Sci. U.S.A.* 84 (1987) 2565.
- [30] J.C. Chambron, C.O. Dietrich-Buchecker, J.P. Sauvage, in: J.P. Sauvage, M.W. Hosseini (Eds.), *Templating, Self-assembly and Self-organization*, vol. 9, Pergamon Press, Oxford, 1996.
- [31] (a) A. El-ghayoury, L. Douce, A. Skoulios, R. Ziessel, *Angew. Chem. Int. Ed. Engl.* 37 (1998) 2205;
(b) L. Douce, A. El-ghayoury, A. Skoulios, R. Ziessel, *Chem. Commun.* (1999) 2033;
(c) L. Douce, R. Ziessel, *Mol. Cryst. Liq. Cryst.* 362 (2001) 133;
(d) R. Ziessel, *Coord. Chem. Rev.* 216–217 (2001) 195.
- [32] K. Nakanishi, N. Berova, R.W. Woody, *Circular Dichroism: Principles and Applications*, VCH Publishers, Inc, New York, NY, 1994.
- [33] M.R. de la Fuente, B. Palacios, M.A. Pérez-Jubindo, R. Iglesias, J.L. Serrano, T. Sierra, *Liq. Cryst.* 25 (1998) 481.
- [34] K.R. Villazor, T.M. Swager, 19th International Liquid Crystal Conference, Edinburgh, UK, 30 June–5 July, 2002.
- [35] (a) A.M. Levelut, *J. Physique Lett.* 40 (1979) 81;
(b) A.M. Levelut, P. Oswald, A. Ghanem, J. Malthête, *J. Physique* 45 (1984) 745;
(c) A.M. Levelut, J. Malthête, A. Collet, *J. Physique* 47 (1986) 351.
- [36] H. Engelkamp, C.F. van Nostrum, S.J. Piken, R.J.M. Nolte, *Chem. Commun.* (1998) 979.