

Cooperative Chirality in Columnar Liquid Crystals: Studies of Fluxional Octahedral Metallomesogens

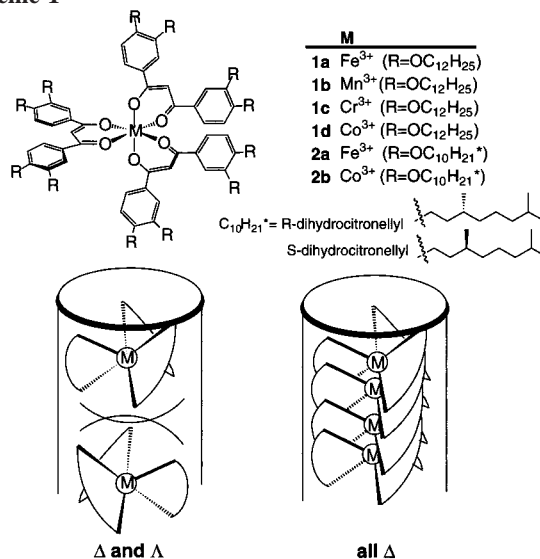
Scott T. Trzaska, Hsiu-Fu Hsu, and Timothy M. Swager*

Department of Chemistry
Massachusetts Institute of Technology, 77 Massachusetts Ave.
Cambridge, Massachusetts 02139

Received January 6, 1999
Revised Manuscript Received March 8, 1999

Chirality is a powerful element for creating novel organizations and functions in liquid crystalline materials. Optically active liquid crystals often display polar structures, frustration, and periodic structures with mesoscale dimensions.¹ Chiral nematic and smectic liquid crystals have been widely investigated,¹ whereas chiral columnar liquid crystals have received limited investigation. Nevertheless, chiral columnar phases have proved interesting, and recent reports include demonstrations of unusual liquid crystalline structures,² ferroelectricity,³ and exceptional second-order nonlinear optical susceptibilities.⁴ We have been investigating liquid crystals with racemic octahedral metallomesogenic cores having D_3 symmetry, **1**, which were recently discovered to display columnar phases (Col).^{5,6} These materials have a low aspect ratio for a thermotropic liquid crystal, and as a result the dipolar interactions necessary to stabilize the mesophase likely arise from interdigitation of the pendant aromatic rings on the ligands. Considering the structure of **1** and the highly birefringent nature of the mesophases, it is plausible that the molecules in the Col mesophase align with the pseudo- C_3 molecular axis coincident with that of the column as shown in Scheme 1. This organization promotes interactions between the pendant aromatic rings that depend on chiral sense (Δ or Λ) of the nearest neighbors.^{7,8} When nearest neighbors have the same absolute configuration about the transition metal, we expect efficient packing and a helical columnar structure. A mismatched structure will concurrently limit the dipolar interactions between mesogens (Scheme 1). In this contribution, we demonstrate that octahedral metallomesogen-based liquid crystals can spontaneously resolve into microdomains with net chirality (Δ or Λ). Additionally, we address the importance of the supramolecular symmetry, and our studies suggest that a hexagonal columnar phase, Col_h, facilitates this resolution, whereas a lower symmetry rectangular columnar phase, Col_r, better accommodates equal amounts of Δ and Λ isomers.

Scheme 1



The barriers for interconversion between the Δ and Λ enantiomers of D_3 first-row transition-metal complexes are understood to arise from ligand field stabilization. As a result, compounds **1a** and **1b**, which are high-spin Fe^{3+} and Mn^{3+} species, are fluxional, whereas the analogous Cr^{3+} and Co^{3+} complexes, **1c** and **1d**, are conformationally locked. These differences and the phase behavior of series **1** suggest that chirality is an important determinant of nearest neighbor interactions. All of the compounds of series **1** have similar clearing points, and in each case the initial phase observed with cooling is a Col_h phase (Table 1). At lower temperatures the intermolecular correlations, and consequently the influence of chirality, become stronger and produce different behaviors. Compounds **1a** and **1b** display an additional Col_h phase, whereas **1c** and **1d** display a Col_r phase.⁹ The significance of hexagonal and rectangular symmetries is important (Scheme 2). A perfect hexagonal organization is a close-packed columnar structure wherein each column is indistinguishable from its neighbors. In other words, a simple two-dimensional hexagonal unit cell contains only one column, and there is a preference for uniformity among all columns. There is also the possibility that a hexagonal superlattice will form wherein both enantiomers can exist, but one dominates (Scheme 2).¹⁰ In the case of a fluxional octahedral complex in a Col_h phase, microdomains can form where a Δ or Λ isomer dominates. However, in the case of a rectangular phase, there are two columns with different environments in a unit cell. It is important to note that the proposed driving force for a homogeneous chirality involves synergistic intracolumnar as well as intercolumnar interactions. If the chirality is static and equal amounts of Δ and Λ isomers must be preserved, a rectangular structure that can accommodate two different columns with opposite chirality is favored.

To test this structural model, we have investigated the effect of additional static chiral centers on the behavior of octahedral metallomesogens. Compounds **2** have the same cores as series **1** but have citronellyl side chains with *R* or *S* chiral centers. The chiral centers are not directly adjacent to the mesogenic core to prevent a strong bias for the Δ or Λ isomer, and **2** should be a

(1) Goodby, J. W. In *Handbook of Liquid Crystals: Fundamentals*; Demus, D., Goodby, J., Gray, G. W., Spiess, H.-W., Vill, V., Eds.; Wiley-VCH: Weinheim, 1998; Vol. 1, Chapter 5.

(2) (a) Nuckolls, C.; Katz, T. J. *J. Am. Chem. Soc.* **1998**, *120*, 9541. (b) van Nostrum, C. F.; Bosman, A. W.; Gelinck, G. H.; Schouten, P. G.; Warman, J. M.; Kentgens, A. P. M.; Devillers, M. A. C.; Meijerink, A.; Picken, S. J.; Sohling, U.; Schouten A.-J.; Nolte, R. J. M. *Chem.—Eur. J.* **1995**, *1*, 171. (c) Maltete, J.; Jacques, J.; Tinh, H. N.; Destrade, C. *Nature* **1982**, *298*, 46.

(3) (a) Barbera, J.; Iglesias, R.; Serrano, J. L.; Sierra, T.; de la Fuente, M. R.; Palacios, B.; Perez-Jubindo, M. A.; Vazquez, J. T. *J. Am. Chem. Soc.* **1998**, *120*, 2908. (b) Scherowsky, G.; Chen, X. H. *Liq. Cryst.* **1994**, *17*, 803. (c) Bock, H.; Helfrich, W. *Liq. Cryst.* **1995**, *18*, 707. (d) Bock, H. Helfrich, W. *Liq. Cryst.* **1995**, *18*, 387.

(4) Verbiest, T.; Elshocht, S. V.; Kauranen, M.; Hellemans, L.; Snauwaert, J.; Nuckolls, C.; Katz, T. J.; Persoons, A. *Science* **1998**, *282*, 913.

(5) (a) Zheng, H.; Swager, T. M. *J. Am. Chem. Soc.* **1994**, *116*, 761. (b) Swager, T. M.; Zheng, H. *Mol. Cryst. Liq. Cryst.* **1995**, *260*, 301. (c) Zheng, H. Ph.D. Dissertation, University of Pennsylvania, 1995.

(6) These liquid-crystal phases were previously labeled with a different nomenclature (ref 5). Col is currently the preferred designation.

(7) Crystallographic analysis of the methoxy analogue of **1d** (see Supporting Information) indicates that the complexes stack in enantiomerically pure columns.

(8) Recent studies of discoid molecules have also established the preference for a single chiral conformer in a columnar stack: Palmans, A. R. A.; Vekemans, J. A. J. M.; Havinga, E. E.; Meijer, E. W. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2648.

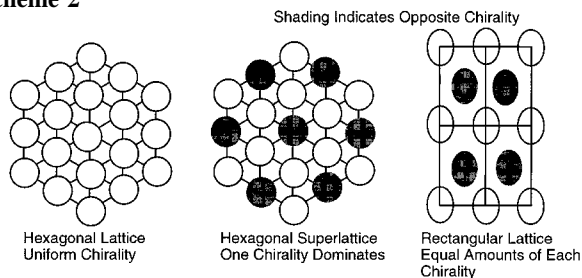
(9) The transition to the Col_r phase is not observable by DSC or in the optical microscope for the Co^{3+} material, **1d**. The Cr^{3+} analogue, **1c**, was previously shown (ref 5) to display large textural changes. In all cases, the phase assignment is supported by low-angle X-ray diffraction.

(10) The interdigitation and fluctuations of side chains in a helical hexagonal system will produce frustration, which may give rise to a three-column superlattice. Fontes, E.; Heiney, P. A.; de Jeu, W. H. *Phys. Rev. Lett.* **1988**, *61*, 1202.

Table 1. Phase Behavior and Variable Temperature XRD^c

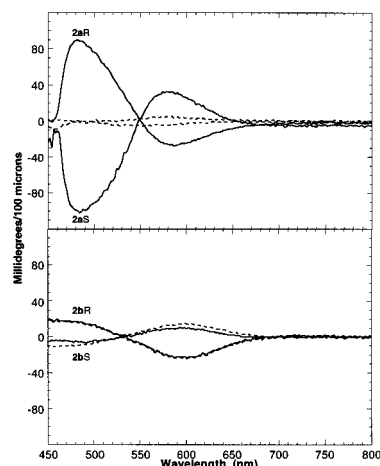
	Phase Behavior	Phase	Lattice Constant (Å) ^b	Spacing Observed
1a^a	Col _h $\xrightleftharpoons[84.3(9.46)]{91.1(9.89)}$ Col _h	Col _h , 92°C	30.72	26.60(100)
		Col _h , 65°C	32.92	28.50(100) 16.42(110)
1b^a	Col _h $\xrightleftharpoons[53.6(2.50)]{62.1(3.10)}$ Col _h	Col _h , 90°C	31.01	26.85(100) 15.51(110) 13.55(200)
		Col _h , 40°C	33.96	29.40(100)
1c^d	Col _h $\xrightleftharpoons[43.6(2.59)]{64.6(3.12)}$ Col _h	Col _h , 90°C	30.43	26.35(100)
		Col, 35°C	a=63.86 b=33.12	31.93(200) 29.40(110)
1d	Col _h $\xrightleftharpoons[Not\ Observed]{61.4(3.3)}$ Col _h	Col _h , 80°C	29.72	25.74(100) 14.94(110)
		Col, 25°C	a=63.58 b=32.83	31.79(200) 29.17(110)
2aR	Col _h $\xrightleftharpoons[76.5(-2.4)]{83.8(2.4)}$ I	Col _h , 70°C	26.26	22.74(100)
2aS	Col _h $\xrightleftharpoons[73.8(-2.1)]{81.0(2.1)}$ I	Col _h , 70°C	26.26	22.74(100)
2bR	Col _h $\xrightleftharpoons[82.9(-2.4)]{88.9(2.5)}$ I	Col _h , 70°C	26.47	22.92(100)
2bS	Col _h $\xrightleftharpoons[74.0(-2.0)]{81.4(2.2)}$ I	Col _h , 70°C	26.47	22.92(100)

^a Data from reference 5c. ^b At wide angle only diffuse scattering is observed (4.45 Å for series 1 and 4.8 Å for series 2). ^c The transition temperatures (°C) and enthalpies, in parentheses (kcal/mole), are given above and below the arrows.

Scheme 2

mixture of diastereomers with nearly equal heats of formation. Consistently, **2a**, which contains a fluxional Fe³⁺ core, displays no apparent circular dichroism (CD) spectrum (450–700 nm) in solution. The Co³⁺ analogue, **2b**, was found to display a small CD signal in solution, with a near mirror image relationship for the *R* and *S* forms of the citronellyl side chains. The origin of the latter CD is likely due to a small enrichment of either the Δ or Λ diastereomer in the synthesis, which involved thermolysis of Co(acac)₃ in a melt of the chiral ligand. Hence, the chiral ligand solvent templates the complex formation.

Consistent with the trends observed for series 1, complexes **2a** and **2b** display similar clearing transition temperatures and Col_h phases with essentially identical lattice constants (Table 1). However, in the mesophase the CD spectra of **2a** and **2b** are very different. CD studies of the liquid-crystal phases were done under carefully controlled conditions to prevent linear dichroism effects. Samples were rapidly cooled from the isotropic phase, producing small liquid crystalline domains that in effect produce a “powder-like” spectrum with an ensemble of orientations. This fact is confirmed by the reproducibility of the spectra and the fact that mirror image relationships for *R* and *S* isomers were consistently

**Figure 1.** CD spectra of **2a** (top) and **2b** (bottom) in the Col_h phase at 25 °C (solid line) and in the isotropic phase at 105 °C (dashed line).

obtained. In the isotropic melt, the CD spectrum (Figure 1) for **2a** is similar to that obtained in solution indicating negligible bias for a particular chiral conformation. However, the supramolecular order imposed by cooling into the Col_h phase produces a dramatic enhancement in **2a**'s circular dichroism signal (Figure 1). The principal chiral induction for **2a** occurs at the I–Col_h phase transition, but a continued increase in CD intensity is observed with lowering temperature. In contrast, **2b** displays no apparent increase in its CD spectrum upon transforming from the isotropic (I) to the Col_h phase or with continued cooling throughout the Col_h phase. As mentioned earlier, the small CD signal for **2b** is the result of the synthesis.

The different CD behavior of **2a** and **2b** can only be rationalized by considering that the fluxional behavior of **2a** allows the system to resolve into a dominantly Δ or Λ domains depending upon the *R* or *S* stereochemistry of the citronellyl side chain. It is important to note that both **2a** and **2b** have structurally equivalent Col_h phases, hence the CD is not the result of different liquid crystalline properties. The driving force for this resolution is the result of both intracolumnar stacking of the mesogenic cores^{7,8} as well as intercolumnar interactions. Such a situation should also display cooperative behavior with a large chiral induction resulting from the addition of a small amount of **2a** to **1a**. This fact is observed experimentally (see Supporting Information), where the CD signal increases rapidly with the addition of small concentrations of the chiral dopant (**2a**). The data are indicative of a cooperative interaction because a purely unimolecular process would result in a linear change in the CD signal with the mole fraction of **2a**.

In summary, we have demonstrated that liquid crystals displaying a Col_h phase can display a cooperative chiral state. In our model the hexagonal symmetry is an integral feature that favors the chiral state. This latter point is also supported by our recent work on fluxional eight vertex Zr⁴⁺ mesogens¹¹ with the same ligands as used in **2**, wherein we found no increase in the CD signal upon cooling from the isotropic phase into an oblique columnar phase.¹²

Acknowledgment. This research was part of the doctoral dissertation of STT at the University of Pennsylvania. This work was supported by the Office of Naval Research and the National Science Foundation (DMR-9811377). We acknowledge the use of the Central Facilities in the Center for Materials Science and Engineering at MIT which is supported by NSF-DMR-94-00334.

JA9900609

(11) Trzaska, S. T.; Zheng, H.; Swager, T. M. *Chem. Mater.* **1999**, *11*, 130.

(12) Trzaska, S. T. Ph.D. Dissertation, University of Pennsylvania, 1998.