

## Octahedral Metallomesogens: Liquid Crystallinity in Low Aspect Ratio Materials

Hanxing Zheng and Timothy M. Swager\*<sup>†</sup>

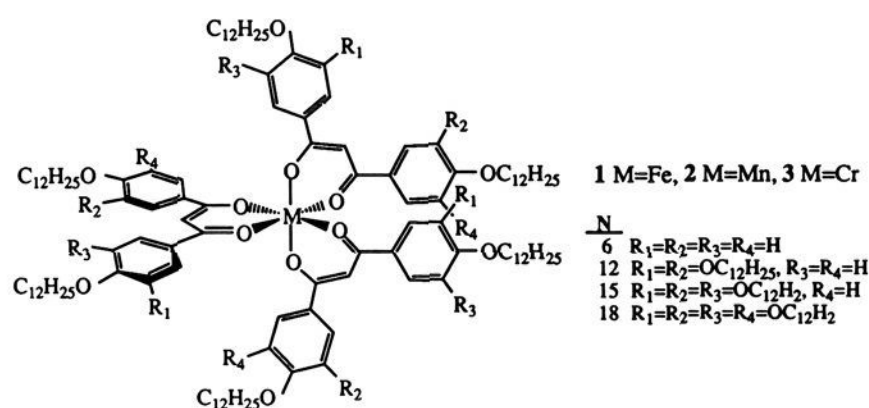
Department of Chemistry, University of Pennsylvania  
Philadelphia, Pennsylvania 19104-6323

Received September 15, 1993

Revised Manuscript Received November 29, 1993

Interest in liquid crystals incorporating transition metals has primarily arisen from the special magnetic and electronic properties of these materials.<sup>1</sup> However, metallomesogens also provide geometric shapes not readily attainable in purely organic materials and thus present opportunities to test the structural boundaries which will support known thermotropic phases. The most common structural guideline in the design of a liquid crystal has been to choose molecules or associations of molecules which display a high aspect ratio. Hence, most liquid crystals exhibit anisotropic rodlike (calamitic) or disclike (discotic) shapes which facilitate attractive dipolar interactions. In this report we describe low aspect ratio transition-metal complexes with octahedral structures and average  $D_3$  symmetry<sup>2</sup> which exhibit liquid crystallinity.

We inadvertently began our investigations of octahedral metallomesogens as part of our program in polar discotics<sup>3,4</sup> when we endeavored to synthesize liquid crystalline analogs of the square-pyramidal complex  $\text{FeCl}(\text{acac})_2$ .<sup>5</sup> However, reactions of alkoxyphenyl-substituted 1,3-diketones with  $\text{FeCl}_3$  under a variety of conditions gave complexes containing no Cl and C:H:Fe ratios, consistent with a tris(diketonate) complex. After confirming the octahedral structures and mesomorphic properties, we synthesized complexes with various numbers ( $N$ ) of dodecyloxy side chains. We have investigated Fe complexes **1** ( $N = 6, 12, 15, 18$ ), Mn complexes **2** ( $N = 12, 15, 18$ ), and Cr complexes **3** ( $N = 12, 15, 18$ ). In spite of their nonplanar low aspect structures, which reduce the attractive dipolar forces, all of these complexes exhibit mesomorphism (Figure 1).

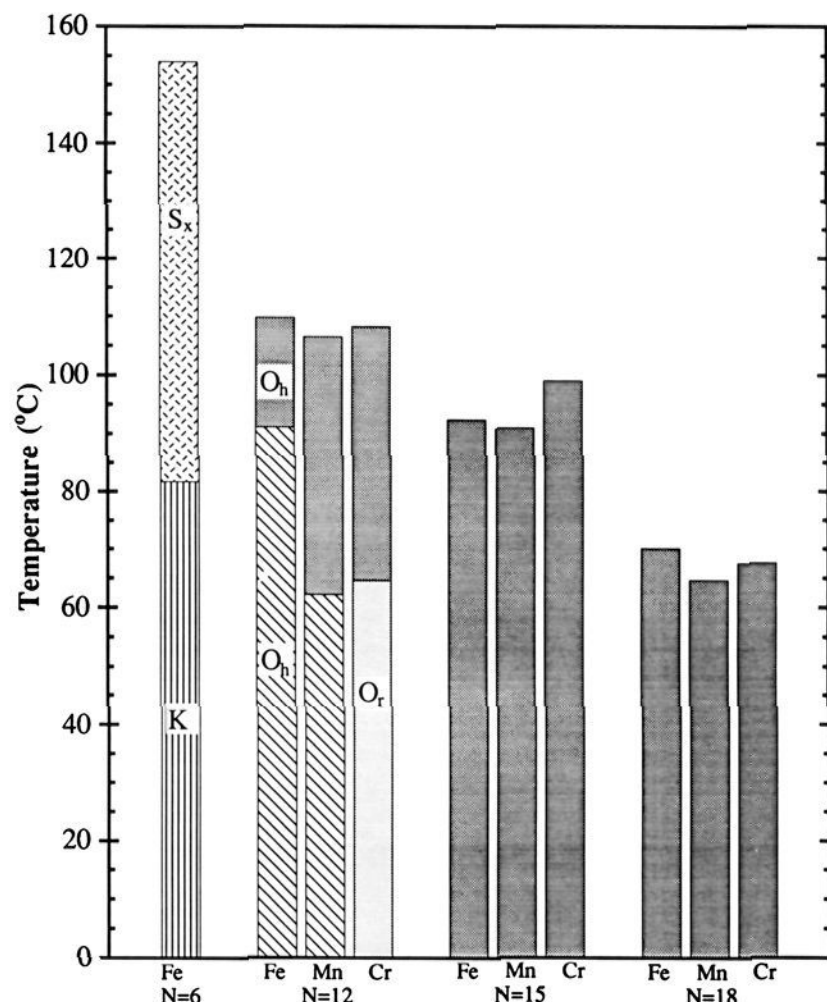


The  $N = 6$  derivative of **1** is very similar in structure to a complex which was previously reported to display multiple differential scanning calorimetry (DSC) transitions.<sup>6</sup> Indeed, when heated above 82 °C this compound transforms to a viscous birefringent fluid phase and to an isotropic phase above 154 °C. However, the isotropic phase is prone to supercooling, which suggests that this fluid phase may actually be crystalline. This is also consistent with our polarizing microscope results, which reveal a mosaic texture with irregular curved domains indicative of an ordered smectic phase.<sup>7</sup> Indeed, X-ray diffraction (XRD)

<sup>†</sup> Office of Naval Research Young Investigator 1992-1995; NSF-Young Investigator 1992-1997; DuPont Young Faculty Grantee.

(1) (a) Giroud-Godquin, A. M.; Maitlis, P. M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 375. (b) Hudson, S. A.; Maitlis, P. M. *Chem. Rev.* **1993**, *93*, 861.

(2) Not all of the compounds have rigorous  $D_3$  symmetry since the manganese complexes likely have Jahn-Teller distortions, and one series of ligands is asymmetric, thereby producing a complex series of isomers.



**Figure 1.** Bar graph showing the phase behavior of octahedral metallomesogens. The shading indicates that the phases have similar character.  $S_x$  indicates an unidentified ordered smectic phase,  $K$  indicates a crystal phase, and the labels  $O_h$  and  $O_r$  indicate hexagonal columnar and rectangular columnar phases, respectively.

indicates a lamellar structure with a (001) peak ( $d = 29.1 \text{ \AA}$ ) accompanied by (002) and (003) peaks, a halo at wide angle ( $d = 4.43 \text{ \AA}$ ), and weak peaks in the midangle region.<sup>8</sup>

All the  $N = 12$  complexes display well-behaved mesomorphism with relatively small (6.4-7.2 kJ/mol) mesophase-to-isotropic transition enthalpies. The high-temperature mesophases of **1**, **2**, and **3** display fan textures with regions of uniform extinction and linear birefringent defects, both which are often observed in discotic hexagonal phases.<sup>3</sup> XRD confirms a hexagonal columnar phase, and **1**, **2**, and **3** display (100) peaks at 26.60, 26.85, and 26.35  $\text{\AA}$ , respectively, and halos centered at approximately 4.48  $\text{\AA}$ . Further confirmation of the hexagonal structure is found in the XRD pattern of **2**, which also displays (200) and (110) reflections.

While the mesophase-to-isotropic transitions are very similar for all of the  $N = 12$  complexes, the phase transitions at lower temperature phases are different. In the case of **1** ( $N = 12$ ), cooling the high-temperature mesophase results in a large exothermic transition (37.6 kJ/mol), which also produces an abrupt decrease in the birefringence but gives no other noticeable textural changes. DSC shows this phase to undergo supercooling (5 °C at 10°/min), but XRD establishes that it is a hexagonal disordered mesophase with a (100) peak at 28.50  $\text{\AA}$ , a (110) peak

(3) For reviews on discotics, see: (a) Destrade, C.; Foucher, P.; Gasparoux, H.; Nguyen, H. T.; Levelut, A. M.; Malthete, J. *Mol. Cryst. Liq. Cryst.* **1984**, *106*, 121. (b) Billard, J. In *Liquid Crystals of One- and Two-Dimensional Order*; Springer Series in Chemical Physics; Springer: Berlin, 1980; p 383. (c) Chandrasekhar, S.; Ranganath, G. S. *Rep. Prog. Phys.* **1990**, *53*, 57.

(4) (a) Xu, B.; Swager, T. M. *J. Am. Chem. Soc.* **1993**, *115*, 1159. (b) Zheng, H.; Carroll, P. J.; Swager, T. M. *Liq. Cryst.* **1993**, *14*, 1421. (c) Serrette, A. G.; Swager, T. M. *J. Am. Chem. Soc.* **1993**, *115*, 8879.

(5) Puri, D. M.; Mehrotra, R. C. *J. Less Common Met.* **1963**, *5*, 2.

(6) Giroud-Godquin, A.-M.; Rassat, A. C. *R. Acad. Sci. Paris, Ser. 2* **1982**, *294*, 241.

(7) Gray, G. W.; Goodby, J. W. G. *Smectic Liquid Crystals: Textures and Structures*; Leonard Hill Publishers: Glasgow, 1984.

(8) Additional XRD studies are necessary to determine the exact structure of this phase.

at 16.42 Å, and a halo centered at 4.41 Å. The large change in birefringence suggests that the ligands of **1** change conformation to give a more isotropic molecular polarizability at lower temperature. Indeed variable temperature infrared spectroscopy confirms that this phase transition is coupled to the rotational preferences and dynamics of the alkoxyphenyl groups. In **1**'s isotropic and high-temperature hexagonal columnar phase, the 1,3-diketonate portion of the ligands exhibit a strong C=C stretching band<sup>9</sup> at 1531 cm<sup>-1</sup>. However, in the low-temperature mesophase, this band shifts to 1516 cm<sup>-1</sup>, thereby indicating an increased conjugation between the phenyl groups and the diketonate functionality.

The high-temperature hexagonal columnar phases of **2** and **3** ( $N = 12$ ) have a greater range of stability than that of **1** ( $N = 12$ ). For **2**, a new hexagonal phase is formed at 62 °C ( $\Delta H = 13.0$  kJ/mol) with an expanded intercolumnar distance ( $(100) = 29.4$  Å). This phase transition does not display as dramatic a reduction in birefringence as is observed for **1** and gives no clear changes in the IR spectrum. The low-temperature hexagonal columnar phase of **2** is also prone to supercooling (9 °C at 10 deg/min); however, this is likely the result of the large mass of the complexes and the relatively low temperature. Complex **3** displays a different mesophase at lower temperature, and with the transition to this phase, the fans which display radial patterns are transformed into fans with concentric arc patterns. Additionally, the smooth boundaries between different fans are transformed into jagged boundaries, which indicates that the columns are prone to being redirected in these regions. These features are suggestive of a transformation to a rectangular columnar phase which was confirmed by XRD ( $a = 68.86$  Å,  $b = 33.12$  Å). This transition is also accompanied by a shift of the 1,3-diketone's C=C stretching frequency from 1532 cm<sup>-1</sup> to two different bands at 1527 and 1523 cm<sup>-1</sup>. Hence, **3** ( $N = 12$ ) displays behavior similar to that of **1** ( $N = 12$ ), whereby at lower temperature it adopts a conformation which increases the conjugation between the phenyl groups and the 1,3-diketonate groups. However, in this case the conformational changes of ligands result in a shape which favors an elliptical projection along the column axis characteristic of a rectangular columnar phase.

For the  $N = 15$  and 18 side-chain derivatives of **1**, **2**, and **3**, the greater number of side chains leads to stronger dispersion forces, lower isotropic transitions, and room temperature mesomorphism. The characteristic textures of these materials display spine and digitized leaf patterns with small amounts of fans and linear birefringent defects. These features and the fact that the textures display large regions of uniform extinction suggest that these phases are optically uniaxial and thus have hexagonal symmetry. This assignment is confirmed by XRD, and structures **1**,  $N = 15$  and 18, exhibit (100) diffraction peaks at 26.85 and 27.35 Å, respectively, with halos at 4.46 Å. The transition enthalpies increase with the mass of the complexes and range from 11.0 to 14.0 kJ/mol for  $N = 15$  and from 25.1 to 36.0 kJ/mol for  $N = 18$ . The large masses (ca. 3500–4000) of these complexes and the relatively low clearing temperature also produce a tendency for supercooling (ca. 5–9 °C at 10 deg/min for  $N = 15$  and 19–21 °C at 10 deg/min for  $N = 18$ ). Infrared analysis of **1** ( $N = 15, 18$ ) reveals that the 1,3-diketonate C=C bands are insensitive to temperature and have a frequency of 1532 cm<sup>-1</sup>.

Given the data presented thus far, one might conclude that these octahedral complexes display phases which should be simply classified with the standard discotic hexagonal and discotic rectangular labels (i.e.,  $D_{hd}$  and  $D_{rd}$ ). However, we have avoided using these labels since these phases are not miscible with discotic



**Figure 2.** Photograph of a contact preparation showing the lack of miscibility of the  $O_h$  phase of **3**,  $N = 12$  (bottom) with a  $D_{hd}$  phase of a square-planar copper diketonate complex (top) viewed with a polarizing microscope at 90 °C (polarizers oriented vertical and horizontal).

columnar materials. A contact preparation between **3** ( $N = 12$ ) and a square-planar bis(diketonate) complex of copper containing the ligand used to produce the  $N = 18$  octahedral complexes (i.e.,  $R_1 = R_2 = R_3 = R_4 = C_{12}H_{25}$ ) is shown Figure 2.<sup>10</sup> The 12-side-chain copper complex displays a classical  $D_{hd}$  phase between 59.9 and 101.5 °C and an intercolumnar spacing which is within 3% of that of **3** ( $N = 12$ ). In spite of the similarities, these complexes are not miscible and display an abrupt change in the texture at the interface. Contact preparations with all of the other octahedral complexes show similar results. We believe that this lack of miscibility with discotic materials is due to the fact that the clefts of one complex are necessary to accommodate those side chains of neighboring complexes that cannot be directed outside the column core. Consistent with this idea is the fact that the  $N = 18$  derivatives, which have 50% more side chains than the  $N = 12$  complexes, exhibit an intercolumnar spacing only 3% larger. Hence, the extra side chains fill voids within the columns rather than expanding the column's diameter. As a result of these differences with discotics, we have labeled these new mesophases as octahedral hexagonal ( $O_h$ ) and octahedral rectangular ( $O_r$ ) (Figure 1).

In summary, we have shown that octahedral coordination complexes exhibit novel mesomorphism. These results suggest that new types of metallomesogens previously considered unlikely liquid crystal candidates may reveal a number of novel phases.

**Acknowledgment.** We are grateful for financial support provided by the National Science Foundation (DMR-9258298 and DMR-9119045) and the Office of Naval Research.

(9) The assignment of this band has been previously determined: Singh, P. R.; Sahai, R. *Aust. J. Chem.* **1967**, *20*, 639.

(10) This copper compound and a number of other discotic diketonate complexes will be the subject of future reports.