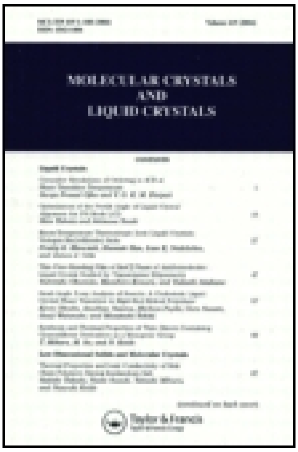

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Liquid Crystalline Behavior in Octahedral Metal Complexes

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LIQUID CRYSTALLINE BEHAVIOR IN OCTAHEDRAL METAL COMPLEXES

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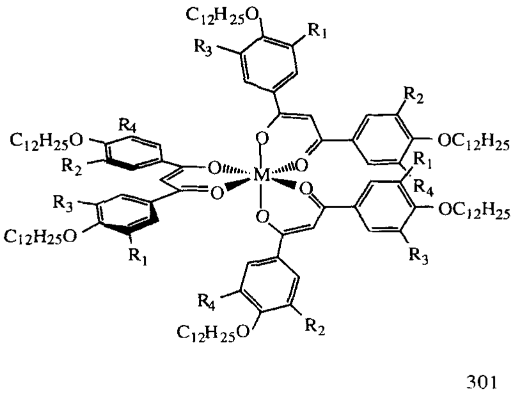
Abstract Octahedral liquid crystals based upon diketonate complexes of Fe^{+3}, Mn^{+3}, and Cr^{+3} are reported. *These materials display columnar phases with* ≥*12* sidechains and an ordered smectic phase with 6 sidechains.

INTRODUCTION

Metallomesogens 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 and thereby can lead to the discovery of new 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. In this report we describe low aspect ratio metallomesogens with octahedral structures.[1,2]

RESULTS

We have performed a systematic study in which we synthesized diketonate complexes with various numbers (N) of dodecyloxy sidechains. We also investigated the effect of the transition metal and have studied Fe complexes **1** (N=6,12,15,18), Mn complexes **2** (N=12,15,18), and Cr complexes **3** (N=12,15,18).



1 M=Fe, **2** M=Mn, **3** M=Cr

N	
6	$R_1=R_2=R_3=R_4=H$
12	$R_1=R_2=OC_{12}H_{25}$, $R_3=R_4=H$
15	$R_1=R_2=R_3=OC_{12}H_2$, $R_4=H$
18	$R_1=R_2=R_3=R_4=OC_{12}H_2$

The liquid crystalline behavior is summarized in Figure 1. The N=6 derivative of **1** is very similar in structure to a complex which was previously reported to display multiple DSC transitions.[3] Indeed after the first heat-cool cycle, which is generally unique from all other cycles, when heated above 82°C this compound transforms to a viscous birefringent fluid phase and to a isotropic phase above 154°C. However, the isotropic phase is prone to supercooling and displays broad DSC transitions in the cooling cycle 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. Indeed X-ray diffraction (XRD) indicates a lamellar structure with a (001) peak (d=29.1 Å) accompanied by (002) and (003) peaks, a halo at wide angle (d=4.43 Å), and weak peaks in the mid-angle region confirming that this is a highly organized smectic phase.[4]

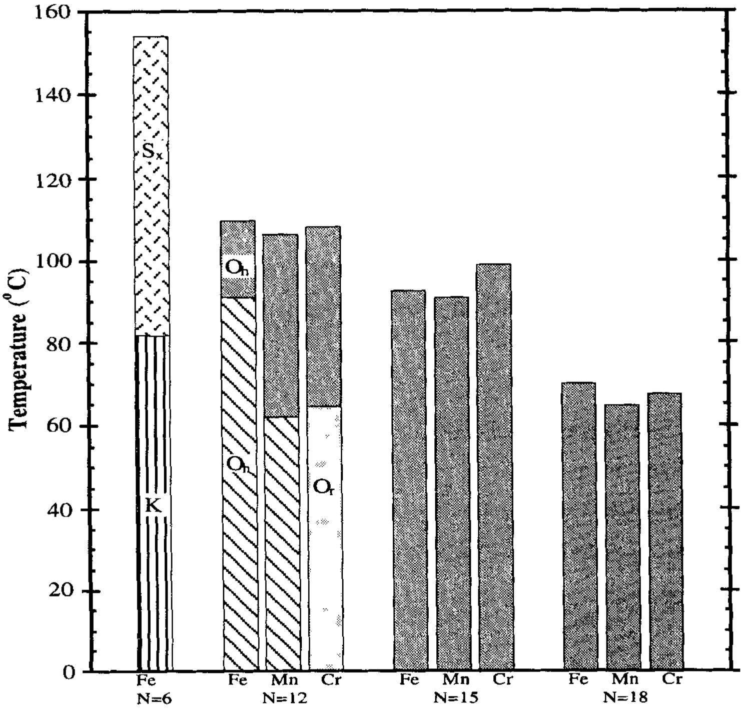


FIGURE 1. Bar graph showing the phase behavior of octahedral metallomesogens, and the shading indicates that the phases have similar character. S_x indicates an unidentified ordered smectic phase, K indicates a crystal phase, and the labels O_h and O_r indicate hexagonal columnar rectangular columnar phases respectively with liquid like order within the columns.

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 typical of columnar phases. These materials also display regions of uniform extinction and linear birefringent defects, both which are often observed in discotic hexagonal phases. XRD confirms a hexagonal columnar phase, and **1**, **2**, and **3** display (100) peaks at 26.60, 26.85, and 26.35 Å respectively and halos centered at approximately 4.48 Å. 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 gave no other noticeable textural changes. DSC shows this phase to undergo supercooling (5° at 10°/min), but XRD establishes that it is a hexagonal disordered mesophase with a (100) peak at 28.50 Å, a (110) peak 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 (Figure 2) 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[5] at 1531 cm^{-1}. In the low temperature mesophase this bands shifts to 1516 cm^{-1} thereby indicating a 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 (ΔH=13.0 kJ/mol) with an expanded intercolumnar distance ((100)=29.4Å). This phase transition doesn't display as dramatic a reduction in birefringence as is observed for **1** and gave no clear changes in the IR spectrum. The low temperature hexagonal columnar phase of **2** is also prone to supercooling (9° at 10°/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^{-1} to two different bands at 1527 cm^{-1} and 1523 cm^{-1}. Hence **3** (N=12) displays behavior similar to **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.

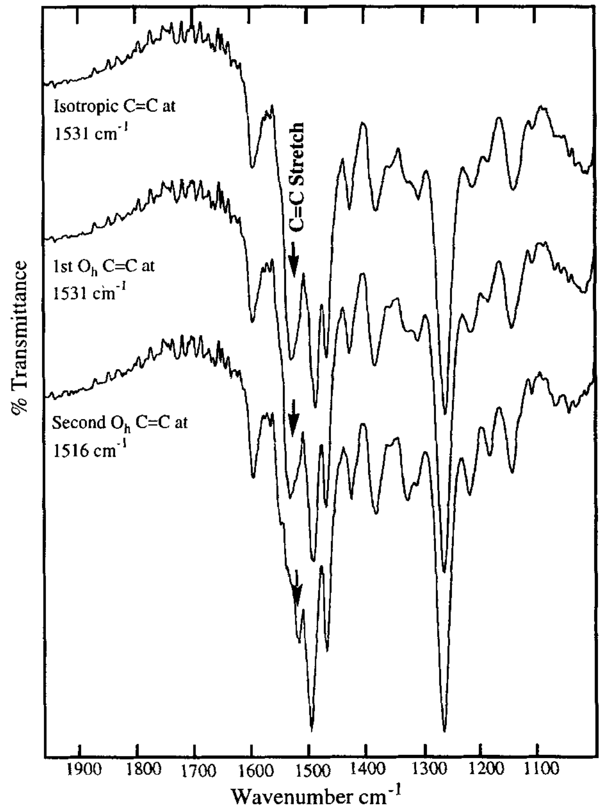


FIGURE 2. VT-IR data showing changes in **1** (N=12).

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 (ΔH=13.0 kJ/mol) with an expanded intercolumnar distance ((100)=29.4Å). This phase transition doesn't display as dramatic a reduction in birefringence as is observed for **1** and gave no clear changes in the IR spectrum. The low temperature hexagonal columnar phase of **2** is also prone to supercooling (9° at 10°/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^{-1} to two different bands at 1527 cm^{-1} and 1523 cm^{-1}. Hence **3** (N=12) displays behavior similar to **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 sidechain derivatives of **1**, **2**, and **3**, the greater number of sidechains 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 **1** N=15 and 18 exhibit (100) diffraction peaks at 26.85Å and 27.35Å 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/mo for N=18. The large masses (ca. 3,500-4,000) of these complexes and the relatively low clearing temperature also produce a tendency for supercooling (c.a. 5-9° at 10°/min for N=15 and 19-21° at 10°/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^{-1}.

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 columnar materials. Contact preparations 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. $R_1=R_2=R_3=R_4=C_{12}H_{25}$) were investigatee.[1] The 12 sidechain copper complex displays a classical D_{hd} phase between 59.9 and 101.5°C a intercolumnar spacing which is within

3% of **3's** (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 sidechains of neighboring complexes that can not be directed outside the column core. Consistent with this idea is the fact that the N=18 derivatives which have 50% more sidechains than the N=12 complexes exhibit an intercolumnar spacing only 3% larger than the high temperature hexagonal phases of the N=12 complexes. Hence, the extra sidechains 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. Additionally, the chiral nature of these octahedral bidentate complexes is of interest due to the technological importance of chiral liquid crystals and related compounds will be the subject of future work.

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REFERENCES

1. H. Zheng, T. M. Swager J. Am. Chem. Soc., 116, 761-2, (1994).
2. For other examples of octahedral metallomesogens see: S. Schmidt, G. Lattermann, R.
Kleppinger, J. H. Wendorff, Liq. Cryst., 16, 693-702, (1994).
3. Giroud-Godquin, A-M.; Rassat, A. C. R. Acad. Sc. Paris, Series II, 294, 241, (1992).
4. Additional XRD studies are necessary to determine the exact structure of this phase.
5. The assignment of this band has been previously determined. Singh, P. R.; Sahai, R. Aust. J. Chem., 20, 639, (1967).