CHEMISTRY of
MATERIALS®

VOLUME 6, NUMBER 2 FEBRUARY 1994

Communications

Transition Metals in Highly Correlated Discotic Phases: Designing Metallomesogens with Selected Intermolecular Organizations

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Received October 19, 1993

The extension of important bulk material properties, which have been largely limited to the solid materials, into fluid phases presents new challenges for materials design. Nevertheless, complex fluids can contribute a new dimension to these properties and provide opportunities for novel technologies and applications.[1,2] Thermotropic liquid crystals containing transition-metal coordination complexes (metallomesogens) offer a wealth of opportunities from which to develop advanced materials with novel properties.[1] Many coordination compounds are stable in multiple oxidation states, exhibit paramagnetism, and have electronic excitations coincident with visible light. These properties if harnessed effectively can be used to produce novel conductors, magnetic materials, and display devices. Square planar metal complexes are particularly important building blocks for new materials since the open axial coordination sites allow for intermetallic communication via direct metal–metal or ligand-mediated interactions. To design materials exhibiting specific properties it is critical to develop methods which can control this communication. As part of our program to develop advanced materials based upon metallomesogens we have been investigating square-planar and square-pyramidal 1,3-diketonate Schiff-base complexes. In this program we seek not only to produce materials with well-behaved mesomorphism but to also design liquid-crystalline superstructures which provide a degree of control over the nature of the intermolecular interactions. We demonstrate herein an approach utilizing correlated columnar mesophases to produce low-viscosity phases which maintain metal centers in closer proximity than typically observed in fluid columnar phases.

The tendency for a given molecule to display a particular liquid-crystalline superstructure is related to its shape, aspect ratio, and dipolar properties.[3] Rod-shaped molecules generally assemble into nematic or smectic phases whereas disc-shaped molecules tend to display columnar phases. While the guiding principle of shape is extensively used in the design of liquid crystals, a less commonapproach in discotic materials has been to generate the desired disc-shaped and aspect ratio with noncircular yet complementary shaped molecules. The use of complementary shapes has the advantage that an understanding of the assembly of these materials into highly correlated liquid-crystal phases provides opportunities to control the nature and degree of the intermolecular interactions.[4,5] An additional feature of correlated columnar mesophases

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[†] Office of Naval Research Young Investigator 1992–1995, NSF-Young Investigator 1992–1997, duPont Young Professor 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. (c) Espinet, P.; Esteruelas, M. A.; Oro, L. A.; Serrano, J. L.; Sola, E. *Coord. Chem. Rev.* **1992**, *117*, 215.

(2) For example, ferroelectric liquid crystals not only display the classical ferroelectric property of bistable polar order but also can be used to create high-performance displays and electrooptical devices. Goodby, J. W.; Blinc, R.; Clark, N. A.; , S. T.; Osipov, M. A.; Pikin, S. A.; Sakurai, T.; Yoshino, K.; Zeks, B. *Ferroelectric Liquid Crystals: Principles, Properties, and Applications*; Gordon and Breach Science Publishers: Amsterdam, 1991.

(3) *Thermotropic Liquid Crystals: Critical Reports on Applied Chemistry*; Gray, G. W., Ed.; Society of Chemical Industry: 1987; Vol. 22.

(4) (a) Serrette, A. G.; Swager, T. M. *J. Am. Chem. Soc.* **1993**, *115*, 8879. (b) Lai, C. K.; Serrette, A.; Swager, T. M. *J. Am. Chem. Soc.* **1992**, *114*, 7948–7949.

(5) (a) The asymmetry of correlated structures has previously been shown to dramatically reduce the melting points of liquid crystals. Rourke, J. P.; Fanizzi, F. P.; Bruce, D. W.; Dunmur, D. A.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1992**, 3009. (b) Complementary shapes have also been used in the formation of discotic phases of dimeric thallium diketonate complexes. Barbera', J.; Cativiela, C.; Serrano, J. L.; Zurbano, M. M. *Adv. Mater.* **1991**, *3*, 602.

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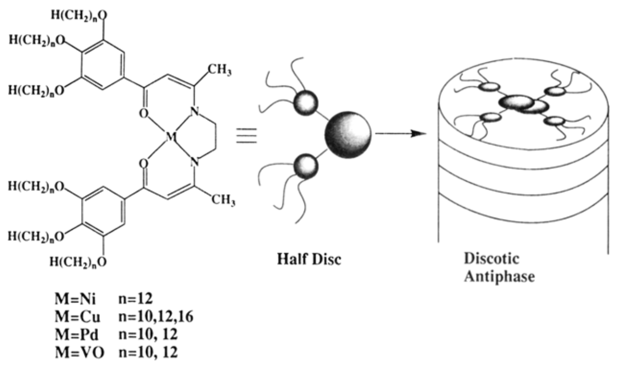

Figure 1. Structure of the diketonate Schiff-base complexes investigated (left), shape analysis of the complexes (center), and assembly of the complexes into a discotic antiphase superstructure.

is that they may be composed of smaller molecules which have greater freedom of movement than those in standard discotic phases. This latter feature can be used to produce materials exhibiting lower viscosities.

The best known class of highly correlated mesophases are the smectic antiphases of cyanobiphenyl mesogens.[6] In these phases, strong dipolar forces cause the cyanobiphenyls to display a time-averaged antiparallel organization of nearest neighbors. We have been examining a similar concept using discotic liquid crystals in which molecules exhibiting a half-disc shape assemble to form antiparallel correlated discotic phases.[4] The compounds investigated in this study, shown in Figure 1, have weaker dipoles than the cyanobiphenyls. Hence we consider that shape effects and/or dative interactions between neighboring complexes are the dominant factors in producing an antiparallel organization. On the basis of the similarities with the smectic materials, we refer to these structures as discotic antiphases.

We have investigated coordination complexes of the 1,3-diketonate Schiff-base ligands shown in Figure 1 with square planar Pd, Ni, and Cu centers as well as with square-pyramidal vanadyl centers. The relatively low melting points, below 50 °C for most of the compounds, are a desirable attribute. Most metallomesogens have high melting points which limit potential applications. The melting points are lower for the Cu complexes, and the n = 10 and 12 derivatives are room-temperature liquid crystals. We find that all of the square-planar compounds display mesomorphism over a fairly broad temperature range, and the phase behavior is summarized in Table 1. For the square-planar complexes, the DSC traces display crystal-to-mesophase transitions with variable enthalpies (3.5–109.6 kJ/mol) and small mesophase-to-isotropic transition enthalpies (2.3–3.8 kJ/mol) indicating relatively disordered mesophases. In the case of the Cu (n = 16) derivative, we observe an unusual but reproducible crystal-to-crystal transition upon heating. This effect is influenced by the rate of cooling and has kinetic origins. The vanadyl complexes exhibit larger isotropic transition enthalpies (17–25 kJ/mol). These enthalpies and the fact that the isotropic phase may be supercooled (≈15 °C at 10 °C/min) indicates that these complexes are not liquid crystals. The fact that a square pyramidal metal center inhibits the liquid crystallinity indicates that efficient interactions between the metal-containing portion of the core groups are critical to mesophase stability.

Table 1. Phase Behavior of Diketonate Schiff-Base Complexes[a]

M	behavior
Ni (n = 12)	$K \underset{31.8\ (17.6)}{\overset{44.5\ (19.7)}{\rightleftharpoons}} \underset{31.94}{D_{hd}} \underset{86.8\ (3.0)}{\overset{91.0\ (3.1)}{\rightleftharpoons}} I$
Cu (n = 10)	$K \underset{15.8\ (13.3)}{\overset{36.7\ (16.0)}{\rightleftharpoons}} \underset{29.86}{D_{hd}} \underset{104.4\ (3.08)}{\overset{106.9\ (3.2)}{\rightleftharpoons}} I$
Cu (n = 12)	$K \underset{25.8\ (21.0)}{\overset{44.0\ (22.1)}{\rightleftharpoons}} \underset{31.31}{D_{hd}} \underset{100.2\ (3.8)}{\overset{103.5\ (3.9)}{\rightleftharpoons}} I$
Cu (n = 16)	$K \xrightarrow{42.0\ (2.6)} K \xrightarrow{44.4\ (109.6)} \underset{35.85}{D_{hd}} \underset{84.2\ (2.6)}{\overset{88.0\ (3.0)}{\rightleftharpoons}} I$ $K \xleftarrow[34.9\ (91.1)]{} D_{hd}$
Pd (n = 10)	$K \underset{50.0\ (6.6)}{\overset{83.6\ (6.8)}{\rightleftharpoons}} \underset{30.15}{D_{hd}} \underset{119.3\ (2.3)}{\overset{123.6\ (2.3)}{\rightleftharpoons}} I$
Pd (n = 12)	$K \underset{31.8\ (92.7)}{\overset{49.0\ (89.3)}{\rightleftharpoons}} K \underset{50.0\ (3.5)}{\overset{78.0\ (6.5)}{\rightleftharpoons}} \underset{32.58}{D_{hd}} \underset{111.9\ (2.6)}{\overset{116.2\ (2.6)}{\rightleftharpoons}}$
VO (n = 10)	$K \underset{84.6\ (23.0)}{\overset{99.7\ (25.3)}{\rightleftharpoons}} I$
VO (n = 10)	$K \overset{42.7\ (81.5)}{\rightleftharpoons} K \underset{79.3\ (16.9)}{\overset{93.9\ (16.1)}{\rightleftharpoons}} I$

[a] The transition temperatures (°C) and enthalpies (in parentheses, kJ/mol) were determined by DSC (10 °C/min) and are given above and below the arrows. The lattice constants (Å) are given below the D_{hd} mesophase designation. **K** and **I** indicate crystal and isotropic phases, respectively.

Polarizing microscope observations of these mesophases produced by slow cooling of the isotropic phases show textures dominated by areas of uniform extinction. This observation indicates that the materials are optically uniaxial and that they have a strong tendency to orient with their optic axis perpendicular to surface of the untreated glass microscope slides. The optical textures of thick preparations contained minor amounts of weakly birefringent fan shaped regions which displayed highly colored linear birefringent defects. These observations combined with low clearing point enthalpies are indicative of a discotic hexagonal disordered phase (D_{hd}).[7] The ease of alignment suggests that the mesophases have a low surface tension. Generally only highly disordered fluid phases with low surface tensions such as S_A, N, or lyotropic phases are so easy to align. It is also noteworthy that the viscosities of these phases are qualitatively lower than those of most discotic phases.

The assignment of these phases as D_{hd} is also supported by X-ray diffraction and by the typical patterns shown in Figure 2. A summary of the lattice constants is also given in Table 1. Most of these samples display the typical signature of a two-dimensional hexagonal lattice with a strong (100) peak and two weak (110) and (200) peaks with relative d spacings of 1, $3^{-1/2}$, and $^1/_2$, respectively. The wide-angle region displays halos indicating liquidlike correlations between the rigid cores. The intercolumnar distances are metal dependent, Ni exhibits slightly larger distances than Cu, and the Pd complexes are noticeably larger than both Ni and Cu. The origin of the increased lattice constant for Pd may be due to greater association

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(6) Gray, G. W.; Goodby, J. W. G. *Smectic Liquid Crystals: Textures and Structures*; Leonard Hill Publishers: Glasgow, 1984; pp 143–149.

(7) 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, Berlin, 1980; p 383. (c) Chandrasekhar, S.; Ranganath, G. S. *Rep. Prog. Phys.* **1990**, *53*, 57 and references therein.

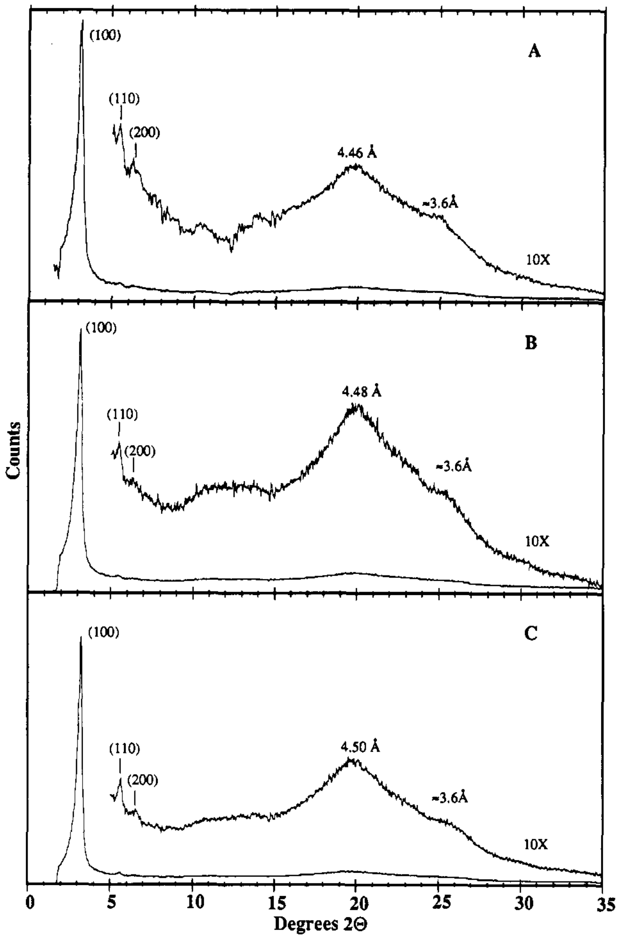

Figure 2. X-ray diffraction of the $n = 12$ complexes of Pd (A), Ni (B), and Cu (C). The low-angle region reveals (100), (110), and (200) diffraction peaks associated with the two-dimensional hexagonal lattice. The mid- and wide-region shows the overlapping halos discussed in the text.

between complexes. An association with the Schiff-base nitrogens would produce an offset which is consistent with the difference in intercolumnar distances. A greater association between the Pd complexes would also account for the higher clearing temperatures exhibited by these derivatives.

The hexagonal columnar arrangement is a close-packed structure and indicates that these molecules assemble so as to project a circular shape along the column's axis. The large preference for this organization confirms that although the molecules do not individually present a circular shape, they are very effective in forming correlated structures which do. Close inspection of our X-ray results shown in Figure 2 provides additional evidence for the discotic antiphase structure. Although the wide- and mid-angle regions do not show sharp peaks, this region displays overlapping halos. The broad and overlapping nature of these halos makes it difficult to assign the exact *d* spacing; however, for all of the compounds the largest peak of the halo is centered at ≈4.5 Å with a shoulder at ≈3.6 Å. The peak at 4.5 Å is typical of liquid correlations between molten hydrocarbon side chains, and the peak at 3.6 Å is assigned to core–core correlations. Hence it appears that the intermesogen spacing is closer than would be expected for a D_{hd} phase with such high fluidity. The Cu and Ni samples display an interesting additional halo at mid-angle (9–15° 2θ) which is centered at roughly twice the core–core correlation distance or ≈7.2 Å. This halo is likely due to a doubling of the period along the columns axis which further confirms the antiphase structure. The Pd complexes do not display this mid-angle halo, and this result may be related to the larger lattice constant displayed by the Pd analogs.

In summary, we have developed new correlated columnar liquid crystals which are based upon square-planar 1,3-diketonate Schiff-base complexes. These compounds exhibit a number of desirable liquid-crystalline properties such as ease of alignment, low melting points, and low viscosity. The complexes are correlated into a discotic antiphase structure in which the complexes are oriented antiparallel. This structure facilitates very close intermesogen contacts of 3.6 Å since the antiphase structure directs the sterically bulky side chains away from those of the nearest neighbors.

Acknowledgment. We are grateful for financial support provided by the National Science Foundation (DMR-9258298 and DMR-9119045) and the Office of Naval Research. We are also thankful for funds provided by the Office of Naval Research, the University of Pennsylvania, and the Laboratory for Research on the Structure of Matter (DMR-9120668) for funds used to create a variable-temperature XRD facility.