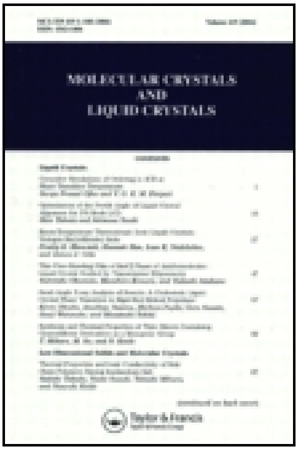

Molecular Crystals and Liquid Crystals

Mesogenic Properties of Binucleating Schiff-Base Ligands with Long Side Chains and Their Binuclear Cu(II) and Ni(II) Complexes

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Mesogenic Properties of Binucleating Schiff-Base Ligands with Long Side Chains and Their Binuclear Cu(II) and Ni(II) Complexes

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Liquid-crystalline binucleating ligands, 1,4-[bis(2-hydroxy-4-(n-alkoxy)benzaldimino]benzene, and their binuclear nickel and copper complexes have been synthesized, with the aim to study the effect of the long alkoxy chain substituents on the mesogenic properties of the ligand and on the extent of electronic interaction between the two paramagnetic metal centers for binuclear Cu(II) complexes. The ligand and the complexes have been characterized by elemental analyses, IR, ^1H NMR, and FAB mass and electronic spectral studies. Magnetic moment studies of the Cu (II) complexes show that there is antiferromagnetic spin-exchange interaction between the two Cu (II) centers through the phenyl bridge. The variable temperature magnetic studies show that the extent of spin-exchange interaction decreases with the increase in the length of the alkoxy side chain. The ligands 1,4-bis-(2-hydroxy-4-(n-alkoxy)benzaldimino)benzene exhibit liquid-crystalline properties with the smectic C phase. The mesogenic property of the ligand disappears on complex formation.

Keywords: binuclear complex, liquid crystal, metallomesogen, spin exchange interaction

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INTRODUCTION

Incorporation of the metal ions in the mesogenic or nonmesogenic ligands can make the resulting metal complexes more polarizable and the complex molecules may become suitably oriented for the fortification or generation of mesogenic properties. Such metallomesogens combine the unique properties of liquid-crystalline anisotropic fluids with the electronic and optical properties of metal complexes [1–3].

However, in some cases, binding with the metal ion may lead to the loss of the mesogenic property of the ligand because of the unfavorable orientation and the polarizability of the resulting complex [1].

In the present report, mesogenic Schiff-base ligands have been synthesised by the condensation of the 2-hydroxy-4-(*n*-alkoxy)benzaldehydes with *p*-phenylenediamine. Furthermore, the syntheses of the doubly bridged, binuclear complexes of copper and nickel, with the liquid-crystalline Schiff bases, have been carried out, and their properties have been studied to see the effect of the liquid-crystalline character on the complex formation and also to observe the effect of the long alkoxy side chains on the long-range spin-exchange interaction between the two paramagnetic Cu(II) centers through the two aromatic bridges.

The magnetic exchange between two paramagnetic Cu(II) centers in the binuclear complexes can occur through multiatom bridge(s). The bridging ligands often mediate the long-range spin-exchange interaction between the paramagnetic centers, and this results in subnormal magnetic properties at room temperature. Study of this type of magnetic exchange is important in order to understand the mechanism of the electron transfer between paramagnetic centers, well separated by organic moiety [4] and also to understand the mechanism of biological electron transport over long distances [5].

Another interesting feature of the binuclear complexes with the binucleating ligands (L) that have a spacer between the two coordinating sites is the formation of helical structure [6]. In case of M_2L_2 complexes of the Schiff-base ligands of *p*-phenylenediamine with salicylaldehyde, there exists the possibility of the formation of a helical structure [6]. In the binuclear complexes of the Schiff-base ligands with long side chains, as studied in this article, the helical structure may be further stabilized because of the intramolecular hydrophobic interaction between the long alkoxy chains of the binucleating Schiff-base ligands and this may affect the mesogenic character of the complexes and also the extent of antiferromagnetic interaction between the two paramagnetic Cu(II) centers.

EXPERIMENTAL

Physical Measurements and Materials

Microanalyses (C, H, N) were carried out using a Perkin-Elmer 240C elemental analyzer. IR spectra were obtained on a Perkin-Elmer 783 spectrophotometer as KBr pellets. ^{1}H NMR spectra were obtained using a 300 MHz varian FT-spectrophotometer in CDCl3 solution using TMS as the internal standard. Electronic spectra were recorded on a Shimadzu UV-240 UV-visible spectrophotometer. Magnetic susceptibilities were measured using a PAR 155 vibrating sample magnetometer. The EPR spectra were recorded using a Varian model 109C E-Line X band spectrophotometer fitted with a quartz Dewar for measurement at 77 K (liquid nitrogen). The EPR spectra were calibrated using tetracyanoethylene (TCEN; $g = 2.3003$) in dichloromethane. Cyclic voltametric studies were carried out using a PC-controlled EG&G/PAR 273A electrochemistry system. A glassy carbon working electrode, a platinum wire auxiliary electrode, and an Ag/AgCl reference electrode were used in the three-electrode configuration. Tetraethylammonium perchlorate (TEAP) was the supporting electrolyte and the concentration of the solution was $\sim 10^{-3}$ M. The fast atom bombertment (FAB) mass spectra were recorderd on a JEOL SX 102/DA-6000 mass spectrometer using argon as the FAB gas. The phase behaviors of all the complexes were examined by Lietz Laborlux 12 Pol polarizing microscope fitted with a Kofler heating stage and were confirmed by differential scanning calorimetric study using a DSC-822e Mettler TOLFDO apparatus.

$Cu(CH_3COO)_2 \cdot 2H_2O$ and $Ni(CH_3COO)_2 \cdot 4H_2O$ (Loba, India), 1,4-diaminobenzene (S. D. Fine, India) and other chemicals and solvents of reagent grade were used as received. Alkyl bromides (Sisco Chem, India) were used after distillation.

Syntheses

Syntheses of 4-n-alkoxy-2-hydroxybenzaldehyde

The ligands, 2-hydroxy-4-(n-alkoxy)benzaldehydes were synthesized following a method reported by Marcos *et al.* [7,8] by reacting n-alkyl bromide with 2,4-dihydroxybenzaldehyde in presence of $KHCO_3$ in anhydrous acetone. The products were purified by flash column chromatography, using hexane–ethylacetate (96:4 v/v) as the eluent. The purity of the product thus obtained was checked by TLC and the melting point of the compounds were found to be same as previously reported [2,9].

Syntheses of 1,4-bis-(2-Hydroxy-4-(n-alkoxy)benzaldimino) benzene

The Schiff-base ligands, 1,4-bis-(2-hydroxy-4-(*n*-alkoxy)benzaldimino)benzene, were synthesized by condensation of two equivalents of 2-hydroxyl-4-(*n*-alkoxy)benzaldehyde, with one equivalent of 1,4-diaminobenzene, in dry ethanol. Specific details for one representative compound are as follows:

1,4-bis-(2-hydroxy-4-(*n*-hexyloxy)benzaldimino)benzene: Into a 25-ml ethanolic solution of 1,4-bis-(2-hydroxy-4-(*n*-hexyloxy)benzaldehyde (1.033 g, 0.2 mmol), a 10-mL ethanolic solution of 1,4 diaminobenzene (0.108 g, 0.1 mmol) was added dropwise under stirring conditions at room temperature. The yellow-colored tetradentate Schiff-base compound, which precipitated immediately, was filtered, washed with 10 ml of ethanol and 10 mL of hexane, and dried in air. The purity of the product was checked by TLC.

Mp 272°C, anal. found: C, 74.10; H, 7.50; N, 5.30. Calc, for $C_{32}H_{40}O_4N_2$: C, 74.39; H, 7.80; N, 5.41. IR $\nu_{C=N}$ 1640, ν_{OH} 3550.

1,4-bis-(2-hydroxy-4-(*n*-decoxy)benzaldimino)benzene: Mp 239°C, anal. found: C, 75.95; H, 9.26; N, 4.23. Calc. for $C_{40}H_{56}O_4N_2$: C, 75.95; H, 9.56; N, 4.23. IR $\nu_{C=N}$ 1630, ν_{OH} 3560.

1,4-bis-(2-hydroxy-4-(*n*-tetradecoxy)benzaldimino)benzene: Mp 231°C, anal. found: C, 78.10; H, 9.21; N, 3.60. Calc. for $C_{32}H_{40}O_4N_2$: C, 78.22; H, 9.30; N, 3.80. IR $\nu_{C=N}$ 1635, ν_{OH} 3550.

Syntheses of 1,4-bis-(2-Hydroxy-4-(n-alkoxy)benzaldimino) benzenecopper(II) Complexes (Series I)

All the complexes of series **I** were prepared by the same method. Specific details of one representative complex are given here and the spectral and analytical data of the complexes are collected in Table I.

1,4-bis-(2-hydroxy-4-(*n*-hexyloxy)benzaldimino)benzenecopper(II): Into a 50.0-mL ethanolic solution of $Cu(CH_3COO)_2 . 2H_2O$ (0.199 g, 0.1 mmol), a solution of 1,4-bis-(2-hydroxy-4-(*n*-hexyloxy)benzaldimino)benzene (0.384 g, 0.1 mmol) in 10 mL of dichloromethane was added. The reaction mixture was refluxed for 5 h and the resulting solution was subjected to distillation to reduce the volume to 5.0 mL. On cooling, brown-colored crystalline solid separated. The complex was isolated by filtration, washed with 10 mL of ethanol and 10 mL of hexane, and dried in air. The complex was further purified by crystallization from dichloromethane.

The complexes, 1,4-bis-(2-hydroxy-4-(*n*-alkoxy)benzaldimino)benzenenickel(II) (series **II**), were synthesized by following the same method as described for series **I**, using an equivalent amount of $Ni(CH_3COO)_2 \cdot 4H_2O$ instead of $Cu(CH_3COO)_2 \cdot 2H_2O$.

TABLE I Characterization Data

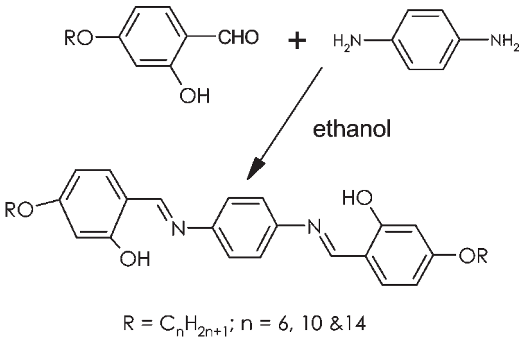
Complexes	Microanalytical data (%)[a] C	H	N	Electronic spectral data[b] λ nm (ε mol^{-1} dm^3 cm^{-1} [c])	IR data $\nu_{C=N}$ cm^{-1}
Series I					
CP6	66.34 (66.49)	6.27 (6.58)	5.01 (4.84)	645(641), 370(56147), 310(50933)	1609
CP10	69.95 (69.61)	7.46 (7.83)	4.24 (4.06)	650(551), 370(52871), 310(52870)	1920
CP14	71.66 (71.86)	8.73 (8.55)	3.49 (3.30)	645(567), 355(33741), 330(31761)	1611
Series II					
NP6	67.44 (67.05)	6.32 (6.63)	4.66 (4.68)	360(23207), 285(13849)	1612
NP10	70.23 (70.12)	7.79 (7.88)	3.99 (4.23)	360(13781), 285(9474)	1608
NP14	71.97 (72.29)	8.73 (8.78)	3.71 (3.51)	360(48004), 305(32684)	1609

[a] Calculated values in parentheses.
[b] In acetonitrile solution.
[c] Extinction coefficient.

RESULTS AND DISCUSSION

The formation of tetradentate Schiff-bases is shown in Scheme 1.

In the IR spectra of the free ligands, the $\nu_{C=N}$ stretching frequency appears at ca. 1640 cm^{-1} and the OH stretching band of the phenolic hydroxyl groups of the free ligand appears at 3550 cm^{-1}. In the ^{1}H NMR spectrum of the ligand, the singlet at δ 13.1, which integrates



SCHEME 1

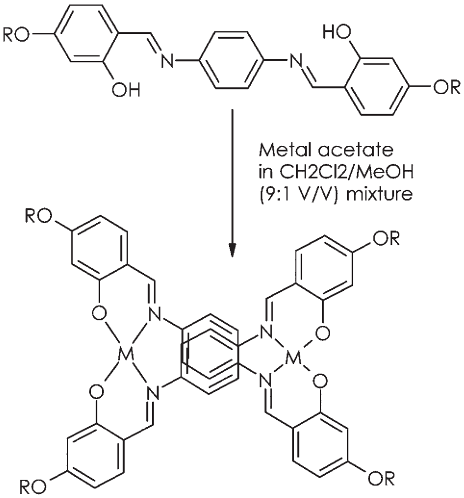
TABLE II Transition Temperatures (°C) of the Ligands (1,4-bis(2-hydroxy-4-(*n*-alkoxy)benzaldimino)benzene

	Transition temperatures (°C)	
R = *n*-alkyl group	C-Iso	SmC
Hexyl	274	(100)
Decyl	238	(105)
Tetradecyl	232	(102)

two protons, has been assigned to the aldimine protons. The aromatic, as well as the aliphatic regions, of the ^{1}H NMR spectra of the ligand appear to be very complicated, owing to significant overlaps of the signals resulting from the aromatic and aliphatic protons.

The phase-transition temperatures of all the ligands are recorded in Table II. The phase-transition temperatures indicate that all the ligands exhibit mesogenic behavior. They are monotropic in nature and exhibit the smectic C phase.

These mesogenic ligands have been used to prepare the binuclear complexes of copper(II) and nickel(II) (series **I** and **II**) in the present study. The probable structures of the ligands and complexes are shown in Scheme 2.



R = C_nH_{2n+1}; n = 6, 10 &14
M = Cu(II) Series **I**,& Ni(II) Series **II**

SCHEME 2

The microanalytical data (C, H, N), as collected in Table I, correspond to the expected compositions of these complexes.

Mass Spectral Studies

The FAB mass spectra of two representative complexes, one each from of the two series, were recorded to support the structure of the complexes, as shown in Scheme 2.

In the mass spectrum of CP10, the peak with the maximum intensity at $m/z = 1382$ corresponds to the molecular ion $(Cu_2L_2)^+$. The calculated molecular weight of the complex is 1380.74. The peak at $m/z = 753$ corresponds to (Cu_2L), and the peak observed at $m/z = 689$ corresponds to $(CuL)^+$. The peak at $m/z = 549$ corresponds to $(Cu\{L{-}C_{10}H21\})$ and the peak at $m/z = 409$ corresponds to $(Cu\{L{-}(C_{10}H_{21})_2\})$, indicating loss of one and of both the alkyl side chains, respectively.

In the mass spectrum of NP10, the peak with the maximum intensity at $m/z = 1372$ corresponds to the molecular ion $(Ni_2L_2)^+$. The calculated molecular weight of the complex is 1371.03. The peak at $m/z = 685$ corresponds to (NiL) and the peak at $m/z = 544$ corresponds to $(Ni\{L{-}C_{10}H_{21}\})$ showing the loss of one of the alkyl side chains.

The sequences of the formation of the fractions, in both cases, support the structure of the complexes as shown in Scheme 2.

IR Spectral Studies

Comparison of the IR spectral data of the free ligands with that of the complexes of the series **I** and **II** indicates that the $\nu_{C=N}$ stretching frequency of the free ligands is shifted to ca. $1609\,cm^{-1}$ in the IR spectra of the complexes. This observation is in accordance with the coordination of azomethine nitrogen atoms to the metal ions [10].

Furthermore, the OH stretching band of the phenolic hydroxyl groups of the free ligand disappears in the IR spectra of complexes supporting the deprotonation of the phenolic hydroxyl groups of the ligand during complexation.

^{1}H NMR Spectral Studies

Comparison of the ^{1}H NMR spectrum of one representative complex, NP10 of series **II**, with that of the corresponding ligand shows that there is a shift in the position of the signals. In the ^{1}H NMR spectrum of NP10, the signal from aldimine protons appears at δ 13.7 as a singlet. As for the ligand, in the ^{1}H NMR spectra of the complex, the aromatic as well as the aliphatic regions appear to be complicated owing to significant overlaps of the signals. However, in the NMR spectrum of the complex NP10, the signals in the both the aromatic and aliphatic regions integrate to the 84 protons, confirming to the required number of protons of the ligands for 2:2 metal-ligand complex. This observation further supports the M_2L_2 composition of complex (series **I**) as proposed on the basis of the elemental and FAB mass spectral studies.

Electronic Spectral Studies

All the complexes are insoluble in nonpolar solvents such as benzene and petroleum ether, as well as polar solvents such as ethanol, methanol, acetone, acetonitrile, dimethylformamide, and dimethylsulphoxide. The electronic spectra of all the complexes were recorded in dichloromethane solution, with concentrations of 10^{-4} to 10^{-5}(M), and the spectral data are collected in Table I. In the electronic spectra of all the Cu(II) complexes, a band of low intensity appears at ca. 645 nm. On the basis of the low value of extinction coefficient, this band has been assigned to the electronic transition between the *d*-orbitals of the metal ions. The occurrence of one band indicates distorted octahedral geometry around the Cu(II) centers. This indicates that there is intermolecular interaction of the Cu(II) with O^- of the ligands of two other complex molecule occupying the axial positions around it. In case of Ni(II) complexes, the *d*–*d* transition band could not be observed because of the poor solubility of the complexes.

In the UV region of the electronic spectra of all the complexes of series **I**, two bands appear at ca. 365 nm and 320 nm, whereas the same bands in the UV region of the electronic spectra of the complexes of series **II** appear at ca. 360 nm and 285 nm. The values of the extinction coefficients of these bands are of the order of 10^5. These bands in the UV region have been attributed to the intraligand electronic transitions, as the same bands appear in the electronic spectra of the free ligands. In the electronic spectra of the complexes, the positions of the intraligand transition bands undergo a shift compared to the same for the free ligands. This change of the electronic energy levels of the ligand may be attributed to the complexation of the ligands to the metal ions.

Magnetic Properties

The Cu(II) complexes are paramagnetic, whereas Ni(II) complexes are diamagnetic, as expected for tetragonal structure.

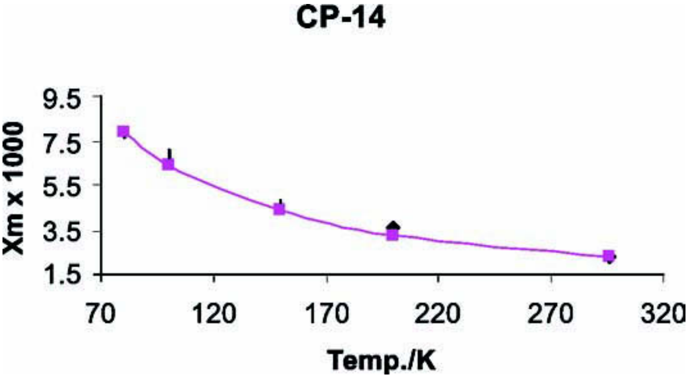


FIGURE 1 Temperature dependence of molar magnetic susceptibility, Xm (♦) for CP-14. The solid line (━ ■ ━) is the calculated curve.

The room-temperature magnetic moment values of the Cu(II)complexes are lower than expected for two Cu(II) centers with one unpaired electron each. This indicates that there is spin-exchange interaction between the two centers through the bridge. The extent of electronic interactions between the two copper centers in the binuclear complexes of the series **I** was studied with the help of temperature-dependent magnetic susceptibility measurements. The magnetic susceptibility was measured in the temperature range 80–300 K

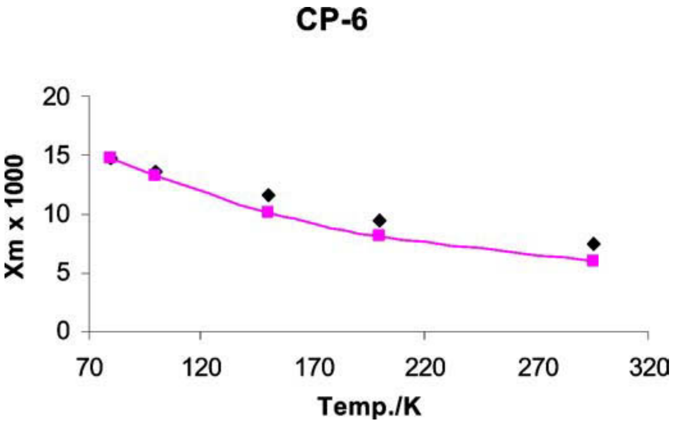


FIGURE 2 Temperature dependence of molar magnetic susceptibility, Xm (♦) for CP-6. The solid line (━ ■ ━) is the calculated curve.

and the results of the magnetic susceptibility measurements for the complexes CP6 and CP14 are given as a function of temperature in Figures 1 and 2 along with the values of χ_m calculated at different temperature using the Bleaney–Bowers equation [11].

The best fits for the experimental data with the calculated data were obtained for $2J = -70\,\text{cm}^{-1}$ for CP6 and $-20\,\text{cm}^{-1}$ for CP14, considering $g = 1.8649$ for CP6 and 1.9047 for CP14, as obtained from the electron spin resonance (ESR) spectral data.

Although the J values are not high, it is indicated that there is antiferromagnetic interaction between the two metal centers and this should be through the σ and π orbitals of the bridging ligand. The extent of antiferromagnetic interaction parameter increases from $-70\,\text{cm}^{-1}$ to $-20\,\text{cm}^{-1}$ with the increase in the chain length of the alkoxy substituent at the 4-position of the 2-hydroxybenzaldimino moiety of the ligand in the complexes. The more negative value of the antiferromagnetic interaction parameter, $2J$ for the complex CP6, compared to the same for CP14, indicates relatively large antiferromagnetic interaction in the former. The lower antiferromagnetic interaction in CP14 may be attributed to the structural constraint imposed by the long alkoxy chains of the ligands, which affects the extent of orbital overlap between the bridging orbital and magnetic orbital of the metal ions. The hydrophobic interaction between the side chains of the two ligands may affect the helical coiling of the ligands and may also affect the extent of spin exchange interaction between the metal centers through the bridge. The complexes could not be obtained in the suitable crystalline form for X-ray studies and hence the presence of helical structure, as suggested in Scheme 1, could not be confirmed.

ESR Spectral Studies

In the ESR spectrum of the Cu(II) complexes, CP6 and CP14, a single signal is obtained, showing that the complexes are paramagnetic. The g values are 1.8649 and 1.9047 for the complexes CP6 and CP14, respectively. This shows that there is an average octahedral field around the metal ion, as discussed in the electronic spectral study. The Ni(II) complexes are EPR silent, as expected.

The cyclic voltammetric studies show that the voltammograms are not reproducible, probably because of the deposition of the complexes with long chains on the electrodes [12].

Thus, the microanlytical data, along with mass, ^{1}H NMR, IR, ESR, electronic spectral, and magnetic moment studies, support the proposed structure of the complexes.

Mesogenic Behavior

None of the Cu(II) or Ni(II) complexes exhibit mesogenic character. This shows that although the free tetradentate Schiff-base ligands exhibit liquid-crystalline properties, the corresponding binuclear Cu(II) and Ni(II) complexes are nonmesogenic. This is because the structural orientation and hydrophobicity of the binuclear complex do not favor the mesogenic character. Thus, in these systems, the liquid-crystal behavior of the ligand is lost on the formation of the binuclear complex.

REFERENCES

[1] Serrano, J. L. (Ed.) (1996). *Metallomesogens, Synthesis, Properties and Applications*, VCH: Weinhein.

[2] Hudson, S. A. & Maitlis, P. M. (1993). *Chem. Rev.*, *93*, 861 and refers therein.

[3] Liebsch, S., Oakley, M. A., Paschke, R., & Sinn, E. (2002). *Inorg. Chem. Comm.*, *5*, 525.

[4] Haim, A. (1983). *Pure and Appl. Chem.*, *55*, 89.

[5] Moor, G. R. & Williams, R. J. P. (1976). *Coord. Chem. Rev.*, *18*, 125.

[6] Youinou, M. T., Ziessel, R., & Lehn, J. M. (1991). *Inorg. Chem.*, *30*, 2144.

[7] Artigas, M., Marcos, M., Melendez, E., & Serrano, J. L. (1985). *Mol. Cryst. Liq. Cryst.*, *130*, 337.

[8] Marcos, M., Melendez, E., & Serrano, J. L. (1983). *Mol. Cryst. Liq. Cryst.*, *91*, 157.

[9] Lai, C. K. & Leu Y. F. (1998). *Liquid Crystals*, *25*, 689–698.

[10] Hariram, R., Santra, B. K., & Lahiri, G. K. (1997). *J. Organomet. Chem.*, *155*, 540.

[11] Kahn, O. (1993). *Molecular Magnetisim*, VCH: New York.

[12] Armaroli, N., Accorsi, G., Gisselbrecht, J. P., Gross, M., Eckert, J., & Nirengarten, J. F. (2003). *New. J. Chem.*, *27*, 1470.