Synthesis, Mesomorphism, and Spectroscopic Characterization of Bis[4-(*n*-alkoxy)-5-(*p*-*n*-tetradecylphenylazo)]-Substituted (*N*,*N*'-Salicylidenediaminato)nickel(II) Complexes

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The bis[4-(n-C_mH_{2m+1}O)-5-(p-C₁₄H₂₉C₆H₄N=N)]-substituted N,N'-salicylidenediamines H₂[L_N(m,14)] (N = 1: 1,2-diaminoethane; N = 2: 1,3-diaminopropane; N = 3: 1,3-diamino-2,2-dimethylpropane; m = 6 or 18) have been synthesized. Both the N = 2 and 3 series of compounds display a smectic C (SmC) mesophase, with clearing points well below 100 °C. By treating the H₂[L_N(m,14)] ligands with an Ni^{II} salt, liquid crystalline mononuclear complexes with

Introduction

The photoisomerization of liquid crystals containing an azobenzene core has been envisaged as useful tool in designing optical switching materials based on light-induced isothermal phase transitions.^[1,4] In an endeavour to improve or explore possible new applications of mesomorphic species, metal atoms have been incorporated into mesogenic molecular structures and a further class of materials (*metallomesogens*), for which some physical properties (e.g. optical, electrical, or magnetic) depend on the nature of the metal centre, is now available.^[5] In principle, new materials can be obtained from compounds whose molecular structures combine different features; thus, in particular, photoisomerizable metal-based liquid crystals could be relevant for applications in electrooptic devices.

We are currently concerned with the design and synthesis of metallomesogens^[6,7] and with reference to the abovementioned uses have recently reported^[8] rod-like thermotropic complexes of Ni^{II}, Cu^{II}, or VO²⁺ with a series of bis[5-(*p*-*n*-alkylphenylazo)]-substituted *N*,*N'*-salicylidenediamines (see Scheme 1). The results of such a comparative investigation indicate that: i) the mesomorphism appears for N[∩]N = 1,2-diaminoethane or 1,3-diaminopropane only; ii) the lowest clearing temperatures are shown by the Ni^{II} species and iii) the better mesomorphic properties (namely larger mesomorphic range) are obtained for the li-

^[a] Dipartimento di Chimica, Università della Calabria, I-87030 Arcavacata (CS), Italy "unconventional" (lateral-tailed) molecular shape form. These Ni[$L_N(m, 14)$] complexes, showing nematic and smectic disordered phases, are stable over a quite large temperature range and have been characterized by different spectroscopic techniques. The newly synthesized mesogens exhibit lower transition temperatures and higher thermal stability than homologous complexes Ni[$L_N(14)$] with a "conventional" rod-like molecular geometry.

gands bearing the n-C₁₄H₂₉ alkyl chains. However, all these mesogens display poor thermal stability, and strong decomposition is observed when, at about 300 °C, the mesophase to isotropic liquid transition occurs. This drawback severely limits any practical applications; therefore, in order to preserve chemical stability, the melting transition temperatures of these materials must decrease – i.e. a different molecular structure has to be considered.



Scheme 1. General formula of the $M[L_N(n)]$ complexes (ref.^[8])

The relationship between chemical structure and mesogenic properties is an extensively investigated area in the field of liquid crystal chemistry and, although the greater part of the available data concerns organic species,^[9] some rules could also be of use for the metallomesogens. In particular, it has been proven that lateral addition of long alkyl chains to a rod-like molecular structure gives rise to a class of "nonconventional" liquid crystals, whose mesophase-isotropic transition temperatures are significantly lower than those of the corresponding rod-like compounds.^[10] Thus, speculating on this trend, low-temperature phase transitions could be predicted for metallomesogens with similar structural features.

The target of the research work we are presently involved in is to obtain thermally stable photoactive metal-contain-

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 1: N=1, m=6
 2: N=1, m=18

 3: N=2, m=6
 4: N=2, m=18

 5: N=3, m=6
 6: N=3, m=18

Scheme 2. Synthetic route to Ni[$L_N(m, 14)$] complexes 1–6; reagents and conditions: i) KOH, n- $C_mH_{2m+1}Br$, ethanol; ii) 4-(n-tetradecyl)aniline, HCl, NaNO₂, NaOH, water; iii) N = 1,2-diaminoethane or 1,3-diaminopropane or 1,3-diamino-2,2-dimethylpropane, ethanol; iv) Ni(CH₃COO)₂ · 4 H₂O, ethanol

ing liquid crystals. As an extension of the previous study,^[8] this paper reports on the synthesis, mesomorphic behaviour, and spectroscopic properties of the complexes that the Ni^{II} ion forms with a series of salicylidenediamino ligands obtained by the symmetric addition of two aliphatic tails to the bis[5-(*p*-*n*-tetradecylphenylazo)]-substituted N,N'-salicylidenediamine skeleton (see Scheme 2).

Results and Discussion

Synthesis

The $H_2[L_N(m, 14)]$ ligands were synthesized in satisfactory yields as outlined in Scheme 2. The starting material, 2,4-dihydroxybenzaldehyde, was treated first with the ap-

propriate alkyl bromide n-C_mH_{2m+1}Br [intermediates I(6) for m = 6 and I(18) for m = 18], and then coupled with the diazonium chloride obtained from the 4-*n*-tetradecylaniline. Finally, the new formed intermediates II(6,14) and II(18,14) were condensed with the selected diamines (namely 1,2-diaminoethane, N = 1; 1,3-diaminopropane, N = 2; and 1,3-diamino-2,2-dimethylpropane, N = 3). The H₂[L_N(m,14)] compounds are orange solids which, by treatment with nickel(II) acetate tetrahydrate, give the corresponding Ni[L_N(m,14)] complexes 1-6 (Scheme 2) as brown to red solids.

The ligands and complexes were characterized by IR and ¹H-NMR spectroscopies and their purity confirmed by elemental analysis (see Experimental Section). These data as a whole account for the general formula shown in

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Scheme 2. Moreover, both the IR and ¹H-NMR spectra, except for the signal attributable to the n- $C_mH_{2m+1}O$ chain, compare well with those of the previously described $H_2[L_N(n)]$ and Ni[$L_N(n)$] compounds (see Scheme 1).^[8] Thus, for complexes **1**–**6**, an [$L_N(m, 14)$] bonding mode, like that which the [$L_N(n)$] groups exhibit in Ni[$L_N(n)$] and expected for ligands containing the salicylidenediaminato core, is proposed (see Scheme 2).

Mesomorphism

The thermal behaviour of all the newly synthesized compounds belonging to the three homologous series N = 1-3, was investigated by combining polarized optical microscopy (POM), miscibility tests with reference compounds, differential scanning calorimetry (DSC) and variable-temperature low-angle X-ray diffraction (XRD) measurements.

The transition temperatures and associated enthalpies for both the ligands $H_2[L_N(m, 14)]$ and their related Ni^{II} complexes are reported in Tables 1 and 2, respectively.

Table 1. Transition temperatures, phase assignments^[a] and enthalpy changes for the $H_2[L_N(m, 14)]$ ligands

Ligand	Transition	<i>T</i> [°C]	ΔH [kJmol ⁻¹]
$H_{2}[L_{1}(6, 14)]$	Cr–I	94.5	69.1
$H_2[L_1(18,14)]$	Cr-Cr'	85.6	28.4
	Cr'-I	106.4	72.7
$H_2[L_2(6,14)]$	Cr-SmC	61.8	83.3
	SmC-I	83.4	39.5
H ₂ [L ₂ (18,14)]	Cr-Cr'	52.5	47.9
	Cr'-I	65.9	2.7
	I-SmC ^[b]	61.7	2.5
	SmC-Cr	42.5	44.6
$H_2[L_3(6,14)]$	Cr-SmC	49.7	27.5
	SmC-I	62.9	18.0
$H_2[L_3(18, 14)]$	Cr-SmC	48.1	4.1
	SmC-I	51.9	24.1

^[a] Cr: crystal; Sm: smeetic; I: isotropic liquid. – ^[b] Monotropic transition.

Table 2. Transition temperatures, phase assignments^[a] and enthalpy changes for the Ni[L_N(m,14)] complexes **1–6**

Compound	Transition	<i>T</i> [°C]	ΔH [kJmol ⁻¹]
$ \frac{1 \{ Ni[L_1(6,14)] \}}{2 \{ Ni[L_1(18,14)] \} } $	Cr-I	213.7	46.7
	Cr-SmC	05.5	46.0
3 {Ni[L ₂ (6,14)]}	Cr-N N-I	101.2 127.3 226 0 ^[b]	2.5 49.6
4 {Ni[L ₂ (18,14)]}	Cr-SmC SmC-SmA SmA-I	89.5 102.2 180 0 ^[b]	29.9 1.0
5 {Ni[L ₃ (6,14)]}	Cr-SmA SmA-I	128.1 293 0 ^[b]	61.8
6 {Ni[L ₃ (18,14)]}	Cr–SmA SmA–I	117.8 190.1	31.1 5.0

^[a] Cr: crystal; Sm: smectic; N: nematic; I: isotropic liquid. – ^[b] From optical microscopy.

Ligands

None of the H₂[L₁(m,14)] ligands displays mesomorphic behaviour, melting directly to an isotropic liquid at about 100°C; a crystal-to-crystal transition at 86°C (DSC, XRD) appears only for the m = 18 homologues.

Increasing the bridge size promotes liquid crystalline behaviour (N = 2 and 3 series). The smectic C (SmC) mesophase is the only one observed in these compounds, irrespective of the bridging diamine or the length of the lateral $n-C_mH_{2m+1}O-$ group. In particular, an enantiotropic (m =6) or monotropic (m = 18) SmC phase, featuring the typical schlieren texture, is exhibited by the $H_2[L_2(m, 14)]$ couple, showing clearing temperatures ranging from 66°C (m = 18) to 83°C (m = 6). Worthy of note is an exothermic peak detected at 65°C (DSC) for the $H_2[L_2(6,14)]$ sample just after the formation of the SmC phase, indicating a transition to a thermodynamically more stable form before reaching the isotropic liquid. In contrast, in the $H_2[L_2(18,14)]$ compound, a crystal-to-crystal transition is observed at 52°C (DSC, XRD). For both the H₂[L₂(m,14)] species, an SmC mesophase first appears on cooling from the isotropic liquid but, on further cooling, crystallization does not occur and the samples solidify into a glassy state retaining the structure of the SmC phase.

Finally, both the N = 3 compounds give an SmC phase showing a sanded texture. On cooling down from the isotropic liquid, the SmC phase is not restored for H₂[L₃(6,14)] and the sample becomes an amorphous solid (POM, DSC, XRD).

At room temperature, the compound with the longest lateral chain, $H_2[L_3(18,14)]$, is a viscous material, slightly birefringent when sheared, whose XRD patterns reveals a semicrystalline structure with a hexagonal smectic-like structure. As the temperature is increased, the material becomes more fluid and an SmC phase is observed at 48°C, before reaching the clearing point at 52°C. Upon cooling, the SmC phase reappears at 41°C and the SmC texture remains until solidification (without crystallization) occurs.

As expected, the results obtained for the N = 2 and 3 series demonstrate that longer lateral tails or bulkier bridges gradually decrease the transition temperatures, whereas the thermal stability of the mesophase progressively reduces. Moreover, since liquid crystalline properties were not observed for any of the $[L_N(14)]$ series,^[8] the $H_2[L_N(m,14)]$ thermal behaviour is a further example of the role the lateral *n*-C_mH_{2m+1}O- chains could play in mesomorphism.^[9]

Complexes

All the Ni[$L_N(m, 14)$] complexes (except for 1) are liquid crystals which exhibit higher clearing points and larger mesomorphic ranges than those of the corresponding ligands.

Of the N = 1 species, 1 (m = 6) melts directly to the isotropic liquid at 214°C but the lengthening of the lateral aliphatic chain to m = 18 (complex 2), induces mesomorphism. Indeed 2 shows an enantiotropic SmC phase, stable in

the range 65-101 °C. Upon cooling, this mesophase reappears at 88 °C and is supercooled to room temperature.

The mesomorphic behaviour of the Ni[$L_2(m, 14)$] series proves to be quite sensitive to changes in the lateral alkoxy tail length and confirms the general trend that longer chains promote more ordered phases. Thus, compound 3 (m = 6) displays a nematic (N) phase showing a homeotropic texture over its entire temperature range, whereas the upper homologues 4 (m = 18) exhibits an SmC (blurred "schlieren" texture) followed by an SmA phase. This latter mesophase becomes more and more fluid and displays homeotropic zones as the temperature is increased. However, both complexes exhibit mesogenic behaviour over a temperature range of about 100°C; the corresponding clearing peaks, only detected by POM observations, were not observed in the DSC scans. When cooled from the isotropic liquid to room temperature, both compounds 3 and 4 transformed into an amorphous solid (XRD).

Finally, of the N = 3 derivatives, the Ni[L₃(*m*,14)] complexes **5** and **6** exhibit an SmA phase, identified from the appearance, via batônnetes, of the focal conic fan texture at 128 °C (**5**) and 118 °C (**6**). On cooling from the isotropic liquid, in compound **5** the SmA phase develops at 280 °C and remains stable until, at 103 °C, crystallization takes place (POM, XRD). In contrast, for compound **6** no crystallization or glass transition was observed until -20 °C.

However, for these three series of Ni[L_N(m,14)] complexes it is possible to conclude that the clearing points decrease by about 50°C (for N = 2) or 100°C (for N = 1,3) as the lateral chain changes from C₆H₁₃O to C₁₈H₃₇O, while they rise only slightly as the number of the carbon atoms of the bridging diamine increases (from 2, N = 1, to 3, N = 2, 3). A similar trend is not observed for the melting transitions and, consequently, for the stability range of the different mesophases.

Azobenzene (E)/(Z) Photoisomerization Measurements

Experiments concerning the (E)/(Z) photoisomerization were performed at room temperature in dichloromethane solutions on Ni[L₂(18,14)] and, for the sake of comparison, on its rod-like homologues Ni[L₂(14)] and on both of the uncomplexed ligands H₂[L₂(18,14)] and H₂[L₂(14)].

The absorption spectra of azobenzenes in their thermally stable (*E*) configuration exhibit absorption maxima at about 350 and 450 nm, and it was observed that irradiation at about 360 nm induces (E)/(Z)-N=N isomerization.^[11] Absorptions at similar wavelengths were also recognized in the spectra of the azo compounds considered; nevertheless under the experimental conditions used, no spectral changes attributable to (*Z*) isomers were detected after irradiation.

Based on the spectral features, Rau^[11] classified the substituted azobenzenes into three different classes depending on the electronic effects the different substituents exert: namely, the azobenzene type, the aminobenzene type, and the

pseudo stilbenes, the latter class containing the azobenzenes substituted with electron-donating and -accepting groups. Each of these classes behave differently as far as the (Z)/(E)isomerization is concerned and, in particular, the donoracceptor azobenzenes isomerize on a millisecond time scale at room temperature.^[11] The lack of spectral evidence for the (E)/(Z) isomerization of Ni[L₂(18,14)], Ni[L₂(14)], $H_2[L_2(18,14)]$, or $H_2[L_2(14)]$ could therefore be ascribed to a very fast (Z)/(E) thermal isomerization process which takes place in the time required to move the sample from the irradiating lamp to the spectrometer (see Experimental Section). These results suggest that in the compounds examined each molecular half (see Scheme 2) behaves as a pseudo stilbene. Moreover, since the n-C14H19 chain is a common feature of these species, an investigation comparing the ligands with the corresponding Ni^{II} complexes and the rod-like molecules with the lateral alkoxy-substituted ones indicates that neither complexation to an Ni^{II} ion nor the addition of a lateral alkoxy chain to the aromatic ring A (Scheme 2) changes the photophysical properties of these N=N-containing molecules significantly.

Conclusions

The present investigation was planned in order to explore a convenient synthetic route to prepare thermally stable photoisomerizable metallomesogens. All the members of the Ni[$L_N(m,14)$] series display thermotropic mesomorphism except for the complex Ni[$L_1(6,14)$]. In no case was decomposition observed, the mesophases are stable over a rather large temperature range, and the clearing temperatures decrease as the lateral chains increase in length.

These results prove that the addition of two lateral nalkoxy tails to bis[5-(p-n-alkylphenylazo)]-substituted N,N'salicylidenediaminato species produces the correct molecular geometry for nematic and smectic metal-containing liquid crystalline compounds with good thermal stability. Indeed, a comparison of the newly synthesized mesogens with the corresponding rod-like complexes^[8] (Scheme 1) shows that the lateral chains i) lower both the melting and clearing temperatures by some 100 °C (N = 2) or 200 °C (N = 1), ii) promote mesomorphism in the N = 3 derivatives, and iii) cause more disordered mesophases (N and S_A) to appear in the N = 1 and 2 series. Thus, as far as the thermal behaviour is concerned, the addition of lateral groups to metallomesogens with a rod-like structure induces effects similar to those observed for organic liquid crystals.^[10]

Practical applications which require metal-based mesogenic optical switching materials can now be considered. Moreover, it has been recently reported that some complexes containing the (salicylidenediaminato)nickel(II) core display second-order nonlinear optical properties,^[12] and this makes coordination compounds such as those reported herein even more attractive materials.

Experimental Section

General: IR: Perkin–Elmer F.T.2000; as KBr pellets. – ¹H NMR: Bruker WH-300 spectrometer; in CDCl₃ solutions, with TMS as internal standard. - Elemental analyses: Perkin-Elmer 2400 analyzer. - Phase transitions and optical textures: Zeiss Axioscope polarizing microscope equipped with a Linkam C0 600 heating stage. - Transition temperatures and enthalpies: Perkin-Elmer DSC-7 differential scanning calorimeter (DSC) operating at a scanning rate of 10.0°C/min; the apparatus was calibrated with indium (156.6°C, 3.3 kJ mol). - X-ray diffraction: INEL CPS-120 powder diffractometer using a monochromatized Cu- K_{α} radiation (λ = 1.54 Å). - Room-temperature absorption spectra of aerated dichloromethane solutions: Perkin-Elmer Lambda 5 spectrometer. - Irradiation experiments: At selected wavelengths by using the 150-W xenon lamp of a Spex Fluorolog II Spectrofluorimeter. -All the commercially available chemicals were used without further purification. The reference compounds $H_2[L_2(14)]$ and $Ni[L_2(14)]$ were prepared as previously reported.^[8]

4-(*n***-Hexyloxy)-2-hydroxybenzaldehyde [I(6)]:** KOH (0.81 g, 14.5 mmol) and subsequently an ethanolic solution (10 mL) of 1bromohexane (3.5 mL, 21.7 mmol) was added to a solution of 2,4dihydroxybenzaldehyde (2.0 g, 14.5 mmol) in ethanol (30 mL). The resulting mixture was heated at reflux for 24 h, allowed to cool to room temp. and 15 mL of H₂O was added. The brownish solid formed was filtered and washed with diethyl ether. The organic layer was dried with Na₂SO₄ and the solvent removed under reduced pressure to afford a yellow oil, which was purified by column chromatography on silica gel (diethyl ether/petroleum ether, 1:1 v:v). Yield 1.82 g (55%). – IR (KBr): $\tilde{v} = 1677 \text{ cm}^{-1}$ (CHO). – ¹H NMR (CDCl₃): $\delta = 11.49$ (s, 1 H, H²), 9.70 (s, 1 H, H¹), 7.42 (d, 1 H, H⁶), 6.53 (dd, 1 H, H⁵), 6.41 (d, 1 H, H³), 4.03 (t, 2 H, OCH₂).

2-Hydroxy-4-(*n***-octadecyloxy)benzaldehyde [I(18)]:** Compound I(18) was prepared according to the procedure decribed for I(6). The white solid afforded was purified by recrystallization from ethanol. Yield 2.86 g (50)%. M.p. 60 °C. – IR (KBr): $\tilde{v} = 1676$ cm⁻¹ (CHO). – ¹H NMR (CDCl₃): $\delta = 11.50$ (s, 1 H, H²), 9.70 (s, 1 H, H¹), 7.41 (d, 1 H, H⁶), 6.52 (dd, 1 H, H⁵), 6.41 (d, 1 H, H³), 4.00 (t, 2 H, OCH₂). – C₂₅H₄₂O₃ (390.6): calcd. C 76.87, H 10.84; found C 76.67, H 10.84.

4-(n-Hexyloxy)-2-hydroxy-5-{[p-(n-tetradecyl)phenyl]azo}benzaldehyde [II(6,14)]: 4-(n-Tetradecylyl)aniline (1.3 g, 45.0 mmol) was dissolved in water (15 mL) and HCl (1.12 mL, 13.49 mmol). The solution was cooled to 0°C and an aqueous solution (8 mL) of NaNO₂ (0.3 g, 48.6 mmol) was added dropwise. I(6) (1 g, 48.6 mmol)45.0 mmol), dissolved in NaOH (5.17 mL, 2 N) and ethanol (3 mL), was added to the solution of the diazonium salt. The reaction mixture was stirred for 1 h at 0°C and then allowed to warm slowly to room temp. The brown solid formed was filtered, washed several times with H₂O and dissolved in dichloromethane. The organic layer was dried with anhydrous Na2SO4, the solvent removed and the crude product purified by column chromatography on silica gel (diethyl ether/petroleum ether, 1:4 v:v). Further purification by recrystallization from methanol afforded the pure product as a yellow solid. Yield 0.70 g (30%). M.p. 81 °C. – IR (KBr): $\tilde{v} = 1653$ cm⁻¹ (CHO). – ¹H NMR (CDCl₃): δ = 14.62 (s, 1 H, H²), 9.81 (s, 1 H, H¹), 7.93 (s, 1 H, H⁶), 7.81 (d, 2 H, H^{b,c}), 7.30 (d, 2 H, H^{a,d}), 6.58 (s, 1 H, H³), 4.21 (t, 2 H, OCH₂), 2.67 (t, 2 H, CH₂). $C_{33}H_{50}N_2O_3$ (522.77): calcd. C 75.82, H 9.64, N 5.36; found C 75.78, H 9.60, N 5.15.

2-Hydroxy-4-(*n*-octadecyloxy)-5-{[4-(*n*-tetradecyl)phenyl]azo}benzaldehyde [II(18,14)]: Compound II(18,14) was prepared ac-

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cording to the procedure decribed for **II(6,14**). Yellow. Yield 0.70 g (40%). M.p. 79 °C. – IR (KBr): $\tilde{\nu} = 1653 \text{ cm}^{-1}$ (CHO). – ¹H NMR (CDCl₃): $\delta = 11.63$ (s, 1 H, H²), 9.82 (s, 1 H, H¹), 7.95 (s, 1 H, H⁶), 7.82 (d, 2 H, H^{b.c}), 7.31 (d, 2 H, H^{a.d}), 6.59 (s, 1 H, H³), 4.22 (t, 2 H, OCH₂), 2.68 (t, 2 H, CH₂). – C₄₅H₇₄N₂O₃ (691.09): calcd. C 78.21, H 10.19, N 4.05; found C 78.31, H 10.15, N 4.34.

N,N'-Bis[4-(*n*-hexyloxy)-2-hydroxy-5-{[*p*-(*n*-tetradecyl)phenyl]azo}benzylidene]ethylenediamine {H₂[L₁(6,14)]}: A mixture of **II**(6,14) (0.25 g, 0.47 mmol) and 1,2-diaminoethane (0.016 mL, 0.23 mmol) in ethanol (15 mL) was refluxed for 4 h. The precipitate was then filtered off and purified by recrystallization from chloroform/ethanol to yield 0.21 g (82%) of a red solid. $- {}^{1}$ H NMR (CDCl₃): $\delta =$ 14.07 (br. s, 2 H, H²), 8.31 (s, 2 H, H¹), 7.78 (d, 4 H, H^{b,c}), 7.69 (s, 2 H, H⁶), 7.28 (d, 4 H, H^{a,d}), 6.54 (s, 2 H, H³), 4.16 (t, 4 H, OCH₂), 3.90 (s, 4 H, NCH₂), 2.67 (t, 4 H, CH₂). $- C_{68}H_{102}N_6O_4$ (1069.61): calcd. C 76.36, H 9.80, N 7.86; found C 76.39, H 9.83, N, 7.24.

H₂[L₁(18,14)]: Prepared according to the procedure described for H₂[L₁(6,14)] with the appropriate diamine. Yellow orange. Yield 0.230 g (75%). - ¹H NMR (CDCl₃): δ = 14.10 (br. s, 2 H, H²), 8.31 (s, 2 H, H¹), 7.77 (d, 4 H, H^{b,c}), 7.68 (s, 2 H, H⁶), 7.27 (d, 4 H, H^{a,d}), 6.53 (s, 2 H, H³), 4.17 (t, 4 H, OCH₂), 3.69 (s, 4 H, NCH₂), 2.66 (t, 4 H, CH₂). - C₉₂H₁₅₂N₆O₄ (1404.26): calcd. C 78.58, H 10.89, N 5.98; found C 78.88, H 11.24, N 5.80.

H₂[L₂(6,14)]: Prepared as described for H₂[L₁(6,14)] with the appropriate diamine. Orange, yield 0.21 g (81%). - ¹H NMR (CDCl₃): δ = 14.30 (br. s, 2 H, H²), 8.28 (s, 2 H, H¹), 7.77 (d, 4 H, H^{b,c}), 7.68 (s, 2 H, H⁶), 7.27 (d, 4 H, H^{a,d}), 6.52 (s, 2 H, H³), 4.17 (t, 4 H, OCH₂), 3.69 (t, 4 H, NCH₂), 2.66 (t, 4 H, CH₂), 2.12 (m, 2 H, NCH₂CH₂). $- C_{69}H_{104}N_6O_4$ (1081.62): calcd. C 76.62, H 9.69, N 7.77; found C 76.70, H 9.70, N 7.75.

H₂[L₂(18,14)]: Prepared according to the procedure decribed for H₂[L₁(6,14)] with the appropriate diamine. Yellow orange, yield 0.28 g (90%). – ¹H NMR (CDCl₃): δ = 14.26 (br. s, 2 H, H²), 8.29 (s, 2 H, H¹), 7.78 (d, 4 H, H^{b,c}), 7.69 (s, 2 H, H⁶), 7.27 (d, 4 H, H^{a,d}), 6.53 (s, 2 H, H³), 4.17 (t, 4 H, OCH₂), 3.69 (t, 4 H, NCH₂), 2.66 (t, 4 H, CH₂), 2.13 (m, 2 H, NCH₂CH₂). – C₉₃H₁₅₄N₆O₄ (1420.28): calcd. C 78.65, H 10.93, N 5.92; found C 78.60, H 10.70, N 5.99.

 $\begin{array}{l} \textbf{H_2[L_3(6,14)]:} \mbox{ Prepared according to the procedure decribed for} \\ \textbf{H_2[L_1(6,14)]} \mbox{ with the appropriate diamine. Dark red, yield 0.21 g} \\ (70\%). - {}^1\mbox{H}\ NMR\ (CDCl_3): \delta = 14.48\ (br. s, 2\ H, H^2), 8.25\ (s, 2\ H, H^1), 7.78\ (d, 4\ H, H^{b,c}), 7.70\ (s, 2\ H, H^6), 7.27\ (d, 4\ H, H^{a,d}), \\ 6.53\ (s, 2\ H, H^3), 4.18\ (t, 4\ H, CH_2), 3.46\ (s, 4\ H, NCH_2), 2.66\ (t, 4\ H, OCH_2), 1.32\ [s, 6\ H, C(CH_3)_2]. - C_{71}H_{108}N_6O_4\ (1109.68): \\ \mbox{calcd. C}\ 76.85, H\ 9.81, N\ 7.50; \ found\ C\ 76.81, H\ 9.79, N\ 7.55. \end{array}$

 $H_2[L_3(18,14)]$: Prepared according to the procedure decribed for $H_2[L_1(6,14)]$ with the appropriate diamine. Dark orange, yield 0.23 g (73%). - 1H NMR (CDCl_3): δ = 14.51 (br. s, 2 H, H²), 8.25 (s, 2 H, H¹), 7.77 (d, 4 H, H^{b,c}), 7.70 (s, 2 H, H⁶), 7.27 (d, 4 H, H^{a,d}), 6.53 (s, 2 H, H³), 4.17 (t, 4 H, OCH_2), 3.46 (s, 4 H, NCH_2), 2.66 (t, 4 H, CH_2), 1.25 [s, 6 H, C(CH_3)_2]. - C₉₅H₁₅₈N₆O₄ (1448.34): calcd. C 78.78, H 5.80, N 11.00; found C 78.72, H 5.90, N 11.50.

Ni[L₁(6,14)] (1): A mixture of nickel(II) acetate tetrahydrate (0.02 g, 0.09 mmol) and an equimolar amount of H₂[L₁(6,14)] (0.1 g) in ethanol (15 mL) was refluxed for 4 h. The dark red solid formed was filtered off and the pure product was obtained by recrystallization from chloroform/ethanol. Yield 0.09 g (86%). - ¹H NMR (CDCl₃): $\delta = 7.70$ (d, 4 H, H^{b,c}), 7.55 (s, 2 H, H⁶), 7.32 (br. s, 2 H, H¹), 7.19 (d, 4 H, H^{a,d}), 6.60 (s, 2 H, H³), 4.09 (t, 4 H, OCH₂), 3.33 (s, 4 H, NCH₂), 2.61 (t, 4 H, CH₂). - C₆₈H₁₀₂N₆NiO₄

(1126.29): calcd. C 72.52, H 9.13, N 7.46; found C 72.62, H 9.12, N 7.46.

Ni[L₁(18,14)] (2): Prepared according to the procedure decribed for Ni[L₁(6,14)] with the appropriate ligand. Brick red, yield 0.073 g (70%). – ¹H NMR (CDCl₃): δ = 7.72 (d, 4 H, H^{b,c}), 7.57 (s, 2 H, H⁶), 7.39 (d, 2 H, H¹), 7.22 (d, 4 H, H^{a,d}), 6.62 (s, 2 H, H³), 4.09 (t, 4 H, OCH₂), 3.37 (s, 4 H, NCH₂), 2.63 (t, 4 H, CH₂). - $C_{92}H_{150}N_6NiO_4$ (1462.93): calcd. C 75.53, H 10.33, N 5.74; found C 75.60, H 10.59, N 5.88.

Ni[L₂(6,14)] (3): Prepared according to the procedure decribed for Ni[L₁(6,14)] with the appropriate ligand. Brown, yield 0.057 g(53%). – ¹H NMR (CDCl₃): δ = 7.73 (d, 4 H, H^{b,c}), 7.57 (s, 2 H, H⁶), 7.25 (d, 6 H, H^{a,d} and H¹), 6.60 (s, 2 H, H³), 4.10 (t, 4 H, OCH₂), 3.50 (t, 4 H, NCH₂), 2.64 (t, 4 H, CH₂), 1.89 (m, 2 H, NCH₂CH₂). - C₆₉H₁₀₂N₆NiO₄ (1138.30): calcd. C 72.81, H 9.03, N 7.38; found C 72.80, H 9.10, N 7.40.

Ni[L₂(18,14)] (4): Prepared according to the procedure decribed for Ni[L₁(6,14)] with the appropriate ligand. Ochre yellow, yield 0.095 g (92%). - ¹H NMR (CDCl₃): $\delta = 7.73 \text{ (d, 4 H, H^{b,c})}, 7.57$ (s, 2 H, H⁶), 7.25 (d, 6 H, H^{a,d} and H¹), 6.60 (s, 2 H, H³), 4.10 (t, 4 H, OCH₂), 3.50 (t, 4 H, NCH₂), 2.64 (t, 4 H, CH₂), 1.89 (m, 2 H, NCH₂CH₂). - C₉₃H₁₅₂N₆NiO₄ (1476.96): calcd. C 75.63, H 10.37, N 5.69; found C 75.73, H 10.46, N 5.70.

 $Ni[L_3(6,14)]$ (5): Prepared according to the procedure decribed for Ni[L₁(6,14)] with the appropriate ligand. Brown, yield 0.060 g(57%). - ¹H NMR (CDCl₃): $\delta = 7.74$ (d, 4 H, H^{b,c}), 7.59 (s, 2 H, H^{6}), 7.26 (d, 4 H, $H^{a,d}$), 7.13 (s, 2 H, H^{1}), 6.62 (s, 2 H, H^{3}), 4.11 (t, 4 H, CH₂), 3.26 (s, 4 H, NCH₂), 2.65 (t, 4 H, OCH₂), 1.48 (s, 6 H, C(CH₃)₂). - C₇₁H₁₀₆N₆NiO₄ (1166.37): calcd. C 73.11, H 9.16, N 7.21; found C 73.40, H 9.25, N 7.32.

Ni[L₃(18,14)] (6): Prepared according to the procedure decribed for Ni[L₁(6,14)] with the appropriate ligand. Red, yield 0.097 g (94%). $- {}^{1}H$ NMR (CDCl₃): $\delta = 7.74$ (d, 4 H, H^{b,c}), 7.59 (s, 2 H, H⁶), 7.26 (d, 4 H, H^{a,d}), 7.12 (s, 2 H, H¹), 6.62 (s, 2 H, H³), 4.10 (t, 4 H, CH₂), 3.25 (s, 4 H, NCH₂), 2.65 (t, 4 H, OCH₂), 1.26 [s, 6 H, C(CH₃)₂). - C₉₅H₁₅₆N₆NiO₄ (1505.01): calcd. C 75.82, H 10.45, N 5.58; found C 75.73, H 10.75, N 5.83.

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- ^[1] S. Xie, A. Natansohn, P. Rochon, Chem. Mater. 1993, 5, 403 - 411.
- ^[2] J. Newton, H. Walton, H. Coles, P. Hodge, Mol. Cryst. Liq. Cryst. 1995, 260, 107-113.
- ^[3] O. Tsutsumi, T. Shiono, T. Ikeda, G. Galli, J. Phys. Chem. B 1997, 101, 1332-1337 and references therein.
- ^[4] S. Furumi, H. Akiyama, S. Morino, K. Ichimura, J. Mater. Chem. 1998, 8, 65-70.
- ^[5] ^[5a] D. W. Bruce in: Inorganic Materials (Eds.: D.W. Bruce, D. O'Hare), Wiley, Chichester, **1992**. – ^[5b] J. L. Serrano, *Metallomesogens*, VCH, Weinheim, **1996**. – ^[5c] A. M. Giroud-Godquin in Handbook of Liquid Crystals, vol. 2B (Eds.: D. Demus, J. Goodby, G. W. Gray, H. W. Spiess, V. Vill), Wiley-WCH, Weinheim, 1998.
- ^[6] F. Neve, M. Ghedini, O. Francescangeli, S. Campagna, Liq. Cryst. 1998, 24, 673-680.
- [7] M. Ghedini, F. Neve, D. Pucci, Eur. J. Inorg. Chem. 1998, 501 - 504.
- [8] I. Aiello, M. Ghedini, F. Neve, D. Pucci, Chem. Mater. 1997, 9, 2107-2112
- ^[9] D. Demus in Handbook of Liquid Crystals, vol. 1 (Eds.: D. Demus, J. Goodby, G. W. Gray, H. W. Spiess, V. Vill), Wiley-WCH, Weinheim, 1998.
- ^[10] W. Weissflog in Handbook of Liquid Crystals, vol. 2B (Eds.: D. Demus, J. Goodby, G. W. Gray, H. W. Spiess, V. Vill), Wiley-WCH, Weinheim, 1998.
- ^[11] H. Rau in Photochromism (Eds.: H. Durr, H. Bouas-Laurent),
- Elsevier, Amsterdam, 1990, chapter 4. ^[12] S. Di Bella, I. Fragalà, I. Ledoux, M. A. Diaz-Garcia, T. J. Marks, J. Am. Chem. Soc. 1997, 119, 9550-9957. Received December 21, 1998

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