

Mixed f-d Metallomesogens with an Extended Rigid Core

Koen Binnemans,^{*,[a]} Katleen Lodewyckx,^[a] Bertrand Donnio,^[b] and Daniel Guillon^[b]**Keywords:** Copper / Lanthanides / Liquid crystals / Metallomesogens / Nickel

The liquid-crystalline behaviour of copper(II) and nickel(II) complexes of a mesogenic Schiff-base ligand derived from *N,N'*-disalicylidene-1,2-phenylenediamine (salophenH₂) and of the corresponding trinuclear mixed copper(II)/lanthanum(III) and nickel(II)/lanthanum(III) complexes was investigated. High-temperature X-ray diffraction studies revealed that both the parent transition metal complexes and the mixed f-d complexes exhibit a hexagonal columnar phase (Col_h) over an extended temperature range. Complex forma-

tion with lanthanum(III) nitrate resulted in an increase of the transition temperatures. The geometrical parameters (lattice parameters and column cross-section) of all the metal complexes are very similar, which indicates that the local organisation in the mesophase is the same despite their structural differences.

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Introduction

Liquid-crystalline metal complexes (metallomesogens) combine the unique properties of both transition metals or rare-earth metals and liquid crystals, and these compounds form an intriguing class of new materials.^[1] In this way, it is, for instance, possible to obtain paramagnetic liquid crystals,^[2] or redox-active liquid crystals.^[3] Nearly all metallic elements of the periodic table have been used to create metallomesogens, but examples of liquid crystals that contain both an f-block metal ion (lanthanide or rare-earth ion) and a d-block metal ion are rare. The first examples of such mixed f-d metallomesogens have been reported recently (Figure 1).^[4] A copper(II) complex of a mesogenic 2,2'-*N,N'*-bis(salicylidene)ethylenediamine (salen) derivative was used to form adducts with lanthanide(III) nitrates. This work was extended further in the sense that the copper(II) was replaced by nickel(II) (Figure 2), and that the influence of the chain length on the transition temperatures was investigated.^[5] In all cases, both the parent transition metal complexes and the f-d complexes exhibit a hexagonal columnar mesophase (Col_h). It should be noticed that salen-type ligands are of interest not only for preparing liquid-crystalline f-d complexes, but also for the design of many types of liquid-crystalline transition metal complexes.^[6] The salen-type Schiff-base complexes are important as catalysts.^[7]

In this paper we have modified the salen-type ligand that has been used in earlier studies on f-d metallomesogens by replacing 1,2-ethylenediamine as the linking group by 1,2-diaminobenzene. The aim of the work was to investigate the influence of the extension of the rigid part of the core of the ligand on the thermal behaviour of the ligand and metal complexes. Four mesogenic metal complexes were prepared, namely two copper(II) and nickel(II) ones, and two binuclear copper(II)/lanthanum(III) and nickel(II)/lanthanum(III) complexes (Figure 3). Their liquid-crystalline properties were investigated in detail by X-ray diffraction.

Results and Discussion

The synthesis of the *N,N'*-disalicylidene-1,2-phenylenediamine (salophenH₂) Schiff-base ligand (H₂L) and of the metal complexes is outlined in Scheme 1. The first step is the synthesis of 3,4,5-tris(tetradecyloxy)benzoic acid by alkoxylation of 3,4,5-trihydroxybenzoic acid ethyl ester (Williamson ether synthesis), followed by formation of the free acid by saponification of the ethyl ester and acidification of the carboxylate salt. The second step is the coupling of 3,4,5-tris(tetradecyloxy)benzoic acid to the 4-position of 2,4-dihydroxybenzaldehyde by an ester bond (with DCC, DMAP). The aldehyde was transformed into the Schiff-base ligand by condensation with 1,2-diaminobenzene in toluene. The water formed during the condensation reaction was removed azeotropically in a Dean–Stark trap. The copper(II) complex CuL and the nickel(II) complex NiL were formed by reaction between the Schiff-base H₂L and copper(II) acetate monohydrate and nickel(II) acetate tetrahydrate, respectively, in a methanol/chloroform mixture.

[a] Katholieke Universiteit Leuven, Department of Chemistry, Celestijnenlaan 200F, 3001 Leuven, Belgium
Fax: +32-16-327-992
E-mail: Koen.Binnemans@chem.kuleuven.ac.be

[b] Institut de Physique et Chimie des Matériaux de Strasbourg – Groupe Matériaux Organiques, UMR 7504 CNRS-Université Louis Pasteur,
B. P. 43, 23 rue du Loess, 67034 Strasbourg, Cedex 2, France

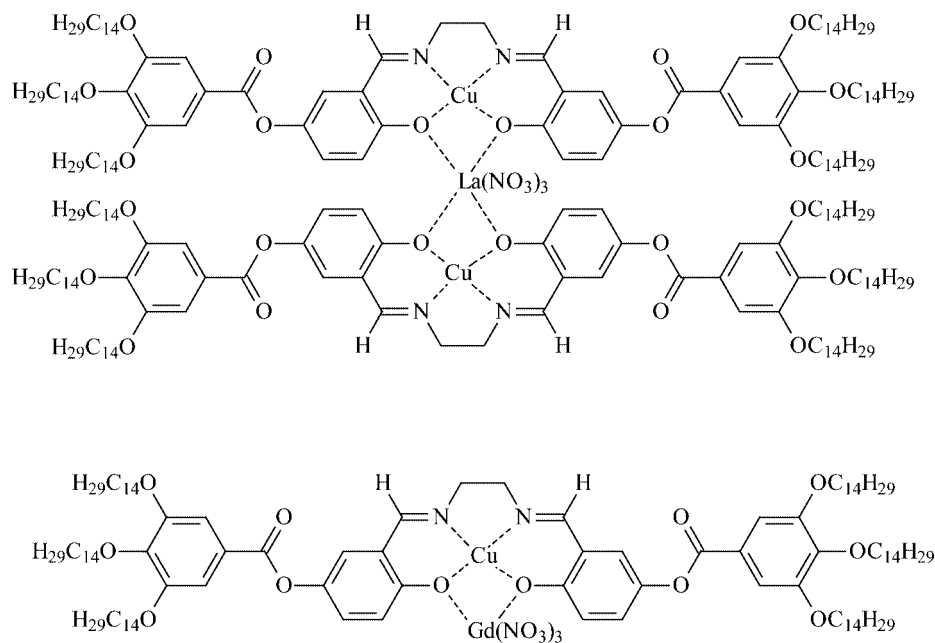


Figure 1. Structure of the first examples of mixed f-d metallomesogens, a trinuclear copper(II)/lanthanum(III) complex and a dinuclear copper(II)/gadolinium(III) complex with a mesogenic 2,2'-N,N'-bis(salicylidene)ethylenediamine (salen) ligand, reported by Binnemans et al.^[4]

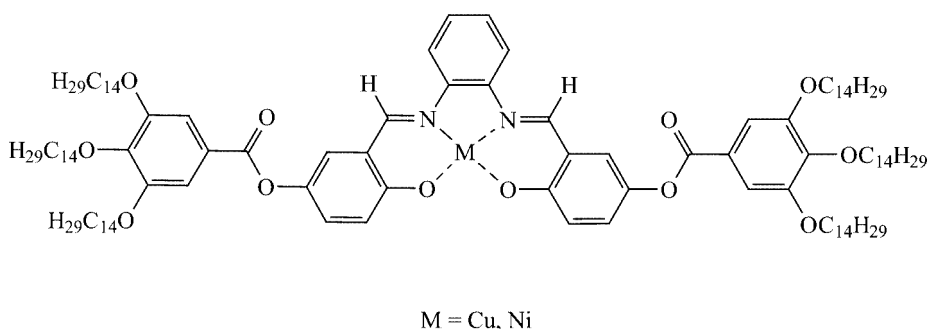


Figure 2. Structure of the copper(II) complex CuL (M = Cu) and the nickel(II) complex NiL (M = Ni) of the mesogenic N,N'-disalicylidene-1,2-phenylenediamine (salophenH₂) ligand.

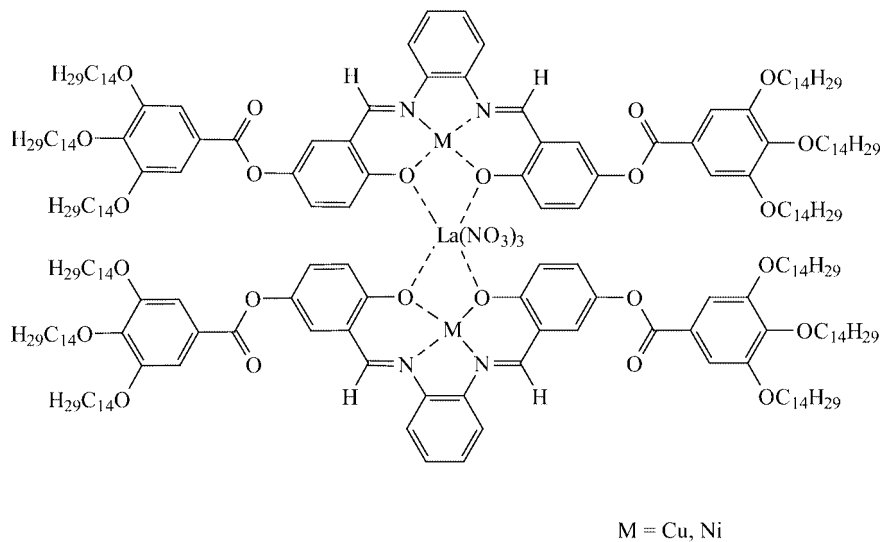
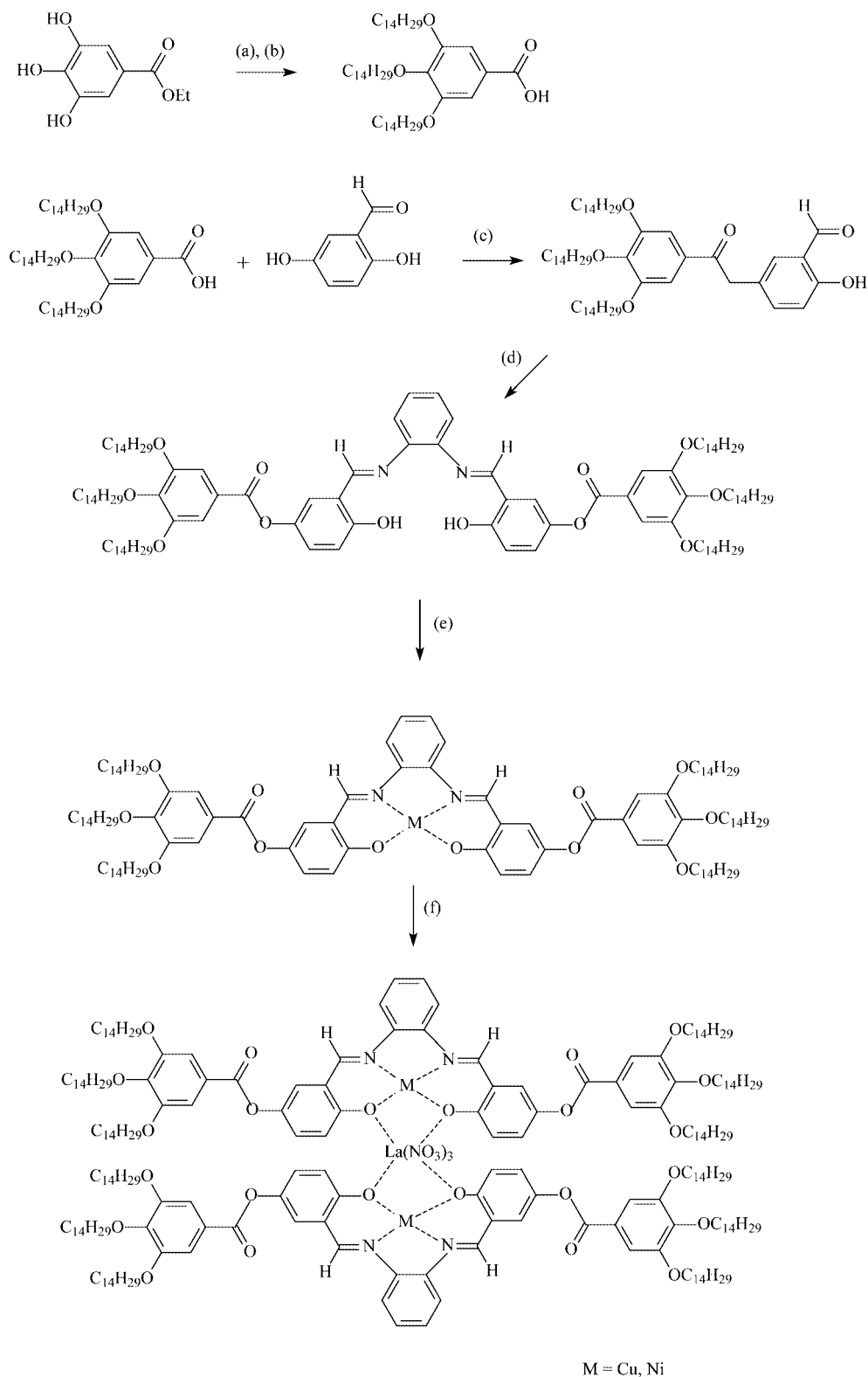


Figure 3. Structure of the trinuclear copper(II)/lanthanum(III) complex CuLaL (M = Cu) and of the trinuclear nickel(II)/lanthanum(III) complex NiLaL (M = Ni) of the mesogenic N,N'-disalicylidene-1,2-phenylenediamine (salophenH₂) ligand H₂L described in this study.



Scheme 1. Synthesis of the Schiff-base ligand H_2L and of the metal complexes. Reagents and conditions: (a) RBr (3 equiv.), K_2CO_3 (6 equiv.), TBAB (phase-transfer catalyst), methyl isobutyl ketone, reflux overnight; (b) NaOH, ethanol, reflux for 4 h; acidification with dilute HCl solution; (c) DCC, DMAP, dichloromethane, 24 h at room temp.; (d) 1,2-diaminobenzene (1/2 equiv.), glacial acetic acid (catalyst), toluene, Dean–Stark trap, 3 h at reflux; (e) $Cu(OOCCH_3)_2 \cdot H_2O$ ($M = Cu$) or $Ni(OOCCH_3)_2 \cdot 4H_2O$ ($M = Ni$) (1 equiv.), methanol/chloroform, reflux overnight; (f) $La(NO_3)_3 \cdot 6H_2O$, acetone, room temp., 24 h.

The acetate ions act as the base to deprotonate the Schiff-base ligand. The copper(II)/lanthanum(III) complex CuLaL and the nickel(II)/lanthanum(III) complex NiLaL were prepared by reaction between the copper(II) complex CuL or the nickel(II) complex NiL and lanthanum(III) nitrate hexahydrate in acetone. The metal complexes were characterised by infrared spectroscopy and by elemental analysis. Both the copper(II)/lanthanum(III) complex CuLaL and the nickel(II)/lanthanum(III) complex NiLaL were found to be trinuclear species consisting of two transition metal ions [either copper(II) or nickel(II)] and one trivalent lanthanum(III) ion per molecule. The nitrogen content of the lanthanum(III) complexes, as determined by CHN microanalysis, is lower than the calculated value. This discrepancy is due to a systematic error in the CHN microanalysis procedure, and can be attributed to incomplete reduction of the nitrates to dinitrogen gas or to the formation of lanthanum(III) oxonitrides. Although we could not obtain single crystals of our compounds for X-ray structure determination, we can nevertheless deduce some data about the coordination sphere of the lanthanum(III) by referring to the crystal structures published by Kahn et al. for f-d complexes of the salen ligand.^[8] The three nitrate ions are coordinated to the lanthanum(III) ion in a bidentate fashion. The coordination number of lanthanum(III) is ten, with six oxygen atoms from the three nitrate groups and four oxygen atoms of the two copper(II) salophen complexes [or nickel(II) salophen complexes]. The coordination polyhedron of lanthanum(III) is irregular and cannot be approximated by a highly symmetric coordination polyhedron. Coordination number 10 is rather unusual for lanthanide complexes, but can in this case be achieved by the small bite angle of the nitrate groups.

The Schiff-base ligand H₂L is not mesomorphic, and it melts directly to an isotropic liquid at 67 °C. All the metal complexes are enantiotropic liquid crystals. The mesophases were studied by polarising optical microscopy (POM), differential scanning calorimetry (DSC) and by high-temperature X-ray diffraction. For the copper and nickel complex, a typical texture of a hexagonal columnar mesophase (Col_h) could be seen by POM upon slow cooling from the isotropic liquid. Only atypical textures were observed for the trinuclear complex CuLaL and for the trinuclear complex NiLaL, so that it was impossible to determine the mesophase unambiguously by POM. Observation of the texture of the copper/lanthanum complex CuLaL was also hampered by the thermal decomposition of the complex in the mesophase before the clearing point was reached. Just above the melting point, the viscosity of the samples is quite high, but the viscosity decreases with increasing temperature. Because no well-resolved DSC curves could be recorded (a problem also encountered in the past for similar complexes),^[4] no enthalpy data could be obtained. These problems could be due to the high viscosity of the complexes, and to the low crystallinity of the complexes in the solid phase. The transition temperatures of the complexes were determined by optical microscopy, and the values are given in Table 1.

Table 1. Transition temperatures and mesophase behaviour of the Schiff-base complexes.

Complex	Transition temperatures [°C] ^[a]
CuL	Col _{ho} · 39 · Col _h · 170 · I
NiL	Cr · 40 · Cr' · 61 · Col _h · 133 · I
CuLaL	Cr · 69 · Col _h · 192 · dec.
NiLaL	Cr · 85 · Col _h · 218 · I

[a] Cr, Cr': crystalline phases; Col_{ho}: ordered hexagonal columnar phase; Col_h: hexagonal columnar phase; I: isotropic liquid; dec.: decomposition.

Table 2. Characteristic X-ray data of the copper(II) complex CuL.

Temperature [°C]	$d_{\text{measd.}}$ [Å]	[<i>h</i> <i>k</i>]	$d_{\text{calcd.}}$ [Å]	Mesophase and parameters
30	37.3	[10]	37.25	Col _{ho} $a = 43 \text{ Å}$ $s = 1600 \text{ Å}^2$
	21.4	[11]	21.5	
	18.7	[20]	18.6	
	10.3	<i>h</i> 1		
	4.5	<i>h</i> 2		
50	4.1	<i>s</i> 1		Col _h $a = 43.65 \text{ Å}$ $s = 1650 \text{ Å}^2$
	37.8	[10]	37.8	
	21.8	[11]	21.8	
	9.8	<i>h</i> 1		
	4.5	<i>h</i> 2		
100	37.05	[10]	36.9	Col _h $a = 42.6 \text{ Å}$ $s = 1570 \text{ Å}^2$
	21.35	[11]	21.3	
	18.3	[20]	18.45	
	9.8	<i>h</i> 1		
	4.5	<i>h</i> 2		

Table 3. Characteristic X-ray data of the nickel(II) complex NiL at 100 °C.

$d_{\text{measd.}}$ [Å]	[<i>h</i> <i>k</i>]	$d_{\text{calcd.}}$ [Å]	Mesophase and parameters
36.5	[10]	36.5	Col _h $a = 42.15 \text{ Å}$ $s = 1540 \text{ Å}^2$
21.05	[11]	21.1	
9.4	<i>h</i> 1		
4.5	<i>h</i> 2		

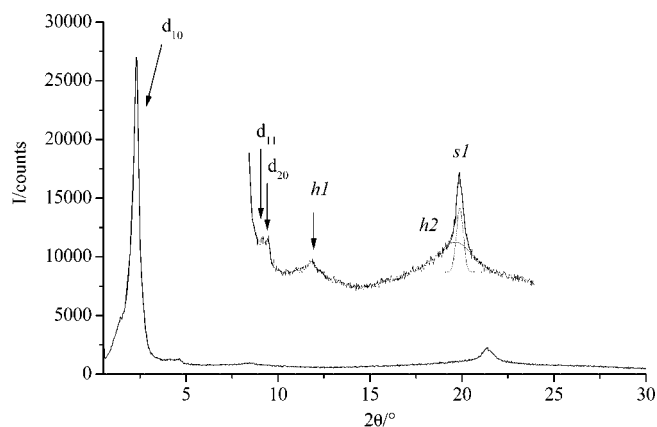
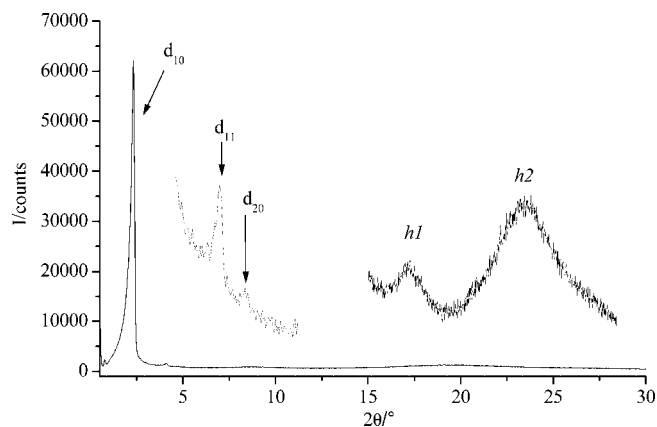
Table 4. Characteristic X-ray data of the copper(II)/lanthanum(III) complex CuLaL.

Temperature [°C]	$d_{\text{measd.}}$ [Å]	[<i>h</i> <i>k</i>]	$d_{\text{calcd.}}$ [Å]	Mesophase and parameters
100	36.7	[10]	36.7	Col _h $a = 42.4 \text{ Å}$ $s = 1560 \text{ Å}^2$
	21.2	[11]	21.2	
	18.4	[20]	18.35	
	9.8	<i>h</i> 1		
	4.5	<i>h</i> 2		
150	35.7	[10]	35.6	Col _h $a = 41.1 \text{ Å}$ $s = 1460 \text{ Å}^2$
	20.5	[11]	20.55	
	17.8	[20]	17.8	
	13.5	[21]	13.45	
	9.9	<i>h</i> 1		
	4.5	<i>h</i> 2		

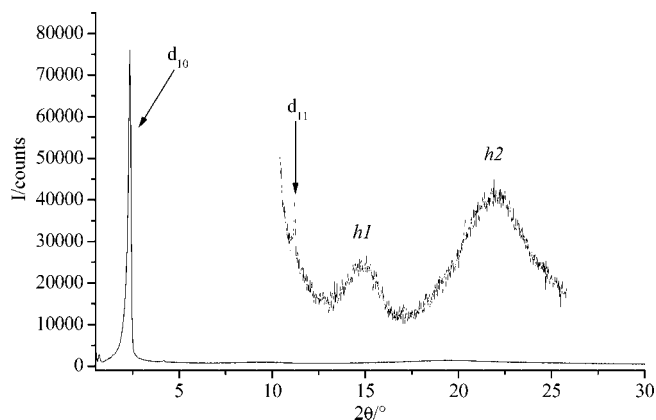
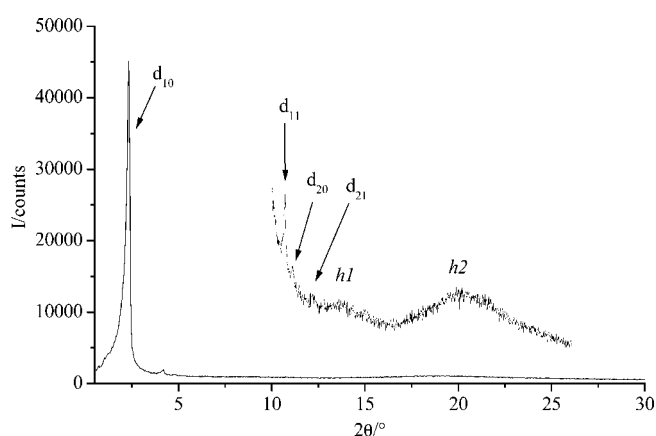
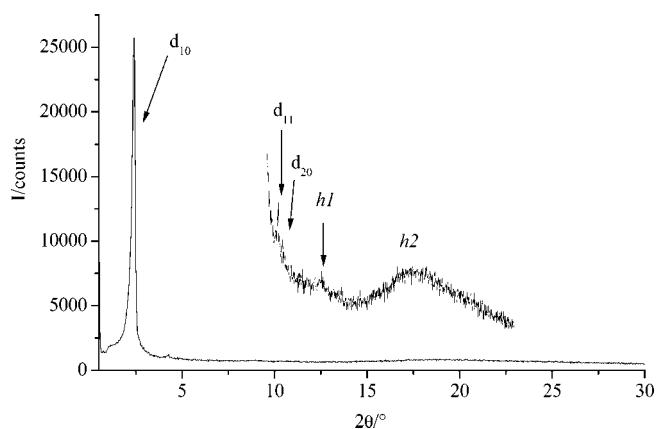
The mesophase behaviour of the metal complexes was studied in detail by temperature-dependent X-ray measurements. The results of the X-ray measurements are summarised in Tables 2–5. X-ray patterns of the complexes are shown in Figures 4–8. X-ray diffractograms were recorded at 30 °C (Figure 4) and at 50 °C and 100 °C (Figure 5) for

Table 5. Characteristic X-ray data of the nickel(II)/lanthanum(III) complex NiLaL.

Temperature [°C]	$d_{\text{measd.}}$ [Å]	$[hk]$	$d_{\text{calcd.}}$ [Å]	Mesophase and parameters
100	36.8	[10]	36.65	Col_h
	21.15	[11]	21.15	$a = 42.3 \text{ Å}$
	18.25	[20]	18.3	$s = 1550 \text{ Å}^2$
	9.8	$h1$		
	4.5	$h2$		
	3.8	$h3$		
150	35.5	[10]	35.45	Col_h
	20.45	[11]	20.45	$a = 40.9 \text{ Å}$
	17.7	[20]	17.7	$s = 1450 \text{ Å}^2$
	9.4	$h1$		
	4.5	$h2$		

Figure 4. X-ray diffractogram of the copper(II) complex CuL at 30 °C in the Col_{ho} phase.Figure 5. X-ray diffractogram of the copper(II) complex CuL at 100 °C in the Col_h phase.

the mononuclear copper complex CuL (Table 2) and the mononuclear nickel complex NiL (Table 3), and at 100 °C (Figure 6) and 150 °C for the trinuclear copper/lanthanum complex CuLaL (Figure 7, Table 4) and the nickel/lanthanum complex NiLaL (Figure 8, Table 5). All the samples gave similar X-ray patterns when the experiments were performed in the mesomorphic temperature ranges. The X-ray patterns consist of: (a) a diffuse scattering halo ($h2$) in the wide-angle region, corresponding to the liquid-like disorder

Figure 6. X-ray diffractogram of the nickel(II) complex NiL at 100 °C in the Col_h phase.Figure 7. X-ray diffractogram of the copper(II)/lanthanum(III) complex CuLaL at 150 °C in the Col_h phase.Figure 8. X-ray diffractogram of the nickel(II)/lanthanum(III) complex NiLaL at 150 °C in the Col_h phase.

of the aliphatic chains and rigid parts, at about 4.5 Å, a distance corresponding to $\langle h \rangle$ in Figure 9 and Figure 10; (b) another, slightly less intense diffuse band ($h1$) seen at about 9.4 Å, which could be an indication of a dimeric structure; and (c) three or four sharp, intense reflections in the small-angle region, with the reciprocal spacings in the

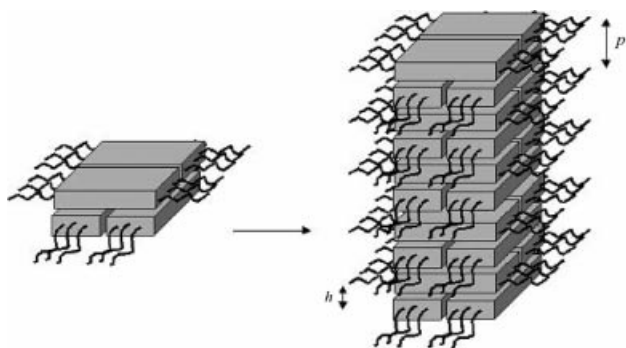


Figure 9. Molecular organisation of the copper(II) complex CuL and the nickel(II) complex NiL within the hexagonal columnar mesophase. The columnar repeat unit is given by $\langle p \rangle$, and $\langle h \rangle$ is the average distance between adjacent molten chains.

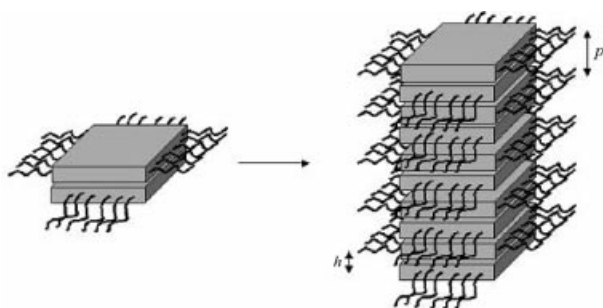


Figure 10. Molecular organisation of the copper(II)/lanthanum(III) complex CuLaL and the nickel(II)/lanthanum(III) complex NiLaL within the columnar mesophase. The columnar repeat unit is given by $\langle p \rangle$, and $\langle h \rangle$ is the average distance between adjacent molten chains.

ratio 1, $\sqrt{3}$, $\sqrt{4}$ and $\sqrt{7}$, corresponding to the indexation $[hk] = [10]$, $[11]$, $[20]$ and $[21]$, respectively. Such features are characteristic of a two-dimensional hexagonal packing of columns; that is, a hexagonal columnar mesophase (Col_h). The phase is disordered since there is no long-range correlation order within the columns, as evident from the absence of a sharp peak in the wide-angle region which would have corresponded to a more regular stacking along the columnar axis. However, for the copper complex CuL, an ordered columnar mesophase with a hexagonal symmetry (Col_{ho}) was observed below 39 °C. A typical feature in the X-ray diffractogram of this compound is the sharp diffraction peak in the wide-angle region at about 4.1 Å (Figure 4). The corresponding nickel complex NiL is crystalline at temperatures below 61 °C, and undergoes a crystal-to-crystal transition between 35 and 40 °C. The crystalline character of this compound at ambient temperature is evident from the large number of sharp diffraction peaks in the X-ray pattern. For the complexes in the mesophase, the lattice parameter, a , and the column cross-section, s , were determined from the positions of the small angle diffraction peaks (10), (11), (20) and (21): $a = 2/\sqrt{3}[1/4(d_{10} + \sqrt{3}d_{11} + 2d_{20} + \sqrt{7}d_{21})]$ and $s = 2/\sqrt{3}[1/4(d_{10} + \sqrt{3}d_{11} + 2d_{20} + \sqrt{7}d_{21})]$.^[2] The lattice parameters and thus the column cross-sections of all the complexes are very similar. This similarity indicates that the local organisation within the mesophase

is the same despite the structural differences. The hexagonal symmetry of the columnar mesophase implies that the hard, columnar core (i.e. the aromatic part) is cylindrical, and that therefore the cross-section is circular. These hard columns are separated from one another by the liquid paraffinic continuum formed by the molten alkyl chains. As far as the copper(II)/lanthanum(III) complex and the nickel(II)/lanthanum(III) complex are concerned, they both have a square-like shape, and it is evident that upon their stacking into an alternated orthogonal fashion (the halo hI corresponds to a dimerisation, as shown in Figure 10) and due to the free rotation around the molecular axis, the apparent cross-sections of the columns will appear circular, thus satisfying the geometrical requirements for the formation of the Col_h phase. Moreover, and in agreement with this proposal, we found that the molecular volume considering a density of about 0.95 for each of these two trinuclear compounds corresponds exactly to the volume of one single columnar stratum with a thickness of 4.5–4.6 Å (or to two complexes per portion of column with a thickness of 9.2–9.4 Å). Note also that the molecular dimensions of these two mixed complexes are in good agreement with the lattice parameters of the Col_h phases, and thus they both lie almost flat in the 2D hexagonal lattice. However, due to the lath-like shape of the mononuclear copper and nickel complexes, it is probable that they initially associate into face-to-face dimers (Figure 9) approximating the shape of a large, flat square, which then self-organise into columns as for the trinuclear complexes (Figure 9). Again, considering a density close to unity for both the complexes, it was found that the volume of a portion of column with a thickness of about 4.5 Å can contain two mononuclear complexes, and that the length of the complexes is of the order of the diameter of the columns, a . As mentioned above, the presence of the halo hI at about 9.4 Å in the X-ray patterns of the mesophases indicates that the repeating unit along the columnar axis $\langle p \rangle$ is about twice the thickness of the complexes. Thus, the repeating unit is formed by two molecules stacked on top of each other (dimeric structures). A similar behaviour was also observed for the copper complexes and for the copper/lanthanide complexes we reported previously.^[4] Structural models for the different metal complexes are shown in Figures 9 and 10. Moreover, a change of the linking group formed by ethylenediamine to a linking group formed by 1,2-diaminobenzene in the Schiff-base ligand has a negligible effect on the column lattice parameters. This is not unexpected due to the presence of the (disordered) alkyl chains in the complexes in the mesophase. For all the complexes, the lattice parameter a decreases with increasing temperature.

Conclusions

We have studied the mesophase behaviour of new copper(II), nickel(II), copper(II)/lanthanum(III) and nickel(II)/lanthanum(III) complexes of a mesogenic N,N' -disalicylidene-1,2-phenylenediamine (salophenH₂) ligand. The cop-

per(II)/lanthanum(III) and the nickel(II)/lanthanum(III) complexes are trinuclear. All the Schiff-base complexes exhibited a hexagonal columnar mesophase (Col_h). X-ray diffraction measurements on samples in the mesophase indicate that the geometrical parameters (lattice parameter *a* and column cross-section *s*) are largely independent of the type of complex. This indicates that the structure of the mesophase is more or less identical for all the complexes. The metal has an influence on the transition temperatures: higher transition temperatures have been observed, and thus a substantial enhancement of the mesophase stability achieved, for the mixed f-d metallomesogens with respect to the parent transition metal complexes. The replacement of the ethylenediamine linking group present in the first type of mixed f-d metallomesogens by a more rigid 1,2-diaminobenzene linking group has a negligible influence on the mesophase behaviour. This is probably due to the fact that the linking group constitutes only a small part of the total ligand. One could have expected that the enhanced π - π stacking of the aromatic cores would result in higher transition temperatures, but this is not the case. The difference between the copper(II) or nickel(II) ion as the d-block metal is reflected in the thermal stability of the f-d complexes, in the sense that the nickel(II)/lanthanum(III) complex is thermally more stable than the corresponding copper(II)/lanthanum(III) complex. The presence of the rigid linking group is not a sufficient condition to induce a mesophase in the Schiff-base ligand.

Experimental Section

Equipment: The NMR spectra were recorded on a Bruker Avance 300 spectrometer (operating at 300 MHz) and Bruker AMX-400 (operating at 400 MHz), using CDCl₃ as solvent and tetramethylsilane (TMS) as internal standard. FTIR spectra were recorded on a Bruker IFS-66 spectrometer, using the KBr pellet method. Elemental analyses were obtained on a CE-Instrument EA-1110 elemental analyzer. The optical textures of the mesophases were observed with an Olympus BX60 polarizing microscope equipped with a LINKAM THMS600 hot stage and a LINKAM TMS93 programmable temperature-controller. DSC traces were recorded with a Mettler-Toledo DSC821e module. The XRD patterns were obtained with two different experimental set-ups, and in all cases the powdered sample was filled in Lindemann capillaries of 1 mm diameter. A linear monochromatic Cu-K α_1 beam ($\lambda = 1.5405 \text{ \AA}$) obtained with a sealed-tube generator (900 W) and a bent quartz monochromator were used (both generator and monochromator were manufactured by Inel). One set of diffraction patterns was registered with a curved counter Inel CPS 120, for which the sample temperature was controlled to within $\pm 0.05 \text{ }^\circ\text{C}$; periodicities up to $60 \text{ \AA}$ could be measured. The other set of diffraction patterns was registered on an Image Plate detector. The cell parameters were calculated from the position of the reflection at the smallest Bragg angle, which is in all cases the most intense. Periodicities up to $90 \text{ \AA}$ could be measured, and the sample temperature was controlled to within $\pm 0.3 \text{ }^\circ\text{C}$.

Synthesis of 3,4,5-Tris(tetradecyloxy)benzoic Acid: Ethyl 3,4,5-trihydroxybenzoate (19.82 g, 0.1 mol), K₂CO₃ (55.28 g, 0.4 mol), tetrabutylammonium bromide (TBAB, phase-transfer catalyst) (1.61 g, 5 mmol), methyl isobutyl ketone (MIBK; 300 mL) and 1-bromo-

tetradecane (97.05 g, 0.35 mol), were added to a 1 L flask. Subsequently, the reaction mixture was heated to reflux and stirred overnight. The brown mixture was cooled below $100 \text{ }^\circ\text{C}$, and water (300 mL) was added. The aqueous layer was separated, and the organic layer was washed with water (300 mL), dilute HCl solution (300 mL, 1.0 M), and water (300 mL) again. The solvent was removed on a rotary evaporator and the crude product was recrystallised from acetone. This product was redissolved in an ethanol solution of NaOH (16 g, 0.4 mol) and refluxed for 4 h. After allowing the solution to cool to room temperature, the reaction mixture was poured into cold water. The solution was acidified with dilute HCl. The precipitate was filtered off, recrystallised from dichloromethane and washed with ethanol. Yield: 57% (42.67 g), m.p. $72 \text{ }^\circ\text{C}$. C₄₉H₉₀O₅ (749.24): calcd. C 77.52, H 11.95; found C 77.56, H 11.98. ¹H NMR (CDCl₃, 300 MHz): $\delta = 0.89$ (t, *J* = 6.3 Hz, 9 H, CH₃), 1.27 (m, 30 H, CH₂), 1.49 (m, 6 H, CH₂CH₂CH₂O), 1.81 (m, 6 H, CH₂CH₂O), 4.03 (t, *J* = 6.3 Hz, 6 H, CH₂O), 7.33 (s, 2 H, H-aryl) ppm.

Synthesis of 3-Formyl-4-(hydroxyphenyl)-3,4,5-tris(tetradecyloxy)benzoate: 3,4,5-Tris(tetradecyloxy)benzoic acid (15.16 g, 0.02 mol) and DMAP [4-(dimethylamino)pyridine; 0.24 g, 0.002 mol] were added to a mixture of 2,5-dihydroxybenzaldehyde (2.76 g, 0.02 mol) and *N,N'*-dicyclohexylcarbodiimide (DCC; 4.60 g, 0.022 mol) in 600 mL of dichloromethane. The solution was stirred at room temperature for 24 h. The precipitated *N,N'*-dicyclohexylurea was filtered off and washed with a saturated NaHCO₃ solution (2 $\times$ 400 mL) and water (2 $\times$ 400 mL). The aqueous layers were back-extracted with dichloromethane (200 mL). The combined organic layers were dried with MgSO₄ and the solvent was removed on a rotary evaporator. The crude compound was purified by column chromatography (silica, with dichloromethane as the eluent). Yield: 49% (8.60 g), m.p. $70 \text{ }^\circ\text{C}$. C₅₆H₉₄O₇ (879.34): calcd. C 76.49, H 10.77; found C 76.56, H 10.83. ¹H NMR (CDCl₃, 300 MHz): $\delta = 0.89$ (t, 9 H, CH₃), 1.27 (m, 30 H, CH₂), 1.50 (m, 6 H, CH₂CH₂CH₂O), 1.81 (m, 6 H, CH₂CH₂O), 4.05 (t, 6 H, CH₂O), 7.06 (d, *J*_o = 9.15 Hz, 1 H, H-aryl), 7.36 (dd, *J*_o = 8.91, *J*_m = 2.84 Hz, 1 H, H-aryl), 7.40 (s, 2 H, H-aryl), 7.44 (d, *J*_m = 2.58 Hz, 1 H, H-aryl), 9.89 (s, 1 H, CHO), 10.96 (s, 1 H, OH) ppm.

Synthesis of the Schiff-Base Ligand H₂L: 1,2-Diaminobenzene (54 mg, 0.5 mmol) and five drops of glacial acetic acid (as the catalyst) were added to a solution of 3-formyl-4-(hydroxyphenyl)-3,4,5-tris(tetradecyloxy)benzoate (0.88 g, 0.001 mol) in 150 mL of toluene. The mixture was heated for 3 h at reflux, and the water formed by the reaction was removed azeotropically (Dean-Stark trap). After allowing the solution to cool to room temperature, the solvent was removed under reduced pressure. The crude product was purified by recrystallisation from absolute ethanol. Yield: 92% (0.84 g), m.p. $67 \text{ }^\circ\text{C}$. C₁₁₈H₁₉₂N₂O₁₂ (1830.8): calcd. C 77.41, H 10.57, N 1.53; found C 76.94, H 10.57, N 1.54. IR (KBr): $\tilde{\nu} = 1626 \text{ cm}^{-1}$ (C=N), 1209 (C=O). ¹H NMR (CDCl₃, 300 MHz): $\delta = 0.88$ (t, 18 H, CH₃), 1.26 (m, 60 H, CH₂), 1.49 (m, 12 H, CH₂CH₂CH₂O), 1.83 (m, 12 H, CH₂CH₂O), 4.05 (m, 16 H, CH₂O, CH₂N), 6.80–7.45 (m, 14 H, H-aryl), 8.59 (s, 2 H, CH=N), 13.01 (s, 2 H, OH) ppm.

Synthesis of the Copper(II) Complex CuL: A hot solution of copper(II) acetate monohydrate, (30 mg, 0.15 mol) in methanol was added dropwise to a hot solution of the Schiff-base ligand H₂L (0.24 g, 0.13 mmol) in chloroform. The reaction mixture was refluxed overnight. After allowing the solution to cool to room temperature, the solvent was removed under reduced pressure. The crude product was crystallised from ethyl acetate, washed with methanol and dried in vacuo. Yield: 92% (0.23 g). IR (KBr): $\tilde{\nu} =$

1606 cm^{-1} (C=N), 1203 (C–O). $\text{C}_{118}\text{H}_{196}\text{CuN}_2\text{O}_{15}$ (1892.3): calcd. C 72.82, H 10.15, N 1.44; found C 72.88, H 10.24, N 1.49.

Synthesis of the Nickel(II) Complex NiL: A hot solution of nickel(II) acetate tetrahydrate (70 mg, 0.28 mmol) in methanol was added dropwise to a hot solution of the Schiff-base ligand H_2L (0.46 g, 0.25 mmol) in chloroform. The reaction mixture was heated at reflux temperature overnight. After allowing the solution to cool to room temperature, the solvent was removed under reduced pressure. The crude product was crystallised from ethyl acetate, washed with methanol and dried in vacuo. Yield: 86% (0.41 g). IR (KBr): $\tilde{\nu}$ = 1606 cm^{-1} (C=N), 1203 (C–O). $\text{C}_{118}\text{H}_{190}\text{N}_2\text{NiO}_{12}$ (1887.5): calcd. C 75.09, H 10.15, N 1.48; found C 74.68, H 10.28, N 1.50.

Synthesis of the Copper(II)/Lanthanum(III) Complex CuLaL: A solution of lanthanum(III) nitrate hexahydrate (0.048 g, 0.11 mmol) in acetone was added to a solution of the copper complex CuL (0.189 g, 0.1 mmol) in acetone. The reaction mixture was stirred at room temperature for 24 h. The precipitate was filtered off, washed with cold methanol and dried in vacuo. Yield: 40% (164 mg). IR (KBr): $\tilde{\nu}$ = 1629 cm^{-1} (C=N), 1306 (C–O). $\text{C}_{236}\text{H}_{380}\text{Cu}_2\text{LaN}_7\text{O}_{33}$ (4105.59): calcd. C 68.98, H 9.33, N 2.39; found C 68.45, H 9.23, N 1.97.

Synthesis of the Nickel(II)/Lanthanum(III) Complex NiLaL: A solution of lanthanum(III) nitrate hexahydrate (0.048 g, 0.11 mmol) in acetone was added to a solution of the nickel complex NiL (0.189 g, 0.1 mmol) in acetone. The reaction mixture was stirred at room temperature for a period of 24 h. The precipitate was filtered off, washed with cold methanol and dried in vacuo. Yield: 46% (187 mg). IR (KBr): $\tilde{\nu}$ = 1627 cm^{-1} (C=N), 1205 (C–O). $\text{C}_{236}\text{H}_{380}\text{LaN}_7\text{Ni}_2\text{O}_{33}$ (4095.60): calcd. C 69.15, H 9.35, N 2.39; found C 69.23, H 9.36, N 2.06.

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