Mixed Copper–Lanthanide Metallomesogens

Koen Binnemans,*[a] Katleen Lodewyckx,[a] Bertrand Donnio,[b] and Daniel Guillon[b]

Abstract: This paper describes the first examples of heteropolynuclear metallomesogens that contain both a transition metal ion and a trivalent lanthanide ion. Adducts were formed between a mesomorphic [Cu(salen)] complex (salen = 2,2′-*N*,*N*′-bis(salicylidene)ethylenediamine) with six terminal tetradecyloxy chains and a lanthanide nitrate (Ln = La, Gd). Different stoichiometries were found, depending on the lanthanide ion: a trinuclear copper–lanthanum–copper complex [La$(NO_3)_3$\{Cu(salen)\}$_2$] and a binuclear copper-gadolinium complex [Gd$(NO_3)_3$Cu(salen)]. The compounds exhibit a hexagonal columnar mesophase (Col_H) over a wide temperature-range with rather low melting temperatures. Although the clearing point could be observed for the parent [Cu(salen)] complex, the mixed f–d complexes decomposed in the high-temperature part of the mesomorphic domain before clearing. On the basis of X-ray diffraction measurements and molecular modelling, a structural model for the mesophase of the metal complexes is proposed.

Keywords: copper · lanthanides · liquid crystals · metallomesogens · supramolecular chemistry

Introduction

During recent years, considerable research effort has been invested in the design of new metal-containing liquid crystals (*metallomesogens*) with the aim of combining the unique properties of anisotropic fluids (anisotropy of physical properties and fast orientational response to external fields) with the specific properties of metals (magnetic, electronic).[1] Furthermore, metals offer multiple structural possibilities for novel molecular architectures, which in turn may lead to new types of molecular organisations or mesophases. For example, mesomorphism has been achieved in nonconventional metal complexes, with octahedral,[2] square-antiprismatic,[3] trigonal-bipyramidal[4] and tetrahedral[5] coordination geometry. Recently, the synthesis of mesomorphic metallacrowns,[6] butterfly compounds,[7] metallodendrimers[8] and polynuclear systems[9] opened up the field for the construction of original structures able to contain a large number of metallic centres.

Liquid crystals incorporating paramagnetic metal ions are of particular interest in the sense that they can be switched by weak external magnetic fields and can find new applications in the display and communication technologies. Examples of such paramagnetic metal ions include Cu^{II} ,[10] oxovanadium,[11] and the trivalent lanthanide ions.[12]

Although several mixed f–d complexes have been synthesised and their magnetic behaviour studied in detail,[13] there is still no report on heteropolynuclear metallomesogens that contain both a transition metal ion and a lanthanide (rare-earth) ion. Such mixed f–d metallomesogens could represent an intriguing new class of materials, since they combine specific magnetic interactions of f–d coordination compounds (such as magnetic exchange interactions) with the properties of liquid crystals. Furthermore, from a materials processing point of view, such f–d metallomesogens could be advantageous because of the strong tendency of the lanthanide-based metallomesogens to form a glassy state on cooling rather than to crystallise, and thus giving the possibility to freeze-in the mesomorphic order, whereas common non-mesomorphic f–d coordination complexes are obtained as crystalline powders.

In this paper, we report on the structural design and on the thermal behaviour of two novel mixed f–d metallomesogens, based on binuclear or trinuclear copper–lanthanide complexes.

Results and Discussion

To obtain these mixed f–d metallomesogens, our approach consisted of modifying the structures of previously described non-mesomorphic f–d complexes in such a way that a sufficient structural anisotropy was obtained to favour the formation of mesophases. This can be achieved by extending

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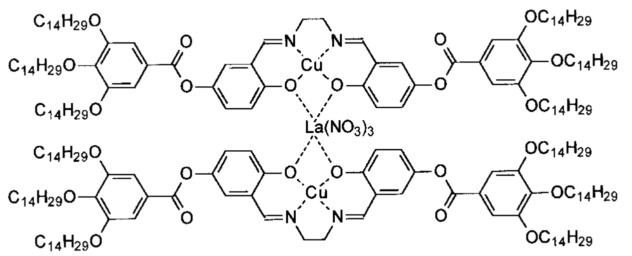
Supporting information for this article is available on the WWW under http://wiley-vch.de/home/chemistry/ or from the author: Experimental details of the synthesis of the salen ligand L and additional X-ray diffraction data.

0947-6539/02/0805-1101 $ 17.50+.50/0

the aromatic parts of the central rigid core on the one hand and to attach long alkyl chains to the extremities of the core complex on the other hand. Recently, Kahn et al. described adducts of lanthanide(III) nitrates with the [Cu(salen)] complex (salen = 2,2′-*N*,*N*′-bis(salicylidene)ethylenediamine).[14] For the light lanthanides, they obtained heterotrinuclear $[Ln(NO_3)_3\{Cu(salen)\}_2]$ compounds, whereas for gadolinium and for the heavier lanthanides heterobinuclear $[Ln(NO_3)_3\{Cu(salen)\}]$ complexes were formed. These types of complexes stood model for the mixed copper–lanthanide metallomesogens described in this paper. Let us recall that suitably designed [Cu(salen)] complexes have yielded mesomorphic properties and have already been previously described,[15] though they structurally differ from the [Cu(salen)] complexes used here as ligand for the mesomorphic f–d complexes.

The synthesis of the substituted salen ligand (L) and of the parent [Cu(salen)] complex **1** is shown in Scheme 1. The copper–lanthanum complex **2** and the copper–gadolinium complex **3** were obtained by reaction of complex **1** with $La(NO_3)_3 \cdot 6H_2O$ and $Gd(NO_3)_3 \cdot 6H_2O$, respectively, in acetone. Two different stoichiometries were found, in agreement with the findings of Kahn et al. for the unsubstituted complexes.[14]

Observation of the textures by polarised-light optical microscopy (POM) showed that the copper complex **1** gives an enantiotropic liquid crystal, melting at 58 °C and clearing at 159 °C. Just above the melting point, despite the high viscosity, flow could nevertheless be induced by pressing the cover slip with a needle. However, on further heating, the viscosity was found to gradually decrease up to the clearing-point temperature, at which the texture appeared totally fluid. On cooling from the isotropic phase, a characteristic texture of a columnar phase was formed (as evidence by the growth of dendritic features). On further cooling, the viscosity gradually increased, and the mesophase could still be observed at room temperature; crystallization was observed at around 0 °C. The copper–lanthanum complex **2** was found by POM to melt at 77 °C into a viscous mesophase with an atypical texture, with the viscosity gradually decreasing upon heating. Around 170 °C a sharp decrease in viscosity was observed. At this temperature, a step in the baseline of the differential scanning calorimetry (DSC) thermogram was detected. Above 220 °C, the compound started to decompose. The copper–gadolinium complex **3** shows a similar mesophase behaviour to that of the complex **2**, with a melting point at 95 °C. The mesophase persisted up to 210 °C, at which the compound started to decompose without clearing.



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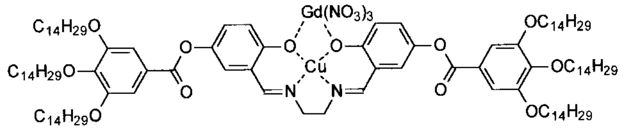

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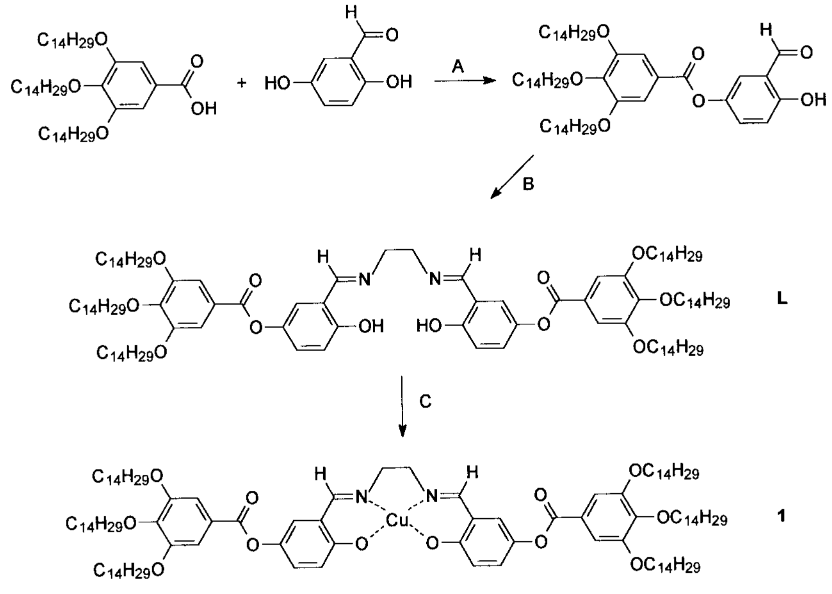
Temperature-dependent X-ray diffraction (XRD) measurements were carried out systematically within the crystalline and the mesomorphic temperature ranges, every 10 °C between 40 and 180 °C for **1**, and between 30 and 200 °C for **2** and **3**. The time exposure was varied from 30 minutes up to 4 hours, depending on the specific reflections being sought (weaker reflections taking longer to expose). The X-ray diagrams were not reproducible on cooling for the two mixed complexes **2** and **3**, due to the fast decomposition on reaching the isotropic liquid, the long-time exposure at high temperature and the X-ray beam. Nevertheless, a good agreement was found between the temperatures determined by POM and by DSC, and those determined by XRD. Practically identical X-ray patterns were obtained for all samples, when the experiments were performed in the mesomorphic temperature



Scheme 1. Synthesis of copper complex **1**, used for adduct formation with the lanthanide nitrates. Reagents and conditions A) DCC, DMAP, DCM, 24 hours at RT; B) ethylene diamine (1/2 equiv), glacial acetic acid (catalyst), toluene, Dean-Stark trap, 3 hours at reflux; C) $Cu(OOCCH_3)_2 \cdot H_2O$ (1 equiv), methanol/chloroform, reflux overnight.

ranges. They consist of: a) a diffuse scattering halo (**II**) in the wide-angle region, which corresponds to the liquidlike disorder of the aliphatic chains and rigid parts, at about 4.5 Å (this distance corresponds to $\langle h\rangle$); b) another, slightly less intense diffuse band (**I**) seen at approximately 9.4 Å, which could be an indication of a dimeric structure, and thus of the periodicity along the column, $\langle p\rangle$; and c) two or three sharp, intense reflections in the small-angle region, with the reciprocal spacings in the ratio 1, $\sqrt{3}$ and $\sqrt{4}$, corresponding to the indexation $[hk] = [10]$, [11] and [20], respectively. Such features are characteristic of a two-dimensional hexagonal packing of columns, that is, to 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 perfect and regular stacking along the columnar axis. Characteristic data have been selected and are reported in Table 1, with, in addition, a representative diffractogram for the copper–lanthanum complex **2** (Figure 1).

Table 1. Characteristic XRD data (at 100 °C) and mesophase behaviour of copper complex **1**, of the mixed copper-lanthanum complex **2** and of the mixed copper-gadolinium complex **3**.

	d_{exptl} [Å]	I[a]	[hk]	d_{calcd} [Å]	Mesophase and parameters[b]
1	36.3	VS	[10]	36.3	Crys 58 Col_H 159 I
	21.1	S	[11]	20.9_5	$a = 41.9$ Å
	18.3	M	[20]	18.1_5	$s = 1521$ Å^2
	9.4	br	–		
	4.5	br	–		
2	36.7	VS	[10]	36.7	Crys 77 Col_H 220 decomp
	21.2	S	[11]	21.2	$a = 42.4$ Å
	18.3	M	[20]	18.3	$s = 1555$ Å^2
	9.4	br	–		
	4.5	br	–		
3	37.2	VS	[10]	37.2	Crys 95 Col_H 210 decomp
	21.4_5	S	[11]	21.5	$a = 42.9_5$ Å
	18.5	M	[20]	18.6	$s = 1598$ Å^2
	9.3	br	–		
	4.6	br	–		

[a] Intensities (I): VS = very strong; S = strong; M = medium; br = broad. [b] Transition temperatures are those obtained from polarised optical microscopy and expressed in °C (in good agreement with those determined by DSC and XRD). Crys = solid, crystalline phase; Col_H = hexagonal columnar mesophase; I = isotropic liquid; decomp = decomposition.

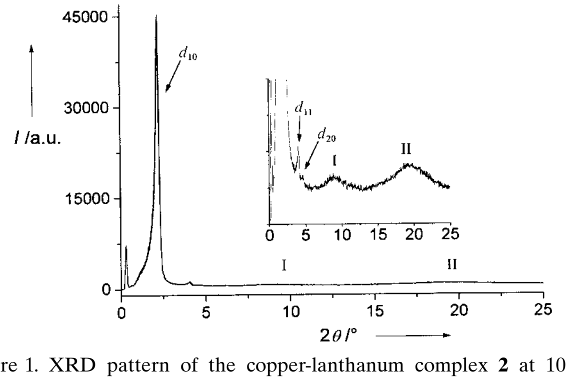


Figure 1. XRD pattern of the copper-lanthanum complex **2** at 100 °C, showing the three sharp small angle reflections, d_{10}, d_{11} and d_{20} and the two diffuse halos (**I** and **II**).

The systematic observation of a hexagonal columnar mesophase for the three compounds as well as the similarity in the measured geometrical parameters suggest strongly that the local organisation within the mesophase is the same despite their structural differences. Furthermore, the formation of what seems likely to be some kind of dimeric structure is also present in the three cases. Only the thermal stability of the compounds in the mesophase is different, probably in relation to the intrinsic structure of each complex. The hexagonal symmetry of the mesophase implies the necessary condition that the hard columnar core (i.e., the aromatic parts) is cylindrical, and, therefore, has a circular cross section (these hard columns are separated from each other by the liquid paraffinic continuum—see Figure 2). To generate such circular cross sections with these large lathlike molecules, the complexes are likely to be self-organised into molecular assemblies (clusters) with a flat, more or less square shape, which will then stack on top of each other to yield the columns. The rotation of these supramolecular slices, and thus of the hard columnar core with respect to the columnar axis, lead to apparent cylindrical rigid columns (with a circular cross section s_0 of diameter ϕ_0), as in the case of classical polycatenar mesogens.[16]

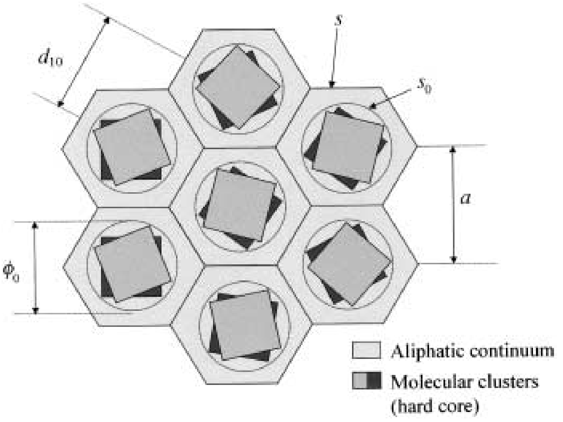


Figure 2. Schematic representation of the columnar periodicity d_{10}, the lattice parameter a ($a = 2d_{10}/\sqrt{3}$), the cross section s ($s = ad_{10} = 2d_{10}^2/\sqrt{3}$) and the apparent hard-core cross section s_0, with diameter ϕ_0.

The number of complexes (or dimers) contained in each molecular cluster can be estimated using the equation for N_{Mol} [Eq. (1) below].[17, 18] In their fluid state, the density of these complexes can be approximated to be close to 1 g cm^{-3}. In this case, the molecular volumes (V_{Mol}) of the three complexes are 3100, 6700, and 3600 Å^3, respectively. Thus, in order to calculate the number of molecules (N_{Mol}) contained within the hexagonal cell of thickness $\langle p\rangle$, one just needs to divide the volume of this cell (V_{cell}) by the molecular volume [Eq. (1)].

$$N_{Mol} = V_{cell}/V_{Mol} = s\langle p\rangle/V_{Mol} = 2\,d_{10}^2\langle p\rangle/(\sqrt{3}\,V_{Mol}) \qquad (1)$$

Here, s corresponds to the cross section of the hexagonal columnar phase and $\langle p\rangle$ to the average columnar repeat unit, both values being determined by X-ray diffraction (from d_{10}, $s = 2d_{10}^2/\sqrt{3}$ and from the centre position of the halo **I**—given by a Lorentzian fit—$\langle p\rangle \cong 9.4$ Å). The results of these calculations showed that on average, slightly more than four copper complexes **1** (two dimers), two copper–lanthanum complexes **2** (one dimer) and four mixed gadolinium–copper complexes **3** (or two dimers) are needed to fill a columnar slice approximately 9.4 Å thick.

A good agreement with a geometrical approach was also found. The approach implies the calculation of an interface Σ associated with the repeat unit along the column (as above the repeat unit is taken as the columnar slice with the thickness $\langle p\rangle$), and to calculate the number of aliphatic chains (N_{ch}) radiating out off this interface. Knowing the number of chains per slice, one can deduce the number of molecules per slice, N_{Mol} (see below). Prior to the calculation, the following parameters have to be defined (Figure 2): ϕ_0 is the diameter of the apparent circular cross section of the hard column core, deduced from the length of the rigid molecular part of the copper complex **1**, l_0 ($l_0 \cong 27$ Å, determined by computer modelling). With the hypothesis of a square cluster, the diameter of s_0 equals its diagonal according to $\phi_0 = l_0\sqrt{2}$). Γ_0 is the hard core perimeter associated to s_O ($\Gamma_0 = \pi\phi_0$), and Σ is the interface of thickness $\langle p\rangle$ ($\Sigma = \pi\phi_0\langle p\rangle$). From the average distance between adjacent molten chains, $\langle h\rangle$, the cross-section area of one methylene group σ can be calculated: $\sigma = 2\langle h^2\rangle/\sqrt{3}$.[17] Thus, the number of chains radiating out of such an interface is expressed by: $N_{ch} = \Sigma/\sigma$. Only half of the interface has to be considered, because, looking at the molecular shape and the stacking, the chains occupy only two sides of the square-shaped molecules. The other sides are filled by the chains of the molecules belonging to adjacent columns. Of course, the whole clusters of molecules rotate around the column axis (circular cross section, see Figure 2). Thus, the number of chains per platelike slice can be expressed by: $N_{ch} = \pi\phi_0\sqrt{3}\langle p\rangle\langle h^{-2}\rangle/4$. Knowing the total number of chains per slice, the number of corresponding molecules (N_{Mol}) forming the cluster is $N_{Mol} = N_{ch}/n$ ($n = 6$ for **1** and **3**, and 12 for **2**). Therefore, $N_{ch} = \pi\phi_0\sqrt{3}\langle p\rangle\langle h^{-2}\rangle/(4n)$. As mentioned above, comparable results were obtained, in that more or less four copper or mixed copper–gadolinium complexes (two dimers) and only two copper–lanthanum complexes (or one dimer) form the molecular clusters approximately 9.4 Å thick.

The following molecular organisation within the columnar mesophase can now be proposed: four molecules of type I (complexes **1** and **3**) self-arrange into a platelike molecular clusters, while only two molecules of type II (complex **2**, itself having a platelike shape) fulfill the geometrical requirements. They then self-assemble to form the columns by an alternating stacking (at right angles, see Figures 3 and 4) in order to maximise the space occupied by the aliphatic chains. Note that the orientational molecular ordering in these clusters within the column and with those of neighbouring columns is not correlated over a long range, allowing some freedom for the molecules to fill the space in a more efficient way, as confirmed by the d_{10} temperature variation. Indeed, for complexes **1** and **3**, the d spacing decreases linearly with T, and is almost temperature independent for **2**. This is in agreement with the probable presence of undulations of the columns in order to compensate the thermal expansion of the paraffinic chains.[18] On increasing temperature T, the space filling of the chains is optimised, and the columns become less and less ondulating. The columnar phase results from the self-organisation of the columns into a two-dimensional hexagonal lattice. The disordered chains ensure at the same time the gliding of the columns, one with respect to the other, and thus the fluidity and the liquid-crystalline nature of the mesophase. A schematic representation of the molecular organisation of the complexes within the columnar mesophase is shown in Figure 3 and 4. This is only a schematic representation at one given moment, as the system is fluid and the molecular clusters rotate around the column axis (see text above and Figure 2).

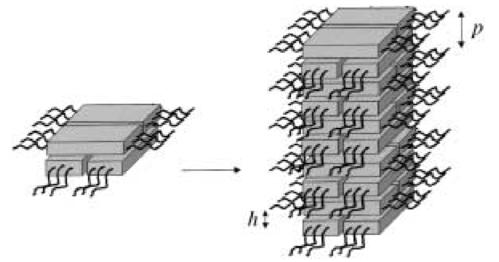


Figure 3. Molecular organisation of the complexes **1** and **3** (type I) within the columnar mesophase. The columnar repeat unit is given by $\langle p\rangle$, and $\langle h\rangle$ is the average distance between adjacent molten chains.

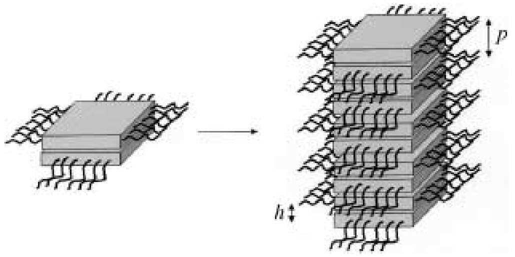


Figure 4. Molecular organisation of complex **2** (type II) within the columnar mesophase. The columnar repeat unit is given by $\langle p\rangle$, and $\langle h\rangle$ is the average distance between adjacent molten chains.

Conclusion

In conclusion, we prepared the first examples of heteropolynuclear metallomesogens that contain both a transition metal ion and a trivalent lanthanide ion. Adducts were formed between a mesomorphic [Cu(salen)] complex and a lanthanide nitrate. Different stoichiometries were found, depending on the lanthanide ion: a trinuclear copper–lanthanum–copper complex and a binuclear copper–gadolinium complex. The compounds exhibit an hexagonal columnar mesophase ($\mathrm{Col_H}$) over a wide temperature-range with rather low melting temperatures. Although the clearing point could be observed for the parent [Cu(salen)] complex, the mixed f–d complexes decomposed in the high-temperature part of the mesomorphic domain before clearing. Further work is in progress to prepare new complexes by varying some structural parameters, such as varying the metal ions by the use of different metal combinations, the structure of the ligands and the type of counterions in order to obtain more thermally stable compounds and to analyse the magnetic properties.

Experimental Section

General procedures: CHN elemental analyses were performed on a CE Instruments EA-1110 elemental analyser. FTIR spectra were recorded on a Bruker IFS-66 spectrometer, by using the KBr pellet method. Optical textures of the mesophase were observed with an Olympus BX60 polarised optical microscope equipped with a Linkam THMS 600 hot stage and a Linkam TMS 93 programmable temperature controller. The XRD patterns were obtained with two different experimental set-ups, and in all cases the crude powder was filled in Lindemann capillaries of 1 mm diameter. A linear monochromatic $\mathrm{Cu}_{\mathrm{K}\alpha 1}$ beam ($\lambda = 1.5405$ Å) 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 within $\pm 0.05\,^{\circ}\mathrm{C}$; periodicities up to 60 Å could be measured. The other set of diffraction patterns was registered on an image plate. The cell parameters are calculated from the position of the reflection at the smallest Bragg angle, which was the most intense in all cases. Periodicities up to 90 Å could be measured, and the sample temperature was controlled within $\pm 0.3\,^{\circ}\mathrm{C}$.

The calculation of the rigid aromatic segment length was done by molecular mechanics with the Discover 3 software from MSI with the esff forcefield. The length l_o was taken between the two opposite oxygen atoms of the alkoxy chains in the *para*-position the copper complex **1**.

Synthesis of salen ligand L: A detailed description of the synthesis of the substituted salen ligand L (salen = 2,2'-*N*,*N*'-bis(salicylidene)ethylenediamine) is available as Supporting Information. L melts at 70 °C, without forming a mesophase.

Synthesis of 1: A hot solution of $\mathrm{Cu(OOCCH_3)_2 \cdot H_2O}$ (0.20 g; 1 mmol) in methanol was added dropwise to a hot solution of L (1.78 g; 1 mmol) in chloroform. The reaction mixture was heated at reflux 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: 81 % (1.50 g); IR (KBr): $\tilde{\nu} = 1640$ (C=N), 1206 $\mathrm{cm^{-1}}$ (C–O); elemental analysis (%) calcd for $\mathrm{C_{114}H_{190}O_{12}N_2Cu}$ (1844.28): C 74.24, H 10.38, N 1.52; found: C 74.38, H 10.59, N 1.30.

Synthesis of 2: A solution of $\mathrm{La(NO_3)_3 \cdot 6H_2O}$ (0.143 g; 0.33 mmol) in acetone was added to a solution of **1** (0.553 g; 0.3 mmol) in acetone. The reaction mixture was stirred at room temperature for 24 hours. The precipitate was filtered, washed with cold methanol and dried in vacuo. Yield: 96 % (578 mg); IR (KBr): $\tilde{\nu} = 1639$ (C=N), 1198 $\mathrm{cm^{-1}}$ (C–O); elemental analysis (%) calcd for $\mathrm{C_{228}H_{380}O_{33}N_7Cu_2La}$ (4013.48): C 68.23, H 9.54, N 2.44; found: C 68.19, H, 9.70, N 2.47.

Synthesis of 3: The same procedure as for compound **2** was used: **1** (0.553 g; 0.3 mmol), $\mathrm{Gd(NO_3)_3 \cdot 6H_2O}$ (0.149 g; 0.33 mmol). Yield: 97 % (635 mg); IR (KBr): $\tilde{\nu} = 1647$ (C=N), 1198 $\mathrm{cm^{-1}}$ (C–O); elemental analysis (%) calcd for $\mathrm{C_{114}H_{190}O_{21}N_5CuGd}$ (2187.54): C 62.59, H 8.75, N, 3.20; found: C 62.40, H 9.15, N 2.93.

Acknowledgements

K.B. is a Postdoctoral Fellow of the Fund for Scientific Research-Flanders (Belgium). Funding by the K.U.Leuven (GOA 98/3 and PhD grant to K.L.) and by the F.W.O.-Vlaanderen (G.0243.99) is gratefully acknowledged. K.B. and K.L. wish to thank Prof. C. Görller-Walrand for providing laboratory facilities. CHN microanalyses were performed by Ms. P. Bloemen. B.D. and D.G. would like to thank Dr C. Bourgogne for his help in the computer molecular modelling.

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[1] a) A. M. Giroud-Godquin, P. M. Maitlis, *Angew. Chem.* **1991**, *103*, 370; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 375; b) *Metallomesogens, Synthesis, Properties and Applications* (Ed. J. L. Serrano), VCH, Weinheim, **1996**; c) D. W. Bruce in *Inorganic Materials*, 2nd ed. (Eds.: D. W. Bruce, D. O'Hare), Wiley, Chichester, **1996**, Chapter 8, p. 429,; d) B. Donnio, D. W. Bruce, *Struct. Bond.* **1999**, *95*, 193.

[2] a) S. Schmidt, G. Lattermann, R. Kleppinger, J. H. Wendorff, *Liq. Cryst.* **1994**, *16*, 693; b) H. Zheng, T. M. Swager, *J. Am. Chem. Soc.* **1994**, *116*, 761; c) S. Morrone, D. W. Bruce, D. Guillon, *Inorg. Chem.* **1996**, *35*, 7041; d) R. Deschenaux, B. Donnio, G. Rheinwald, F. Stauffer, G. Süss-Fink, J. Velker, *J. Chem. Soc. Dalton Trans.* **1997**, 4351; e) X. H. Liu, I. Manners, D. W. Bruce, *J. Mater. Chem.* **1998**, *8*, 1555.

[3] S. T. Trzaska, H. Zheng, T. M. Swager, *Chem. Mater.* **1999**, *11*, 130, and references therein.

[4] a) L. Ziminski, J. Malthête, *J. Chem. Soc. Chem. Commun.* **1990**, 1495; b) U. Stebani, G. Lattermann, M. Wittenberger, J. H. Wendorff, *Angew. Chem.* **1996**, *108*, 1941; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1859.

[5] a) F. Neve, M. Ghedini, *J. Inclusion Phenom.* **1993**, *15*, 259; b) A. El-ghayoury, L. Douce, A. Skoulios, R. Ziessel, *Angew. Chem.* **1998**, *110*, 2327; *Angew. Chem. Int. Ed.* **1998**, *37*, 2205; c) L. Douce, A. El-ghayoury, A. Skoulios, R. Ziessel, *Chem. Commun.* **1999**, 2033; d) R. Ziessel, L. Douce, A. El-ghayoury, A. Harriman, A. Skoulios, *Angew. Chem.* **2000**, *112*, 1549; *Angew. Chem. Int. Ed.* **2000**, *39*, 1489.

[6] a) J. Barbera, A. Elduque, R. Gimenez, L. A. Oro, J. L. Serrano, *Angew. Chem.* **1996**, *108*, 3048; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2832; b) J. Barbera, A. Elduque, R. Gimenez, F. J. Lahoz, J. A. Lopez, L. A. Oro, JL Serrano, *Inorg Chem.* **1998**, *37*, 2832.

[7] T. Hegmann, B. Neumann, J. Kain, S. Diele, C. Tschierske, *J. Mater. Chem.* **2000**, *10*, 2244.

[8] J. Barbera, M. Marcos, A. Omenat, J. L. Serrano, J. I. Martinez, P. J. Alonso, *Liq. Cryst.* **2000**, *27*, 255.

[9] J. Szydlowska, A. Krowczynski, E. Gorecka, D. pociecha, *Inorg. Chem.* **2000**, *39*, 4879.

[10] a) Yu. G. Galyametdinov, I. V. Ovchinnikov, B. M. Bolotin, N. B. Etingen, G. I. Ivanova, L. M. Yagfarova, *Bull. Acad. Sci. USSR Div. Chem. Sci.* **1984**, *33*, 2174; b) J. Barberá, A. M. Levelut, M. Marcos, P. Romero, J. L. Serrano, *Liq. Cryst.* **1991**, *10*, 119.

[11] a) Yu. G. Galyametdinov, I. G. Bikchantaev, I. V. Ovchinnikov, *J. Gen. Chem.* **1988**, *58*, 1180; b) E. Campillos, M. Marcos, J. L. Serrano, J. Barberá, P. J. Alonso, J. I. Martínez, *Chem. Mater.* **1993**, *3*, 1518.

[12] a) Yu. G. Galyametdinov, G. I. Ivanova, I. V. Ovchinnikov, *Bull. Acad. Sci. USSR Div. Chem. Sci.* **1991**, *40*, 1109; b) Yu. G. Galyametdinov, M. A. Athanassopoulou, K. Griesar, O. Kharitonova, E. A. Soto Bustamante, L. Tinchurina, I. Ovchinnikov, W. Haase, *Chem. Mater.* **1996**, *8*, 922; c) K. Binnemans, Yu. G. Galyametdinov, R. Van Deun, D. W. Bruce, S. R. Collinson, A. P. Polishchuk, I. Bikchantaev, W. Haase, A. V. Prosvirin, L. Tinchurina, I. Litvinov, A. Gubajdullin, A. Rakhmatullin, K. Uytterhoeven, L. Van Meervelt, *J. Am. Chem. Soc.* **2000**, *122*, 4335; d) Yu. G. Galyametdinov, W. Haase, L. Malykhina, A. Prosvirin, I. Bikchantaev, A. Rakmatullin, K. Binnemans, *Chem. Eur. J.* **2001**, *7*, 99; e) K. Binnemans, K. Lodewyckx, *Angew. Chem.* **2001**, *113*, 248; *Angew. Chem. Int. Ed.* **2001**, *40*, 242..

[13] a) A. Bencini, C. Benelli, A. Caneshi, R. L. Carlin, A. Dei, D. Gatteschi, *J. Am. Chem. Soc.* **1985**, *107*, 8128; b) A. Benelli, A. Caneshi, A. Dei, D. Gatteschi, *Inorg. Chem.* **1986**, *25*, 572; c) M. Sakamoto, M. Hashimura, K. Matsuki, N. Matsumoto, K. Inoue, H. Okawa, *Bull. Chem. Soc. Jpn.* **1991**, *64*, 3639; d) O. Guillou, P. Bergerat, O. Kahn, E. Bakalbassis, K. Boubekeur, P. Batail, M. Guillot, *Inorg. Chem.* **1992**, *31*, 110; e) J. P. Costes, F. Dahan, A. Dupuis, J. P. Laurent, *Inorg. Chem.* **1996**, *35*, 2400; f) J. P. Costes, F. Dahan, A. Dupuis, J. P. Laurent, *Inorg. Chem.* **1997**, *36*, 3429; g) C. Piguet, E. Rivara-Minten, G. Bernadinelli, J.-C. G. Bünzli, G. Hopfgartner, *J. Chem. Soc. Dalton Trans.* **1997**, 421; h) R. E. P. Winpenny, *Chem. Soc. Rev.* **1998**, *27*, 447; i) J. P. Costes, F. Dahan, A. Dupuis, *Inorg. Chem.* **2000**, *39*, 165.

[14] M. L. Kahn, T. M. Rajendiran, Y. Jeannin, C. Mathonière, O. Kahn, *C. R. Acad. Sci. II C* **2000**, *3*, 131.

[15] a) R. Paschke, H. Zaschke, A. Mädicke, J. R. Chipperfield, A. B. Blake, P. G. Nelson, G. W. Gray, *Mol. Cryst. Liq. Cryst. Lett.* **1988**, *6*, 81; b) T. D. Shaffer and K. A. Sheth, *Mol. Cryst. Liq. Cryst.* **1989**, *172*, 27; c) N. Hoshino, *Coord. Chem. Rev.* **1998**, *174*, 77.

[16] H. T. Nguyen, C. Destrade, J. Malthête, *Adv. Mater.* **1997**, *9*, 375.

[17] M. Marcos, R. Giménez, J. L. Serrano, B. Donnio, B. Heinrich, D. Guillon, *Chem. Eur. J.* **2001**, *7*, 1006.

[18] B. Donnio, B. Heinrich, T. Gulik-Krzywicki, H. Delacroix, D. Guillon and D. W. Bruce, *Chem. Mater.* **1997**, *9*, 2951.

Received: September 13, 2001 [F3554]