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Influence of the lanthanide contraction on the transition temperatures of rare-earth containing metallomesogens with Schiff base ligands

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Abstract

We have synthesised liquid–crystalline rare-earth complexes with Schiff base ligands. The stoichiometry of these complexes is $Ln(LH)_3(NO_3)_3$, where Ln is a trivalent rare-earth ion (Y^{3+}, La^{3+}–Lu^{3+}, except Ce^{3+} and Pm^{3+}), LH is the protonated form of the Schiff base 4-alkoxy-*N*-octadecyl-2-hydroxybenzaldimine. The mesophases were studied by optical microscopy and by differential scanning calorimetry (DSC). For the complexes with the 4-octyloxy-*N*-octadecyl-2-hydroxybenzaldimine ligand, a gradual increase in the melting point and a gradual decrease in the clearing point is found when going from La^{3+} to Lu^{3+}. In this way, the mesophase range narrows over the lanthanide series. This is due to the lanthanide contraction. The textures observed by optical microscopy reveal the presence of a smectic A mesophase. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

The investigation of liquid–crystalline metal complexes (metallomesogens) is a fast growing branch of coordination chemistry [1–7]. Metallomesogens are not restricted to mesomorphic ligands, because the metal ion can induce mesomorphism in non-mesomorphic ligands. In the past, the majority of the newly synthesised metallomesogens contained Cu(II), Ni(II), Pt(II) and Pd(II) as the central metal ion, since the coordination of the central metal ion in the complexes is square planar (coordination number = 4). In this way, the flat molecular structure of the ligands is retained and even extended, so that the structural anisotropy necessary for the formation of the mesophase is not destroyed. Square planar coordination is however only observed for a limited number of transition metal ions, and it is desirable to incorporate other transition metal ions into liquid crystals in order to take full advantage of the unique physical properties of these elements.

Only a few examples of lanthanide-containing metallomesogens have been described in the literature. The first mesomorphic lanthanide compounds were the substituted bis(phthalocyaninato)lutetium (III) complexes, described by Piechocki et al. [8]; these compounds exhibit columnar mesophases. Later, Galyametdinov and coworkers described

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calamitic lanthanide complexes with Schiff bases [9,10] and β-enaminoketones [11] as the ligands, showing a smectic A mesophase. We showed that the transition temperatures of the Schiff base complexes are greatly influenced by the choice of the counter-ion [12]. Wang et al. reported complexes with hemicyanine ligands, showing an unspecified mesophase with a mosaic texture [13].

The elements of the lanthanide series (La–Lu) are chosen as the central metal ion for several reasons: (1) Because of the high coordination number (coordination number = 8 or 9), the coordination polyhedra in lanthanide complexes are different from those observed for transition metal complexes. This opens new possibilities for investigation of the structure-mesomorphism relation, (2) the lanthanide ion can induce mesomorphism in non-mesomorphic ligands [10], (3) the different elements of the lanthanide series show strong luminescence and/or interesting magnetic properties (paramagnetism).

In this Letter, we report on liquid–crystalline rare-earth complexes with Schiff base ligands. Special attention is paid to the influence of the lanthanide contraction on the mesomorphic properties of the rare-earth containing metallomesogens. The lanthanide contraction is the gradual decrease in the ionic radius of the rare earths over the lanthanide series. This smooth contraction has several consequences. For instance, the ionic radius of the rare-earth ion Y^{3+} is close to the ionic radius of Ho^{3+}, although Y^{3+} belongs to the fifth period of the periodic system and Ho^{3+} to the sixth period. We investigate whether the lanthanide contraction is also reflected by differences in the transition temperatures (and enthalpies) of rare-earth containing liquid crystals. The Schiff base we worked with is 4-octyloxy-*N*-octadecyl-2-hydroxybenzaldimine (Fig. 1). To avoid confusion: the *lanthanides* are the elements with an atomic number between 57 (lanthanum) and 71 (lutetium). By *rare earths* we understand the lanthanides together with element 21 (scandium) and element 39 (yttrium). In general, the properties of the 3d-element scandium significantly differ from the properties of the other rare-earth elements. Therefore, we do not consider scandium in this systematic study.

2. Experimental details

All chemicals were used as received, without further purification. Hydrated rare earth nitrates were purchased from Aldrich. ^{1}H NMR spectra were recorded on a Bruker AMX400 spectrometer (400 MHz). Elemental analyses (CHN) were performed on a Perkin-Elmer 2400 Elemental Analyser. The mesophases were investigated by optical microscopy and by differential scanning calorimetry (DSC). Microscopy was performed on an Olympus BX60 polarising microscope, equipped with a Linkam TMS600 hot stage and a Linkam TMS93 temperature controller. DSC-thermograms were recorded on a Mettler-Toledo DSC-821e module. The temperature and heat flow were calibrated by indium (T_m = 156.6 ± 0.3°C; $\Delta H = 28.45 \pm 0.6$ J g^{-1}). The heating and cooling rates were 10°C min^{-1}, except when the melting and clearing peaks showed an overlap. In those cases, the rate was reduced to 1°C min^{-1}. The samples were sealed in a 40 μl aluminium pan with a pierced lid. Dry nitrogen was used as the oven atmosphere.

3. Synthesis of the ligand and complexes

4-Octyloxy-2-hydroxybenzaldehyde was prepared by refluxing (for 3 h) 2,4-dihydroxybenzaldehyde (50 mmol, 6.91 g) with 1-bromooctane (50 mmol, 9.68 g) in DMF, and with $KHCO_3$ (50 mmol, 5.01 g) as the base. The raw aldehyde was transformed to the Schiff base without further purification by refluxing in absolute ethanol (3 h) with octadecylamine

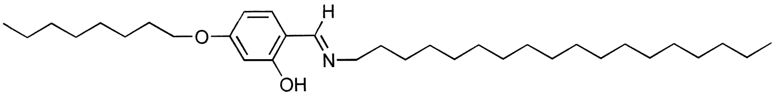

Fig. 1. The Schiff base ligand 4-octyloxy-*N*-octadecyl-2-hydroxybenzaldimine (LH).

(50 mmol, 13.48 g), using a few drops of glacial acetic acid as the catalyst. The Schiff base 4-octyloxy-*N*-octadecyl-2-hydroxybenzaldimine was purified by recrystallising three times from absolute ethanol. The overall yield was 46% (11.60 g). The ligand was characterised by NMR and IR spectroscopy. The rare earth complexes were prepared by dissolving the Schiff base in absolute ethanol and adding a solution of the hydrated rare-earth nitrate in absolute ethanol. Although a complex is formed in a 1:3 metal:ligand ratio, we used an excess of the hydrated rare-earth nitrate, in order to take the uncertainty of the water content of these reagents into account. For the calculations, it was assumed that the compounds were hexahydrates (Y, La–Sm) or pentahydrates (Eu–Lu). The dissolution of the Schiff base can be assisted by heating the ethanolic solution, but reproducible results for the complexes could only be obtained if the solution is cooled beneath 50°C before the solution of the rare-earth salt is added dropwise. About 15 min after mixing, the solution turns cloudy and the complex starts to precipitate. Stirring was continued for at least 3 h. After filtration, the complex was washed with ice-cold ethanol and dried in vacuo. The yield of the complexes varied between 70 and 80%. The complexes were characterised by CHN elemental analysis. No reproducible results could be obtained for the cerium complex, probably because of a redox reaction due to Ce(III,IV). Promethium was excluded from the study, because this element is radioactive.

Although Galyametdinov et al. [10] proposed that the empirical formula of this type of complexes is $[\mathrm{Ln(LH)_2L}](\mathrm{NO_3})_2$, we now have strong evidence that the empirical formula is $\mathrm{Ln(LH)_3(NO_3)_3}$. It is difficult to differentiate between $[\mathrm{Ln(LH)_2L}](\mathrm{NO_3})_2 \cdot 3\mathrm{H_2O}$ and $\mathrm{Ln(LH)_3(NO_3)_3}$ by CHN microanalysis only. However, the ^{1}H NMR spectrum of the lanthanum complex shows that all the ligands are identical and that the OH-group of the ligand remains protonated. Recently, a single crystal X-ray structure of an analogous non-mesomorphic derivative ($\mathrm{LH} = \mathrm{CH_3OC_6H_3(OH)CH{=}NC_4H_9}$) was obtained [14]. The crystal structure shows that three coordinating nitrate anions are present and that all three nitrates are bound in a bidentate, chelating fashion. The Schiff base ligands are bound through the phenol oxygen.

4. Mesomorphic properties: results and discussion

The ligand 4-octyloxy-*N*-octadecyl-2-hydroxybenzaldimine itself does not show mesomorphism, melting directly to an isotropic liquid at 50°C. However, all the rare-earth complexes exhibit a mesophase. The mesophase was identified as a smectic A phase by optical microscopy, using a hot stage and polarised light. The sample was placed between two untreated cover glasses. By cooling from the isotropic melt bâtonnets form, which coalesce to form a focal–conic fan structure. In the same sample extinct regions were also observed, indicating homeotropic alignment of the molecules. This supports the identification as the smectic A phase. The mesophases show a high viscosity, which is evident if one tries to shear the cover glasses at a temperature close above the melting point. At higher temperatures the viscosity gradually decreases, and a strong increase in fluidity is observed at the clearing point. When cooling the mesophase (5°C min^{-1}), no crystallisation is observed in the microscope and the texture of the mesophase is frozen into the solid state. A glassy mesophase is formed. The glass formation is noticed from the fact that it is no longer possible to shear the cover glasses between which the sample is sandwiched. Moreover, when cooling further, conchoidal fractures are observed in the texture. These conchoidal fractures also indicate the presence of a glassy state. The glass state in the mesophase is closer to the glassy state in polymers than the real inorganic glasses. In contradistinction to inorganic glasses which are optically isotropic, the vitreous mesophase is an anisotropic glass. It should be noted that by a glass, we mean a structural glass, and not a spin glass. The DSC traces show crystallisation at a cooling rate of 10°C min^{-1}, although a strong supercooling is observed. This difference in behaviour between the microscopic and DSC observations do not contradict each other, because we are studying a thin film under the microscope, whereas a bulk sample is used for the DSC measurements. The glassy film is transparent at room temperature. When the aluminium crucible is opened after the DSC measurement, the sample is translucent, indicating its polycrystalline state. No crystallisation of the thin films was observed, not even after a day. Galyametdinov and coworkers [10] describe supercooling of similar complexes and they observed that the texture is stable between -20°C and 60°C. Metallomesogens, and especially ionic complexes, show a strong tendency to form glassy mesophases. Among the first to draw attention to this behaviour were Bruce et al. [15], who observed glass formation for silver(I) complexes. The potential of vitreous metallomesogens is discussed in a review by Neve [16].

The mesomorphic properties of the rare-earth complexes are summarised in Table 1. The DSC traces for the praseodymium and the erbium complex are shown in Fig. 2. The reported temperatures were determined by DSC, whereas the clearing points have been determined by optical microscopy. The onset of the clearing peak could not be determined for the complexes of the heavier rare-earth complexes, because of the overlap of the melting and clearing peaks. In all cases, it was possible to determine the clearing peak maximum in the heating run, although at the end of the lanthanide series the heating rate had to be reduced to 1°C min^{-1} in order to resolve the peaks. At a heating rate of 10°C min^{-1}, clearing was only observed as a shoulder of the melting peak. Microscopy shows that all the complexes form a mesophase after melting, so that all our compounds are enantiotropic liquid crystals. The complexes in the series from lanthanum to europium show a crystal–crystal transition, which is absent in the second heating run. No crystal–crystal transition was observed for the complexes of the heavier lanthanides. Fig. 3 shows that the melting temperatures smoothly increase when going from the lanthanum to the lutetium complex. At the same time, a decrease is observed for the clearing point. Therefore, an overall trend is a narrowing of the mesophase range over the lanthanide series. Since the clearing point decreases, the mesophase stability also decreases. The change in the transition temperatures is more pronounced in the beginning of the lanthanide series than at the end. Whereas an increase in the melting point of 52°C is observed when going from the lanthanum complex to the lutetium complex, the decrease of the clearing point is only 26°C. These trends in mesomorphic behaviour can be correlated to the ionic radius of the central rare-earth ion. The radius of the lanthanide ion steadily decreases over the lanthanide series (lanthanide contraction). The fact that a correlation exists between the ionic radius and the mesomorphic properties of the complexes is also illustrated by comparison of the transition temperatures of the holmium complex (Crys $\rightarrow$ S_A: 134°C, $S_A \rightarrow$ I: 144°C) and the yttrium complex (Crys $\rightarrow$ S_A: 132°C, $S_A \rightarrow$ I: 142°C). The ionic radii of Ho^{3+} and Y^{3+} are nearly identical. The ion gets smaller over the lanthanide series and the charge remains, so that the electrostatic attraction between the lanthanide ion and the coordinating groups become stronger and therefore the melting temperature increases. The rapid increase of the melting point when going from the europium to the

Table 1
Mesomorphic properties of the rare-earth complexes $Ln(LH)_3(NO_3)_3$, where Ln represents the rare-earth ion and LH the protonated Schiff base ligand 4-octyloxy-*N*-octadecyl-2-hydroxybenzaldimine

Ln	Transition[a]	Temperature[b] (°C)	ΔH^b (kJ mol^{-1})
Y	Crys–S_A	132	22.7
	S_A–I	141	11.0
La	Crys–S_A	83	2.5
	S_A–I	165	11.8
Pr	Crys–S_A	90	8.7
	S_A–I	163	13.2
Nd	Crys–S_A	95	12.4
	S_A–I	159	11.8
Sm	Crys–S_A	105	12.4
	S_A–I	154	12.4
Eu	Crys–S_A	108	15.5
	S_A–I	151	13.3
Gd	Crys–S_A	121	16.9
	S_A–I	150	12.7
Tb	Crys–S_A	128	17.6
	S_A–I	148	10.6
Dy	Crys–S_A	131	21.4
	S_A–I	146	11.8
Ho	Crys–S_A	134	22.2
	S_A–I	144	10.8
Er	Crys–S_A	135	–[c]
	S_A–I	142	–[c]
Tm	Crys–S_A	139	–[c]
	S_A–I	142	–[c]
Yb	Crys–S_A	138	–[c]
	S_A–I	141	–[c]
Lu	Crys–S_A	135	–[c]
	S_A–I	139	–[c]

[a] Crys: crystalline phase; S_A: smectic A phase; I: isotropic liquid.
[b] The error on the temperature measurements is ±0.5°C and on the heat flow 0.2 kJ mol^{-1}.
[c] No transition enthalpies could be determined for the Er–Lu complexes, because of overlapping peaks.

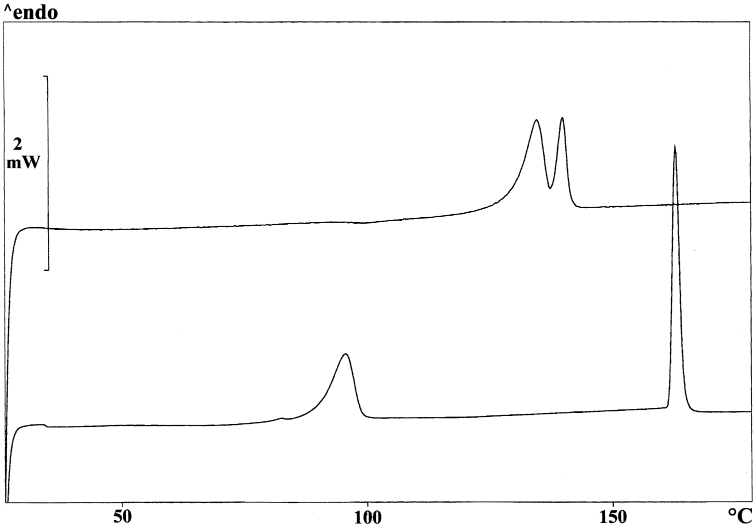

Fig. 2. DSC curves of the praseodymium complex (lower trace) and erbium complex (upper trace) (2nd heating run). Endothermic peaks are pointing upwards (^ endo).

gadolinium complex is most likely due to a difference in crystal structure between the complexes of the light and those of the heavy lanthanides. It is more difficult to explain the reduction of the clearing point over the lanthanide series. Probably, the reduction in ion size leads to steric problems in the mesophase and thus more structural distortions occur, leading to a less anisotropic complex and reduction of the clearing point.

Because of the overlap between melting and clearing peaks, the melting and clearing enthalpy could not be determined separately for the complexes at the end of the lanthanide series (Er–Lu). The melting enthalpy exhibits the same trend as the melting temperature: ΔH_m increases over the lanthanide series from 2.2 kJ mol^{-1} for the lanthanum complex to 22.5 kJ mol^{-1} for the holmium complex (Table 1). However, no distinct trend is observed for the clearing enthalpies. The values are rather constant and scattered between 10.6 and 13.3 kJ mol^{-1}.

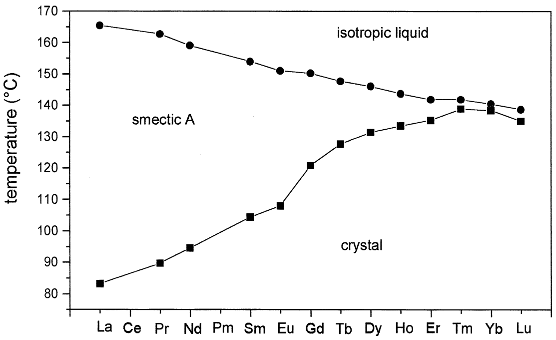

Fig. 3. Change of the mesomorphic properties of the complexes $Ln(LH)_3(NO_3)_3$ over the lanthanide series.

5. Conclusions

We have synthesised rare-earth complexes with the Schiff base 4-octyloxy-*N*-octadecyl-2-hydroxybenzaldimine as the ligand, for all the rare-earth ions, except scandium, cerium and promethium. The complexes have the stoichiometry $Ln(LH)_3(NO_3)_3$, where Ln represents the trivalent rare-earth ion. All the complexes form an enantiotropic mesophase. The mesophase could be identified as a smectic A phase (S_A) by optical thermomicroscopy. The melting temperatures smoothly increase when going from the lanthanum to the lutetium complex, whereas a decrease is observed for the clearing point. Therefore, the mesophase range narrows over the lanthanide series. This trend can be correlated to the lanthanide contraction. The melting enthalpy follows the same trend as the melting temperature, whereas the clearing enthalpy is rather constant over the lanthanide series. A thin film of the complexes supercools to a glassy mesophase. Further work is in progress to check whether the trends observed for the 4-octyloxy-*N*-octadecyl-2-hydroxybenzaldimine ligand and the nitrate ion, are also present in ligands with other chain lengths and for complexes with other counter-ions.

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