Mesomorphic lanthanide complexes with azomethine ligands

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Abstract

The synthesis and mesophase behaviour of lanthanide complexes with azomethine (Schiff base) ligands is described. The ligands are 4-tetradecyloxy-*N*-alkyl-2-hydroxybenzaldimines, where the alkyl chain on the imine nitrogen is C_8H_{17}, $C_{12}H_{25}$ or $C_{18}H_{37}$. The stoichiometry of the complexes formed by the reaction of the hydrated nitrates of the lanthanides with the azomethines is $[Ln(LH)_3(NO_3)_3]$. All these coordination compounds exhibit liquid-crystalline properties. A viscous smectic A (SmA) mesophase is formed. The mesophase of these metallomesogens can be supercooled to a glassy state. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Lanthanides; Rare earths; Metallomesogens; Liquid crystals; Schiff base; Smectic mesophases

1. Introduction

When a rare-earth complex is heated, normally it either decomposes or melts to an isotropic liquid. However, it is possible to design rare-earth complexes which will pass, on heating, through a so-called mesophase before melting to the isotropic liquid. A compound in a mesophase can be considered to be a strongly disordered solid or an ordered liquid, and is termed a "liquid crystal". Metal-containing liquid crystals (*metallomesogens*) have attracted a lot of attention [1–7], but only a limited number of liquid-crystalline lanthanide complexes has been reported in the literature [8]. The first mesomorphic lanthanide compounds were the substituted bis(phthalocyaninato)lutetium(III) complexes, described by Piechocki et al. [9]; these compounds exhibit columnar mesophases. Later, Galyametdinov and coworkers described calamitic lanthanide complexes with Schiff bases [10,11] and β-enaminoketones [12] as the ligands, showing a smectic A mesophase. Binnemans et al. showed that the transition temperatures of the Schiff base complexes are greatly influenced by the choice of the counter-ion [13], and they were able to show that the lanthanide contraction has a distinct influence on the transition temperatures of this type of compound [14].

In the paper, we describe the synthesis and thermal behaviour of other examples of mesomorphic rare-earth complexes with azomethine (Schiff base) ligands. The ligands are 4-tetradecyloxy-*N*-alkyl-2-hydroxybenzaldimines, where the alkyl chain on the imine nitrogen is C_8H_{17}, $C_{12}H_{25}$ or $C_{18}H_{37}$. The influence of this chain length on the transition temperatures is discussed.

2. Experimental details

2.1. Techniques

^{1}H-NMR spectra were obtained on a Bruker DRX-400 spectrometer (400 MHz), a Bruker AMX-400 spectrometer (400 MHz), or a Bruker WM-250 spectrometer (250 MHz), using $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal standard. The δ values are expressed in ppm. IR spectra were recorded on a Bruker FTIR spectrometer IFS66. KBr pellets of the samples were used for the FTIR spectra. Elemental analyses (CHN) were performed on a CE Instruments EA-1110 elemental analyser. Differential scanning calorimetry (DSC) measurements were carried out on a Mettler-Toledo DSC821e module. Samples of 2–5 mg in solid form were placed in aluminium pans (40 μl) with a pierced lid, and heated or cooled at a scan rate of 10°C min^{-1} under a nitrogen flow. Indium metal was used as standard for the calibration of the instrument ($T_m = 156.6\pm0.3$°C, $\Delta H_m = 28.45\pm0.6$ J g^{-1}). Optical textures of the mesophases were observed with an

Olympus BX60 polarising microscope equipped with a LINKAM TMS600 hot stage and a LINKAM TMS93 programmable temperature-controller. All chemicals were used as received, without further purification. Organic reagents were obtained from ACROS. Hydrated rare-earth nitrates were purchased from Aldrich.

2.2. Synthesis of the compounds

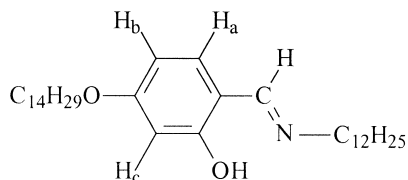### 2.2.1. 4-Tetradecyloxy-2-hydroxybenzaldehyde (**1**)
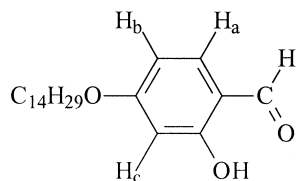
4-Tetradecyl-2-hydroxybenzaldehyde (**1**) was prepared by heating 2,4-dihydroxybenzaldehyde (20.73 g, 0.15 mol) for 3 h at reflux with 1-bromotetradecane (41.59 g, 0.15 mol) in DMF, and with $KHCO_3$ (15.04 g, 0.15 mol) as the base. The crude aldehyde was purified by crystallisation from hot acetonitrile. Yield: 54% (27 g). ^{1}H-NMR (250 MHz, CDCl$_3$, δ ppm): 0.90 (t, 3H, CH$_3$), 1.0–1.6 (m, 22H, CH$_2$), 1.80 (quintet, 2H, $-CH_2-CH_2-O-$), 4.00 (t, 2H, $-CH_2-O-$), 6.40 (d, 1H, H$_c$), 6.50 (dd, 1H, H$_b$), 7.40 (d, 1H, H$_a$), 9.70 (s, 1H, CHO).

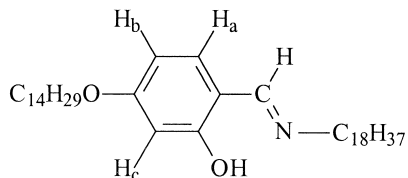### 2.2.2. 4-Tetradecyloxy-N-octyl-2-hydroxybenzaldimine (**2**)
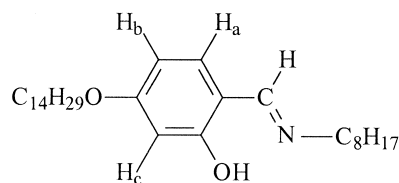
4-Tetradecyloxy-*N*-octyl-2-hydroxybenzaldimine (**2**) was prepared by heating 7.75 g (23 mmol) of aldehyde **1** with 2.95 g (23 mmol) of n-octylamine in absolute ethanol for 3 h at reflux, with a few drops of glacial acetic acid as the catalyst. The crude product was crystallised several times from hot absolute ethanol. Yield: 30% (3.07 g). ^{1}H-NMR (400 MHz, CDCl$_3$, δ ppm): 0.88 (t, 6H, CH$_3$), 1.24–1.46 (m, 32H, CH$_2$), 1.67 (quintet, 2H, $-CH_2-CH_2-$ N$-$), 1.77 (quintet, 2H, $-CH_2-CH_2-O-$), 3.51 (t, 2H, $-CH_2-N-$), 3.96 (t, 2H, $-CH_2-O-$), 6.33 (dd, 1H, H$_b$), 6.37 (d, 1H, H$_c$), 7.05 (d, 1H, H$_a$), 8.09 (s, 1H, CH=N), 14.1 (s, 1H, OH), $J_o = 8.5$ Hz, $J_m = 2.5$ Hz. Calc. for C$_{29}$H$_{51}$NO$_2$: C 78.14%, H 11.53%, N 3.14%. Found: C 78.11%, H 11.56%, N 2.99%.

2.2.3. 4-Tetradecyloxy-N-dodecyl-2-hydroxybenzaldimine (**3**)

4-Tetradecyloxy-*N*-dodecyl-2-hydroxybenzaldimine (**3**) was prepared by heating for 3 h at reflux 4.12 g (12.3 mmol) of aldehyde **1** with 2.29 g (12.3 mmol) of n-dodecylamine in absolute ethanol, with a few drops of glacial acetic acid as the catalyst. The crude product was crystallised several times from hot absolute ethanol. Yield: 88% (5.42 g). ^{1}H-NMR (250 MHz, CDCl$_3$, δ ppm): 0.88 (t, 6H, CH$_3$), 1.03–1.56 (m, 40H, CH$_2$), 1.67 (quintet, 2H, $-CH_2-CH_2-N-$), 1.77 (quintet, 2H, $-CH_2-CH_2-O-$), 3.51 (t, 2H, $-CH_2-N-$), 3.95 (t, 2H, $-CH_2-O-$), 6.33 (dd, 1H, H$_b$), 6.36 (d, 1H, H$_c$), 7.04 (d, 1H, H$_a$), 8.09 (s, 1H, CH=N), 14.1 (s, 1H, OH), $J_o = 8.5$ Hz, $J_m = 2.5$ Hz. Calc. for C$_{33}$H$_{59}$NO$_2$: C 78.98%, H 11.85%, N 2.79%. Found: C 78.93%, H 11.90%, N 2.56%.

2.2.4. 4-Tetradecyloxy-N-octadecyl-2-hydroxybenzaldimine (**4**)

4 - Tetradecyloxy - *N* - octadecyl - 2 - hydroxybenzaldimine (**4**) was prepared by heating for 3 h at reflux 16.73 g (50 mmol) of aldehyde **1** with 13.50 g (50 mmol) of n-octadecylamine in n-heptane, with a few drops of glacial acetic acid as the catalyst. The crude product was crystallised several times from hot n-heptane. Yield: 40% (11.6 g). ^{1}H-NMR (400 MHz, CDCl$_3$, δ ppm): 0.88 (t, 6H, CH$_3$), 1.10–1.50 (m, 52H, CH$_2$), 1.67 (quintet, 2H, $-CH_2-CH_2-$ N$-$), 1.77 (quintet, 2H, $-CH_2-CH_2-O-$), 3.50 (t, 2H, $-CH_2-N-$), 3.95 (t, 2H, $-CH_2-O-$), 6.32 (dd, 1H, H$_b$), 6.36 (d, 1H, H$_c$), 7.05 (d, 1H, H$_a$), 8.08 (s, 1H, CH=N), 14.1 (s, 1H, OH), $J_o = 8.5$ Hz, $J_m = 2.5$ Hz. Calc. for C$_{39}$H$_{71}$NO$_2$: C 79.94%, H 12.21%, N 2.39%. Found: C 80.23%, H 12.16%, N 2.30%.

2.2.5. La complex (**11**)

Compound **11** was prepared by adding a solution of 0.37 g (0.85 mmol) of La(NO$_3$)$_3 \cdot 6H_2O$ in absolute ethanol dropwise to a stirred solution of 0.50 g (0.85 mmol) of the ligand LH in absolute ethanol, at a temperature not higher than 50°C. After ca. 15 min, the solution turned cloudy,

indicating that the product started to precipitate. Stirring was continued for at least 3 h. The pale yellow precipitate was filtered on a crucible, washed with ice-cold absolute ethanol and dried in vacuo. Yield: 76% (0.45 g). ^{1}H-NMR (250 MHz, CDCl$_3$, δ ppm): 0.88 (m, 6H, CH$_3$), 1.10–1.40 (m, 52H, CH$_2$), 1.62 (m, 4H, N–CH$_2$–**CH$_2$** and **CH$_2$**–CH$_2$–O), 3.46 (t, 2H, N–**CH$_2$**), 3.64 (t, 2H, **CH$_2$**–O), 6.15 (dd, 1H, H$_b$), 6.33 (d, 1H, H$_c$), 6.90 (d, 1H, H$_a$), 7.60 (d 1H, CH=N), 12.2 (s, 1H, OH), $J_o = 8.5$ Hz, $J_m = 2.5$ Hz. IR (KBr pellet, cm^{-1}): 3200 (m, ν(OH)), 2920, 2860 (s, aliphatic C–H stretch), 1620 (s, ν(C=N)), 1530 (s, ν(C=C)), 1290 (s, ν(C$_{Ph}$–O)), 1230 (s, ν_{as}(C–O–C)), 1030 (s, ν_s(C–O–C)), 590 (m, ν(La–O)). The elemental analysis results are given in Table 1. All the other rare-earth complexes were synthesised in an analogous way.

3. Results and discussion

Ligands **2**–**4** were synthesised in a two-step reaction, in which the hydroxy group in the 4-position in 2,4-dihydroxybenzaldehyde is first replaced by an alkoxy chain, followed by formation of the Schiff base by reaction of the aldehyde with an alkyl amine (Scheme 1). 4-Tetradecyloxy-2-hydroxybenzaldehyde (**1**) was prepared by refluxing (for 3 h) 2,4-dihydroxybenzaldehyde (1 eq.) with 1-bromotetradecane (1 eq.) in DMF, with KHCO$_3$ (1 eq.) as the base. The crude aldehyde was crystallised from acetonitrile and transformed to the Schiff base by refluxing in absolute ethanol (3 h) with the respective alkyl amine (1 eq.), using a few drops of glacial acetic acid as the catalyst. The Schiff bases 4-tetradecyloxy-*N*-alkyl-2-hydroxybenzaldimines were purified by crystallising several times from absolute ethanol. The overall yield varied between 30 and 88%. The ligands were characterised by NMR, IR spectroscopy and by CHN analysis. The rare-earth complexes **5**–**14** 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. 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 was cooled below 50°C before the solution of the rare-earth salt was added dropwise. About 15 min after mixing, the solution turned cloudy and the complex started 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 56 and 96%. The complexes were characterised by CHN elemental analysis (Table 1). All the complexes have the stoichiometry [Ln(LH)$_3$(NO$_3$)$_3$] [14,15]. In the complexes, the Schiff base is present in a zwitterionic form. The phenolic hydrogen is transferred to the imine nitrogen and coordination occurs through the phenolic oxygen only. The imine nitrogen is not coordinated. For each lanthanide ion, three nitrate groups are present as counter-ions.

The azomethine ligands do not show liquid-crystalline properties, but melt directly to an isotropic liquid. However, all the rare-earth complexes exhibit a mesophase (Table 2). The compounds are enantiotropic liquid crystals, except for the Ho complex (**7**), which is a monotropic liquid crystal. A typical DSC trace is shown in Fig. 1. The mesophase was identified as a smectic A (SmA) 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 formed, which coalesced 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. In a smectic A mesophase, the complexes form layers, and the long molecular axis of the complexes is, on average, perpendicular to the layer planes [16]. When cooling the mesophase, no crystallisation was observed under the microscope and the texture of the mesophase
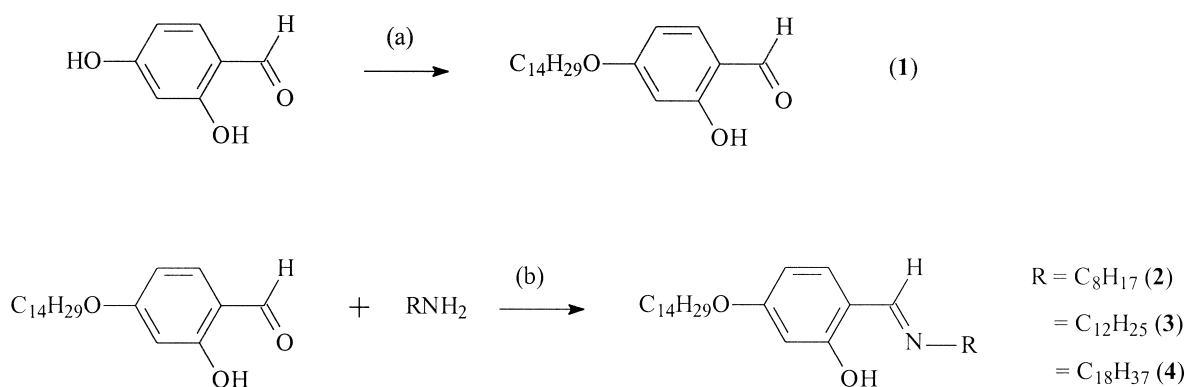
Scheme 1. Synthesis of the azomethine ligands **2**–**4**. Experimental conditions: (a) C$_{14}$H$_{29}$Br, KHCO$_3$, DMF (reflux, 3 h); (b) ethanol or n-heptane (reflux, 3 h), glacial acetic acid (catalyst).

Table 1
Overview and analysis results for the mesomorphic rare-earth complexes [Ln(LH)$_3$(NO$_3$)$_3$] with azomethine ligands

Compound	Ln	LH[a]	%C[b]	%H[b]	%N[b]	Yield (%)
5	Nd	**2**	62.31 (62.27)	9.21 (9.25)	4.90 (5.04)	57
6	Gd	**2**	62.20 (62.18)	9.20 (9.18)	4.86 (5.00)	56
7	Ho	**2**	61.85 (61.90)	9.14 (9.14)	4.82 (4.98)	62
8	Nd	**3**	64.08 (64.77)	9.65 (9.72)	4.44 (4.58)	71
9	Gd	**3**	63.52 (64.32)	9.49 (9.65)	4.43 (4.54)	74
10	Ho	**3**	63.80 (64.05)	9.52 (9.61)	4.43 (4.53)	63
11	La	**4**	68.38 (67.47)	10.46 (10.31)	3.63 (4.03)	76
12	Nd	**4**	66.84 (67.29)	10.16 (10.28)	3.98 (4.02)	96
13	Gd	**4**	66.73 (66.88)	10.21 (10.22)	3.78 (4.00)	91
14	Ho	**4**	66.59 (66.64)	10.19 (10.18)	3.75 (3.98)	92

[a] Ligands: **2**, 4-tetradecyloxy-*N*-octyl-2-hydroxybenzaldimine; **3**, 4-tetradecyloxy-*N*-dodecyl-2-hydroxybenzaldimine; **4**, 4-tetradecyloxy-*N*-octadecyl-2-hydroxybenzaldimine.

[b] Calculated values are given in parentheses.

was frozen into the solid state. A glassy mesophase was formed. Glass formation was noticed from the fact that it was no longer possible to shear the cover glasses between which the sample was sandwiched. Moreover, when cooling further, conchoidal fractures were observed in the texture. These conchoidal fractures also indicate the presence of a glassy state. The DSC traces showed crystallisation at a cooling rate of 10°C min^{-1}, although a strong supercooling was observed. These differences in behaviour between the microscopic and DSC observations do not contradict each other, because we were studying a thin film under the microscope, whereas a bulk sample was used for the DSC measurements.

When going from the neodymium(III) complex, to the gadolinium(III) complex, to the holmium(III) complex, the mesophase stability range decreases. In fact, the melting point gradually increases over the lanthanide series, and at the same time the clearing point decreases. This is in agreement with the findings of Binnemans et al. [14] for other nitrate complexes. The length of the alkyl chain has considerably less influence on the transition temperature than the central metal ion.

4. Conclusions

In this paper, the mesomorphic properties of some lanthanide complexes with azomethine ligands are discussed. It is shown that the lanthanide ion can induce mesomorphism in non-mesomorphic azomethine ligands, by forming complexes with stoichiometry [Ln(LH)$_3$(NO$_3$)$_3$], where Ln is a lanthanide ion, LH is the ligand and NO$_3$ is the counter ion. These complexes all show smectic A mesophases on cooling from the isotropic melt. The mesophase can be supercooled to a glassy state.

Table 2
Thermal behaviour of the azomethine ligands and the rare-earth complexes

Compound	Transition[a]	Temperature (°C)	ΔH (kJ mol^{-1})
2	Crys→I	37	74.5
3	Crys→I	50	87.6
4	Crys→I	73	86.0
5	Crys→SmA	116	15.6
	SmA→I	158	10.9
6	Crys→SmA	125	21.4
	SmA→I	143	10.2
7[b]	Crys→I	143	42.7
	I→SmA	133	9.6
8	Crys→SmA	106	19.0
	SmA→I	160	12.2
9	Crys→SmA	130	23.0
	SmA→I	150	12.5
10	Crys→SmA	138	33.3
	SmA→I	144	9.9
11	Crys→SmA	92	5.2
	SmA→I	138	10.8
12	Crys→SmA	102	14.7
	SmA→I	155	10.6
13	Crys→SmA	115	25.6
	SmA→I	145	10.6
14	Crys→SmA	132	30.9
	SmA→I	141	11.9

[a] Crys, crystalline phase; SmA, smectic A phase; I, isotropic phase.

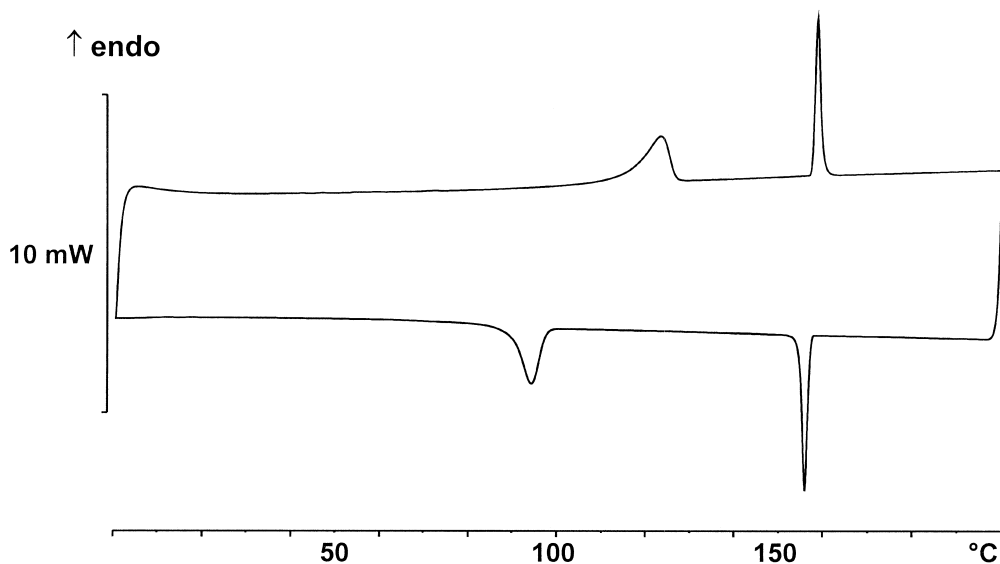[b] Compound **7** shows a SmA mesophase on cooling from the isotropic liquid only (monotropic liquid crystal).

Fig. 1. DSC trace of compound **5**. Endothermic peaks point upwards. The upper trace shows the second heating run, the lower trace shows the second cooling run.

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