Rare-earth complexes of mesomorphic Schiff's base ligands

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Rare-earth complexes of mesomorphic Schiff's bases, 4-[(alkylimino)methyl]-3-hydroxyphenyl 4-alkyloxybenzoates, were synthesized. Whereas the ligands LH display a nematic and/or a smectic C phase, the metal complexes show a viscous smectic A phase and decompose at the clearing point. The mesophase was investigated by hot-stage polarizing optical microscopy, by differential scanning calorimetry and by high temperature X-ray diffraction. Two types of complex were found, $[\mathrm{Ln(LH)_3(NO_3)_3}]$ and $[\mathrm{Ln(LH)_2 L(NO_3)_2}]$, depending on the ligand or the central metal ion. The first coordination sphere of the rare-earth ion in these metallomesogens is comparable to that in the structure of complexes with 4-alkoxy-*N*-alkyl-2-hydroxybenzaldimine ligands.

1. Introduction

The majority of the metal-containing liquid crystals (metallomesogens) described in the literature contain Cu(II), Ni(II), Ag(I), Pd(II) or Pt(II) as the central metal ion [1]. The first calamitic rare-earth-containing liquid crystals were described in 1991 by Galyametdinov and co-workers [2]. These complexes contained Schiff's base ligands with two aromatic rings (figure 1). It was thought that the stoichiometry of these complexes was $[\mathrm{Ln(LH)_2 L X_2}]$, with Ln being the rare-earth ion, LH being the Schiff's base ligand (L is the deprotonated form) and X being the counterion (nitrate or chloride). The ligands are mesogenic, forming a SmC phase. The rare-earth complexes form a highly viscous smectic mesophase (which was not further identified in the original paper). Later Galyametdinov and coworkers synthesized rare-earth complexes of non-mesogenic Schiff's base ligands with one aromatic ring (4-alkoxy-*N*-alkyl 2-hydroxybenzaldimines). Although the ligands did not display liquid crystalline properties, the rare-earth complexes did (SmA phase) [3–6]. It took several years before the molecular structure of these complexes could

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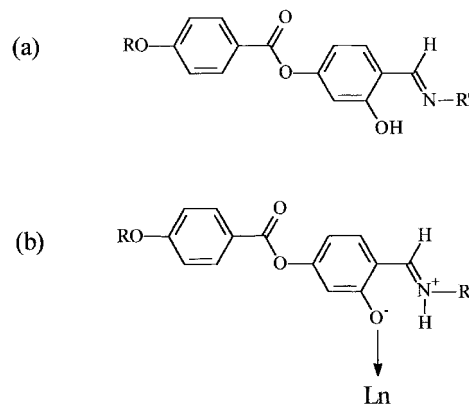
Figure 1. 4-[(alkylimino)methyl]-3-hydroxyphenyl 4-alkyloxy-benzoate Schiff's base ligand in the normal form (*a*) and in the zwitterionic form showing coordination to a lanthanide centre (*b*). *R* and *R'* represent long chain alkyl groups.

be determined. At first, it was assumed that the stoichiometry of the complexes is $[\mathrm{Ln(LH)_2 L X_2}]$ (just as for the complexes of Schiff's base ligands with two aromatic rings), but Binnemans *et al.* were able to show that the stoichiometry of the complexes with nitrate counterions should be reformulated as $[\mathrm{Ln(LH)_3(NO_3)_3}]$. The Schiff's base ligands are present in a zwitterionic form,

with a negative charge on the phenolic oxygen and a positive charge on the imine nitrogen [7, 8]. The metal ion is surrounded by three monodentate Schiff's base ligands (binding via the phenolic oxygen) and three bidentate nitrate groups. It was found that the transition temperature of these complexes is strongly dependent on the size of the central metal ion [9]. So far little is known about the structure of the chloride complexes, but Binnemans *et al.* could obtain metallomesogens with reduced transition temperatures by replacing chloride by dodecyl sulphate (DOS) counter ions [10]. Later, it was possible to obtain the DOS complexes via a direct route using Ln(DOS)$_3$ salts as the reagents [11]. Other rare-earth-containing metallomesogens have been described in the literature [12], but in less detail than the salicylaldimine Schiff's base complexes.

Although we now have a good understanding of the structure of the rare-earth complexes of Schiff's bases with one aromatic ring and with nitrate counterions, the properties of the corresponding complexes of Schiff's bases with two aromatic rings were much less intensively investigated [2, 13]. In this paper, we present the synthesis, characterization and mesomorphic behaviour of rare-earth complexes with these 4-[(alkylimino)methyl]-3-hydroxyphenyl 4-alkyloxybenzoate Schiff's base ligands (figure 1). An overview of the ligands can be found in table 1. Answers will be given to the questions: (1) What is the stoichiometry of the complexes? (2) What can we say about the structure of the first coordination sphere around the rare-earth ion? (3) What is the exact identity of the smectic mesophase? (4) What is the influence of the chain length and the central metal ion on mesophase behaviour? (5) Are the complexes thermally stable?

2. Experimental

2.1. *Apparatus and methods*

^{1}H NMR spectra were obtained on a Bruker WM-250 spectrometer (250 MHz) or on a Bruker AMX 400 spectrometer (400 MHz). Elemental analyses (CHN) were carried out on a CE Instruments EA-1110 elemental analyser. Differential scanning calorimetry (DSC) measurements were made on a Mettler-Toledo DSC821e module (heating rate 10°C min^{-1}). 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. High temperature X-ray diffraction (XRD) was measured on a STOE transmission powder diffractometer system STADI P, with a high temperature attachment version 0.65.1 (temperature range from room temperature to 1000°C). Monochromatic CuK$_{\alpha_1}$ radiation ($\lambda = 1.5406$ Å) was obtained with the aid of a curved germanium primary monochromator. Diffracted X-rays were measured by a linear position sensitive detector (PSD). The sample was placed in a quartz glass capillary (outer diameter 0.3 mm, wall thickness 0.01 mm) and spun during the measurement. In general, data were collected in the range $1 \leqslant 2\theta \leqslant 30°$. FTIR spectra were recorded on a Bruker IFS-66 spectrometer, using KBr pellets. Thermogravimetric curves were obtained on a Polymer Laboratories STA 1000H TG-DTA apparatus. The sample (*c.* 15 mg) was heated in a static air atmosphere from 30 to 1000°C, at a rate of 10°C min^{-1}. All chemicals were used as received, without further purification. Hydrated rare earth nitrates were purchased from Aldrich.
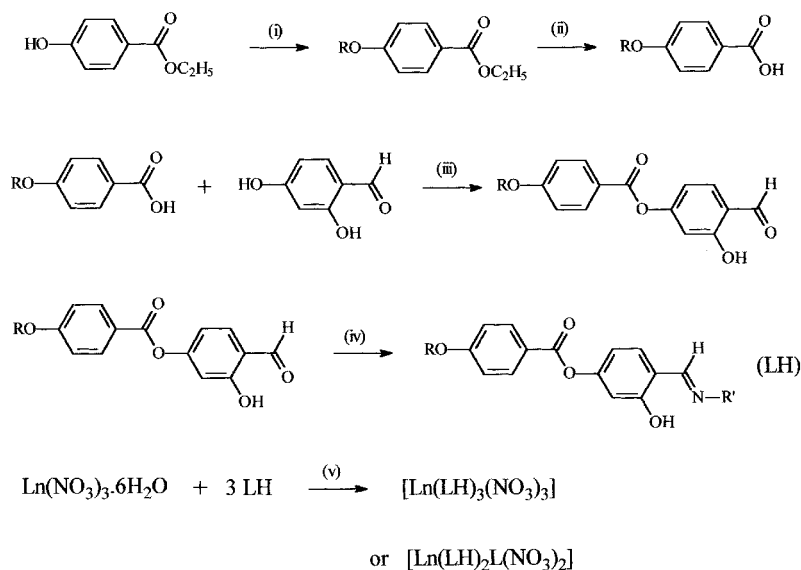
2.2. *Synthesis*

The Schiff's base ligands were synthesized via a three-step reaction (see the scheme). The 4-alkoxybenzoic acids were obtained by reaction between ethyl 4-hydroxybenzoate and the corresponding 1-bromoalkane in 2-butanone, with K$_2$CO$_3$ as the base and KI as catalyst, followed by saponification of the ester and work-up in acidic solution. Alternatively we used a method described by Berdagué *et al.* [14], namely direct alkylation of 4-hydroxybenzoic acid in PEG-200 (polyethylene glycol with average molecular weight 200) as the solvent. 4-Hydroxybenzoic acid is deprotonated with two equivalents of KOH. Addition of one equivalent of a 1-bromoalkane results in selective ether formation, instead of

Table 1. Overview of the Schiff's base ligands and their mesomorphic behaviour.

Ligand[a]	R	R′	Transition temperatures/°C[b]
L^{1}H	C$_6$H$_{13}$	C$_{12}$H$_{25}$	Cr$_I$ • 42 • Cr$_{II}$ • 66 • N • 75 • I
L^{2}H	C$_{10}$H$_{21}$	C$_{12}$H$_{25}$	Cr • 65 • SmC • 77 • N • 80 • I
L^{3}H	C$_{12}$H$_{25}$	C$_{12}$H$_{25}$	Cr • 73 • SmC • 82 • I
L^{4}H	C$_6$H$_{13}$	C$_{18}$H$_{37}$	Cr$_I$ • 53 • Cr$_{II}$ • [SmC • 57] • 68 • N • 73 • I
L^{5}H	C$_8$H$_{17}$	C$_{18}$H$_{37}$	Cr$_I$ • 56 • Cr$_{II}$ • 69 • SmC • 73 • N • 77 • I
L^{6}H	C$_{10}$H$_{21}$	C$_{18}$H$_{37}$	Cr$_I$ • 59 • Cr$_{II}$ • 70 • SmC • 79 • I
L^{7}H	C$_{12}$H$_{25}$	C$_{18}$H$_{37}$	Cr$_I$ • 63 • Cr$_{II}$ • 66 • Cr$_{III}$ • 76 • SmC • 83 • I

[a] A general structure of the Schiff's base ligands can be found in figure 1.
[b] Cr, Cr$_I$, Cr$_{II}$ = crystalline solid phases; SmC = smectic C phase; N = nematic phase; I = isotropic liquid.

Scheme. Synthesis of the Schiff's base ligands and rare-earth complexes. Reaction conditions and reagents: (i) K_2CO_3, RBr, 2-butanone, KI (catalyst), reflux, 48 h; (ii) (a) KOH, ethanol, reflux, 2.5 h, (b) H_3O^+; (iii) DCC, DMAP, DCM, room temperature, 24 h; (iv) $R'NH_2$, toluene, acetic acid (5 drops), 3 h reflux (Dean–Stark trap); (v) absolute ethanol, 50°C, 3 h.

esterification. Although the method of Berdagué *et al.* is much faster than the classical Williamson etherification, a disadvantage is that it is difficult to remove the PEG-200 solvent after the reaction. The 4-(4-alkyloxy-benzoyloxy)-2-hydroxybenzaldehydes were synthesized by esterification of the corresponding 4-alkoxybenzoic acid and 2,4-dihydroxybenzaldehyde, with DCC and DMAP in dichloromethane [15]. The Schiff's bases were obtained by condensing the aldehydes with a primary amine in toluene, with removal of water via a Dean–Stark trap. The purity of the ligands was checked by ^1H NMR and by CHN elemental analysis. The rare-earth complexes were prepared by reaction of the Schiff's base ligand with an excess of hydrated rare-earth nitrate in absolute ethanol.

As an example, the syntheses of ligand L^1H and complex **1** is described.

2.2.1. *4-[(Dodecylimino)methyl]-3-hydroxyphenyl 4-hexylbenzoate, L^1H*

To a solution of 4-(4-hexyloxybenzoyloxy)-2-hydroxy-benzaldehyde (8 mmol, 2.75 g) in toluene (400 ml) was added *n*-dodecylamine (8 mmol, 1.49 g) and 5 drops of acetic acid. The solution was heated at reflux for 3 h, and the water evolved during the reaction was collected by a Dean–Stark trap. After leaving the solution to cool to room temperature, the solvent was removed under reduced pressure. The crude Schiff's base was recrystallized from absolute ethanol; yield 72% (2.94 g). ^1H NMR (δ_H, CDCl$_3$, 250 MHz): 0.91 (6H, m, $2 \times CH_3$), 1.1–1.5 (24H, m, CH$_2$), 1.66 (2H, quintet, NCH$_2$CH$_2$), 1.80 (2H,

quintet, OCH$_2$CH$_2$), 3.57 (2H, t, NCH$_2$), 4.06 (2H, t, OCH$_2$), 6.70 (1H, dd, H–aryl, $J_o = 8.5$ Hz, $J_m = 2.0$ Hz), 6.78 (1H, d, H–aryl, $J_m = 2.0$ Hz), 6.95 (2H, dd, H–aryl, $J = 9$ Hz), 7.25 (1H, d, H–aryl, $J_o = 8.5$ Hz; overlap with CHCl$_3$ peak), 8.10 (2H, dd, H–aryl, $J = 9$ Hz), 8.30 (1H, s, CH=N), 14.0 (1H, s (broad), OH). IR (v_{max}/cm^{-1}, KBr): 1718 (s, C=O), 1604 (s, C=N), 1284 (m, Ph–OH), 1255 (s, asymm C–O–Ph), 1072 (m, symm C–O–Ph). Elemental analysis: calc. for C$_{32}$H$_{47}$NO$_4$ ($M_w = 509.72$), C 75.40, H 9.29, N 2.75; found C 75.25, H 9.29, N 2.63%.

2.2.2. *[La(L^1H)$_3$(NO$_3$)$_3$], 1*

To a stirred solution of L^1H (0.49 mmol, 250 mg) in absolute ethanol at 50°C was added an excess of La(NO$_3$)$_3$.6H$_2$O (0.49 mmol, 220 mg). The solution was stirred during 3 h at 50°C, and the complex precipitated. After leaving the mixture to cool to room temperature, the complex was collected on a fritted-glass funnel, washed with cold absolute ethanol and dried *in vacuo*. The complex was obtained as a light yellow powder; yield 15% (45 mg). ^1H NMR (δ_H, CDCl$_3$, 250 MHz): 0.88 (18H, m, $2 \times CH_3$), 1.1–1.5 (72H, m, CH$_2$), 1.78 (6H, m, NCH$_2$CH$_2$), 1.81 (6H, m, OCH$_2$CH$_2$), 3.55 (6H, t, NCH$_2$), 4.01 (6H, t, OCH$_2$), 6.40 (3H, dd, H–aryl, $J_o = 8.5$ Hz, $J_m = 2.0$ Hz), 6.65 (3H, d, H–aryl, $J_m = 2.0$ Hz), 6.92 (6H, dd, H–aryl, $J = 9$ Hz), 7.03 (3H, d, H–aryl, $J_o = 8.5$ Hz), 7.89 (3H, broad doublet, CH=N), 8.01 (6H, dd, H–aryl, $J = 9$ Hz), 12.80 (3H, s (broad), OH). IR (v_{max}/cm^{-1}, KBr): 1730 (s, C=O), 1606 (s, C=N), 1479 (s, NO$_3$), 1319 (m, Ph–OH), 1255 (s, asymm C–O–Ph), 1063 (m, symm C–O–Ph), 1028 (s, NO$_3$), 764

(m, NO_3). Elemental analysis: calc. for $C_{96}H_{141}N_6O_{21}La$ ($M_w = 1854.08$), C 62.19, H 7.67, N 4.53; found C 62.26, H 7.68, N 4.15%.

3. Results and discussion

The metal complexes were prepared as described in §2 and the CHN analysis results (table 2) are consistent with the stoichiometry $[Ln(LH)_3(NO_3)_3]$ or $[Ln(LH)_2L(NO_3)_2]$, Ln being the rare-earth ion, LH the Schiff's base ligand and L the deprotonated form of the ligand. The factor influencing the stoichiometry of the complexes is not known. The stoichiometry depends on the ligands (different lengths of the terminal chains), but also to some extent on the central metal ion. The complexes of type $[Ln(LH)_3(NO_3)_3]$ have very similar structural properties in comparison with the corresponding complexes of Schiff's bases with one aromatic ring [8, 9]. It was possible to show by ^1H NMR experiments on the La(III) complexes **1**, **6** and **7** and on the corresponding ligands, that in the metal complexes the Schiff's bases are present in a zwitterionic form, figure 1(*b*). In the ligand, the signal of the OH proton is observed at 14.0 δ. Irradiation of the NH resonance did not influence the CH=N proton signal. In the complexes, the CH=N signal was not only shifted from 8.30 δ to 7.89 δ, but was also broadened or even sometimes showed a doublet splitting. Selective homo-decoupling at 12.3 δ led to a collapse of the CH=N doublet or to a significant reduction of the linewidth. The Schiff's base ligand coordinates to the rare-earth ion via the phenolic oxygen only (monodentate coordination). It can be assumed that the three nitrate groups bind in a bidentate fashion to the rare-earth ion, so that the total coordination number of the rare-earth ion is nine. In the complexes of type $[Ln(LH)_2L(NO_3)_2]$, it was also possible to find evidence for the presence of a zwitterionic form for the ligands.

In principle, the deprotonated Schiff's base ligand L can be either monodentate (coordination via phenolic oxygen) or bidentate (coordination via phenolic oxygen and via the imine nitrogen). In the first case, the coordination number of the lanthanide ion is seven, in the second case the coordination number would be eight. A molecular structure suggested for the lanthanide complexes is shown in figure 2.

All the Schiff's base ligands are liquid crystals. The mesomorphism depends on the chain length: short chains stabilize the nematic phase, while long chains induce a smectic C phase. The nematic phase (N) exhibited the typical schlieren-texture with two and four brushes, or a marbled texture. The smectic C phase gave a paramorphotic texture when obtained by cooling the nematic phase, but the transition could be determined from the fingerprint-like transition lines at the SmC↔N transition point. When a compound displayed only the smectic C phase, a schlieren-texture was observed (points with 4 schlieren). Although the smectic C phase has a higher viscosity than the nematic phase, it was still possible to observe the Brownian motion. The mesomorphic behaviour of the Schiff's base ligands is summarized in table 1. For some ligands, crystal–crystal transitions were observed in the DSC-thermogram of the solid phase.

The mesophase behaviour of the Schiff's bases was changed by complex formation with rare-earth ions. In comparison with their parent ligands, the metallomesogens have a mesophase with a very high viscosity. The viscosity is much higher than in the case of complexes of Schiff's base ligands with one aromatic ring [8, 9]. It was not easy to obtain a good texture by hot-stage polarizing optical microscopy, because of the high viscosity of the mesophase and because the texture could only be obtained by heating the compound. Therefore, the mesophase was identified by high temperature XRD.

Table 2. Overview of the rare-earth complexes (including microanalysis data) and their mesomorphism[a].

Complex	Stoichiometry[a]	%C[b]	%H[b]	%N[b]	Transition temperatures/°C[c]
1	$[La(L^1H)_3(NO_3)_3]$	62.26 (62.19)	7.68 (7.67)	4.15 (4.53)	Cr • 70 • SmA • 184 • dec.
2	$[Tb(L^1H)_3(NO_3)_3]$	61.42 (61.52)	7.44 (7.58)	4.04 (4.48)	Cr • 75 • SmA • 172 • dec.
3	$[La(L^2H)_2L^2(NO_3)_2]$	65.73 (66.20)	8.25 (8.43)	3.25 (3.57)	Cr • 87 • SmA • 178 • dec.
4	$[La(L^3H)_2L^3(NO_3)_2]$	66.70 (67.00)	8.52 (8.68)	3.17 (3.43)	Cr • 87 • SmA • 187 • dec.
5	$[Nd(L^3H)_3(NO_3)_3]$	66.49 (66.83)	8.43 (8.66)	3.01 (3.41)	Cr • 96 • SmA • 164 • dec.
6	$[La(L^4H)_3(NO_3)_3]$	64.87 (65.00)	8.46 (8.47)	3.66 (3.99)	Cr • 71 • SmA • 192 • I (dec.)
7	$[La(L^5H)_3(NO_3)_3]$	65.46 (65.79)	8.70 (8.70)	3.53 (3.84)	Cr • 66 • SmA • 199 • I (dec.)
8	$[La(L^6H)_2L^6(NO_3)_2]$	67.73 (68.42)	9.15 (9.11)	3.34 (3.17)	Cr • 70 • SmA • 177 • dec.
9	$[Nd(L^6H)_2L^6(NO_3)_2]$	67.61 (68.25)	8.88 (9.09)	2.98 (3.16)	Cr • 74 • SmA • 173 • dec.
10	$[La(L^7H)_2L^7(NO_3)_2]$	68.75 (69.05)	9.33 (9.31)	3.24 (3.05)	Cr • 88 • SmA • 169 • dec.
11	$[Nd(L^7H)_2L^7(NO_3)_2]$	68.46 (68.89)	9.19 (9.29)	2.88 (3.04)	Cr • 85 • SmA • 170 • dec.

[a] An overview of the ligands can be found in Table 1.
[b] Calculated values are given in brackets.
[c] Abbreviations: Cr = crystalline phase; SmA = smectic A phase; I = isotropic liquid; dec. = decomposition.
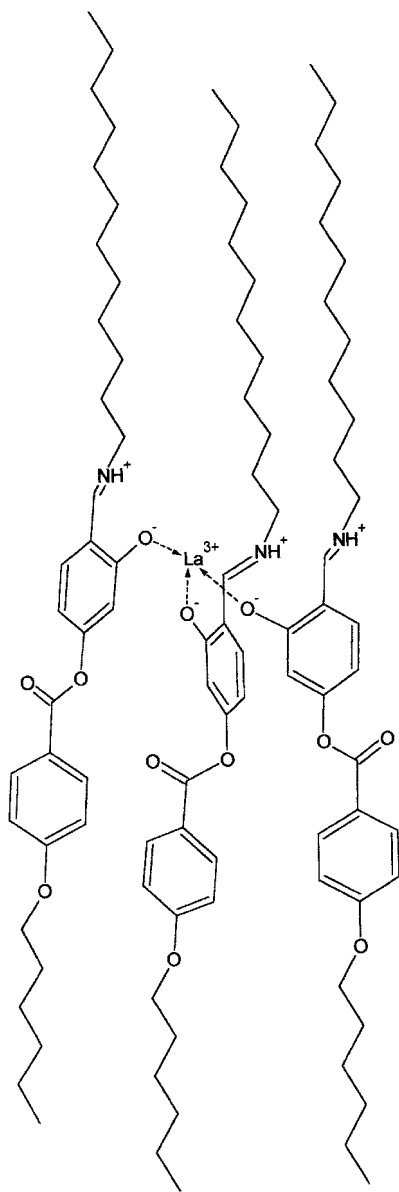
Figure 2. Molecular structure suggested for the Schiff's base complexes. For the sake of clarity, the nitrate groups have been omitted.
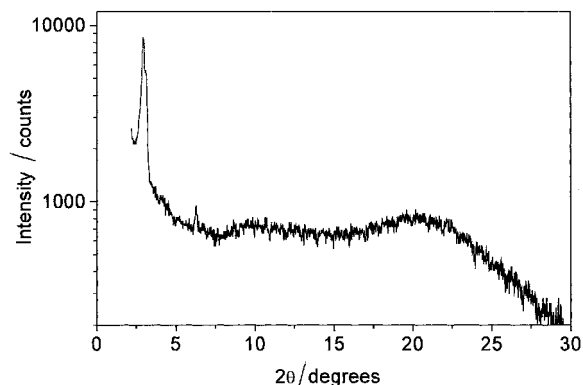

Figure 3. X-ray diffractogram of Tb(III) complex **2** in the mesophase at 110°C.
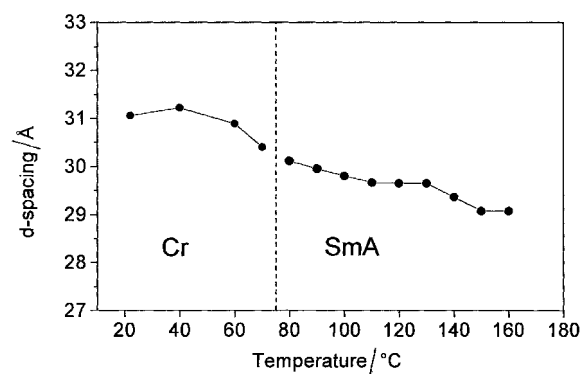
Figure 4. Temperature dependence of the *d*-spacing in Tb(III) complex **2**.

Figure 3 shows the X-ray diffractogram of Tb(III) complex **2** at 110°C. This diffractogram indicates the presence of a lamellar structure. In the small angle region, an intense peak is observed at $2\theta = 2.98°$, corresponding to a layer thickness of 29.65Å. This peak represents the (0 0 1) reflection. The second order peak at $2\theta = 6.00°$ is very weak, which indicates that the smectic layers are not well defined [16]. The diffuse peak in the wide angle region (at *c.* 4.6 Å) points to a disordered smectic phase. In figure 4, the temperature dependence of the *d*-spacing is shown. In the solid state, the *d*-spacing increases slightly from 20 to 40°C, and then decreases towards the melting point. No distinct jump in *d*-spacing is observed at the solid to mesophase transition (75°C). A similar behaviour was observed by Binnemans *et al.* for lanthanum(III) dodecanoate [17]. In the mesophase (75–172°C), the *d*-spacing decreases with increasing temperature. This behaviour is typical for the presence of a SmA phase. At *c.* 140°C, a break is observed in the smooth decrease of the *d*-spacing; this may be due to structural changes in the molecular complexes in the mesophase.

The melting point of the rare-earth complexes is fairly low (for some complexes as low as 70°C) and the smectic A phase is stable over about 100°C. However, most of the metal complexes decompose without clearing (between 170 and 200°C). The DSC thermogram of La(III) complex **7** is shown in figure 5. It is one of the few complexes for which the clearing point could be observed (at a heating rate of 10°C min^{-1}). No X-ray diffractograms could be measured close to the clearing point, because of decomposition of the metal complexes. Thermogravimetry shows that thermal decomposition of the ligands themselves only starts above 220°C. The dependence of the transition temperature on the rare-earth ion is much less pronounced than in the case of the
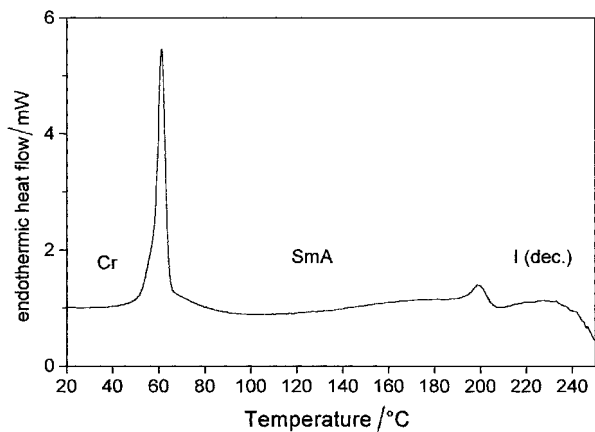
Figure 5. DSC thermogram of La(III) complex **7** (heating rate 10°C min⁻¹). Endothermic peaks point upwards.

complexes with one-ring ligand [10]. On the other hand, the transition temperatures depend on the stoichiometry of the metal complexes. Whereas $[La(L^7H)_2 L^7(NO_3)_2]$ and $[Nd(L^7H)_2 L^7(NO_3)_2]$ have virtually the same transition temperatures, a significant difference is found for the complexes $[La(L^3H)_2 L(NO_3)_2]$ and the $[Nd(L^3H)_3(NO_3)_3]$ complexes. The rare-earth ions have a very strong tendency to induce or stabilize SmA mesophases. Hitherto, only a SmA phase could be observed for calamitic lanthanide complexes. Although the mesomorphism of the ligands depends on the length of the terminal chains, this is no longer the case for the lanthanide complexes. The mesophase behaviour of the rare-earth complexes is summarized in table 2.

4. Concluding remarks

The new complexes have two different types of stoichio-metries: $[Ln(LH)_3(NO_3)_3]$ and $[Ln(LH)_2 L(NO_3)_2]$. The type formed depends on the ligand (different terminal chain lengths), but to some extent also on the lanthanide ion. All the complexes form a smectic A mesophase (determined by polarizing microscopy and high temper-ature XRD). In complexes of the type $[Ln(LH)_3(NO_3)_3]$, the three Schiff's base ligands coordinate in a zwitter-ionic form to the metal ion. Three monodentate Schiff's bases and three bidentate nitrate groups make the coordi-nation number of the rare-earth ion nine. The chain length has an influence on the transition temperatures and the mesomorphic behaviour of the ligand (N, SmC or both phases present depending on the terminal chain lengths), but only one type of mesophase is observed for the rare-earth complexes (SmA).

Although the metal complexes described in the work are structurally related to the salicylaldimine ligands with one aromatic ring, and although they form the same type of mesophase [8, 9], they have an unfavour-ably high viscosity and a low thermal stability. Further work on the liquid crystalline lanthanide complexes with Schiff's base ligands will be concentrated on structural variation in ligands with one aromatic ring.

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