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Influence of the ligand structure on the liquid crystalline properties of lanthanide-containing salicylaldimine mesogens

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Influence of the ligand structure on the liquid crystalline properties of lanthanide-containing salicylaldimine mesogens

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The synthesis and liquid crystalline properties of lanthanide complexes with different but structurally related Schiff's base ligands are described. The complexes all contain nitrate counterions and have the stoichiometry $[Ln(LH)_3(NO_3)_3]$, where Ln is a trivalent rare-earth ion (La, Nd, Gd or Ho) and LH is a Schiff's base ligand. None of the Schiff's base ligands exhibits mesomorphism, but some of the complexes do (SmA phase). It is shown that the presence or absence and the position of substituents on the ligand determine whether or not the complexes show mesomorphism. The thermal behaviour of these compounds has been investigated by hot stage polarizing microscopy and differential scanning calorimetry.

1. Introduction

Since the discovery of metal-containing liquid crystals (metallomesogens), an increasing number of researchers have described the advantages of these compounds when compared with their metal-free counterparts. The fluidity, physical anisotropy and response to external electric and magnetic fields, which are all characteristic properties of conventional liquid crystals, are combined with the redox and magnetic properties of the metal in metallomesogens, giving a combination which cannot be found in other materials [1–9]. Following on from the early metallomesogens which contained transition metals, lanthanide mesogens combine the typical properties of lanthanides, such as paramagnetism, possible high magnetic anisotropy and the bright photoluminescence of high colorimetric purity, with those of liquid crystals. Lanthanide mesogens containing Schiff's bases as ligands have been studied intensively [10–20].

We have performed a systematic study of lanthanide metallomesogens consisting of the ligand LH1 shown in figure 1, with nitrate as the counterion, and found an overall stoichiometry $[Ln(LH)_3(NO_3)_3]$ for this type of compound [12, 13]. Nitrate is often chosen as the counterion, because it can coordinate in a bidentate fashion, allowing the lanthanide ion easily to obtain a high coordination number, without the need to form dimeric or oligomeric complexes. A later study of similar compounds but with dodecyl sulphate (DOS) counterions instead of nitrate showed a similar stoichiometry for these complexes: $[Ln(LH)_3(DOS)_3]$ [14]. Finally, in liquid crystalline lanthanide-containing Schiff's base complexes with chloride counterions, this stoichiometry $[Ln(LH)_3Cl_3]$ was found, although at first it remained unclear as to how the monodentate chloride ions could provide the lanthanide ion with a sufficiently high coordination number [15]. It was later shown by 2D COSY ^{1}H NMR

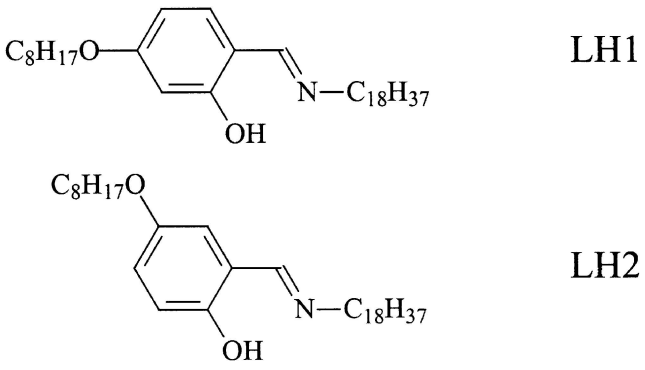

Figure 1. Schiff's base ligands discussed in this paper.

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that there exist two forms of the complexes in solution [16]. In one structure, the Schiff's base coordinates in a monodentate zwitterionic way, as is the case in the nitrate and DOS complexes. In the other form, the ligands coordinate in a bidentate fashion, involving not only the phenol oxygen atoms, but also the imine nitrogen atoms in the coordination. These studies had one aspect in common: they all varied either the lanthanide, the counterion, or the chain length of the terminal chain, while the structure of the ligand was kept constant. In that way, either the influence of the lanthanide contraction on the thermal behaviour of the mesogens, or the influence of varying the counterion could be studied in detail [12, 17–19].

In this paper, we report an investigation of the thermal properties of lanthanide-containing Schiff's base complexes in which attention is paid to varying the Schiff's base ligand. Three different variations of the same ligand type have been selected, as can be seen in figure 1 (LH1 to LH3; LH4 will be needed for comparison).

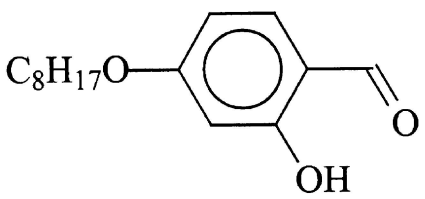
2. Experimental

2.1. *Characterization*

^{1}H NMR spectra were recorded on either a Bruker Avance 300 spectrometer (300 MHz) or a Bruker AMX-400 spectrometer (400 MHz) using $CDCl_3$ as solvent and tetramethylsilane as the internal standard. Elemental analyses (CHN) were performed on a CE-Instrument EA-1110 elemental analyser. Differential scanning calorimetry (DSC) measurements were made using a Mettler-Toledo DSC822e module (scan rate 10°C min^{-1} under a helium flow). Optical textures of the mesophases were observed with an Olympus BX60 polarizing microscope equipped with a Linkam THMS600 hot stage and Linkam TMS93 programmable temperature controller. Organic reagents were purchased from ACROS; lanthanide salts were obtained from Aldrich. All solvents and chemicals were used as received.

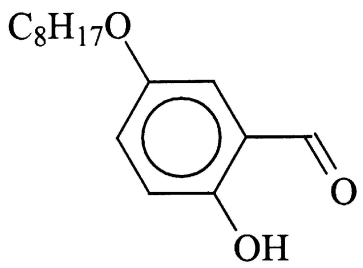
2.2. *Synthesis*

2.2.1. *2-Hydroxy-4-(octyloxy)benzaldehyde*



A solution of 2,4-dihydroxybenzaldehyde (6.91 g, 50 mmol), 1-bromooctane (9.66 g, 50 mmol) and $KHCO_3$ (5.01 g, 50 mmol) in DMF was heated at reflux for 3 h. After cooling to room temperature, the reaction mixture was poured into a mixture of 100 ml of 38% HCl and 300 ml of deionized water. The aqueous layer was extracted three times with diethyl ether. The organic fractions were combined and dried over $MgSO_4$. The crude 2-hydroxy-4-(octyloxy)benzaldehyde was purified by column chromatography, using a 90/10 mixture of *n*-heptane/ethylacetate as the eluent. Yield 63% (7.88 g), light yellow oil. ^{1}H NMR ($CDCl_3$, δ/ppm): 0.88 (t, 3H, CH_3), 1.00–1.55 (m, 10H, CH_2), 1.79 (m, 2H, C**H**$_2$–CH_2–O), 4.00 (t, 2H, CH_2–O), 6.40 (d, 1H, H_{arom}), 6.52 (dd, 1H, H_{arom}), 7.41 (d, 1H, H_{arom}), 9.70 (s, 1H, CHO), 11.50 (s, 1H, OH). Calculated for $C_{15}H_{22}O_3$ ($M_w = 250.33$) C 72.0, H 8.9; found C 72.2, H 8.9%.

2.2.2. *2-Hydroxy-5-(octyloxy)benzaldehyde*



To a solution of hydroquinone (33.01 g, 300 mmol) in 300 ml of a H_2O/dioxane mixture and K_2CO_3 (13.82 g, 100 mmol) was added 1-bromooctane (19.29 g, 100 mmol). Stirring was continued for 12 h at 110°C, under an argon atmosphere. After cooling to room temperature, the dioxane was evaporated under reduced pressure. The remaining residue was acidified with a 6M HCl solution and extracted three times with ether. The ether layers were washed three times with deionized water, and dried over $MgSO_4$ overnight. The crude 4-octyloxyphenol was purified on a silica column using a 1/1 mixture of ether/*n*-heptane as eluent. Yield 60% (13.41 g), white crystalline powder. ^{1}H NMR ($CDCl_3$, δ/ppm): 0.88 (t, 3H, CH_3), 1.23–1.46 (m, 10H, CH_2), 1.75 (m, 2H, C**H**$_2$–CH_2–O), 3.89 (t, 2H, CH_2–O), 4.48 (s, 1H, OH), 6.77 (m, 4H, H_{arom}). Calculated for $C_{14}H_{22}O_2$ ($M_w = 222.32$) C 75.6, H 10.0; found C 75.4, H 10.0%.

To introduce the aldehyde function tributylamine (4.45 g, 24 mmol), was added to a solution of 4-octyloxyphenol (13.39 g, 60 mmol) in 200 ml of dry toluene, the reaction mixture was evacuated and an argon atmosphere introduced. Anhydrous $SnCl_4$ (0.70 ml, 6 mmol) was added through a septum, using an oven-dried glass syringe. The reaction mixture was stirred for 20 min at room temperature. Paraformaldehyde was then added under a continuous argon flow (3.96 g, 132 mmol), and stirring continued for 10 h at 100°C. After cooling to room temperature, the reaction mixture was poured into 500 ml of deionized water and acidified with a 2M HCl solution to pH 2. Diethyl ether was added to extract the aldehyde from the reaction mixture; during this step, an emulsion formed, containing a very fine Sn-containing

byproduct, which had to be filtered through Celite®. After the solid byproduct had been removed, the water layer was extracted with diethyl ether, the combined organic fractions were washed with a saturated NaCl solution (twice) and dried over $MgSO_4$ overnight. The crude 2-hydroxy-5-(octyloxy)benzaldehyde was purified on a silica column using dichloromethane as eluent. Yield 49% (7.30 g), light yellow oil. ^{1}H NMR ($CDCl_3$, δ/ppm): 0.87 (t, 3H, CH_3), 1.23–1.54 (m, 10H, CH_2), 1.77 (m, 2H, C**H**$_2$–CH_2–O), 3.93 (t, 2H, CH_2–O), 6.91 (d, 1H, H_{arom}), 6.98 (d, 1H, H_{arom}), 7.13 (dd, 1H, H_{arom}), 9.83 (s, 1H, CHO), 10.63 (s, 1H, OH).

2.2.3. *Ligands LH1–LH4*

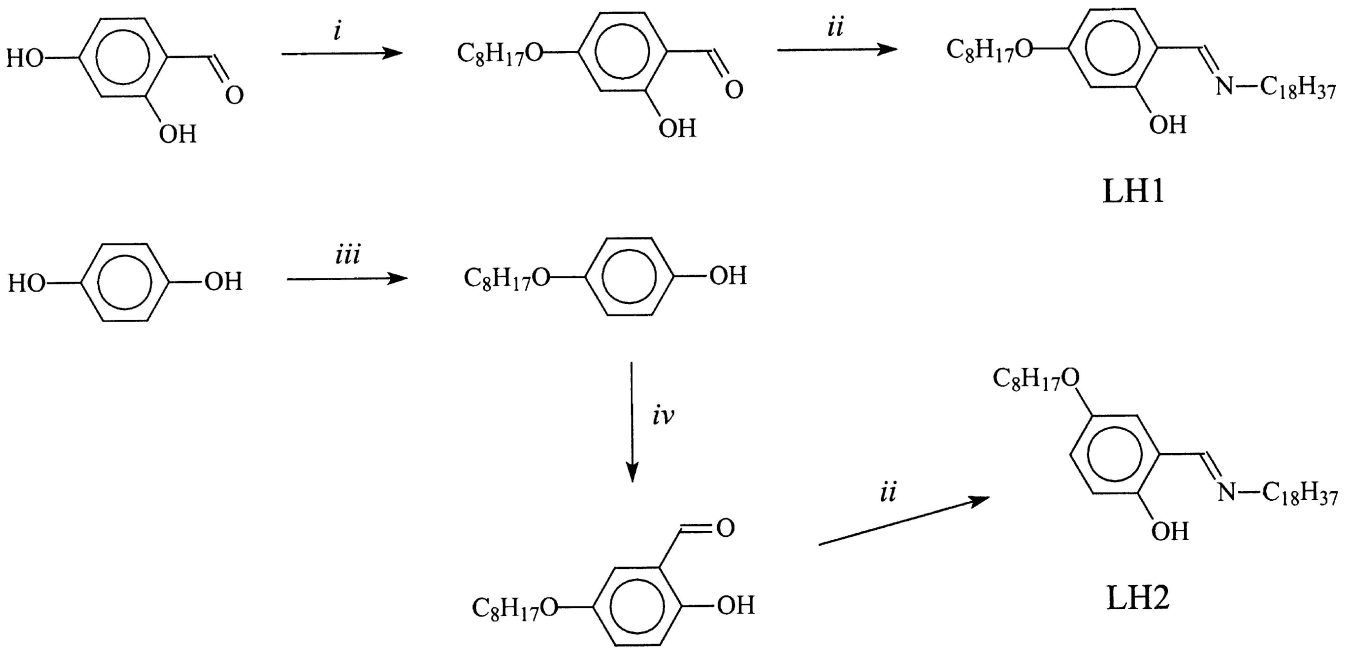
The ligands were synthesized by condensing the appropriate aldehyde with octadecylamine (stearylamine) in absolute ethanol with a few drops of glacial acetic acid as catalyst. The solution was heated at reflux for 3 h. After cooling to room temperature, the ligands were collected by filtration as yellow crystalline precipitates and were purified by recrystallization from hot absolute ethanol solution. The synthesis of ligands LH1 and LH2 is outlined in more detail in the scheme.

2.2.3.1. *2-{(E)-[(E)-Octadecylimino]methyl}-5-(octyloxy)-phenol LH1*. Yield 48% (7.56 g), m.p. 50.3°C. ^{1}H NMR ($CDCl_3$, δ/ppm): 0.88 (m, 6H, CH_3), 1.25–1.44 (m, 40H, CH_2), 1.67 (m, 2H, N–CH_2–C**H**$_2$), 1.77 (m, 2H, C**H**$_2$–CH_2–O), 3.50 (t, 2H, N–CH_2), 3.95 (t, 2H, CH_2–O), 6.31 (dd, 1H, H_{arom}), 6.35 (d, 1H, H_{arom}), 7.04 (d, 1H, H_{arom}), 8.09 (s, 1H, CH=N), 14.1 (s, 1H, OH). Calc. for $C_{33}H_{59}NO_2$ ($M_w = 501.83$) C 79.0, H 11.8, N 2.8; found C 79.1, H 12.3, N 2.8%.

2.2.3.2. *2-{(E)-[(E)-Octadecylimino]methyl}-4-(octyloxy)-phenol LH2*. Yield 84% (7.96 g), m.p. 54.4°C. ^{1}H NMR ($CDCl_3$, δ/ppm): 0.86 (t, 6H, CH_3), 1.19–1.44 (m, 40H, CH_2), 1.73 (m, 4H, N–CH_2–C**H**$_2$ and C**H**$_2$–CH_2–O), 3.56 (t, 2H, N–CH_2), 3.90 (t, 2H, CH_2–O), 6.76 (s, 1H, H_{arom}), 6.89 (s, 2H, H_{arom}), 8.27 (s, 1H, CH=N). Calc. for $C_{33}H_{59}NO_2$ ($M_w = 501.83$) C 79.0, H 11.8, N 2.8; found C 79.3, H 12.2, N 2.8%.

2.2.3.3. *2-{(E)-[(E)-Octadecylimino]methyl}phenol LH3*. Yield 63% (5.90 g), m.p. 43.1°C. ^{1}H NMR ($CDCl_3$, δ/ppm): 0.88 (t, 3H, CH_3), 1.25 (m, 30H, CH_2), 1.69 (m, 2H, N–CH_2–C**H**$_2$), 3.58 (t, 2H, N–CH_2), 6.68 (t, 1H, H_{arom}), 6.95 (d, 1H, H_{arom}), 7.24 (d, 1H, H_{arom}), 7.29 (t, 1H, H_{arom}), 8.33 (s, 1H, CH=N), 13.7 (s, 1H, OH). Calc. for $C_{25}H_{43}NO$ ($M_w = 373.62$) C 80.4, H 11.6, N 3.8; found C 80.0, H 11.9, N 3.8%.

2.2.3.4. *5-Methoxy-2-{(E)-[(E)-octadecylimino]methyl}-phenol LH4*. Yield 71% (14.33 g), m.p. 60.9°C. ^{1}H NMR ($CDCl_3$, δ/ppm): 0.88 (t, 3H, CH_3), 1.18–1.33 (m, 30H, CH_2), 1.67 (m, 2H, N–CH_2–C**H**$_2$), 3.50 (t, 2H, N–C**H**$_2$), 3.80 (s, 3H, CH_3O), 6.35 (m, 2H, H_{arom}), 7.06



Scheme. Ligand synthesis. *i* $C_8H_{17}Br$, $KHCO_3$, 3 h reflux in DMF, argon atmosphere; *ii* $C_{18}H_{37}NH_2$, trace of glacial acetic acid, 3 h reflux in abs. ethanol; *iii* $C_8H_{17}Br$, K_2CO_3, 12 h, 110°C in H_2O/dioxane, argon atmosphere; *iv* $(CH_2O)_n$, $N(C_4H_9)_3$, anhydrous $SnCl_4$, 10 h, 100°C in dry toluene, argon atmosphere.

(d, 1H, H_{arom}), 8.09 (s, 1H, CH=N). Calc. for $C_{26}H_{45}NO_2$ ($M_w = 403.64$) C 77.4, H 11.2, N 3.5; found C 77.4, H 11.3, N 3.5%.

2.2.4. *Complexes **1**–**12***

All complexes were synthesized using the same procedure. A solution of either $La(NO_3)_3 \cdot 6H_2O$, $Nd(NO_3)_3 \cdot 6H_2O$, $Gd(NO_3)_3 \cdot 6H_2O$ or $Ho(NO_3)_3 \cdot 5H_2O$ in absolute ethanol was added dropwise to a stirred absolute ethanolic solution of the appropriate ligand at 50°C. After addition, the solution was left to stir overnight. The precipitate formed was filtered on a Gooch crucible, washed with absolute ethanol and dried *in vacuo*. The yields and elemental analysis data can be found in table 1.

3. Results and discussion

The preparation of the complexes discussed in this paper was achieved in a multi-step synthesis. The complexes were synthesized by reaction of the appropriate Schiff's base with the appropriate lanthanide nitrate in absolute ethanol. The Schiff's bases were made by condensing the corresponding aldehyde with octadecylamine (stearylamine). Depending on the commercial availability of the aldehyde, the synthesis of the Schiff's base consisted of one or more steps. The starting aldehydes for the preparation of ligands LH3 and LH4 are salicylaldehyde and 2-hydroxy-4-methoxybenzaldehyde, respectively, and both are commercially available. The aldehydes needed for the synthesis of ligands LH1 and LH2 are not commercially available. These are 2-hydroxy-4-(octyloxy)-benzaldehyde and 2-hydroxy-5-(octyloxy)benzaldehyde, respectively, and their syntheses differ quite dramatically. 2-Hydroxy-4-(octyloxy)benzaldehyde can be prepared by heating at reflux 2,4-dihydroxybenzaldehyde with 1-bromooctane and $KHCO_3$ in DMF for 3 h (see the scheme). Although both the 2- and 4-hydroxy groups are equally active towards alkylation, alkylation mainly occurs in the 4-position because of hydrogen bonding of the 2-hydroxy group with the aldehyde oxygen.

Following a similar strategy, one can imagine preparing 2-hydroxy-5-(octyloxy)benzaldehyde by the alkylation of 2,5-dihydroxybenzaldehyde. However, the 5-hydroxy group is much less active towards alkylation than the 2-hydroxy group, so considerable amounts of dialkylated product are obtained, and this is difficult to separate from the monoalkylated product. Thus, the synthesis of 2-hydroxy-5-(octyloxy)benzaldehyde had to be performed using a different route. Starting from hydroquinone, one can selectively alkylate one of the hydroxy groups by using K_2CO_3 as the base and a mixture of water and dioxane as the solvent in combination with 1-bromooctane as the alkylating species [21]. The crude 4-octyloxyphenol was purified on a silica column using a 1/1 mixture of ether/heptane as eluent. The second step in the synthesis is the introduction of an aldehyde group in the position *ortho* to the remaining OH group of the alkylated hydroquinone [22]. The active species in this synthesis is paraformaldehyde, in combination with tributylamine as the base and anhydrous $SnCl_4$ as the catalyst (see the scheme). The resulting 2-hydroxy-5-octyloxybenzaldehyde was purified on a silica column with dichloromethane as eluent.

Complexes **1**–**12** were prepared by dissolving 500 mg of the appropriate ligand in absolute ethanol at temperatures not exceeding 50°C and adding dropwise a solution of the appropriate lanthanide nitrate in absolute ethanol. Stirring continued without further heating for several hours, after which the complexes appeared as a fine precipitate. Completion of precipitation was achieved by placing the flasks in a refrigerator. The complexes were collected by filtration on a crucible, washed with absolute ethanol and dried under reduced pressure. This method proved satisfactory for the preparation of all

Table 1. Yields and elemental analysis data for the complexes $[Ln(LH)_3(NO_3)_3]$.

				Elemental analysis: calculated (found)/%		
Compound	LH	Ln	Yield/%	C	H	N
1	LH1	La	85	65.0 (64.7)	9.8 (10.0)	4.6 (4.5)
2	LH3	La	41	62.3 (62.0)	9.0 (9.3)	5.8 (5.6)
3	LH1	Nd	92	64.8 (64.4)	9.7 (10.0)	4.6 (4.5)
4	LH2	Nd	48	64.8 (64.3)	9.7 (10.1)	4.6 (4.5)
5	LH3	Nd	70	62.1 (61.5)	9.0 (9.2)	5.8 (5.7)
6	LH4	Nd	90	60.8 (60.7)	8.8 (8.9)	5.4 (5.4)
7	LH1	Gd	92	64.3 (64.4)	9.6 (9.6)	4.5 (4.5)
8	LH2	Gd	60	64.3 (63.8)	9.6 (10.0)	4.5 (4.5)
9	LH3	Gd	68	61.5 (61.5)	8.9 (9.4)	5.7 (5.7)
10	LH1	Ho	95	64.0 (63.8)	9.6 (9.6)	4.5 (4.4)
11	LH2	Ho	74	64.0 (63.8)	9.6 (9.8)	4.5 (4.4)
12	LH3	Ho	84	61.2 (60.9)	8.8 (8.9)	5.7 (5.5)

but one compound. Specifically, the synthesis of the lanthanum compound of ligand LH2 caused major problems. When the standard procedure was used, precipitation indeed occurred, but when the compound was analysed, either by CHN or DSC, the precipitate turned out to be pure ligand LH2 and not the assumed lanthanum(III) complex. Repeating the synthesis gave the same results. A more severe method, namely heating at reflux in absolute ethanol for several hours (which is too severe for the preparation of complexes with ligand LH1, because of the decomposition of the ligand by the strong Lewis acid lanthanide ions), resulted in a smaller amount of precipitate, but when analysed, it was again identified as the ligand LH2. Even more remarkable is the fact that the standard procedure did show to be adequate for the preparation of complexes **4**, **8** and **11** of Nd, Gd and Ho with the same ligand LH2. This unusual behaviour of the lanthanum ion has been noted in the past [12, 13, 16, 18] and has to be related to the large ionic radius of La^{3+} (with $r = 1.18$ Å, La^{3+} is the largest lanthanide ion), resulting in a lower charge density. Since lanthanide coordination chemistry mainly concerns electrostatic interactions, this reduced charge density may account for the lower reactivity of the lanthanum ion.

All compounds studied in this paper have been analysed by CHN elemental analysis (table 1) and DSC (table 2). For complexes **1**–**12**, the stoichiometry can be concluded to be $[Ln(LH)_3(NO_3)_3]$, which is in agreement with our earlier findings for similar nitrate complexes [12, 13]. Each lanthanide ion is surrounded by three Schiff's base ligands and three bidentate nitrate ions. The ligands are present as zwitterions and coordinate to the lanthanide ion through the phenol oxygen only. Thus the coordination number of the lanthanide ion is 9.

The thermal results of ligands LH1–LH4 in table 2 show that each ligand melts directly from the crystalline phase to the isotropic liquid. The DSC thermograms show one peak only, corresponding to the melting point. The Schiff's base ligand LH1 has been shown to induce mesomorphism in lanthanide complexes [12] and here, it does also. When the thermal data of LH1 are compared with those of compounds **1**, **3**, **7** and **10**, it is immediately apparent that the latter compounds do not melt directly

Table 2. Transition temperatures and thermal data for ligands LH1–LH4 and complexes **1**–**12**.

Compound	Transition[a]	T/°C	ΔH/kJ mol^{-1}	ΔS/J mol^{-1} K^{-1}
LH1	Cr → I	50	89.8	277.8
LH2	Cr → I	54	76.4	233.4
LH3	Cr → I	43	67.3	213.0
LH4	Cr → I	61	70.4	210.9
1	Cr(I) → Cr(II)	52	80.7	248.4
	Cr(II) → SmA	83	2.5	7.0
	SmA → I	165	11.8	26.9
2	Cr(I) → Cr(II)	67	64.2	188.8
	Cr(II) → I	88	71.3	197.5
3	Cr(I) → Cr(II)	53	89.7	275.1
	Cr(II) → SmA	98	15.0	40.4
	SmA → I	159	11.8	27.3
4	Cr(I) → Cr(II)	34	81.2	264.3
	Cr(II) → I	138	64.1	156.0
5	Cr → I	98	90.2	243.0
6	Cr(I) → Cr(II)	82	59.2	166.6
	Cr(II) → SmA	119	37.9	96.9
	SmA → I	127	3.8	9.4
7	Cr(I) → Cr(II)	52	86.0	264.5
	Cr(II) → SmA	121	16.9	42.9
	SmA → I	150	12.7	30.0
8	Cr(I) → Cr(II)	35	86.0	279.8
	Cr(II) → I	142	71.6	172.7
9	Cr → I	103	97.4	259.4
10	Cr(I) → Cr(II)	48	98.5	306.4
	Cr(II) → SmA	134	22.2	54.5
	SmA → I	144	10.8	25.9
11	Cr(I) → Cr(II)	46	85.3	277.1
	Cr(II) → I	139	76.8	186.6
12	Cr → I	103	106.4	282.6

[a] Cr = crystalline solid, SmA = smectic A mesophase, I = isotropic liquid.

to the isotropic liquid, but pass through a mesophase before clearing to the isotropic liquid. This mesophase was identified by polarizing optical microscopy as a smectic A (SmA) phase by the observation of bâtonnets growing from the isotropic liquid upon cooling and homeotropic regions coexisting with fan-shaped regions in the texture. This is shown for compound **3** in figure 2. All four complexes, **1**, **3**, **7** and **10**, show a crystal-to-crystal transition before melting to the SmA phase. This is identified by the peak in the DSC thermogram and the fact that no changes are observed in the microscope at that temperature. This crystal-to-crystal transition only occurs in the first heating run, indicating that the complex crystallizes in a different crystal structure upon cooling in the DSC than that obtained after synthesis, which is often the case. All four complexes **1**, **3**, **7** and **10** show an enantiotropic SmA mesophase.

When similar complexes are considered with the structurally related ligand LH2, an entirely different situation occurs. By placing the octyloxy chain in the 5-position instead of the 4-position of the aromatic ring, the liquid crystalline properties are destroyed, as can be seen from the data for complexes **4**, **8** and **11** in table 2. All three compounds melt directly to an isotropic liquid. Nor do they form a mesophase upon cooling from the isotropic liquid, i.e. a monotropic mesophase cannot be observed. The reason for this behaviour is clear. A major factor in the design of calamitic (or rod-like) liquid crystals is to obtain a sufficiently high length-to-breadth ratio of the molecules. When the resulting molecules do not sufficiently resemble rods, the arrangement of the molecules in a mesophase cannot be achieved. The bulky arrangement of the ligands LH1, which is the most elongated of the ligands discussed here, around the lanthanide ion, already hampers the realization of an elongated molecule. When this is then even further hampered by increasing the width of the ligand by placing the octyloxy chain in a less ideal position (5 instead of 4) in ligand LH2, the resulting complex is no longer sufficiently rod-like to permit the interactions which are necessary for the formation of a mesophase.

Finally, no mesomorphism is seen in complexes **2**, **5**, **9** and **12**. It seems that ligand LH3 cannot provide sufficient stability to the resulting lanthanide complex for the formation of a mesophase. While the only difference between ligand LH3 and LH1 is the absence of the alkoxy chain in the 4-position of the aromatic ring, it can be assumed that this would not alter the width of the complexes. Of course, the calculated length of the all-*trans* conformation of the ligands differs significantly ($l = 40.1$ Å for LH1 and $l = 28.8$ Å for LH3).

In figure 3, the DSC heating curves for compounds **3**–**6** are shown. This figure allows for the easy comparison of the complexes $[Nd(LH)_3(NO_3)_3]$, with LH being LH1, LH2, LH3 and LH4 respectively. In combination with the thermal data from table 2, it is easy to see that only two complexes are liquid crystalline (**3** and **6**) and that compound **3** shows the highest mesophase stability.

It seems that for these types of compounds, the presence of an alkoxy chain in the 4-position of the aromatic ring, however short, is of central importance to the existence of a mesophase. As we have shown previously, varying the alkoxy chain length $C_nH_{2n+1}O$ in ligand LH1 (figure 1) between $C_{20}H_{41}O$ and CH_3O does not significantly influence the transition temperatures and the corresponding mesophase stability in the complexes

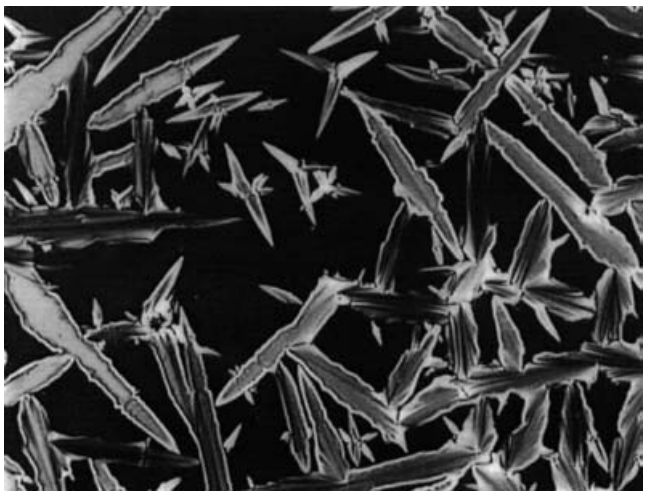


Figure 2. Texture of compound **3**, observed at the clearing point upon cooling from the isotropic liquid (158°C, 100×). Bâtonnets growing from the isotropic liquid, coalescing to a fan-shaped texture, illustrate the presence of a SmA phase.

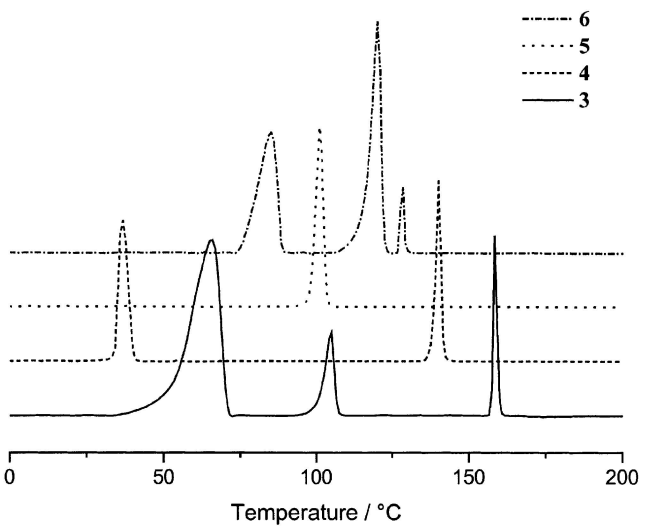


Figure 3. DSC traces for compounds **3**–**6**. Heat flow (*Y*-axis, endothermic peaks pointing upwards) has been scaled for optimal visibility and easy comparison.

$[Nd(LH1)_3(NO_3)_3]$, except for the shortest chain lengths [18]. However, all these complexes, even those with the shortest chain length CH_3O, show a SmA mesophase. Thus, decreasing the chain length by one more unit (thus omitting the chain) destroys the liquid crystalline properties. Compound **6** has been included in this paper for the sake of comparison. It contains the shortest chain variant of ligand LH1, namely ligand LH4.

Figure 4 shows a bar graph of the thermal behaviour of compounds **3**–**6**. Starting with compound **5**, the absence of an alkoxy chain (ligand LH3) prevents the existence of a mesophase. The complex melts directly to the isotropic liquid: Cr 98 I. Introducing a chain with minimal length (compound **6**, ligand LH4) results in the formation of a SmA phase, albeit over a very narrow temperature range: Cr 119 SmA 127 I. Increasing the chain length to eight carbon units (compound **3**, ligand LH1) has a stabilizing effect on the mesophase: Cr 98 SmA 159 I. Finally, placing the chain in a less favourable position (compound **4**, ligand LH2) again destroys the mesophase: Cr 138 I.

When the transition temperatures of compounds **1**, **3**, **7** and **10** are compared, it can be seen that the melting points increase from the lanthanum(III) compound **1** (Cr 83 SmA 165 I) via the neodymium(III) compound **3** (Cr 98 SmA 159 I) and the gadolinium(III) compound **7** (Cr 121 SmA 150 I) to the holmium(III) compound **10** (Cr 134 SmA 144 I), whereas the clearing points decrease in the same way. This trend has been observed for the entire lanthanide series [12]. The increasing charge density on going from La^{3+} to Lu^{3+} was believed to cause stronger interactions between individual complex molecules towards the heavier lanthanides and thereby increasing the melting points. A similar argument could be used to explain the behaviour of the LH3 derivatives **2**, **5**, **9** and **12**. Here also, the melting point increases from La towards Ho.

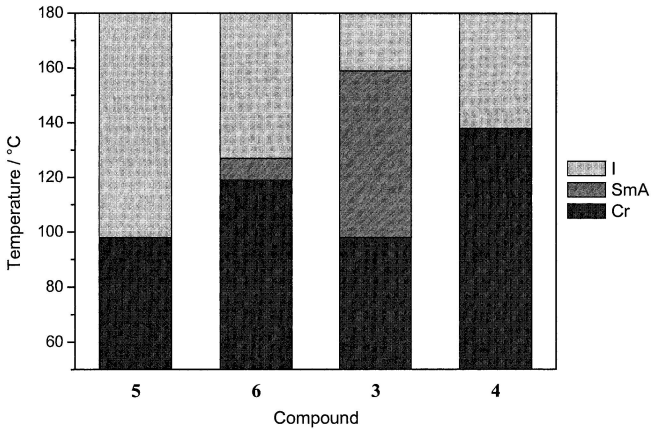


Figure 4. Bar graph showing the mesophase stability of the neodymium(III) complexes.

4. Conclusions

The thermal properties of the lanthanide complexes $[Ln(LH)_3(NO_3)_3]$, with different but structurally related Schiff's base ligands LH, have been investigated. It was found that the presence or absence and the position of substitutents on the aromatic core determine to a great extent whether these compounds are liquid crystalline. The 4-substituted ligand with a long alkoxy chain provides the most stable mesophase. Decreasing the length of the alkoxy chain to a minimum of one carbon unit reduces the stability of the mesophase, but does not destroy it, whereas omitting the chain does. When the alkoxy chain is placed in the 5-position instead of the 4-position, the resulting complex is no longer liquid crystalline.

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