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Mesomorphism of lanthanide-containing Schiff's base complexes with chloride counterions

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Liquid crystalline complexes [Ln(LH)$_3$Cl$_3$] have been synthesized, where Ln is a trivalent lanthanide ion (Pr–Lu, except Pm) and where LH is the Schiff's base ligand *N*-octadecyl-4-tetradecyloxysalicylaldimine. Although the ligand does not exhibit mesomorphism, the complexes do (SmA phase). The mesophase behaviour of these compounds has been investigated by polarizing optical microscopy, differential scanning calorimetry and high temperature X-ray diffraction. The lanthanide complexes have much higher melting and clearing points than comparable complexes with nitrate or dodecyl sulphate counterions. In addition, the transition temperatures are virtually independent of the type of lanthanide ion. This behaviour is opposite to that observed for similar complexes with nitrate counterions [Ln(LH)$_3$(NO$_3$)$_3$]. The differences in temperature dependence can be related to structural differences. Whereas in the nitrate complexes the Schiff's base ligand binds in a zwitterionic form, two-dimensional ^{1}H NMR correlation spectroscopy (COSY) of [Lu(LH)$_3$Cl$_3$] gives an indication that in the chloride complexes, besides coordination via the oxygen of molecules in the zwitterionic form, some of the Schiff's base ligands bind in a bidentate fashion (via the phenolic oxygen and the imine nitrogen).

1. Introduction

The idea behind the incorporation of transition metal ions into liquid crystals (forming metallomesogens) is to design materials which have both the properties of liquid crystals (fluidity, anisotropic physical properties, possibility of switching by external fields, …) and the properties due to the metal centre (redox properties, magnetic properties, …) [1–6]. There is an interest in developing lanthanide-containing liquid crystals, mainly because of the unique magnetic properties of some of the trivalent ions of the lanthanide series. Not only are these ions paramagnetic and have a high magnetic moment, but also more importantly, the trivalent lanthanide ions can have a very high magnetic anisotropy. A high value for the magnetic anisotropy is desirable if one wants to switch liquid crystals by an external magnetic field. The best investigated lanthanide-containing liquid crystals are those with Schiff's base ligands (salicylaldimine) [7–19]. In these compounds the Schiff's base ligands bind in a zwitterionic form to the lanthanide ion. The lanthanide complexes exhibit a smectic A mesophase and the transition temperatures depend on the type of counterion. Types of counterion which have been studied include: nitrate, chloride, triflate, alkyl sulphates (especially dodecyl sulphate) and perfluorinated alkyl sulphates. For some counterions, the trend in the transition temperatures over the lanthanide series is known. For instance, for the complexes with nitrate counterions, the mesophase stability range decreases over the lanthanide series [12], whereas the opposite trend is observed for compounds with the perfluorinated alkyl sulphates as the counterions [17].

In this paper we describe the synthesis, characterization and mesophase behaviour of a series of lanthanide complexes of the Schiff's base ligand *N*-octadecyl-4-tetradecyloxysalicylaldimine (LH) with chloride as the counterion (figure 1). Special attention will be paid to the influence of the lanthanide ion on the transition temperatures. This work is an extension of other recent work on chloride complexes [19].

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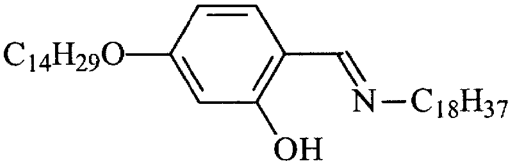

Figure 1. The Schiff's base ligand LH.

2. Experimental

^{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 (TMS) as internal standard. Infrared spectra were recorded on a Bruker IFS66 FTIR spectrometer, using a nujol mull of the samples between KBr windows. Elemental analyses (CHN) were performed on a CE-Instrument EA-1110 elemental analyser. Differential scanning calorimetry (DSC) was done on a Mettler-Toledo DSC821e module (scan rate 10°C min^{-1} under a nitrogen flow). 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) measurements were made on a STOE transmission powder diffractometer system STADI P, with a high temperature attachment version 0.65.1 (temperature range from room to 1000°C). Monochromatic Cu K$_{\alpha 1}$ 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 $1 < 2\theta < 30°$. Organic reagents were purchased from ACROS; lanthanide salts were obtained from Aldrich. All solvents and chemicals were used as received.

2.1. *Synthesis of the Schiff's base ligand N-octadecyl-4-tetradecyloxysalicylaldimine (LH)*

A mixture of 2,4-dihydroxybenzaldehyde (0.20 mol, 27.62 g), 1-bromotetradecane (0.20 mol, 55.46 g) and KHCO$_3$ (0.20 mol, 20.02 g) in DMF (400 ml) was heated at reflux temperature for 3 h in a nitrogen atmosphere. After leaving the mixture to cool to room temperature, 500 ml of 6M HCl was added. The organic layer was washed three times with diethyl ether. The combined organic layers were washed with saturated brine and the diethyl ether was evaporated on a water bath. The crude 2-hydroxy-4-tetradecyloxybenzaldehyde was crystallized from hot acetonitrile and dried *in vacuo*; yield 83% (55.40 g). ^{1}H NMR δ (CDCl$_3$): 0.80 (t, 3H, CH$_3$); 1.18–1.45 (m, 22H, CH$_2$); 1.80 (m, 2H, **CH$_2$**–CH$_2$–O); 4.0 (t, 2H, **CH$_2$**–O); 6.41 (d, 1H, H$_{\text{arom}}$); 6.52 (dd, 1H, H$_{\text{arom}}$); 7.41 (d, 1H, H$_{\text{arom}}$); 9.70 (s, 1H, CHO); 11.5 (s, 1H, OH). Elemental analysis calculated for C$_{21}$H$_{34}$O$_3$ (334.49) C 75.4, H 10.2; found C 75.1, H 10.4%.

The purified aldehyde (164 mmol, 54.93 g) was converted into the Schiff's base by reaction with octadecylamine (stearylamine, 164 mmol, 44.20 g) in a 1 : 1 mixture of absolute ethanol and n-heptane, with a few drops of acetic acid as the catalyst. After heating at reflux for 3 h and cooling, the yellow precipitate was filtered off, crystallized from a 1 : 1 mixture of absolute ethanol and n-heptane and dried *in vacuo*; yield 69% (66.30 g), m.p. 73–74°C. ^{1}H NMR δ (CDCl$_3$): 0.88 (m, 6H, CH$_3$); 1.10–1.50 (m, 52H, CH$_2$); 1.67 (m, 2H, N–CH$_2$–**CH$_2$**); 1.77 (m, 2H, **CH$_2$**–CH$_2$–O); 3.50 (t, 2H, N–**CH$_2$**); 3.95 (t, 2H, **CH$_2$**–O); 6.32 (dd, 1H, H$_{\text{arom}}$); 6.36 (d, 1H, H$_{\text{arom}}$); 7.05 (d, 1H, H$_{\text{arom}}$); 8.08 (s, 1H, CH=N); 14.1 (s, 1H, OH). IR (nujol, cm^{-1}): 1627 (C=N stretch), 1579 (arom. C=C stretch), 1520 (arom C=C stretch), Elemental analysis: calculated for C$_{39}$H$_{71}$NO$_2$ (599.99) C 79.9, H 12.2, N 2.4; found C 79.5, H 12.2, N 2.3%.

2.2. *Synthesis of lanthanide complex [Sm(LH)$_3$Cl$_3$]*

Ligand LH (0.25 mmol, 150 mg) was dissolved in absolute ethanol (150 ml), with heating. The ligand solution was cooled to a temperature lower than 50°C and a solution of SmCl$_3$.6H$_2$O (0.50 mmol, 91 mg) in absolute ethanol was added dropwise. The mixture was stirred during 3 h at room temperature. Part of the solvent was removed *in vacuo*. After the metal complex started to precipitate, the solution was stirred for another 24 h. The precipitate was filtered on a Gooch crucible (P4), washed with ice cold ethanol, and dried *in vacuo*; yield 136 mg (81%). Elemental analysis: calculated for C$_{117}$H$_{213}$Cl$_3$N$_3$O$_6$Sm (2014.67) C 69.8, H 10.7, N 2.1; found C 69.7, H 10.5, N 2.0%.

All the other lanthanide complexes were prepared in a similar way. NMR data for [Lu(LH)$_3$Cl$_3$]: ^{1}H NMR δ (CDCl$_3$): 0.88 (m, 6H, CH$_3$); 1.10–1.50 (m, 52H, CH$_2$); 1.61 (m, 2H, N–CH$_2$–**CH$_2$**); 1.75 (m, 2H, **CH$_2$**–CH$_2$–O); 3.55 (t, 2H, N–**CH$_2$**); 3.65 (t, 2H, **CH$_2$**–O); 6.16 (d, 1H, H$_{\text{arom}}$); 6.83 (b, 1H, CH=N); 6.92 (d, 1H, H$_{\text{arom}}$); 7.58 (d, 1H, H$_{\text{arom}}$); 12.3 (b, 1H, OH).

3. Results and discussion

The Schiff's base ligand LH (figure 1) was prepared by condensation of 2-hydroxy-4-tetradecyloxybenzaldehyde with n-octadecylamine. Reaction of excess of LnCl$_3$.6H$_2$O with LH in absolute ethanol led to formation of [Ln(LH)$_3$Cl$_3$], (Ln = Pr–Lu, except Pm). No reproducible results could be obtained for the lanthanum and cerium complexes. From the elemental analysis results (table 1) it is evident that three Cl anions are present in each complex. The question arises whether the ligands

Table 1. Yields and elemental analysis data for $[Ln(LH)_3Cl_3]$.

Compound	Yield/%	Elemental analysis: calc. (found)/% C	H	N
$[Pr(LH)_3Cl_3]$	43	70.1 (69.6)	10.7 (10.5)	2.1 (1.9)
$[Nd(LH)_3Cl_3]$	56	70.0 (69.9)	10.7 (10.5)	2.1 (2.0)
$[Sm(LH)_3Cl_3]$	81	69.8 (69.7)	10.7 (10.5)	2.1 (2.0)
$[Eu(LH)_3Cl_3]$	80	69.7 (69.7)	10.7 (10.4)	2.1 (2.0)
$[Gd(LH)_3Cl_3]$	78	69.5 (69.4)	10.6 (10.6)	2.1 (1.9)
$[Tb(LH)_3Cl_3]$	82	69.5 (69.6)	10.6 (10.7)	2.1 (2.0)
$[Dy(LH)_3Cl_3]$	79	69.3 (69.3)	10.6 (10.6)	2.1 (1.9)
$[Ho(LH)_3Cl_3]$	85	69.3 (69.1)	10.6 (10.6)	2.1 (1.9)
$[Er(LH)_3Cl_3]$	86	69.2 (68.9)	10.6 (10.6)	2.1 (1.9)
$[Tm(LH)_3Cl_3]$	86	69.0 (68.6)	10.5 (10.5)	2.1 (1.9)
$[Yb(LH)_3Cl_3]$	87	68.9 (68.4)	10.5 (10.5)	2.1 (2.0)
$[Lu(LH)_3Cl_3]$	79	68.9 (68.4)	10.5 (10.5)	2.1 (2.0)

LH coordinate to the lanthanide ion in a monodentate way (through the phenol oxygen only) or a bidentate way (phenol oxygen and imine nitrogen). It has been shown earlier by means of single crystal XRD as well as by NMR studies that in the case of the analogous nitrate complexes coordination occurs through the phenol oxygen only, the ligand being present in a zwitterionic form [15]. The three nitrate counterions, coordinated in a bidentate fashion, bring the coordination number of the lanthanide ion to nine. Obviously, chloride coordinates in a monodentate way, so this is one significant difference between the chloride complexes and the nitrate compounds. Numerous efforts have already been made by us to crystallize an analogous short chain derivative made from the ligand *N*-butyl-4-methoxysalicylaldimine for XRD studies. However, until now, no single crystals have been obtained, so that we can only make assumptions with regard to the coordination mode of the lanthanide ion in the complexes $[Ln(LH)_3Cl_3]$. First, CHN analysis shows no evidence of molecules of water of crystallization. The coordination number of the lanthanide ion is 6 (which is very low) in the case of three monodentate chloride counterions and three monodentate ligands LH, coordinating through the phenol oxygen only. The second possibility is that the ligands LH are present in a bidentate form, so that a coordination number of nine is obtained. A third possibility is the presence of bridging chlorides, where a chloride ion is shared by two lanthanide ions. In the case of two bridging and two non-bridging chloride ions (six chlorides for two lanthanide ions) with LH acting as a monodentate ligand, a coordination number 7 is obtained.

In order to gain more insight into the coordination mode of the lanthanide ion in solution we measured 1D and 2D NMR spectra of both the ligand and the diamagnetic lutetium(III) complex $[Lu(LH)_3Cl_3]$ in $CDCl_3$ solution. All proton resonances of the free ligand are sharp and show the expected splitting, with the exception of the phenolic proton resonance which is extremely weak and broad, probably due to its fast exchange with the protons in the solvent. A list of NMR resonances is given in the experimental part of this paper. The ^1H NMR spectrum of the $[Lu(LH)_3Cl_3]$ complex showed that protons close to the potential coordination sites, i.e. adjacent to either phenolic oxygen or imine nitrogen, were shifted and broadened. Upon complexation with Lu^{3+}, the imine CH proton of the ligand shifted by 1.14 ppm upfield and became very broad. This shift is much larger than in analoguous nitrate complexes [11, 13]. Another proton which is most significantly affected by complexation is the aromatic proton next to the phenolic group, which exhibited a downfield shift of 1.25 ppm. Moreover, the phenolic proton which in the ligand was barely detectable, gives a strong, broad peak at 12.3 ppm. The expected range for phenolic protons is between 4.5 and 7 ppm, and the large downfield shift is a clear indication that the proton is involved in hydrogen bonding with the nearby nitrogen [20]. The hydrogen bonding probably slowed down exchange of the phenolic proton with the protons in the solvent, so that it could be detected. In contrast to the nitrate complexes [11, 13], selective irradiation of the signal at 12.3 ppm did not remove the broadening of the imine signal. This gives rise to doubt that the Schiff's base ligand is in a zwitterionic form in the chloride complexes.

Two-dimensional ^1H NMR correlation spectroscopy (COSY) has been shown to be a useful tool in understanding the coordination mode in the $[Lu(LH)_3Cl_3]$ complex. Figure 2 shows the ^1H COSY spectrum of $[Lu(LH)_3Cl_3]$ measured in $CDCl_3$ at room temperature. The spectrum shows that the broad peak at 12.3 ppm consists actually of two overlapping peaks, which on the one hand show coupling to the aromatic proton adjacent to the phenolic group, and on the other hand, show

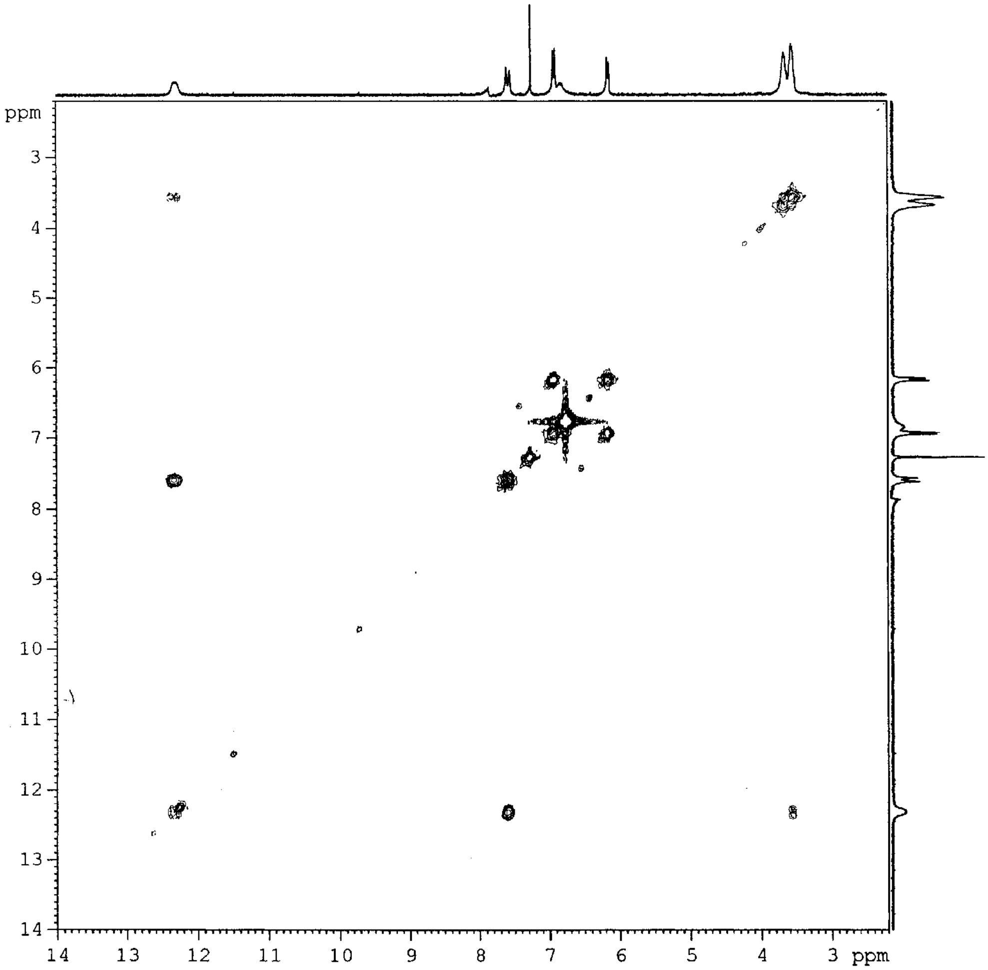

Figure 2. Part of the ^{1}H COSY spectrum of [Lu(LH)$_3$Cl$_3$]. The coupling between the different protons can be deduced from the off-diagonal peaks.

coupling to the CH$_2$ group next to the nitrogen. These results are consistent with the existence of two types of complex which in solution exist as an equilibrium mixture (figure 3). The difference between the two complexes is the position of the proton, which through hydrogen bonding has been 'shared' between the phenolic oxygen and the imino nitrogen.

In complex B, the proton is shifted more to nitrogen, and therefore it couples to the adjacent CH$_2$ group (cross-peak at 12.3 and 3.65 ppm in the COSY spectrum). Hence, the coordination can occur only through the phenolic oxygen as in analogous nitrate complexes in which the ligand is present in a zwitterionic form. However, this mode of binding leaves the Ln^{3+} ion

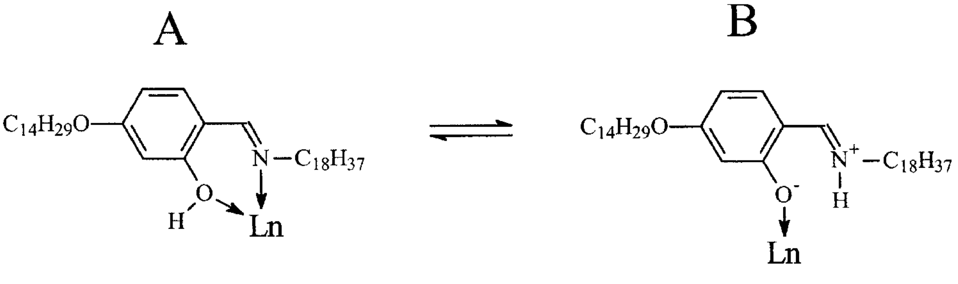

Figure 3. In solution, an equilibrium exists between structures A and B. In A, the Schiff's base ligand acts as a bidentate ligand and the phenolic group remains protonated. In B, the ligand is in a zwitterionic form and acts as a monodentate ligand.

coordinatively unsaturated (a coordination number of six only), and therefore the ligand has a tendency to coordinate in a bidentate mode as in complex A. In this complex the phenolic proton remains bound to oxygen, and therefore it couples to an adjacent aromatic proton (cross-peak at 12.3 and 7.65 ppm in the COSY spectrum). In this case, the nitrogen can also bind to the Ln^{3+} and form 9-coordinated complexes.

The structure which can be proposed is that of a tricapped trigonal prism, with the Schiff's base ligands forming the trigonal prism and the chlorides the three capping ligands in the equatorial plane. It seems likely that we were unsuccessful in obtaining single crystals by crystallization from solution because of the existence of two inter-converting isomers A and B in the solution.

The solid state structure of the complexes was probed by IR spectrometry. In order to avoid halogen exchange, we preferred to record the IR spectra of the complexes using nujol mulls, rather than KBr pellets. Full interpretations of the IR spectra of both the ligand and the metal complexes is difficult, because of the large number of absorption bands. Tentative assignments were made by comparing our data with those reported by Teyssie and Charette [21] and by Bullock and Tajmir-Riahi [22]. Major differences are observed between the IR spectrum of the ligand LH and that of the metal complexes. One distinct feature of the complexes is the appearance of a strong broad band at 3146 cm^{-1}, which can be assigned to N^{+}–H stretching. Whereas in the ligand the C=N stretching vibration is observed at 1627 cm^{-1}, the complexes show two bands in this region: 1658 and 1614 cm^{-1}. Notice that in zwitterionic complexes (for instance the lanthanide complexes with nitrate counter ions [13], [22]) the C=N stretch is shifted to higher wavenumbers in comparison with the position of this vibration in the free ligand; whereas in the complexes with deprotonated ligands (for instance colbalt(II) and copper(II) complexes, [21]) the C=N vibration is shifted to shorter wavenumbers. This dual behaviour is in agreement with the NMR data for the complexes in solution, where an equilibrium between two structures exists. No IR absorptions corresponding to Ln–Cl vibrations could be observed above 400 cm^{-1}.

A schematic picture of the proposed structure for the lanthanide complexes, assuming bidenate coordination by the Schiff's base ligands, is shown in figure 4. This structure is closely related to the molecular structure originally proposed by Galyametdinov and coworkers for the complexes with nitrate counterions [8]. Although we first thought that the complexes were oligomeric or even polymeric [19], the fact that the complexes are readily soluble in chloroform or dichloromethane points to the chloride complexes being monomeric. Trials to

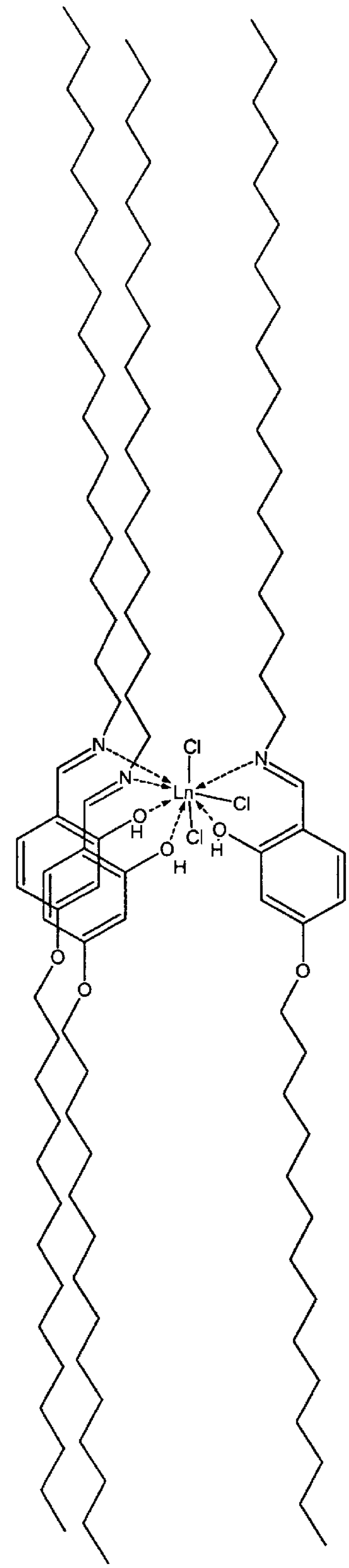

Figure 4. Schematic presentation of the molecular structure of the [Ln(LH)$_3$Cl$_3$] complexes assuming coordination of the Schiff's base ligands through both the oxygen and nitrogen.

obtain evidence for this from mass spectrometry measurements were unsuccessful. It should be mentioned that the complexes described in this work are closely related to the yttrium(III) salicylideneimines described by Kuma and Yamada [23]. These authors argue that their complexes should be formulated as [YCl$_2$(LH)$_3$]Cl, a structure in which the yttrium ion probably achieves coordination number eight with two monodentate chloride ions and three bidentate Schiff's base molecules. Furthermore they assume that hydrogen bonding occurs between two adjacent molecules and not in an intramolecular way. However, these authors too were unable to obtain single crystals of their compounds.

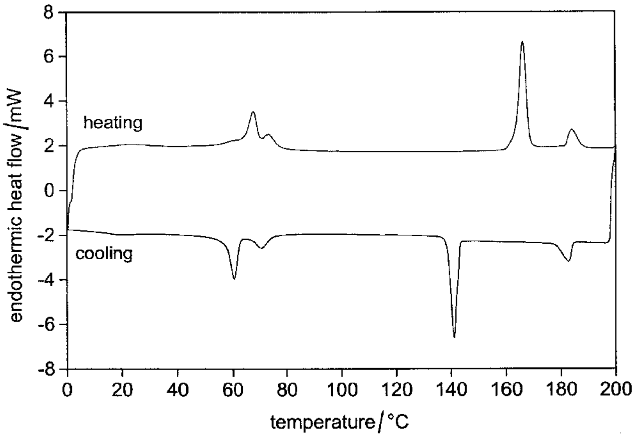

Figure 5. DSC trace (2nd heating and cooling run) of [Sm(LH)$_3$Cl$_3$]. Endothermic peaks are pointing upwards. The thermal effects between 50 and 80 °C are due to reversible crystal–crystal transitions.

As for the thermal properties, all complexes show an enantiotropic SmA phase (table 2). The DSC trace of a typical compound [Sm(LH)$_3$Cl$_3$] (figure 5) shows the melting point at 166 °C ($\Delta H = 56.12$ kJ mol^{-1}) and the clearing point at 184 °C ($\Delta H = 10.94$ kJ mol^{-1}). Although these transition temperatures are rather high, the compounds do not decompose at temperatures several tens of degrees above the clearing point, not even if these temperatures are maintained for several hours. In addition to the melting and clearing points, reversible crystal to crystal transitions can be observed between 50 and 80 °C. The effect of changing the counter ion is clearly illustrated: the similar nitrate complex [Nd(LH)$_3$(NO$_3$)$_3$] shows significantly lower transition temperatures (Cr.102.SmA.155.I), while the decrease in the temperatures is even more spectacular in the case of the dodecyl sulphate compound [Nd(LH)$_3$(DOS)$_3$] (Cr.65.SmA.79.I). Changing the counterion has been shown to be a very efficient way of influencing the transition temperatures [17–19]. A plot of the transition temperatures as a function of the lanthanide ion in compounds [Ln(LH)$_3$Cl$_3$] is shown in figure 6. In contrast to similar complexes with nitrate counterions, where a very pronounced influence of the lanthanide ion on the transition temperatures was found [8], in the case of the chloride complexes this

Table 2. Transition temperatures and thermal data for [Ln(LH)$_3$Cl$_3$] complexes.

Ln	Transition[a]	T/°C	ΔH/kJ mol^{-1} [b]
Pr	Cr → SmA	159	50.06
	SmA → I	179	11.31
Nd	Cr → SmA	161	52.07
	SmA → I	183	12.66
Sm	Cr → SmA	166	56.12
	SmA → I	184	10.94
Eu	Cr → SmA	167	55.18
	SmA → I	184	9.64
Gd	Cr → SmA	168	61.31
	SmA → I	185	10.96
Tb	Cr → SmA	170	73.94
	SmA → I	185	11.76
Dy	Cr → SmA	171	67.88
	SmA → I	186	10.36
Ho	Cr → SmA	169	65.98
	SmA → I	185	11.46
Er	Cr → SmA	170	59.42
	SmA → I	186	10.38
Tm	Cr → SmA	171	57.78
	SmA → I	187	10.47
Yb	Cr → SmA	172	58.91
	SmA → I	187	10.14
Lu	Cr → SmA	173	60.17
	SmA → I	185	10.17

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

[b] Enthalpy data were determined from the DSC thermogram of the second heating run.

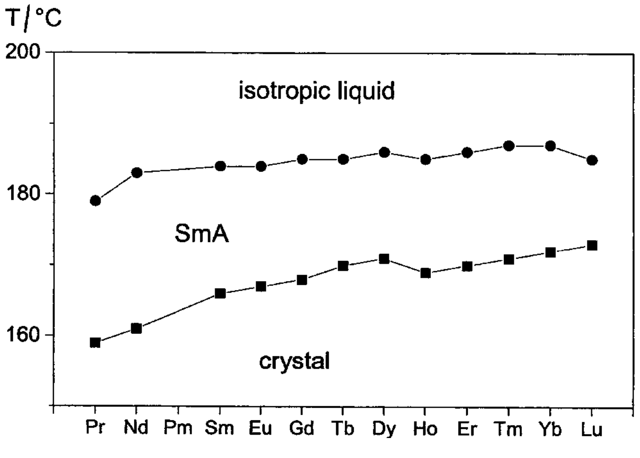

Figure 6. Evolution of the melting and clearing temperatures of the complexes [Ln(LH)$_3$Cl$_3$] over the lanthanide series.

dependence of the lanthanide ion on the transition temperatures is much smaller. One can even say that the transition temperatures remain more or less constant over the lanthanide series. This and the fact that the transition temperatures are higher than for nitrate or dodecyl sulphate complexes, can be attributed to structural differences between the chloride and the previously described lanthanide complexes.

The compound [Sm(LH)$_3$Cl$_3$] was investigated by high temperature XRD (figure 7). At room temperature, the compound exists in a lamellar state with crystallized chains. The *d*-spacing at 25°C is 38.1 Å, which is less than the all-*trans*-length of the ligand (calculated by molecular modelling to be 45.5 Å). This could mean that the complex molecules are interdigitated, as is often seen for this kind of compound. Because of the quite large space occupied by the lanthanide ion surrounded by aromatic groups, interdigitation of the chains could fulfill the need for space filling in the aliphatic part of the complex. Another possible explanation for the shorter *d*-spacings could be a folding of the long alkyl chains. We are against a hypothesis that the shorter *d*-spacing could be due to tilting of the layers (and the presence of a SmC phase as suggested in a recent paper by Alexandrov *et al.* [24]). At 175°C in the SmA mesophase, the *d*-value is 32.2 Å. The identity of the mesophase as SmA is confirmed by the decrease of the layer spacing with increasing temperature in the mesophase, together with the observation of a typical focal-conic texture with homeotropic regions.

The transition temperatures of our compounds are similar, although somewhat lower, than those of complexes with *N*-octadecyl-4-octyloxysalicylaldimine as the ligand [19]. Just as in the case of the nitrate complexes [13], the chain length has little influence on the transition temperatures of the chloride complexes.

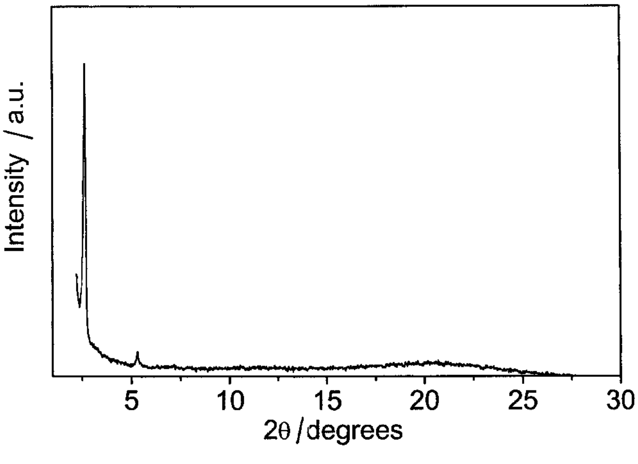

Figure 7. X-ray diffractogram of [Sm(LH)$_3$Cl$_3$] in the SmA mesophase at 175°C.

4. Conclusions

A series of lanthanide complexes with Schiff's base ligands and chloride counterions, [Ln(LH)$_3$Cl$_3$] have been synthesized. All the complexes exhibit an enantiotropic SmA mesophase. Whereas in the nitrate complexes [Ln(LH)$_3$(NO$_3$)$_3$] the Schiff's base ligand binds in a zwitterionic form, two-dimensional ^{1}H NMR correlation spectroscopy (COSY) of [Lu(LH)$_3$Cl$_3$] gives an indication that in the chloride complexes, besides coordination via the oxygen by molecules in the zwitterionic form, also a proportion of the Schiff's base ligands bind in a bidentate fashion (via the phenolic oxygen and the imine nitrogen). This can account for the higher transition temperatures of the chloride complexes in comparison with the nitrate or dodecyl sulphate complexes, and to the absence in the chloride series of any pronounced dependence of the transition temperatures on the lanthanide ion is found. It is evident that by varying the counterions in this type of complex, and based on the fact that the lanthanide ion wants to adopt a high coordination number, not only can the transition temperatures of these mesogenic metal complexes be modified, but also their molecular structures.

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