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

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Liquid crystalline complexes of the formula [Ln(LH)$_3$(DOS)$_3$] have been synthesized, where Ln is a trivalent rare earth-ion (Y, La–Lu, except Pm), LH is the ligand *N*-octadecyl-4-tetradecyloxysalicylaldimine and DOS is the dodecyl sulphate counterion. Although the Schiff's base ligands do not exhibit mesomorphism, the complexes do (SmA phase). The mesophase behaviour of these compounds has been investigated by polarizing optical microscopy, differential scanning calorimetry, high temperature X-ray diffraction and thermogravimetric analysis. The stoichiometry of the complexes remains constant throughout the lanthanide series.

1. Introduction

Metal-containing liquid crystals (metallomesogens) have received considerable attention recently, due to the ability of the metal to change the liquid crystalline properties of the materials in which it is embedded [1–9]. Liquid crystalline metal complexes can be made not from liquid crystalline ligands alone, because the metal can also induce mesomorphism in non-mesomorphic ligands. The majority of metallomesogens that have been studied to date contain d-block metals such as Cu(II), Ni(II), Pt(II) and Pd(II), because they coordinate in a square planar fashion with the ligands used. In this way, the molecular structure of the complexes can still be rod-like, so that the structural anisotropy necessary for the formation of a mesophase is retained. However, only a limited number of metals exhibit square planar coordination, therefore efforts were made to obtain liquid crystalline metal complexes with metals other than those mentioned earlier.

Lanthanides are well-known for their rich coordination chemistry, their ions obtaining coordination numbers between 6 and 12, with most complexes having coordination number 8 or 9. Such high coordination numbers, however, did seem to be incompatible with the structural anisotropy that is necessary to exhibit liquid crystalline behaviour. However, after the discovery of the first columnar liquid crystalline lanthanide complex by Piechocki *et al.* in 1985 [10], Galyametdinov and coworkers synthesized the first calamitic lanthanide-containing liquid crystal in 1991 [11]. These compounds consisted of a central trivalent lanthanide ion surrounded by three Schiff's base ligands. The reported stoichiometry was [LnL′(L′H)$_2X_2$], where Ln is the trivalent lanthanide ion, L′H is the Schiff's base **1** (figure 1) and X is a counterion (nitrate or chloride). The ligand itself is mesomorphic, exhibiting a nematic phase: Cr–43–N–71–I (°C). The complexes were shown to exhibit a highly viscous SmA mesophase, e.g. the Gd complex with nitrate counterions showed the following mesomorphic behaviour: Cr–98–SmA–192–I. Later, mesomorphic lanthanide complexes with non-mesomorphic ligands LH were discovered.

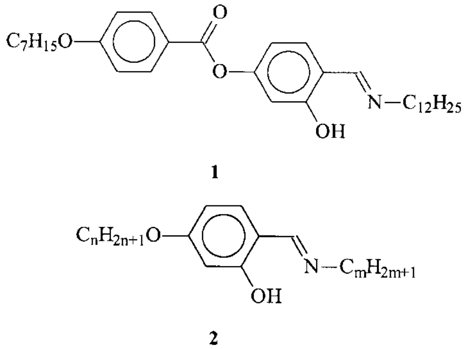

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Figure 1. Structures of Schiff's base ligands **1** and **2**.

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When Gd is taken again as the central lanthanide and nitrate as the counterion, the complex $[Gd(LH)_3(NO_3)_3]$ with LH being the Schiff's base **2** (figure 1, $n = 8$, $m = 18$) the transition temperatures are Cr–121–SmA–150–I.

The major drawback so far preventing metallomesogens from finding use in devices is their relatively high transition temperatures. It was found that changing the counterion in the complex $[Gd(LH)_3(NO_3)_3]$ from nitrate to chloride significantly altered the transition temperatures, but in the wrong sense: Cr–171–SmA–194–I [12]. The finding, however, that changing the counterion could drastically change the transition temperatures led to more extensive research aimed especially at this topic. Starting from a complex with chloride as the counterion, Binnemans *et al.* obtained low melting metallomesogens by exchanging chloride for dodecyl sulphate [13]. Using ligand LH (**2**, figure 1, $n = 12$, $m = 18$) and $GdCl_3\ 6H_2O$, a complex with stoichiometry $[GdL(LH)_2Cl_2]\ 3H_2O$ was obtained, which showed an enantiotropic smectic A phase: Cr–164–SmA–188–I. This compound was allowed to react with silver dodecyl sulphate AgDOS to replace the two chloride anions with two dodecyl sulphate counterions. The resulting complex $[GdL(LH)_2(DOS)_2]$ showed significantly lower transition temperatures: Cr–59–SmA–112–I. Galyametdinov *et al.* later found that dodecyl sulphate complexes could be synthesized by direct reaction between lanthanide dodecyl sulphate and the Schiff's base ligand [14]. These findings inspired us to undertake a more systematic study of Schiff's base complexes of lanthanides with dodecyl sulphate counterions.

2. Experimental

All ^1H 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. Elemental analyses (CHN) were performed on a CE-Instrument EA-1110 elemental analyser. Differential scanning calorimetry (DSC) measurements were 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) studies were performed 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 $1 < 2\theta < 30°$. Thermogravimetric analyses were performed with a Polymer Laboratories STA1000H TG-DTA apparatus, using a static air atmosphere. Organic reagents were purchased from ACROS; lanthanide salts were obtained from Aldrich. All solvents and chemicals were used as received.

All complexes were synthesized by direct addition of the lanthanide dodecyl sulphate $Ln(DOS)_3$ in absolute ethanol to a stirred absolute ethanolic solution of the ligand LH (**2**, figure 1, $n = 14$, $m = 18$) at a temperature of about 50°C. Lanthanide dodecyl sulphates were prepared by the reaction of sodium dodecyl sulphate NaDOS with the appropriate hydrated lanthanide chloride $LnCl_3\ xH_2O$ ($x = 6$ or 7) in deionized water. Ligand LH was prepared by condensation of stearylamine with 2-hydroxy-4-tetradecyloxybenzaldehyde in an absolute ethanol: *n*-heptane 1:1 mixture.

2.1. *Synthesis of neodymium tri(dodecyl sulphate), Nd(DOS)*$_3$

To a stirred aqueous solution (50 cm^3) of sodium dodecyl sulphate NaDOS (6 mmol, 1.73 g), a solution of $NdCl_3\ 6H_2O$ (2 mmol, 0.72 g) in water (20 cm^3) was added dropwise at room temperature. The solution was left to stir for about 1 h. The pale lilac precipitate was then filtered on a crucible, washed thoroughly with water and dried in a vacuum oven at 40°C over night; yield 95% (1.83 g). Elemental analysis calculated for $C_{36}H_{75}O_{12}S_3Nd\ H_2O$: C 45.1, H 8.1; found: C 45.1, H 8.0%.

All the other lanthanide dodecyl sulphate salts were prepared in an analogous manner to the synthesis of $Nd(DOS)_3$. The salts are either monohydrates or dihydrates (table 1) and have the typical colour of the trivalent lanthanide ion they contain [15].

2.2. *Synthesis of ligand LH, N-octadecyl-4-tetradecyloxysalicylaldimine*

A solution of 2,4-dihydroxybenzaldehyde (50 mmol, 6.91 g), 1-bromotetradecane (50 mmol, 13.86 g) and $KHCO_3$ (50 mmol, 5.01 g) in DMF was heated under reflux for 3 h. The crude 2-hydroxy-4-tetradecyloxybenzaldehyde was crystallized from hot acetonitrile and dried *in vacuo*; yield 59% (9.82 g). ^1H NMR δ ($CDCl_3$): 0.9 (t, 3H, CH_3); 1.0–1.6 (m, 22H, CH_2); 1.8 (quintet, 2H, $CH_2{-}CH_2{-}O$); 4.0 (t, 2H, $CH_2{-}O$); 6.4 (d, 1H, H_{arom}); 6.5 (dd, 1H, H_{arom}); 7.4 (d, 1H, H_{arom}); 9.7 (s, 1H, CHO); 11.5 (s, 1H, OH). Elemental analysis calculated for $C_{21}H_{34}O_3$: C 75.4, H 10.2; found: C 75.5, H 10.2%.

The purified aldehyde (10 mmol, 3.34 g) was converted into the Schiff's base by reaction with octadecyl amine (stearylamine, 10 mmol, 2.70 g) in a 1:1 mixture

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

Compound	Yield/%	Elemental analysis: calc. (found)/% C	H	N
Y(DOS)$_3$ 2H$_2$O	92	46.9 (46.9)	8.6 (8.7)	
La(DOS)$_3$ H$_2$O	96	45.4 (45.6)	8.1 (8.1)	
Ce(DOS)$_3$ H$_2$O	92	45.3 (45.6)	8.1 (8.1)	
Pr(DOS)$_3$ H$_2$O	93	45.3 (45.6)	8.1 (8.3)	
Nd(DOS)$_3$ H$_2$O	95	45.1 (45.1)	8.1 (8.0)	
Sm(DOS)$_3$ H$_2$O	94	44.8 (44.5)	8.0 (8.2)	
Eu(DOS)$_3$ H$_2$O	92	44.8 (44.5)	8.0 (8.0)	
Gd(DOS)$_3$ H$_2$O	95	44.5 (44.5)	8.0 (8.2)	
Tb(DOS)$_3$ 2H$_2$O	92	43.6 (43.7)	8.0 (8.0)	
Dy(DOS)$_3$ H$_2$O	90	44.3 (44.2)	8.0 (8.1)	
Ho(DOS)$_3$ 2H$_2$O	91	43.4 (43.4)	8.0 (8.1)	
Er(DOS)$_3$ 2H$_2$O	91	43.3 (43.3)	8.0 (8.1)	
Tm(DOS)$_3$ 2H$_2$O	92	43.2 (43.2)	8.0 (7.9)	
Yb(DOS)$_3$ 2H$_2$O	91	43.0 (43.2)	7.9 (7.9)	
Lu(DOS)$_3$ 2H$_2$O	94	42.9 (42.9)	7.9 (7.9)	
[Y(LH)$_3$(DOS)$_3$]	70	69.5 (69.2)	11.0 (11.0)	1.6 (1.5)
[La(LH)$_3$(DOS)$_3$]	61	68.2 (68.2)	10.8 (10.8)	1.6 (1.5)
[Ce(LH)$_3$(DOS)$_3$]	48	68.2 (68.2)	10.8 (10.9)	1.6 (1.5)
[Pr(LH)$_3$(DOS)$_3$]	57	68.2 (68.2)	10.8 (10.9)	1.6 (1.5)
[Nd(LH)$_3$(DOS)$_3$]	54	68.1 (68.2)	10.8 (10.8)	1.6 (1.5)
[Sm(LH)$_3$(DOS)$_3$] 2H$_2$O	77	67.0 (66.7)	10.7 (10.7)	1.5 (1.4)
[Eu(LH)$_3$(DOS)$_3$] 2H$_2$O	78	67.0 (66.9)	10.7 (10.6)	1.5 (1.5)
[Gd(LH)$_3$(DOS)$_3$] 2H$_2$O	74	66.9 (66.7)	10.7 (10.4)	1.5 (1.4)
[Tb(LH)$_3$(DOS)$_3$] 2H$_2$O	73	66.8 (67.0)	10.7 (10.5)	1.5 (1.4)
[Dy(LH)$_3$(DOS)$_3$] 2H$_2$O	74	66.8 (66.8)	10.7 (10.9)	1.5 (1.4)
[Ho(LH)$_3$(DOS)$_3$]	49	67.6 (67.6)	10.7 (10.9)	1.5 (1.5)
[Er(LH)$_3$(DOS)$_3$]	58	67.5 (67.4)	10.7 (10.6)	1.5 (1.4)
[Tm(LH)$_3$(DOS)$_3$]	58	67.5 (67.0)	10.7 (10.4)	1.5 (1.5)
[Yb(LH)$_3$(DOS)$_3$]	56	67.4 (67.2)	10.6 (10.8)	1.5 (1.5)
[Lu(LH)$_3$(DOS)$_3$]	66	67.3 (67.2)	10.6 (10.4)	1.5 (1.4)

of absolute ethanol and *n*-heptane, with a few drops of acetic acid as catalyst. The reaction mixture was stirred at reflux for 3 h, cooled, and the yellow precipitate filtered, crystallized from a 1 : 1 mixture of absolute ethanol and *n*-heptane and dried in a vacuum dessicator; yield 82% (4.80 g). ^{1}H NMR δ (CDCl$_3$): 0.9 (m, 6H, CH$_3$); 1.2–1.5 (m, 52H, CH$_2$); 1.7 (quintet, 2H, N–CH$_2$–**CH**$_2$); 1.8 (quintet, 2H, **CH**$_2$–CH$_2$–O); 3.5 (t, 2H, N–CH$_2$); 3.9 (t, 2H, CH$_2$–O); 6.3 (dd, 1H, H$_{\mathrm{arom}}$); 6.4 (d, 1H, H$_{\mathrm{arom}}$); 7.0 (d, 1H, H$_{\mathrm{arom}}$); 8.1 (s, 1H, CH=N); 14.1 (s, 1H, OH). Elemental analysis calculated for $C_{39}H_{71}NO_2$: C 79.9, H 12.2, N 2.4; found: C 80.2, H 12.2, N 2.3%).

2.3. *Synthesis of complex [Nd(LH)$_3$(DOS)$_3$]*

A solution of Nd(DOS)$_3$ H$_2$O (0.43 mmol, 0.40 g) in absolute ethanol was added dropwise to a stirred absolute ethanolic solution of the ligand LH (**2**, figure 1, $n = 14$, $m = 18$) (0.43 mmol, 0.25 g) at 50°C; the solution was left to stir overnight. A yellow precipitate formed, which was filtered on a crucible, washed with absolute ethanol and dried *in vacuo*; yield 54% (0.21 g). Elemental analysis calculated for $C_{153}H_{288}N_3O_{18}S_3Nd$: C 68.1, H 10.8, N 1.6; found: C 68.2, H 10.8, N 1.5%.

All the other lanthanide complexes [Ln(LH)$_3$(DOS)$_3$] were obtained by the same synthetic method as [Nd(LH)$_3$(DOS)$_3$], and are all yellow powders (colour of the Schiff's base ligand).

3. Results and discussion

The starting material for our investigation was the Schiff's base ligand LH (**2**, figure 1, $n = 14$, $m = 18$), which was prepared by condensing 2-hydroxy-4-tetradecyloxybenzaldehyde with octadecylamine. Unlike Binnemans *et al.* [13], we did not first make chloride complexes, but instead took a direct approach by using lanthanide dodecyl sulphates Ln(DOS)$_3$ as salts for complexation with the ligand [14]. The reaction of excess Ln(DOS)$_3$ with LH in absolute ethanol led to the formation of [Ln(LH)$_3$(DOS)$_3$]. From the elemental analysis results in table 1, it is clear that three DOS anions are present in each complex, which thus differ from the compounds obtained by the two-step method used by Binnemans *et al.* The question arises whether the ligands coordinate to the lanthanide ion in a monodentate way (through the phenol oxygen only) or in a bidentate way (phenol oxygen and imine nitrogen). It was shown earlier [16] 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. The three nitrate counterions coordinate in a bidentate fashion, bringing the coordination number of the lanthanide ion to nine. We are now attempting to synthesize a short chain alkyl sulphate in order to obtain a short chain complex which may be crystallized for XRD studies. In this way, the coordination of both ligands and counterions could be determined. ^{1}H NMR studies of the diamagnetic complex $[La(LH)_3(DOS)_3]$ have already shown that the coordination of the ligands to the lanthanum ion is identical to that of the analogous nitrate complex: specifically, homodecoupling of the signal at 12.4 ppm resulted in a sharpening of the imine signal at 7.6 ppm, indicating that coordination occurs through the phenol oxygen only, the ligands being present in the zwitterionic form. A sketch of the structure of the compounds is given in figure 2. This diagram, in which the third ligand and the third DOS counterion have been omitted for clarity, clearly reflects the layered structure of the mesophase.

As for thermal properties, all the complexes show an enantiotropic SmA phase (table 2) with a range of 13–27°C and with melting points decreasing slightly from 67°C (La-compound) to 59°C (Lu-compound). The DSC trace of a typical compound $[Er(LH)_3(DOS)_3]$ (figure 3) shows two transitions: the melting point at 60.6°C ($\Delta H = 83.0\,\mathrm{kJ\,mol^{-1}}$) and the clearing point at 84.8°C ($\Delta H = 6.2\,\mathrm{kJ\,mol^{-1}}$). The transitions are very sharp and well defined, indicating that all parts of the compound (alkyl chains and core) melt at the same temperature. The mesophase range increases on going from the La-compound to the Lu-compound (figure 4). This behaviour is contrary to that of similar nitrate complexes (DOS anion replaced by nitrate), which exhibit the opposite trend [17]: i.e, the mesophase stability decreases on going from La to Lu, with decreasing ionic radius. We assumed that a higher charge density (+ 3 charge for each lanthanide ion, but La^{3+} being larger than Lu^{3+}) for the smaller lanthanide ions caused the electrostatic interactions between the molecules to be stronger and therefore the melting point to be higher towards the end of the lanthanide series. In the case of the DOS complexes this higher charge density obviously cannot be the main effect, because here the melting points slightly decrease towards the end of the lanthanide series. The reason for this opposing behaviour has to be the difference in size between the small nitrate ions and the bulky dodecyl sulphate ions. It seems to be easier to gather three ligands and three large counterions around a large lanthanide ion like lanthanum (ionic radius r of the trivalent ion = 1.16 Å) than it is to fit the same ligands and counterions around a small ion like lutetium ($r = 0.98$ Å). It is more difficult to explain the observed trend in the clearing points.

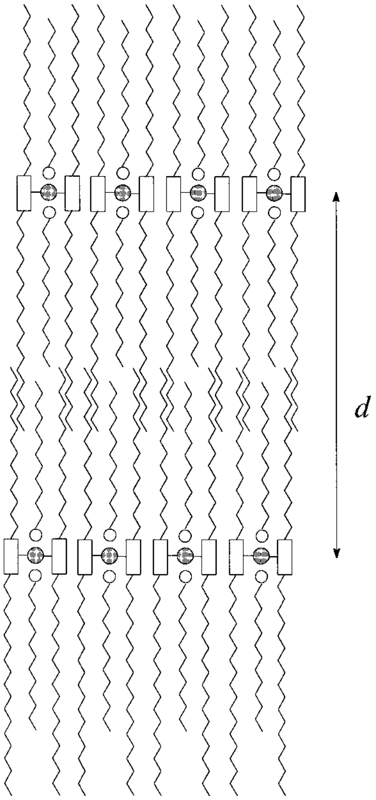

Figure 2. Diagram of the mesophase structure, showing the layer thickness *d*. For clarity, each third ligand (represented by the rectangular structures bearing two alkyl chains) and each third DOS counterion (represented by the circular structures bearing one chain) have been omitted.

The identity of the mesophase has also been investigated by high temperature XRD. Figure 5 shows the X-ray diffractogram of $[Er(LH)_3(DOS)_3]$ at room temperature. The compound exists in a lamellar state with crystallized chains. The *d*-spacings of the Bragg reflections vary as 1:2:3, corresponding to the (0 0 1) to (0 0 3) reflections. The bulky dodecyl sulphate groups, as well as the alkyl and alkoxy chains of the ligands, probably prevent the crystalline material from obtaining a very high order of symmetry, thus showing no higher than the third order reflections in the diffractogram. The wide angle region contains a diffuse reflection at about 4.5 Å originating from the in-plain scattering of the alkyl chains. Figure 6 shows the diffractogram of the same

Table 2. Transition temperatures and thermal data for [Ln(LH)$_3$(DOS)$_3$] complexes (second heating run). Cr = crystalline solid, SmA = smectic A mesophase, I = isotropic liquid.

Ln	Transition	T/°C	ΔH/kJ mol^{-1}	ΔS/J mol^{-1} K^{-1}
Y	Cr → SmA	61.0	85.4	255.7
	SmA → I	86.0	6.1	17.0
La	Cr → SmA	67.3	88.8	260.9
	SmA → I	79.9	7.0	19.8
YCe	Cr → SmA	66.4	89.6	264.0
	SmA → I	80.2	6.6	18.7
Pr	Cr → SmA	65.7	87.0	256.9
	SmA → I	80.0	6.2	17.6
Nd	Cr → SmA	65.1	87.9	260.0
	SmA → I	78.7	6.3	17.9
Sm	Cr → SmA	62.4	85.4	254.6
	SmA → I	78.0	5.8	16.5
Eu	Cr → SmA	62.2	88.6	264.3
	SmA → I	78.4	5.9	16.8
Gd	Cr → SmA	61.3	84.0	251.3
	SmA → I	77.7	5.7	16.2
Tb	Cr → SmA	61.3	84.9	254.0
	SmA → I	80.3	5.7	16.1
Dy	Cr → SmA	61.1	88.3	264.3
	SmA → I	82.2	5.9	16.6
Ho	Cr → SmA	61.5	84.2	251.7
	SmA → I	83.5	5.8	16.3
Er	Cr → SmA	60.6	83.0	248.8
	SmA → I	84.8	6.2	17.3
Tm	Cr → SmA	60.1	79.3	238.1
	SmA → I	86.1	6.1	17.0
Yb	Cr → SmA	59.7	76.2	229.0
	SmA → I	87.4	6.3	17.5
Lu	Cr → SmA	59.3	74.9	225.4
	SmA → I	85.8	6.1	17.0

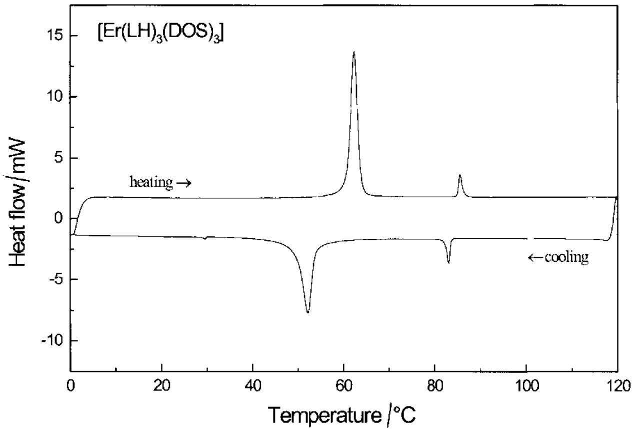

Figure 3. DSC trace (second heating and cooling run) of [Er(LH)$_3$(DOS)$_3$]. Endothermic peaks are upwards.

compound at 75°C, a temperature above the melting point. In the small angle region, only the first order reflection can be easily observed. The wide angle reflection has become even more diffuse, indicating the melting

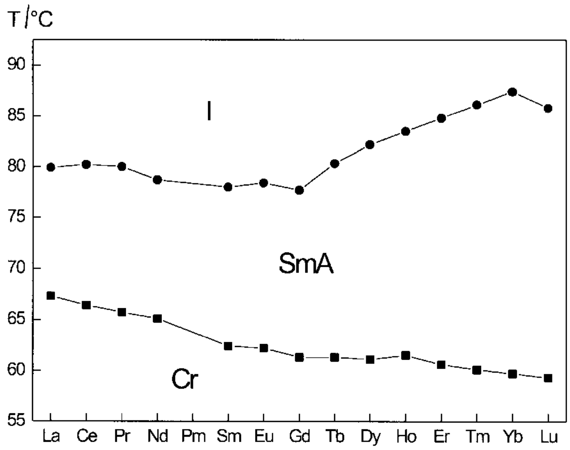

Figure 4. The melting and clearing temperatures of complexes [Ln(LH)$_3$(DOS)$_3$] over the lanthanide series (temperatures are taken from the second heating run).

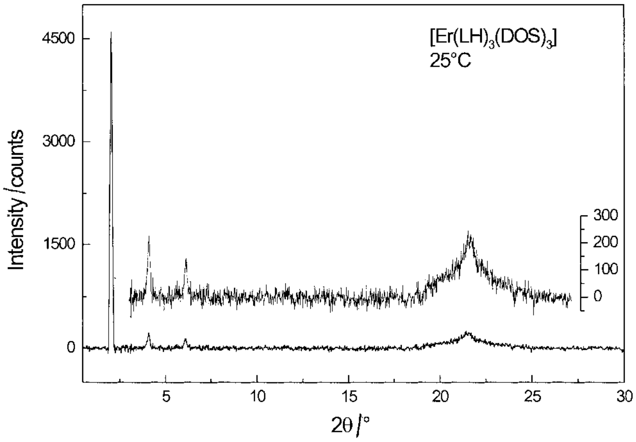

Figure 5. X-ray diffractogram of compound [Er(LH)$_3$(DOS)$_3$] at 25°C.

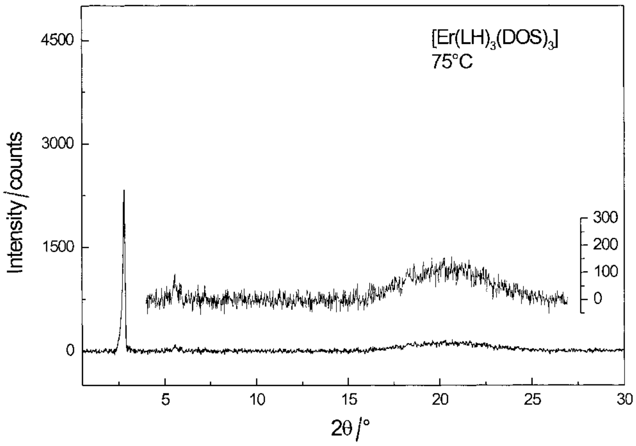

Figure 6. X-ray diffractogram of compound [Er(LH)$_3$(DOS)$_3$] at 75°C.

of the alkyl chains. At this temperature, the compound exists in the mesophase. The fact that one reflection can still be seen in the small angle region indicates that the material has a lamellar structure, which is of course less ordered than in the solid state (25°C).

The lamellar layer spacing *d* of compound $[Er(LH)_3(DOS)_3]$ as a function of temperature is shown in figure 7. At 25°C the value of *d* is 42.8 Å, slightly less than the length of the ligand in its all-*trans*-conformation (calculated to be 47 Å). The value of *d* varies by no more than 0.5 Å when heating the lamellar solid phase towards the melting point. At the melting point, however, there is a sharp decrease of the lamellar layer spacing by almost 9 Å. At 75°C, the value of *d* is 31.5 Å. Considering the all-*trans* length of the ligand, this *d*-value indicates that the complex molecules are interpenetrated in the mesophase, as indicated in figure 2. The assignment of the mesophase as a SmA phase is confirmed by the fact that the mesophase layer spacing decreases with increasing temperature, together with the observation of the characteristic focal-conic texture with coexisting homeotropic regions when viewed in the microscope. A plot of the layer spacing *d* versus temperature of the analogous complex $[Sm(LH)_3(DOS)_3]$ shows very similar behaviour, suggesting the same mesomorphism as that observed for $[Er(LH)_3(DOS)_3]$. Thermogravimetric analyses of $[Sm(LH)_3(DOS)_3]$ and $[Er(LH)_3(DOS)_3]$ reveal that both compounds are thermally stable up to 200°C.

4. Conclusions

Lanthanide-containing complexes of Schiff's base ligands with dodecyl sulphate counterions have been synthesized by direct addition of lanthanide dodecyl sulphates to the Schiff's base *N*-octadecyl-4-tetradecyloxysalicylaldimine. All complexes have the stoichiometry $[Ln(LH)_3(DOS)_3]$ where Ln is a trivalent lanthanide ion, LH is the Schiff's base ligand and DOS is the dodecyl sulphate counterion. These compounds all exhibit an enantiotropic SmA phase, as characterised by polarizing optical microscopy, DSC and high temperature XRD measurements. The complexes are examples of metallomesogens with rather low melting and clearing temperatures.

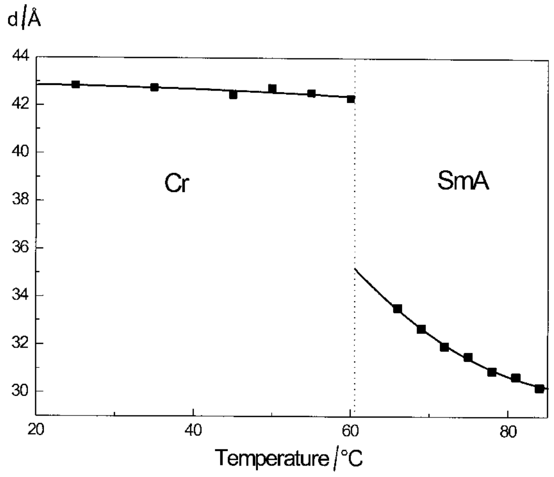

Figure 7. Plot of the layer spacing *d* of compound $[Er(LH)_3(DOS)_3]$ as a function of temperature.

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