Liquid Crystals
Publication details, including instructions for authors and subscription information:
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To cite this Article Martin, Francoise , Collinson, Simon R. and Bruce, Duncan W.(2000) 'The synthesis of low melting liquid crystalline lanthanide complexes with triflate counter-anions', Liquid Crystals, 27: 6, 859 — 863

To link to this Article: DOI: 10.1080/026782900202363

URL: http://dx.doi.org/10.1080/026782900202363

LIQUID CRYSTALS, 2000, VOL. 27, NO. 6, 859–863

The synthesis of low melting liquid crystalline lanthanide complexes with triflate counter-anions

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(*Received 1 December 1999; accepted 27 January 2000*)

Paramagnetic liquid crystalline complexes of the formula $[\mathrm{LnL(LH)_2}][\mathrm{CF_3SO_3}]_2$ have been synthesised, where LH is the ligand *N*-dodecyl-4-(3′,4′-didodecyloxybenzoyloxy)salicylaldimine and Ln is a lanthanide metal. When compared with analogous nitrate complexes, the transition temperatures are rather low.

1. Introduction

Metal-containing liquid crystals have been intensively studied in recent years [1] as the inclusion of a metal atom provides one way of changing the properties of liquid crystals for particular requirements. For example, the creation of liquid crystals with a large magnetic anisotropy based on paramagnetic lanthanide mesogens is possible. It is well known that the anisotropic properties of liquid crystals determine their response to external fields, and switching by magnetic fields is determined by the anisotropy in the magnetic susceptibility. Thus, the preparation of mesogens with a large magnetic anisotropy will provide liquid crystalline materials which can be addressed by weak magnetic fields. In 1991, Galyametdinov *et al.* [2] reported the first liquid crystalline lanthanide complex with Schiff's base ligands with the stoichiometry $[\mathrm{Ln(LH')_3}][X_3]$ where Ln = Pr, Gd, Dy and $X = \mathrm{NO_3}$ and $[\mathrm{Ln(L)(LH')_2}][X_2]$, where Ln = Eu, L = ligand minus the phenolic proton and $X = \mathrm{Cl}$ (figure 1). The ligand itself, LH′ (figure 1), is mesomorphic with a monotropic nematic phase [Cr (N • 71 •) • 143 • I] (for $n = 7$ and $m = 12$), while the corresponding gadolinium nitrate complex, for example, shows a rather viscous smectic A phase at higher temperatures [Cr • 98 • SmA • 192 • I] (°C).

Subsequently, Galyametdinov *et al.* reported [3] the synthesis of mesomorphic lanthanide complexes with non-mesomorphic Schiff's bases $[\mathrm{LnL''(LH'')_2}][X_2]$ (figure 1), and La, Gd, Dy, Er, Nd, Ho, Eu, Pr and Gd were used as the lanthanide ions with nitrate and chloride as the counter-ions. For the gadolinium nitrate complex (with $n = 12$ and $m = 18$) the transition temperatures are Cr • 135 • SmA • 146 • I. The work indicated that not only does the length of the terminal chains or the type of lanthanide ion have an influence on the transition temperatures, but that the choice of counter-ion was also important. For example, if the above-mentioned gadolinium complex was prepared as the chloride rather than the nitrate, the transition temperatures increased significantly: Cr • 164 • SmA • 185 • I.

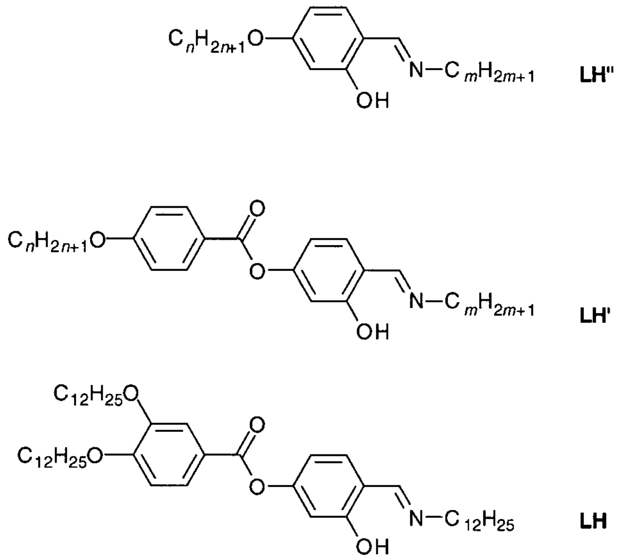

Figure 1. Structures of salicylaldimine ligands discussed in the paper.

Magnetic studies were carried out on complexes of both salicylaldimine [4] and enaminoketone [5] ligands, and very high magnetic anisotropies were found, particularly for the dysprosium derivatives, which could be aligned in an external magnetic field [3]. Since the high transition temperatures of these metallomesogens are a major drawback for future applications, it is important to decrease the melting points using whatever means are available.

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Liquid Crystals ISSN 0267-8292 print/ISSN 1366-5855 online © 2000 Taylor & Francis Ltd
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In our studies of silver(I) mesogens [6], we had shown that incorporation of the dodecylsulphate (DOS) ion could reduce transition temperatures [7] when compared with, say, nitrate or tetrafluoroborate [8]. Ziessel *et al.* [9] has also used this anion to generate mesomorphic complexes of palladium(II) and we have shown that it can be useful in reducing transition temperatures in lanthanide systems [10]. Effective as the DOS anion is, it can have some drawbacks, namely that extra chains can add to viscosity, it is not always a straightforward matter to incorporate it as an anion and it can hydrolyse to the related alcohol under acidic conditions. Further, its incorporation inevitably adds an extra step to the synthesis. Thus, while low temperatures and rich polymorphism can and do result from its use, we were keen to see if other counter-anions might also be effective in these lanthanide systems.

2. Results and discussion

In these studies, we first developed a modified salicylaldimine ligand, *N*-dodecyl-4-(3,4-didodecyloxybenzoyloxy)salicylaldimine (LH, figure 1), containing a dialkoxybenzoate function. Initially, we made some complexes of lanthanide nitrates and found that the materials obtained had the formula $[LnL(LH)_2][NO_3]_2$. They all showed a columnar hexagonal phase with a range of 30–60°C with melting points around 85°C and decomposition observed often while clearing above 110°C (table 1). The stoichiometry of these materials is interesting. The formula we have found here, which is based upon the evidence from elemental analysis (we have not yet been able to grow single crystals for X-ray diffraction studies), is the same as that reported initially by Galyametdinov for his nitrate systems. However, it has subsequently been shown by single crystal X-ray diffraction studies that complexes of LH″ have the composition $[Ln(LH'')_3(NO_3)_3]$ in which there are three bidentate nitrate groups and the ligand has rearranged itself into a zwitterionic form (figure 2) and bound itself to the lanthanide via the phenate oxygen [11]. At the present time, we do not have any detailed knowledge of the mode of coordination of the complexes with the formula $[LnL(LH)_2][NO_3)_2]$, but we can say that the stoichiometry is obtained reproducibly for a given ligand and lanthanide salt.

Table 1. Transition temperatures and thermal data for $[LnL(LH)_2][CF_3SO_3]_2$.

Ln	Transition	T/°C	ΔH/kJ mol^{-1}	ΔS/J mol^{-1} K^{-1}
Triflates				
Nd	Cr–Col_h	57	90.3	27
	Col_h–I	88	9.2	3
Gd	Cr–Col_h	51	44.9	14
	Col_h–I	89	3.7	1
Tb	Cr–Col_h	48	43.8	14
	Col_h–I	88	2.2	1
Dy	Cr–Col_h	51	37.6	16
	Col_h–I	88	4.3	1
Er	Cr–Col_h	51	44.6	14
	Col_h–I	88	0.54	0.1
Nitrates				
Nd	Cr–Col_h	84	35.3	10
	Col_h–I	112	—	—
Dy	Cr–Col_h	85	20.0	6
	Col_h–I	146	—	—
Er	Cr–Col_h	77	71.2	20
	Col_h–I	128	—	—

As we were aware that chloride salts had been shown by Galyametdinov to give rather high transition temperatures, we then considered what other lanthanide salts might be available. We were drawn first to lanthanide trifluoromethanesulphonates (triflates) both because previous work had shown that triflate materials could be mesomorphic [8, 12] and also because it was known that triflates could act as suitable precursor materials for anion metathesis [13].

Thus, the yellow triflate complexes were synthesized by reaction of three equivalents of the ligand with the lanthanide triflate in THF at room temperature and then purified by crystallization. All of the complexes had the formula $[LnL(LH)_2][CF_3SO_3]_2$, established by elemental analysis, which did not vary with the metal, unlike the situation found with nitrate complexes. However, the formula implied that there ought to be two different types of ligand in the complex which, at least for the diamagnetic lanthanum complexes, ought to be visible in the ^{1}H NMR. However, the ^{1}H NMR spectra showed well resolved signals and no suggestion that there were two types of ligand present. This situation remains to be clarified. However, it is absolutely clear that complexes with the above formula were obtained reproducibly and always with the same liquid crystal transition temperatures (*vide infra*).

As we had hoped, the complexes were all mesomorphic and showed a columar hexagonal phase (see figure 3). However, we were surprised to find that the transition temperatures were rather low, with most complexes melting just above 50°C and clearing just below 90°C. In fact, what was remarkable was that the melting and clearing points showed almost total insensitivity to the lanthanide

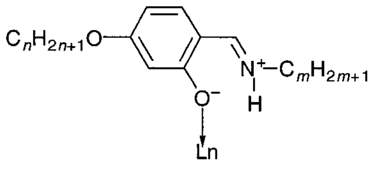


Figure 2. Schematic drawing to show the coordination of the zwitterionic form of the salicylaldimine to a lanthanide centre.

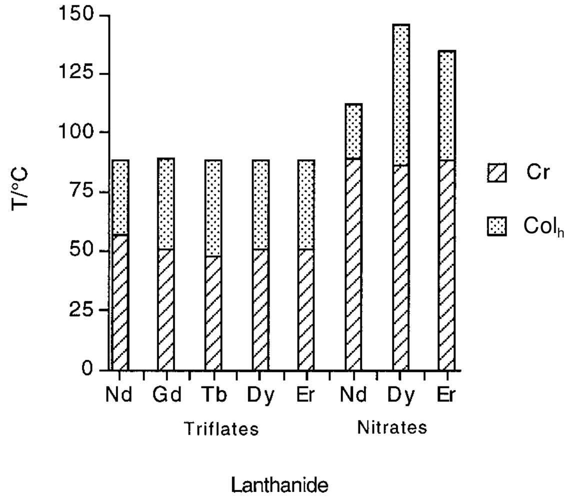


Figure 3. Mesomorphic properties of the complexes [LnL(LH)$_2$][X_2] (X = OTf or NO$_3$).

employed. This is in stark contrast to Binneman‘s work with lanthanide nitrate complexes of salicylaldimines which showed a pronounced decrease in the mesomorphic range as the lanthanide series was traversed, resulting from stabilization of the crystal phase and destabilization of the smectic A phase [14]. The behaviour of the complexes is also remarkable as they represent rare examples of a situation where, on complexation, the transition temperatures of the ligands are *reduced*, the reverse normally being the case with metallomesogens.

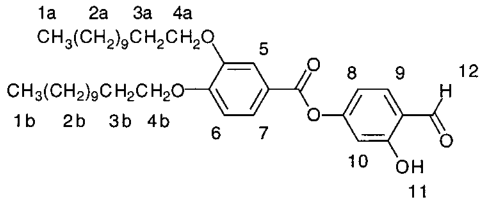
This anion is then clearly advantageous for the study of lanthanide complexes of salicylaldimines; the transition temperatures of the complexes, at just above ambient temperature, have facilitated study of their physical responses, in particular their optical [15] and magnetic [16] properties. That the transition temperatures are so low with the triflate anion we tentatively assign to its relatively large size which we assume reduces the structural anisotropy of the complexes. Of course, there is a fine balance between this anisotropy being sufficiently large to give rise to an effect such as this and its being too large so that mesomorphism is suppressed. Triflate would, therefore, appear to be happily placed in this regard.

3. Experimental

NMR spectra were recorded on either a Bruker ACF-300 or a Bruker DRX-400 spectrometer and chemical shifts are reported relative to the internal standard of the deuteriated solvent used. Analysis by hot stage microscopy was carried out with an Olympus BH40 microscope equipped with a Linkam HFS91 hot stage, TMS92 controller and LNP2 cooling unit. DSC data were recorded on a Perker Elmer DSC7 instrument using heating and cooling rates of 10 K min^{-1}. Elemental analyses were recorded by the University of Exeter Elemental Analytical Service. All solvents and chemical were used as received, except THF which was dried by distillation from sodium and benzophenone under nitrogen. 3,4-Didodecyloxybenzoic acid was synthesized as previously described [9].

3.1. *Synthesis of 4-(3′,4′-didodecyloxybenzoyloxy)-2-hydroxybenzaldehyde*

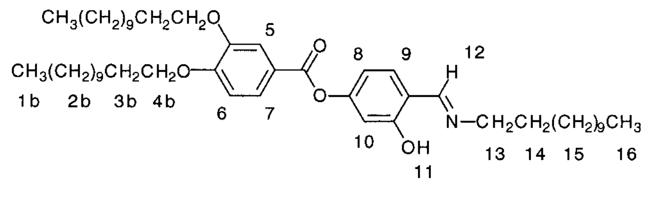
Under a nitrogen atmosphere 3,4-didodecyloxybenzoic acid (4 g, 8.2 mmol) was dissolved in CH$_2$Cl$_2$ (100 cm^3) and added dropwise to a solution of 2,4-dihydroxybenzaldehyde (0.58 g, 4.2 mmol), 4-(*N*,*N*-dimethylamino)-pyridine (DMAP, 20 mg) and dicyclohexylcarbodiimide (DCC, 1.69 g, 8.2 mmol) in CH$_2$Cl$_2$ (80 cm^3). Then, the mixture was allowed to stir for 24 h. Afterwards, the salts were removed by filtration and the filtrate was reduced to dryness under reduced pressure. The yellowish residue was purified by column chromatography on silica with CH$_2$Cl$_2$ as eluant. The colourless compound was then dried under vacuum; yield 78%.



^{1}H NMR δ (CDCl$_3$): 0.88 (2 × t, 6H, $^{\text{H1a and 1b}}$); 1.27–1.48 (m, 36H, $H^{2a\text{ and }2b}$); 1.85 (qt. 4H, $H^{3a\text{ and }3b}$); 4.07 (2 × t, 4H, $H^{4a\text{ and }4b}$ $^3J_{HH}$ 6.6 Hz); 6.90 (m, 1H, $H^{6,\,8\text{ and }10}$); 7.62 (d, 1H, H^5, $^4J_{HH}$ 2.0 Hz); 7.80 (dd, 1H, H^7, $^3J_{HH}$ 8.4 Hz, $^4J_{HH}$ 2.0 Hz); 9.88 (s, 1H, H^{12}); 11.24 (s, 1H, H^{11}). Elemental analysis for $C_{50}H_{83}O_5N_1$: calc, C 74.8, H 9.4; found, C 74.9, H 9.7%.

3.2. *Synthesis of N-dodecyl-4-(3′,4′-didodecylbenzoyloxy)salicylaldimine (LH)*

Under a nitrogen atmosphere, 4-(3′,4′-didodecyloxybenzoyloxy)-2-hydroxybenzaldehyde (2.85 g, 4.67 mmol) and dodecylamine (0.87 g, 4.67 mmol) were dissolved in ethanol (absolute, 100 cm^3) with a few drops of glacial acetic acid as a catalyst. The yellow solution was heated at reflux for 3 h and on cooling, a yellow precipitate was obtained. This precipitate was washed with a little cold absolute ethanol before crystallization from hot ethanol. The resulting crystals were dried *in vacuo*; yield 89%.



^{1}H NMR δ ($CDCl_3$): 0.88 (3 × t, 9H, $H^{1a,\,1b\text{ and }16}$); 1.26–1.88 (m, 54H, $H^{2a,\,2b,\,3a,\,3b\;14\text{ and }15}$); 3.58 (t, 2H, H^{13}); 4.08 (2 × t, 4H, $H^{4a\text{ and }4b}$); 6.72 (dd, 1H, H^{10}, $^3J_{HH}$ 2.2 Hz, $^4J_{HH}$ 8.4 Hz); 6.79 (d, 1H, H^8, $^4J_{HH}$ 2.2 Hz); 6.92 (d, 1H, H^6, $^3J_{HH}$ 8.6 Hz); 7.26 (d, 1H, H^9, $^3J_{HH}$ 8.4 Hz); 7.65 (d, 1H, H^5, $^4J_{HH}$ 2.0 Hz); 7.80 (dd, 1H, H^7, $^3J_{HH}$ 8.6 Hz, $^4J_{HH}$ 2.0 Hz); 8.31 (s, 1H, H^{12}). Elemental analysis for $C_{50}H_{83}O_5N_1$: calc, C 77.2, H 10.7, N 1.8; found, C 77.2, H 10.7, N 1.6%.

3.3. *Synthesis of the lanthanide triflate complexes*

Under a nitrogen atmosphere, a solution of $Ln(CF_3SO_3)_3$ (0.31 mmol, 0.18 g) in THF (10 cm^3) was added to a solution of *N*-dodecyl-4-(3′,4′-didodecyloxybenzoyloxy)salicylaldimine (0.84 mmol, 0.54 g) in THF. The solution was stirred at room temperature for 3 h before the solvent was removed under reduced pressure. The resulting yellow solid was crystallized from ethyl acetate/hexane before being dried *in vacuo*.

^{1}H NMR δ ($CDCl_3$): 0.88 (3 × t, 9H); 1.25–1.50 (m, 72H); 3.57 (t, 2H); 4.08 (2 × t, 4H); 6.72 (dd, 1H, $^3J_{HH}$ 8.4 Hz, $^4J_{HH}$ 2.2 Hz); 6.80 (d, 1H, $^4J_{HH}$ 2.2 Hz); 6.92 (d, 1H, $^3J_{HH}$ 8.4 Hz); 7.25 (d, 1H, $^3J_{HH}$ 8.4 Hz); 7.65 (d, 1H, $^4J_{HH}$ 2.0 Hz); 7.80 (dd, 1H, $^3J_{HH}$ 8.4 Hz, $^4J_{HH}$ 2.0 Hz); 8.02 (s, 1H); 13.75 (s, 1H, $O\underline{H}$). Elemental analysis for $C_{170}H_{284}O_{21}N_3F_6S_2La_1$: calc, C 67.5, H 9.5, N 1.4; found, C 68.5, H 10.3, N 1.5%.

3.4. *Synthesis of the lanthanide nitrate complexes*

Under a nitrogen atmosphere, a solution of $La(NO_3)_3.6H_2O$ (0.31 mmol, 0.13 g) in acetonitrile was added to a solution of *N*-dodecyl-4-(3,4-didodecyloxybenzoyloxy)salicylaldimine (0.84 mmol, 0.54 g) in THF (10 cm^3). The reaction mixture was stirred at room temperature for 3 h. The solvent was then removed under reduced pressure and the yellow solid crystallized from chloroform/ethanol before being dried *in vacuo*.

Table 2. Microanalytical data for the new complexes.

Metal	Yield/%	Calc (found)/% C	H	N
Triflates				
Nd	23	65.8 (65.4)	8.9 (9.6)	1.6 (1.5)
Gd	47	65.6 (65.3)	8.8 (9.2)	1.6 (1.5)
Tb	60	65.5 (65.5)	8.9 (9.1)	1.5 (1.3)
Dy	43	65.4 (65.4)	8.9 (9.3)	1.5 (1.3)
Er	68	65.3 (66.1)	8.8 (9.4)	1.5 (1.4)
Nitrates				
Nd	42	68.8 (68.7)	9.5 (9.9)	2.7 (2.6)
Dy	63	68.3 (68.2)	9.6 (9.7)	2.6 (2.7)
Er	67	67.8 (67.2)	9.6 (9.7)	2.6 (2.7)

^{1}H NMR δ ($CDCl_3$): 0.88 (3 × t, 9H); 1.25–1.50 (m, 72H); 3.56 (t, 2H); 4.04 (2 × t, 4H); 6.43 (dd, 1H, $^3J_{HH}$ 8.6 Hz, $^4J_{HH}$ 1.9 Hz); 6.65 (d, 1H, $^4J_{HH}$ 1.9 Hz); 6.87 (d, 1H, $^3J_{HH}$ 8.6 Hz); 7.01 (d, 1H, $^3J_{HH}$ 8.6 Hz); 7.55 (d, 1H, $^4J_{HH}$ 2.0 Hz); 7.68 (dd, 1H, $^3J_{HH}$ 8.6 Hz, $^4J_{HH}$ 2.0 Hz); 7.88 (s, 1H); 12.90 (s, 1H, $O\underline{H}$). Elemental analysis for $C_{112}H_{190}O_{19}N_5La_1$: calc, C 65.6, H 9.3, N 3.4; found, C 65.4, H 9.6, N 3.1%.

We thank the EPSRC (FM) and the Leverhulme Trust (SRC) for support.

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