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Reduction of the transition temperatures in mesomorphic lanthanide complexes by the exchange of counter-ions

Koen Binnemans,[a] **Yury G. Galyametdinov,**[b] **Simon R. Collinson**[c] **and Duncan W. Bruce**[c]*†

[a]*K.U.Leuven, Department of Chemistry, Coordination Chemistry Division, Celestijnenlaan 200F, B-3001 Heverlee (Leuven), Belgium*

[b]*Physical-Technical Institute, Russian Academy of Science, Sibirsky Tract 10/7.420029, Kazan, Russia*

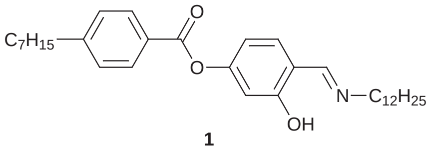
[c]*Department of Chemistry, University of Exeter, Stocker Road, Exeter, UK EX4 4QD*

Metathesis of the chloride anion in the mesomorphic lanthanide complexes $[LnL(LH)_2][Cl]_2$ (LH = salicylaldimine; Ln = lanthanide element) by dodecyl sulfate (DOS) leads to the complexes $[LnL(LH)_2][DOS]_2$, which have wider mesomorphic ranges and lower clearing points.

Introduction

The study of metal-containing liquid crystals (metallomesogens) is a flourishing branch of liquid-crystal research, and the work in this area has been reviewed extensively.[1] The majority of the calamitic metallomesogens so far synthesised contain metal ions in a d^8–d^{10} configuration (*e.g.* Ag^I, Cu^{II}, Ni^{II}, Pd^{II}), thus exhibiting a geometry which is either linear (CN = 2) or planar (CN = 4), and the core of these compounds can easily satisfy the basic structural requirements for a calamitic mesogen of a highly anisotropic structure. Because complexes with coordination numbers higher than four do not form planar, and therefore highly anisotropic, structures, then the design of metallomesogens with a coordination number higher than four is a challenge. However, it is necessary to undertake such a challenge because in this way it is possible to take full advantage of the rich coordination chemistry of a much wider range of transition metal ions.

Progress has been made in this direction, and mesomorphic iron and vanadyl complexes with a square pyramidal geometry (CN = 5) have been reported by Galyametdinov[2] and others,[3] while Malthête[4] has reported mesomorphic butadiene iron tricarbonyl complexes, and Deschenaux mesomorphic ferrocenes.[5] Calamitic metallomesogens with octahedral geometry have been reported based on Mn^I and Re^I tetracarbonyl fragments complexed to imines,[6] or based on bromorheniumtricarbonyl fragments complexed to diazabutadienes[7] and bipyridines.[8] On the other hand, during the last few years a lot of attention has been paid to ionic metallomesogens due to the new structures which become possible and because of an interest in the way ionic interactions can influence mesomorphism.[9] In this respect, lanthanide-containing liquid crystals are of interest, because they combine a high coordination number with the tendency to form ionic compounds. Moreover, lanthanide ions have interesting spectroscopic and magnetic properties. Although liquid-crystalline lanthanide complexes forming columnar phases have been studied for more than 10 years,[10] calamitic lanthanide mesogens have only been reported more recently. In 1991, Galyametdinov[11] reported the first liquid-crystalline lanthanide complex with Schiff base ligands with the stoichiometry $[LnL'(L'H)_2]X_2$, ($L'H = \mathbf{1}$), where Ln = Pr, Eu, Gd, Dy and X = Cl, NO_3 (L′ is a deprotonated ligand).



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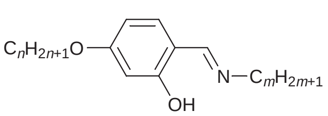

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These complexes form S_A mesophases, with a high viscosity. The ligand itself is a mesogen: Cr • 43 N • 71 • I (for $R = C_7H_{15}$ and $R' = C_{12}H_{25}$). The corresponding transition temperatures of the gadolinium complex with nitrate counter-ions are: Cr • 98 • S_A • 192 • I.

Subsequently, Galyametdinov reported[12] the synthesis of mesomorphic lanthanide complexes with non-mesomorphic Schiff base ligands (**2**), and Gd, Dy and La were used as the lanthanide ions with nitrate as the counter-ion. For the gadolinium complex (with $R = C_{12}H_{25}$ and $R' = C_{18}H_{37}$) the transition temperatures are Cr • 135 • S_A • 146 • I. The work indicated that not only the length of the terminal chains or the type of lanthanide ions had an influence on the transition temperatures, but also the type of counter-ion. If in the above mentioned gadolinium complex, the nitrate ion was replaced by a chloride ion, the transition temperatures increased significantly: Cr • 164 • S_A • 185 • I. Magnetic studies were carried out on derivatives of both salicylaldimate[13] and enaminoketone,[14] and very high magnetic anisotropies were found for the dysprosium derivatives.

Since the high transition temperatures of metallomesogens are a major drawback for future applications, we asked ourselves if it would not be possible to decrease the melting points of these complexes by an alternative choice of the counter-ion. Previous work on silver complexes of stilbazoles showed that when the dodecyl sulfate (DOS) anion was incorporated in place of the BF_4, NO_3 or CF_3SO_3 anions, both melting and clearing points were reduced.[15] Therefore, the DOS anion seemed to be a good candidate for obtaining low-melting, liquid-crystalline lanthanide complexes.

Results and Discussion

We prepared the ligand (LH) of type **2** ($n = 12$, $m = 18$), which was readily obtained in two steps from 2,4-dihydroxybenzal-

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†E-mail: d.bruce@exeter.ac.uk

Table 1 Transition temperatures (2nd heating run) and phase behaviour of the lanthanide complexes with general formula $[LnL(LH)_2][X]_2$ [where LH = 4-(dodecyloxy)-*N*-octadecyl-2-hydroxybenzaldimine]

Ln	transition/°C (ΔH/kJ mol^{-1})	
	X = Cl	X = DOS
Nd	Cr • 162 (56.6) • S_A • 187 (9.1) • I	Cr • 61 (59.7) • S_A • 98 (9.7) • I
Gd	Cr • 164 (58.7) • S_A • 188 (11.6) • I	Cr • 59 (55.9) • S_A • 112 (9.0) • I
Dy	Cr • 166 (55.6) • S_A • 186 (11.9) • I	Cr • 61 (65.6) • S_A • 89 (13.3) • I
Ho	Cr • 168 (56.0) • S_A • 185 (11.7) • I	Cr • 59 (71.1) • S_A • 81 (12.0) • I
Yb	Cr • 169 (51.8) • S_A • 185 (11.3) • I	Cr • 59 (65.1) • S_A • 111 (14.5) • I

dehyde. Reaction[7] of three equivalents of LH with $YbCl_3 \cdot 6H_2O$ in absolute ethanol led to $[YbL(LH)_2]Cl_2 \cdot 3H_2O$. That the complex is a trihydrate was evidenced both by elemental analysis and by the observation of a broad, weak endothermic peak between 80 and 90 °C in the first DSC heating run; all other chloride salts were also found to be trihydrates. The complex exhibits an enantiotropic smectic S_A phase: Cr • 169 • S_A • 185 • I [ΔH (Cr$\rightarrow S_A$) = 51.8 kJ mol^{-1}; $\Delta H(S_A \rightarrow I)$ = 5.7 kJ mol^{-1}]. The ytterbium complex was then treated with two equivalents of AgDOS which led to a precipitate of AgCl and the formation of the target complex, $[YbL(LH)_2][DOS]_2$. This and the other DOS salts were obtained as anhydrous materials which can be explained by the much higher affinity of lanthanide ions for oxygen donors over chloride donors.

The corresponding ytterbium(III) complex with the DOS anion, $[YbL(LH)_2][DOS]_2$, also shows an enantiotropic smectic S_A phase, but the transition temperatures have been reduced dramatically: Cr • 59 • S_A • 111 • I [ΔH (Cr$\rightarrow S_A$) = 65.1 kJ mol^{-1}; ΔH (S_A)$\rightarrow$I = 14.5 kJ mol^{-1}]. A similar behaviour was found for complexes with other lanthanide ions, and the optical and thermal data for the Nd, Gd, Dy, Ho and Yb complexes are summarised in Table 1. Thus, the exchange of the chloride anion by the dodecyl sulfate anion reduces the melting temperature by about 100 °C, and the clearing point to a lesser extent (about 70–90 °C), so that the dodecyl sulfate salts have a wider mesomorphic range than the corresponding chloride salts. Further, while neither the transition temperatures of the chloride salts nor the melting points of the DOS salts are significantly influenced by the lanthanide ion (although there is a small increase in the melting point of the chlorides across the series of lanthanides studied), the clearing temperatures of the DOS salts vary over a much broader range. The origin of this effect is, for the time being, unclear.

Whereas the transition temperatures of covalent metallomesogens can be tuned by an appropriate choice of the number and the length of the terminal chains and by substituents on the rigid core, we have pointed out the fact that the transition temperatures of ionic metallomesogens can be changed by a proper choice of the counter-ion. This principle has been illustrated in this case of lanthanide complexes with Schiff base ligands.

Experimental

^{1}H NMR spectra were recorded on a Brüker ACF-300 spectrometer (300 MHz). Elemental analyses (CHN) were performed on a Perkin-Elmer 2400 Elemental Analyser. The mesophases were investigated by optical microscopy and by differential scanning calorimetry (DSC). Microscopy was performed on a Olympus BX50 polarising microscope, equipped with a Linkam TMS600 hot stage and a Linkam TMS93 temperature controller. DSC thermograms were recorded on a Perkin-Elmer DSC-7 or on a Mettler-Toledo DSC-821e. X-Ray fluorescence spectra were run on a Tracor X-ray Spectrace 450. All chemicals were used as received, without further purification. Hydrated rare earth chlorides were purchased from Aldrich.

4-(Dodecyloxy)-2-hydroxybenzaldehyde

Potassium hydrogen carbonate (0.04 mol, 4.00 g) and 2,4-dihydroxybenzaldehyde (0.036 mol, 5.00 g) were dissolved in acetone (100 cm^3) with stirring. 1-Bromododecane (0.04 mol, 9.96 g) was then added to the mixture before heating at reflux for 48 h. The solution was allowed to cool and was then filtered to remove the solid precipitate of potassium bromide and the solvent was then evaporated under reduced pressure. The residue was added to acidified water (200 cm^3) and extracted with diethyl ether (3×100 cm^3). The combined organic layer were washed with brine (100 cm^3) and dried with anhydrous sodium sulfate, before the diethyl ether was removed under reduced pressure. The brown oil was purified by column chromatography on silica, with hexane : ethyl acetate (9 : 1) as the eluent (total volume: 750 cm^3). The yellowish oil obtained solidified when placed in an ice bath. The crude aldehyde was then recrystallised from hot ethanol (95% v/v). The yellow powder obtained was then washed with a little cold ethanol and dry *in vacuo*; yield 60%. δ_H (300 MHz, $CDCl_3$): 0.88 (t, 3H, CH_3); 1.27–1.47 [m, 18H, $(CH_2)_9$]; 1.80 (q, 2H, CH_2); 4.01 (t, 2H, CH_2O); 6.41 (d, 1H, H-aryl); 6.52 (dd, 1H, H-aryl); 7.40 (d, 1H, H-aryl); 9.70 (s, 1H, CHO); 11.45 (s, 1H, OH); J_o = 8.7 Hz, J_m = 2.3 Hz.

4-(Dodecyloxy)-*N*-octadecyl-2-hydroxybenzaldimine

4-(Dodecyloxy)-2-hydroxybenzaldehyde (2 mmol, 0.60 g) and octadecylamine (2 mmol, 0.54 g) were dissolved in absolute ethanol (50 cm^3) with a few drops of glacial acetic acid as a catalyst. The solution was then refluxed for 3 hours and after cooling a yellow precipitate was obtained. The precipitate was washed with a little cold absolute ethanol, before recrystallisation from hot ethanol and the resulting crystals were dried *in vacuo*; yield 82%. δ_H (300 MHz, $CDCl_3$): 0.89 (t, 6H, CH_3); 1.2–1.8 (m, 52H, CH_2); 3.51 (t, 2H, NCH_2); 3.96 (t, 2H, OCH_2); 6.33 (dd, 1H, H-aryl); 6.37 (d, 1H, H-aryl); 7.05 (d, 1H, H-aryl); 8.09 (s, 1H, CH=N); 14.1 (s, br, 1H, OH); J_o = 8.5 Hz, J_m = 2.5 Hz.

[Bis(4-dodecyloxy)-*N*-octadecylbenzaldimino-2-hydroxy][4-(dodecyloxy)-*N*-octadecylbenzaldimino-2-olato]ytterbium(III) dichloride trihydrate

4-(Dodecyloxy)-*N*-octadecyl-2-hydroxybenzaldimine (1 g, 1.8 mmol) was dissolved in warm absolute ethanol and to this was added dropwise a solution of $YbCl_3 \cdot 6H_2O$ (1.8 mmol; 0.70 g) in absolute ethanol. The reaction was stirred at room temperature for 5 hours, before it was placed in an ice bath. The yellow powder obtained was collected by filtration, washed with a little cold ethanol and dried *in vacuo*. Yield: 76% (0.9 g).

$[YbL(LH)_2][O_3SOC_{12}H_{25}]_2$

The complex $[YbL(LH)_2][Cl]_2 \cdot 3H_2O$ (250 mg, 0.13 mmol) was dissolved in dichloromethane (10 cm^3). This solution was added dropwise to a stirred solution of silver(I) dodecyl sulfate (97 mg; 0.26 mmol) in dichloromethane (10 cm^3) and was stirred for 4 hours with the vessel protected from light. A precipitate of silver(I) chloride was formed and removed by filtration of the mixture through a Celite path and washed with dichloromethane (2×20 cm^3), the solvent was then removed from the combined organic solutions under reduced pressure. The product was then recrystallised from a ethanol : dichloromethane mixture (10 : 1) and dried *in vacuo.* The absence of significant amounts of chloride and silver ions was proved by X-ray fluorescence spectrometry. Yield: 81% (0.25 g).

All other complexes were prepared as above and on a similar

Table 2 Yields and analytical data for the new complexes

compound	yield/%	elemental analyses: calc. (found)% C	H	N
Nd-Cl ($3H_2O$)	54	68.7 (69.0)	10.7 (10.9)	2.2 (2.1)
Gd-Cl ($3H_2O$)	90	68.2 (68.4)	10.6 (10.9)	2.2 (2.1)
Dy-Cl ($3H_2O$)	75	68.0 (68.2)	10.6 (10.5)	2.1 (2.1)
Ho-Cl ($3H_2O$)	88	67.9 (67.9)	10.6 (10.8)	2.1 (2.1)
Yb-Cl ($3H_2O$)	76	68.1 (68.2)	10.6 (10.8)	2.2 (2.1)
Nd-DOS	76	69.2 (69.6)	10.7 (11.1)	1.8 (2.0)
Gd-DOS	80	68.7 (68.6)	10.7 (10.9)	1.8 (2.0)
Dy-DOS	91	68.5 (68.2)	10.7 (11.1)	1.8 (2.0)
Ho-DOS	68	68.5 (68.5)	10.6 (11.0)	1.8 (1.9)
Yb-DOS	81	68.2 (68.2)	10.6 (11.1)	1.8 (2.0)

scale. Yields and analytical data for the complexes are given in Table 2.

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