THE ROYAL SOCIETY

Towards magnetic liquid crystals

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In this paper, we present the results of studies on the synthesis and properties of a series of liquid-crystalline lanthanide complexes of imine ligands. We describe the liquid-crystalline behaviour as a function of the metal, ligand and anion employed and we report on the nature of the coordination between different ligand types and the metal centre.

Keywords: lanthanides; liquid crystals; metallomesogens; Schiff bases

1. Introduction

In this paper, we intend to present an introduction to the study of metal-based paramagnetic liquid crystals concentrating primarily on our own work with lanthanide-based materials. The development of this subject goes largely hand-in-hand with the development of the synthesis of the so-called *metallomesogens*—metal-based liquid crystals—which has developed strongly in the last 15 years or so (Bruce 1996).

The liquid-crystal state is the fourth state of matter and exists between the solid and liquid states for certain molecules. As such, it has properties reminiscent of both phases and so like a liquid it has fluidity and like a solid it has order. It is perhaps convenient to consider a liquid crystal as a rather ordered liquid which is, therefore, an anisotropic fluid stabilized by anisotropic dispersion forces consequent on it being composed of anisotropic molecules. If the molecules are rod-like, then nematic and lamellar phases tend to result, while disc-like molecules tend to give rise to nematic and columnar phases.

The most disordered of the liquid crystal mesophases is the nematic phase in which the unique molecular axes are orientationally correlated about a director ($\boldsymbol{n}$) in one dimension in the absence of positional order. A schematic of a nematic phase of rods is given in figure 1.

For rod-like molecules, lamellar or *smectic* phases are also known which differ from the nematic phase in that they possess partial translational ordering. Thus, in the smectic A ($\mathrm{S_A}$) phase, the molecules are on average ordered in one direction while be partly ordered into layers (lamellae). The smectic C ($\mathrm{S_C}$) phase is analogous except that the molecules are tilted within these layers. In fact, these layers are not real, being better described by sinusoidal molecular distribution functions as described

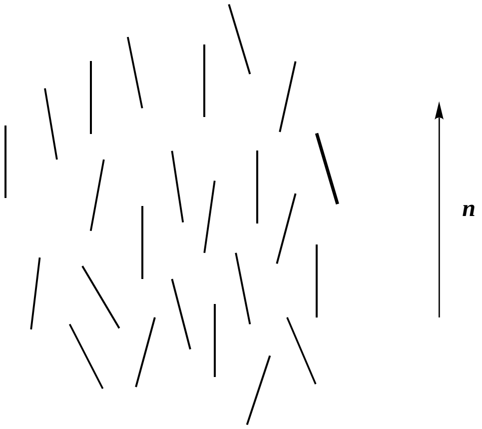

Figure 1. Schematic of a nematic mesophase.

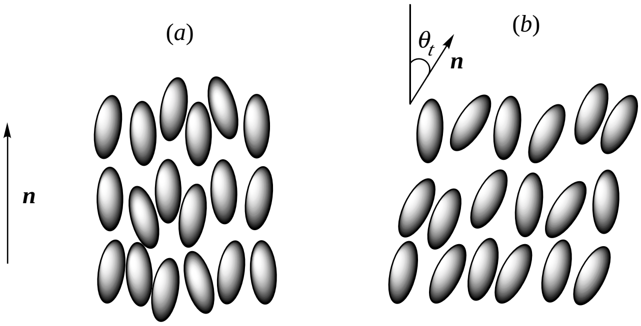

Figure 2. Schematic of a smectic A (*a*) and smectic C (*b*) phase.

well in Leadbetter (1987). The $\mathrm{S_A}$ and $\mathrm{S_C}$ phases are illustrated schematically in figure 2.

Because the phases are anisotropic, their physical properties are also anisotropic. Most commonly, we might consider the anisotropy of dielectric response ($\Delta\varepsilon$), refractive index (Δn) and diamagnetism ($\Delta\chi$), which are defined as (example for diamagnetism):

$$\Delta\chi = \chi_{\parallel} - \chi_{\perp},$$

where $\chi_{\parallel}$ is the diamagnetic susceptibility *parallel* to the director and $\chi_{\perp}$ is the diamagnetic susceptibility *perpendicular* to the director. For $\Delta\chi > 0$, the diamagnetic anisotropy is termed positive. It is already possible to use this diamagnetism, and cooling a liquid crystalline material into its nematic phase from the normal or isotropic liquid state in the presence of a magnetic field of, say, 0.7 T will produce a macroscopically ordered sample.

However, the interaction of a paramagnetic material with an external magnetic field will be stronger than that of a diamagnetic material, which means that any alignment or *re*alignment might be realized with a much smaller field. Thus, it may in turn be possible to look at the orientational switching of a liquid-crystalline material by using an external magnetic field.

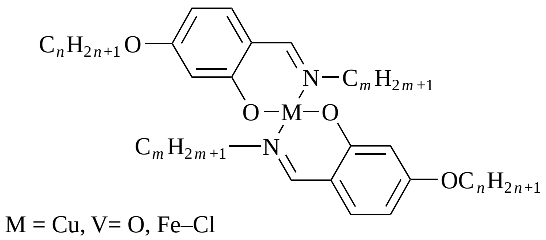

Figure 3. Early paramagnetic complexes.

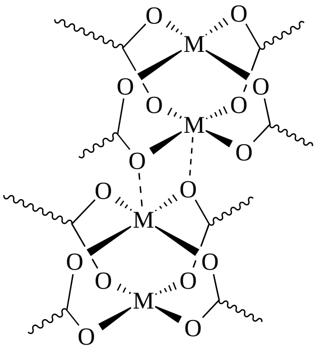

Figure 4. Mesomorphic dinuclear metal carboxylates (M = Cu, Rh, Ru, Mo).

2. Non-lanthanide liquid crystals

In terms of paramagnetic rod-like metallomesogens, the earliest examples were the Cu(II) and V(IV) complexes of salicylaldimines (figure 3) originally described by Galyametdinov and co-workers (Ovchinnikov *et al*. 1984). A large number of groups then became involved in the study of salicylaldimine-based mesogens, and Fe(III) complexes were added to the collection of paramagnetic systems available (Hoshino 1998). A wider discussion of other paramagnetic metallomesogens is found in Alonso (1996).

Metallomesogens forming columnar phases are also known, and probably the best-studied examples are the dinuclear dicoppertetra(alkanoates) studied by Marchon, Giroud-Godquin, Guillon and Skoulios in the early 1980s (figure 4). The dinuclear Cu(II) structure allows for antiferromagnetic exchange between the two copper centres and, consequently, the complex is diamagnetic, although SQUID studies did show an abrupt change in $\chi(T)$ at the transition from the solid to columnar phase. Later, the dinuclear Ru(II)–Ru(II) and Ru(II)–Ru(III) analogues were investigated and it was possible to evaluate the magnitude of the zero-field splitting energy between the $M_{\mathrm{S}} = 0$ ground state and $M_{\mathrm{S}} = \pm 1$ excited state in the Ru(II)–Ru(III) system ($D \approx 300\,\mathrm{cm}^{-1}$) (Giroud-Godquin 1998).

3. Lanthanide liquid crystals

One of the great attractions for some groups in the field has been to incorporate lanthanide elements into liquid-crystalline systems. The reasons for this relate not only to the magnetic and photophysical properties which will result, but also to the

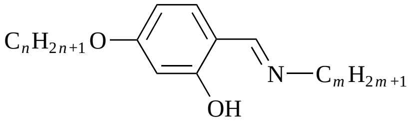

Figure 5. Salicylaldimine ligands.

synthetic challenge of building a metal with a high coordination requirement into a highly anisotropic molecule (Bruce 1994).

The first example of a lanthanide-based liquid crystal was a lutetium phthalocyanine sandwich described by Simon (Piechocki *et al.* 1985), which showed an anisotropy of conductivity in the columnar phase of the order of 10^7 and an absolute conductivity of 3.9×10^{-5} S cm^{-1} at 10 GHz.

There was later a report of mesomorphic salicylaldimine complexes of some lanthanides by Galyametdinov. These complexes were remarkable in that they seemed to take very straightforward ligands (figure 5) which generated, in combination with the metal, a species which was sufficiently anisotropic to show a smectic A phase (Galyametdinov *et al.* 1991). The formula of the complexes was given as $[\mathrm{Ln(L-H)(L)_2}][\mathrm{X}]_2$, where L is the salicylaldimine ligand, $\mathrm{L-H}$ its deprotonated form and X a nitrate or chloride counter anion. It was assumed that the ligands were arranged around the metal in a trigonal prismatic geometry to give a toblerone-shaped mesogen. Indeed, some magnetic data obtained for related complexes were not inconsistent with such a hypothesis (Bikchantaev *et al.* 1996).

Through collaborations supported under INTAS, the team from Exeter began to work with Galyametdinov's team and also with Binnemans in Leuven (supported by the FWO-Flanders and the British Council); this paper gives an overview of some of what we have achieved in collaboration; however, this is very much an ongoing effort and so much of what is here is in the form of preliminary results. A primary aim was to extend the number and type of the complexes and to see how changing the ligand, metal and any anion would affect the properties. These factors are treated separately below, following a brief discussion of the synthesis.

4. Synthesis and structure

One fact that quickly came to light during these studies was that while the initial synthetic work had been accomplished using ethanol as a solvent, in many cases the results were unsatisfactory resulting in low yields or no yield at all. We eventually settled on THF as a solvent although even so, in some systems yields and purity are not always reliable and crystallization is not always a readily available option as the purity of the complex often decreases thereafter. The reason for this irreproducibility is certainly related to the ability of lanthanide ions to act as rather effective Lewis acids which can catalyse the hydrolysis of the imine bond. Such an effect has previously been observed (Smith *et al.* 1998; Berg *et al.* 1991).

Having looked at *N*-alkyl-substituted ligands and bearing in mind the wealth of liquid-crystalline metal complex chemistry based on *N*-aryl-substituted ligands, we next looked to this latter series of ligands for complexes. However, in whichever laboratory the chemistry was carried out, we were not able to complex *N*-aryl-salicylaldimines to lanthanide centres and the reason for this is not entirely clear. However, one clue comes from a single crystal X-ray structure obtained on a dyspro-

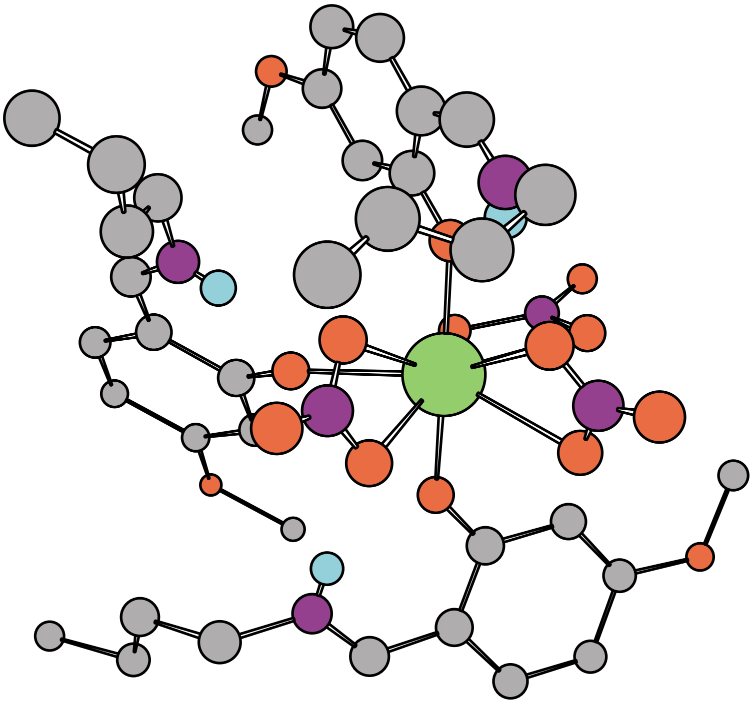

Figure 6. X-ray single-crystal structure of a dysprosium complex of a salicylaldimine with all except the iminium hydrogens removed for clarity.

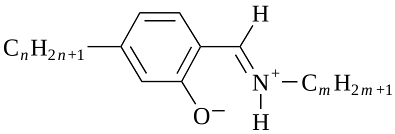

Figure 7. Zwitterionic form of a salicylaldimine.

sium complex of the salicylaldimine shown in figure 6 (Polishuk & Galyametdinov, unpublished work).

The structure seemed to show that, as schematized in figure 7, the phenolic proton of the ligand transferred to the imine nitrogen to give a zwitterion and that the binding of the ligand was entirely through a phenate oxygen. Subsequent re-examination of the ^{1}H NMR spectra of some diamagnetic La derivatives revealed that the imine proton was often broad and, one on occasion, was found to be split into a doublet. What we had presumed to be the phenolic proton was found just above $\delta 12$. If in the complex the zwitterionic form were present, then we would expect a coupling between the N—H and imine protons. We found that selective irradiation of the signal at about $\delta 12$ removed the broadening in the imine signal, showing conclusively that the protons are coupled and, therefore, that in many cases it is the zwitterionic form which coordinates (figure 8). Thus, it may be that the difference in basicity between the nitrogens of *N*-alkyl and *N*-aryl imines is sufficient to tip the balance, allowing the zwitterion (and therefore complexes) to form in one case and not the other.

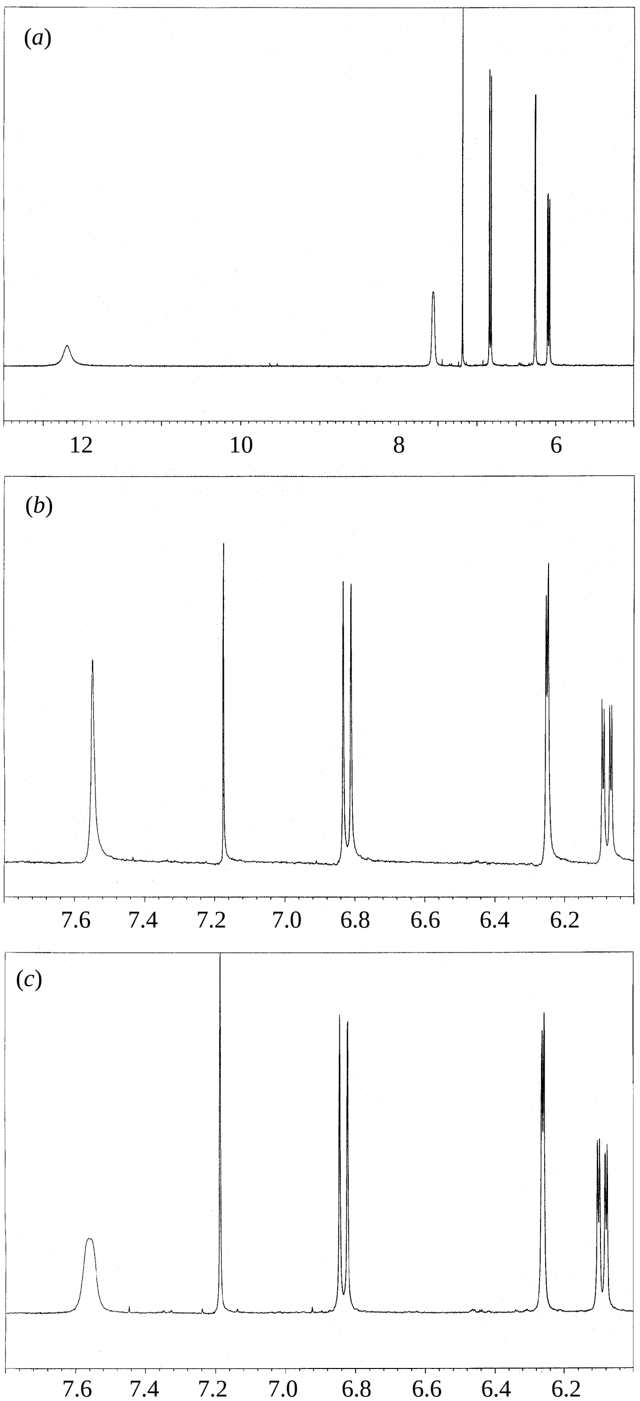

Figure 8. Lower field portion of the ^{1}H NMR spectrum of $[\mathrm{La(L)_2(L{-}H)}][\mathrm{NO_3}]_2$ (main spectrum (*a*)); with enlargement of area of imine signal with (*b*) and without (*c*) decoupling of the N—H$^+$ proton at $\delta 12.3$.

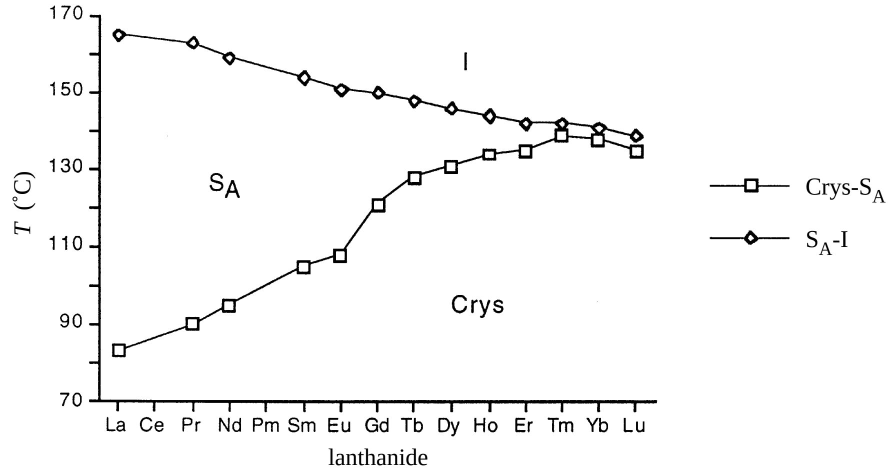

Figure 9. Plot of transition temperature as a function of lanthanide.

However, another major feature shown by the structure determination is that the initially proposed formula of [Ln(L)$_2$(L—H)][X]$_2$ was in error as the complex clearly contained three nitrate groups, bound in a bidentate fashion to the central dysprosium. Thus, the formula for these complexes is clearly more appropriately represented as [Ln(L*)$_3$][X]$_3$, where L* implies a rearranged (i.e. the zwitterionic) ligand. We now suppose that for simple ligands of the type shown in figure 5 complexed to lanthanide nitrates, this formula is correct and appropriate. However, we would note at this stage that preliminary data from other related complexes made in Exeter show that this situation is not necessarily common to all salicylaldimine complexes of lanthanides. A full investigation of the structure of these complexes is currently underway.

5. The effect of metal

In order to examine systematically the effect of the metal on the mesomorphism, a complex of each lanthanide (with the exceptions of cerium and promethium) was made using the ligand shown in figure 5 ($n = 8$, $m = 18$), starting from the lanthanide nitrate (Binnemans *et al.* 1999).

The complexes, all of which had the formula [Ln(L)$_3$][NO$_3$]$_3$, each showed only a smectic A mesophase which was readily characterized by the appearance of a focal conic fan texture and the presence of homeotropic areas consistent with a uniaxial smectic phase.

However, when the transition temperatures were plotted (figure 9) it was readily evident that the metal was having a profound effect on the mesophase range and that while the melting point was increasing with increasing atomic number, the clearing point was decreasing, reducing the mesomorphic range. The explanation for this is not entirely clear. Of course, as the lanthanide series is crossed, the ionic radius decreases (the lanthanide contraction) and so it may be possible to explain the increase in crystal-phase stability in terms of the smaller metal ion leading to a more compact arrangement of the ligands around the metal leading to a more efficient packing. This point will be difficult to delineate as, from the crystal structure shown

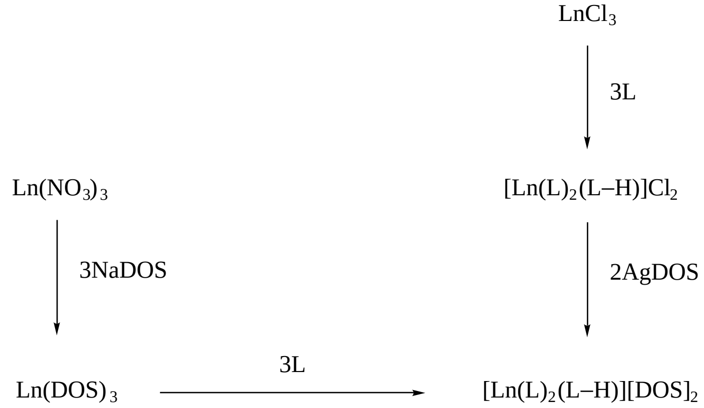

Figure 10. Preparation of the DOS salts.

above in figure 7, it is apparent that the ligand is bound to the metal only via a single atom (the phenate oxygen) and so the orientation of the ligand will be determined by the alkyl chains on the ligand and how they are required to pack under the control of lattice energy forces. Thus, crystal structures of model complexes with shorter alkyl chains will not necessarily provide a guide to what is happening in these systems.

If the arrangement of the ligands were to become more compact about the metal as its radius decreased, then the more compact anisotropic arrangement would be expected to lead to a higher clearing point which is the opposite of what is observed. However, it is possible to argue that with the increasing charge density on the metal as the lanthanide series in crossed, the polarizability due to the metal will decrease due to the higher charge density, which would lead to a destabilization of the smectic A phase. We have previously shown (Bertram *et al.* 1991) that the metal has a major contribution to make to the polarizability of metallomesogens and so we feel that such an effect could well contribute to the observed behaviour.

6. Effect of the anion

In the initial studies of these metallomesogens, Galyametdinov *et al.* (1991) had synthesized nitrate and chloride salts and had typically found transition temperatures ranging from 120 to 180 °C. While physical studies of materials at such temperatures are possible, they become easier if the temperature can be moderated somewhat. In previous studies of complexes of silver(I), we had found previously that the replacement of a small anion such as nitrate or triflate by the long-chain dodecylsulphate (DOS) led to greatly reduced transition temperatures as well as to interesting mesomorphism (Bruce *et al.* 1992; Donnio *et al.* 1997). With this in mind, we set about the introduction of the dodecylsulphate anion into these complexes.

Two approaches were employed. In the first, the chloride complex was reacted with silver dodecylsulphate, precipitating silver chloride and leading smoothly to the complex (Binnemans *et al.* 1998). In the second (Galyametdinov *et al.* 1999), $Ln(DOS)_3$ was prepared in advance from $Ln(NO_3)_3$ and NaDOS in water and then reacted with the ligand (figure 10).

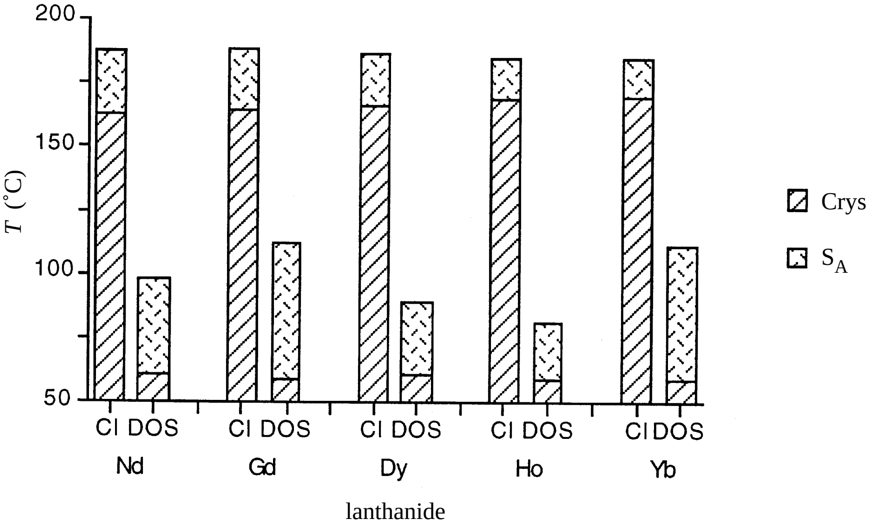

Figure 11. Graphical representation of the thermal behaviour of chloride and DOS salts of some lanthanide complexes.

The result was as we had predicted and the transition temperatures of the complexes were significantly reduced. This is shown graphically in figure 11.

The transition temperatures for these complexes show the starkest difference with melting points reducing from *ca.* 160 to 60 °C and clearing points from *ca.* 180 °C to *ca.* 100 °C. However, it is interesting to note that the transition temperatures for the chloride salts are rather insensitive to the metal, while those for the DOS salts do show a metal dependence. The high temperatures and metal insensitivity lead us to suggest that these former complexes may have a significant ionic character (strong interaction between the hard lanthanide acids and the borderline chloride base would not be expected). For the purposes of comparison, the transition temperatures of the related nitrate complexes are somewhat intermediate between those of the chlorides and dodecylsulphates. Another possibility would be a chlorobridged, dimeric structure (*vide infra*).

7. Effect of the ligand

As it appeared that the use of N-arylamines was out of the question, it was therefore necessary to extend the salicylaldimines at the other end of the molecule. Thus, in another strategy aimed at reducing transition temperatures, we introduced a 3,4-dialkoxybenzoate group (figure 12) as the alkoxy chain in the 3-position of the terminal ring would lower the anisotropy of the complex.

With this ligand, a systematic approach to the structure was adopted. Thus, initially n and m were systematically varied using lanthanum nitrate as the lanthanide source in order that NMR data could be readily obtained. Some selected data are recorded in table 1.

Several things are of note from these initial results. First, it does not appear as though there is a ready correlation between the two chain lengths, n and m, and the transition temperatures; a fuller picture will emerge as more derivatives

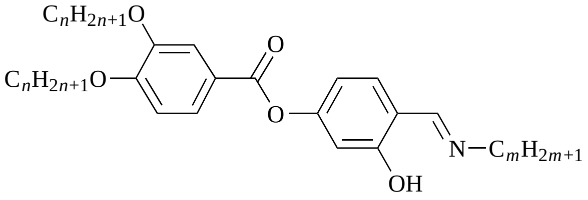

Figure 12. Structure of the 3,4-dialkoxysalicylaldimines.

Table 1. *Transition temperatures for some lanthanum nitrate salts*

n	m	complex formula	mesomorphism
4	4	$[LaL_2][NO_3]_3$	Crys · 84 · S_A · 124 · I
4	18	$[LaL_2][NO_3]_3$	Crys · 103 · S_A · 191 · I
8	4	$[LaL_2][NO_3]_3 \cdot H_2O$	Crys · 100 · S_A · 200 · I
8	12	$[LaL_2(L{-}H)][NO_3]_2 \cdot 2H_2O$	Crys · 83 · S_A · 123 · I

Table 2. *Selected transition temperatures for lanthanide complexes of the ligand with* $n = m = 12$

complex formula	mesomorphism
$[Dy(L)_2(L{-}H)][NO_3]_2$	Crys · 103 · S_A · 144 · I
$[Dy(L)_2(L{-}H)][OTf]_2$	Crys · 51 · S_A · 84 · I
$[Nd(L)_2(L{-}H)][NO_3]_2 \cdot H_2O$	Crys · 84 · S_A · 112 · I
$[Nd(L)_2(L{-}H)][OTf]_2$	Crys · 57 · S_A · 87 · I
$[Ho(L)_2][NO_3]_3$	Crys · 85 · S_A · 155 · I
$[Er(L)_2(L{-}H)][OTf]_2$	Crys · 51 · S_A · 81 · I

become available. Second, note that the first three complexes in table 1 possess only two ligands. If we assume that each nitrate is bound in a bidentate fashion to the lanthanum taking up a total of six coordination sites, and that the ligands are bound in the zwitterionic form, then the metal is eight-coordinate (we are assuming for now that in the third entry, the water is in the lattice). To our knowledge, this stoichiometry has not previously been observed with salicylaldimine ligands bound to lanthanide centres. However, in the final table entry, a more familiar stoichiometry appears in which the metal appears bound both to the neutral (zwitterionic) ligand and to the ligand anion.

Next, we used a particular ligand ($n = m = 12$) in complexes with a range of lanthanides using both nitrate and triflate anions. Two patterns emerged. First, the stoichiometry of the triflate complexes was reliable, being $[Ln(L)_2(L{-}H)][OTf]_2$, occasionally with a water of crystallization, while the stoichiometry of the nitrate complexes varied between $[Ln(L)_2(L{-}H)][NO_3]_2$ and $[Ln(L)_2][NO_3]_3$ with no apparent pattern. Second, the transition temperatures of the triflate complexes were always lower than those of the corresponding nitrate complex, almost approaching room temperature. Some examples are shown in table 2.

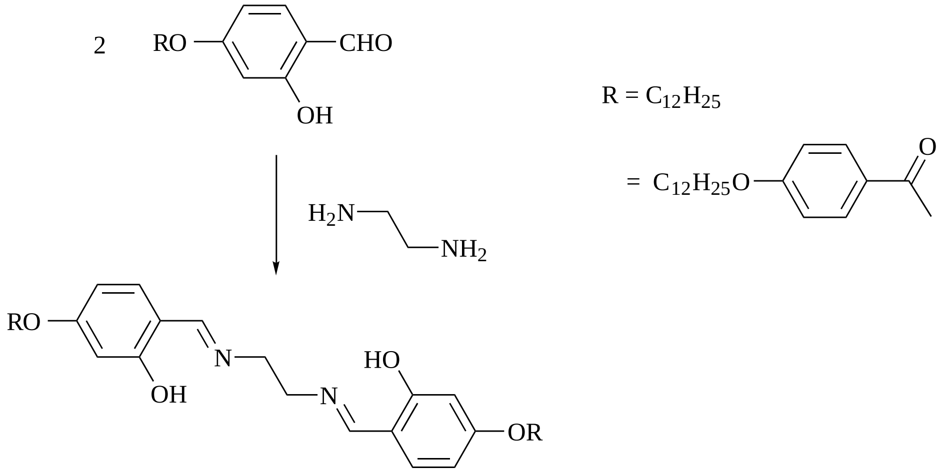

Figure 13. Structure of the dimeric ligands.

Table 3. *Mesomorphism of lanthanide complexes of dimeric ligands*

R	complex formula	mesomorphism
$C_{12}H_{25}$	[Nd(L—2H)(L—H)]	Crys · 150 · S · 190 · I
$C_{12}H_{25}$	[Er(L—2H)(L—H)] · $3H_2O$	Crys · 165 · S · 230 · I
$C_{12}H_{25}$	[Eu(L—2H)(L—H)] · $2H_2O$	Crys · 150 · S · 190 · I
$C_{12}H_{25}OC_6H_4CO$	[Nd(L—2H)(L—H)]	Crys · 140 · S · 200 · dec

8. Complexes of dimeric ligands

Previously, Paschke had synthesized (Paschke *et al.* 1990) dimeric salicylaldimine ligands which he had used to form complexes of nickel(II) and copper(II). We then made modifications of such ligands (figure 13) and used them to form complexes of various lanthanides.

The ligands themselves were mesomorphic (Cerrada *et al.* 1989) and with R = $C_{12}H_{25}$, a smectic C phase was found between 85 and 107 °C, while for R = $C_{12}H_{25}O$ C_6H_4CO, a smectic A phase was seen from 140 to 230 °C.

With these ligands, we were able to form neutral complexes in which the metal was bound to one monoanionic ligand and one dianionic ligand, the base used in the synthesis being piperidine. The mesomorphism of these complexes is shown in table 3.

For these complexes, we have not yet been able to identify the mesophase, as it is somewhat viscous, preventing the establishment of a well-defined texture; X-ray diffraction measurements are in progress. The mesophase is seen at slightly elevated temperatures, which is perhaps a little surprising since we might have expected that a totally neutral complex might be mesomorphic at lower temperatures. However, a possible explanation is found in the next section, on tripodal ligands.

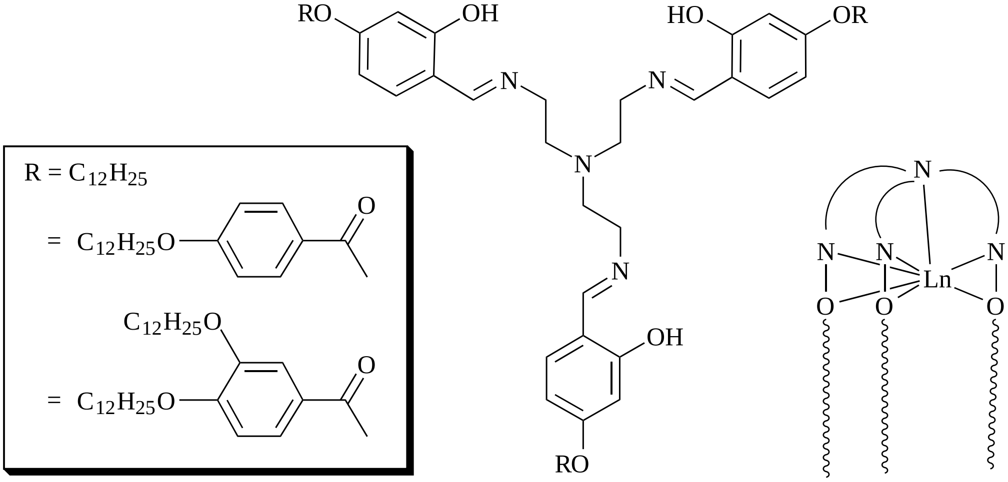

Figure 14. Structure of the tripodal ligands and a schematic of how they might coordinate.

9. Complexes of tripodal ligands

We then took the ligand design a stage further and thought about how we might encapsulate the lanthanide within a ligand system. We felt that this might be possible using a tripodal ligand to give a coordination geometry as shown in figure 14; the ligand used is shown in the same figure. The same ligand has also been used by the Zaragoza group for the synthesis of metallomesogens (Serrano, personal communication).

In one case (with R = Me), we were able to grow single crystals and the results of the structure determination are shown in figure 15 (Slawin, unpublished work). Thus, figure 15*a* shows what turned out to be half of the molecule, and reveals that while a tripodal geometry is adopted, the ligand appears insufficiently large to encapsulate the metal entirely and there is an open face with a phenolic oxygen protruding. Note that in this case, the ligand coordinates through the imine (and apical) nitrogen and a phenate anion, i.e. the zwitterion does not form. The presence of the open face suggests the full structure of a dimer which is held together through two bridging oxygen atoms and which is shown in figure 15*b*.

While we have not yet been able to determine whether the ligands are mesomorphic, their complexes, obtained as neutral materials of the general empirical formula [Ln(L—3H)], showed liquid crystal phases, although again here we do not yet have an unequivocal identification of the nature of what we believe to be the smectic phase. Representative data are collected in table 4.

In this case, the transition temperatures are rather higher than we might have anticipated, but the result of the crystal structure determination suggests a possible explanation for this, both for the tripodal ligands and for the dimeric ligands above. In the former case, we see clearly the dimeric arrangement of the complex and we suspect that such a large species would indeed have rather high transition temperatures. Of course, the dimeric ligands are closely related to the tripodal ligands and so it may well be that the neutral complexes of the dimer ligands also give rise to dimeric complexes which, being similarly large, lead to high melting systems.

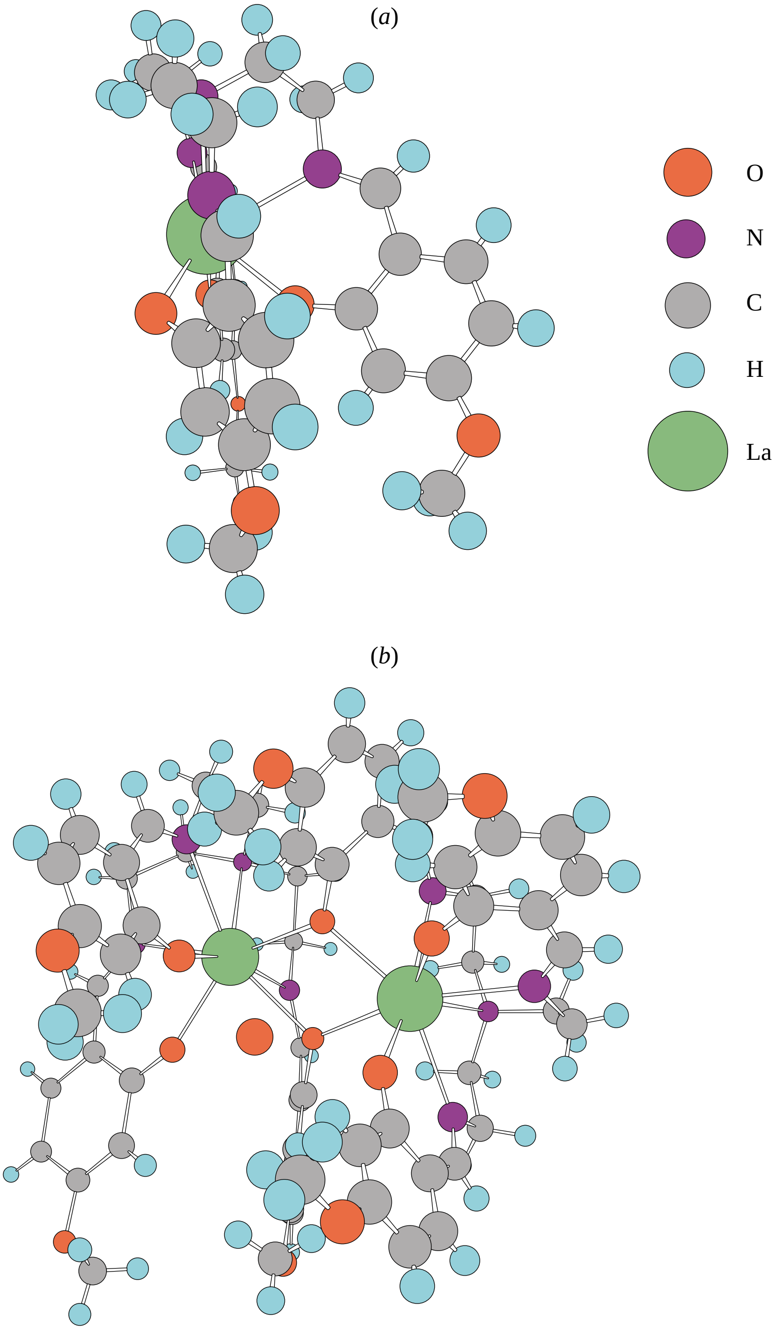

Figure 15. Molecular structure of a tripodal lanthanum complex.

10. Conclusion

In this paper, we have shown that there are several ways in which liquid-crystalline complexes of lanthanide elements can be realized, although a full development and

Table 4. *Mesomorphism of lanthanide complexes of trimeric ligands*

R	complex formula	mesomorphism
$C_{12}H_{25}$	$[La(L—3H)] \cdot H_2O$	Crys · 209 · S · 221 · I
$C_{12}H_{25}$	$[Gd(L—3H)] \cdot H_2O$	Crys · 205 · S · 278 · I
$C_{12}H_{25}$	$[Er(L—3H)] \cdot 2H_2O$	Crys · 230 · S · 270 · I
$C_{12}H_{25}OC_6H_4CO$	$[La(L—3H)] \cdot 4H_2O$	Crys · 216 · S · 230 · I
3,4-$(C_{12}H_{25}O)_2C_6H_3CO$	$[La(L—3H)] \cdot H_2O$	Crys · 122 · S · 180 · I

appreciation of the subject will need to go hand-in-hand with some fundamental lanthanide coordination chemistry. At the time of writing, we await with anticipation the results of the first physical measurements made on our new complexes and look forward to exploiting the phenomenon of magnetism in the anisotropic environment that is a liquid crystal mesophase.

The authors thank the following agencies for their support: the Leverhulme Trust, the EPSRC, FWO Flanders, IWT (Flanders), the British Council and INTAS (contract: INTAS 96-1198). Crystal structure data from Professor A. Polishuk (Kiev University) and Dr A. Slawin (Loughborough University) are gratefully acknowledged, as is expert NMR assistance from Dr V. Sik (Exeter).

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