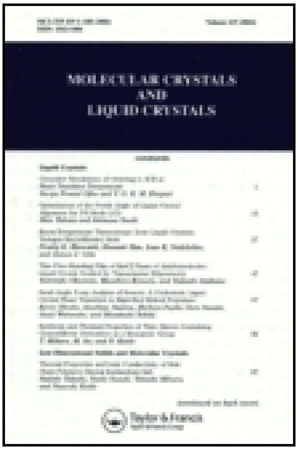

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Mesomorphic Complexes of the Lanthanide Elements

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Mesomorphic Complexes of the Lanthanide Elements

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Mesomorphic lanthanide(III) complexes of salicylaldimine ligands have been synthesised. The effect upon the mesomorphic behaviour is discussed with variation of the counter-anion, number of alkoxy chains and the nature of the ligand framework. Complexes displaying either smectic or columnar mesophases have been realised.

Keywords: metallomesogens; lanthanide(III) complexes; salicylaldimine ligands; polycatenar

In recent years, metal-containing liquid crystals, so-called metallomesogens, have developed into an extensive and ever-increasing field of exciting new materials.[1] The sub-set of metallomesogens incorporating lanthanide(III) complexes has developed at a slower rate. This is hardly surprising, when one considers that the high coordination number requirements of the lanthanide ions complicates the design of such metallomesogens with respect to maintaining the structural anisotropy requisite for promoting mesophase formation. Importantly though, certain lanthanide(III) complexes exhibit a large paramagnetism[2] and strong luminescent properties.[3]

The first example of metallomesogens containing a lanthanide(III) ion were bis(phthalocyaninato)lutetium(III) complexes.[4] Furthermore, it was demonstrated that there was an anisotropy of the conductivity of these materials in the columnar mesophase of the order of 10^7, with a conductivity of 3.9×10^{-5} S cm^{-1} at 10 GHz associated with intracolumnar processes. We have also recently reported that soaps of the lanthanide elements, specifically lanthanum(III) alkanoates, display an enantiotropic smectic A phase.[5] This report will concentrate on our successes in developing mesomorphic complexes of the lanthanide elements incorporating salicylaldimine ligands (Figure 1); related mesomorphic complexes were reported initially by Galyametdinov.[6] Interestingly, Haase and coworkers have demonstrated the alignment of terbium(III) and dysprosium(III) metallomesogens of salicylaldimine ligands HL^1 ($R = C_{12}H_{25}$ and $R' = C_{18}H_{37}$) *via* an external magnetic field of 1.2 T. This was facilitated by the fact that these lanthanide complexes display large magnetic anisotropies, which are two orders of magnitude greater than for organic liquid crystals or metallomesogens containing transition metals [7]

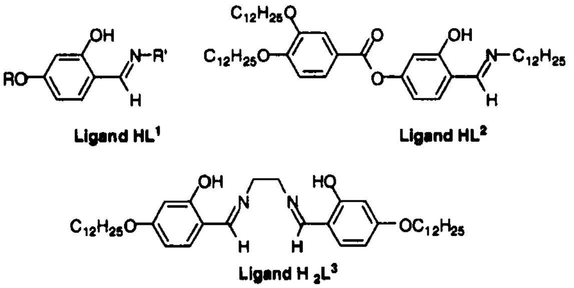

Figure 1. Salicylaldimine ligands used in this study.

Complexes of simple salicylaldimines.

One of the difficulties associated with the study of metallomesogens is the high transition temperatures often encountered. Having shown previously that appropriate choice of anion could beneficially affect transition temperatures,[8] we applied the same methodology to these lanthanide systems. Thus, we found that the dodecylsulphate (DOS) anion reduced temperatures considerably compared to analogous nitrate and chloride salts (Table 1).[9] We similarly found the triflate anion to be beneficial in this regard. This effect is thought to arise as the mobility of the alkyl chains in the alkylsulphate anions acts to destabilise the crystalline and liquid-crystalline states leading to a reduction in the melting and clearing temperatures compared to the analogous nitrate and chloride complexes.

Table 1: Examples of the effect of altering the counter-anions (Ligand HL^1 where $R = C_{12}H_{25}$ and $R' = C_{18}H_{37}$).

Compound	Transition (*T*/°C)	Δ*H*/ kJ mol^{-1}	Δ*S*/ J K^{-1} mol^{-1}
$[NdL^1(HL^1)_2]Cl_2.3H_2O$	Crys • 162 • S_A	56.6	130
	S_A • 187 • I	9.1	20
$[NdL^1(HL^1)_2](DOS)_2$	Crys • 61 • S_A	59.7	179
	S_A • 98 • I	9.7	26
$[YbL(LH)_2]Cl_2.3H_2O$	Crys • 169 • S_A	51.8	117
	S_A • 185 • I	11.3	25
$[YbL(LH)_2](DOS)_2$	Crys • 59 • S	65.	19
	S_A • 111 • I	14.5	38

With similar aims, we have also investigated the effect of increasing the number of alkoxychains on the salicylaldimine ligand (HL^2), obtaining complexes of formula $[LnL^2(HL^2)_2](X)_2$ ($X = NO_3$ or CF_3SO_3). These polycatenar complexes[10] now display a viscous columnar hexagonal mesophase, as identified by optical microscopy and X-ray diffraction (Table 2). The stabilisation of a hexagonal columnar mesophase is consistent with our studies of platinum(II) and palladium(II) di- and tri-alkoxystilbazole metallomesogens.[11] Thus, for these metallomesogens we demonstrated that in order to observe columnar mesophases, the alkoxychains had to be of sufficient density (and thus volume) to contribute at least 60% of the molecular weight, in agreement with previously reported observations.[12] Similarly, if we apply the same reasoning to our polycatenar lanthanide(III) salicylaldiminato complexes, then for $[NdL^2(HL^2)_2(NO_3)_2]$ the alkoxychains contribute 64% and for $[NdL^2(HL^2)_2](CF_3SO_3)_2$ the alkoxychains contribute 60% of the molecular weight. Accordingly, the analogous lanthanide(III) salicylaldiminato complexes of HL^2, where there is not an alkoxy chain at the 3'-position, have been reported by Galyametdinov to display a S_A mesophase.[6]

These polycatenar complexes are also significant as they display lower melting points compared to the ligand itself, with the opposite situation being observed more frequently with metallomesogens.[1] Interestingly, here again an anion effect is observed with the complexes with triflate anions exhibiting transition temperatures lower than those of the analogous nitrate complexes.[13] This effect shows that triflate complexes are perhaps a synthetically easier alternative to alkylsulphate complexes for metallomesogens with low melting points.

Table 2: Transition temperatures and thermal data for $[LnL^2(HL^2)_2]X_2$ ($X = NO_3$ or CF_3SO_3).

Compound	*Transition* *(T/°C)*	Δ*H*/ kJ mol^{-1}	Δ*S*/ J K^{-1} mol^{-1}
$[NdL^2(HL^2)_2](CF_3SO_3)_2$	Crys • 57 • Col$_h$	90.3	270
	Col$_h$ • 88 • I	9.2	30
$[GdL^2(HL^2)_2](CF_3SO_3)_2$	Crys • 51 • Col$_h$	44.9	140
	Col$_h$ • 89 • I	3.7	10
$[TbL^2(HL^2)_2](CF_3SO_3)_2$	Crys • 48 • Col$_h$	43.8	140
	Col$_h$ • 88 • I	2.2	10
$[DyL^2(HL^2)_2](CF_3SO_3)_2$	Crys • 51 • Col$_h$	37.6	160
	Col$_h$ • 88 • I	4.3	10
$[ErL^2(HL^2)_2](CF_3SO_3)_2$	Crys • 51 • Col$_h$	44.6	140
	Col$_h$ • 88 • I	0.5	1
$[NdL^2(HL^2)_2(NO_3)_2]$	Crys • 84 • Col$_h$	35.3	100
	Col$_h$ • 112 • I	–	–
$[DyL^2(HL^2)_2(NO_3)_2]$	Crys • 85 • Col$_h$	20.0	60
	Col$_h$ • 146 • I	–	–
$[ErL^2(HL^2)_2(NO_3)_2]$	Crys • 77 • Col$_h$	71.2	200
	Col$_h$ • 128 • I	–	–

Complexes of bifunctional salicylaldimines

We were also interested in obtaining neutral complexes *via* deprotonation of the salicylaldimine ligands, in order to determine the effect upon the mesomorphism. Frustratingly, we were unable to synthesise such complexes with ligands HL^1 and HL^2 after employing a range of bases, lanthanide(III) salts and reaction conditions.

Table 3: Transition temperatures and thermal data for lanthanide(III) salen complexes (d = decomposition)

Compound	Transition (*T*/°C)	Δ*H*/ kJ mol^{-1}	Δ*S*/ J K^{-1} mol^{-1}
H_2L^3	Crys • 65.1 • Crys'	2.7	8
	Crys' • 81 • Crys"	20.7	58
	Crys" • 84.6 • S_C	21.7	61
	S_C • 106.9 • I	9.0	24
$[La(H_2L^3)_2]Cl_3.4H_2O$	Crys • 220 • S	–	
	S • 288 • d	–	
$[La(H_2L^3)_2](CF_3SO_3)_3.4H_2O$	Crys • 170 • S	–	
	S • 240 • I^d	–	
$[La(L^3)(HL^3)].H_2O$	Crys • 134.5 • Crys'	0.1	0
	Crys' • 175.8 • S	4.3	10
	S • 190 • I^d	–	
$[Nd(L^3)(HL^3)]$	Crys • 181.9 • S	14.5	32
	S • 209.4 • I^d	30.2	63
$[Er(L^3)(HL^3)].3H_2O$	Crys • 65.1 • Crys'	1	3
	Crys' • 111.6 • S	0.5	1
	S • 155 • I	–[a]	
$[Eu(L^3)(HL^3)].2H_2O$	Crys • 87.9 • Crys'	20.8	58
	Crys' • 95.9 • Crys"	2.8	8
	Crys" • 137.7 • S	20.4	50
	S • 165.8 • d		

We were, however, inspired by a report in the literature of an erbium(III) bis(salen) complex where all the phenolic protons had been removed using piperidine as base.[14] Consequently, we synthesised the mesomorphic ligand H_2L^3, which itself displays a S_C phase.[15] This ligand when reacted with either lanthanum(III) chloride or lanthanum(III) triflate then forms complexes of the type $[La(H_2L^3)][X]_3.4H_2O$ (X = Cl or CF_3SO_3). Significantly though, when reacted with the appropriate lanthanide(III) triflate in the presence of three equivalents of piperidine then complexes of the type $[Ln(HL^3)(L^3)].H_2O$ are obtained.[16] These complexes are mesomorphic (Table 3) displaying a viscous smectic mesophase at higher temperatures in comparison to the free ligand. The nature of the mesophase was difficult to determine unequivocally by optical microscopy, but subsequent X-ray studies supported the assignment as a smectic mesophase, although the studies were hampered by sample deterioration upon prolonged heating. The transition temperatures are higher for the complexes of formula $[La(H_2L^3)]X_3.4H_2O$ (X = Cl or CF_3SO_3)

compared to those of [La(HL^3)(L^3)], presumably due to the stronger intermolecular interactions associated with the more ionic structure in the former case.

We have previously shown that for the mesomorphic lanthanide(III) nitrate complexes of ligands HL^1, where [Ln(HL^1)$_3$](NO$_3$)$_3$, R = C_8H_{17} and R' = $C_{18}H_{37}$, the transition temperatures correlate against the size of the lanthanide(III) ion (Figure 2).[17] Consequently, as the lanthanide series is traversed there is a gradual increase in the melting temperatures and a reduction in the clearing temperatures, leading to a reduction in the mesophase range observed. This phenomenon is explained in terms of the lanthanide contraction, so that as the ionic radius of the lanthanide(III) ion gets smaller across the lanthanide series, whilst the charge remains constant, consequently there is an increase in the electrostatic interaction between the lanthanide ion and the coordinating ligands leading to the observed increase in the melting temperature. The decrease in the clearing point presumably reflects the increase of steric interactions between the ligands coordinated to the lanthanide(III) ion as the ionic radius falls, which results in greater structural distortions and consequently a reduction in the overall structural anisotropy and therefore the stability of the mesophase. The fact that the correlation exists between the ionic radius and the mesomorphic properties, is clearly demonstrated by comparison of the properties of the holmium complex (Crys • 134 • S$_A$ • 144 • I) with the yttrium complex (Crys • 132 • S$_A$ • 142 • I), as these two complexes have nearly identical ionic radii.

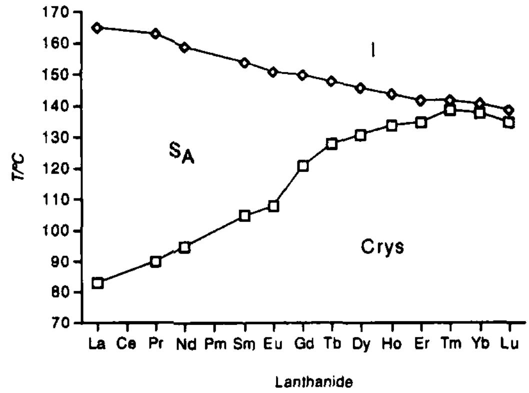

Figure 2. Influence of the ionic radius upon the mesomorphic properties of [Ln(HL^1)$_3$](NO$_3$)$_3$, R = C_8H_{17} and R' = $C_{18}H_{37}$.

Any influence of the size of the lanthanide(III) ion upon the transition temperatures is, however, absent for the complexes of $[LnL^2(HL^2)_2]X_2$ ($X = NO_3$ or CF_3SO_3) and $[Ln(L^3)(HL^3)].H_2O$. The difference between these lanthanide complexes and the $[Ln(HL^1)_3(NO_3)_3]$ complexes arises in the coordination mode of the salicylaldimine ligands, with those of the $[Ln(HL^1)_3](NO_3)_3$ series of complexes containing the salicylaldimine ligands coordinated only in a monodentate mode *via* a phenate oxygen.[18] Consequently, there is no interaction between the imine nitrogen and the metal ion. In fact the phenolic hydrogen is transferred to the imine nitrogen, so that a zwitterionic form of the Schiff base is formed (negative charge on the oxygen atom, positive charge on the nitrogen atom). For the complexes of $[LnL^2(HL^2)_2]X_2$ ($X = NO_3$ or CF_3SO_3) and $[Ln(L^3)(HL^3)].H_2O$ at least one of the ligands is deprotonated, leading to the formation of a more rigid chelate structure between the lanthanide(III) cation and the ligand. Presumably, this increased rigidity acts to maintain a more uniform molecular structure as the lanthanide series is traversed because the ligands are unable to rotate about the central lanthanide cation. This in turn leads to a more constant mesophase range being observed due to the mesomorphic properties being determined principally by the ligand framework, which remains constant for a given series of lanthanide(III) complexes.

In summary, we have discussed the beneficial lowering of the transition temperatures when dodecylsulphate is used as counter-anion when compared to chloride. Furthermore, we have shown that the addition of an extra alkoxy chain to the ligand results in the observance of lanthanide(III) salicylaldiminato complexes displaying an hexagonal columnar mesophase. For these complexes, where triflate is the counter-anion then the melting temperatures are lower than when the counter-anion is nitrate. For a series of lanthanide(III) bis(salen) complexes we observe that deprotonation of the ligands leads to a smectic mesophase at lower temperatures than for the related complexes where inorganic anions are present. Where the salicylaldimine ligands coordinate only in a mono-dentate mode then the mesomorphism is strongly influenced by the lanthanide contraction, whilst such an effect is absent where the ligands co-ordinate in a chelating mode.

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