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X-ray and magnetic birefringence studies of some lanthanide metallomesogens with Schiff's base ligands

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Preliminary Communication

X-ray and magnetic birefringence studies of some lanthanide metallomesogens with Schiff's base ligands

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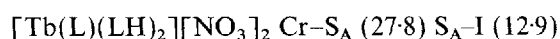
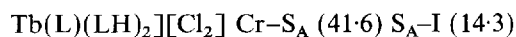
Low angle X-ray scattering studies have been used to identify the mesophase of some calamitic lanthanide mesogens as smectic A, while magnetic birefringence studies have shown a huge magnetic anisotropy for these complexes.

Metallomesogens represent a new and very promising field of liquid crystal science [1]. One of the most unusual and intriguing properties of some of these substances is the presence of a paramagnetic moment and magnetic anisotropy, which determines the behaviour of the liquid crystals in a magnetic field. The vast majority of metallomesogens include d-block transition elements, although it is known that the maximum values of magnetic moments, and especially of magnetic anisotropy, are inherent in f-block transition element complexes.

The synthesis of the first calamitic lanthanide mesogens has recently been described [2]. Here we report the synthesis and some preliminary characterization of some lanthanide complexes, $[(LH)_2(L)LnX_2]$ (LH = salicylal-dimine), shown in figure 1 and table 1. The given formulation, $[(LH)_2(L)Ln][X]_2$, reflects the observed stoichiometry of the complexes and shows that one ligand coordinates as its deprotonated form, while two ligands coordinate as neutral species, resulting in the retention of two anions. Although it has not been possible to grow single crystals of these complexes to

prove the structure, the ligand coordination about the metal is regarded as being trigonal prismatic (the molecular long axis contains a C_3 rotational axis), giving a 'Toblerone'-shaped complex (figure 2). The location of the anions is not clear, but given the high coordination numbers associated with lanthanides, it is likely that they are either bound to, or at least closely associated with, the metal cation.

The chemical composition was determined by elemental analysis (table 2), vapour pressure osmometry measurements (Eu complex), magnetic susceptibility, and by infrared spectroscopy. The liquid crystalline properties were measured using polarizing optical microscopy and calorimetric data were obtained. For example, enthalpic values (in kJ mol^{-1}) for the Tb-Cl and Tb- NO_3 systems were as follows and were typical of the data obtained.



We observed the homeotropic and fan-shaped texture typical for a S_A phase. As seen from table 1, the substitution of NO_3 group by Cl ion results in an increase in the transition temperatures for the Tb complex.

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As complexes of this type are rather new and as the molecular structure of the mesogen was unsure, low angle X-ray scattering patterns were obtained for the complexes with Ln = La, Tb; X = NO₃, and Ln = Tb; X = Cl, and were consistent with the smectic A phase structure as determined by polarizing microscopy. The patterns contained two sharp reflections in the spacing ratio 1:2 in the small-angle region, and one broad reflection, corresponding to a spacing of 4.6 Å, in the wide-angle region. It was also possible to obtain some diffraction data from samples which were partially

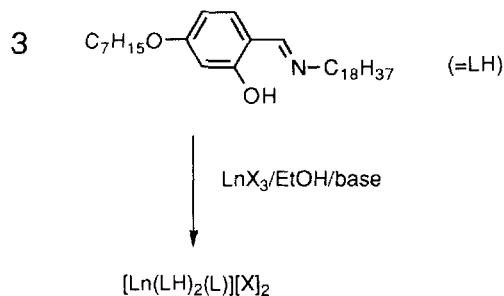


Figure 1. Proposed structure of the lanthanide complexes.

Table 1. Transition temperatures and magnetic moments for the complexes $[\text{Ln}(\text{LH})_2(\text{L})][\text{X}]_2$

X	Ln	Transition	T/°C	$\mu_{\text{eff}}(\text{exp})/\text{BM}$	$\mu_{\text{eff}}(\text{theor})/\text{BM}$
NO ₃	La	Cr → S _A	127	0	0
		S _A → I	165		
NO ₃	Tb	Cr → S _A	148	9.8	9.7
		S _A → I	151		
NO ₃	Dy	Cr → I	151	10.3	10.5
		(S _A → I)	(150)		
NO ₃	Nd	Cr → S _A	142	3.4	3.6
		S _A → I	155		
NO ₃	Eu	Cr → S _A	140	3.2	3.4
		S _A → I	153		
NO ₃	Gd	Cr → S _A	148	7.7	7.9
		S _A → I	155		
Cl	Tb	Cr → S _A	182	9.5	9.7
		S _A → I	203		

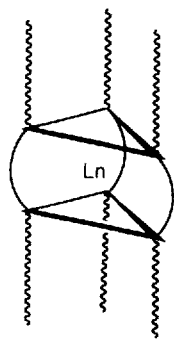


Figure 2. Synthetic scheme to the lanthanide complexes.

Table 2. Analytical data for the new complexes

Formula	Calculated(%)			Found(%)		
	C	H	N	C	H	N
C ₉₆ H ₁₇₀ N ₅ O ₁₂ La	66.8	9.9	4.1	67.0	9.9	4.1
C ₉₆ H ₁₇₀ N ₅ O ₁₂ Dy	65.9	9.8	4.0	66.3	9.8	4.1
C ₉₆ H ₁₇₀ N ₅ O ₁₂ Tb	66.1	9.8	4.0	66.0	9.5	4.1
C ₉₆ H ₁₇₀ N ₅ O ₁₂ Nd	66.7	9.9	4.1	66.6	9.8	4.1
C ₉₆ H ₁₇₀ N ₅ O ₁₂ Eu	66.3	9.9	4.0	66.7	9.8	4.1
C ₉₆ H ₁₇₀ N ₅ O ₁₂ Gd	66.1	9.8	4.0	66.4	9.8	4.1
C ₉₆ H ₁₇₀ N ₃ O ₆ Cl ₂ Tb	68.1	10.1	2.5	68.3	9.8	2.5

aligned on cooling from the I to S_A phase in a transverse magnetic field of 1.2 T. The data so obtained from these experiments were consistent with the assignment as a S_A phase.

No other sharp reflection was observed in the patterns, but there was an additional broad reflection (figure 3) at about 8.7 Å for the La and Tb compound (X = NO₃) and at about 9.1 Å for the Tb compound (X = Cl). These 8–9 Å reflections were interpreted as corresponding to the mean side-to-side distance between the rigid parts of the complexes, while the diffuse reflection at about 4.6 Å resulted from the mean distance between molten aliphatic chains. The layer thicknesses (Ln = La, X = NO₃: 30.0 Å; Ln = Tb, X = NO₃: 28.6 Å; Ln = Tb, X = Cl: 30.0 Å) were very similar for all complexes and much smaller than the length of the ligand in its fully extended conformation which was evaluated as 39 Å by molecular modelling using the Sybil package. If it is assumed that the anions are located in the rigid core, closely associated with the rare earth cation, then as a consequence, the aliphatic chains, confined within their sublayer have to cover a larger area than in the case of the ligand, leading to a reduced layer thickness. The reflection at about 9 Å is then explained as a side-to-side distance if a cation

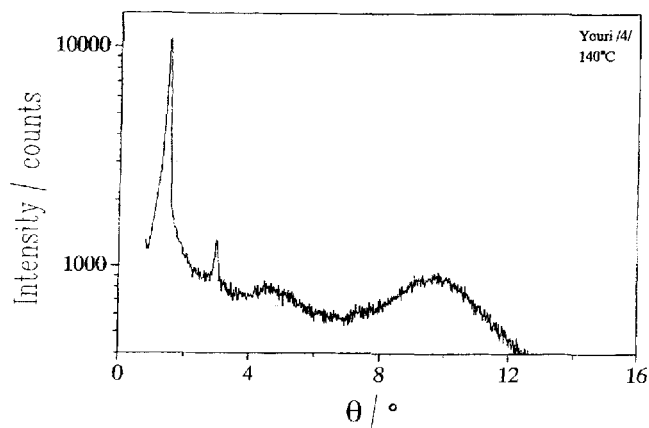


Figure 3. X-ray pattern obtained from $[\text{La}(\text{L})(\text{LH})_2][\text{NO}_3]_2$ at 140°C.

diameter of 2.5 Å and a ligand parameter of about 5.5 Å (the average value of the mean distance separating hard cores in a smectic phase) are assumed.

To estimate the scale of magnetic anisotropy for our compounds, we have measured the magnetic birefringence of La, Gd and Dy complexes in CCl₄ (CARE, carcinogen), CHCl₃ and in C₆H₆ (CARE, carcinogen) solutions. The results obtained in different solutions were very similar. Thus, the diamagnetic La^{III} complex, and paramagnetic Gd^{III} complex in an 8S_{7/2} ground state, possess a small magnetic anisotropy in the range typical for liquid crystalline molecules. The small anisotropy results from diamagnetism in the case of La^{III} and the isotropic spin of the f⁷ Gd^{III} ion. In contrast, a large magnetic anisotropy is expected for the Dy^{III} complex which has a 6H_{15/2} ground state resulting from an f⁹ configuration.

We have observed that the magnetic birefringence, $C_{m(HO)}$, of none of the solutions is the molecular (Cotton–Mouton) effect, even for the minimal complex concentrations (2×10^{-4} mol dm⁻³ for the Dy complex) available from our measurements, and is therefore due to molecular association (Majorane effect). We will not discuss here any specific features of this effect, which is four orders of magnitude stronger than the molecular effect and which is a macroscopic magnetic birefringence, but will simply use the fact that its value is proportional to the magnetic anisotropy, $\Delta\chi$, of molecular associates, at

least in the low field region. The molar constant of magnetic birefringence, $C_{m(HO)} \approx \Delta\alpha \times \Delta\chi$ approximated to zero field proved to be 6×10^{-11} , 7×10^{-11} and 10^{-7} cm³ mol⁻¹ Oe⁻² for La, Gd and Dy, respectively. Spectroscopic data indicate that the structures of the molecular associates for complexes of the different ions are probably similar, and so we can expect the equality of electronic polarizability, $\Delta\alpha$, of molecular associates with different ions. We can therefore conclude that the magnetic anisotropy of Dy associates and even that of the separate Dy complexes (in the axial symmetry approximation) is 10³ times greater than that of the La and Gd complexes.

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References

- [1] (a) BRUCE, D. W., 1993, *J. chem. Soc. Dalton Trans.*, 2983; (b) BRUCE, D. W., *Inorganic Materials*, 1992, edited by D. W. Bruce and D. O'Hare (Chichester: Wiley); (c) ESPINET, P., SERRANO, J. L., ORO, L. A., and ESTERUELAS, M. A., 1992, *Coord. Chem. Rev.*, **117**, 215; (d) MAITLIS, P. M., and GIROUD-GODQUIN, A.-M., 1991, *Angew. Chem. Int. Ed. Engl.*, **30**, 402; (e) POLISHCHUK, A. P., and TIMOFFEEVA, T. V., 1993, *Russ. Chem. Rev.*, **62**, 291.
- [2] GALYAMETDINOV, Y. G., IVANOVA, G. I., and OVCHINNIKOV, I. V., 1991, *Izv. Akad. Nauk USSR, ser. Khim.*, 1232; Eng. trans.: *Bull. Acad. Sci. USSR Div. Chem. Sci.*, 1991, **40**, 1109.