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Magnetic properties of rare-earth β-enaminoketone metallomesogens

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Reaction of β-enaminoketones with lanthanide salts leads to mesomorphic complexes displaying an S_A mesophase. The mesophase was characterized using X-ray scattering, EPR and magnetic susceptibility. A very high magnetic anisotropy was deduced for a complex containing dysprosium.

Metal-containing liquid crystals have been intensively studied in recent years [1]. The inclusion of a metal atom in a mesogenic molecule 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 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.

The first synthesis of lanthanide-containing calamitic mesogens with Schiff's base ligands was described by Galyametdinov *et al.* [2]. The successful use of β-enaminoketone ligands for the synthesis of mesogenic copper complexes [3] gave us an opportunity to use this ligand for the synthesis of the lanthanide complexes $[(LH)_2(L)Ln][X]_2$ (see the table). Below we report some preliminary results of an investigation of these metallomesogens, whose composition was determined by means of elemental analysis and magnetic susceptibility measurements. The phase transition temperatures and the type of mesophase were determined by polarizing optical microscopy (fan-shaped texture, typical for S_A phase). The phase transition temperatures increased noticeably when substituting the NO_3^- ion by the Cl^- ion, as can be seen from the table.

Synthesis of the ligand with $R = C_{12}H_{25}$ was described in reference [4]. The complexes $[(LH)_2(L)Tb][X]_2$ were prepared (figure 1) by reaction of the ligand with the metal salt (nitrate or chloride) in ethanol from which the product precipitated as an analytically pure material. Other complexes were synthesized in a similar way and transition temperatures are collected in the table. Although we have been unable as yet to grow single crystals suitable for X-ray measurements and therefore unequivocally assign the coordination geometry around the metal, we believe that the ligand arrangement is essentially trigonal prismatic with the counter anions also bound to, or at least closely associated with, the lanthanide. Thus, the length of the molecular long axis corresponds to the length of an isolated ligand.

X-ray measurements on the mesophase of La and Dy compounds ($R = C_7H_{15}$, $X = NO_3$) allowed us to estimate the layer thickness (30·7 and 30 Å, respectively, for La and Dy), which is much smaller than the length of the

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

n	X	Ln	Transition	T/°C	μ_{eff} (exp)	μ_{eff} (theor)
12	NO_3	La	$Cr\rightarrow S_A$ $S_A\rightarrow I$	101 143	0	0
12	NO_3	Tb	$Cr\rightarrow S_A$ $S_A\rightarrow I$	109 139	9·2	9·7
12	NO_3	Dy	$Cr\rightarrow I$ $(S_A\rightarrow I)$	116 151	10·4	10·5
12	NO_3	Gd	$Cr\rightarrow S_A$ $S_A\rightarrow I$	105 146	7·9	7·9
12	NO_3	Er	$Cr\rightarrow S_A$ $S_A\rightarrow I$	110 145	9·4	9·5
12	Cl	Tb	$Cr\rightarrow S_A$ $S_A\rightarrow I$	161 165	9·3	9·7
12	Cl	Gd	$Cr\rightarrow S_A$ $S_A\rightarrow I$	159 173	7·8	7·9
7	NO_3	La	$Cr\rightarrow S_A$ $S_A\rightarrow I$	82 140	0	0
7	NO_3	Dy	$Cr\rightarrow S_A$ $S_A\rightarrow I$	121 135	10·3	10·5

ligand in its fully stretched conformation (estimated to be ~40 Å by molecular modelling). To explain the discrepancy, it is assumed that the anions are located in the rigid core, closely associated with, or bound to, the rare earth cation. As such, the ligand aliphatic chains, confined within their sub-layer, have to cover the higher area, defined by the complex, than is the case in the isolated ligand, leading to a reduced layer thickness. Similar observations were made by us in another publication [5]. The X-ray patterns also contained broad reflections in the wide angle region at about 8·8 Å (La), 8·4 Å (Dy) and 4·6 Å (La and Dy). The reflection at about 8 Å probably corresponded to the mean distance between the rigid parts of the complex, while the 4·6 Å reflection was characteristic of the mean distance between molten aliphatic chains.

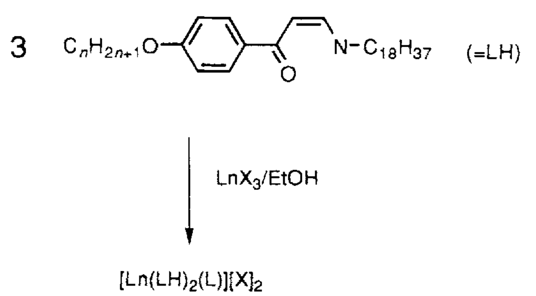

Figure 1. Synthetic scheme for lanthanide complexes.

We have recorded the X-band EPR spectra of the Dy complex ($R=C_{12}H_{25}$ and C_7H_{15}) at liquid helium temperatures. Each spectrum consisted of a broad, asymmetric line having a g value around 11, together with a more symmetric line with g value ~2. The latter was attributed to very small amounts of copper (<0·15%) in the starting materials. No other spectral lines were detected at magnetic fields up to 1·2 T. Further interpretation of the low temperature EPR spectra is in progress.

It is likely that the structures of rare-earth complexes involving different kinds of metal ions (but identical ligands) should be similar, so, we carried out a more detailed EPR investigation on Gd complexes whose EPR spectra are easier to interpret and can be observed even at room temperature.

The typical Q-band EPR spectra of Gd complexes ($R=C_{12}H_{25}$, $X=NO_3$) are shown in figure 2. The EPR spectrum of a toluene solution was a narrow single line. $\Delta H=31$ Oe ($3{\cdot}1\times10^{-3}$ T, figure 2(*a*)), the fine structure of which had been completely averaged by fast molecular tumbling. The g value of 1·990 confirmed that the Gd ion was in its $^8S_{7/2}$ ground state [6]. The EPR spectrum of the powder displayed fine structure and consisted of three lines of different intensity, figure 2(*b*). Two symmetrically-arranged outer lines corresponded to the spin transition $S_z=\pm7/2\rightarrow S_z=\pm5/2$ for a molecular orientation parallel to the field direction, while the central peak resulted from all other spectral lines—five for parallel orientations and seven for perpendicular molecular orientations. This spectrum may be described with

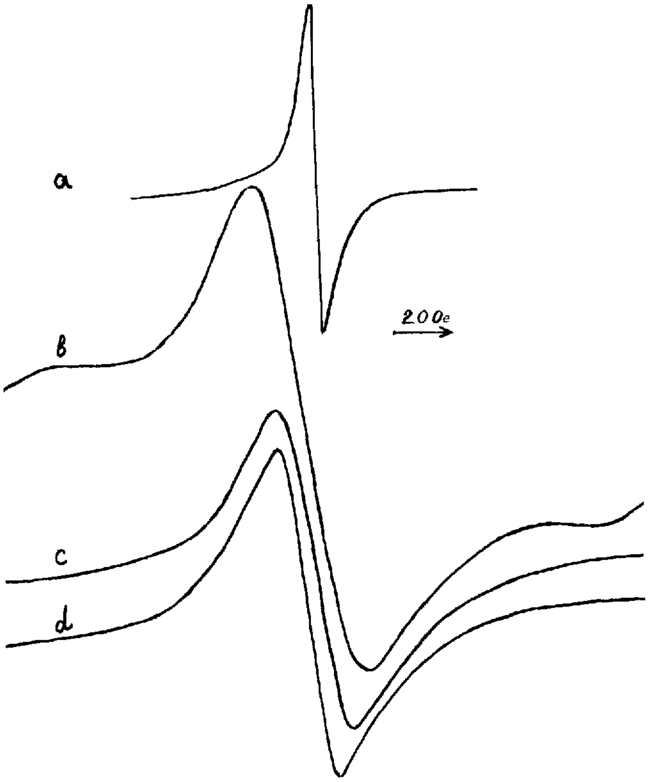

Figure 2. EPR spectra of the Gd complex with $R=C_{12}H_{25}$, $X=NO_3$ (*a*) in toluene solution (*b*) as a powder, (*c*) in the mesophase, (*d*) in the isotropic phase.

the usual axially-symmetric spin-Hamiltonian for Gd compounds [6]:

$$\mathscr{H}=g\beta\mathbf{H}\cdot\mathbf{S}+\tfrac{1}{3}b_2^0O_2^0+\tfrac{1}{60}b_4^0O_4^0$$

where the first term is the Zeeman energy, and the other two terms (spin operators O_2^0 and O_4^0) describe the influence of ligands on the magnetic energy of the Gd ion and reflect the symmetry and strength of interactions in the local environment. The spin-Hamiltonian parameters were evaluated as:

(1) $g=1{\cdot}986$; $b_2^0=131\times10^{-4}\,\mathrm{cm}^{-1}$; $b_4^0=7\times10^{-4}\,\mathrm{cm}^{-1}$ for the Gd complex with $R=C_{12}H_{25}$ and $X=NO_3$, and

(2) $g=1{\cdot}988$; $b_2^0=123\times10^{-4}\,\mathrm{cm}^{-1}$; $b_4^0=0$ for the same complex with $X=\mathrm{Cl}$.

Similar results have been obtained for the complex with $R=C_7H_{15}$.

When heating the sample, one observes (in the mesophase and the isotropic phase) a gradual narrowing of the EPR spectrum and disappearance of the fine structure, figure 2 (*c*, *d*), associated with increasing rotational mobility of the molecules. The much greater line width in the isotropic phase, figure 2 (*d*), as compared with that in toluene solution, figure 2 (*a*), indicated that the fine structure had not been completely averaged because of the high viscosity of the isotropic phase.

The results indicate that the local environment of the Gd ion possesses a rotational axis of order at least three ($\geqslant C_3$). It is worth mentioning that the values of the magnetic parameters for the Gd ion are not remarkable, being close to those for the hydrated chloride of Gd(III) [6] or for the Gd(III) ion incorporated into the crystal lattice of bismuth magnesium nitrate, [7]. A special EPR experiment on an oriented sample showed that the mean direction of the 'axial axis' coincides with the director axis of the liquid crystal.

To estimate the anisotropy of magnetic susceptibility in the mesophase, the temperature dependence of the magnetic susceptibility of the Dy complex with $R=C_7H_{15}$, $X=NO_3$ was measured with a SQUID magnetometer. Below the mesophase transition the measured susceptibility $\chi=\chi_{\mathrm{iso}}$ showed a Curie-type temperature dependence, decreasing with increasing temperature. However, at the mesophase transition, there was an increase in the measured component of the susceptibility due to the alignment of the liquid crystalline phase in the magnetic field of 5 T; this increase in χ_{obs} was 12% of its value at 122°C. The susceptibility measured in the mesophase χ_{obs} is equal to (or less than, if orientation is incomplete) the greater of two components $\chi_\parallel$ or $\chi_\perp$. So $\Delta\chi=|\chi_\parallel-\chi_\perp|\geqslant(\chi_{\mathrm{obs}}-\chi_{\mathrm{iso}})K$, where $K=3/2$ if $\chi_\parallel>\chi_\perp$ and $K=3$ if $\chi_\parallel<\chi_\perp$. The estimated value of the anisotropy is between 18% and 36% of $\chi_{\mathrm{iso}}=345\times10^{-4}$ ($T=394\,\mathrm{K}$); that is $\Delta\chi$ is in the region $60\text{–}120\times10^{-4}\,\mathrm{cm}^3\,\mathrm{mol}^{-1}$ ($T=395\,\mathrm{K}$). The magnetic anisotropy deduced for the Dy compound with $R=C_7H_{15}$ and $X=NO_3$ was very large, and is related to the high anisotropy of the *g*-tensor, which may have been anticipated from the approximately measured value of $g=11$ from EPR measurements. Further investigation of this high anisotropy is clearly necessary, and will open up the way for magneto-active liquid crystals responding to very low magnetic fields.

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