The synthesis of liquid crystalline lanthanide complexes and their magnetic birefringence

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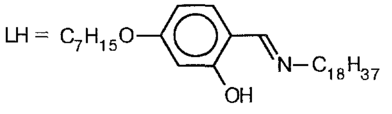
Liquid crystalline complexes of the type $[ML(LH)_2](NO_3)_2$, where LH = $C_7H_{15}O$—$C_6H_3(OH)CH{=}N$—$C_{18}H_{37}$ and M = Gd, Dy, and La, have been obtained. All of them exhibit the S_A phase and have high magnetic birefringence constants due to the association of the complexes in solution. In the case of the dysprosium derivative, the effect is much stronger (four orders of magnitude greater than the usual value) because of the high magnetic anisotropy of the particles of the complex.

Key words: liquid crystals; lanthanide complexes; magnetic birefringence.

In recent years, liquid crystals containing transition metals have been studied as media with birefringence[1] and high polarizability[2] controlled by external electric fields. They are also considered to be promising materials for non-linear optics.[3] However, magnetooptical studies of metallomesogens are difficult due to the absence of compounds controlled by weak magnetic fields. This is mainly because of the low magnetic anisotropy of the metals in the structure of metallomesogens.[4,5] It is known that some lanthanides have the greatest magnetic anisotropy. The orbital moment connected with the molecular framework directly through the electric fields of ligands[6] is an important factor determining molecular paramagnetic anisotropy. The purpose of this work is to prepare liquid crystals containing lanthanides and study their magnetooptical properties. The preparation of viscous, almost non-orienting dyscotics[5] and some smectics of high molecular weights[7] has been described in communications about the syntheses of lanthanum-containing mesogens. In order to decrease the viscosity of the products, we used a non-liquid crystalline ligand of relatively small molecular weight for the synthesis of mesogenic complexes.



The complexes were prepared by reacting LH with the corresponding metal nitrates in ethanol according to a procedure described previously.[7] The compounds obtained are light-yellow powders soluble in CCl_4 and $CHCl_3$. According to the data of elemental analysis and mass spectrometry,* these substances are complexes of the composition $[ML(LH)_2](NO_3)_2$, where LH = ligand, M = Dy, Gd, and La. The DTA data indicates the absence of water or alcohol molecules in the structure of the complexes. The good correlation between the theoretical and experimental values of the magnetic moments (Table 1, μ_{eff}) also confirms the composition of these complexes.

Liquid crystalline properties have been studied by the method of polarization polythermal microscopy. All of the compounds obtained exhibit the S_A phase (see Table 1) and low viscosity as compared with that of the metallomesogens described previously.[5,7] Unlike enantiotropic Dy and Gd derivatives, the La compound is monotropic, *i.e.*, it forms the mesophase when its isotropic melt is cooled. The method of magnetic birefringence was used to study the behavior of the complex compounds in magnetic fields. The molar constant of the magnetic birefringence is expressed by the formula:[8]

$$ {}_mS = \Delta R/H^2 \qquad (1) $$

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* Mass spectra were recorded for a complex obtained similarly to the one described but with a shorter length of the N-alkyl chain in the ligand, LH = 2-hydroxy-4-heptyloxiacetophenone N-decylimine. This is connected with the technical possibilities of the device used, which did not allow us to obtain spectra for compounds with molecular weight higher than 1500.

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Table 1. Temperatures of phase transitions, magnetic moments (μ_{eff}) and molar constants ($_{m}S$) of magnetic birefringence for lanthanide complexes $ML(LH)_2 \cdot 2NO_3$

M	Temperatures of phase transitions/°C		μ_{eff}/μ_B		$_{m}S$/cm^3 mol^{-1}	
	C→S_A^*	S_A→I	theor	exp	theor	exp
La	145	146	—	0	$5.94 \cdot 10^{-15}$	$1.1 \cdot 10^{-10}$
Gd	135	146	7.94	7.88	$5.94 \cdot 10^{-15}$	$1.5 \cdot 10^{-10}$
Dy	138	141	10.65	10.64	$-1.35 \cdot 10^{-12}$	$-2.9 \cdot 10^{-8}$

* Phase C, crystalline; S_A, smectic A; and I, isotropic phases.

The difference between the molar refractions ΔR of normal and unusual beams is determined from the expression:

$$\Delta R = 4/45\pi N_a \cdot \Delta a \Delta\chi / KT \cdot H^2, \qquad (2)$$

where Δa and $\Delta\chi$ are the anisotropy of electronic polarizability and anisotropy of magnetic susceptibility. As follows from formulas (1) and (2), the value of the effect depends on the magnetic anisotropy of the complex. In the chosen series of lanthanide derivatives, La^{3+} and Gd^{3+} ions do not contribute to $\Delta\chi$, and the value of the birefringence of the complex is determined by the anisotropy of its ligands. The anisotropies for the La and Gd complexes calculated by the additive schemes[8—10] are $\Delta a = 16.7 \cdot 10^{-24}$ cm^{-3} molec. and $\Delta\chi = 8.7 \cdot 10^{-29}$ cm^{-3} molec. The Dy^{3+} ion possesses magnetic anisotropy which is 2—3 orders of magnitude higher than that of the ligands. Therefore, the corresponding increase in the magnetooptical effect should be expected for its complex. A typical dependence of the magnetic birefringence (ΔR) on the magnetic field strength (H^2) obtained for the Dy compound is presented in Fig. 1; the theoretical curve calculated by formula (2) is presented by the dotted line. As can be seen from Fig. 1, a sharp increase in the effect (four orders of magnitude higher than the calculated value) is observed even under weak fields (up to 100 Oe). Such a phenomenon was previously observed for lyotropic liquid crystals without metal, colloids, and biological macromolecules; usually, it was related to particle association.[11,12] The molar constants of the magnetic birefringence, calculated theoretically by formula (1), and the experimental values approximated to zero field are presented in Table 1. Judging by the ratio between $_{m}S_{theor}$ and $_{m}S_{exp}$, in CCl_4 the associates of the compounds studied contain not less than $2 \cdot 10^4$ molecules of the complexes. According to the ^1H NMR and IR spectroscopic data, the hydroxyl proton (δ(OH) = 12.6 ppm, ν(OH) = 3200 cm^{-1}) participating in the hydrogen bond, does exist in the solutions of the compounds under study. A bond of this type seems to favor the association of the complex molecules described above. It is likely that the associated particles are not charged, because the DMF solutions of the complexes ($C = 10^{-3}$ mol L^{-1}) display no electrical conductivity. It should be mentioned that the IR spectra of all of the complexes in vaseline oil and in CCl_4 are almost the same. This indicates that their structures in crystal and solution are essentially the same.

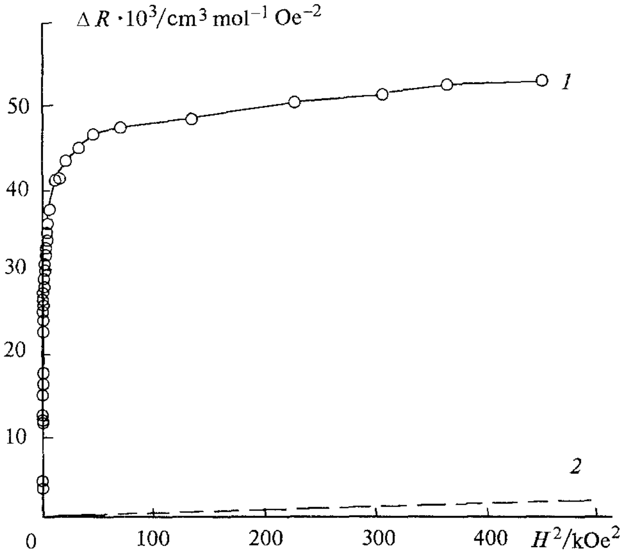

Fig. 1. Dependence of the difference between the molar refractions of normal and unusual beams (ΔR) of compound $DyL(LH)_2 \cdot 2NO_3$ on the magnetic field strength (H^2): *1*, obtained in the experiment (λ = 632.8 nm, $C = 2.3 \cdot 10^{-7}$ mol cm^{-3}); *2*, theoretically calculated by formula (2).

The molar constant of the complex of Dy and Schiff's base (see Table 1, $_{m}S = -2.9 \cdot 10^{-8}$ cm^3 mol^{-1}) is four orders of magnitude higher than those of the lanthanide complexes described in literature.[8—10] Thus, for the Dy derivative, the strength of the effect is determined by the high values of the magnetic anisotropy of the metal ion, the electronic polarization of ligand L, and the association of the molecules of the complexes in solution.

Experimental

Electrical conductivity was measured at 20 °C in a 20-mL cell with platinum electrodes. The constant of the cell was determined against a 0.001 mol L^{-1} KCl solution. The DTA experiments were performed on a DSM-2M differential scanning calorimeter. The thermooptical studies were carried out using a Boetius polarization microscope with a heated plate. IR spectra were recorded in vaseline oil on a Specord 75 IR spectrometer, and ^{1}H NMR spectra were measured on a Unity-300 (Varian) device. Magnetic susceptibilities were determined by Faraday's method at 25 °C at magnetic field strength H = 1.5 kOe. Magnetic birefringence was measured on a previously described[8] setup at 25 °C, at H = 0 to 20 kOe in CCl_4, $C = 2 \cdot 10^{-7}$ to $4 \cdot 10^{-5}$ mol cm^{-3}. A laser with wavelength l = 632.8 nm was used as the light source. Mass spectra were obtained on a Finnigan MAT-212 spectrometer by the method of field desorption (chloroform was used as the solvent, the intensity was 2 kV).

Tris(*N*-octadecyl-2-hydroxy-4-heptyloxibenzaldiminate)lanthanum dinitrate. A solution of lanthanum nitrate ($0.2 \cdot 10^{-3}$ mole) was added dropwise to an alcohol solution of 0.24 g of ligand LH ($0.5 \cdot 10^{-3}$ mole) with continuous stirring at 30 °C. The mixture was stirred for 1 h at ~20 °C. The residue was filtered off and washed with ethanol. 0.22 g (80 %) of the product was isolated. Found (%): C, 66.89; H, 9.89; N, 4.10. $C_{126}H_{170}LaN_5O_{12}$. Calculated (%): C, 66.82; H, 9.92; N, 4.06. ^{1}H NMR ($CDCl_3$), δ: 1.3—1.7 (m, 42 H, CH_2); 3.51 (m, 2 H, NCH_2); 3.71 (t, 2 H, OCH_2, J = 5.86 Hz); 6.23 (d, 1 H, Ph, J = 8.68 Hz); 6.37 (s, 1 H, Ph); 6.97 (d, 1 H, Ph, J = 8.68 Hz); 7.75 (s, 1 H, CH=N); 12.58 (s, 1 H, OH).

Mass spectrum for tris(*N*-decyl-2-hydroxy-4-heptyloxiacetopheniminate)lanthanum dinitrate (PD, $CHCl_3$ 2 kV), m/z (I_{rel} (%)): 1432 $[M^+ + H]$ (100). Dy and Gd derivatives were obtained similarly.

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