Synthesis and magnetooptical properties of mesomorphic complexes of lanthanides with β-aminovinyl ketones

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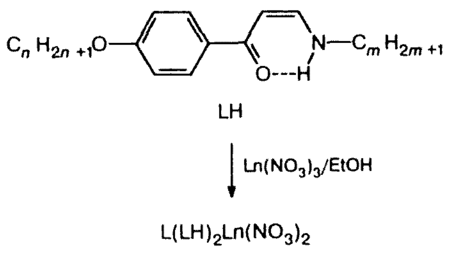
Complexes of the composition $L(LH)_2Ln(NO_3)_2$ (Ln = La, Dy, Gd, Er, Eu, or Tb) were obtained by the reaction of β-aminovinyl ketone (LH) with rare earth metal nitrates. All the compounds synthesized are thermotropic liquid crystals having the smectic S_A phase. The values of magnetic anisotropy of these complexes measured by magnetic birefringence are fairly high.

Key words: lanthanides, β-aminovinyl ketones, complexes; liquid crystals; magnetooptical properties.

Interest in the synthesis of metal-containing liquid crystals (metallomesogens) continuously increases. This class of compounds attracts attention of researchers owing to their combination of the optical (linear and nonlinear) and electric properties peculiar to liquid crystals, and the magnetic and electronic characteristic features of transition metal complexes.[1,2] In some papers, the high polarizability[3] and birefringence[4] of metallomesogens as well as prospects for using them as materials for nonlinear optics have been noted.[5]

Recently, in studies dealing with mesogenic complexes of Schiff's bases, it was shown that the introduction of lanthanides into a molecule is favorable for the appearance of high optical nonlinearity in the substance[6] and for the attainment of the highest magnitudes of magnetic anisotropy and magnetic birefringence.[7,8] Therefore, it seems reasonable to extend the range of mesogenic complexes of lanthanides by using new ligands, for example, β-aminovinyl ketones, whose structure is similar to that of Schiff's bases.[9]

In the present paper, we have synthesized complexes of the lanthanide series with LH ligands:[10]

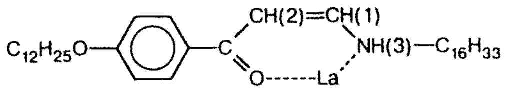


Ln = La, Dy, Gd, Er, Eu, Tb; n = 7, 12; m = 12, 16, 18

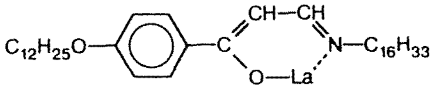
The ^1H NMR and IR spectra of the LH compounds are close to those reported previously.[9,10] This fact and the data of elemental analysis make it possible for one to believe that the structure of the ligands corresponds to that presented in the Scheme. The chelate ring is formed through an intramolecular hydrogen bond. No compounds possessing mesomorphic properties were detected among the β-aminovinyl ketones synthesized.

We prepared $L(LH)_2Ln(NO_3)_2$ complexes by the reactions of the LH β-aminovinyl ketones with the corresponding metal nitrates in ethanol. The reaction products were isolated as finely crystalline precipitates soluble in benzene and chloroform. According to the elemental analysis data and to ^1H NMR and IR spectroscopy, the coordination number of the central atom is 8. The ligands can be coordinated in two ways leading to structures **A** and **B**. Two ligands (LH) are coordinated to the metal in a type **A** structure, and the third ligand (L) is bound in a type **B** structure.

The ^1H NMR spectrum (Table 1) of the lanthanum compound $L(LH)_2La(NO_3)_2$ exhibits a multiplet at 10.38 ppm, corresponding to the protons of the NH group, and a doublet of doublets at 7.13 ppm (CH—N). The presence of these signals and their integral intensities indicate that two ligands (LH) incorporated in the complex have the ketoamine structure **A**, while the third ligand (L) has the enolimine structure **B**.



A



B

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Table 1. Temperatures of phase transitions (T) and magnetic moments (μ_{eff}) of lanthanide complexes with β-aminovinyl ketones $L(LH)_2Ln(NO_3)_2$

Complex			T/°C		μ_{eff}		L/d
Ln	n	m	K → S_A	S_A → I	experimental	calculated	
La	7	12	142	153	0	0	2.9
La	12	12	121	149	0	0	3.5
Tb	12	12	123	147	9.4	9.7	3.5
Dy	12	12	125	147	10.4	10.5	3.5
Gd	12	12	127	152	7.3	7.9	3.5
La	12	16	153	164	0	0	3.6
Tb	12	16	143	154	9.5	9.7	3.6
Dy	12	16	131	160	10.3	10.5	3.6
Er	12	16	124	158	9.2	9.5	3.6
Eu	12	18	140	160	3.1	3.4	3.8

Note. K is the crystalline phase, S_A is the smectic phase, and I is the isotropic phase.

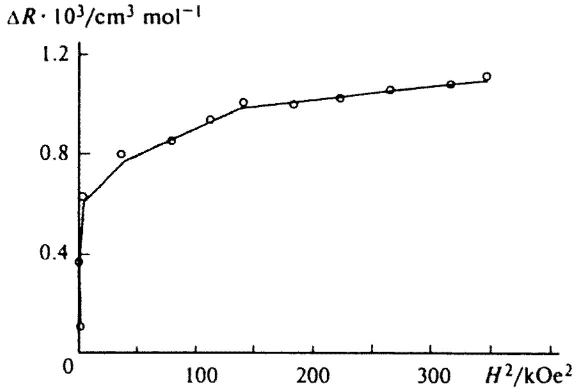

Fig. 1. Dependence of the difference between the refractions (ΔR) of ordinary and extraordinary rays on the squared applied field strength (H^2) for the complex $L(LH)_2Dy(NO_3)_2$ (n = 12, m = 16).

The good correlation between the calculated magnetic moments $\mu_{eff}{}^2 = g^2J(J+1)$ and the μ_{eff} values found (see Table 1) also confirm the above composition of the complexes.

The mesomorphic properties (phase transition temperatures and types of mesophases) were studied by polarization polythermal microscopy. All the coordination compounds obtained are thermotropic liquid crystals, since on heating, their melts exhibit the fan-shaped texture in polarized light, which is typical of a smectic A-mesophase. An interesting feature of the complexes synthesized compared to other metallomesogens is that the temperatures of their phase transitions depend only slightly on the type of metal. This confirms the known similarity of the physicochemical properties of lanthanide compounds.

The insignificant effect of the length of the substituent (see Table 1) on the phase transition temperatures is caused by the fact that, when there are large numbers of C atoms in the hydrocarbon radical, their contributions to the anisotropy of the polarizability of the molecule level off. For example, this phenomenon smooths out the effect of the odd-even alternation of phase transition temperatures in liquid crystals when the number of C atoms in the alkyl fragment is greater than 12. Calculations of the geometry of complexes by the method of atom-atom potentials[11] taking into account the rotation of alkyl chains indicate that as the length of the radical varies from C_7 to C_{12} (see Table 1), the anisotropy L/d (the ratio of the length to the width of the rotation cylinder of the molecule) varies only slightly, *viz.*, from 2.9 (C_7) to 3.5 (C_{12}).

The fact that anisotropy of polarizability and the geometrical anisotropy of the complexes are similar accounts for their close clarification points (the S_A—I transition, see Table 1). Note that the anisotropy factors of β-aminovinyl ketones LH are quite close to those of the previously studied *N*-alkylsalicylaldimines.[8] The clarification points of lanthanide complexes of these ligands also lie in the 140—160 °C range.

The magnetooptical properties of complexes were studied using the magnetic birefringence method. Figure 1 shows the typical dependence of the difference between the molar refractions of the ordinary and extraordinary rays $\Delta R = 6n(n_0 - n_e)/[C(n^2+2)^2]$ (n_0, n_e, and n are the refraction indices of the ordinary ray and the extraordinary ray, and their mean value, respectively; C is the concentration) on the squared magnetic field strength for the dysprosium complex (see Table 1). Even in weak fields (up to 100 Oe), a dramatic increase in the birefringence, exceeding that expected theoretically by four orders of magnitude, is observed. The shape of the curve shown in Fig. 1 indicates that associates of the molecules of the complexes exist in the solutions studied. A similar plot was obtained for the lanthanum complex (see Table 1).

Although the effect observed is not the molecular Cotton—Mouton effect, the limiting (at $H \to 0$) value of the birefringence constant $C_m = \Delta R/H^2$ is proportional to the anisotropy ($\Delta\chi$) of the molecular associates. The ratio of the constants extrapolated to zero field $C_m(Dy)/C_m(La) \geq 10^2$ demonstrates the real magnitude of the ratio between the magnetic anisotropies of the paramagnetic dysprosium complex and the diamagnetic lanthanum complex. This ratio is lower than that obtained previously for similar complexes with Schiff's bases;[7] nevertheless, it indicates that the dysprosium derivative studied possesses high magnetic anisotropy, which markedly exceeds the anisotropy of known mesogens.

Experimental

Thermooptical studies (textures and phase transition temperatures) were carried out using a polarization microscope with a Boetius hot-stage apparatus. IR spectra were recorded on a Specord-75 IR instrument; ^{1}H NMR spectra were obtained on a Varian Unity-300 spectrometer. The magnetic susceptibility was determined by the Faraday method at 25 °C in the magnetic field H = 1.5 kOe. The magnetic birefringence of solutions of the complexes in chloroform and acetone was measured using a setup described previously[12] at 25 °C, in magnetic fields with H ranging from 0 to 20 kOe. A laser with a wavelength of 632.8 nm served as the light source.

The ligands were synthesized by a previously described procedure.[10] The complexes were prepared by a general procedure, which is presented below for the lanthanum derivative.

Synthesis of the complex $L(LH)_2La(NO_3)_2$. At 36 °C, a slight excess of $La(NO_3)_3$ (0.06 g, 0.13 mmol) was added to an ethanolic solution of LH (0.2 g, 0.36 mmol). Several hours later, the precipitate was filtered off, washed with ethanol, and dried *in vacuo* over P_2O_5 to give 0.17 g (79 %) of the product. Found (%): C, 69.48; H, 10.16; N, 3.52. $C_{111}H_{194}LaN_5O_{12}$. Calculated (%): C, 69.12; H, 10.07; N, 3.63. IR (Vaseline oil), ν/cm^{-1}: 1620 (C_{Ph}—O_M); 1585 (C—C). ^{1}H NMR, δ: 1.01 (t, 6 H, CH_3); 1.24 (m, 44 H, CH_2); 1.69 (m, 2 H, CH_2CH_2N); 1.92 (m, 2 H, CH_2CH_2O); 3.43 (q, 24 H, CH_2N); 4.15 (q, 2 H, CH_2O); 5.73 (d, 1 H, PhC(O)CH); 7.13 (dd, 1 H, CH—N, $^3J_{1,2}$ = 7.5 Hz, $^3J_{1,3}$ = 12.3 Hz); 6.99, 8.91 (both d, 4 H, Ph); 10.38 (m, 1 H, NH).

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References

1. S. A. Hudson and P. Maitlis, *Chem. Rev.*, 1993, **93**, 861.
2. D. W. Bruce, in *Inorganic Materials*, Eds. D. W. Bruce and D. O'Hare, Chichester (England), 1992, 405.
3. C. Versace, G. Gipparrone, D. L. Lucchetta, D. Pucci, and M. Ghedini, *Condens. Matter News*, 1992, **1**, 13.
4. C. Bertram, D. W. Bruce, D. A. Dunmur, S. E. Hunt, P. M. Maitlis, and M. McCann, *J. Chem. Soc., Chem. Commun.*, 1991, 69.
5. G. Gipparrone, D. Duca, D. Pucci, M Ghedini, and V. Meton, *Condens. Matter News*, 1992, **1**, 14.
6. L. H. Gao, K. Z. Wang, C. H. Huang, X. S. Zhao, X. H. Xia, T. K. Li, and J. M. Xu, *Chem. Mater.*, 1995, **7**, 1047.
7. I. V. Ovchinnikov, Yu. G. Galyametdinov, and A. V. Prosvirin, *Izv. Akad. Nauk, Ser. Khim.*, 1995, 787 [*Russ. Chem. Bull.*, 1995, **44**, 768 (Engl. Transl.)].
8. Yu. G. Galyametdinov, M. Atanassopoulo, V. Khaaze, and I. V. Ovchinnikov, *Koord. Khim.*, 1995, **21**, 751 [*Russ. J. Coord. Chem.*, 1995, **21** (Engl. Transl.)].
9. Yu. G. Galyametdinov, O. A. Kharitonova, O. N. Kadkin, and I. V. Ovchinnikov, *Izv. Akad. Nauk, Ser. Khim.*, 1994, 1685 [*Russ. Chem. Bull.*, 1994, **43**, 1595 (Engl. Transl.)].
10. Yu. G. Galyametdinov, G. I. Ivanova, and I. V. Ovchinnikov, *Zh. Obshch. Khim.*, 1991, **61**, 234 [*J. Gen. Chem. USSR*, 1991, **61** (Engl. Transl.)].
11. V. G. Dashevskii, *Konformatsii organicheskikh molekul* [*Conformations of Organic Molecules*], Khimiya, Moscow, 1974, 431 pp. (in Russian).
12. I. R. Abdullin, S. G. Vul'fson, and E. Kh. Kazakova, *Izv. Akad Nauk SSSR, Ser. Khim.*, 1987, 2573 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1987, **36**, 2551 (Engl. Transl.)].

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