

PHOTOCHEMISTRY
AND MAGNETOCHEMISTRY

Anisotropy of the Magnetic Susceptibility
of Mesogeneous Lanthanide Complexes

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Abstract—Liquid crystalline adducts of lanthanide tris(β -diketonates) with 5,5'-diheptadecyl-2,2'-bipyridine forming a nematic mesophase were obtained. Molar constants of magnetic birefringence and the magnetic susceptibility anisotropy of synthesized complexes were determined according to the magnetic birefringence in solution. The values of magnetic susceptibility anisotropy are two orders of magnitude higher than those of organic liquid crystals.

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INTRODUCTION

Lanthanide complexes attract the attention of researchers as materials for creating molecular magnets [1], data storage devices [2], contrast agents in magnetic resonance tomography [3], and shift reagents in NMR studies [4] due to the unique magnetic properties of some lanthanides [5]. The anisotropy of magnetic susceptibility of lanthanide mesogens is higher by several orders of magnitude than those of organic liquid crystals [6], so is possible on the basis of such mesogens to create materials controlled by weak external magnetic fields [3–5, 7–9]. The main problem in producing lanthanide-containing magnetic liquid crystals is that the formed mesophases (usually smectic or discotic) are very viscous, which hampers control over the molecules in a magnetic field. We recently succeeded, however, in obtaining lanthanide mesogens that possess a stable nematic mesophase [10] that is least viscous with respect to other mesophase types [11].

The main parameter defining the behavior of a mesophase in a magnetic field is the anisotropy of the magnetic susceptibility of a molecule $\Delta\chi = \chi_{\parallel} - \chi_{\perp}$, where χ_{\parallel} and χ_{\perp} are the components of tensor of magnetic susceptibility, parallel and perpendicular to the maximal axis of the molecule's magnetic susceptibility ellipsoid, respectively. The larger the absolute value of $\Delta\chi$, the simpler it is to control the spatial orientation of a molecule. Ions Tb(III), Dy(III), Ho(III), Er(III), and Tm(III) [11] have the largest values of magnetic susceptibility anisotropy.

The main methods for determining magnetic anisotropy susceptibility are the Faraday method [12] and EPR spectroscopy [8]. The sign of magnetic

anisotropy susceptibility can be found from an experiment on magnetic birefringence: one measures the birefringence of light passing through the material under investigation in a magnetic field (the Cotton–Mouton effect [13–16]).

The behavior of molecules in a magnetic field is characterized by their anisotropic magnetic susceptibility $\Delta\chi_{ij}$, and the optical properties of particles depend on the anisotropy of electric polarizability Δb_{ij} . In an arbitrary coordinate system, molar paramagnetic constant ${}_mP$ connecting these parameters is defined as follows [16]:

$${}_mP = \frac{2\pi N_A}{45kT} \sum \Delta b_{ij} \Delta\chi_{ij}, \quad (1)$$

where ${}_mP$ is the molar constant of birefringence; N_A is the Avogadro number; k is the Boltzmann constant; T is the temperature; $\Delta\chi_{ij}$ is the magnetic susceptibility anisotropy; and Δb_{ij} is the electric polarizability anisotropy.

Hence, the value of molecular magnetic susceptibility anisotropy can be determined, provided that ${}_mP$ is found in the experiment and Δb_{ij} is calculated.

EXPERIMENTAL

The synthesis of Ln(CPDk_{3–5})₃bpy₁₇ complexes was performed in ethanol at 60–70°C following the procedure in [17]. Data confirming the structure are presented for tris[1-(4-(4-propylcyclohexyl)phenyl)octane-1,3-diono]-[5,5'-diheptadecyl-2,2'-bipyridine]europium:

C₁₁₃H₁₇₅EuN₂O₆: yield 61%, found (in %): C, 75.3; H, 9.82; N, 1.56;

$C_{113}H_{175}EuN_2O_6$: calculated (in %): C, 75.00; H, 9.75; N, 1.55;

Frequencies ν in the IR-spectrum, cm^{-1} : Eu–O, 421; Eu–N, 205. The textures and temperatures of the phase transitions were determined on a Boetius polarization microscope equipped with a temperature unit.

Measurements of the magnetic birefringence effect were performed on the original apparatus described in [18].

The molar constant of birefringence was calculated using the formula:

$${}_mP = \frac{2\lambda n_{12} C_{12} M_2}{3(n_{12}^2 + 2)^2 d_{12} \omega_2}, \quad (2)$$

where λ is the light source wavelength; C_{12} is the magnetic birefringence (MB) constant of the solution; M_2 is the molecular mass of the solute; n_{12} is the refraction index of the solution; d_{12} is the density of the solution; and ω_2 is the mass fraction of the solute.

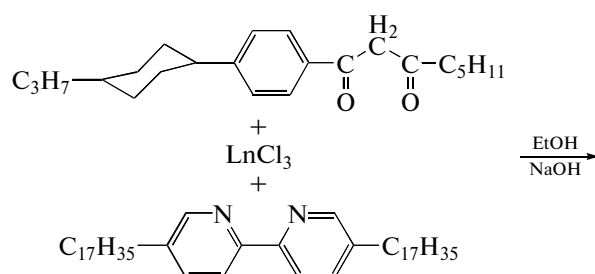
The magnetic birefringence constant of the solution was determined by the relative method using the value of magnetic birefringence for benzene:

$$C_{\text{benz}} = a\Delta\varphi, \quad (3)$$

where a is the cell constant; C_{benz} is the MB constant for benzene; and $\Delta\varphi$ is the MB value for benzene.

The anisotropy of magnetic susceptibility of the studied tris- β -diketonate complexes was calculated from the formula:

$$\Delta\chi = \frac{45kTmP}{2\pi N_A \Delta b}, \quad (4)$$



where Ln = Eu, Gd, Tb, Ho, Tm, Dy; CPDK₃₋₅ is β -diketonate (1-(4-(4-propylcyclohexyl)phenyl)octane-1,3-dione); and Bpy₁₇ is 5,5'-di(heptadecyl)-2,2'-bipyridine.

All of the synthesized complexes were polymorphous and exhibited smectic and nematic mesomorphism. The temperatures of the phase transitions are given in Table 1.

Earlier, we investigated the magneto-optical properties of liquid crystalline complexes of lanthanides with Schiff bases [15, 21]. It was shown that in CCl_4 solutions, compounds of this class were associated, the dependence of birefringence on the square of magnetic field intensity was nonlinear, and the Majorane

Table 1. Temperatures t of phase transitions of Ln(CPDK₃₋₅)₃Bpy₁₇ complexes

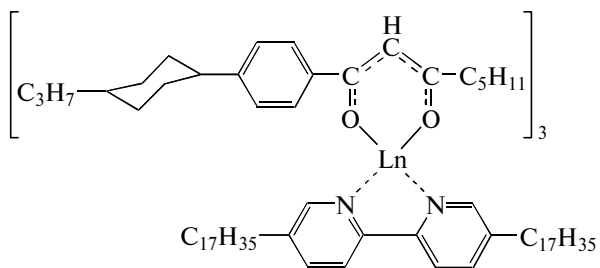
Ln	$T, ^\circ C$		
	Cr \rightarrow SmA	SmA \rightarrow N	N \rightarrow I
Eu	80	114	144
Tb	76	103	153
Dy	70	106	142
Ho	76	98	147
Er	77	103	141
Tm	73	113	149

where ${}_mP$ is the molar constant of magnetic birefringence; k is the Boltzmann constant; T is the absolute temperature; N_A is the Avogadro number; and Δb is the anisotropy of polarizability.

The polarizability anisotropy of molecules of the complexes was found using the tensor additive scheme of Le Fevre [19]. The geometry of the molecular structure of the complexes was determined by means of quantum-chemical calculations [20].

RESULTS AND DISCUSSION

A series of liquid crystalline adducts of lanthanide tris(β -diketonates) with 5,5'-diheptadecyl-2,2'-bipyridine Ln(CPDK₃₋₅)₃Bpy₁₇ was obtained following the procedure [17],



effect was observed [15]. It was therefore not possible to use the magnetic birefringence effect to determine the value of the molecular magnetic susceptibility anisotropy.

The complexes studied in this work had a saturated coordination sphere that has no counterion and is filled with ligands without active functional groups. The ability of the adducts to form associations in solution was therefore hampered. The presence of large number of alkyl and aryl fragments in the ligand structure also made it difficult to form intermolecular associates such as Ln–Ln, due to the shielding of the lanthanide ion. In accordance with the above, it is possible to estimate molecular anisotropy of magnetic

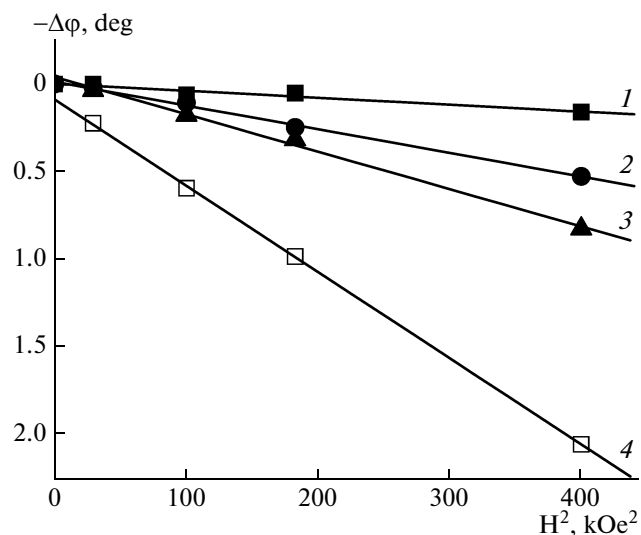


Fig. 1. Dependence of the magneto-optical effect ($\Delta\phi$) on the square of magnetic field intensity for complexes $\text{Dy}(\text{CPDk}_{3-5})_3\text{Bpy}_{17}$ with various concentrations: 1, 1×10^{-6} ; 2, 5×10^{-6} ; 3, 1×10^{-5} ; 4, 2.25×10^{-5} mol/l.

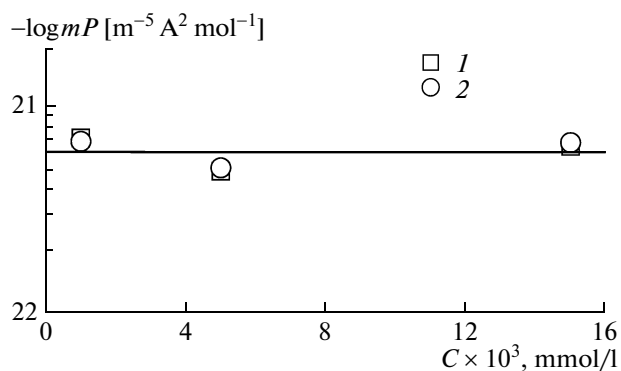


Fig. 2. Dependence of the molar constant of magnetic birefringence on the concentration of $\text{Dy}(\text{CPDk}_{3-5})_3\text{Bpy}_{17}$ solution at different magnetic field intensities: 1, 20; 2, 10.8 kOe.

susceptibility by measuring the magnetic birefringence in solution.

A series of five experiments with various intensities of the magnetic field (20, 16.2, 10.8, 5.4 kOe) and without a field was performed for each solution con-

Table 2. Molar constants of magnetic birefringence of lanthanide complexes $\text{Ln}(\text{CPDk}_{3-5})_3\text{Bpy}_{17}$

Ln	$mP \times 10^{12}$, emu.	Ln	$mP \times 10^{12}$, emu.
Eu	0.99	Ho	-1.32
Tb	-3.46	Er	2.46
Dy	-4.04	Tm	1.53

centration. For further calculations, the magnetic birefringence of benzene was determined, using which we found the magnetic birefringence constants of a solution. The dependence of the magnetic birefringence values on the square of magnetic field intensity is plotted in Fig. 1.

The linearity of the obtained curves proves that there are no intermolecular associates in the studied compounds, in contrast to the earlier described complexes with Schiff bases [15, 21].

The molar constants of magnetic birefringence were found using Eq. (2). The dependence of the molar constant of magnetic birefringence on concentration is shown in Fig. 2 for the example of $\text{Dy}(\text{CPDk}_{3-5})_3\text{Bpy}_{17}$.

As can be seen from Figs. 1, 2, the molar magnetic birefringence constant is independent of both complex concentration and magnetic field intensity. This fact supports the possibility of applying of Eq. (4) for calculation of anisotropy of magnetic susceptibility.

The calculated molar constants of magnetic birefringence are presented in Table 2. Complexes of Tb(III) and Dy(III) exhibit the greatest magneto-optical effect, while the complex of Eu(III) shows no effect of magnetic birefringence in a weak magnetic field (5.4 kOe).

The constant of magnetic birefringence is positive when the maximum axes of magnetic susceptibility and electronic polarizability ellipsoids of the complexes coincide; i.e., they are collinear. A negative value occurs when the maximum axes of the ellipsoids are perpendicular.

Calculations within the additive tensor scheme yielded a value of 36.6 \AA^3 for the polarizability anisotropy of $\text{Eu}(\text{CPDk}_{3-5})_3\text{Bpy}_{17}$. Allowing for the known isostructurality of lanthanide coordination compounds, this value (36.6 \AA^3) was used in further calculations for the entire series of studied complexes.

The molecular values of magnetic susceptibility anisotropy of complexes $\text{Ln}(\text{CPDk}_{3-5})_3\text{Bpy}_{17}$ were found from Eq. (4) using the determined molar paramagnetic constants (Table 3). The obtained values were compared with the magnetic susceptibility anisotropies described in the literature for lanthanide coordination compounds having different structures of the coordination sphere [22–24].

It is known that magnetic susceptibility anisotropy of lanthanide complexes are defined not only by the metal, but also by distortions in the coordination sphere. According to [25], the values of magnetic susceptibility anisotropy for, e.g., complexes of Dy(III), can vary from -4×10^{-2} to $8 \times 10^{-2} \text{ cm}^3/\text{mol}$, depending on the geometry of the coordination center. As compared to organic paramagnetic liquid crystals containing stable radicals [26], the orientation of which is stable in magnetic fields of intensity 1.5–2 T, the magnetic susceptibility anisotropy of lanthanide

Table 3. Values of molecular anisotropy of magnetic susceptibility of lanthanide complexes ($\Delta\chi \times 10^6$, cm³/mol)

Complex	Ln(CPDk ₃₋₅) ₃ bpy ₁₇	Ln(dpm) ₃ (pic) ₂ [22]	Ln(antip) ₆ I ₃ [23]	LnL ₃ CHF ₂ (CF ₂) ₅ CH ₂ [24]
Eu(CPDk ₃₋₅) ₃ bpy ₁₇	-3981	—	-915	-700
Tb(CPDk ₃₋₅) ₃ bpy ₁₇	-13923	-15838	-26810	-8220
Dy(CPDk ₃₋₅) ₃ bpy ₁₇	-16253	-24606	-12002	-19470
Ho(CPDk ₃₋₅) ₃ bpy ₁₇	-5311	—	-7353	-12840
Er(CPDk ₃₋₅) ₃ bpy ₁₇	9894	3655	6540	5980
Tm(CPDk ₃₋₅) ₃ bpy ₁₇	6154	1831	12803	—

complexes is larger by two orders of magnitude, which should allow us to orient a layer of lanthanide mesogen according to weak external magnetic fields.

CONCLUSIONS

It was shown that lanthanide complexes Ln(CPDk₃₋₅)₃bpy₁₇ in CCl₄ solution do not form associates; this is proved by the linear dependence of magnetic birefringence on the square of field intensity. The molecular anisotropy of the magnetic susceptibility of liquid crystalline lanthanide adducts with a non-viscous nematic mesophase was determined for the first time. The obtained values were two orders of magnitude larger than those of organic liquid crystals.

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