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Synthesis and Luminescence Properties of the Pr(III), Sm(III), Eu(III), Nd(III), and Yb(III) Complexes with Propane-1,3-dione Derivatives

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Abstract—The luminescence method, mass spectrometry, and elemental analysis are used to reveal that under optimal conditions (pH 5–8) Ln^{3+} ions (Ln = Pr, Sm, Eu, Nd, and Yb) with 1-(2-hydroxy-4-methylphenyl)-3-(5-methyl-1-phenyl-^1H-1,2,3-triazol-4-yl)propane-1,3-dione form complexes with the mole ratio Ln : ligand = 2 : 3. According to the IR spectral data, Ln^{3+} ions coordinate three oxygen atoms of two carbonyl groups and one hydroxyl group. In the IR spectra of the complexes, an intense band at 628.7 cm^{-1} is assigned to the Ln–O bond vibrations. The X-ray diffraction patterns of the complexes contain no lines corresponding to the ligand. The luminescence intensity of the complexes in the visible spectral range changes in the series Eu(III) > Sm(III) > Pr(III), whereas in the IR region the order is Yb(III) > Nd(III). In all cases, luminescence of the solid complexes is considerably more intense than that of their solutions.

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INTRODUCTION

Narrow 4*f*-luminescence bands, which are rigidly characteristic of each Ln^{3+} ion, provide both radiation color purity and rather high luminescence intensity of elements of this series in complexes with many organic reagents [1]. There is a recent tendency to synthesize reagents with many cycles (photoantennas) and branched structures, providing the possibility of coordinating two and more Ln^{3+} ions, being luminescence emitters [2–6]. Thus increased luminescence quantum yield favors the enlargement of potentialities of using Ln complexes in biology and medicine as bioprobes (biomarkers) and contrast agents and for the construction of new materials for UV and IR lasers, active light guides, etc. [7–9]. The Ln (Sm, Eu, Nd, and Yb) compounds with β-diketones are best studied. Tris(chelates) formed are characterized by high stability constants ($\log\beta$ = 14–18) and luminescence intensity [10]. The β-diketone fragment in the structures of the synthesized organic compounds with two or several cycles favors the formation of strong six-membered rings including the central ion and the efficient absorption by the ligand of the light energy, the transfer of which to the Ln^{3+} ion allows one to observe luminescence.

The purpose of the present work is to study the formation conditions, compositions, and spectral luminescence properties of the Pr(III), Sm(III), Eu(III), Nd(III), and Yb(III) complexes with 1-(2-hydroxy-4-methylphenyl)-3-(5-methyl-1-phenyl-1*H*-1,2,3-triazol-4-yl)propane-1,3-dione (**L**).

EXPERIMENTAL

The ligand was synthesized by the acylation of 1-(2-hydroxy-5-methylphenyl)ethanone with 1-phenyl-5-methyl-1*H*-1,2,3-triazole-4-carboxylic acid chloride followLed by the Baker–Vankataraman rearrangement of the ester formed

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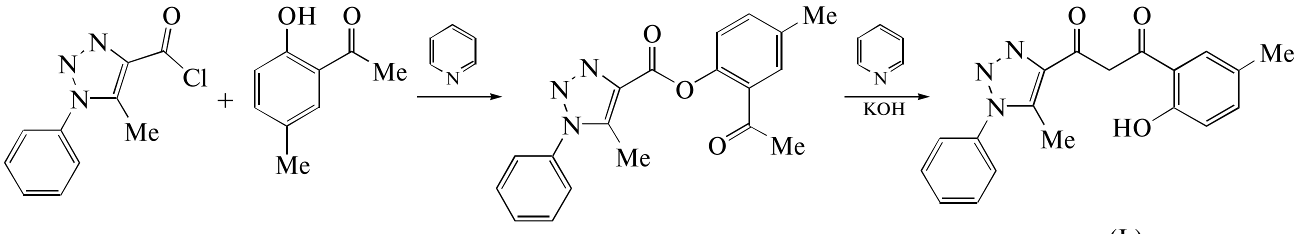

(L)

The compound synthesized was identified and its purity was checked by elemental analysis, NMR spectroscopy, and chromatography combined with mass detection. The ^{1}H NMR spectra were recorded on a Mercury 400 instrument with the working frequency 400 MHz using DMSO-d_6 (deuterated dimethyl sulfoxide) as a solvent. Chemical shifts are presented relatively to the signal from tetramethylsilane. Mass spectra were obtained on an Agilent 1100 LC/MD chromatograph coupled with a mass spectrometer using chemical ionization. ^{1}H NMR for ligand L (δ, ppm): 2.32 (s, 3H, CH_3), 2.64 (s, 3H, CH_3), 4.82 (br.s, 1H, CH_2), 6.88 (d, $J = 8.37$ Hz, 1H, H_{Ar}-4), 7.20 (dd, $J = 8.35$ Hz, 1.68, 1H, H_{Ar}-5). 7.60–7.67 (m, 5H, H_{Ph}), 7.71 (s, 1H, H_{Ar}-3). 10.71 (br.s, 1H, OH), 11.26 (br.s, 1H, OH). Mass spectrum (*m/z*): 336 $[M + H]^+$.

For $C_{19}H_{17}N_3O_3$

anal. calcd., %:	C, 68.05;	H, 5.11;	N, 12.53.
Found, %:	C, 68.19;	H, 5.03;	N, 12.75.

A 0.01 M solution of the ligand in acetonitrile prepared by an exact weighed sample of the ligand was used. Aqueous 0.1 M solutions of praseodymium, neodymium, samarium, europium, and ytterbium perchlorates were prepared from the corresponding oxides (Ln_2O_3, 99.98%) by the dissolution of the oxides in perchloric acid with removal of its excess by evaporation to the wet salts. The dry residue was dissolved in bidistilled water, and the solution was brought to a necessary volume in a volumetric flask. An exact concentration of Ln(III) was determined by titration with a solution of Trilon B in the presence of the indicator arsenazo I. Solutions with a lower concentration were obtained by the dilution of the starting solutions.

Other reactants used were reagent or analytical grade. Organic solvents of grades lower than analytical grade were purified by distillation [11].

Solutions of the complexes were prepared by mixing of an aqueous solution of $Ln(ClO_4)_3$ with an acetonitrile solution of the ligand in the presence of the buffer with a necessary pH value. Acetate–ammonia buffer solutions were used. The pH values were measured using an OP 211/1 pH meter (Hungary) with an ESL-43-07 glass electrode and a silver chloride reference electrode.

The solid complexes were obtained by the dropwise addition of an acetonitrile solution (1×10^{-1} M) of Ln(III) perchlorate to an acetonitrile solution (1×10^{-2} M) of the ligand in the mole ratio Ln : L = 2 : 3 followed by vigorous stirring. After stirring for 1 h, the solution was left in air at room temperature until the solvent was completely removed. The precipitate that formed was dried at 70°C (1 h) and stored in a desiccator.

Elemental analyses for C and H were carried out by the Helcher method [12]. Control combustion was carried out using N-methyl-D-glucamine (Fluka) as a reference sample. Elemental analysis for N was carried out by the Dumas method [12]. Lanthanides were analyzed complexonometrically using arsenazo I as an indicator.

The IR spectra of the ligand and complexes were recorded on a FTIR-8400S Shimadzu spectrometer (KBr pellets). Mass spectra were measured on a VG-7070 mass spectrometer (VG ANALYTICAL, Great Britain). Desorption ionization was carried out using a beam of argon atoms with an energy of 8 keV. 3-Nitrobenzyl alcohol served as a matrix.

X-ray diffraction studies were carried out by the powder method on a DRON diffractometer (CuK_α radiation, nickel filter). Interplanar spacings were determined using the published tables [13].

The UV spectra of the ligand and complexes were recorded on a Lambda-9 UV/VIS/NIR spectrophotometer (PerkinElmer) using a quartz cell with l = 1 cm.

The excitation and luminescence spectra of the ligand and complexes were recorded on a Fluorolog FL 3-22 spectrofluorimeter (HORIBA Jobin-Yvon Inc., France) with a 450W ozoneless Xe lamp. For measurements in the IR spectral range, the spectrofluorimeter was equipped with an InGaAs photoresistance (DSS-IGAO20L, Electro-Optical Systems, Inc.) cooled with liquid nitrogen. In addition, luminescence spectra were also recorded on an SDL-1 diffraction spectrometer (LOMO, St. Petersburg) with a DRSh-250 mercury lamp, and the emission of the most intense line of the lamp at 365 nm was picked out with the UFS-2 light filter. The energy of the triplet level of the ligand (E_{T1}, cm^{-1}) was determined by the phosphorescence spectrum of the Gd(III) complex at 77 K. The luminescence quantum yield of the complexes was determined by comparing with references, namely, tris(2,2'-bipyridine)ruthenium(II) chloride ($Ru(Bipy)_3Cl_2$) and zinc *meso*-tetraphenylporphyrinate (ZnTPP).

The luminescence of the lanthanide complexes with the ligand as a suspension of precipitates in solutions [1] was detected for Pr^{3+} (in the range from 580 to 630 nm), Sm^{3+} (550–670 nm), Eu^{3+} (570–660 nm), Nd^{3+} (850–1100 nm), and Yb^{3+} (920–1100 nm). A quartz cell (l = 1 cm) was used for solutions of the complexes, and a cell with a hole 7 mm in diameter was used for solid samples.

RESULTS AND DISCUSSION

It was found by the luminescence method from the radiation intensity maximum that the complex formation of Ln^{3+} ions with the ligand occurred in the pH region from 4 to 8, thereat pH 5–6 is optimal for Pr^{3+}, pH 6–7 is optimal for Sm^{3+} and Eu^{3+}, and pH 6–8 is optimal for Nd^{3+} and Yb^{3+}.

The mole ratio of the components in the complexes determined by independent methods is Ln : L = 2 : 3.

Table 1. Spectral luminescence characteristics of the complexes Ln_2L_3 (aqueous solutions + 1% acetonitrile ($c_{Pr,\,Sm,\,Nd,\,Yb} = 1 \times 10^{-5}$, $c_{Eu} = 1 \times 10^{-6}$, and $c_L = 1 \times 10^{-4}$ mol/l)

Complex	λ_{max}, nm	$\varepsilon \times 10^{-3}$, $mol^{-1}\,l\,cm^{-1}$	λ_{exc}, nm	ΣI, arb. units*	$\varphi \times 10^3$ **
Pr_2L_3	382.7	9.4	361	197.7	2.19
Sm_2L_3	378.7	8.3	360	777.0	4.62
Eu_2L_3	377.5	9.0	366	196.8	10.79
Nd_2L_3	377.7	8.2	365	92.3	0.08
Yb_2L_3	377.4	9.6	365	99.4	0.11

* ΣI is the integral luminescence intensity.

** $\varphi = 0.042$ for $(Ru(Bipy)_3Cl_2)$ and 0.0315 for ZnTPP.

This was confirmed by the data of mass spectrometry of the complexes (m/z, found/calculated for Sm, Eu, and Yb: 1305/1301, 1307/1304, and 1347/1346, respectively) and by elemental analysis data.

For $C_{57}H_{47}N_9O_{10}Sm_2$ ($Sm_2L_3 \cdot H_2O$)

anal. calcd., %:	C, 52.63;	H, 3.49;	N, 9.69;	Sm, 23.12.
Found, %:	C, 52.44;	H, 3.57;	N, 9.72;	Sm, 23.01.

For $C_{57}H_{47}N_9O_{10}Eu_2$ ($Eu_2L_3 \cdot H_2O$)

anal. calcd., %:	C, 52.50;	H, 3.49;	N, 9.67;	Eu, 23.31.
Found, %:	C, 53.02;	H, 3.38;	N, 9.59;	Eu, 23.25.

For $C_{57}H_{47}N_9O_{10}Yb_2$ ($Yb_2L_3 \cdot H_2O$)

anal. calcd., %:	C, 50.85;	H, 3.38;	N, 9.37;	Yb, 25.71.
Found, %:	C, 50.63;	H, 3.31;	N, 9.28;	Yb, 25.61.

(Hereinafter, molecules of water of crystallization in all complexes are omitted for clarity.)

The X-ray diffraction data for the Eu_2L_3 complex confirm that the compound is pure and a ligand admixture is absent.[1]

The dentate and coordination modes of Ln^{3+} ions in the complexes were determined by the IR spectral data. IR for L (ν, cm^{-1}): 1624, 1593, 1554 ν(CO), 1497 ν(C=C), 1284 ν(C_6H_5–OH), 1170 δ(C–H of phenyl ring); IR for Eu_2L_3 (ν, cm^{-1}): 1621, 1566, 1520 ν(CO), 1485 ν(C=C), 1284 ν(C_6H_5–OH), 1146 ν_{benc}(C–H of phenyl ring), 628 ν(Eu–O). A comparative analysis of the IR spectra of the ligand and Eu(III) complex in the region of characteristic vibrational frequencies of functional groups forming the coordination node with the central ion indicates the coordination of the lanthanide ion with all CO groups, whose vibrational frequencies decrease in the complex, whereas the intensities of the bands corresponding to ν(CO) vibrations decrease threefold. The intensity of the band corresponding to ν(C_6H_4–OH) decreases sharply without shifting in the spectrum of the complex and is accompanied by the appearance of an intense band at 628.7 cm^{-1} due to Eu–O bond vibrations. A molecule of the europium complex includes water of crystallization, which is indicated by the band with a maximum at 3360 cm^{-1}. Similar low-intensity bands were also observed for the Pr(III), Sm(III), Nd(III), and Yb(III) complexes. Thus, in the Ln(III) complexes the ligand is bound to the central ion by three oxygen atoms through the tridentate cyclic mode.

The structure of the Ln(III) complex with the ligand was established from the elemental analysis and IR and mass spectral data using the HyperChem program (Fig. 1).

The luminescence characteristics of the lanthanide complexes Ln_2L_3 are presented in Table 1. The absorption band maxima of the complexes, their molar coefficients, and the luminescence excitation wavelengths differ insignificantly, but the values of luminescence and quantum yield differ substantially. As it should be expected, the Ln_2L_3 complex is characterized by the highest luminescence quantum yield (**φ**). The order of changing φ in the series Eu > Sm > Pr > Yb > Nd, which is mainly determined by their spectroscopic characteristics, is also observed for the complexes with other organic reagents.

The luminescence spectra of the Sm(III) and Eu(III) complexes (visible spectral region, spectrometer gaps 0.1–0.2) and the Nd(III) and Yb(III) complexes (IR region, gaps 0.5–1.0) are shown in Fig. 2. The splitting of the bands corresponding to hypersensitive transitions, which is observed in the luminescence spectra of Eu^{3+} (two maxima at 590 and 594 nm; transition $^5D_0 \longrightarrow {}^7F_1$ and three maxima at 612, 618, and 626 nm; transition $^5D_0 \longrightarrow {}^7F_2$) and in the spectrum of Nd(III) (two pronounced maxima at 879 and 902 nm; transition $^4F_{3/2} \longrightarrow {}^4I_{9/2}$), indicates the low symmetry of the coordination polyhedron [1].

It should be mentioned that the determined value of the triplet level energy of the ligand (E_{T1} = 18180 cm^{-1}) is considerably lower than the energy of radiating levels of dysprosium (20963 cm^{-1}) and terbium (20500 cm^{-1}). Therefore, the intramolecular

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[1] The X-ray diffraction data are available from the authors.

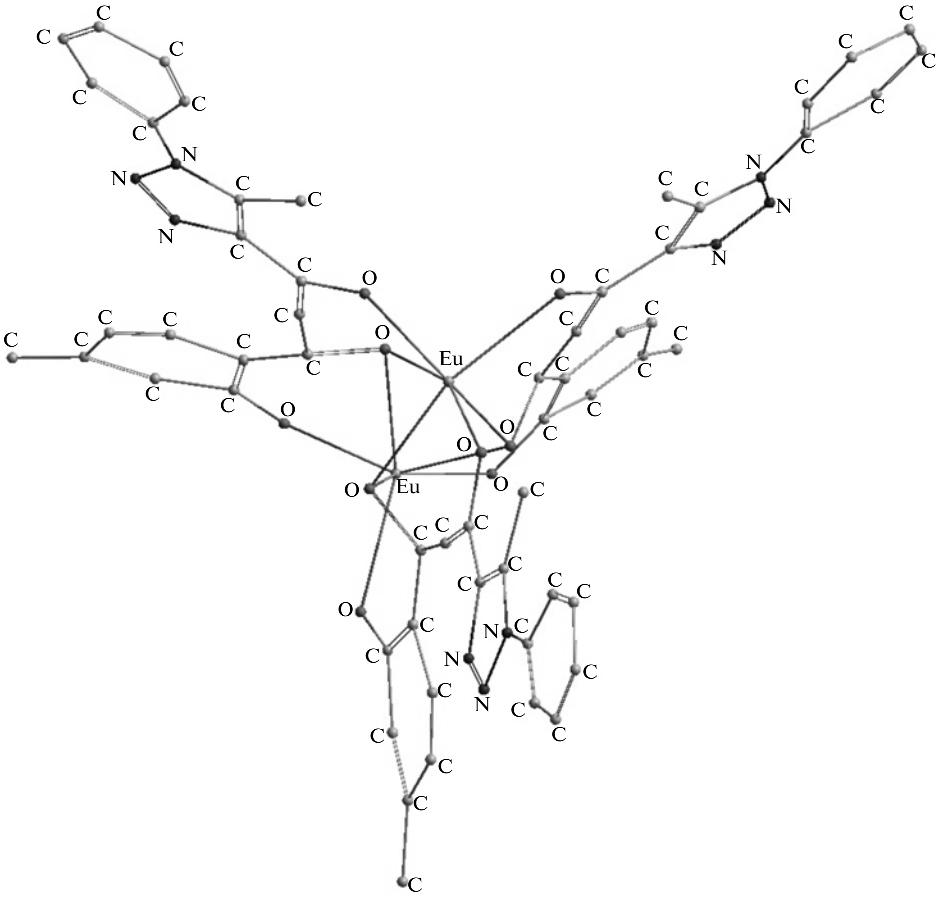

Fig. 1. Molecular structure of the Eu_2L_3 complex optimized by the MM^+ method (HyperChem).

energy transfer from the excited ligand to Dy and Tb cannot occur in principle as for other Ln^{3+}, which exhibit characteristic luminescence upon the transition to the ground state.

In the most part of cases, ions Ln^{3+} coordinate from one to several water molecules along with the main ligand. The high-frequency vibrations of these molecules (OH oscillators) strongly quench luminescence. In particular, the introduction of the second ligand or an organic solvent favors the displacement of the water molecules from the internal coordination sphere of the complex [1, 14]. According to the IR spectra and the results of analyses, the europium complex includes the water molecule and, hence, the introduction of the second ligand (Table 2) increases the luminescence intensity. For example, in the presence of batho-

Table 2. Increase in the luminescence intensity of the Pr(III), Sm(III), Eu(III), Nd(III), and Yb(III) complexes with 1-(2-hydroxy-4-methylphenyl)-3-(5-methyl-1-phenyl-1*H*-1,2,3-triazol-4-yl)propane-1,3-dione (L) upon the introduction of the second ligand (L')* ($c_{Pr,\ Sm,\ Nd,\ Yb} = 2 \times 10^{-5}$, $c_{Eu} = 1 \times 10^{-6}$, and $c_{L,L'} = 2 \times 10^{-4}$ mol/l)

Complex	$I(Ln_2L_3L')/I(Ln_2L_3)$						
	α,α'-Bipy	Phen	Batophen	TPPO	TOPO	DAPM	GMP
Pr_2L_3	1.3	1.1	1.9	2.6	2.7	1.7	1.4
Sm_2L_3	1.4	1.3	6.1	4.1	5.1	3.2	0.9
Eu_2L_3	2.8	1.4	8.3	4.6	5.5	2.1	1.0
Nd_2L_3	1.5	1.5	2.2	2.0	2.2	2.7	1.6
Yb_2L_3	1.0	1.1	1.7	1.1	1.0	0.9	1.0

* L' is α,α'-bipyridine (Bipy), 1,10-phenanthroline (Phen), 4,7-diphenyl-1,10-phenanthroline (Batophen), triphenylphosphine oxide (TPPO), trioctylphosphine oxide (TOPO), diantipyrylpropylmethane (DAPM), and hexamethapol (GMP).

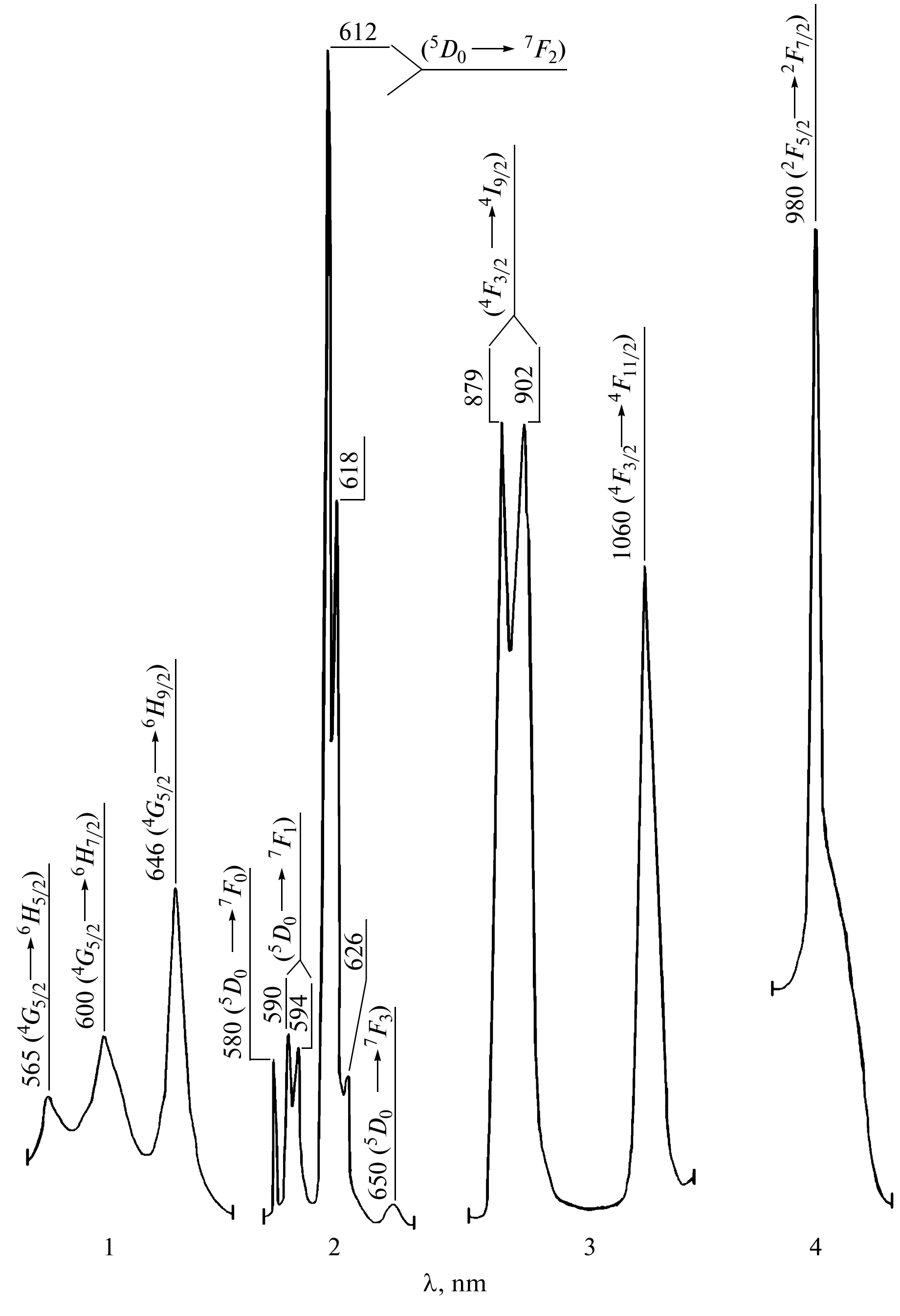

Fig. 2. Luminescence spectra of the complexes (1) Sm_2L_3, (2) Eu_2L_3, (3) Nd_2L_3, and (4) Yb_2L_3.

phenanthroline, the luminescence intensity increases by 8.3 times. In the case of complexes of other lanthanides, the introduction of the second ligands either exerts no effect or enhances their luminescence to a smaller extent. Organic solvents affect the luminescence of the Ln_2L_3 complexes in different way, depending on the concentration (Fig. 3). In the presence of ethanol (40 vol %), the luminescence of Yb_2L_3 increases by 4.5 times, and its luminescence is enhanced to a smaller extent by dioxane (3.5 times), acetonitrile (3 times), and DMSO (2 times) at a concentration of 30 vol %. Probably, the weak enhancement of the luminescence in the presence of DMSO is due to its high donor ability competing with that of the ligand.

Photostability is an important characteristic of the Ln(III) complexes, which determines the possibility of using these complexes as luminescent probes. The plots presented in Fig. 4 show the change in the luminescence intensity of the synthesized complexes upon continuous UV irradiation (λ = 365 nm) for 30 min. The Nd_2L_3 complex is characterized by the highest

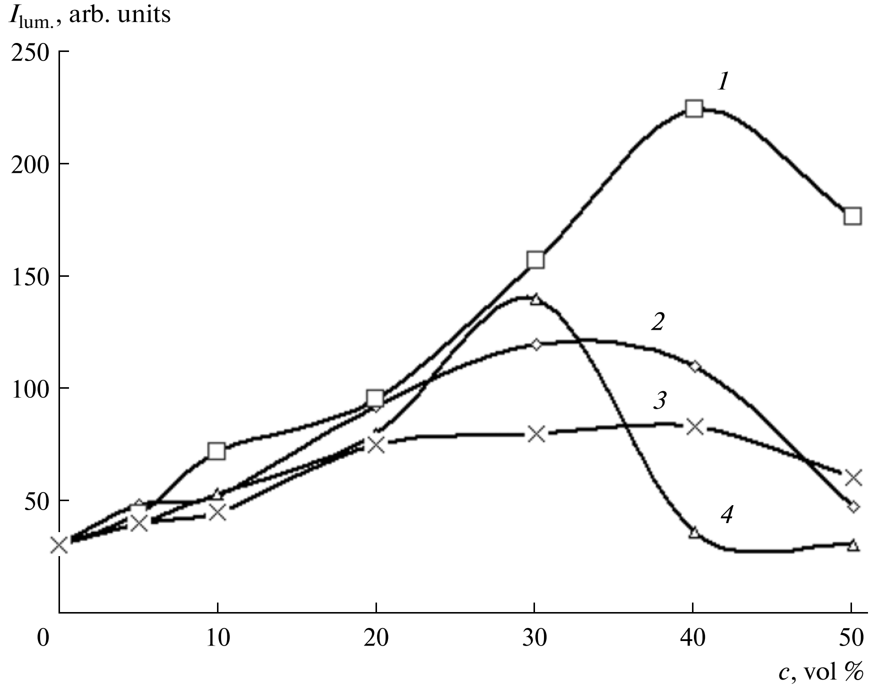

Fig. 3. Effect of organic solvents on the luminescence intensity of the complex Yb_2L_3: (*1*) ethanol, (*2*) acetonitrile, (*3*) DMSO, and (*4*) dioxane ($c_{Yb} = 1 \times 10^{-5}$ and $c_L = 1 \times 10^{-4}$ mol/l).

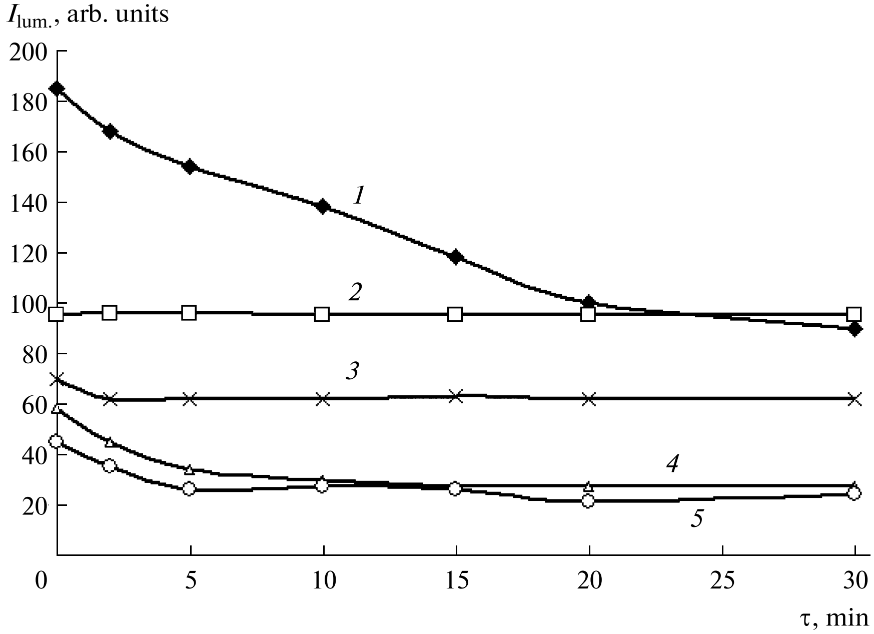

Fig. 4. Plots of the luminescence intensity of the solid complexes (*1*) Yb_2L_3, (*2*) Nd_2L_3, (*3*) Pr_2L_3, (*4*) Eu_2L_3, and (*5*) Sm_2L_3 vs. time of continuous UV irradiation.

photostability. During the first 5 min of irradiation, the luminescence intensity of Pr_2L_3 decreases by 15% and that of Eu_2L_3 and Sm_2L_3 decreases by 50% and then remains unchanged. The luminescence of Yb_2L_3 decreases continuously, and an approximately 50% decrease occurs within the first 20 min of irradiation.

Thus, the synthesis of reagents containing β-diketone fragments provides the formation of stable six-membered rings, and the presence of aryl substituents (photoantennas) results in the intense absorption of the exciting radiation. On the one hand, the ligands synthesized are branched and shield the central ion from water molecules entering into the internal coordination sphere. On the other hand, they prevent the formation of tris-chelate. Three ligand molecules coordinate two lanthanide ions (luminescence emitters) instead of one ion, which increases the luminescence quantum yield.

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