Temperature-Dependent Luminescence Quenching in New Water-Soluble Europium Complexes in Water and Heavy Water

Anastasiia V. Kharcheva*, Dmitriy A. Kharitonov, Vitaliy A. Ioutsi, Nataliya E. Borisova, and Svetlana V. Patsaeva
Lomonosov Moscow State University, Moscow 119991, Russian Federation

***e-mail:** harcheva.anastasiya@physics.msu.ru

Abstract. The luminescent properties of three novel water-soluble europium complexes with organic ligands based on 2,2'-bipyridyl substituted with phosphonic acids were studied in water and heavy water at temperatures from 293 to 333 K. With an increase in temperature, a decrease in the intensity of europium luminescence was observed both in water and heavy water. The luminescence intensity in the studied temperature range is well described by the van't Hoff plot for each solution. For all complexes, the luminescence lifetime in heavy water was much longer than in water due to effective quenching of the excited states by the OH oscillators of water molecules located in the first coordination sphere of the europium. The number of water molecules in the first coordination sphere of the europium at different temperatures was calculated; it did not vary with temperature. We conclude that the main mechanism of luminescence quenching is the enhanced energy back transfer from the excited state of europium to the triplet level of the ligand or the charge transfer state. The energy back transfer probability rises simultaneously with a displacement of the position of the europium ion relative to the inverse center in the complex upon solution heating.

Keywords: rare-earth complexes; trivalent europium; phosphorescence; temperature dependence; luminescence lifetime; luminescence quantum yield; van't Hoff plot.

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1 Introduction

Studying the optical properties of new rare-earth complexes is an important task, since their unique luminescent properties provide a wide range of applications. We will emphasize their high stability, intense luminescence with a high quantum yield and long lifetimes. Over time, rare-earth complexes have become indispensable in many field. They are used in optoelectronics to develop displays, light diodes and lasers [1−5], as luminescent markers and security labels [6], in night vision devices [7], photocatalysis [8], nanoscopy [9], bioprobes and biosensors [10−11], contrast agents in magnetic resonance imaging [12], as well in targeted drug delivery [13]. The possibility of doping various glasses with europium complexes opens up applications in the optical industry: in solar energy, in the production of amplifiers and waveguides, and in the development of lasers [14−17]. A feature of *f-f* transitions in rare-earth ions is manifested in relatively long luminescence lifetime, in the millisecond range. This, in turn, leads to interesting prospects for optical analysis and imaging of biological systems, where the effect of interfering tissue fluorescence can be eliminated by the time offset between light emission and detection [18−19].

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Changes in the external conditions and environmental composition can have a great impact on the luminescence characteristics of rare-earth complexes; therefore, the study of the luminescence spectra of rare-earth complexes under various experimental conditions is very important. Measuring the temperature dependences of luminescence of rare-earth complexes is especially important, since these properties are necessary for most applications. All these determines the relevance of the goal of this work focused in the studying the temperature dependences of luminescent characteristics of new water-soluble europium complexes with organic ligands based on N-heterocyclic compounds.

1.1 Mechanism of Luminescence in Trivalent Europium Complexes with Organic Ligands

Although the luminescence in the rare-earth complexes is due to the emission of the rare-earth ion, the organic ligand is an important component of the luminescing system. An organic ligand attached to a rare-earth ion can significantly increase the molar extinction of the complex compared to the same rare-earth ion due to the so-called antenna effect. Thus, in the complex, light is absorbed by the ligand (antenna) and photoexcitation energy is transferred from the ligand to the lanthanide ion [20].

The luminescence mechanism of europium complexes involves excitation of the singlet state of the ligand upon absorption of a photon, followed by the energy transfer through the triplet state of the ligand to the lanthanide ion (Fig. 1). Emission occurs during the transition of the europium ion from the excited state $^5D_0$ to several levels of the ground term ^7F_J [21]. The generally accepted energy transfer mechanism was first proposed by Crosby and Whan [22−24]. It is shown schematically in Fig. 1 with additives characteristic of europium complexes. After absorption of a photon, the ligand moves to the vibrational level of the singlet state S_1 or S_2. From the higher energy S_2 state there is an internal conversion (IC) to the lower energy S_1 state. The transition process from S_1 state can occur in several ways: intersystem crossing (ISC) to the T_1 triplet level, emission of ligand fluorescence, or non-radiative relaxation to the ground state.

In europium complexes, it is also possible to transfer energy directly to the excited state of the rare-earth ion, for example, from the S_1 level to the $^5D_1$ level with subsequent relaxation to the $^5D_0$ state [25]. After intersystem crossing, non-radiative deactivation of the ligand triplet state or ligand phosphorescence emission can occur, as well as energy transition to the charge transfer (CT) states (ILCT or LMCT) or the excited state of the rare-earth ion [23].

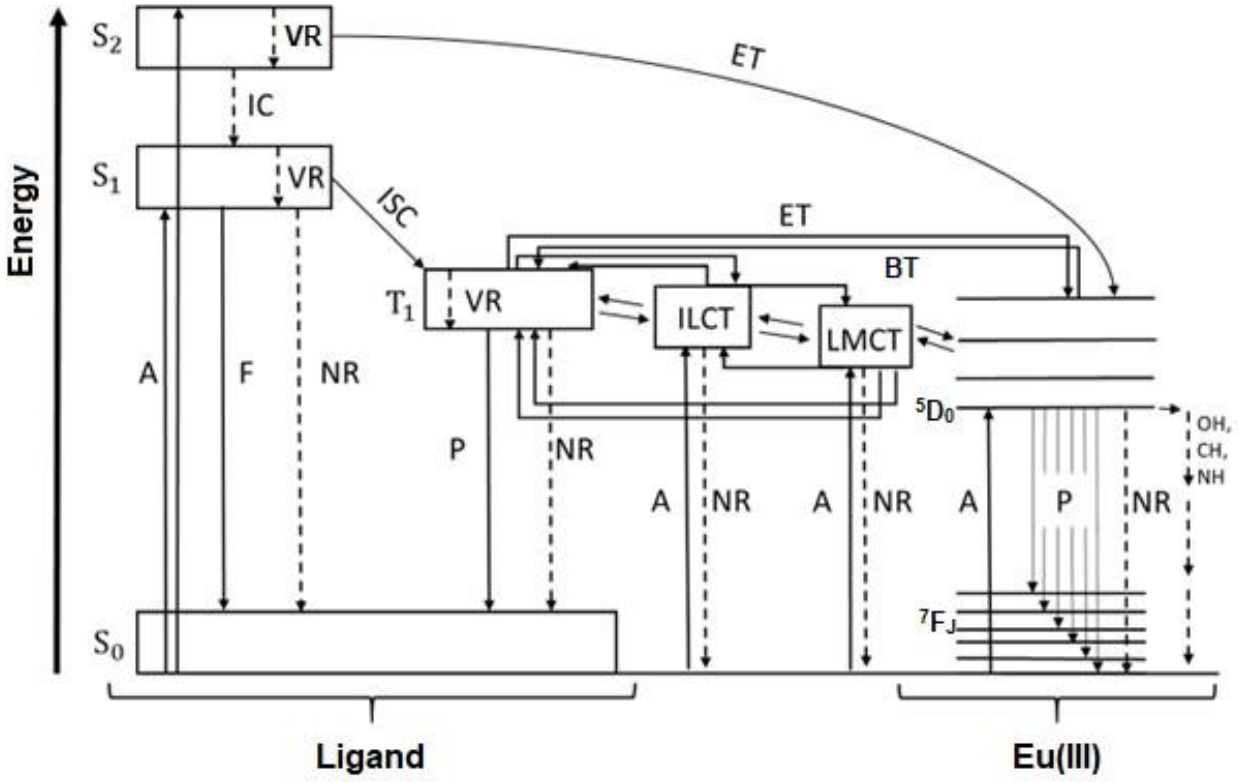


Fig. 1 The scheme of energy transfers in europium complex with an organic ligand (S_0, S_1, S_2 – singlet states, T_1 – triplet state, ILCT (intra ligand charge transfer) and LMCT (ligand to metal charge transfer) – charge transfer states, A – absorption, F – fluorescence, P – phosphorescence, NR − non-radiative transfer, IC − internal conversion, ISC − intersystem crossing, ET − energy transfer from the ligand to the europium ion, BT − back energy transfer, VR − vibrational relaxation.

It is important to note that all energy transfers between the ligand triplet level, the excited level of the rare-earth ion, and the CT states can occur in both the forward and reverse directions. The probability of reverse transfer depends on the energy gap between the states, and if the energy difference between the excited state of the lanthanide ion and the upper triplet energy level of the ligand is too small, then the probability of the reverse transfer increases significantly, reducing the quantum yield of lanthanide luminescence. Moreover, in a situation where the excited state of the metal ion has a higher energy than the triplet state of the ligand, the probability of a transfer will be extremely low, and lanthanide luminescence cannot be observed [26].

In some compounds, the absorption of photons leads to direct excitation of vibrational levels of the ligand singlet state or the CT states, and non-radiative relaxation from all these states can also occur. After transferring energy to the excited state of the europium, the lanthanide ion emits the characteristic radiation. The luminescence spectrum of the trivalent europium consists of the lines in the red, corresponding to the transitions from the excited state $^5D_0$ to the states ^7F_J: $^5D_0 \rightarrow {}^7F_1$ (585−600 nm), $^5D_0 \rightarrow {}^7F_2$ (610−630 nm), $^5D_0 \rightarrow {}^7F_3$ (640−660 nm), $^5D_0 \rightarrow {}^7F_4$ (680−710 nm), $^5D_0 \rightarrow {}^7F_5$ (740−770 nm) and $^5D_0 \rightarrow {}^7F_6$ (810−840 nm) [27].

1.2 Luminescent Sensors for Temperature Measurement

A huge number of thermally sensitive nanoscale materials were developed, such as organic molecules based on boron [28], gold [29], semiconductor quantum dots [30], photonic crystal fiber [31], as well as luminescent rare-earth complexes [32]. Luminescent probes for temperature measurement have advantages over other existing methods and are widely used in marine, geochemical, biotechnological and other studies [33−34]. The paper [35] proposes the use of fluorescent water-soluble compounds based on porphyrins to control the temperature of body tissues during phototherapy in the course of antitumor treatment. Linear calibration curves were obtained from the ratios of two fluorescence peaks, peak-to-valley, or fluorescence lifetime, which provides a fairly high accuracy of temperature determination, up to 0.1 K, in the biologically important range. The colloidal CdSe (ZnS) quantum dots in a SiO_2 dielectric matrix were examined in Ref. [36]. The maximum of the luminescence emission of this sensor was shifted to the red region, the width of the luminescent band increased upon heating in the range from 295 to 525 K. The paper [37] describes the effect of temperature on the luminescence spectra of lanthanide-grafted bipyridine periodic mesoporous organosilica in the biological temperature range. The advantage of using such a sensor is low toxicity; therefore, in the future, it is planned to use them to control intracellular temperature during drug delivery.

Compounds with europium ions (complexes, films, MOFs, etc.) have found the greatest application as luminescent temperature sensors due to the high intensity and duration of europium luminescence. It was established in the work [38] that the luminescence intensity of a vitrified film from the mesogenic complex of europium β-diketonate ($Eu(CPDK_{3\text{-}5})_3$phen, where "$CPDK_{3\text{-}5}$" stands for 1-(4-(4-propylcyclohexyl)phenyl) octane-1,3-dione and "phen" stands for 1,10-phenathroline) decreases linearly on average in 10 times when heated from 298 to 348 K, and the luminescence lifetime decreases in 2.6 times. The process is reversible, i.e. the film can be reused as a temperature sensor. In addition to recording the temperature dependence, the authors also suggested that the LMCT state is responsible for the strong quenching of the europium luminescence from the $^5D_0$ level at high temperatures, and the activation energy was determined in accordance with the Arrhenius equation. The films with β-diketonate complex of similar structure ($Eu(DK_{12\text{–}14})_3$phen, $DK_{12\text{–}14}$ = 1-(4-(dodecyloxy)phenyl)-3-(4-(tetradecyloxy)phenyl) propane-1,3-dione, phen = 1,10-phenanthroline) in an extended temperature range of 214–370 K were studied [39]. It has been found that the film luminescence lifetime can be the main parameter of a reusable temperature sensor in the temperature range of 270–370 K with high sensitivity.

In the work [40] temperature dependence of binuclear europium complex ($[BP\text{-}(EuIII)_2\text{-}(ODA)_3]$ (BP = 2,20-bipyridine-6,60-dicarboxylic acid bis(N-hydroxysuccinimide) ester, ODA = diglycolic acid)) was studied in the range of 283–333 K. It was found that when the temperature of the solution of the binuclear europium complex in H_2O or D_2O changes, the shape of the luminescence emission band corresponding to the energy transition $^5D_0 \rightarrow {}^7F_2$ changes as well. When the complex solution is heated, the luminescence intensity of two bands corresponding to the Stark splitting of the $^5D_0$ energy level increases, and their ratio depends not only on temperature, but also on the type of the solvent (light or heavy water). Thus, one can speak about the influence of water molecules in the first coordination sphere of the europium ion on the temperature-dependent processes.

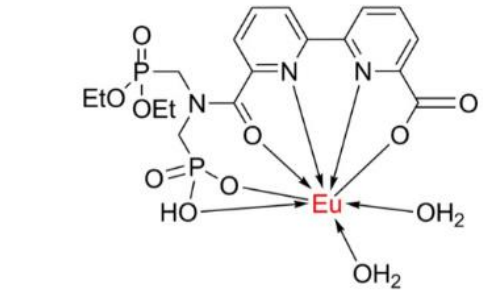
The authors of the paper [41] studied the tetranuclear Na^+–Eu^{3+} complex, $[Eu_2Na_2(nta)_2(CF_3CO_2)_4(naphCO_2)_2(tpm^*)_2]\cdot H_2O$ [where nta^- = 1-(2-naphthoyl)-3,3,3-trifluoroacetonate, $naphCO_2^-$ = naphthalene-2-carboxylate, tpm* = tris(3,5-dimethyl-1-pyrazolyl)methane], and suggested using it as a temperature sensor in the range of 273−233 K. The authors consider the temperature dependences of the luminescence integral intensity and lifetime, and the dependence of the luminescence lifetime on temperature was well described by the Mott-Seitz model. This made it possible to calculate the activation energy and propose a model for the quenching of the excited state $^5D_0$ of the europium ion by the back energy transfer to the singlet energy level S_1 of the ligand.

The method for determining the temperature for many optical thermometers is based on measuring the ratio of luminescence emission of the ions, for example, Eu(III) and Tb(III), or Eu(III) and Sm(III)) in multicenter compounds [42−46].

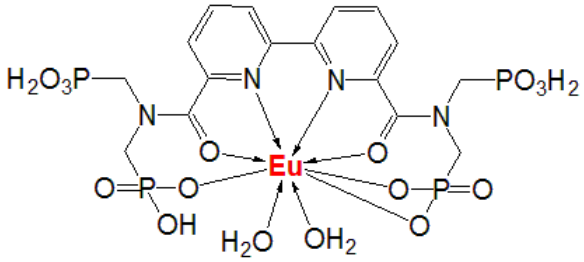
2 Materials and Methods

2.1 Synthesis of Europium Complexes

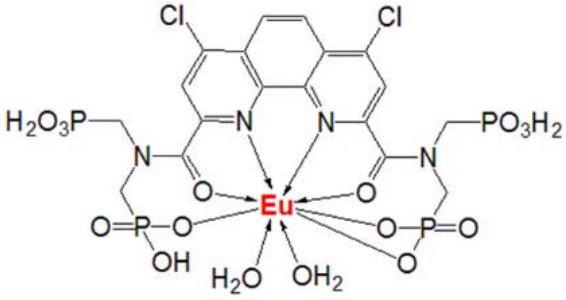
The Fig. 2 shows the chemical structures of the studied water-soluble europium complexes with organic ligands based on 2,2′-bipyridyl and 1,10-phenanthroline substituted with phosphonic acids [47−48].



(a)



(b)



(c)

Fig. 2 Chemical structures of the studied europium complexes: (a) complex 1, (b) complex 2, (c) complex 3.

The complex 1 was isolated as a white powder, practically insoluble in water and other polar solvents suitable for recording NMR spectra; therefore, IR and luminescent spectrometry, as well as high-resolution mass spectrometry, were used to determine the structure of the substance. According to the ESI-HR-MS, the composition of the complex corresponds to the hydrolysis product of the amide group and two ester groups of phosphoric acid. According to the IR spectrometry, a broad intense band is observed in the region of 1646–1595 cm^{-1} with a maximum at 1617 cm^{-1}, corresponding to the stretching vibrations of the C=O group in the uncoordinated tertiary amide group, and a narrower intense band at 1573 cm^{-1}, corresponding to carboxylate anion. The presence of residual ester groups was confirmed by the presence of intense absorption bands in the region of 1078 and 1151 cm^{-1}, corresponding to the stretching vibrations of C-O bonds in esters of phosphonic acids. The presence of phosphonic acid after partial hydrolysis of ester groups was confirmed by the presence of a weak band at 1272 cm^{-1}. In the spectrum there are observed also absorption bands, characteristic of C-H stretching vibrations in the region of 2856–2958 cm^{-1}.

The presence of water molecules in the coordination sphere of complex 1 was established on the basis of luminescent studies (Section 3.4).

Complex 1 was synthesized by the following algorithm. A solution of $Eu(NO_3)_3 \cdot 6H_2O$ (45 mg, 0.1 mmol) in deionized water (1 ml) was added to a solution of octaethyl phosphonic ester (0.1 g, 0.1 mmol) [42] in 3 ml of acetonitrile. Then the 0.1 ml of 1M HCl were added dropwise under vigorous stirring. After addition is complete, the reaction mixture stirred about 1 h. White precipitate appeared were filtered off and washed twice by 1 ml of deionized water and air dried. The product yield was 40 mg (65%). High resolution electrospray ionization mass spectrometry showed the presence of a product $[LEu]^-$ with a mass-to-charge ratio 734. 9875 (calc. for $C_{18}H_{20}EuN_3O_9P_2$). The lines in the IR spectra (detected using KBr pellet) were the following: 2958, 2927, 2856 (ν_{C-H}),1617 (ν_{CON}), 1432, 1488, 1571 ($\nu_{C=O}$), 1274 (ν_{P-O}), 1078, 1151 (ν_{C-OP}) cm^{-1}.

The complexes 2 and 3 were synthesized according to the Fig. 3 using the previously described procedures [47−48]. In the process of optimizing the preparation of complex 2, an attempt was made to perform metal-assisted deethylation of the octakisethyl bisphosphonic ester intermediate using the 2,2'-bipyridyl derivatives as an example. As a result of the treatment of the europium complex formed in situ with a 1 M HCl solution at room temperature, complex 1 was isolated, which is the product of partial hydrolysis of the ester groups and the amide fragment (Fig. 3).

Solutions of europium complexes were prepared by dissolving a small amount of the complex powder in water or heavy water to obtain a concentration $(1 \div 3) \cdot 10^{-5}$ M.

2.2 Registration of Absorption and Luminescence Spectra, Calculation of Asymmetry Coefficient

The absorption spectra of solutions of the complexes were measured by a Solar PB 2201 spectrophotometer in the temperature range from 293 to 333 K relative to a pure solvent (water or heavy water). The studies were carried out in the spectral range of 200−800 nm using quartz cuvettes with an optical path length of 10 mm.

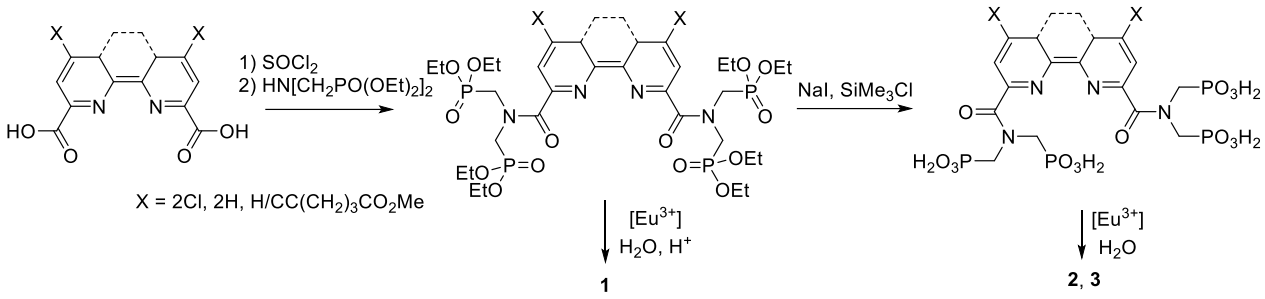


Fig. 3 The scheme of the synthesis of studied compounds.

Luminescence spectra were recorded using a Solar CM2203 luminescence spectrometer (Belarus). To set and maintain the required temperature of the solutions in the temperature range from 293 to 333 K, a thermostatic cell compartment was used. The measurements were carried out in standard quartz cuvettes with an optical path length of 10 mm. For more accurate temperature control, an external thermometer was used lowered into the cuvette.

The luminescence emission spectra were registered in the spectral range from 280 to 800 nm with a step of 1 nm upon excitation at 270 or 320 nm. The spectral width of the excitation and registration monochromator slits was set to 5 nm. The luminescence excitation spectra were measured upon excitation within the spectral range 250–600 nm when recorded at 613 nm. After measuring the luminescence spectra, the effect of the internal filter was corrected using the following Eq. (1):

$$I_{corr} = I_0 \times 10^{(\frac{D_{ex}+D_{em}}{2})}, \quad (1)$$

where I_{corr} – luminescence intensity corrected for the internal filter effect, I_0 – registered luminescence intensity, D_{ex} and D_{em} – absorbance of the solution at the wavelength of excitation and registration, respectively.

The luminescence quantum yield was calculated by the reference dye method using the values of the quantum yield of solutions of these complexes in water and heavy water at room temperature (297 K) as a reference (the corresponding values were obtained earlier, using Rhodamine as a reference [49]).

The so-called asymmetry coefficient (or asymmetry ratio) R was calculated as the ratio of the intensities of the peaks corresponding to the "supersensitive" ($^5D_0 \rightarrow {}^7F_2$) and magnetic dipole ($^5D_0 \rightarrow {}^7F_1$) transitions. R characterizes the specific crystallographic site symmetry of the europium ion. Distortions or deviations from centrosymmetric geometry of Eu^{3+} generally increase R [50].

2.3 Luminescence Lifetime Measurement

The luminescence decay kinetics were measured by a Solar CM2203 luminescence spectrometer upon excitation with a wavelength of 270 or 320 nm and a recording wavelength of 618 nm. The spectral slit width of the excitation and recording monochromators was 10 nm, the measurements were carried out with a period of 0.02 s (accumulation time of one decay cycle), 5 repetitions of 40 cycles each. Based on the luminescence decay kinetics obtained for each repetition, the luminescence lifetime τ_{obs} of the excited state of europium was calculated as following:

$$\tau_{obs} = \frac{t}{\ln I(0) - \ln I(t)}, \quad (2)$$

where $I(0)$ and $I(t)$ are the phosphorescence intensities at the start and time t, respectively. Subsequently, the lifetime values obtained in different repetitions for one sample were averaged.

2.4. Determination of the Number of Water Molecules in the First Coordination Sphere of the Europium Ion

Using the observed luminescence lifetime τ_{obs} of compounds with europium, one can determine, for example, the number of water molecules included in the first coordination sphere of the complex (hydration number). This number provides information on the composition of europium complexes in aqueous solutions. The method for determining the hydration number is based on the fact that OH groups can quench the excited state $^5D_0$, while OD groups of D_2O quench it less efficient. Therefore, one can observe an increase in the observed luminescence lifetime in heavy water compared to light water [51].

For the case when it is required to determine the number of water molecules in the first coordination sphere of complexes, one can use the formula for solutions of complexes obtained empirically [52]:

$$q = A(\frac{1}{\tau_{H_2O}} - \frac{1}{\tau_{D_2O}} - B), \quad (3)$$

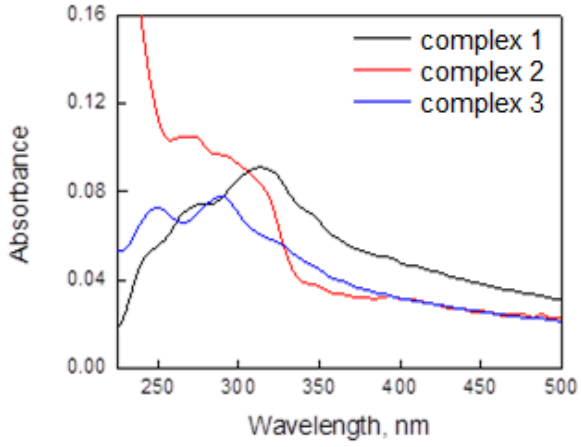
where the coefficients A = 1.11 ms and B = 0.31 ms^{-1}.

3 Results

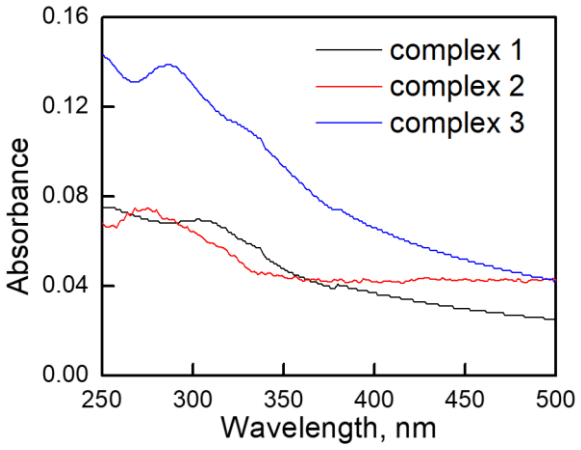
3.1 Absorption Spectra of Solutions of Europium Complexes

The absorption spectra of solutions of water-soluble europium complexes in water and heavy water represent

a broad spectral band in the UV range. In Fig. 4 they are shown for solutions at a temperature of 297 K. Local absorption maxima corresponding to the absorption of the ligand are located in the wavelength range of 270−320 nm, depending on the complex and solvent. Experiments have shown that the absorption spectrum does not change shape with increasing temperature, but the absorbances decrease slightly with increasing temperature.



(a)



(b)

Fig. 4 Absorption spectra of studied complexes in (a) H_2O and (b) in D_2O at 297 K.

The absorption spectrum of the complex 1 has a maximum at a wavelength of 315 nm, which corresponds to the ligand absorption to the S_1 state; in heavy water the absorption maximum of the complex solution is slightly broadened and shifted to the shorter wavelengths by 5 nm; otherwise, the absorption spectrum remains practically unchanged. Taking into account that the concentrations of solutions are almost identical, in heavy water and in water absorbances are comparable. The absorption spectrum of a solution of complex 2 in water has a broad peak in the wavelength range of 250−340 nm with a noticeable shoulder at 320 nm; in heavy water it has a noticeable peak at 270 nm and a shoulder at a wavelength of 320 nm. The absorption spectrum of a solution of the complex 3 in water has a peak with a maximum at a wavelength of 290 nm, the absorption spectrum of a solution in heavy water is red shifted and is significantly broadened. The absorption spectra of solutions of complexes 1 and 2 have similar peaks at 315−320 nm, either in water and in heavy water. The fact that these two complexes are also similar in structure confirms the assumption that the N-heterocyclic part of the ligand common to them is responsible for the nature of the absorption spectrum [27]: for complexes 1 and 2, this part is bipyridine, while for the complex 3, the N- heterocyclic part is phenanthroline.

3.2 Luminescence Emission and Excitation Spectra of Solutions of Europium Complexes

Emission spectra were measured with an excitation wavelength of 270 nm (complex 3 in D_2O) and 320 nm (other complexes), which corresponds to the wavelength at the maximum of the excitation spectrum. Emission spectra were recorded in the spectral range from 500 to 800 nm in the phosphorescence measurement mode with a delay respect to the lamp pulse. A typical phosphorescence emission spectrum of the europium complex is a set of spectral lines in the region of 570−720 nm corresponding to the energy transitions $^5D_0 \rightarrow {}^7F_J$ (where J = 0…6, only the first five of them were observed in the experiment). Emission spectra were recorded in the fluorescence measurement mode (with simultaneous excitation and registration of spectra) at the same excitation parameters in a wider spectral range from 330 to 800 nm (Fig. 5). The spectra obtained in this measurement mode have a broad peak in the short-wavelength region, which corresponds to the fluorescence of the organic ligand.

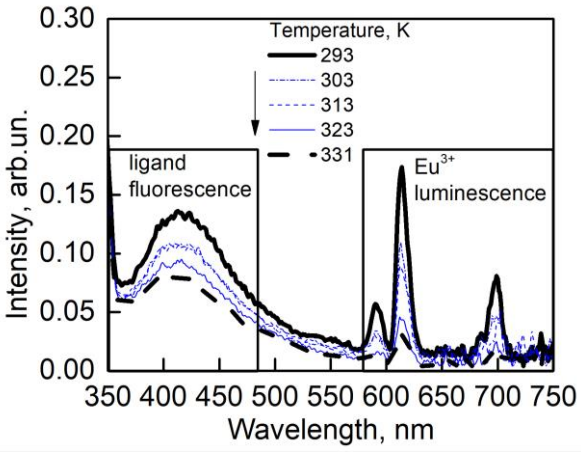


Fig. 5 Luminescence emission spectra of the complex 2 in heavy water at different temperatures recorded in the fluorescence measurement mode, λ_{ex} = 320 nm. The spectra of other studied samples are presented in the Supplementary Material, Figs. S1.

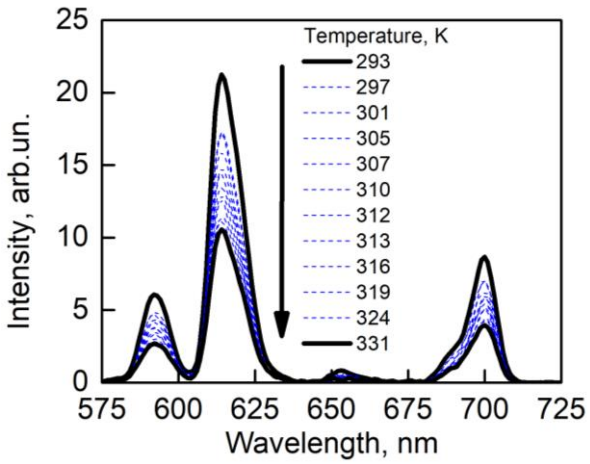


Fig. 6 Luminescence emission spectra of the complex 1 in water at different temperatures recorded in the phosphorescence measurement mode, λ_{ex} = 320 nm.

The most intense peak in the luminescence spectrum of the investigated solutions of europium complexes corresponds to the transition from the $^5D_0$ level to the $^7F_2$ level, the so called "supersensitive" transition. Two other peaks are also clearly visible, corresponding to transitions to the $^7F_1$ and $^7F_4$ levels with the peak wavelengths of 595 and 700 nm, respectively. In addition, the forbidden transitions to the $^7F_0$ and $^7F_3$ levels can be distinguished, but their intensity is much lower compared to the others. The shape is characteristic of all europium complexes, regardless of the solvent (Fig. 6).

With an increase in the temperature of solutions of europium complexes in both solvents, a decrease in the intensity of europium luminescence was observed (Fig. 7). The dependence of the wavelength-integrated luminescence intensity of europium complexes on temperature in the temperature range under study was found to be non-linear.

The wavelength-integrated luminescence intensity of solutions of the complexes 1 and 3 in water drops by 40% as the temperature increases from 293 to 313 K, and this drop is practically the same for these two complexes. Further, with an increase in the temperature of the solutions above 313 K, the integrated luminescence intensity decreases by only 5%. The strongest drop in the luminescence intensity was observed for a solution of the complex 2 in water; its luminescence decreases by 80% along with temperature rising from 293 to 313 K. With further heating, the luminescence decreases by no more than 10%. A solution of the complex 1 in heavy water is characterized by a linear dependence over the entire temperature range from 293 to 333 K with a decrease in the wavelength-integrated luminescence intensity by 58%.

The complex 2 in heavy water, as well as in water, has a large change in the luminescence intensity; this temperature dependence consists of two linear sections. In the temperature range from 293 to 313 K, the integrated luminescence intensity of the europium complex drops about 5 times. Then the rate of fall decreases, and the intensity decreases twofold as the temperature rises up to 333 K. Thus, it can be seen that the behavior of the luminescence of the complex 2 is practically independent of the solvent. A solution of the complex 3 in heavy water is characterized by a dependence with a weakly pronounced change in the angle of inclination at 313 K, and with a general decrease in the wavelength-integrated luminescence intensity by 66%.

In general, decreasing with temperature luminescence intensity was observed earlier for other europium complexes. In a number of studies, a characteristic linear decrease in intensity followed by its break is observed [36, 48]. However, in the mentioned papers, the temperature range under investigation mainly affected the first linear section of the dependence; there were no data on how the dependence of the integrated luminescence intensity behaves at higher temperatures.

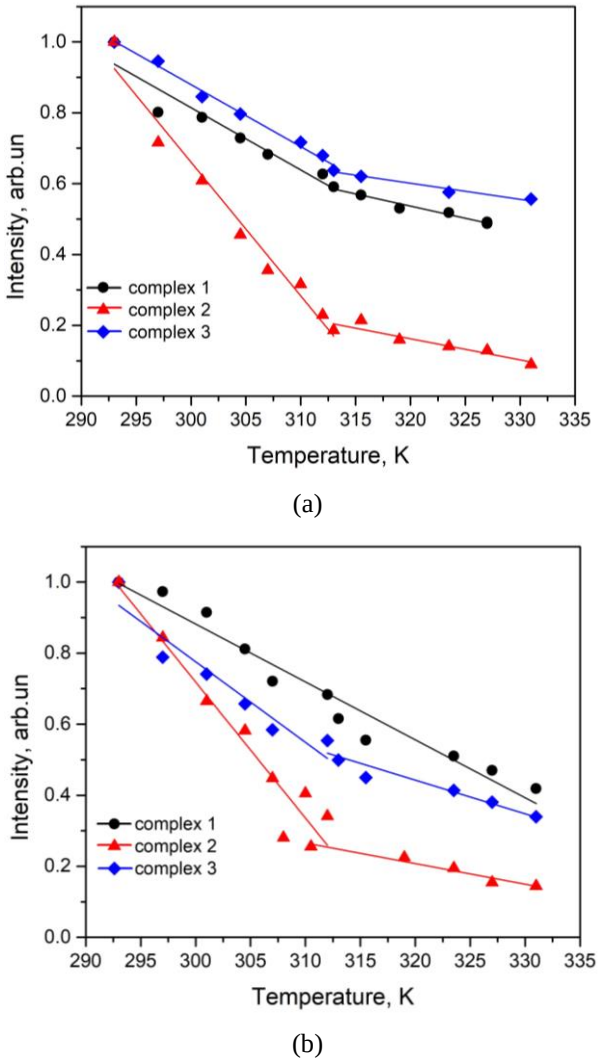


Fig. 7 Dependences of the wavelength-integrated luminescence intensity for solutions of complexes in water (a) and heavy water (b).

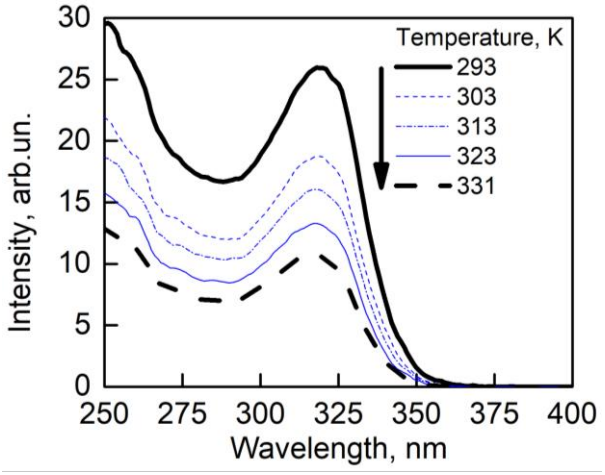


Fig. 8 Luminescence excitation spectra of the complex 1 in heavy water at various temperatures.

The dependence of luminescence quenching on temperature in the article [48] is explained by electron-phonon pairing and/or a change in the crystal field due to thermal contraction of the lattice. The second, in our case, can probably be associated with a change in the conformation of the complex under the action of temperature. Based on the linear dependence of the change in the energy of the $^5D_0 \rightarrow {}^7F_0$ transition, it is assumed in the article that electron-phonon pairing is the main mechanism. In Ref. [36], the dependence of the integral intensity on temperature is explained by a change in the energy transfer to the singlet S1 state of the ligand, which in our case is impossible according to the energy conservation law.

The luminescence excitation spectra of europium complexes in water and heavy water were obtained upon excitation with wavelengths ranging from 250 to 600 nm and registration at a wavelength of 613 or 614 nm, which corresponds to an ultrasensitive energy transition (registration was carried out in the phosphorescence measurement mode). As an example, the Fig. 8 shows the change in the excitation spectrum for the complex 1 when the solution is heated.

The intensity maximum for the luminescence excitation spectra falls at a wavelength of 320 or 270 nm (for the complex 3 in heavy water). The band-shape of the excitation spectra, the position of the maximum did not change significantly with temperature. We observed only a uniform decrease in intensity occurred along with rising temperature. Changes in the maximum intensity in the excitation spectra with temperature alteration corresponded to changes in the wavelength-integrated intensity in the emission spectra.

3.3 Van't Hoff Plots

According to the obtained dependences of the wavelength-integrated luminescence intensity, van't Hoff plots were calculated as dependences of the logarithm of the normalized luminescence intensity on the reciprocal absolute temperature (Fig. 9).

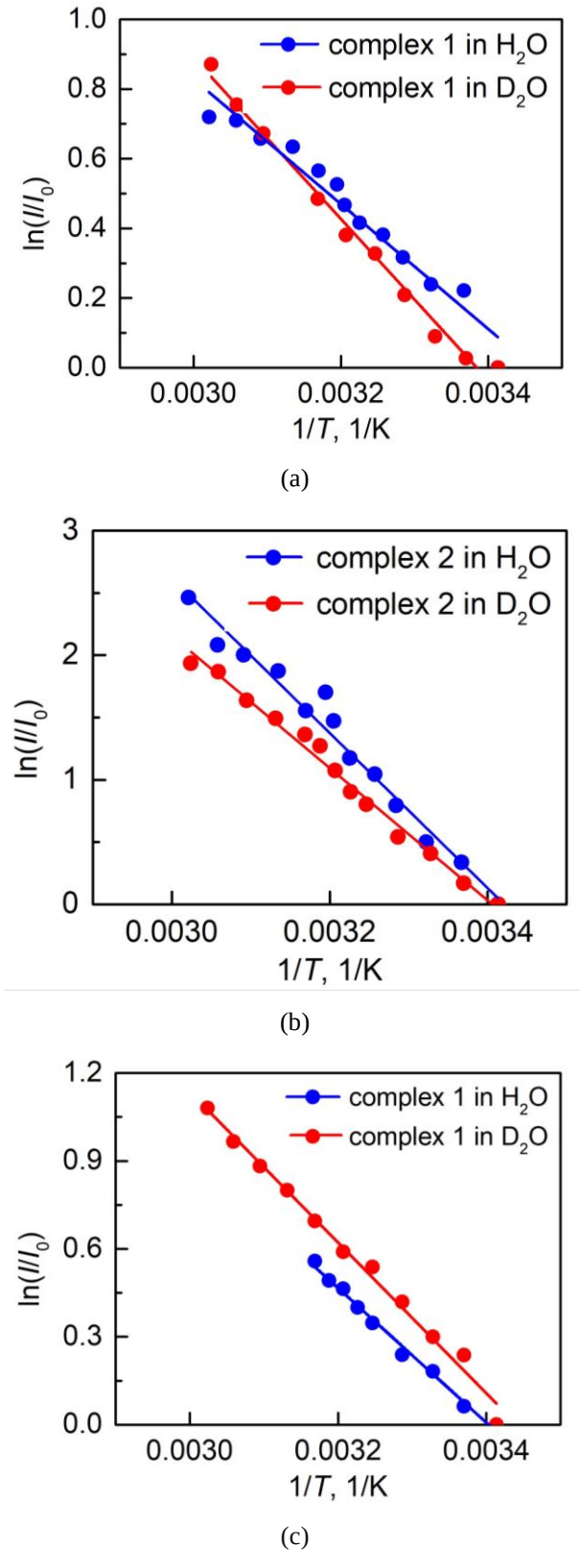


Fig. 9 Dependence of the logarithm of the normalized integral luminescence intensity of solutions of europium complexes on the reciprocal absolute temperature: (a) complex 1, (b) complex 2, (c) complex 3.

The obtained dependences for the three complexes 1, 2 and 3 were found to be linear for both solvents, water and heavy water, which indicates that the Arrhenius law for the van't Hoff plots is fulfilled [38]. Linear dependences with similar regression coefficients for the complexes 1 and 3, both in water and in heavy water, indicate the predominance of the same mechanism of thermal luminescence quenching in these complexes with a constant activation energy. Most likely, such a mechanism is the back energy transfer between the europium excited level and the ligand triplet level or the CT state.

3.4 Luminescence Kinetics and Lifetime

A typical luminescence decay at various temperatures is shown in Fig. 10. The kinetics of luminescence decay was recorded at a wavelength of 618 nm, which corresponds to the emission line of the supersensitive energy transition $^5D_0 \rightarrow {}^7F_2$. Excitation was carried out at a wavelength of 320 nm. The luminescence decay for all complexes proceeded according to an exponential function with good accuracy.

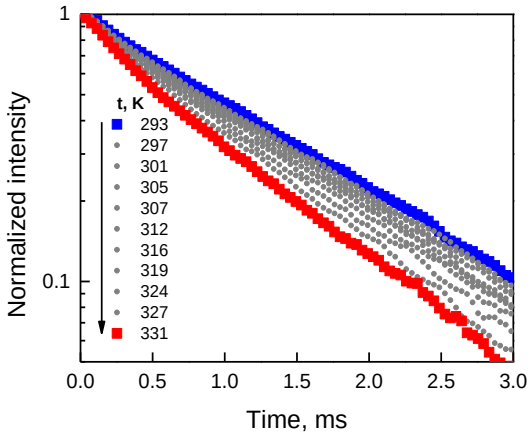


Fig. 10 Luminescence decay in logarithmic scale for the complex 3 in heavy water at various temperatures.

From the luminescence decay plotted in logarithmic scale, the luminescence lifetime of the europium complexes was calculated. The observed lifetimes had different trends along with temperature rising depending on the europium complex (Fig. 11).

The resulting dependences of the luminescence lifetime on temperature for all complexes are almost linear. The luminescence lifetime of a solution of the complex 3 in heavy water drops by 25% from 1.34 ms to 1.01 ms. The luminescence lifetime of the remaining europium complexes is practically independent of temperature in the studied range. In heavy water, it was 1.69 ± 0.01 ms for the complex 1 and 1.35 ± 0.02 ms for the complex 2. For solutions in water, the luminescence lifetime of the complexes 2 and 3 coincided and turned out to be 1.34 ± 0.01 ms, and for the complex 1, the value was also practically unchanged and amounted to 1.6 ± 0.01 ms.

For all complexes, the luminescence lifetime in heavy water is much longer than in water, that is explained by the effective quenching of the excited state by the OH groups of water molecules located in the first coordination sphere of the europium ion.

Thus, we conclude that for two from three of the studied complexes, the lifetime does not depend on temperature. Since the luminescence intensity is reduced for all complexes with increasing temperature, the growing luminescence quenching is not due to the non-radiative deactivation of the excited state of europium ion, but is caused by a rise in the back energy transfer to the triplet state of the ligand or the state with charge transfer with increasing temperature.

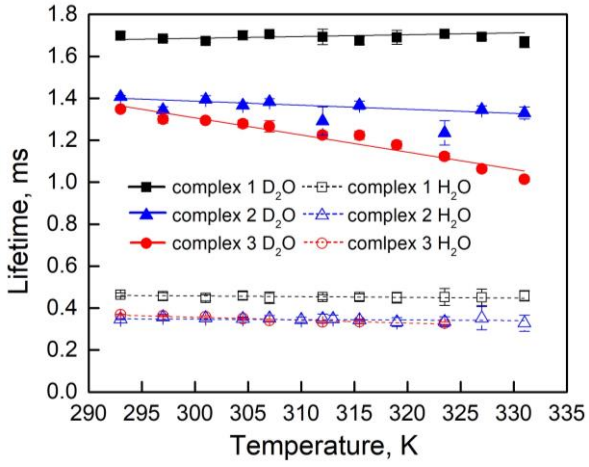


Fig. 11 Observed luminescence lifetimes of europium complexes in water and heavy water at different temperatures.

3.5 Estimation of the Number of Water Molecules in the First Coordination Sphere of Europium Ion

The number of water molecules (q) included in the first coordination sphere of the europium ion was estimated at different temperatures from the calculated values of luminescence lifetime (Fig. 12). For all three complexes (complexes 1, 2 and 3), the number of water molecules in the first coordination sphere of europium practically did not vary with temperature. The calculated q value was 1.44 ± 0.03 for the complex 1, while for the complexes 2 and 3 the value was 2.03 ± 0.07 and 1.97 ± 0.09, respectively. This suggests that the first coordination sphere of the europium in the complex 1 contains one or two water molecules with almost equal probability, while the nearest environment of the europium in complexes 2 and 3 contains two water molecules. The number of water molecules in the first coordination sphere of the europium for all studied complexes did not depend on temperature.

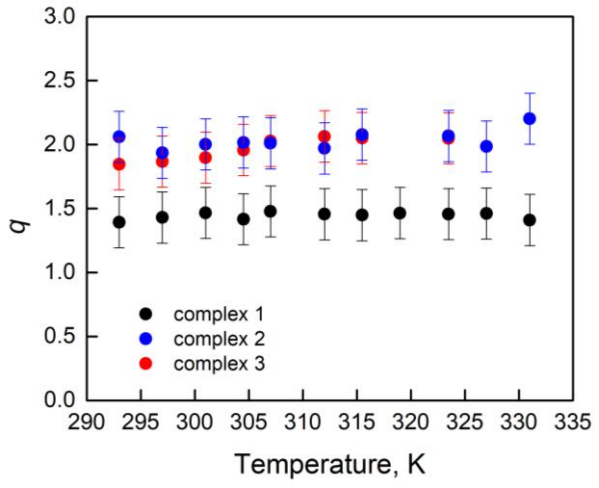


Fig. 12 The number of water molecules (q) incorporated in the first coordination sphere of the europium ion at different solution temperatures.

3.6 Luminescence Quantum Yield Φ and Asymmetry Coefficient R

Based on the values of the wavelength-integrated luminescence intensity, the luminescence quantum yield (Φ_L, %) was calculated, and its temperature dependences were plotted for each complex (Fig. 13). It can be seen from the obtained temperature dependences that for all the complexes the luminescence quantum yield decreases almost linearly along with rising temperature. The highest luminescence quantum yield (13.5%) and the most significant drop (more than twofold from 13.5% to 5.6% with an increase in temperature from 293 to 333 K) was observed for the complex 3 in both solvents and for the solution of the complex 1 in heavy water. The mentioned temperature dependences were found almost linear with the same slope. The lowest luminescence quantum yield was observed for the solutions of the complex 2 in heavy water; with an increase in temperature by 40 K the luminescence quantum yield decreased from 2.7% to 0.5%. In aqueous solution the luminescence quantum yield was even lower and dropped from 1.3% to 0.1% within the same temperature range. All obtained dependences have a decreasing, almost linear character.

From the luminescence emission spectra of solutions of europium complexes, the values of the asymmetry coefficients R were obtained as the ratio of the intensities of the energy transitions $^5D_0 \rightarrow {}^7F_2$ and $^5D_0 \rightarrow {}^7F_1$. The temperature dependences of the R values are shown in Fig. 14.

As the temperature rises, the asymmetry coefficient grows quite smoothly and almost linearly. In this case, the growth is practically the same for solutions in water and heavy water, and depends rather on the europium complex itself. For the complexes 1 and 3, the increase in the asymmetry coefficient with an increase in temperature from 293 to 333 K in both solvents was insignificant: in heavy water by about 8% and 12%, respectively, in water for both complexes by about 7%. For the complex 2, the growth was more significant, about 30% for all solutions.

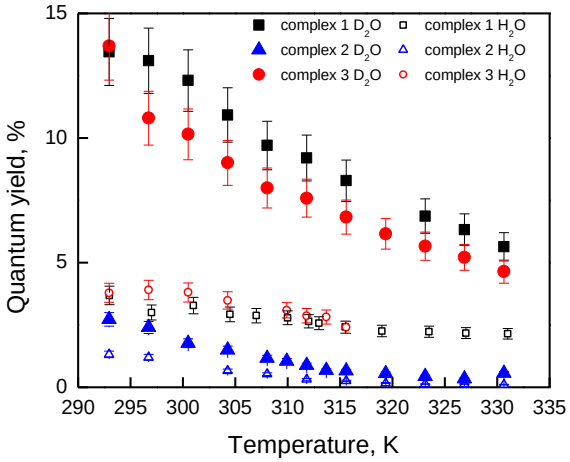


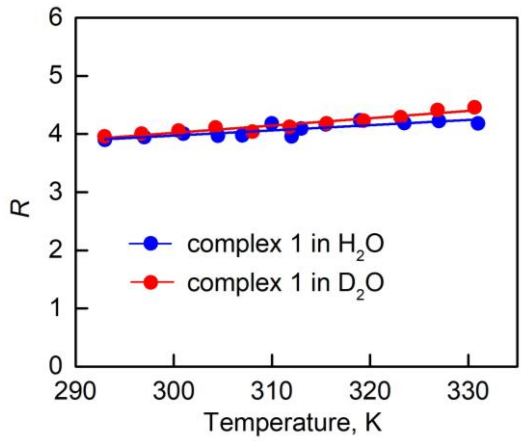
Fig. 13 Luminescence quantum yield (Φ_L, %) of europium complexes with N-heterocyclic ligands substituted with phosphonic acids at different solution temperatures.

Thus, we conclude that the wavelength-integrated intensity of the $^5D_0 \rightarrow {}^7F_1$ transition falls faster than the intensity of the $^5D_0 \rightarrow {}^7F_2$ transition. This suggests that an increase in temperature leads to a change in the conformation of the complexes upon heating and a shift of the europium ion from centrosymmetric geometry. These changes are more noticeable for the complex 2 than for the complexes 1 and 3.

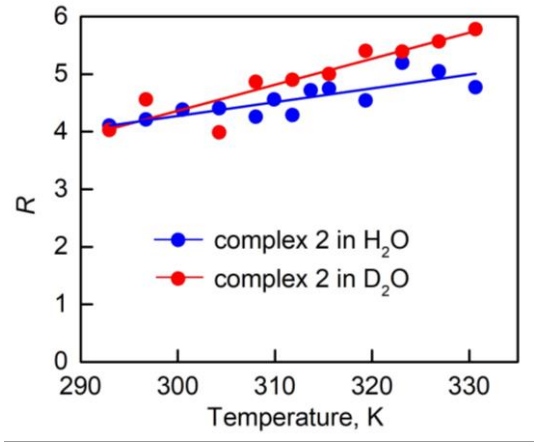
4 Conclusions

We studied the dependence of spectral-luminescent properties of europium complexes with organic ligands substituted with phosphonic acids (based on 2,2'-bipyridyl and 1,10-phenantroline) in water and heavy water on temperature ranged from 293 to 333 K. The following main results were obtained:

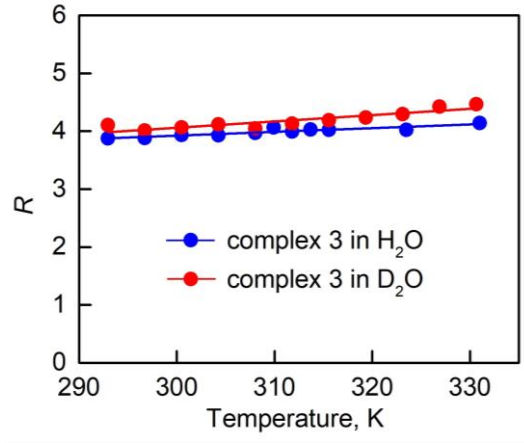
1. The shape of the luminescence excitation and emission spectra of the studied europium complexes was found practically independent of temperature. The main maxima in the emission spectrum were observed at 592 nm ($^5D_0 \rightarrow {}^7F_1$), 614 nm ($^5D_0 \rightarrow {}^7F_2$) and 700 nm ($^5D_0 \rightarrow {}^7F_4$), in the excitation spectrum at 320 nm (except for the complex 3 in heavy water, for which the luminescence excitation maximum was located at 270 nm).
2. With increasing solution temperature, a decrease in the intensity of europium luminescence was observed both in water and heavy water. The change in the luminescence intensity in the studied temperature range is described by the Arrhenius law and is expressed by a linear function on van't Hoff plots. The linear regression coefficient of the van't Hoff plots turned out to be close for both solvents (water and heavy water).



(a)



(b)



(c)

Fig. 14 The asymmetry coefficient *R* of the europium complexes with N-heterocyclic ligands substituted with phosphonic acids at different solution temperatures: (a) complex 1, (b) complex 2, (c) complex 3.

3. The dependence of the luminescence lifetime of solutions of europium complexes in water and heavy water upon heating from 293 to 333 K has been established. For all complexes, the luminescence lifetime in heavy water was significantly longer than in water, which is explained by the effective quenching of the excited state by the OH groups of water molecules incorporated in the first coordination sphere of the europium ion. The luminescence lifetime of the complex 3 in heavy water dropped from 1.34 ms to 1.01 ms with increasing temperature, and for other solutions it was practically independent of temperature: in heavy water it was 1.69 ± 0.01 ms (the complex 1), 1.35 ± 0.02 ms (the complex 2); and for solutions in water 1.34 ± 0.01 ms (the complexes 2 and 3) and 1.6 ± 0.01 ms (the complex 1). Thus, since the luminescence intensity decreases for all complexes with rising temperature, we conclude that the increased efficiency of luminescence quenching is not caused by nonradiative deactivation of the europium ion, but is explained by the enhanced back energy transfer to the triplet state of the ligand or the state with charge transfer.

4. The luminescence quantum yield for all complexes was found decreasing almost linearly along with rising temperature. The highest luminescence quantum yield (13.5%) and the most significant its drop (more than twofold with temperature rising from 293 to 333 K) was observed for the complex 3 in both solvents and for a solution of the complex 1 in heavy water.

5. The calculated number of water molecules *q* in the first coordination sphere of the europium ion for all three complexes did not depend on temperature: $q=1.44 \pm 0.03$ in the complex 1 (which means coexistence of complexes with one and two water molecules, which relative concentration does not vary with temperature), and in the complexes 2 and 3 two water molecules are present in the nearest environment of the europium.

6. It has been established that the asymmetry coefficient of the studied water-soluble europium complexes, which characterizes the displacement of the position of the europium ion relative to the inversion center, slowly increased with rising temperature. The largest increase in the asymmetry coefficient (up to 30%) was observed for the complex 2.

Thus, we concluded that the main mechanism of luminescence quenching in the studied water-soluble europium complexes with increasing temperature is the reverse energy transfer between the excited level of the europium and the triplet level of the ligand or charge transfer state. The probability of reverse energy transfer upon solution heating increases simultaneously with the displacement of the position of the europium ion relative to the inversion center.

A practical application of the findings could be development of molecular temperature sensors for multiple biological applications, since the studied compounds are soluble in water.

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Disclosures

The authors declare no conflict of interest.

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