Temperature dependence of the luminescence of two-center REE complexes with N-heterocyclic ligands at an excess of metal ions with respect to the ligand

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The temperature dependence of the spectral-luminescent characteristics of rare earth element (REE) complexes with an N-heterocyclic ligand based on $2,2'$-bipyridyldicarboxamide in the simultaneous presence of two emitting centers (europium + terbium) was studied. Measurements were conducted in a physiological temperature range $(20-60°C)$. Solutions of the ligand, europium nitrate hexahydrate and terbium nitrate pentahydrate in acetonitrile (with concentrations of $3 \cdot 10^{-5}$ mol/l) were mixed in the ratio of $1:1:1$. In order to reveal the features of energy transitions in such compounds, the results obtained were compared with similar results for solutions of the europium or terbium complex with the same ligand. For the studied compounds, the lifetimes of europium and terbium ions in solutions at different temperatures were obtained. The temperature dependences of the luminescence quantum efficiency of the compounds are obtained. The ratios of the integrated luminescence intensities of europium and terbium ions are calculated as functions of temperature. It has been found that the luminescence lifetime of europium and terbium ions in solution at the recording wavelengths of europium and terbium (615 and 545 nm) does not depend on the mixing order of the ligand, europium, and terbium. Also, based on the experimental data, a conclusion is made that the luminescence lifetime remains unchanged in the temperature range from 20 to 60°C.

Keywords: luminescence, organic ligands, europium, terbium, lanthanides, temperature sensor.

1. Introduction

The study of complexes of rare earth elements (REE) with N-heterocyclic ligands based on $2,2'$-bipyridyldicarboxamides is a relevant task. Compounds of this type can have temperature-sensitive luminescence spectra and, due to this, are promising in practical applications, such as, for example, optical thermometers, radiation detectors of various nature, analytical reagents [1,2]. Due to the antenna effect, i.e. the attachment of chelate ligands to the REE ion with the formation of coordination bonds, luminescent parameters of REE ions can be improved: the extinction coefficient can be increased, as well as the efficiency of the ion luminescence excitation [3]. Therefore, organic ligands based on $2,2'$-bipyridyl are promising compounds for studying the luminescent properties of REE complexes and producing highly sensitive luminescent sensors based on them [3,4]. Also due to the formation of coordination bonds in REE complexes with ligands on the basis of $2,2'$-bipyridyldicarboxamides, it is possible to accurately select optical parameters taking into account changes in the structure of the nearest environment of the metal [5]. Also, complexes of such ligands with REE ions are of interest as potential luminescent materials [6], whose properties depend on the ligand molecule substitution with the amide part [7].

In REE complexes with organic ligands, the luminescence occurs due to the absorption of light by the organic part (ligind) and the transfer of photoexcitation energy to the REE ion, and is emitted in the form of a spectral line of the ion. Such complexes exhibit high stability, good solubility in organic solvents or water (depending on the type of ligand), intense luminescence with a high quantum yield, and long luminescence duration.

Trivalent europium ions have narrow spectral lines in the red wavelength range, and also have a relatively large energy difference between their resonant and ground levels, which provide radiation in the visible range [8]. This provides a good opportunity for a theoretical description of the processes occurring in materials containing europium ions.

The emission bands of trivalent terbium ions have narrow spectral bands in the green wavelength range, and all its emission bands do not show high sensitivity outside the first coordination sphere [9]. In earlier studies, it was found that trivalent terbium ions in the composition of salts of unsaturated acids have a temperature dependence of luminescence that is atypical for most rare earth elements: in negative temperature ranges, when heated to room temperature, the luminescence of terbium increases [10].

In the literature, the luminescent properties of compounds of rare earth metals and organic ligands have been studied quite extensively. Currently, the luminescent

properties of such complexes have been studied at negative temperatures [1,11]. For example, in combination with europium and terbium bimetallic fluorides, the luminescence lifetime at negative temperatures decreases with an increase in the percentage of europium in the solution and changes almost linearly [1]. Also, Tb^{3+} compounds have a more complex temperature behavior of luminescence compared to Eu^{3+} complexes in the negative temperature range [10].

Currently, the main characteristics of luminescence for compounds of europium, terbium and organic ligands are known for the range from extremely low temperatures (25 K) to room temperature (300 K), as well as at temperatures much higher than the physiological range [12,13]. An important feature of such complexes is the temperature-dependent luminescence. In this temperature range, the emission intensity of europium and terbium at excitation wavelengths of 615 and 545 nm, respectively, is inversely proportional to the temperature [12]. Between Eu^{3+} and Tb^{3+} ions, the energy transfer takes place, which increases with increasing temperature. The main mechanism underlying the temperature-dependent energy transfer between Eu^{3+} and Tb^{3+} ions is the Förster energy transfer.

The role of ligands in the luminescence of REE complexes is also very important. Rare-earth metal ions themselves have a very low luminescence intensity because they have low extinction coefficients. The attachment of ligands with high extinction coefficients to rare-earth metal ions due to the antenna effect makes it possible to solve the problem of low luminescence intensity of metals. Also, the role of the ligand is to shield the lanthanide ion from the solvent in order to avoid the processes of nonradiative energy deactivation [14].

Intramolecular energy transfer in solutions containing lanthanide ions or complexes can occur from singlet or triplet excited states of organic molecules to lanthanide ions or chelates, from excited lanthanide ions to organic molecules or to other lanthanide ions. In [15] it was suggested that the mechanism of excitation of trivalent lanthanide ions is a diffusion-controlled collision process. According to this mechanism, the energy from the lowest triplet state populates one of the levels of the lanthanide ion through an intermediate level, which subsequently results in the luminescence. The purpose of this work is to study the luminescence characteristics of complexes composed of diamide L containing additional donor centers in the amide fragment for the coordination of f-element ions, europium and terbium in a wide temperature range $(20-60°C)$ and the search for mechanisms of temperature changes in the luminescence in such complexes.

2. Subjects of the study and methods of investigation

In this study, the luminescence characteristics of solutions of diamide L, europium, and terbium are compared at different mixing orders with an excess of REE ions, as
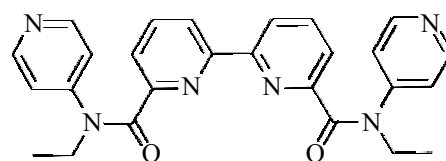

Figure 1. Structure of N, N'-diethyl-N, N'-di(pyrid-4-yl)diamide 2, 2′-bipyridyl-6, 6′-dicarboxylic acid L.

well as a comparison is carried out between the spectra for solutions of diamide L and europium, diamide L, and terbium and pure solutions of europium and terbium. The structure of the diamide L used is shown in Fig. 1 (the synthesis of the ligand is described in [16]).

For the studied solutions, the absorption spectra, emission spectra, luminescence excitation spectra (in modes without time delay and with time delay), phosphorescence kinetics (phosphorescence kinetics was averaged over five measurements for each temperature point) were measured. The measurements were carried out in the temperature range from 20 to 60°C, where the recording started from 20°C and the spectra were recorded every 5°C.

The absorption spectra were recorded using a Solar PB2201 spectrophotometer. Luminescence spectra and luminescence decay kinetics were recorded by a Solar CM2203 spectrometer under excitation by light with a wavelength of 320 nm. To maintain the required temperature of the under-study solution in the range from 20 to 60°C, a thermostated cell compartment was used.

Luminescence spectra were recorded using solutions of diamide L, europium nitrate hexahydrate, and terbium nitrate pentahydrate in acetonitrile (with concentrations of $3 \cdot 10^{-5}$ mol/l), which were mixed in the ratio of 1 : 1 : ,1 at different sequence of addition of europium and diamide solutions. The mixture was prepared immediately before the study.

The luminescence quantum yield was determined by the reference dye method, where the reference luminescence quantum yield (Φ_{et}) was taken to be the luminescence quantum yield of a solution of the ligand and europium in acetonitrile with a concentration of $1 \cdot 10^{-5}$ mol/l (notation: „L : Eu") [16]:

$$\Phi = \frac{I_x}{D_x} \frac{D_{et}}{I_{et}} \Phi_{et}.$$

Here I_x and I_{et} are integrated luminescence intensities of the solutions of the studied sample and the reference sample, respectively, D_x and D_{et} are optical densities of the solutions of the studied sample and the standard, respectively, at the excitation wavelength.

Due to the fact that the phosphorescence kinetics turned out to be monoexponential, the luminescence lifetime was calculated from the data on the phosphorescence kinetics:

$$I_{FF} \sim \exp\left(-\frac{t}{\tau}\right),$$

where I_{FF} is luminescence intensity at time t, τ is luminescence lifetime. This value was used to find the luminescence
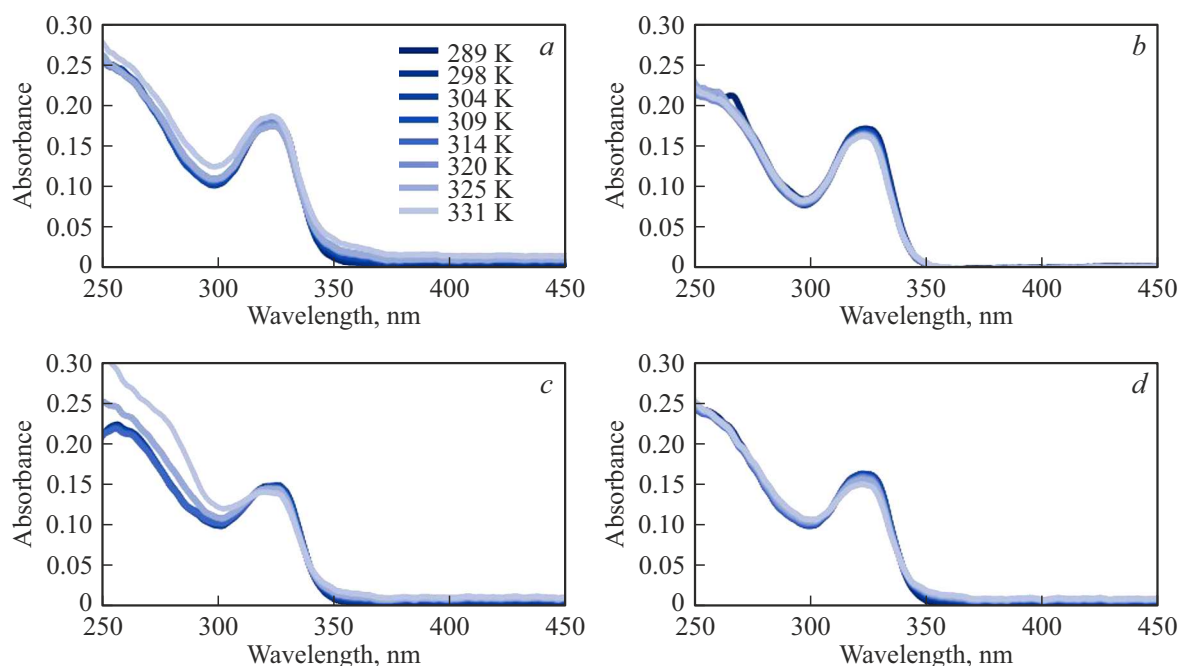
Figure 2. Absorption spectra of solutions in a temperature range of $280-330$ K: a — absorption spectrum for a solution of diamide, europium, terbium (notation: L : Eu : Tb, where the order of substances in the notation coincides with the order of mixing when preparing the solution), b — for L : Tb : Eu, c — for L : Eu (a mixture of diamide, europium and acetonitrile in equal proportions), d — for L : Tb (similar to the L : Eu solution).

lifetime as a quantity inverse to the slope coefficient of the graph of the time-dependence of the phosphorescence intensity logarithm:

$$\tau = \frac{1}{A}, \quad A = \frac{\ln(I_{FF})}{t}.$$

3. Experimental results

3.1. Absorption spectra

The absorption spectra of the studied solutions have a broad peak in the region of $325-330$ nm, which corresponds to the absorption of light by the ligand in the complex with the lanthanide ion [7]. Thus, it can be argued that when the solutions of diamide, europium nitrate hexahydrate, and terbium nitrate pentahydrate were mixed, the complexation took place, i.e. the studied solutions contained europium and/or terbium complexes in their composition.

According to the experimental data, the absorption capacity of the studied substances is almost independent on the sequence of mixing europium and terbium with diamide. (Fig. 2, *a, b*). Fig. 2, *c, d* shows similar absorption spectra of europium and terbium solutions with diamide (i.e. solutions of europium and terbium complexes). It is clearly seen that the difference between them and the spectra of the two previous samples is weak.

Based on the data obtained, it can be concluded that even if the excess (compared to the ligand) lanthanide

ions present in the solution are able to coordinate with the already formed europium and/or terbium complexes, then the complexation constant for these tertiary complexes is low (lower than 1000), which leads to a very low concentration of such tertiary complexes in the solution and, consequently, very weak changes in the absorption spectra.

When the temperature of the studied samples changes, no noticeable changes take place in the absorption spectra of all four studied solutions. This is indicative of the fact that temperature variation in the range of $20-60°$C has little effect on the absorption capacity of lanthanide complexes.

3.2. Luminescence emission spectra

Luminescence emission spectra of solutions of ligands with europium and terbium ions were obtained (Fig. 3). The luminescence spectra of europium complexes in a range of $450-720$ nm include typical bands corresponding to transitions from the level $^5D_0$ to levels ^7F_J, where $J = 0-4$ (with peaks at wavelengths in the regions of $570-585$, $585-600$, $610-630$, $640-660$ and $680-710$ nm, respectively) [17]. The luminescence spectra of terbium complexes contain lines corresponding to transitions from the level $^5D_4$ to levels ^7F_J, where $J = 6-3$ (with peaks at wavelengths in the regions of $485-500$, $540-555$, $580-595$ and $615-625$ nm, respectively) [12,18].

If the solution simultaneously contains ions of both types (europium and terbium), the luminescence emission spectrum of such a sample simultaneously contains luminescence bands of both ions.
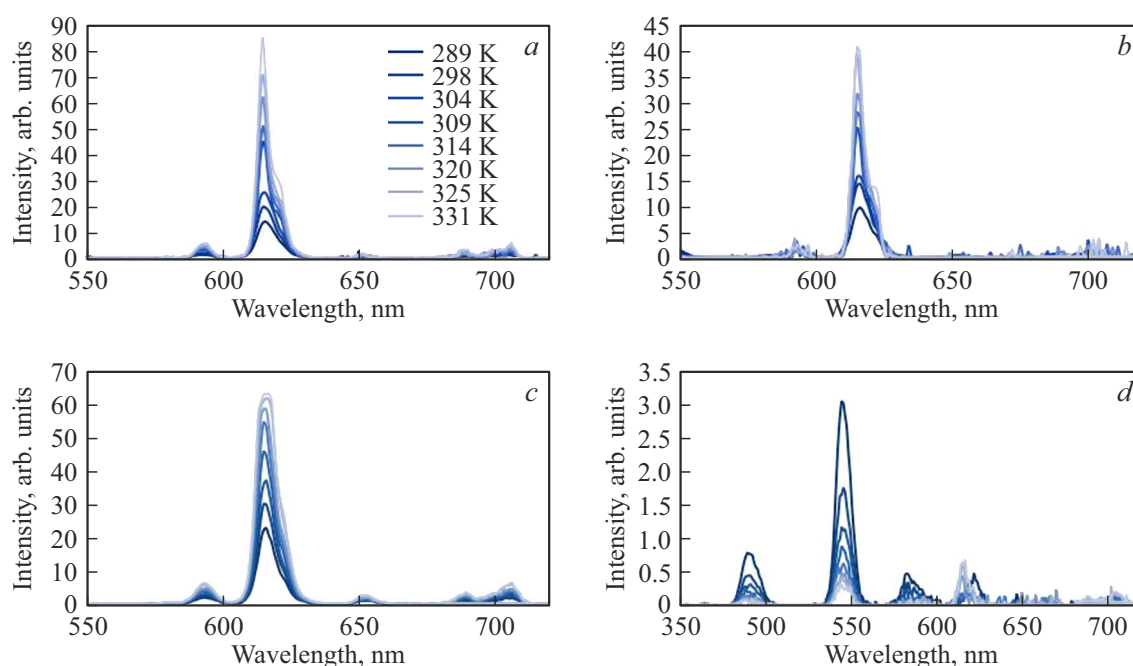
Figure 3. Luminescence emission spectra of solutions: a — L:Eu:Tb, b — L:Tb:Eu, c — L:Eu, d — L:Tb in the temperature range of $280-330$ K, measured in the phosphorescence mode (i. e. with a time delay).

It follows from Fig. 3, *a, b* that when changing the order of mixing the solutions from „diamide←europium←terbium" to „diamide←terbium←europium" the luminescence intensity of europium ion with a peak at 615 nm corresponding to the energy transition $^5D_0 \rightarrow {}^7F_2$ is about 2 times less than that in the first case, and the luminescence intensity of the terbium ion at 545 nm corresponding to the $^5D_4 \rightarrow {}^7F_5$ energy transition, is only slightly lower. A likely cause for the change in the photophysical properties upon changing the mixing order of the reagents is the formation of tertiary complexes due to the coordination of the lanthanide ion with additional pyridine donor centers in the amide fragments of the ligand already complexed with another ion.

It follows from Fig. 3 that as the solution temperature increases, the europium luminescence intensity increases in all solutions, while the terbium luminescence intensity decreases. Such a temperature-dependent increase in the luminescence intensity of europium was also observed in earlier studies of REEs, and this was called the effect of temperature enhancement of luminescence [19,20]. In [19] it has been found that in europium carboxylates the enhancement in the intensity of europium luminescence is associated with an increase in the concentration of the radical anion of the neutral ligand due to an increase in the time of UV irradiation.

In [20], where the luminescence of Eu^{3+} in trifluoroacetates was studied, it has also been found that the effect of the enhancement of europium luminescence is associated with an increase in the irradiation time. The cause was an increase in the free radical signal of the neutral ligand. In this case, electrons from the Eu^{2+} ions transferred to the

ligand radical, thereby increasing the concentration of the radical and the number of Eu^{3+} ions in the excited state and leading to an increase in the luminescence intensity. Since studies [19,20] were carried out at low temperatures (~ 77 K), then in the case of our study, it is impossible to state exactly about the similar effect of irradiation time on the luminescence build-up, therefore in the future, this effect should be refined for our experimental conditions (Fig. 3).

3.3. Luminescence excitation spectra

In the course of the experiment, the luminescence excitation spectra of terbium ions (with recording at 545 nm) and europium ions (with recording at 615 nm) in solutions were obtained (Fig. 4). On the one hand, the excitation spectra of europium and terbium ions have significant differences: in the case of recording at 615 nm, the intensity of the excitation light flux in a range of $250-350$ nm is approximately 10 times higher than at a recording wavelength of 545 nm. This indicates a difference in the processes of energy transfer to different ions in the solutions under study. On the other hand, neither the order of mixing the solutions (Fig. 4, *a, b*), nor the absence of the second ion in the solution (Fig. 4, *c, ,d*) generally has an effect on the shapes of the luminescence excitation spectra, which is indicative of the fact that the processes of energy transfer to the same lanthanide ions occur in a similar way in all the samples under study.

It can also be seen from the graphs that the luminescence excitation spectra of the terbium ion are similar in shape to the absorption spectra of the same solutions (Fig. 4, *b, d* and Fig. 2, *b, d*). It has been established that changes
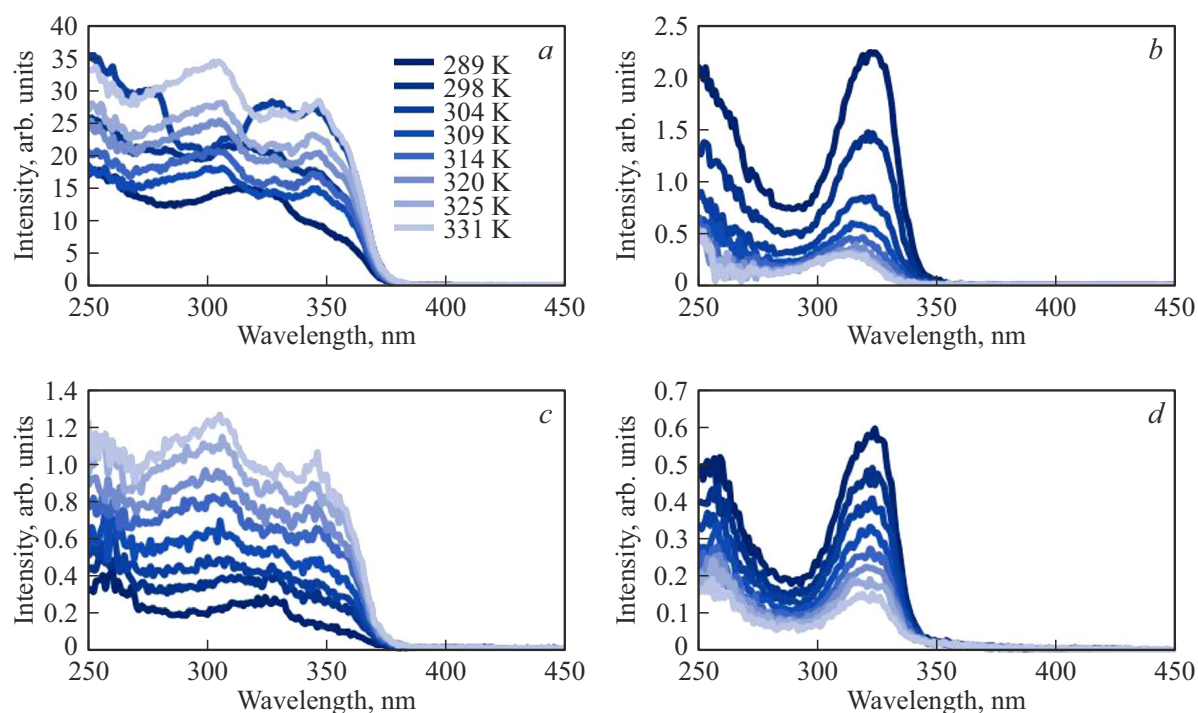
Figure 4. Luminescence excitation spectra of solutions: a, b — L:Eu:Tb; c, d — L:Tb:Eu in a temperature range of $280-330$ K. Recording wavelength: a, c — 615 nm; b, d — 545 nm.

in the luminescence intensities in the excitation spectra of europium and terbium ions with a change in the temperature of the solutions are similar to changes in the luminescence emission spectra.

3.4. Phosphorescence lifetimes

Fig. 5 shows temperature dependences of the phosphorescence lifetimes of europium and terbium ions in the solutions under study. A dependence of the luminescence lifetime of europium and terbium ions in complexes with the studied ligand was found (Fig. 5, c, d). The phosphorescence lifetime of a solution of the europium complex (ligand←europium) decreases from 1.8 to 1.5 ms upon heating in a temperature range of $290-330$ K, however, for the terbium complex, an inverse dependence of this parameter was found: the lifetime increases from 2.5 to 5.6 ms upon heating in the same temperature range. On the other hand, the phosphorescence lifetimes of europium and terbium ions for solutions containing both europium and terbium ions are almost independent on the solution temperature. Also, the mixing order does not affect the phosphorescence lifetime of both ions. (Fig. 5, a, b).

3.5. Quantum yield of luminescence

The dependences of the quantum yield of the luminescence of solutions are shown in Fig. 6. The luminescence quantum yield for solutions of diamide, eu-

ropium, and terbium increases with increasing temperature (Fig. 6, a). When the mixing order L:Eu:Tb→L:Tb:Eu is changed, the quantum yield remains nearly unchanged with increasing temperature (Fig. 6, b). Such dependences can be related to the features of the luminescence emission spectra of these solutions: when changing the mixing order L:Eu:Tb→L:Tb:Eu the maximum intensity of europium and terbium luminescence decreased by about 2 times (from ~ 80 to 40 arb.units for europium luminescence, from ~ 8 to 4 arb.units for terbium).

The luminescence quantum yield of the solution of europium complex linearly increases upon heating, which corresponds to the dependence of the luminescence intensity of this sample on temperature (Fig. 6, c). The luminescence quantum yield of the terbium complex, on the contrary, decreases linearly with increasing temperature, which is probably due to the reverse energy transfer from the terbium ion to the ligand (Fig. 6, d).

3.6. Intensity ratio of europium and terbium phosphorescence bands

In order to understand how the luminescence intensities of europium and terbium correlate with each other, the ratios of intensity of the luminescence bands of europium and terbium were calculated depending on temperature. To calculate the intensity ratio of the bands, the values of the integral intensities were taken from Fig. 3, a, b.
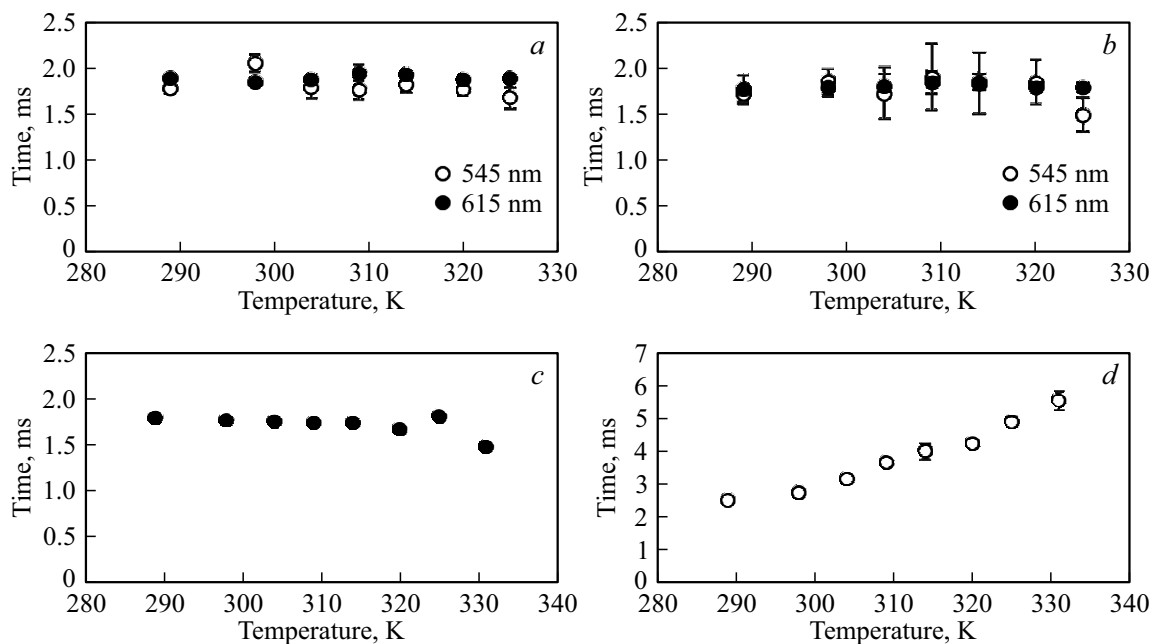
Figure 5. Dependences of the phosphorescence lifetime of solutions: a — L:Eu:Tb, b — L:Tb:Eu, c — L:Eu, d — L:Tb on temperature in a temperature range of 280−330 K. Recording wavelengths: a, b — 615 and 545 nm; c — 615 nm; d — 545 nm.
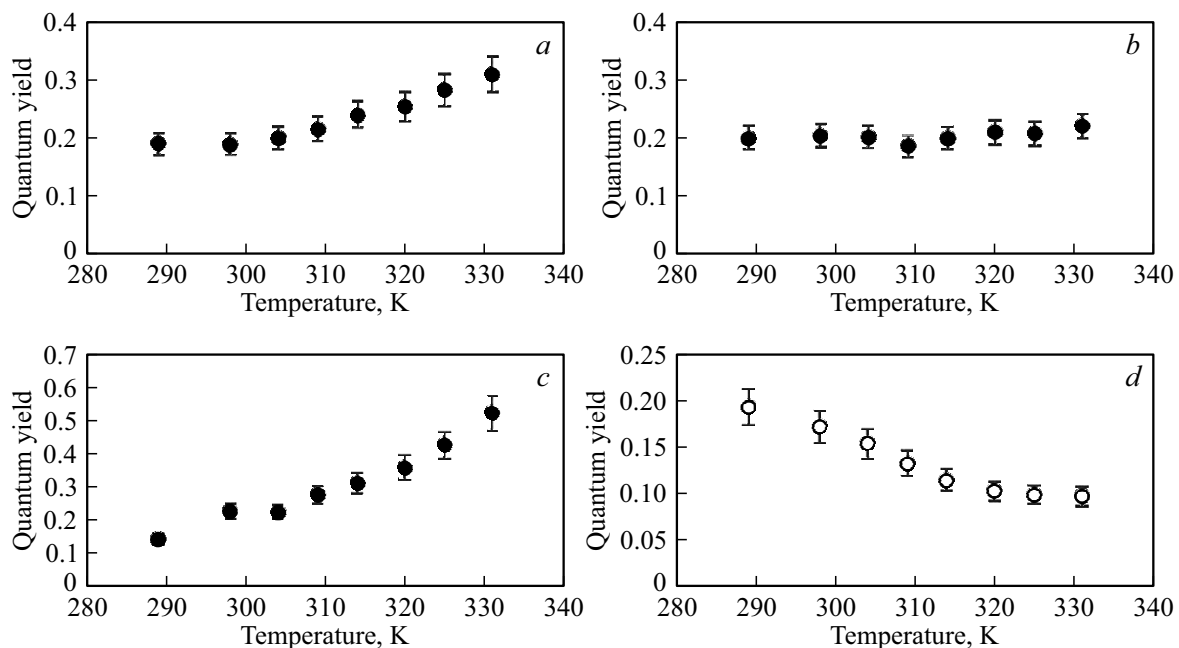

Figure 6. Dependence of the luminescence quantum yield of solutions: a — L:Eu:Tb, b — L:Tb:Eu, c — L:Eu, d — L:Tb on temperature in a temperature range of 280−330 K.

It follows from Fig. 7 that as the temperature increases, the intensity ratio of the bands increases because the europium luminescence intensity increases and the terbium intensity decreases. In the case of fluorescence (Fig. 7, a) this dependence is very similar to a linear one. When the mixing order is changed (L:Eu:Tb→L:Tb:Eu), the ratio of fluorescence bands decreases approximately by a factor of 2 for corresponding temperature points. This is indicative

that the binding of diamide and europium, diamide and terbium molecules in solution occurs in different ways.

In the case of the ratio of phosphorescence bands, no explicit correlation between the two dependences is observed, therefore, according to the data in Fig. 7, b, it can be only said that the temperature leads to an increase in the difference between the europium and terbium phosphorescence intensities.
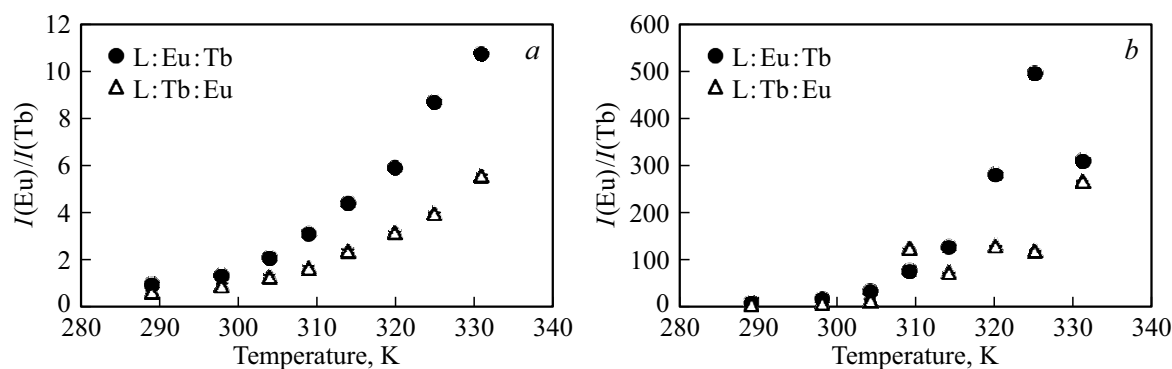
Figure 7. Temperature dependence of the ratio of intensities of the luminescence bands of europium and terbium ions in solutions of diamide, europium and terbium with different orders of addition of europium and terbium in a temperature range of 280−330 K (when measured in the mode of: *a* — fluorescence (i.e. without time delay), *b* — phosphorescence (i.e. with time delay)).
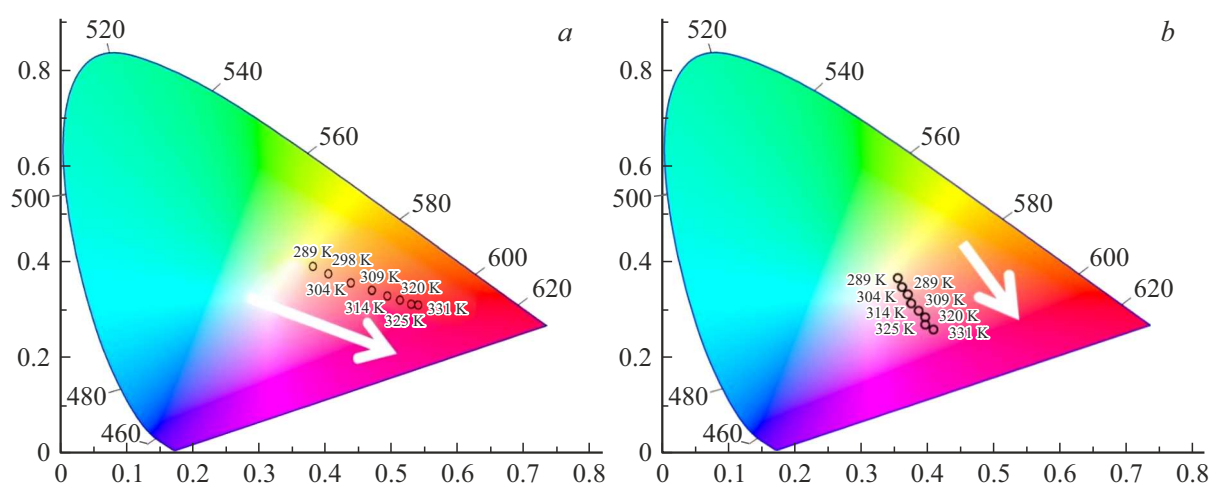

Figure 8. CIE diagram showing the change in color of light emission when observing the luminescence of solutions at different temperatures for samples: *a* — L:Eu:Tb, *b* — L:Tb:Eu.

3.7. Chromaticity diagram

The CIE chromaticity diagram is very useful for absolute and quantitative comparison of emission colors [21]. In our case, it allowed for qualitative estimation of the contribution of europium and terbium ions in the complex to the luminescence, which is important for a fundamental understanding of the processes of energy transfer between REE ions. It was also important for us to obtain a qualitative estimation of the effect of temperature on the color of the radiation, which is of practical interest for the use of these complexes as organic luminescent sensors [22].

To estimate the relationship between the distributions of wavelengths in the electromagnetic visible spectrum for the solutions of diamide, europium and terbium, the radiation coordinates in the CIE chromaticity diagram (Fig. 8) are calculated [12]. In the process of heating the solution, the color of the radiation changes from yellow to crimson; this occurs due to an increase in the luminescence intensity of europium and a decrease in the intensity of terbium. Changing the mixing order affects the change in the color of the luminescence depending on the temperature.

In the case of L:Eu:Tb (Fig. 8, *a*) the color changes from orange to almost red, which is due to the large contribution of europium to the emission spectrum, and in the case of L:Tb:Eu (Fig. 8, *b*) it changes from yellow to crimson, because despite the large luminescence intensity of europium, at temperatures close to room temperature the contribution of the terbium ion luminescence is significant.

As a result of the experiments, the temperature dependences of the luminescence spectra were found. It is shown that the absorption spectra of solutions remain almost unchanged with increasing temperature (Fig. 2). It can be seen from the luminescence emission spectra that the luminescence intensity of terbium (emission intensity at 545 nm) decreases with increasing temperature, while for europium (luminescence at a recording wavelength of 615 nm) it varies in direct proportion to temperature (Fig. 3, *c, d*).

Thus, the temperature enhancement of the europium luminescence was found. Such an effect is presumably due to the direct influence of temperature and (or) an increase in the irradiation time, which can lead to a change in the

intramolecular structure of the ligand and an increase in the number of Eu^{3+} ions, a change in the rate of energy transfer between europium and terbium in the solution.

4. Conclusion

The order of mixing of the ligand, europium, and terbium has almost no effect on the shape of the absorption spectra and luminescence excitation spectra, as well as on the luminescence lifetimes of two-center REE complexes with N-heterocyclic ligands at an excess of metal ions with respect to the ligand. Therefore, the binding of the ligand to the Eu^{3+} and Tb^{3+} ions occurs in a similar way. We believe that associates of europium or terbium complexes, which contain several ligand molecules, are not formed in these solutions because when the concentration of any of the components changes, the Bouguer−Lambert−Beer law is fulfilled, i. e. the optical density at the absorption wavelength of the complex is directly proportional to the concentration of the component (according to the data not included in the article). As a result of mixing the solutions in different sequences, complexes with the ion contained in the first added salt predominate in the solution, while the ion of the second added salt almost does not enter into the complexation reaction with the ligand. Changing the sequence of mixing the components of the solution made it possible to obtain two different solutions with different radiation characteristics.

When studying the temperature dependence of luminescence, it was found that the luminescence lifetimes of the solutions of diamide, europium, and terbium remain nearly unchanged with temperature variations. The absorption spectra of the solutions of the complexes remain almost unchanged with increasing temperature, while the intensity of the luminescence of REE ions turned out to be the most sensitive parameter to temperature changes. The luminescence intensity of terbium (545 nm) decreases with increasing temperature. This is due to the reverse charge transfer from the terbium ion to the ligand with increasing temperature. The luminescence intensity of europium (615 nm), on the contrary, increases linearly with temperature, which is probably due to the relaxation of the high-energy levels of the europium ion (^5D_j, $^5L_6$ and others) through the charge transfer state [10]. A change in temperature has no effect on the energies of the singlet level of the ligand, as well as the rate of energy transfer processes between the levels of REE ions, therefore, the absorption spectra and luminescence lifetimes of the compounds remain unchanged.

In the process of heating the solution of complexes, the color of the radiation changes from yellow to crimson; this occurs due to an increase in the luminescence intensity of europium and a decrease in the intensity of terbium and is reflected on the chromaticity diagram.

Based on the measurements, it was assumed that these compounds are potentially applicable for luminescent temperature sensors, molecular thermometers, because they show temperature-dependent behavior of luminescence and have pronounced linear temperature dependences of the ratio of luminescence band intensities, which can be used as a measurement parameter.

Conflict of interest

The authors declare that they have no conflict of interest.

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