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# Photoluminescence of Lanthanide Aromatic Carboxylates

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**Abstract**—Energy transfer processes affecting the luminescence properties and methods of controlling them by a change in the compositions and structures of luminescent compounds are analyzed in the review on example of lanthanide aromatic carboxylates. The analysis demonstrates clearly how the understanding of the physical regularities of the processes leading to luminescence makes it possible to perform the purposeful design of organic ligands and their brightly luminescing complexes with lanthanides.

**Keywords:** lanthanide aromatic carboxylates, mixed ligand complexes, bimetallic complexes, luminescence
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A luminescence phenomenon finds an increasing number of applications in the modern world. Coordination compounds of lanthanides, whose luminescence is caused by *f–f* transitions inside individual ions, occupy a special place among luminescent compounds. The geometry of the molecule remains almost unchanged upon excitation due to a strong shielding of the 4f shell of lanthanides by the external crystal field of ligands, and the shape of the luminescence spectrum is nearly independent of the nature of ligands except for the Stark splitting of bands caused by the splitting of the *J* levels by the crystal fields of ligands [1]. The spin-orbit coupling in lanthanide ions substantially exceeds the value of the crystal field and, therefore, the spectrum of the lanthanide compounds is quasi-monochromatic and corresponds to transitions between the states with different values of total angular moment *J* inside the shielded *f* shell (Fig. 1).

Although luminescence of inorganic salts was discovered in 1908, its significance was not evaluated for a long time because of a low intensity caused by a low absorbance induced by the forbiddance of *f–f* transitions. The use of coordination compounds with an organic ligand capable of efficient absorbing the energy and transmitting it to the excited level of lanthanide from which luminescence occurs makes it possible to avoid the direct excitation of the lanthanide ion forbidden by selection rules [2]. The discovery of this phenomenon, namely, sensitization of the luminescence of the lanthanide ion by the organic ligand or "antenna effect," resulted in the obtaining of coordination compounds of lanthanides, whose luminescence by orders of magnitude exceeded that of inorganic salts by brightness. This was a reason for inextinguishable interest in luminophores based on compounds of this class.

A rich experience was accumulated from the moment of "antenna effect" discovery in studying the luminescence properties of coordination compounds of rare-earth elements with ligands of different classes, including β-diketonates [3–6] and related acyl pyrazolonates [7–10] and phosphoryl phenolates [11–13], complexes with Schiff bases [14–18], and aromatic carboxylates [19–26]. However, a complex analysis of the accumulated data is often impeded because of a huge number of factors affecting the luminescence properties. One of classes of compounds that are convenient for this analysis is composed of rare earth element aromatic carboxylates known by the high stability and intense luminescence. On the one hand, aromatic carboxylate anions, consisting of the aromatic ring with one or more carboxyl groups, provide a possibility of the introduction of substituents with different electron natures into the ring and of heteroatoms into the aromatic ring, which directly affect the structure and properties of the formed complex. On the other hand, aromatic carboxylate anions in tris(carboxylates) cannot provide the saturation of the coordination sphere of lanthanide ions, which allows the introduction of an additional neutral ligand and the further purposeful variation of the luminescence properties. This synthetic approach is widely known in the coordination chemistry of rare-earth elements as the formation of mixed-ligand complexes.

Design of organic ligands, which can purposefully result in the synthesis of brightly luminescing compounds, requires the understanding of the physical regularities of the luminescence properties of the coordination compounds of lanthanides. The Jablon-

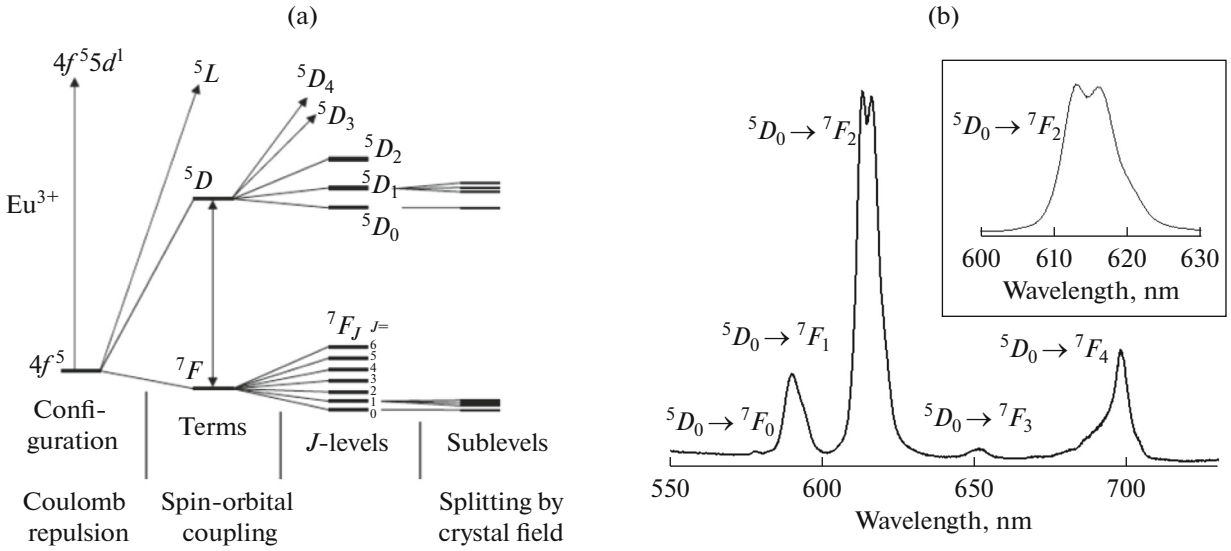



**Fig. 1.** (a) Energy structure of the europium ion taking into account various factors (interelectron repulsion, spin-orbital coupling, and crystal field of ligands); (b) the luminescence spectrum of europium tetrafluorobenzoate (the bands correspond to the transitions between the *J* levels; the band splitting corresponds to the splitting of the *J* levels by the crystal field). Insert: Stark splitting of the band $^5D_0 \rightarrow {}^7F_2$.

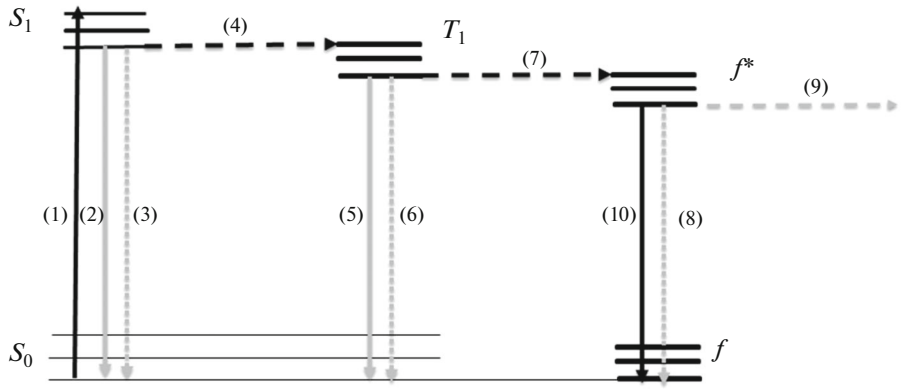



**Fig. 2.** Jablonski diagram for the lanthanide coordination compounds.

ski diagram (Fig. 2) shows the main energy transfer processes that can occur in the rare-earth element coordination compounds during luminescence: energy absorption by the organic ligand (**1**), fluorescence of the ligand (**2**), nonradiative relaxation of the singlet excited state of the ligand (**3**), intersystem crossing (**4**), phosphorescence of the ligand (**5**), nonradiative relaxation of the triplet excited state of the ligand (**6**), sensitization of the lanthanide ion (**7**), nonradiative relaxation of the excited state of lanthanide (**8**), other routes of quenching of the excited state of lanthanide (**9**), and luminescence of lanthanide (**10**).

The goal of this review is to analyze the role of processes (1)–(10) using our and literature data and to show methods for changing their contributions to the photoluminescence of rare-earth element coordination compounds using aromatic lanthanide carboxylates as examples, the variability of which makes it possible to control their role in the general scheme in Fig. 2.

**Excitation (1).** Brightness of luminescence (*B*) is the most important characteristic for any practical application. The value of *B* is directly proportional to the number of emitted photons

$$B = \frac{dI}{d\sigma \cos\alpha}, \quad (1)$$

$$I = \frac{d\Phi}{d\Omega} = \frac{d^2Q}{dtd\Omega}, \quad (2)$$

**Table 1.** Photometric characteristics of selected compounds

| No. | Compound | $\lambda_{max}$, nm | ε, $cm^{-1}$ $mol^{-1}$ L |
|---|---|---|---|
| 1 | Benzene | 225 | 180 |
| 2 | Naphthalene | 286 | 360 |
| 3 | Anthracene | 375 | 7100 |
| 4 | Tetracene | 477 | 110000 |
| 5 | Pyrene | | 54000 |
| 6 | Ethylene | 171 | 15530 |
| 7 | 1-Octene | 177 | 12600 |
| 8 | *trans*-2-Hexene | 184 | 10000 |
| 9 | Cyclohexene | 182 | 7600 |
| 10 | Sodium *p*-azidotetrafluorobenzoate | 255 | 15700 |
| 11 | Sodium *p*-(methoxycarboxyl)tetrafluorobenzoate | 282 | 3220 |
| 12 | Sodium pentafluorobenzoate | 260 | 608 |
| 13 | Potassium *p*-aminotetrafluorobenzoate | 249 | 3380 |
| 14 | Sodium *p*-(hydroxymethyl)tetrafluorobenzoate | 270 | 764 |
| 15 | Sodium benzoate | 267 | 2640 |
| 16 | 1,10-Phenanthroline | 264 | 31000 |
| 17 | 2,9-Diphenyl-1,10-phenanthroline | 306 | 29500 |
| 18 | 2,9-Dianizyl-1,10-phenanthroline | 323 | 32900 |
| 19 | 4,7-Diphenyl-1,10-phenanthroline (bathophenanthroline) | | 22350 |
| 20 | Tris(4,7-diphenyl-1,10-phenanthroline)ruthenium(II) | | 30000 |

$$Q = K_m \int_{380\ nm}^{780\ nm} Q_\lambda(\lambda)V(\lambda)d\lambda, \quad (3)$$

where $I$ is the luminous intensity, $d\sigma\cos\alpha$ is the projection of the surface with the incident light, $\Phi$ is the luminous flux, $\Omega$ is solid angle, $t$ is time, $Q$ is the radiation energy, $K_m$ is the maximum luminous efficiency of radiation, $V(\lambda)$ is the relative spectral luminous efficiency of the monochromatic radiation for daylight vision, and $Q_\lambda(\lambda)$ is the luminous energy depending on the number of emitted photons [27].

It follows from the definition of the photoluminescence quantum yield, which is equal to the ratio of the number of emitted photons to the number of absorbed photons, that the higher the absorption and quantum yield, the higher the number of emitted photons. Therefore, it is convenient to choose luminosity ($L$) as a characteristic of brightness

$$L = \varepsilon \times \mathrm{PLQY}, \quad (4)$$

where ε is the molar absorption coefficient characterizing absorption, and PLQY is photoluminescence quantum yield. Therefore, the design of new luminophores should be aimed at both enhancing their quantum yield (efficiency of radiative relaxation of the excited state) and increasing the absorption, i.e., efficiency of their transition to the excited state.

The values of ε for organic compounds are known to be higher by orders of magnitude ($\varepsilon \approx 10^3$–$10^5$ $cm^{-1}$ $mol^{-1}$ L [28]) than those for lanthanide ions ($\varepsilon < 12.5$ $cm^{-1}$ $mol^{-1}$ L [29, 30]). This results in the situation where at comparable quantum yields the luminosity of coordination compounds of lanthanides with organic ligands is considerably higher than that of their inorganic salts. However, the values of ε for various organic compounds differ by several orders of magnitude. To increase them, one should understand the factors affecting ε.

In the case of aromatic compounds, among these factors are, first, the extension of the conjugation degree of the aromatic ring: both the energy of the excited state and the molar absorption coefficient change on going from benzene to naphthalene, anthracene, and tetracene (Table 1, nos. 1–4; Fig. 3) [31, 32].

The second, less efficient method for enhancing absorption is the introduction of various substituents into the aromatic ring. An appreciable change in ε can be achieved only in the case where the introduced substituent participates in conjugation [28] while the introduction of unconjugated aliphatic (Table 1, nos. 6–7) and even aromatic (Table 1, nos. 16, 17, and 19) substituents exerts a noticeably lower effect and can even decrease absorption [33]. It should be taken

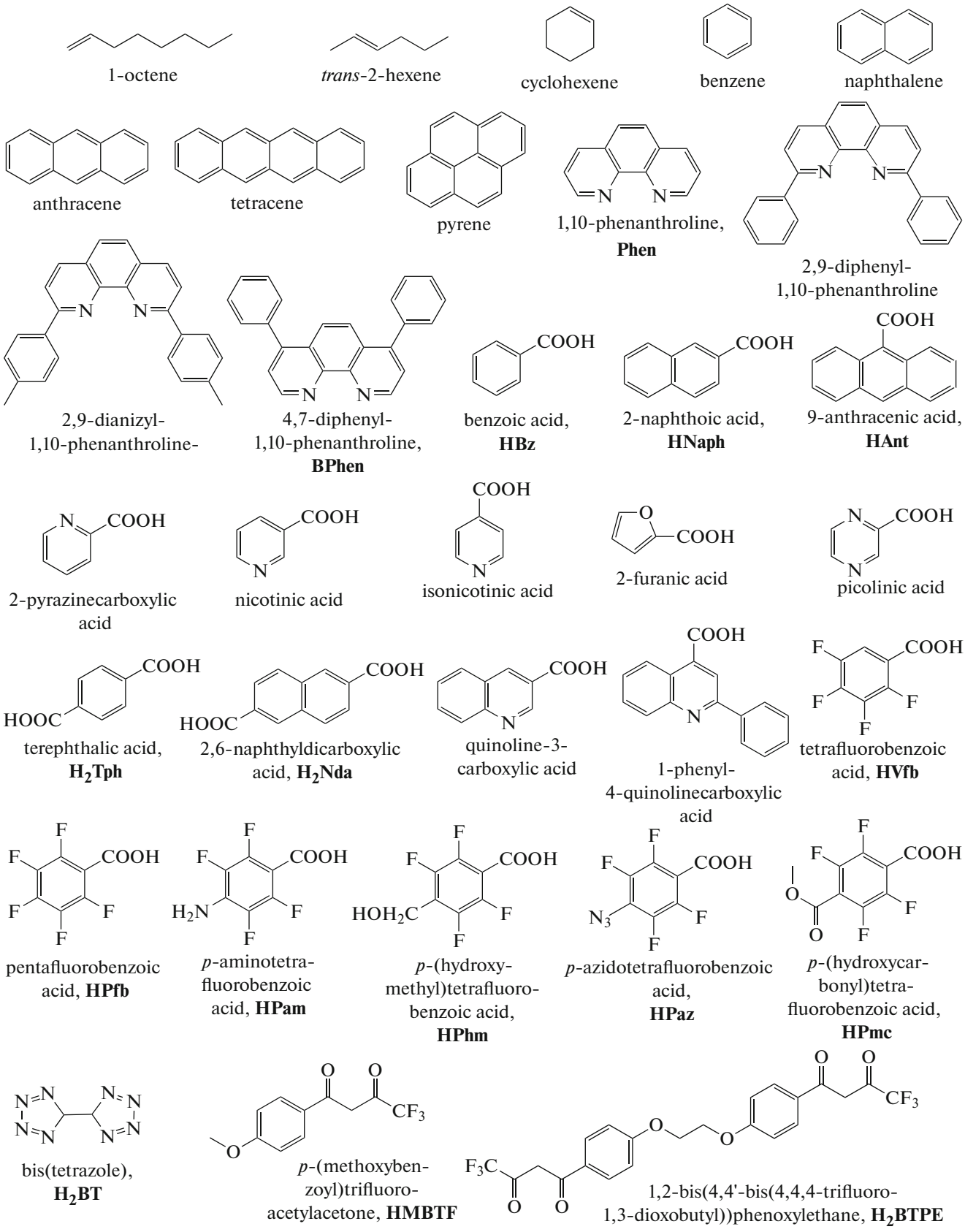



**Fig. 3.** Structural formulas of the organic compounds presented in the text.

**Table 2.** Luminescence characteristics of selected terbium complexes

| Compound | $\varepsilon_L$, $cm^{-1}$ $mol^{-1}$ L | PLQY, % | $L$, $cm^{-1}$ $mol^{-1}$ L |
|---|---|---|---|
| $Tb(Paz)_3(H_2O)_2$ | 15700 | 0 | 0 |
| $Tb(Pmc)_3(H_2O)_6$ | 3220 | 62 | 2000 |
| $Tb(Pfb)_3(H_2O)$ | 608 | 38 | 230 |
| $Tb(Pam)_3(H_2O)_4$ | 3380 | 14 | 470 |
| $Tb(Phm)_3(H_2O)_4$ | 764 | 36 | 275 |
| $Tb(Bz)_3(H_2O)_2$ | 2640 | 100 | 2600 |

into account that the absorption of various isomers can also differ (Table 1, nos. 7–9).

The influence of the substituents in the benzene ring on the absorption coefficient of the ligand and luminosity of the lanthanide complexes can be monitored for *para*-substituted terbium benzoates compared with benzoate and pentafluorobenzoate. The absorption spectra of dilute solutions of sodium or potassium salts of the corresponding acids were studied to determine ε (Table 1, nos. 10–15). It turned out that ε decreases more than fourfold on going from NaBz to NaPfb due to the replacement of the hydrogen atoms by fluorine atoms. The introduction of substituents capable of participating in conjugation, namely, $NH_2$, $N_3$, and $C(O)OCH_3$ groups, into the *para*-position of the fluorinated ligand increases the value of ε by 5–25 times, whereas the introduction of the hydroxymethyl group exerts almost no effect on ε (Table 2, Fig. 3).

As a result, the values of $L$ for the $Tb(Pmc)_3(H_2O)_6$ and $Tb(Bz)_3(H_2O)_2$ complexes nearly coincide, although their quantum yields (62 and 100%) differ noticeably (Table 2). Among $Tb(Pam)_3(H_2O)_4$, $Tb(Phm)_3(H_2O)_4$, and $Tb(Pfb)_3(H_2O)$, the maximum luminosity is characteristic of $Tb(Pam)_3(H_2O)_4$, although its quantum yield is minimum in this series. At the same time, both the quantum yield and specific luminosity of $Tb(Paz)_3(H_2O)_2$ are equal to zero (Table 2).

The absorption of a lanthanide complex can be enhanced by the formation of a mixed-ligand complex with a neutral ligand having high ε. For the Phen ligand, the value of ε is at least an order of magnitude higher than those of substituted benzoate anions (Table 1). As a result, the absorption of the heteroligand complex with this ligand is higher than that of homoligand complexes. Complexes of *d* metals, mainly iridium or ruthenium, can be used as auxiliary ligands, i.e., an approach of formation of heterometallic *d–f* complexes can be used [34–38]. The absorption of the *d*-metal to ligand charge transfer state is usually characterized by higher ε. For example, for the $[Ru(BPhen)_3]^{2+}$ cation $\varepsilon = 30000$ $cm^{-1}$ $mol^{-1}$ L, and for BPhen itself $\varepsilon = 22350$ $cm^{-1}$ $mol^{-1}$ L (Table 1, nos. 19 and 20).

**Intersystem crossing (4) and relaxation of ligand (2) and (3).** After the rare-earth element coordination compound was transformed into the excited state, its quantum yield should be maximized, which is achieved by an increase in the efficiency of processes (4), (7), and (10) over other, competing processes (Fig. 2). The photoluminescence quantum yield of lanthanide coordination compounds can be expressed as

$$Q_{Ln}^{L} = \eta_{ISC}\eta_{sens}Q_{Ln}^{Ln}, \quad (5)$$

where $Q_{Ln}^{L}$ is the quantum yield upon excitation through the ligand, or the external quantum yield; $\eta_{ISC}$ is the efficiency of Intersystem crossing (4); $\eta_{sens}$ is the efficiency of sensitization (7); and $Q_{Ln}^{Ln}$ is the quantum yield upon excitation through lanthanide, or internal quantum yield (10). Although in many works the efficiency of sensitization implies the resulting efficiency ($\eta_{ISC}\eta_{sens}$), these values should be distinguished, because the methods of their enhancement are different.

The efficiency of intersystem crossing (4) is enhanced by an increase in the ratio of constant $k_4$ for this process ($S_1 \xrightarrow{k_4} T_1$) and constants of radiative or nonradiative relaxation of the ligand ($S_1 \xrightarrow{k_2,k_3} S_0$): $\eta_{sens} = \dfrac{k_4}{k_2 + k_3 + k_4}$.

It is usually very difficult to distinguish process (4) from the general scheme (Fig. 2). If the fluorescence of the ligand (2) is observed along with the luminescence of lanthanide, the efficiency of intrasystem transfer is low. However, the absence of fluorescence does not necessarily indicate a high efficiency of intersystem crossing and can be a consequence of the nonradiative relaxation of the excited state of the ligand (3).

The efficiency of intersystem crossing in the ligand can be estimated by comparing the luminescence properties of the complexes of diamagnetic rare-earth elements (yttrium, lanthanum, and lutetium) and the most paramagnetic lanthanide (gadolinium). The

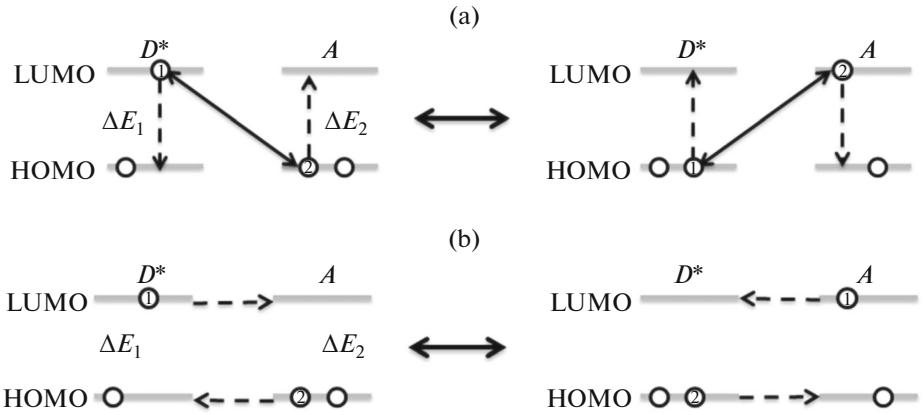
presence of the latter favors intersystem crossing (4), which is related to the use of the gadolinium complexes for the determination of the ligand triplet state energy a phosphorescence band appears in the luminescence spectra at a low temperature (77 K) or even at room temperature. The triplet state energy is determined by the position of this band.

The efficiency of intersystem crossing was studied [39] for lanthanum, gadolinium, and lutetium methyl salicylates. The luminescence spectra of these coordination compounds exhibit a fluorescence band, whereas an additional phosphorescence band is observed in the spectrum of the gadolinium complex. The appearance of this band is related to an increase in the efficiency of intersystem crossing, since a decrease in the lifetime of the excited state in the gadolinium coordination compound (0.24 ns) compared to the lanthanum and lutetium coordination compounds (2.2 and 2.4 ns) indicates the appearance of an additional transfer process.

The limiting factor in the resulting efficiency can be distinguished by studying the bimetallic complexes $M^1_xM^2_{1-x}L_3$, which are the product of partial substitution of luminescent ion $M^1$ by non-luminescent ion $M^2$. The replacement produces ligands spatially remote from the luminescent ion. This substantially decreases the efficiency of process (7), due to which the luminescence of the ligand can be observed even if it was not manifested in the spectrum of the luminescent lanthanide $M^1L_3$. If the intersystem crossing is insufficiently efficient, the partial replacement of luminescent ions by ions of paramagnetic gadolinium ($M^2$ = Gd) results in an increase in the efficiency of intersystem crossing compared to the complexes with diamagnetic ions ($M^2$ = La, Y, and Lu). This effect is observed in the whole series of complexes [4, 35, 38, 40, 41] and leads to an increase in the luminescence intensity of the $Eu^{3+}$, $Tb^{3+}$, and $Sm^{3+}$ ions in the heterometallic coordination compounds with the paramagnetic auxiliary ion compared to the heterometallic coordination compounds with the diamagnetic ion [42, 43].

**Energy transfer (7) and ligand relaxation (5) and (6).** One of the most important processes that occur during the luminescence of the lanthanide coordination compounds is sensitization, i.e., energy transfer from the sensitizer (organic ligand) to the activator (lanthanide ion). As in intersystem crossing, the maximum efficiency of sensitization can be provided by increasing the ratio of constant $k_7$ for this process ($T_1 \xrightarrow{k_7} f^*$) and the constants of radiative and nonradiative relaxation of the ligand ($T_1 \xrightarrow{k_5,k_6} S_0$): $\eta_{ISC} = \dfrac{k_7}{k_5 + k_6 + k_7}$.

Sensitization is a nonradiative and additional route of relaxation of the excited state of the ligand and, hence, unlike reabsorption, results in a decrease in the lifetime of the excited state of the sensitizer. Energy transfer can proceed via the Dexter exchange mechanism (a) [44] or via the Förster mechanism (b) due to the Coulomb interaction [45] (Scheme 1)




**Scheme 1.**

The exchange mechanism requires the overlap of the electron clouds of the sensitizer and activator and, hence, it is short-range. The Coulomb interaction is longer-range and, therefore, the energy can be transferred via the Förster mechanism to distances up to hundreds of Angström units. The energy transfer between the sensitizer and activator needs the overlap of the emission spectrum of the sensitizer and the absorption spectrum of the activator that would differ from zero. The energy transfer is most efficient in the case of the resonance $\Delta E_1 = \Delta E_2$. When the resonance condition is not fulfilled, decoupling in energy gaps is compensated by the birth of phonons (lattice vibrations).

The determination of an exact route of energy transfer is a particular problem. For instance, in the

**Table 3.** Energies of triplet levels ($E(T_1)$, $cm^{-1}$) for selected aromatic carboxylates

| Anion | $E(T_1)$ | Anion | $E(T_1)$ |
|---|---|---|---|
| Benzoate | 23200<br>23200<br>21700<br>21300 | Terephthalate | 23300 * |
| 2-Naphthoate | 22000* | 2,6-Naphthyl dicarboxylate | 18300* |
| 9-Anthracenate | 20300 | Quinoline-3-carboxylate | 23830 |
| | | 1-Phenyl -4-quinolinecarboxylate | 19557 |
| 2-Furanate | 29155 | Nicotinate | 26385 |
| Picolinate | 25773 | Isonicotinate | 26595 |
| 2-Pyrazinecarboxylate | 24000 | | |

case of the europium complexes, three states, namely, $^5D_0$, $^5D_1$, and $^5D_2$, can act as resonance levels of lanthanide to which the energy is transferred. Therefore, where the energy transfer occurred can finally be determined only using time resolution luminescence spectroscopy.

Since the description of energy excitation and emission processes in the rare-earth element coordination compounds is mathematically complicated, the empirical regularities predicting the photophysical properties remain to be an important prediction tool in spite of many restraints. Latva's empirical rule determining the optimal value of the energy gap between the triplet level of the ligand and the resonance level of lanthanide remains to be one of the most popular methods. Latva's rule was derived only for terbium and europium ions, whose luminescence intensity in the coordination compounds was the highest and, therefore, these compounds were most studied. The optimal value is 2500–3500 $cm^{-1}$ for $Eu^{3+}$ and 2500–4000 $cm^{-1}$ for $Tb^{3+}$ (Fig. 2) [46]. This rule has a good predictive force, and the position of the triplet level of the ligand is the key factor for the enhancement of the sensitization efficiency.

The triplet level energy is usually determined from the phosphorescence spectra of the gadolinium complexes. However, there are two procedures for its determination [47]: (1) from the position of the short-wavelength edge of the phosphorescence band, which is accepted to correspond to the 0–0 transition [48, 49] and (2) from the maximum of the peak with the maximum energy for phosphorescence band deconvolution [13, 50]. The obtained values of energy usually differ by 1500–3000 $cm^{-1}$, which is seen for benzoate and hydroxybenzoate anions (Tables 3, 4) [26, 47, 50–52]. Therefore, when comparing the energies of the triplet levels obtained in different works, one should pay attention to the procedure used.

The triplet level position can be varied by two main methods: a change in the aromatic ring and the introduction of substituents into the aromatic ring. The first method is based on the principle of decreasing the energy of the excited state with an increase in the degree of conjugation as, for example, in the series of anions: benzoate → 2-naphthoate → 9-anthracenate (Table 3, Fig. 3). As a consequence, the benzoate anion can sensitize luminescence of both terbium ($E(^5D_4)$ = 20 400 $cm^{-1}$) and europium ions ($E(^5D_0)$ = 17 200 $cm^{-1}$) with different efficiencies. The 2-naphthoate anion sensitizes only the luminescence of the europium ion, whereas the luminescence spectrum of terbium 2-naphthoate contains only the broad luminescence band of the ligand. A similar decrease in the triplet level energy is observed in the series terephthalate → 2,6-naphthyl dicarboxylate (Table 3, Fig. 3). The former can sensitize luminescence of both terbium and europium [53], and the latter sensitizes only europium luminescence [54].

The aromatic ring can be changed also by the introduction of heteroatoms. The electron-acceptor nature of heteroatoms results in an increase in the energy of the excited state, which is confirmed by an analysis of literature data. The energy of the triplet level of anions

**Table 4.** Energies of triplet levels ($cm^{-1}$) for selected benzoate anions $C_6H_4XCOO^-$

| X | *para* | *meta* | *ortho* |
|---|---|---|---|
| Methyl | 24630 | 25316 | 27397 |
| Phenyl | 20492 | | 23095 |
| Nitro | 22321 | 22321 | 22272 |
| Hydroxy | 29851<br>22700 | 29940<br>22200<br>22500 | 27027<br>23300 |
| Methoxy | 24876 | 20942 | 23095 |
| Amino | 22779 | 27634 | 23753 |
| Fluoro | | | 22000 |

of pyridinic acids (picolinic, nicotinic, and isonicotinic acids) is noticeably higher than that of the benzoate anion and depends slightly on the position of the carboxy group [55]. The energy of the triplet level also increases on going from 2-naphthoate to quinoline-3-carboxylate (Table 3) [56, 57].

The introduction of donor and acceptor substituents into the aromatic system can increase or decrease the energy of the triplet level depending on the position in the aromatic ring. Being an electron-acceptor group, the carboxyl substituent activates the *meta*-position and, on the contrary, decreases the electron density on the *ortho*- and *para*-carbon atoms of the benzene ring. Therefore, a change in the positions of the HOMO and LUMO levels for different positions of the introduced substituents is expectable, but the value of the changes is hardly predictable. For example, according to [51], the introduction of the methyl group into the *ortho*-position increases the position of the triplet level of the ligand (27400 $cm^{-1}$) compared to that for the initial benzoate (25600 $cm^{-1}$). However, the introduction of the same substituent into the *para*- and *meta*-positions, on the contrary, decreases the triplet level position (24630 and 25300 $cm^{-1}$, respectively) [51]. The position of the nitro group exerts almost no effect on the triplet level energy, the value of which for all the three isomers of nitrobenzoic acid lies at ~22300 $cm^{-1}$ (Table 4) [52]. The introduction of fluorine into the benzene ring exerts the same effect on the energy of the triplet level regardless of its position (22000 $cm^{-1}$) [58]. Moreover, we showed that the value remained unchanged depending on the number of fluorine substituents (from one to five) and when other substituents, such as Cl, $NH_2$, $NO_2$, $N_3$, $C(O)OCH_3$, and $CH_2OH$, are introduced additionally to fluorine atoms.

In several cases, the influence of the substituent position on the triplet level energy is explained by structural features of the formed complex. For example, the amino group in europium(III) and terbium(III) *para*-aminobenzoates is coordinated by the lanthanide ion, unlike other isomers, which affects its donor ability [52]. The structures of lanthanide methoxybenzoates are also substantially different: *ortho*-methoxybenzoate is a dimer, whereas *meta*- and para-methoxybenzoates are polymers [59].

The formation of bimetallic *d–f* complexes also makes it possible to affect the energy of the excited state if the MLCT energy is lower than the energy of the excited state localized on the ligand [34–38]. As a result, the energy of the excited state can be decreased rather strongly to provide the efficient sensitization of luminescence of NIR-emitting ions, the choice of ligands for which is a particular complicated problem. The luminescent ytterbium, erbium, and neodymium complexes were obtained using this approach, and Re(I), Ru(II), Os(II), Ir(III), Pd(II), and Pt(I) recommended themselves best of all among the *d* metals [60, 61]. A substantial distinction in the chemistry of *d* metals and lanthanides makes it possible to choose ligands containing spatially separated nitrogen- and oxygen-containing donor groups coordinating *d* and *f* metals, respectively, as linkers between different metals.

At the same time, it seems unreasonable to prepare bimetallic *d–f* complexes for luminescence sensitization of terbium and europium that radiate in the visible range. Too low energy of the MLCT state is close to the position of the excited state of lanthanide. As a result, the energy is transferred incompletely, and the phosphorescence of "*d*-block" (5) competes with the energy transfer to lanthanide (7) (Fig. 2). In several cases, this competition finds practical use: the color coordinates of the luminescence of the bimetallic iridium and europium complexes appeared as bands in the blue range (due to emission from the MLCT level of the "*d*-block") and red range (due to the ion luminescence of europium) correspond to the white color [38, 40, 41].

Undoubtedly, the choice of the ligand should primarily be dictated by the search for a correspondence between the energy of the triplet level of the ligand and the energy of the excited state of lanthanide, which is almost independent of the composition of the compound and is constant for a chosen ion. At the same time, there are situations where the ligand is chosen from certain functional properties, such as solubility or stability, and a problem arises of increasing the efficiency of energy transfer for this metal–ligand pair. The main approach used in this situation is the introduction of an additional energy transfer step. The excited state of an auxiliary ligand (when preparing mixed ligand complexes) or an auxiliary rare-earth element ion (when synthesizing heterometallic complexes) can act as the additional transfer step.

The first method is most popular and makes it possible to increase the quantum yield multiply. In [51, 59, 62, 63], Phen was used as an additional step for energy transfer from the aromatic carboxylate anion to the europium ion. However, its introduction is not restricted by the participation in the two-step process of energy transfer: the neutral ligand also substitutes quenching water molecules in the coordination sphere and affects the coordination environment of the lanthanide ion. In addition, the use of phenanthroline, one of the most efficient sensitizers of europium luminescence, prejudices the role of anionic carboxylate ligands as sensitizers.

Another approach to the formation of this "energy step" is the introduction of an additional metal and bimetallic complex formation. This approach was widely discussed [4, 64]. However, terbium and europium form the single pair of lanthanides the energy transfer between which finds practical use [64]. The obvious conditions for the efficiency of this approach are as follows: (1) low luminescence quantum yield of

the europium complex, (2) high efficiency of the terbium → europium energy transfer, and (3) high internal quantum yield of the europium ion in the complex. As shown in [53], in spite of the fact that the energies of the excited states of the terephthalate anion, terbium, and europium lie in the series $E[T_1(Tph^{2-})] > E[^5D_4(Tb^{3+})] > E[^5D_0(Eu^{3+})]$, it is impossible to increase the quantum yield of $Eu_2(Tph)_3(H_2O)_4$ by the partial replacement of europium by terbium. This is related to the fact that the quantum yield of $Eu_2(Tph)_3(H_2O)_4$ (25%) is limited by the internal quantum yield of europium (25%) rather than the efficiency of the energy transfer $Tph^{2-} \rightarrow Eu^{3+}$ (100%). Although all complexes $Tb_xEu_{1-x}(Tph)_{3/2}(H_2O)_2$ ($x$ = 0...0.9) demonstrate only ionic luminescence of europium, its quantum yield is also 25%.

In some cases, this approach leads, on the contrary, to a decrease in the luminescence quantum yield, since the fraction of emitting centers (europium ions) decreases simultaneously with an increase in the efficiency of the transfer due to the partial substitution of europium ions by terbium ions. A twofold decrease in the quantum yield was observed on going from $Eu(Vfb)_3(H_2O)$ to $Eu_{0.5}Tb_{0.5}(Vfb)_3(H_2O)$. No ion luminescence of terbium was observed, indicating the completeness of the energy transfer $Tb^{3+} \rightarrow Eu^{3+}$, and the quantum yield decrease is only connected with the twofold decrease in the ratio of emitting ions and ligands $Vfb^-$ absorbing energy.

There are examples for the successful application of the approach of heterometallic compound formation. The quantum yield of pentafluorobenzoates $Eu(Pfb)_3(H_2O)$ and $Eu_{0.5}Tb_{0.5}(Pfb)_3(H_2O)$ is 15 and 29%, respectively, i.e., increases upon the introduction of terbium ions [58]. Ion luminescence of terbium in the bimetallic complex is almost absent, and the lifetime of the excited state of the terbium ion decreases from 2 ms for $Tb(Pfb)_3(H_2O)$ to 0.12 ms for $Eu_{0.5}Tb_{0.5}(Pfb)_3(H_2O)$, indicating a high efficiency of the energy transfer $Tb^{3+} \rightarrow Eu^{3+}$.

**Quenching (8) and (9).** The higher the internal quantum yield $Q_{Ln}^{Ln} = k_{rad}/(k_{rad} + k_{nr})$, the higher the photoluminescence quantum yield $Q_{Ln}^{L} = \eta_{ISC}\eta_{sens}Q_{Ln}^{Ln}$. Here $k_{rad}$ is the radiative relaxation constant, and $k_{nr}$ is the nonradiative relaxation constant. Vibrational quenching and energy transfer to levels of quenchers, which can be both organic ligands and metal ions, can be assigned to processes of nonradiative relaxation of the excited state or, in other words, quenching of luminescence.

**Vibrational relaxation (8).** Collective vibrations of molecules in crystal (phonons) and intramolecular vibrations (vibrations of particular bonds) are distinguished among the vibrations that become a reason for vibrational relaxation. During vibrational quenching, the excited state energy can be expensed to the birth of several phonons and perturbation of various vibration modes of groups of atoms. The higher the number of phonons or vibration mode, whose birth or perturbation is necessary to expense the stored energy, the lower the probability of quenching. In molecular crystals, the typical value of the energy of phonons is ~$10^2$ $cm^{-1}$ [65, 66], and gaps between the excited and ground states of lanthanide ions is ~$10^4$ $cm^{-1}$. Therefore, the mechanism of phonon quenching for lanthanide coordination compounds has low efficiency. On the contrary, the energy of intramolecular vibrations is about $10^3$ $cm^{-1}$, and only the fourth vibration mode of the O–H bond ($4 \times 3400 = 13600$ $cm^{-1}$) is sufficient for the quenching of even the luminescence of the terbium ion (the gap between the $^5D_4$ and $^7F_0$ terms is ~14750 $cm^{-1}$) (Fig. 4). The third vibration mode is enough for luminescence quenching of the ytterbium ion (~10 000 $cm^{-1}$). The replacement of hydrogen by deuterium results in a decrease in the vibration energy, and the quenching probability decreases.

The most representative methods for the evaluation of vibrational quenching are provided by a comparison of the luminescence properties of a deuterated and non-deuterated compound or solutions in deuterated and non-deuterated solvents. For example, the luminescence intensity of an aqueous solution of europium pentafluorobenzoate is 8 times lower than that in a $D_2O$ solution of the same concentration [58]. The replacement of water by $D_2O$ during the synthesis of hydrates of *para*-substituted europium tetrafluorobenzoates resulted in an increase in the quantum yield of powdered complexes $Eu(Phm)_3(D_2O)_6$ and $Eu(Pmc)_3(D_2O)_6$ containing heavy water (Table 5). At the same time, the quantum yields of $Eu(Pfb)_3(D_2O)$ and $Eu(Pfb)_3(H_2O)$ coincide, because in the absence of an efficient vibrational quenching the lifetime of the excited state of the europium ion increases so strongly that the sensitization efficiency decreases [58].

The method for the determination of the number of inner-sphere water molecules is based on the deuteration effect. The influence of inner-sphere molecules only is caused by the fact that the excitation of these vibrations proceeds via the dipole-dipole mechanism, and the efficiency of the process decreases with distance directly proportionally to $1/r^6$ [45, 67, 68]. Since, as shown in [69, 70], all water molecules act independently of each other, the degree of quenching is directly proportional to the number of O–H vibrations. Since O–D vibrations almost do not participate in quenching processes, one can estimate the number of water molecules in the first coordination sphere by comparing the luminescence properties of the lanthanide complexes with the properties of a similar complex with $D_2O$:

$$\text{for europium ion} \begin{cases} n_{H_2O} = 1.05\left(\frac{1}{\tau_{H_2O}} - \frac{1}{\tau_{D_2O}}\right) \\ n_{H_2O} = 1.1\left(\frac{1}{\tau_{H_2O}} - \frac{1}{\tau_{D_2O}} - 0.31\right) \end{cases}, \quad (6)$$

$$\text{for terbium ion } n_{H_2O} = 4.2\left(\frac{1}{\tau_{H_2O}} - \frac{1}{\tau_{D_2O}}\right). \quad (7)$$

These empirical equations were experimentally derived for solutions [71], but they are also fulfilled for powders with good accuracy [58]. The difference in the hydrate composition of europium and terbium bis(tetraazolates) ($[(Eu(BT)(H_2O)_7]_2[BT]$ and $[Tb(H_2O)_8]_2[BT]_3$) is consistent with the data obtained from the luminescence decay curves of the solid samples ($n_{H_2O}(Eu) = 7.1$ and $n_{H_2O}(Tb) = 8.3$).

High vibration modes are excited more difficultly than the low ones and, hence, it is substantially simpler to obtain efficiently luminescing compounds based on $Tb^{3+}$ than those based on $Eu^{3+}$. For example, the quantum yield of terbium benzoate hydrate is 100% [72]. The absence of quenching due to water molecules is shown for terbium *para*-hydroxobenzoate hydrate: the lifetime of the excited state during dehydration remains unchanged, indicating the absence of vibrational relaxation [50]. Vibrational quenching exerts the highest effect on the luminescence of the IR emitters, namely, the $Er^{3+}$, $Yb^{3+}$, and $Nd^{3+}$ complexes, due to the smallest energy gap between the excited and highest from below lying states. The luminescence characteristics of the erbium complexes with benzoic and pentafluorobenzoic acids and of their heteroligand complexes with bipyridine were compared [73]. When water in the coordination sphere of lanthanide is replaced by bipyridine, the luminescence intensity of the complexes increases tenfold, and the fluorination of the benzene ring leading to the disappearance of C–H vibrations increases the intensity by 1.5 times. An increase in the luminescence intensity on going from ytterbium 2,6-naphthyl dicarboxylate $Yb_2(Nda)_3(H_2O)_4$ to 9-anthracenate $Yb(Ant)_3$ was shown [54]. In spite of the fact that the energies of the triplet level of both ligands are close and substantially higher than the energy of the excited state of the ytterbium ion, the quantum yields of the complexes differ substantially. This is related to the fact that $Yb(Ant)_3$ is formed in the anhydrous state, whereas $Yb_2(Nda)_3(H_2O)_4$ is hydrate.

On the whole, a decrease in the number of functional groups near the emitter ion [74, 75] and the replacement of functional groups with a high vibration frequency by groups with lower-frequency vibrations [67, 74] result in an increase in the luminescence efficiency.

**Quenchers of luminescence (9).** The energy transfer to the quencher levels is also an important process of luminescence quenching. Both molecules located in the immediate vicinity of the luminophore and organic ligands and metal ions in the luminophore composition can act as quenchers. For example, triplet oxygen capable of efficient quenching excited triplet states is among the first ones [76–79].

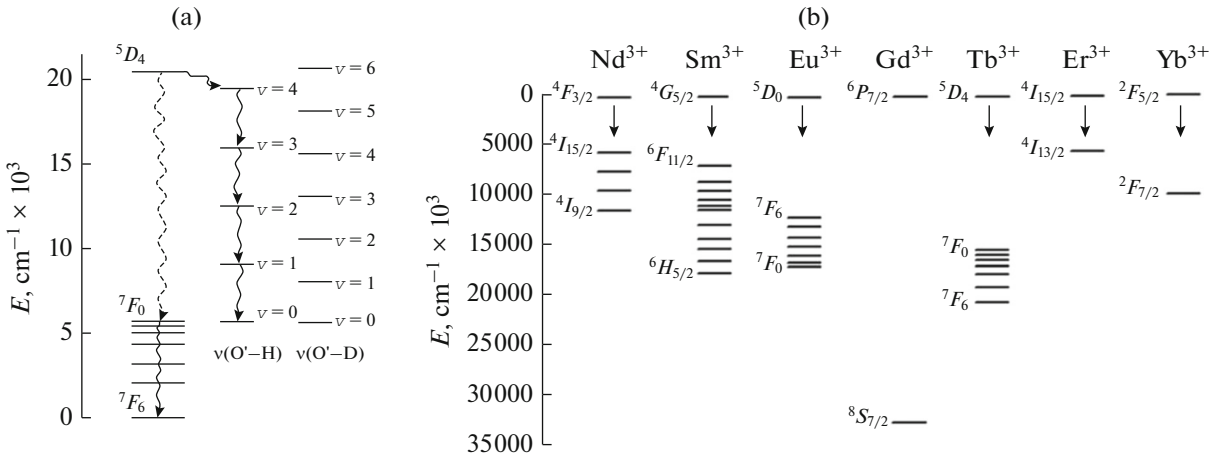



**Fig. 4.** (a) Alternative routes of the relaxation of the excited state of the $Tb^{3+}$ ion via the excitation of vibrations of the (*1*) O–H and (*2*) O–D groups; (b) the Dicke diagram with electronic states of some $Ln^{3+}$ ions.

The terbium complexes with phenanthroline represent an example of the quenching of luminescence of lanthanide coordination compounds by their ligands [50]. Luminescence quenching by aromatic carboxylate $Tb(Carb)_3(Phen)$ at 300 K occurs due to the efficient energy transfer to the triplet level of Phen, whose energy coincides with the energy of the terbium level $^5D_4$ ($T_1$ = 20 400 cm$^{-1}$). The subsequent nonradiative relaxation proceeds via vibrations of the O–H groups of the carboxylate anion and, hence, their number substantially affects the luminescence intensity. Since vibrational quenching is substantially less efficient on cooling, almost no quenching is observed at 77 K. As a result, the simultaneous introduction of O–H substituents into the carboxylate anion and of *o*-phenantroline into the terbium heteroligand compound provides a high thermal sensitivity of luminescence up to $I_{77}/I_{300}$ = 80 for the terbium mixed ligand compound with 2,4-dihydroxybenzoate anion and phenanthroline. In this case, the energy transfer can occur from both the excited state of the terbium ion, which is indicated by a noticeable decrease in the lifetime of the excited state [50, 80], and the excited level of the carboxylate anion, which is shown by the shift of the 'red boundary" of the excitation spectrum to the short-wavelength range [80].

Since the terbium ion efficiently sensitizes the europium luminescence, the europium ion in the terbium–europium heterometallic complex also acts a luminescence quencher for the terbium ion. No appreciable luminescence of the terbium ion is observed up to $(1 - x) = 0.9$ in bimetallic terephthalates $Eu_xTb_{1-x}(Tph)_{3/2}(H_2O)_2$ [53]. The relaxation rate of the excited state $^5D_4$ of the terbium ion $Tb^{3+}$ increases with an increase in the fraction of europium in the sample. This indicates that the energy transfer occurs due to the nonradiative energy transfer rather than reabsorption.

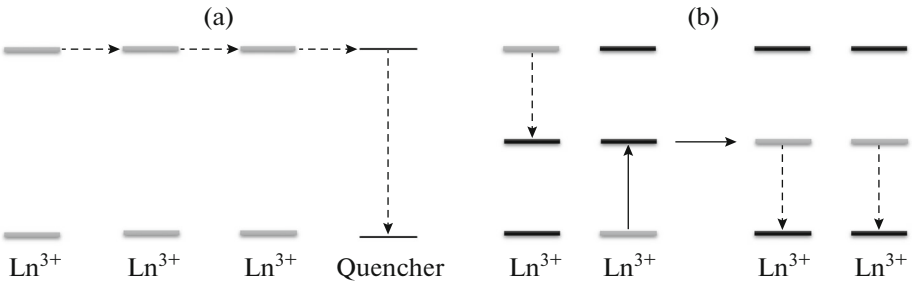
**Table 5.** Luminescence characteristics of europium aromatic carboxylates

| Compound | *n** | $Q_{Ln}^{Ln}$, % | $\eta_{sens}$, % | $Q_{Ln}^{L}$, % |
|---|---|---|---|---|
| $Eu_2(Tph)_3(H_2O)_4$ | 2 | 25 | 100 | 25 |
| $Eu_2(Nda)_3(H_2O)_4$ | 2 | 7.2 | 53 | 3.8 |
| $Eu(Bz)_3(H_2O)_2$ | 2 | 10.5 | | |
| $Eu(Pfb)_3(H_2O)$ | 1 | 23 | 65 | 15 |
| $Eu(Pfb)_3(D_2O)$ | | | | 15 |
| $Eu(Pmc)_3(H_2O)_6$ | 2 | 14 | 74 | 10 |
| $Eu(Pmc)_3(D_2O)_6$ | | | | 25 |
| $Eu(Phm)_3(H_2O)_6$ | 3 | 9 | 78 | 7 |
| $Eu(Phm)_3(D_2O)_6$ | | | | 21 |

* *n* is the number of inner-sphere water molecules, calculated by Eq. (6).

**Concentration quenching (9).** Concentration quenching can be considered as a particular case of quenching of one lanthanide ion by another [81–83]. It is assumed rather frequently that the effect of concentration quenching is not characteristic of lanthanide coordination compounds because of the remoteness of radiative centers (lanthanyl ions) from each other [84, 85]. However, there are studies demonstrating an opposite situation [4].

Two main mechanisms of concentration quenching are distinguished: energy migration (a) and cross relaxation (b) (Scheme 2).




(defect acting as acceptor is designated by black)

**Scheme 2.**

Energy migration is the energy transfer inside the crystal to a substantial distance to quenching defects. Cross relaxation is the energy redistribution between emitting ions in the excited and non-excited states. Owing to this redistribution, both activators are in the intermediate excited state the probability of vibrational relaxation from which is substantially higher.

An increase in the concentration of activating ions decreases the average distance and enhances the interaction between the ions, which makes it possible to perform mechanisms of concentration quenching. Unlike the energy migration characteristic of any lanthanide ions, cross relaxation needs an intermediate excited state equally remote by energy from the ground

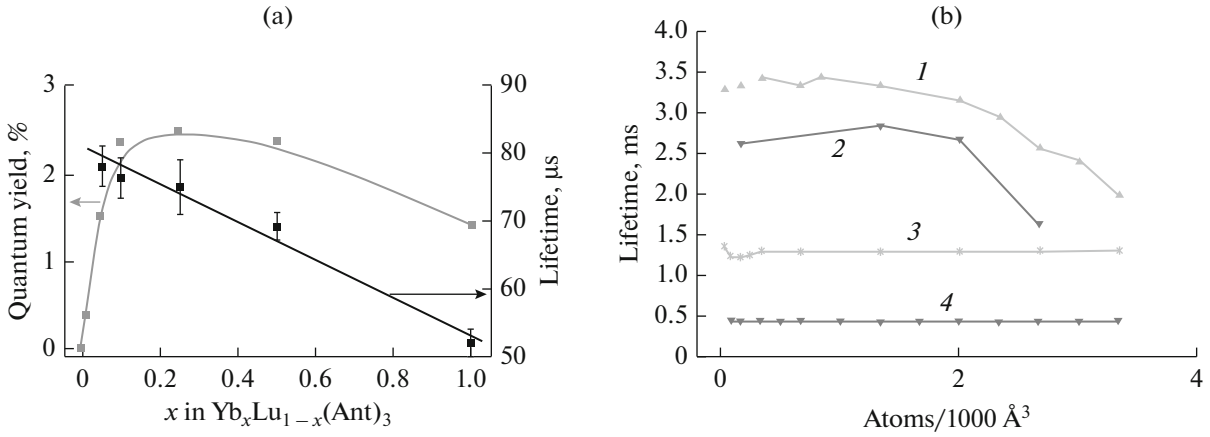



**Fig. 5.** (a) Lifetimes of the excited state and quantum yields of the $Yb_xLu_{1-x}(Ant)_3$ complexes; (b) the lifetimes of the excited states $Eu^{3+}(^5D_0)$ and $Tb^{3+}(^5D_4)$ in heterometallic terephthalates: (*1*) $Tb_xY_{1-x}(Tph)_{3/2}$, (*2*) $Eu_xY_{1-x}(Tph)_{3/2}$, (*3*) $Tb_xY_{1-x}(Tph)_{3/2}(H_2O)_2$, and (*4*) $Eu_xY_{1-x}(Tph)_{3/2}(H_2O)_2$.

and excited states. Cross relaxation is not characteristic of the $Eu^{3+}$ and $Tb^{3+}$ coordination compounds but can substantially affect the luminescence efficiency of $Sm^{3+}$ [4].

Thus, the effect of concentration quenching in the coordination compounds of luminescent lanthanide cannot be denied and should be taken into account for the formation of materials based on these compounds. We showed that the luminescence intensity of dysprosium terephthalate increased upon the partial replacement of dysprosium by ytterbium. Similarly, the maximum of the quantum yield of ytterbium–lutetium anthracenate falls onto the composition $Yb_{0.3}Lu_{0.7}(Ant)_3$ (Fig. 5a).

Concentration quenching, as any other competitive process of excited state relaxation, necessarily results in a decrease in the lifetime of the excited state with an increase in the fraction of the luminescing ion. This is observed, for example, for ytterbium–lutetium anthracenate (Fig. 6a). At the same time, terbium and europium terephthalates undergo no concentration quenching, and the lifetimes of the excited state of the terbium and europium ions in terephtalates $M_xY_{1-x}(Tph)_{3/2}(H_2O)_2$ (M = Eu, Tb) are independent of the fraction of terbium and europium, respectively (Fig. 6b).

The absence of concentration quenching in $M_xY_{1-x}(Tph)_{3/2}(H_2O)_2$ is associated with shorter lifetimes of the excited state in the coordination compound unlike inorganic salts [76]. Indeed, the dehydration of these compounds increased the lifetimes of the excited states ($\tau_{obs}$) of the luminescing $Tb^{3+}$ and $Eu^{3+}$ ions due to the removal of quenchers (water molecules). As a result, concentration quenching was manifested: $\tau_{obs}$ decreases with an increase in the fraction of the luminescing ion in dehydrated terephthalates $M_xY_{1-x}(Tph)_{3/2}$.

**Quenching due to the charge-transfer state (9).** The states acting as quenchers of luminescence due to energy transfer (9) can be localized (on the metal or ligand) or be the charge transfer states. The d-metal compounds, for example, the iridium and rhodium coordination compounds, exhibit the states with charge transfer from the metal to ligand (MLCT) responsible for luminescence. In the case of lanthanide coordination compounds, the charge transfer occurs from the ligand to metal (LMCT), which is characteristic of coordination compounds of the ions that can rather easily be reduced to the oxidation state +2 ($Eu^{3+}$, $Sm^{3+}$, and $Yb^{3+}$) [68]. In the most cases, this energy level acts as an efficient quencher of luminescence of the central lanthanide ion. It is assumed that the LMCT state is singlet [86]. The presence of the LMCT can be determined from the appearance of an additional band in the diffuse reflectance spectrum of the lanthanide complexes containing the LMCT ($Eu^{3+}$, $Sm^{3+}$, and $Yb^{3+}$). This band was not observed in the diffuse reflectance spectrum of the lanthanide coordination compounds containing no LMCT [87]. For example, unlike luminescent $Eu(Phm)_3(H_2O)_6$, complex $Eu(Pam)_3(H_2O)_4$ has almost no luminescence, which is related to quenching due to the LMCT. This state appears in the diffuse reflectance spectrum (Fig. 6a) of $Eu(Pam)_3(H_2O)_4$ as an additional band, whereas the diffuse reflectance spectra of $Eu(Phm)_3(H_2O)_6$ and $Gd(Phm)_3(H_2O)_2$ coincide except for the bands corresponding to the transitions in the europium ions (Fig. 7b). The presence of the LMCT state in a complex with the amino-containing ligand is related to the possibility of amino group oxidation.

**Radiative constant increase (10).** The internal quantum yield $Q_{Ln}^{Ln} = k_{rad}/(k_{rad} + k_{nr})$ can be increased due to both the elimination of quenching

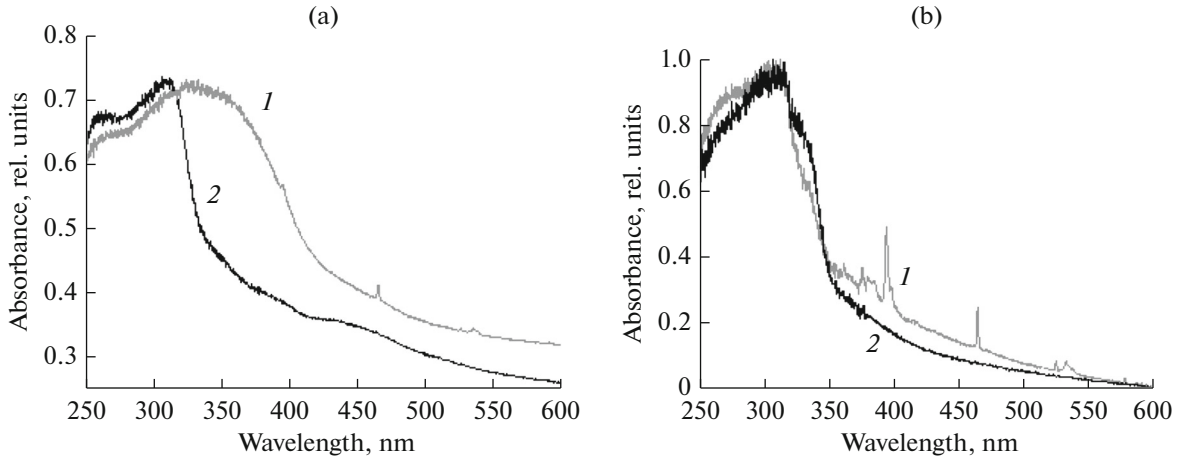



**Fig. 6.** Diffuse reflectance spectra of complexes (a) (*1*) $Eu(Pam)_3(H_2O)_4$ and (*2*) $Gd(Pam)_3(H_2O)_4$ (*2*); (b) (*1*) $Eu(Phm)_3(H_2O)_6$ and (*2*) $Gd(Phm)_3(H_2O)_2$.

(decreasing $k_{nr}$ in the denominator) and an increase in the numerator ($k_{rad}$). The radiative constant $k_{rad}$, or the Einstein coefficient, relates the radiative relaxation rate of the excited state to its population. Its value is usually low (~$10^{-6}$ s) due to the Laporte selection (forbiddance) rule, the partial elimination of which is possible in the noncentrosymmetric environment. Thus, a decrease in the symmetry of the coordination environment of the lanthanide ion should result in an increase in the radiative constant and quantum yield.

The most complete quantum mechanical description of energy emission was given by Judd and Ofelt in 1961. The description is based on the assumption that the prohibition of *f–f* transitions is partially eliminated due to admixing wave functions of an opposite evenness to the considered wave functions of lanthanide ions [88, 89]. In spite of mathematical complicatedness of this theory, it is simplified in several cases thus making possible an analysis of the luminescence properties. A special place is occupied by the europium compounds, whose luminescence occurs from the $^5D_0$ level that is not split in the crystal field as any level with $J = 0$, which substantially simplifies the analysis. The spectrum contains pure magnet-dipole transitions ($D_{ED} = 0$), the most intense of which is the transition $^5D_0 \rightarrow {}^7F_1$. Thus, for these transitions, the dipole force $D_{MD}$ is independent of the environment [90], and the equation for the Einstein coefficient $A(\psi J, \psi' J')$ is substantially simplified:

$$A(\psi J, \psi' J') = \frac{64\pi^4\tilde{\nu}^3}{3h(2J+1)} \times \left[\frac{n(n^2+2)^2}{9} D_{ED} + n^3 D_{MD}\right] = \frac{64\pi^4\tilde{\nu}^3}{3h(2J+1)} n^3 D_{MD}. \quad (8)$$

This allows one to obtain an information on stoichiometry [91–93], binding constants of the metal with ligand [94–96] and binding constants of other metals (due to competition) [95], distances between the metal ion and donor atoms of the ligand [97], and exchange rate of ligands [98] from the data of luminescence spectroscopy of lanthanide coordination compounds.

For example, the europium compounds are characterized by the constant force of dipole $D_{MD}$ for the transition $^5D_0 \rightarrow {}^7F_1$, which means the constancy of the Einstein coefficient and integral intensity of the corresponding band

$$D_{MD} = \frac{3h(2J+1)}{64\pi^4\tilde{\nu}^3 n^3} A_{MD} = \frac{3h(2J+1)}{64\pi^4\tilde{\nu}^3 n^3} \frac{8\pi^2 e^2 \sigma^2}{m} P_{MD} = \frac{3h(2J+1)}{64\pi^4\tilde{\nu}^3 n^3} \frac{8\pi^2 e^2\sigma^2}{m} \frac{mc^2}{\pi e^2 N \overline{\lambda^2}} \int k(\lambda) d\lambda, \quad (9)$$

$$\int k(\lambda) d\lambda = \frac{3(2J+1)\sigma^2}{8\pi^3 \nu n^3 N h} D_{MD}. \quad (10)$$

Unlike $^5D_0 \rightarrow {}^7F_1$, the intensity of the $^5D_0 \rightarrow {}^7F_2$ transition depends substantially on the symmetry of the environment, which can be evaluated from the ratio of intensities of the $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_4$ transitions. The luminescence spectra of solutions containing $Eu^{3+}$ ions change substantially upon the addition of dipicolinic acid anions [99]. The magnetic dipole transition $^5D_0 \rightarrow {}^7F_1$ and electric dipole transition $^5D_0 \rightarrow {}^7F_4$ are most intensive in the luminescence spectrum in the absence of a ligand. The relative intensity of the "hypersensitive" transition $^5D_0 \rightarrow {}^7F_2$ increases substantially after a ligand was added.

The constancy of the Einstein coefficient for one of the transitions leads to the possibility of calculation of the radiative lifetime of the excited state $\tau_{rad}$ from the luminescence spectrum of the europium compound.

Its value is the reciprocal sum of the Einstein coefficients of all transitions from this state

$$\frac{1}{\tau_{rad}} = \Sigma_{J'} A_{J,J'}. \quad (11)$$

The normalization of this value to the Einstein coefficient $A_{0-1}$ of the magnetic dipole transition ${}^5D_0 \rightarrow {}^7F_1$ allows one to express $\tau_{rad}$ as follows:

$$\frac{1}{\tau_{rad}} = \Sigma_{J'} A_{J,J'} = \left(\frac{\Sigma_{J'} A_{J,J'}}{A_{0-1}}\right) A_{0-1} = A_{0-1,0} n^3 \left(\frac{I_{tot}}{I_{MD}}\right). \quad (12)$$

The branching factor ($B_{0-1}$) is determined from the spectrum: $B_{0-1} = \frac{A_{0-1}}{\Sigma'_J A_{J,J'}} = \frac{I_{MD}}{I_{tot}}$, and the Einstein coefficient $A_{0-1,0} = \frac{64\pi^4 \tilde{\nu}^3}{3h(2J+1)} D_{0-1}$ is constant ($14.65\ s^{-1}$).

In the case of lanthanides differed from europium, all transitions contain both components: electron-dipole and magnet-dipole. Therefore, there is no such an "internal standard" for them. However, the radiative lifetime of the excited state can be determined from the absorption spectrum corresponding to the radiative transition, since the oscillator force $P$ is calculated directly from this spectrum

$$\frac{1}{\tau_{rad}} = A = \frac{8\pi^2 e^2 \sigma^2}{m} P = 2303 \frac{8\pi c n^2 \bar{\nu}_{ul}^2}{N_A} \frac{g_l}{g_u} \int \varepsilon(\nu) d\nu, \quad (13)$$

where $c$ is the velocity of light in vacuum, $\bar{\nu}$ is the transition frequency, $n$ is the refractive index of the medium, $N_A$ is Avogadro's number, $\varepsilon(\nu)$ is the absorption spectrum of the transition, and $g_l$ and $g_u$ is the degeneration of the ground and excited states, respectively, in the case of lanthanide ions $(2J + 1)$. Using Eq. (13), we believe that the $(2J + 1)$ levels are degenerate or, at least, they have the same population, which, in turn, can be violated because of the Stark splitting. Different populations of the Stark sublevels result in deviations up to 20% [100]. The photophysical parameters of europium dipicolinate obtained experimentally were compared [101] with those theoretically calculated using the Judd–Ofelt theory and simplified Eq. (12) [99], and the coincidence of the experimentally obtained values with theoretical ones with good accuracy was shown.

It is known that the lower the symmetry of the environment, the lower $\tau_{rad}$ [102]. Therefore, the quantum yield of the europium compounds can be increased. For example, the monomeric $[Eu(MBTF)_3(DMSO)(H_2O)]$ and dimeric $[Eu_2(BTPE)_3(DMSO)_4]$ europium complexes with β-diketones (*p*-methoxybenzoyl)trifluoroacetylacetone (HMBTF) and its dimer 1,2-bis(4,4'-bis(4,4,4-trifluoro-1,3-dioxobutyl))phenoxylethane ($H_2BTPE$) (Fig. 3) were synthesized [102]. In spite of resemblance of the functional groups in both ligands, the quantum yields of the europium complexes differed by 1.5 times. A less symmetric coordination environment of europium in the monomer (triangular dodecahedron) gave a higher quantum yield ($Q = 38\%$) than the more symmetric environment in the dimer (square antiprism, $Q = 25\%$). The comparison of the luminescence properties of heteroligand β-diketonates $Eu(\beta\text{-dik})_3(L)_2$ and complexes $Eu(\beta\text{-dik})_3(L^1)(L^2)$ showed [103] that the quantum yield of the complex with two different neutral ligands $L^1$ and $L^2$ was higher than the half-sum of the quantum yields of two complexes containing only one of these ligands. The authors also ascribe this behavior to a decrease in the symmetry of the environment.

Thus, the luminescence of rare-earth element coordination compounds is a complicated phenomenon caused by a set of competing processes (Fig. 2). The efficiency of each process should purposefully be affected to obtain an intense luminescence. The analysis of literature data on the luminescence of lanthanide aromatic carboxylates and our results makes it possible to distinguish several main approaches for the modification of the composition of coordination compounds affecting the luminescence properties. First, among them are (1) variation of the composition of the carboxylate anion itself, which can be achieved by the introduction of substituents or a change in the aromatic moiety due to changing the conjugated fragment or introducing heteroatoms, (2) introduction of neutral auxiliary ligands, including *d*-metal complexes acting as ligands, and (3) synthesis of heterometallic *f*–*f* complexes.

It is important that the use of any approach in order to affect the efficiency of one of the steps would inevitably change the efficiency of all energy transfer processes involved in luminescence. A distinct understanding of both the nature of particular processes and the method for controlling their efficiency is necessary for the purposeful synthesis of the brightly luminescing coordination compounds of lanthanides.

The use of the whole set of approaches for a change in the efficiency of particular stages allows their purposeful combination to perform in order to achieve the maximum possible luminescence efficiency. The approaches can be chosen taking into account the assumed method of application and additional requirements imposed on the luminescent material for its practical use.

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