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Peculiarities of the excitation energy transfer in europium and terbium aromatic carboxylates and nitrate complexes with sulfoxides: Blocking effect

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Abstract

The influence of modification of the aromatic ligands on the excitation energy transfer to Ln^{3+} ions in europium and terbium carboxylates and nitrates was examined. The luminescence excitation spectra of three groups of the europium and terbium compounds: phenyl-, diphenyl-, triphenylacetates, phenoxyacetates and triphenylpropionates; 1- and 2-naphthylcarboxylates and 2-naphthoxyacetates; lanthanide nitrates with diarylsulfoxides (diphenyl- and dibenzylsulfoxides) and dialkylsulfoxides were investigated. The spectra of adducts of terbium phenylcarboxylates with 1,10-phenanthroline were also analyzed. The effect of the aliphatic bridges, which decouple the π–π- or p–π-conjugation in the ligand, on the energy transfer to Ln^{3+} ions (so-called blocking effect) was investigated. It was shown, that this decoupling leads to significant lowering of the energy of "ligand–metal ion" charge transfer states (LM CTS) in the europium carboxylate salts, just down to ∼27,800 cm^{-1} in europium 2-naphthoxyacetate. As a consequence, the probability of the LM CTS participation in the excitation energy dissipation processes increases. A channel of the excitation energy dissipation in the region of ∼31,750 cm^{-1} related to ligand electronic transitions was found in the europium and terbium nitrates with sulfoxides. It was demonstrated that a part of the energy absorbed by the aromatic ligand having aliphatic bridge can be emitted as the ligand fluorescence.

Keywords: Tb^{3+}; Eu^{3+}; Luminescence; LM CTS; Aromatic carboxylates; Nitrates

1. Introduction

Studies of the processes of transfer and dissipation of excitation energy in lanthanide coordination compounds with organic ligands are important in the search of materials for molecular electronics devices, light transforming materials, engineering of the sensors for monitoring environment, elaboration of green chemistry methods, for the application of the lanthanide compounds in clinical medicine and biology, etc. Spectroscopic characterization of the energy transfer depends on many factors, which can overlap and are very difficult to be predicted and taken into consideration. Many papers, in particular [1–8], were consecrated to studies of the influence of the location of ligand triplet levels and the states of "ligand–metal ion" charge transfer state (LM CTS) on the processes of the excitation energy transfer to Ln^{3+} ions. The triplet state of europium compound can be populated very poorly, if there is a competition with the LM CTS. Some communications demonstrate a direct excitation energy transfer from the singlet levels of the ligands to the levels of the lanthanide ions [9], and consider the energy transfer through the excited states of the intraligand charge transfer state (IL CTS) [10].

Methods of regulation of excitation and luminescence efficiencies of europium and terbium compounds by the ligand modification are discussed in our papers [11–15]. This modification can change the energies and reciprocal positions of the ligand metastable triplet state, LM CTS, IL CTS, and 5d-states of Ln^{3+} ion. In particular, it was demonstrated that participation of LM CTS "β-diketonate–europium" in processes of the excitation energy degradation in com-

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pounds $Eu(\beta)_3\cdot Phn$ (Phn—derivatives of 1,10-phenanthroline) increases with strengthening the Eu–O bonds, when the donor ability of the radicals of β-diketone increases, or at weakening the Eu–N bonds [11]. Low luminescence efficiency of europium anthranylates and salicylates including their adducts with 1,10-phenanthroline is connected with the participation of the LM CTS "carboxylate–europium" in the processes of the excitation energy degradation [13]. At the same time, low luminescence efficiency of both europium and terbium nitrocarboxylates is explained by the existence of the channel of the excitation energy degradation through π*–n transition of nitrogroup [13].

The blocking influence of the methylene bridges on the excitation energy transfer to Eu^{3+} ions and, correspondingly, on luminescence efficiency of the europium ions was demonstrated on examples of europium aromatic carboxylates and europium nitrates with sulfoxides [11,15]. It was attributed to substantial weakening of the interaction of two parts of molecule upon the introduction of aliphatic bridge breaking π–π- or p–π-conjugation. A related blocking effect of the energy transfer was observed in fluorescence spectra of methylene-linked naphthalene and anthracene [16]. In the europium aromatic carboxylates channels of the excitation energy degradation were found in the region of 280–400 nm (35,700–25,000 cm^{-1}) [15]. In paper cited we have placed these degradation channels to ligand electronic transitions or LM CTS.

A comparison of the luminescence excitation spectra of Eu^{3+} and Tb^{3+} was undertaken in present work in the hope of providing better understanding of the mechanisms of the energy transfer to the lanthanide ion in presence of the aliphatic blocking bridge in the ligand. The main attention is given to carboxylates with aromatic substituents: europium and terbium phenyl- and naphthylcarboxylates. Besides, the spectra of europium and terbium nitrates with dialkyl- and diarylsulfoxides are considered. It was demonstrated, that the weakening of π–π-conjugation in aromatic carboxylate ligands can lead to substantial lowering of the energy of LM CTS in europium carboxylate salts and, correspondingly, to more active influence of these states on the processes of the energy transfer from the ligand to Eu^{3+} ion.

2. Experimental

The luminescence and luminescence excitation spectra of europium and terbium phenylcarboxylates: phenylacetates $Ln(PhAc)_3\cdot H_2O$, diphenylacetates $Ln(DPhAc)_3\cdot 2H_2O$, triphenylacetates $Ln(TPhAc)_3\cdot 2H_2O$, phenoxyacetates $Ln(PhOAc)_3\cdot 2H_2O$, triphenylpropionates $Ln(TPhProp)_3\cdot nH_2O$ and their adducts $LnLig_3Phen$, Lig-phenylcarboxylate anion, Phen-1,10-phenanthroline, were investigated. The spectra of europium and terbium 1- and 2-naphthylcarboxylates, $Ln(1\text{-}Napht)_3$ and $Ln(2\text{-}Napht)_3\cdot 3H_2O$, and 2-naphthoxyacetates $Ln(2\text{-}NaphtOAc)_3\cdot 4H_2O$ were also analyzed.

The luminescence excitation spectra of europium and terbium compounds related to the different class: nitrates with sulfoxides $Ln(NO_3)_3\cdot 3DRSO$ (R = $-C_2H_5$ (DESO, diethylsulfoxide), $-C_5H_{11}$ (DASO, diamylsulfoxide), $-C_6H_{13}$ (DHSO, dihexylsulfoxide), $-C_6H_5$ (DPhSO, diphenylsulfoxide), $-CH_2C_6H_5$ (DBSO, dibenzylsulfoxide)) and $Ln(NO_3)_3\cdot 4DMSO$ (DMSO, dimethylsulfoxide) were examined to come to the heart of the problem of luminescence excitation of compounds containing aromatic radicals.

The aromatic carboxylate salts were synthesised by the exchange of cations in water or ethanol solutions of the lanthanide chloride and the sodium salt of corresponding aromatic acid. The adducts were obtained by mixing ethanol solution of 1,10-phenanthroline with solution of the lanthanide salt of aromatic acid. The compounds with sulfoxides were synthesised by mixing ethanol or isopropanol solutions of the lanthanide nitrate and corresponding sulfoxide. The precipitates were recrystallized from isopropanol. Composition of compounds synthesised and the details of their structures were controlled by the elemental analysis, vibrational spectroscopy, comparison of the europium and terbium luminescence spectra and available X-ray data [17].

The luminescence and luminescence excitation spectra of europium and terbium compounds were measured with LOMO UM-2 monochromator (low resolution), SPECTRA-PRO-750 monochromator (high resolution) and SLM Aminco SPF 500 spectrofluorimeter (middle resolution) at 77 and 300 K. The registration of excitation spectra was realized in the regions of $^5D_0$–$^7F_2$ (Eu^{3+}) and $^5D_4$–$^7F_5$ (Tb^{3+}) transitions. The absorption spectrum of the nujol emulsion of 1,10-phenanthroline at 300 K was recorded using Cary-Varian 500 spectrophotometer.

3. Results and discussion

3.1. Luminescence spectra of phenylacetates

The luminescence spectra of europium salts of phenylacetic acids presented in Fig. 1 witness to different symmetry of the charge arrangement around the lanthanide ion in these compounds. Broadening of the Stark components of electronic transitions of Eu^{3+} ions in the diphenylacetate spectrum and their excess number in the triphenylacetate spectrum (Fig. 1c and d) reflect existence of nonequivalent centres in these compounds. This nonequivalence is conditioned by the influence of steric factor concerned with voluminous aromatic radicals. The identity of the structure of pairs of europium and terbium compounds was confirmed by the comparison of the $^5D_0$–^7F_J and $^5D_4$–^7F_J (J = 1, 2, 4) transitions in the spectra of corresponding Eu^{3+} and Tb^{3+} compounds. Such a comparison is demonstrated in Fig. 1a and b for phenylacetates $Eu(PhAc)_3\cdot H_2O$ and $Tb(PhAc)_3\cdot H_2O$. Here the patterns of the Stark splittings of $^7F_1$ and $^7F_2$ multiplets of Eu^{3+} and Tb^{3+} ions are the same. The broadening of lines in the spectrum of $Tb(PhAc)_3\cdot H_2O$ is conditioned by occupation of several low-energy Stark components of $^5D_4$ multiplet and by low resolution of spectrometer used.

Judging from the spectra, lanthanide compounds $LnLig_3Phen$ have dimeric structures with coordination number of the Ln^{3+} ion equal to nine, analogous to many known lanthanide carboxylates with Phen [17], in particular, europium capronate [18], acetate [19], benzoate [20]. This conclusion follows from likeness of the luminescence spectra of compounds $LnLig_3Phen$ (Ln = Eu, Tb) investigated with the typical spectra of europium compounds [13,15,19] having known structures.

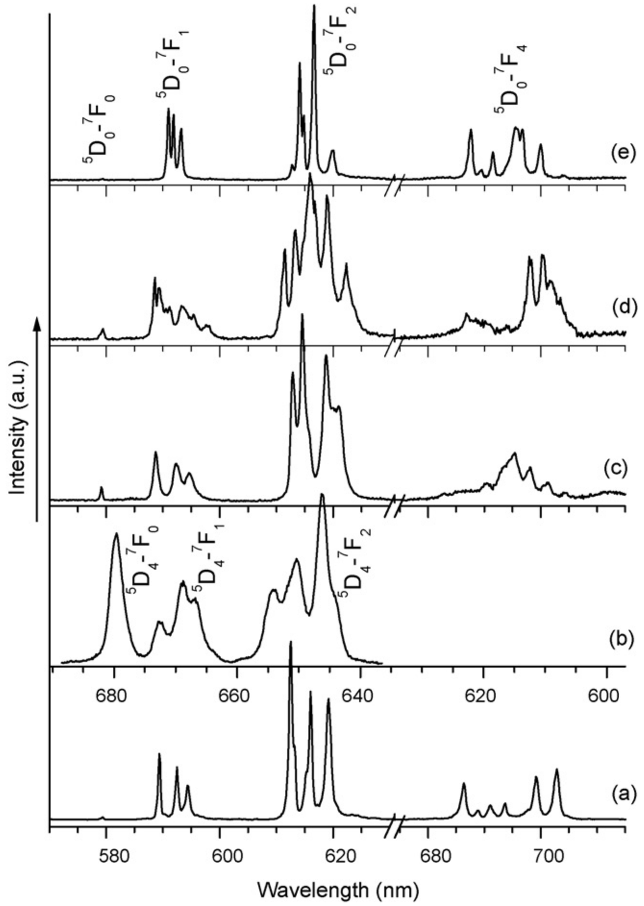

Fig. 1. Luminescence spectra of Eu(PhAc)$_3$·H$_2$O (a), Tb(PhAc)$_3$·H$_2$O (b), Eu(DPhAc)$_3$·2H$_2$O (c), Eu(TPhAc)$_3$·2H$_2$O (d) and Eu(PhOAc)$_3$·2H$_2$O (e) obtained with ~10 cm^{-1} resolution at 77 K. The spectrum (b) was registered with ~20 cm^{-1} resolution.

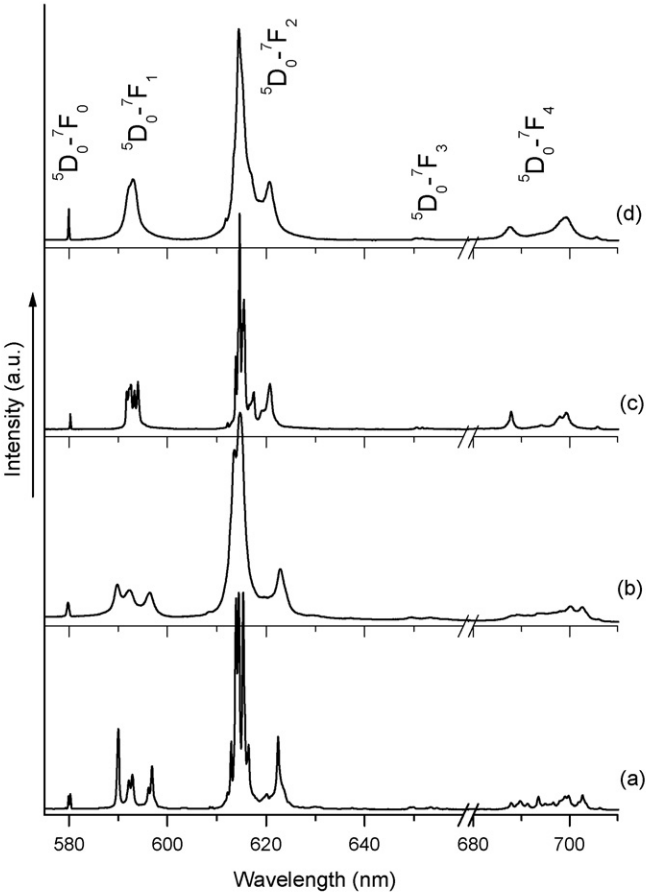

Fig. 2. Luminescence spectra of Eu(TPhAc)$_3$·Phen (a and b) and Eu(PhOAc)$_3$·Phen (c and d) obtained with ~2 cm^{-1} resolution at 77 K (a and c) and 300 K (b and d), respectively.

Only the structure of phenoxyacetate Ln(PhOAc)$_3$·Phen (Ln = Nd, Eu) [21] is known in the series of the lanthanide carboxylates with phenanthroline investigated here. This structure is equivalent to the structures of compounds enumerated above. Two Ln^{3+} cations are connected by four phenoxyacetate anions, of which two are involved in bidentate bridging bonds through carboxylic group and two others in tridentate bridging-cyclic ones. Moreover, the metal cation is connected with two oxygen atoms of bidentate-cyclic carboxylic group of phenoxyacetate anion and with two nitrogen atoms of one phenanthroline molecule. The oxygen atom of phenoxy-group is not coordinated. The coordination number of the Ln^{3+} ion is equal to nine. The nonequivalence of the luminescence centres of Eu^{3+} is seen quite clearly in the luminescence spectrum of Eu(PhOAc)$_3$·Phen recorded at 77 K (Fig. 2). It is smoothed at 300 K owing to broadening the lines and averaging-out the crystal field. There are no indications of nonequivalence of the nearest surroundings of the lanthanide ions in the X-ray data obtained for Eu(PhOAc)$_3$·Phen at 300 K [21].

The luminescence spectrum of europium phenylacetate Eu(PhAc)$_3$·Phen belongs to the only luminescence centre [15]. A strengthening of the crystal field and a growth of the difference of the Ln^{3+} nonequivalent luminescence centres are observed at increase of the number of phenyl radicals in phenylacetate series, in particular, in transition to europium diphenylacetate Eu(DPhAc)$_3$·Phen and then to europium triphenylacetate Eu(TPhAc)$_3$·Phen (Fig. 2). The growing steric influence should lead first of all to more prominent nonequivalence of the centres in dimers. Because of this nonequivalence, decay curves of the metastable levels $^5D_0$ (Eu^{3+}) and $^5D_4$ (Tb^{3+}) measured for europium and terbium diphenyl- and triphenylacetate compounds could not be fitted to a mono-exponential law. Vibrational IR spectra point out a significant asymmetry of carboxylic groups in the lanthanide triphenylacetic salts and their adducts. Still, at increase of the length of the aliphatic bridge between carboxylic group and phenyl rings in transition from triphenylacetate to triphenylpropionate the influence of the steric factor is weakening. So, nonequivalence of the luminescence centres is not observed in the spectrum of triphenylpropionate Eu(TPhProp)$_3$·Phen.

3.2. *Effects of the luminescence excitation*

Earlier we had pointed out the effect of the blocking of the energy transfer from phenyl or naphthyl radicals to Eu^{3+} ion by the introduction of aliphatic bridge, in particular, methylene group –CH$_2$– between the radical and coordinated group of the ligand [11,15]. A consequence of this effect is the lowering of the luminescence efficiency of europium compounds. At the introduction of the bridge a broad band of aromatic radicals disappears from the luminescence excitation spectra of europium carboxylates and europium nitrates with diarylsulfoxides. Besides, the intensity of narrow lines of short-wavelength transitions of Eu^{3+} ions lowers, and sometimes these lines vanish completely. This can be taken as a sign of appearance of some channels of the excitation quenching. Comparison of the excitation spectra of related europium and terbium compounds can help to determine the origin of these energy degradation channels.

3.2.1. Luminescence excitation spectra of europium and terbium nitrates with sulfoxides

At first, let us turn to the family of europium and terbium nitrates with sulfoxides. The luminescence spectra of $Eu(NO_3)_3 \cdot n$DRSO ($n = 3$, 4) had been published earlier [22]. The X-ray data on the structures of $Ln(NO_3)_3 \cdot n$DRSO compounds are well known [17]. The nearest surroundings of the Ln^{3+} ion in $Ln(NO_3)_3 \cdot 3$DRSO is formed by nine atoms of oxygen, six of them belong to three nitrate anions and three last of them belong to sulfoxide molecules.

The excitation spectra of europium and terbium nitrates $Ln(NO_3)_3 \cdot 3$DRSO with dialkylsulfoxides DESO, DASO, DHSO, and $Ln(NO_3)_3 \cdot 4$DMSO consist of narrow bands of Eu^{3+} or Tb^{3+} ions. This is shown in Fig. 3a and d for the compounds with DHSO. The ligand bands are absent there. Moreover, the narrow bands of electronic transitions of both Eu^{3+} and Tb^{3+} are absent in the wavelength range shorter than 315 nm. So, some quenching channel at ~31,750 cm^{-1} in europium and terbium compounds with dialkylsulfoxides, which can be related to π*–n transition of one of the ligands, takes part in the processes of energy dissipation.

In the range of 250–370 nm of the excitation spectra of compounds containing diphenylsulfoxide $Ln(NO_3)_3 \cdot 3$DPhSO (Ln = Eu, Tb) a broad band is observed (Fig. 3b and e). This range of the spectrum is formed by overlapping bands of π–π* and n–π* transitions of diphenylsulfoxide [23]. The short-wavelength part of the band is related mainly to π–π* transitions of the phenyl rings, the long-wavelength part of the band—to the IL CT (p–π-conjugation). In the excitation spectrum of terbium nitrate with dibenzylsulfoxide $Tb(NO_3)_3 \cdot 3$DBSO the intensity of broad band of phenyl radical sharply decreases (Fig. 3c). Only a relatively weak band with maximum at 320 nm remains there. In the spectrum of $Eu(NO_3)_3 \cdot 3$DBSO broad bands of the ligands disappear completely (Fig. 3f). Higher excitation efficiency of Tb^{3+} luminescence through absorption band of the ligand in comparison with Eu^{3+} is conditioned by lower probability of multiphonon relaxation in Tb^{3+} ions [24]. The energy transfer from phenyl rings to the metal ions in compounds of both lanthanides is blocked by methylene bridges of the benzyl radicals located between S=O-group and phenyl rings. As a result, the luminescence efficiency of Ln^{3+} ions lowers dramatically at pumping in the range of phenyl absorption band. The effect revealed in europium and terbium compounds with diarylsulfoxides may be connected with the participation of the same channel in the energy transfer processes as above-mentioned quenching channel in the compounds with dialkylsulfoxides.

3.2.2. Luminescence excitation spectra of europium and terbium phenyl- and naphthylcarboxylates

Patterns of intensity distribution in the excitation spectra of europium phenyl- and naphthylcarboxylates (Figs. 4 and 5) look

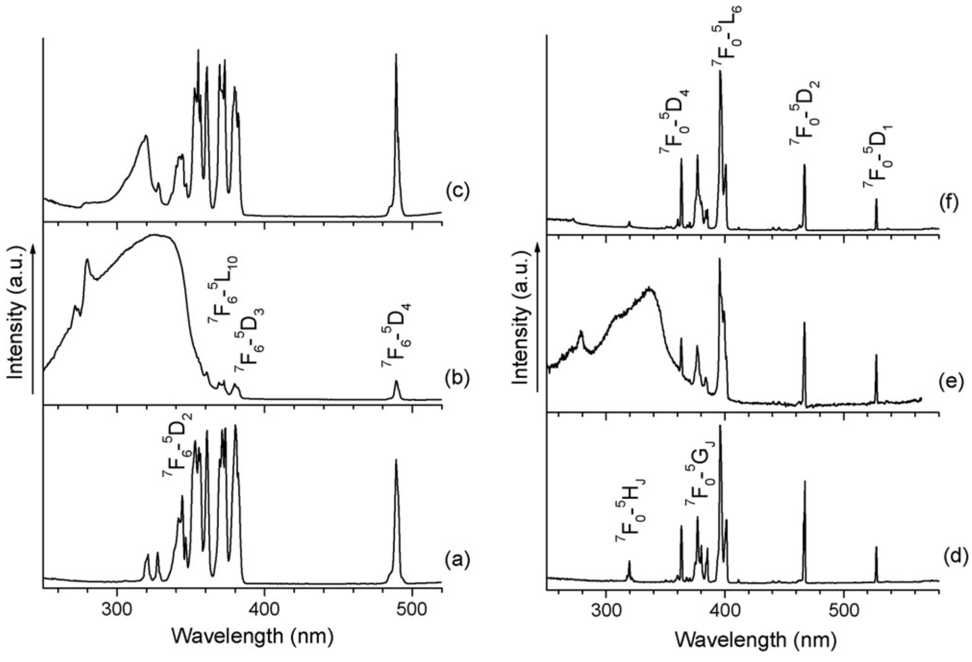

Fig. 3. Luminescence excitation spectra of nitrates $Tb(NO_3)_3 \cdot 3$DHSO (a), $Tb(NO_3)_3 \cdot 3$DPhSO (b), $Tb(NO_3)_3 \cdot 3$DBSO (c), $Eu(NO_3)_3 \cdot 3$DHSO (d), $Eu(NO_3)_3 \cdot 3$DPhSO (e) and $Eu(NO_3)_3 \cdot 3$DBSO (f) at 77 K.

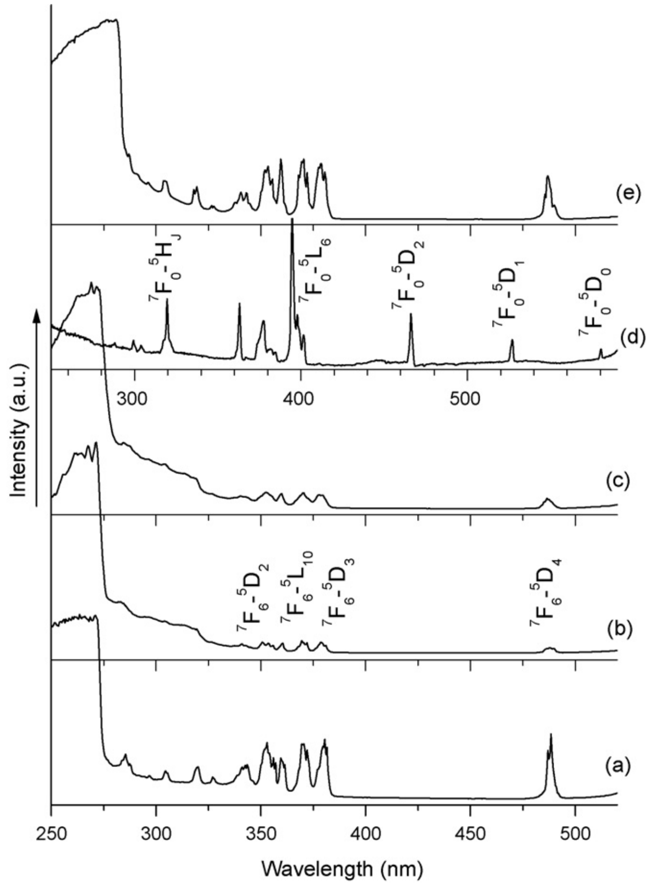

Fig. 4. Luminescence excitation spectra of $Tb(PhAc)_3{\cdot}H_2O$ (a), $Tb(DPhAc)_3{\cdot}2H_2O$ (b), $Tb(TPhAc)_3{\cdot}2H_2O$ (c), $Eu(TPhAc)_3{\cdot}2H_2O$ (d) and $Tb(PhOAc)_3{\cdot}2H_2O$ (e) at 77 K.

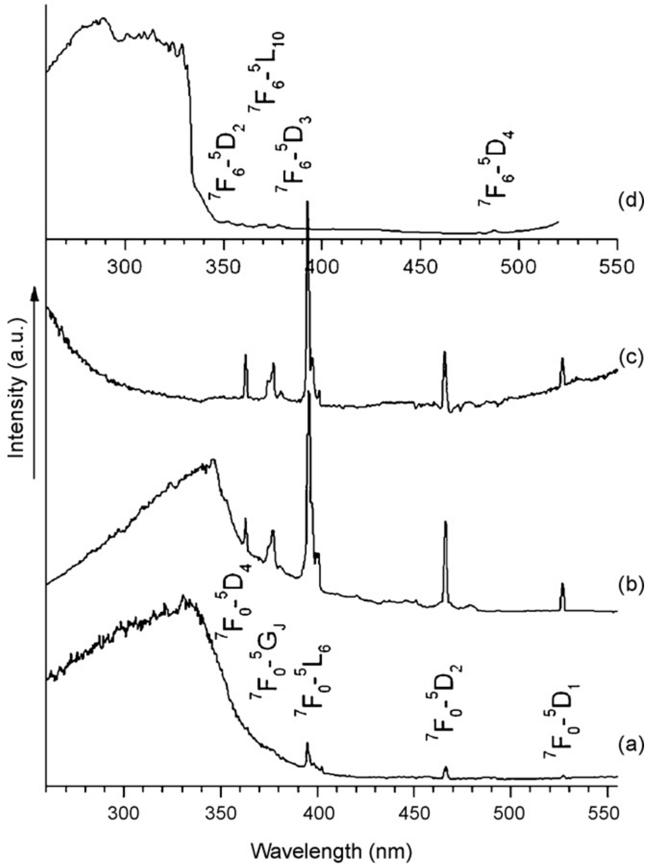

Fig. 5. Luminescence excitation spectra of $Eu(1\text{-}Napht)_3$ (a), $Eu(2\text{-}Napht)_3{\cdot}3H_2O$ (b), $Eu(2\text{-}NaphtOAc)_3{\cdot}4H_2O$ (c) and $Tb(2\text{-}NaphtOAc)_3{\cdot}4H_2O$ (d) at 77 K.

like the patterns of europium and terbium nitrates with diarylsulfoxides discussed above. But, as it will follow, the origin of the quenching channels in carboxylates is different.

When the blocking bridge is absent, broad band of the aromatic ligand is observed in the excitation spectra of europium carboxylates, for example, in benzoate spectra $Eu(Benz)_3{\cdot}2H_2O$ [13], 1- and 2-naphthylcarboxylates $Eu(1\text{-}Napht)_3$ and $Eu(2\text{-}Napht)_3{\cdot}3H_2O$ (Fig. 5a and b). The excitation spectrum of terbium benzoate $Tb(Benz)_3{\cdot}2H_2O$ is analogous to the spectrum of europium benzoate [13]. $Tb(1\text{-}Napht)_3$ and $Tb(2\text{-}Napht)_3{\cdot}3H_2O$ compounds are not luminescent as the energy of the first triplet level of the ligand is lower than the energy of $^5D_4$ level of Tb^{3+} ion [14]. That is why there are no excitation spectra of these compounds.

The bands related to aromatic radicals of the ligand are absent or have very low intensity in the spectra of europium carboxylates with the aliphatic bridge in the ligand. This is typical for the spectra of europium phenylacetate $Eu(PhAc)_3{\cdot}H_2O$, phenoxyacetate $Eu(PhOAc)_3{\cdot}2H_2O$ [15], triphenylacetate $Eu(TPhAc)_3{\cdot}2H_2O$ (Fig. 4d) and 2-naphthoxyacetate $Eu(2\text{-}NaphtOAc)_3{\cdot}4H_2O$ (Fig. 5c). The role of the bridge in the triphenylacetate ligand $(Ph)_3C\text{–}COO^-$ is performed by the carbon atom located between the phenyl radicals and the carboxylic group.

In contrast to situation in the europium excitation spectra, an intense π–π*-band of aromatic part of the ligand appears in the short-wavelength region of the excitation spectra of terbium phenylacetates and naphthoxyacetate presented in Figs. 4 and 5. The band is expanding to the long-wavelength side in transition from phenylacetates (Fig. 4a–c) to phenoxyacetate (Fig. 4e) and then to naphthoxyacetate (Fig. 5d). The bathochromic shift of the band of the phenoxyacetate anion is conditioned by the interaction of the phenyl with unshared pair of electrons of oxygen atom (p–π-conjugation) [23]. In the case of naphthoxyacetate anion the corresponding band is located in longer wavelength region owing to the increase of the dimensions of π-conjugated system. The hypsochromic shift of the band in transition from benzoate to phenylacetates is related to substantial weakening of the conjugation in the ligand, caused by the introduction of the blocking bridge and to complete lack of the coplanarity of the ligand [17]. The increase of the relative intensity of this band in the spectra of diphenyl- and triphenylacetates as well as appearance of a weak band in the region of 275–325 nm, probably, due to IL CT transition, can be conditioned by the increase of the number of phenyl rings and some strengthening of the conjugation. The weakening of the conjugation between carboxylic group and the phenyl rings in phenylacetates in comparison with the benzoates should lead to strengthening of the Ln–O bonds and, as a consequence, to lowering of the LM CTS energy in the europium phenylacetates. The bands of the ligand are lacking in the excitation spectra of europium phenylacetates and naphthoxyacetate, as the LM CTS having sufficiently low energy takes part in process of excitation energy dissipation. The LM CTS energy is lowering from ~35,700 to ~27,800 cm^{-1} in the row of europium salts with ligands: PhAc–TPhAc–PhOAc–2-NaphtOAc.

A noticeable part of the energy absorbed by the aromatic ligand with built-in aliphatic bridge should be emitted as fluorescence. Besides the weak narrow lines of Ln^{3+} transitions a broad band of the ligand fluorescence can be observed in the emission spectra of the lanthanide salts under investigation. The emission spectra of europium and terbium triphenylacetates and triphenylpropionates as well as fluorescence spectrum of triphenylpropionic acid are shown in Fig. 6. One can see quite clear here blocking of the luminescence excitation by the elongated bridge in the $(Ph)_3C–CH_2–$ radical of triphenylpropionate anion in comparison with $(Ph)_3C–$ radical of the triphenylacetate anion. A broad fluorescence band coinciding with the fluorescence band of uncoordinated ligand appears in the spectra of lanthanide triphenylpropionates.

In transition from benzoates to phenylacetates the value of the relative luminescence efficiency evaluated under the experimental conditions described earlier [13], when a region of 300–380 nm of the spectrum of DRSh-250 mercury high pressure lamp including the intense Hg 365 nm line was applied for luminescence excitation, becomes four to five times lower for europium compounds and only two to three times lower for terbium compounds. This is in accordance with the conclusion on participation of LM CTS in the degradation of the excitation energy in the europium salts. While using more intense excitation source in the 250–275 nm region the difference of the luminescence efficiencies of europium benzoate and phenylacetates may be about ten times higher.

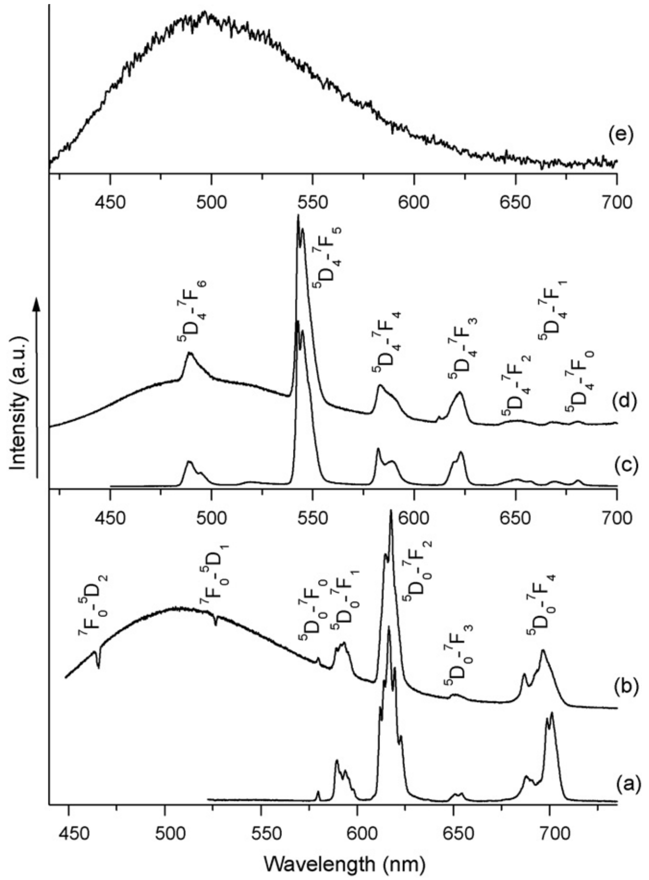

Fig. 6. Emission spectra of $Eu(TPhAc)_3·2H_2O$ (a), $Eu(TPhProp)_3·nH_2O$ (b), $Tb(TPhAc)_3·2H_2O$ (c), $Tb(TPhProp)_3·nH_2O$ (d) and triphenylpropionic acid (e) at 77 K.

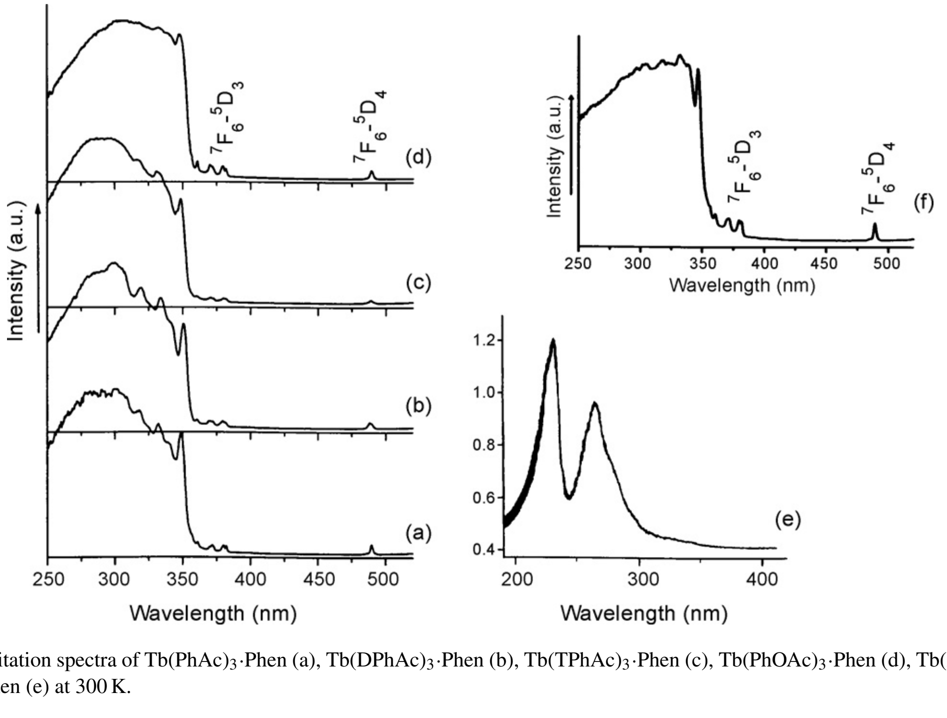

Fig. 7. Luminescence excitation spectra of $Tb(PhAc)_3·Phen$ (a), $Tb(DPhAc)_3·Phen$ (b), $Tb(TPhAc)_3·Phen$ (c), $Tb(PhOAc)_3·Phen$ (d), $Tb(Ac)_3·Phen$ (f) at 77 K and absorption spectrum of Phen (e) at 300 K.

The introduction of heterocyclic diimines in europium and terbium aromatic carboxylates changes the processes of luminescence excitation and energy transfer and results in spectacular increase of excitation and luminescence efficiencies [13–15]. The luminescence excitation spectra of europium and terbium phenylcarboxylates with phenanthroline are practically the same. This is true also for naphthylcarboxylates. A broad band of phenanthroline, probably, overlapping with the band of aromatic carboxylate is observed in the excitation spectra of the series of terbium phenylacetates with phenanthroline, presented in Fig. 7a–d, as well as in the spectra of corresponding europium compounds [15]. The bands related to phenanthroline can be identified if we use for comparison the excitation spectra of the nitrates, acetates or chlorides of europium and terbium with phenanthroline. The spectra of these compounds are formed by phenanthroline bands as the bands of the second ligand are absent in the wavelength region concerned. The absorption spectrum of the nujol emulsion of the 1,10-phenanthroline powder and the luminescence excitation spectrum of terbium acetate $Tb(Ac)_3{\cdot}Phen$ are shown in Fig. 7e and f. A row of very weak bands is observed in the phenanthroline absorption spectrum besides two intense bands at 228 and 265 nm. The longest wavelength weak bands ($S–S^*$–n–π^*, π–π^*) are situated at 324 and 338 nm, respectively, in accordance with published data [25]. The efficiency of the Eu^{3+} luminescence excitation through these Phen bands is higher than that through the intense short-wavelength bands.

The luminescence efficiencies measured for adducts of europium and terbium carboxylates with phenanthroline are 20–30 times higher than for carboxylates without auxiliary heterocyclic ligand. They have a drop of about four times for adducts of both the europium and terbium aromatic carboxylates having aliphatic bridge in comparison with benzoate adducts. Similar changes of europium and terbium luminance witness about the absence of the influence of LM CTS on the energy transfer processes in the adducts investigated.

In general, a comparative study of the excitation spectra of europium and terbium aromatic carboxylates with aliphatic bridge in ligand testifies to the participation of LM CTS in excitation energy degradation in europium salts.

4. Conclusions

The luminescence and luminescence excitation spectra of three groups of europium and terbium coordination compounds containing ligands with aromatic radicals: phenyl- and naphthylcarboxylates, europium and terbium nitrates with sulfoxides were investigated. It was demonstrated, that an increase of the number of phenyl radicals in phenylacetates results in the rise of nonequivalence of Ln^{3+} luminescence centres.

The influence of the aliphatic bridges decoupling the π–π- or p–π-conjugation in the ligand on the energy transfer to Ln^{3+} ions (blocking effect) was examined. It was shown that this decoupling leads to significant lowering of the LM CTS energy in the europium carboxylate salts, just down to $\sim$27,800 cm^{-1}. Accordingly, the probability of the LM CTS participation in the excitation energy dissipation processes increases and the luminescence quantum yield of europium compounds lowers.

A channel of the excitation energy dissipation in the region of $\sim$31,750 cm^{-1} related to ligand electronic transitions was found in the europium and terbium nitrates with sulfoxides.

It was shown that a part of the energy absorbed by the aromatic ligand having aliphatic bridge can be emitted as the ligand fluorescence.

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References

[1] M. Latva, H. Takalo, V.-M. Mukkala, C. Matachescu, J.C. Rodriguez-Ubis, J. Kankare, J. Lumin. 75 (1997) 149.

[2] B. Yan, H. Zhang, S. Wang, J. Ni, J. Photochem. Photobiol. A: Chem. 116 (1998) 209.

[3] S. Petoud, J.-C.G. Bünzli, T. Glanzman, C. Piguet, Q. Xiang, R.P. Thummel, J. Lumin. 82 (1999) 69.

[4] X. Yu, Q. Su, J. Photochem. Photobiol. A: Chem. 155 (2003) 73.

[5] F. Gutierrez, Ch. Tedeschi, L. Maron, J.-P. Daudey, R. Poteau, J. Azema, P. Tisnes, C. Picard, Dalton Trans. (2004) 1334.

[6] P. Gawryszewska, O.L. Malta, R.L. Longo, F.R. Goncalves e Silva, S. Alves, K. Mierzwicki, Z. Latajka, M. Pietraszkiewicz, J. Legendziewicz, Chem. Phys. Chem. 5 (2004) 1577.

[7] G.K. Liu, M.P. Jensen, P.M. Almond, J. Phys. Chem. 110 (2006) 2081.

[8] W.M. Faustino, O.L. Malta, G.F. de Sa, Chem. Phys. Lett. 429 (2006) 595.

[9] C. Yang, L.-M. Fu, Y. Wang, J.-P. Zhang, W.-T. Wong, X.-C. Ai, Y.-F. Qiao, B.-S. Zou, L.-L. Gui, Angew. Chem. Int. Ed. 43 (2004) 5010.

[10] Y.H. Kim, N.S. Baek, H.K. Kim, Chem. Phys. Chem. 7 (2006) 213.

[11] V. Tsaryuk, V. Zolin, J. Legendziewicz, J. Lumin. 102–103 (2003) 744.

[12] V.F. Zolin, L.N. Puntus, V.I. Tsaryuk, V.A. Kudryashova, J. Legendziewicz, P. Gawryszewska, R. Szostak, J. Alloys Compd. 380 (2004) 279.

[13] V. Tsaryuk, K. Zhuravlev, V. Zolin, P. Gawryszewska, J. Legendziewicz, V. Kudryashova, I. Pekareva, J. Photochem. Photobiol. A: Chem. 177 (2006) 314.

[14] V.I. Tsaryuk, K.P. Zhuravlev, V.F. Zolin, V.A. Kudryashova, J. Legendziewicz, R. Szostak, J. Appl. Spectrosc. 74 (2007) 51.

[15] V. Tsaryuk, V. Zolin, K. Zhuravlev, V. Kudryashova, J. Legendziewicz, R. Szostak, J. Alloys Compd. 451 (2008) 153.

[16] S. Speiser, M. Hasegawa, S. Enomoto, T. Hoshi, K. Igarashi, Y. Nishimura, A. Yasuda, T. Yamazaki, I. Yamazaki, J. Lumin. 102-103 (2003) 278.

[17] Cambridge Structural Database System, v.5.28, 2006.

[18] M.A. Porai-Koshits, A.S. Antsyshkina, G.G. Sadikov, E.N. Lebedeva, S.S. Korovin, R.N. Shchlelokov, V.G. Lebedev, Zh. Neorg. Khim. 40 (1995) 748.

[19] V. Tsaryuk, I. Turowska-Tyrk, J. Legendziewicz, V. Zolin, R. Shostak, L. Puntus, J. Alloys Compd. 341 (2002) 323.

[20] S.-Y. Niu, B. Yang, J.-Q. Cao, G.-D. Yang, Chem. J. Chin. Univ. 18 (1997) 1917 (Chinese edition).

[21] H. Deng, Y.-P. Cai, H. Chao, C.-L. Chen, C.W. Jiang, C.-Q. Chen, L.-N. Ji, Chin. J. Chem. 21 (2003) 409.

[22] V.I. Tsaryuk, Proc. SPIE, v.5507, 2004, p. 62.

[23] O.V. Sverdlova, Electronic Spectra in Organic Chemistry, Chemistry, Leningrad, 1985 (in Russian).

[24] V.F. Zolin, L.G. Koreneva, Lanthanide Probe in Chemistry and Biology, Nauka, Moscow, 1980 (in Russian).

[25] E.F. Gudgin Templeton, A. Pollak, J. Lumin. 43 (1989) 195.