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## Role of methylene spacer in the excitation energy transfer in europium 1- and 2- naphthylcarboxylates

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### ABSTRACT

A series of compounds  $\text{Ln}(\text{RCOO})_3 \cdot \text{Phen}$  ( $\text{Ln} = \text{Eu}, \text{Gd}, \text{Tb}$ ;  $\text{RCOO}^- = 1\text{- and } 2\text{-naphthoate}$ , 1- and 2-naphthylacetate, 1- and 2-naphthoxyacetate anions, Phen = 1,10-phenanthroline) was investigated by methods of optical spectroscopy. Compounds of composition  $\text{Ln}(\text{RCOO})_3 \cdot n\text{H}_2\text{O}$  with the same carboxylate ligands are also considered. Results of studies of the effects of methylene spacer decoupling the  $\pi$ - $\pi$ - or  $p$ - $\pi$ -conjugation in the naphthylcarboxylate ligand on the structure of  $\text{Eu}^{3+}$  coordination centre, on the lifetime of  $^5\text{D}_0$  ( $\text{Eu}^{3+}$ ) state, and on processes of the excitation energy transfer to  $\text{Eu}^{3+}$  or  $\text{Tb}^{3+}$  ions are presented. Introduction of the methylene bridge in the ligand weakens the influence of the steric hindrances in forming of a crystal lattice and results in lowering the distortion of the  $\text{Eu}^{3+}$  luminescence centre, and in elongation of the observed  $^5\text{D}_0$  lifetime  $\tau_{\text{obs}}$ . The latter is caused by decrease in contribution of the radiative processes rate  $1/\tau_r$ . This is confirmed by the correlation between the lifetimes  $\tau_{\text{obs}}$  and the quantities " $\tau_r \cdot \text{const}$ " inversely proportional to the total integral intensities of  $\text{Eu}(\text{RCOO})_3 \cdot \text{Phen}$  luminescence spectra. The methylene spacer performs a role of regulator of sensitization of the  $\text{Ln}^{3+}$  luminescence efficiency by means of an influence on mutual location of lowest triplet states of the ligands, the ligand–metal charge transfer (LMCT) states, and the emitting states of  $\text{Ln}^{3+}$  ions. The lowest triplet state in lanthanide naphthylcarboxylate adducts with Phen is related to carboxylate anion. A presence of the methylene spacer in naphthylcarboxylate ligand increases the triplet state energy. At the same time, the energy of "carboxylic group– $\text{Eu}^{3+}$  ion" charge transfer states falls, which can promote the degradation of excitation energy. In naphthylcarboxylates investigated a range of the carboxylate triplet state energies from 19 150 to 20 600  $\text{cm}^{-1}$  was demonstrated in dependence on the type of the carboxylate anion. The interligand energy transfer from Phen to carboxylate lowest triplet state was revealed in complexes with Phen ligand. The effect of OH-group inserted in 1- or 3-position of 2-naphthoate ligand on the excitation energy transfer is also analyzed.

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### 1. Introduction

Strategies for the design of highly luminescent lanthanide compounds, which can be used in photonic applications such as organic light emitting diodes, physical and biological sensors, light transforming materials, plastic lasers and amplifiers, should include disclosure and minimizing of the factors preventing the effective excitation energy transfer to  $\text{Ln}^{3+}$  ion. The blocking influence of the methylene bridges on the excitation energy transfer between two fragments of an organic system or of a lanthanide complex with organic ligand giving rise to an abrupt decrease of the emission of acceptor part of the system is well known [1–4]. Embedding of the

methylene groups in aromatic carboxylate ligand can cause substantial lowering in the energy of ligand–metal charge transfer (LMCT) states in europium carboxylates and, correspondingly, more active influence of these states on the processes of the excitation energy degradation [2,4]. These effects are conditioned by interrupting the  $\pi$ - $\pi$ - or  $p$ - $\pi$ -conjugation in organic system and by substantial weakening of the interaction of two parts of the molecule in the presence of aliphatic bridge. One of the design principles of luminescent sensors and switches employs the format "fluorophore–spacer–receptor" [5,6]. In polymer films, the rate of photoinduced electron transfer through the methylene chain and the intensity of fluorescence of the linked monomers can be enhanced by an electric field in contrast to situation in the films without the methylene groups [7,8]. Examples cited indicate an important role of the methylene groups in the energy transfer in organic molecules and coordination compounds.

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In present work, the effects of methylene spacer situated in 1- and 2-naphthylcarboxylate ligands in several europium complexes with 1,10-phenanthroline (Phen) on the structure of  $\text{Eu}^{3+}$  luminescence centre, on the lifetime of  $^5\text{D}_0$  ( $\text{Eu}^{3+}$ ) state and on the excitation energy transfer to  $\text{Ln}^{3+}$  ion are discussed. Contributions of radiative and nonradiative processes to the lifetimes measured are analyzed. The ligand lowest triplet state in lanthanide naphthylcarboxylate complexes belongs to carboxylate anion in contrast to many lanthanide phenylcarboxylates and aliphatic carboxylates with Phen, in which the lowest triplet state is related to Phen ligand [9,10]. Relation between the type of naphthylcarboxylate anion and the carboxylate triplet state energy is investigated. Processes of the energy transfer between two different ligands of compound are considered. Correlations between spectroscopic properties and peculiarities of the structure of lanthanide naphthylcarboxylates obtained can extend opportunities for the search of the rare earth materials with high quantum yield of luminescence for applications in devices of molecular electronics and photonics.

## 2. Experimental

Lanthanide carboxylates  $\text{Ln}(\text{RCOO})_3 \cdot \text{Phen}$  ( $\text{Ln} = \text{Eu}, \text{Gd}, \text{Tb}$ ) containing 1- and 2-naphthoic ( $\text{C}_{10}\text{H}_7\text{COO}^-$ ), 1- and 2-naphthylacetic ( $\text{C}_{10}\text{H}_7\text{CH}_2\text{COO}^-$ ), 1- and 2-naphthoxyacetic ( $\text{C}_{10}\text{H}_7\text{OCH}_2\text{COO}^-$ ) anions were synthesized and investigated. Carboxylates of composition  $\text{Ln}(\text{RCOO})_3 \cdot n\text{H}_2\text{O}$  with the ligands indicated and with 1- and 3-hydroxy-2-naphthoic anions ( $\text{C}_{10}\text{H}_6\text{OHCOO}^-$ ) were also considered. Chemical formulae of the ligands are shown in Fig. 1. A list of compounds investigated with the corresponding abbreviations is given in Tables 1 and 2. The carboxylate salts were obtained by the exchange of cations in water or ethanol solutions of the lanthanide

chloride and the sodium salt of corresponding carboxylic acid. The adducts with phenanthroline were synthesized by admixing of ethanol solution of Phen to solution of the lanthanide salt of carboxylic acid. All reagents used for syntheses were purchased from Sigma-Aldrich. Composition of compounds synthesized was controlled by the elemental analysis and IR vibrational spectroscopy. Eu, Gd, and Tb compounds with the same carboxylate ligand are isostructural. The europium adduct with 1-NaphthOAc and Phen ligands was obtained in two compositions: as hydrated and anhydrous compounds. After keeping the hydrate for 2 h at  $\sim 100^\circ\text{C}$  temperature, the weakly bound  $\text{H}_2\text{O}$  molecules evaporated, and the compound transformed to anhydrous form. All the other adducts with Phen were synthesized as anhydrous compounds. X-ray data are known only for dimeric  $\text{Eu}(\text{1-Napht})_3 \cdot \text{Phen}$  having  $\text{Eu}^{3+}$  C.N.=9 [11]. Judging from the spectra, the lanthanide carboxylates with Phen form a group of related compounds similar in a structure to this naphthoate. The lanthanide carboxylate salts (without Phen) contain various numbers of water molecules. They have noticeably differing luminescence spectra that testify to individual crystal structures.

The luminescence, phosphorescence, and luminescence excitation spectra of compounds under investigation were measured with LOMO UM-2 monochromator, LOMO DFS-12 spectrophotometer and SLM Aminco SPF 500 spectrofluorimeter. The former experimental set was supplied with highly sensitive photomultiplier H6780-20. The energy of the lowest excited triplet state of the ligands was obtained from phosphorescence spectra recorded with 1 ms time delay at 77 K, and lifetimes of  $^5\text{D}_0$  ( $\text{Eu}^{3+}$ ) state in europium compounds were determined at 77 and 295 K with UM-2 setup. The exponential fitting with Origin 7.0 was used for analysis of decay process. Decay curves of the  $^5\text{D}_0$  level could be fitted to a mono-exponential law. Relative error of determination of lifetimes is  $\pm 2\%$ . The relative integral intensities of the  $\text{Eu}^{3+}$  electronic transitions were estimated with correction on the spectral sensitivity distribution of the experimental setup.

## 3. Results and discussion

### 3.1. Luminescence spectra and lifetime of $^5\text{D}_0$ ( $\text{Eu}^{3+}$ ) state

In the crystal structure of  $\text{Eu}(\text{1-Napht})_3 \cdot \text{Phen}$  (1) two  $\text{Ln}^{3+}$  ions of dimer are bonded by two bridging and two bridging-cyclic carboxylic groups [11]. Each  $\text{Ln}^{3+}$  ion coordinates also cyclic carboxylic group and Phen molecule. The degree of distortion of lanthanide coordination polyhedron taken as distorted three-capped trigonal prism in this compound is more pronounced than for many analogous dimeric europium carboxylates with Phen having  $\text{Eu}^{3+}$  C.N.=9 [9]. In this compound main distortions of Ln coordination polyhedron display as considerable ( $\sim 0.7 \text{ \AA}$ ) range in the Ln–O distances related to bridging-cyclic  $\text{COO}^-$ -group. The

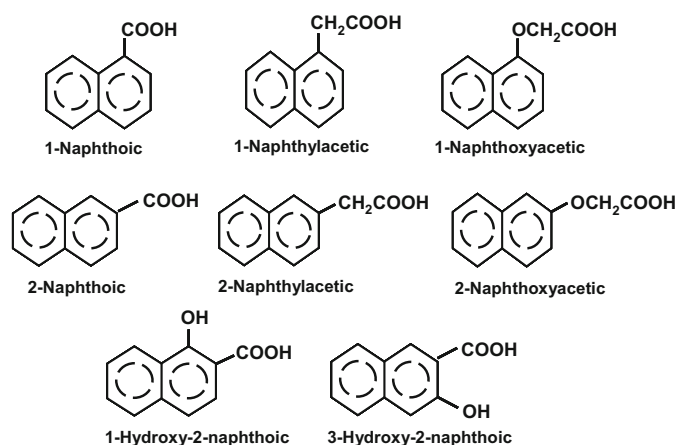


Fig. 1. Structures of the molecules of naphthylcarboxylic acids.

**Table 1**  
Relative integral intensities of electronic transitions in the  $\text{Eu}^{3+}$  luminescence spectra  $I = ^5\text{D}_0 \rightarrow ^7\text{F}_j / ^5\text{D}_0 \rightarrow ^7\text{F}_1$ , total integral intensity  $\Sigma I$  at 77 K and lifetimes  $\tau_{\text{obs}}$  of  $^5\text{D}_0$  state.

| No. | Compound                                                                     | $I$ (a.u.) |       |       | $\Sigma I$<br>( $J=0-6$ ) | $\tau_{\text{obs}}$ (ms) |       |
|-----|------------------------------------------------------------------------------|------------|-------|-------|---------------------------|--------------------------|-------|
|     |                                                                              | $J=2$      | $J=4$ | $J=6$ |                           | 77 K                     | 295 K |
| 1   | $\text{Eu}(\text{1-Napht})_3 \cdot \text{Phen}$                              | 6.95       | 2.1   | 1.25  | 11.4                      | 1.12                     | 1.02  |
| 2   | $\text{Eu}(\text{2-Napht})_3 \cdot \text{Phen}$                              | 5.0        | 1.8   | 1.0   | 8.95                      | 1.15                     | 1.11  |
| 3   | $\text{Eu}(\text{1-NaphtAc})_3 \cdot \text{Phen}$                            | 3.1        | 1.66  | 0.77  | 6.63                      | 1.94                     | 1.83  |
| 4   | $\text{Eu}(\text{2-NaphtAc})_3 \cdot \text{Phen}$                            | 3.5        | 1.44  | 0.85  | 6.89                      | 1.63                     | 1.46  |
| 5   | $\text{Eu}(\text{1-NaphtOAc})_3 \cdot \text{Phen}$                           | 3.43       | 1.42  | 0.78  | 6.72                      | 1.59                     | 1.56  |
|     | $\text{Eu}(\text{1-NaphtOAc})_3 \cdot \text{Phen} \cdot 2\text{H}_2\text{O}$ | 2.27       | 1.38  | 0.58  | 5.33                      | 0.87                     | 0.75  |
| 6   | $\text{Eu}(\text{2-NaphtOAc})_3 \cdot \text{Phen}$                           | 3.23       | 1.37  | 0.66  | 6.36                      | 1.71                     | 1.60  |

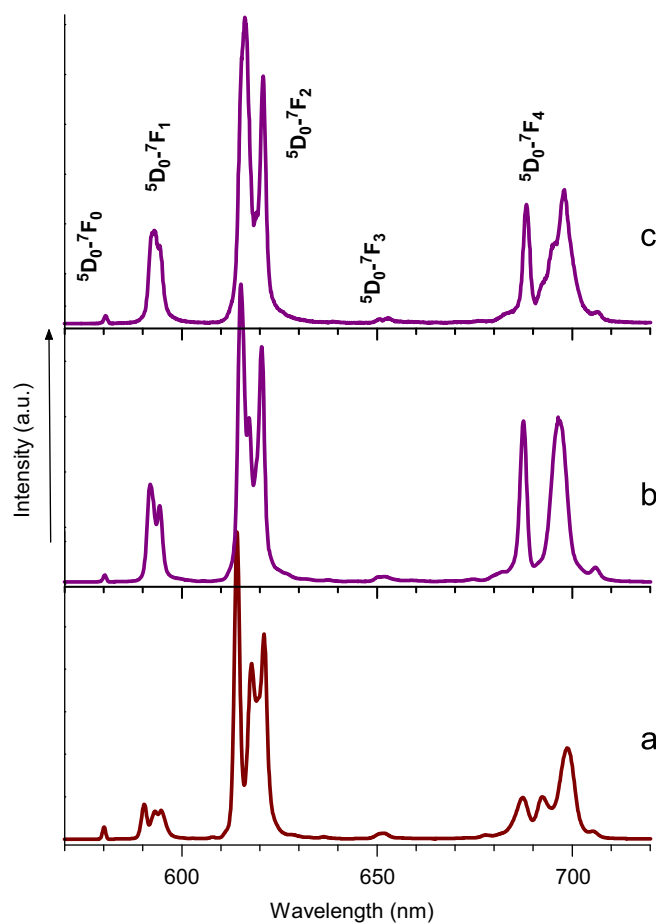
**Table 2**Energies of ligand triplet states and  $\text{Ln}^{3+}$  electronic states.

| Ligand                                                           | Compound                                                      | Energy ( $\text{cm}^{-1}$ ) | $\text{Ln}^{3+}$ state              |
|------------------------------------------------------------------|---------------------------------------------------------------|-----------------------------|-------------------------------------|
| 1,10-Phenanthroline<br>1,10-Phenanthroline<br>2-Naphthoxyacetate | $\text{GdCl}_3 \cdot \text{Phen}_2 \cdot n\text{H}_2\text{O}$ | 21 470                      | $^5\text{D}_2$ ( $\text{Eu}^{3+}$ ) |
|                                                                  | Carboxylate complexes [9,10]                                  | 21 050                      |                                     |
|                                                                  | $\text{Gd}(\text{2-NaphtOAc})_3 \cdot \text{Phen}$            | 20 850–22 300               |                                     |
|                                                                  | $\text{Gd}(\text{2-NaphtOAc})_3 \cdot 4\text{H}_2\text{O}$    | 20 470                      |                                     |
|                                                                  |                                                               | 20 600                      |                                     |
| 1-Naphthoxyacetate                                               | $\text{Gd}(\text{1-NaphtOAc})_3 \cdot \text{Phen}$            | 20 500                      | $^5\text{D}_4$ ( $\text{Tb}^{3+}$ ) |
|                                                                  | $\text{Gd}(\text{1-NaphtOAc})_3 \cdot 3\text{H}_2\text{O}$    | 19 850                      |                                     |
|                                                                  | $\text{Gd}(\text{2-NaphtAc})_3 \cdot \text{Phen}$             | 19 920                      |                                     |
|                                                                  | $\text{Gd}(\text{2-NaphtAc})_3 \cdot 3\text{H}_2\text{O}$     | 19 700                      |                                     |
|                                                                  | $\text{Gd}(\text{1-NaphtAc})_3 \cdot \text{Phen}$             | 19 850                      |                                     |
| 2-Naphthylacetate                                                | $\text{Gd}(\text{1-NaphtAc})_3 \cdot 2.5\text{H}_2\text{O}$   | 19 600                      | $^5\text{D}_1$ ( $\text{Eu}^{3+}$ ) |
|                                                                  | $\text{Gd}(\text{2-Napht})_3 \cdot \text{Phen}$               | 19 800                      |                                     |
|                                                                  | $\text{Gd}(\text{2-Napht})_3 \cdot 3\text{H}_2\text{O}$       | 19 500                      |                                     |
| 1-Naphthylacetate                                                | $\text{Gd}(\text{1-Napht})_3 \cdot \text{Phen}$               | 19 300                      | $^5\text{D}_0$ ( $\text{Eu}^{3+}$ ) |
|                                                                  | $\text{Gd}(\text{1-Napht})_3$                                 | 19 150                      |                                     |
| 2-Naphthoate                                                     | $\text{Gd}(\text{1-OH-2-Napht})_3 \cdot n\text{H}_2\text{O}$  | 19 750                      | $^5\text{D}_1$ ( $\text{Eu}^{3+}$ ) |
|                                                                  |                                                               | 18 975                      |                                     |
| 1-Naphthoate                                                     | $\text{Gd}(\text{3-OH-2-Napht})_3 \cdot n\text{H}_2\text{O}$  | 17 550                      | $^5\text{D}_0$ ( $\text{Eu}^{3+}$ ) |
|                                                                  |                                                               | 17 250                      |                                     |

shift of Ln atom from the centre of its coordination polyhedron is 0.15 Å, the rotation angle between the bases of trigonal prism is 13.1°, and torsion and bending angles between “pyridine” rings in Phen are 8.6° and 4.2°, respectively [9,11].

The main changes in the structure of Ln coordination polyhedron and in the charge distribution in the nearest surroundings of  $\text{Ln}^{3+}$  ion in dimeric carboxylates with Phen or 2,2'-bipyridine (Bpy) of the kind are conditioned by high “sensitivity” of bonding of the bridging-cyclic carboxylic group to the type and size of carboxylate ligand [9,12]. Introduction of the methylene group in the carboxylate ligand leads to weakening the steric hindrances and to decrease in the distortions of the lanthanide coordination polyhedron thanks to moving the voluminous fragment from the  $\text{Ln}^{3+}$  ion and to bending of the ligand. This appears in dimeric europium phenoxyacetate with Phen [13] in comparison with corresponding benzoate complex [14] and in europium 1-naphthylacetate solvate with dimethylformamide  $\text{Eu}(\text{1-NaphtAc})_3 \cdot \text{Phen} \cdot (\text{C}_3\text{H}_7\text{NO})$  [15] in comparison with  $\text{Eu}(\text{1-Napht})_3 \cdot \text{Phen}$  compound. In the solvate mentioned, the Eu–O bond lengths related to the bridging-cyclic carboxylic group are close to that in europium acetate with Phen having relatively small distortions of Eu coordination polyhedron [16].

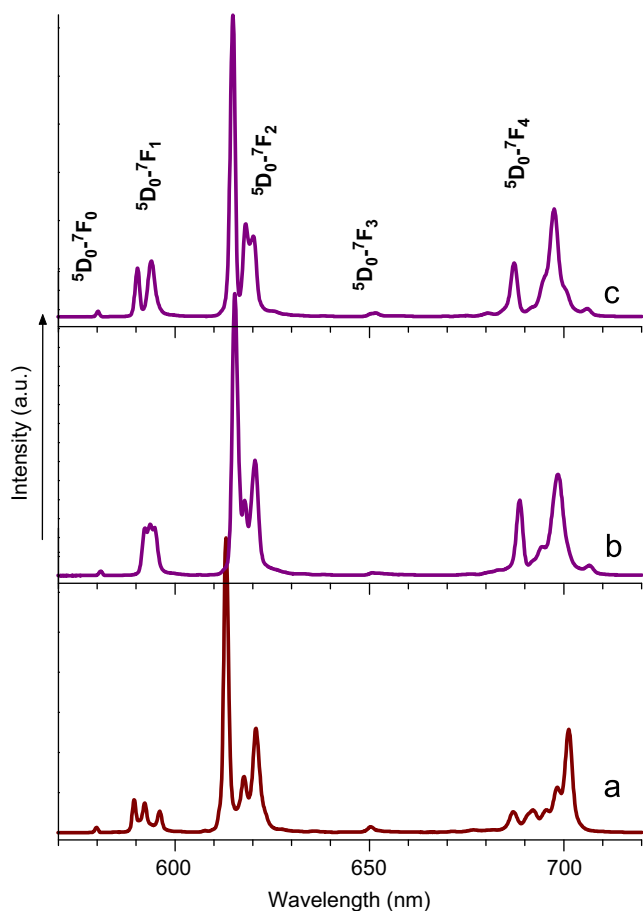
So, the introduction of the methylene bridges between the COO-group and naphthalene rings in compounds investigated must weaken the effect of the size factor on the  $\text{Eu}^{3+}$  ion nearest surroundings, and the distortions of the crystal field should be lowered. In the  $\text{Eu}^{3+}$  luminescence spectra of two series of compounds containing 1- and 2- naphthylcarboxylate anions one can observe the degeneration of Stark components and two-three times decrease in the relative intensity of hypersensitive  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  transition in going from naphthoates to compounds with the methylene bridge in the ligand (Figs. 2 and 3, Table 1). The luminescence centres in  $\text{Eu}(\text{1-Napht})_3 \cdot \text{Phen}$  (1) and  $\text{Eu}(\text{2-Napht})_3 \cdot \text{Phen}$  (2) have the largest distortions. The least distorted centres were found for  $\text{Eu}(\text{1-NaphtOAc})_3 \cdot \text{Phen} \cdot 2\text{H}_2\text{O}$  hydrate (Fig. 4). The difference between the frequencies of antisymmetric  $\nu_{as}$  and symmetric  $\nu_s$  components of the stretching vibration  $\nu(\text{COO}^-)$  in the IR spectrum of this compound is the smallest in the family of naphthylcarboxylates investigated. This points to increase in equivalence of effective charges on oxygen atoms of carboxylic groups and decrease in the degree of polarization of carboxylate anions in this compound. Judging from the IR spectra,



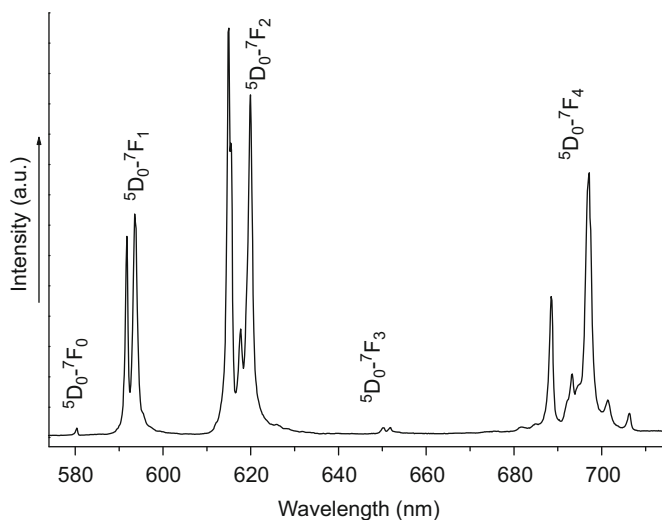
**Fig. 2.** Luminescence spectra of europium 1-naphthylcarboxylates:  $\text{Eu}(\text{1-Napht})_3 \cdot \text{Phen}$  (a),  $\text{Eu}(\text{1-NaphtAc})_3 \cdot \text{Phen}$  (b) and  $\text{Eu}(\text{1-NaphtOAc})_3 \cdot \text{Phen}$  (c) recorded with  $\sim 20 \text{ cm}^{-1}$  resolution at 77 K.

in other compounds more strongly distorted and polarized carboxylic groups are present.

The rise in the symmetry of the nearest surroundings of  $\text{Eu}^{3+}$  ion should lead to the decrease in the probability of the induced electric-dipole transitions and, therefore, to decrease in



**Fig. 3.** Luminescence spectra of europium 2-naphthylcarboxylates: Eu(2-Napht)<sub>3</sub> · Phen (a), Eu(2-NaphtAc)<sub>3</sub> · Phen (b) and Eu(2-NaphtOAc)<sub>3</sub> · Phen (c) recorded with  $\sim 20 \text{ cm}^{-1}$  resolution at 77 K.

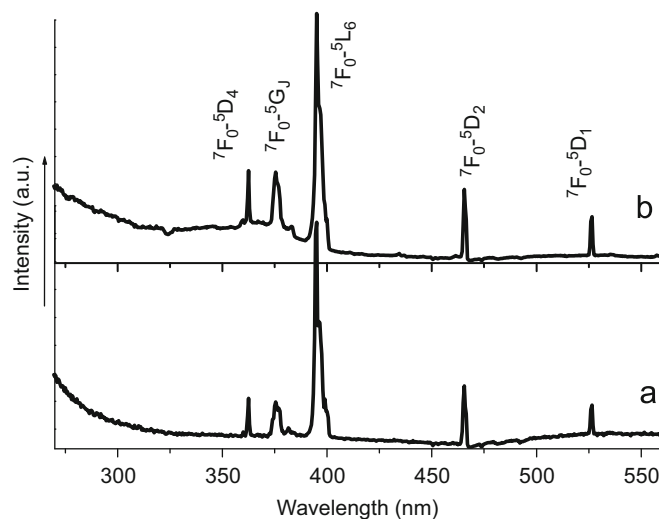


**Fig. 4.** Luminescence spectrum of Eu(1-NaphtOAc)<sub>3</sub> · Phen · 2H<sub>2</sub>O recorded with  $\sim 10 \text{ cm}^{-1}$  resolution at 77 K.

the rate of radiative (natural) processes, i.e. to increase in the radiative lifetime  $\tau_r$  of the  $^5\text{D}_0$  state of  $\text{Eu}^{3+}$  ion. The lifetimes of the  $^5\text{D}_0$  state  $\tau_{obs}$  measured for europium naphthylcarboxylate adducts with Phen are given in Table 1. The lifetime observed for  $\text{Eu}^{3+}$  ion electronic state is defined usually by the rates of radiative and of various nonradiative processes: multiphonon

relaxation, the quenching with participation of LMCT states, the quenching by back energy transfer from the metastable level of  $\text{Ln}^{3+}$  ion to the ligand lowest triplet state, and the Ln–Ln concentration quenching [17–21]. A question arises, how large is a contribution of the radiative processes to the  $^5\text{D}_0$  state lifetime  $\tau_{obs}$  measured for europium naphthylcarboxylates. As the lifetimes are the shortest for compounds Eu(1-Napht)<sub>3</sub> · Phen and Eu(2-Napht)<sub>3</sub> · Phen having the least symmetric luminescence centres, one can suppose the prevailing contribution of the radiative processes rates in these systems. Let us analyze contributions of the listed potential quenching processes to the lifetime of  $^5\text{D}_0$  state in naphthylcarboxylates.

- (i) It was demonstrated [9] that in the anhydrous dimeric europium carboxylates with Phen the Ln–Ln self-quenching can decrease the lifetime of  $^5\text{D}_0$  state only by 3–4%.
- (ii) The luminescence quenching by back energy transfer from  $^5\text{D}_0$  state in europium compounds is possible. The authors of communication [19] investigated such processes for europium Schiff base complexes, in which the lowest triplet states were situated close to the  $^5\text{D}_0$  state, and the back energy transfer was active. This case of quenching can be realized only in europium 3-hydroxy-2-naphthoate, where the triplet state energy is very low (Table 2).
- (iii) Judging from the  $\text{Eu}^{3+}$  excitation spectra (Fig. 5 and Figs. in Ref. [4]), LMCT state can participate in the degradation of the excitation energy in europium naphthylcarboxylate hydrates  $\text{Ln}(\text{RCOO})_3 \cdot n\text{H}_2\text{O}$  having methylene spacer, in contrast to Eu(1-Napht)<sub>3</sub> and Eu(2-Napht)<sub>3</sub> · 3H<sub>2</sub>O salts, where spacers of the kind are absent. The weakening in the conjugation between the carboxylic group and the naphthalene fragment in naphthylacetates and naphthoxyacetates in comparison with the naphthoates should lead to strengthening the Ln–O bonds and, as a consequence, to lowering the LMCT state energy for europium salts, but not for corresponding terbium salts (see the excitation spectra of Eu(2-NaphtOAc)<sub>3</sub> · 4H<sub>2</sub>O and Tb(2-NaphtOAc)<sub>3</sub> · 4H<sub>2</sub>O in Ref. [4]). The bands of the ligand and  $\text{Eu}^{3+}$  electronic lines above  $^7\text{F}_0$ – $^5\text{D}_4$  transition are lacking in the excitation spectra of europium naphthylacetate and naphthoxyacetate salts, as the LMCT state having sufficiently low energy takes part in process of excitation energy dissipation. Such nonradiative processes will influence



**Fig. 5.** Luminescence excitation spectra of Eu(1-NaphtOAc)<sub>3</sub> · 3H<sub>2</sub>O (a) and Eu(2-NaphtAc)<sub>3</sub> · 3H<sub>2</sub>O (b) at 77 K.



on the efficiency of the sensitization and the overall  $\text{Eu}^{3+}$  luminescence quantum yield. But the energy of LMCT state is too high for the quenching of the  $^5\text{D}_0$  ( $\text{Eu}^{3+}$ ) electronic state. Therefore, nonradiative processes due to the LMCT states should not contribute to the  $^5\text{D}_0$  lifetime and to the intrinsic quantum yield of the  $\text{Eu}^{3+}$  ion in naphthylcarboxylates. The case of participation of low-energy LMCT state in the quenching of  $^5\text{D}_0$  state in europium dipivaloylmethanate  $\text{Eu}(\text{DPM})_3$  at high temperatures is well known [22].

- (iv) It can be supposed, that a contribution of the multiphonon relaxation with participation of high-frequency vibrations to the  $^5\text{D}_0$  lifetime  $\tau_{\text{obs}}$  for europium naphthylcarboxylates  $\text{Eu}(\text{RCOO})_3 \cdot \text{Phen}$  should not be higher than for europium acetates with Phen and Bpy, where it is 21% because of the  $\text{CH}_3$ -stretching vibrations [9]. The quenching due to Phen and Bpy ligands in such compounds should be less effective. Judging from our data on the measurements of  $^5\text{D}_0$  state lifetimes for europium carboxylates with deuterium substituted Bpy ligand [9], contribution of the quenching with participation of the high-frequency CH-vibrations of heterocyclic diimine molecules to the  $^5\text{D}_0$  lifetime  $\tau_{\text{obs}}$  is 1–5%. The main potential quencher in the naphthylacetates and naphthoxyacetates is the  $-\text{CH}_2-$  group proximal to the  $\text{Ln}^{3+}$  ion. Still its contribution to the multiphonon relaxation must be smaller than contribution of  $\text{CH}_3$ -group, as it has lower frequencies of stretching vibrations than the  $\text{CH}_3$ -group.

The participation of high-frequency stretching vibrations of water molecules in the luminescence quenching is noticeably greater. When the compound  $\text{Eu}(\text{1-NaphtOAc})_3 \cdot \text{Phen} \cdot 2\text{H}_2\text{O}$  loses the water molecules at heating, the  $^5\text{D}_0$  lifetime  $\tau_{\text{obs}}$  increases from 0.87 to 1.59 ms at 77 K. The rate of multiphonon relaxation owing to  $\text{H}_2\text{O}$  vibrations is also high for naphthylcarboxylate  $\text{Eu}(\text{RCOO})_3 \cdot n\text{H}_2\text{O}$  hydrates. The  $^5\text{D}_0$  lifetime  $\tau_{\text{obs}}$  for these compounds varies from 0.4 to 0.8 ms at 77 K and practically does not change on increasing the temperature to 295 K.

Thus, two main contributions to  $\tau_{\text{obs}}$  exist in the europium adducts with Phen: the maximal one associated with the radiative processes and the smaller one conditioned by multiphonon quenching. The increase of  $\tau_{\text{obs}}$  at introduction of the  $-\text{CH}_2-$  bridge in the carboxylate ligand can be mainly caused by the rise of symmetry of  $\text{Eu}^{3+}$  ion nearest surroundings, which is in agreement with the decrease of relative integral intensities of the  $\text{Eu}^{3+}$  induced electric-dipole transitions  $^5\text{D}_0 \rightarrow ^7\text{F}_J$  ( $J=2, 4, 6$ ) (Table 1).

One can analyze the behavior of the radiative lifetimes  $\tau_r$  of  $^5\text{D}_0$  state for compounds 1–6 using the known relation for determination of quantities  $\tau_r$  from the integral intensities of the  $\text{Eu}^{3+}$  luminescence spectra  $\Sigma I(J=0-6)/I(J=1)$  (formula (7) in [20]). Meanwhile, the application of this simplified method is obstructed because of dependence of the radiative processes rate  $1/\tau_r$  on the cube of refractive index  $n$ . As a rule, the authors of publications use  $n=1.5$  for determination of the  $\tau_r$  in solid europium coordination compounds that is unfounded. Available rough correlations between the index  $n$  and the density  $D$  of compounds permit to estimate a potential error of determination of the radiative lifetime  $\tau_r$ . The density  $D$  for many crystalline compounds is contained in the tables of crystallographic data. For example, the  $D$  values for europium carboxylates can fall in the interval from 1.2 to  $2.6 \text{ g cm}^{-3}$  [23,24] that entails an appreciable range of  $n$  values. In accordance with the  $n$  value, which is used for calculation, the lifetime  $\tau_r$  can exhibit the range up to a few tens percent. Therefore, the best path to avoid fallibility in the interpretation of experimental data is in measurement of the

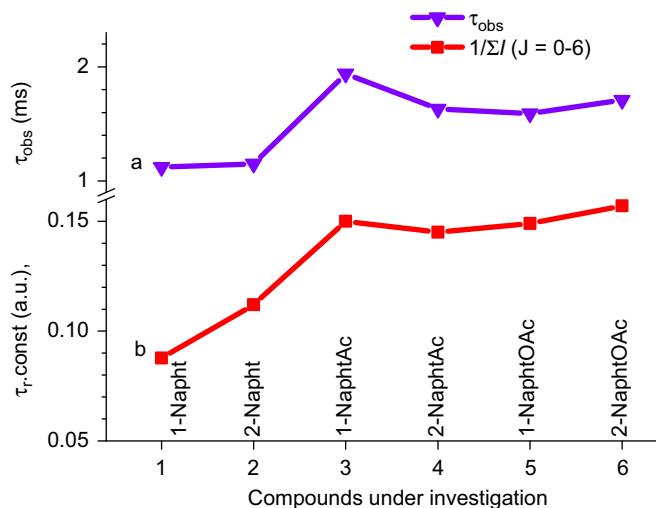


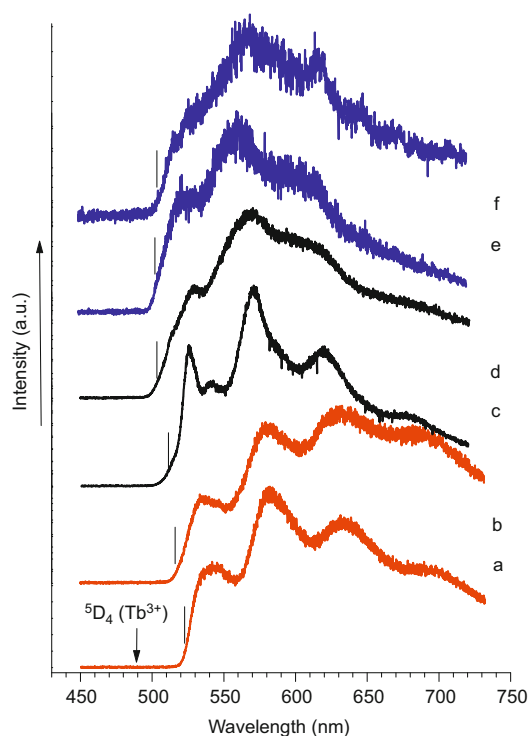
Fig. 6. The change of lifetime  $\tau_{\text{obs}}$  of  $^5\text{D}_0$  state at 77 K (a) and the change of the quantity " $\tau_r \cdot \text{const}$ " (b) in the row of europium compounds with Phen.

refractive index  $n$  in every particular case of the determination of  $\tau_r$  from the  $\text{Eu}^{3+}$  luminescence spectrum. The important role of the refractive index was recently stressed in Ref. [25].

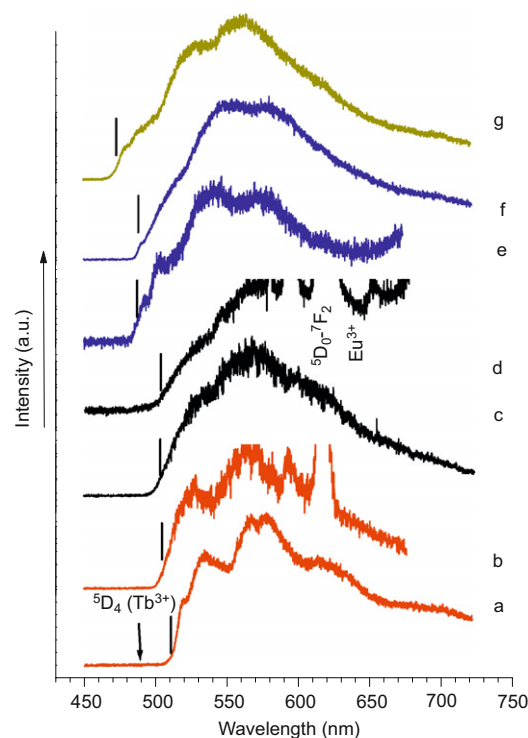
As the refractive indexes  $n$  for polycrystalline compounds under investigation are not known, we resort to the same assumptions taken into account for the different family of europium carboxylates [9]. One can suppose that the refractive indexes  $n$  are not different significantly in the family of naphthylcarboxylates  $\text{Eu}(\text{RCOO})_3 \cdot \text{Phen}$  that permit to determine the quantities inverse to the relative integral intensities  $\Sigma I$ . They are proportional to the radiative lifetimes  $\tau_r$  multiplied by a constant, " $\tau_r \cdot \text{const}$ ", ( $\text{const} = A_{\text{MD},0} n^3$ , where  $A_{\text{MD},0}$  is the spontaneous luminescence probability for the magnetic-dipole  $^5\text{D}_0 \rightarrow ^7\text{F}_1$  transition in vacuo ( $14.65 \text{ s}^{-1}$ ) [20]). To visualize the behavior of the quantities " $\tau_r \cdot \text{const}$ " and  $\tau_{\text{obs}}$  in the series of europium naphthylcarboxylates with Phen they are presented as gradual plots in Fig. 6. The plot "b" describes a tendency of the change in the  $\tau_r$  for the row of compounds 1–6. In crude approximation, one can see a correlation between the two plots. As the  $\tau_{\text{obs}} = 1/(k_r + k_{\text{nr}})$  ( $k_r$  and  $k_{\text{nr}}$  are the rates of radiative and nonradiative processes), this correlation can serve as a confirmation of the principal contribution of radiative processes to  $\tau_{\text{obs}}$ . The different slopes of two plots can be caused by both different contributions of the multiphonon relaxation to the  $\tau_{\text{obs}}$  for compounds 1–6 (plot "a" in Fig. 6) and differing values of the refractive index  $n$  for 1–6 (plot "b").

### 3.2. Triplet states and excitation energy transfer

Let us consider the effect of methylene spacer in the naphthylcarboxylate anion on the energy of lowest triplet state of ligands and on the excitation energy transfer. In series of lanthanide naphthylcarboxylates with Phen the lowest triplet state is related to carboxylate ligand. The affiliation of triplet state was defined by comparison of the phosphorescence spectra of gadolinium naphthylcarboxylates  $\text{Gd}(\text{RCOO})_3 \cdot \text{Phen}$  and  $\text{Gd}(\text{RCOO})_3 \cdot n\text{H}_2\text{O}$ . These spectra for 1- and 2- naphthylcarboxylates are shown in Figs. 7 and 8. The energies of T-S<sub>0</sub> zero-phonon transition obtained from short-wavelength edge of broad vibronic band are given in Table 2. They are also presented in Fig. 9 for visualization. As the fine structure was absent in phosphorescence spectra, the accuracy of determination of the triplet state energy was not high. Nevertheless, one



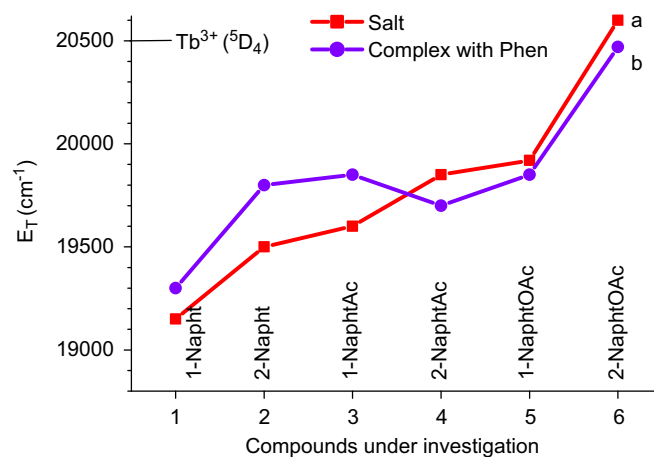
**Fig. 7.** Phosphorescence spectra of gadolinium 1-naphthylcarboxylates: Gd(1-Napht)<sub>3</sub> (a), Gd(1-Napht)<sub>3</sub>·Phen (b), Gd(1-NaphtAc)<sub>3</sub>·2.5H<sub>2</sub>O (c), Gd(1-NaphtAc)<sub>3</sub>·Phen (d), Gd(1-NaphtOAc)<sub>3</sub>·3H<sub>2</sub>O (e) and Gd(1-NaphtOAc)<sub>3</sub>·Phen (f) recorded with 1 ms time delay at 77 K.



**Fig. 8.** Phosphorescence spectra of gadolinium 2-naphthylcarboxylates: Gd(2-Napht)<sub>3</sub>·3H<sub>2</sub>O (a), Gd(2-Napht)<sub>3</sub>·Phen (b), Gd(2-NaphtAc)<sub>3</sub>·H<sub>2</sub>O (c), Gd(2-NaphtAc)<sub>3</sub>·Phen (d), Gd(2-NaphtOAc)<sub>3</sub>·4H<sub>2</sub>O (e), Gd(2-NaphtOAc)<sub>3</sub>·Phen (f) and GdCl<sub>3</sub>·Phen·nH<sub>2</sub>O (g) recorded with 1 ms time delay at 77 K.

can clearly see a gradual change in the triplet energy. It was demonstrated [9,10] that the range of energy of phenanthroline lowest triplet state in lanthanide carboxylates is sufficiently wide: 20 850–22 300 cm<sup>-1</sup>. Still the energy of naphthylcarboxylate ligand triplet is always lower than the energy of Phen triplet.

Decoupling of the  $\pi$ - $\pi$ - or  $p$ - $\pi$ - conjugation in the carboxylate ligand by the methylene bridge built in and by following potential turning of the naphthalene fragment results in increasing in the triplet energy in the following succession of compounds with ligands: Napht (**1**, **2**)–NaphtAc (**3**, **4**)–NaphtOAc (**5**, **6**). The lowest triplet state energy for the lanthanide naphthoates (19 150–19 800 cm<sup>-1</sup>) and naphthylacetates (19 600–19 840 cm<sup>-1</sup>) is substantially lower than the energy of <sup>5</sup>D<sub>4</sub> state of Tb<sup>3+</sup> ions (20 500 cm<sup>-1</sup>), so the luminescence intensity for these terbium carboxylates is very low. The increase in the triplet energy to 20 500–20 600 cm<sup>-1</sup> for 2-naphthoxyacetates changes conditions of the excitation energy transfer, and the luminescence intensity of terbium compounds can become high. This trend of developments serves as the definite proof of the interligand energy transfer process in the adducts under investigation. The excitation spectra of europium naphthylcarboxylates with Phen are a typical spectra having the intense broad band of Phen with long-wavelength edge at  $\sim$ 350 nm [4,16]. The energy absorbed by Phen ligand goes via Phen lowest triplet state to naphthylcarboxylate triplet. In the opposite case, the luminescence of Tb<sup>3+</sup> ions should be observed for all the assembly of terbium naphthylcarboxylates. Analogous interligand energy transfer, for example, from aromatic carboxylate anion to Phen and from hexafluoroacetylacetone ligand to 9-diisopropylphosphorylanthracene was found for lanthanide complexes having two types of ligands [26,27]. In the europium naphthylacetate and naphthoxyacetate compounds with Phen, one should not rule out a possibility of transfer of the excitation energy absorbed by the carboxylate



**Fig. 9.** The change of triplet state energy of naphthylcarboxylate ligand in the rows of gadolinium salts and gadolinium complexes with Phen.

ligand to “COO<sup>-</sup>–Eu<sup>3+</sup>” LMCT state with the following dissipation to the crystal lattice.

Increase in the triplet state energy in the series of salts with the ligands Napht–NaphtAc–NaphtOAc (**1**–**6**) (Fig. 9) is caused by growing the interruption of conjugation. Stronger interruption of conjugation for 2-naphthylcarboxylates (**2**, **4**, **6**) can be conditioned, probably, by more effective withdrawal of electronic charge from the naphthalene rings by the carboxylic group and by a larger freedom of turning and bending of the naphthalene fragment in the lanthanide complexes. It has been shown by calculations that in the 2-naphthoic acid the electronic charge shifts more strongly from the aromatic rings towards carboxylic

group in comparison with the case of 1-naphthoic acid [28]. The triplet energies for europium adducts with three first naphthylcarboxylate anions (1–3) are larger than those for the salts, and for three following anions (4–6) this is vice versa. It may be because of the increase of conjugation in the carboxylate anion for three last-named adducts (4–6) in comparison with the corresponding salts that can be caused by steric factors. However, the breaking of a common system of delocalized  $\pi$ -electron orbitals resulting in splitting of the naphthylcarboxylate triplet in two components can be also possible [29]. In this case, the energy transfer to  $\text{Ln}^{3+}$  ion emitting state should be realized through low-energy component related to naphthalene rings. The energy of high-energy component related to carboxylic group should roughly coincide with the energy of triplet state of lanthanide aliphatic carboxylates (acetate, propionate, and caproate) at  $\sim 22\,000\text{ cm}^{-1}$  [9] that is higher than the Phen triplet energy.

### 3.3. Europium hydroxy-2-naphthylcarboxylates

To determine the influence of electron-donating OH-group in naphthoic ligand on excitation energy transfer to  $\text{Ln}^{3+}$  ion, the compounds  $\text{Ln}(1\text{-OH-2-Napht})_3 \cdot n\text{H}_2\text{O}$  and  $\text{Ln}(3\text{-OH-2-Napht})_3 \cdot n\text{H}_2\text{O}$  ( $\text{Ln}=\text{Eu, Gd, Tb}$ ) were investigated. The energies of the lowest triplet states for the 1- and 3-hydroxy-carboxylates were determined as  $\sim 19\,750$  and  $\sim 17\,550\text{ cm}^{-1}$ , respectively, that is suitable for excitation of both the europium compounds.

But the appreciable luminescence was only observed for  $\text{Eu}(3\text{-OH-2-Napht})_3 \cdot n\text{H}_2\text{O}$  at 77 K. The luminescence excitation and luminescence spectra of this compound are shown in Fig. 10. It can be supposed, that processes of the luminescence excitation for  $\text{Eu}(1\text{-OH-2-Napht})_3 \cdot n\text{H}_2\text{O}$  are similar to those for salicylates  $\text{Eu}(2\text{-OH-Benz})_3 \cdot n\text{H}_2\text{O}$  [30]. The low-energy LMCT state participates in the excitation energy dissipation in both these compounds, so, they have very low luminescence efficiency. In  $\text{Eu}(3\text{-OH-2-Napht})_3 \cdot n\text{H}_2\text{O}$  the lowest excited singlet and triplet levels shift to low-energy side and LMCT state shifts to high-energy side. So, the excitation energy reaches  $^5\text{D}_0$  ( $\text{Eu}^{3+}$ ) state, and the luminescence efficiency for  $\text{Eu}(3\text{-OH-2-Napht})_3 \cdot n\text{H}_2\text{O}$  becomes high enough at 77 K. The cause of poor luminescence of this compound at 295 K is the quenching by back energy transfer from  $^5\text{D}_0$  state to triplet state located about  $300\text{ cm}^{-1}$  higher. Similarity of the luminescence spectra of europium 3-hydroxy-2-naphthoate and europium 4-amino-benzoate synthesized at  $\text{pH}=5$  (Fig. 10) testifies to identical structures of the coordination centres in both the compounds and to the absence of coordination centres of the OH-group in the former. The last is confirmed by vibrational IR spectra. Such peculiarity of the structure of  $\text{Eu}(3\text{-OH-2-Napht})_3 \cdot n\text{H}_2\text{O}$  can give rise to appearance of the intense band of intraligand charge transfer in the 370–410 nm region of the excitation spectrum.

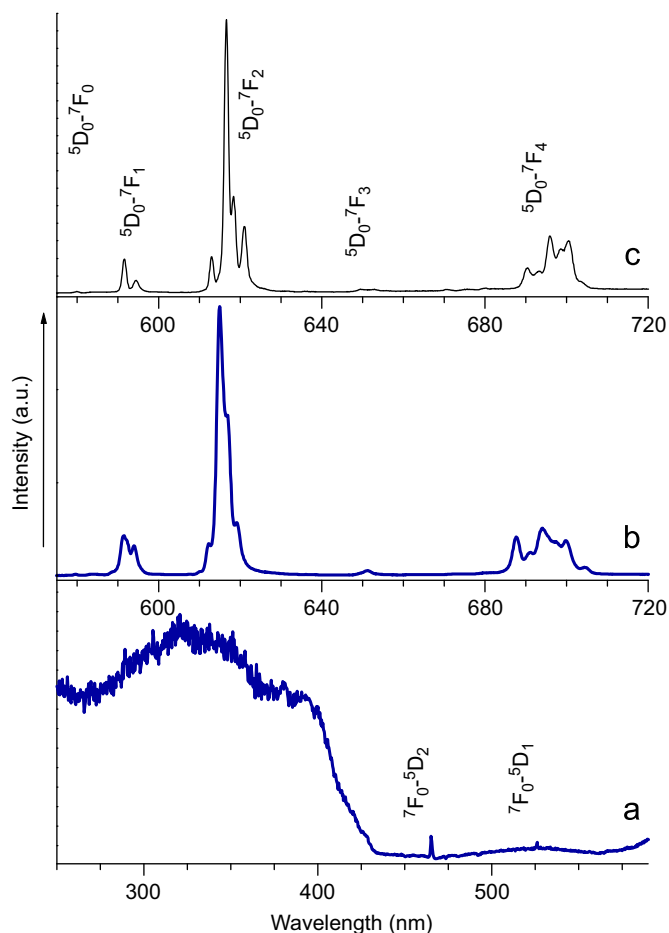
### 4. Conclusions

The effects of the methylene spacer in the carboxylate ligand in series of europium 1- and 2-naphthylcarboxylates on the structure of  $\text{Eu}^{3+}$  ion nearest surroundings, on the lifetime of  $^5\text{D}_0$  electronic state, on the energies of the ligand lowest triplet state and LMCT state, and on processes of the excitation energy transfer to  $\text{Ln}^{3+}$  ions were studied.

It was demonstrated that introduction of the methylene bridge between the carboxylic group and naphthalene rings of ligand weakens the steric hindrances in the structures of lanthanide naphthylcarboxylates with 1,10-phenanthroline. The nearest surroundings of  $\text{Eu}^{3+}$  ion become more symmetric, that results in decrease in the probability of the induced electric-dipole transitions and increase in the measured lifetime of the  $^5\text{D}_0$  state  $\tau_{\text{obs}}$ . The latter is explained by decrease in contribution of the radiative processes rate to the lifetime. This is confirmed by the correlation between the lifetimes  $\tau_{\text{obs}}$  and the quantities “ $\tau_r \cdot \text{const}$ ” obtained from the total integral intensities of  $\text{Eu}(\text{RCOO})_3 \cdot \text{Phen}$  luminescence spectra. A necessity of the measurement of refractive index  $n$  in every particular case of the determination of radiative lifetime through  $\text{Eu}^{3+}$  luminescence spectrum was noted.

The decoupling of ligand  $\pi$ – $\pi$ - or  $p$ – $\pi$ -electronic system gives rise to lowering the energy of “carboxylic group– $\text{Eu}^{3+}$  ion” LMCT states that can promote the degradation of excitation energy. At the same time, a presence of the methylene spacer in the ligand can increase the energy of carboxylate lowest triplet state by  $\sim 1500\text{ cm}^{-1}$ . That allows the energy transfer to  $^5\text{D}_4$  ( $\text{Tb}^{3+}$ ) state and appearance of the luminescence of terbium compounds. It was shown that the lowest triplet state in lanthanide naphthylcarboxylate adducts with Phen is related to carboxylate anion. The interligand energy transfer from Phen molecule to naphthylcarboxylate anion was demonstrated.

Role of the methylene spacer in the excitation energy transfer to  $\text{Ln}^{3+}$  ion consists in its influence on mutual location of the LMCT state, triplet states of both the ligands and  $\text{Ln}^{3+}$  emitting states, and, as a result, on the efficiency of the lanthanide luminescence. To increase the luminescence efficiency of europium aromatic carboxylates one had to eliminate the methylene groups from the ligand. But to increase the luminescence



**Fig. 10.** Luminescence excitation spectrum of  $\text{Eu}(3\text{-OH-2-Napht})_3 \cdot n\text{H}_2\text{O}$  (a) and luminescence spectra of  $\text{Eu}(3\text{-OH-2-Napht})_3 \cdot n\text{H}_2\text{O}$  (b),  $\text{Eu}(4\text{-NH}_2\text{-Benz})_3 \cdot n\text{H}_2\text{O}$  ( $\text{pH}=5$ ) (c) at 77 K.



efficiency of terbium naphthylcarboxylates one should introduce the methylene groups into the ligand.

An addition of hydroxy-groups in the naphthoate ligand can appreciably change the energies of the ligand lowest triplet state and LMCT state and, as a consequence, can change the luminescence efficiency of europium naphthylcarboxylates.

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