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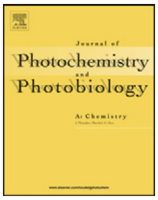

Europium and terbium ortho-, meta-, and para-methoxybenzoates: Structural peculiarities, luminescence, and energy transfer

Konstantin P. Zhuravlev[a], Vera I. Tsaryuk[a,*], Irina S. Pekareva[a], Jerzy Sokolnicki[b], Zinaida S. Klemenkova[c]

[a] V.A. Kotelnikov Institute of Radioengineering and Electronics of RAS, 1 Vvedenskii sq., Fryazino, Moscow reg. 141190, Russia
[b] Faculty of Chemistry, University of Wrocław, 14 F. Joliot-Curie str., Wrocław 50-383, Poland
[c] A.N. Nesmeyanov Institute of Organoelement Compounds of RAS, 28 Vavilov str., Moscow 119991, Russia

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ABSTRACT

A series of methoxybenzoates $Ln(MOBA)_3 \cdot nH_2O$ and $Ln(MOBA)_3 \cdot L$ (Ln = Eu, Gd, Tb; MOBA – 2-, 3-, and 4-methoxybenzoate anions, L – 1,10-phenanthroline (Phen) and 2,2′-bipyridine (Bpy)) was investigated by methods of optical spectroscopy. The effects of methoxy groups located in different positions of the benzene ring on the structure of Eu^{3+} luminescence centers, the lifetimes of $^5D_0$ (Eu^{3+}) and $^5D_4$ (Tb^{3+}) states, the energies of the lowest singlet and triplet states of the ligands, and on processes of the excitation energy transfer to Eu^{3+} and Tb^{3+} ions are examined. The spectroscopic data for lanthanide methoxybenzoates are in accordance with known structural peculiarities: the lanthanide–oxygen bond lengths and the Ln^{3+} coordination polyhedron distortions. The low-energy ligand–metal charge transfer state was identified in the compound $Eu(4\text{-}MOBA)_3$. It was shown that the distortions of Ln^{3+} luminescence centers are the smallest for 2-methoxybenzoates. The enhancement of Tb^{3+} luminescence efficiency by 2–2.5 times for terbium methoxybenzoates with phenanthroline $Tb(MOBA)_3 \cdot Phen$ in comparison with benzoate $Tb(Benz)_3 \cdot Phen$ at 295 K is caused by a decrease in the rate of back energy transfer due to an increase in the energy of the lowest Phen triplet state. The highest luminescence efficiency was observed for $Tb(4\text{-}MOBA)_3 \cdot Phen$. Judging from the results presented, the $Tb(4\text{-}MOBA)_3 \cdot Phen$ can be potentially more preferable for the fabrication of emitter layers in organic light emitting diodes (OLEDs) than the $Tb(2\text{-}MOBA)_3 \cdot Phen \cdot H_2O$, which has been tested before.

1. Introduction

Lanthanide coordination compounds and lanthanide-based hybrid materials with a high quantum yield of luminescence can be used in various devices of the molecular electronics: organic light emitting diodes, plastic lasers, molecular switches, as well as in light transforming materials, sensors, etc. [1–10]. Terbium carboxylates [11–13], in particular, the terbium-yttrium complex with 2-methoxybenzoate and 1,10-phenanthroline ligands $TbY(2\text{-}MOBA)_6 \cdot Phen_2 \cdot 2H_2O$ [12], have been tested as components forming the light-emitting layers in electroluminescent devices (OLEDs). An optimization of spectroscopic characteristics of lanthanide compounds through variations of fragments of their crystal structures is an important stage in the fabrication of highly luminescent lanthanide materials, which can be used in photonic applications. Factors obstructing an effective excitation energy transfer to Ln^{3+} ions have to be minimized by means of a rational design of the lanthanide material.

This paper is a continuation of our studies on the connection between structural regularities and luminescence properties of europium and terbium carboxylates in search for methods of increasing the quantum yield of luminescence [14–17]. Recently, the series of dimeric aromatic and aliphatic lanthanide carboxylates with Phen having the coordination number (C.N.) of Ln^{3+} ion equal to 9 has been investigated, and the types of distortions of Ln^{3+} polyhedron responsible for a brightness of the Eu^{3+} and Tb^{3+} luminescence have been determined [14]. It was shown that increasing the probability of induced electric-dipole transitions of Ln^{3+} ion in compounds of the kind can be assigned to substantial distortions of the Ln coordination polyhedron due to voluminous carboxylate ligands. These polyhedron distortions are caused by a range of Ln–O bond lengths related to the bridging–cyclic carboxylic groups. At the same time, the luminescence efficiency for terbium compounds at high temperatures depends on the rate of back energy transfer process, which in its turn depends on the bonding strength of Phen ligand with the Tb^{3+} ion.

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* Corresponding author at: V.A. Kotelnikov Institute of Radioengineering and Electronics of RAS, Laboratory of Molecular Electronics, 1 Vvedenskii sq., Fryazino, Moscow reg. 141190, Russia. Tel.: +7 4965652577; fax: +7 4957029572.
E-mail addresses: vtsaryuk@mail.ru, vit225@ire216.msk.su (V.I. Tsaryuk).

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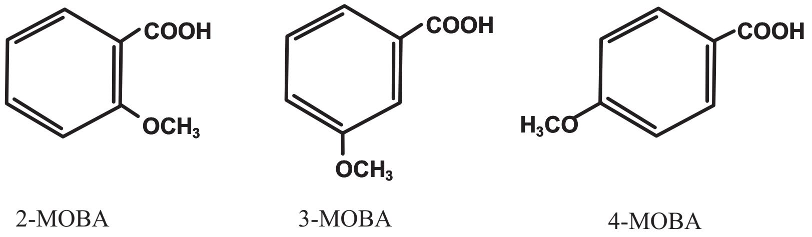

Fig. 1. Structures of molecules of methoxybenzoate ligands.

In the present work, series of europium and terbium 2-, 3-, and 4-methoxybenzoates with heterocyclic diimines $Ln(MOBA)_3 \cdot L$ (L – 1,10-phenanthroline (Phen) and 2,2′-bipyridine (Bpy)) and $Ln(MOBA)_3 \cdot nH_2O$ were investigated by methods of optical spectroscopy. The effects of methoxy groups ($–OCH_3$) located in different positions of the benzene ring on the structure of Ln^{3+} coordination centers, on the lifetimes of $^5D_0$ (Eu^{3+}) and $^5D_4$ (Tb^{3+}) states, and on the processes of the excitation energy transfer to Eu^{3+} and Tb^{3+} ions are examined. The weak donating methoxy group situated in the 2-, 3-, or 4-positions of the benzoate anion can change a mutual location of the lowest singlet and triplet states of the ligands, the ligand–metal charge transfer (LMCT) states, and the emitting states of the Ln^{3+} ions. It is caused by a different distribution of electron density in the benzoate ligand and in its three MOBA derivatives [18], by the type of L ligand and by peculiarities of the crystal packing. The Ln^{3+} quantum yield can depend on a position of $–OCH_3$-group in the benzene ring. The $–OCH_3$-group may perform a role of regulator of sensitization of the Ln^{3+} luminescence.

2. Structural regularities of dimeric lanthanide methoxybenzoates $Ln(MOBA)_3 \cdot L$

In process of an examination of the spectroscopic characteristics of lanthanide methoxybenzoates selected for this paper some known structural data are taken into account. Chemical formulae of the methoxybenzoate ligands are shown in Fig. 1. Crystals of most of the ternary lanthanide carboxylates with heterocyclic diimines: 1,10-phenanthroline, 2,2′-bipyridine and their derivatives consist of dimers [19]. There are dimers with C.N. of Ln^{3+} ion equal to 8 and 9. In compounds with C.N. = 9, as, for example, in the europium benzoate $Eu(Benz)_3 \cdot Phen$ [20], two Ln^{3+} ions of the dimer are bonded by two bridging and two bridging–cyclic carboxylic groups. In compounds with C.N. = 8 two Ln^{3+} ions of the dimer are bonded by four bridging carboxylic groups. In both cases each Ln^{3+} ion coordinates also a cyclic carboxylic group and a molecule of heterocyclic diimine. Overwhelming majority of lanthanide carboxylates with heterocyclic diimines including europium, gadolinium and terbium methoxybenzoates with Phen and Bpy belongs to two dimeric structures described above. The crystal structures of ternary methoxybenzoates with Ln^{3+} C.N. = 8 under investigation are given in Refs. [19,21–24], the structures of ternary methoxybenzoates with Ln^{3+} C.N. = 9 are presented in Refs. [19,25–27].

In addition to these two principal types of dimers, there are also different types of dimers [19]. In particular, in the compound $Sm(2\text{-}MOBA)_3 \cdot Phen \cdot H_2O$ (C.N. = 9) coded as CEVTON in the Cambridge structural database (CSD) [19,28] two Ln^{3+} ions of the dimer are bonded by the two bridging–cyclic carboxylic groups. Each Ln^{3+} ion coordinates also the cyclic and monodentate carboxylic groups as well as the Phen and H_2O molecules. In the structures of brominated benzoate $Eu(3\text{-}BrBenz)_3 \cdot Phen \cdot H_2O$ coded as IJICOT [19,29] and fluorinated benzoate $Eu(2\text{-}FBenz)_3 \cdot Phen \cdot C_2H_5OH$ [30] having C.N. = 8 two Ln^{3+} ions of the dimer are bonded by the four bridging carboxylic groups. Each Ln^{3+} ion coordinates also a monodentate carboxylic group, the Phen molecule and the molecule of a solvent. In the structure of $[Tb(4\text{-}NH_2\text{-}Benz)_3 \cdot Bpy \cdot H_2O] \cdot 2H_2O$ coded as KALDOR [19,31] having C.N. = 8 two Ln^{3+} ions are bonded in the dimer by the two bridging carboxylic groups, and, additionally, each Ln^{3+} ion coordinates the cyclic and monodentate carboxylic groups, the Bpy and H_2O molecules.

The CSD does not contain much data for binary lanthanide methoxybenzoates. Only the structures of 2-methoxybenzoates of neodymium (FEXVEJ) [32] and dysprosium $[Dy(2\text{-}MOBA)_3 \cdot 2H_2O] \cdot 2H_2O$ (VOPJEQ) [33], and the structure of europium 3-methoxybenzoate $Eu(3\text{-}MOBA)_3 \cdot 2H_2O$ (NEMXEI) [34] are known. Recently, the authors of the paper [35] solved X-ray crystal structures of binary terbium 2-, 3-, and 4- methoxybenzoates. The dimeric structure of $[Tb(2\text{-}MOBA)_3 \cdot 2H_2O] \cdot 2H_2O$ is identical to the VOPJEQ structure. The structure of $Tb(3\text{-}MOBA)_3 \cdot 2H_2O$ is polymeric, and it is identical to the NEMXEI structure. The anhydrous compound $Tb(4\text{-}MOBA)_3$ have also the chained structure. The binary lanthanide 3-methoxybenzoates contain only the bridging and cyclic carboxylic groups, in contrast to the lanthanide 2-, and 4-MOBA compounds having in their structures the bridging–cyclic carboxylic groups in parallel with different types of COO^- coordination.

Now we will analyze the distortions of Ln^{3+} coordination polyhedron for the family of ternary methoxybenzoates of lanthanides (relating to the middle of lanthanide row) with C.N. = 9 in analogy to the analysis for the more numerous series of related europium aromatic and aliphatic carboxylates with the same C.N. [14]. In the row of such dimeric compounds, the largest changes in Ln–O bond lengths are observed for the bridging–cyclic COO^--groups. The transformation of Ln–O bonds related to these COO^--groups and the change in dimer Ln–Ln distance for the row of methoxybenzoates with known crystal structures are given in Fig. 2. The names of compounds are included in this figure and, later, in Table 1. Main distortions of the Ln^{3+} coordination polyhedron display as a considerable spread in the Ln–O distances related to the bridging–cyclic carboxylic groups COO^-. A spread in the Ln–O bond lengths due to the bridging and cyclic carboxylic groups, and a spread in the Ln–N bond lengths are appreciably smaller. The Δ(Ln–O) spread for lanthanide polyhedron decreases gradually from 0.580 Å in **1** to 0.331 Å in **5** compound. The tendency to equalization of the “2” and “3” Ln–O bonds of the bridging–cyclic COO^--group leads to an approach of the lanthanide ions in the dimer from 4.076 Å in **1** to 4.0 Å in **4** and **5** (Fig. 2). It should be noted that the average Ln–N bond length being equal to 2.633, 2.629 and 2.603 Å in europium compounds **1**, **3** and **5**, respectively, decreases in this row. In the compound $Sm(2\text{-}MOBA)_3 \cdot Phen \cdot H_2O$ (**6**), in which two Ln^{3+} ions of the dimer are only bonded by the two bridging–cyclic carboxylic groups, three Ln–O bonds due to these groups are equalized and the Ln–Ln distance increases to 4.26 Å.

In the case of dimeric europium and terbium methoxybenzoates with C.N. = 8, the Δ(Ln–O) spread for Ln^{3+} polyhedron being equal to 0.15–0.19 Å is appreciably smaller than for the compounds with

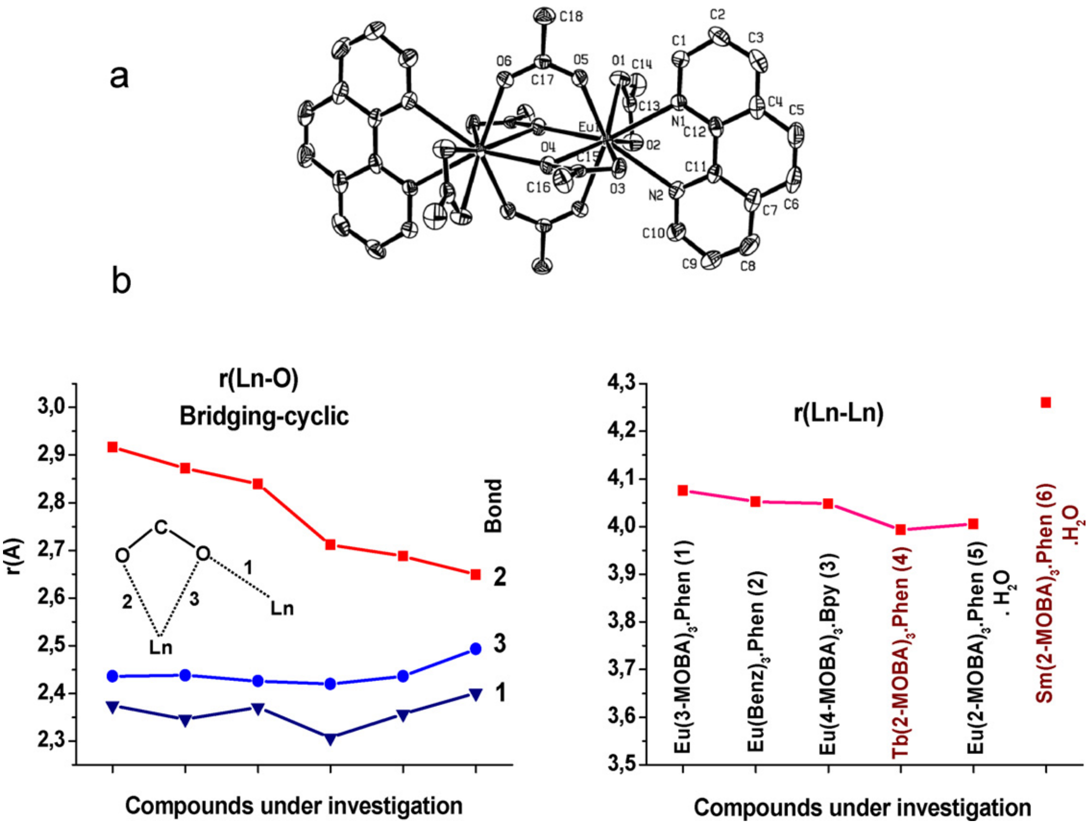

Fig. 2. General view of dimers in the structures of ternary lanthanide carboxylates with Phen (Ln^{3+} C.N. = 9) (a). The changes in Ln–O bond lengths due to the bridging–cyclic COO^- groups and in the dimer Ln–Ln distances in the row of $Ln(MOBA)_3{\cdot}L$ (C.N. = 9). The points on the axis *X* of the left part of b relate to the same compounds listed in the right part of (b).

Table 1
Relative integral intensity *I* of $^5D_0$–$^7F_2$ transition (Eu^{3+}), lifetimes of $^5D_0$ (Eu^{3+}) and $^5D_4$ (Tb^{3+}) states, and triplet state energy of L ligand for ternary compounds $Ln(MOBA)_3{\cdot}L$.

No.	Compound[a]	C.N., Ref. structure	I (Eu)$^5D_0$–$^7F_2$	τ_{obs} (ms) (Eu)		τ_{obs} (ms) (Tb)		k_{BET} (ms^{-1})	E_T (cm^{-1})	$\Delta = E_T - E(^5D_4)$
				77 K	295 K	77 K	295 K			
1	$Ln(3\text{-}MOBA)_3{\cdot}Phen$	9 [25]	6.61			1.12	0.75	0.44	21,750	1250
2	$Ln(Benz)_3{\cdot}Phen$	9, SIBCUP [20]	5.70	1.3	1.26	1.26	0.28	2.78	20,850	350
3	$Ln(4\text{-}MOBA)_3{\cdot}Bpy$ (D-Bpy)	9, MEBDUS [26]	6.1	1.19 (1.35)[b]	1.182 (1.29)[b]				22,400	1900
5	$Ln(2\text{-}MOBA)_3{\cdot}Phen{\cdot}H_2O$	9 [27]	5.63	1.52	1.47				≈21,500	≈1000
7	$Ln(2\text{-}MOBA)_3{\cdot}Bpy$ (D-Bpy)	9	5.79	1.25 (1.281)[b]	1.27 (1.277)[b]				22,800	2300
8	$Ln(3\text{-}MOBA)_3{\cdot}Bpy$ (D-Bpy)	8 [21]	5.45	1.19 (1.35)[b]	1.185 (1.30)[b]	1.19	1.22		22,000	1500
9	$Ln(4\text{-}MOBA)_3{\cdot}Phen$	8 [23]	7.63	1.16	1.19	1.25	1.15	0.07	22,100	1600
10	$Tb(2\text{-}MOBA)_3{\cdot}Phen$	8				1.79	1.05	0.39	≈21,500	≈1000
	$^5D_4(Tb^{3+})$								20,500	

[a] Ln = Eu, Gd, Tb for compounds **2**, **8**, **9**; Ln = Eu, Gd for compounds **3**, **5**, **7**; Ln = Gd, Tb for compounds **1**, **10**.

[b] The values of τ_{obs} given in brackets are related to europium compounds with D-Bpy.

C.N. = 9, but the Ln–Ln distance being equal to 4.25–4.35 Å is appreciably larger.

The visualized changes in the Ln–O and Ln–Ln distances in the dimeric methoxybenzoates **1**–**5** with Ln^{3+} C.N. = 9 presented as plots in Fig. 2 lay well on analogous plots for the more numerous group of carboxylates investigated in [14]. They lay in the region of the bond lengths for compounds with voluminous carboxylate ligands: between europium 1-naphthylcarboxylate and phenoxyacetate. However, it should be noted, that judging from the bond lengths in methoxybenzoates, the minimum steric hindrances are specific for the 2-MOBA compounds (**4**, **5**, **6**). Probably, this is conditioned by a feature of the structures of 2-MOBA compounds, when the carboxylic group is not situated in the plane of benzene ring [19].

3. Experimental

3.1. Compounds

A series of ternary lanthanide methoxybenzoates with heterocyclic diimines $Ln(MOBA)_3{\cdot}L$ (MOBA – 2-, 3-, and 4-methoxybenzoate anions, L – 1,10-phenanthroline (Phen) and 2,2′-bipyridine (Bpy), Ln = Eu, Gd, Tb) was synthesized and examined. Binary lanthanide methoxybenzoates $Ln(2\text{-}MOBA)_3{\cdot}3H_2O$, $Ln(3\text{-}MOBA)_3{\cdot}2H_2O$ and $Ln(4\text{-}MOBA)_3$ (Ln = Eu, Gd, Tb) having known crystal structures [34,35] were also synthesized and investigated. The compounds $Ln(MOBA)_3{\cdot}L$ (**1**, **3**, **5**, **7**–**10**) under investigation and the benzoate $Ln(Benz)_3{\cdot}Phen$ (**2**) related to eight dimeric crystal structures with Ln^{3+} C.N. = 8 [21,23] and 9

Table 2
Energies of the lowest excited singlet (E_{S^*}) and triplet (E_T) states of the ligands (cm^{-1}).[a]

Compound	E_{S^*}	E_T	$\Delta_1 = E_{S^*} - E_T$	E_{LMCT}
$Ln(Benz)_3 \cdot 2H_2O$	34,500	≥23,300	≤11,200	
$Ln(2\text{-}MOBA)_3 \cdot 3H_2O$	31,250	24,500	6750	
$Ln(3\text{-}MOBA)_3 \cdot 2H_2O$	31,250	23,000	8250	
$Ln(4\text{-}MOBA)_3$	33,300	≥25,600	≤7700	~28,500
$Ln(Benz)_3 \cdot Phen$	28,700	20,850	7850	
$Ln(MOBA)_3 \cdot Phen$	~29,000	21,500–22,100	7500–6900	
$Ln(MOBA)_3 \cdot Bpy$	~30,000–32,000	22,000–22,800	~8000–9000	

[a] Energies of the electronic states for ternary compounds are related to L ligand.

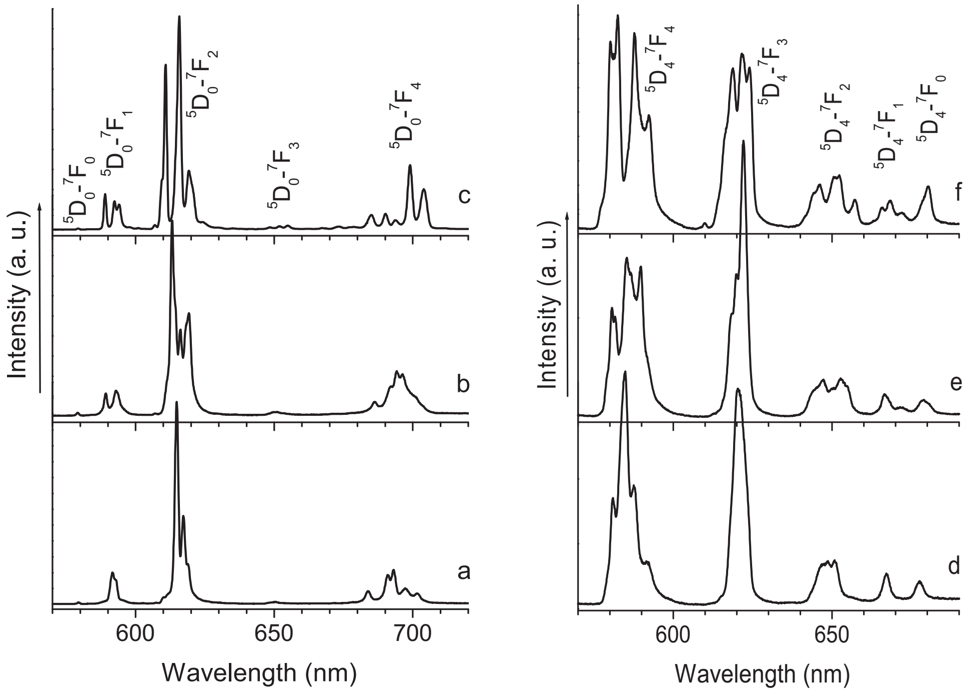

Fig. 3. Luminescence spectra of $Eu(2\text{-}MOBA)_3 \cdot 3H_2O$ (a), $Eu(3\text{-}MOBA)_3 \cdot 2H_2O$ (b), $Eu(4\text{-}MOBA)_3$ (c), $Tb(2\text{-}MOBA)_3 \cdot 3H_2O$ (d), $Tb(3\text{-}MOBA)_3 \cdot 2H_2O$ (e), and $Tb(4\text{-}MOBA)_3$ (f) recorded with ~20 cm^{-1} resolution at 77 K.

[20,25–27] are collected in Table 1. The two ternary compounds with C.N. = 9, $Tb(2\text{-}MOBA)_3 \cdot Phen$ (**4**) [27] and $Sm(2\text{-}MOBA)_3 \cdot Phen\ H_2O$ (**6**) [28], for which the structural data were analyzed in Section 2, were not synthesized for spectroscopic studies. The ternary europium and terbium compounds studied have a high luminescence efficiency. To estimate contributions of multiphonon relaxation to lifetimes of Ln^{3+} metastable electronic states three europium methoxybenzoates (**3**, **7**, **8**) with deuterium substituted 2,2′-bipyridine $C_{10}N_2D_8$ (D-Bpy) having 99.9% isotope enrichment were synthesized.

Binary carboxylates were obtained by exchange of cations in water or ethanol solutions of the lanthanide chloride and the sodium salt of corresponding carboxylic acid. Adducts with heterocyclic diimines were synthesized by admixing of an ethanol solution of Phen or Bpy to a solution of the lanthanide salt of methoxybenzoic acid. All of the reagents used for syntheses were purchased from Sigma–Aldrich. The composition of compounds synthesized was controlled by the elemental analysis, the IR vibrational spectroscopy, and a comparison of the Stark splittings of electronic transitions in the Eu^{3+} and Tb^{3+} luminescence spectra. In most cases, Eu, Gd, and Tb compounds with the same methoxybenzoate ligand are isostructural. In a number of cases, to be sure in accordance of the compounds under investigation with published X-ray crystal structure data, the measured vibrational IR and Eu^{3+} luminescence spectra were compared with the IR and low-resolution luminescence spectra given in these publications.

3.2. *Optical spectroscopy*

Luminescence, phosphorescence, and luminescence excitation spectra of compounds under investigation were measured on a LOMO UM-2 monochromator and a SLM Aminco SPF 500 spectrofluorimeter. The former experimental set was supplied with a highly sensitive photomultiplier H6780-20. Energies of the lowest excited triplet states of ligands were obtained from phosphorescence spectra of gadolinium compounds recorded with 1 ms time delay at 77 K. The lowest triplet energies of L ligands were determined from the spectra of ternary gadolinium compounds. The lowest excited singlet energies of the ligands were taken from the Eu^{3+} and Tb^{3+} luminescence excitation spectra recorded at 77 K. Lifetimes of $^5D_0$ (Eu^{3+}) and $^5D_4$ (Tb^{3+}) states were measured at 77 and 295 K. The exponential fitting with Origin 7.0 was used for analysis of decay process. Decay curve for the $^5D_0$ level could be fitted to a mono-exponential law. A relative error of determination of lifetimes is ±2%. Relative integral intensities of the Eu^{3+} electronic transitions were estimated with correction for the spectral sensitivity distribution of the experimental set-up. Luminescence efficiencies were measured in accordance with the procedure described in Ref. [17]. IR spectra in the 400–4000 cm^{-1} region were obtained on a Nocolet Magna 750 FTIR spectrophotometer using the KRr pellets technique. The principal spectroscopic characteristics for the compounds under study are collected in Tables 1 and 2.

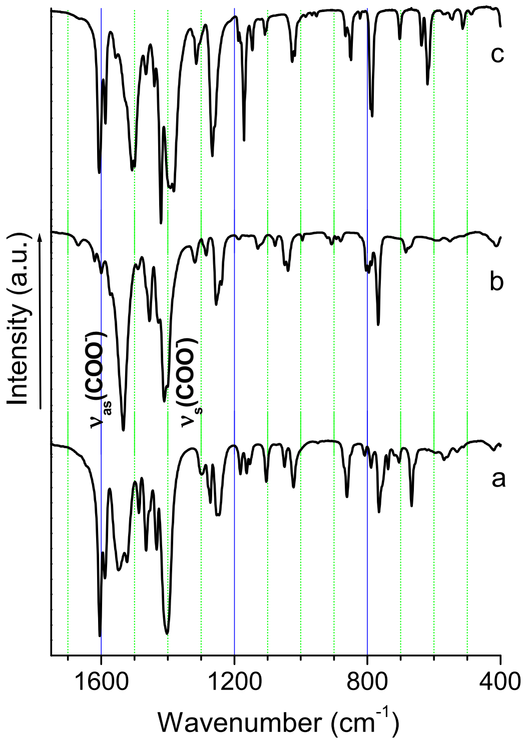

Fig. 4. Vibrational IR spectra of Eu(2-MOBA)$_3$·3H_2O (a), Eu(3-MOBA)$_3$·2H_2O (b), and Eu(4-MOBA)$_3$ (c) at 295 K.

4. Results and discussion

4.1. Luminescence, luminescence excitation and vibrational IR spectra of europium and terbium 2-, 3-, and 4-methoxybenzoates Ln(MOBA)$_3$·nH_2O

The luminescence spectra of binary europium and terbium 2-, 3-, and 4-methoxybenzoates Ln(MOBA)$_3$·nH_2O (Ln = Eu, Tb) are presented in Fig. 3. An identity of Stark splittings of the electronic transitions in Eu^{3+} and Tb^{3+} luminescence spectra that can be especially well seen for the $^5D_0$–$^7F_{1,2}$ (Eu^{3+}) and $^5D_4$–$^7F_{1,2}$ (Tb^{3+}) transitions, proves a similarity of the europium and terbium compounds. The spectra testify to different symmetries of the Ln^{3+} ion nearest surroundings in the compounds with three MOBA derivatives. Judging from the spectra, the symmetry of Eu^{3+} luminescence center tends to a raise in going from 4- to 2-MOBA compound. In the indicated row of europium compounds one can clearly observe the degeneration of Stark components and the decrease in the relative intensity of electric-dipole $^5D_0$–$^7F_2$ transition. Moreover, the crystal field in the Ln(2-MOBA)$_3$·3H_2O compounds is weaker than in the 3-, and 4- methoxybenzoates that corresponds to the longest average Tb–O distance in the Tb^{3+} coordination polyhedron of this compound [35].

The vibrational IR spectra of the binary europium 2-, 3-, and 4-methoxybenzoates (Fig. 4) agree with peculiarities of coordination of carboxylic groups. In Eu(3-MOBA)$_3$·2H_2O, where only bridging and cyclic coordinations of the COO$^-$ groups are present, the small splitting (Δ = 120 cm^{-1}) of the ν(COO$^-$) stretching vibration in ν_{as} and ν_s components points to an equivalence of effective charges on the oxygen atoms of COO$^-$ groups and to a small polarization of these anions [36,37]. In the compounds with 2- and 4-MOBA ligands, where bridging–cyclic carboxylic groups are present, Δ = 205 cm^{-1} and Δ = 235 cm^{-1}, respectively. This is an evidence of a stronger distortion and polarization of COO$^-$ groups in these two compounds.

The Eu^{3+} and Tb^{3+} luminescence excitation spectra of binary compounds given in Fig. 5 clarify to some extent the processes of excitation energy transfer from the ligands to Ln^{3+} ions. The LMCT state can be identified in the Eu(4-MOBA)$_3$ compound by means of comparison of the Eu^{3+} excitation spectra recorded at 77 and 295 K and the Tb^{3+} spectrum at 77 K. This state can serve as one of quenching channels of the excitation energy transfer in Eu(4-MOBA)$_3$. The low energy of the LMCT state can be caused by the stronger Eu–O (COO$^-$ groups) bonds in Eu(4-MOBA)$_3$ in comparison with other compounds [35]. Distinctions in the bonding strengths of carboxylic groups with the metal ion in the three binary compounds are conditioned by a different distribution of the electron density in three methoxybenzoate derivatives and by effects of the crystal packing. Interaction of two or several substituents with the benzene framework in ligands of lanthanide compounds generates as a rule a variety of substituent phenomena, which cannot be described by a simple universal theory. The following classical concept [18] permits to explain distinctions in the spectra of three lanthanide methoxybenzoate derivatives. Polar substituent effects transmitted through the benzene ring are similar in the cases of substituents in the ortho and para positions, and are different from effects for substituents in the meta position. However, both polar and steric effects form the main part of the ortho effect.

The strong and weak broad bands relating to S–S* (π–π*) and intraligand charge transfer (ILCT) transitions, respectively, are observed best of all in the excitation spectra of terbium compounds. The ILCT band with the long-wavelength edge at 380 nm is the strongest in the spectrum of Tb(4-MOBA)$_3$, and it is feeble in the spectrum of Tb(2-MOBA)·3H_2O. The ILCT band is also well seen in the spectrum of Eu(4-MOBA)$_3$. The intensity of this band is in line with a shift of electron density from the weak donating –OCH$_3$-group situated in different positions of the benzene ring to the acceptor carboxylic group. One can observe a shift of the strong S–S* (π–π*) band to a short-wavelength side in the Tb(4-MOBA)$_3$ excitation spectrum in comparison with the spectra of 2-, and 3-MOBA compounds, i.e. the energy of the lowest excited singlet state in the 4-MOBA compound is the highest (Table 2). At the same time, the presence of the –OCH$_3$-group at the fourth position of aromatic ring increases the triplet state energy to 25,600 cm^{-1} in comparison with the lower triplets of the lanthanide 2- and 3-MOBA compounds (24,500 and 23,000 cm^{-1}). These can indicate “a less expanded” system of π-electron density in the 4-MOBA ligand bonded stronger with the Ln^{3+} ion. The luminescence efficiencies of anhydrous europium and terbium Ln(4-MOBA)$_3$ compounds are somewhat higher than an approximately identical efficiencies of different two binary methoxybenzoates and benzoate Ln(Benz)$_3$·2H_2O containing the water molecules. The low-energy LMCT state in the Eu(4-MOBA)$_3$ compound and the more profitable energy gap Δ_1 for S*–T intersystem crossing [38] in the methoxybenzoates than in the benzoate do not exert key influence on the luminescence efficiency. Probably, the rate of multiphonon relaxation k_{vibr} because of the H_2O stretching vibrations contributing to the decay rates of emitting states of the Ln^{3+} ions τ_{obs} is a decisive factor influencing the rate of nonradiative processes and the luminescence quantum yield.

4.2. Luminescence properties of dimeric europium and terbium methoxybenzoates Ln(MOBA)$_3$·L

The list of ternary compounds investigated together with their spectroscopic characteristics is presented in Table 1. The luminescence spectra of europium and terbium methoxybenzoates with Phen and Bpy, Ln(MOBA)$_3$·L, are given in Figs. 6 and 7. The spectrum “a” in Fig. 6 belongs to doped Eu^{3+} ions, which serve as a luminescent probe in the Gd(3-MOBA)$_3$·Phen (**1**) compound. We could not

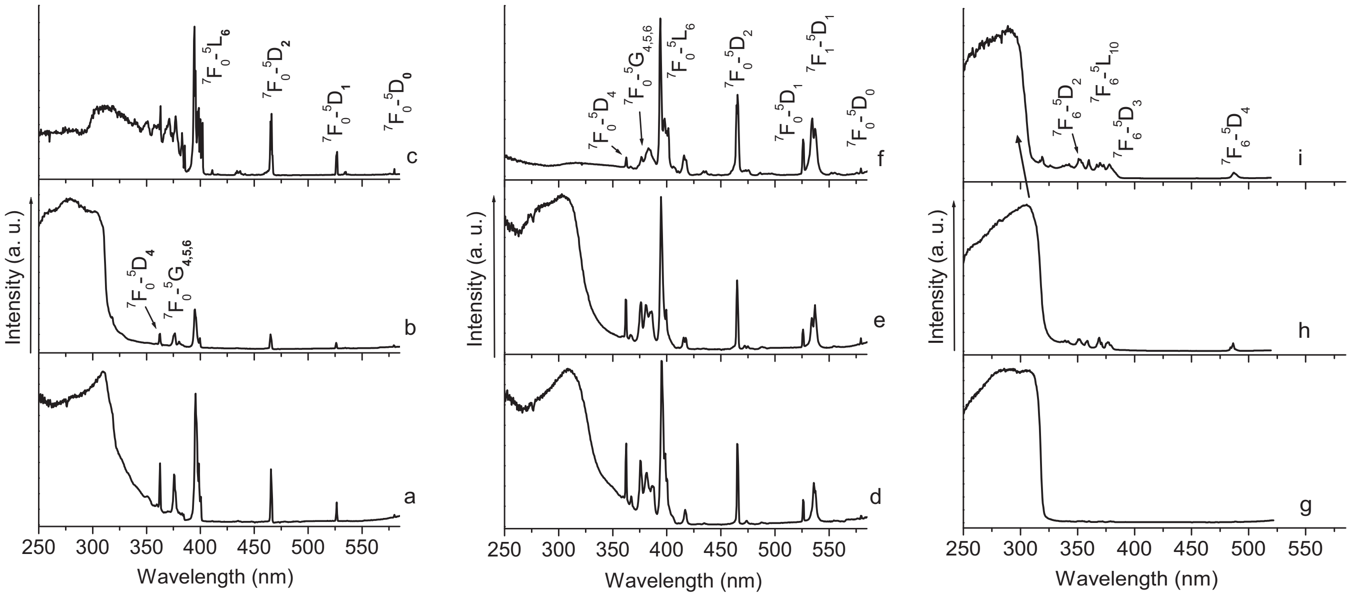

Fig. 5. Luminescence excitation spectra of Eu(2-MOBA)$_3$·3H$_2$O (a and d), Eu(3-MOBA)$_3$·2H$_2$O (b and e), Eu(4-MOBA)$_3$ (c and f), Tb(2-MOBA)$_3$·3H$_2$O (g), Tb(3-MOBA)$_3$·2H$_2$O (h), and Tb(4-MOBA)$_3$ (i) at 77 (a–c and g–i) and 295 K (d–f).

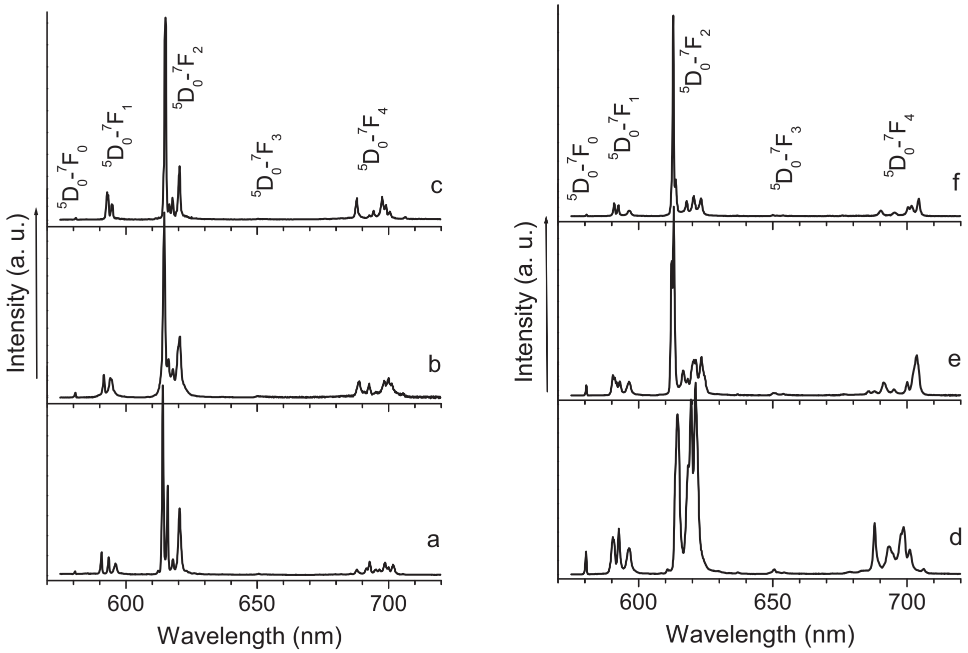

Fig. 6. Luminescence spectra of Gd(Eu)(3-MOBA)$_3$·Phen (**1**) (a), Eu(4-MOBA)$_3$·Bpy (**3**) (b), Eu(2-MOBA)$_3$·Phen·H$_2$O (**5**) (c), Eu(2-MOBA)$_3$·Bpy (**7**) (d), Eu(3-MOBA)$_3$·Bpy (**8**) (e), and Eu(4-MOBA)$_3$·Phen (**9**) (f) recorded with ~10 cm^{-1} resolution at 77 K.

synthesize the europium compound identical to this gadolinium one. The spectra “a”, “b”, “c” and “d” in Fig. 6 and the spectrum “a” in Fig. 7 are related to compounds with Ln^{3+} C.N. = 9, the spectra “e” and “f” in Fig. 6 and the spectra “b”, “c” and “d” in Fig. 7 are related to compounds with Ln^{3+} C.N. = 8. One can see a similarity of Stark splittings of the electronic transitions in the Eu^{3+} and Tb^{3+} luminescence spectra of the compounds with C.N. = 9, and the same is for the compounds with C.N. = 8. The maximal possible number of Stark components in the Eu^{3+} electronic transitions witness about a low symmetry of charge distribution in the nearest surroundings of Eu^{3+} ion. The presence of two non-equivalent luminescence centers in the compound Eu(3-MOBA)$_3$·Bpy (**8**) (spectrum “e” in Fig. 6) is in agreement with X-ray data [21]. Judging from the spectrum “d”, the compound Eu(2-MOBA)$_3$·Bpy (**7**) has also two non-equivalent centers. Besides, the intense line of $^5D_0$–$^7F_0$ transition in this spectrum can, probably, testify about an influence of J–J mixing. A specific Stark splitting of $^5D_0$–$^7F_4$ transition in all spectra of the dimeric europium compounds with C.N. = 9, which are investigated in the present work as well as in the previous paper [14], is a characteristic feature of such compounds.

In the series of methoxybenzoates Eu(MOBA)$_3$·L (**1**, **3**, **5**) having C.N. = 9, one can see a decrease in the integral intensity *I* of hypersensitive electric-dipole $^5D_0$–$^7F_2$ transition in relation to the intensity of magnetic-dipole $^5D_0$–$^7F_1$ transition from ~6.6 to ~5.6 that is demonstrated in Fig. 8. These values *I* fall into the region of values *I* for the europium compounds with voluminous aromatic carboxylate ligands and Phen studied in Ref. [14]. In contrast to this, for aliphatic carboxylates with C.N. = 9 the values *I* were

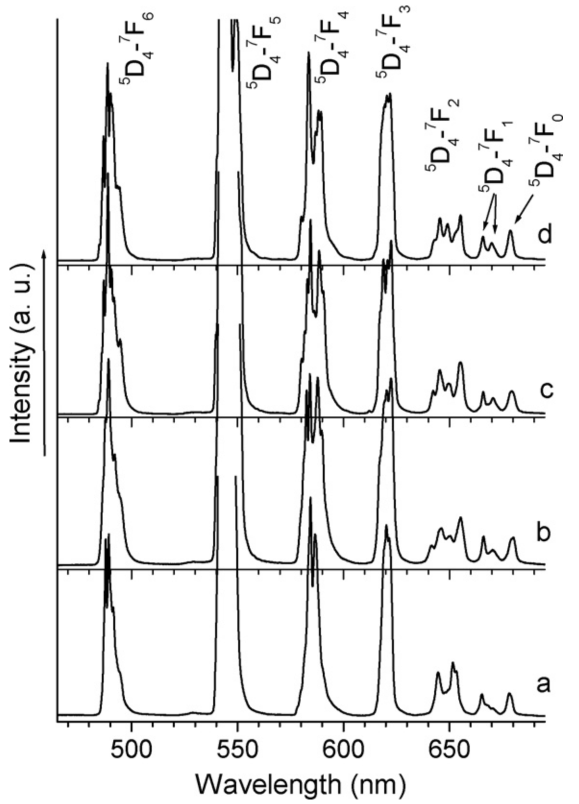

Fig. 7. Luminescence spectra of Tb(3-MOBA)$_3$·Phen (**1**) (a), Tb(3-MOBA)$_3$·Bpy (**8**) (b), Tb(4-MOBA)$_3$·Phen (**9**) (c), and Tb(2-MOBA)$_3$·Phen (**10**) (d) recorded with ~20 cm^{-1} resolution at 77 K.

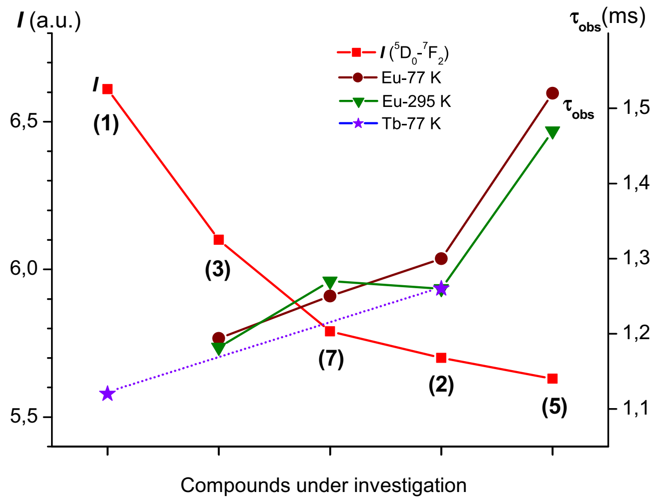

Fig. 8. Visualization of the changes in relative integral intensity I of $^5D_0$–$^7F_2$ transition of Eu^{3+} ion at 77 K and lifetimes τ_{obs} of the $^5D_0$ (Eu^{3+}) and $^5D_4$ (Tb^{3+}) states for compounds Ln(MOBA)$_3$·L with C.N. = 9.

determined as equal to 3.2–4 [14]. The change in intensity I in the row of compounds **1**, **3**, **5** is in accordance with the degeneration of Stark components of the $^5D_0$–$^7F_1$ and $^5D_0$–$^7F_4$ electronic transitions, and, correspondingly, with lowering the distortions of luminescence centers. One should note that distortions of Eu^{3+} luminescence centers are minimum for the Eu(2-MOBA)$_3$·Phen (**5**) compound. The value I for Eu(2-MOBA)$_3$·Bpy (**7**) witnesses about the same. These are the identical features for the 2-MOBA ternary and binary compounds. As it was supposed above, the minimum distortions for these compounds are conditioned by decreasing the steric hindrances under a lack of coplanarity of the 2-MOBA ligand and at the crystal packing. Lowering the Eu^{3+} luminescence center distortions in going from **1** to **3**, and then to **5** resulting from the spectra correlate with decreasing the Δ(Ln–O) coordination polyhedron distortions caused by a difference in the bond strengths of Eu^{3+} ion with the bridging–cyclic carboxylic groups. The plot for I in Fig. 8 agrees with the plots for distortions of the Ln^{3+} coordination polyhedron shown in Fig. 2.

Raising the symmetry of the charge distribution in the nearest surroundings of Eu^{3+} ion resulting in lowering the probabilities of induced electric-dipole transitions should correspond to a decrease in the rate of radiative processes (or an increase in the natural lifetimes of radiative states of the Eu^{3+} and Tb^{3+} ions). One can see from Fig. 8 that a tendency to change in the decay rates τ_{obs} is in agreement with the plot for the intensity I of $^5D_0$–$^7F_2$ transition. These τ_{obs} fall into the region of values τ_{obs} for the compounds with voluminous carboxylate ligands [14], and it is also right for the intensity I.

As it follows from [14] for the series of dimeric lanthanide carboxylates with C.N. = 9, $\tau_{obs} = 1/(k_r + k_{vibr})$ for europium compounds at 77 and 295 K and for terbium compounds at 77 K. Here, k_r is the rate of pure radiative process, k_{vibr} is the rate of nonradiative process conditioned by the multiphonon relaxation. However, the contribution of k_{vibr} to τ_{obs} is not very high. There is opportunity to evaluate a contribution of multiphonon relaxation to τ_{obs} due to the Bpy high-frequency vibrations using the isotopic substitution. The lifetimes τ_{obs} of $^5D_0$ (Eu^{3+}) state for the compounds with natural Bpy and deuterium substituted D-Bpy ligands are given in Table 1. The increase in the lifetime at the isotopic substitution amounts to 12–14%. We suppose that a contribution of the multiphonon relaxation with participation of vibrations of the methoxybenzoate anion to τ_{obs} is also not high, as the –CH and –OCH$_3$ groups of this ligand being quenchers locate farther from the Ln^{3+} ions, than the –CH groups of Bpy ligand [39]. So, a contribution of k_{vibr} to τ_{obs} should not distort strongly a tendency to the change in the natural lifetimes τ_r of the radiative states of Eu^{3+} and Tb^{3+} ions in the row of compounds, i.e. this tendency should agree with the tendency to the changes in τ_{obs} and $1/I$ (Fig. 8). The changes in the lifetimes τ_{obs} and, probably, τ_r, as well as the behavior of the luminescence spectra are in an agreement with values of distortions of the Ln^{3+} coordination polyhedron, and first of all with the bond strengths of Ln^{3+} ion with oxygens of the bridging–cyclic carboxylic groups. The increase in the τ_{obs} values for 2-MOBA compounds correlates with the decrease in Ln^{3+} polyhedron distortions.

The lifetimes of $^5D_4$ state in the methoxybenzoates Tb(MOBA)$_3$·L (**1**, **9**, **10**) at 295 K differ from ones obtained at 77 K. At high temperatures a back energy transfer from the $^5D_4$ level of Tb^{3+} ion to the lowest triplet level of terbium compound can arise by a thermal activation [40–43]. In this case the $^5D_4$ decay rate $\tau_{obs} = 1/(k_r + k_{vibr} + k_{BET})$, where k_{BET} is the rate of back energy transfer. To analyze the contribution of k_{BET} to τ_{obs} it is necessary to know the energy of the lowest triplet state and to consider its position in relation to the $^5D_4$ electronic state. The comparison of the phosphorescence spectra of ternary and binary gadolinium compounds allows to attribute the lowest triplet state in Gd(MOBA)$_3$·L to the Phen or Bpy ligands (Tables 1 and 2). The triplet state energy of the Phen ligand in the ternary compounds is situated in the 21,500–22,100 cm^{-1} region, this energy of the Bpy ligand lies in the 22,000–22,800 cm^{-1} region. The triplet state energy of Phen in the methoxybenzoates is higher than that in the benzoate Gd(Benz)$_3$·Phen (**2**), where it is equal to 20,850 cm^{-1}.

The Phen ligand in the ternary methoxybenzoates **1**, **9** and **10** is responsible for a fall of the lifetime of $^5D_4$ (Tb^{3+}) state by reason of the back energy transfer at increasing the temperature from 77 to 295 K. This fall for the Tb(MOBA)$_3$·Phen compounds is substantially smaller than for the benzoate Tb(Benz)$_3$·Phen (**2**). The value

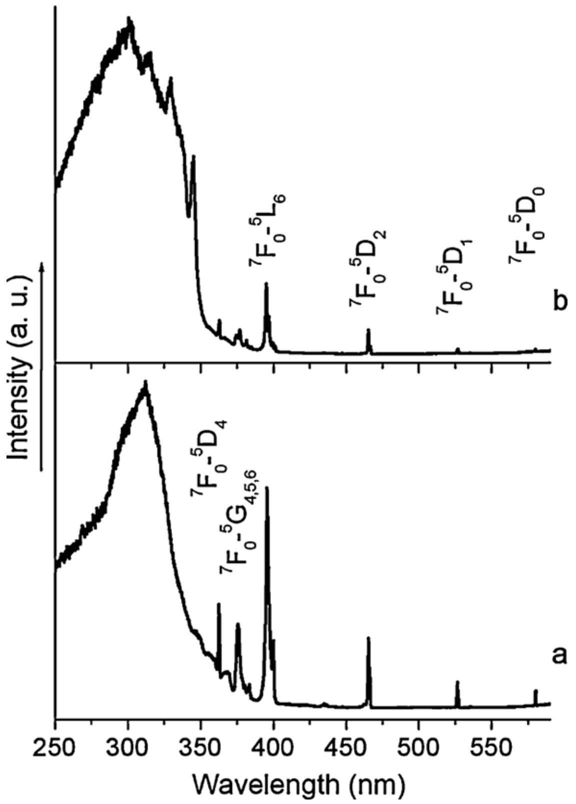

Fig. 9. Luminescence excitation spectra of Eu(4-MOBA)$_3$·Bpy (**3**) (a) and Eu(4-MOBA)$_3$·Phen (**9**) (b) at 77 K.

$\Delta = E_T - E(^5D_4)$ being equal to 1000–1600 cm^{-1} for the methoxybenzoates is lower than the empirically determined value of the limit difference Δ = 1850 cm^{-1} [40–43], at which the rate of back energy transfer k_{BET} becomes inessential. The k_{BET} rates determined from the difference of the values $1/\tau_{obs}$ (Tb^{3+}) at 295 and 77 K are presented in Table 1. These rate constants supplement the k_{BET} set found for Δ = 350–1250 cm^{-1} region in the series of terbium carboxylates with Phen studied in Ref. [14].

The luminescence efficiencies observed for the Tb(MOBA)$_3$·Phen compounds at 77 K are lower than for Tb(Benz)$_3$·Phen, while ones measured for the methoxybenzoates at 295 K are by 2–2.5 times higher than for the benzoate. The cause of increasing the Tb^{3+} luminescence efficiency at room temperature at introduction of methoxy group in the benzoate ligand should consist in processes of the Tb^{3+} sensitization including the back energy transfer. It can be connected with relative energies of the lowest excited singlet and triplet electronic states of the ligands (Tables 1 and 2) and of the emitting Ln^{3+} states. The energies of singlet levels S* of L ligands were determined from the broad band relating to the Phen or Bpy in the luminescence excitation spectra of the Eu(MOBA)$_3$.L compounds, in particular, from this band in the spectra of Eu(4-MOBA)$_3$·Phen (**9**) and Eu(4-MOBA)$_3$·Bpy (**3**) (Fig. 9). The energy of Phen singlet state for different ternary carboxylates is roughly the same. The principal distinction of schemes of energy levels for the Tb(MOBA)$_3$·Phen and Tb(Benz)$_3$·Phen (**2**) compounds is in a difference of the values Δ and Δ_1 for these two systems. As it is following from the larger energy gap Δ_1 for Tb(Benz)$_3$·Phen (**2**), the less effective intersystem crossing S*–T may occur in **2**, as it is widely believed, for example, in Ref. [38]. However, this does not give rise to a decrease in the Tb^{3+} luminescence efficiency for the benzoate. The higher luminescence efficiency for this compound at 77 K in comparison with the methoxybenzoates can be caused by an effective energy transfer to the Tb^{3+} ion due to the narrower energy gap Δ = 350 cm^{-1}. But this small energy gap is responsible for the high rate of back energy transfer and the sharp decrease in the luminescence efficiency for **2** at 295 K. On the contrary, an ineffective dissipation of the excitation energy through this channel in the Tb(MOBA)$_3$·Phen compounds having Δ = 1000–1600 cm^{-1} can provide the higher overall quantum yield of the Tb^{3+} luminescence. Moreover, the maximum energy gap Δ for Tb(4-MOBA)$_3$·Phen (**9**) should be responsible for the most effective luminescence of this compound.

5. Conclusions

The influence of three methoxybenzoate derivatives, ortho-, meta-, and para-, on the luminescence spectra, on the lifetimes of $^5D_0$ (Eu^{3+}) and $^5D_4$ (Tb^{3+}) states, and on the energy transfer processes in the europium and terbium binary Ln(MOBA)$_3$·nH$_2$O and ternary Ln(MOBA)$_3$·L (L – 1,10-phenanthroline and 2,2′-bipyridine) compounds was analyzed. It was shown that the spectroscopic peculiarities of lanthanide methoxybenzoates are in accordance with known X-ray data: with the Ln–O bond lengths and with the Ln^{3+} coordination polyhedron distortions. In particular, the distortions of Ln^{3+} luminescence centers are minimum for the binary and ternary 2-methoxybenzoates that is confirmed by X-ray data. The low-energy LMCT state was found in the binary Eu(4-MOBA)$_3$ compound. But this state does not become apparent in the ternary europium 4-methoxybenzoates, as it was seen in the ternary europium salicylates and anthranylates [17].

It was demonstrated that the enhancement of the Tb^{3+} luminescence efficiency by 2–2.5 times obtained for the Tb(MOBA)$_3$·Phen compounds at 295 K at insertion of the methoxy group in the aromatic ring of benzoate anion is caused by the increase in the lowest triplet state energy of Phen molecule, and, as consequence, by the decrease in the rate of non-radiative processes related to the back energy transfer. The maximum luminescence efficiency was found for the Tb(4-MOBA)$_3$·Phen compound having the highest Phen triplet state. So, judging from the results obtained, the Tb(4-MOBA)$_3$·Phen can be potentially more preferable for the fabrication of light-emitting layers in OLEDs than the Tb(2-MOBA)$_3$·Phen·H$_2$O compound, which has been sampled in Ref. [12].

The results presented in this work for the ternary dimeric lanthanide compounds with voluminous methoxybenzoate ligands having Ln^{3+} C.N. = 9 complete excellent the data published in our previous paper for the numerous series of related carboxylates with the more strongly discriminated distortions of the Ln^{3+} coordination polyhedron [14].

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