Journal of Photochemistry and Photobiology A: Chemistry 211 (2010) 7–19

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem

Structural regularities and luminescence properties of dimeric europium and terbium carboxylates with 1,10-phenanthroline (C.N. = 9)

Vera I. Tsaryuk [a,*], Konstantin P. Zhuravlev [a], Anna V. Vologzhanina [b], Valentina A. Kudryashova [a], Vladislav F. Zolin [a]

[a] *V. A. Kotelnikov Institute of Radioengineering and Electronics, Russian Academy of Sciences, 1 Vvedenskii Square, 141190 Fryazino, Moscow reg., Russia*
[b] *A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 Vavilov st., Moscow, 119991, Russia*

ARTICLE INFO

Article history:
Received 18 November 2009
Received in revised form
30 December 2009
Accepted 21 January 2010
Available online 1 February 2010

Keywords:
Europium
Terbium
Gadolinium
Carboxylates
1,10-Phenanthroline
Luminescence
Lifetime
Back energy transfer
X-ray crystal structure

ABSTRACT

A systematic comparison of the spectroscopic and structural data for series of related dimeric lanthanide carboxylates with 1,10-phenanthroline $Ln(RCOO)_3\cdot Phen$ (Ln = Eu, Gd, Tb): 1-naphthylcarboxylates, benzoates, 2-furancarboxylates, phenoxyacetates, caproates, acetates, propionates, 3-nitropropionates was undertaken in search for methods of regulation of quantum yield of the Ln^{3+} luminescence and for paths of the control of excitation energy transfer. The crystal structures of europium propionate and europium and terbium 3-nitropropionates were solved by X-ray diffraction methods. Effect of stepwise distortions of Ln coordination polyhedron derived from X-ray data of the succession of compounds, which determine details of the charge distribution in the surroundings of the Ln^{3+} ion, on luminescence spectra, on lifetimes of Ln^{3+} states, and on efficiency of Ln^{3+} luminescence was investigated. Polyhedron distortions are to a great extent caused by the range of the Ln–O bond lengths related to bridging-cyclic carboxylic group that is conditioned by the type and the size of carboxylate anion. Relative contributions of the rates of radiative and various nonradiative processes to the lifetimes of europium $^5D_0$ and terbium $^5D_4$ metastable states were estimated. Multiphonon relaxation is the main nonradiative process in europium compounds at temperatures from 77 to 295 K and in terbium compounds at low temperatures, but the radiative processes are appreciably prevailing. Dependence of the lifetimes due to radiative processes determined from the integral intensity of europium $^5D_0$–^7F_J transitions related to the intensity of magnetic-dipole $^5D_0$–$^7F_1$ transition on distortions of Eu polyhedron in the sequence of compounds is in agreement with the same dependence obtained from the measured lifetimes, if nonradiative processes are taken into account. A back energy transfer from $^5D_4$ state of Tb^{3+} ions to the lowest triplet state related to Phen molecule in most of compounds studied is another nonradiative process contributing to quenching in terbium compounds at high temperatures. An influence of this process on luminescence intrinsic quantum yield can be predominant. It leads to abrupt lowering the luminescence intensity of some terbium carboxylates, for example, benzoate at increasing the temperature. It was found, that lifetime of $^5D_4$ state and luminescence efficiency of terbium compounds at high temperatures depend on the bonding strength of Phen ligand with Tb^{3+} ion. A range of the lowest triplet state energies of Phen ligand, from 20,850 to 21,750 cm^{-1}, was revealed in lanthanide carboxylates under investigation. Closeness of the natural lifetimes of $^5D_0$ and $^5D_4$ states of Eu^{3+} and Tb^{3+} ions, respectively, in the same charge surroundings was demonstrated.

1. Introduction

Study of correlation between the structure and properties of lanthanide coordination compounds is an issue of the day of physical chemistry. Many such compounds, in particular, carboxylates can be ranked among supramolecular systems, in which the fragments of the structure are self-assembled in an unified system by weak interactions, such as H-bonding, stacking of aromatic fragments, Van der Waals forces, etc. [1]. Rational selection of the components of supramolecular system can give opportunity to design light transforming materials, materials for emitter layers of organic light emitting diodes and molecular switches, microporous materials of the type of synthetic zeolites that can be applied in sensors, catalysts, adsorbents, separators [2–14].

A principal task at elaboration of new compounds having high luminescence efficiency is optimization of their structures and opti-

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[*] Corresponding author at: Institute of Radioengineering and Electronics of RAS, Molecular Engineering Laboratory, 1, Vvedenskii Square, 141190 Fryazino, Moscow reg., Russia. Tel.: +7 496 5652577; fax: +7 495 7029572.
E-mail addresses: vit225@ire216.msk.su, vtsaryuk@mail.ru (V.I. Tsaryuk).

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doi:10.1016/j.jphotochem.2010.01.012

cal characteristics. The most effective method of solution of the problems of the kind is forming and spectroscopic investigation of groups of related compounds differing by a definite structural factor. Step-by-step change of the nearest surroundings of the Ln^{3+} ion and its influence on the luminescence spectra and other photophysical characteristics can be obtained by several methods. In particular, it can be done by variation of the counterions in the outer coordination sphere or by the changing the concentration of compound in solution [15–18]. But most often the modification of substituents on coordinated ligands is used. Recently, the strong influence of the steric hindrances on the structure of the Eu^{3+} luminescence centre has been observed in series of related europium phenyl- and naphthylcarboxylates [19]. The excitation spectra of quite a number of europium and terbium aromatic carboxylates have been investigated [20–22]. In these papers the effects of modification of $RCOO^-$ anion on the processes of excitation energy transfer to Ln^{3+} ions were discussed. Unfortunately, the X-ray data on the structures of complete set of compounds studied were absent there and this hampered to some extent the interpretation of the spectroscopic results. To the time being Cambridge structural database [1] has a plenty of structures of the lanthanide coordination compounds, so, that made possible a systematic comparison of spectroscopic and structural data for some groups of compounds.

In work presented, luminescence properties of a series of dimeric lanthanide carboxylates with 1,10-phenanthroline (Phen) of composition $Ln(RCOO)_3 \cdot Phen$ with Ln^{3+} C.N. = 9: naphthylcarboxylates, benzoates, furancarboxylates, phenoxyacetates, caproates, acetates, propionates and nitropropionates, with known crystal structures [23–28] were examined. In enumerated compounds two Ln^{3+} ions of dimer are bonded by two bridging and two bridging-cyclic carboxylic groups. Each Ln^{3+} ion coordinates also cyclic carboxylic group and Phen molecule. Both a distorted three-capped trigonal prism and a distorted one-capped tetragonal antiprism may be considered as coordination polyhedron of Ln^{3+} ion in these compounds. Many other lanthanide carboxylates with Phen: chloro-, fluoro-, methoxybenzoates, trimethylacetates, etc., and some lanthanide carboxylates with 2,2′-bipyridine (Bpy) have such a structure [1]. We were guided by following principal motives in selection of compounds for this investigation. (i) The compounds must have sufficiently high quantum yield of luminescence. (ii) The compounds must have related structures with the same C.N. of Ln^{3+} ion and with the same kind of coordination polyhedron at broad variation of carboxylate ligand. (iii) The compounds of Eu, Gd and Tb must be isostructural. (iv) Molecules of water and other solvents being strong luminescence quenchers must be absent there. (v) Simplicity and good repeatability of synthesis and crystallization of compounds. (vi) Presence of structural data in Cambridge database.

So, 10 crystal structures were chosen for this study. At the first stage of investigation, under modification of carboxylate ligand $L = RCOO^-$ the regularities of distortions for the lanthanide coordination polyhedron were analyzed. Then, isostructural compounds of Eu, Gd and Tb related to every structure (with the exception of one case) were examined with methods of optical spectroscopy. Using variation of the carboxylate anion within the series organized one can change peculiarities of the structure of coordination centres, the distribution of the electron density in the nearest surroundings of the Ln^{3+} ions, and, therefore, shape of the luminescence spectra and conditions of the excitation energy transfer, changing in this way the efficiency of luminescence at the same C.N. and the type of Ln coordination polyhedron.

It is known, that the overall quantum yield of luminescence of lanthanide compound is determined by the intrinsic quantum yield of the Ln^{3+} ion and by the efficiency of the sensitization. To obtain a new material with high overall quantum yield of luminescence one has to find methods of regulation of intrinsic quantum yield of the Ln^{3+} ion and of steering the ways of excitation energy transfer, i.e. influence the efficiency of sensitization. The task of this study includes the investigation of effect of distortions of coordination polyhedron on radiative (natural) and nonradiative decay rates of $^5D_0$ and $^5D_4$ levels, respectively, in europium and terbium compounds in the sequence formed. The Eu^{3+} and Tb^{3+} ions differ by energy intervals between ^5D_J and ^7F_J states and by combinations of contributions of matrix elements of electric- and magnetic-dipole moments to probability of electronic transitions. If it is possible to determine the rate of radiative processes from the integral intensity of $^5D_0$–^7F_J transitions in luminescence spectrum of europium compound related to the intensity of magnetic-dipole $^5D_0$–$^7F_1$ transition, but the applicability of this method is questionable in the case of terbium compounds [29], as there is not “pure” magnetic-dipole $^5D_4$–^7F_J transition in Tb^{3+} spectrum. A question arises, to what extent differ the rates of radiative processes for Eu^{3+} and Tb^{3+} ions in the same ligand surroundings. Can be the experimental rate of Eu^{3+} radiative processes used for evaluation of the intrinsic quantum yield of luminescence of terbium compound? Another question arises at analysis of the rates of nonradiative processes related to back energy transfer from metastable radiative states of Ln^{3+} ions to the lowest triplet state of compound. These rates can be very high and can abruptly decrease the quantum yield of luminescence, if the energy gap between the states mentioned is sufficiently small. One should know, to which ligand of the complex is related the lowest triplet state, and how significant is the change in its energy at modification of the carboxylate ligand. It is also important to discuss the contributions of rates of other nonradiative processes to the lifetimes measured: quenching through ligand–metal charge transfer states (LM CTS) in europium compounds, multiphonon relaxation and concentration quenching.

2. Experimental

2.1. Compounds

Lanthanide carboxylates with 1,10-phenanthroline $Ln(RCOO)_3 \cdot Phen$: 1-naphthylcarboxylates $Ln(1\text{-}Napht)_3 \cdot Phen$ (**1**), benzoates $Ln(Benz)_3 \cdot Phen$ (**2**), 2-furancarboxylates $Ln(2\text{-}Fura)_3 \cdot Phen$ (**3**), phenoxyacetates $Ln(PhOAc)_3 \cdot Phen$ (**4**), caproates (hexanoates) $Ln(Capr)_3 \cdot Phen$ (**5**), acetates $Ln(Ac)_3 \cdot Phen$ (**7**), propionates $Ln(Prop)_3 \cdot Phen$ (**10**), 3-nitropropionates $Ln(3\text{-}NProp)_3 \cdot Phen$ (**11**) (Ln = Eu, Gd, Tb) and $Eu(3\text{-}NProp)_3 \cdot Phen$ (**6**) were synthesized. Europium 3-nitropropionate was obtained in two crystal forms (**6** and **11**). All the compounds have dimeric structures described above, and all the dimers with the exception of ones in **3** are centrosymmetrical. Chemical formulae of compounds and codes in Cambridge structural database for europium compounds [23–28,30] are given in Table 1. Succession of compounds in Table 1 corresponds to lowering the distortions of the Ln coordination polyhedron and to gradual changes of the bond lengths of Ln^{3+} ions with bridging-cyclic carboxylic group that agrees with the type and the size of the fragment R of carboxylate ligand. The data on the structure of europium succinamate having two non-equivalent dimers in the unit cell (**8** and **9**) were used for completeness of analysis of the Ln coordination polyhedron in the series of compounds. This compound was not used in experimental investigations.

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

Table 1
Lanthanide carboxylates under investigation.

No.	Ligand (L)	Compound, Ln = Eu, Gd, Tb	Compound with known structure (abbreviation)	CSD code, Refs.
1	1-Naphthylcarboxylate	$Ln(C_{10}H_7COO)_3{\cdot}(C_{12}H_8N_2)$	$Eu(1\text{-}Napht)_3{\cdot}Phen$	VAQWAM [23]
2	Benzoate	$Ln(C_6H_5COO)_3{\cdot}(C_{12}H_8N_2)$	$Eu(Benz)_3{\cdot}Phen$	SIBCUP [24]
3	2-Furancarboxylate	$Ln(C_5H_4OCOO)_3{\cdot}(C_{12}H_8N_2)$	$Eu(2\text{-}Fura)_3{\cdot}Phen$	LUHFUP [25]
4	Phenoxyacetate	$Ln(C_6H_5OCH_2COO)_3{\cdot}(C_{12}H_8N_2)$	$Eu(PhOAc)_3{\cdot}Phen{\cdot}1/2C_2H_5OH$	ESESIE [26]
5	Caproate (Hexanoate)	$Ln(C_5H_{11}COO)_3{\cdot}(C_{12}H_8N_2)$	$Eu(Capr)_3{\cdot}Phen$	ZASWUL [27]
6	3-Nitropropionate	$Eu(NO_2C_2H_4COO)_3{\cdot}(C_{12}H_8N_2)$	$Eu(3\text{-}NProp)_3{\cdot}Phen$	This work
7	Acetate	$Ln(CH_3COO)_3{\cdot}(C_{12}H_8N_2)$	$Eu(Ac)_3{\cdot}Phen$	[28]
8, 9	Succinamate	$Eu(NH_2COC_2H_4COO)_3{\cdot}(C_{12}H_8N_2){\cdot}3H_2O$	$Eu(Succ)_3{\cdot}Phen{\cdot}3H_2O$	WUWVOZ [30]
10	Propionate	$Ln(C_2H_5COO)_3{\cdot}(C_{12}H_8N_2)$	$Eu(Prop)_3{\cdot}Phen$	This work
11	3-Nitropropionate	$Ln(NO_2C_2H_4COO)_3{\cdot}(C_{12}H_8N_2)$	$Tb(3\text{-}NProp)_3{\cdot}Phen$	This work

of Phen to solution of the lanthanide salt of carboxylic acid. All reagents were purchased from Sigma–Aldrich. To avoid as much as possible the influence of rare earth impurities on energy transfer Eu_2O_3 and Tb_2O_3 oxides with 99.999% purity were used as precursors. All solvents were purified by standard techniques. To extend the series of compounds investigated the crystal structures of nitropropionates $Eu(3\text{-}NProp)_3{\cdot}Phen$ (**6**), propionate $Eu(Prop)_3{\cdot}Phen$ (**10**) and $Tb(3\text{-}NProp)_3{\cdot}Phen$ (**11**) were determined by X-ray diffraction method. The crystals of these compounds were grown from water solution at slow evaporation of the solvent.

Eu, Gd, and Tb compounds with the same carboxylate ligand L are isostructural. This was assured with the help of the luminescent probe, vibrational spectroscopy and X-ray powder diffraction. Phenoxyacetates $Ln(PhOAc)_3{\cdot}Phen$ (**4**) synthesized were related to the series of compounds investigated, but, judging from the X-ray powder diffraction data, differed from the published $Ln(PhOAc)_3{\cdot}Phen.1/2C_2H_5OH$ solvate [26]. Compounds $Ln(Prop)_3{\cdot}Phen$ (**10**) (Ln = Eu, Gd, Tb) were not isostructural to known compound $Sm(Prop)_3{\cdot}Phen$ [1,31]. The compounds investigated were characterized by the elemental analysis.

To estimate contributions of multiphonon relaxation to lifetimes of Ln^{3+} metastable electronic states several lanthanide compounds with deuterium substituted ligands having 99.9% isotope enrichment, acetic acid CD_3COOD (D-Ac) and 2,2′-bipyridine $C_{10}N_2D_8$ (D-Bpy), were synthesized. We used D-Bpy for this purpose, as could not obtain deuterated 1,10-phenanthroline.

2.2. *Optical spectroscopy*

The luminescence and phosphorescence spectra were measured with LOMO UM-2 monochromator (~20 cm^{-1} resolution) and LOMO DFS-12 spectrophotometer (2 cm^{-1} resolution, when it required) at 77 and 295 K. The former experimental set was supplied with highly sensitive photomultiplier H6780-20. The luminescence excitation source was DRSh-250 high-pressure mercury lamp. For excitation of luminescence, we used the 300–380 nm region of the spectrum of this lamp (isolated by light filters), which contains the intense Hg 365 nm line. The samples were placed under strictly identical conditions. The energy of the lowest excited triplet state of the ligands was obtained from phosphorescence spectra recorded with 1 ms time delay. The relative integral intensities of the Eu^{3+} electronic transitions were estimated with correction on the spectral sensitivity distribution of the experimental set-up. The relative luminescence intensity $I_{295\,K}/I_{77\,K}$ for terbium compounds was measured in accordance with the procedure described in Ref. [32]. Lifetimes of $^5D_0$ (Eu^{3+}) and $^5D_4$ (Tb^{3+}) states in europium and terbium compounds were usually determined at 77 and 295 K, and sometimes at different temperatures. The exponential fitting with Origin 7.0 was used for analysis of decay process. Decay curves of the $^5D_0$ and $^5D_4$ levels could be fitted to a mono-exponential law. Relative error of determination of lifetimes is ±2%.

2.3. *X-ray crystallography*

The single-crystal X-ray diffraction data for the complexes **6**, **10** and **11** were collected on a Bruker SMART APEX II CCD diffractometer at 100 K, using graphite monochromated Mo – Kα radiation ($\lambda = 0.71073$ Å) [33]. Absorption correction was performed with SADABS program [34], using multiple measurements of equivalent reflections. The structures were solved by direct methods and refined by the full-matrix least squares technique against F^2 of all data. Non-hydrogen atoms were located from the Fourier density synthesis and refined in the anisotropic approximation. The positions of hydrogen atoms were calculated, the H(C) atoms were included in refinement in isotropic approximation with the riding model with the $U_{iso}(H) = 1.2U_{eq}(C)$, where $U_{eq}(C)$ is the equivalent thermal parameter of carbon atom to which the corresponding H atoms are bound. All calculations were performed with SHELXTL software package [35]. Details of the crystal data collection and refinement parameters for the crystals **6**, **10** and **11** are listed in Table 2.

3. Results and discussion

3.1. *Crystal structures of compounds **6**, **10** and **11***

The nitropropionates **6** and **11** crystallize in triclinic system, while propionate **10** – in monoclinic (Table 2). The crystals consist of dimers with composition $Ln_2(L)_6(C_{12}H_8N_2)_2$, (Ln = Eu or Tb for L = $NO_2C_2H_4COO$ and Ln = Eu for L = C_2H_5COO), Fig. 1. The symmetrically independent part of unit cell includes a half of dimer and the other is obtained by the inversion operation. Each Ln atom coordinates a 1,10-phenanthroline molecule in bidentate-cyclic mode. Phen molecules in **6**, **11** and **10** are almost planar, the mean deviation of atoms from the least-squares plane is 0.06(1), 0.02(1) and 0.03(1) Å. Besides, Ln ligates five 3-nitropropionates (**6** and **11**) or five propionates (**10**). All six L ligands in the dimer are involved in coordination by Ln through their carboxylic groups, thus, they act as bidentate ligands. At the same time, coordination modes of L include cyclic, bridging and bridging-cyclic ones. As a result, coordination numbers of Eu and Tb atoms are equal to 9. Coordination polyhedron LnN_2O_7 adopts distorted three-capped trigonal prismatic geometry. It is worth mentioning that Ln–N and Ln–O pair distances in a given phenanthroline or carboxylic group are usually not equal within 3σ (Table 3).

All three crystals display a supramolecular organization arising from stacking interactions and a rich network of C–H···O contacts. Stacking interaction in all the cases is represented by that between parallel Phen rings of neighboring molecules, where the least-squares planes of Phen are situated 3.3 Å from each other. Both Phen molecules of the dimers are involved in stacking interaction, thus in crystal structures of **6**, **11** and **10** infinite chains can

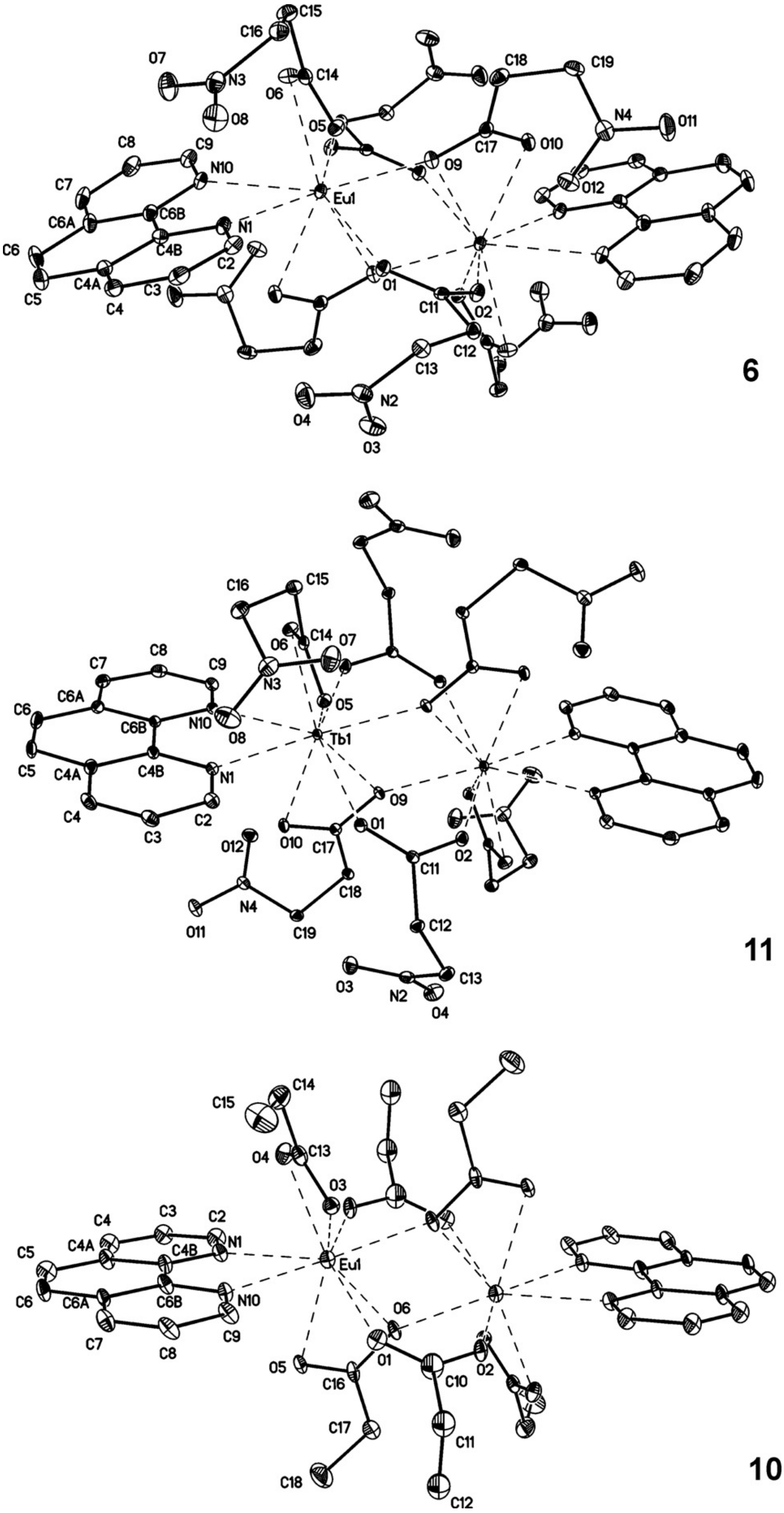

Fig. 1. General view of dimers in the structures of compounds **6**, **11** and **10** in thermal ellipsoids (given with 30% probability level). Only symmetrically independent atoms are labeled. Hydrogen atoms are omitted.

Table 2
Crystallographic data and experimental details for the crystals **6**, **10** and **11**.

Compound	6	11	10
Chemical formula	$C_{42}H_{40}Eu_2N_{10}O_{24}$	$C_{42}H_{40}N_{10}O_{24}Tb_2$	$C_{42}H_{46}Eu_2N_4O_{12}$
Formula weight	1372.76	1386.68	1102.75
Colour, habit	Colorless, prism	Colorless, prism	Colorless, prism
Crystal dimensions (mm)	0.30 × 0.20 × 0.20	0.29 × 0.14 × 0.13	0.18 × 0.15 × 0.08
Temperature (K)	100 (2)	100 (2)	100 (2)
F(000)	680	684	2192
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$C\,2/c$
a (Å)	8.4676(8)	10.0094(7)	23.4635(15)
b (Å)	10.5393(9)	11.5769(8)	9.6802(6)
c (Å)	13.4681(13)	12.2513(9)	21.1512(13)
α (°)	93.281(2)	114.807(2)	90
β (°)	92.836(2)	97.052(2)	113.195(1)
γ (°)	94.3076(17)	106.693(2)	90
Volume (Å^3)	1194.82(19)	1185.04(15)	4415.8(5)
Z	1	1	4
D_{calc} (g cm^{-3})	1.908	1.943	1.659
μ (mm^{-1})	2.70	3.06	2.88
$T_{\min}$	0.498	0.601	0.600
$T_{\max}$	0.614	0.678	0.796
Collected reflections	12,696	13,437	35,933
Independent reflections	6304 (R_{int} = 0.045)	6267 (R_{int} = 0.025)	6595 (R_{int} = 0.107)
Observed reflections	5374	5774	4407
No. of parameters	352	352	244
$\theta_{\max}$ (°)	29.0	29.0	30.4
$R[F^2 > 2\sigma(F^2)]$	0.039	0.023	0.089
$wR(F^2)$	0.074	0.053	0.248
GOF	1.04	1.01	1.02
Weighting scheme	Calculated $w = 1/[\sigma^2(F_o^2) + (0.023P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$	Calculated $w = 1/[\sigma^2(F_o^2) + (0.0287P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$	Calculated $w = 1/[\sigma^2(F_o^2) + (0.12P)^2 + 180P]$ where $P = (F_o^2 + 2F_c^2)/3$
Largest diff. peak and hole (e Å^{-3})	1.63, −2.19	1.20, −1.12	2.58, −3.08

be discriminated, which are parallel with, respectively, crystallographic axis c, (0 1 1) direction and crystallographic axis a.

3.2. Structural regularities of dimeric compounds Ln(RCOO)$_3$·Phen (C.N. = 9)

Let us consider features of the lanthanide coordination polyhedron taken as distorted three-capped trigonal prism in the structures of dimeric carboxylates **1**–**11** (Table 1). Transformation of Ln–O, Ln–N and dimer Ln–Ln bonds in transition from **1** to **11** is presented in Fig. 2. For most of compounds of the kind [1], in particular, for **1**–**8** the distribution of the Ln–O bond lengths is the following. The longest bond is one of the bonds of Ln with bridging-cyclic COO$^-$-group marked as “3” in Fig. 2b, the shortest bond is “1” one of Ln with the same COO$^-$-group. In the structure **6** those bonds are Eu(1)–O(9) and Eu(1A)–O(9) (Table 3). At that, the length of the short bond of the bridging-cyclic COO$^-$-group with Ln is about equal to the Ln–O bond lengths related to the bridging COO$^-$-group (“1” and “2” in Fig. 2c). The lengths of two Ln–O bonds left with the bridging-cyclic COO$^-$-group are on average somewhat longer than that with the cyclic ligand (“1” and “2” in Fig. 2a). That is, the Ln–O bond lengths with the bridging-cyclic ligand correlate with corresponding Ln–O bonds related to the ligands representing “pure” bridging or cyclic type of coordination. However, supplementary bridging coordination of the bridging-cyclic ligand weakens rather the cyclic coordination that shows in increase in the mean bond lengths with the cyclic fragment. Simultaneously, the “drawing back” of the carboxylic group by the second lanthanide of dimer may increase the asymmetry of Ln–O bonds in the cyclic fragment. The analysis realized for coordination of COO$^-$-groups in **1**–**8** crystals agrees with previous discussion of lanthanide carboxylates [27,36].

Table 3
Selected geometric parameters (Å) of coordination polyhedra in compounds **6**, **10** and **11**.

Bond	**6** (Ln = Eu)	**11** (Ln = Tb)	**10** (Ln = Eu)
Bridging L			
Ln(1)–O(1)	2.401(3)	2.348(2)	2.392(8)
Ln(1**A**[a])–O(2)	2.359(2)	2.374(2)	2.385(8)
Cyclic L			
Ln(1)–O(5)[b]	2.504(3)	2.482(2)	2.446(8)
Ln(1)–O(6)[b]	2.455(3)	2.396(2)	2.426(9)
Bridging-cyclic L			
Ln(1)–O(9)[b]	2.612(3)	2.484(2)	2.525(8)
Ln(1**A**[a])–O(9)[b]	2.359(3)	2.357(2)	2.348(7)
Ln(1)–O(10)[b]	2.500(3)	2.540(2)	2.551(8)
Phen			
Ln(1)–N(1)	2.558(3)	2.543(2)	2.619(9)
Ln(1)–N(10)	2.646(3)	2.614(2)	2.576(9)

[a] Symmetry code **A** to generate equivalent atoms for **6**, **11** and **10** are, respectively, 1 − x, 1 − y, −z; 2 − x, 1 − y, 1 − z; 0.5 − x, 0.5 − y, −z.

[b] The atoms O(5), O(6), O(9) and O(10) in the structures of **6** and **11** correspond to O(3), O(4), O(6) and O(5) in the structure of **10**.

At the same time, in Cambridge structural database [1] there is a number of compounds, in which the “2” and “3” Ln–O bond lengths related to cyclic coordination of the bridging-cyclic ligand are about equal. But in compounds coded as RISMIQ (Sm(Prop)$_3$·Phen), YAGGIX and FAYLAT (lanthanum and cerium N-acetyl-N-phenylglycinate with Phen), and also in Eu(Prop)$_3$·Phen (**10**) and Tb(NProp)$_3$·Phen (**11**) the bond “2” of bridging-cyclic COO$^-$-group is the longest (Fig. 2b). This corresponds to bonds Eu(1)–O(5) in **10** and Tb(1)–O(10) in **11**. The presence of the strong intermolecular C–H···O bond with Phen ligand of a neighboring molecule is characteristic feature of all these compounds. Eu(Succ)$_3$·Phen·3H$_2$O (WUWVOZ), which has two independent dimers (**8** and **9**), is especially interesting in this relation. The distribution of the “2” and “3” bonds with the bridging-cyclic ligand in **8**

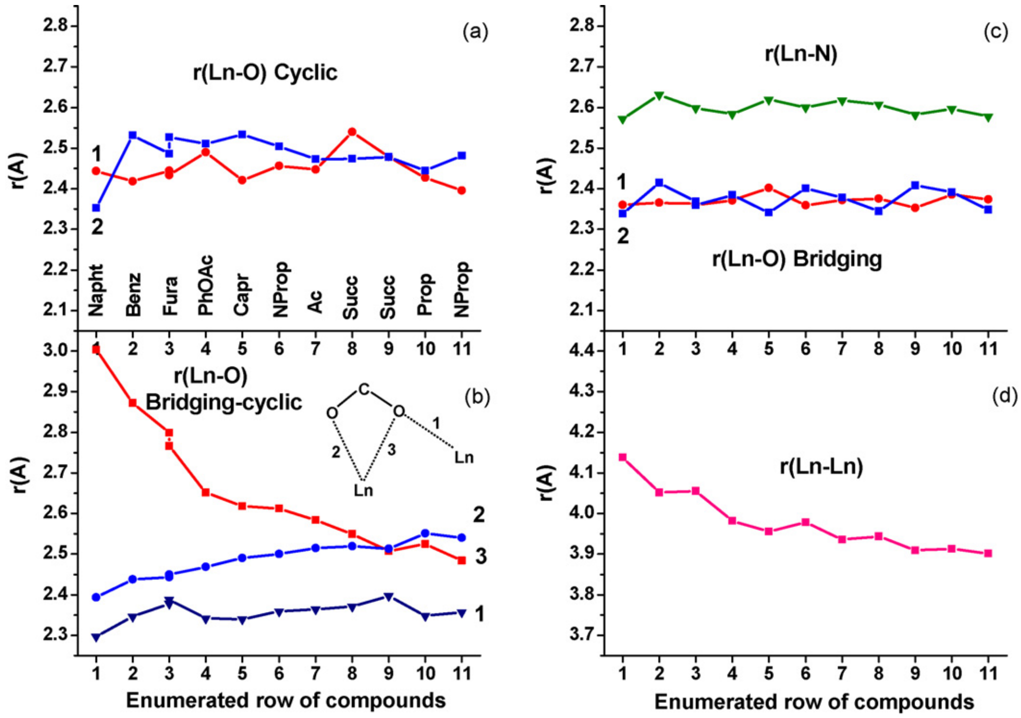

Fig. 2. The changes of Ln–O, Ln–N and dimer Ln–Ln bond lengths in the row of compounds **1**–**11** (Ln = Eu for **1**–**10**, Ln = Tb for **11**).

and **9** is different. If the contact C–H···O is absent, the distribution of the bond lengths is usual, but if the contact exists, the distribution is "inverted". However, in compound Eu(2-Fura)$_3$·Phen (**3**) (LUHFUP) these contacts have place but the distribution of the bond lengths is usual. One can conclude that the presence of strong intermolecular bond C–H···O with Phen ligand of the neighboring molecule is a necessary but not sufficient condition of displacement of bridging-cyclic COO$^-$-group, at which the bond "2" becomes longer than the bond "3".

It should be pointed that in the succession of compounds investigated the equalization of "2" and "3" Ln–O bonds of the bridging-cyclic carboxylic group and the transition to their "inverted" distribution leads to approach of lanthanide ions in dimer from 4.138 Å in **1** to 3.901 Å in **11** (Fig. 2d).

In compounds **1**–**3** with voluminous carboxylate ligands and in some other compounds, such as europium trimethylacetate and 3-methoxybenzoate with Phen [1], main distortions of Ln coordination polyhedron display as considerable spread in the Ln–O distances related to bridging-cyclic COO$^-$-group (Fig. 2b). This spread decreases gradually from ~0.7 Å in **1** to ~0.1 Å in **9** compound, and then slightly increases in **10** and **11** under the bonds inversion. The spread in the Ln–O bond lengths due to bridging and cyclic carboxylic groups, and the spread in Ln–N bond lengths are appreciably less than 0.1 Å in the majority of the compounds investigated. Nevertheless, these changes look significant for aliphatic carboxylates, where the spread in the Ln–O bonds related to bridging-cyclic group is relatively small. So, the main changes of the structure of Ln coordination polyhedron and of the charge distribution in the nearest surroundings of Ln^{3+} ion are conditioned by high "sensitivity" of bonding of the bridging-cyclic carboxylic group to the type and size of entire carboxylate ligand. Embedding of the methylene bridge in the ligand between voluminous R-fragment and carboxylic group in europium phenoxyacetate (**4**) leads to weakening the steric hindrances and to decrease of the coordination polyhedron distortion thanks to moving the voluminous fragment off the Ln^{3+} ion and to bending of the ligand [26].

The distortions of lanthanide coordination polyhedron as three-capped trigonal prism (Fig. 3) in the structures **1**–**11** are given in Table 4 and in Fig. 4. Δr(Ln–O) and Δr(Ln–N) are the ranges between the longest and the shortest distances in coordination polyhedron. D_{CP} was calculated as the displacement of Ln atom from the centre of its coordination polyhedron. Besides, the rotation angle φ between the bases of trigonal prism and distortions of Phen molecule: the torsion angle δ between "pyridine" rings and the bending angle of "pyridine" rings (DB) shown schematically in Fig. 3 were determined. Systematic changes of φ, δ and DB distortions were not disclosed in the enumerated row of compounds. Nevertheless, the degree of lanthanide coordination polyhedron distortion is more pronounced for **1** and **2** (D_{CP} = 0.15, 0.14 Å) and remains approximately constant (D_{CP} ≈ 0.10 Å) for other compounds. In general case the distortion of coordination polyhedron depends on composition of the complex and, to a lesser extent, on the effects of crystal packing. In the crystal structures of **3**–**11** infinite chains can be distinguished due to stacking contacts between

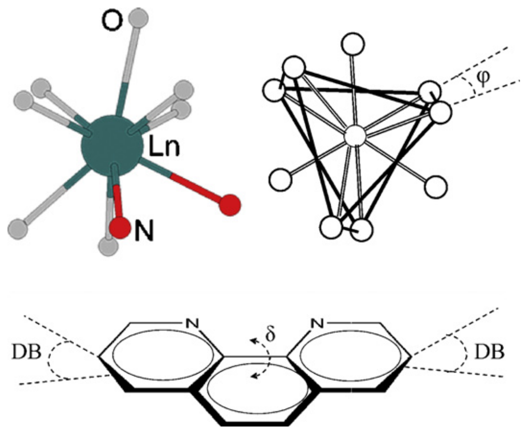

Fig. 3. Schematic representation of φ, δ and DB distortions in Ln polyhedron and Phen molecule.

Table 4
Distortions of the Ln coordination polyhedra in the compounds **1**–**11** and conformation parameters for Phen[a].

No.	Compound	D_{CP}, Å	Ln–O range/Ln–N range, Å	φ,°	δ,°	DB,°
1	Eu(1-Naphth)$_3$·Phen	0.150	2.297–3.003/2.567–2.576	13.1	8.6	4.2
2	Eu(Benz)$_3$·Phen	0.141	2.346–2.872/2.619–2.644	8.0	4.6	2.3
3	Eu(2-Fura)$_3$·Phen	0.104	2.363–2.799/2.578–2.613	19.5	5.4	2.7
		0.107	2.359–2.766/2.594–2.615	18.4	6.1	3.1
4	Eu(PhOAc)$_3$·Phen	0.087	2.342–2.652/2.567–2.602	9.4	1.5	0.5
5	Eu(Capr)$_3$·Phen	0.098	2.340–2.618/2.619–2.621	21.4	4.4	2.2
6	Eu(3-NProp)$_3$·Phen	0.102	2.359–2.613/2.557–2.646	12.8	7.8	3.6
7	Eu(Ac)$_3$·Phen	0.105	2.364–2.584/2.587–2.649	10.9	3.0	1.3
8	Eu(Succ)$_3$·Phen	0.090	2.345–2.549/2.592–2.624	20.0	3.9	1.9
9		0.089	2.353–2.513/2.555–2.610	13.7	2.4	1.2
10	Eu(Prop)$_3$·Phen	0.115	2.348–2.551/2.575–2.619	13.4	3.6	1.5
11	Tb(3-NProp)$_3$·Phen	0.078	2.347–2.540/2.542–2.614	15.3	2.9	1.3

[a] D_{CP} is the shift of Ln atom from the centre of its coordination polyhedron; Ln–X range is the range between the longest and the shortest distances in coordination polyhedron; φ is the rotation angle between the bases of trigonal prism (see Fig. 3); δ is the torsion angle between "pyridine" rings; DB is the bending angle of "pyridine" rings.

parallel Phen rings. The distance between the least-squares planes of Phen molecules varies from 3.3 to 3.6 Å. In the crystal structures of **1** and **2** only weak C–H···C and C–H···O contacts are present. Thus, the degree of distortion of Ln coordination polyhedron in **1**–**11** can be viewed mainly as an intrinsic feature of the complex.

3.3. Luminescence spectra of europium carboxylates

Earlier, the luminescence spectra of europium compounds under investigation were separately published without systematic comparison with structural data [19–21,28]. The luminescence spectra of Eu(RCOO)$_3$·Phen presented in Fig. 5 have the maximal possible number of Stark components in the Eu^{3+} electronic transitions that witness about low symmetry of charge distribution in the nearest surroundings of Eu^{3+} ion. This symmetry belongs to one of point groups inside the triclinic, monoclinic or rhombic syngonies, that agrees with X-ray data. Judging from characteristic features of the spectra, the carboxylates investigated can be assigned to two subgroups: compounds **1**–**4** with voluminous aromatic carboxylate ligands and aliphatic carboxylates **5**–**7**, **10**, **11**. Against the background of similarity of the crystal field Stark splitting of Eu^{3+} electronic transitions in **1**–**4** one can see a prominent fall of the intensity of hypersensitive electric-dipole $^5D_0$–$^7F_2$ transition in relation to the intensity of magnetic-dipole $^5D_0$–$^7F_1$ transition $I(^5D_0–^7F_2)/I(^5D_0–^7F_1)$ from compound **1** to **4** (Fig. 6). The intensity of $^5D_0$–$^7F_2$ transition is extremely sensitive to the nature and symmetry of the effective charge distribution on atoms of the nearest surroundings of Eu^{3+} ion in contrast to $^5D_0$–$^7F_1$ transition. The value $I(^5D_0–^7F_2)/I(^5D_0–^7F_1)$ is the highest in the spectrum of Eu(1-Napht)$_3$·Phen (**1**). It decreases gradually and becomes about two times lower in aliphatic carboxylates. "Deviation" of the point **3** is connected with distortion of Eu(2-Fura)$_3$·Phen dimer symmetry from centrosymmetrical accompanied by the appearance of non-equivalent luminescence centres. Lowering the $^5D_0$–$^7F_2$ intensity in the row of compounds **1**–**4** must be caused by decrease of the distortions of coordination polyhedron conditioned by substantial difference in the bond strengths of Eu^{3+} ion with the bridging-cyclic carboxylic group (Figs. 2 and 4). In comparison with this strong distortion the influence of the other distortions of polyhedron on the luminescence spectra of compounds **1**–**4** seems significantly smaller. At the same time, in the spectra of aliphatic compounds beginning from **5** the intensity distribution between Stark components of every electronic transition changes, but the changes of relative intensity of $^5D_0$–$^7F_2$ transition are not too high. This is determined first of all by smaller values of distortions of coordination polyhedron concerned with bridging-cyclic carboxylic group. Against the background of equalization of "2" and "3" bonds of Eu^{3+} ion with bridging-cyclic group (Fig. 2b) the distortions due to non-equivalence of Eu^{3+} bonds with cyclic and bridging carboxylic groups and due to a torsion of polyhedron φ concerned with the rotation of one base of trigonal prism in relation to the other should display more clearly. Equalization of the pair bonds Eu–O related to cyclic and bridging groups is observed in compounds from **5** to **7** and **10**. Then, in compound **11** the distortions connected with these groups increase. The angle φ decreases gradually in the compounds **5**–**7**, then increases in **10** and **11**. The minimal distortions of europium coordination polyhedron were found in acetate (**7**). This agrees with the luminescence spectra showing the highest symmetry of the crystal field influencing the Eu^{3+} ion in this compound.

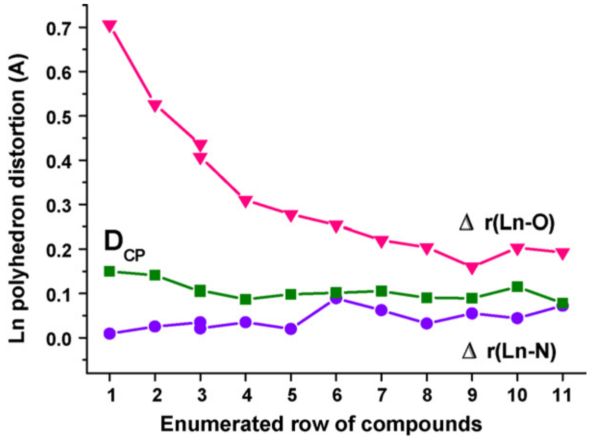

Fig. 4. The changes of distortions of the Ln coordination polyhedron Δr(Ln–O), Δr(Ln–N) and D_{CP} in the row of compounds **1**–**11** (Ln = Eu for **1**–**10**, Ln = Tb for **11**).

In general, lowering the symmetry of the nearest surroundings of Eu^{3+} ion should lead to the increase in the probability of the induced electric-dipole transitions and, therefore, to increase in the rate of radiative processes. The correlation between the features of the luminescence spectra and the distortions of coordination polyhedron of Ln^{3+} ion has to be in accordance with behavior of the natural lifetimes of the radiative states of Eu^{3+} and Tb^{3+} ions.

3.4. Lifetimes of $^5D_0$ (Eu^{3+}) and $^5D_4$ (Tb^{3+}) states. Luminescence efficiency

Let us consider the lifetimes of metastable states of Eu^{3+} and Tb^{3+} ions in the series of europium and terbium compounds under investigation Ln(RCOO)$_3$·Phen. The observed luminescence decay at the excitation in the ligand is the result of a balance between rates of all the radiative and nonradiative processes in the lanthanide system. Various cases of the balance between all the rates in lanthanide coordination compounds were perfectly treated by adequate sys-

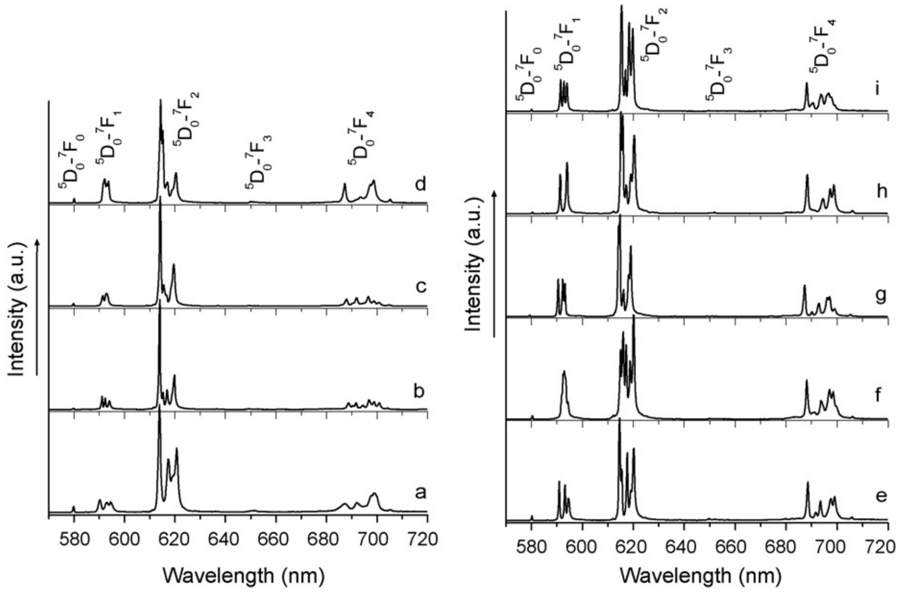

Fig. 5. Luminescence spectra of Eu(1-Napht)$_3$·Phen – **1** (a), Eu(Benz)$_3$·Phen – **2** (b), Eu(2-Fura)$_3$·Phen – **3** (c), Eu(PhOAc)$_3$·Phen – **4** (d), Eu(Capr)$_3$·Phen – **5** (e), Eu(3-NProp)$_3$·Phen – **6** (f), Eu(Ac)$_3$·Phen – **7** (g), Eu(Prop)$_3$·Phen – **10** (h) and Eu(3-NProp)$_3$·Phen – **11** (i) at 77 K.

tems of rate equations [37,38]. It is obvious that the slower step in the system determines the overall velocity of kinetic processes. We suppose that the decay rates of $^5D_0$ and $^5D_4$ levels of Ln^{3+} ion in the carboxylates under investigation are low in comparison with the decay rates of the ligand lowest triplet states including intramolecular energy transfer rates, by analogy with the complexes studied in many works, in particular, in Ref. [38]. This assumption was verified by rough experimental estimation of the lifetimes of the ligand lowest triplet states at 77 K, which was not higher than the $^5D_0$ and $^5D_4$ lifetimes in our systems. So, we describe the lifetime observed for Ln^{3+} ion electronic state as $\tau_{obs} = 1/(k_r + k_{nr})$, where k_r is the rate of pure radiative processes, k_{nr} is the rate of nonradiative processes listed in Eq. (1).

$$k_{nr} = k_{vibr} + k_{LMCT} + k_{BET} + k_{Ln-Ln}, \tag{1}$$

where k_{vibr}, k_{LMCT}, k_{BET} and k_{Ln-Ln} are the rates of nonradiative processes, conditioned by the quenching with participation of high-frequency vibrations of the crystal lattice (multiphonon relaxation), the quenching with participation of LM CTS in europium compounds, the quenching by back energy transfer from the metastable level of Ln^{3+} ion to the ligand lowest triplet state and the Ln–Ln concentration quenching, respectively [29,39,40].

Measured lifetimes τ_{obs} of $^5D_0$ state of Eu^{3+} ion and $^5D_4$ state of Tb^{3+} ion are given in Table 5. One can see only ~5% differences between the values of τ_{obs} ($^5D_0$) for every europium compound Eu(RCOO)$_3$·Phen at 77 and 295 K and τ_{obs} ($^5D_4$) for corresponding terbium compound Tb(RCOO)$_3$·Phen at 77 K. To visualize the behavior of the lifetimes in the series of compounds **1**–**11** it was presented as gradual plots in Fig. 7. The lifetimes for terbium compounds at 295 K are substantially lower than their values at 77 K, they cannot be superimposed on the gradual plot, and they will be considered a bit later. Successive "coincidence" of every three points relating to different diagrams in Fig. 7 gives the evidence for following:

(i) The quenching conditioned by the participation of LM CTS in energy transfer processes in europium compounds is absent. In the opposite case, the lifetime τ_{obs} (Eu) should be lower than τ_{obs} (Tb), and τ_{obs} (Eu) at 295 K should be lower than τ_{obs} (Eu) at 77 K [41]. Besides, at presence of the quenching LM CTS the intensities of some of the narrow f–f bands in the Eu^{3+} excita-

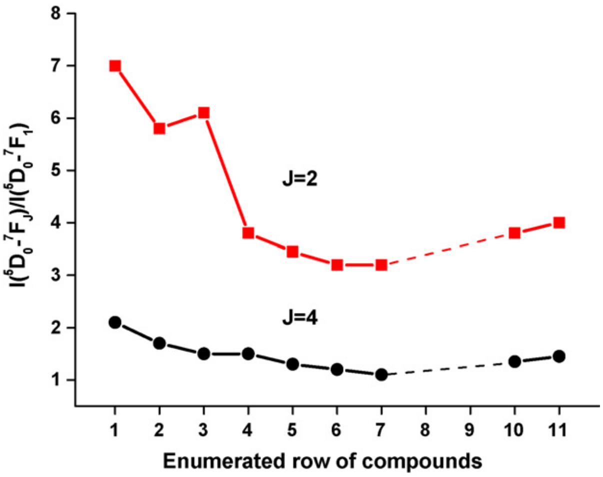

Fig. 6. The changes of relative integral intensities of $^5D_0$–^7F_J transitions of Eu^{3+} ion in the investigated row of compounds at 77 K.

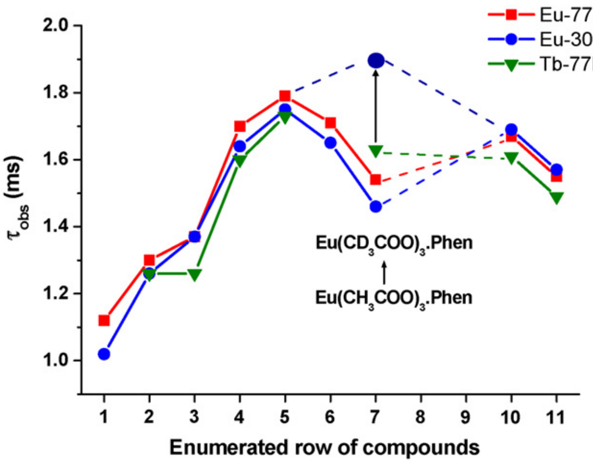

Fig. 7. The changes of lifetimes τ_{obs} of $^5D_0$ (Eu^{3+}) state at 77 and 295 K and $^5D_4$ (Tb^{3+}) state at 77 K for row of europium and terbium carboxylates.

Table 5
Lifetimes τ_{obs} of $^5D_0$ (Eu^{3+}) and $^5D_4$ (Tb^{3+}) states, rate constant k_{BET} (Tb^{3+}) at 295 K, energy of the ligand lowest triplet state E_T and relative intensity of the Tb^{3+} luminescence $I_{295\,K}/I_{77\,K}$.

No.	Compound	τ_{obs} (ms) (Eu^{3+})		τ_{obs} (ms) (Tb^{3+})		k_{BET} (ms^{-1})	E_T (cm^{-1})	$\Delta = E_T - E(^5D_4)$ (cm^{-1})	$I_{295\,K}/I_{77\,K}$, (Tb^{3+})
		77 K	295 K	77 K	295 K	295 K			
1	Ln(1-Napht)$_3$·Phen	1.12	1.02	Low intensity	Low intensity		19,200 (Napht)	−1300	
2	Ln(Benz)$_3$·Phen	1.30	1.26	1.26	0.28	2.78	20,850	350	0.26
3	Ln(2-Fura)$_3$·Phen	1.37	1.37	1.26	0.75	0.54	21,500	1000	0.92
4	Ln(PhOAc)$_3$·Phen	1.70	1.64	1.60	0.78	0.66	21,270	770	0.94
5	Ln(Capr)$_3$·Phen	1.79	1.75	1.73	0.54	1.26	20,950	450	0.39
6	Eu(3-NProp)$_3$·Phen	1.71	1.65						
7	Ln(Ac)$_3$·Phen	1.54	1.46	1.63	0.98	0.41	21,100	600	0.87
	Eu(D-Ac)$_3$·Phen	1.96	1.93						
10	Ln(Prop)$_3$·Phen	1.67	1.69	1.61	1.05	0.33	21,700	1200	0.89
11	Ln(3-NProp)$_3$·Phen	1.55	1.57	1.49	0.87	0.48	21,750 (Phen)	1250	0.78
							21,000 (NProp)	500	
	$^5D_4$ (Tb^{3+})						20,500		

tion spectra as well as the intensity of the ligand broad band usually fall down [20,21,42,43] that is not observed in the row of compounds examined [20,21,28].

(ii) Contribution of the quenching owing to the back energy transfer is the most actual for Tb^{3+} ions. At 295 K, the reverse energy transfer from $^5D_4$ state of Tb^{3+} to the lowest triplet state is a principal mechanism of the luminescence quenching in investigated terbium complexes with Phen, but at 77 K the contribution of k_{BET} in k_{nr} is negligible.

(iii) The Ln–Ln self-quenching in the dimers is one of potential contributors to the quenching of luminescence, especially for compounds at the end of the succession investigated, where the Ln^{3+} ion pairs are maximal close (Fig. 2d). To determine this contribution the lifetimes of $^5D_0$ state of Eu^{3+} ions contained as "traces" in carboxylates Gd(RCOO)$_3$·Phen (originated from commercial precursor Gd_2O_3) were measured. The lifetimes τ_{obs} obtained for those Eu^{3+} ions at 295 K were 3–4% higher than the τ_{obs} for Eu(RCOO)$_3$·Phen compounds. So, for europium compounds studied here the contribution of concentration quenching is low.

(iv) Judging from our data, k_{vibr} gives a principal contribution to k_{nr} for Eu^{3+} ions at 77 and 295 K and for Tb^{3+} ions at 77 K. To evaluate contribution of multiphonon relaxation to τ_{obs} with participation of high-frequency vibrations, the lifetimes of $^5D_0$ (Eu^{3+}) state in several natural and deuterium substituted compounds were compared. The increase in the τ_{obs} (Eu) in acetate Eu(D-Ac)$_3$·Phen in comparison with Eu(Ac)$_3$·Phen amounted to 21%. This agrees well with our results for a pair of acetates Eu(D-Ac)$_3$·Bpy and Eu(Ac)$_3$·Bpy and with the data obtained before for solutions of europium H- and D-acetates [44]. In contrast to this, the quenching due to Bpy ligand and, probably, due to Phen is less effective. The increase in the lifetime τ_{obs} for Eu(Ac)$_3$·D-Bpy and Eu(Benz)$_3$·D-Bpy in comparison with protonated analogues amounted to ~1 and ~5%, respectively. This increase for Eu(NO$_3$)$_3$·D-Bpy$_2$ is ~12%. It can be supposed, that results for europium compounds with Phen ligand will be similar. We guess also, that the contribution of the multiphonon relaxation to τ_{obs} in other compounds of the sequence studied should be smaller than in acetates. The main quencher in the aliphatic compounds is the –CH$_2$– group proximal to the Ln^{3+} ion having lower frequencies of stretching vibrations than CH$_3$– group. The rest of potential quenchers (–CH$_2$– and CH$_3$– groups) are far from Ln^{3+} ions and their contribution to the rate of multiphonon relaxation substantially diminishes with the distance [45].

If the contribution of multiphonon relaxation to k_{nr} were significant, the values of τ_{obs} (Tb) in carboxylates investigated would be substantially higher than τ_{obs} (Eu) caused by higher energy gap between ^5D_J and ^7F_J states in terbium compounds in comparison with europium compounds. Only in Ln(Ac)$_3$·Phen the value of τ_{obs} (Tb) is somewhat higher than the value of τ_{obs} (Eu). For comparison, in hydrates of terbium and europium carboxylates, where the quenching is determined predominantly by contribution of stretching vibrations of water molecules to multiphonon relaxation, τ_{obs} (Tb) at 77 K is above 40–60% higher, than τ_{obs} (Eu) [46]. Moreover, it must be noted that the rate of muliphonon relaxation with participation of high-energy C–H and O–H stretching vibrations is essentially temperature independent between 77 and 295 K [41].

So, the points on the plots of Fig. 7 are mainly related to $\tau_{obs} = 1/(k_r + k_{vibr})$. Three close values of τ_{obs} for every compound witness about nearness of the natural lifetimes for Eu^{3+} and Tb^{3+} ions. At the absence of contribution of CH$_3$– vibrations to the luminescence quenching in acetate (**7**) at substitution CD$_3$– for CH$_3$– group lifetime τ_{obs} increases. That changes the course of the plot (see the change for compound **7** in Fig. 7). The changes of the plots because of the contributions of k_{vibr} in the quenching in other compounds should be substantially lower. If one takes the amendments for all points on axes *x* into account, the plots in Fig. 7 should demonstrate the tendency to the change in the pure radiative lifetimes of the $^5D_0$ (Eu^{3+}) and $^5D_4$ (Tb^{3+}) states in the sequence of compounds investigated.

To be sure in correctness of the predicted changes we will define the behavior of the radiative lifetimes τ_r of $^5D_0$ state of Eu^{3+} ion by comparison of integral intensities of $^5D_0$–^7F_J and $^5D_0$–$^7F_1$ transitions using a treatment of europium luminescence spectra [29,47–50] and a relation formulated in Refs. [29,47]:

$$1/\tau_r = A_{MD,0} \cdot n^3 \cdot (I_{tot}/I_{MD}). \tag{2}$$

Here, *n* is refractive index of the medium, $A_{MD,0}$ is the spontaneous luminescence probability for the magnetic-dipole $^5D_0$–$^7F_1$ transition in vacuo (14.65 s^{-1}), (I_{tot}/I_{MD}) is the ratio of the integral intensity of the Eu^{3+} luminescence spectrum (all electronic transitions $\Sigma I(^5D_0–^7F_J)$) to the integral intensity of the magnetic-dipole transition $I(^5D_0–^7F_1)$. It will be supposed that refraction indexes *n* are not different significantly in the row of polycrystalline compounds under investigation, and the $^5D_0$–$^7F_1$ transition is a pure magnetic-dipole transition [51,52], i.e., the value $A_{MD,0}$. n^3 will be taken as a constant:

$$1/\tau_{r(Eu)} \approx \text{const} \cdot (\Sigma I(^5D_0–^7F_J)/I(^5D_0–^7F_1)). \tag{3}$$

The quantities reverse to relative integral intensity will be proportional to the values of the radiative lifetimes for compounds of the row formed:

$$1/(\Sigma I(^5D_0–^7F_J)/I(^5D_0–^7F_1)) \sim \tau_{r(Eu)}. \tag{4}$$

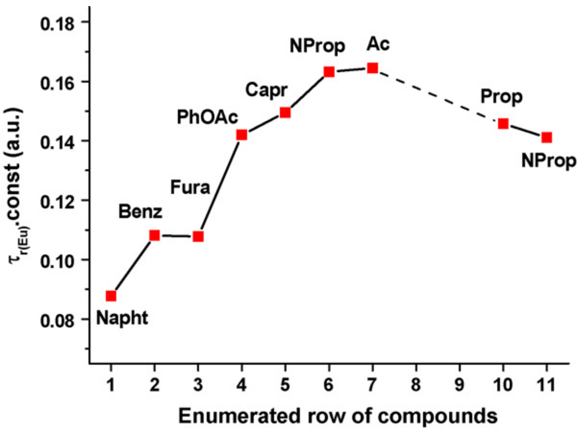

Fig. 8. The changes of the values "$\tau_{r(\mathrm{Eu})}$·const" for row of europium carboxylates (const = $A_{\mathrm{MD},0}\cdot n^3$, see formulae (2) and (3)).

These quantities for europium compounds **1**–**11** are presented in Fig. 8. Correction for spectral sensitivity of the experimental set-up was made. With every faults and assumptions admitted, the plots presented in Figs. 7 and 8 conform to each other satisfactorily. They describe a general tendency of the change in the natural lifetimes of the radiative states of Eu^{3+} and Tb^{3+} ions in succession of compounds.

The radiative lifetime τ_r is determined by distribution of the electron density in the nearest surroundings of Eu^{3+} ion and by the degree of anisotropy of the crystal field [29,47–50,53]. The behavior of the lifetimes τ_{obs} with k_{vibr} correction as well as that of ($\tau_{r(\mathrm{Eu})}$·const) values calculated from the luminescence spectra come to an agreement with values of distortions of Eu^{3+} coordination polyhedron (Figs. 2 and 4). Judging from the Eu–O distances, the radiative lifetime of Ln^{3+} ion correlate first of all with the bond strengths of Eu^{3+} ion with the oxygen atoms of bridging-cyclic carboxylic groups. When the main contribution in polyhedron distortions caused by these carboxylic groups is lowering, the radiative lifetime of Ln^{3+} ion is increasing. This correlation is entirely compatible with behavior of the luminescence spectra considered above.

Let us return to Table 5. As we mentioned earlier, the behavior of the lifetimes of $^5D_4$ state in the row of compounds $Tb(RCOO)_3$·Phen (**1**–**11**) at 295 K is spectacularly different from their behavior at 77 K. Parallel with the energy transfer from the lowest triplet level to metastable $^5D_4$ level of Tb^{3+} ion at high temperatures a back energy transfer is possible from $^5D_4$ level to the triplet of compound by thermal activation [39,54–56]. In contrast to the values τ_{obs} (Tb, 77 K) depending mainly on the symmetry of the charges distribution in the nearest surroundings of Ln^{3+} ions and on their polarizability, a linear dependence of the ratio τ_{obs} (Tb, 295 K)/τ_{obs} (Tb, 77 K) on the energy of the lowest triplet state is observed [46].

It is necessary to define the affiliation of the lowest triplet state of the terbium complexes and to consider its position in relation to $^5D_4$ (Tb^{3+}) electronic state. The phosphorescence spectra of some gadolinium compounds $Gd(RCOO)_3$·Phen used for determination of the energies of the lowest triplet states of the ligands are presented in Fig. 9. The energy of T – S_0 zero-phonon transition is obtained from short-wavelength edge of broad vibronic band. As the fine structure is absent in the majority of phosphorescence spectra examined, the accuracy of determination of the triplet state energy is not high. In some of the spectra, the lines of the electronic transitions of Eu^{3+} and Tb^{3+} ions contained as admixture in commercial precursor Gd_2O_3 are superimposed on broad band of the ligand. The comparison of the $Gd(RCOO)_3$·Phen phosphorescence spectra with spectra of corresponding hydrate salts without phenanthroline $Gd(RCOO)_3\cdot nH_2O$ gives evidence of belonging of the lowest triplet state in the range of 20,850–21,750 cm^{-1} to Phen ligand. However, one should keep in mind that the carboxylate triplet state energy in the salt can differ from that in corresponding adduct with Phen. Only in two of compounds investigated, $Gd(1\text{-}Napht)_3$·Phen (**1**) and $Gd(3\text{-}NProp)_3$·Phen (**11**), the energies of the lowest triplet state of carboxylate ligand having, respectively, the values 19,200 and 21,000 cm^{-1} are lower than the energy of triplet state T of Phen. In the first compound, the carboxylate triplet energy is substantially lower than the energy of $^5D_4$ state of Tb^{3+} ions, so, the luminescence of $Tb(1\text{-}Napht)_3$·Phen is not observed at all.

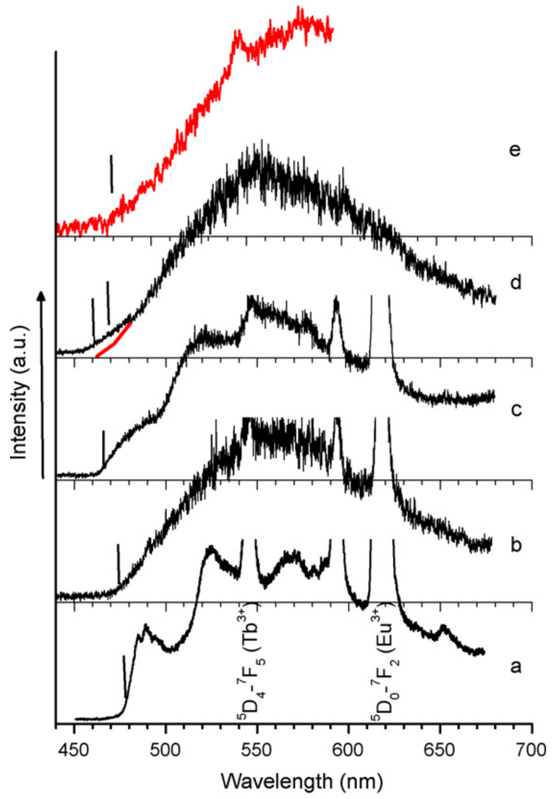

Fig. 9. Phosphorescence spectra of $Gd(Benz)_3$·Phen – **2** (a), $Gd(Ac)_3$·Phen – **7** (b), $Gd(2\text{-}Fura)_3$·Phen – **3** (c), $Gd(3\text{-}NProp)_3$·Phen – **11** (d) and $Gd(3\text{-}NProp)_3\cdot nH_2O$ (e) registered with 1 ms time delay at 77 K.

The triplet level of Phen molecule in the majority of $Tb(RCOO)_3$·Phen compounds is responsible for the fall of the lifetime of $^5D_4$ (Tb^{3+}) state owing to back energy transfer at a rise of the temperature. The value $\Delta = E_T - E(^5D_4) = 350\text{–}1250\ cm^{-1}$ is lower than empirically determined value of the limit difference $\Delta = 1850\ cm^{-1}$ [54–56], at which the rate of the back energy transfer becomes inessential. For example, in corresponding terbium compounds with 2,2′-bipyridine $Tb(RCOO)_3$·Bpy, where the Bpy triplet is situated ~1000 cm^{-1} higher than the Phen triplet, the decrease of the lifetime of $^5D_4$ state of Tb^{3+} ion at 295 K is not observed. Triplet states of the majority of terbium carboxylate salts investigated in this work have also too high an energy (22,000–23,000 cm^{-1}) for active participation in the back energy transfer.

The energies of the ligand lowest triplet state E_T and the quantities $\Delta = E_T - E(^5D_4)$ are given in Table 5. At increasing the temperature the efficiency of processes related to back energy transfer grows, the contribution of k_{BET} in the value of the lifetime τ_{obs} (Tb) increases. In particular, at heating from 77 to 335 K of the specimen $Tb(PhOAc)_3$·Phen (**4**) having $\Delta = 770\ cm^{-1}$ a fall of the lifetime τ_{obs} of $^5D_4$ state from 1.60 to 0.17 ms occurs. In benzoate $Tb(Benz)_3$·Phen (**2**) with $\Delta = 350\ cm^{-1}$ the $\tau_{obs} = 0.17$ ms is reached at lower temperature, 305 K. Table 5 includes the rate

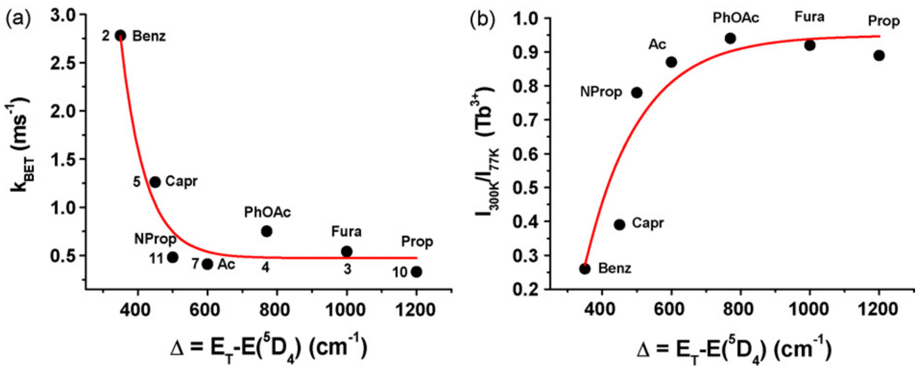

Fig. 10. Rate constant of the back energy transfer k_{BET} (a) and the relative luminescence intensity $I_{295\,K}/I_{77\,K}$ (b) for terbium compounds as functions of $\Delta = E_T - E(^5D_4)$. The circles represent the experimental data, and the solid line represents the exponential fitting.

constants k_{BET} obtained from the difference of the values $1/\tau_{obs}$ (Tb) = $k_r + k_{vibr} + k_{BET}$ at 295 K and $1/\tau_{obs}$ (Tb) = $k_r + k_{vibr}$ at 77 K, and the relative intensities of Tb^{3+} luminescence $I_{295\,K}/I_{77\,K}$. The behaviors of values k_{BET} and $I_{295\,K}/I_{77\,K}$ depended upon Δ can be approximated by exponential fitting (Fig. 10). In the case of nitropropionate $Tb(3\text{-}NProp)_3{\cdot}Phen$, the triplet of NProp ligand ($\Delta = 500\,cm^{-1}$) takes more active part in the back energy transfer in comparison with the triplet of Phen ($\Delta = 1250\,cm^{-1}$). Satisfactory accordance of the plots "a" and "b" testifies to a paramount influence of the back energy transfer processes on the intensity of Tb^{3+} luminescence at 295 K.

It is possible to evaluate the intrinsic quantum yield of luminescence $\Phi = k_r/(k_r + k_{nr})$ for acetates $Ln(Ac)_3{\cdot}Phen$. Taking into account the change in the lifetimes at deuterium substitution one can with good accuracy determine the rate of radiative processes k_r, which is equal ~0.46 ms^{-1} for Eu^{3+} ions in acetate. As, judging from our data, k_r for Eu^{3+} and Tb^{3+} ions should not be substantially different (τ_{obs} (Tb, 77 K) < τ_{obs} (Eu, 77 K) by ~5%), the intrinsic quantum yield Φ for $Tb(Ac)_3{\cdot}Phen$ at 77 K is equal to ~0.75. At room temperature it drops to ~0.45 caused by more active the back energy transfer. Overall luminescence quantum yield should be lower as the efficiency of the excitation energy transfer from the ligands to the Ln^{3+} ion usually is less than one.

It is interesting to look for correlation between the quenching rate constant k_{BET} (Tb^{3+}) at 295 K dependent on the ligand triplet energy and details of the structure of complexes. One can see a considerable change in the Phen triplet energy in the family of dimeric compounds investigated at changing the second ligand, carboxylate anion. Broad range of the Phen triplet energy, from 20,850 cm^{-1} in gadolinium benzoate to 22,300 cm^{-1} in gadolinium triphenylpropionate with Phen [46], demonstrates extraordinary sensitivity of this state to the structure of compound. The energies of the electronic states of Phen molecule depend on its interaction with the Ln^{3+} ion and to the lesser degree on weaker intermolecular interactions, in particular, on stacking interaction. In crude approximation, with allowance made for low accuracy of determination of the triplet energy a linear dependence between the experimental value of Phen triplet energy T and the mean distance Eu–N in the electronic ground state of complexes is observed (Fig. 11). The shorter is the bond Ln–N, the higher is the energy of the lowest triplet state of Phen. The increase in the triplet energy can indicate "a less expanded" system of π-electron density in the Phen ligand bonded stronger with the metal cation. In accordance with the correlation demonstrated for T state of Phen the rate constant k_{BET} also should depend on the distance Ln–N (Fig. 11). High value of k_{BET} and significant lowering the luminescence intensity at increase of the temperature correspond to terbium benzoate with relatively long Ln–N bonds.

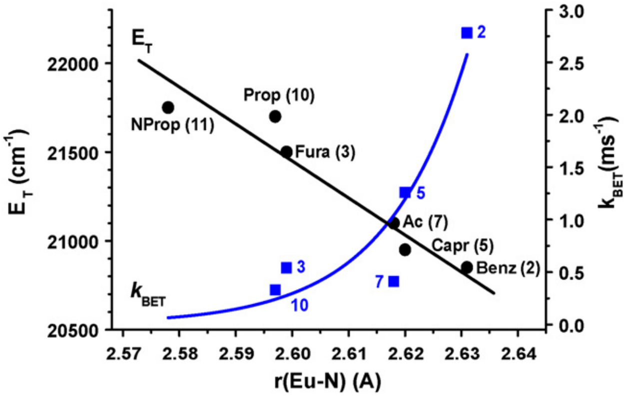

Fig. 11. Phenanthroline triplet state energy E_T and k_{BET} values as functions of average Eu–N distance. The solid lines represent the linear and exponential fittings.

4. Conclusions

The influence of the distortions of the lanthanide coordination polyhedron in dimeric carboxylates with 1,10-phenanthroline $Ln(RCOO)_3{\cdot}Phen$ on photophysical properties of compounds such as the luminescence spectra, lifetimes of $^5D_4$ (Tb^{3+}) and $^5D_0$ (Eu^{3+}) electronic states, features of the excitation energy transfer from the ligands to Ln^{3+} ions and efficiency of luminescence was examined.

The relative contributions of the rates of the radiative and nonradiative processes to the lifetimes were determined. The lifetime of $^5D_0$ (Eu^{3+}) state in the temperature interval from 77 to 295 K and the lifetime of $^5D_4$ (Tb^{3+}) state at low temperatures are mainly determined by radiative processes and depend on details of the charge distribution in the nearest surroundings of the Ln^{3+} ion that are connected with distortions of coordination polyhedron of Ln^{3+} ion. Polyhedron distortions are to a great extent caused by the range of the Ln–O bond lengths related to bridging-cyclic carboxylic group that depends on the type and the size of carboxylate anion. At prominent polyhedron distortions, as in naphthylcarboxylates, benzoates and furancarboxylates, the rates of the radiative processes become higher and the intensity of Eu^{3+} $^5D_0$–$^7F_2$ hypersensitive transition increases.

Multiphonon relaxation is the main nonradiative process in europium compounds at 77–295 K and in terbium compounds at 77 K. The contribution of multiphonon relaxation to the lifetimes measured is high enough in acetates, but it is substantially lower in other compounds. A back energy transfer from $^5D_4$ state of Tb^{3+} ion to the lowest triplet state related to Phen in most of compounds is the principal nonradiative process contributing noticeably to quenching in terbium compounds at high temperatures. In particular, this process leads to fourfold decrease in the intensity of terbium benzoate in transition from 77 to 295 K. It was found, that the lifetime of $^5D_4$ (Tb^{3+}) state and the luminescence efficiency of terbium compounds at high temperatures depend substantially on the bonding strength of phenanthroline with Ln^{3+} ion. The stronger is the Ln–N bond, the higher is the relative intensity of luminescence of terbium compounds $I_{295\,K}/I_{77\,K}$.

To increase the probability of induced electric-dipole transitions, first of all, hypersensitive transitions in the lanthanide carboxylates with Phen, one needs to create substantial distortions of Ln coordination polyhedron with the help of voluminous carboxylate ligands. In the same time, to decrease the influence of the back energy transfer processes on the quantum yield of luminescence, relatively small changes in the Ln–N bond strengths are sufficient.

In dimeric carboxylates $Ln(RCOO)_3{\cdot}Phen$, a range of the phenanthroline triplet state energy, from 20,850 to 21,750 cm^{-1}, was demonstrated in dependence on the type of carboxylate anion. That points to necessity of measurements of the triplet energy in every particular case of analysis of processes of the energy transfer.

Closeness of the radiative lifetimes of $^5D_0$ and $^5D_4$ metastable states of Eu^{3+} and Tb^{3+} ions, respectively, located in the same crystal field was demonstrated. That is, the experimental rate of Eu^{3+} radiative processes can be used for evaluation of the intrinsic quantum yield of luminescence of Tb^{3+} ions.

CCDC 766008 (**6**), 766009 (**11**) and 766010 (**10**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

The authors are indebted to Prof. K. A. Lyssenko for helpful discussions. The work was supported by the Russian Foundation for Basic Research (Grant No. 08-02-00424-a).

Appendix A. Supplementary experimental confirmation of theoretical considerations presented in Ref. [29]

Experimental values of τ_{obs} ($^5D_0$) observed for carboxylates $Eu(RCOO)_3{\cdot}Phen$ at 77 K (equated roughly to natural lifetimes) are presented in Fig. 12 as a function of the ratio $\Sigma I(^5D_0{-}^7F_J)/I(^5D_0{-}^7F_1)$. In spite of the assumption made the curve in this figure agrees closely with the curve in Fig. 3 of Ref. [29].

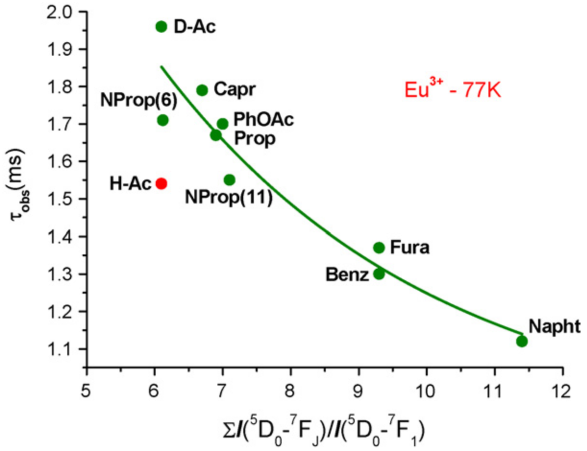

Fig. 12. Dependence of the values τ_{obs} (Eu^{3+}, 77 K) on the ratio $\Sigma I(^5D_0{-}^7F_J)/I(^5D_0{-}^7F_1)$.

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