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Vibronic spectra and details of the structure of europium nitrates with derivatives of 1,10-phenanthroline

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Abstract

Luminescence and excitation of luminescence vibronic spectra as well as IR and Raman spectra of europium nitrates with 1,10-phenanthroline derivatives of formula $Eu(NO_3)_3.Ph_2$ were studied. The effect of size of ligands and their effective charges on crystal structure and, as a consequence, on spectroscopic characteristics was investigated under conditions where one type of ligand (NO_3^- group) is sufficiently rigid. The second ligand, heterocyclic diimine, can change its size and donor-acceptor properties when the substituents are varied. Stark splittings and relative intensities of the Eu^{3+} electronic transitions, the behaviour of vibration frequencies, and vibronic interaction were studied. It was demonstrated that nitrates under investigation have identical composition but form two different structural groups with small and bulky phenanthroline derivatives due to the influence of steric factor. All nitrate anions in the compounds are coordinated and the Eu-O (NO_3^-) bonds are relatively strong. The values of the splitting of stretching vibrations of the NO_3^--anions ($\triangle = \nu_4 - \nu_1$) and position of the band of ν(Eu–O) vibration show that the strongest Eu–O bonds are formed in $Eu(NO_3)_3.Nphen_2$, $Eu(NO_3)_3.Tmphen_2$ and $Eu(NO_3)_3.Dphphen_2$ due to high acceptor properties of nitro-phenanthroline and large size of tetramethyl- and diphenyl-phenanthroline molecules. Weak vibronic mixing of electronic and vibronic states was demonstrated in the region of $^5D_0–^7F_2$ transition of Eu^{3+}. The vibronic satellites of $^5D_0–^7F_0$ -transition due to vibrations of the NO_3^--group borrow about 1–2% of the intensity of the electric-dipole $^5D_0–^7F_2$ transition yielding the increase of their relative intensity of 100 times in the Stokes sideband.

Keywords: Crystal and ligand fields; Electron-phonon interaction; Luminescence

1. Introduction

This work belongs to the series of spectroscopic investigations of europium compounds with 1,10-phenanthroline derivatives [1–3]. In earlier studies of $Eu(\beta)_3.Ph$ adducts of europium tris(β-diketonate) with derivatives of 1,10-phenanthroline, both the ligands were highly polarizable, 'soft'. In this case the changes of the electronic density on nitrogen atoms of phenanthroline molecules when varying the substituents were influencing the value of electronic density on the oxygen atoms of β-diketones and vice versa. An important role in formation of the structure of β-diketonates refers to donor-acceptor properties of ligands as well as to steric factor. In this paper the influence of size of ligands and effective charges on atoms in the nearest surroundings of Eu^{3+} ion on spectroscopic characteristics and structure of mixed complexes of europium nitrates with derivatives of 1,10-phenanthroline is investigated. In these compounds one of two kinds of ligands, namely the nitrate ion, is sufficiently rigid. Stark splitting and relative intensities of the Eu^{3+} electronic transitions, vibration frequencies, and vibronic interaction are considered.

2. Experimental

The luminescence and the excitation of luminescence spectra, as well as IR and Raman spectra of europium nitrates with 1,10-phenanthroline derivatives of formula $Eu(NO_3)_3.Ph_2$ (Ph-3,4,7,8-tetramethyl-phenanthroline (Tmphen), 5-methyl-phenanthroline (Mphen), phenanthroline (Phen), 5-phenyl-phenanthroline (Phphen), 4,7-diphenyl-phenanthroline (Dphphen), 5-nitro-phenanthroline (Nphen)) were examined. Phenanthroline derivatives are arranged in such the manner that their acceptor properties increase. The appreciable withdrawal of electronic density from the nitrogen atoms occurs in transitions

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from the first to the second and from the fifth to the sixth members of the row (in accordance with values of the polar Taft's constants σ^* of the substituents $-CH_3$ (0), –H (+0.49), $-C_6H_5$ (+0.6), $-NO_2$(+3.9) [4]).

To assign the vibration bands in IR spectra and the vibronic satellites of Eu^{3+} transitions, isotopic substitution of ^{15}N for ^{14}N in NO_3^- groups, as well as quasi isotopic substitution of Ln^{3+} and Y^{3+} host metal ions for Eu^{3+} ones were used [5]. Comparison of the spectra of $Eu(NO_3)_3.Ph_2$ with the spectra of $Eu(NO_3)_3.Bpy_2$ (Bpy-H- or D-2,2′-bipyridine) [6] and $Eu(NO_3)_3.6\ H_2O$ one [7] were made.

The compounds were obtained by mixing of ethanol solutions of europium nitrate $Eu(NO_3)_3.6\ H_2O$ and heterocyclic diimine. The elemental analysis confirms the composition of all the substances as $Eu(NO_3)_3.Ph_2$. It should be noted that europium compounds with Dphphen can form isomers, whose structure probably differs by a different deviation of phenyl rings from the plane of three condensed rings. Their luminescence spectra slightly differ in the Stark splitting of electronic levels. Two isomers was observed earlier in studies of $Eu(NO_3)_3.Bpy_2$ compound [8].

The luminescence and excitation of luminescence spectra were measured on SLM Aminco SPF 500 spectrofluorimeter and on ISP-51 spectrograph. Excitation vibronic spectra in region of $^7F_0$-$^5D_0$ transition of Eu^{3+} were obtained on MDR-23 monochromator or DFS-12 spectrometer using a tuneable dye laser on the Rhodamine 6G or a xenon lamp for optical pumping of the samples. Luminescence and excitation of luminescence spectra were studied at 300, 77 and at 4.2 K. IR spectra in 70–4000 cm^{-1} region were recorded using Brucker FS 88 FTIR and UR-20 spectrometers. Nujol and fluorinated oil were used for preparation of samples. Raman spectra were registered on a Nicolete FT Raman module coupled to Nicolet Magna 860 FTIR spectrometer.

3. Results and discussion

3.1. Excitation of luminescence and luminescence spectra

The structure of $Eu(NO_3)_3.Phen_2$ [9] is analogous to the structure of $Eu(NO_3)_3.Bpy_2$ [8,10]. The crystal lattice consists of neutral molecules bonded by Van der Vaals forces. The coordination polyhedron of the Eu^{3+} ion is dodecahedron formed by six oxygens of three bidentate nitrate anions and four nitrogen atoms of two heterocyclic diimine molecules.

At insertion of substituents with different donor-acceptor properties into the phenanthroline molecule the effective charges on nitrogen atoms and correspondingly the strength of the Eu–N bonds change. The above should reflect in the bonds of europium with the second ligand, NO_3^- ion. However, this influence should not be as strong as in the case of β-diketonates due to lower polarizability of NO_3^- -groups. Besides, at preservation of the high coordination number, equal to 10, (judging from IR spectra all the NO_3^- -groups are coordinated) in the row of the compounds investigated, an influence of the steric factor of bulky molecules of the heterocyclic diimines should appear.

Let us consider the changes in the excitation and luminescence spectra of $Eu(NO_3)_3.Ph_2$ when changing the phenanthroline substituents. These spectra are presented in Figs. 1–4. The short-wavelength part (less than 350 nm) of the ligand excitation band in Fig. 1 is filtered off by glass walls of the sample ampoule. It is known that the strong band in absorption spectrum of the nitrate ion is situated at ~320 nm [11]. To determine the position of the absorption bands of the phenanthroline derivatives the spectra of ethanolic solutions of this derivatives were obtained in UV region. The most long-wavelength bands in the absorption spectrum of 1,10-phenanthroline (S–S*) are situated at 324 and 338 nm in accordance with the data of [12] obtained for solid state specimen. The bands practically do not shift in the spectra of methyl-derivatives and shift by

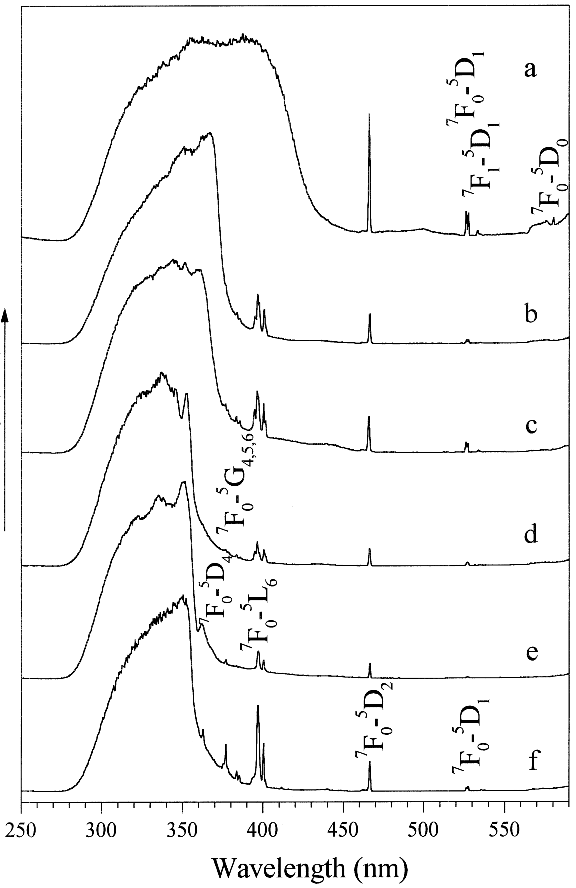

Fig. 1. Excitation spectra of $Eu(NO_3)_3.Nphen_2$ (a), $Eu(NO_3)_3.Dphphen_2$ (b), $Eu(NO_3)_3.Phphen_2$ (c), $Eu(NO_3)_3.Tmphen_2$ (d), $Eu(NO_3)_3.Mphen_2$ (e), $Eu(NO_3)_3.Phen_2$ (f) at 77 K.

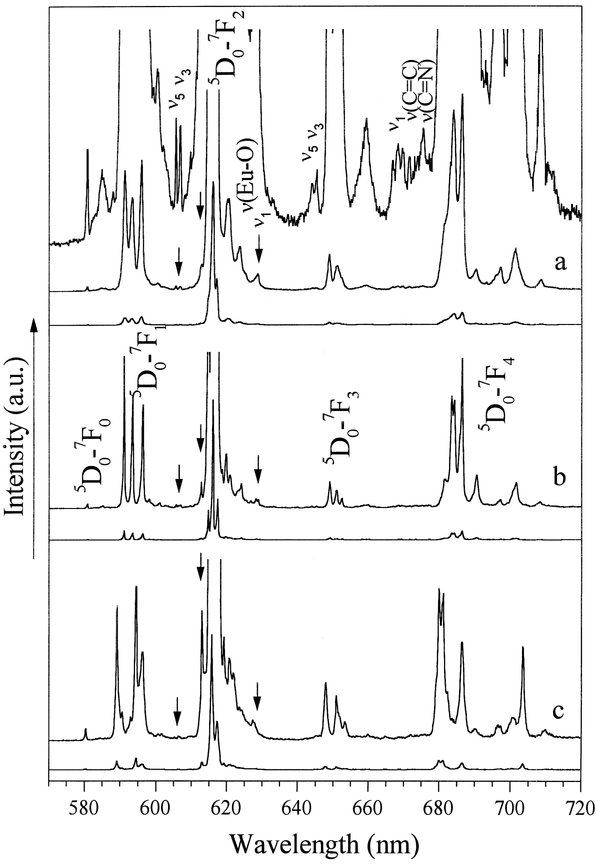

Fig. 2. Luminescence spectra of $Eu(NO_3)_3.Mphen_2$ (a), $Eu(NO_3)_3.Phen_2$ (b), $Eu(NO_3)_3.Nphen_2$ (c) at 77 K.

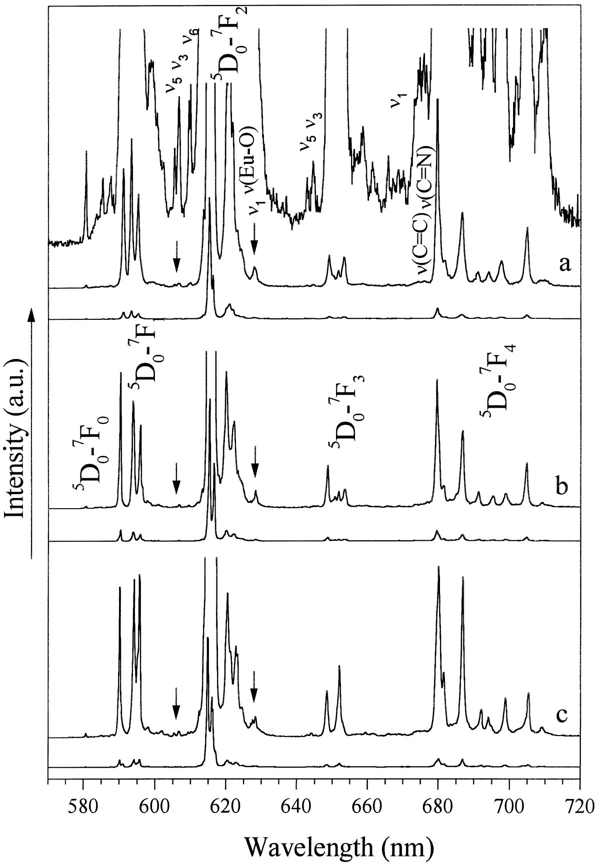

Fig. 3. Luminescence spectra of $Eu(NO_3)_3.Tmphen_2$ (a), $Eu(NO_3)_3.Phphen_2$ (b), $Eu(NO_3)_3.Dphphen_2$ (c) at 77 K.

~10–15 nm towards the long-wavelength side in the phenyl-derivatives due to the increase of the conjugated π-electrons system. The presence of the NO_2-radicals leads to extending of the wide ligand band to 410 nm. A slight long-wavelength shift of the bands by ~10 nm is observed at coordination. The efficiency of the europium luminescence excitation through the diimine absorption bands depends on the kind of the substituents. At 77 K $Eu(NO_3)_3.Mphen_2$ has the highest efficiency, $Eu(NO_3)_3.Phphen_2$ has the lowest one. Coincidence of the singlet levels of Phphen and $^5D_4$-levels of Eu^{3+} has no significant influence on the process of the excitation energy transfer. The differences in the efficiency of the transfer, is probably conditioned by different strength of the Eu-N bonds and by variations of the energy of the triplet levels of Ph that leads to changes in the efficiency of the cascade processes of the energy transfer from excited ligand singlet to the $^5D_0$ emitting level of Eu^{3+}.

The maximum number of the Stark components of the f–f transitions of the Eu^{3+} ion shows low rhombic symmetry of the nearest surroundings of that ion in all the compounds under investigation. This results corresponds well to the X-ray data [9]. Judging from Stark splitting and intensity of Eu^{3+} transitions in the excitation (Fig. 1) and luminescence spectra (Figs. 2–4, Table 1) one can conclude that compounds with the relatively small heterocyclic diimine molecules (Mphen, Phen and Nphen) form a subgroup of complexes. The compounds, containing bulky diimine molecules, such as Tmphen, Phphen and Dphphen, form another subgroup. The compounds containing Nphen could be classified into the first subgroup in spite of the fact that by $^5D_0$–$^7F_4$-transition is close to the second group. The substantial influence of the donor–acceptor properties was detected in the first group of complexes. The distortion of the nearest surroundings of Eu^{3+} ion in $Eu(NO_3)_3.Mphen_2$ is somewhat weaker than in the case of $Eu(NO_3)_3.Phen_2$, so that the effective charges on the atoms in the nearest surroundings are better equalised. Weakening of the Eu–N bonds leads to a strengthening of the Eu–O bonds due to higher electronegativity of the Phen and Nphen radicals. Among compounds of the second subgroup, the values of the even crystal field harmonics of the second order are somewhat lower, and the values of the odd ones – somewhat higher in comparison to the first subgroup. That could point out on the influence of the steric factor in above systems.

The analysis of the vibration spectra shows the differences in the structure of the nearest surroundings of Eu^{3+} in the nitrates studied and will be discussed in the next paragraph.

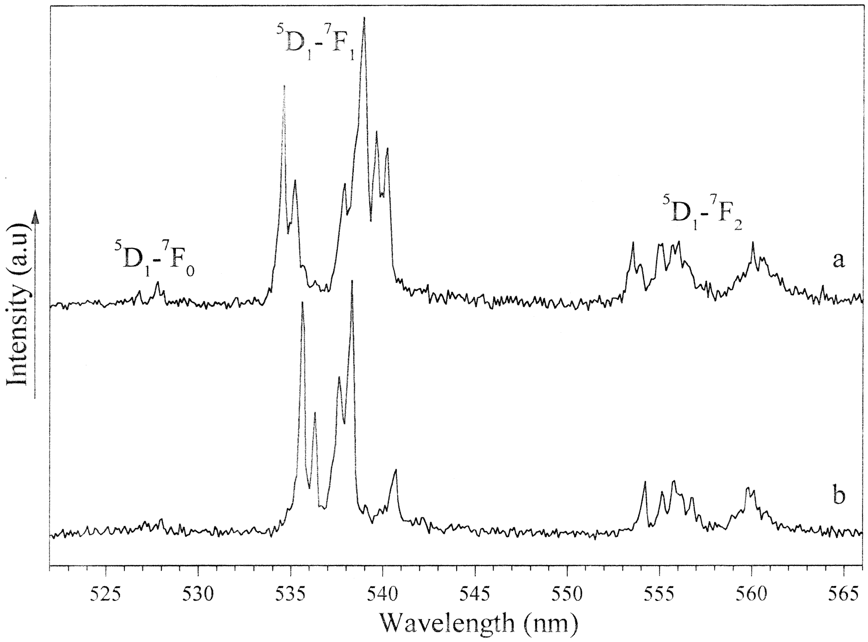

Fig. 4. Luminescence spectra of $Eu(NO_3)_3$.Dphphen$_2$ (a), $Eu(NO_3)_3$.Phen$_2$ (b) in the region of $^5D_1$-^7F_J transitions at 77 K.

3.2. IR and Raman spectra

Infrared and Raman spectra of the investigated compounds are presented in Figs. 5–7. In the Table 2 the frequencies of IR and Raman bands of $Eu(NO_3)_3$.Phen$_2$ and the frequencies of vibrations active in the vibronic sideband of the $^7F_0$–$^5D_0$ transition in the excitation spectra (Fig. 8) are given. Using the isotopic substitution and the literature data [13–16] the assignment of the bands was done. In the 700–900 cm^{-1} region the bands related to out-of-plane C-H bending vibrations are situated. The bands in the 720–770 cm^{-1} region are due to out-of-plane motions of the hydrogen atoms of heterocyclic rings, whereas those in the 840–900 cm^{-1} range are connected with the motions of two hydrogen atoms of the central ring. In the 1340–1630 cm^{-1} region the ν(C=C), ν(C=N) vibrations of the aromatic rings are observed. The frequencies 708, 740–745, 810, 1030, 1310 and 1470–1500 cm^{-1} were assigned to the ν_5, ν_3, ν_6, ν_2, ν_1 and ν_4 vibrations of the nitrate group.

The major differences in the vibrational spectra of phenanthroline derivatives are observed in the vicinity of C–H out-of-plane vibrations [17] and in the region of vibrations of substituents, namely, NO_2-group (the bands at 837, 1355, 1533 cm^{-1} appear [18]), CH_3-groups and the phenyl rings [13]. In the Raman spectra (Fig. 5b,d) the most intense lines are those related to the stretching vibrations ν(C=C), ν(C=N) and to breathing vibrations of the rings. The bands of the nitrate group vibrations are very weak, except for the totally symmetric stretching ν_2 mode at 1030–1035 cm^{-1}.

The IR spectra (Figs. 5,6) confirm the coordination of all the three nitrate anions, as no strong band of the stretching vibration of free NO_3^- -anion (D_{3h}) at 1390 cm^{-1} is observed, a weak band at 1380–1395 cm^{-1} is related to the heterocyclic diimine vibrations. The anion symmetry is lowered due to coordination and instead of one band, two bands, ν_1 and ν_4 are observed at ~1300 and ~1485 cm^{-1}. The mean value of the $\Delta=\nu_4-\nu_1$ splitting in the spectra of investigated compounds is equal to 175–180 cm^{-1} (Table 3). This frequency difference is usually used as a measure of the strength of the coordination bond of the NO_3^- group with the metal ion [19,20]. Large value of this splitting in $Eu(NO_3)_3$.Ph$_2$ evidence that Eu–O bonds are relatively strong [21], stronger than those in the europium nitrate hexahydrate ($\Delta=150$ cm^{-1}). Judging

Table 1
Relative integral intensities of electronic transitions $^5D_0$-^7F_J in luminescence spectra of $Eu(NO_3)_3$.Ph$_2$ at 77 K

Compound	$^5D_0$–$^7F_0$	$^5D_0$–$^7F_1$	$^5D_0$–$^7F_2$	$^5D_0$–$^7F_3$	$^5D_0$–$^7F_4$
$Eu(NO_3)_3$.Mphen$_2$	0.007	1	7.25	0.23	2.32
$Eu(NO_3)_3$.Phen$_2$	0.01	1	8.07	0.24	2.43
$Eu(NO_3)_3$.Nphen$_2$	0.02	1	6.24	0.39	1.93
$Eu(NO_3)_3$.Tmphen$_2$	0.007	1	9.36	0.33	2.01
$Eu(NO_3)_3$.Phphen$_2$	0.008	1	8.16	0.43	2.13
$Eu(NO_3)_3$.Dphphen$_2$	0.007	1	9.53	0.38	2.14

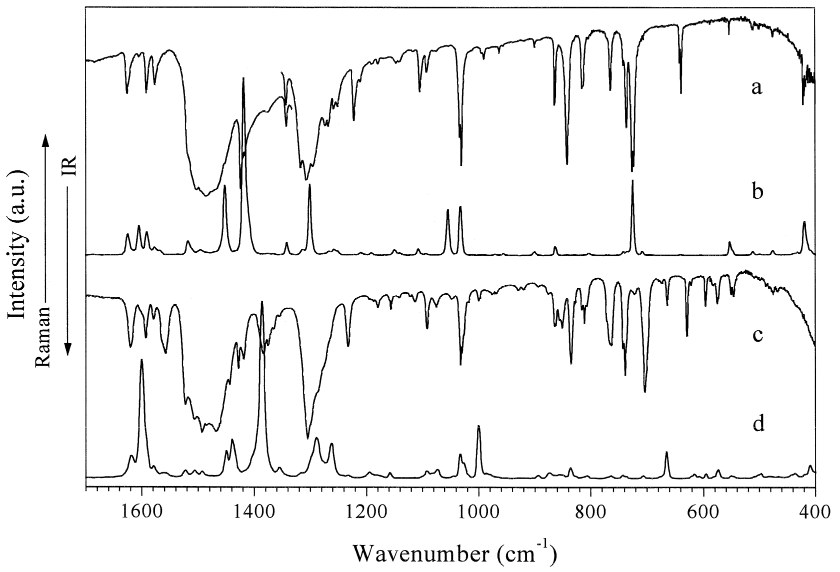

Fig. 5. IR (a,c) and Raman (b,d) spectra of $Eu(NO_3)_3$.$Phen_2$ (a,b), $Eu(NO_3)_3$.$Dphphen_2$ (c,d) at 300 K.

from the value of Δ the Eu–O bond in case of $Eu(NO_3)_3$.$Nphen_2$ compound is somewhat stronger than in cases of $Eu(NO_3)_3$.$Mphen_2$ and $Eu(NO_3)_3$.$Phen_2$, what is in accordance with higher electronegativity of Nphen radicals. In the second group the strongest Eu–O bond is observed in compounds with the bulky Tmphen and Dphphen ligands, which can not arrange tight-fitting to metal cation. The weakening of the Eu–O bonds in $Eu(NO_3)_3$.$Phphen_2$ is caused by the ability of the Phphen ligand containing only one phenyl substituent to come nearer to the europium ion.

These conclusions must correlate with the behavior of the ‘metal–ligand’ bands in the far IR spectra. Let us analyse the positions of the bands related to Eu–O(NO_3^-) vibrations, which unlike the Eu–N(Ph) vibrations, posses almost constant effective mass.

To find the bands connected with the largest contribution of the metal ion motions let us consider the far IR spectra of a series of isomorphous compounds $Ln_{0.96}Eu_{0.04}(NO_3)_3$.$Phen_2$, Ln=La, Eu, Gd, Y, Yb, presented in Fig. 7. The position of the most intense band in the $Eu(NO_3)_3$.$Phen_2$ spectrum, at 213 cm^{-1}, changes appreciably with the mass of the metal ion. It shifts by 37 cm^{-1} from 207 cm^{-1} for ytterbium to 244 cm^{-1} for yttrium derivative. One can see that the position of 172 cm^{-1} band changes also. It should be noted that in

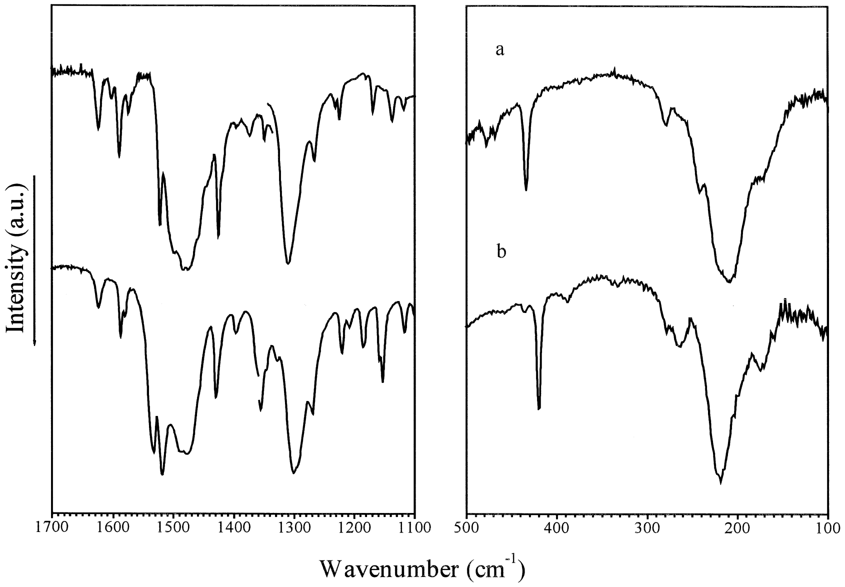

Fig. 6. IR spectra of $Eu(NO_3)_3$.$Mphen_2$ (a), $Eu(NO_3)_3$.$Nphen_2$ (b) at 300 K.

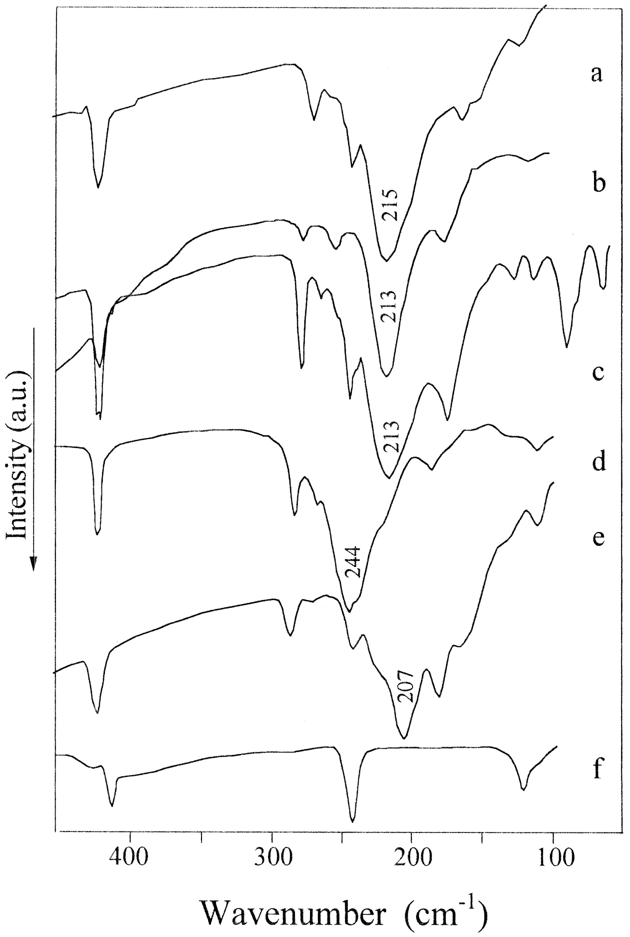

Fig. 7. FIR spectra of $Ln_{0.96}Eu_{0.04}(NO_3)_3.Phen_2$, Ln=La (a), Eu (b), Gd (c), Y (d), Yb (e) and of 1,10-phenanthroline (f) at 300 K.

vibronic spectra of europium doped lanthanide compounds, in contrast to IR spectra of the compounds with molecular structure, the effect of the host ion mass on the position of these bands is absent [5]. It can be illustrated by the example of the vibronic spectra of $Ln_{0.96}Eu_{0.04}(NO_3)_3.Phen_2$.

Deuteration of Bpy in $Eu(NO_3)_3.Bpy_2$ causes 5–10 cm^{-1} shift of the bands in the 120–160 and 350 cm^{-1} regions of the vibronic spectrum, while the bands in the 200–225 cm^{-1} region do not change their position. That is why the former group of bands was assigned to the metal–ligand vibrations with substantial contribution of the bipyridine molecules.

Comparison of the IR spectra of $Eu(NO_3)_3.Ph_2$, $Eu(NO_3)_3.Bpy_2$ and $Eu(NO_3)_3.6\ H_2O$ enables determination of the position of the metal–ligand bands connected with the vibrations with crucial contribution of the oxygen atom motions. As in the spectrum of europium nitrate hexahydrate these bands have maxima at 165 cm^{-1} and 200 cm^{-1}, one should observe them in europium nitrate complexes with heterocyclic diimine derivatives at higher frequencies because of strengthening of the Eu–O bonds, compare the Δ values in Table 3. That is why the bands

Table 2
The vibronic sideband of $^7F_0$–$^5D_0$ transition at 77 K, IR and Raman spectra at 300 K of $Eu(NO_3)_3.Phen_2$[a]

Vibr	IR	Raman	Assignment
60 vw	59		
	89		
115	110	105	
129	125	125	
	135		
146	142	144	
153			
		157	
172	172	175	
192		197	
203			ν(Eu–O)
212	213vs		
218			
226			
	242		
253	250 sh	248 w	
263 w	260	260 w	
276	276	274 m	
412			
420	418	419 m	ring tors.
479	476 w	476	
	512 w	512 v w	
	553 w	553 w	
	639 s		δ ring i.p.
708	706 v w	708 v w	$\nu_5(NO_3^-)$
	723 v s	725 s	δ(CH) o.p.
738	736 s	735 v w	$\nu_3(NO_3^-)$
745		742 v w	
	765 s		δ(CH) o.p.
	813		$\nu_6(NO_3^-)$
	842 s		
	864	864	δ(CH) o.p.
	901 w	901 w	
	963 w		
	990 w		
1032	1030 s	1033 s	$\nu_2(NO_3^-)$
1039			
1058		1055 s	ring 'breath'
	1092	1094 v w	
1110	1103	1108 v w	δ(CH) i.p.
		1151 v w	
1185			
1197			
	1210	1210 v w	
1220 v w	1222		δ(CH)+ν(C=C)
1250 v w	1250		
	1258	1258 v w	
	1267		
1278	1274		ν(C=C)+δ(CH)
	1290 s		
1300	1303 s	1302	$\nu_1(NO_3^-)$
1318	1318 sh	1314 v w	
1350	1343 w	1342	ν(C=C), ν(C=N)
1425	1425	1420 v s	
1450	1450 sh	1453	ν(C=C)+δ(CH)
1480	1485		$\nu_4(NO_3^-)$
1495		1497 v w	
	1505		
1524		1519 w	
	1577	1578 v w	
1583			ν(C=C), ν(C=N)
	1592	1592	
1600	1605 v w	1606	
1633	1627	1626	

[a] Note: vw, w, m, s, vs$^-$, very weak, weak, medium, strong, very strong lines in spectra; sh-shoulder.

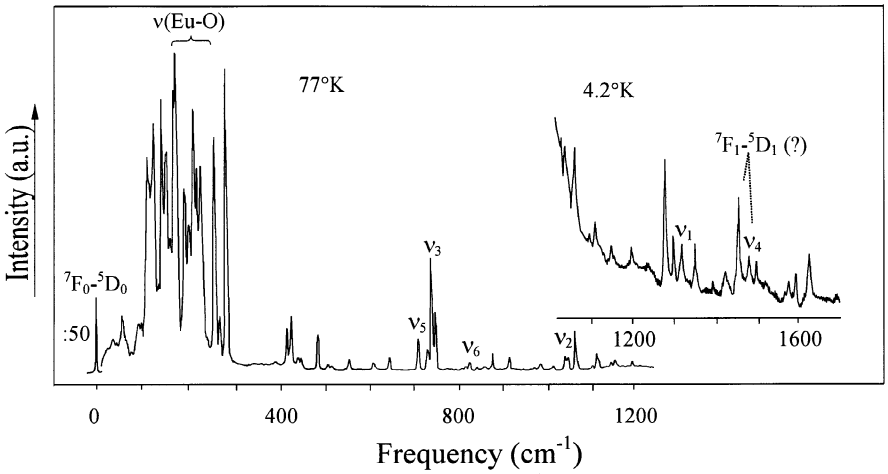

Fig. 8. Excitation spectrum of $Eu(NO_3)_3.Phen_2$ in the region of vibronic sideband of ${}^7F_0-{}^5D_0$ transition.

Table 3
Splitting of the stretching vibrations of NO_3^- group

Compound	ν_1	ν_4	Δ
$Eu(NO_3)_3.6\ H_2O$	1330	1480	150
$Eu(NO_3)_3.Mphen_2$	1310	1487	177
$Eu(NO_3)_3.Phen_2$	1308	1485	177
$Eu(NO_3)_3.Nphen_2$	1300	1483	183
$Eu(NO_3)_3.Tmphen_2$	1305	1490	185
$Eu(NO_3)_3.Phphen_2$	1313	1484	171
$Eu(NO_3)_3.Dphphen_2$	1305	1488	183

connected with metal ions vibrations in the 205–220 cm^{-1} region and around 175 cm^{-1} are at the same time bands due to nitrate oxygen atoms motions.

The increase of ν(Eu–O) vibration frequencies of the europium nitrate compounds with phenanthroline derivatives, within the first subgroup of compounds, due to augmentation of the bond force constant, accompanying the Eu–O bonds strengthening is observed (Fig. 6, Table 4). In the second subgroup, in the case of compounds containing bulky Tmphen and Dphphen ligands, the frequencies of ν(Eu–O) modes are higher and correspondingly, the Eu–O bonds are stronger. As can be seen, there is a correlation between the data obtained from different regions of IR spectra for Eu–O bonds.

3.3. Vibronic interaction

In the luminescence and the excitation of luminescence spectra of the nitrates a large number of vibronic satellites related to vibrations of both types of ligands is observed. The detailed attribution of the vibronic luminescence spectra presented in Figs. 2 and 3 is difficult due to the overlap of the vibronic sidebands belonging to the different electronic transitions ${}^5D_0-{}^7F_J$. To assign the vibronic satellites we used isotopic substitutions like in the case of IR spectra. In the excitation spectra at low temperatures when the population of ${}^7F_1$ and ${}^7F_2$ levels is lowered, the overlap of the different electronic transitions decrease. At 77 K the attribution of the bands in the vibronic sideband of ${}^7F_0-{}^5D_0$-transition with frequencies higher than 1300 cm^{-1} is hindered by overlap of the zero-phonon bands of the ${}^7F_1-{}^5D_1$ transition. Fig. 8 and Table 2 present the data on the vibronic sideband of ${}^7F_0-{}^5D_0$-transition in the luminescence excitation spectrum of $Eu(NO_3)_3.Phen_2$ obtained with high resolution. A high-frequency region obtained at 4.2 K is given there, too. At 300 K rich structure of the low-frequency region of the sideband formed by 'metal–ligand' vibrations is smoothed out and the observed lines correspond well to the bands of IR spectrum. In Fig. 9 the vibronic sidebands of the ${}^7F_0-{}^5D_0$-transition in the excitation spectra of $Eu(NO_3)_3.Tmphen_2$

Table 4
'Metal–Ligand' vibrations in IR spectra

Compound	ν(Eu–O)					
$Eu(NO_3)_3.6\ H_2O$		165	200			
$Eu(NO_3)_3.Mphen_2$		173	210 s	242	279	
$Eu(NO_3)_3.Phen_2$	143	173	212 s	241	260, 275	
$Eu(NO_3)_3.Nphen_2$	138	176	219 s		265, 279	
$Eu(NO_3)_3.Tmphen_2$	134	178	214 s		271	311
$Eu(NO_3)_3.Phphen_2$	136		211 s		254	298
$Eu(NO_3)_3.Dphphen_2$	130	175, 188	210 m, 222 s	237	252	308

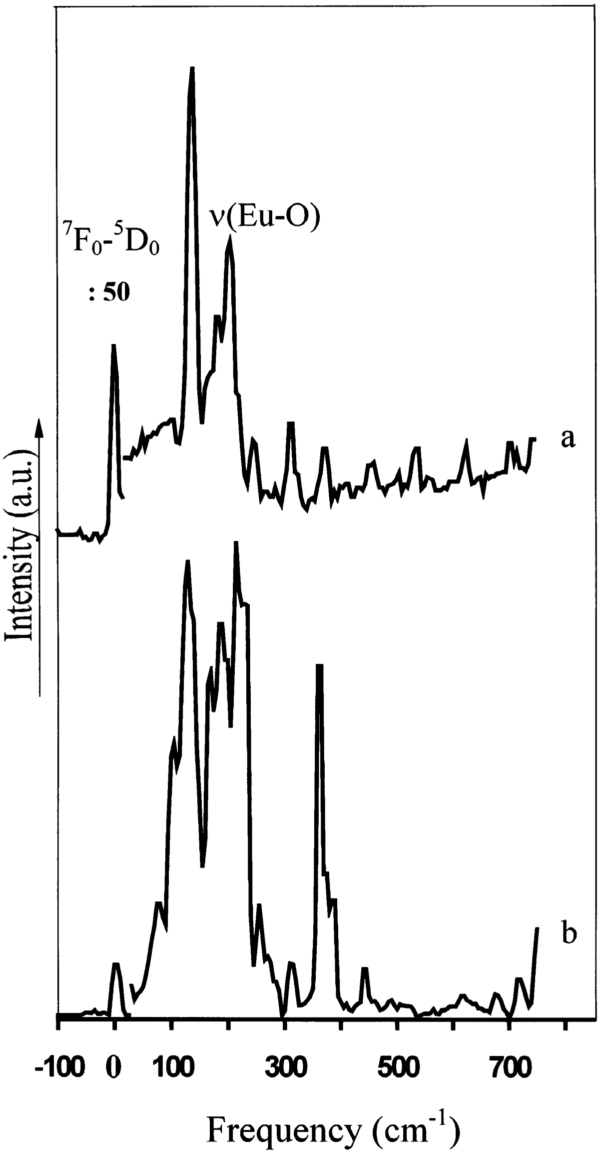

Fig. 9. Excitation spectra of $Eu(NO_3)_3$.Tmphen$_2$ (a), $Eu(NO_3)_3$.Dphphen$_2$ (b) in the region of vibronic sideband of $^7F_0$ -$^5D_0$ transition at 77 K.

and $Eu(NO_3)_3$.Dphphen$_2$ obtained at lower resolution are presented. The ν(Eu–O) band in the spectrum of the second compound is somewhat shifted towards the high-frequency side. That shift could indicate a strengthening of the europium bonds with NO_3^- groups. Intense bands in the region of ~360 cm^{-1} absent in IR and present in Raman spectra of this compound are assigned to the out-of-plane ring bending vibrations. Analogous bands are observed in the vibronic spectrum of $Eu(NO_3)_3$.Bpy$_2$ [6] and in the Raman spectrum of Bpy [22].

In the overlap region of zero-phonon lines of $^5D_0$–$^7F_2$-transition and vibronic sideband of $^5D_0$–$^7F_0$-transition the conditions of the vibronic mixing of states and vibronic resonance appear [2,23]. The data on intensity of some vibronic satellites of the $^5D_0$–$^7F_0$-transition situated in vicinity of the zero-phonon lines of $^5D_0$-$^7F_2$-transition (marked with arrows in Figs. 2,3) are presented in Table 5. In the luminescence spectra of compounds belonging to the first subgroup, Fig. 2, an elevated vibronic satellite situated at a short-wavelength side of the $^5D_0$–$^7F_2$-transition was observed. The distance between this line and the most intense Stark component of $^5D_0$–$^7F_2$-transition is equal to 83 and 68 cm^{-1} in $Eu(NO_3)_3$.Phen$_2$ and $Eu(NO_3)_3$.Nphen$_2$, respectively. It corresponds to the vibration with frequencies 898 and 920 cm^{-1} and can be assigned to an out-of-plane C–H vibrations. The relative intensity I_{vibr}/I_{0-0} is equal to 3.7 and 4.4. In the excitation spectra (anti Stokes sidebands) the relative intensity of those vibronic satellites is of the order of 10^{-2}–10^{-3}.

Table 5
Relative integral intensities of some vibronic satellites of $^5D_0$–$^7F_0$ transitions I_{vibr}/I_{0-0}

Compound	ν_5, ν_3	δ(CH)	ν_1
$Eu(NO_3)_3$.Mphen$_2$	3.0		8.0
$Eu(NO_3)_3$.Phen$_2$	2.3	3.7	3.5
$Eu(NO_3)_3$.Nphen$_2$	0.9	4.4	2
$Eu(NO_3)_3$.Tmphen$_2$	3.5		11.8
$Eu(NO_3)_3$.Phphen$_2$	3.2		12
$Eu(NO_3)_3$.Dphphen$_2$	3.8		10.6

Vibronic mixing of states caused also increasing intensity of the vibronic satellites of $^5D_0$–$^7F_0$ transition that are situated at both sides of zero-phonon lines of $^5D_0$–$^7F_2$ transition at distances about 300 cm^{-1}. This is observed in luminescence spectra of $Eu(NO_3)_3$.Ph$_2$ (Figs. 2, 3) for lines associated with vibrations ν_5,ν_3 and ν_1 of the nitrate group. Intensities of these lines are about 1–2% of the intensity of the zero-phonon $^5D_0$–$^7F_2$ transition. The intensity relation of these bands in the Stokes sideband of $^5D_0$–$^7F_0$ transition of $Eu(NO_3)_3$.Phen$_2$ to that of the parent line is a hundred times higher than the corresponding relation for the anti Stokes sideband. It should be noted that in spectra of the second subgroup (Fig. 3) the maximum Stark splitting of the $^5D_0$–$^7F_2$-transition increases together with the increasing the transition intensity. It is possible that this is the cause of the increase of borrowing of intensity by ν_5,ν_3 vibrations and especially by ν_1 resulting in the increase of the intensity of corresponding vibronic satellites.

4. Conclusions

Analysis of the luminescence, excitation of luminescence, IR and Raman spectra of europium nitrates containing 1,10-phenanthroline derivatives $Eu(NO_3)_3$.Ph$_2$ was performed. Information on the details of the structure of compounds was obtained. These compounds form two subgroups, with relatively small (Mphen, Phen, Nphen) and bulky (Tmphen, Phphen, Dphphen) molecules of phenanthroline derivatives. No gradual changes of the spectra corresponding to the variations of donor-acceptor properties of the substituents were observed. The steric factor has the prevailing effect on the spectra.

Elemental analysis proves similar overall composition of compounds. From the IR spectra it was found that all nitrate anions are coordinated and the Eu–O(NO_3^-) coordination bonds are relatively strong. From the values of splitting of the stretching vibrations of NO_3^--anions and from the position of the band of ν(Eu–O) vibration it was shown that $Eu(NO_3)_3.Nphen_2$ with high electronegativity of the $-NO_2$-group of nitro-phenanthroline and a pair of compounds $Eu(NO_3)_3.Tmphen_2$, $Eu(NO_3)_3.Dphphen_2$ with bulky substituents in phenanthroline molecules have the strongest Eu–O bonds.

Weak vibronic mixing between electronic state and a remote vibration states related to different Eu^{3+} transitions was demonstrated.

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