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Spectra and details of the structure of europium acetates with derivatives of 1,10-phenanthroline

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Abstract

Luminescence, excitation of luminescence, IR and Raman spectra of europium acetates with 1,10-phenanthroline derivatives (Ph), $Eu(CH_3COO)_3.Ph$, were studied. Crystal field parameters for model complexes were calculated. Some conclusions about details of the structure of the compounds were obtained. It was shown that both steric hindrances due to ligand–ligand crowding and donor–acceptor properties of the ligands are significant in creation of the structure. Maximum inequivalence of Eu–O bonds in compound containing 5-nitro-phenanthroline with electrophilic NO_2-group was noted as well as in compounds with 3,4,7,8-tetramethyl- and 5-phenyl-phenanthroline having bulky substituents. There is the strongest polarisation of the carboxyl groups in these compounds. Nearly equalised Eu–O bonds were found in compound with 4,7-diphenyl-phenanthroline. Here a steric factor was minimised due to rotation of phenyl radicals in relation to the phenanthroline nucleus. © 2001 Elsevier Science B.V. All rights reserved.

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

1. Introduction

The present work reports new results of spectroscopic investigation of the mutual influence of inequivalent ligands in lanthanide compounds with derivatives of heterocyclic diimine [1–3]. In earlier studies, the effect of the steric factor and of donor–acceptor properties of different substituents in the 1,10-phenanthroline molecule on peculiarities of the structure of the nearest surroundings of the europium ions in nitrates $Eu(NO_3)_3.Ph_2$ (Ph, heterocyclic diimine) [2] and dipivaloylmethanates $Eu(DPM)_3.Ph$ [3] was examined. The prevailing contribution of the size of ligands was observed in both groups of compounds. This effect is conditioned by bulky radicals of 1,10-phenanthroline derivatives in the case of high coordination number in the nitrates (C.N.=10) or by voluminous molecules of both types of ligands in the case of smaller coordination number in dipivaloylmethanates (C.N.=8). Spectroscopic methods were used in this work to study details of the structure of europium acetates $Eu(CH_3COO)_3.Ph$ hypothetically having a dimeric structure.

The influence of donor–acceptor and steric properties of the substituents in the phenanthroline molecules on effective charges in the nearest surroundings of Eu^{3+} ions and on the relative strength of the europium bonds with two kinds of ligands was examined. The degree of polarisability of the carboxyl groups and inequivalence of bonds 'metal–oxygen' in a row of compounds were analysed. Dependence of the Stark splittings of the Eu^{3+} electronic levels, positions of the excitation bands, vibration frequencies in the IR, Raman and vibronic spectra on variation of the phenanthroline substituents was studied. The data obtained were compared with the results of analogous investigations of europium nitrates and dipivaloylmethanates with 1,10-phenanthroline derivatives.

2. Experimental

The luminescence and excitation of luminescence spectra, as well as IR absorption and Raman spectra of europium acetates with 1,10-phenanthroline derivatives of formula $Eu(CH_3COO)_3.Ph$ (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. Ph are arranged in such a manner that acceptor properties of their sub-

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stituents increase (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]). The compounds were obtained by heating of the mixture of water solutions of europium acetate $Eu(CH_3COO)_3.H_2O$ and ethanol solution of Ph. The crystals of $Eu(CH_3COO)_3$.Phen were grown.

The luminescence and excitation of luminescence spectra were measured on a SLM Aminco SPF 500 spectrofluorimeter and DFS-12 spectrometer at 300 and 77 K. IR spectra were registered using Brucker FS 88 FTIR and UR-20 spectrometers. Raman spectra were recorded on a Nicolet Raman accessory attached to a Nicolet Magna 860 spectrometer. To assign the vibration and vibronic lines in spectra, comparison of the spectra of the related $Eu(CH_3COO)_3$.Phen and $Eu(CH_3COO)_3$.Bpy (Bpy — H- or D-2,2′-bipyridine) were carried out. The isotopic substitution of D for H in CH_3COO^- groups, as well as quasi isotopic substitution of Ln^{3+} and Y^{3+} host metal ions for Eu^{3+} ions, by analogy to Ref. [2], were also used.

3. Results and discussion

Preliminary X-ray data on the crystal structure of acetate $Eu(CH_3COO)_3$.Phen were obtained on our request, and these results will be published elsewhere. It occurred that the nearest surroundings of the Eu^{3+} ion and types of the coordination of the carboxyl groups in $Eu(CH_3COO)_3$.Phen are analogous to the same features of the structure of europium capronate $Eu(C_5H_{11}COO)_3$.Phen [5]. Previous studies of the luminescence spectra and data on kinetics of the luminescence quenching of Eu^{3+} ions by other Ln^{3+} ions demonstrated the presence of the dimeric metal ions and similarity of their nearest surroundings in anhydrous aliphatic europium carboxylates with 1,10-phenanthroline (excluding formates) [6]. Judging from the spectra, the europium acetates with phenanthroline derivatives $Eu(CH_3COO)_3$.Ph have similar nearest surroundings of the Eu^{3+} ions. The structures of the series of acetates investigated probably consist of centrosymmetric four-bridged dimeric molecules like the structures of capronate and acetate with phenanthroline. The coordination polyhedron of Eu^{3+} is formed by seven oxygens of carboxylate anion and two nitrogen atoms of 1,10-phenanthroline molecule (C.N.=9). One can see a distorted one-capped tetragonal antiprism or a three-capped trigonal prism as this polyhedron [5]. Three types of the coordination of the carboxyl groups by the lanthanide ions exist here: bidentate–cyclic, bidentate bridging, tridentate bridging–cyclic. The groups of the latter type form the most extended bonds $Ln-O(COO^-)$, but the bridging bonds are much shorter than the third bond giving the cyclic function to the tridentate group [5,7].

At insertion of substituents, having different donor–acceptor properties and different sizes, into the phenanthroline molecule, the effective charges on nitrogen atoms in compounds $Eu(CH_3COO)_3$.Ph change. That must be reflected in the bonds of europium with both kinds of ligands and somewhat change the nearest surroundings of the Eu^{3+} ions.

3.1. Luminescence spectra

Judging from Stark splitting of the electronic transitions in the luminescence spectra of $Eu(CH_3COO)_3$.Ph (Fig. 1), the site symmetry of the lanthanide ion is not higher than rhombic. These results do not conflict with the available X-ray data. The prevailing influence of the steric factor can be seen in the series of acetates. The hindrance because of ligands crowding is less pronounced than in the cases of $Eu(NO_3)_3.Ph_2$ [2] and $Eu(DPM)_3$.Ph [3]. Schematically the compounds can be separated into two groups by their luminescence spectra: a, b, c and d, e, f of Fig. 1. In a different way, excluding the compounds with voluminous

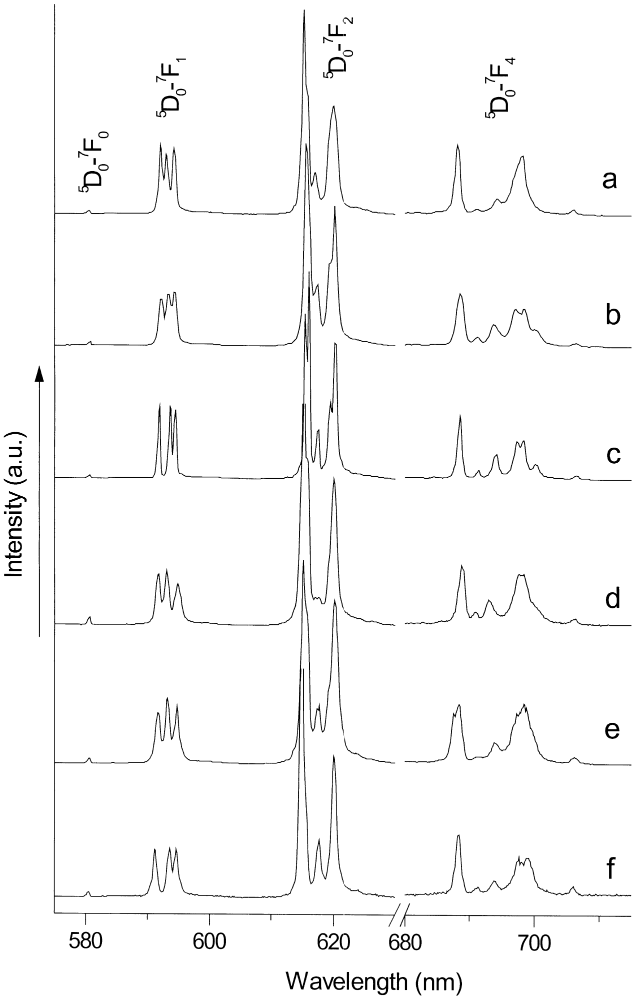

Fig. 1. Luminescence spectra of $Eu(CH_3COO)_3$.Tmphen (a), $Eu(CH_3COO)_3$.Mphen (b), $Eu(CH_3COO)_3$.Phen (c), $Eu(CH_3COO)_3$.Phphen (d), $Eu(CH_3COO)_3$.Dphphen (e), and $Eu(CH_3COO)_3$.Nphen (f) at 77 K.

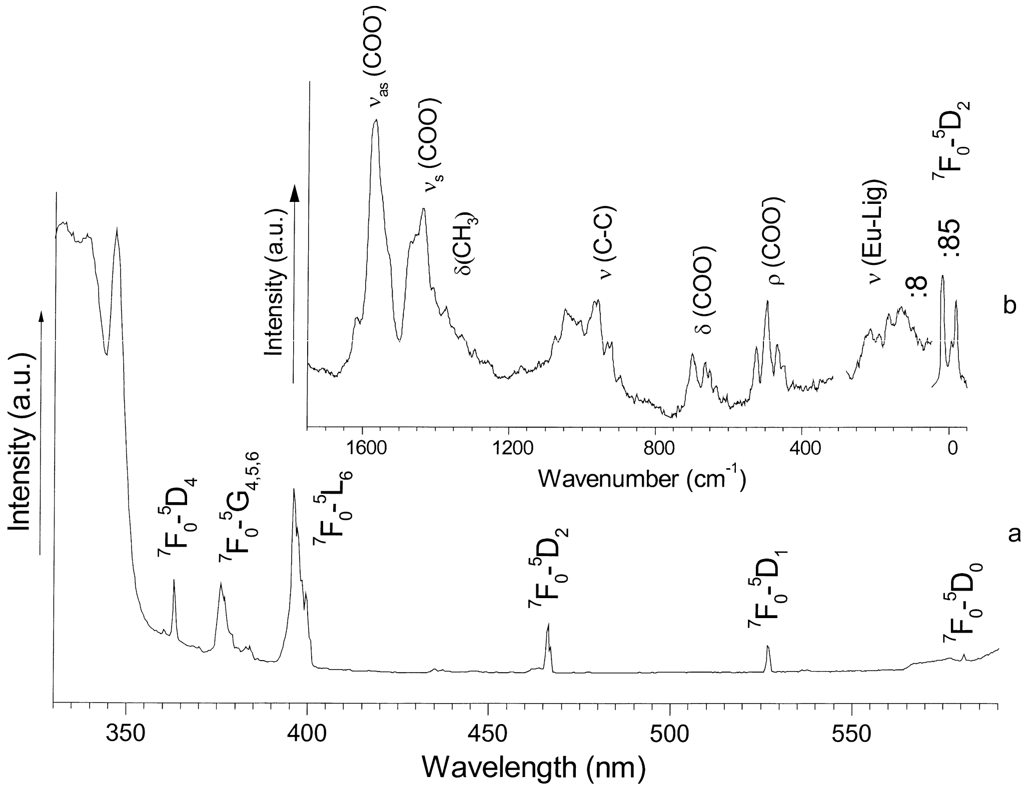

Fig. 2. Excitation spectrum (a) and vibronic sideband of $^7F_0$–$^5D_2$ transition (b) of Eu$(CH_3COO)_3$.Phen at 77 K.

substituents one can arrange the rest according to increasing acceptor influence of the Ph radicals [1]. Crystal field parameters B^k_q (in Wybourne notation, [3] and references therein) for a point-charge model complexes of C_{2v} symmetry, calculated with use of the root-mean-square criterion from the energy levels of Eu^{3+} ions obtained from luminescence and excitation of luminescence spectra (Fig. 2a), are presented in the Table 1. Variations of B^k_q in the row of acetates can be connected with the changes of bond strengths and the effective charges on oxygen atoms due to the cyclic function of the tridentate carboxyl groups.

The resonant vibronic effect with participation of the acetate anion vibrations is observed in the Eu$(CH_3COO)_3$.Ph luminescence spectra [1]. To understand this effect, anti-Stokes vibronic sidebands of $^7F_0$–$^5D_0$ and $^7F_0$–$^5D_2$ transitions were obtained. One of these of Eu$(CH_3COO)_3$.Phen is presented in Fig. 2b. They are formed principally by vibrations of the acetate anion. Intensity redistribution between the lines in the region of the Eu^{3+} electronic transitions due to the resonant interaction was taken into account in attribution of the Eu^{3+} electronic levels.

3.2. IR spectra

To identify the carboxyl coordination function and to obtain the degree of inequivalence of the ligands in the acetate series Eu$(CH_3COO)_3$.Ph, one can use the characteristics of the vibration bands in IR and Raman spectra (Figs. 3 and 4). The intense lines in Raman spectra are attributed to vibrations of the Ph molecules by analogy to europium nitrates [2]. The bands in IR spectra at ~1550–1560, and ~1590–1615 cm^{-1} are related to the antisymmetric stretching vibrations $\nu_{as}(COO^-)$, ones in 1410–1455 cm^{-1} region belong to symmetric stretching vibrations $\nu_s(COO^-)$, and bands at 640–680 cm^{-1} belong

Table 1
Crystal field parameters (cm^{-1}), 77 K

Compound	$\hat{B}^2_0$	$\hat{B}^2_2$	$\hat{B}^4_0$	$\hat{B}^4_2$	$\hat{B}^4_4$	$\hat{B}^6_0$	$\hat{B}^6_2$	$\hat{B}^6_4$	$\hat{B}^6_6$
Eu$(CH_3COO)_3$.Tmphen	−155	80	−780	35	300	749	802	−140	203
Eu$(CH_3COO)_3$.Mphen	−165	40	−800	35	280	600	193	−349	758
Eu$(CH_3COO)_3$.Phen	−195	50	−700	120	260	702	755	−198	298
Eu$(CH_3COO)_3$.Phphen	−210	106	−840	100	230	769	658	−219	149
Eu$(CH_3COO)_3$.Dphphen	−215	65	−950	90	220	695	655	−160	358
Eu$(CH_3COO)_3$.Nphen	−290	60	−950	80	200	669	643	−200	253

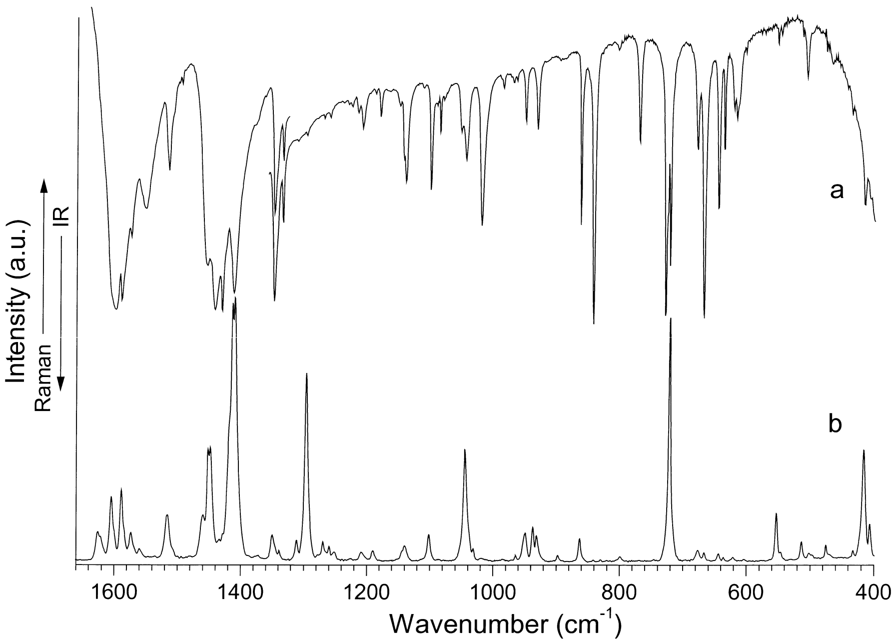

Fig. 3. IR (a) and Raman (b) spectra of Eu($CH_3COO)_3$.Phen at 300 K.

to the bending vibrations $\delta(COO^-)$ of carboxyl groups [8,9]. Overlap of bands makes difficult the determination of the $\nu_s(COO^-)$ vibration. Three lines in the region of $\delta(COO^-)$ vibrations (645, 668 and 679 cm^{-1} in spectrum of Eu($CH_3COO)_3$.Phen) indicate about three types of acetate groups, moreover low-frequency line is associated

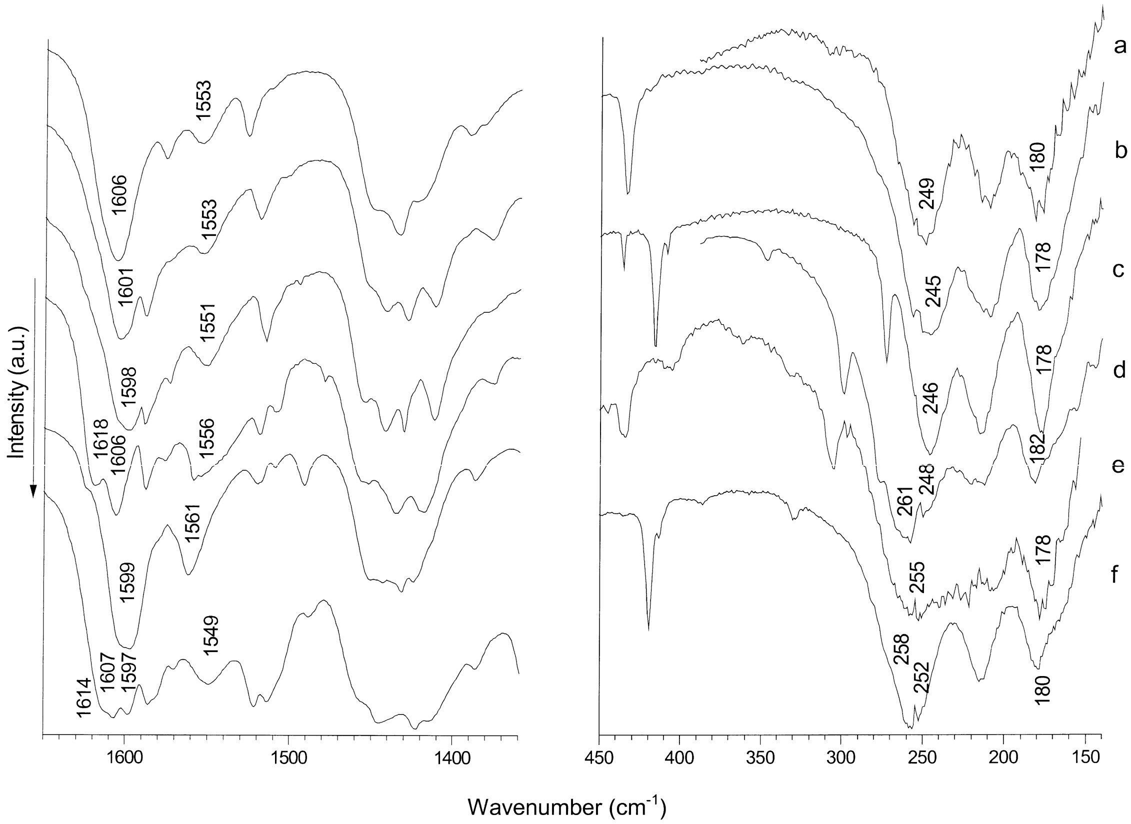

Fig. 4. Fragments of IR spectra of Eu($CH_3COO)_3$.Tmphen (a), Eu($CH_3COO)_3$.Mphen (b), Eu($CH_3COO)_3$.Phen (c), Eu($CH_3COO)_3$.Phphen (d), Eu($CH_3COO)_3$.Dphphen (e), and Eu($CH_3COO)_3$.Nphen (f) at 300 K. Fluorinated oil was used for preparation of samples for IR measurements in the region of COO^- stretching vibrations.

with tridentate bridging–cyclic groups [10]. This agrees with the X-ray data. The value of splitting of $\nu(\mathrm{COO}^-)$ stretching vibration correlates with the strength of binding the carboxylate anions and the degree of their polarisation by metal. Splitting of both $\nu_{as}(\mathrm{COO}^-)$ and $\nu_s(\mathrm{COO}^-)$ bands (Fig. 4) demonstrates the inequivalence of the carboxyl groups. The most prominent changes are observed in the region of high-frequency component of $\nu_{as}(\mathrm{COO}^-)$ vibration. As a rule, high frequency of $\nu_{as}(\mathrm{COO}^-)$ vibration (up to ~1600 cm^{-1}) is attributed to strongly polarised carboxyl groups and to inequivalence of two M–O bonds [8]. Probably, this band may be concerned with the presence of the tridentate carboxyl groups in the compounds under investigation [10]. With variation of the Ph-ligands, the strength and inequivalence of three Eu–O bonds related to the tridentate groups has to change the most easily. In the case of the Eu–N bonds weakening at the depletion of π-electron density of the Nphen by electrophilic $\mathrm{NO_2}$-group or because of the steric hindrance of bulky Ph molecules, the conditions for stronger binding of one of the oxygen atoms by a supplementary bond with Eu^{3+} ion may arise. That must lead to maximum polarisation of tridentate carboxyl groups and to a high-frequency shift of $\nu_{as}(\mathrm{COO}^-)$ to 1614 (Nphen), 1606 (Tmphen) and 1618 (Phphen) cm^{-1}. In europium acetates containing bulky Dphphen this supplementary bond Eu–O is weaker (1599 cm^{-1}), as phenyl radicals may turn out of the plane of the phenanthroline nucleus. The steric hindrance is displayed in a different part of the molecule. The shift of the low-frequency component of $\nu_{as}(\mathrm{COO}^-)$ to 1561 cm^{-1} shows the maximum polarisation for some of the bidentate carboxyl groups.

There are three bands in the 165–270 cm^{-1} region of far IR spectra (Fig. 4). Using the attribution methods mentioned in the experimental section, we related the high- and low-frequency bands of these three to 'europium–oxygen' vibrations. Far IR spectra of $\mathrm{Eu(CH_3COO)_3}$.Ph compounds can be separated into two groups by positions of the bands: spectra a, b, c with lower frequencies of ν(Eu–O) vibrations and d, e, f — with higher frequencies of these vibrations. Judging from these frequencies, compounds of the first group with Mphen, Phen must have more equivalent Eu–O bonds (small spread in bond lengths). There are the strongest Eu–O bonds and, accordingly, the shortest Eu–O bonds in compounds of the second group (large spread in bond lengths). These conclusions about the details of the structure of the nearest surroundings of Eu^{3+} ions with variation of Ph molecules agree with the data obtained from the middle IR region.

3.3. Spectra and details of the structure of europium acetates and nitrates

Let us return to the excitation spectra of complex acetates $\mathrm{Eu(CH_3COO)_3}$.Ph (Fig. 2a). The long-wavelength edge of the broad band of phenanthroline- and its methyl-derivatives is ~345 nm, phenyl-derivatives is ~362 nm, nitro-phenanthroline is ~420 nm. It was observed that the excitation band of Ph ligands has the short-wavelength shift by 5–15 nm in acetates in comparison with nitrates [2]. This demonstrates that the Eu–N bonds are somewhat weaker in the case of acetates. Raman spectra of complex europium acetates and nitrates indicate about the same. Low-frequency shifts up to 12 cm^{-1} for different lines, assigned to Ph vibrations, are observed in the acetate spectra in comparison with the nitrate ones. The value of shift depends on the kind of substituents and their positions. For example, as to substituents in the fifth position the shifts of Raman lines in the 1280–1460 cm^{-1} region (ν(C=C, ν(C=N), $\nu(\mathrm{C{=}C})+\delta(\mathrm{CH})$) may be minimum, ~0–3 cm^{-1} (Mphen) and maximum, ~5–12 cm^{-1} (Nphen). Changes in the excitation and Raman spectra indicate a lower polarising effect of Eu^{3+} ions on the phenanthroline molecules in acetates and, accordingly, weaker Eu–N bonds.

No shift of the ligand band in the $\mathrm{Eu(CH_3COO)_3}$.Dphphen excitation spectrum is observed in comparison with the spectrum of $\mathrm{Eu(CH_3COO)_3}$.Phphen, but an intensity redistribution can be seen. At the same time a long-wavelength shift of this band by ~6 nm was seen in the spectrum of $\mathrm{Eu(NO_3)_3}$.Dphphen in comparison with $\mathrm{Eu(NO_3)_3}$.Phphen [2]. In contrast to nitrates, a substantially smaller difference of the π-electron system dimensions is observed in both acetates. It may be associated with turning of the phenyl radicals attached to the phenanthroline ligand in $\mathrm{Eu(CH_3COO)_3}$.Dphphen. The small value of the intensity of line 1600 cm^{-1} (ν(C=C, C=N) phenyl ring vibration) in relation to the intensity of line 998 cm^{-1} (phenyl ring breathing vibration) in Raman spectrum of $\mathrm{Eu(CH_3COO)_3}$.Dphphen shows the absence of conjugation of the rings [11].

4. Conclusions

The luminescence, excitation of luminescence, IR and Raman spectra of a variety of europium acetates containing 1,10-phenanthroline derivatives $\mathrm{Eu(CH_3COO)_3}$.Ph were studied. Crystal field parameters for model complexes were calculated. Information on the peculiarities of the structure was obtained. Both donor–acceptor properties and the size of ligands have an influence on the structure. The effect of phenanthroline substituents on the nearest surroundings of Eu^{3+} ion is small.

There are carboxyl groups with different kinds of coordination in acetates under investigation. Inequivalence of the carboxyl groups and the bond strengths 'metal–ligand' change in the row of compounds. The acetates $\mathrm{Eu(CH_3COO)_3}$.Nphen with electrophilic $\mathrm{NO_2}$-groups and $\mathrm{Eu(CH_3COO)_3}$.Tmphen, $\mathrm{Eu(CH_3COO)_3}$.Phphen with bulky substituents in the phenanthroline molecules can be characterised by the highest inequivalence of Eu–O bonds. Strongly polarised carboxyl groups are present in these compounds. Nearly equalised Eu–O bonds are indicated in $Eu(CH_3COO)_3$.Dphphen. Turns of the phenyl radicals are needed to reach the optimal packing of the latter compound.

It was demonstrated that the complex acetates have weaker bonds of Eu^{3+} with the molecules of heterocyclic diimines in comparison with corresponding nitrates.

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