Russian Journal of Coordination Chemistry, Vol. 29, No. 8, 2003, pp. 574–581. Translated from Koordinatsionnaya Khimiya, Vol. 29, No. 8, 2003, pp. 617–624.
Original Russian Text Copyright © 2003 by Puntus, Zolin.

Modeling of Eu^{3+} Energy Levels in Complexes with 1,10-Phenanthroline Derivatives

L. N. Puntus and V. F. Zolin

Institute of Radio Engineering and Electronics, Russian Academy of Sciences, Moscow, Russia

Received August 22, 2002

Abstract—The experimental electronic spectra of the Eu^{3+} ion in three groups of the Eu complexes (β-diketonates, acetates, and nitrates) with the 1,10-phenanthroline derivatives were used to calculate the crystal field parameters for the model of the nearest environment of this ion with the C_{2v} point group symmetry. It was shown that these parameters can be used for estimating the coordination number of the metal cation and establishing the structural peculiarities.

The correlations between the spectra and structures of the lanthanide β-diketonates, acetates, and nitrates with the 1,10-phenanthroline were studied in [1–4] by IR, Raman, and optical spectroscopies (luminescence and excitation spectra). The crystal field parameters (CFP) were not used in these studies, since the experimental data on the Stark splittings of the Eu^{3+} levels for each of the group under consideration were insufficient for reliable estimation of the CFP, particularly, the sixth-order parameters. In this work, the combined use of the energies of the Eu^{3+} levels in the spectra of all three groups of compounds, which differed in the coordination numbers of the lanthanide ions, made it possible not only to calculate these parameters, but to apply the calculation results for establishing the structure of the nearest surrounding of the lanthanide ions and determining their interaction with ligands.

EXPERIMENTAL

The europium compounds with the 1,10-phenanthroline (Ph) derivatives $[Eu(L)_3Ph]$ were synthesized as described elsewhere [2–4]. Here L is dipivaloylmethanate (DPM) or acetate anions; Ph are the 1,10-phenanthroline derivatives: 3,4,7,8-tetramethyl-1,10-phenanthroline (Tmphen), 5-methyl-1,10-phenanthroline (Phphen), 4,7-diphenyl-1,10-phenanthroline (Dphphen), 5-nitro-1,10-phenanthroline (Nphen). The europium nitrates with Ph of the composition $[Eu(NO_3)_3(Ph)_2]$ were obtained by mixing the ethanol solutions of $Eu(NO_3)_3 \cdot 6H_2O$ and of the phenanthroline derivatives. The compositions of the compounds were confirmed by the elemental analysis data.

The luminescence and excitation spectra were recorded on a SLM Aminco SPF 500 spectrometer and DFS-12 spectrograph at 77 and 300 K. The Raman spectra were recorded on a Nicolet Magna 860 FTIR spectrometer at 300 K. IR absorption spectra of the compound emulsions in vaseline oil and hexachlorobutadiene were taken on the UR-20 and Nicolet Magna 750 FTIR spectrophotometers at 300 K.

RESULTS AND DISCUSSION

The $[Eu(DPM)_3Phen]$ structure described in [5] is similar to the structures of the other lanthanide β-diketonates with heterocyclic diimines [6–8]. The coordination polyhedron of Eu^{3+} in these compounds is the distorted square antiprism formed by six oxygen atoms and two nitrogen atoms (the coordination number (CN) of the europium ion being eight). The point group symmetry of the coordination polyhedron is close to C_2. The additional deformation of the antiprism caps due to the rotation of the ligand planes can increase the polyhedron symmetry to C_{2v}. This assumption agrees with the use of the model of the complex with the distorted coordination polyhedron.

The $[Eu(CH_3COO)_3Phen]$ crystals are built of the dimeric molecules. All the three acetate groups perform different structural functions [9]. One of them acts as the bidentate bridge, the second is the tridentate-bridging-cyclic group, while the third is the bidentate-cyclic group. The coordination polyhedron of the Eu^{3+} ion is formed by seven oxygen atoms of the carboxylate anions and two nitrogen atoms of the 1,10-phenanthroline molecule (CN 9). The polyhedron can be represented as a distorted tetragonal one-capped antiprism or as a three-capped trigonal prism. The symmetry of the model coordination polyhedron will be close to C_{2v} as the tridentate bridging-cyclic acetate groups change their positions.

The coordination polyhedron of the Eu^{3+} ion in the nitrate complexes with the phenanthroline derivatives of the composition $[Eu(NO_3)_3(Phen)_2]$ [10] is a two-capped dodecahedron formed by six oxygen atoms of three bidentate nitrate anions and four nitrogen atoms of two molecules of heterocyclic diimine (CN 10). All the three nitrate groups lie above, while the phenanthroline molecules, below the equatorial plane of the complex. One nitrate group is on the two-fold symmetry axis, whereas the other two are in the general positions. The symmetry of the model coordination polyhedron will be close to C_{2v} as the coordinated phenanthroline molecules are respectively rotated.

In order to calculate the CFP, we selected the model of the nearest environment of the lanthanide ion with the point symmetry C_{2v}. The CFP calculated for such a model provide sufficiently adequate agreement between the theoretical energies of the europium ion levels and the experimental values (standard deviation of the calculated values from the experimental values being ~12 cm^{-1}). The selected model is supported by the effect of leveling of interaction of the charges at the oxygen atoms and of the charges at the nitrogen atoms (more exactly, the dipole moments of the phenanthroline molecules) with the lanthanide ion due to the strong dependence of this interaction on the reverse distances between the interacting charges. As the result of this leveling, the symmetry of the effective nearest environment of the lanthanide ion becomes higher than the symmetry of the real distribution of ions.

The Stark splitting of the levels of the lanthanide ions in the lattice crystal field was described by the Hamiltonian of a crystal field [11], which is the sum of the products of the CFP B_k^q by the C_k^q operators, proportional to the normalized spherical harmonics Y_k^q:

$$H_{cf} = \Sigma_k^q[B_k^q(C_k^q + (-1)^q C_k^q) + iS_k^q(C_k^q - (-1)^q C_k^q)],$$

$$C_k^q(4\pi/2n + 1)^{1/2} Y_k^q.$$

For the C_{2v} symmetry, all S_k^q values are equal to zero, and therefore only nine CFP remain.

The CFP were calculated by adjusting the theoretical values of the Stark splittings using the experimental data. In this case, the CFP calculation is an inverse problem that can give many solutions depending on the conditions and restrictions of the model used, for example, the direction of the quantization axis, etc. [12]. We imposed the following additional conditions.

The fixed sign of the B_0^2 parameter, i.e., positive for the β-diketonates (in this case, proceeding from X-ray diffraction data, one can expect large values of the axial component of the crystal field (CF) of a second order) and negative sign for the europium acetates and nitrates with Ph.

According to Lea, Leask, and Wolf [13], the value of X, which is determined by the relationship $\frac{X}{1-|X|} = \frac{F(4)B_0^4}{F(6)B_0^6}$, where $F(4)$ and $F(6)$ are the numerical coefficients for $J = 4$, and used for describing the structure of the levels of the $^5D_0$–$^7F_4$ transition in the cubic-symmetry crystal field, is close to unity in the case of the β-diketonates and acetates and is zero for nitrates (Fig. 1).

The B_0^4/B_4^4 and B_0^6/B_4^6 values have different signs, which corresponds to an increased contribution of the cubic components of the crystal field.

The most accurate experimental data on the Stark splittings of the levels in CF are provided by the $^7F_1$, $^7F_2$, and $^7F_4$ levels of the ground ^7F_J ($J = 0$–6) multiplet of the Eu^{3+} ion. At the same time, even in this case, one cannot always establish all the Stark components of these levels, for instance, the $^7F_4$ level for the europium β-diketonates or the $^7F_2$ level for the europium nitrates. That is why the positions of the Stark components of the Eu^{3+} levels are determined using the linear dependences of the centers of gravity of different levels on the position of the center of gravity of the $^7F_1$ or any other level, for which they are reliably estimated [14]. We used our experimental data and constructed the plots of the linear dependence between the positions of the centers of gravity of the $^5D_0$–$^7F_1$ and $^5D_0$–$^7F_2$ transitions, which are similar to the plot previously reported in [14], and of the $^5D_0$–$^7F_1$ and $^5D_0$–$^7F_4$ transitions (Fig. 2). In Table 1, the energies (E) of the Stark components of the transitions determined from these plots are marked by asterisk.

The plots of the center of gravity of the $^5D_0$–$^7F_4$ transition on the center of gravity of the $^5D_0$–$^7F_1$ transition for the considered groups of compounds are the parallel straight lines that cannot be laid in one line (Fig. 2). It is known that the degeneration of the centers of gravity of the electron levels, which differ in the full angular momentum J, inside multiplets, whose energy is determined by the repulsion of the $4f$ electrons, in particular, inside the ^7F multiplet of the Eu^{3+} ion, is removed by the spin–orbit coupling. In this case, the energies of the centers of gravity ($\bar{E}$) for the levels with different J depend linearly on the spin–orbit coupling constant. Apparently, when constructing the plots of the energies of the centers of gravity of some levels in a multiplet vs. the energies of the centers of gravity of the other levels in the same multiplet, the linear dependence will be obtained, since the former and the latter energies depend linearly on the spin–orbit coupling constant. The real dependence of the centers of gravity of the levels on the spin–orbit coupling constant will be linear only with the assumption that the parameters of the electrostatic repulsion (the Slater radial integrals [11]) are constant. This partially holds for the single-type crystal lattices (for isomorphic crystals of compounds with almost identical composition). This condition is likely to be observed in each of the three groups under study, but is violated when going from one group to the other one.

The $^5D_0$–$^7F_3$ transition is forbidden, and in the most spectra of the investigated compounds, it contains only 3 or 4 weak lines instead of seven possible lines. That

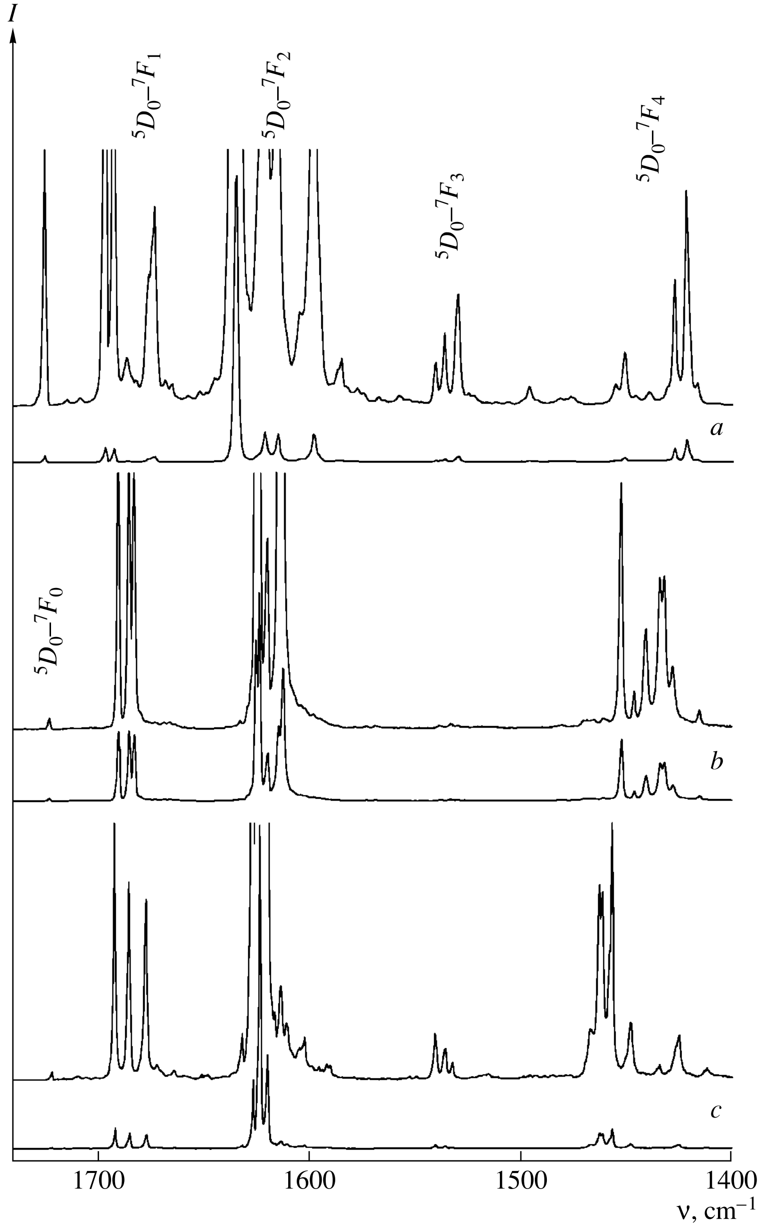

Fig. 1. Luminescence spectra of (*a*) [Eu(DPM)$_3$Phen], (*b*) [Eu(CH$_3$COO)$_3$Phen], and (*c*) [Eu(NO$_3$)$_3$(Phen)$_2$] at 77 K.

is why the data on the Stark structure of this level were not taken for the CFP calculations. The experimental and calculated values of the Eu^{3+} energy levels in different compounds with 1,10-phenanthroline are given in Table 1. The values of the CFP for the studied three groups are presented in Table 2.

Among the investigated compounds, [Eu(DPM)$_3$Ph] have the lowest symmetry of the europium coordination polyhedra. In order to establish the Stark components of the $^5D_0$–$^7F_4$ transition, we had to separate weak lines of the electronic transitions and intense electron-vibration (EV) components of the Stokes band of the $^5D_0$–$^7F_2$ transition and isolate the EV bands by comparing with the phonon-free lines of the $^5D_0$–$^7F_2$ transition displaced by the value of the Stokes shift of the EV bands (Fig. 3). The frequency of the respective vibration assigned to a combined vibration including the symmetric extension of the chelate ring of the β-diketonate is equal to: 1380 in [Eu(DPM)$_3$Mphen], 1385 in [Eu(DPM)$_3$Phen] and [Eu(DPM)$_3$Nphen], 1393 in [Eu(DPM)$_3$Tmphen], and 1399 cm^{-1} in [Eu(DPM)$_3$Phphen] and [Eu(DPM)$_3$Dphphen]. Hence, in the [Eu(DPM)$_3$Ph] series, this frequency, as well as the Stark splittings of the Eu^{3+} level, depends on the size of substituents in Ph.

The variation of one ligand (phenanthroline derivatives), with the second ligand (dipivaloylmethanate) remaining unchanged, mainly affects the amplitudes of

Table 1. The experimental (E_{exp}) and calculated (E_{calcd}) energies (cm^{-1}) of the Eu^{3+} levels in different Eu complexes with Phen

Levels	[Eu(DPM)$_3$Phen]			[Eu(CH$_3$COO)$_3$Phen]			[Eu(NO$_3$)$_3$[Phen]$_2$]		
	symmetry type	E_{exp}	E_{calcd}	symmetry type	E_{exp}	E_{calcd}	symmetry type	E_{exp}	E_{calcd}
$^7F_0$	A_1	0	0	A_1	0	0	A_1	0	0
$^7F_1$	A_2	286	285	B_1	327	330	B_1	297	301
	B_1	329	331	B_2	374	378	B_2	366	362
	B_2	519	518	A_2	400	393	A_2	447	448
$^7F_2$	A_1	901	903	A_2	974	976	A_2	952	951
	B_2	909	910	A_1	990	980	A_1	981	985
	A_2	1032	1039	A_1	1027	1021	A_1	1018	1010
	B_1	1099	1096	B_2	1080	1085	B_2	1083	1083
	A_1	1267	1263	B_1	1100	1108	B_1	1193	1197
$^7F_3$	B_2		1812	B_2		1809	B_2		1781
	A_2	1845	1850	A_2	1836	1847	A_2	1808	1821
	A_1	1886	1892	B_2		1885	B_2	1856	1862
	B_1		1923	A_1	1893	1893	B_1	1889	1893
	A_2		1943	B_1		1900	A_1		1876
	B_2	1950	1952	B_1	1925	1903	B_1		1902
	B_1		1984	A_2	1945	1943	A_2		1978
$^7F_4$	B_2	2683	2680	B_2	2698	2680	B_2	2584	2586
	A_1	2735	2728	B_1	2698*	2694	B_1	2599	2595
	B_1	2735*	2743	A_1	2698*	2714	A_1	2635	2636
	A_2	2785	2778	A_1	2758	2761	A_1	2734	2739
	B_1	2850	2860	B_2	2817	2841	B_2	2869	2866
	A_1	2971	2968	A_2	2882	2869	A_2	2869*	2873
	B_2	3026	3024	B_1	2904	2900	A_1	2943	2941
	A_2	3026*	3026	A_2	2941	2942	B_1	2961	2960
	A_1	3077	3075	A_1	3068	3060	A_2	3096	3094
$^5D_0$	A_1	17241		A_1	17222		A_1	17215	

the CF rhombic components (Table 2). These values are likely to correlate with the sizes of substituents. They are at minimum for the compounds with methylphenanthroline and at maximum for the compounds with more bulky phenyl derivatives of phenanthroline. In general, the CF changes in the series of the phenanthroline derivatives are insignificant. The CFP for [Eu(DPM)$_3$Tmphen] and [Eu(DPM)$_3$Nphen] were not calculated, since the spectra of the nonequivalent luminescence centers were not separated in these cases. The values of the sixth-order CFP, i.e., B_0^6–B_6^6, for DPM family are minimum, which illustrates the tendency of the sixth-order CFP to decrease with a decrease in the coordination number of the lanthanide ion observed when comparing these values for the three groups under consideration.

The negative sign of the CFP B_0^2 (Table 1) for the acetate group agrees with X-ray diffraction data and corresponds to an increased distribution density of a negative charge in the equatorial region. The calculations gave the increased values of the CF tetragonal components, i.e., the large values of B_0^4 and B_4^4. This fact is likely to point to two bidentate-bridging and to two tridentate bridging-cyclic carboxyl groups in the equatorial region of the dimeric compound (four bridging carboxyl groups of our model with the C_{2v} point symmetry). When going across the Ph series in the direction of increasing of the acceptor properties of their radicals (except for the bulky Ph, such as Tmphen, Dphphen), the B_0^2 and B_0^4 parameters gradually increase in this group, which suggests that the bond between the Eu^{3+} ion and the oxygen atoms becomes

Table 2. Crystal field parameters of the Eu^{3+} ion (cm^{-1}) in different Eu complexes with the 1,10-phenanthroline derivatives

Compound	B_0^2	B_2^2	B_0^4	B_2^4	B_4^4	B_0^6	B_2^6	B_4^6	B_6^6
[Eu(DPM)$_3$Mphen]	700	17	–1412	959	327	–304	191	–87	86
[Eu(DPM)$_3$Phen]	701	94	–1190	1046	385	–255	299	–288	–16
[Eu(DPM)$_3$Phphen]	685	155	–1242	976	484	–59	334	–124	62
[Eu(DPM)$_3$Dphphen]	660	150	–1050	1089	393	–289	194	–164	15
[Eu(CH$_3$COO)$_3$Tmphen]	–135	81	–718	59	347	–1067	536	–266	528
[Eu(CH$_3$COO)$_3$Mphen]	–171	42	–720	75	299	–873	443	–237	647
[Eu(CH$_3$COO)$_3$Phen]	–186	30	–726	60	320	–1031	489	–232	545
[Eu(CH$_3$COO)$_3$Phphen]	–194	85	–855	73	314	–1034	398	–259	501
[Eu(CH$_3$COO)$_3$Dphphen]	–214	73	–768	68	280	–919	456	–357	650
[Eu(CH$_3$COO)$_3$Nphen]	–252	57	–802	25	285	–968	443	–279	575
[Eu(NO$_3$)$_3$(Tmphen)$_2$]	–295	127	–807	372	399	–1177	491	–1227	706
[Eu(NO$_3$)$_3$Mphen)$_2$]	–298	158	–803	–49	740	–1177	705	–544	805
[Eu(NO$_3$)$_3$(Phen)$_2$]	–347	176	–730	–72	780	–1229	736	–329	819
[Eu(NO$_3$)$_3$(Phphen)$_2$]	–418	109	–762	307	415	–1218	461	–1308	624
[Eu(NO$_3$)$_3$(Dphphen)$_2$]	–483	97	–720	344	342	–1306	549	–1246	572
[Eu(NO$_3$)$_3$(Nphen)$_2$]	–507	119	–964	222	376	–1096	405	–1301	377

stronger. In this group, the B_0^4/B_4^4 and B_0^6/B_4^6 ratios are very close to those typical for CF with a high, for example, cubic, symmetry.

Judging from the CFP values, the most symmetric charge distribution in the nearest environment of the Eu^{3+} ion is observed in the europium acetate with Mphen, which agrees with IR and Raman spectra. Although the [Eu(CH$_3$COO)$_3$Phen] and [Eu(CH$_3$COO)$_3$Mphen] spectra are similar (the B_q^k values are close), the former compound has the higher symmetry. Such a decrease in the symmetry, when going from the acetate with the methyl derivative of phenanthroline to the acetate with phenanthroline, probably occurs due to an increase in the nonequivalent charge distribution in the nearest environment of the europium ions. Such nonequivalence can be explained, for example, by a growing difference in the functions of the bidentate-bridging and tridentate bridging-cyclic groups resulting from the steric hindrances of the ligands in the coordination core and increasing due to a decrease in the total volume of the complex with the removed CH$_3$ radical.

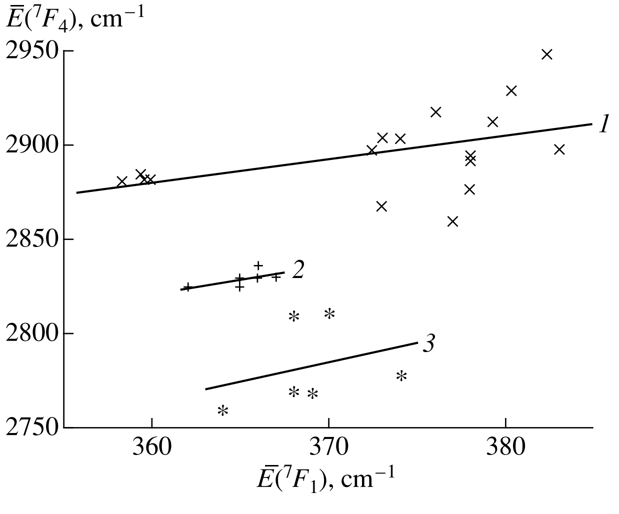

Fig. 2. The center of gravity of the $^7F_4$ level as a function of the center of gravity of the $^7F_1$ level for (*1*) [Eu(DPM)$_3$Ph], (*2*) [Eu(CH$_3$COO)$_3$Ph], and (*3*) [Eu(NO$_3$)$_3$(Ph)$_2$].

The broadening of the lines from the Eu^{3+} electron transitions in the luminescence spectra of the acetates with the bulky substituents (such as Phphen, Dphphen) is likely to be due to the steric hindrances arising during crystal lattice packing. This made the assignment of the lines in the region of the $^5D_0$–$^7F_4$ transition difficult. Therefore, we had to use the similarity of the luminescence spectra when going across the Ph series.

The luminescence spectra of the nitrates with Ph contain minimum number of intense lines, therefore the nearest surrounding of the europium ion in these compounds has the highest symmetry (Fig. 1). As was previously reported in [3], this group of compounds exhibit significant value of the electron-vibration interaction. In the region of the overlapping of the phonon-free lines of the $^5D_0$–$^7F_2$ transition with the electron-vibration band of the $^5D_0$–$^7F_0$ transition, the conditions for the EV mixing of states are fulfilled and the EV res-

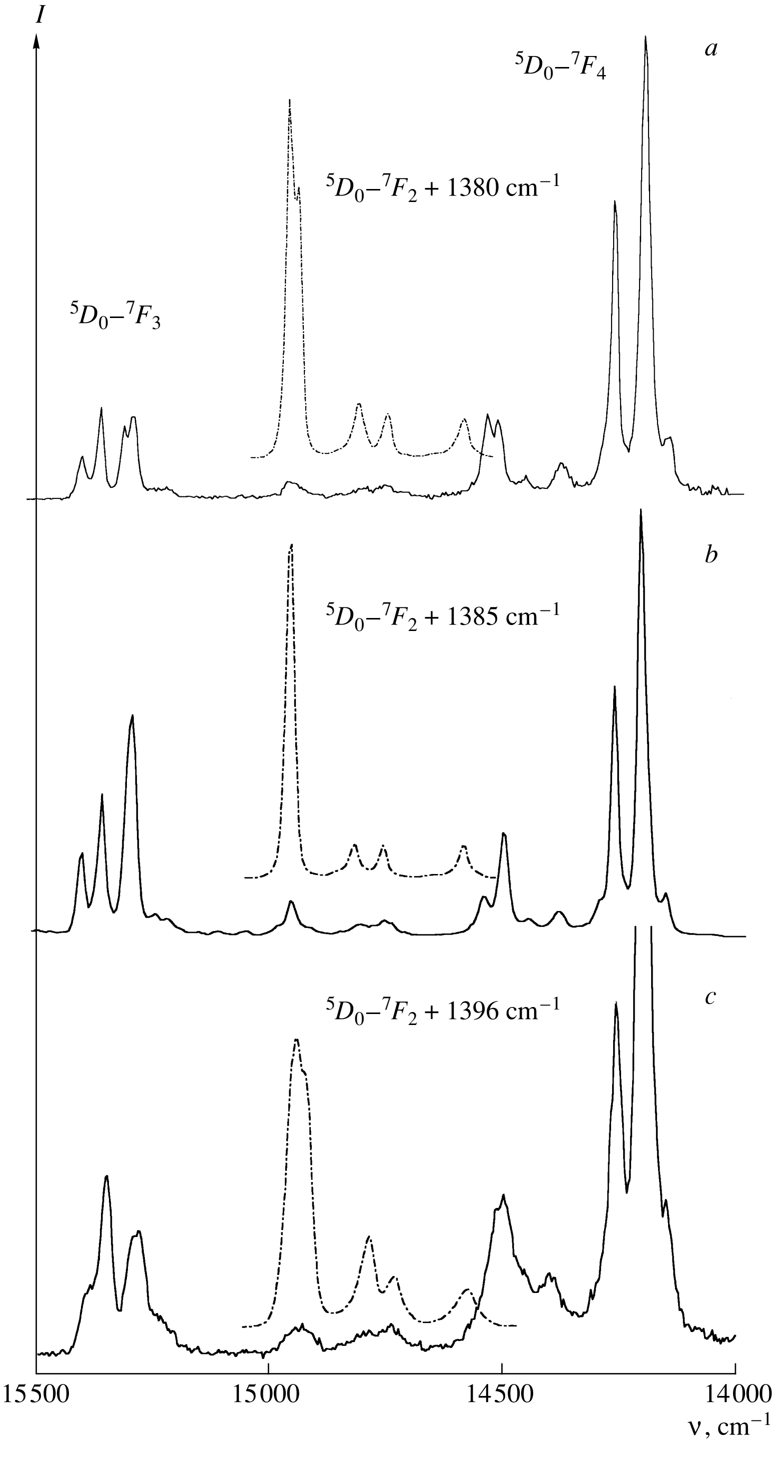

Fig. 3. Luminescence spectra of (*a*) [Eu(DPM)$_3$Mphen], (*b*) [Eu(DPM)$_3$Phen], and (*c*) [Eu(DPM)$_3$Phphen] in the region of the $^5D_0$–$^7F_4$ transition at 77 K.

onance is observed, which complicates the study of the Stark structure of the $^7F_2$ level. The separation of the Stark components of this level and EV lines was performed using IR and Raman spectra for estimation of the Stokes displacements of the EV lines and was compared with the data obtained from the plot of the centers of gravity of the $^7F_2$ level.

The europium nitrates with Ph have the greatest (~530 cm^{-1}) splitting of the $^5D_0$–$^7F_4$ transition (for the β-diketonates and acetates, it is ~395 and ~380 cm^{-1}, respectively). Because of the increased number of the spectral lines (more than nine) in the region of the $^5D_0$–$^7F_4$ transition, we had to turn to the plot of the centers of gravity of the $^5D_0$–$^7F_4$ transition and select the Stark components of the transition. After the analysis of the vibration spectra, we could separate the phonon-free electronic and EV lines in the region of this transition. The electron-vibration mixing of states results in an increase in the intensity of the EV satellites of the $^5D_0$–$^7F_2$ transition that lie in the region of the phonon-free $^5D_0$–$^7F_4$ transition. The Stokes displacement of these satellites with respect to the most intense Stark component of the $^5D_0$–$^7F_2$ transition is equal to 1525 and 1530 cm^{-1} in the case of [Eu(NO$_3$)$_3$(Phen)$_2$] and [Eu(NO$_3$)$_3$(Mphen)$_2$], respectively. The satellites observed in this region can be assigned to the stretching vibrations ν(C=C) and ν(C=N) of the condensed aromatic rings in phenanthroline. A number of peculiarities of the [Eu(NO$_3$)$_3$(Ph)$_2$] luminescence spectra that determine the relative values of the different-order CFP are explained probably by the high coordination number (CN 10) of the Eu^{3+} ion in these compounds. The significant changes in the CFP values, particularly, B_2^2, B_2^4, B_2^6 for the europium nitrates with Ph allow one to divide the group under consideration into two subgroups identified previously by the authors of [3].

The comparison of three groups of compounds in terms of the calculated CFP reveals the correlation between the relative values of the CFP of different orders and the coordination number of the Eu^{3+} ion. The least sixth-order CFP (B_0^6 ~ 250 cm^{-1}) and the greatest second-order CFP (B_0^2 ~ 690 cm^{-1}) are observed for [Eu(DPM)$_3$Ph] (CN 8). The europium acetates with Ph (CN 9) have the intermediate sixth-order CFP values and the minimum second-order CFP values (B_0^6 ~ 980 cm^{-1}, B_0^2 ~ 190 cm^{-1}). The greatest CFP values of the sixth order and the intermediate CFP values of the second order (B_0^6 ~ 1200 cm^{-1}, B_0^2 ~ 390 cm^{-1}) are observed in the europium nitrates with Ph (CN 10).

The relatively high and constant CFP values of the sixth order for some europium nitrates with Ph as compared with the CFP for the other two groups indicate that as the coordination number increases (to nine and higher), the contributions of different sorts of atoms in the nearest environment of the lanthanide ion to the CFP of the lowest orders are averaged, but give the increased values to the sixth-order CFP. This tendency can be explained by the limiting resolving capability of the 4*f* orbitals and states with the low angular momentum *J* bringing about the averaging of contributions of different atoms to the CFP of the least orders as compared to the sixth-order CFP upon the reduction in the solid angles occupied by these atoms in the first coordination sphere with an increase in the cation coordination number. One should note that the mutual repulsion of the ligands also results in the averaging, weakening, and symmetrization of the effect of the nearest surrounding on the ligand ion with an increase in the coordination number.

The analysis of the vibration spectra and the plots of the centers of gravity of the $^7F_2$ and $^7F_4$ levels vs. the center of gravity of the Eu^{3+} $^7F_1$ level made it possible to establish some Stark components of the Eu $^5D_0$–$^7F_2$ and $^5D_0$–$^7F_4$ transitions in the case of the nitrates and β-diketonates with Ph, respectively. As the result, the CFP were calculated for the models of luminescence centers with the C_{2v} symmetry for three groups of the europium compounds with the phenanthroline derivatives: the β-diketonates, acetates, and nitrates with different coordination numbers.

The comparison of the obtained crystal field parameters for these groups shows that the relative values of the CFP depend on the coordination number of the lanthanide ion. In particular, as the coordination number of the Eu^{3+} ion increases, the amplitudes of harmonics of the second-order crystal field are decreased, while the amplitudes of harmonics of the sixth-order crystal field increase. The discovered correlation can be useful when studying complexes with the unknown coordination number of the metal cation.

ACKNOWLEDGMENTS

The authors are grateful to V.I. Tsaryuk for synthesizing the europium acetates and nitrates with the 1,10-phenanthroline derivatives we used in this study and for recording the luminescence spectra and to professor Ya. Legendziewicz and doctor R. Shostak from the Wroclaw University for providing IR and Raman spectra of the investigated compounds.

This work was supported by the Russian Foundation for Basic Research (projects nos. 01-02-16837 and 02-02-06316).

REFERENCES

1. Tsaryuk, V., Zolin, V., and Legendziewicz, J., *Spectrochim. Acta, Part A*, 1998, vol. 54, no. 9, p. 2247.
2. Tsaryuk, V., Legendziewicz, J., Puntus, L., *et al.*, *J. Alloys Compd.*, 2000, vols. 300–301, p. 464.
3. Tsaryuk, V., Zolin, V., Puntus, L., *et al.*, *J. Alloys Compd.*, 2000, vols. 300–301, p. 184.
4. Tsaryuk, V., Legendziewicz, J., Zolin, V., *et al.*, *J. Alloys Compd.*, 2001, vols. 323–324, p. 661.
5. Malta, O.L., Couto dos Santos, M.A., Thompson, L.C., and Ito, N.K., *J. Lumin.*, 1996, vol. 69, no. 1, p. 77.
6. Watson, W.H., Williams, R.J., and Stemple, N.R., *J. Inorg. Nucl. Chem.*, 1972, vol. 34, no. 3, p. 501.

7. Korytnyi, E.F., Dzubenko, N.G., Aslanov, L.A., and Martynenko, L.N., *Zh. Neorg. Khim.*, 1981, vol. 26, no. 1, p. 72.
8. Leipoldt, J.G., Bok, L.D.C., Basson, S.S., and Laubscher, A.E., *J. Inorg. Nucl. Chem.*, 1976, vol. 38, no. 6, p. 1477.
9. Tsaryuk, V., Turowska-Tyrk, I., Legendziewicz, J., *et al.*, *J. Alloys Compd.*, 2002, vol. 341, p. 323.
10. Frechette, M., Butler, I.R., Hynes, R., and Detellier, Ch., *Inorg. Chem.*, 1992, vol. 31, no. 5, p. 1650.
11. Wybourne, B.G., *Spectroscopic Properties of Rare Earth Ions*, New York: Interscience, 1965.
12. Tikhonov, A.N. and Arsenin, V.Ya., *Metody resheniya nekorrektnykh zadach* (Methods of Solution of Ill-Posed Problems), Moscow: Nauka, 1986.
13. Lea, K.R., Leask, M.J.M., and Wolf, W.P., *J. Phys. Chem. Solids*, 1962, vol. 23, no. 5, p. 1381.
14. Antic-Fidancev, E., *J. Alloys Compd.*, 2000, vols. 300–301, p. 2.