

The Dependence of the Luminescence Intensity of Lanthanide Complexes with β -Diketones on the Ligand Form

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The influence of β -diketone forms on the luminescence intensity of lanthanide compounds in a series of ligands, acetylacetone (trifluoroacetylacetone, benzoylacetone)—their unsaturated analogues (monomeric form)—copolymers of the latter with styrene (methylmethacrylate), was studied. Lanthanides in compounds with copolymers have been established to demonstrate the brightest luminescence. It was found that its intensity depends not only on the character of the substituent (CH_3 , CF_3 , C_6H_5) in the β -diketone molecule, but also on the distance between the β -diketone fragments in the copolymer. Reasons explaining the high intensity of luminescence in lanthanide-copolymer compounds are considered.

KEY WORDS: Luminescence; lanthanides; β -diketones; copolymers.

INTRODUCTION

The unique ability of lanthanide (Ln) ions to emit luminescence has provided for their extensive application in laser techniques as transformers of light energy, phosphors, etc. For more than three decades, lanthanide complex compounds have been used for the express and highly sensitive determination of these elements in various objects, as the shift reagents in NMR spectroscopy, for luminescence labels in immunofluorescence assays, etc. [1,2].

In phosphors sufficiently intensive luminescence can be observed for all lanthanides with from 2 to 13 electrons in the 4f-shell, while in solutions of β -diketonates only Sm^{3+} , Eu^{3+} , Tb^{3+} , Nd^{3+} , and Yb^{3+} ions display luminescence (the latter two in the IR spectral region) [2]. It is known [3] that the luminescence of trivalent lanthanide

ions is realized as a result of the energy transfer from the excited organic moiety of the complex molecule. The formation of the stable complex compound is a necessary but insufficient condition; it is important that the energy of the lower triplet level of the ligand is equal to or higher than the energy of the excited level of the lanthanide ion.

One of the factors limiting the possibility of observing the intensive luminescence of lanthanides in aqueous solutions is its quenching by the vibrations of the OH groups (OH oscillators) of water molecules entering into the inner coordination sphere of the complex [4]. The substitution of H_2O with D_2O [5] as well as the introduction of a second ligand to obtain a mixed-ligand complex leads to partial or complete elimination of the H_2O influence. In the case of lanthanide β -diketonates, the organic bases are mainly used as the second ligands, which effectively replace the water molecules to stimulate a considerable increase in the luminescence intensity [2]. The same effect may be achieved by crowding out the water molecule from the inner and outer coordination sphere when the organic solvents are added [2,6] or when the molecule

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of lanthanide β -diketonate is introduced into the micelle of the surfactant [7]. As found previously [8], screening of the central ion increases noticeably with lengthening of the fluorinated aliphatic substituent (R_F) in the series of acetylacetonate (acac) derivatives. The absence of H_2O in the inner coordination sphere of the complex has been observed at $R_F = C_6F_{13}-C_8F_{17}$, and the luminescence intensity of lanthanide *tris*-chelates with these β -diketonates is actually equal to that of mixed-ligand complexes [9].

The energy losses resulting from the thermal blows of the complex molecules in solutions [10] play an important role in the quenching of lanthanide luminescence that is removed by freezing of the solutions to 77K [2], sorption of the complex by the polymeric sorbent [11], or its introduction into the polymeric matrix [1]. Here, the quenching of luminescence connected with OH oscillators also decreases to some extent.

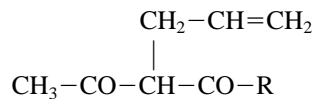
The available odd literature data regarding lanthanide complexation with polymeric and monomeric β -dicarbonylic compounds [1,12] does not allow us to form a conclusion on the influence of the substituent nature and position of the β -dicarbonylic unit in the polymeric chain on lanthanide luminescence, while both the possibility of the formation of the coordination saturated chelated lanthanide compound and the intensity of its luminescence depend on these factors. Moreover, comparative data on the luminescence of lanthanide β -diketonates in different aggregate states are absent.

The purpose of the present work is to study the influence of the form of ligands on the luminescence intensity of lanthanide compounds in the series, acac and its derivatives—their unsaturated analogues (monomeric form)—copolymers of the latter with styrene or methylmethacrylate (MMA). It was also of interest to compare the luminescence intensity of lanthanide β -diketonates and their sorbates on the polymeric sorbent (PMMA) with its value for lanthanide compounds with copolymers containing the same β -diketone units and MMA.

EXPERIMENTAL

Samarium, europium, neodymium, ytterbium oxides, and β -diketonates [acac, trifluoroacetylacetonate (tfacac), benzoylacetonate (bzac)] were purchased from Aldrich (Gillungham, Dorsent) and used as received. Stock solutions of $1 \times 10^{-1} \text{ mol dm}^{-3}$ concentrations of the lanthanides were prepared by dissolving a known amount of oxide in hydrochloric acid. After evaporation of the acid, the residue was dissolved in water (final pH, 3–4) and the metal concentration was determined by titration with EDTA [13].

Synthesis of monomeric forms of β -diketonates was performed by the Claisen condensation method [14].



where $R = \text{CH}_3$ -allylacetylacetonate (al-acac), $R = \text{CF}_3$ -allyltrifluoroacetylacetonate (al-tfacac), and $R = \text{C}_6\text{H}_5$ -allylphenylacetylacetonate (al-phenacac)

The synthesized compounds were identified by IR and NMR spectroscopy, GLC, and elemental analysis.

Copolymers were obtained using the reaction of radical copolymerization of synthesized monomeric β -diketone forms with styrene and methylmethacrylate at different comonomer ratios (1:1, 1:2, 1:5).

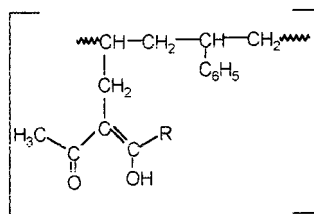
Stock solutions of $1 \times 10^{-2} \text{ mol dm}^{-3}$ β -diketonates, their monomer forms, and 1 mg ml^{-1} solutions of the copolymers were prepared by dissolving the appropriate amount in acetone.

In the lanthanide complexes with β -diketonates, the monomeric and polymeric forms were obtained by mixing the LnCl_3 and ligand solutions in the presence of acetic–ammonium buffer solution (pH 7.5). A 10-fold excess of β -diketonates [2] and monomers was taken (ratio of Ln: β -diketone, monomer = 1:3). The necessary amount of copolymers was established by the maximal intensity of the luminescence of the compounds formed.

Luminescence measurements were carried out on an SDL-2 spectrofluorimeter equipped with a photon counting system (Leningrad, Optic-Mechanical Association, St. Petersburg, Russia) [15]. The spectra were corrected with a standard lamp. A xenon lamp was used as the excitation source. Registration of luminescence spectra was carried out within the following regions: Sm^{3+} , 630–670 nm ($\lambda_{\text{max}} = 645 \text{ nm}$, $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{9/2}$ transition); Eu^{3+} , 590–630 nm ($\lambda_{\text{max}} = 614 \text{ nm}$, $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition); Nd^{3+} , 860–940 nm ($\lambda_{\text{max}} = 903 \text{ nm}$, $^4\text{F}_{3/2} \rightarrow ^4\text{I}_{9/2}$ transition); and Yb^{3+} , 950–1000 nm ($\lambda_{\text{max}} = 980 \text{ nm}$, $^2\text{F}_{5/2} \rightarrow ^2\text{F}_{7/2}$ transition). In all cases, the hypersensitive transitions were used.

RESULTS AND DISCUSSION

The copolymers used contain the chelating groups in the side chains, for example, with styrene



where R = CH₃, CF₃, C₆H₅.

The difficulty due to the formation of *tris*-chelate will be determined by the loading of a copolymer with β -diketone units. We have supposed that within the interval of ratios β -diketone:styrene (MMA) = 1:1, 1:2, and 1:5, the optimal one at which the lanthanide ion will coordinate the maximal number of β -diketone groups is present. Such a compound in a series of the same type has to demonstrate the most intensive luminescence.

It was found experimentally that the amount of copolymers as well as nonpolymerized β -diketones [2] affects the luminescence intensity of the formed compounds (Fig. 1). It should be noted that the pH, 7.5, of the complexation of lanthanide ions with all the monomers and copolymers corresponds to its value for compounds with nonpolymerized β -diketones [2].

A list of the studied copolymers and the luminescence intensity of their compounds with Eu³⁺ ions is presented in Table I.

From a comparison of the obtained luminescence intensity (I_{lum}) values, it can be seen that Eu³⁺ compounds with copolymers including al-acac (Nos. 1–6) show the lowest I_{lum} . Their luminescence may be observed at a Eu³⁺ concentration in solution of 1×10^{-4} mol dm⁻³, which is higher by two orders of magnitude than in the case of copolymers containing al-tfacac (Nos. 7–12) and al-phenacac (Nos. 13–18). For the first two groups of copolymers including β -diketones with alkyl substituents (CH₃, CF₃), the maximal luminescence is observed for Eu³⁺ compounds with copolymers in which the ratio of β -diketone:styrene (MMA) = 1:2 (Nos. 2, 5, 8). The minimal luminescence corresponds to a ratio of components 1:1 (Nos. 1, 4, 7). The minimum of I_{lum} is also at a ratio of β -diketone:styrene (MMA) = 1:1 (Nos. 10, 13,

Table I. List of the Studied Copolymers and the Luminescence Intensity of Their Eu³⁺ Compounds^a

No.	Copolymer		I_{lum} (arb. units)
	Abbreviation	Component ratio	
1	Al-acac–styrene	1:1	1.4
2	Al-acac–styrene	1:2	7.0
3	Al-acac–styrene	1:5	4.5
4	Al-acac–MMA	1:1	3.1
5	Al-acac–MMA	1:2	13.5
6	Al-acac–MMA	1:5	11.0
7	Al-tfacac–styrene	1:1	5.4
8	Al-tfacac–styrene	1:2	21.4
9	Al-tfacac–styrene	1:5	18.0
10	Al-tfacac–MMA	1:1	6.5
11	Al-tfacac–MMA	1:2	27.6
12	Al-tfacac–MMA	1:5	22.8
13	Al-phenacac–styrene	1:1	21.1
14	Al-phenacac–styrene	1:2	49.6
15	Al-phenacac–styrene	1:5	74.1
16	Al-phenacac–MMA	1:1	23.7
17	Al-phenacac–MMA	1:2	69.3
18	Al-phenacac–MMA	1:5	100

^a C_{Eu} (1–6) = 1×10^{-4} mol dm⁻³, C_{CP} = 0.4 mg cm⁻³; C_{Eu} (7–18) = 1×10^{-6} mol dm⁻³, C_{CP} = 0.2 mg cm⁻³.

16) in the case of copolymers including β -diketone with an aryl substituent (C₆H₅). However, the most intensive luminescence is observed for Eu³⁺ compounds with copolymers in which the ratio of components is 1:5 (Nos. 12, 15, 18) at the longer linking bridge between β -diketone units. The latter may result from the large steric hindrances caused by phenyl radicals on complexation.

It is obvious that under otherwise equal conditions the luminescence of Eu³⁺ in compounds with copolymers β -diketone–MMA is more intensive than with their styrene analogues (compare Nos. 1–3 with Nos. 4–6, Nos. 7–9 with Nos. 10–12, and Nos. 13–15 with Nos. 16–18). The explanation for this circumstance evidently consists of the additional coordination of Eu³⁺ ions with oxygen atoms of the carbonylic group of MMA [11].

The differences in the luminescence intensity of Eu³⁺ compounds with similar copolymers distinguished by different loadings of the polymer chain by β -diketone units are likely caused by the steric difficulties which hinder the formation of *tris*-chelate, in which the luminescence of Eu³⁺ (other Ln) is most intensive due to the energy transfer from the maximum possible number of β -diketone units in the coordination sphere of the complex. Indirect confirmation of this supposition could be the experimentally established fact that the luminescence intensity of Eu³⁺ compounds with copolymers (1:5) is increased by 1.3–1.5 times when the appropriate “free”

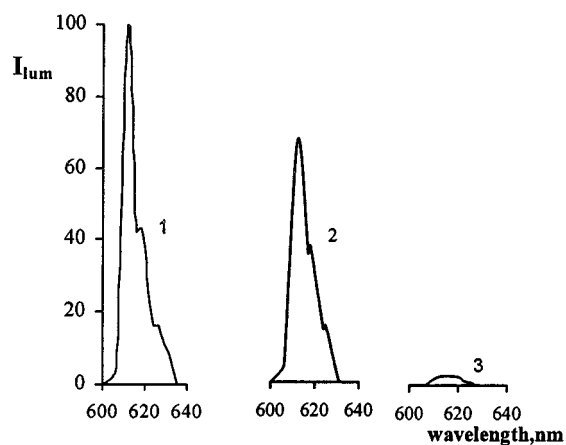
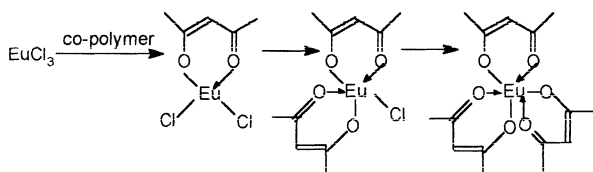


Fig. 1. Dependence of the luminescence intensity of Eu³⁺ compounds on the copolymer amounts: (1) al-phenacac–styrene (1:5); (2) al-tfacac–MMA (1:2); (3) al-acac–styrene (1:2).

β -diketone (acac, tfacac, bzac) is added to solutions. In the case of copolymers characterized by more loading with β -diketone units (1:1; 1:2), the introduction of β -diketone into the solution leads to some decrease in I_{lum} , probably owing to the extraction of the Eu^{3+} ion from a compound with a copolymer in the solution and the formation of weakly luminescent acetylacetonates (trifluoroacetylacetonates, benzoylacetonates).



The results obtained are in accordance with the conclusions of other authors [12] that when the β -diketone units are introduced into the polymeric chain, the formation of complexes with the composition $\text{Eu}^{3+}:\text{Lig} = 1:3$ is difficult. Therefore, the complex 1:2 (and, to a lesser degree, 1:1) becomes the predominant one, characterized by a lower luminescence intensity compared with *tris*-chelate.

Taking Sm^{3+} , Eu^{3+} , Nd^{3+} , and Yb^{3+} compounds as an example, it was shown how their I_{lum} changes in the series of ligands, β -diketone—its monomeric analogue—copolymer with styrene. As shown in Table II, the lanthanide compounds with all copolymers (Nos. 3, 6, 9) demonstrate significantly higher luminescence intensity compared with other forms of the same β -diketone. The luminescence intensity of lanthanide complexes with monomeric ligands containing allyl substituents (CH_3 ,

CF_3) is less intensive than for the complexes with appropriate β -diketones (acac, tfacac): $I_2/I_1 < 1$ (compare No. 1 with No. 2 and No. 4 with No. 5). When there is one aryl substituent (C_6H_5) the I_{lum} of compounds is higher than the value for the corresponding β -diketonates: $I_2/I_1 > 1$ (compare No. 8 with No. 7).

When the structure of the chelate ring is identical and the substituents are different, the observed difference in I_{lum} can probably be explained by the different arrangement of charges in the chelate cycle, which, as known [16], correlate with I_{lum} values in a series similar in construction to that of β -diketones.

In compounds with copolymers, the lanthanide ions demonstrate the most intensive luminescence, which is higher by one order of magnitude compared with that for Ln^{3+} complexes with β -diketones ($I_3/I_1 > 1$) and their monomeric analogues ($I_3/I_2 > 1$). Although the formation of *tris*-chelates with copolymers is difficult, the high luminescence intensity of their Ln^{3+} compounds compared with β -diketone and monomeric ones is likely caused by the following factors. First, the Ln^{3+} ions are rigidly fixed in the copolymer structure. Second, the molecular mass of the Ln^{3+} compounds with copolymers is significantly higher than that of complexes with the same β -diketones and monomeric analogues, owing to the fact that the energy losses connected with thermal blows are dramatically decreased.

Finally, it was of interest to compare the luminescence intensity of Eu^{3+} compounds with copolymers in solids with the sorbates of the same β -diketonates on PMMA [11]. As shown in Fig. 2, under identical conditions (solid phase, the same Eu^{3+} amount) the lumines-

Table II. Variations in Luminescence Intensity of Sm^{3+} , Eu^{3+} , Nd^{3+} , and Yb^{3+} Complexes in the Series of Ligands, β -Diketone— β -Diketone Allyl Derivatives (Monomer; mmm)—Their Copolymers with Styrene^a

No.	Ligand	I_{lum} (arb. units)					I_{lum} enhancement (times)				
		I_{1-3}	Sm^{3+}	Eu^{3+}	Nd^{3+}	Yb^{3+}	$I_{2,3}/I_{1,2}$	Sm^{3+}	Eu^{3+}	Nd^{3+}	Yb^{3+}
1	Acac	I_1	1.6	1.7	2.9	4.2	I_2/I_1	0.5	0.7	0.6	0.8
2	Al-acac	I_2	0.8	1.2	1.9	3.2	I_3/I_1	6.1	7.1	5.7	6.8
3	Al-acac–styrene (1:2)	I_3	9.8	12.1	16.5	28.4	I_3/I_2	12.2	10.1	8.7	8.9
4	Tfacac	I_1	2.4	2.1	3.9	5.3	I_2/I_1	0.7	0.6	0.7	0.8
5	Al-tfacac	I_2	1.6	1.2	2.9	4.2	I_3/I_1	12.9	10.5	9.7	10.5
6	Al-tfacac–styrene (1:2)	I_3	30.9	22.1	37.9	55.8	I_3/I_2	19.3	18.4	13.1	13.3
7	Bzac	I_1	4.1	2.5	4.8	5.3	I_2/I_1	1.8	2.8	2.0	1.8
8	Al-phenacac	I_2	7.3	7.1	9.7	9.5	I_3/I_1	24.4	40.0	20.1	18.9
9	Al-phenacac–styrene (1:5)	I_3	100	100	100	100	I_3/I_2	13.7	14.1	10.3	10.5

^a $C_{\text{Sm}}(1-3) = 1 \times 10^{-3} \text{ mol dm}^{-3}$, $C_{\beta\text{-dik,mmr}} = 1 \times 10^{-3} \text{ mol dm}^{-3}$; $C_{\text{Sm}}(4-9) = 1 \times 10^{-5} \text{ mol dm}^{-3}$, $C_{\beta\text{-dik,mmr}} = 1 \times 10^{-4} \text{ mol dm}^{-3}$; $C_{\text{Eu}}(1-3) = 1 \times 10^{-4} \text{ mol dm}^{-3}$, $C_{\beta\text{-dik,mmr}} = 1 \times 10^{-3} \text{ mol dm}^{-3}$; $C_{\text{Eu}}(4-9) = 1 \times 10^{-6} \text{ mol dm}^{-3}$, $C_{\beta\text{-dik,mmr}} = 1 \times 10^{-4} \text{ mol dm}^{-3}$; $C_{\text{Nd,Yb}}(1-3) = 1 \times 10^{-3} \text{ mol dm}^{-3}$, $C_{\beta\text{-dik,mmr}} = 1 \times 10^{-2} \text{ mol dm}^{-3}$; $C_{\text{Nd,Yb}}(4-9) = 1 \times 10^{-4} \text{ mol dm}^{-3}$, $C_{\beta\text{-dik,mmr}} = 1 \times 10^{-3} \text{ mol dm}^{-3}$; $C_{\text{CP}}(3) = 0.4 \text{ mg cm}^{-3}$; $C_{\text{CP}}(6, 9) = 0.2 \text{ mg cm}^{-3}$.

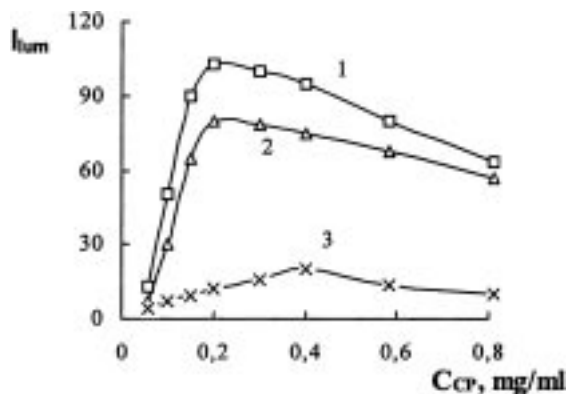


Fig. 2. Luminescence spectra: (1) Eu^{3+} compound with al-phenacac-MMA (1:5); (2) sorbate $\text{Eu}(\text{bzac})_3$ on PMMA; (3) $\text{Eu}(\text{bzac})_3$ in solution. $C_{\text{Eu}} = 1 \times 10^{-6} \text{ mol dm}^{-3}$.

cence intensity of Eu^{3+} in a compound with al-phenacac-MMA (spectrum 1) is almost two times higher than that of $\text{Eu}(\text{bzac})_3$ sorbate on PMMA (spectrum 2). Since the possibility of energy losses from the thermal blows is removed in the solid phase, such differences in I_{lum} may be due to the following. In a compound with a copolymer, the Eu^{3+} ions are separated from each other by polymeric links. The reabsorption of energy is actually excluded. On the contrary, when sorption of Eu^{3+} benzoylacetonate by PMMA takes place, their conglomerates are present on the sorbent, in which the energy transfer between the lanthanide ions leads to its nonradiative losses. For comparison, the spectrum of Eu^{3+} benzoylacetonate in solution, the luminescence intensity of which is very weak under the same conditions, is also given in Fig. 2.

CONCLUSION

Thus, a comparison of the luminescence intensity of Sm^{3+} , Eu^{3+} , Nd^{3+} , and Yb^{3+} ions in the series of ligands, β -diketones—their monomer derivatives—copolymers with styrene or MMA, has demonstrated the absolute advantage of the latter ones. In spite of the fact

that the complexation energy is insufficient to orient the neighboring β -diketone units and, simultaneously, to fold the polymeric chain for the formation of *tris*-chelate, the I_{lum} in the lanthanide compounds with copolymers is significantly higher than that in solutions of their complexes with β -diketones and monomers in which the Ln^{3+} ion is bonded with three chelate rings.

The compounds with copolymers represent a rigid structure in which the Ln^{3+} ions situate at a fixed distance from each other in accordance with the arrangement of β -diketone units, which exclude, to a significant degree, reabsorption of the emitted light. The increase in the molecular mass of the formed compounds is caused by reduction of the energy losses from the thermal blows. The absolute advantage of the copolymers may be used in the luminescence determination of Sm^{3+} , Eu^{3+} , Nd^{3+} , and Yb^{3+} in the presence of lanthanides-quenchers.

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