

Research Article

Electrochemiluminescence Study of Europium (III) Complex with Coumarin3-Carboxylic Acid

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Received 4 May 2008; Revised 12 June 2008; Accepted 22 July 2008

Recommended by Mohamed Sabry Abdel-Mottaleb

The europium (III) complex of coumarin-3-carboxylic acid (C3CA) has been prepared and characterized on the basis of elemental analysis, IR, and emission (photoluminescence and electrochemiluminescence) spectroscopy. The synthesised complex having a formula $\text{Eu}(\text{C3CA})_2(\text{NO}_3)(\text{H}_2\text{O})_2$ was photophysically characterized in solution and in the solid state. Electrochemiluminescence, ECL, of the system containing the $\text{Eu}(\text{III})/\text{C3CA}$ complex was studied using an oxide-covered aluminium electrode. The goal of these studies was to show the possibility of the use of electrochemical excitation of the $\text{Eu}(\text{III})$ ion in aqueous solution for emission generation. The generated ECL emission was very weak, and therefore its measurements and spectral analysis were carried out with the use of cut-off filters method. The studies proved a predominate role of the ligand-to-metal energy transfer (LMET) in the generated ECL.

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1. INTRODUCTION

Coumarins and their derivatives due to their biological activities, interesting photophysical and photochemical, and metal binding properties have been a subject of numerous investigations [1–12]. This group of compounds is known to have diverse applications in biology and medicine, due to their anticancer, antibiotic, anticoagulant, and anti-inflammatory [1, 2] properties. It has been found that the binding of a metal to the coumarin moiety retains or even enhances its biological activity [2, 3].

The coumarin-3-carboxylic acid (HC3CA) has previously been used as a ligand in complexation reactions with d-electron metal ions [5–7] and series of lanthanide cations ($\text{Dy}(\text{III})$, $\text{Er}(\text{III})$, $\text{Eu}(\text{III})$, $\text{Gd}(\text{III})$, $\text{Tb}(\text{III})$, and $\text{Sm}(\text{III})$) [8–12]. The binding mode of coumarin-3-carboxylic acid in its $\text{La}(\text{III})$ complex has been investigated both experimentally and theoretically [8], the studies indicated strong ionic metal-ligand bonding in $\text{La}-\text{C3CA}$ complex and insignificant donor acceptor interaction. A sensitized emission and an effective ligand to metal energy transfer in the samarium complex with 7-acetoxy coumarin 3-carboxylic acid [9], and efficient emission with long lifetimes although with low quantum yield values in the systems of Eu^{3+} and Tb^{3+}

with crown ethers and iminodiacetic subunits attached to 3-arylcoumarins in methanol [10] have been observed. The samarium (III) complex of coumarin-3-carboxylic acid proved to be the most active antiproliferative agent among the complexes [11]. Erbium (III) and europium (III) luminescent lanthanide complexes based on a coumarin showing effective energy transfer between the coumarin ligand and the lanthanide ions were designed and characterized by Kim et al. [12].

Coumarin derivatives have been a subject of electrochemiluminescence its mechanisms, induced by injection of hot electrons into aqueous electrolyte solution [13]. The studies showed that coumarins can be suitable candidates as ECL labels for bioaffinity assays or other analytical applications [13].

In our recent investigations, we have applied specific electrogenerated luminescence, ECL, which can be observed in $\text{Ln}(\text{III})$ ($\text{Ln} = \text{Tb}$, Dy and Eu) complexes with organic ligands containing aromatic rings forming stable complexes, in studying mechanisms of energy transfer [14, 15]. The ECL was obtained by producing highly oxidizing and reducing species as: hydrated electrons, hydroxyl, and sulfate radicals. These strong redox reactants efficiently excite the complexed $\text{Ln}(\text{III})$ ions by ligand to metal energy transfer.

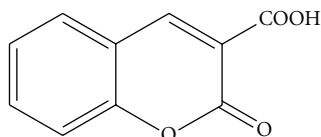


FIGURE 1: The structure of the ligand (coumarin-3-carboxylic acid, C3CA) studied.

The present work contains results of photoluminescence (PL) and electrochemiluminescence (ECL) studies concerning the complex of Eu (III) with the C3CA ligand. The goal of these studies was to show the possibility of ECL generation with the use of electroexcitation resulting in the ligand-to-metal energy transfer (LMET) in aqueous solution with participation of the Eu (III) ion.

2. EXPERIMENTAL

2.1. Synthesis of compounds

All chemicals were used of AR grade. The europium oxide Eu_2O_3 (Merck 99.99%, KGaA, Germany) was dissolved in a slight excess of HNO_3 or H_2SO_4 . Obtained europium nitrate was dried and its appropriate amount dissolved in ethanol (spectroscopic grade) and europium sulphate was dried and dissolved in water (doubly distilled).

Synthesis of Eu(III) complex with coumarin-3-carboxylic acid.

The complex was synthesized by reaction of the Eu (III) salt, $\text{Eu}(\text{NO}_3)_3$, with coumarin-3-carboxylic acid (Merck, Figure 1) in a 1:2 metal to ligand molar ratio. The complex was prepared by adding ethanol solution of $\text{Eu}(\text{NO}_3)_3$ into ethanol solution of the ligand. The reaction mixture was stirred for 2 hours at room temperature. The precipitate was filtered, washed four times with ethanol, and dried in a desiccator to constant weight. The obtained Eu/C3CA complex was very limited soluble in water and ethanol ($<10^{-4} \text{ mol} \times \text{dm}^3$).

2.2. Methods

The carbon, hydrogen, and nitrogen content of the compounds were determined by elemental analysis on an elemental analyser model VARIO ELIII. The IR spectra ($4000\text{--}400 \text{ cm}^{-1}$) were obtained by means of an FTIR Bruker IFS 113v spectrophotometer (resolution 1 cm^{-1}), and the samples ($\sim 2 \text{ mg}$) were prepared in KBr. The water content was determined by luminescence lifetime measurement of the solid complex and was confirmed by TGA.

The luminescence lifetime measurements were carried out using the detection system consisting of a nitrogen laser (KB6211) and a tuneable dye laser [16].

The fluorescence spectra were recorded using a Perkin-Elmer MP3 and Aminco Bowman AB2 spectrofluorimeters.

ECL measurements were carried out using the experimental setup described recently [14]. Detection of the emitting light was possible through the use of a spectrometer Triax 180 (Horiba Jobin YVON GmbH, Germany) and a

photon-counting head Hamamatsu H4730-01. The spectrometer allows for spectral recording in the range of $200\text{--}800 \text{ nm}$ with a step of 0.15 nm . The spectrometer control is executed using a built-in digital controller. This controller enables one to operate the position of a diffraction grating and the width of the entrance and exit slits by controlling of the respective stepping motors. It also allows for sharp tuning of an emission wavelength and its change during measurements. The detection module of this system also allows the measurements of ultra weak emission (chemi- and electrochemiluminescence) spectra with a standard resolution of a moderate quality spectrofluorimeter. The recording module of this equipment consists of a photon-counting head Hamamatsu H4730-01 and a scalar cart attached to a PC. The ECL spectra, because of their weak emission, were recorded using the method of cut-off filters [17]. The ECL measurements were made in a double electrode system: $\text{Al}/\text{Al}_2\text{O}_3$ as the working electrode and a Pt-wire as the counter electrode, in aqueous solution. The aluminium plate electrode ($5 \text{ mm} \times 25 \text{ mm} \times 1 \text{ mm}$) was covered with a natural oxide film (ca. 2 nm thick) and was made of an aluminium stripe (99.999%, Merck). The platinum anode was made of a Pt-wire (1.5 mm diameter). The ECL measurements were recorded with the use of the earlier described equipment [14].

3. RESULTS AND DISCUSSION

Characterization of the Eu (III) complex with coumarin-3-carboxylic acid.

The elemental analysis of the Eu/C3CA compound showed the following data: C = 39.07%; H = 2.14%; N = 2.16%, which are in a very good agreement with the calculated values, C = 38, 23%; H = 2.25%; N = 2.24%, for $\text{Eu}(\text{C3CA})_2(\text{NO}_3)(\text{H}_2\text{O})_2$, $\text{EuC}_{20}\text{H}_{14}\text{NO}_{13}$. The formation of this Eu (III) complex was also confirmed by IR spectroscopy (see Figure 2) and luminescence of lifetime measurement.

3.1. FTIR spectra analysis

Detailed analysis of vibrational frequencies, the IR spectra of the HC3CA ligand and its Eu (III) complex, showed a very good agreement with the literature data [8] and gave evidence for bidentate coordination of C3CA ligand to Eu (III) ions through the carbonylic oxygen and the carboxylic oxygen. The bands in the $3580\text{--}3440 \text{ cm}^{-1}$ range are observed in the Eu/C3CA complex IR spectrum due to the $\nu(\text{OH})$ modes of the coordinated water molecules, while the broad band at $\sim 3180 \text{ cm}^{-1}$ in the IR spectrum of the ligand is assigned to the $\nu(\text{OH})$ vibrational mode. This band is not observed in the spectra of the complexes, indicating that the deprotonated ligand form participates in the complexes.

The following bands, observed in the IR spectra of the Eu/C3CA complex, are assigned to the vibrational modes of the NO_3 group: 1260 cm^{-1} for $\nu(\text{NO})_{\text{bonded}}$; 790 cm^{-1} and 725 cm^{-1} for $\delta(\text{ONO})$. These bands indicate the presence of the nitrate group in the Eu/C3CA complex molecule. On the basis of the above detailed vibrational study, we

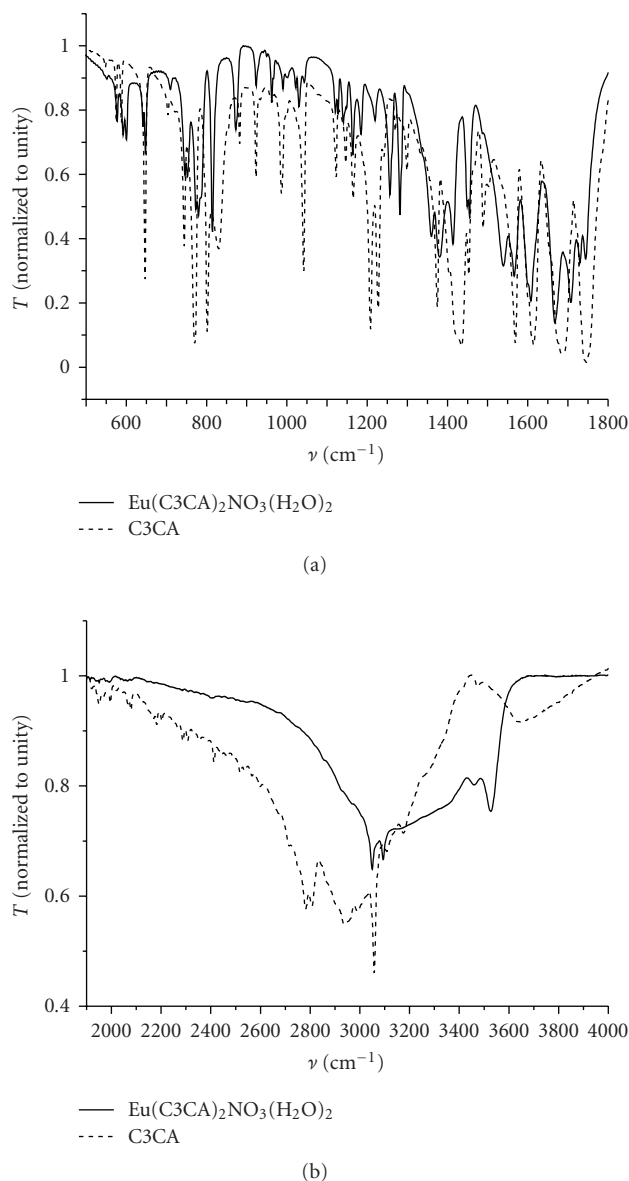


FIGURE 2: FTIR spectra of the C3CA ligand and $\text{Eu}(\text{C3CA})_2(\text{NO}_3)(\text{H}_2\text{O})_2$ complex recorded in the range of 500–1800 cm⁻¹ (a) and 2000 and 4000 cm⁻¹ (b).

can conclude that the metal-ligand bonding in Eu(III) complexes of coumarin-3-carboxylic acid appeared to be strongly ionic with very small donor-acceptor character, which is in agreement with the previously reported data for the Gd (III), Sm (III), and Dy (III) complexes with the C3CA ligand [11].

3.2. Luminescence and electrochemiluminescence studies

The Eu(III) luminescence lifetime measured as 411 ± 6 microseconds (average of 6 measurements) for the solid Eu/C3CA complex was used to calculate the number of water

molecules, bond in the inner sphere of the Eu(III) ion, from the equation below [18]:

$$n_{\text{H}_2\text{O}} = 1.05 \times \tau^{-1} - 0.7. \quad (1)$$

The decay rate ($k = 1/\tau$, τ in milliseconds) of the $5\text{D}_0 \rightarrow 7\text{F}_j$ emission is proportional to the number of aqua ligands, coordinating the Eu(III) ion, due to the vibronic coupling of the 5D_0 excited state with vibrational states of the high frequency OH oscillators of the aqua ligands. The calculated $n_{\text{H}_2\text{O}}$ based on the value of τ (0.411 millisecond) measured for the Eu/C3CA complex indicates the presence of two water molecules in the Eu(III) inner coordination sphere. This hydration number ($n_{\text{H}_2\text{O}} \approx 2$) confirms the formula $\text{Eu}(\text{C3CA})_2(\text{NO}_3)(\text{H}_2\text{O})_2$ of the complex-formed Eu(III) with coumarin-3-carboxylic acid ligand. The studied complex $\text{Eu}(\text{C3CA})_2(\text{NO}_3)(\text{H}_2\text{O})_2$ is weakly soluble in water and alcohol ($< 10^{-4}$ mol/dm³ in water).

The electrochemiluminescence of the europium(III) ion is the least known among the lanthanide series [13, 19]. Studies being done so far, considering europium chelates with the use of cathodic-generated ECL in aqueous solution, indicate two possible mechanisms of excitation of the Eu(III) ions: (1) in the process of energy transfer from electrochemically excited ligand the Eu(III) ion, or (2) in the electroreduction process of Eu^{3+} to Eu^{2+} following its oxidation with the use of a strong radical oxidizer generated as a result of decomposition of a coreactant (e.g., $\text{S}_2\text{O}_8^{2-}$). It has been previously shown that this oxidizing excitation process of Eu(II) occurs mainly in chemiluminescence systems [20, 21].

Luminescence excitation and emission spectra of the solid $\text{Eu}(\text{C3CA})_2(\text{NO}_3)(\text{H}_2\text{O})_2$ complex are presented in Figure 3. These photoluminescence studies show that the emission spectrum of the complex ($\lambda_{\text{ex}} = 370$ nm) exhibits typical narrow sharp emission bands corresponding to the characteristic $5\text{D}_0 \rightarrow 7\text{F}_j$ transition of Eu(III) ion with the strongest emission band of the characteristic $5\text{D}_0 \rightarrow 7\text{F}_2$ transition of the Eu(III) ion at 615 nm. This observation confirms the crucial role of the C3CA ligand in the transfer of the absorbed energy to the central ion of the complex.

In order to find optimal conditions for the ECL process, we studied the dependence of pH on the photoluminescence (PL) intensity of Eu(III) in the solution of Eu/C3CA complex. As shown in Figure 4, the PL intensity of Eu(III) in the complex solution considerably decreases above the value of pH > 5 with a simultaneous change of the intensity ratio of the bands $5\text{D}_0 \rightarrow 7\text{F}_1$ and $5\text{D}_0 \rightarrow 7\text{F}_2$. The observed changes, especially in the range of pH > 6, indicate ligand replacements in the inner coordination sphere of the Eu(III) ion, due to progressive hydrolysis occurring in the aqueous solution of the complex.

The ECL studies of systems containing the Eu(III) ion, both in the complex with C3CA ligand and uncomplexed (as $\text{Eu}_2(\text{SO}_4)_3$), were investigated.

The quantum yield of the ECL ultraweak emission is assessed (as $\sim 5 \times 10^{-8}$, for $\text{Eu}_2(\text{SO}_4)_3$). The quantum yield of this ultraweak emission is given as the ratio of the number of electric charges introduced into the system, resulting of ECL process, to the number of photons generated in the

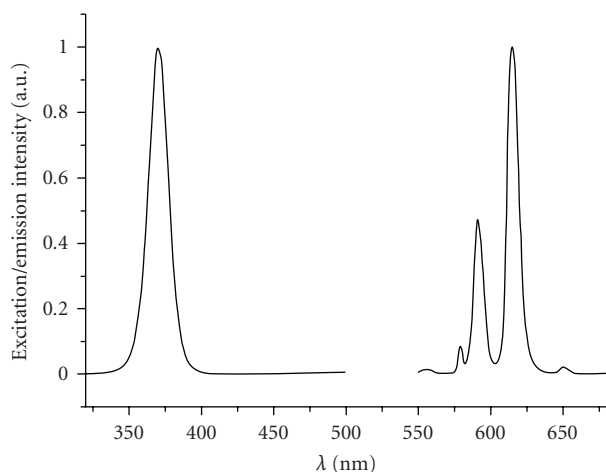


FIGURE 3: Normalized excitation and emission spectra of solid state of $\text{Eu}(\text{C3CA})_2(\text{NO}_3)(\text{H}_2\text{O})_2$ complex ($5 \times 10^{-5} \text{ mol} \times \text{dm}^{-3}$), $\lambda_{\text{exc}} = 365 \text{ nm}$.

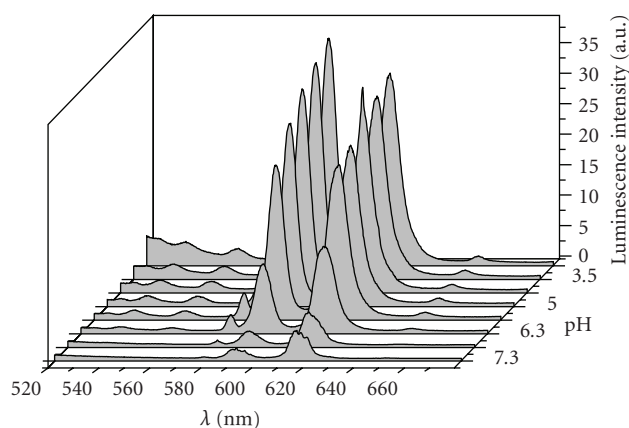
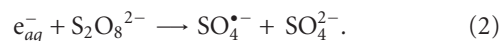
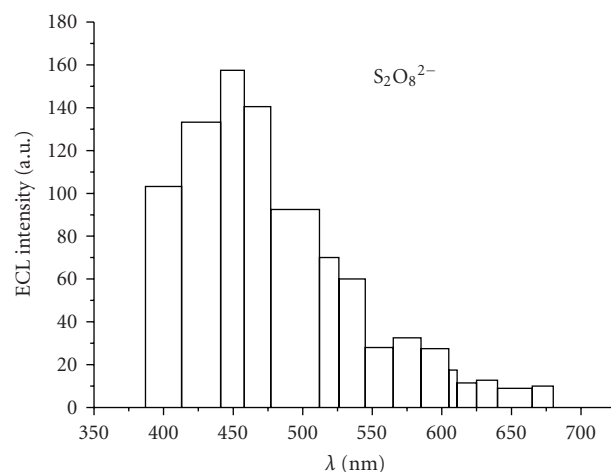


FIGURE 4: Photoluminescence spectrum of aqueous solution of ($5 \times 10^{-5} \text{ mol} \times \text{dm}^{-3}$), $\lambda_{\text{exc}} = 355 \text{ nm}$ as a function of pH.

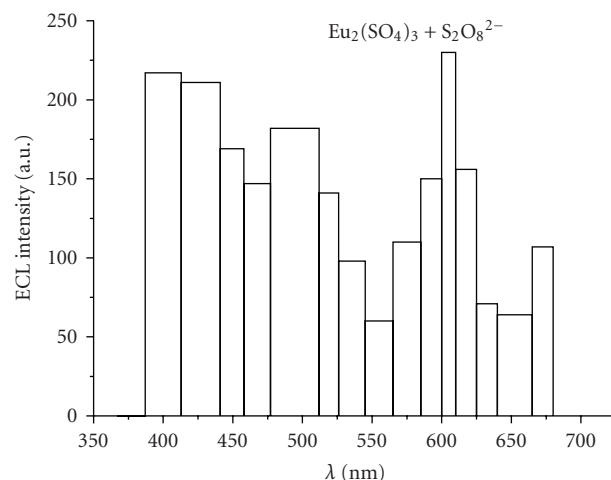
process, in the same geometrical conditions. The excitation mechanism of the coumarin 3-carboxylic acid molecules via the ECL method involves emission of “hot” electrons from the electrode into the Eu(III) complex. This assists in the formation of active radicals on the electrode surface in solutions containing peroxodisulfate $\text{S}_2\text{O}_8^{2-}$ ions, as a coreactant, which can be easily decomposed in the following reaction:



Under air-saturated solutions, and due to oxygen evolution at the counter electrode, oxyradicals and hydrogen peroxide can be formed, if hydrated electrons are produced at the working electrode [13]. The ECL spectra were recorded in aqueous solution containing: only the coreactant $\text{K}_2\text{S}_2\text{O}_8$ (Figure 5(a)), and $\text{Eu}_2(\text{SO}_4)_3$ (as uncomplexed Eu(III)) plus the coreactant $\text{K}_2\text{S}_2\text{O}_8$ (see Figure 5(b)). The ECL spectra



(a)



(b)

FIGURE 5: ECL spectra of system containing $\text{K}_2\text{S}_2\text{O}_8$ ($2 \times 10^{-2} \text{ mol} \times \text{dm}^{-3}$). (a) and $\text{K}_2\text{S}_2\text{O}_8 + \text{Eu}_2(\text{SO}_4)_3$ ($5 \times 10^{-2} \text{ mol} \times \text{dm}^{-3}$). (b) Experimental conditions: $\text{Al}/\text{Al}_2\text{O}_3$ as a working electrode, Pt wire as a counter electrode, applied pulse voltage -50 V , frequency 40 Hz , pulse charge $30 \mu\text{C}$, pH of solution 4.5 .

and spectral analysis, due to a very weak ECL intensity observed in the studied system, were complete using the method of cut-off filters [17].

In the case of ECL, spectrum recorded for the coreactant ($\text{K}_2\text{S}_2\text{O}_8$) predominates a band with maximum at $\sim 450 \text{ nm}$, corresponding to radiative relaxation from the ^3P excited state to the ^1S ground state of the active F-center in Al_2O_3 [22]. The ECL spectrum containing additionally the Eu(III) ions exhibits characteristic emission in the region around 600 nm . The ECL spectrum characteristic for Eu(III), generated in the system without an organic ligand, shows that Eu(III) can be excited by the reduction-oxidation process. The Eu(III) ions are easily reduced to Eu(II) (E_0 for $\text{Eu}(\text{III})/\text{Eu}(\text{II}) = -0.35 \text{ V}$) and then are oxidized by sulfate

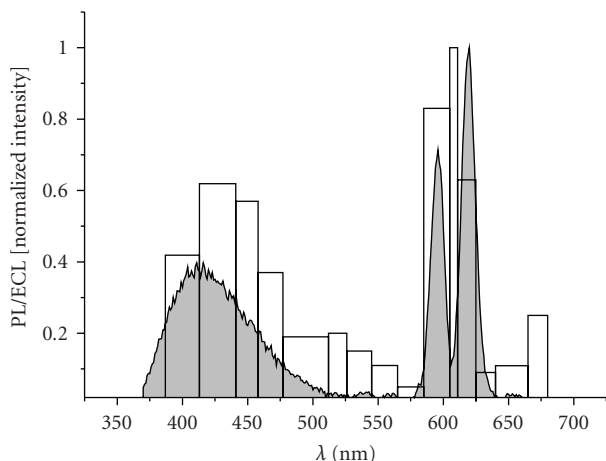
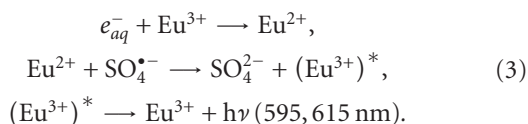


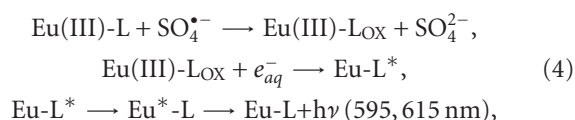
FIGURE 6: Photoluminescence ($\lambda_{\text{exc}} = 355 \text{ nm}$) and electrochemiluminescence spectra of $\text{Eu}(\text{C3CA})_2(\text{NO}_3)(\text{H}_2\text{O})_2$ complex in aqueous solution. Experimental conditions: $\text{Al}/\text{Al}_2\text{O}_3$ as a working electrode, Pt wire as a counter electrode, applied pulse voltage -50 V , frequency 40 Hz , pulse charge $30 \mu\text{C}$, pH of solution 4.5 , concentration of the complex $5 \times 10^{-5} \text{ mol} \times \text{dm}^{-3}$.

and hydroxyl radicals present in solution leading to $\text{Eu}(\text{III})$ excitation

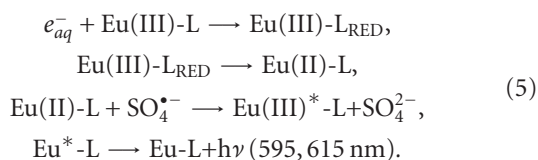


The ECL spectrum of the $\text{Eu}(\text{C3CA})_2(\text{NO}_3)(\text{H}_2\text{O})_2$ complex shows, additionally to the characteristic emission of $\text{Eu}(\text{III})$, also a broad emission band in the range of $370\text{--}500 \text{ nm}$, corresponding to radiative transitions in the ligand molecule (see Figure 6). In the case of complexes containing phenyl group(s), the radical excitation of the aromatic ring can be accomplished on the way of redox reactions. Therefore, the studied system consisting of $\text{Eu}(\text{C3CA})_2(\text{NO}_3)(\text{H}_2\text{O})_2$ complex and $\text{S}_2\text{O}_8^{2-}$ the central ion can be potentially excited according to two ways:

(I) as a result of energy transfer from the excited state (singlet or triplet) of the ligand to the $\text{Eu}(\text{III})$ ion:



(II) on the way of reduction and oxidation of the complexed $\text{Eu}(\text{III})$:



The ECL intensity ($\lambda = 615 \text{ nm}$) observed in the system containing the complex studied is over one order of magnitude higher than in that with the uncomplexed $\text{Eu}(\text{III})$ ions. This observation proves the predominate role of the ligand to metal energy transfer on the total efficiency of the electrochemiluminescence.

4. CONCLUSIONS

$\text{Eu}(\text{III})$ forms with the ligand of coumarin-3-carboxylic acid (C3CA) the complex of composition $\text{Eu}(\text{C3CA})_2(\text{NO}_3)(\text{H}_2\text{O})_2$. This complex is one of a few examples in which ECL characteristic for the $\text{Eu}(\text{III})$ ion can be observed [13, 15, 19]. The mechanism of excitation of the central ion can be completed as a result of energy transfer from the excited state of the ligand to the $\text{Eu}(\text{III})$ ion (LMET), which is predominant, and on the way of reduction and oxidation reactions of the complexed $\text{Eu}(\text{III})$ ion. The observed ECL in this system is utraweak, due to a very limited solubility of C3CA, and therefore can be detected with the use of a single photon counting method. Coumarin derivatives having important biological activities, of better than C3CA solubility in aqueous solution should exhibit more intensive ECL. This ECL generated with the participation of the LMET, can be potentially used in analytical applications of biologically active agents, for example, in pharmaceutical preparations, as we recently have shown using the chemically generated emission for the determination of tetracycline derivatives [23].

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