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Review

Chemiluminescence of systems containing lanthanide ions

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Abstract

A review of the chemiluminescent reactions in the systems containing lanthanide ions as emitters and different chemical compounds is presented. The systems in which lanthanide ions enhance the chemiluminescence intensity, thanks to the energy transfer processes, as well as the systems in which redox reactions involving lanthanide ions cause chemiluminescence and the systems showing electrogenerated luminescence and lyoluminescence are discussed. ©2000 Elsevier Science S.A. All rights reserved.

Keywords: Chemiluminescence; Electroluminescence; Energy transfer; Lanthanide complexes; Lyoluminescence

1. Introduction

The method of chemiluminescence (CL) has been increasingly used in the studies of kinetics and mechanisms of different reactions as well as in qualitative and quantitative analyses of various systems, including biological ones. The method relying on the effects related to the chemical reaction only, i.e. without the need of external energy supply, has been found to be more advantageous than other luminescence methods. It is characterised by high sensitivity, a large dynamic range of concentrations of the substances determined, minimum background, no disturbances and light scattering, reproducibility and the possibility of simple and quick analysis [1–5].

The lanthanide ions, thanks to their spectroscopic properties and the ability to react with many biologically active compounds (in which they replace the cations of Ca, Zn, Mg and Fe), have been widely used as structural and analytical luminescent probes providing information on these materials and the biochemical processes occurring therein [6,7]. The combination of the advantages of the method of chemiluminescence with the use of lanthanide ions as luminescent probes offers new possibilities in investigation of the reaction mechanism and provides information on the spectral and structural properties of organic compounds in systems with lanthanide ions, mainly Eu(III).

This review is concerned with the following CL-systems in which lanthanide ions act as emitters:

1. systems in which lanthanide ions enhance the CL intensity due to the energy transfer processes (Fig. 1);
2. systems in which redox reactions involving lanthanide ions bring about CL; and
3. systems showing electrogenerated luminescence and lyoluminescence.

The inclusion of the latter phenomena is based on the fact that in chemiluminescence (emission of light as the result of chemical reaction), electroluminescence (light emission as the result of electrolysis of a solution) and lyoluminescence (light emission as the result of dissolution of a solid), the excitation occurs as a result of intermolecular energy transfer or electron transfer in homogeneous solution or at a solid/solution interface containing energetic intermediates.

2. Chemiluminescence sensitized by lanthanide ions

The β-diketonates of Eu(III) and Tb(III) are effective activators of the CL of 1,2-dioxetanes (four-membered cyclic peroxides) whose thermal decomposition leads to the formation of triplet-excited carbonyl compounds at a high yield (~30%). In the presence of coordinatively saturated Eu(III) chelates, such as europium tris(thenoyltrifluoroacetonate)-1,10-phenanthroline, a narrow and highly intense CL band at 613 nm is observed. The excitation of europium takes place through the intermolec-

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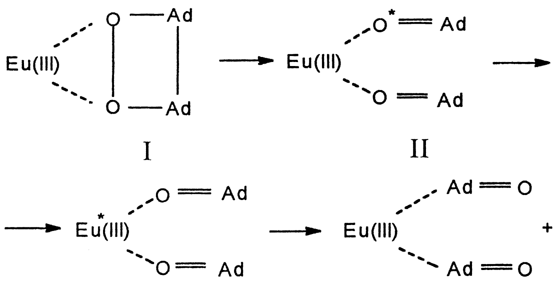
ular energy transfer triplet–triplet from the excited product of dioxetane decomposition to the ligand (in complex with Eu) and then an intramolecular energy transfer to Eu(III) [8]. The coordinatively unsaturated lanthanide chelates, such as Eu(fod)$_3$ (fod = heptafluorodimethyloctanedione), additionally catalyse the peroxide decomposition through weakening of the O–O bond as a result of the complex formation with chelate [9–12].

Many works are concerned with CL appearing during thermal decomposition of dispiro(adamantane-2,3′-1′,2′-dioxetane-4′,2″)(**I**) in the presence of lanthanides (Ln). In the presence of terbium nitrate the energy is transferred from the excited adamantanone (**II**) (a product of the decomposition of **I**) to a Tb(III) ion, while in the presence of Eu(fod)$_3$ — the energy is transferred with simultaneous acceleration (100 times) of the reaction of excited adamantanone formation [10]. Apart from Eu(fod)$_3$, Eu(dpm)$_3$, Eu(TTA)$_3$ and Eu(acac)$_3$ chelates (dpm = dipivaloylmethane; TTA = thenoyltrifluoroacetone; acac = acetylacetone) also catalyse the decomposition of dioxetane to adamantanone in *o*-xylene solution. Besides the bands attributed to the $^5D_0$–^7F; transitions, the CL spectra revealed the signal ascribed to the $^5D_1$ level of Eu(III) ion, in the 535–550 nm range. The CL accompanying thermal decomposition of **I** in the presence of Eu(fod)$_3$ was found to be significantly affected by the process of complex formation with dioxetane **I** and adamantanone **II**. The stability constants for [Eu(fod)$_3$·**I**] and [Eu(fod)$_3$·**II**] complexes were determined as 18 ± 3 and 64 ± 20 l/mol, respectively, and the rate constant of [Eu(III)·**I**] decomposition (3.8×10^{-4} s^{-1}) was found from the quenching kinetic data. The emission from the $^5D_1$ level of Eu(III) ion observed in the CL spectrum was attributed to the process of direct (without ligand triplet) transfer of the excitation energy from **II*** to the luminescent Eu(III) levels in the geometrically distorted [Eu(fod)$_3$·**II**] complex. Owing to the disturbed geometry of the complex [Eu(III)·**II**] in which the geometry of the previous compound [Eu(III)·**I**] is preserved, the energy of excitation of **II** is transferred directly to the levels $^5D_1$ and $^5D_0$ of Eu(III) ion [11,12]:



Similar mechanisms are discussed in the successive works concerning the CL accompanying the decomposition of **I** in the presence of lanthanide compounds [13–23].

The complexation of excited Eu(fod)$_3$ chelate with adamantanone in *o*-xylene has been studied by kinetic luminescence spectroscopy [13]. The stability constant of the excited [Eu(III)·**II**] complex exceeds by a factor of three to that in the ground state. The high stability of the excited [Eu(III)*·**II**] complex is attributed to an increase in the acceptor ability of the Lewis Eu(fod)$_3$ acid upon its excitation. In [14], the photophysical properties of triplet excited adamantanone was studied and the yield of Eu(III) chemiexcitation in a nonequilibrium complex of adamantanone with Eu(fod)$_3$ in o-xylene was estimated ($0.015 < \phi_{\mathrm{Eu}^*} < 0.04$).This yield was found to be lower than the triplet yield upon dioxetane thermolysis. The difference between the yields is explained by a decrease in the activation energy for thermal degradation of the dioxetane in the complex.

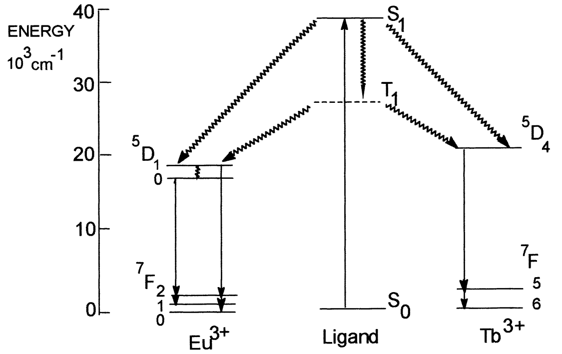


Fig. 1. Scheme of the energy transfer processes concerning the Eu(III) and Tb(III) ions.

CL accompanying the decomposition of **I** in acetonitrile solutions of Eu(III), Gd(III), Tb(III), Pr(III) and Ce(III) perchlorates was studied [15,16]. In the presence of Eu(III), Tb(III) and Pr(III) ions, the CL spectra showed the luminescence bands characteristic of these ions. In the case of Gd(III) and Ce(III), the CL is caused by deactivation of singlet-excited adamantanone **II**. The excitation of the lanthanide depends on the existence of a suitable energy level at which the intracomplex excitation transfer from the $^3n, \Pi^*$-state of the ketone is possible. The yields of CL and excitation of lanthanide ions in the decomposition of **I** in the [**I**·Eu(III)] and [**I**·Tb(III)] complexes were determined ($\phi_{\mathrm{Eu}^*} = 0.013, \phi_{\mathrm{Tb}^*} = 0.08$). The fact that the efficiency for the population of the $^5D_4$ level of Tb(III) was higher than those for the $^5D_1$- and $^5D_0$-levels of Eu(III) is related to the difference in the energy gap between the triplet level of **II** and the excited levels of the lanthanides [15] (see Fig. 1). The stability constants of the [**I**·Ln(III)] complexes and the thermodynamic parameters of the complex formation as well as the rate constants of the **I** decomposition in complexes [**I**·Ln(III)] were determined. It was established that the value of rate constant of the **I** decomposition increased with increasing value of the [**I**·Ln(III)] complex stability constant. Higher values of the complex stability constants among the lanthanides investigated point to a more stable coordination bonding between Ln(III) and the peroxide, resulting in a weakening of the O–O bond in dioxetane. The values of the stability constant, entropy and enthalpy of the complex formation increase with decreasing Ln(III) ionic radius ($K_{[\mathbf{I}\cdot\mathrm{Ce(III)}]} = 5.5\,\mathrm{l\,mol^{-1}}$, $K_{[\mathbf{I}\cdot\mathrm{Tb(III)}]} = 11.6\,\mathrm{l\,mol^{-1}}$) [16].

CL and catalysis of decomposition of **I** in the presence of Eu(III) and Tb(III) tris(benzoyltrifluoroacetonate) (btfa) complexes in toluene were investigated. The thermodynamic parameters of complex formation, stability constants of the complexes [**I**·Ln(btfa)$_3$] and yields of excitation of Ln(btfa)$_3$ chelates ($\phi_{\mathrm{Eu}^*} = 0.021, \phi_{\mathrm{Tb}^*} = 0.12$) were estimated. A higher efficiency of population of the $^5D_4$ -level of Tb(III) than that of $^5D_1$- and $^5D_0$ -levels of Eu(III) follows from different efficiency of nonradiative dissipation energy in Ln(III) ions after intracomplex energy transfer from ^3n, Π^*-state of **II** to the resonance excited levels of the lanthanides [17].

CL of Pr(III) (in visible and infrared regions) upon decomposition of **I** catalysed by β-diketonates PrL$_3$ (L = fod or dpm) in toluene were also observed. In the case of Pr(fod)$_3$, the efficiency of excitation was estimated to be $\phi_{\mathrm{Pr}^*} \leq 10\%$. The branched quantum chain reaction was observed on thermal decomposition of **I** in the presence of an excess amount of Pr(fod)$_3$. Branching of the chain may be realized through the quenching of Pr(fod)$_3$*, where Pr(III) is in the $^3P_0$ or $^3P_1$-excited states by the [**I**·Pr(fod)$_3$] complex with the preservation of excitation energy of Pr(III) in the lower lying $^1D_2$-state. Energy transfer on the [**I**·Pr(fod)$_3$] complex results in the decomposition of **I** with excitation of Pr(III) into $^3P_1$, $^3P_0$ or $^1D_2$ states [18,19].

The Eu(fod)$_3$ activated CL upon degradation of **I** sorbed on Silipore was studied and compared with CL in solution [20,21]. The reactions of thermolysis of **I** on Silipore in the presence of Eu(fod)$_3$ as well as the CL spectrum and mechanism were found in the same way as those in solution. However, in solution the CL intensity increases proportionally to Eu(fod)$_3$ concentration, while the dependence of CL intensity on Eu(fod)$_3$ content on Silipore is described by the exponential function. The observed concentration dependence of CL intensity is explained by the branched quantum-chain process in the dioxetane-Eu(fod)$_3$ system. The interaction of Eu*(fod)$_3$ in its $^5D_1$ state with the complex [dioxetane·Eu(III)] with retention of excitation in the $^5D_0$ state and formation of another excited Eu(fod)$_3$ molecule is a key step in the quantum-chain reaction.

CL accompanying the impact of the mechanical effect on solid particles of the complex of Eu(fod)$_3$ with **I** was detected and studied. The CL has a complex structure and its spectrum is attributed to excited Eu(III) ions. Light emission was observed only for a mechanical mixture of Eu(fod)$_3$ complex with **I** and their co-crystallised form while it was absent for the separate components. Analysis of the mechanism of CL caused by the mechanical impact revealed that the CL was not triboluminescence, but was induced by decomposition of dioxetane **I** [22].

CL in near IR region upon thermolysis of melts consisting of Nd(III) or Yb(III) perchlorates and **I** was first observed. The CL spectra correspond to the $^4F_{3/2}$–$^4I_{9/2}$ and $^4F_{3/2}$–$^4I_{11/2}$ transitions in Nd(III) and $^2F_{5/2}$–$^2F_{7/2}$ transition in Yb(III) [23].

The CL activated by lanthanide ions in biochemical systems was analysed. The intensity of CL appearing as a result of peroxide oxidation of the lipids of biomembranes (liposome suspension) was observed to increase in the presence of Tb(III) ions or the complex of Eu(III) with tetracycline and the CL spectrum showed the bands characteristic of Tb(III) ($^5D_4$–$^7F_5$) or Eu(III) ($^5D_0$–$^7F_2$) interpreted as the result of energy transfer from primary emitters to Ln(III) ions [24,25]. The process of energy transfer to Tb(III) ions as well as Dy(III) ions was also observed during the chemiluminescent reaction of histamine oxidation by potassium bromate in the presence of these ions [26].

CL appearing during oxidation of hydrazine by hypochlorite in the presence of europium tris(thenoyltrifluoroacetonate)(T) chelate was studied. The chemical excitation in this system (at a quantum yield about 7%) was found to be the result of the three-molecular thermal reaction:

$$\mathrm{EuT_2[N_2H_4]} + 2\mathrm{ClO^-} \rightarrow \mathrm{EuT_2[^3N_2{}^*]},$$

followed by the energy transfer from the excited nitrogen in the triplet state to the triplet level of the ligand and light emission from Eu(III) [27].

The CL reactions of Ce(IV) ions with drugs containing a thiol-group, sensitized by fluorescent dyes are also known. They have been used for determination of these drugs in combination with the flow-injection method [28,29]. The mechanism of these reactions is as follows: the oxidation of the drug (e.g. captopril, hydrochlorothiazine) by Ce(IV) ions leads to the appearance of excited Ce(III) ions, from them the energy is transferred to the dye present in the solution (e.g. rhodamine B, rhodamine 6G) which emits CL.

3. Chemiluminescence in redox reactions of the lanthanides

In 1983, a series of studies on CL emitted during oxidation of Eu(II) ions in complexes with organic ligands by hydrogen peroxide was begun. This reaction, involving radicals, leads to the appearance of excited Eu(III) ions [30]:

$$\mathrm{Eu(II)} + \mathrm{H_2O_2} \rightarrow \mathrm{Eu(III)} + \mathrm{HO^-} + \mathrm{HO^\bullet}$$

$$\mathrm{HO^\bullet} + \mathrm{Eu(II)} \rightarrow \mathrm{Eu(III)^*} + \mathrm{HO^-}$$

$$\mathrm{Eu(III)^*} \rightarrow \mathrm{Eu(III)} + h\nu$$

The emission observed is a result of the energy transition from $^5D_0$ to $^7F_1$ and $^7F_2$ levels of Eu(III) and its intensity significantly increases after complexation of Eu(II) ions and depends on pH of the solution and concentration of H_2O_2.

The study of CL emitted from the systems Eu(II)/Eu(III) — adenine nucleotide — hydrogen peroxide were reported [31,32]. The integral intensity and quantum yield of CL ($\phi_{\mathrm{CL}} = 5\times10^{-12}$, 1×10^{-11} and 3×10^{-10} for uncomplexed Eu or Eu/cAMP, Eu/ADP and Eu/ATP, respectively) were found to be dependent mainly on the number of P–O-groups occurring in particular nucleotides and on the values of stability constants of the europium complexes with the nucleotides (ATP > ADP > c-AMP > AMP). Analysis of the fluorescence of the system Eu(III)-ATP indicated the intramolecular energy transfer process from ATP molecule to Eu(III) ion.

Chemiluminescence and the mechanism of its generation (using typical radical quenchers) was also studied in the systems containing europium ions, hydrogen peroxide and deoxyribonucleic acid or nicotinamide adenine dinucleotide reduced disodium salt [33,34]. The spectrum of CL shows bands attributed to Eu(III) ions ($\lambda = 590$–620 nm) and to excited molecules of singlet oxygen ($\lambda = 460$–480 and 625–640 nm), appearing as the products of simultaneous processes of hydrogen peroxide decomposition and radical recombination. The results testify to the radical character of the reaction leading to the generation of CL.

Attempts were made to use the CL-generating systems with europium ions for the characterisation of properties of human blood plasma introduced to the system. Differences in the intensity and spectral distribution of CL were noted between the systems with plasma from the patients with chronic renal failure put to hemodialysis before, and after, that procedure as well as between those samples and the samples taken from healthy people. Unfortunately, a great variety of natural components of plasma has not permitted so far to offer a complete explanation of the observed change in CL spectra. CL was also studied in the system with plasma's water (obtained by means of the dry ultrafiltration process) and the dialysate (i.e. the dialysing physiological liquid, containing mainly salts). Differences were found in the course of the kinetic CL curves for the dialysate samples taken before, and after, the contact with circulating blood of particular patients. Moreover, the influence of creatinine on the courses of CL generated in the plasma's water systems was noted [35,36]. CL characteristics of some plasma components (creatinine, creatine and urea, as well as lactic, malic and citric acids) in the presence of europium ions were analysed [37].

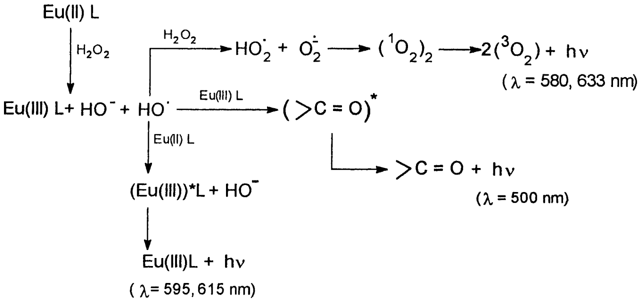
The CL-generating system of Eu(II)/Eu(III) - hydrogen peroxide was studied in the presence of N_3^- ions responsible for a considerable increase in Eu(III) emission. The excitation of Eu(III) in this system was found to occur not only as a result of the radical reaction of Eu(II) oxidation to Eu(III), but also due to the energy transfer from the singlet oxygen through the complexing N_3^- ions to the europium ions [38]. Similar phenomena and relationships were found in the systems also containing, apart from europium ions and hydrogen peroxide, aminopolycarboxylic acids (e.g. ethylenediaminetetraacetic or diethylenetriaminepentaacetic or ethyleneglycol-bis(2-aminoethyl)tetraacetic acid). It was established that in all systems studied the only emitters were europium ions, and the long duration of CL was related to the process of energy transfer from the dimols of singlet oxygen to Eu(III) ions through the mediation of the complexing aminopolycarboxylic acids. The mechanism of CL did not depend on the kind of the aminopolycarboxylate ligand, but the intensity of emission did [39,40]. The scheme of the reaction mechanism is as follows:

$$({}^1O_2)_2 + [\mathrm{Eu(III)L}]^{n-} \rightarrow [\mathrm{Eu(III)L}]^{n-} \cdots ({}^1O_2)_2 \rightarrow$$

$$\begin{array}{c} \rightarrow [\mathrm{Eu(III)^*L}]^{n-} + 2\,{}^3O_2 \\ \downarrow \\ h\nu\ (600\ \mathrm{nm}) \end{array}$$

where $L = N_3$ or aminopolycarboxylic acid.

The introduction of coronands (1,4,10,13-tetraoxa-7,16-diazacyclooctadecane or 1,4,10-trioxa-7,13-diazacyclo pentadecane or 1,4,7,10-tetraoxa-13-azacyclopentadecane or 1,4,7,10,13-pentaoxa-16-azacyclooctadecane) to the above-described CL-generating system resulted in the process in which three kinds of CL-emitters were distinguish: excited Eu(III) ion responsible for the emission at 615 nm; dimers of singlet oxygen responsible for emission at 580 and 633 nm; and excited carbonyl fragments emitting in the 450–500 nm range [41]:



The intensity and shape of the emission decay as well as the spectral distribution of CL were found to depend on the number of nitrogen atoms in the ring of the macrocycle and the size match between the macrocycle cavity and the europium ions.

The cryptands 2.2.1 and 2.2.2 (4,7,13,16,21-pentaoxa-1,10-diazabicyclo[8.8.5]tricosane and 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane, respectively) introduced into the CL-generating system stabilise the Eu(II) ions. The complexation of Eu(II) inside the three-dimensional cavity of the cryptand causes the elongation of the CL duration and a decrease in the CL intensity when compared with that in the systems with coronands, which is accounted for by a slowing down of the process of Eu(II) oxidation to Eu(III). The duration of CL generated by these systems depends on the stabilisation of Eu(II) by the cryptands and the stability of the macrocyclic complex formed with these ions [42].

Other examples of CL-generating redox reactions leading to the emission from the lanthanide have been also described. The CL characteristic of Yb(III) is observed as the result of the reaction between tetrahydrofuran adducts of pentamethylcyclopentadienylytterbium with O_2 and O_2^- [43]. Emission from Eu(III) and Sm(III) is generated by the oxidation reaction of cyclopentadienyleuropium(II) and cyclopentadienylsamarium(II) by oxygen and the reactions of cyclopentadienyleuropium(III) and cyclopentadienylsamarium(III) and their peroxides with water [44]. CL-generation was also described in the reactions of reduction of Tb(IV) and Pr(IV) in water solutions of isopoly- and heteropolytungstates $Na_5HW_6O_{21}$, $K_8SiW_{11}O_{39}$, $K_7PW_{11}O_{39}$ [45], $K_{10}P_2W_{17}O_{61}$ [46] and in the reaction of dissolving double lithium and terbium(IV) oxide in acids [47], where the emitters were Ln(III) ions. CL was, moreover, observed in the reduction of xenone trioxide with Eu(II) ions in aqueous $HClO_4$ solution, but then europium ions are not the sources of emission [48].

4. Electrogenerated luminescence and lyoluminescence with the lanthanides

As a result of the electrogenerated reaction of tri-*p*-tolylamine radical cation ($D^{\bullet+}$) and benzophenone (or dibenzoylmethane) radical anion ($A^{\bullet-}$) only the exciplex $^1(A^-D^+)^*$ emission is observed (broad band with a maximum at 581 nm). After addition of the europium chelates (EuL_3) with dibenzoylmethide and piperidine or dinaphtoylmethide and piperidine to these systems, the characteristic emission of Eu(III) (narrow band at 612 nm) appears. This emission is a result of energy transfer from the exciplex (excited charge-transfer complex) directly to an europium chelate [49]:

$$^1(A^-D^+)^* + EuL_3 \rightarrow A + D + EuL_3{}^*$$

$$EuL_3{}^* \rightarrow EL_3 + h\nu$$

Electrolysis of an aqueous electrolyte containing nitrate and europium(III) at the oxide-covered aluminium electrode produces surface-bound Eu(III) in the excited- level $^5D_0$ which, on return to the ground level, generates emission from the Eu(III) ions. This cathodic europium(III) electroluminescence is highly sensitive to Eu(III) ion concentration (down to 10^{-8} M) [50].

Generation of highly intense cathodic Tb(III) electrogenerated luminescence at an oxide-covered aluminium electrode in aqueous electrolytes additionally containing potassium peroxydisulphate or hydrogen peroxide was demonstrated. Electrochemical excitation of Tb(III) is a multi-step process comprising adsorption of Tb(III) on the oxide-covered aluminium electrode, formation of the sulphate monoanion and hydroxyl radicals and generation of Tb(III) emission. In the last step, sulphate monoanion and hydroxyl radicals oxidise the oxide-bound Tb(III) to oxide-bound Tb(IV) which is highly unstable under these conditions and is immediately reduced to oxide-bound Tb(III). This reduction process is energetically enough to produce the excited terbium(III), whose emission allows to determine the Tb(III) ions at levels $\geq 10^{-8}$ M [51].

In [52] the mechanism of electrogenerated luminescence of Tb(III) — {2,6-bis[*N*,*N*-bis(carboxymethyl)aminomethyl]-4-benzoylphenol} (L) chelate is presented. Generation of hydrated electrons at an oxide-covered aluminium electrode may be the primary step of the electrogenerated luminescence of aromatic Tb(III) chelates. In the presence of appropriate precursors, hydrated electrons produce secondary oxidising radicals. The aromatic moiety of a Tb(III) chelate is excited by its consecutive interactions with hydrated electron and the secondary oxidising radical followed by an intramolecular transfer of this excitation energy to the $^5D_4$ level of coordinated terbium(III), leading to the $^5D_4$–^7F_j transitions. Electrogenerated luminescence of yttrium, samarium and dysprosium bonded with the same heptadentate chelating agent L, which forms stable dimer-like dinuclear chelates, has been presented in [53]. At a pulse-polarized oxide-covered aluminium cathode in the presence of peroxydisulphate, the homodinuclear L-Y-Y-L chelate generates a weak Y(III)-initiated ligand-centered emission (at 322 nm), while the homodinuclear L-Ln-Ln-L (Ln = Sm, Dy) and heterodinuclear L-Y-Ln-L chelates initiate intense ligand-sensitised Dy(III)- and Sm(III)-specific, $^4F_{9/2}$–^6H_j and $^4G_{5/2}$–^6H_j transitions, respectively.

A thin-film electroluminescent device has been prepared using a divalent europium species. This system exhibits a bright orange photoluminescence with a high quantum efficiency in the solid state. The volatility of used compound (e.g. bis[tris(dimethylpyrazolyl)borate]europium(II)) enabled to prepare multi-layer electroluminescent devices, in which the phosphor was sandwiched between an electron-transporting layer and a hole-transporting layer. Thin-film electroluminescent devices showed a visible emission comparable to the photoluminescence spectrum of pure europium complex, indicating that emission is based in the phosphor layer. The observed intense emission band at $\lambda_{max} = 596$ nm is assigned as a ligand-to-metal charge transfer (LMCT) band from low-lying ligand orbitals into the high energy f-orbitals of Eu(II). This new organolanthanide material offers promise as a volatile phosphor for thin film devices [54]. Another interesting paper is devoted to an electroluminescent device containing the Eu(II) silicate layer on the silicon substrate. This electroluminescent device exhibits the characteristics of broad spectral band, large-area uniform emission, high external quantum efficiency, fast response and low threshold. The europium silicate appears a promising candidate material for the production of flat panel displays and the optoelectronic integrated circuits on the silicon substrate [55]. Recently, an organic electroluminescence devices using a neodymium complex (tris(dibenzoylmethanato)(monobathophenanthroline)-neodymium(III)) as an emitting layer showing sharp near-infrared emission bands assigned to f-f transitions of Nd(III) ion were obtained. This system could lead to new possibilities for the realisation of the neodymium organic electroluminescence laser [56].

Lyoluminescence of terbium(III) has been observed as a result of dissolution in Tb(III)-containing aqueous solution of potassium peroxydisulphate previously irradiated by UV or X-rays. This dissolution produces a solid/solution interface rich in hydrated sulphate radicals. Pathway of this lyoluminescence consists of the following steps:

1. hydrated sulphate radical oxidizes Tb(III) to Tb(IV);
2. Tb(IV) is immediately reduced by water and this reaction is energetically enough to produce the excited Tb(III) ($^5D_4$); and
3. radiative transitions $^5D_4$–^7F_j [57].

Excitation of Tb(III) as a result of energy transfer process and $^5D_4$–^7F_j transitions has also been observed as a consequence of the dissolution of X-ray irradiated sodium chloride in aqueous solution containing the hydrated Tb(III) ions (intermolecular energy transfer) [58] or the Tb(III) chelates [59,60], as well as a dissolution of additively coloured (i.e. treated in elevated temperature and pressure with alkali metal vapour) potassium chloride in aqueous solutions of peroxydisulphate ions in the presence of the Tb(III) chelate [61]. In the last three examples, the chemical excitation of the aromatic ligand is followed by an intramolecular transfer of this excitation energy to the ($^5D_4$) state of Tb(III).

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