Monatshefte für Chemie 130, 1443–1451 (1999)

Monatshefte für Chemie
Chemical Monthly

The Influence of the Donor Atom on the Chemiluminescence of Eu(III) Ions in the System Eu(II)/(III)-Ligand-H_2O_2

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Summary. The chemiluminescence (CL) of the system Eu(II)/(III)-*L*-H_2O_2 ($L = EGTA$, *NTA*, *TETA*, *K22DA*, *MA*, *DGA*) has been studied. Kinetic curves of CL decay and CL spectral distributions were determined. Differences in CL intensity and the time of its duration allowed to draw conclusions on the influence of the donor atoms (N, O) on the intensity of the Eu(III) chemiluminescence.

Keywords. Chemiluminescence; Europium ions; Aminopolycarboxylic acid.

Einfluß des Donoratoms auf die Chemilumineszenz von Eu(III)-Ionen im System Eu(II)/(III)-Ligand-H_2O_2

Zusammenfassung. Die Chemilumineszenz (CL) im System Eu(II)/(III)-*L*-H_2O_2 ($L = EGTA$, *NTA*, *TETA*, *K22DA*, *MA*, *DGA*) wurde untersucht. Zerfallskurven der CL sowie Chemilumineszenzspektren wurden gemessen. Die Unterschiede in den CL-Intensitäten sowie den Lebensdauern erlaubt Rückschlüsse auf den Einfluß der Donoratome (N, O) auf die Intensität der CL der Eu(III)-Ionen.

Introduction

The luminescence properties of lanthanide ions *Ln*(III), in particular Eu(III), encouraged their use as luminescence [1] and chemiluminescence [2] probes in the investigation of organic compounds. The intensity of emission of the lanthanide ions strongly depends on the composition of the inner coordination sphere of the metal ion. Luminescence quenching is a result of coupling between the electron excited state of *Ln*(III) with OH oscillators from water molecules coordinated in the inner sphere [1, 3]. During complexation, water molecules are gradually replaced by molecules or ions of another ligand. The tervalent lanthanide ions form a number of complexes with cyclic as well as acyclic ligands [1, 4, 5], and their coordination involves oxygen and nitrogen atoms [1].

We were especially interested in the application of the redox system Eu(II)/(III)-H_2O_2 in connection with the investigation of organic compounds [6, 7]. In

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chemiluminescent systems containing H_2O_2 as an oxidizer, decomposition of H_2O_2 and recombination of radicals leads to the generation of singlet oxygen [8–10] whose quenching by amines involves nitrogen atoms and formation of a charge-transfer intermediate [11].

This paper reports the results of chemiluminescence and spectrophotometric studies of systems containing europium ions, hydrogen peroxide and cyclic (*TETA*, *K22DA*) or acyclic (*NTA*, *EGTA*) aminopolycarboxylic acids or dicarboxylic acids (*DGA*, *MA*). The choice of ligands enabled us to determine the influence of the donor atoms (N, O) on the chemiluminescene of Eu(III) ions.

Results and Discussion

Chemiluminescence emitted by systems containing Eu(II)/(III) ions, H_2O_2, and one of the ligands *EGTA*, *NTA*, *K22DA*, *TETA*, *DGA*, and *MA* was observed. Figures 1 and 2 show the kinetic curves of decay of the CL of these systems. Curve 1 in Figs. 1 and 2 characterizes the CL decay of the system Eu(II)/(III)-H_2O_2, which in this case is of short duration – about 7 minutes – and low intensity.

Introduction of cyclic and acyclic aminopolycarboxylic acids (*TETA*, *K22DA*, *EGTA*, *NTA*) into the systems of europium ions and H_2O_2 resulted in an increase in CL intensity and duration (up to 2 hours). For all systems with aminopolycarboxylic acid as a ligand the course of the kinetic curves of CL was similar with a maximum 3 minutes after initiation of the reaction by introducing hydrogen peroxide (Fig. 1, curves 2–4). This course of CL decay is different from that obtained for the basic system Eu(II)/(III)-H_2O_2. The highest intensity of CL was recorded for the solution with *TETA* as a ligand. For systems with *EGTA*, *K22DA*, and *NTA* (under conditions of ML_2 complex prevalence) the CL intensities are comparable (Fig. 1, curves 2, 3).

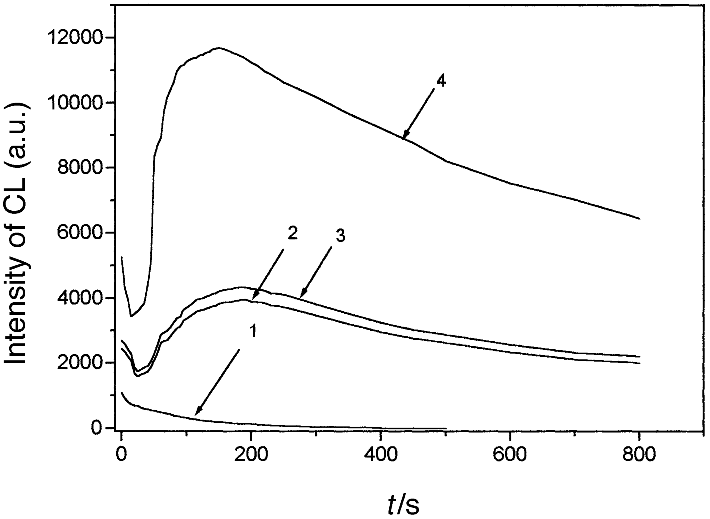


Fig. 1. Kinetic curves of CL of the systems Eu(II)/(III)-H_2O_2 (1) Eu(II)/(III)-*EGTA*-H_2O_2 (2), Eu(II)/(III)-*K22DA*-H_2O_2 (3), Eu(II)/(III)-*TETA*- H_2O_2 (4); initial concentration of Eu(II) ions: $2 \cdot 10^{-3}$ mol $\cdot$ l^{-1}, molar ratio of Eu(II):L:H_2O_2 = 1:1:1, $pH = 7.0$

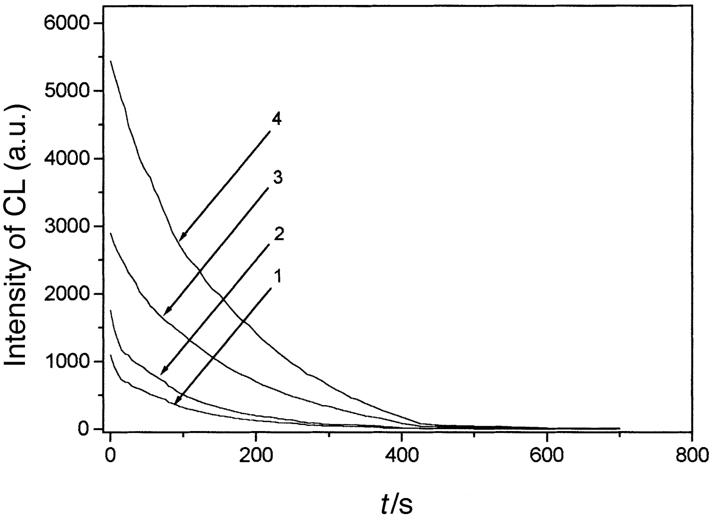


Fig. 2. Kinetic curves of CL of the systems Eu(II)/(III)-H_2O_2 (1) and Eu(II)/(III)-*DGA*-H_2O_2 for different molar ratios of metal to ligand: 1:1 (2, *ML*), 1:2 (3, ML_2), 1:4 (4, ML_3); complex forms dominant in particular solutions are given in parentheses; initial concentration of Eu(II) ions and $H_2O_2: 2 \cdot 10^{-3}\,\mathrm{mol \cdot l^{-1}}$, $pH = 7.0$

For the systems with Eu(II)/(III) ions, H_2O_2, and *DGA* or *MA*, the CL intensity was highest at the moment of the reaction initiation and then decreased. Exemplary CL kinetic curves obtained for the system Eu(II)/(III)-*DGA*-H_2O_2 are shown in Fig. 2. The presence of *DGA* and *MA* in the system Eu(II)/(III)-H_2O_2, irrespective of their concentration, was not found to affect the CL duration. In the systems Eu(II)/(III)-*DGA*-H_2O_2 and Eu(II)/(III)-*MA*-H_2O_2, chemiluminescence was recorded for about 7 minutes from the introduction of H_2O_2. For the former system the highest intensity of CL was found for a solution of the molar ratio Eu(II):*DGA* = 1:4, containing exclusively ML_3 type complexes (Fig. 2, curve 4). For the systems in which ML_2 and *ML* type complexes were dominant, the intensity of CL was lower. Moreover, for the systems with *MA* in the ML_2 and *ML* type regime the emission was similar to that obtained for the complexes of the same type with diglycolic acid.

The chemiluminescence systems of interest were also subjected to spectral analysis. Spectra of their emission were recorded after the maximum on CL decay curve, and for the systems with aminopolycarboxylic acids also 30, 60, and 90 minutes after initiation of the reaction. All spectra revealed considerable resemblance. An exemplary spectrum recorded for the system Eu(II)/(III)-*EGTA*-H_2O_2 is presented in Fig. 3.

The spectrum shows only the band characteristic of Eu(III) ions, with a maximum at about 600 nm, ascribed to the transitions $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$, proving that these ions are the only source of emission in these systems [5, 14].

All ligands used absorb far ultraviolet radiation with a maximum absorption at $\lambda \cong 210\,\mathrm{nm}$. The absorption spectrum of europium(II) chloride shows a characteristic broad band with a maximum at $\lambda = 251\,\mathrm{nm}$. With regard to the fact that the absorbance of the ligand and the complex Eu(III)-*L* at the concentrations studied

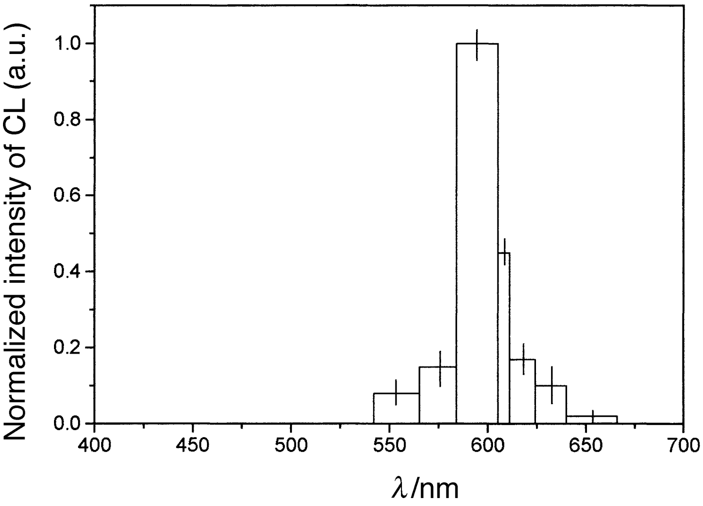


Fig. 3. Spectral distribution of CL of the system Eu(II)/(III)-*EGTA*-H_2O_2; initial concentration of Eu(II) ions and $H_2O_2: 2 \cdot 10^{-3}\,\mathrm{mol} \cdot \mathrm{l}^{-1}$, molar ratio of Eu(II) to ligand: 1:1, $pH = 7.0$

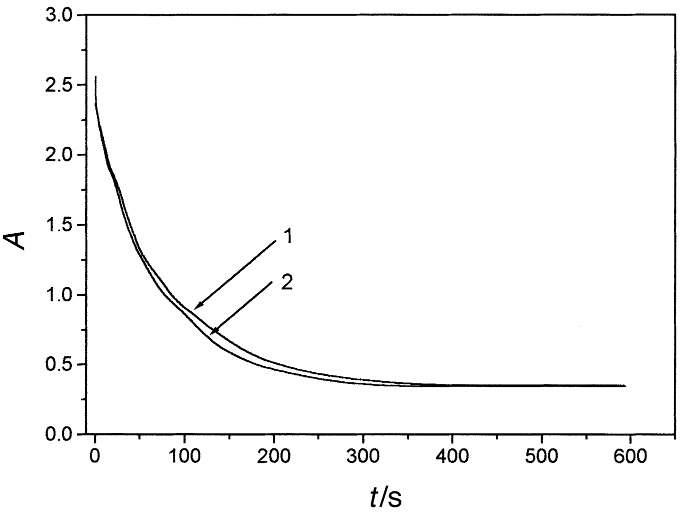


Fig. 4. Time changes in absorbance for $\lambda = 251$ nm in the fundamental system (1) and Eu(II)/(III)-*EGTA*-H_2O_2 (2); concentrations of all components of the system were the same and equal to $2 \cdot 10^{-3}\,\mathrm{mol} \cdot \mathrm{l}^{-1}$

$(2 \cdot 10^{-3}\,\mathrm{mol} \cdot \mathrm{l}^{-1})$ is negligible at 251 nm, the changes in the absorbance at this wavelength in the systems Eu(II)/(III)-Ligand-H_2O_2 were used to detect changes in the Eu(II) ion concentration. The results are presented as time dependencies of absorbance which are of similar character for all ligands used.

Figure 4 presents exemplary curves illustrating time changes in absorbance for the system Eu(II)/(III)-*EGTA*-H_2O_2 and the fundamental system. As they are very similar in character we conclude that in the systems containing the ligands used the process of decay of Eu(II) ions is similar to their decay in the fundamental system, and the cyclic ligands employed (*TETA* and *K22DA*) do not stabilize Eu(II) ions. A comparable character of the decay of Eu(II) ions in all systems together with the fact that no chemiluminescence was observed in the systems Eu(II)/(III)-H_2O_2, Eu(II)/(III)-*DGA*-H_2O_2, and Eu(II)/(III)-*MA*-H_2O_2 seven minutes after the initiation of the reaction leads to the conclusion that after this time europium ions occur at a concentration at which the reaction of their oxidation ($\mathrm{Eu(II)}+\mathrm{OH}\rightarrow\mathrm{Eu(III)}^*+\mathrm{OH}^-$) cannot be a source of detectable CL. Moreover, taking into account the fact that *EDTA* and its complexes with *d*-electron metals have been used as quenchers of singlet oxygen [14, 15], and regarding the energy levels of singlet oxygen dimols $(^1O_2)_2$ and excited Eu(III) ions [5], the long time of emission in systems with cyclic and acyclic aminopolycarboxylic acids is a result of the energy transfer from dimers of singlet oxygen (products of the reaction of recombination of radicals [4, 8, 9, 14]) to the complexed Eu(III) ions, similarly as it happens in the system with azide ions [5].

In order to confirm the occurrence of energy transfer, the chemiluminescence studies were carried out in the so called *Fenton* system (Fe(II)/(III)-H_2O_2). In this system, similar to Eu(II)/(III)-H_2O_2, the radical reactions leading to formation of singlet oxygen molecules take place [10]. Introduction of europium (III) ions and one of the ligands: *TETA*, *K22DA*, *NTA*, *EGTA*, *MA* and *DGA* into the *Fenton* system produces an environment in which the Eu(III) ion complexes are subjected to radicals and singlet oxygen dimers.

The kinetic curves of CL decay in the systems Fe(II)/(III)-H_2O_2, Fe(II)/(III)-Eu(III)-*DGA*-H_2O_2, and Fe(II)/(III)-Eu(III)-*MA*-H_2O_2 are very similar. The emission practically decayed already 4 minutes after the initiation of the reaction (curve 1 in Fig. 5), and the relevant emission spectra revealed bands characteristic of singlet oxygen dimers (520, 580, and 630 nm). The presence of these bands in the CL spectra as well as the comparable intensities and courses of the kinetic CL

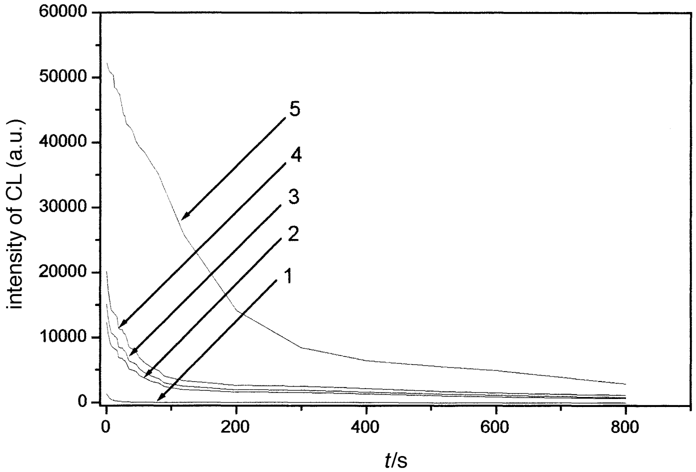


Fig. 5. Kinetic curves of CL of the systems Fe(II)/(III)-H_2O_2 (1), Fe(II)/(III)-Eu(III)-*K22DA*-H_2O_2 (2), Fe(II)/(III)-Eu(III)-*NTA*-H_2O_2 (3), Fe(II)/(III)-Eu(III)-*EGTA*-H_2O_2 (4), and Fe(II)/(III)-Eu(III)-*TETA*-H_2O_2 (5); initial concentration of Fe(II) ions: $2\cdot10^{-3}\,\mathrm{mol}\cdot\mathrm{l}^{-1}$, molar ratios: Fe(II):Eu(III):*L*:H_2O_2 ($L=EGTA$, $K22DA$, $TETA$): = 1:1:2:1, Fe(II):Eu(III):*L*:H_2O_2 ($L=NTA$) = 1:1:4:1, $pH=7.0$

curves testify that the Eu(III) ions complexed by *DGA* and *MA* do not undergo excitation in the *Fenton* system. Different effects were observed upon introduction of Eu(III) ions complexed by cyclic and acyclic aminopolycarboxylic acids into the system Fe(II)/(III)-H_2O_2. The presence of these complexes resulted in a significant increase in emission intensity and duration (Fig. 5, curves 2–5) and produced some changes in the CL spectrum. The CL spectra of solutions containing Fe(II)/(III), Eu(III), H_2O_2 and the ligands: *EGTA*, *TETA*, *K22DA*, and *NTA* showed only the band corresponding to Eu(III) ions with a maximum at 600 nm and thus were similar to those of the systems Eu(II)/(III)-*L*-H_2O_2 ($L = TETA$, *NTA*, *K22DA*, *EGTA*) (Fig. 3). The disappearance of the emission bands ascribed to singlet oxygen dimers and the appearance of the emission bands attributed to Eu(III) ions points to an energy transfer from the singlet oxygen dimers to Eu(III) ions complexed with *EGTA*, *TETA*, *K22DA*, and *NTA* as well as to the fact that the strong increase in CL intensity in the systems Fe(II)/(III)-Eu(III)-*L*-H_2O_2 ($L = TETA$, *NTA*, *K22DA*, *EGTA*) is a result of radiative deactivation of excited lanthanide ions. The occurrence of energy transfer in systems with cyclic and acyclic aminopolycarboxylic acids which coordinate the *Ln*(III) ion through oxygen and nitrogen atoms and the absence of this process in systems where coordination of the *Ln*(III) ions involves only oxygen atoms (*DGA* and *MA* acids) confirms the participation of nitrogen atoms in the process of energy transfer and thus in singlet oxygen dimer quenching [11, 16, 17].

As follows from the results reported, the intensity of Eu(III) chemiluminescence strongly depends on the kind of the ligand used. The differences are illustrated in Table 1, which presents the light sums of CL (*S*) of the systems Eu(II)/(III)-aminopolycarboxylic acid-H_2O_2, the hydration number (*n*) of the complexed Eu(III) ions, the stability constants values of the complexes ($\log K$), and the number of nitrogen atoms (L_{nitrogen}) taking part in coordination of the lanthanide ion.

According to the data from Table 1, the values of *S* are comparable for the systems with *EGTA*, *NTA*, and *K22DA* which are characterized by the same

Table 1. CL light sums (*S*) of the systems Eu(II)/(III)-aminopolycarboxylic acid-H_2O_2, hydration number (*n*) of the complexed Eu(III) ions, values of complex stability constants ($\log K$), and number of nitrogen atoms (L_{nitrogen}) involved in coordination of the lanthanide ion

Ligand	Type of complex	$\log K^a$	n^b	L_{nitrogen}	*S* (a.u.)	$S/S_{\mathrm{fund.system}}$
–	–	–	9	–	14±1	1
TETA	*ML*	15.46	1	4	12500±320	893
K22DA	*ML*	12.02	1	2	3460±180	247
EGTA	*ML*	17.77	1	2	3700±140	264
NTA	ML_2	20.64	1	2	3580±150	258
DGA	*ML*	5.53	6	–	22±2	1.6
	ML_2	10.04	3	–	98±7	7
	ML_3	13.20	0	–	168±12	12
MA	*ML*	4.85	6	–	18±2	1.3
	ML_2	8.11	3	–	89±6	6.3

[a] Ref. [18]; [b] Refs. [19–21]

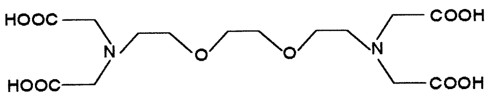
hydration number and the same number of nitrogen atoms taking part in the lanthanide ion coordination, but by different values of stability constants. This means that the stability of the complex does not affect significantly the intensity and duration of CL of Eu(III) ions. The quenching of luminescence of *Ln*(III) ions is a result of the coupling between the electron excited state of *Ln*(III) ions with OH oscillators from water molecules coordinated in the inner sphere [1]. In the systems containing Eu(III) complexes with *EGTA*, *NTA*, *TETA*, and *K22DA*, the coordination number of the metal ion is 1 (Table 1), and 2 or 4 nitrogen atoms are involved in the coordination of the europium ion. In the systems with *EGTA*, *NTA*, and *K22DA*, the value of *S* is 250 times greater than for the fundamental system, and when 4 nitrogen atoms involved in the coordination, this factor rises to about 890. Significantly lower light sums were obtained for the systems in which only oxygen atoms are involved in the coordination of the lanthanide ion (*MA*, *DGA*).

In conclusion, the intensity of CL of europium(III) ions increases as a result of their complexation by the ligand. In systems in which the energy transfer occurs from singlet oxygen dimers to Eu(III) ions, the intensity and duration of CL of europium (III) ions strongly depend on the nature and number of nitrogen atoms present in the cyclic and acyclic aminopolycarboxylic acids complexing the Eu(III) ions. When this energy transfer is absent (systems with *DGA* and *MA*), the intensity of CL from europium ions depends on the coordination properties of the ligand and, in particular, on the number of water molecules pushed out by the ligand from the inner coordination sphere of the Eu(III) ion. The values of light sums increase in the following sequence: $S_{ML} < S_{ML_2} < S_{ML_3}$, *i.e.* with decreasing hydration number of the Eu(III) ion (6, 3, 0).

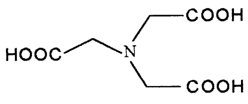
Experimental

The $EuCl_3$ solution was prepared by dissolving Eu_2O_3 (spectral purity, obtained at our laboratory) in HCl (pure for analysis, Merck). Reduction of $EuCl_3$ to $EuCl_2$ was performed by the *McCoy* method [12]. The degree of reduction was determined by the iodometric method directly prior to measurement. The solutions of the appropriate acids *EGTA* (pure for analysis, Fluka), *NTA* (pure for analysis, POCh, Gliwice), *TETA* (pure for analysis, Fluka), *K22DA* (pure for analysis, Fluka), *DGA* (pure for analysis, Fluka), and *MA* (pure for analysis, Fluka) were prepared by dissolving the compounds in distilled water with addition of tetraethylammonium hydroxide. The structural formulae of the ligands used are given below.

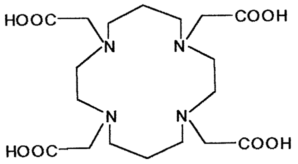
Measurements were carried out for *pH* values from 6 to 8. Using the acids *NTA*, *DGA*, and *MA*, which apart from *ML* form also ML_2 or ML_3 complexes with lanthanide ions, the measurements were performed under conditions ensuring a maximum concentration of the desired form of the complexes. These conditions were determined using the SPECA computer program on the basis of curves describing percent contribution of particular forms of complexes depending on *pH* for different metal:ligand ratios obtained from the known protonation constants of the ligand and the stability constants of Eu(III) ion complexes. Chemiluminescence measurements were carried out using the equipment described earlier [5], whereas the spectral distribution of CL was determined by the cut-off filter method [13]. The CL light sum was defined as the area under the kinetic CL curve, taking into account the fragment till the background emission level is reached. All chemiluminescence measurements were carried out in the same way. Proper amounts of the ligand, tetraethylammonium hydroxide, and water were placed in a measuring cell whose contents were mixed by argon (99.99%). Then, the $EuCl_2$ and hydrogen peroxide were added. When the *Fenton* system was used, the first substance introduced into the measuring cell was the ligand solution; then



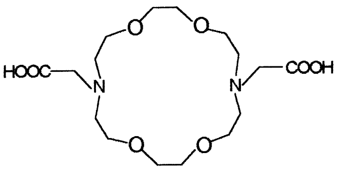
EGTA



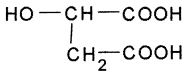
NTA



TETA

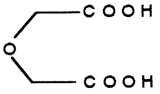


K22DA



$$\begin{array}{l} HO-CH-COOH \\ \quad\quad\;\, | \\ \quad\quad\;\, CH_2-COOH \end{array}$$

MA



DGA

EGTA: ethyleneglycol-*bis*-(2-aminoethyl)-N,N,N′,N′-tetraacetic acid; *NTA*: nitrilotriacetic acid; *TETA*: 1,4,8,11-tetraazacyclo-tetradecane-1,4,8,11-tetraacetic acid; *K22DA*: 7,16-*bis*-(carboxymethyl)-1,4,10,13-tetraoxa-7,16-diazacycloocta-decane; *MA*: malic acid (2-hydroxysuccinic acid); *DGA*: diglycolic acid (2,2′-oxydiacetic acid)

$EuCl_3$ was added, and mixing was effected by a stream of Ar. After mixing, the solutions of $FeCl_2$ and H_2O_2 were introduced. The absorption spectra of the ligands, europium ions, and the chemiluminescence systems were recorded using a UVVis 2401 PC Shimadzu spectrometer (quartz, 1×1 cm).

Acknowledgements

This work was supported by the *Polish State Committee for Scientific Research*, Grant No. 3 T09A 026 10.

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Received March 16, 1999. Accepted May 17, 1999