ELSEVIER

Journal of Alloys and Compounds 275–277 (1998) 225–229

Journal of ALLOYS AND COMPOUNDS

The influence of aminopolycarboxylic acids on the chemiluminescence of the Eu(II)/Eu(III)–H_2O_2 system

Marian Elbanowski*, Małgorzata Kaczmarek, Krzysztof Staninski

Department of Rare Earth, Faculty of Chemistry, A. Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland

Abstract

The chemiluminescence (CL) of the systems Eu(II)/Eu(III)–EDTA–H_2O_2, Eu(II)/Eu(III)–DTPA–H_2O_2 and Eu(II)/Eu(III)–TTHA–H_2O_2 was studied. The kinetic curves of CL decay and CL spectral distributions were obtained. On the basis of differences in the CL intensity and its duration, as well as characteristics of the CL spectra, a mechanism of the processes occurring in the studied systems is proposed. © 1998 Elsevier Science S.A.

Keywords: Aminopolycarboxylic acids; Chemiluminescence; Eu(III) ions

1. Introduction

Chemiluminescence (CL) measurements provide information on the spectral and structural properties of organic compounds in systems with lanthanide ions, mainly europium [1–3]. A product of Eu(II) ion oxidation by hydrogen peroxide is excited Eu(III) ions which, on returning to the ground state, emit radiation of wavelength $\lambda=594$ and 615 nm corresponding to the transitions $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$. The intensity of emission of lanthanide ions depends on the stability of the complex formed with the ligand and the Ln(III) hydration number [4,5]. In the chemiluminescence of systems containing H_2O_2 as oxidiser, the products of the simultaneous processes of H_2O_2 decomposition and radical recombination are molecules of singlet oxygen $^1O_2$ [6]. In order to determine their effect on the CL emission, they are quenched by different quenchers, e.g. amines. For singlet-oxygen quenching by amines, a mechanism involving electron transfer or the formation of a partial charge-transfer intermediate was suggested [7,8]. Hessler, studying singlet-oxygen quenching by EDTA and its complexes, demonstrated that the formation of the intermediate product between amine and $^1O_2$ is affected by the complexed metal ion. For instance, complexes of Cu(II) and Fe(III) with EDTA are much more effective quenchers of singlet oxygen than EDTA alone [9].

This paper reports the results of an investigation of systems composed of europium ions, hydrogen peroxide and one of the acids ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepentaacetic acid (DTPA) or triethylenetetraaminehexaacetic acid (TTHA), and a mechanism of the processes taking place in the systems is proposed.

2. Experimental

A solution of $EuCl_2$ was obtained by reduction of $EuCl_3$ according to the McCoy method [10]. A solution of $EuCl_3$ was obtained by dissolving Eu_2O_3 (of spectral purity, prepared in our laboratory) in HCl (pure for analysis, Merck). Solutions of EDTA, DTPA and TTHA (all pure for analysis, Fluka) were prepared by adding portions of NaOH (pure for analysis, POCh, Gliwice). The other agents used in the studies were: $FeCl_2$ (pure for analysis, Merck), H_2O_2 (35% solution, pure for analysis, Merck) and $Na_2B_4O_7 \cdot 10H_2O$ as a buffer (pure for analysis, Merck).

2.1. Procedure

Into a solution containing Eu(II) ions, ligand and borax buffer, H_2O_2 was added in equimolar amounts with respect to Eu(II). The desired solution pH was obtained by addition of an appropriate amount of borax buffer. The presence of borax buffer (borax ions) does not affect the intensity of CL in the system Eu(II)/Eu(III)–H_2O_2 (Table 1). It can be used in studies of CL in systems with

---

*Corresponding author.

0925-8388/98/$19.00
PII: S0925-8388(98)00308-9

Table 1
Influence of borax buffer on the CL intensity of the system Eu(II)/Eu(III)–H_2O_2. The concentration of europium ions was 2×10^{-3} mol l^{-1}; the pH of the solutions was 5.5

Concentration of borax ions (mol l^{-1})	Light sum $\Sigma I\Delta t$ (a.u.)
0	347 ± 23
5×10^{-4}	335 ± 22
2×10^{-3}	339 ± 25
1×10^{-2}	329 ± 26
5×10^{-2}	346 ± 25

aminopolycarboxylic acids. The pH was measured before and after the CL reactions.

The effect of pH on the chemiluminescence of the systems Eu(II)/Eu(III)–L–H_2O_2, where L=EDTA, DTPA, TTHA, for molar ratio metal/ligand 1:1, was studied. For the systems with TTHA and DTPA, with pH increasing up to about 6, the intensity of CL increased when the pH increased to >6; no changes were observed in the intensity of CL and in the course of the kinetic curves. In the systems containing EDTA, the pH 7.5 solution revealed the greatest intensity of CL. Further increase of pH in this system did not affect the intensity of CL, therefore CL measurements were performed for solutions at pH 7.5.

When applying the Fenton system, solutions of Fe(II) and Eu(III) were mixed with the ligand solution in the molar ratio Fe(II)/Eu(III)/L 1:1:2, and borax buffer was added. A solution of H_2O_2 was then added to the system in equimolar ratio to Fe(II). The reaction mixtures were stirred by flowing argon (99.99%) through them.

The kinetic curves of the CL decay (CL intensity vs. time) were recorded using the apparatus described in detail in Ref. [11]. Spectral distributions were obtained using the method of cutoff filters. The light sum of chemiluminescence ($\Sigma I\Delta t$) was defined as the area under the kinetic curve and calculated from the time of reaction initiation to the time of reaching the background level.

Spectrophotometric measurements were performed using a UV-2401 PC spectrophotometer Shimadzu.

3. Results and discussion

The chemiluminescence emitted from systems containing europium ions, hydrogen peroxide and EDTA or DTPA or TTHA, which form 1:1 complexes with europium ions [4,12], was measured. Structural formulae of the ligands are given in Fig. 1.

The kinetic curves of CL decay recorded for the systems studied

$$\mathrm{Eu(II)/Eu(III)–H_2O_2} \tag{1}$$

$$\mathrm{Eu(II)/Eu(III)–EDTA–H_2O_2} \tag{2}$$

$$\mathrm{Eu(II)/Eu(III)–DTPA–H_2O_2} \tag{3}$$

$$\mathrm{Eu(II)/Eu(III)–TTHA–H_2O_2} \tag{4}$$

are shown in Fig. 2. Curve 1 in Fig. 2 characterises the decay of CL of the system Eu(II)/Eu(III)–H_2O_2; its intensity is small and its duration very short, only about 8 min. The introduction of aminopolycarboxylic acids into the system of europium ions and hydrogen peroxide resulted in an increase in CL intensity and duration (up to a few hours). The highest CL intensity was recorded for the system with TTHA as a ligand; curve 4 in Fig. 2.

In order to identify the emitter in the systems studied, their CL spectral distributions (Fig. 3) were recorded by the method of cutoff filters [15]. For all systems studied, (1)–(4), the CL spectrum was the same.

As shown in the exemplary spectral CL distribution for the Eu(II)/Eu(III)–TTHA–H_2O_2 system (Fig. 3) the dominant band is the maximum for $\lambda=600$ nm characteristic of the transitions ${}^5D_0\rightarrow{}^7F_1$ and ${}^5D_0\rightarrow{}^7F_2$ for the Eu(III) ion. The minimum width of the spectral intervals

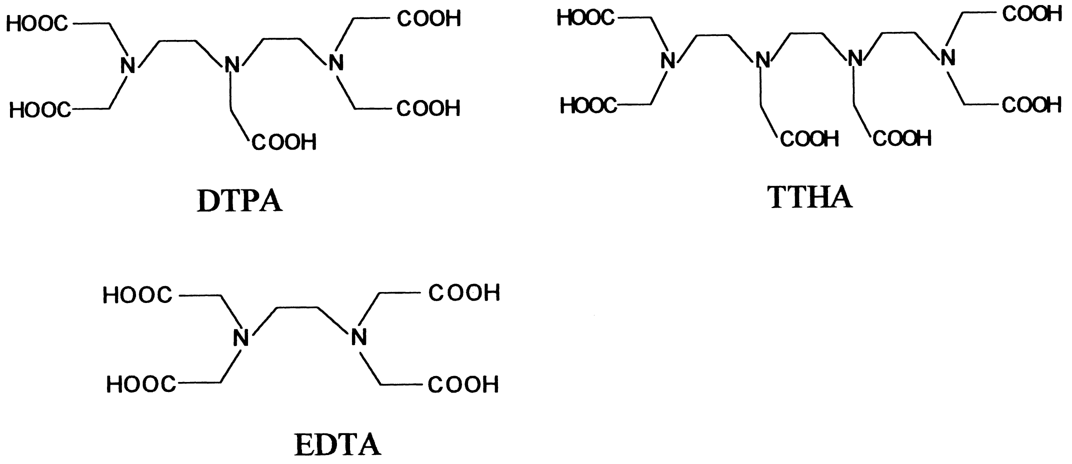


Fig. 1. Structural formulae of DTPA, TTHA and EDTA.

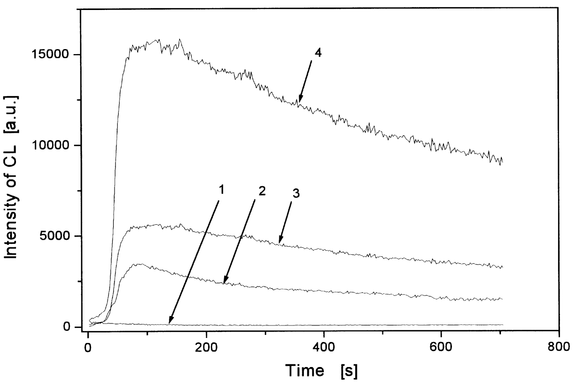


Fig. 2. Kinetic curves of CL decay for the systems (1) Eu(II)/Eu(III)–H_2O_2 (pH 5.5); (2) Eu(II)/Eu(III)–EDTA–H_2O_2; (3) Eu(II)/Eu(III)–DTPA–H_2O_2; (4) Eu(II)/Eu(III)–TTHA–H_2O_2. The concentration of europium ions was 2×10^{-3} mol l^{-1}; the molar ratio Eu(II)/L was 1:1; the pH of the solutions was 7.5.

obtainable by the cutoff filter method is 10–15 nm, so it was not possible to obtain a better separation of the two bands in the spectrum. In addition to the spectral distributions, the absorption spectra of Eu(II) ions and the aminopolycarboxylic acids were also recorded. Fig. 4A presents absorption spectra for Eu(II) ions and the ligand TTHA.

The maximum absorption of europium ions falls at $\lambda=248$ nm. At this wavelength the absorbance due to TTHA as well as the other ligands is negligible, so the intensity of emission at this wavelength can be taken as a measure of changes in the europium ion concentration in all systems studied. Fig. 4B presents the decay of the band at $\lambda=248$ nm for the systems Eu(II)/Eu(III)–H_2O_2 and Eu(II)/Eu(III)–TTHA–H_2O_2, which is the same as for the other systems studied, (2) and (3). This indicates that the introduction of a ligand to the system Eu(II)/Eu(III)–H_2O_2 does not change the kinetics of decay of the band at $\lambda=248$ nm, and thus does not affect the concentration of Eu(II) ions.

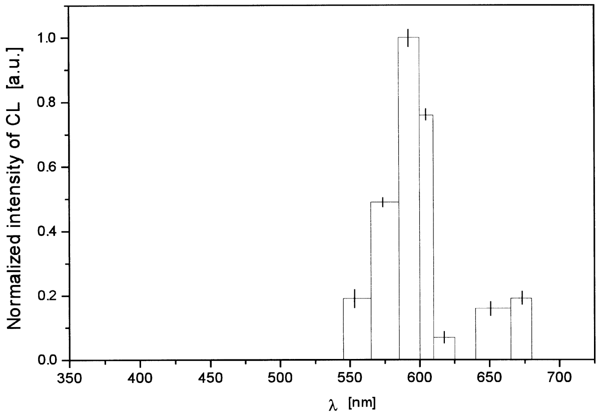


Fig. 3. Spectral distribution of CL for the system Eu(II)/Eu(III)–TTHA–H_2O_2. The concentration of europium ions was 2×10^{-3} mol l^{-1}; the molar ratio of Eu(II)/L was 1:1; the pH of the solutions was 7.5.

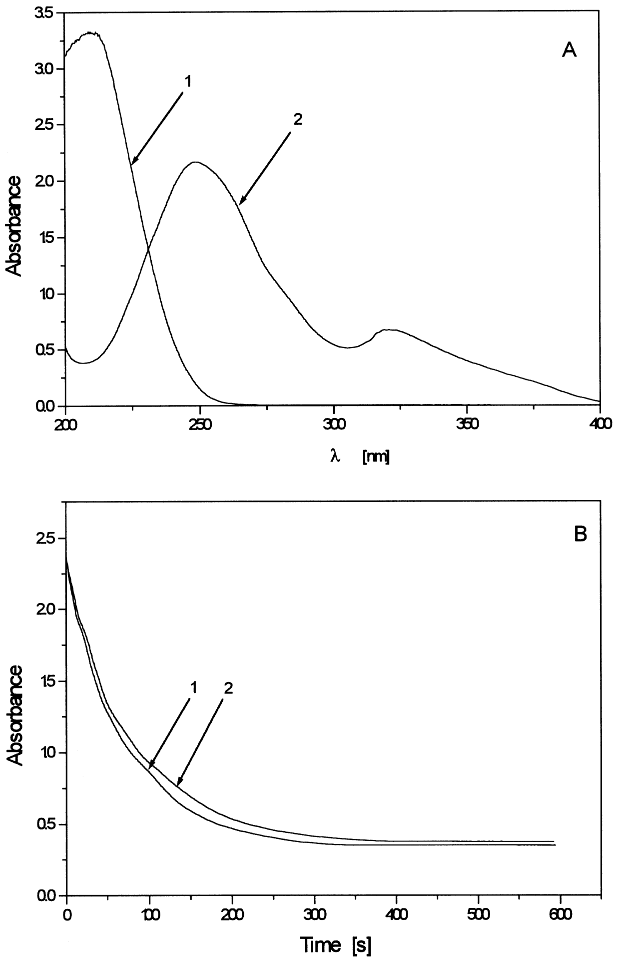


Fig. 4. (A) The absorption spectrum of (1) TTHA and (2) Eu(II) ions. The concentration of TTHA and Eu(II) ions was 2×10^{-3} mol l^{-1}. (B) The decay curves of the absorbance at $\lambda=248$ nm for the systems (1) Eu(II)/Eu(III)–H_2O_2 and (2) Eu(II)/Eu(III)–TTHA–H_2O_2. The concentration of europium ions was 2×10^{-3} mol l^{-1}; the molar ratio Eu(II)/L/H_2O_2 was 1:1:1.

The system Eu(II)/Eu(III)–H_2O_2 is a source of $HO^{\cdot}$ radicals forming during the decomposition of hydrogen peroxide:

$$\mathrm{Eu(II)} + H_2O_2 \rightarrow \mathrm{Eu(III)} + HO^{-} + HO^{\cdot} \qquad \text{(I)}$$

Similar transformations take place in the Fenton system (Fe(II)/Fe(III)–H_2O_2). In both systems the products of the radical reactions are, among others, molecules of singlet oxygen in the states $^1\Delta_g^+$ and $^1\Sigma_g^+$ [12,13]. By introducing europium (III) ions and one of the ligands EDTA or DTPA or TTHA into the Fenton system, we obtain an environment in which the europium complexes with aminopolycarboxylic acids are subject to the activity of radicals and singlet oxygen (Fig. 5).

In Fig. 5, curve 1 corresponds to CL decay in the Fenton system Fe(II)/Fe(III)–H_2O_2, and its character indicates a low intensity of CL emission and fast decay. The presence

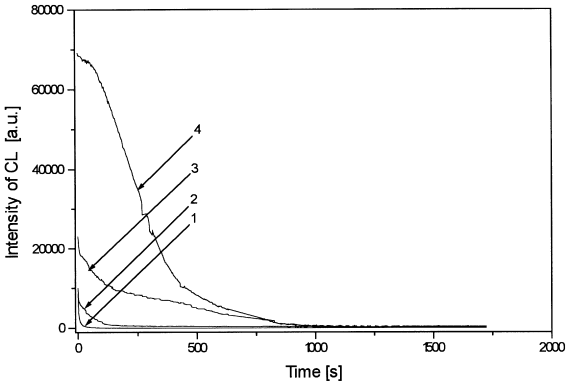


Fig. 5. Kinetic curves of CL decay for the systems (1) Fe(II)/Fe(III)–H_2O_2; (2) Fe(II)/Fe(III)–Eu(III)–EDTA–H_2O_2; (3) Fe(II)/Fe(III)–Eu(III)–DTPA–H_2O_2; (4) Fe(II)/Fe(III)–Eu(III)–TTHA–H_2O_2. The concentration of europium ions was 2×10^{-3} mol l^{-1}; the molar ratio Eu(III)/Fe(II)/L was 1:1:2, the pH of the solutions was 7.5.

of Eu(III) ions and EDTA or DTPA or, particularly, TTHA in the Fenton system results in a significant increase in CL emission; see curves 2, 3, 4 in Fig. 5.

The introduction of the aminopolycarboxylic acids into the Fenton system quenched its CL by 25% (EDTA or DTPA) and by 35% (TTHA).

The spectral distributions of CL measured for the systems

$$\text{Fe(II)/Fe(III)–Eu(III)–EDTA–}H_2O_2 \qquad (5)$$

$$\text{Fe(II)/Fe(III)–Eu(III)–DTPA–}H_2O_2 \qquad (6)$$

$$\text{Fe(II)/Fe(III)–Eu(III)–TTHA–}H_2O_2 \qquad (7)$$

proved identical. An exemplary spectral distribution obtained for (7) is shown in Fig. 6.

The dominant band is that attributed to Eu(III) with the maximum at about 600 nm, which indicates that these ions are the only emitters in the systems studied.

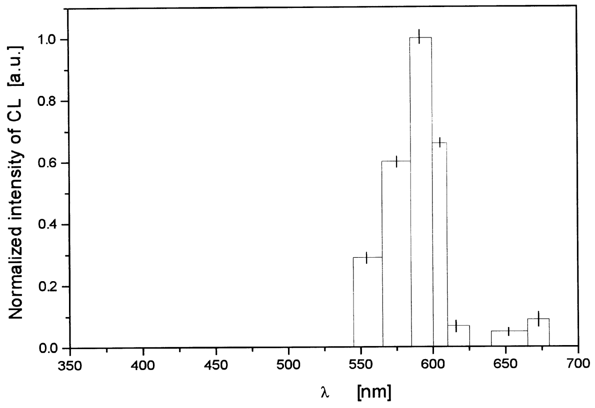


Fig. 6. Spectral distribution of CL for the system Fe(II)/Fe(III)–Eu(III)–TTHA–H_2O_2. The concentration of europium ions was 2×10^{-3} mol l^{-1}; the molar ratio Eu(III)/Fe(II)/L was 1:1:2; the pH of the solutions was 7.5.

On the basis of the curves for the decay of the band at $\lambda=248$ nm (Fig. 4B) it can be concluded that, 10 min after initiation of the reaction, in systems (1) to (4), no Eu(II) ions are detected. Thus, the strong increase in CL intensity and its long duration for systems (2) to (4) (Fig. 2) are mainly a result of the energy transfer process.

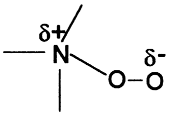
EDTA and its complexes with Cu(II) or Fe (III) were used as quenchers of singlet oxygen [9]. Analysis of the favourable position of the energy levels of singlet-oxygen dimols and exited Eu(III) ions suggests that the excitation of the lanthanide ions occurs due to the action of ${}^1O_2$ dimols, as established analogously for azide ions [11]. The observed long duration of CL is due to the reproduction of singlet oxygen in the reactions of recombination of radicals [6]:

$$O_2^{-\cdot} + HO^{\cdot} \rightarrow {}^1O_2 + HO^-$$

$$O_2^{-\cdot} + HO^{\cdot} + H^+ \rightarrow {}^1O_2 + H_2O$$

$$HO_2^{\cdot} + HO_2^{\cdot} \rightarrow {}^1O_2 + H_2O_2$$

It should be mentioned that quenching of singlet oxygen by amines and EDTA occurs partly through the formation of an intermediate charge transfer [7–9]:



The gradual increase in CL intensity observed in the systems Eu(II)/Eu(III)–H_2O_2 with EDTA, DTPA or TTHA (Fig. 2) is caused by an increasing concentration of Eu(III) ions formed as a result of reaction (I). The increasing concentration of Eu(III) ions increases the probability of formation of the intermediate charge transfer, {Eu(III)–aminopolycarboxylic acid}–singlet oxygen, and energy transfer.

On the basis of the results obtained, the following mechanism of the reaction can be proposed:

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

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

where L=EDTA ($n=1$), DTPA ($n=2$) and TTHA ($n=3$). The final effect is emission from the Eu(III) ions observed in the spectrum at about $\lambda=600$ nm.

After introducing aminopolycarboxylic acids (APA) into the solution containing Eu(II)/(III) ions and H_2O_2, because of the high stability of Eu–APA complexes, the concentration of free (uncomplexed) europium ions is negligibly low and no hydrolysis is observed.

For the systems Fe(II)/Fe(III)–Eu(III)–H_2O_2 with EDTA, DTPA or TTHA, the course of the kinetic changes in CL was different (Fig. 5). The chemiluminescence was very intensive at the instant of reaction initiation and lasted for a much shorter time. Taking into account the similar course of hydrogen peroxide decomposition in the Fenton system and in the system Eu(II)/Eu(III)–H_2O_2, the differences in the course of the kinetic curves follow from the different number of Eu(III) ions in the initial stage of the reaction. The much faster decay of CL in the Fenton system containing additionally Eu(III) ions and EDTA, DTPA or TTHA, is a result of singlet-oxygen quenching by the complexes of iron ions with aminopolycarboxylic acids.

In the systems studied the intensity of CL increases in the order EDTA<DTPA<TTHA. The only emitters in these systems are Eu(III) ions forming with EDTA complexes with stability constants of the order of 10^{17}; with TTHA and DTPA they form complexes with stability constant 10^{22} [11]. In these complexes, in the inner coordination sphere of the Eu(III) ions, there are different numbers of water molecules and their effect on the CL intensity must be taken into account (Table 2).

The significant differences in the CL intensity of the systems containing DTPA and TTHA, in view of the fact that these ligands form complexes with Eu(III) ions of similar stability, indicates that the effect of the number of coordinated water molecules must be important. With decreasing hydration number, the CL intensity increases. The highest CL intensity was recorded for the system with TTHA (curve 4 in Fig. 2 and curve 4 in Fig. 5).

The increase in CL intensity in the order EDTA<DTPA<TTHA indicates that it can also depend on the number of nitrogen atoms in the ligand molecule involved in formation of the intermediate product {Eu(III)–aminopolycarboxylic acid}–singlet oxygen.

Table 2
The number of water molecules in the inner coordination sphere of Eu(III) ions in Eu(III)L complexes

Ligand L	Hydration number of Eu(III)L complexes
EDTA	2.6[a]
DTPA	1.1[a]
TTHA	0[b]

[a] Ref. [4].
[b] Ref. [14].

In conclusion, it can be stated that in all systems studied the only emitters are europium ions, and the long duration of CL is related to the process of energy transfer from the dimols of singlet oxygen to europium(III) ions through the mediation of the complexing aminopolycarboxylic acids. The chemiluminescent method, chosen for studies on complexes of europium ions with aminopolycarboxylic acids, provides an explanation of the mechanism of the reactions in these systems.

Acknowledgements

This work was supported by the Polish Committee for Scientific Research, grant No. 3 T09A 026.

References

[1] V.S. Sharov, Yu.A. Vladimirov, Biofizyka 27 (1982) 327.

[2] M. Elbanowski, J. Wierzchowski, M. Paetz, J. Sławinski, Z. Naturforsch. 38a (1983) 808.

[3] M. Elbanowski, K. Staninski, M. Kaczmarek, Acta Phys. Pol. A 84 (1990) 993.

[4] H.G. Brittain, G.R. Choppin, P.P. Barthelemy, J. Coord. Chem. 26 (1992) 143.

[5] M. Elbanowski, S. Lis, B. Makowska, J. Konarski, Monatsh Chem. 116 (1985) 901.

[6] A. Singh, Can. J. Physiol. Pharmacol. 60 (1982) 1330.

[7] E.A. Ogryzlo, C.W. Tang, J. Am. Chem. Soc. 92 (1970) 5034.

[8] I. Saito, T. Matsuura, K. Inoue, J. Am. Chem. Soc. 105 (1983) 3200.

[9] D.P. Hessler, F.H. Frimmel, E. Oliveros, A.M. Braun, Helv. Chim. Acta 77 (1994) 859.

[10] H.N. McCoy, J. Am. Chem. Soc. 57 (1935) 1756.

[11] M. Elbanowski, K. Staninski, M. Kaczmarek, Acta Phys. Pol. A 90 (1996) 101.

[12] R.M. Smith, A.E. Martell, Critical Stability Constants, Plenum Press, New York, 1989.

[13] A. Singh, Photochem. Photobiol. 28 (1978) 429.

[14] R.C. Holz, W.DeW. Horrocks, Inorg. Chim. Acta 171 (1990) 193.

[15] R.F. Vassilev, Nature 196 (1962) 668.