Available online at www.sciencedirect.com

ScienceDirect

Inorganica Chimica Acta 360 (2007) 3748–3755

Inorganica Chimica Acta

www.elsevier.com/locate/ica

Kinetic study of dissociation of Eu(III) complex with H_8dotp (H_8dotp = 1,4,7,10-tetraazacyclododecane-1,4,7,10-tetrakis(methylphosphonic acid))

Z. Piskula [a,b], I. Svobodová [a], P. Lubal [a,*], S. Lis [b], Z. Hnatejko [b], P. Hermann [c]

[a] *Department of Chemistry, Faculty of Science, Masaryk University, Kotlářská 2, 611 37 Brno, Czech Republic*
[b] *Department of Rare Earths, Faculty of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, Poznan 60 780, Poland*
[c] *Department of Inorganic Chemistry, Faculty of Science, Charles University, Hlavova 2030, 128 40 Prague, Czech Republic*

Received 14 December 2006; received in revised form 22 March 2007; accepted 8 May 2007
Available online 13 May 2007

Abstract

The dissociation kinetics of the europium(III) complex with H_8dotp ligand was studied by means of molecular absorption spectroscopy in UV region at ionic strength 3.0 mol dm^{-3} (Na,H)ClO_4 and in temperature region 25–60 °C. Time-resolved laser-induced fluorescence spectroscopy (TRLIFS) was employed in order to determine the number of water molecules in the first coordination sphere of the europium(III) reaction intermediates and the final products. This technique was also utilized to deduce the composition of reaction intermediates in course of dissociation reaction simultaneously with calculation of rate constants and it demonstrates the elucidation of intimate reaction mechanism. The thermodynamic parameters for the formation of kinetic intermediate ($\Delta H^0 = 11 \pm 3$ kJ mol^{-1}, $\Delta S^0 = 41 \pm 11$ J K^{-1} mol^{-1}) and the activation parameters ($E_a = 69 \pm 8$ kJ mol^{-1}, $\Delta H^{\neq} = 67 \pm 8$ kJ mol^{-1}, $\Delta S^{\neq} = -83 \pm 24$ J K^{-1} mol^{-1}) for the rate-determining step describing the complex dissociation were determined. The mechanism of proton-assisted reaction was proposed on the basis of the experimental data.

Keywords: Macrocyclic complexes; Cyclen derivatives; Phosphonate complex; Europium(III) complex; Dissociation kinetics; Molecular absorption spectroscopy; Time-resolved laser-induced fluorescence spectroscopy (TRLIFS)

---

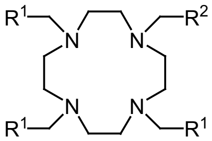
1. Introduction

Lanthanide(III) complexes of macrocyclic ligands having acetic (H_4dota) or phosphonic acid (H_8dotp) (see Chart 1) pendant arms, and their derivatives are studied for possible applications in medicine. Nowadays, the majority of contrast agents in magnetic resonance imaging (MRI) is based on gadolinium(III) complexes of acyclic (H_5dtpa) and cyclic (H_4dota) ligands [1,2] while the complexes of some lanthanide(III) ions (e.g. Eu^{3+}/Tb^{3+} emitting in the VIS and Yb^{3+}/Nd^{3+} in the NIR regions, respectively) are employed as luminescent probes [3–6]. Macrocyclic ligands binding metal radioisotopes (e.g. ^{90}Y, ^{153}Sm, ^{166}Ho, ^{177}Lu) are utilized as carriers in nuclear medicine [7]. These lanthanide(III) complexes with macrocyclic ligands can be attached to bioactive molecules responsible for a desired distribution in an organism (e.g. monoclonal antibodies, small peptides, hormones, sugars, etc.) in a form of so-called *bifunctional chelates* (BFCs). Since free lanthanide(III) ions are very toxic [3], the macrocyclic unit of the BFCs should sequester lanthanide(III) ions with a high thermodynamic stability, and the complexes formed should exhibit a high kinetic inertness under physiological conditions [1,2,7]. These properties are strongly influenced by the type of derivatization of the ligand skeleton [8]. By introducing the phosphorus atom into the pendant arms (phosphonic/phosphinic acid groups in acid or ester forms), some similarities to the acetic parent compounds

---

[*] Corresponding author. Tel.: +420 549 49 5637; fax: +420 541 211 214/549 492 494.
E-mail address: lubal@chemi.muni.cz (P. Lubal).

0020-1693/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.ica.2007.05.009



R^1	R^2	
CO_2H	CO_2H	H_4dota
$P(O)(OH)_2$	$P(O)(OH)_2$	H_8dotp
CO_2H	$P(O)(OH)_2$	H_5do3ap

Chart 1.

are preserved due to acid character of both types of groups, but the other properties (bulkiness, basicity, hydrogen bond formation ability, etc.) are different [8,9]. Generally, phosphonate ligands form more stable complexes with lanthanide(III) ions than do macrocyclic H_4dota-like ligands [8,9].

The first synthesis of H_8dotp was described by Kabachnik et al. [10,11]. The protonation and stability constants of the complexes with alkaline, alkaline earth and transition metal ions as well as with lanthanide(III) ions have been determined by several research groups [12–15]. The last dissociation constants of H_8 dotp are unusually high in comparison with those of H_4 dota due to the large negative charge of the ligand anion [12–15]. These values are strongly influenced by the presence of alkali and alkali earth metal ions due to the strong affinity of the deprotonated phosphonate groups for these cations [12–14]. The ability to strongly interact with these metal ions is retained also in the lanthanide(III) complexes of H_8 dotp in aqueous solution [14,16] or in the solid state [17].

For any application of the lanthanide(III) complexes in biology, it is important and, usually decisive, to have thermodynamically stable and, in particular, kinetically inert complexes. There is only one paper related to the study of the kinetic properties of the gadolinium(III) complex of H_8 dotp [18]. In this paper, the europium(III) ion was chosen, having similar chemical properties to gadolinium(III), in order to follow the dissociation kinetics by means of absorption and/or luminescence spectroscopy. It is also possible to compare our experimental data with results obtained for other lanthanide(III) complexes (mostly for gadolinium(III) or cerium(III) complexes described in the literature).

2. Experimental

Stock solutions of europium(III) perchlorate or chloride (0.05 mol dm^{-3}) were obtained by dissolving Eu_2O_3 (spectroscopically pure, prepared in the Department of Rare Earths, Faculty of Chemistry, Adam Mickiewicz University, Poznań or Alfa, Darmstadt, Germany) in perchloric or hydrochloric acid solutions (Analar grade, Fluka). The caution should be taken during work with metal perchlorates and concentrated perchlorate solutions [19].

The H_8dotp was prepared according to a previously described procedure [20,21]. The complex was prepared by mixing the metal ion solution and the ligand in the solid state in molar ratio 1:1.1 (10% ligand excess was used to ensure complete complex formation). The pH of the complex stock solutions ($c_{\mathrm{EuL}} \sim 0.015$ mol dm^{-3}) was adjusted to approximately 10 by NaOH. All other chemicals of the highest available purity were used as received.

The experimental methodology and details for the kinetic study of the lanthanide(III) complex reaction were the same as described elsewhere [9]. All kinetic measurements were carried out on a diode array spectrophotometer HP-8453A (Hewlett-Packard, USA) or a two-beam spectrometer UV 2 (Pye Unicam, UK). Dissociation kinetics of the europium(III) complex was measured in the proton concentration range of 0.10–3.00 mol dm^{-3} and an ionic strength $I = 3.0$ mol dm^{-3} (H,Na)ClO_4 ($c_{\mathrm{EuL}} \sim 1 \times 10^{-3}$ mol dm^{-3}). The decomplexation reaction was followed by a change in the CT band of the $[Eu(dotp)]^{5-}$ complex (275 nm). Data from kinetic experiments were processed by non-linear regression using EXCEL, HP and/or PROK-II [22] software with identical results. The measured values of the absorbances were corrected for a background signal.

The corrected luminescence spectra were recorded on an Aminco Bowman AB2 (Aminco Bowman, USA) spectrofluorimeter in 1 cm quartz cells ($\lambda_{\mathrm{exc}} = 394$ nm, ${}^7F_0 \rightarrow {}^5L_6$ transition [23]) at room temperature. The luminescence lifetime measurements, using the same excitation wavelength, were carried out using a detection system, consisting of a nitrogen pump laser and a tuneable dye laser, as described earlier [24,25]. The kinetics of acid-assisted dissociation of the europium(III) complexes ($c_{\mathrm{EuL}} \sim 0.001$ mol dm^{-3}) was followed by TRLIFS in perchloric or hydrochloric acids ($I = 3.0$ mol dm^{-3}). The reaction was initiated by the addition of the complex stock solution into the cell containing the acid. The first measurement was usually done between the 30th and the 60th second after mixing (reaction dead-time). Experiments were stopped when a measured luminescent lifetime became constant. All lifetime experiments were repeated at least three times in order to get an average value and the data were corrected for the dead-time for following kinetic treatment. The experimental luminescence decay data were fitted by a one-term equation (1)

$$I_t = I_0 \times e^{-\frac{t}{\tau}} \tag{1}$$

or by using the linearized logarithmic form (2) of the previous equation in order to prove monoexponential behaviour.

$$\ln(I_t) = \ln(I_0) - \frac{1}{\tau} \times t. \tag{2}$$

The I_t is the measured intensity of luminescence as a function of time (μs), I_0 is the initial luminescence intensity and τ is the lifetime of the luminescence decay. The logarithmic analysis of the experimental luminescence decay for all data points of the kinetic study shows that decays follow a mono-exponential dependence (see Eqs. (1) and (2)). The determined lifetimes of luminescence decay were used for an estimation of the number of water molecule as discussed earlier [25–32]. In this work, the hydration numbers (q) of the europium(III)-containing species were determined by means of Eq. (3) [26]

$$q = 1.05 \times \tau^{-1} - 0.7 \qquad (3)$$

which is a simplified modification of Horrock's equation [25–32] where no need of data from deuterated solvents are necessary. It was demonstrated in our previous work that results obtained by using Eq. (3) and more common equations [25–32] are in reasonable agreement [25].

3. Results and discussion

3.1. Thermodynamic stability of complexes

The acidobasic and complexing behaviour of H_8dotp and its lanthanide(III) complexes has been studied. It was found that the value ($\log K_1$) of the first protonation constant 13.7 [12–14] or 14.65 [15] is rather high. The thermodynamic stabilities ($\log \beta_{\mathrm{LnL}}$) of the lanthanide(III) complexes increase in the series from light (Ce(III) 27.7, Nd(III) 27.3) through middle (Eu(III) 28.1, Gd(III) 28.8) to heavy lanthanide(III) ions (Tm(III) 29.5, Yb(III) 29.5) [14]. In addition, ^{6,7}Li, ^{23}Na, or ^{133}Cs NMR spectroscopy were utilized for the determination of equilibrium constants for the association of alkaline and alkaline earth metal ions with lanthanide(III) complexes [14,16]. The strong interaction of the $[\mathrm{Tm(dotp)}]^{5-}$ complex with alkali metal ions (Li^+, Na^+, Cs^+) was described by a model where deprotonated, monoprotonated, and diprotonated species with several binding sites having different affinities for the alkali metal ions were postulated [16]. The strong affinity for sodium(I) ions is also supported by results obtained for the $[\mathrm{Gd(dotp)}]^{5-}$ complex in the solid state [17]. The literature values for the protonation and stability constants determined in $I = 0.1$ mol dm^{-3} $(NMe_4)Cl$ [14–16,18] were used for the construction of equilibrium distribution diagram valid for the Gd(III)–H_8dotp system (Fig. 1) to illustrate a species abundance as a function of solution acidity. Comparing the protonation constants of the $[\mathrm{Tm(dotp)}]^{5-}$ complex in Na^+- and NMe_4^+-containing ionic media (7.6 versus 6.8, 6.3 versus 5.6 or 5.4 versus 4.7 for $(NMe_4)Cl$ and NaCl, respectively) [14,16], it is clear that protonations are shifted to a lower $-\log[H^+]$ values in the NaCl-containing medium. Assuming the same effect of the sodium(I) ion on the complexation of the other $[\mathrm{Ln(dotp)}]^{5-}$ complexes [16] and also taking into account an ionic strength effect ($I = 0.1 \rightarrow 3.0$ mol dm^{-3}) with increased sodium(I) ion concentration, it can be surmised that it would be more difficult to protonate the complexes in NaCl or $NaClO_4$ media than it would in the $(NMe_4)Cl$ medium, mainly in the case when cationic species are formed.

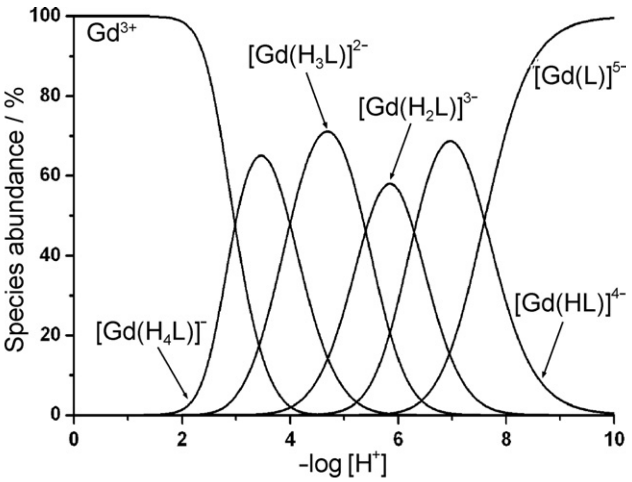


Fig. 1. The species distribution diagram for the gadolinium(III)-H^+-dotp^{8-} system under equilibrium conditions ($c_{\mathrm{Gd}} = c_{\mathrm{L}} = 0.001$ mol dm^{-3}). The protonation and stability constants were taken from the literature [14,15,18] for ionic strength $I = 0.1$ mol dm^{-3} NMe_4Cl.

3.2. Structure of complexes

The structure of the $[\mathrm{Ln(dotp)}]^{5-}$ complexes is well known in solution [33,34] as well as in the solid state [17]. The metal ions are sandwiched between the N4- and O4-planes, and the donor atoms are aligned in a twisted square antiprismatic (TSA) arrangement leading to octacoordination of the ligand. No water molecule is directly bound in the first coordination sphere as was shown by luminescence measurements done on $[\mathrm{Eu(dotp)}]^{5-}$ complex [25,35]. The same results were also obtained in the frozen state at temperature 77 K [25]. The second-sphere containing water molecules is present in these complexes as was shown by NMR and NMRD measurements on the gadolinium(III) complex [36,37].

3.3. Dissociation kinetics study

The acid-assisted decomplexation is commonly investigated in order to determine the kinetic inertness of the lanthanide(III) complexes with H_4dota-like macrocyclic ligands since the rate of complex dissociation at physiological pH is very low [9,18,38–42]. First, the course of the dissociation reaction of the europium(III) complex with H_8dotp was followed by molecular absorption spectroscopy in UV region. An example of the experimental dissociation data is given in Fig. 2. In some solution acidities, the decomposition of europium(III) was also followed by luminescence spectroscopy (Fig. 3). It can be seen that the europium(III) complex shows only one absorption maximum at about 275 nm, and this band decreased monotonically in the course of the dissociation reaction, similarly to that found for the analogous H_4dota complex [39]. The dissociation reaction of the europium(III) complex is slow at ambient temperature, and it is accelerated by increasing temperature.

The proton-assisted dissociation kinetics is usually studied in strongly acidic media since the Ln(III) complexes are thermodynamically unstable under these experimental conditions (see Fig. 1). In the literature, a mechanism for the dissociation of the gadolinium(III) complex of H_8dotp has been suggested [18]. Generally [18,39,40], the dissociation of the lanthanide(III) complexes of H_4dota-like ligands can be postulated as reaction (A), where charges are omitted for the sake of clarity.

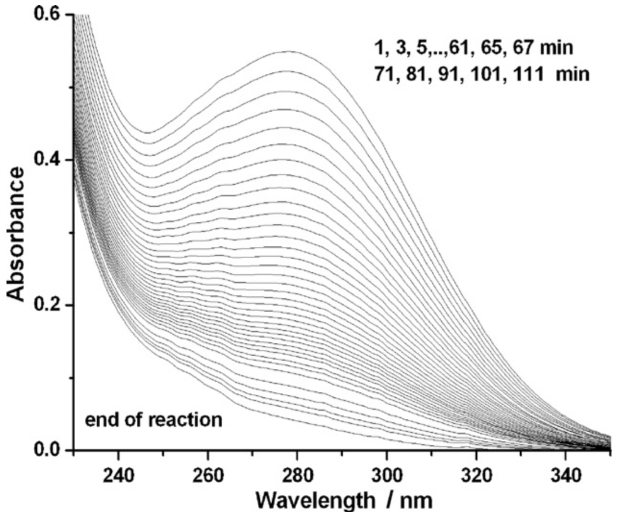


Fig. 2. An example of the time change in the absorption spectra in the course of the dissociation of the europium(III) complex ($[H^+] = 3.0$ mol dm^{-3}, $c_{EuL} = 0.001$ mol dm^{-3}, $I = 3.0$ mol dm^{-3} (H,Na)ClO_4, $t = 25$ °C).

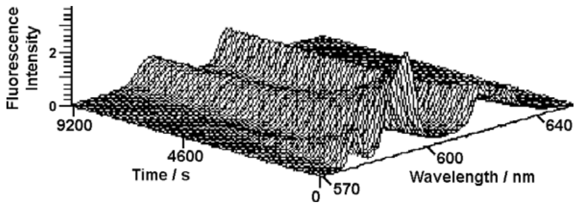


Fig. 3. An example of the time change in the emission spectra in the course of the dissociation of the europium(III) complex ($\lambda_{exc} = 394$ nm, $[H^+] = 3.0$ mol dm^{-3}, $c_{EuL} = 3 \times 10^{-3}$ mol dm^{-3}, $I = 3.0$ mol dm^{-3} (H,Na)ClO_4, $t = 25$ °C).

$$\mathrm{LnL} + n\mathrm{H}^+ \overset{K}{\rightleftarrows} \mathrm{Ln(H}_n\mathrm{L)} \xrightarrow{k} \mathrm{Ln}^{3+} + \mathrm{H}_n\mathrm{L} \tag{A}$$

The rate of dissociation of the Ln(III) complexes is defined by Eq. (4).

$$-\frac{\mathrm{d[complex]}}{\mathrm{d}t} = {}^{\mathrm{Ln}}k_{\mathrm{d,obs}} \times [\mathrm{complex}]_{\mathrm{tot}}. \tag{4}$$

As it was given above, the protonated $[\mathrm{Ln(H}_n\mathrm{L)}]^{n-5}$ ($n = 1$–4) complex species are thermodynamically stable [14,18]. Therefore, the analogous $[\mathrm{Ln(H_4L)}]^-$ and $[\mathrm{Ln(H_5L)}]$ complex species should be formed under our experimental conditions. Assuming that the $[\mathrm{Ln(H_5L)}]$ complex is an active kinetic species in the dissociation process, Eq. (5) can be postulated. The ${}^{\mathrm{H}}K_5$ is the corresponding protonation constant defining the concentration of the $[\mathrm{Ln(H_5L)}]$ species (Eq. (6)).

$$-\frac{\mathrm{d[complex]}}{\mathrm{d}t} = k_{\mathrm{Ln(H_5L)}} \times [\mathrm{Ln(H_5L)}], \tag{5}$$

$${}^{\mathrm{H}}K_5 = \frac{[\mathrm{Ln(H_5L)}]}{[\mathrm{Ln(H_4L)}] \times [\mathrm{H}^+]}. \tag{6}$$

Taking into account the following mass balance equation (7):

$$\begin{aligned}[\mathrm{complex}]_{\mathrm{tot}} &= [\mathrm{Ln(H_5L)}] + [\mathrm{Ln(H_4L)}] \\ &= [\mathrm{Ln(H_4L)}] \times (1 + {}^{\mathrm{H}}K_5 \times [\mathrm{H}^+])\end{aligned} \tag{7}$$

and combining Eqs. (4), (5) and (7), a shortened relationship (7) can be derived

$${}^{\mathrm{Ln}}k_{\mathrm{d,obs}} = \frac{k_{\mathrm{Ln(H_5L)}} \times {}^{\mathrm{H}}K_5 \times [\mathrm{H}^+]}{1 + {}^{\mathrm{H}}K_5 \times [\mathrm{H}^+]}. \tag{8}$$

The experimental data obtained for the complex dissociation could be explained by a one-step reaction mechanism. The measured pseudo-first order rate constants ${}^{\mathrm{Ln}}k_{\mathrm{d,obs}}$ for the europium(III) complex were fitted using Eq. (8) (see the example in Fig. 4), and the values for the different temperatures are given in Table 1. One can verify the postulated reaction mechanism (reaction (A)) for the europium(III) complex at 25 °C by treatment of a set of experimental data for all acidities using ProK-II software [22] program; the following parameters were calculated: $k_{(\mathrm{EuH5L})} = (6.13 \pm 0.07) \times 10^{-4}\ \mathrm{s}^{-1}$ and $\log({}^{\mathrm{H}}K_5) = 0.42 \pm 0.01$ (i.e. ${}^{\mathrm{H}}K_5 = 2.6 \pm 0.4\ \mathrm{M}^{-1}$). These values agree with values given in Table 1 obtained by fitting the data to Eq. (8). In addition, the parameters determined for temperature 25 °C (Table 1) are in a fair agreement with the values obtained for the gadolinium(III) complex: $k_{(\mathrm{GdH5L})} = (5.4 \pm 0.2) \times 10^{-4}\ \mathrm{s}^{-1}$ and ${}^{\mathrm{H}}K_5 = 1.7 \pm 0.2\ \mathrm{M}^{-1}$ [18] measured under a different ionic strength ($I = 1.0$ mol dm^{-3} (H, $\mathrm{NMe_4}$)Cl). The protonation constant ${}^{\mathrm{H}}K_5$ is roughly of the same order of magnitude as ${}^{\mathrm{H}}K_1$ for the Ln(III)–$\mathrm{H_4}$dota complexes [39,44]. In addition, the activation and thermodynamic parameters calculated from the temperature dependence of the parameters were estimated, and they are given in Table 1. In order to compare our results with literature data, the activation parameters were also calculated for the k_{H} rate constant (Tables 1 and 2).

Comparing the reactivity of the $[\mathrm{Ce(dotp)}]^{5-}$ and $[\mathrm{Eu(dotp)}]^{5-}$ complexes, the europium(III) complex is slightly less inert than the cerium(III) complex [43]. This is also reflected in values of the pseudo-first order rate con-

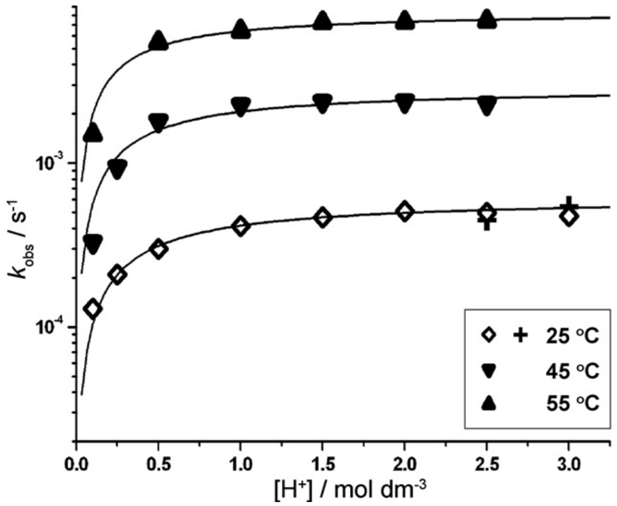


Fig. 4. The dependence of the pseudo-first rate constants for dissociation of the europium(III) complex on the acidity of the solutions ($I = 3.0$ mol dm^{-3} (H,Na)ClO_4). The experimental data marked by crosses were obtained by luminescence spectroscopy (see Fig. 3) while the other data points were determined by molecular absorption spectroscopy (see Fig. 2). The full lines are the best fits according to Eq. (8) using parameters given in Table 1.

Table 1
The parameters determined (see Eq. (8)) for the description of acid-assisted decomplexation of the $[Eu(dotp)]^{5-}$ complex ($I = 3.00$ mol dm^{-3} (H,Na)ClO_4) obtained by molecular absorption spectroscopy in UV region[a]

t (°C)	$k_{Ln(H5L)}$($\times 10^{-4}$) (s^{-1})	$^{H}K_5$ ($dm^3\ mol^{-1}$)	k_H ($\times 10^{-3}$) ($dm^3\ mol^{-1}\ s^{-1}$)
25	6.2 ± 0.3	2.0 ± 0.2	1.3
45	29 ± 2	2.4 ± 0.7	7.04
55	85 ± 3	3.1 ± 0.5	26.12
Activation/thermodynamic parameters	$E_a = 69 \pm 8$ kJ mol^{-1} $\Delta H^{\neq} = 67 \pm 8$ kJ mol^{-1} $\Delta S^{\neq} = -83 \pm 24$ J K^{-1} mol^{-1}	$\Delta H^0 = 11 \pm 3$ kJ mol^{-1} $\Delta S^0 = 41 \pm 11$ J K^{-1} mol^{-1}	$E_a = 80 \pm 11$ kJ mol^{-1} $\Delta H^{\neq} = 77 \pm 11$ kJ mol^{-1} $\Delta S^{\neq} = -41 \pm 34$ J K^{-1} mol^{-1}

$k_{Ln(H5L)}$: $E_a = 100$ kJ mol^{-1}; $\Delta H^{\neq} = 97$ kJ mol^{-1}; $\Delta S^{\neq} = 0.9$ J K^{-1} mol^{-1}.
$^{H}K_5$: $\Delta H^0 = 8.7$ kJ mol^{-1}; $\Delta S^0 = 36.8$ J K^{-1} mol^{-1}.
k_H: $E_a = 111 \pm 20$ kJ mol^{-1}; $\Delta H^{\neq} = 108 \pm 20$ kJ mol^{-1}; $\Delta S^{\neq} = 32 \pm 62$ J K^{-1} mol^{-1}.

[a] The activation parameters for the cerium(III) complex (Ref. [43]).

Table 2
Overview of the parameters describing the dissociation of the Ln(III)-H_4dota and Ln(III)-H_8dotp complexes ($t = 25$ °C, $I = 3.00$ mol dm^{-3} (H,Na)ClO_4, unless stated otherwise in text)

Ligand	Ce^{3+}[a,b]	Eu^{3+}[a,b]	Gd^{3+}[a,b]
H_4dota	$k_{H1} = 8 \times 10^{-4}$ M^{-1} s^{-1} $k_{H2} = 2 \times 10^{-3}$ M^{-2} s^{-1} (refs. [38,39])	$k_{H1} = 1.4 \times 10^{-5}$ M^{-1} s^{-1} $k_{H2} = 1.0 \times 10^{-3}$ M^{-2} s^{-1} $k_{d,1} = 1 \times 10^{-6}$ s^{-1} $k_{d,2} = 6.2 \times 10^{-4}$ s^{-1}	$k_{H1} = 2.0 \times 10^{-5}$ M^{-1} s^{-1} $k_0 = 5 \times 10^{-10}$ s^{-1} (ref. [39])[c]
	$k_{H1} = 3.373 \times 10^{-4}$ M^{-1} s^{-1}[e] $k_{H2} = 1.605 \times 10^{-3}$ M^{-2} s^{-1}[e] (ref. [41])	$K_1 = 14$ M^{-1} $K_2 = 0.12$ M^{-1} (ref. [39])[d]	$k_{H1} = 8.4 \times 10^{-6}$ M^{-1} s^{-1} $k_0 < 5 \times 10^{-8}$ s^{-1} (ref. [42])[d]
H_8dotp	$k_{H1} = 4.18 \times 10^{-3}$ M^{-1} s^{-1}[f] $k_{d,1} = 1.15 \times 10^{-3}$ M^{-1} s^{-1}[f] $K_{1(5)} = 3.6$ M^{-1}[f] (ref. [43])	$k_{H1} = 1.3 \times 10^{-3}$ M^{-1} s^{-1} $k_{d,1} = 6.2 \times 10^{-4}$ M^{-1} s^{-1} $K_{1(5)} = 2.0$ M^{-1} (this work)	$k_{H1} = 9.2 \times 10^{-4}$ M^{-1} s^{-1}[g] $k_1 = 5.4 \times 10^{-4}$ M^{-1} s^{-1}[g] $K_{1(5)} = 1.7$ M^{-1}[g] (ref. [18])

[a] $k_{d,obs} = k_0 + k_{H1} \times [H^+] + k_{H2} \times [H^+]^2$.
[b] $k_{d,obs} = \frac{k_{d,1} \times K_1 \times [H^+] + k_{d,2} \times K_1 \times K_2 \times [H^+]^2}{1 + {}^{H}K_1 \times [H^+] + {}^{H}K_1 \times {}^{H}K_2 \times [H^+]^2}$.
[c] pH 3.2–5.0, $t = 37$ °C, non-specified ionic strength.
[d] $I = 1.0$ mol dm^{-3} (NaCl).
[e] $I = 1.0$ mol dm^{-3} (H,K)Cl (estimate, in paper $I = 0.1$ mol dm^{-3}) k_{H1}: $\Delta H^{\neq} = 71.5$ kJ mol^{-1}, $\Delta S^{\neq} = -71$ J K^{-1} mol^{-1} k_{H2}: $\Delta H^{\neq} = 40.0$ kJ mol^{-1}, $\Delta S^{\neq} = -164$ J K^{-1} mol^{-1}.
[f] $t = 60$ °C.
[g] $I = 1.0$ mol dm^{-3} (H,NMe_4)Cl.

stant, $^{Ln}k_{d,obs}$, measured in 3.0 mol dm^{-3} $HClO_4$ (25 °C): 1.39×10^{-4} s^{-1} (Ce(III), Ref. [43]) and 4.76×10^{-4} s^{-1} (Eu(III), this work). The value of the pseudo-first order rate constant, $^{Ln}k_{d,obs}$, for the europium(III) complex is comparable to the value of 5.41×10^{-4} s^{-1} found by treatment of the kinetic data obtained by luminescence measurements (crosses in Fig. 3; see also below). A similar kinetic inertness for lanthanide(III) complexes was also observed for cerium(III) and gadolinium(III) complexes of the monophosphonate derivative H_5do3ap under identical experimental conditions, i.e. 3.00 mol dm^{-3} $HClO_4$ and temperature 25 °C ($^{Ln}k_{d,obs} = 3.7 \times 10^{-3}$ s^{-1} for Ce(III) and 7.3×10^{-3} s^{-1} for Gd(III) [9], respectively) while the kinetic inertness of $[Ce(dota)]^-$ and $[Eu(dota)]^-$ complexes is much different ($^{Ln}k_{d,obs} = 2.04 \times 10^{-2}$ s^{-1} for Ce(III) [38] and 1.62×10^{-4} s^{-1} for Eu(III) [39], respectively).

3.4. Mechanism of dissociation

In order to gain further insight on the detailed reaction mechanism of such a complex dissociation, time-resolved laser-induced fluorescence spectroscopy (TRLIFS) was employed. The luminescence decay traces of the europium(III) complex recorded during the course of the acid-assisted dissociation were used for the determination of the time dependence of an average number of water molecules in the inner sphere of the $[Eu(dotp)]^{5-}$ complex (Fig. 5). Analyzing the experimental data, some surprising facts should be noted. The final product of the complex dissociation (on our measurement time scale) is not a free europium(III) aqua ion as it was observed for the $[Eu(dota)]^-$ complex [39,40,44,45]. Our final product was a long-lived reaction intermediate having four (for perchlorate medium) or five (for chloride medium) water molecules in its inner coordination sphere. In addition, spectrum of the final product of the $[Eu(dotp)]^{5-}$ complex dissociation is different from spectrum of the europium(III) aqua ion (formed e.g. in the dissociation of the $[Eu(dota)]^-$ complex [39]). The existence of a similar stable reaction intermediate formed in course of europium(III) complexation by H_4dota in a slightly acidic solution was detected and the intermediate contains about five water molecules in its inner

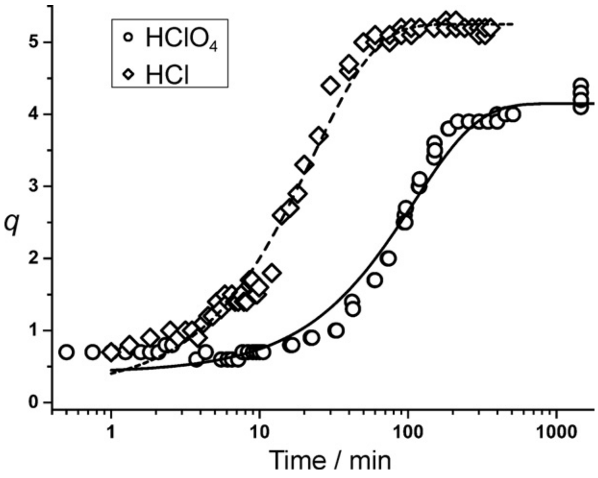


Fig. 5. The time course for the change in the number of water molecules (q) during the acid-assisted dissociation of the europium(III) complex ($c_{\mathrm{EuL}} = 0.01\ \mathrm{mol\ dm^{-3}}$, $[H^+]_{\mathrm{tot}} = 3.0\ \mathrm{mol\ dm^{-3}}$). The full ($HClO_4$) and dashed (HCl) lines are the best fits according to Eq. (10).

coordination sphere; it is stable up to several days under the used conditions [45].

Let us consider the reaction mechanism (reaction (A)) describing the Eu(III) complex dissociation. The average number of the inner-sphere water molecules is a weighted value defined as a function of time by Eq. (9)

$$
\begin{aligned}
q_t &= q_{t=0}(\mathrm{EuL}^*) \times \mathrm{e}^{-{}^{\mathrm{Eu}}k_d \times t} + q_{t=\infty}(\mathrm{Eu}) \times (1 - \mathrm{e}^{-{}^{\mathrm{Eu}}k_d \times t}) \\
&= \mathrm{e}^{-{}^{\mathrm{Eu}}k_d \times t}(q_{t=0}(\mathrm{EuL}^*) - q_{t=\infty}(\mathrm{Eu})) + q_{t=\infty}(\mathrm{Eu}), \qquad (9)
\end{aligned}
$$

where $[\mathrm{EuL}]^*$ complex is a reaction intermediate and hydrated the Eu(III) ion is considered as the final product according to the reaction (A). For H_8dotp, the general relationship (9) had to be modified as Eq. (10)

$$
\begin{aligned}
q_t &= q_{t=0}(\mathrm{EuL}^*) \times \mathrm{e}^{-{}^{\mathrm{Eu}}k_d \times t} + q_{t=\infty}(\mathrm{EuL}^{**}) \times (1 - \mathrm{e}^{-{}^{\mathrm{Eu}}k_d \times t}) \\
&= \mathrm{e}^{-{}^{\mathrm{Eu}}k_d \times t}(q_{t=0}(\mathrm{EuL}^*) - q_{t=\infty}(\mathrm{EuL}^{**})) + q_{t=\infty}(\mathrm{EuL}^{**}), \qquad (10)
\end{aligned}
$$

where the $[\mathrm{EuL}]^*$ and $[\mathrm{EuL}]^{**}$ complexes are short-lived and long-lived intermediates, respectively. However, the long-lived intermediate is not decomposed under the condition employed. The experimental data (Fig. 5) were fitted by means of a non-linear least-square algorithm using Eq. (10). The following parameters were estimated together with number of the inner-sphere water molecules in both reaction intermediates (the precision of the q determination is ±0.5): $k_{\mathrm{d,obs}} = (1.53 \pm 0.08) \times 10^{-4}\ \mathrm{s^{-1}}$, $q_{t=0}$ (EuL*) = 0.4, $q_{t=\infty}$ (EuL^{**}) = 4.1 (in $3.0\ \mathrm{mol\ dm^{-3}}$ $HClO_4$) and $k_{\mathrm{d,obs}} = (7.4 \pm 0.3) \times 10^{-4}\ \mathrm{s^{-1}}$, $q_{t=0}$ (EuL^*) = 0.2, $q_{t=\infty}$ (EuL^{**}) = 5.2 (in $3.0\ \mathrm{mol\ dm^{-3}}$ HCl). It is difficult to decide if the difference in the number of water molecules for the perchlorate and chloride media is a consequence of the formation of mixed ternary complex species and/or the effect of an anion of the supporting electrolyte as it was discussed very recently in the literature [46–50]. Nevertheless, the effect of chloride ions on the dissociation kinetics is evident ($k_{\mathrm{d,obs}}$ ($3.00\ \mathrm{mol\ dm^{-3}}$ HCl)/$k_{\mathrm{d,obs}}$ ($3.00\ \mathrm{mol\ dm^{-3}}$ $HClO_4$) = $7.4 \times 10^{-4}/1.53 \times 10^{-4} = 4.85$). The rate constant $k_{\mathrm{d,obs}}$ measured for $3.00\ \mathrm{mol\ dm^{-3}}$ $HClO_4$ by TRLIFS differs from the values determined by UV and luminescence spectroscopies (see Fig. 5); however, the above value for $3.0\ \mathrm{mol\ dm^{-3}}$ HCl is much closer to the results obtained by the spectroscopies. Chloride ions can accelerate the dissociation reaction as it was shown in a study of the acid-assisted dissociation of the copper(II) complexes of bis(methylphosphonic acid) derivatives of cyclam [51,52]. For the copper(II) complexes in chloride-containing solutions, an interaction of chloride anions with protonated phosphonic group(s) was suggested similarly to the analogous interactions found in the solid-state structures of the nickel(II) complexes of the ligands [53]. Recently, it was also demonstrated on the hydrophilic cationic gadolinium(III)–dotam complex (dotam = tetraamide of H_4dota) that different anions interacting with the complex in the second coordination sphere have an influence on water exchange rate of the metal-bound water molecule [54]. Assuming an effect of such interaction(s) on luminescent decay of the $[\mathrm{Eu(H}_n\mathrm{dotp)}]^{(5-n)-}$ complexes, it can be supposed that the long-lived intermediate species (the final product under our experimental conditions) has also cationic character.

The dissociation mechanism of europium(III) complex can be explained by the fact that the dissociation reaction proceeds through several reaction pathways having similar rate constants. The molecular absorption spectroscopy in UV region employed in this study can detect decomposition (Fig. 2) of all in-cage europium(III) species taking part in this reaction as an average signal (see Scheme 1) and this technique determines the rate constant of complex dissociation as a total value. On the contrary, TRLIFS detects sensitively only europium(III) complex species having a different number of water molecules and changing their hydration number in course of the complex dissociation. Thus the reaction pathways where species are not changing hydration number are "invisible" (e.g. isomerisation reaction (D)) due to no change in hydration number. The rate constant determined by this technique should be lower as it follows only the changes of concentrations of "active" species with time. In addition, this luminescence behaviour can

$$[\mathrm{Eu(dotp)}]^{5-} + 4\mathrm{H}^+ \underset{fast}{\overset{{}^{\mathrm{H}}K_1.{}^{\mathrm{H}}K_2.{}^{\mathrm{H}}K_3.{}^{\mathrm{H}}K_4}{\rightleftarrows}} [\mathrm{Eu(H_4dotp)}]^- \qquad (\mathrm{B})$$

$$[\mathrm{Eu(H_4dotp)}]^- + \mathrm{H}^+ \underset{fast}{\overset{{}^{\mathrm{H}}K_5}{\rightleftarrows}} [\mathrm{Eu(H_5dotp)}]^* \qquad (\mathrm{C})$$

$$[\mathrm{Eu(H_5dotp)}]^*(\mathtt{I}) \xrightarrow[\text{slow}]{\mathrm{H_2O}} [\mathrm{Eu(H_5dotp)}]^*(\mathtt{II}) \qquad (\mathrm{D})$$

$$[\mathrm{Eu(H_5dotp)}]^*(\mathtt{I}) + \mathrm{H}^+ \xrightarrow[\text{slow}]{\mathrm{H_2O}} [\mathrm{Eu(H_6dotp)(H_2O)_4}]^{(+)}{**} \qquad (\mathrm{E})$$

$$[\mathrm{Eu(H_5dotp)}]^*(\mathtt{II}) + \mathrm{H}^+ \xrightarrow[\text{slow}]{\mathrm{H_2O}} [\mathrm{Eu(H_6dotp)(H_2O)_4}]^{(+)}{**} \qquad (\mathrm{F})$$

$$[\mathrm{Eu(H_6dotp)(H_2O)_4}]^{(+)}{**} \xrightarrow[\text{very slow}]{\mathrm{H_2O}} \mathrm{Eu(H_2O)_9^{3+}} + \mathrm{H_6dotp^{2-}} \qquad (\mathrm{G})$$

Scheme 1.

be influenced by the choice of excitation and emission wavelengths for some special cases (e.g. ternary europium(III) complexes of H_4cdta and H_2ida [55]).

Combining all the known facts, the following reaction mechanism can be proposed for perchlorate medium (see Scheme 1). It is assumed that the reaction(s) (D)–(F) proceeds in a time scale of hours while reaction (G) takes place in a longer scale of weeks or months.

Thus, the reaction starts with formation of the thermodynamically stable protonated $[Eu(H_n dotp)]^{(5-n)-}$ species where n can be up to four (see distribution diagram; Fig. 1). As the main emission bands (see Fig. 3) decrease their intensities only, except of the diminished band at 579 nm, inner coordination sphere remains intact upon protonation, i.e. all protonated complexes $[Ln(H_n L)]^{(5-n)-}$ ($n = 1$–4) are nine coordinated without any water molecules in the first hydration sphere, and they have very similar structure to that of the starting complex (Scheme 1). In the following pre-equilibrium step, the neutral $[Eu(H_5dotp)]^*$ intermediate species is formed having five bound protons. This $[Eu(H_5dotp)]^*$ reaction intermediate should contain no water molecule (as it was found for the thermodynamic species $[Eu(H_n dotp)]^{(5-n)-}$) and it probably contains one double-protonated phosphonate moiety (isomer **I**) and its structure should be similar to previous protonated species. Other alternative structure of the $[Eu(H_5dotp)]^*$ intermediate is that of isomer **II** in which nitrogen donor atom can be protonated via proton transfer which has been already postulated in the literature [56]. The short-lived $[Eu(H_5dotp)]^*$ intermediate slowly rearranges to a long-lived intermediate $[Eu(H_6dotp)]^{(+)**}$ with participitation of one proton (the final product under our reaction conditions). The $[Eu(H_6dotp)]^{(+)**}$ species contains 4–5 water molecules in the inner coordination sphere and, therefore, we can assume that central ion binds only four oxygen atoms of four phosphonate groups and 4–5 water molecules. The $[Eu(H_6dotp)]^{(+)**}$ species itself is very slowly decomposed to the Eu(III)-aqua ion and the free ligand, highly protonated under such acid conditions (Scheme 1). More probably, the $[Eu(H_6dotp)]^{(+)**}$ species can be very slowly decomposed to the same product with an assistance of the next proton(s).

Formation of a similar stable reaction intermediate was proposed in mechanism for dissociation of the $[Gd(dotp)]^{5-}$ complex; the long-lived reaction intermediate $[Gd(H_5dotp)]^{**}$ was decomposed within four months [18]. In addition, monitoring of structure of the $[Eu(dota)]^-$ complex, inert in acidic region ($c_{H+} = 1 \times 10^{-5}$ – 0.56 mol dm^{-3}), by molecular absorption spectroscopy in VIS region ($^7F_0$–$^5D_0$ band) and by ^{1}H NMR spectroscopy suggested that the inner coordination sphere is intact to an extent of protonation [44]. Therefore, it was suggested that both non-protonated and protonated complexes are nine-coordinated with one inner-sphere water molecule [44]. Taking into account activation and thermodynamic parameters discussed above, the high kinetic inertness of the $[Eu(H_6dotp)(H_2O)_4]^{(+)**}$ intermediate can be explained. Since the complex protonation (reaction (C)) is endothermic and entropically driven, the formation of the $[Eu(H_5dotp)]^*$ intermediate is favoured at higher temperatures. The transformation of this intermediate to a relatively kinetically inert $[Eu(H_6dotp)(H_2O)_4]^{(+)**}$ intermediate (some of the reactions (D)–(F)) has a high energetic barrier which is, of course, higher for the rate-determining step (rds) than for other slow reactions. The rds has very probably an associative character ($\Delta S^{\neq} < 0$) with a participation of water molecule(s) and resulting to a simultaneous transfer of the phosphonate-bound proton(s) to nitrogen atom(s) of the ring [56]. Thus, the dissociation is more favoured at higher temperatures as a consequence of both thermodynamic and kinetic aspects. The difference in activation parameters obtained for the $[Ce(dotp)]^{5-}$ and $[Eu(dotp)]^{5-}$ complexes can be explained by structural variability of both complexes leading to difference in reactivity. The former complex probably coordinates one water molecule and it leads to lower kinetic inertness of complex decomposing probably to cerium(III) aqua ion [43]. The similar difference in acidic inertness was observed for $[Y(dota)]^-$, $[La(dota)]^-$ and $[Eu(dota)]^-$ complexes [44].

Generally, the most studied Ln(III) complexes are those of cerium(III), europium(III), and gadolinium(III) ions. Comparing properties of the $[Ln(dota)]^-$ and $[Ln(dotp)]^{5-}$ complexes (Table 2), it seems that the dissociation reaction of the $[Ln(dota)]^-$ complexes are slower than those for the $[Ln(dotp)]^{5-}$ complexes. However, the decomposition of $[Ln(dotp)]^{5-}$ complex cannot be assigned to a simple dissociation step, but it can be a reaction having a more complex character such as dissociation accompanied by an isomerization of the complex. This hypothesis is supported by the high values of the activation parameters which are higher than those for the corresponding $[Ln(dota)]^-$ complex [41], and they are in a fair agreement with the published values, mostly determined for copper(II) complexes of phosphonic acid derivatives of cyclam [51,52].

4. Conclusions

The dissociation kinetics of the $[Eu(dotp)]^{5-}$ complex was studied in detail. Dissociation of the complex under ambient conditions is faster than that $[Eu(dota)]^-$ complex; see half-times of complex decomposition in 0.01 mol dm^{-3} acid at 25 °C and $I = 3.00$ mol dm^{-3}: 899 h ($[Eu(dota)]^-$) [39] versus 15.8 h ($[Eu(dotp)]^{5-}$) [this work], respectively. Activation parameters of the complex dissociation were determined for the first time for this class of Ln(III) complexes and they still remain very rare in the literature. Surprisingly, the dissociation of the europium(III) complex of H_8dotp leads to a long-lived intermediate where the nitrogen atoms are (partly) protonated, and the central ion is coordinated by phosphonate pendant arms and some water molecules. This probably cationic intermediate is decomposed only after a long time (months) to the final europium(III) aqua complex due to a hindered excess of the next proton(s) necessary for a full ligand protonation and, thus, complex decomposition. This constitutes a proof that phosphonic acid pendant arms are able to bind lanthanide(III) ions even in strongly acidic conditions as it was observed for lanthanide(III) complexation by diphosphonate ligands [57]. This new methodology can be used for the study of reaction mechanism of lanthanide(III) complex with macrocyclic ligands having luminescent properties on at least minute time scale.

Acknowledgements

This work was supported by Ministry of Education, Youth and Sports (Czech–Polish KONTAKT Bilateral Program CZ/PL 2006/2007/9) and was performed in frame of the EU COST D18/D38 Action.

References

[1] A.E. Merbach, É. Tóth (Eds.), The Chemistry of Contrast Agents in Medical Magnetic Resonance Imaging, Wiley, New York, 2001.
[2] P. Caravan, J.J. Ellison, T.J. McMurry, R.B. Lauffer, Chem. Rev. 99 (1999) 2293.
[3] J.C.G. Bünzli, G.R. Choppin (Eds.), Lanthanide Probes in Life, Chemical and Earth Sciences, Theory and Practice, Elsevier, Amsterdam, 1989.
[4] D. Parker, Coord. Chem. Rev. 205 (2000) 109.
[5] D. Parker, R.S. Dickins, H. Puschmann, C. Crossland, J.A.K. Howard, Chem. Rev. 102 (2002) 1977.
[6] S. Faulkner, J.L. Matthews, in: J.A. McCleverty, T.J. Meyer (Eds.), Comprehensive Coordination Chemistry II, vol. 9, Elsevier, Amsterdam, 2004, p. 913.
[7] S. Liu, D.S. Edwards, Bioconjugate Chem. 12 (2001) 7.
[8] I. Lukeš, J. Kotek, P. Vojtíšek, P. Hermann, Coord. Chem. Rev. 216–217 (2001) 287.
[9] P. Táborský, P. Lubal, J. Havel, J. Kotek, J. Rudovský, P. Hermann, I. Lukeš, Collect. Czech. Chem. Commun. 70 (2005) 1909.
[10] M.I. Kabachnik, T.Ya. Medved, F.I. Belskii, S.A. Pisareva, Izv. Akad. Nauk SSSR, Ser. Khim. (1984) 844.
[11] M.I. Kabachnik, Yu. M. Polikarpov, Zh. Obsch. Khim. 58 (1988) 1937.
[12] R. Delgado, L. Siegfried, T.A. Kaden, Helv. Chim. Acta 73 (1990) 140.
[13] C.F.G.C. Geraldes, A.D. Sherry, W.P. Cacheris, Inorg. Chem. 28 (1989) 3336.
[14] A.D. Sherry, J. Ren, J. Huskens, E. Brücher, É. Tóth, C.F.G.C. Geraldes, M.M.C.A. Castro, W.P. Cacheris, Inorg. Chem. 35 (1996) 4604.
[15] F. Marques, L. Gano, M.P. Campello, S. Lacerda, I. Santos, L.M.P. Lima, J. Costa, P. Antunes, R. Delgado, J. Inorg. Biochem. 100 (2006) 270.
[16] J. Ren, A.D. Sherry, Inorg. Chim. Acta 246 (1996) 331.
[17] F. Avecilla, J.A. Peters, C.F.G.C. Geraldes, Eur. J. Inorg. Chem. (2003) 4179.
[18] L. Burai, R. Király, I. Lázár, E. Brücher, Eur. J. Inorg. Chem. (2001) 813.
[19] A.A. Schilt, Perchloric Acid and Perchlorates, G.F. Smith Company, Columbus, 1979.
[20] I. Lázár, D.C. Hrncir, W.D. Kim, G.E. Kiefer, A.D. Sherry, Inorg. Chem. 31 (1992) 4422.
[21] X. Sun, M. Wuest, Z. Kovacs, A.D. Sherry, R. Motekaitis, Z. Wang, A.E. Martell, M.J. Welch, C.J. Anderson, J. Biol. Inorg. Chem. 8 (2003) 217.
[22] M. Maeder, Y.M. Neuhold, G. Puxty, P. King, Phys. Chem. Chem. Phys. 5 (2003) 2836.
[23] K. Binnemans, C. Görller-Walrand, Chem. Phys. Lett. 235 (1995) 163.
[24] S. Lis, Z. Hnatejko, Z. Stryła, Opt. Appl. 31 (2001) 643.
[25] P. Táborský, I. Svobodová, Z. Hnatejko, P. Lubal, S. Lis, M. Försterová, P. Hermann, I. Lukeš, J. Havel, J. Fluoresc. 15 (2005) 507.
[26] P. Barthelemy, G.R. Choppin, Inorg. Chem. 28 (1989) 3354.
[27] E.N. Rizkalla, G.R. Choppin, in: K.A. Gschneidner Jr., L. Eyring (Eds.), Handbook on the Physics and Chemistry of Rare Earth, vol. 15, Elsevier, Amsterdam, 1991, p. 393 (Chapter 103).
[28] S. Lis, J. Alloys Compnd. 341 (2002) 45.
[29] I. Billard, in: K.A. Gschneidner Jr., J.-C.G. Bünzli, V.K. Pekharsky (Eds.), Handbook on the Physics and Chemistry of Rare Earth, vol. 33, Elsevier, Amsterdam, 2003, p. 465 (Chapter 216).
[30] A. Beeby, I.M. Clarkson, R.S. Dickins, S. Faulkner, D. Parker, L. Royle, A.S. de Sousa, J.A.G. Williams, M. Woods, J. Chem. Soc., Perkin Trans. 2 (1999) 493.
[31] R.M. Supkowski, W. De W. Horrocks Jr., Inorg. Chim. Acta 340 (2002) 44.
[32] W. De W. Horrocks Jr., D.R. Sudnick, J. Am. Chem. Soc. 101 (1979) 334.
[33] C.F.G.C. Geraldes, A.D. Sherry, G.E. Keifer, J. Magn. Reson. 97 (1992) 290.
[34] J. Ren, S. Zhang, A.D. Sherry, C.F.G.C. Geraldes, Inorg. Chim. Acta 339 (2002) 273.
[35] R.S. Dickins, D. Parker, J.I. Bruce, D.J. Tozer, Dalton Trans. (2003) 1264.
[36] M. Botta, Eur. J. Inorg. Chem. (2000) 399.
[37] P. Caravan, M.T. Greenfield, X. Li, A.D. Sherry, Inorg. Chem. 40 (2001) 6580.
[38] E. Brücher, G. Laurency, Z. Makra, Inorg. Chim. Acta 139 (1987) 141.
[39] E. Tóth, E. Brücher, I. Lázár, I. Tóth, Inorg. Chem. 33 (1994) 4070.
[40] E. Brücher, Top. Curr. Chem. 221 (2002) 103.
[41] C.A. Chang, Y.-H. Liu, J. Chin. Chem. Soc. 47 (2000) 1001.
[42] X. Wang, J. Tianzhu, V. Comblin, A.L. Mut, E. Merciny, J.F. Desreux, Inorg. Chem. 31 (1992) 1095.
[43] I. Svobodová, Z. Piskula, P. Lubal, S. Lis, P. Hermann, J. Alloys Compnd. in press, doi:10.1016/j.jallcom.2007.04.052.
[44] E. Szylagyi, E. Tóth, E. Brücher, A.E. Merbach, J. Chem. Soc., Dalton Trans. (1999) 2481.
[45] J. Moreau, E. Guillon, J.-C. Pierrard, J. Rimbault, M. Port, M. Aplincourt, Chem. Eur. J. 10 (2004) 5218.
[46] P.J. Breen, W. De W. Horrocks Jr., Inorg. Chem. 22 (1983) 536.
[47] S. Lis, G.R. Choppin, Mater. Chem. Phys. 31 (1992) 159.
[48] T. Kimura, Y. Kato, J. Alloys Compnd. 278 (1998) 92.
[49] P.G. Allen, J.J. Bucher, D.K. Shuh, N.M. Edelstein, I. Craig, Inorg. Chem. 39 (2000) 595.
[50] A. Nehlig, M. Elhabiri, I. Billard, A.-M. Albrecht-Gary, K. Lutzenkrichen, Radiochim. Acta 91 (2003) 37.
[51] J. Kotek, P. Lubal, P. Hermann, I. Císařová, I. Lukeš, T. Godula, I. Svobodová, P. Táborský, J. Havel, Chem. Eur. J. 9 (2003) 233.
[52] P. Lubal, J. Maleček, P. Hermann, J. Kotek, J. Havel, Polyhedron 25 (2006) 1884.
[53] J. Kotek, P. Vojtíšek, I. Císařová, P. Hermann, I. Lukeš, Collect. Czech. Chem. Commun. 66 (2001) 363.
[54] A.L. Thompson, D. Parker, D.A. Fulton, J.A.K. Howard, S.U. Pandya, H. Puschmann, K. Senanayake, P.A. Stenson, A. Badari, M. Botta, S. Avedano, S. Aime, Dalton Trans. (2006) 5605.
[55] W. De W. Horrocks Jr., V.K. Arkle, F.J. Liotta, D.R. Sudnick, J. Am. Chem. Soc. 105 (1983) 3455.
[56] M. Försterová, I. Svobodová, P. Lubal, P. Táborský, J. Kotek, P. Hermann, I. Lukeš, Dalton Trans. (2007) 535.
[57] K.L. Nash, J. Alloys Compnd. 249 (1997) 33.