

Kinetic study of dissociation of Eu(III) complex with H₈dotp (H₈dotp = 1,4,7,10-tetraazacyclododecane-1,4,7,10-tetrakis(methylphosphonic acid))

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Abstract

The dissociation kinetics of the europium(III) complex with H₈dotp ligand was studied by means of molecular absorption spectroscopy in UV region at ionic strength 3.0 mol dm⁻³ (Na,H)ClO₄ 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 ($\Delta H^0 = 11 \pm 3 \text{ kJ mol}^{-1}$, $\Delta S^0 = 41 \pm 11 \text{ J K}^{-1} \text{ mol}^{-1}$) and the activation parameters ($E_a = 69 \pm 8 \text{ kJ mol}^{-1}$, $\Delta H^\ddagger = 67 \pm 8 \text{ kJ mol}^{-1}$, $\Delta S^\ddagger = -83 \pm 24 \text{ J K}^{-1} \text{ mol}^{-1}$) 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.

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1. Introduction

Lanthanide(III) complexes of macrocyclic ligands having acetic (H₄dota) or phosphonic acid (H₈dotp) (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 (H₅dtpa) and cyclic (H₄dota) ligands [1,2] while the complexes of some lanthanide(III) ions (e.g. Eu³⁺/Tb³⁺ emitting in the VIS and Yb³⁺/Nd³⁺ in the NIR regions, respectively) are employed as luminescent probes [3–6]. Macrocyclic ligands

binding metal radioisotopes (e.g. ⁹⁰Y, ¹⁵³Sm, ¹⁶⁶Ho, ¹⁷⁷Lu) 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

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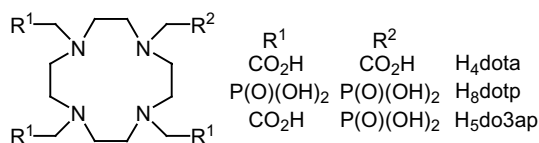


Chart 1.

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 H₄dota-like ligands [8,9].

The first synthesis of H₈dotp 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 H₈dotp are unusually high in comparison with those of H₄dota 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 H₈dotp 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 H₈dotp [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 Eu₂O₃ (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 H₈dotp 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 ($c_{\text{EuL}} \sim 0.015 \text{ mol dm}^{-3}$) 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 $I = 3.0 \text{ mol dm}^{-3}$ (H,Na)ClO₄ ($c_{\text{EuL}} \sim 1 \times 10^{-3} \text{ mol dm}^{-3}$). 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 ($\lambda_{\text{exc}} = 394 \text{ nm}$, ${}^7\text{F}_0 \rightarrow {}^5\text{L}_6$ 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 ($c_{\text{EuL}} \sim 0.001 \text{ mol dm}^{-3}$) was followed by TRLIFS in perchloric or hydrochloric acids ($I = 3.0 \text{ mol dm}^{-3}$). 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)

$$I_t = I_0 \times e^{-t/\tau} \quad (1)$$

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

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

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]

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