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SPECTROSCOPIC CHARACTERIZATION OF ETHYLENEDIAMINE- DI(*o*-HYDROXYPHENYL)ACETIC ACID AND ITS COMPLEXES WITH LANTHANIDE(III) IONS

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Binding properties of ethylenediaminedi(*o*-hydroxyphenyl)acetic acid (EHPG) with lanthanide(III) ions were studied using spectroscopic methods. Luminescence intensity and lifetime of the Tb(III) ion were measured in a wide pH range in order to characterize the Ln-EHPG complexation. The calculated hydration number of the Tb-EHPG system proved the replacement of six water molecules by the EHPG ligand in the inner coordination sphere of Tb(III). Energy transfer from Tb(III) to Eu(III) in the Tb(III)-EHPG-Eu(III) system indicated an existence of only monomeric form of the Tb-EHPG complex. Analysis of the ^1H NMR and FTIR spectra of the EHPG ligand and its complexes with lanthanide(III) ions confirmed the hexadentate manner of EHPG complexation with the lanthanides. The system of Dy(III)-EHPG, showing a linear dependence of luminescence intensity ($\lambda_{em} = 578 \text{ nm}$) of Dy(III) on its concentration, in the range of 3.3×10^{-7} to $1 \times 10^{-5} \text{ mol}\cdot\text{l}^{-1}$, can be applied for spectrofluorimetric determination of Dy(III).

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1. Introduction

The spectroscopic properties of trivalent lanthanides have attracted much attention in studying a variety of complexes in solution [1-3]. Ion luminescence and absorption (in the UV-visible and the near IR region) of certain lanthanide(III) ions make these ions useful in the characterization of lanthanide complexation in solution [2-4]. The luminescence intensity and lifetime of Eu(III) and Tb(III) ions have been used to gain information on the composition and structure of the first coordination sphere of these ions in a variety of systems [3-6]. Studies using ^1H NMR have been valuable to elucidate the nature and structures of La(III) or Lu(III) complexes [7].

Previously we reported the use of Eu(III) lifetime measurements to identify the residual hydration of the Eu(III) ion in aminopolycarboxylate complexes [8] and to characterize the bonding properties of the nitrogen, oxygen and sulfur donors to lanthanide ions with dicarboxylate ligands [9].

This paper is concerned with spectroscopic characterization of ethylenediaminedi(*o*-hydroxyphenyl)acetic acid (EHPG) and its complexation study with lanthanide ions. Complexation of EHPG with rare earth(III) ions were studied using pH-potentiometric and spectrophotometric methods [10] and potentiometric, luminescence intensity and lifetime measurements [11]. We report a study of hydration of the Tb(III) ion using the Tb(III) luminescence intensity and lifetime measurements, in the Tb-EHPG system, and energy transfer from Tb(III) to Eu(III) in the Tb(III)-EHPG-Eu(III) system. The ^1H NMR and FTIR spectra of the EHPG ligand and its complexes with lanthanide(III) ions are analysed in order to explain the binding properties of the ligand and a possibility of the Dy(III)-EHPG system for the spectrofluorimetric determination of Dy(III) is tested.

2. Experimental

2.1. Solutions

The reagent grade of the ethylenediaminedi(*o*-hydroxyphenyl)acetic acid was obtained from Sigma and used as received. Solutions of $\text{Tb}(\text{ClO}_4)_3$, $\text{Eu}(\text{ClO}_4)_3$ and $\text{La}(\text{ClO}_4)_3$ were prepared by dissolving Tb_4O_7 , Eu_2O_3 and La_2O_3 (spectral pure, made in our laboratory), respectively, in hydrochloric acid. Aliquots were added to solutions of the ligand such that the concentration of Eu(III) was $0.01 \text{ mol}\cdot\text{l}^{-1}$ and all solutions had a final ionic strength $0.1 \text{ mol}\cdot\text{l}^{-1} \text{ NaClO}_4$. The pH values of the solutions were adjusted by addition of aliquots of standard solutions of NaOH or of HCl. For the studies in D_2O (purity > 99.8%), aliquots of TbCl_3 solution were evaporated to dryness, followed by dissolution in D_2O . This procedure was repeated four times. Solutions of NaOD and DCl were used to adjust the pD values in these systems. During handling, the experimental vessels were protected with parafilm to avoid absorption by the samples of H_2O from the air. Solutions of EHPG and $\text{La}(\text{ClO}_4)_3$ for NMR studies in D_2O were prepared in the same way. The solid Eu-EHPG^- complex was prepared in a reaction of EHPG with $\text{Eu}(\text{ClO}_4)_3$ from equimolar water solutions at $\text{pH} \approx 11$.

2.2. Equipment

The Tb(III) corrected luminescence spectra were registered using Perkin-Elmer MPF-3 spectrofluorimeter and the exciting wavelength was 368 nm.

The luminescence lifetime measurements of Eu(III) were carried out with the use of the detection system described earlier [12] consisting of a nitrogen laser (KB6211) and a tunable dye laser. The luminescence decay curves observed in this work could be analysed by a single exponential relation (semilogarithmic plots of the luminescence intensity versus time were linear, providing the decay constants).

The ^1H NMR spectra were recorded using a Gemini 300 VT Varian spectrometer operating at 300 MHz at room temperature. The chemical shift values are in ppm (with accuracy of ± 0.01 ppm) in δ scale relative to DSS.

The IR spectra were obtained by means of FTIR Bruker JFS 113v spectrophotometer, and the samples (1.5 mg) were prepared in KBr (200 mg).

3. Results and discussion

The EHPG ligand forms a metal–ligand 1:1 complex [10, 11]. Schematic presentation of the EHPG ligand is shown in Fig. 1.

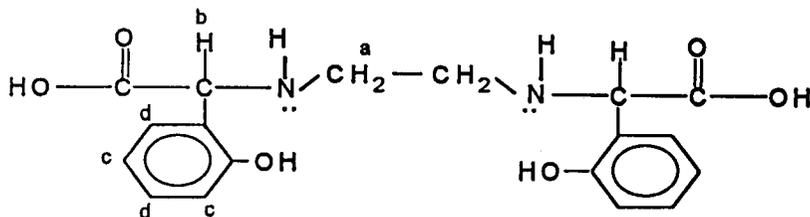


Fig. 1. Schematic presentation of the EHPG ligand.

The ligand has six potential ligating groups: two carboxylate groups, two phenolate oxygens and two amino nitrogens. Lanthanide ion binding to EHPG is of particular interest as an analogue of lanthanide binding to proteins, since the ligating groups of EHPG are similar to those in many proteins [11].

The luminescence intensity (I_{lum}) of the most intense band for Tb(III) at 545 nm, corresponding to the ${}^5D_4 \rightarrow {}^7F_5$ transition, and Tb(III) luminescence lifetime (τ) in the system containing Tb:EHPG = 1:1, depending on the pH value was investigated. A plot of the I_{lum} and τ dependence on varying pH (in the pH range 5–12) is shown in Fig. 2. The data plotted in Fig. 2 demonstrate the strong pH dependence of terbium luminescence intensity in the Tb-EHPG⁻ complex. The increasing intensity follows the binding of all the ligand moieties. The extent of direct Tb-phenolate binding and Tb-nitrogen donor binding increases with in-

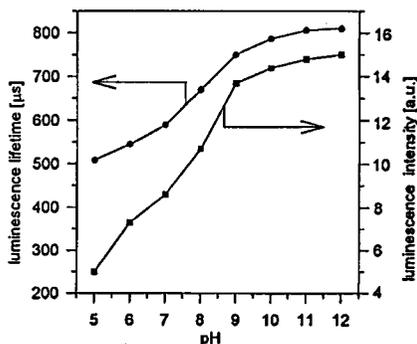


Fig. 2. Luminescence intensity and lifetime of Tb(III) ion in the Tb-EHPG system as a function of pH.

creasing pH, and the terbium luminescence intensity also increases with increasing pH.

The luminescence lifetime of Tb(III) in complexes with the EHPG ligand has been measured in H₂O and D₂O solutions and used to calculate the number of water molecules coordinated to Tb(III) in the Tb-EHPG⁻ complex.

The number of water molecules coordinated to Tb(III) in this system was determined from the reciprocal excited-state lifetime, τ^{-1} , separately in H₂O and D₂O solutions. The number of coordinated water molecules, $n_{\text{H}_2\text{O}}$, has been calculated from Eq. (1), regarding the contribution of the N-H vibration [4, 13, 14]:

$$n_{\text{H}_2\text{O}} = 4.2(\tau_{\text{H}_2\text{O}}^{-1} - \tau_{\text{D}_2\text{O}}^{-1}). \quad (1)$$

The total coordination number of the Tb(III) ion is 8 or 9 [2, 3, 11], and in this study it was found to be 8.7. The hydration number of the Tb-EHPG⁻ (1:1) complex depends on pH solution. The obtained results show that the Tb-EHPG⁻ complex has less than five water molecules of hydration in pH < 6 region and less than three water molecules of hydration when pH > 9. This indicates that EHPG coordinates as a hexadentate ligand in the basic region of pH, where its all potentially ligating groups are deprotonated.

In the ¹H NMR spectrum of EHPG solution in D₂O there are observed signals of nonlabile protons of methylene, methine groups and aromatic ring protons, denoted in Fig. 1 as a, b, c and d, respectively, in the dependence on pD. An increase in pD causes a successive dissociation of four D⁺ ions of the EHPG functional (carboxylic and phenolic) groups (see Table I). This dissociation contributes to the increase in the electron density at nonlabile protons, which is observed as the decrease in their chemical shift values. Dependence of chemical shifts of the ¹H NMR signals of nonlabile protons of EHPG in D₂O solutions on pD is shown in Fig. 3. The formation of the La-EHPG⁻ complex was found from the pD de-

TABLE I
Calculated values of the Stern-Volmer quenching constants (K_{SV}^{ϕ} and K_{SV}^{τ}) and the intramolecular association constant (K_{C}) as a function of pH in solution of the Tb-EHPG⁻ complex.

pH	K_{SV}^{ϕ}	K_{SV}^{τ}	K_{C}
6.0	626	620	4
7.0	567	497	73
8.0	492	379	93
9.0	288	284	15
10.0	239	148	86
11.0	370	264	97

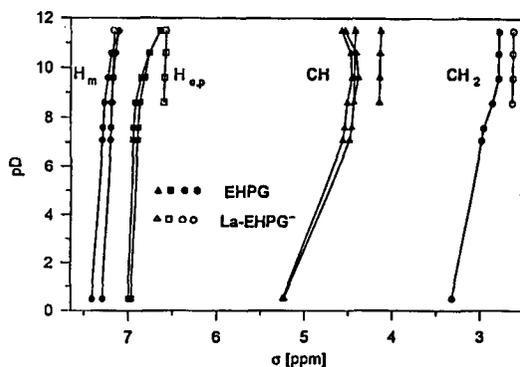


Fig. 3. Calculated hydration number of Tb(III) for Tb-EHPG⁻ complex (1:1) depending on pH.

pendence of proton chemical shifts in the system where the ratio of La(III):EHPG equals 1:1. Comparing the values of chemical shifts of nonlabile protons of EHPG ligand with those of La-EHPG⁻ complex, there is observed a substantial decrease in electron density at these protons as the ligand became coordinated. The central atom-carboxylate oxygen bond has an ionic nature and the electron density of nonlabile protons of carboxymethyl groups in the complex depends mainly on an electric potential of the metal ion. Signals of other protons of La-EHPG⁻ complex are observed upfield when compared to those for noncomplexed EHPG⁴⁻ ion.

Using the FTIR spectra an effect of a rigidity of the complexing system has been studied. On the basis of the FTIR spectra a strength of vibrations of these parts of the ligands, which take a part in complexation, was analysed. The observed shifts of characteristic bands corresponding to vibrations of: C-OO⁻, C-O⁻ (in aromatic ring) and C-NH, recorded for the EHPG ligand and Eu-EHPG⁻ complex (prepared as a solid 1:1 at pH ≈ 11), as shown in Table II, proved a weakening of the vibration bands involving N and O (both carboxylic and phenolic) atoms.

TABLE II

Chemical shifts of nonlabile protons of ionic forms of EHPG and their changes caused by the dissociation of functional group protons.

EHPG ionic form	pD	-CH ₂ - Δδ [ppm]	-NH- Δδ [ppm]	H _{o,p} Δδ [ppm]	H _m Δδ [ppm]
H ₄ L	0.5				
H ₃ L ⁻	7.1	0.34	0.71	0.068	0.097
H ₂ L ²⁻	8.6	0.028	0.055	0.024	0.013
HL ³⁻	10.6	0.002	-0.020	0.085	0.030
L ⁴⁻	11.5	0.005	-0.095	0.120	0.060

Energy transfer from Tb(III) to Eu(III) in the Tb(III)-EHPG-Eu(III) system was studied using the Stern-Volmer analysis of Tb(III) luminescence quenching (K_{SV}^{ϕ}) and its lifetime measurements (K_{SV}^{τ}) as a function of the Eu(III) (quencher) concentration $[Q]$. The values of K_{SV}^{ϕ} and K_{SV}^{τ} were calculated from Tb(III) luminescence intensity or lifetime using the following equations:

$$\frac{I_0 - I}{I} = K_{SV}^{\phi}[Q], \quad (2)$$

$$\frac{\tau_0 - \tau}{\tau} = K_{SV}^{\tau}[Q], \quad (3)$$

where I and τ are the Tb(III) luminescence intensity and lifetime in the presence, and I_0 and τ_0 in the absence of Eu(III) (quencher), respectively.

The intermolecular association constant, K_C , was calculated from the equation below

$$(I_0 - I)/I = (K_{SV}^{\tau} + K_C)[Q] + (K_{SV}^{\tau} K_C)[Q]^2. \quad (4)$$

The obtained values of K_{SV}^{ϕ} , K_{SV}^{τ} and K_C are presented in Table III. The results show that the energy transfer proceeds dominantly via a dynamic mechanism since $K_{SV}^{\phi} \approx K_{SV}^{\tau}$ and the value of K_C is low ($K_C \approx 100$), thus proving the monomeric nature of the Tb-EHPG⁻ complex in the whole pH (6-11) range studied.

TABLE III

IR spectroscopic data for EHPG and Eu-EHPG⁻ complex.

Assignment of vibration	λ_{\max} [cm ⁻¹] ligand	λ_{\max} [cm ⁻¹] complex	$\Delta\nu$ [cm ⁻¹]
COO ⁻ asymmetric	1645	1595	50
COO ⁻ symmetric	1415	1395	20
C-O ⁻ (phenol)	1175	1145	30
C-NH	3380	3320	60

Complexation of the lanthanide ions with EHPG results in enhancement of lanthanide ion luminescence. We have tested the possibility of applying the spectrofluorimetric method for determination of luminescent lanthanide ions in aqueous solution of the Ln-EHPG system. The greatest enhancement of luminescence intensity has been observed in the system of Dy(III)-EHPG. The luminescence intensity ($\lambda_{em} = 578$ nm) of Dy(III) was a linear function of its concentration, in the range of 3.3×10^{-7} to 1×10^{-5} mol·l⁻¹, and this system can be applied for spectrofluorimetric determination of Dy(III).

Changes of the luminescence intensity of the Tb(III) complex and determined hydration number for the Tb-EHPG⁻ complex proved that the EHPG ligand coordinates as a hexadentate ligand. The results show that in the Tb-EHPG⁻ (1:1) complex the hydration number is ≈ 2 and therefore the EHPG ligand replaces six water molecules in the inner sphere of Tb(III) indicating that both the nitrogen donors and oxygen (in carboxylic and phenolic groups) atoms are bonded to the

metal ion. It is consistent with the ^1H NMR results obtained from chemical shifts of protons of EHPC coordinated with La(III) ions. Also the results obtained from the analysis of the IR spectra proved complexation of Eu(III) by functional (carboxylic and phenolic) groups and the nitrogen donors.

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