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Spectroscopic studies of the complexes formed between lanthanide ions and N-(2-hydroxyethyl)iminodiacetic acid in solution

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Abstract

The solution coordination chemistry associated with 1 : 1 and 1 : 2 complexes of lanthanide ions with N-(2-hydroxyethyl)iminodiacetic acid (HIDA, H_2hida) has been studied by means of luminescence spectroscopy. The luminescence lifetime of Tb(III) in complexes with HIDA have been measured in H_2O and D_2O solutions of varying pH (ranging from pH 1.5 to 11) and lanthanide(III)–HIDA ratio. The lifetime has been used to determine the number of water molecules bound in the inner coordination sphere to the Tb(III) ion. In addition, energy transfer from Tb(III) to Eu(III) in the Ln(III)–HIDA system has been investigated. The results obtained show that HIDA acts as a tetradentate ligand. It was also concluded that at low pH values, the Tb(HIDA) complex is mononuclear and contained an average of $\sim$5 molecules of coordinated water, whereas at high pH values, this complex is self-associated. The Tb(HIDA)$_2$ complexes below pH 9 were monomeric and contained one or two coordinated water molecules.

Keywords: N-(2-hydroxyethyl)iminodiacetic acid complexes; Luminescence; Europium(III); Terbium(III); Energy transfer

1. Introduction

From among all metallic cations, lanthanide (and certain actinide) ions are distinguished by their luminescence properties in solution at ambient temperature [1]. An inner coordination sphere of the Ln(III) cations, studied by luminescence spectroscopy, provides significant information regarding the coordination environment of the chemical species in solution and solid [1–5]. A correlation between the luminescence decay constants, k_{H_2O} (the reciprocal of the excited state lifetime) and the hydration number, n_{H_2O}, of Ln(III) ions studied in H_2O–D_2O solution and in crystalline compounds [6–8], were employed in studies of the structures of lanthanide complexes. Complexes formed by Ln(III) with ligands containing a negatively charged oxygen atom as a donor are the most stable [9]. The structures of lanthanide complexes can be different depending on interactions between donor groups of the ligand, competition between the donor groups and solvent molecules [10,11].

Aminopolycaboxylic acids (APA) are particularly suitable ligands for investigation of their complexes with rare earth ions as they absorb radiation in the far ultraviolet range making sure that the absorption bands of the ligands will not overlap the emission bands of Ln(III) [11].

The lanthanide(III) complexes are characterised by high stability and well water solubility which facilitates their investigation by various methods.

Previously [10,11], we have characterised complexes of Sm(III), Eu(III), Tb(III) and Dy(III) with APA in aqueous solution using luminescence spectroscopy. Dependence of the lanthanide(III) ion luminescence intensity on pH, ligand concentration and temperature have been discussed. The hypersensitivity of the Eu(III) luminescence band and energy transfer in systems with APA have also been studied. Luminescence lifetime measurements of excited states of Ln(III) ions, were used to determine the number of water molecules coordinated in the inner sphere with the lanthanide ion in a series of complexes with aminopolycarboxylic acids [12–15] following the procedure developed by Horrocks and Sudnick [6].

This paper is a continuation of our luminescence studies on complexes of lanthanide(III) ions with aminopolycarboxylic acids. Here we report a study of the solution coordination chemistry of Eu(III) and Tb(III) ions with HIDA.

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2. Experimental

2.1. Chemicals

The N-(2-hydroxyethyl)iminodiacetic acid, analytical grade, was used as received from Fluka. Perchlorate solutions of europium(III) and terbium(III) were prepared by dissolving weighed amounts of Eu_2O_3 or Tb_4O_7 (spectrally pure, obtained in our laboratory), respectively, in perchloric acid (Merck). For the studies in D_2O aliquots of $Eu(ClO_4)_3$ solution were evaporated to dryness, followed by dissolution in D_2O. This procedure was repeated four times. During handling the D_2O solutions were covered with parafilm to protect absorption of H_2O from the air and kept in a desiccator. In the solution used for luminescence studies the concentration of Ln(III) ions was 1×10^{-2} mol l^{-1}, while in the one used for the lifetime measurements it was 2×10^{-3} mol l^{-1}. For investigation of energy transfer processes, very small amounts (microlitres) of EuHIDA solutions of a concentration of 6×10^{-3} mol l^{-1} and the metal to ligand ratio the same as in TbHIDA solutions, were added to the latter. The value of pH of the solutions was adjusted by $HClO_4$/DCl or NaOH/NaOD, using a pH-meter (26, Radiometer, Copenhagen) and a combined electrode GK 2401C.

2.2. Spectroscopic measurements

Emission measurements were conducted using Perkin-Elmer MPF-3 spectrofluorimeter in a quartz cuvette (1 × 1 cm). Luminescence spectra of the aqueous solutions of Ln(III) and LnHIDA were obtained with wavelengths corresponding to that of the maximum absorption of the lanthanide ion, that is $\lambda = 394$ or 368 nm for Eu(III) and Tb(III), respectively. Absorption spectra were recorded on a UV-VIS 160 Shimadzu spectrophotometer. The luminescence lifetime measurements of Tb(III) were carried out with the use of the detection system described earlier [16]. It consisted of a nitrogen laser pumping the LD390 (or BPBD365) dye (Exciton Chemicals) in methanolic (or ethanol–toluene) solution in a tunable dye laser. Experiments were conducted at room temperature. The luminescence decay curves observed in this work could be analysed by a single exponential relation providing the decay constants.

3. Results and discussion

Luminescence spectra of three positive lanthanide ions are composed of narrow and well resolved bands corresponding to ff transitions. Spectra of Eu(III) and Tb(III) (Fig. 1) show the greatest increase of emission intensity after complexation of the ions, and therefore they are most frequently used in luminescence studies.

HIDA is a potentially tetradentate ligand containing two carboxylic groups, a hydroxyl group and a donating nitrogen atom, Fig. 2.

Absorption and luminescence spectra of HIDA and its complexes with Ln(III) ions were recorded in aqueous solution. With the help of a computer program, written in Basic, which uses the ligand protonation and complexation stability constants [17], the percentage of M, ML and ML_2 species were calculated as a function of the variation of pH and metal–ligand ratios. This procedure, described in [11], allowed us to choose the optimum experimental conditions (metal–ligand ratio and pH) to measure also the luminescence lifetime of each species. The absorption spectra of the

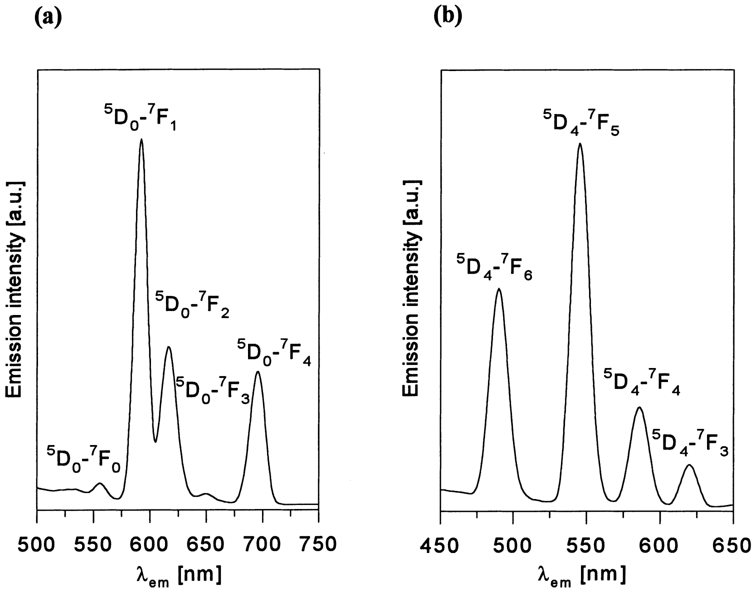

Fig. 1. Luminescence spectra of Eu(III) (a) and Tb(III) (b).

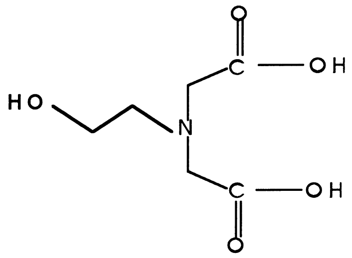

Fig. 2. Structure of the N-(2-hydroxyethyl)iminodiacetic acid.

HIDA ligand and its complex with Eu(III) show the maxima of absorption at $\lambda = 235$ and 250 nm, respectively, so the bands do not interfere with luminescence bands of Ln(III) ions.

3.1. Luminescence vs. pH

Luminescence spectra of the LnHIDA solutions were recorded for the M : L molar composition of 1 : 1, 1 : 2 and 1 : 4 in a wide range of pH. The dependence of the intensity of Tb(III) luminescence for $\lambda = 545$ nm $^5D_4 \rightarrow {}^7F_5$ transition) on pH and the Tb : HIDA molar ratio is shown in Fig. 3.

The intensity of luminescence of the complex solutions increases with increasing pH and the metal-ligand ratio. Increasing intensity of Tb(III) luminescence of the 1 : 1 complex solution was observed for pH varying from 1.5 to 4 and from 9 to 11. In the case of the molar ratio 1 : 2 and 1 : 4 solutions the greatest increase of the luminescence intensity was observed for the pH values from 1.5 to 6. Further increase of pH up to 10 did not produce any significant increase in the luminescence intensity, a slight increase only above this value was noted. The luminescence spectrum of Eu(III) ion in solution shows two strongest bands at 593 and 615 nm, associated with $^5D_0 \rightarrow^7 F_1$ and $^5D_0 \rightarrow^7 F_2$ (exhibiting hypersensitivity) transitions, respectively (Fig. 1). The intensity of Eu(III) aqua ion at 615 nm is weaker than that at 593 nm and the relative intensities are sensitive to the environment of the inner coordination sphere of the Eu(III) ion [11]. We calculated the ratios η of the intensities I_{615}/I_{593}, (Table 1) as a function of metal–ligand ratio and pH.

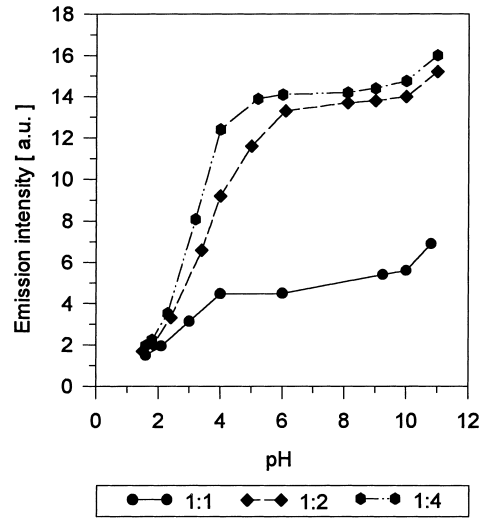

Fig. 3. Intensity of Tb(III) ions emission in solutions of complexes with HIDA as a function of pH and molar ratio of the components.

As follows from the Table 1 data, complexation of the lanthanide ions by HIDA takes place already at pH lower than 2, however, in these conditions the degree of complexation of Ln(III) ions is low. The highest values of η equal to ~1.90 were obtained for the systems of the molar ratio of respective components of 1 : 2 and 1 : 4. The same values of η can indicate the presence of the same forms of complexes. For the system with MIDA (N-methyliminediacetic acid), forming ML, ML_2 and ML_3, the situation was different, that is the values of η increased with increasing metal to ligand ratio up to 1 : 3 [12].

Table 1
Characteristics of luminescence of Eu(III) – HIDA complexes depending on the composition of the solution and its pH

Molar ratio	pH of solution	% of the complex form			I_{lum593}(a. u.)	I_{lum615} (a.u.)	$\eta = \frac{I_{lum}615}{I_{lum}593}$	$\frac{I_{lumEu/HIDA}}{I_{lumEu(ClO_4)_3}}$
		M	ML	ML_2				
1 : 1	1.5	91	9	-	7.0	3.1	0.44	1.3
	2.2	48	48	4	9.0	7.5	0.84	3.0
	3.5	19	66	15	13.9	18.7	1.34	7.5
	5.8	17	66	17	14.8	20.4	1.38	8.2
1 : 2	1.5	74	25	1	7.0	3.2	0.45	1.3
	1.8	48	48	4	8.0	5.4	0.68	2.2
	2.4	17	66	17	13.0	16.4	1.26	6.6
	3.2	2	44	54	21.4	62.5	1.58	12.9
	10.0	–	–	100	33.0	62.5	1.90	25.0
1 : 4	1.5	56	42	2	7.6	3.4	0.45	1.4
	2.3	7	67	26	13.8	15.7	1.14	6.3
	3.1	1	20	79	20.0	32.8	1.64	13.1
	7.7	–	–	100	27.1	50.2	1.85	20.1
	10.0	–	–	100	33.9	64.1	1.89	25.6

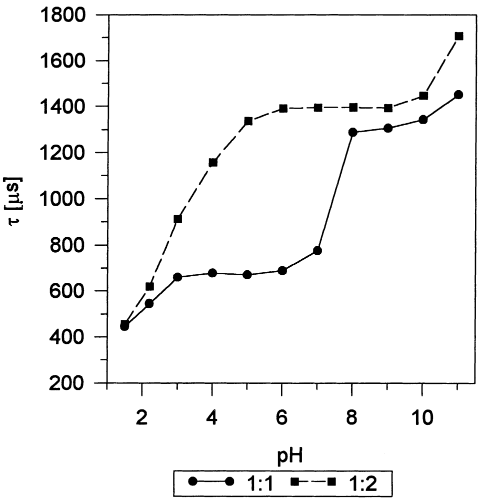

Fig. 4. Tb(III) ions lifetime in solutions of complexes with HIDA as a function of pH and molar ratios of the components.

The lifetime of Tb(III) ions in the complexes with HIDA measured against pH and for different metal – ligand molar ratios are collected in Fig. 4.

3.2. The number of the coordinated water molecules

The average number of water molecules coordinated to Tb(III) ion in the TbHIDA system was determined by measuring excited state lifetime, τ, separately in H_2O (k_{H_2O}) and D_2O (k_{D_2O}) solutions. The decay constants ($k = \tau^{-1}$) were used to calculate the hydration number, n_{H_2O}, by the relationship [6]:

$$n_{H_2O} = 4.2(k_{H_2O} - k_{D_2O})$$

The uncertainty of the calculated n is ±(0.4) unit.

Calculated hydration number of TbHIDA complexes for different pH and metal–ligand ratio are shown in Table 2.

As shown in Table 2, in the system of TbHIDA at the molar ratio 1 : 1 the number of water molecules coordinated in the inner sphere quickly decreases with pH increasing from 1.5 to 3, and then remains constant for pH from 3 to 6. With the further increase of pH the number of water molecules decreases to take $n = 1.8$ at pH 8. This indicates the presence of two forms of complexes in this system, the first one for pH from 1.5 to 3 where the number of water molecules in the first coordination sphere is about 4.7, and the second for pH varying from 6 to 8 where the corresponding number of water molecules is 1.9. For the TbHIDA system of the molar ratio 1 : 2 the number of relevant water molecules decreases with pH increasing up to 6, and then takes a constant value of 1.6. The results are in agreement with the data reported for NTA [14] and this agreement proves that two HIDA molecules are involved in the coordination (with participation of hydroxyl groups) and formation of $Ln(HIDA)_2^{3-}$ complexes. Our results have confirmed the reports of Kostromina [18] who determined a contribution of the OH group from HIDA in the coordination. The author claims that the Ln–OH bond is responsible for a shift of protons from the $-CH_2$ group which is the neighbour closest to the OH group of the acid.

3.3. Intermolecular energy transfer

Determination of the association degree is of particular importance in investigation of lanthanide complexes [13]. Measurements of intermolecular energy transfer for different pH values and metal to ligand ratio can be used for determination of the degree of association of a given lanthanide complex in solution [13–15]. The structure of the associated forms depends on pH, at low pH values they take the form of the bridged ligands and for high pH the complexes are formed through hydroxy bridges [19].

In the next step of our studies, the quenching of the excited state of Tb(III) ion, used as a donor, by Eu(III) was studied. The Eu(III) ion having the excited $^5D_0$ level, lying ~3000 cm^{-1} below the excited $^5D_4$ level of Tb(III), is a very good quencher for the Tb(III) luminescence. On the basis of the known changes in the lifetime and luminescence intensity of Tb(III) ions, the Stern-Volmer constants, K_{sv},

Table 2
The number of water molecules, n, bound in the inner coordination sphere of the Tb(III) ion in solutions of Tb–HIDA complexes

pH solution	Tb / ligand mole ratio					
	1 : 1			1 : 2		
	$\tau^{-1}_{H_2O}$[ms^{-1}]	$\tau^{-1}_{D_2O}$[ms^{-1}]	n_{H_2O}	$\tau^{-1}_{H_2O}$[ms^{-1}]	$\tau^{-1}_{D_2O}$[ms^{-1}]	n_{H_2O}
1.5	2.25	0.31	8.2	2.20	0.29	8.0
2	1.84	0.35	6.2	1.62	0.30	5.5
3	1.52	0.35	4.9	1.10	0.31	3.3
4	1.48	0.35	4.7	0.86	0.35	2.1
5	1.49	0.34	4.8	0.75	0.34	1.7
6	1.45	0.34	4.7	0.72	0.34	1.6
7	1.29	0.33	4.0	0.72	0.34	1.6
8	0.78	0.32	1.9	0.72	0.34	1.6
9	0.77	0.32	1.9	0.72	0.34	1.6
10	0.75	0.32	1.8	0.69	0.34	1.5
11	0.69	0.33	1.5	0.59	0.35	1.0

Table 3
Stern–Volmer constants and intermolecular association constants, K_c, for different pH values and molar ratios

Molar ratio of the components						
pH	1 : 1			1 : 2		
	K_{sv}^{ϕ}	K_{sv}^{τ}	K_c	K_{sv}^{ϕ}	K_{sv}^{τ}	K_c
1.5	281	165	127	152	119	30
2.5	374	253	118	182	140	32
3.0	462	330	122	1208	269	734
4.0	571	436	128	2069	806	1074
5.0	765	243	393	925	892	38
6.0	1189	302	726	586	512	70
7.0	2698	746	1779	159	100	62
8.0	3503	701	2584	288	187	85
9.0	3142	282	2789	858	329	531
10.0	2669	137	2501	1289	305	971
11.0	2444	161	2238	1739	304	1428

were calculated. On the basis of K_{sv} values the ranges of pH, within which the monomeric and dimeric forms of the complexes occur, were found. The Stern–Volmer constants were calculated from the formulas:

$$\frac{I_o - I}{I} = K_{sv}^{\phi}[Q]; \; \frac{\tau_o - \tau}{\tau} = K_{sv}^{\tau}[Q] \tag{2}$$

where, I_o and τ_o are the intensity of emission and lifetime of Tb(III) ions without the quencher, while I and τ are the corresponding values in the presence of a quencher at a concentration $[Q]$.

The quenching of the donor emission can occur according to the mechanism of dynamic or static quenching. In many cases the luminescence quenching is a result of a combination of static and dynamic quenching [13–15]. In such circumstances:

$$\frac{I_o}{I} - 1 = (K_{sv}^{\tau} + K_c)[Q] + (K_{sv}^{\tau} \times K_c)[Q]^2 \tag{3}$$

where, K_c is the intermolecular association constant.

The forms of complexes occurring in solution can be characterized by the values of K_c [14,15]. The calculated K_c values are presented in Table 3. The error of K_c resulting from inaccuracy of K_{sv}^{τ} and luminescence intensity, in all the cases, is less than 5%.

In a solution of the molar ratio of its components 1 : 1 and within the pH range from 1.5 to 4, the dynamic quenching of luminescence is observed since the calculated K_c values are low for the TbHIDA complex, having five water molecules of hydration. It suggests that the complex has the monomeric form (Table 3) in this range of pH and is responsible for the observed static quenching characterized by the same values of K_{sv}^{ϕ} and K_{sv}^{τ}. With a further increase of pH the association of the system growth and the static mechanism of quenching is set on. This kind of behaviour, characterized by much higher values of the self-associated constant ($K_c \sim 2600$), indicates the formation of a new type of species. The existence of this new species is also evident from the lifetime measurements. The calculated hydration number for the basic pH range (above seven) gives two water molecules of hydration. It means that the formation of the new species must result in expulsion of three coordinated water molecules, and as a result the oligomeric species is formed. Most probably in the basic pH range this oligomeric species is hydroxy bridged dimer complex with two water of hydration. A similar observation of the appearance of a self-association form in the range of pH values from 4.0 to 6.0 for TbNTA (1 : 2) complex has been reported by Brittain [14]. In the case of the Tb to HIDA ratio of 1 : 2, the dynamical quenching is observed for pH in the range from 1.5 to 2.5 and from 5.0 to 8.0, while for pH from 3.0 to 4.0 and above 8.0, in which the K_c values are much higher, the quenching occurs according to the static mechanism.

4. Conclusions

In conclusion, the luminescence techniques used in this work have provided detailed information regarding the nature of TbHIDA complexes in solution. The luminescence data obtained for the TbHIDA complexes indicate the formation of both 1 : 1 and 1 : 2 metal–ligand complexes. Determined hydration numbers for the TbHIDA and Tb(HIDA)$_2$ complexes shown that the HIDA acts as a tetradentate ligand, replacing four and seven or eight water molecules from the inner sphere of Tb(III), indicating that both the nitrogen donors and oxygen (of carboxylic and hydroxyethyl groups) atoms are bonded to the metal ion.

Energy transfer results obtained for the Tb/HIDA/Eu system prove the presence of both monomeric and oligomeric – hydroxy bridged forms of the TbHIDA complexes, depending on pH and metal–ligand ratio.

References

[1] J.-C.G. Bünzli, in: J.-C.G. Bünzli, G.R. Choppin (Eds.), Lanthanide Probes in Life, Chemical and Earth Sciences: Theory and Practice, chap. 9, Elsevier, Amsterdam, The Netherlands, 1989.

[2] S.T. Frey, M.L. Gong, W. DeW. Horrocks Jr., Inorg. Chem. 33 (1994) 3229.

[3] J.V. Beitz, J. Alloys Comp. 207/208 (1994) 41.

[4] L. Soderholm, G. K Liu, J. Muntean, J. Malinsky, M.R. Antonio, J. Phys. Chem. 99 (1995) 9611.

[5] S. Lis, Z. Wang, G.R. Choppin, Inorg. Chim. Acta 239 (1995) 139.

[6] W. DeW. Horrocks Jr., D.R. Sudnick, J. Am. Chem. Soc. 101 (1979) 334.

[7] P. Barthelemy, G.R. Choppin, Inorg. Chem. 28 (1989) 3354.

[8] T. Kimura, G.R. Choppin, Y. Kato, Z. Yoshida, Radiochim. Acta 72 (1996) 61.

[9] T. Moeller, Inorg. Chem. Ser. One 7 (1972) 275.

[10] M. Elbanowski, S. Lis, J. Konarski, Mąkowska, B., Monatsh. Chem. 118 (1987) 907.

[11] S. Lis, J. Konarski, Z. Hnatejko, M. Elbanowski, J. Photochem. Photobiol., A: Chem. 79 (1994) 25.

[12] M. Elbanowski, Z. Hnatejko, Z. Stryła, S. Lis, J. Alloys Comp. 225 (1995) 515.

[13] H.G. Brittain, in: C.E. Carraher, J. Sheats, C. Pittman (Eds.), Intermolecular Energy Transfer as a means for the Characterization of Polymeric Lanthanide Complexes in Solution, in Metal Containing Polymeric Systems, Plenum Press, New York, 1985, p. 451.

[14] H.G. Brittain, J.P. Jasinski, J. Coord. Chem. 18 (1988) 279.

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

[16] Z. Stryła, S. Lis, M. Elbanowski, Opt. Appl. 23 (1993) 163.

[17] A.E. Martell, R.M. Smith, Critical Stability Constants, vol. 1, Plenum Press, New York, 1989.

[18] N.A. Kostromina, Usp. Khim. 32 (1973) 585.

[19] R. Prados, L.G. Stadtherr, H. Donato, R.B. Martin, J. Inorg. Nucl. Chem. 36 (1974) 689.