

Spectroscopy of Heavy Lanthanide Complexes with NTA

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Abstract

Spectroscopic properties of Ho^{3+} -NTA and Er^{3+} -NTA systems were investigated for different M:L ratios and different concentrations of M within a broad pH range. Analysis of the oscillator strength values of the 'hypersensitive' transitions and of the Judd-Ofelt intensity parameters τ_{λ} allowed us to investigate the formation and the type of bonding of the Ln^{3+} -NTA species occurring in solution. These results are in good agreement with the results of luminescence measurements.

Introduction

Lanthanide complexes with polyamino acids have been the subject of several investigations. Almost all physical methods available have been applied to the elucidation of their structures in solid phase and/or in solution. Lanthanide complexes with polyamino acids are mainly entropy stabilized; ligands are relatively weakly bonded with the central lanthanide ion. As was shown in NMR studies [1–4] only M–N bonding is relatively inert and complexation processes could be investigated by this method. Once formed the M–N bond is relatively weakly affected (with the exception maybe of solutions with very high pH) by the additional processes which can occur in solution. NMR in this case is not a particularly sensitive method. In such a case additional independent methods are necessary because no unequivocal conclusions can be drawn from any data from this particular method. Significant progress in the better understanding of the structure and the reaction of polyaminocarboxylate lanthanide complexes (both in solid phase and in solution) was achieved by applying the luminescence spectroscopy method [5–8]. It was proved that both total luminescence intensities and luminescence decay constants of several polyaminoacetic complexes are related to the structure of species existing in solution. Together with the luminescence studies of crystals, some important information is obtainable – especially that concerning the presence of water molecules (or OH groups) in the particular lanthanide

ion coordination sphere. The luminescence intensity of lanthanide (Sm, Eu, Gd, Tb, Dy) polyamino acid complexes (EDTA and NTA) in solution for different M:L ratios at different pH values were measured recently by Elbanowski *et al.* [6–8].

In our opinion, electronic absorption spectroscopy is still underrated as a source of important information on the coordination state in solution. In our recent papers [9–11] we concluded that this method was quite sensitive when intensity changes of f–f transitions were considered. Several authors have found differences in the structures of heavy and light lanthanide complexes with some ligands. This fact is caused by the increasingly effective electric charge on the lanthanide ion across the series. This effect should be distinctly noted for the large ligands for which the packing effect around the small cation is particularly important. Among different polyaminoacetic ligands nitrilotriacetic acid has a particular position. The only nitrogen atom has strong donor properties and the size of the molecule is relatively small in comparison with such polyamino acids as EDTA and their derivatives.

In our recent papers [9, 10] we presented some spectral data which could be explained by the assumption of the influence of the solution coordination state on both intensities and band shapes of Nd^{3+} -polyamino acid ligand systems in solution. It was reasonable to test if this method is sensitive when changes in the coordination mode of the ligand by lanthanide ion are possible. Since we can expect such a change for the heavy lanthanide ions we have chosen Ho^{3+} - and Er^{3+} -NTA systems. For these lanthanide ions several electronic f–f transitions are available for absorption spectroscopy measurements.

Experimental

Reagents

The stock solutions of Ho^{3+} and Er^{3+} perchlorates were prepared from 99.9% lanthanide oxides (Merck). Concentrations of the Ln^{3+} ions were determined gravimetrically. The stock solution of NTA, because of its solubility, was prepared using NaOH with a

ratio NTA:NaOH = 1:2. A carbonate-free NaOH solution was used to adjust the pH of the ligand solutions to appropriate values.

Measurements and Calculations

All spectral measurements were made on a Cary 14 spectrophotometer within the region 10 000–41 000 cm^{-1} . All the measured solutions were prepared with the same ionic strength (0.5 M NaClO_4). The pH values of the solutions investigated spectroscopically were measured on a Radelkis pH-meter (with an accuracy ± 0.05 pH unit). Experimental oscillator strength values were obtained by graphic

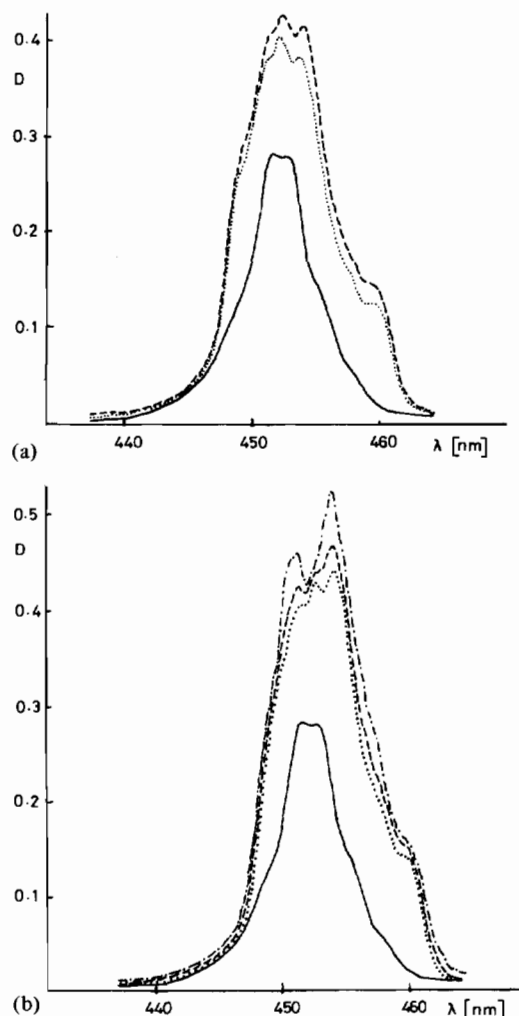


Fig. 1. The effect of pH on the 'hypersensitive' transition $^5G_6 \leftarrow ^5I_8$ in the absorption spectrum of the Ho^{3+} ion for: (a) Ho^{3+} :NTA ratio of 1:1 ($c_{\text{Ho}^{3+}} = 1.489 \times 10^{-2}$ M, $c_{\text{NTA}} = 1.5 \times 10^{-2}$ M): $\text{Ho}(\text{ClO}_4)_3$, — (pH = 2.86); $\text{Ho}(\text{ClO}_4)_3 + \text{NTA}$, (pH = 1.43); $\text{Ho}(\text{ClO}_4)_3 + \text{NTA}$, - - - (pH = 6.75). (b) Ho^{3+} :NTA ratio of 1:2 ($c_{\text{Ho}^{3+}} = 1.489 \times 10^{-2}$ M, $c_{\text{NTA}} = 3.0 \times 10^{-2}$ M): $\text{Ho}(\text{ClO}_4)_3$, — (pH = 2.86); $\text{Ho}(\text{ClO}_4)_3 + \text{NTA}$, (pH = 1.61); $\text{Ho}(\text{ClO}_4)_3 + \text{NTA}$, - - - (pH = 2.06); $\text{Ho}(\text{ClO}_4)_3 + \text{NTA}$, - · - (pH = 5.16–12.16).

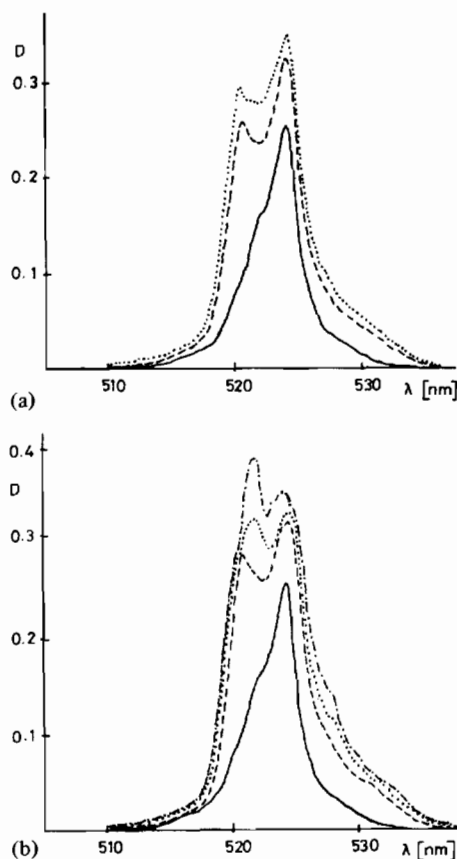


Fig. 2. The effect of pH on the 'hypersensitive' transition $^2H_{11/2} \leftarrow ^4I_{13/2}$ in the absorption spectrum of the Er^{3+} ion for: (a) Er^{3+} :NTA ratio of 1:1 ($c_{\text{Er}^{3+}} = 1.496 \times 10^{-2}$ M, $c_{\text{NTA}} = 1.5 \times 10^{-2}$ M): $\text{Er}(\text{ClO}_4)_3$, — (pH = 1.61); $\text{Er}(\text{ClO}_4)_3 + \text{NTA}$, - - - (pH = 1.55); $\text{Er}(\text{ClO}_4)_3 + \text{NTA}$, (pH = 7.10). (b) Er^{3+} :NTA ratio of 1:2 ($c_{\text{Er}^{3+}} = 1.496 \times 10^{-2}$ M, $c_{\text{NTA}} = 3.0 \times 10^{-2}$ M): $\text{Er}(\text{ClO}_4)_3$, — (pH = 1.61); $\text{Er}(\text{ClO}_4)_3 + \text{NTA}$, - - - (pH = 1.55); $\text{Er}(\text{ClO}_4)_3 + \text{NTA}$, (pH = 2.64); $\text{Er}(\text{ClO}_4)_3 + \text{NTA}$, - · - (pH = 4.57–12.30).

integration of the area under the absorption curves after appropriate corrections for the base line.

The τ_λ parameters were calculated from the experimental oscillator strengths and the Judd–Ofelt equation in the following modified form:

$$P = \sum_{\lambda} \tau_{\lambda} \sigma(f_{\psi_J}^N \| U^{(\lambda)} \| f_{\psi'_J}^N)^2 / (2J + 1) \quad (1)$$

where σ is the wave number (cm^{-1}), $U^{(\lambda)}$ are matrix elements of the unit tensor calculated by Carnall *et al.* [12] in the intermediate coupling scheme, $f_{\psi_J}^N$, $f_{\psi'_J}^N$ are the initial and final states of electronic transitions, respectively, and J is the total quantum number.

Results and Discussion

The spectra of Ho^{3+} – and Er^{3+} –NTA systems were examined over a large pH range for different

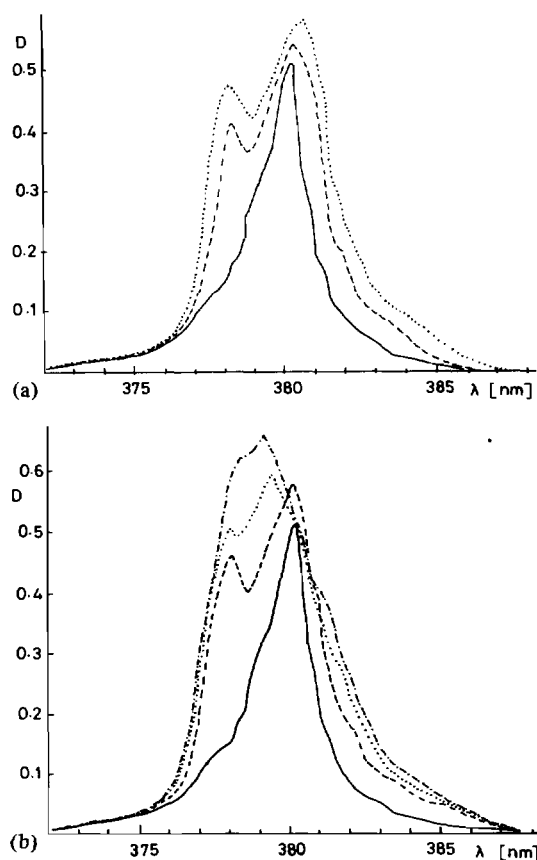


Fig. 3. The effect of pH on the 'hypersensitive' transition ${}^4G_{11/2} \leftarrow {}^4I_{13/2}$ in the absorption spectrum of the Er^{3+} ion for: (a) $\text{Er}^{3+}:\text{NTA}$ ratio of 1:1 ($c_{\text{Er}^{3+}} = 1.496 \times 10^{-2}$ M, $c_{\text{NTA}} = 1.5 \times 10^{-2}$ M): $\text{Er}(\text{ClO}_4)_3$, — (pH = 1.61); $\text{Er}(\text{ClO}_4)_3 + \text{NTA}$, - - - (pH = 1.55); $\text{Er}(\text{ClO}_4)_3 + \text{NTA}$, ····· (pH = 7.10). (b) $\text{Er}^{3+}:\text{NTA}$ ratio of 1:2 ($c_{\text{Er}^{3+}} = 1.496 \times 10^{-2}$ M, $c_{\text{NTA}} = 3.0 \times 10^{-2}$ M): $\text{Er}(\text{ClO}_4)_3$, — (pH = 1.61); $\text{Er}(\text{ClO}_4)_3 + \text{NTA}$, - - - (pH = 1.55); $\text{Er}(\text{ClO}_4)_3 + \text{NTA}$, ····· (pH = 2.64); $\text{Er}(\text{ClO}_4)_3 + \text{NTA}$, - · - · (pH = 4.57–12.30).

lanthanide ion concentrations and different M:L ratios.

The typical picture of intensity and shape changes of 'hypersensitive' transitions as a function of the pH

TABLE II. Oscillator Strength Values (P) of the ${}^5G_6 \leftarrow {}^5I_8$ 'Hypersensitive' Transition and the Judd–Ofelt Parameter Values (τ_λ) of Ho^{3+} for an $\text{Ho}^{3+}:\text{NTA}$ Ratio of 1:1 at Different pH Values ($c_{\text{Ho}^{3+}} = 2.002 \times 10^{-2}$ M, $c_{\text{NTA}} = 2 \times 10^{-2}$ M)

pH	$P \times 10^6$	$\tau_2 \times 10^9$	$\tau_4 \times 10^9$	$\tau_6 \times 10^9$
1.34	9.8765	2.01 ± 0.38	4.76 ± 0.55	4.37 ± 0.39
1.61	10.5231			
2.04	10.5419	2.46 ± 0.36	4.54 ± 0.53	4.53 ± 0.37
3.18	10.4053	2.30 ± 0.31	4.70 ± 0.45	4.58 ± 0.32
4.36	11.3163	2.52 ± 0.40	5.19 ± 0.59	4.64 ± 0.41
6.35	10.7099	2.18 ± 0.56	5.20 ± 0.56	4.67 ± 0.39
6.85	11.2980			
6.96	11.5473			

and M:L concentration ratios are presented in Fig. 1 for the ${}^5G_6 \leftarrow {}^5I_8$ transition of Ho^{3+} and in Figs. 2 and 3 for the ${}^4G_{11/2} \leftarrow {}^4I_{13/2}$ and ${}^2H_{11/2} \leftarrow {}^4I_{13/2}$ transitions of Er^{3+} .

The Judd–Ofelt intensity parameters for the solutions examined were evaluated from the set of all available f–f transitions. Results are collected in Tables I–III for Ho^{3+} – and in Tables IV–VI for Er^{3+} –NTA systems.

Solutions with Ratio of $\text{Ln}^{3+}:\text{NTA} = 1:1$

For these systems at low pH values below 2.25 for Ho^{3+} and 3.25 for Er^{3+} (Fig. 4) some equilibria between aqua ions and 1:1 complex species are observed. At such a low pH value the effective concentration of unprotonated polyamino acid ligand is very low. Formation of the 1:1 complex species is demonstrated by the intensity changes of the 'hypersensitive' transition and distinct changes of the 'hypersensitive' transition band shape (Figs. 1, 2 and 3). Above these pH values, oscillator strength values are nearly constant, which indicates full complexation of Ln^{3+} ions as a 1:1 $\text{Ln}(\text{NTA})$ species. NTA is bonded with lanthanide ion both by one nitrogen atom and three carboxylic groups. This is in good agreement with the luminescence spectroscopy

TABLE I. Oscillator Strength Values (P) of the ${}^5G_6 \leftarrow {}^5I_8$ 'Hypersensitive' Transition and the Judd–Ofelt Parameter Values (τ_λ) of Ho^{3+} at Different Ligand Excesses and Constant Metal Concentration ($c_{\text{Ho}^{3+}} = 2.002 \times 10^{-2}$ M)

$c_{\text{Ho}^{3+}}:c_{\text{NTA}}$	c_{NTA} [M]	pH	$P \times 10^6$	$\tau_2 \times 10^9$	$\tau_4 \times 10^9$	$\tau_6 \times 10^9$
1:0		2.65	6.1975			
1:0.5	0.010	1.45	8.1991			
1:1	0.020	1.34	9.8765	2.01 ± 0.38	4.76 ± 0.55	4.37 ± 0.39
1:1.25	0.025	1.43	10.6740			
1:1.5	0.030	1.47	11.0389			
1:1.75	0.035	1.50	11.2890			
1:2	0.040	1.69	11.5467	2.50 ± 0.42	5.48 ± 0.62	4.73 ± 0.43
1:3	0.060	2.03	11.2823	2.27 ± 0.47	5.57 ± 0.70	5.01 ± 0.49
1:4	0.080	2.18	11.7644	2.41 ± 0.40	5.70 ± 0.59	5.18 ± 0.41

TABLE III. Oscillator Strength Values (P) of the ${}^5G_6 \leftarrow {}^5I_8$ 'Hypersensitive' Transition and the Judd-Ofelt Parameter Values (τ_λ) of Ho^{3+} for $\text{Ho}^{3+}:\text{NTA}$ Ratios of 1:2, 1:3, and 1:4 at Different pH Values ($c_{\text{Ho}^{3+}} = 2.002 \times 10^{-2}$ M, $c_{\text{NTA}} = 4 \times 10^{-2}$ M, 6×10^{-2} M and 8×10^{-2} M)

pH	$P \times 10^6$	$\tau_2 \times 10^9$	$\tau_4 \times 10^9$	$\tau_6 \times 10^9$
1:2				
1.69	11.5467	2.50 ± 0.42	5.48 ± 0.62	4.73 ± 0.43
2.04	11.5327			
5.44	11.6729	2.17 ± 0.43	5.98 ± 0.63	5.54 ± 0.45
5.91	11.4107	2.08 ± 0.44	6.00 ± 0.64	5.11 ± 0.45
9.40	11.9161	2.26 ± 0.44	6.05 ± 0.65	5.48 ± 0.46
11.25	11.9787			
11.67	12.0864	2.23 ± 0.42	6.27 ± 0.62	5.65 ± 0.44
12.30	11.8664			
12.41	11.2571	1.88 ± 0.46	6.17 ± 0.68	5.49 ± 0.48
1:3				
2.03	11.2823	2.27 ± 0.47	5.57 ± 0.70	5.01 ± 0.49
2.62	11.8371			
10.53	11.4333	2.11 ± 0.45	5.96 ± 0.66	5.34 ± 0.46
11.01	11.4952	2.06 ± 0.45	6.07 ± 0.67	5.51 ± 0.47
12.24	11.7688			
12.71	11.9656			
12.97	11.1844	1.86 ± 0.64	6.20 ± 0.94	5.64 ± 0.66
13.21	12.0311	2.48 ± 0.39	5.80 ± 0.58	5.44 ± 0.41
1:4				
2.18	11.7644	2.41 ± 0.40	5.70 ± 0.59	5.18 ± 0.42
11.20	11.7256	2.00 ± 0.61	6.42 ± 0.89	5.63 ± 0.63

copy data. Under similar conditions Horrocks *et al.* [5] assumed the existence of $\text{Tb}(\text{NTA}) \cdot 5\text{H}_2\text{O}$ species. Elbanowski *et al.* [6–8] measured intensity of fluorescence as a function of M:L ratios and pH values for NTA systems with Eu^{3+} , Gd^{3+} , Tb^{3+} and Dy^{3+} ions. Results for Tb^{3+} and Dy^{3+} are particularly convenient for comparison with our absorption spectroscopy data because of the similarities in effective charge and ionic radius, particularly between Dy^{3+} and Ho^{3+} ions. For the 1:1 complex the constant

TABLE IV. Oscillator Strength Values (P_1) of the ${}^2H_{11/2} \leftarrow {}^4I_{13/2}$ and (P_2) of the ${}^4G_{11/2} \leftarrow {}^4I_{13/2}$ 'Hypersensitive' Transitions and the Judd-Ofelt Parameter Values (τ_λ) of Er^{3+} at Different Ligand Excesses and Constant Metal Concentration ($c_{\text{Er}^{3+}} = 2.007 \times 10^{-2}$ M)

$c_{\text{Er}^{3+}}:c_{\text{NTA}}$	c_{NTA} [M]	pH	$P_1 \times 10^6$	$P_2 \times 10^6$	$\tau_2 \times 10^9$	$\tau_4 \times 10^9$	$\tau_6 \times 10^9$
1:0		1.45	2.7684	6.0791	1.97 ± 0.33	2.74 ± 0.54	2.28 ± 0.31
1:0.5	0.010	1.24	3.7873	8.0993			
1:1	0.020	1.13	4.6246	9.6539	4.07 ± 0.37	3.03 ± 0.60	2.63 ± 0.34
1:1.25	0.025	1.26	4.7607	10.1767			
1:1.5	0.030	1.32	4.8998	10.5359			
1:1.75	0.035	1.37	5.2033	11.2576			
1:2	0.040	1.42	5.3071	10.9598	4.95 ± 0.42	2.97 ± 0.67	2.78 ± 0.39
1:3	0.060	1.66	5.6115	11.4272	5.22 ± 0.44	3.02 ± 0.70	2.99 ± 0.40
1:4	0.080	1.91	5.5394	10.7874	4.96 ± 0.32	2.82 ± 0.51	2.99 ± 0.30

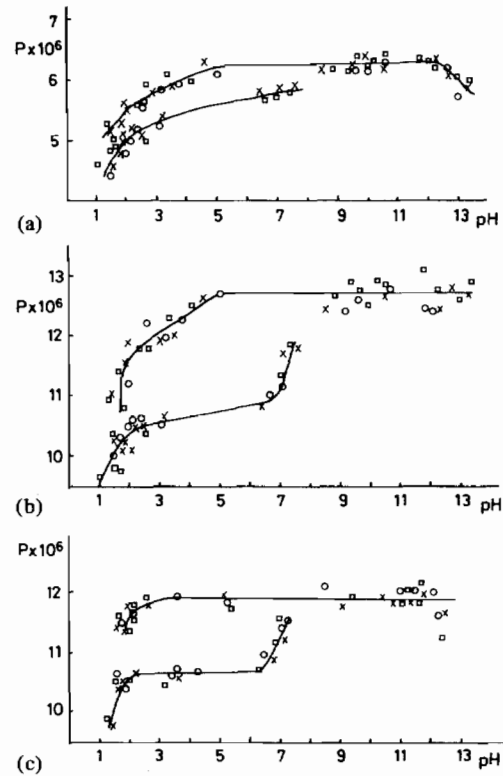


Fig. 4. The oscillator strength value of the 'hypersensitive' transition: (a) ${}^2H_{11/2} \leftarrow {}^4I_{13/2}$ of the Er^{3+} ion; (b) ${}^4G_{11/2} \leftarrow {}^4I_{13/2}$ of the Er^{3+} ion; (c) ${}^5G_6 \leftarrow {}^5I_8$ of the Ho^{3+} ion; as a function of pH value for the $\text{Ln}^{3+}-\text{NTA}$ system. $c_{\text{Er}^{3+}} = 1.004 \times 10^{-2}$ M, \circ ; 1.496×10^{-2} M, \square ; 2.007×10^{-2} M, \times ; 2.002×10^{-2} M, \square .

value is observed within the same pH range as in our measurements. Above $\text{pH} = 6.3$ for Ho^{3+} and 6.7 for Er^{3+} (Fig. 4) the increase of oscillator strength values in absorption spectra is again observed. These changes can be caused by a hydrolysis process and/or by some structural rearrangement of the ligand molecule. Neither of these spectroscopic methods give an

TABLE V. Oscillator Strength Values (P_1) of the ${}^2H_{11/2} \leftarrow {}^4I_{13/2}$ and (P_2) the ${}^4G_{11/2} \leftarrow {}^4I_{13/2}$ 'Hypersensitive' Transitions and the Judd-Ofelt Parameter Values (τ_λ) of Er^{3+} for an Er^{3+} :NTA Ratio of 1:1 at Different pH Values ($c_{Er^{3+}} = 2.007 \times 10^{-2}$ M, $c_{NTA} = 2 \times 10^{-2}$ M)

pH	$P_1 \times 10^6$	$P_2 \times 10^6$	$\tau_2 \times 10^9$	$\tau_4 \times 10^9$	$\tau_6 \times 10^9$
1.13	4.6246	9.6539	4.07 ± 0.37	3.03 ± 0.60	2.63 ± 0.34
1.47	4.6286	10.3527			
1.52	4.8398	10.3405	4.43 ± 0.45	3.16 ± 0.72	2.61 ± 0.41
1.64	4.9794	9.7240	3.93 ± 0.28	3.51 ± 0.44	2.64 ± 0.25
1.74	4.7450	9.6568	4.06 ± 0.33	3.11 ± 0.53	2.68 ± 0.30
1.88	5.0210	10.2610			
2.08	5.1429	10.4446			
2.63	4.9695	10.4218	4.49 ± 0.39	3.16 ± 0.63	2.65 ± 0.36
2.65	5.2730	10.4631			
6.82	5.7430	10.7726			
7.09	5.6887	11.3532	4.83 ± 0.32	3.75 ± 0.52	2.69 ± 0.30
7.43	5.7945	11.8558			

TABLE VI. Oscillator Strength Values (P_1) of the ${}^2H_{11/2} \leftarrow {}^4I_{13/2}$ and (P_2) of the ${}^4G_{11/2} \leftarrow {}^4I_{13/2}$ 'Hypersensitive' Transitions and the Judd-Ofelt Parameter Values (τ_λ) of Er^{3+} for Er^{3+} :NTA Ratios of 1:2, 1:3 and 1:4 at Different pH Values ($c_{Er^{3+}} = 2.007 \times 10^{-2}$ M, $c_{NTA} = 4 \times 10^{-2}$ M, 6×10^{-2} M and 8×10^{-2} M)

pH	$P_1 \times 10^6$	$P_2 \times 10^6$	$\tau_2 \times 10^9$	$\tau_4 \times 10^9$	$\tau_6 \times 10^9$
1:2					
1.42	5.3071	10.9598	4.95 ± 0.42	2.97 ± 0.67	2.78 ± 0.39
1.86	5.3180	11.8532			
2.62	5.6484	11.8917	5.16 ± 0.53	3.54 ± 0.85	2.93 ± 0.49
2.64	5.6333	11.5289	5.38 ± 0.26	2.80 ± 0.67	3.06 ± 0.39
2.70	5.9669	11.7891	5.14 ± 0.62	3.59 ± 0.62	3.08 ± 0.36
2.90	5.9202	11.8880			
3.37	6.0910	12.2784			
4.14	6.0137	12.2354	5.27 ± 0.42	3.79 ± 0.67	3.12 ± 0.38
8.87	6.2081	12.9131	5.75 ± 0.49	3.62 ± 0.79	3.15 ± 0.45
11.83	6.3545	13.0880	5.82 ± 0.49	3.68 ± 0.80	3.28 ± 0.46
13.00	6.0652	12.6327	5.83 ± 0.48	3.15 ± 0.78	3.25 ± 0.45
1:3					
1.66	5.6115	11.4272	5.22 ± 0.44	3.02 ± 0.70	2.99 ± 0.40
2.45	5.5939	11.6288			
9.37	6.1543	12.9144	6.02 ± 0.50	3.08 ± 0.81	3.26 ± 0.46
9.69	6.3822	12.7489	5.77 ± 0.42	3.49 ± 0.68	3.24 ± 0.39
10.31	6.2278	12.9081			
10.59	6.4621	13.1011			
12.30	6.2010	12.7655	5.74 ± 0.44	3.40 ± 0.71	3.33 ± 0.41
13.37	5.9973	12.9014	5.94 ± 0.55	3.14 ± 0.55	3.29 ± 0.51
1:4					
1.91	5.5394	10.7874	4.96 ± 0.32	2.82 ± 0.51	2.99 ± 0.30
10.06	6.2691	12.5555	5.55 ± 0.38	3.67 ± 0.61	3.12 ± 0.35

unequivocal answer, however it is worth noticing that for EDTA complexes [13] for which undoubtedly a hydrolysis process occurs at very high pH values the spectral changes in absorption are distinctly different from those for Ho^{3+} - and Er^{3+} -NTA systems. It is worth pointing out that when the number of water molecules (or OH groups) is constant in the first-coordination sphere of the complex

species, no changes in the fluorescence intensity are observed. The fluorescence intensity changes related to complexation are caused mainly by the substitution of water molecules by the ligand in the first-coordination sphere of the lanthanide ion.

Usually the ligand molecule (at least the part coordinated to the lanthanide ion) does not have such high frequency modes of oscillation as the OH

group of the solvent and participation of other radiation-less mechanisms are far less significant. Therefore it can be suggested that structural changes in the 1:1 species occur in solution. These changes can be caused by hydrolysis, or by formation of the 1:1 complex with the differently bonded NTA molecule. From the X-ray data it is known that in the solid phase the $\text{Dy(NTA)} \cdot 2\text{H}_2\text{O}$ species [14] has all the oxygen atoms of the NTA ligand bonded with the lanthanide ions (three oxygen and one nitrogen atoms bonded with the same lanthanide ion, and a further three oxygen atoms bonded with the adjacent Ln^{3+} ions). This means that the coordination number of each NTA molecule increases to 7, and 7 coordination positions of each lanthanide ion are occupied by the NTA molecule. Such a process should be accompanied by elimination of water molecules from the first-coordination sphere.

The results for EDTA-Ho^{3+} and $-\text{Er}^{3+}$ complexes conform to such a mechanism. Undoubtedly the hydrolysis process changes the shape and intensity of 'hypersensitive' transitions drastically, whereas, as can be seen in Figs. 1–3, in the case of NTA intensity changes are not accompanied by significant shape changes. Some small differences can be caused by exchange of the remaining water molecules in the first-coordination sphere by the OH^- groups.

Solutions with Ratio of $\text{Ln}^{3+}:\text{NTA} = 1:2$

For the system with excess NTA ligand the spectral changes are different than for the $\text{Ln}^{3+}:\text{NTA} = 1:1$ system. This is shown in Fig. 4. The oscillator strength values for solutions with excess NTA (1:2, 1:3 and 1:4) are significantly higher than for the $\text{Ln}:\text{NTA} = 1:1$ system. This is also confirmed by the general spectral changes.

The results collected in Tables III and VI indicate that τ_4 and τ_6 parameter values are higher in this case. It is more clearly visible for Ho^{3+} than for Er^{3+} . Usually, evaluation of the τ_λ parameter values for Ho^{3+} is more accurate thanks to the good resolution of the particular transitions in the spectrum of this ion. It can be assumed that above $\text{pH} = 3$ an equilibrium between 1:1 and 1:2 species occurs. The quantity of the 1:2 species is higher at the higher pH value. In the 1:2 species we can assume that each ligand molecule is coordinated by three oxygen and one nitrogen atoms. This means that

in the first-coordination sphere of the lanthanide ion either no water molecule (if coordination number of the Ho^{3+} is 8) or only one molecule (if coordination number is 9) is preserved. Such a complex hydrolyzes with difficulty because the water molecule in the lanthanide first-coordination sphere is more easily substituted by the OH group. For the L:M ratio higher than 1:2 no distinct spectral differences were observed. This means that under these conditions no higher complexes should exist in the system considered.

These conclusions are in good agreement with the results of luminescence measurements where also a distinct increase of intensity is observed for the solutions with L:M ratio higher than one. It is worth noting, however, that all our solutions were measured at constant ionic strength (0.5 M NaClO_4). We cannot observe any differences caused by the influences of the bulk solution on the intensities of f–f transitions, so all observed spectral changes should be related to the changes in the first lanthanide coordination sphere.

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