

Structure and optical spectroscopy of holmium(III) triethylenetetraaminehexaacetate in single crystal and in solution

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The crystal structure of $[\text{C}(\text{NH}_2)_3]_3[\text{Ho}(\text{ttha})] \cdot 3\text{H}_2\text{O}$ (H_6ttha = triethylenetetraaminehexaacetic acid) has been determined. The coordination environment of the Ho^{III} ion is composed of five carboxylate oxygen atoms and four nitrogen atoms. Electronic absorption spectra of a $[\text{C}(\text{NH}_2)_3]_3[\text{Ho}(\text{ttha})] \cdot 3\text{H}_2\text{O}$ single crystal were measured at room and liquid helium temperatures and compared with those of the $\text{Ho}^{\text{III}}\text{-ttha}$ (1 : 1) complex in solution. The results suggest that a species of coordination geometry similar to that of the $[\text{Ho}(\text{N}_4\text{O}_6)]^{3-}$ type found in the crystal exists predominantly in solution at $\text{pH} > 5$. At lower pH values, as for other $\text{Ln}^{\text{III}}\text{-ttha}$ complexes, coordination equilibria are observed.

This paper is a part of our investigation of lanthanide compounds with triethylenetetraaminehexaacetic acid (H_6ttha), a ligand with four nitrogen and six oxygen donor atoms (N_4O_6). Our previous results based on the electronic absorption spectra of $\text{Nd}^{\text{III}}\text{-ttha}$ crystals and solutions of the complex revealed the existence of two different species at equilibrium in solution.^{1,2} In those species, the inner sphere of the Nd^{III} ion comprises only donor atoms of the ttha ligand, forming $[\text{Nd}(\text{N}_4\text{O}_6)]^{3-}$ and $[\text{Nd}_2(\text{N}_3\text{O}_6)_2]^{6-}/[\text{Nd}(\text{N}_3\text{O}_6)]^{3-}$ entities with coordination numbers of ten and nine, respectively. In order to check how coordination arrangements around the Ln^{III} ion will change across the rare earth series in the ttha complexes, we have performed spectroscopic investigations of the $\text{Ho}^{\text{III}}\text{-ttha}$ complex in solution and in the form of a single crystal. Such studies seem to be essential since previously obtained results on complexes of heavy lanthanide ions with ttha in solution proved the absence of water molecules in the inner sphere of the Ln^{III} ion,^{3–5} formation of oligomeric species⁶ as well as a presence of multiple 1 : 1 species.^{3,7} So far two types of crystal structure of nine-coordinate ttha complexes with heavy lanthanide ions have been determined, namely: $[\text{Ln}(\text{N}_4\text{O}_6)]^{3-}$ (where $\text{Ln}^{\text{III}} = \text{Gd},^8 \text{Dy},^9 \text{Yb}^{10}$) and $[\text{Gd}_2(\text{N}_3\text{O}_6)_2]^{6-}$,¹¹ the latter being similar to that found for the $\text{Nd}^{\text{III}}\text{-ttha}$ complex.² The aim of this paper is to recognize the solution structure of the $\text{Ho}^{\text{III}}\text{-ttha}$ (1 : 1) complex based on a comparison between the spectral properties of this complex in the $[\text{C}(\text{NH}_2)_3]_3[\text{Ho}(\text{ttha})] \cdot 3\text{H}_2\text{O}$ single crystal and in solution.

Experimental

Materials and sample preparation

A stock solution of holmium perchlorate was prepared from Ho_2O_3 (99.9% Merck). The Ho^{III} ion concentration was determined complexometrically using xylenol orange as indicator. The stock solutions of (carboxymethyl)iminobis(ethylenenitrilo)tetraacetic acid (H_5dtpa , Aldrich) and H_6ttha (Merck) were prepared by half-neutralization with NaOH . The NaOH solution was also used to adjust the pH of investigated solutions. All measured solutions were prepared with the same ionic strength (0.5 M NaClO_4).

Crystals of $[\text{C}(\text{NH}_2)_3]_3[\text{Ho}(\text{ttha})] \cdot 3\text{H}_2\text{O}$ were prepared by a slight modification of the method described by Ruloff *et al.*⁹

Guanidinium carbonate (98% ABCR) was added to a hot aqueous suspension of Ho_2O_3 and H_6ttha and stirred for about 5 hours at 70°C . The molar ratio of Ho_2O_3 , H_6ttha and $[\text{C}(\text{NH}_2)_3]_2\text{CO}_3$ was 1 : 2 : 2.5. The undissolved residue was filtered off, the solution adjusted with $[\text{C}(\text{NH}_2)_3]_2\text{CO}_3$ to a final pH of 5 and left to crystallize. Large well-formed crystals, resistant to air and humidity were obtained. The Ho^{III} ion concentration in these crystals was determined by inductively coupled plasma-atomic emission spectroscopy (1.906 M). Anal.(%): found: C, 28.1; H, 5.6; N, 20.1; Ho, 18.7; calc. for $[\text{C}(\text{NH}_2)_3]_3[\text{Ho}(\text{ttha})] \cdot 3\text{H}_2\text{O}$: C, 28.4; H, 5.5; N, 20.5; Ho, 18.6. The refractive index n of the crystal was 1.50 and that of the measured solutions – 1.33.

X-Ray analysis

A suitable crystal was cut from a larger one, placed in a capillary and mounted on a Kuma KM4 diffractometer with κ geometry and a graphite monochromator. The data were corrected for Lorentz and polarization factors, but not for absorption or extinction. The structure was solved in a routine way. The C- and N-bonded hydrogen atoms were placed from geometry. No attempt to localize the O-bonded hydrogen atoms was undertaken. The structure was refined with the full matrix least-squares method with all non-hydrogen atoms anisotropic and hydrogen atoms isotropic with the temperature factors set as 1.2 times the factor for their bonding atoms. The positions of the hydrogen atoms were geometrically constrained. The calculations were performed with the SHELXS¹² and SHELXL-97¹³ programs with commonly used atom scattering factors and anomalous dispersion corrections.¹⁴ Other details of data collection and the structure refinement are given in Table 1.

CCDC reference number 440/190. See <http://www.rsc.org/suppdata/nj/b0/b001480j/> for crystallographic files in .cif format.

Spectroscopic measurements

The absorption spectra were recorded on a Cary 5 UV-vis-near-IR spectrophotometer, equipped with an Oxford CF 1204 continuous-flow helium cryostat for single crystal measurements in the 293–4 K temperature range. The intensities of the 4f–4f transitions (P) and values of the Ω_λ parameters

Table 1 Crystal data and structure refinement for $[\text{C}(\text{NH}_2)_3]_3[\text{Ho}(\text{ttha})] \cdot 3\text{H}_2\text{O}$

Empirical formula	$\text{C}_{21}\text{H}_{48}\text{HoN}_{13}\text{O}_{15}$
Formula weight	887.65
T/K	293(2)
Crystal system	Triclinic
Space group	$P\bar{1}(\text{no. } 2)$
$a/\text{\AA}$	9.535(2)
$b/\text{\AA}$	12.520(3)
$c/\text{\AA}$	17.012(3)
$\alpha/^\circ$	71.89(3)
$\beta/^\circ$	81.55(3)
$\gamma/^\circ$	68.90(3)
$V/\text{\AA}^3$	1799.4(7)
Z	2
μ/mm^{-1}	2.280
Reflections collected	5332
Reflections observed $[I \geq 2\sigma(I)]$	4960
Independent observed reflections	4625 ($R_{\text{int}} = 0.0138$)
Final R , R' indices $[I \geq 2\sigma(I)]$	0.0351, 0.1021

were calculated from the Judd–Ofelt^{15,16} relation:

$$P = \chi \frac{8\pi^2 mc \sigma}{3h(2J+1)} \sum_{\lambda=2,4,6} \Omega_{\lambda} (f^n \psi J \| U^{(\lambda)} \| f^n \psi' J')^2 \quad (1)$$

where P denotes the oscillator strength, $\chi(n^2 + 2)^2/9n$, where n is the refractive index, J is the total quantum number of the ground state, $(f^n \psi J \| U^{(\lambda)} \| f^n \psi' J')$ is the reduced matrix element of the unit tensor operator $U^{(\lambda)}$ tabulated by Carnall *et al.*¹⁷ and Ω_{λ} are empirical least-squares fitted parameters.

Results and discussion

Crystal structure

The coordination geometry of the Ho^{III} ion is presented in Table 2 and is similar to those previously reported for the $[\text{C}(\text{NH}_2)_3]_2[\text{Gd}(\text{Httha})] \cdot 5\text{H}_2\text{O}$,⁸ $[\text{C}(\text{NH}_2)_3]_2[\text{Dy}(\text{Httha})] \cdot 5\text{H}_2\text{O}$ ⁹ and $\text{K}_3[\text{Yb}(\text{ttha})] \cdot 5\text{H}_2\text{O}$ ¹⁰ crystals. The structure consists of complex anions, guanidinium cations and hydration water molecules. The Ho^{III} ion is nine-coordinate. The shortest $\text{Ho} \cdots \text{Ho}$ distance is 9.223(4) Å. The coordination geometry of the lanthanide cation may be defined either as a distorted capped square antiprism (*SAPRS*-9) or a distorted tricapped trigonal prism (*TPRS*-9). In the first case the non-capped base is spanned by N(3), N(2), N(1) and O(7), whereas

O(5), O(1), O(3) and N(4) form the capped one, and O(9) is the cap. The parameter Δ (defined as $\sum d_i^2/9$, $i = 1-9$, where d_i is the distance between the i -th atom and the relevant vertex of the ideal least-squares fitted polyhedron¹⁸) was 0.069 Å². For the *TPRS*-9 case the best fit geometry, with O(1), N(2), O(5) and O(3), O(7), N(4) forming the bases, and N(1), N(3), O(9) occupying the positions of the caps, had $\Delta = 0.086$ Å². The ttha anion does not utilize its full coordination capability; one of its acetate tentacles remains un-coordinated at O(11) and O(12) and is involved only in H-bonds to guanidinium nitrogen atoms. An ORTEP¹⁹ view of the complex anion is presented in Fig. 1. There are three independent guanidinium cations in the structure. One of them, C(20), forms two hydrogen bonds through two of its N atoms with one water molecule and is linked through three other H-bonds to a complex anion, and with one bond to the complex anion in a neighbouring position. The C(30) guanidinium cation links three complex anions *via* two, one and one H-bonds, respectively and is H-bonded to two water molecules. The C(40) cation is involved in H-bonds to three symmetry related complex anions only, forming two bonds with each. In general, the structure is held together by a network of $\text{O} \cdots \text{O}$ and $\text{N} \cdots \text{O}$ hydrogen bonds. The hydrogen bond network and the electrostatic interactions in which the guanidinium cations are engaged, seem to be more advantageous, as far as the forma-

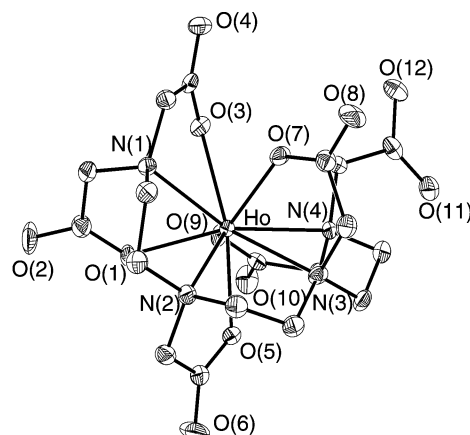


Fig. 1 An ORTEP view of the complex anion, together with the atom numbering scheme. The thermal ellipsoids are drawn at 30% probability. The carbon atom labels have been omitted for the sake of clarity. O(9) is partially eclipsed by Ho.

Table 2 Selected bond lengths (Å) and angles (°) for $[\text{C}(\text{NH}_2)_3]_3[\text{Ho}(\text{ttha})] \cdot 3\text{H}_2\text{O}$

Ho–O(7)	2.307(5)	Ho–N(2)	2.615(6)
Ho–O(9)	2.323(5)	Ho–N(1)	2.626(6)
Ho–O(5)	2.326(5)	Ho–N(4)	2.627(6)
Ho–O(1)	2.340(5)	Ho–N(3)	2.695(6)
Ho–O(3)	2.415(5)		
O(7)–Ho–O(9)	127.8(2)	O(1)–Ho–N(1)	66.53(18)
O(7)–Ho–O(5)	137.28(19)	O(3)–Ho–N(1)	63.11(19)
O(9)–Ho–O(5)	76.41(19)	N(2)–Ho–N(1)	68.7(2)
O(7)–Ho–O(1)	139.81(18)	O(7)–Ho–N(4)	80.4(2)
O(9)–Ho–O(1)	72.22(18)	O(9)–Ho–N(4)	64.58(18)
O(5)–Ho–O(1)	76.25(18)	O(5)–Ho–N(4)	81.79(18)
O(7)–Ho–O(3)	72.09(19)	O(1)–Ho–N(4)	134.96(19)
O(9)–Ho–O(3)	72.97(19)	O(3)–Ho–N(4)	93.81(18)
O(5)–Ho–O(3)	147.79(19)	N(2)–Ho–N(4)	131.71(19)
O(1)–Ho–O(3)	85.07(19)	N(1)–Ho–N(4)	149.42(19)
O(7)–Ho–N(2)	97.3(2)	O(7)–Ho–N(3)	64.76(18)
O(9)–Ho–N(2)	134.9(2)	O(9)–Ho–N(3)	125.21(19)
O(5)–Ho–N(2)	67.49(19)	O(5)–Ho–N(3)	72.55(19)
O(1)–Ho–N(2)	73.6(2)	O(1)–Ho–N(3)	137.71(19)
O(3)–Ho–N(2)	131.74(19)	O(3)–Ho–N(3)	134.84(18)
O(7)–Ho–N(1)	73.6(2)	N(2)–Ho–N(3)	68.5(2)
O(9)–Ho–N(1)	120.76(19)	N(1)–Ho–N(3)	113.9(2)
O(5)–Ho–N(1)	128.53(19)	N(4)–Ho–N(3)	67.2(2)

tion of the crystal is concerned, than those proper to the alkaline cations.

Spectral results

Absorption spectra of the Ho^{III} -ttha (1 : 1) complex were examined in aqueous solution over a wide pH range (2–12) at room temperature and for the $[\text{C}(\text{NH}_2)_3]_3[\text{Ho}(\text{ttha})] \cdot 3\text{H}_2\text{O}$ single crystal at 293 and 4 K. The observed f–f transitions in the 300–700 nm region are shown in Fig. 2. The shape and intensity of the absorption bands in solution changes up to pH 5.43. A further increase of pH gives no changes in the absorption spectra. Changes in the shape and intensity of the bands are best registered for the hypersensitive $^5\text{I}_8 \rightarrow ^5\text{G}_6, ^5\text{F}_1$ transition. The spectral intensities of the f–f transitions and Ω_λ parameters for the studied complexes at 293 K as well as the oscillator strength values for the $[\text{C}(\text{NH}_2)_3]_3[\text{Ho}(\text{ttha})] \cdot 3\text{H}_2\text{O}$ crystal obtained at 4 K are presented in Table 3. For comparison purposes the spectral results of an equimolar Ho^{III} -dtpa solution at pH 8.70 are also included.

As one may note from Table 3, the spectral intensities of all f–f transitions of the $[\text{C}(\text{NH}_2)_3]_3[\text{Ho}(\text{ttha})] \cdot 3\text{H}_2\text{O}$ crystal at 293 K correspond very well with those of the Ho^{III} -ttha complex in solution at pH > 5. When the temperature is lowered from 293 to 4 K an intensity decrease of almost all

transitions in the single crystal is observed. Because of large Ho^{III} J manifolds in the ground and excited states, it is difficult to establish which part of the intensity changes is related to “hot” transitions from the ground state and which ones to the vibronic transitions. The loss of intensity caused by the “hot” transitions is particularly noticeable for transitions with a relatively low J value of the excited states as for example for the $^5\text{I}_8 \rightarrow ^5\text{F}_5$ transition.

In the absorption spectra of the Ho^{III} -ttha complex shown in Figs. 2 and 3 one can observe a very good correspondence between the shape of the bands in solution at pH > 5 and in the single crystal. It should be pointed out that among several very stable lanthanide complexes studied by us so far in solution and as single crystals,^{1,2,20–22} this is the first time such good agreement between spectra of these two phases has been observed. Such a correlation extends into the spectral intensities and energies of the crystal field components, even for the hypersensitive transition which is particularly sensitive to changes in the direct environment of the lanthanide ion. Hence one may conclude that Ho^{III} -ttha species which predominantly exist in aqueous solution at pH > 5 have a very similar coordination geometry around the metal cation to that found in the $[\text{C}(\text{NH}_2)_3]_3[\text{Ho}(\text{ttha})] \cdot 3\text{H}_2\text{O}$ crystal.

The electronic spectra of $\text{Nd}^{\text{III}1,2}$ and $\text{Eu}^{\text{III}3,7}$ complexes with ttha in solution have shown, however, the presence of two different species which exist in equilibrium at different

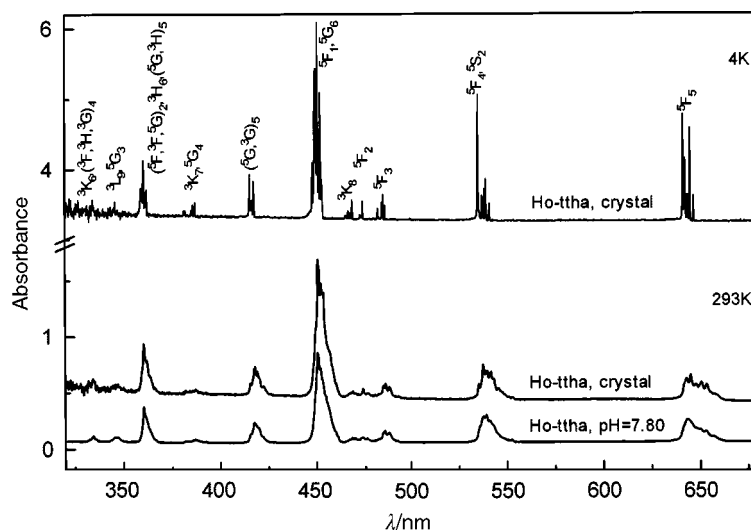


Fig. 2 Absorption spectra of the Ho^{III} -ttha complex in solution and for the single crystal of $[\text{C}(\text{NH}_2)_3]_3[\text{Ho}(\text{ttha})] \cdot 3\text{H}_2\text{O}$ at 293 and 4 K; for solutions: $c_{\text{Ho}} = 2.16 \times 10^{-2}$ M, $c_{\text{ttha}} = 2.40 \times 10^{-2}$ M, $d = 2$ cm; for the crystal: $c_{\text{Ho}} = 1.906$ M, $d = 0.035$ cm.

Table 3 Oscillator strengths (P) and Ω_λ parameters for Ho^{III} complexes with dtpa and ttha in solution as well for the $[\text{C}(\text{NH}_2)_3]_3[\text{Ho}(\text{ttha})] \cdot 3\text{H}_2\text{O}$ crystal at 293 and 4 K (in solution: $c_{\text{Ho}} = 2.16 \times 10^{-2}$ M, $d = 2$ cm; in the crystal: $c_{\text{Ho}} = 1.906$ M, $d = 0.035$ cm)

Transition(s) $^5\text{I}_8 \rightarrow$	$[\text{Ho}(\text{dtpa})]^{2-}$		$[\text{Ho}(\text{ttha})]^{3-}$				crystal, 293 K $10^8 P_{\text{exp.}}$	crystal, 4 K $10^8 P_{\text{exp.}}$
	pH 8.70 $10^8 P_{\text{exp.}}$		pH 3.00 $10^8 P_{\text{exp.}}$	pH 3.96 $10^8 P_{\text{exp.}}$	pH 5.43 $10^8 P_{\text{exp.}}$	pH 9.87 $10^8 P_{\text{exp.}}$		
$^5\text{F}_5$	479.49		497.70	537.82	547.65	552.46	606.37	419.30
$^5\text{S}_2, ^5\text{F}_4$	640.85		669.26	685.55	731.73	705.63	709.53	383.47
$^5\text{F}_3$	242.39		240.55	266.54	277.62	272.13	283.83	126.29
$^5\text{F}_2$	101.01		102.18	95.91	93.79	92.05	89.43	46.87
$^3\text{K}_8$	62.70		72.72	86.39	91.82	91.56	91.67	85.90
$^5\text{F}_1, ^5\text{G}_6$	1217.92		1748.78	2199.78	2460.50	2468.40	2248.38	1728.45
$(^5\text{G}, ^3\text{G})_5$	434.66		447.83	504.47	525.86	533.65	487.25	300.53
$^5\text{G}_4, ^3\text{K}_7$	105.03		104.66	113.61	110.44	119.12	134.96	136.31
$(^5\text{G}, ^3\text{H})_5, ^3\text{H}_6, (^5\text{F}, ^3\text{F}, ^5\text{G})_2$	527.06		646.30	771.20	820.67	816.76	814.92	785.79
$^5\text{G}_3, ^3\text{L}_9$	133.58		159.52	173.86	171.44	170.73	213.82	
$(^3\text{F}, ^3\text{H}, ^3\text{G})_4, ^3\text{K}_6$	99.90		121.91	132.31	129.22	132.39	153.27	
$10^{20}\Omega_2/\text{cm}^2$	2.02 ± 0.33		3.97 ± 0.35	5.41 ± 0.43	6.31 ± 0.42	6.30 ± 0.42	5.82 ± 0.53	
$10^{20}\Omega_4/\text{cm}^2$	4.47 ± 0.49		4.66 ± 0.51	5.24 ± 0.63	5.41 ± 0.62	5.52 ± 0.61	5.54 ± 0.78	
$10^{20}\Omega_6/\text{cm}^2$	3.85 ± 0.34		4.01 ± 0.36	4.13 ± 0.44	4.33 ± 0.43	4.18 ± 0.42	4.72 ± 0.54	
10^7r.m.s.	5.14		5.52	6.74	6.69	6.61	8.03	

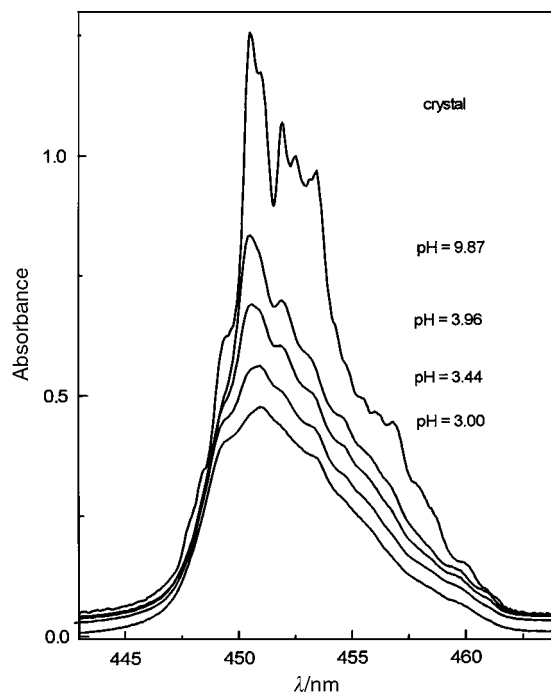


Fig. 3 Absorption spectra of the $^5I_8 \rightarrow ^5G_6, ^5F_1$ hypersensitive transition of the Ho^{III} -ttha complex in solution at different pH values and in the crystal at 293 K; for solutions: $c_{\text{Ho}} = 2.16 \times 10^{-2}$ M, $c_{\text{ttha}} = 2.40 \times 10^{-2}$ M, $d = 2$ cm; for the crystal: $c_{\text{Ho}} = 1.906$ M, $d = 0.035$ cm.

ratios over the entire pH range. Taking into account X-ray investigations, one may assume that in both systems, besides species with 4 N atoms coordinated to the Ln^{III} ion ($[\text{Ln}(\text{N}_4\text{O}_6)]^{3-}$ and $[\text{Ln}(\text{N}_4\text{O}_5)]^{3-}$ for light^{1,9} and heavy^{8–10} Ln^{III} ions, respectively), also species with 3 coordinated N atoms are present ($[\text{Ln}(\text{N}_3\text{O}_6)]^{3-}$). The latter type of coordination was confirmed by the X-ray analysis of the ttha complexes with Nd^{III} and Gd^{III} ions.¹¹ In these complexes, which are nearly centrosymmetric dimers, each Ln^{III} ion coordinates three nitrogens and four carboxylate oxygens from one ttha ligand and two remaining carboxylate oxygens (associated with the terminal un-coordinated amine nitrogen atom) from another ttha molecule which belongs to a second moiety of the complex. It should be pointed out that the existence of two different species as found in the crystal structures of the Nd^{III} -ttha complexes was also detected in solution.^{1,2} The presence of oligomeric species in the Ln^{III} -ttha system in solution was also proved by energy transfer studies carried out on Tb^{III} and Eu^{III} complexes with ttha.⁶ These studies have revealed that polynuclear species are formed below pH 8, and above this pH value only monomeric species exist in solution. Relaxivity studies on the Gd^{III} -ttha complex⁴ also suggest that formation of oligomeric species in this system is particularly effective in the pH range between 3 and 5.

Contrary to the results found for the Nd^{III} and Eu^{III} ions, in which f-f transitions occur between states from which at least one of them is non-degenerate in the crystal field, the heavy lanthanide ions have no such transitions in the spectral region available for UV-vis measurements. This is why for heavy lanthanide complexes it is difficult to determine the number of different species present in solution. In this case, however, the hypersensitive transition may be indicative of the coordination structure of the Ln^{III} ion because the intensity and the peak maximum of this transition is dependent upon the metal ion environment.

Following the results obtained from the energy transfer studies⁶ and absorption spectroscopy^{1,2,7} one can generally assume the presence of $[\text{Ho}_2(\text{N}_3\text{O}_6)_2]^{6-}$ (at pH < 8) and $[\text{Ho}(\text{N}_3\text{O}_6)]^{3-}$ (at pH ≥ 8) species together with the

$[\text{Ho}(\text{N}_4\text{O}_5)]^{3-}$ species, of which the existence was evidenced in this paper. The conspicuous correlation of the crystal field components of the $^5I_8 \rightarrow ^5G_6, ^5F_1$ transition in the solid state and in solution at pH > 5, however, proves that if the $[\text{Ho}_2(\text{N}_3\text{O}_6)_2]^{6-}$ or $[\text{Ho}(\text{N}_3\text{O}_6)]^{3-}$ species were present in solution, their concentrations would have to be very low in comparison to $[\text{Ho}(\text{N}_4\text{O}_5)]^{3-}$. The shift of the most intense crystal field component in the $^5I_8 \rightarrow ^5G_6, ^5F_1$ transition towards the IR region with a decrease in pH (Fig. 3), as well as a considerable loss of intensity of the hypersensitive transitions ($^5I_8 \rightarrow ^5G_6, ^5F_1$ and $^5I_8 \rightarrow (^5G_6, ^3H_5), ^3H_6, (^5F_3, ^5G_2)$) in comparison to the intensity determined at pH 5.43 (Table 3), may indicate a shift of the coordination equilibria. This is consistent with absorption results obtained previously for the Eu^{III} -ttha system⁷ in which two different species exist in comparable amounts in the $3 < \text{pH} < 5$ region. Hence a decrease in hypersensitive transition intensities at pH < 5 may be attributed to the increase of the concentration of the dimeric species^{4,11} with 3 N atoms in the inner sphere of each Ho^{III} ion. It is noteworthy that for all Ln^{III} complexes (Nd^{III} ,²² Eu^{III} ⁷ and Ho^{III} , Table 3) with dtpa, for which only species with three nitrogen atoms coordinated to the Ln^{III} ion of the $[\text{Ln}(\text{N}_3\text{O}_5)(\text{H}_2\text{O})]^{2-}$ are present in solution, the oscillator strengths of the hypersensitive transition are two times lower than those for ttha complexes at pH above 5. The same trend of changes of the hypersensitive transition intensities as seen for Ln^{III} complexes with ttha and dtpa in solution, was also observed in Nd^{III} -ttha crystals with $[\text{Nd}(\text{N}_4\text{O}_6)]^{3-1}$ and $[\text{Nd}(\text{N}_3\text{O}_6)]^{3-2}$ coordination modes. These results indicate that among other factors, the number of coordinated nitrogen atoms which, *e.g.*, may increase electric field inhomogeneity around the Ln^{III} cation²³ or introduce additional covalence contribution²⁴ may also considerably affect the hypersensitive transition intensity.

In summary, we can state that an analysis of spectral properties of well defined species for the complexes of light and heavy lanthanide ions with ttha in single crystals can be very helpful in the elucidation of the equilibria existing in solution of lanthanide complexes with different polyamino polycarboxylic ligands. Extension of the work presented here to other complexes of similar type in their protonated and deprotonated forms is underway.

Conclusions

Continuing our previous studies on complexes of lanthanide ions with polyamino polycarboxylic acids we have obtained crystals of $[\text{CNH}_2]_3[\text{Ho}(\text{ttha})] \cdot 3\text{H}_2\text{O}$. The metal ion is nine-coordinate (4 N and 5 O atoms). Analysis of the electronic spectra of the Ho^{III} -ttha complex in the crystal and in solution at pH > 5 has revealed a close similarity of the coordination spheres in both systems. A comparison of the hypersensitive transition intensities of Ho^{III} complexes with ttha and dtpa in aqueous solution suggests that species with three nitrogen atoms dominate below pH 4, while above pH 5 species with four nitrogen atoms exist mainly for the Ho^{III} -ttha system.

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