New luminescent heteronuclear Ln(III)–Bi(III) complexes (Ln=Nd, Eu, Tb, Yb) based on aminopolycarboxylic acids

S. Smola [a], N. Rusakova [a] & YU. Korovin [a]

[a] Department of Chemistry of Lanthanides, A.V. Bogatsky Physico-Chemical Institute, 65080 Odessa, Ukraine
Published online: 19 Feb 2011.

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis
Taylor & Francis Group

New luminescent heteronuclear Ln(III)–Bi(III) complexes (Ln = Nd, Eu, Tb, Yb) based on aminopolycarboxylic acids

S. SMOLA, N. RUSAKOVA and YU. KOROVIN*

Department of Chemistry of Lanthanides, A.V. Bogatsky
Physico-Chemical Institute, 65080 Odessa, Ukraine

New heteronuclear Ln(III)–Bi(III) complexes (Ln = Nd, Eu, Tb, Yb, Lu) with ethylenediamine-N,N,N′,N′-tetraacetic (H$_4$edta), *trans*-1,2-cyclohexane-diamine-N,N,N′,N′-tetraacetic (H$_4$cdta), diethylenetriamine-N,N,N′,N″,N″-pentaacetic (H$_5$dtpa), and triethylenetetraamine-N,N,N′, N″,N‴,N‴-hexaacetic (H$_6$ttha) acids have been synthesized with a different synthetic approach. Bi(III) is a sensitizer of the 4f-luminescence in visible and near IR region. Emission spectra of Eu(III)–Bi(III) complexes were studied and the asymmetry of Eu(III) coordination environment was estimated, in good agreement with molecular models. The complexes synthesized by self-assembly are characterized by higher values of the 4f-luminescence quantum yield than other Ln(III)–Bi(III) complexes.

Keywords: Heteronuclear complexes; Lanthanides; Bismuth; Aminopolycarboxylic acids; Luminescence

1. Introduction

Heteronuclear complexes of lanthanides enjoy widespread interest due to their optical, magnetic, and catalytic properties [1–3]. The type of metal and organic ligands determines all the above-mentioned properties, in particular, luminescence of the lanthanide ions. The combination of f- and other metal in pair offers opportunities to control the 4f-luminescence. It is also important to find ligands which have the ability to form heteronuclear lanthanide-containing complexes and ensure effective 4f-luminescence. In this respect complexones, are an interesting and promising class of organic ligands. Study of complexation processes in f–p–metal pairs and factors that influence the spectral-luminescent characteristics of heteronuclear complexes is an important modern task of coordination chemistry.

The 4f-luminescence in Ln(III)–Bi(III) systems were studied mainly in solid samples (crystal phosphors, mixed oxides materials, films, etc.) [4–6]; Bi(III) can be a sensitizer of luminescence of lanthanides in the visible and near-infrared (IR) spectral region [7–9]. The presence of the lone pair on Bi(III) and fluorescent properties, as well as a very broad field of practical application of bismuth compounds, causes great interest

---

*Corresponding author. Email: lanthachem@te.net.ua

in the study of Ln(III)–Bi(III) complexes. In this article, we present the first results on the spectral-luminescent studies of heteronuclear Ln(III)–Bi(III) complexes with some complexonates.

2. Experimental

2.1. *Materials and methods*

All chemicals were supplied by Aldrich and used without purification. Doubly-distilled demineralized water was used for the preparation of solutions and for all measurements. Elemental analyses (C, H, and N) were carried out on a Perkin-Elmer CHN-240 analyzer. FT-IR spectra were recorded on a Shimadzu FT–IR 8400S spectrometer using KBr discs. UV-Vis spectra were collected on a Perkin-Elmer Lambda 9 UV/VIS/NIR spectrophotometer. ^{1}H NMR spectra were recorded on a Bruker AM-400 spectrometer; ^{1}H NMR chemical shifts (δ) are referred to tetramethylsilane (TMS) as an internal standard. The structure of the heteronuclear complexes has been optimized using MM+ molecular method (Polak–Ribiere algorithm) by means of the HyperChem program [10].

Emission and excitation spectra were measured using a Horiba Jobin Yvon Fluorolog 3-22 spectrofluorimeter equipped for measurements at both RT and 77 K (detectors Hamamatsu R928 and DSS-IGA020L (Electro-Optical Systems, Inc.) for visible and NIR domain, respectively). The excitation source was a 450 W Xe arc lamp. Emission spectra were corrected for detection and optical response of the spectrofluorimeter and excitation spectra were corrected for the spectral distribution of the lamp intensity using a photodiode reference detector. The relative quantum yields of 4f-luminescence (φ) of Eu(III), Tb(III), Nd(III), and Yb(III) in the complexes were determined as described previously [11, 12]. The phosphorescence spectra of Lu(III) chelates were measured conventionally in glycerol : water (5 : 4 by volume) mixtures at 77 K with different delays after flash. The lifetime measurements at room temperature were acquired with the setup described for luminescence spectra using the FL-1040-UP phosphorimeter accessory with the Fluorolog 3-22 instrument (pulsed Xe–Hg arc lamp, 3 μs bandwidth). Number of water molecules (q) coordinated in the inner sphere of the Eu- and Tb-containing complexes was determined from $\tau(H_2O)$ and $\tau(D_2O)$ using the special equations [13].

2.2. *Synthesis of heteronuclear complexes*

In general, the heteronuclear complexes were synthesized according to a method described earlier [14, 15] with the use of acetates of Ln(III) and homonuclear complexes of Bi(III) with H_4edta, H_4cdta, H_5dtpa, and H_6ttha. The molecular and crystal structures of the latter were already described [16–18].

Heteronuclear Ln(III)–Bi(III) complexes with H_5dtpa and H_6ttha were also synthesized using self-assembly method. Bi_2O_3 (0.466 g, 1 mmol) and $Ln(CH_3COO)_3$ (Ln = Nd, Eu, Tb, Yb, Lu) (1 mmol) were added to a hot aqueous solution of complexone (1 mmol in 150 mL of deionized H_2O). The resulting mixture (pH 1–3) was stirred for 10 h at 90°C, then filtered, evaporated to 30 mL and stored at

room temperature. After 5–7 days the white precipitate (pink in the case of neodymium complexes) can be isolated. The precipitate was filtered off and washed with cold deionized water and diethyl ether and dried in a vacuum oven at $60°C$ for 12 h. For simplification, crystallization of water molecules are not shown in this work. Elemental analysis, $[Nd(H_2O)_2(\mu\text{-}CH_3COO)(\mu\text{-}dtpa)Bi(H_2O)]$, Calcd for $C_{16}H_{27}N_3O_{15}NdBi$: C, 22.49; H, 3.18; N, 4.92; Nd, 16.88; Bi, 24.45. Found: C, 22.39; H, 3.51; N, 4.83; Nd, 16.87; Bi, 24.05. $[Eu(H_2O)_2(\mu\text{-}CH_3COO)(\mu\text{-}dtpa)Bi(H_2O)]$, Calcd for $C_{16}H_{27}N_3O_{15}EuBi$: C, 21.05; H, 3.29; N, 4.92; Eu, 16.13; Bi, 23.25. Found: C, 21.09; H, 3.60; N, 4.58; Eu, 16.54; Bi, 22.86. $[Tb(H_2O)_3(\mu\text{-}CH_3COO)(\mu\text{-}dtpa)Bi(H_2O)]$, Calcd for $C_{16}H_{27}N_3O_{15}TbBi$: C, 20.92; H, 3.90; N, 4.86; Tb, 17.06; Bi, 23.04. Found: C, 20.79; H, 3.61; N, 4.51; Tb, 17.25; Bi, 22.63. $[Lu(H_2O)_2(\mu\text{-}CH_3COO)(\mu\text{-}dtpa)Bi(H_2O)]$, Calcd for $C_{16}H_{27}N_3O_{15}LuBi$: C, 20.28; H, 3.24; N, 4.69; Lu, 19.05; Bi, 21.67. Found: C, 20.47; H, 3.59; N, 4.41; Lu, 18.76; Bi, 22.08. $[Nd(H_2O)(\mu\text{-}ttha)Bi(H_2O)]$, Calcd for $C_{18}H_{28}N_4O_{14}NdBi$: C, 22.53; H, 3.71; N, 6.01; Nd, 16.35; Bi, 23.03. Found: C, 22.74; H, 3.32; N, 6.20; Nd, 16.04; Bi, 23.22. $[Eu(H_2O)(\mu\text{-}ttha)Bi(H_2O)]$, Calcd for $C_{18}H_{28}N_4O_{14}EuBi$: C, 22.49; H, 3.06; N, 6.49; Eu, 16.25; Bi, 23.17. Found: C, 22.56; H, 3.38; N, 6.14; Eu, 16.76; Bi, 23.08. $[Tb(H_2O)(\mu\text{-}ttha)Bi(H_2O)]$, Calcd for $C_{18}H_{28}N_4O_{14}TbBi$: C, 22.23; H, 3.10; N, 6.02; Tb, 17.56; Bi, 22.31. Found: C, 22.34; H, 3.32; N, 6.11; Tb, 17.37; Bi, 22.89. $[Lu(H_2O)(\mu\text{-}ttha)Bi(H_2O)]$, Calcd for $C_{18}H_{28}N_4O_{14}LuBi$: C, 21.82; H, 3.08; N, 6.36; Lu, 18.31; Bi, 22.04. Found: C, 21.89; H, 3.23; N, 6.07; Lu, 18.78; Bi, 22.45.

3. Results and discussion

Two synthetic approaches are commonly used for the synthesis of polynuclear coordination compounds of metals (in particular, lanthanides). One is multistep synthesis based on mononuclear complexes with vacant chelating sites. In this case mononuclear complexes are ligands, forming polynuclear compounds by exo-coordination of the additional metal ions, i.e. mononuclear complexes are the building blocks for polynuclear (and/or heteronuclear) ones [19, 20].

The other approach is the use of polytopic ligands capable of binding metal ions simultaneously through multiple sites. In this case all the reagents are put into the reaction mixture at the same time. Such methods are called self-assemblies [21, 22]. In this work these two methods were used to synthesize heteronuclear complexes, using mononuclear aminopolycarboxylates of Bi(III), i.e. $[Bi(H_2O)_2Hedta]$, $[Bi(H_2O)_2Hcdta]$, and $[Bi(H_2O)H_2dtpa]$ as the building blocks, and using self-assembly method. The elemental analyses are approximately the same as the theoretical data and for heteronuclear complexes the ratio is $Ln : Bi : L = 1 : 1 : 1$.

IR spectra of free ligands and mono- and heteronuclear complexes were analyzed. Bands at $3200–3600 \, cm^{-1}$ belong to the symmetric and asymmetric stretching modes of water. This spectral pattern is very broad with the main contour at $3370 \, cm^{-1}$. Moreover, several shoulders indicate the complex network of hydrogen bonds between carboxylate and water. The $\nu(CH)$ frequency is the same for all complexes $(2970–2990 \, cm^{-1})$ and indicates similar coordination of ligand by Bi(III). These bands are observed in spectra of corresponding building blocks. Bands of the antisymmetrical and symmetrical stretching of the carboxylate group are split into two

components: ν_{as}(C–O) 1620–1660 cm^{-1} and 1590–1605 cm^{-1} and ν_s(C–O) 1430–1440 cm^{-1} and 1370–1385 cm^{-1}. The location and intensity of ν(Bi–O) at 480–490 cm^{-1} does not change in the Ln(III)–Bi(III) complexes and building blocks.

IR spectra of the Ln(III)–Bi(III) complexes, synthesized by self-assembly, were compared to data for the free ligands. The spectra of diethylenetriaminepentaacetates obtained by different synthetic methods are similar, except the antisymmetrical and symmetrical vibration of the carboxylate. These bands are located at 1685–1690 cm^{-1}, 1615–1625 cm^{-1} (ν_{as}(C–O)) and 1385–1390 cm^{-1}, 1335–1345 cm^{-1} (ν_s(C–O)) for the complexes of H$_5$dtpa and H$_6$ttha, respectively. The values $\Delta\nu$(CO) = 340–350 and 225–235 cm^{-1} indicate high covalency of the Bi–O and Ln–O bonds, respectively. IR spectra confirm the coordination of non-ionized carboxylic groups to Ln(III) in species synthesized from Bi(III) aminopolycarboxylates. On the other hand, in complexes synthesized by self-assembly, all donors are coordinated to metal ions.

^{1}H NMR spectra were observed for complexes with Lu(III) in D$_2$O solutions (figure 1). Signals of coordinated ligand from diamagnetic Bi(III) complex are observed in spectra of building blocks: δ 3.80–4.20 ppm from acetate methylene and δ 3.40–3.60 ppm from ethylenic protons (figure 1a). The singlet at δ 1.70–1.71 ppm appears in spectra of heteronuclear complexes due to protons of the acetate-anion (figure 1b). On the formation of bridging bonds between Ln(III) and oxygen of deprotonated carboxylate, singlets at 4.41–4.43 ppm are observed. This group is also linked with Bi(III) by carbonyl oxygen. We suggest that one carboxylate of the Bi(III)–block is bidentate and coordinated to Ln(III) together with acetate. Protons of ethylenediamine and acetate coordinated to Bi(III) are also observed.

In NMR spectra of complexes with H$_5$dtpa, the methylene protons of coordinated carboxylate give two signals at 4.36–4.49 ppm (carboxylate coordinated to Lu(III)) and 4.11–4.25 ppm (coordination to Bi(III)) (figure 1c). Signals attributed to NCH$_2$CH$_2$N group (3.63 and 3.32 ppm) were also assigned. The areas of these signals indicate the coordination of two nitrogens and three carboxylates with Bi(III), one nitrogen and two CH$_2$COO– groups with Lu(III). The peak at 1.73 ppm was assigned to acetate. The spectrum of the Lu(III)–Bi(III) complex with H$_6$ttha is similar except the peak at 4.53 ppm (figure 1d). This signal was assigned to protons of the one bidentate CH$_2$COO coordinated to Lu(III) and Bi(III). The multiplet at 2.99–3.15 ppm was assigned to protons of the ethylenediamine bridge between Lu(III) and Bi(III) coordination polyhedra.

The structures of the Ln(III)–Bi(III) complexes were suggested and the geometry was calculated according to IR-, ^{1}H NMR spectra, and MM+-method (figure 2). The coordination polyhedra of Bi(III) are the same as in mononuclear complexes. Bidentate coordination of CH$_2$COO of the complexones leads to the formation of heteronuclear complexes [Ln(CH$_3$COO)$_2$(H$_2$O)$_3$Bi(H$_2$O)$_2$(μ-edta)] (figure 2a), [Ln(CH$_3$COO)$_2$(H$_2$O)$_3$Bi(H$_2$O)$_2$(μ-cdta)] (figure 2b) and [Ln(CH$_3$COO)$_2$(H$_2$O)$_3$Bi(H$_2$O)(μ-dtpa)] (figure 2c). Two acetates and three water molecules complete the coordination of Ln(III) to six.

The use of the self-assembly method leads to the formation of binuclear Ln(III)–Bi(III) complexes. Evidently, in diethylenetriaminepentaacetates (figure 2d) the Ln(III) is surrounded by oxygens of two carboxylates, one nitrogen, two oxygens of acetate and water. Thus, the coordination of Bi(III) is formed by four oxygens of carboxylates (one of which is bidentate), two nitrogens, and a water molecule.
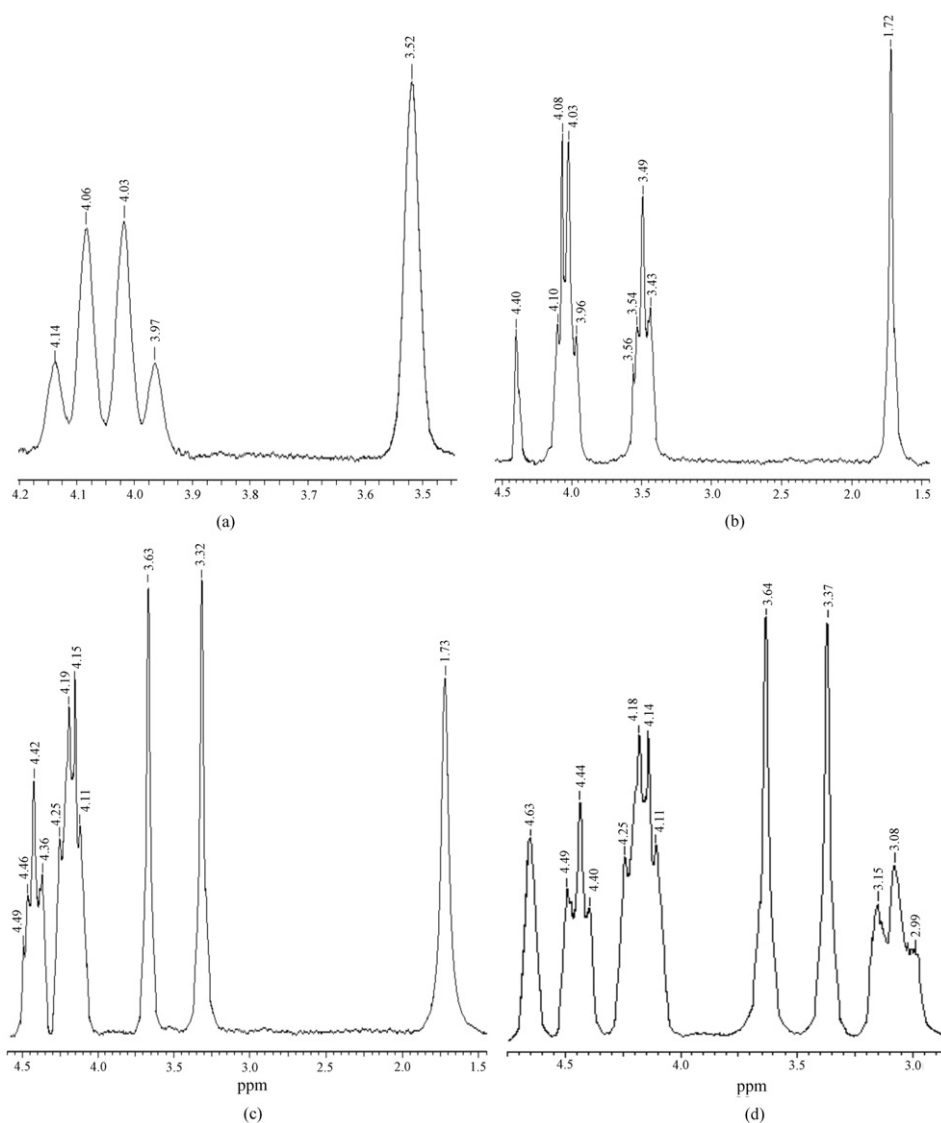
Figure 1. ^{1}H NMR spectra in D$_2$O solution of (a) [Bi(H$_2$O)$_2$Hedta], (b) [Lu(CH$_3$COO)$_2$(H$_2$O)$_3$Bi(H$_2$O)$_2$ (μ-edta)], (c) [Lu(H$_2$O)$_2$(μ-CH$_3$COO)(μ-dtpa)Bi(H$_2$O)], and (d) [Ln(H$_2$O)(μ-ttha)Bi(H$_2$O)].

The coordination polyhedron of Ln(III) in heterometallic complexes with H$_6$ttha (figure 2e) has three oxygens of carboxylates, two nitrogens, and one water molecule. The coordinaion number of Bi(III) is eight and its coordination environment consists of three carboxylate oxygens, one oxygen of bidentate carboxylate, two nitrogens and a water.

The structural parameters obtained from MM+-method are in good agreement with X-ray data [23–25] of homo- and heterometallic Bi(III) and Ln(III) aminopolycarboxylates (table 1). The difference between experimental and theoretical values of the bond lengths is 0.02–0.06 Å (the maximum difference is observed for the Ln–O bonds).
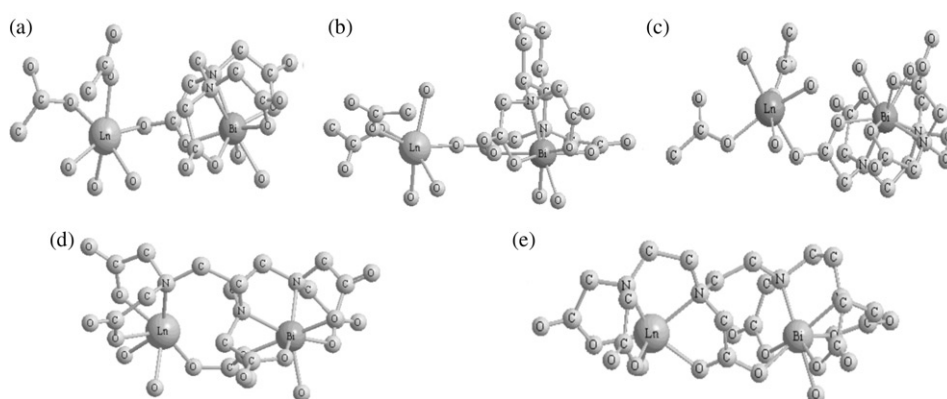
Figure 2. Schematic representation of structures of heteronuclear Ln(III)–Bi(III) complexes: (a) $[Ln(CH_3COO)_2(H_2O)_3Bi(H_2O)_2(\mu\text{-edta})]$, (b) $[Ln(CH_3COO)_2(H_2O)_3Bi(H_2O)_2(\mu\text{-cdta})]$, (c) $[Ln(CH_3COO)_2(H_2O)_3Bi(H_2O)(\mu\text{-dtpa})]$, (d) $[Ln(H_2O)_2(\mu\text{-}CH_3COO)(\mu\text{-dtpa})Bi(H_2O)]$, and (e) $[Ln(H_2O)(\mu\text{-ttha})Bi(H_2O)]$ (Ln = Nd, Eu, Tb, Yb).

Table 1. Comparative characteristics of the experimental (X-ray analysis) and calculated (MM+-method) data of the average bond lengths (Å) in homo- and heteronuclear Bi(III) and Ln(III) complexes.

Bond	[BiHedta] [24]		$Na_4[Dyedta(H_2O)_3]$ [25]		$[(H_2O)_5Nd(\mu_4\text{-edta})Bi(NO_3)_2]$ [15]	
	Exp.	Calcd	Exp.	Calcd	Exp.	Calcd
Bi–O	2.41	2.38	–	–	2.36	2.40
Bi–N	2.52	2.50	–	–	2.49	2.44
Ln–O	–	–	2.38	2.34	2.45	2.39
Ln–N	–	–	2.65	2.64	–	–
Ln–O_w	–	–	2.46	2.49	2.52	2.50

The presence of intermolecular contacts and hydrogen bonds in the crystal structures are ignored in the simulation and cause the deviation of the calculated parameters from the experimental results obtained by X-ray analysis. Thus, it is possible to use computational methods for determining the geometrical characteristics of studied compounds [26–28].

The MM+ calculations were made on heterometallic complexes in order to estimate bond lengths in coordination polyhedra of the metal ions and the Ln⋯Bi distance. The Bi–O and Bi–N bonds do not undergo significant changes in heterometallic complexes: 2.39–2.42 Å (Bi–O) and 2.46–2.47 Å (Bi–N). The Bi–O bridging bonds are slightly longer (2.69–2.86 Å) in complexes with H_4edta, H_4cdta, and H_5dtpa. The Ln–O distances in these complexes are in the range of 2.22–2.31, 2.18–2.27, and 2.22–2.27 Å, respectively. This indicates similar coordination of the Ln(III) ion to a bismuth-containing building block. The Ln–O(water) and Ln–O(acetate) bond distances do not vary significantly. The Ln–O bond lengths in $[Ln(H_2O)(\mu\text{-ttha})Bi(H_2O)]$ and $[Ln(H_2O)_2(\mu\text{-}CH_3COO)(\mu\text{-dtpa})Bi(H_2O)]$ are 2.15–2.26 Å and 2.20–2.33 Å for Ln–N bonds.

Although the coordination number of lanthanides in homonuclear complexes in most cases ranges from eight to ten [23, 25], in heterometallic Ln(III)–Bi(III) species [15]

Table 2. Photophysical parameters of Lu(III)–Bi(III) complexes at 77 K.

Complex	ν_{exc} (cm^{-1})	ν_{lum} (cm^{-1})	$\Delta\nu$ (cm^{-1})	τ (µs)
[Lu(CH$_3$COO)$_2$(H$_2$O)$_3$Bi(H$_2$O)$_2$(µ-edta)]	30,500	26,700	3800	1.1
[Lu(CH$_3$COO)$_2$(H$_2$O)$_3$Bi(H$_2$O)$_2$(µ-cdta)]	30,100	26,200	3900	1.2
[Lu(CH$_3$COO)$_2$(H$_2$O)$_3$Bi(H$_2$O)(µ-dtpa)]	30,400	25,300	5100	0.9
[Lu(H$_2$O)$_2$(µ-CH$_3$COO)(µ-dtpa)Bi(H$_2$O)]	28,400	24,700	3700	1.4
[Lu(H$_2$O)(µ-ttha)Bi(H$_2$O)]	28,000	24,000	4000	1.3

the inner sphere water molecules occupy three to five coordination sites of Ln(III). In Ln(III)–Bi(III) complexes the coordination number six of the lanthanide ion was proposed according to the experimental data. As shown below, the number of coordinated groups of the ligand was determined with the use of the empirical equation, which includes the shift of the band corresponding to $^7F_0 \rightarrow {}^5D_0$ transition in excitation spectra of Eu(III)–Bi(III) complexes and the number of coordinated waters – from Eu(III) and Tb(III) lifetime measurement in H$_2$O and D$_2$O. The structure of the Bi(III) blocks containing a small number of donors able to coordinate Ln(III) ion must also be taken into account. Nevertheless, the results of IR, NMR, absorption, and luminescent spectroscopy strongly indicate the formation of heteronuclear complexes. The models of heterometallic complexes have been proposed to explain the experimental data.

The coordination environment of Ln(III) in heterometallic species synthesized from mononuclear Bi(III) complexes is similar, in contrast to complexes with H$_5$dtpa and H$_6$ttha obtained by self-assembly. Thus, their spectral-luminescent properties are different. Free ligands exhibit an absorption at 260–290 nm due to $n \rightarrow \pi^*$ transition, which is shifted bathochromically ($\sim$30 nm) in spectra of mononuclear Bi(III) complexes (its intensity grows 2.2–2.6 times). This broad absorption undergoes a hypsochromic shift ($\sim$5 nm) in Ln(III)–Bi(III) complexes.

The luminescence spectra of Bi(III) complexes at 77 K consist of one strong band in the near UV and visible spectral range (350–500 nm). The corresponding excitation band is at 270–450 nm (table 2). The decay time of this emission is 0.9–1.4 µs. Values of the Stokes shift are practically the same in [Lu(CH$_3$COO)$_2$(H$_2$O)$_3$Bi(H$_2$O)$_2$(µ-edta)], [Lu(CH$_3$COO)$_2$(H$_2$O)$_3$Bi(H$_2$O)$_2$(µ-cdta)], and [Lu(H$_2$O)(µ-ttha)Bi(H$_2$O)] in contrast to other complexes. This is in good agreement with the dependence of luminescence properties on the coordination environment of Bi(III) [5, 29].

Luminescence of Bi(III) was observed in spectra of heteronuclear complexes. Upon excitation in the $n–\pi^*$-transitions of ligands, the excitation energy transfer occurs from the triplet levels of ligands (29,000–32,000 cm^{-1}) to $^3P_1$ and $^3P_0$ levels, resulting in Bi(III) luminescence. The position of the $^3P_1$ and $^3P_0$ states strongly depends on Bi(III) coordination environment and is different for each type of complex. In the presence of radiative levels of the Ln(III) ions located below the excited states of Bi(III) ($^3P_1$, $^3P_0$) the Bi-to-Ln energy transfer and sensitization of 4f-luminescence is possible. For both radiative and non-radiative energy transfer between sensitizer and activator, an overlap of the emission of the sensitizer and the absorption region of the activator is required. The Bi(III) emission band (figure 3, curve 2) significantly overlaps with the excitation bands of Eu(III) (especially transitions $^7F_0 \rightarrow {}^5D_{4,5,6}$ at 375–383 nm, and $^7F_0 \rightarrow {}^5L_6$ at 393 nm) (figure 3, curve 3). On the whole, the intensity of the broad band at 370–450 nm is low (figure 3, curve 4). Thus, Bi(III) is a sensitizer for 4f-luminescence in heterometallic complexes.
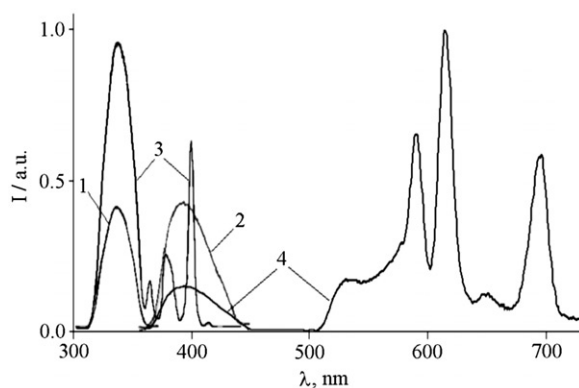
Figure 3. Excitation (1) ($\lambda_{em} = 405$ nm) and emission spectra (2) ($\lambda_{exc} = 329$ nm) of [Bi(H$_2$O)H$_2$dtpa] and excitation (3) ($\lambda_{em} = 614$ nm) and emission spectra (4) ($\lambda_{exc} = 332$ nm) of [Eu(CH$_3$COO)$_2$(H$_2$O)$_3$Bi(H$_2$O)$_2$ (μ-dtpa)] in H$_2$O solution. $C_{Eu} = 1 \times 10^{-4}$ mol dm^{-3}, 295 K.

Table 3. Spectral-luminescent properties of Eu(III)- and Tb(III)-containing hetero-nuclear complexes at 295 K.

Complex	φ^a	τ(H$_2$O) (ms)	τ(D$_2$O) (ms)	q^b
[Eu(CH$_3$COO)$_2$(H$_2$O)$_3$Bi(H$_2$O)$_2$(μ-edta)]	0.071	0.26	0.81	2.6
[Eu(CH$_3$COO)$_2$(H$_2$O)$_3$Bi(H$_2$O)$_2$(μ-cdta)]	0.070	0.25	0.90	2.8
[Eu(CH$_3$COO)$_2$(H$_2$O)$_3$Bi(H$_2$O)(μ-dtpa)]	0.076	0.24	0.77	2.9
[Eu(H$_2$O)$_2$(μ-CH$_3$COO)(μ-dtpa)Bi(H$_2$O)]	0.127	0.33	0.83	1.7
[Eu(H$_2$O)(μ-ttha)Bi(H$_2$O)]	0.196	0.42	0.75	0.8
[Tb(CH$_3$COO)$_2$(H$_2$O)$_3$Bi(H$_2$O)$_2$(μ-edta)]	0.390	0.73	1.37	2.9
[Tb(CH$_3$COO)$_2$(H$_2$O)$_3$Bi(H$_2$O)$_2$(μ-cdta)]	0.442	0.74	1.34	2.7
[Tb(CH$_3$COO)$_2$(H$_2$O)$_3$Bi(H$_2$O)(μ-dtpa)]	0.447	0.72	1.32	2.8
[Tb(H$_2$O)$_2$(μ-CH$_3$COO)(μ-dtpa)Bi(H$_2$O)]	0.519	0.94	1.57	1.8
[Tb(H$_2$O)(μ-ttha)Bi(H$_2$O)]	0.528	1.25	1.80	0.9

[a]Errors in measurement of luminescence quantum yield are $\pm 15\%$.
[b]The number of coordinated water molecules in the inner sphere.

The emission of Bi(III) overlaps with the $^7F_6 \rightarrow {}^5D_3$ excitation band of Tb(III) at 365–379 nm, and typical $^5D_4 \rightarrow {}^7F_j$ transitions of Tb(III) were observed in emission spectra of Tb(III)–Bi(III) complexes.

Similar spectroscopic characteristics of complexes from Bi(III) blocks are realized due to the same coordination of the Eu(III) and Tb(III) ions. More effective excitation energy transfer is observed for [Ln(H$_2$O)$_2$(μ-CH$_3$COO)(μ-dtpa)Bi(H$_2$O)] and [Ln(H$_2$O)(μ-ttha)Bi(H$_2$O)]. For the last ones, the Eu(III) quantum yield is 1.6–2.6 times higher than for complexes with H$_4$edta and H$_4$cdta (table 3). The decay curves display a single-exponential behavior and the number of coordinated water molecules (q) was calculated [13]. The presence of three water molecules in Ln(III) coordination sphere in complexes with H$_4$edta, H$_4$cdta, and H$_5$dtpa causes high non-radiative energy losses on OH–oscillators.

In the complexes from Bi(III) aminopolycarboxylates, the calculated Ln$\cdots$Bi distance is 0.61–0.65 Å and 0.50–0.55 Å for complexes synthesized by self-assembly. This value assumes the dipole–dipole interaction in the Ln(III)–Bi(III) complexes.
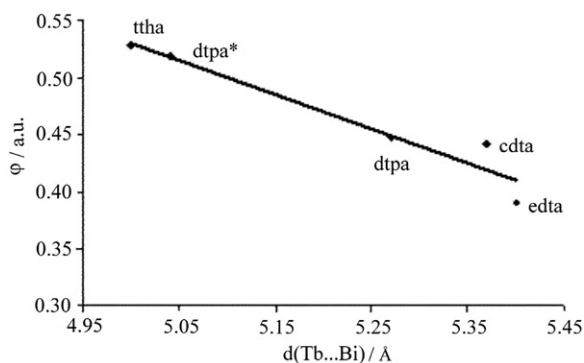
Figure 4. Plot of the 4f-luminescence quantum yield of Tb(III)–Bi(III) complexes against Tb $\cdots$ Bi distance (dtpa* – complex synthesized by self-assembly).

Table 4. Frequencies of the $^5D_0 \to {}^7F_j$ ($j = 0, 1, 2$) bands in excitation spectra of Eu(III)–Bi(III) complexes at 77 K and the ligand coordination number CN_L.

Complexes	ν (cm^{-1})			CN_L
	$^5D_0 \to {}^7F_0$	$^5D_0 \to {}^7F_1$	$^5D_0 \to {}^7F_2$	
[Eu(CH$_3$COO)$_2$(H$_2$O)$_3$Bi(H$_2$O)$_2$(μ-edta)]	17,266	16,891	16,303	3.0
			16,079	
			16,168	
Eu(CH$_3$COO)$_2$(H$_2$O)$_3$Bi(H$_2$O)$_2$(μ-cdta)]	17,266	16,898	16,299	3.0
			16,211	
			16,170	
[Eu(CH$_3$COO)$_2$(H$_2$O)$_3$Bi(H$_2$O)(μ-dtpa)]	17,265	16,896	16,313	3.2
			16,208	
			16,171	
[Eu(H$_2$O)$_2$(μ-CH$_3$COO)(μ-dtpa)Bi(H$_2$O)]	17,263	17,123	16,260	3.7
		17,064	16,194	
			16,051	
[Eu(H$_2$O)(μ-ttha)Bi(H$_2$O)]	17,259	16,920	16,367	4.7
		16,863	16,155	
		16,835	16,129	
			16,090	

It was established that the quantum yield of 4f-luminescence in Tb(III)–Bi(III) complexes increases with decreasing Ln $\cdots$ Tb distance (figure 4).

It is known that the excited $^7F_0$ and ground states $^5D_0$ of Eu(III) are non-degenerate and cannot be split by the ligand field. Moreover, each peak in the spectrum must correspond to a certain Eu(III) environment. The single peak was observed for each Eu(III)–Bi(III) compound in $^7F_0 \to {}^5D_0$ excitation spectra, indicating the presence of one coordination site. The number of ligands coordinated to the Eu-complexes (CN_L) was estimated using the empirical equation $CN_L = 0.237(17276 - \nu) + 0.628$ (where CN_L is the total ligand coordination number and ν is the peak position of the $^5D_0 \leftarrow {}^7F_0$ band) [30]. The maximal shift was observed for [Eu(H$_2$O)(μ-ttha)Bi(H$_2$O)] and CN_L is equal to 4.7, which is in good agreement with its proposed structure. Similar coordination of Bi(III) in complexes with H$_4$edta, H$_4$cdta, and H$_5$dtpa is confirmed by the values of CN_L which are equal to three.
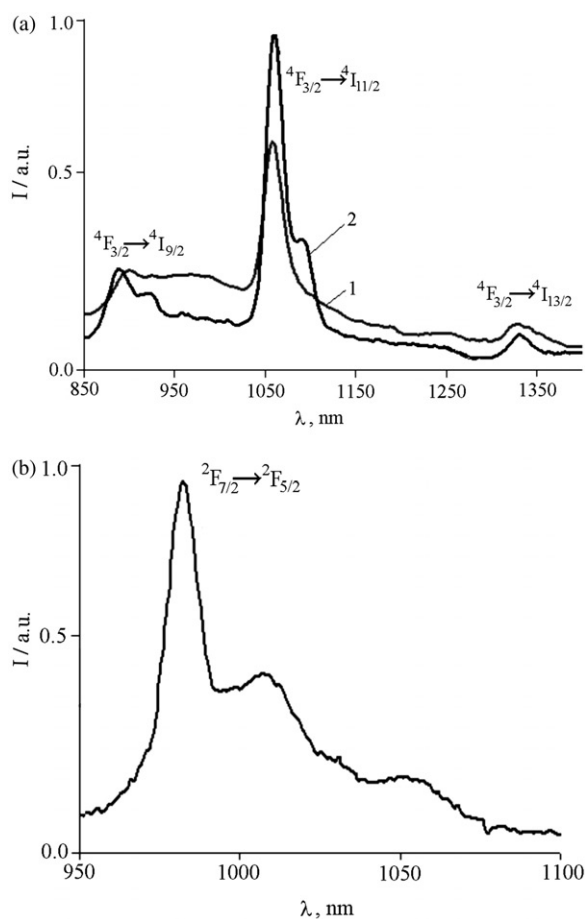
Figure 5. Emission spectra of [Nd(CH$_3$COO)$_2$(H$_2$O)$_3$Bi(H$_2$O)$_2$(µ-edta)] (1) and [Nd(H$_2$O)$_2$(µ-CH$_3$COO)(µ-dtpa)Bi(H$_2$O)] (2) ($\lambda_{exc} = 329$ nm) (a); emission spectra of [Yb(H$_2$O)(µ-ttha)Bi(H$_2$O)] ($\lambda_{exc} = 357$ nm) (b). H$_2$O, $C_{Nd} = 5 \times 10^{-3}$ mol dm^{-3}, $C_{Yb} = 1 \times 10^{-4}$ mol dm^{-3}, 295 K.

Although the proposed coordination number is in good agreement with the CN_L values, the asymmetry of the Eu(III) polyhedron was estimated from splitting of the $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ bands in emission spectra of the Eu(III)–Bi(III) complexes at 77 K (table 4). The emission spectra of the Eu(III)–Bi(III) complexes with H$_4$edta, H$_4$cdta, and H$_5$dtpa contain one peak at 591–593 nm ($^5D_0 \rightarrow {}^7F_1$) and three peaks at 613–621 nm ($^5D_0 \rightarrow {}^7F_2$). C$_{4v}$ symmetry with a square antiprism geometry can be assumed. Distortion of the Eu(III) octahedral configuration was also observed for complexes synthesized by self-assembly. The emission spectrum of [Eu(H$_2$O)$_2$(µ-CH$_3$COO)(µ-dtpa)Bi(H$_2$O)] shows two peaks for $^5D_0 \rightarrow {}^7F_2$ transition and three peaks at the $^5D_0 \rightarrow {}^7F_2$ transition, interpreted in terms of an approximately D$_{4h}$ symmetry with a tetragonal bipyramid geometry. The emission spectrum of [Eu(H$_2$O)(µ-ttha)Bi(H$_2$O)] contains a weak, forbidden $^5D_0 \rightarrow {}^7F_0$ band, three and four peaks due to $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transition, respectively; C$_{2v}$ symmetry was suggested for this complex. To all appearances, in this case the distortion of coordination polyhedra is realized with the formation of a bicapped trigonal prism.

Table 5. Quantum yield of 4f-luminescence of Ln(III)–Bi(III) complexes at 295 K.

Complex	$\varphi(Ln) \times 10^{3a}$	
	Nd	Yb
[Ln(CH$_3$COO)$_2$(H$_2$O)$_3$Bi(H$_2$O)$_2$(μ-edta)]	0.07	0.11
[Ln(CH$_3$COO)$_2$(H$_2$O)$_3$Bi(H$_2$O)$_2$(μ-cdta)]	0.07	0.09
[Ln(CH$_3$COO)$_2$(H$_2$O)$_3$Bi(H$_2$O)(μ-dtpa)]	0.06	0.11
[Ln(H$_2$O)$_2$(μ-CH$_3$COO)(μ-dtpa)Bi(H$_2$O)]	0.11	0.25
[Ln(H$_2$O)(μ-ttha)Bi(H$_2$O)]	0.19	0.29

[a]Errors: ±20%.

Evidently, Bi(III) can sensitize the 4f-luminescence of heterometallic Nd(III) and complexes since Bi(III) emission overlaps with the Nd(III) absorption bands at 354 nm ($^4I_{9/2} \rightarrow {}^4D_{3/2}$) and 432 nm ($^4I_{9/2} \rightarrow {}^2P_{1/2}$). Really, the excitation of the $n \rightarrow \pi^*$ bands of ligand leads to the luminescence of Nd(III)–Bi(III) complexes with the emission bands at 899, 1059, and 1331 nm attributed to transitions from $^4F_{3/2}$ to $^4I_{9/2}$, $^4I_{11/2}$ and $^4I_{13/2}$ sublevels, respectively (figure 5a). One band ($\lambda_{max} = 979$ nm, $^2F_{7/2} \rightarrow {}^2F_{5/2}$ transition) was observed in the emission spectra of Yb(III)–Bi(III) complexes upon excitation at 330–335 nm (figure 5b). The maxima of Yb(III) luminescence is bathochromically shifted (2–3 nm) at 77 K, and also the spectrum contains three bands of the transitions to Stark sublevels of the ground $^2F_{7/2}$ state due to the reduction of symmetry of Yb(III) polyhedra (analogous asymmetry of Ln(III) emission centers are observed in spectra of Eu(III)–Bi(III) complexes). The presence of C–H and O–H oscillators strongly enhances the non-radiative decay pathways giving low 4f-luminescence quantum yields (table 5).

4. Conclusions

New heteronuclear Ln(III)–Bi(III) complexes with aminopolycarboxylic acids have been obtained with different synthetic approaches. Ln(III)–Bi(III) complexes with H$_4$edta, H$_4$cdta, and H$_5$dtpa were obtained based on mononuclear Bi(III) aminopolycarboxylates as building blocks. In these species the structure of bismuth-containing complex anion is preserved and the Ln(III) coordinates with acetate and water molecules. New Ln(III)–Bi(III) complexes with H$_5$dtpa and H$_6$ttha were synthesized by the self-assembly method. In this case aminopolycarboxylate is a bridge between Ln(III) and Bi(III) ions. The structures of the heteronuclear complexes of both types were suggested. Bi(III) is a sensitizer of the 4f-luminescence in visible and near IR region since the bismuth-centered emission overlaps with the f–f absorption bands of the Ln(III) ions. The asymmetry of Ln(III) coordination environment was estimated using the $^5D_0 \rightarrow {}^7F_j$ splitting in Eu(III)–Bi(III) emission spectra. The complexes synthesized by self-assembly are characterized by higher values of the 4f-luminescence quantum yields than other Ln(III)–Bi(III) complexes.

Acknowledgments

References

[1] C. Kremer, J. Torres, S. Dominguez. *J. Mol. Struct.*, **879**, 130 (2008).
[2] J.P. Leonard, C.B. Nolan, F. Stomeo, T. Gunnlaugsson. *Top. Curr. Chem.*, **281**, 1 (2007).
[3] M.D. Ward. *Coord. Chem. Rev.*, **251**, 1663 (2007).
[4] A.E. Hughes, G.P. Pells. *Phys. Status Solidi B*, **71**, 707 (1975).
[5] J. Lin, Q. Su, S. Wang, H. Zhang. *J. Mater. Chem.*, **6**, 265 (1996).
[6] J.-H. Hong, Z.-G. Zhang, C.-J. Cong, K.-L. Zhang. *J. Non-Cryst. Solids*, **353**, 2431 (2007).
[7] N.S. Hussain, Y.R. Prabhakara, S. Buddhudu. *Mater. Lett.*, **53**, 25 (2002).
[8] Q. Xu, B. Lin, Y. Mao. *J. Lumin.*, **128**, 1965 (2008).
[9] G. Lakshminarayana, J. Ruan, J. Qiu. *J. Alloys Compd.*, **476**, 878 (2009).
[10] *HyperChem Professional 7.01 for Windows Molecular Modeling Systems*, Hypercube Inc., Gainesville, FL (2002).
[11] S. Zhuravlyov, N. Rusakova, Yu. Korovin. *J. Alloys Compd.*, **451**, 334 (2008).
[12] N. Rusakova, S. Smola, E. Martsinko, I. Seifullina, E. Ermilov, Yu. Korovin. *J. Fluorescence*, **18**, 247 (2008).
[13] A. Beeby, I.M. Clarkson, R.S. Dickins, S. Faulkner, D. Parker, L. Royle, A.S. De Sousa, J.A.G. Williams, M. Woods. *J. Chem. Soc., Perkin Trans. 2*, **3**, 499 (1999).
[14] H. Wullens, N. Bodart, M. Devillers. *J. Solid State Chem.*, **167**, 494 (2002).
[15] V. Stavila, A. Gulea, N. Popa, S. Shova, A. Merbach, Yu. Simonov, Y. Lipkowski. *Inorg. Chem. Commun.*, **7**, 634 (2004).
[16] V. Stavila, R.L. Davidovich, A. Gulea, K.H. Whitmire. *Coord. Chem. Rev.*, **250**, 2782 (2006).
[17] H. Wullens, M. Devillers, B. Tinant, J.-P. Declercq. *J. Chem. Soc., Dalton Trans.*, **10**, 2023 (1996).
[18] Q.-Y. Jiang, H.-Q. Deg, Y.-M. Hu, J. Shen, G.-Q. Zhong, N.-H. Hu. *Acta Chim. Sinica*, **66**, 1429 (2008).
[19] V.V. Narayanan, G.R. Newkome. *Top. Curr. Chem.*, **197**, 19 (1998).
[20] A.Yu. Tsivadze, G.V. Ionova, V.K. Mikhalko, Yu.N. Kostrubov. *Russ. Chem. Rev.*, **76**, 213 (2007).
[21] M. Fujita. *Struct. Bond.*, **96**, 117 (2000).
[22] J.-C.G. Bünzli. *Acc. Chem. Res.*, **39**, 53 (2006).
[23] J. Wang, P. Hu, B. Liu, X. Jin, Y. Kong, J. Gao, D. Wang, B. Wang, R. Xu, X. Zhang. *J. Coord. Chem.*, **63**, 2193 (2010).
[24] S.P. Summers, K.A. Abboud, S.R. Farrah, G.J. Palenik. *Inorg. Chem.*, **33**, 88 (1994).
[25] J. Wang, G. Gao, Z. Zhang, X. Zhang, Y. Wang. *J. Coord. Chem.*, **60**, 2221 (2007).
[26] T. Le Borgne, P. Altmann, N. André, J.-C.G. Bünzli, G. Bernardinelli, P.-Y. Morgantini, J. Weber, C. Piguet. *Dalton Trans.*, **5**, 723 (2004).
[27] J. Lisowski, M. Paluch, T. Lis. *J. Inclusion Phenom. Macrocyclic Chem.*, **55**, 123 (2006).
[28] Y. Lin, A. Leydier, E. Métay, A. Favre-Réguillon, D. Bouchu, S. Pellet-Rostaing, M. Lemaire. *J. Inclusion Phenom. Macrocyclic Chem.*, **61**, 187 (2008).
[29] A. Wolfert, E.W.J.L. Oomen, G. Blasse. *J. Solid State Chem.*, **59**, 280 (1985).
[30] G.R. Choppin, Z.M. Wang. *Inorg. Chem.*, **36**, 249 (1997).