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ORIGINAL PAPER

The First Observation of 4f-Luminescence in New Heteronuclear Lanthanide–Germanium Complexes

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Abstract New lanthanide–germanium complexes with diethylenetriaminepentaacetic acid (DTPA) have been synthesized and were characterized by means of elemental analysis, IR-, UV-absorption and luminescent spectroscopy. The 4f-luminescence of heteronuclear Ln(Ge-DTPA)2 (Ln=Sm, Eu, Tb, Dy) complexes in aqueous solutions was investigated for the first time.

Keywords Luminescence · Heteronuclear complexes · DTPA · Lanthanides · Germanium

Introduction

Recently lanthanide complexes with diethylenetriamine-*N*,*N*,*N*′,*N*″,*N*″-pentaacetic acid (DTPA) and its derivatives have attracted attention, first of all, as potential contrast agents [1, 2]. But there are only few reports dedicated to the investigation of the spectroscopic properties (in particular, 4f-luminescence) in complexes with DTPA [3, 4]. Is it possible to increase 4f-luminescent characteristics without of functionalization of DTPA by aromatic substituents-sensitizers? We tried to apply non-traditional objects for this purpose, namely heteronuclear *p*-*f*-complexes based on the DTPA. For this moment there is insufficient information about the photophysical properties of the heteronuclear *p*-*f*-complexes [5, 6] and, moreover, practically no data about lanthanide luminescence in them.

Therefore we reported the preliminary results to gain data on the spectroscopic properties of the lanthanide–germanium complexes with DTPA.

Experimental

Synthesis of Ln–Ge heteronuclear complexes with diethylenetriamine-*N*,*N*,*N*′,*N*″,*N*″-pentaacetic Acid

$Ln(CH_3COO)_3{\cdot}H_2O$ (Ln=Sm–Dy) and DTPA were purchased from Aldrich (Gillingham, Dorset) and used as received. Distilled and deionized water (18 MΩ cm^{-1}) was used throughout. The preparation of Ln complexes with DTPA was described previously [7]. The lanthanide–germanium complexes were synthesized by the reaction between corresponding lanthanide acetate hydrate and equimolar quantities of $[Ge(OH)(H_2DTPA)]{\cdot}H_2O$ (the synthesis was reported before [8]) in aqueous solution. The reaction mixture has been heated at 50°C for 1 h. After 48 h complex microcrystals were isolated in 60–65% yield as stable on air compounds. It was proved by elemental analysis and FAB^+ mass spectra data that the complexes were formed with molar ratio Ln/Ge/DTPA=1:2:2. Anal. calcd. for $C_{28}H_{39}N_6O_{22}Ge_2Sm$: C, 28.95; H, 3.87; N, 7.24; Ge, 12.51; Sm, 12.95; found: C, 28.99; H, 3.91; N, 7.35; Ge, 12.44; Sm, 12.59. For $C_{28}H_{39}N_6O_{22}Ge_2Eu$: C, 28.91; H, 3.88; N, 7.22; Ge, 12.49; Eu, 13.08; found: C, 29.32; H, 3.90; N, 7.33; Ge, 12.62; Eu, 13.63. For $C_{28}H_{39}N_6O_{22}Ge_2Tb$: C, 28.74; H, 3.85; N, 7.18; Ge, 12.42; Tb, 13.59; found: C, 29.13; H, 3.89; N, 7.39; Ge, 12.64; Tb, 14.70. For $C_{28}H_{39}N_6O_{22}Ge_2Dy$: C, 28.65; H, 3.84; N, 7.16; Ge,

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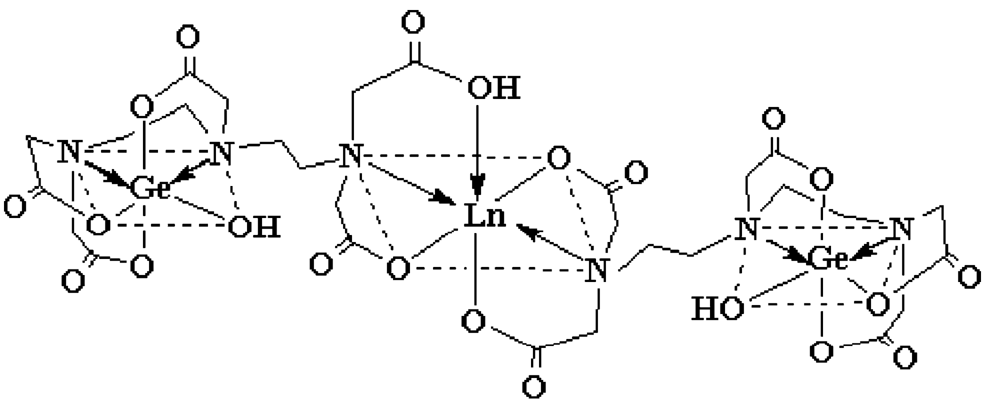


Fig. 1 Schematic structure of the lanthanide–germanium complexes (Ln=Sm–Dy)

12.38; Dy, 13.86; found: C, 29.25; H, 3.87; N, 7.36; Ge, 12.41; Dy, 13.94.

Methods and measurements

Elemental analysis (C, H, N) was carried out by an Perkin-Elmer CHN-240 analyzer. FAB^+ mass spectra were measured on a Varian MAT CH-112 spectrometer (*m*-nitrobenzyl alcohol matrix). All X-ray diffraction (XRD) measurements were made with DRON-2.0 powder diffractometer (CuK_α radiation). The IR spectra were measured on an IR-75 spectrometer (KBr pellets). The UV-Vis absorption spectra were recorded with a Perkin-Elmer Lambda 9 spectrophotometer. The steady-state luminescence spectra were taken in 1 cm×1 cm quartz optical cells using for excitation a combination of a Xe-lamp (XBO 150) and a monochromator (Lot-Oriel), and a polychromator with a cooled CCD matrix as a detector system (Lot-Oriel, Instaspec IV). The luminescence quantum yields (φ) were obtained by the method described by Haas and Stein [9] with the standards $[Ru(bipy)_3]^{2-}$ (φ=0.028 in aerated water) for the Sm^{3+} and Eu^{3+} complexes and quinine sulphate (φ=0.546 in H_2SO_4 1 N) for the Tb^{3+} and Dy^{3+} complexes. The measured values were corrected for the refractive indices. The luminescence lifetime (τ) data were obtained by means of a SDL-1 spectrofluorimeter (LOMO Association, St. Petersburg, Russia) with a LGI-21 nitrogen laser (pulse duration of 8–10 ns at a wavelength of 337 nm) and analyzed by iterative deconvolution and non-linear least-squares method [10]. The triplet level position was obtained from phosphorescence spectrum of gadolinium–germanium complex with DTPA at 77 K.

Results and discussion

The heteronuclear lanthanide complexes were crystalline by results of the XRD. The XRD patterns were characterized by the interplanar distance personal set which differed from mononuclear germanium complex ones. No impurity phases were detected in them. Thus, on the basis of practically identical set of interplanar distances the conclusion that they were isostructural was made.

According to thermogravimetric analysis dehydration starts at 60°C and ends at 210°C. The wide interval of temperatures can be explained by special way of packing of molecules of water due to formation intra- and intermolecular hydrogen bonds in the complexes.

The result showed that a germanium complex with DTPA contains one molecule of water, in contrast to three molecules of H_2O for heteronuclear lanthanide complexes

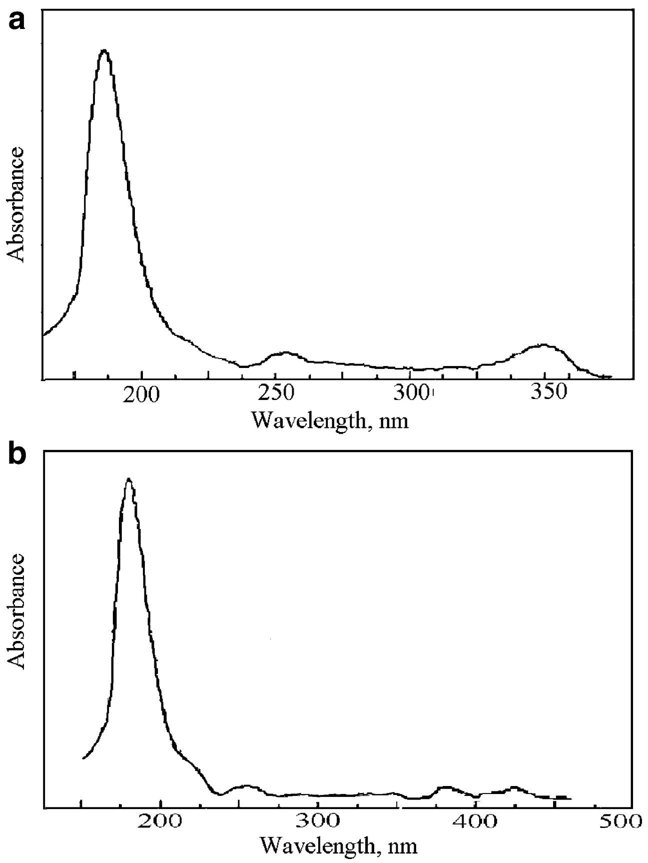


Fig. 2 UV absorption spectra of $Tb(Ge\text{-}DTPA)_2$ (**a**) and $Eu(Ge\text{-}DTPA)_2$ (**b**). 1.0×10^{-3} mol/l in H_2O

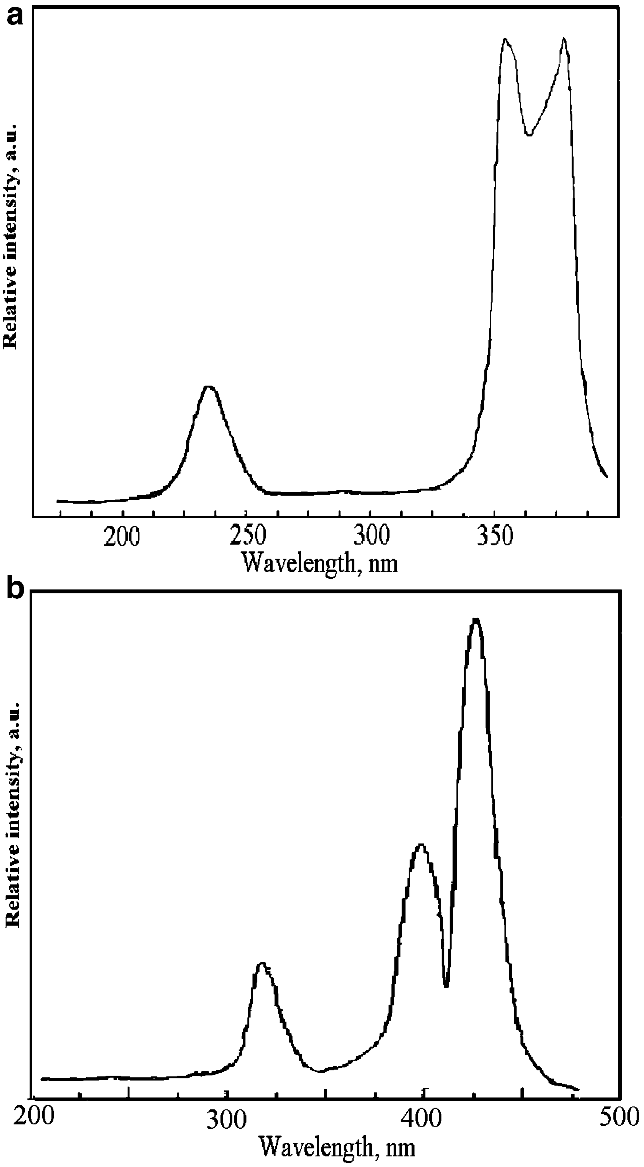


Fig. 3 Excitation spectra of Tb(Ge-DTPA)$_2$ (**a**) (λ_{em}=545 nm) and Eu (Ge-DTPA)$_2$ (**b**) (λ_{em}=612 nm). 1.0×10^{-3} mol/l in H_2O

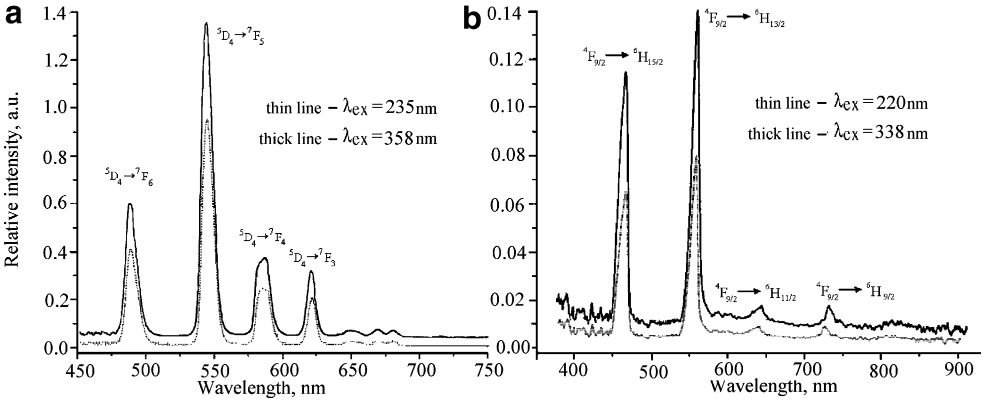
in outer coordination sphere. Pyrolysis proceeds in one single sharp weight loss at 210–260°C while the formation of the inorganic residue is completed at 520–540°C as result of decarboxylation process.

The IR spectra of the heteronuclear complexes were characterized with the following bands (cm^{-1}): in vibration region νCH one (2,990 cm^{-1}), that proves coordination of all three nitrogen atoms of H_5DTPA by metal ions; δGeOH (880), νGe–N (640), νC=O (1,715) coordinated group COOH, ν_{as}C–O (1,595), ν_sC–O (1,400) groups COO$^-$, bounded with *f*-metal; ν_{as}C–O (shoulder is about 1,700) and ν_sC–O (1,330) carboxylate ions bounded with germanium; wide band νOH with maximum about 3,400 cm^{-1}. Thus, it can be concluded that saturation of germanium coordination number up to 6 occurred at the expense of valence linkages with hydroxo- and three carboxylic groups, and also coordinate linkages to two nitrogen atoms of ligand. There was established that all DTPA donor centers are interlinked with metals in complexes. It corresponds to absence of inner sphere water molecules in these heteronuclear complexes.

The analysis of data obtained with the help of different physico-chemical methods allows assuming that *p*-*f*-complexes are three nuclear ones. Coordinated polyhedron of germanium is the same as in complex acid [Ge (OH)(H_2DTPA)]·H_2O [8]. On the basis of experimental data and taking into account the coordination number, oxidation degrees characterized typically for investigated metals, their structure schemes of can be proposed (Fig. 1). Coordination polyhedron of lanthanide is the "distorted octahedron" forming for account of tridentate coordination of two complex anions [Ge(OH)DTPA]$^{2-}$ and [Ge(OH)HDTPA]$^-$ with the closing of four glycine metal cycles which are conjugated by two.

The UV-Vis absorption spectra of heteronuclear terbium– and europium–germanium complexes are shown in Fig. 2. Absorption spectrum of Tb(Ge-DTPA)$_2$ (Fig. 2a) is shifted hypsochromically compared to Ge-DTPA spectrum and consists of three bands (as well as for mononuclear

Fig. 4 Corrected emission spectra of Tb(Ge-DTPA)$_2$ (**a**) and Dy (Ge-DTPA)$_2$ (**b**) complexes (H_2O, 298 K) at different λ_{ex}



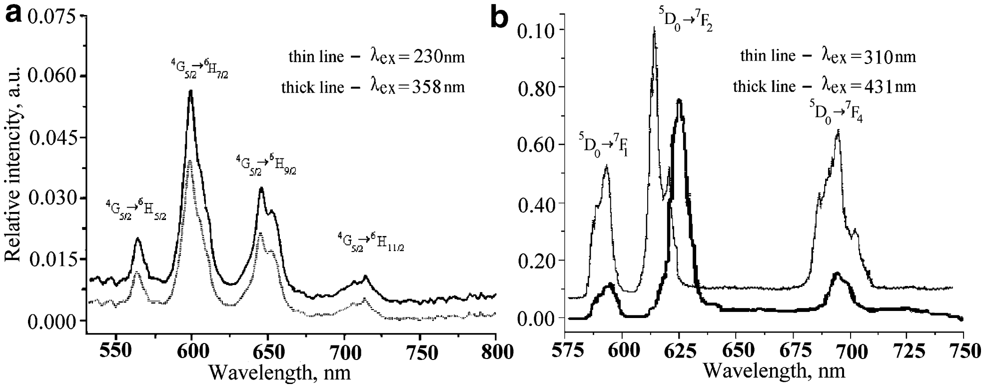


Fig. 5 Corrected emission spectra of Sm(Ge-DTPA)$_2$ (**a**) and Eu(Ge-DTPA)$_2$ (**b**) complexes (H_2O, 298 K) at different λ_{ex}

complexes): intensive one at 195 nm and two less intensive bands at 255 nm and 350 nm. Samarium– and dysprosium–germanium complexes show the similar features. In contrast to previous, a new band in Eu(Ge-DTPA)$_2$ absorption spectrum appears at 427 nm (Fig. 2b), that is not typically for Ge-DTPA. Other three bands noted in the ligand absorption spectrum shift bathochromically.

The excitation spectra (Fig. 3) of lanthanide complexes were measured at 298 K. The excitation spectrum of Tb (Ge-DTPA)$_2$ complex taken at an emission wavelength of 545 nm is shown in Fig. 3a. In the blue spectral region one excitation peak with maximum at 235 nm was resolved. In the long-wavelength region two strong excitation peaks were noted at 358 and 379 nm which practically coincide with excitation bands observed in the spectra of mononuclear complexes. It should be mentioned that the spectral position of the emission bands measured at these selected excitation wavelengths is similar and independent on excitation. The analogous picture is observed in excitation luminescence spectra of samarium and dysprosium heteronuclear complexes. Figure 3b illustrates excitation spectrum of Eu(Ge-DTPA)$_2$ with registration at the red emission band of 617 nm. The excitation spectrum of Eu(Ge-DTPA)$_2$ consists of three peaks in long-wavelength region at 310, 400 and 431 nm, situated separately, unlike a mononuclear complex of europium which is characterized by only two peaks with maxima at 310 and 400 nm.

The steady-state luminescence spectra of heteronuclear lanthanide complexes at room temperature (298 K) are presented in Figs. 4 and 5. The increase of luminescence intensity for heteronuclear complexes in comparison with mononuclear (i.e., Ln-DTPA) complexes was observed (Table 1). It is noteworthy, that the luminescence intensity of heteronuclear samarium, terbium or dysprosium complexes was higher (up to 1.8, 2.1 and 2.5 times, respectively), than in the mono-complexes independent on excitation wavelength. At the same time, the luminescence of heteronuclear europium complex was higher (up to 1.7 times) compared to Eu-DTPA complex only in the excitation region of 310–330 nm.

Two luminescence spectra of the terbium–germanium complex (Fig. 4a) measured with excitation at 235 and 358 nm show the similar pattern of an emission of Tb^{3+} ion. Four main peaks were characterized and emission is originated from the $^5D_4 \rightarrow {}^7F_j$ (j=6, 5, 4, 3) transition of Tb^{3+} ion. The strongest peak (λ_{max}=547 nm; $^5D_4 \rightarrow {}^7F_5$-transition) corresponds to the non-hypersensitive transition.

The luminescence spectrum of Dy(Ge-DTPA)$_2$ (Fig. 4b) shows four apparent emission peaks ($^4F_{9/2} \rightarrow {}^6H_J$; J=15/2, 13/2, 11/2, 9/2) under the short (220 nm) as well as long wavelength (338 nm) excitation. It was found that the luminescence band corresponding to $^4F_{9/2} \rightarrow {}^6H_{13/2}$ hypersensitive transition has the highest emission intensity.

As shown in Table 1, terbium– and dysprosium–germanium complexes are characterized by the more strong emission than other heteronuclear lanthanide complexes.

The luminescence of samarium heteronuclear complex is very weak compared to emission of other lanthanide heteronuclear complexes. Its luminescence spectrum (Fig. 5a) consists of four characteristic emission bands corresponding to the $^4G_{5/2} \rightarrow {}^6H_J$ (J=5/2, 7/2, 9/2, 11/2) transitions of Sm^{3+} ion. The luminescence peak at 601 nm (non-hypersensitive transition $^4G_{5/2} \rightarrow {}^6H_{7/2}$) is the strongest one.

In contrast to other lanthanide complexes, the luminescence spectra of heteronuclear europium complex observed at different excitation wavelength are essentially different (Fig. 5b). The luminescence spectrum of europium complex

Table 1 Photophysical properties of Ln(Ge-DTPA)$_2$ complexes

Complex	Luminescence			Lifetimes τ (μs)[a]
	λ_{ex}(nm)	φ[a]	φ_h/φ_m[b]	
Sm(Ge-DTPA)$_2$	360	0.009	1.8	73
Eu(Ge-DTPA)$_2$	310	0.015	1.7	450
Tb(Ge-DTPA)$_2$	358	0.517	2.1	570
Dy(Ge-DTPA)$_2$	338	0.026	2.5	220

[a] Errors are ±10%.

[b] φ_h and φ_m-Luminescence quantum yield of heteronuclear and mononuclear complexes, respectively.

under the excitation at 310 nm shows three apparent emission peaks, which correspond to the characteristic emission $^5D_0 \rightarrow {}^7F_J$ (J=1, 2, 4) transitions of Eu^{3+} ion, respectively. The peak at 612 nm corresponding to hypersensitive transition ($^5D_0 \rightarrow {}^7F_2$) is the strongest one and the band intensity ratio is 1:2:1. This ratio remains constant when complex is excited at 400 nm, but the luminescent signal decreases approximately twice. With excitation at 431 nm the luminescence band corresponding to $^5D_0 \rightarrow {}^7F_2$ transition shifts bathochromic and its intensity becomes 7 times higher compared to two other emission bands. It should be mentioned, that the 4f-luminescence quantum yield of complex $Eu(Ge\text{-}DTPA)_2$ is lower compared to that values estimated for terbium and dysprosium ones (Table 1). There are different opinions about the efficiency of excitation energy transfer on resonance levels of europium and terbium ions in the complexes with DTPA [3, 11, 12], about which we shall talk further.

The value of the triplet state for considered ligand was estimated to be 24,030 cm^{-1}, as calculated from the spectral position of maximum of the phosphorescence spectrum for aqueous solution of $Gd(Ge\text{-}DTPA)_2$ measured at 77 K. The triplet state of the ligand is higher by 6,730 cm^{-1} than the lowest excited state of Eu^{3+} ion ($^5D_0$), and the ligand strongly sensitized the luminescence of Eu^{3+} ion at excitation wavelength 310 nm. Upon excitation at 400 nm (i.e. factually in absorption band of europium ion-396 nm) low emission from $^5D_0$-level is observed. Apparently, this is due to the presence of the so called "charge transfer level" that as it is known [11] led to essential non-radiative deactivation of triplet state of the complex.

Conclusions

New *p-f* heteronuclear complexes with general formula [Ge(OH)(DTPA)Ln(HDTPA)Ge(OH)] (Ln=Sm^{3+}, Eu^{3+}, Tb^{3+} and Dy^{3+}) were synthesized and their spectroscopic properties were studied. The energy match between the ligand and lanthanide ions has been examined to predict that the energy transfer process occurs between the ligand and Ln^{3+}. It was found that the terbium complex has the most efficient energy transfer, whereas the probability of energy transfer in europium complex strongly depends on excitation wavelength. Since germanium is not the sensitizer of 4f-luminescence then it plays a role of original organizer for the structure of heteronuclear complexes. Undoubtedly, this phenomenon requires the detailed investigations in the future.

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