

A NEW, STRONG ABSORPTION AT 715 NM OBSERVED IN PHOTOACOUSTIC SPECTRUM OF Er(III)-HYDRAZONE COMPLEX

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Received: November 12, 2005

Abstract. The $[\text{Er}(\text{DBH})_2(\text{NO}_3)_2]\text{NO}_3$ complex was synthesized and characterized by elemental analysis, molar conductance, and IR. The photoacoustic (PA) spectra of the f-f transitions in Er(III)-hydrazone have shown that they are over an order of magnitude more intense than similar transitions in the Er(III)-hydrazine complex. A new, very narrow and intense PA absorption line is recorded at 715 nm for Er(III)-hydrazone complex.

1. INTRODUCTION

A large number of hydrazone complexes with metal ions have been investigated because they show a broad spectrum of biological and pharmaceutical activities, such as antimicrobial antitumor, antituberculostatic and anticancer activities [1-3]. The rare earth(III) ions have very high magnetic moment and the organometallic complexes with paramagnetic lanthanide metal ions, especially hydrazone, could be very usefully as a new class of potential magnetic resonance imaging contrast agents [4]. Previously, we reported the structural characterization of lanthanide(III)-hydrazone complexes of higher coordination number [5]. The organic rare earth(III) complexes often have been stud-

ied by using photoacoustic spectroscopy because this technique provides additional, very important information about the dynamical processes, like the intermolecular energy transfer or the heating processes correlated with the electron-phonon interactions [6-10]. The presence of the f-f transitions and intermolecular transfer energy has large influence on the non-radiation processes. Recently, the PA studies of the hydrazone complex of neodymium(III) have evidenced the presence of several very intense PA lines of the f-f type [11].

The new erbium(III)-hydrazone complex belongs to the $[\text{Ln}(\text{DBH})_2(\text{NO}_3)_2]\text{NO}_3$ group with a high coordination number of ten. The PA spectra of this group at room temperature are investigated and especially

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the complex with erbium(III) is expected to show a lot of the f-f transition in the visible region of electromagnetic radiation.

2. EXPERIMENTAL

[Er(DBH)₂(NO₃)₂]NO₃ complex was prepared by the following procedure. A methanolic solution (10 mL) of DBH (4 mmol) was added to a methanolic solution (10 mL) of the appropriate lanthanide nitrate hydrated (2 mmol). The solution was stirred for 1 h. Fine microcrystalline products have been obtained, filtered off, washed with small portions of methanol, and dried in vacuum over anhydrous calcium chloride. The analytical data are presented in Table 1. The preparation of the complexes [Er(DBH)₂(NO₃)₂]NO₃ is summarised in the following general equation: Er(NO₃)₃·5H₂O + 2DBH → [Er(DBH)₂(NO₃)₂]NO₃ + 5H₂O.

Microanalyses (C,H,N) were taken with a Perkin–Elmer analyzer model 2400. The metal contents of the complexes were determined by titration with EDTA volumetric method using xylenol orange as indicator [12]. Melting points were determined with a Bьchi silicon oil bath apparatus and are uncorrected. Molar conductivities were measured by a WTW model LF 530 conductivity bridge employing a calibrated immersion type cell, which had a cell constant of 0.998. This represents a mean value calibrated at 25 °C with potassium chloride solutions. Temperature was controlled with an accuracy

of ±0.1 °C using a Haake thermoelectric circulating system of water. IR spectra were recorded in the 4000–250 cm⁻¹ region on a Perkin–Elmer 1650 FT–IR spectrophotometer using KBr pellets. Calibration of frequency reading was made with polystyrene film.

3. RESULTS AND DISCUSSION

The analytical data of the [Er(DBH)₂(NO₃)₂]NO₃ complex gave the following yield: 91%, mp.: 488K; elemental analyses - determined(calculated): C-45.28% (45.14%), H-3.05% (2.95%), N-16.25% (16.08%), Er-17.51% (17.46%). The indicated 1:2 metal to ligand stoichiometry corresponds to the ErC₃₆H₁₂₈N₁₁O₁₁ molecular formula. The complex is stabilized in crystalline solids, soluble in methanol, ethanol, acetonitrile, DMF, DMSO. It is not insoluble in chloroform, dichloromethane and ether. The molar conductances of 0.001 M acetonitrile, methanol, DMF and DMSO solutions of the Er(III) complex the corresponding values of the compounds is consistent with 1:1 electrolytic behavior with molar conductance: CH₃CN- 146 mho·cm²·mol⁻¹, CH₃OH- 109 mho·cm²·mol⁻¹, DMF- 89 mho·cm²·mol⁻¹, DMSO- 70 mho·cm²·mol⁻¹. Infrared spectral data gives evidence for the coordination of the neutral form of the hydrazone to the lanthanide ion via azomethinic nitrogen, pyridine nitrogen and carbonylic oxygen. The infrared spectra also demonstrates the presence of identity and ionic nitrates in the complex with the erbium(III). Thus the formula of the complex is

Table 1. PA band assignment for hydrazine–Er(III) and hydrazone–Er(III) complexes [9].

Compound	λ [nm]	PA Intensity [arb. units]	Assignment
Hydrazine–Er(III)	300	59	π→π*
	318		π→π*
	405		π→π*
	488	0.10	⁴ I _{15/2} → ⁴ F _{7/2}
	519	0.10	⁴ I _{15/2} → ² H _{11/2} , ⁴ S _{3/2}
	649	0.12	⁴ I _{15/2} → ⁴ F _{9/2}
Hydrazone–Er(III)	375	40	
	422		⁴ I _{15/2} → ⁴ G _{11/2}
	484	5	⁴ I _{15/2} → ² G _{9/2} , ⁴ F _{9/2}
	523	20	⁴ I _{15/2} → ⁴ F _{7/2}
	580	3	⁴ I _{15/2} → ² H _{11/2}
	657	13	⁴ I _{15/2} → ⁴ F _{9/2}
	715	33	?
	744	17	?
	777	16	⁴ I _{15/2} → ⁴ I _{9/2}

[Er(DBH)₂(NO₃)₂](NO₃) (Fig. 1) with coordination number of ten.

The assignments of IR bands were made by comparing the spectra of the complex with those of the free ligand DBH. The broad absorption bands around 3470 cm⁻¹ are assigned to the $\nu(\text{N-H})$ frequency in the spectra of the ligand and its complex. The strong IR bands due to $\nu(\text{C=O})$ (1670 cm⁻¹) is an evidence for the coordination of the hydrazone with the metal via carbonyl oxygen [10]. The band due to $\nu(\text{C=N})$ (1560 cm⁻¹), indicates that azomethine nitrogen is coordinated to the metal. The low energy pyridine ring in-plane and out-of-plane vibrations are observed in the spectrum of the ligand at 615 and 410 cm⁻¹ respectively, but the corresponding bands for the complex are shifted to higher frequencies at 630 and 420 cm⁻¹, respectively, which is a indication of the coordination of the heterocyclic nitrogen [13–15]. The IR spectrum demonstrate the presence of coordinated nitrates. Two strong bands observed at ~1480 and ~1300 cm⁻¹ assigned to the ν_4 and ν_1 vibrations modes of the nitrate group, respectively (C_{2v} symmetry, coordinated nitrate group). The magnitude of the splitting ($\nu_4 - \nu_1$) is ~180 cm⁻¹ and it is typical of bidentate bonding of nitrates [16].

PA spectra of polycrystalline powder samples have been obtained using a modification of the PAS method initially, proposed by G.J.Papadopoulos and G.L.R.Mair [18]. A Xenon arc lamp with 1 kW power and a 1/4m ORIEL monochromator were used as a light source, with bandpass width of 5 nm (at 500 nm). The light, intensity modulated using a mechanical chopper at a frequency of 10 Hz was directed into a photoacoustic cell equipped with a TREVI EM27 microphone. A dual SR830 lock-in amplifier measured amplitude and phase of the PA signal detected by the microphone. Data acquisition ensured that each value was an average of 20 runs at the same wavelength of the incident light. A carbon black was used as a standard to re-calibrate the final spectrum. The PA spectra of all the complexes were recorded at room temperature in the range of 300 – 700 nm.

Fig. 2 presents the PA spectra of hydrazone-Er(III) and hydrazine-Er(III) complexes in the 300–700 nm range. The PA spectra were recorded by detecting the heat generated through the nonradiative transitions by the solid sample after absorbing a periodically varying incident light. The PA absorptions of hydrazine complex below 405 nm are assigned as the $\pi \rightarrow \pi^*$ charge transfer transitions. The absorptions of different energy levels of erbium(III) ions are observed in the UV-VIS region of the PA

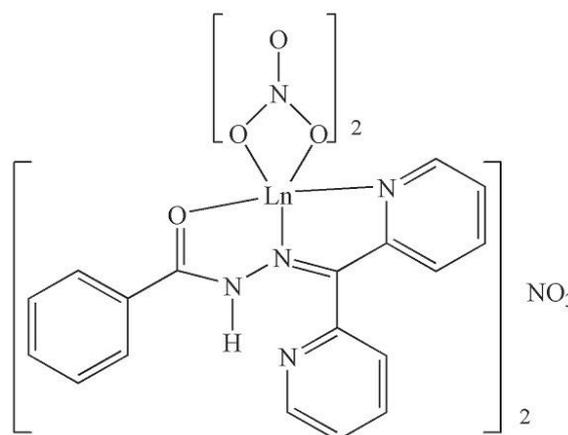


Fig. 1. Structure of the [Ln(DBH)₂(NO₃)₂](NO₃) complexes, where Ln(III)=Gd, Tb, and Er.

spectra. Two kinds of relaxation processes are dominating: the radiative and nonradiative after excitation, but the PA spectrum is formed by the nonradiative processes. The numerous closely packed energy levels of erbium(III) ion (the f-f transitions) are often intermixed and with a high probability the energy can relax by the nonradiative relaxation processes. An electron is promoted from the ground state to 4f excited levels, the 4f→4f resulting intra-configuration transitions give weak and sharp peaks. They are generally electric dipolar transitions forbidden by the parity selection rules and they are forced by the crystal field configuration mixing. If they are not completely hidden by intense absorp-

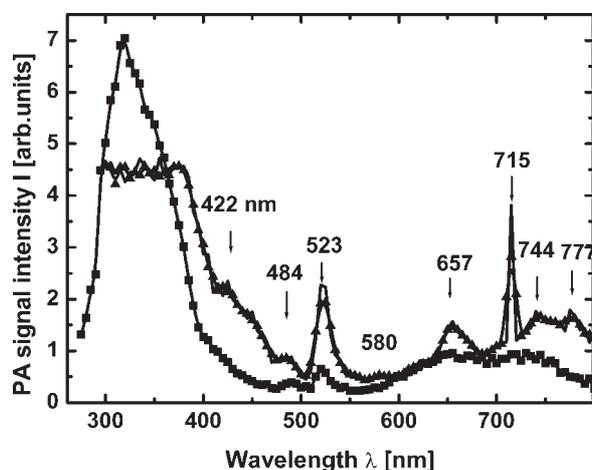


Fig. 2. The PA spectra for Er-hydrazone (▲) and Er-hydrazine (■) complexes.

tion features, they are relatively easy to assign because of the well known electronic structure of the $4f^N$ configuration which is almost independent of the nature of the host. This independence is due to the fact that the maximum of the charge density function for 4f-electrons is well inside the outermost $5s^5$ and $5p^6$ shells which protect the 4f-electrons against the neighbor interactions. The dynamic crystal field, electron-phonon coupling could cause the differences between the free ion spectra and the ion in the lattice [18]. Table 1 gives the obtained PA absorptions of f-f transitions. Two PA absorption lines at 715nm and 744 nm are difficult to assign. In 629-676 nm spectral interval the $^4I_{9/2}$ transitions occur while in 776-830 nm interval the $^4I_{9/2}$ transitions are observed [19]. In the interval were these two extra lines were registered the PA absorption could be forced by a strong coupling of the electron-phonon interaction or we have observed a quit new transitions. These transitions might find application in lasers because these particular excitations could be used for longer wavelength of the electromagnetic radiations.

In conclusion, we have obtained more intense PA spectra of the f-f transitions for the hydrazone-Er(III) complex than for hydrazine-Er(III) complex and for the former complex two new, intense PA absorption lines are observed at 715 nm and 744 nm.

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