

Photoacoustic study of a new neodymium(III) hydrazone complex

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The neodymium(III) hydrazone complex [Nd(DBH)₂(NO₃)₃] has been synthesized and characterized using microanalysis and IR spectroscopy. High-resolution photoacoustic spectrometry has been applied for studying the complex. The obtained photoacoustic spectrum has been analysed and compared to a similar [Nd(PicBH)₂(NO₃)₂]NO₃ complex. The intensities of the f–f transitions in the photoacoustic spectrum of Nd(DBH)₂(NO₃)₃ were two times greater than for the [Nd(PicBH)₂(NO₃)₂]NO₃ complex.

Key words: *photoacoustic spectroscopy; neodymium complex*

1. Introduction

Complexes of hydrazones with paramagnetic lanthanide metal ions have attracted close attention as a new class of potential magnetic resonance imaging contrast agents [1]. A number of hydrazone rare earth(III) complexes have gained wide interest, because they show a broad spectrum of biological and pharmaceutical activities, such as antimicrobial, antitumor, antituberculostatic, and anticancer actions [2–8]. Previously we have reported the structural characterization of lanthanide(III)–hydrazone complexes of higher coordination numbers [9–11]. Recently, rare earth(III) complexes of hydrazones have been studied with a high-resolution photoacoustic (PA) spectrometer [12]. The $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$, and f–f electron transitions with different intensities have been recorded. The PA absorptions of the f–f transitions in the yellow light region have been observed and it has been suggested that they could play a very important role in living matter [13].

The aim of this report is to present the results of PA spectroscopy study of a new kind of coordination compound – the neodymium(III) complex of hydrazone $[\text{Nd}(\text{DBH})_2(\text{NO}_3)_3]$. Special attention will be paid to the intensities of the PA absorptions due to f–f transitions. A comparison will be made with a similar neodymium(III) complex – $[\text{Nd}(\text{NO}_3)_2(\text{PicBH}_2)]\text{NO}_3$ studied previously [12].

2. Experimental

All manipulations were performed in a dry box. The solutions were prepared in a glove box purged with dried nitrogen gas. The complex was prepared by the following general procedure: a methanol solution (10 cm^3) of DBH (4 mmol) was added to a methanolic solution (10 cm^3) of hydrated neodymium nitrate (2 mmol). The solution was stirred for 1 h. A fine microcrystalline product was obtained, filtered off, washed with small amounts of methanol, and dried in vacuum over anhydrous calcium chloride.

All chemicals were purchased from Aldrich Chemicals and used without further purification. All solvents were dried and distilled prior to use. Di-2-pyridylketone benzoylhydrazone was prepared by refluxing a methanolic solution (500 cm^3) of benzoic hydrazide (6.80 g, 50 mmol) and di-2-pyridylketone (9.21 g, 50 mmol) for 24 h. After 24 h of slowly cooling the reaction mixture at room temperature, a crude white product was filtered off, washed with methanol, and recrystallised from methanol. Microanalyses (C, H, N) were taken with a Perkin-Elmer analyzer model 2400. The metal contents of the complexes were determined by titration with the EDTA volumetric method, using xylenol orange as indicator [14]. Melting points were determined with a Büchi silicon oil bath apparatus and are uncorrected. Molar conductivities were measured on a WTW model LF 530 Conductivity Bridge, employing a calibrated immersion type cell, with the cell constant of 0.998 cm^{-1} (mean value calibrated at $25 \text{ }^\circ\text{C}$ with potassium chloride solution). Temperatures were controlled with an accuracy of $\pm 0.1 \text{ }^\circ\text{C}$ using a Haake thermoelectric circulating system of water. IR spectra were recorded in the $4000\text{--}250 \text{ cm}^{-1}$ region with a Perkin-Elmer 1650 FT-IR spectrophotometer using KBr pellets. Frequency readings were calibrated with polystyrene film.

The PA spectra of polycrystalline powder samples were obtained by using a modified PAS (photoacoustic spectroscopy) method initially proposed by Papadopoulos and Mair [15]. A Xenon arc lamp with 1 kW power and a $\frac{1}{4}$ m ORIEL monochromator were used as the light sources, with a band pass width of 5 nm (at 500 nm). The light, whose intensity was modulated with a chopper at 10 Hz, was directed into a photoacoustic cell equipped with a TREVI EM27 microphone. A dual SR830 lock-in amplifier measured the amplitude and phase of the PA signal detected on the microphone. Data acquisition ensured that each value was an average of 20 runs at the same wavelength of the incident light. Carbon black was used as the standard to recalibrate the final spectrum. The PA spectra of all complexes were recorded at room temperature in the range of 300–700 nm.

3. Results and discussion

3.1. Sample preparation and characterization

The analytical data of the complex (with the yield of 88%, m.p. 201 °C; elemental analyses found (calc.): C – 46.37 (46.25), H – 3.00 (3.02), N – 16.52 (16.48) and Nd – 15.60 (15.43)) indicate a 1:2 metal to ligand stoichiometry, corresponding to the molecular formula $\text{NdC}_{36}\text{H}_{28}\text{N}_{11}\text{O}_{11}$. The complex is an air-stable crystalline solid, soluble in methanol, ethanol, acetonitrile, DMF, DMSO, but insoluble in chloroform, dichloromethane and ether. The molar conductances of 0.001 M acetonitrile, methanol, DMF, and DMSO solutions of the neodymium(III) complex lie below $10 \text{ S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$ ($\text{CH}_3\text{CN} - 4 \text{ S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$, $\text{CH}_3\text{OH} - 3 \text{ S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$, $\text{DMF} - 4 \text{ S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$, $\text{DMSO} - 4 \text{ S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$), indicating its non-electrolytic nature. Infrared spectral data give evidence for the coordination of the neutral form of the hydrazone to the neodymium ion via azomethinic nitrogen, pyridine nitrogen and carbonylic oxygen. Infrared spectra also demonstrate the presence of only bidentate coordinated nitrate anions. Thereupon, the formula of the complex becomes $[\text{Nd}(\text{DBH})_2(\text{NO}_3)_3]$ (Fig. 1).

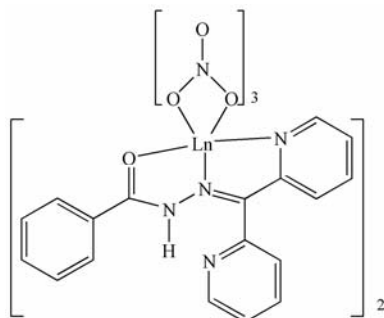


Fig. 1. Schematic structure of the $[\text{Nd}(\text{DBH})_2(\text{NO}_3)_3]$ complex (Ln = Nd)

3.2. IR measurements

The relevant infrared vibration bands are given in Table 1. Assignments were made by comparing the spectra of the complex with those of the free DBH ligand. The broad absorption band at 3415 cm^{-1} was 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}) in the spectra of the complex are the evidence of the coordination of the hydrazone with the metal via carbonyl oxygen [16]. The band due to $\nu(\text{C=N})$ (1576 cm^{-1}) indicates that azomethine nitrogen is coordinated to the metal. Low energy in-plane and out-of-plane vibrations of the pyridine ring were observed in the spectrum of the ligand at 615 and 410 cm^{-1} , respectively, but the corresponding bands for the complexes are shifted to higher frequencies – 622 and 428 cm^{-1} , respectively, indicating

a coordination of heterocyclic nitrogen [17–20]. The spectrum demonstrates the presence of coordinated nitrates. Two strong bands are observed at 1472 and 1300 cm^{-1} and are assigned to the ν_4 and ν_1 vibrations modes of the nitrate group, respectively (C_{2v} symmetry, coordinated nitrate group). The magnitude of splitting in the complex ($\nu_4-\nu_1$) is 172 cm^{-1} , typical of bidentate bonding of nitrates [21].

Table 1. Characteristic IR bands (cm^{-1}) of the ligand DBH and the neodymium(III)–hydrazone complex $\text{Nd}(\text{DBH})_2(\text{NO}_3)_3$

Compound	$\nu(\text{N-H})$	$\nu(\text{C=O})$	$\nu(\text{C=N})$	$\nu_4(\text{NO}_3)$ (C_{2v})	$\nu_3(\text{NO}_3)$ (D_{3h})	$\nu_1(\text{NO}_3)$ (C_{2v})	Low-energy pyridine ring vibrations	
							In plane	Out-of-plane
DBH	3473	1684	1577	–	–	–	615	410
$\text{Nd}(\text{DBH})_2(\text{NO}_3)_3$	3415	1640	1576	1472	–	1300	622	428

3.3. PA spectra

Figure 2 presents the PA spectra of the new neodymium(III) hydrazone–complex, $[\text{Nd}(\text{DBH})_2(\text{NO}_3)_3]$ and a similar neodymium(III)-hydrazone complex studied previously, $[\text{Nd}(\text{PicBH})_2(\text{NO}_3)_2]\text{NO}_3$ [12]. The PA spectra correspond to three kinds of electron transitions: $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$, and f–f. For shorter wavelengths the first two types of transitions dominate and are more intense, whereas in the visible region the less intense f–f transitions appear. The f wavefunctions are mainly localized on rare earth(III) ions, and the position of the PA line for f–f transitions is only very weakly dependent on the kind of matrix. On the other hand, the opposite is true for d–d transitions, because the d wavefunctions are extended over the molecule [22, 23]. The transitions $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ strongly depend on the kind of matrix, because the first one takes part in the bonding processes, and the second could play an important role in the thermodynamic balance of living matter [24]. The intensity of the PA spectrum of f–f transitions is markedly different for the two complexes of neodymium(III) (Fig. 2). Intensity is one of the most important parameters in the photoacoustic spectroscopy of coordination compounds, especially if they are active in biological systems. This is connected to the intermolecular transfer energy as well as to relaxation processes between the excited and the ground states.

The PA spectrum is obtained by detecting the heat generated through non-radiative relaxation, released by a sample absorbing modulated incident light. The PA spectrum intensity, I , could be given by the following relation [25]:

$$I = k A_{\text{abs}} \gamma$$

where A_{abs} is the absorbance of the sample, γ is the probability of a non-radiative transition after excitation, and k is a coefficient determined by the thermal properties of the sample and the spectrometer. In our case, it can be supposed that k and A_{abs} are similar for both samples. The main contribution arises from γ and is connected to non-radiative transitions.

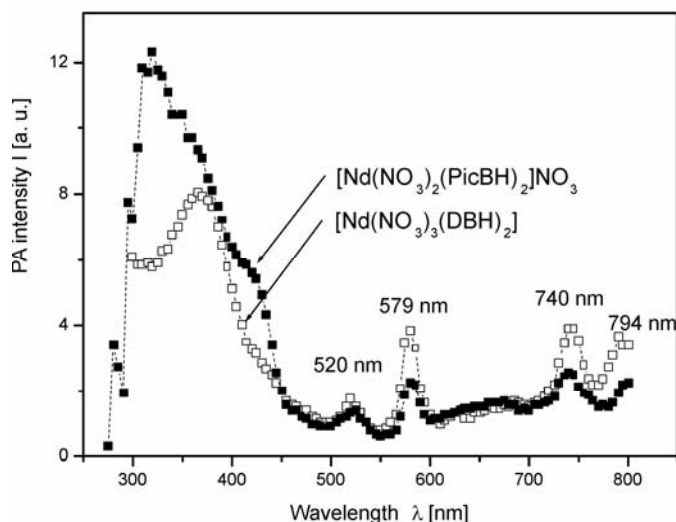


Fig. 2 Photoacoustic spectra of $[\text{Nd}(\text{DBH})_2(\text{NO}_3)_3]$ and, for comparison, $[\text{Nd}(\text{PicBH})_2(\text{NO}_3)_2]\text{NO}_3$

The PA band at shorter wavelengths is shifted to lower energies in both complexes than those observed for the other rare earth(III) organic complexes [26]. It is suggested that the bonds related to $\pi \rightarrow \pi^*$ transitions are weaker in our complexes. The f–f transitions for neodymium complexes are almost at the same positions, but significant differences are observed in the intensities of the PA spectra [26]. More intense PA spectra for the f–f transitions are recorded for the $[\text{Nd}(\text{NO}_3)_3(\text{DBH})_2]$ complex than for the analogous $[\text{Nd}(\text{NO}_3)_2(\text{PicBH})_2]\text{NO}_3$ [12] complex (Fig. 2). This is easily seen by comparing the PAS lines at 520 nm (${}^4G_{9/2} + {}^2D_{7/2}$), 579 nm (${}^4G_{5/2} + {}^2G_{7/2}$), 740 nm (${}^4S_{3/2}$), and 794 nm (${}^4F_{5/2}$). The integrated intensity of all f–f transitions is twice greater for the $\text{Nd}(\text{DBH})_2(\text{NO}_3)_3$ complex.

In conclusion, a new neodymium(III) hydrazone complex has been prepared, characterized by microanalysis and IR measurements, and its PA spectrum recorded at room temperature. Intense lines in the PA spectrum due to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions have been observed to be shifted to lower energies, which suggests that in some parts of the molecule bonding processes are different than in other rare-earth complexes. The integral intensity of f–f transitions in the PA spectrum for the new complex is about two times larger than for an analogous neodymium(III)–hydrazone complex, and thus its intermolecular transfer energy is more robust.

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