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Heteroligand Complexes of Nd(III), Yb(III), and Er(III) Dibenzoyl Methanates with Bis(5-Pyridin-2-yl-1,2,4-Triazol-3-yl)methane

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Abstract—Heteroligand coordination compounds $Ln(Dbm)_2HL \cdot nEtOH$, where Ln is Nd(III), Yb(III), and Er(III); HDbm is dibenzoylmethane; H_2L is bis(5-pyridin-2-yl-1,2,4-triazol-3-yl)methane, are synthesized and studied. The complexes are studied by elemental analysis, TGA, and IR spectroscopy. The structure of complex $[Nd(Dbm)_2 \cdot HL \cdot EtOH] \cdot EtOH$ is determined by X-ray diffraction analysis. The crystals are triclinic, space group $P\bar{1}$, $a = 10.2004(9)$, $b = 11.3809(10)$, $c = 20.9173(18)$ Å, $\alpha = 102.133(1)°$, $\beta = 103.568(1)°$, $\gamma = 100.306(2)°$; $Z = 2$ (8416 reflections with $I > 2\sigma(I)$, $R = 0.053$, $Rw = 0.136$). The luminescence of solid samples of the studied complexes is studied in the near-IR region.

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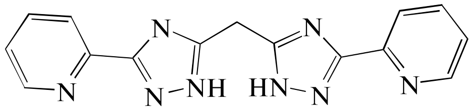
INTRODUCTION

Coordination compounds of lanthanides represent one of the most demanded classes of luminophores due to their efficient monochromatic luminescence necessary for the creation of "pure" colors [1, 2]. One of the main problems in the synthesis of luminescent coordination compounds of lanthanides is the selection of ligands favoring the efficient energy transfer from the organic moiety of the complex to the central atom, being the so-called "photoantenna." The presently best photoluminescence characteristics were obtained for the heteroligand complexes of 4*f* metals in which the central atom is coordinated by a chelating nitrogen-containing Lewis acid along with three anionic bidentate ligands. 1,10-Phenanthroline and 2,2-bipyridine serve most frequently as a Lewis base [3–10]. However, even the most efficient photoluminophores based on the Ln(III) complexes exhibit weak electroluminescence because of low electron-transport properties. Complexes with 3-(pyridin-2-yl)-1,2,4-triazole are promising for the development of electroluminescence devices. On the one hand, these complexes are chelating ligands. On the other hand, they have high electron-transport characteristics. It has earlier been found that the coordination compounds of Eu(III) dibenzoyl methanates with triazoles possess good photoluminescence properties [11]. In continuation of these studies, we synthesized a new series of heteroligand coordination compounds of Nd(III), Yb(III), and Er(III) with dibenzoylmethane (HDbm) and bis(5-pyridin-2-yl-1,2,4-triazol-3-yl)methane (H_2L).



H_2L

EXPERIMENTAL

Bis(5-pyridin-2-yl-1,2,4-triazol-3-yl)methane was synthesized by the reaction of picolinic acid nitrile with malonic acid dihydrazide [12]. Dibenzoyl methanates of Nd(III), Yb(III), and Er(III) were synthesized according to described procedures [13].

Syntheses of the studied coordination compounds were carried out using the following general procedure: $Ln(Dbm)_3 \cdot 2H_2O$ (Ln = Nd(III), Yb(III), and Er(III)) (3 mmol) was dissolved in anhydrous methanol (20 mL). The corresponding triazole (3 mmol) was added to the obtained solution, and the resultant mixture was magnetically stirred on heating for 2 h. Colorless crystals formed on cooling were filtered off, washed with cold methanol, and dried in air. After recrystallization from ethanol, the yield of the complex was 46–67% based on $Ln(Dbm)_3 \cdot 2H_2O$.

Table 1. Crystallographic data and characteristics of the X-ray diffraction experiment for complex **Ia**

Parameter	Value
Molecular Formula	$C_{49}H_{45}N_8O_6Nd$
Molecular weight	986.17
Crystal sizes, mm	0.20 × 0.12 × 0.09
Crystal system	Triclinic
Space group	$P\bar{1}$
Cell parameters:	
a, Å	10.2004(9)
b, Å	11.3809(10)
c, Å	20.9173(18)
α, deg	102.133(1)
β, deg	103.568(1)
γ, deg	100.306(2)
V, Å^3	2240.3(3)
Z	2
Temperature, K	173(2)
ρ_{calcd}, g/cm^3	1.462
μ, mm^{-1}	1.218
F(000)	1006
θ range, deg	2.41–29.61
Ranges of indices	$-13 \leq h \leq 13$, $-15 \leq k \leq 15$, $-27 \leq l \leq 27$
Total number of reflections/independent reflections	23595/11029
T_{min}/T_{max}	0.793/0.898
R ($I > 2\sigma(I)$)	$R_1 = 0.053$ $wR_2 = 0.136$
Goodness-of-fit	0.999
Residual electron density (max/min), e Å^3	1.339/–1.130

$Nd(Dbm)_2 \cdot HL \cdot EtOH$ (**I**)

For $C_{47}H_{40}N_8O_5Nd$

anal. calcd., %: C, 59.98; H, 4.28; N, 11.91.
Found, %: C, 60.19; H, 4.04; N, 12.11.

IR, ν, cm^{-1}: 3414, 3059, 1595, 1549, 1518, 1478, 1456, 1395, 1312, 1225, 1068, 721, 608, 516.

$Yb(Dbm)_2 \cdot HL$ (**II**)

For $C_{45}H_{34}N_8O_4Yb$

anal. calcd., %: C, 58.50; H, 3.71; N, 12.12.
Found, %: C, 58.32; H, 3.95; N, 12.03.

IR, ν, cm^{-1}: 3059, 1595, 1551, 1519, 1476, 1454, 1401, 1310, 1224, 1068, 721, 611, 516.

$Er(Dbm)_2 \cdot HL \cdot EtOH$ (**III**)

For $C_{47}H_{40}N_8O_5Er$

anal. calcd., %: C, 58.55; H, 4.18; N, 11.62.
Found, %: C, 58.65; H, 4.02; N, 12.07.

IR, ν, cm^{-1}: 3056, 1596, 1551, 1519, 1478, 1456, 1395, 1310, 1229, 1068, 724, 611, 519.

Single crystals of complex $[Nd(Dbm)_2 \cdot HL \cdot EtOH] \cdot EtOH$ (**Ia**) suitable for X-ray diffraction analysis were obtained by the crystallization of compound **I** from ethanol.

Elemental analysis was carried out on a Perkin-Elmer 240 C analyzer.

TGA curves were obtained on a *Q* derivatograph (Paulik–Paulik–Erdey system) in a static air atmosphere. The heating rate was 10°C/min, a ceramic crucible without a cap served as a sample holder, and calcined alumina was used as a standard.

IR spectra were recorded in the range from 4000 to 400 cm^{-1} on a Nicolet Nexus 470 FT-IR spectrometer using a standard procedure of sample pressing with potassium bromide.

Absorption spectra were measured on a Lambda-9 UV/VIS/NIR spectrophotometer (PerkinElmer). The luminescence spectra of solid samples were recorded on a Fluorolog-3 instrument with a xenon lamp (450 W).

X-ray diffraction analysis of compound **Ia** was carried out on a Bruker Smart Apex II automated diffractometer (MoK_α radiation, graphite monochromator, $\lambda = 0.71073$ Å). The structure was solved by a direct method and refined by least squares in the full-matrix anisotropic approximation using the SHELXS-97 and SHELXL-97 program packages [14]. One of the dibenzoyl methanate ligands includes the disordered phenyl group occupying two equivalent positions with site occupancies of ~0.5, which differ in the turn about the C–C(Ph) bond. The conditions of the X-ray diffraction experiment and crystallographic parameters are given in Table 1. The full set of X-ray structural data for complex **Ia** was deposited with the Cambridge Crystallographic Data Centre (CCDC no. 888518; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

The complexes were synthesized by the reactions of the corresponding lanthanide dibenzoyl methanates dehydrates with triazole H_2L in a molar ratio of 1 : 1. The elemental analysis results for the reaction products show that the reaction is of the same type for all compounds and proceeds through the displacement of one dibenzoyl methanate anion from $Ln(Dbm)_3 \cdot 2H_2O$ and the coordination of the deprotonated bistriazole molecule. According to the TGA data, the ethanol molecule is removed from complex **I** in the temperature range from 80 to 130°C, which is accompanied by an endothermal effect with a minimum in the DTA curve at 120°C. The high desolvation temperature indirectly indicates the inner-sphere localization of the ethanol molecule. The ethanol molecule is removed from complex **III** at lower temperatures (80–100°C). After the removal of the solvate molecules, the region of thermal stability of the complex is observed up to 310–350°C. The further temperature increase results in the thermal destruction of the sample, which passes to the burning out of the organic residue. This process is accompanied by a series of powerful exotherms in a region of 450–650°C.

The IR spectra of complexes **I**–**III** are of the same type. They exhibit distinct intense bands of stretching vibrations of the pyridyl and triazole rings with maxima at 1596 and 1518 cm^{-1}, respectively. The latter undergoes the upfield shift over its position in the spectra of the free ligands (1497 cm^{-1}), which indirectly indicates the coordination of the nitrogen atoms of the triazole cycles by the metal. The bands of stretching vibrations of the carbonyl groups of the dibenzoyl methanate anion are detected at 1550 cm^{-1}, and their position remains unchanged compared to $Ln(Dbm)_3 \cdot 2H_2O$.

For the objective confirmation of the structures of the studied compounds, we carried out an X-ray diffraction analysis of complex **Ia** obtained by the recrystallization of compound **I** from ethanol. During recrystallization, complex $[Nd(Dbm)_2 \cdot HL \cdot EtOH]$ captures an ethanol molecule and gains the composition $[Nd(Dbm)_2 \cdot HL \cdot EtOH] \cdot EtOH$.

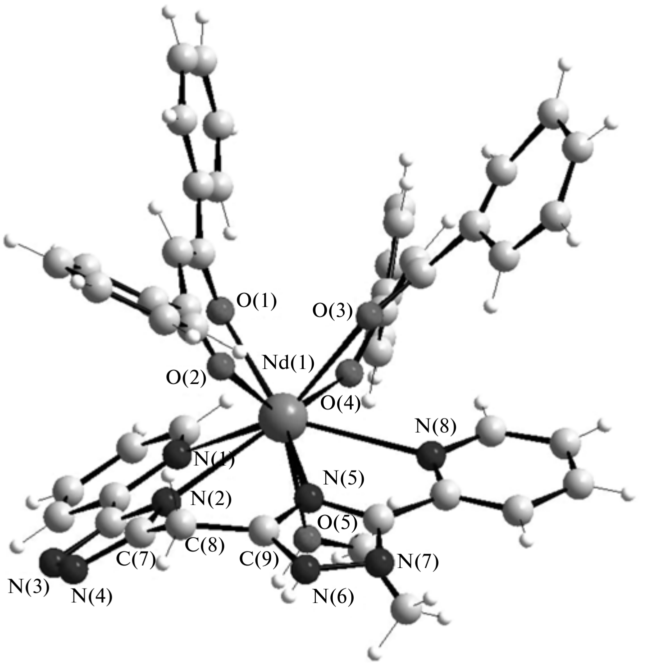


Fig. 1. Molecular structure of complex **Ia**. The most important bond lengths are the following (Å): Nd(1)–O(1) 2.300(3); Nd(1)–O(4) 2.400(3); Nd(1)–O(2) 2.430(3); Nd(1)–O(3) 2.497(3); Nd(1)–O(5) 2.509(3); Nd(1)–N(5) 2.538(4); Nd(1)–N(2) 2.654(4); Nd(1)–N(8) 2.798(4); Nd(1)–N(1) 2.805(4), N(2)–C(7) 1.348(6); N(4)–C(7) 1.381(6); N(3)–N(4) 1.385(6); N(3)–C(6) 1.357(6); N(2)–C(6) 1.390(6); N(5)–C(9) 1.336(6); N(6)–C(9) 1.299(6); N(6)–N(7) 1.380(6); N(7)–C(10) 1.303(6); N(5)–C(10) 1.348(6).

The general view of a complex molecule of **Ia** and the bond lengths within the coordination polyhedron are presented in Fig. 1. The coordination sphere of the neodymium(III) cation is formed by five oxygen atoms (four atoms from the dibenzoyl methanate anions and one atom from the coordinated ethanol molecule) and four nitrogen atoms. The Nd–N bonds are noticeably longer than Nd–O. The coordination polyhedron of the Nd atom can be described by a strongly distorted one-capped (with the N(8) atom in the vertex of the cap) tetragonal antiprism, whose bases are formed by the O(3), O(4), O(5), N(5) and N(1), N(2), O(1), O(2) atoms (the maximum deviation from the best-fit-square plane is 0.064 Å). Two chelate cycles involving 3-(pyridin-2-yl)-1,2,4-triazole are almost planar, and the dihedral angle between their planes is 41.2°. The neodymium ion lies out of the plane of the chelate cycles of the Dbm anions. The dihedral angles between the planes of the O(1), Nd(1), O(2) and O(2), C(24), C(23), C(22), O(1) atoms, as well as of the O(4), C(39), C(38), C(37), O(3) and O(3), Nd(1), O(4) atoms, are 11.93° and 13.53°, respectively. Bistriazole is coordinated in the anionic form due to the deprotonation of one triazole ring. The remained acidic hydrogen atom is localized on the N(6) atom of the second triazole cycle and, as the hydroxyl atoms of the coordinated and solvate ethanol molecules, is involved in intermolecular hydrogen bonds (Table 2). Diverse functions performed by the triazole heterocycles result in a noticeable difference in the nitrogen–carbon bond lengths. The differences in the nitrogen–nitrogen bond lengths range within the determination error for these values (Fig. 1).

An analysis of the diffuse reflectance and excitation spectra of the studied coordination compounds indi-

Table 2. Geometric parameters of the hydrogen bonds with H···A < r(Å) + 2.000 Å and angles DHA > 110°

Contact D–H...A	Distance, Å			Angle D–H···A, deg	Coordinates of atom A
	D–H	H···A	D···A		
O(5)–H(5)···N(3)	0.95(8)	2.17(8)	2.849(7)	128(5)	$-x, y + 1, -z$
N(6)–H(6*A*)···O(1S)	0.88(8)	1.80(8)	2.654(7)	163(5)	$-x, -y, -z$
O(1S)–H(1S)···N(4)	0.73(8)	2.01(8)	2.716(7)	161(5)	x, y, z

Table 3. Spectral luminescence characteristics of complexes **I–III** (the recording conditions are identical)

Complex	Luminescence maximum, nm	$I_{\text{lum}} \times 10^{-3}$, quantum/s	Enhancement of I_{lum} over $\text{Ln(Dbm)}_3 \cdot 2\text{H}_2\text{O}$
I	887	35.17	2.0
	1069	61.70	
II	977	1374.36	9.7
	1032	945.07	
III	1540	35.61	5.0

cates the possibility of luminescence activation due to the absorption of the intense line of mercury (365 nm) with the further energy transfer from the ligand to the Ln(III) ions. The most important characteristics of the luminescence spectra are listed in Table 3. Complexes **I–III** manifest ionic luminescence in the regions characteristic of the corresponding cations. A comparison of the luminescence intensities of the complexes shows that in the compounds with the same ligands the luminescence of the Yb(III) ions is substantially stronger than that of Nd(III) and Er(III), having several sublevels of the ground level on which nonradiative energy losses are possible. The addition of the bistriazole molecule to the Ln(III) cation substantially increases the luminescence intensity over that of $\text{Ln(Dbm)}_3 \cdot 2\text{H}_2\text{O}$, which can be related to both the replacement of water molecules and a decrease in the symmetry of the nearest environment of the central ion. The low symmetry of the coordination polyhedron is also indicated by the Stark splitting of bands in the luminescence spectra of compounds **I** and **II** into several components of the fine structure (Figs. 2 and 3). This is especially pronounced for the Yb(III) complex, whose luminescence spectrum contains two maxima (Fig. 2). Since only one transition $^2F_{5/2} \rightarrow {}^2F_{7/2}$ is possible for the ytterbium complexes, the appearance of several maxima is a result of the low molecular symmetry and the Stark splitting of the term into several sublevels. It should be mentioned that this splitting is poorly characteristic of the Yb(III) complexes [15, 16].

Thus, a new series of the Nd(III), Yb(III), and Er(III) complexes exhibiting the intense luminescence in the near-IR region was synthesized and studied. The use of bis(5-pyridin-2-yl-1,2,4-triazol-3-yl)methane as an additional ligand is shown to be an

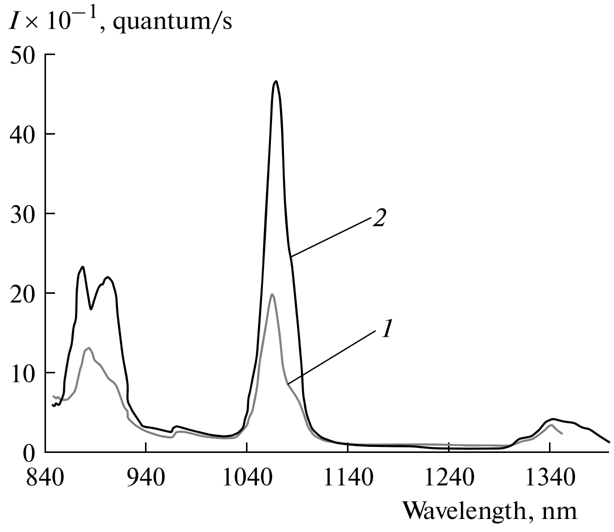


Fig. 2. Luminescence spectra of solid samples of complexes (*1*) $\text{Nd(Dbm)}_3 \cdot 2\text{H}_2\text{O}$ and (*2*) **I** at ambient temperature.

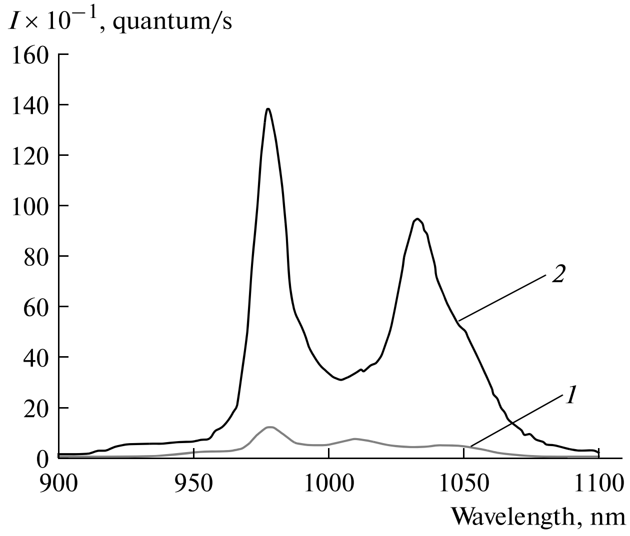


Fig. 3. Luminescence spectra of solid samples of complexes (*1*) $\text{Yb(Dbm)}_3 \cdot 2\text{H}_2\text{O}$ and (*2*) **II** at ambient temperature.

efficient method for increasing the luminescence intensity of Nd(III), Yb(III), and Er(III) dibenzoyl methanates. The efficiency of this ligand is related, most likely, to the displacement of water molecules from the internal coordination sphere and to the decrease in the symmetry of the complexes and, as a consequence, to the elimination of the prohibition of some electron transitions. The data obtained are interesting from the viewpoint of the development of materials for telecommunication devices and luminescent probes.

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