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Synthesis and spectral studies of lanthanides coordination compounds based on N-(diphenylphosphoryl)benzamide. The structure of N-(diphenylphosphoryl)benzamide





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HIGHLIGHTS

- The crystal structure of N-(diphenylphosphoryl)benzamide (HL) was solved.
- The novel highly luminescent lanthanide complexes were synthesized.
- TG analysis and spectral studies were used to characterize synthesized compounds.
- The luminescence properties of Eu(III) and Tb(III) complexes were studied.
- HL efficiency as lanthanide emission sensitizer was evaluated.

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ABSTRACT

N-(diphenylphosphoryl)benzamide (HL), its sodium salt and new lanthanide coordination compounds of general formula LnL₃-*i*-PrOH, LnL₃Dipy LnL₃Phen (Ln = La, Nd, Eu, Gd, Tb; Dipy = α, α' – dipyridyl; Phen = 1,10-phenanthroline) have been synthesized. The crystal structure of HL was solved. The polymeric frame of N-(diphenylphosphoryl)benzamide crystal structure was established. The infinite chains of molecules are formed by the N–H…Ó type hydrogen bonds linking neighboring molecules. The synthesized coordination compounds were studied by means of thermo gravimetric analysis, IR, NMR ¹H, ³¹P, absorption and luminescence spectroscopy at 298 and 77 K. The obtained Eu (III) and Tb (III) complexes luminescence characteristics dependence on triplet states of ligands in complexes is discussed.

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Introduction

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For the last few decades the new luminescent materials for possible application in modern technologies have been actively retrieved. Therein, lanthanides coordination compounds with organic ligands, which can be used in lasers, light emitting diodes and displays devices [1,2], responsive luminescent stains for

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biomedical analysis, medical diagnostics and cell imaging [2–4] are very interesting objects for investigation. Among the most popular and the most intensively investigated lanthanide coordination compounds there are lanthanide β -diketonates and their structural analogs. The explanation is in the variety and relatively easy synthesis of these ligands, and in unique luminescence properties of their complexes [1–5].

It is well known that direct excitation into the 4f excited levels rarely yields highly luminescent materials. Therefore, an alternative path, so called luminescence sensitization or antenna effect, has been worked out. According to the luminescence mechanism, occurred in coordination compounds, which consist of the initial excitation of the chromophore (antenna) and further energy transfer to lanthanide ion, the first and an important step in fluorescent lanthanide complexes creation is the ligand fitting [2]. Effective sensitization of lanthanide luminescence can be expected for complexes with N-(diphenylphosphoryl)benzamide – ligand that contain tree powerful antenna. Besides that it has rather high melting point, which allows us to consider further practical application. The present work is the continuation of systematic investigations of complexes with carbacylamidophosphates (CAPh), compounds of general formula RCONHPOR₂ [6-9] and devoted to new luminescence materials creation. Herein we report the structure of N-(diphenylphosphoryl)benzamide, synthesis and properties of some types of lanthanide coordination compounds based on HL.

Experimental section

Methods

IR measurements were performed on a Perkin–Elmer Spectrum BX spectrometer on samples in form of KBr pellets.

¹H and ³¹P NMR spectra in DMSO-d6 solutions were obtained on a AVANCE 400 Bruker NMR spectrometer at room temperature. Chemical shifts are reported references to SiMe₄ as interior standard for ¹H NMR and H₃PO₄ as exterior standard for ³¹P NMR. Elemental analyses (C, H, N) were performed on an EL III Universal CHNOS Elemental Analyzer.

The diffuse reflection spectra are recorded on UV VIS spectrophotometer Specord M 40 Carl Zeiss.

The thermal stabilities of Eu(III) complexes have been determined between 20 °C and 1000 °C in air with a heating rate of 10 °C min⁻¹ by thermal gravimetric (TG) and differential thermal analyses (DTA).

Emission and excitation spectra of the complexes were measured on «Fluorolog FL 3-22» spectrofluorimeter at 298 and 77 K. The energies of triplet states of ligands in complexes were determined on the base of the phosphorescence spectra registered for La(III) and Gd(III) complexes at 77 K. The f–f-luminescence lifetime measurements at room temperature were obtained using the FL-1040 "Horiba Jobin Yvon" phosphorimeter accessory with the Fluorolog 3-22 instrument (pulsed Xe–Hg arc lamp, 3 µs bandwidth).

Synthesis

N-(diphenylphosphoryl)benzamide – HL – was synthesized according to procedure described previously [10]. Monocrystals suitable for X-ray investigations were obtained by recrystallization from mixture of methanol and isopropanol in ratio 1:1.

NaL was obtained from methanol solution by exchange reaction between NaOMe and HL. NaL: M. p. 255 °C. – UV/Vis (CH₃CN): λ_{max} (lg ε_{max}) = 230 nm (4.37). – IR (KBr): v_{max} = 1590, 1518 (C=O), 1436, 1382, 1175, 1142 (P=O), 1122, 1100, 902, 834, 722, 698, 550, 531 cm⁻¹. – ¹H NMR (DMSO-d6): δ = 7.30 (m, 9H, Ph, Ph2), 7.93 (m, 4H, Ph2), 8.24 (d, 2H, Ph). – ³¹P NMR (DMSO-d6): δ = 17.2 (s). – C₁₉H₁₅NNaO₂P (343.3): calcd. C 66.48, H 4.40, N 4.08; found C 66.54, H 4.32, N 4.01.

Coordination compounds of general compositions LnL₃·*i*-PrOH and LnL₃Q were synthesized according to the following schemes:

 $\begin{array}{l} \text{Ln}(\text{NO}_3)_3 \cdot \text{nH}_2\text{O} + 3\text{NaL} + i - \text{PrOH} \rightarrow \text{LnL}_3 \cdot i - \text{PrOH} \\ + 3\text{NaNO}_3 \downarrow + \text{nH}_2\text{O} \end{array}$

 $\begin{array}{l} Ln(NO_3)_3 \cdot nH_2O + 3NaL + Q \rightarrow LnL_3Q + 3NaNO_3 \downarrow \\ + nH_2O(Q = Dipy \ or \ Phen, Ln = La, Nd, Eu, Gd, Tb) \end{array}$

Preparation of LnL_3 ·i-PrOH (Ln = La, Nd, Eu, Gd, Tb)

Hydrated Ln(III) nitrate (1 mmol) was dissolved in isopropanol (15 ml) and added to the solution of NaL (3 mmol) in 15 ml of acetone and heated to the boiling point. After cooling during ~ 15 min the precipitated NaNO₃ was filtered off. The resulting clear solution was left at ambient temperature in desiccator over anhydrous CaCl₂. In a day the coordination compounds precipitated as powders were filtered, washed with suction by cold *i*-PrOH and finally dried on air (Yield \sim 80%). Anal. Calc. for C60H53N3O6P3La (Mr = 1143,22): C, 63.04; H, 4.67; N, 3.66%. Found: C, 63.09; H, 4.54; N, 3.61%. .M. p. 125 °C. – IR (KBr): v_{max} = 1590, 1509 (C=O), 1438, 1385, 1178, 1128 (P=O), 1066, 910, 726, 694, 549 cm⁻¹. - ¹H NMR (DMSO-d6): $\delta \sim 7.26-7.48$ (m, 27H, Ph, Ph2), 7.88 (m, 12H, Ph2), 8.22 (d, 6H, Ph), 1.06 (d, 6H, CH₃), 3.79 (h, 1H, CH), 4.09 (d. 1H. OH). Anal. Calc. for C60H53N3O6P3Nd (Mr = 1146.22): C, 62.87; H, 4.66; N, 3.67%. Found: C, 62.90; H, 4.60; N, 3.63%. .M. p. 130 °C. – IR (KBr): v_{max} = 1590, 1507 (C=O), 1437, 1383, 1178, 1128 (P=O), 1066, 910, 726, 693, 549 cm⁻¹. Anal. Calc. for C60H53N3O6P3Eu (Mr = 1157.24): C, 62.27; H, 4.62; N, 3.63%. Found: C, 62.34; H, 4.61; N, 3.60%. .M. p. 135 °C. -IR (KBr): v_{max} = 1590, 1508 (C=O), 1438, 1384, 1179, 1128 (P=O), 1066, 909, 727, 693, 549 cm⁻¹. Anal. Calc. for C60H53N3O6P3Gd (Mr = 1157.24): C, 62.01; H, 4.60; N, 3.62%. Found: C, 62.14; H, 4.56; N, 3.59%. .M. p. 135 °C. – IR (KBr): v_{max} = 1591, 1509 (C=O), 1438, 1385, 1179, 1128 (P=O), 1067, 911, 727, 694, 549 cm⁻¹. Anal. Calc. for C60H53N3O6P3Tb (Mr = 1163.24): C, 61.95; H, 4.60; N, 3.61%. Found: C, 62.01; H, 4.57; N, 3.58%. .M. p. 130 °C. -IR (KBr): v_{max} = 1591, 1509 (C=O), 1438, 1385, 1179, 1128 (P=O), 1067, 911, 727, 694, 549 cm⁻¹.

Preparation of LnL_3 ·Dipy (Ln = La, Nd, Eu, Gd, Tb)

Hydrated Ln(III) nitrate (1 mmol) was dissolved in isopropanol (15 ml) and added to the solution of NaL (3 mmol) in 15 ml of acetone. Then 1 mmol of solid Dipy was added. The resulted mixture was boiled for some minutes and then cooled to the room temperature. After 15 min the precipitated NaNO₃ was filtered off. The resulting clear solution was left at ambient temperature in desiccator over anhydrous CaCl₂. In a day the coordination compounds precipitated as powders were filtered, washed with suction by cold i-PrOH and finally dried on air (Yield \sim 90%). Anal. Calc. for C67H53N5O6P3La (Mr = 1255.23): C, 64.11; H, 4.26; N, 5.58%. Found: C, 64.14; H, 4.22; N, 5.55%. .M. p. 130 °C. - IR (KBr): v_{max} = 1590, 1507 (C=O), 1437, 1384, 1178, 1130 (P=O), 1085, 1066, 908, 726, 694, 548 cm $^{-1}$. – 1H NMR (DMSO-d6): $\delta \sim$ 7.27 – 7.49 (m, 29H, Ph, Ph2, Dipy), 7.88 (m, 14H, Ph2, Dipy), 8.21 (d, 6H, Ph), 8.41 (d, 2H, Dipy), 8.64 (d, 2H, Dipy). Anal. Calc. for C67H53N5O6P3Nd (Mr = 1258.23): C, 63.96; H, 4.25; N, 5.57%. Found: C, 63.90; H, 4.26; N, 5.53%. .M. p. 140 °C. - IR (KBr): v_{max} = 1591, 1508 (C=O), 1438, 1384, 1178, 1131 (P=O), 1086, 1066, 909, 726, 695, 548 cm⁻¹. Anal. Calc. for C67H53N5O6P3Eu (Mr = 1269.24): C, 63.40; H, 4.21; N, 5.52%. Found: C, 63.44; H, 4.12; N, 5.50%. .M. p. 130 °C. – IR (KBr): v_{max} = 1591, 1509 (C=O), 1437, 1384, 1178, 1133 (P=O), 1088, 1066, 909, 726, 694, 548 cm⁻¹. Anal. Calc. for C67H53N5O6P3Gd (Mr = 1174.34): C,

63.15; H, 4.19; N, 5.50%. Found: C, 63.12; H, 4.14; N, 5.47%. .M. p. 130 °C. – IR (KBr): $v_{max} = 1592$, 1511 (C=O), 1437, 1385, 1178, 1130 (P=O), 1088, 1067, 910, 724, 696, 546 cm⁻¹. Anal. Calc. for C60H53N3O6P3Tb (Mr = 1175.25): C, 63.10; H, 4.19; N, 5.49%. Found: C, 63.14; H, 4.22; N, 5.44%. .M. p. 135 °C. – IR (KBr): $v_{max} = 1591$, 1511 (C=O), 1438, 1384, 1179, 1132 (P=O), 1089, 1066, 911, 726, 695, 548 cm⁻¹.

Preparation of LnL_3 ·Phen (Ln = La, Nd, Eu, Gd, Tb)

Complexes were obtained in a similar manner to foregoing ones except for the use of 1,10-phenanthroline (1 mmol) instead of 1,2dipyridyl. (Yield ~90%). Anal. Calc. for C69H53N5O6P3La (Mr = 1280.02): C, 64.74; H, 4.17; N, 5.47%. Found: C, 64.81; H, 4.15; N, 5.43%. M.p. 140 °C. – IR (KBr): v_{max} = 1590, 1506 (C=O), 1438, 1384, 1178, 1130 (P=O), 1085, 1066, 908, 725, 695, 548 cm⁻¹. – ¹H NMR (DMSO-d6): $\delta \sim 7.25-7.38$ (m, 27H, Ph, Ph2), 7.69 (m, 2H, Phen), 7.88 (m, 14H, Ph2, Phen), 8.20 (d, 6H, Ph), 8.40 (d, 2H, Phen), 9.12 (d, 2H, Phen). Anal. Calc. for C69H53N5O6P3Nd (Mr = 1285.35): C, 64.47; H, 4.16; N, 5.45%. Found: C. 63.52; H. 4.18; N. 5.43%. M.p. 150 °C. - IR (KBr); v_{max} = 1590, 1508 (C=O), 1438, 1384, 1178, 1130 (P=O), 1085, 1066, 909, 725, 694, 548 cm⁻¹. Anal. Calc. for C69H53N5O6P3Eu (Mr = 1293.07): C, 63.09; H, 4.13; N, 5.42%. Found: C, 64.12; H, 4.12; N, 5.39%. M.p. 190 °C. – IR (KBr): v_{max} = 1590, 1511 (C=O), 1437, 1384, 1179, 1133 (P=O), 1088, 1066, 909, 726, 695, 547 cm^{-1} . Anal. Calc. for C69H53N5O6P3Gd (Mr = 1298.36): C, 63.83; H, 4.11; N, 5.39%. Found: C, 63.84; H, 4.10; N, 5.34%. M. p. 195 °C. – IR (KBr): v_{max} = 1591, 1511 (C=O), 1438, 1384, 1179, 1133 (P=O), 1088, 1066, 910, 726, 694, 547 cm⁻¹. Anal. Calc. for C69H53N3O6P3Tb (Mr = 1300.24): C, 63.75; H, 4.11; N, 5.39%. Found: C, 63.74; H, 4.12; N, 5.36%. .M. p. 200 °C. - IR (KBr): v_{max} = 1590, 1512 (C=O), 1438, 1384, 1179, 1134 (P=O), 1088, 1067, 911, 726, 695, 548 cm⁻¹.

All obtained compounds are stable on air, slightly colored respective to of Ln(III) aqua ion colors. They are soluble in nonpolar aromatic solvents, acetone, chloroform, DMFA, DMSO, soluble poorly in isopropanol and water.

X-ray crystallography

X-ray diffraction data were collected on an XCalibur 3 diffractometer equipped with graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). The structure was solved by direct method and refined against F^2 by full-matrix least-squares method using the SHELXTL package [11]. All non-hydrogen atoms were refined within anisotropic approximation. The H atoms were located from the difference map of electron density and refined by "riding" model with $U_{\rm iso} = 1.2U_{\rm eq}$ of carrier non-hydrogen atom.

Crystals of $C_{19}H_{16}NO_2P$ (Mr = 321.30) at 294(2) K are monoclinic, space group P2₁/c, *a* = 9.464(2), *b* = 16.999(3), *c* = 21.910(3) Å, α = 90.00, β = 91.064(18), γ = 90.0°, *V* = 3524.2 (11) Å³, *Z* = 8, μ (Mo K α) = 0.164 mm⁻¹, *d*_{cal} = 1.211 g/cm³, *F*(000) = 1344, 29,957 reflections measured (Θ_{max} = 55.00°), 8034 unique (R_{int} = 0.0838) and of these 3902 had *F* > 4 σ (*F*) and were considered to be observed. The final R_1 , *w* R_2 values were 0.0729 and 0.1594 respectively, for 415 parameters.

Results and discussion

Description of crystal structure

According to X-ray diffraction data two HL molecules (A and B) with slightly different geometrical parameters are located in asymmetric part of the crystal unit cell (Fig. 1). The carbonyl and the P=O bond have synclinal orientation (the O(2)–P(1)···C(1)–O(1)

pseudo-torsion angle is $-57.8(3)^{\circ}$ and $56.5(3)^{\circ}$ for molecules A and B, respectively). Thus, conformation of ligand is pre-organized for bidentate chelate type of coordination to metal ions.

The amide group is slightly non-planar. The O(1)-C(1)-N(1)-P(1) torsion angle is $-11.3(4)^{\circ}$ in molecule A and $6.3(4)^{\circ}$ in B. The carbonyl bond is not co-planar to phenyl ring (the O(1)-C(1)-C(2)-C(3) torsion angle is $-10.8(5)^{\circ}$ in A and $16.4(5)^{\circ}$ in B).

The geometry around the phosphorus atoms in both molecules can be described as slightly distorted tetrahedron. The P–O and P–N bond lengths have values (Table 1) typical for such the type compounds [12,13]. The phenyl rings at the phosphorous atom have different orientations relatively to the P=O bond. The C(8)--C(13) ring has synperiplanar orientation (the C(9)--C(8)--P(1)--O(2) torsion angle is $-68.4(3)^{\circ}$ and $46.1(3)^{\circ}$ for A and B respectively) while the C(14)--C(19) ring is almost co-planar to the P=O bond (the C(15)--C(14)--P(1)--O(2) torsion angle is $-6.0(3)^{\circ}$ for A and 17.8(3)° for B).

In the crystal phase molecules A and B are bonded by the N—H…O and C—H… π hydrogen bonds (Table 1). This leads to the formation of hydrogen bonded chains along [100] crystallographic direction (Fig. 1b). Neighboring chains are bonded by the C(5A)—H(5A)…C(11B)' (*x*, 0.5–*y*, 0.5 + *z*) hydrogen bonds (H…C 2.75 Å, C—H…C 159°).

IR and electronic spectroscopy

IR investigations of carbasylamidophosphates and their complexes are suitable for a preliminary analysis of coordinating mode



Fig. 1. Structural representation of HL: (a) – atom numbering scheme of molecule A; and (b) – fragment of the crystal packing along [100] axis. (hydrogen atoms are omitted for clarity).

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Selected bond lengths (Å) in the HL structure.

e . ,			
P(1A)-O(2A)	1.475(2)	P(1B)—O(2B)	1.480(2)
P(1A)—N(1A)	1.689(3)	P(1B)—N(1B)	1.682(3)
C(1A)—O(1A)	1.232(4)	C(1B)—O(1B)	1.220(4)
C(1A)-C(2A)	1.486(5)	C(1B)-C(2B)	1.498(4)
N(1A)-C(1A)	1.365(4)	N(1B)-C(1B)	1.376(4)
N(1A)…H(1A)	2.02	H(15A)…C(10B)	2.83
N(1A)-H(1A)O(2B)	168°	C(15A)—H(15A)…C(10B)	158°
N(1B)…H(1B)	1.99	H(19A)…C(9B)	2.84
N(1B)-H(1B)O(2A)	165°	C(19A)—H(19A)…C(9B)	156°
		H(15B)…C(10A)	2.77
		C(15B)-H(15B)C(10A)	158°

Table 2

Averaged values of main vibrational frequencies in the IR spectra^a of synthesized compounds (Ln = La, Nd, Eu, Gd, Tb) and their assignments, cm⁻¹.

HL	NaL	LnL₃iPrOH	LnL₃Phen	LnL ₃ Dipy	Assignment
3064	-	-	-	-	ν(NH)
1670	1518	1508	1508	1510	v(CO)
1199	1143	1128	1130	1131	v(PO)
1456	1382	1384	1384	1384	Amide II
875	902	911	909	909	$\nu(PN)$

^a Positions of the strongest absorption bands are given in section 'Synthesis'.

of the ligands [14]. It was demonstrated that in the neutral form, the CAPh ligands coordinate to the metal ions mostly in a monodentate manner via the oxygen atom of P=O group, whereas in the deprotonated form they coordinate in a bidentate maner via the oxygen atoms of the phosphoryl and carbonyl groups, with the formation of six-membered chelate cycles, which can be inferred from the values of the valence vibrations v(P=O) and v(C=O).

Table 2 lists the averaged values of positions of main absorption bands in IR spectra of synthesized compounds. For all complexes low-frequency shift of v(PO) and v(CO) with respect to spectrum of NaL is observed: $\Delta v(PO) = 12-15 \text{ cm}^{-1}$, $\Delta v(CO) = 8-10 \text{ cm}^{-1}$. That is because of PO and CO bond multiplicity reduction conditioned by chelate cycle formation due to the ligand bidentate coordination. The absence of valence vibrations v(N–H) in region 3064 cm⁻¹ confirms ligand deprotonated form in the complexes.

For neodymium complexes the diffuse reflection spectra (DFS) in the regions of hypersensitive transitions ${}^{4}I_{9/2} - {}^{4}G_{5/2}$, ${}^{2}G_{7/2}$ (**a**) and in the region of ${}^{4}I_{9/2} - {}^{2}P_{1/2}$ (**b**) were studied (see Fig. 2).

Analysis of the form of hypersensitive transitions and the intensity ratios of the bands in DFS allow to conclude about analogous geometry and coordination number eight for neodymium ions in NdL₃Dipy and NdL₃Phen, and coordination number seven in case of NdL₃·*i*-PrOH [15,16]. These conclusions are in agree with ¹H NMR spectroscopy data, obtained for La(III) complexes. The positions of the bands in absorption spectra (in toluene and acetonitrile solutions) and in diffuse reflection for all complexes are very similar, so analogous geometries of the nearest Nd³⁺ environment in solutions and in solid state were suggested.

In the ${}^{4}I_{9/2}-{}^{2}P_{1/2}$ transition region (425–435 nm) for all complexes single bands are observed with the maxima at 430.3 nm for NdL₃Dipy, NdL₃Phen and and at 430.8 nm for NdL₃·*i*-PrOH. This suggests in average more covalent character of the metal–ligand bonds for last complex in comparison to the previous two complexes [17].

Thermal gravimetric analyses

Considering complexes' possible applications, thermal stability of luminescent complexes was examined. TG analysis was performed for europium and terbium complexes LnL₃·i-PrOH, LnL_3Dipy and LnL_3Phen (where Ln = Eu, Tb). The first weight loss 5.3% and 5.1% for EuL₃·*i*-PrOH and TbL₃·*i*-PrOH respectively is observed at 100 °C and is attributed to 2-propanol molecule removal. Increasing of this value in respect to boiling point of *i*-PrOH confirms the solvent coordination to europium ion. Further decomposition of these complexes starts at 290 °C for europium and at 230 °C for terbium complex and occurs in two stages. For europium complex the first stage lays in temperature range 280–360 °C, the second one is in 530–600 °C temperature range. For terbium complex the first stage lays in temperature range 230-350 °C, the second one is in 520-600 °C temperature range. For both europium and terbium complexes the first stage is accompanied with weight loss 28% and the second one - with weight loss 36%.

In case of LnL₃Dipy (Ln = Eu, Tb) complexes, there are no effects on TG curve till 280 and 260 °C respectively. The temperature regions and weight loss percentages on the first stages of decomposition (with indication of corresponding weight loss in brackets) are equal to 280–360 °C (34%) for EuL₃Dipy and 260–320 °C (30%) for TbL₃Dipy respectively, and on the second stages – 550–630 °C (31%) and 490–690 °C (33%) respectively.

Decomposition of LnL₃Phen (Ln = Eu, Tb) complexes occurs in a similar manner to foregoing ones. There are no effects on TG curve till 260 and 250 °C for EuL₃Phen and TbL₃Phen respectively. The temperature regions and weight loss percentages on the first stages of decomposition (with indication of corresponding weight loss in brackets) are equal to 260-310 °C (25%) for EuL₃Phen and 250–400 °C (34%) for TbL₃Phen respectively, and on the second stages – 530-610 °C (43%) and 450-670 °C (33%) respectively.



Fig. 2. Diffuse reflection spectra of synthesized neodymium coordination compounds: 1 - NdL₃·i-PrOH, 2 - NdL₃Dipy, 3 - NdL₃Phen.



Fig. 3. Normalized luminescence spectra of synthesized europium complexes: $EuL_3 \cdot iPrOH(1)$, $EuL_3Dipy(2)$, $EuL_3Phen(3)$. (a) The 5D_1 emission spectra at 77 K; and (b) the 5D_0 emission spectra at 77 K.



Fig. 4. Normalized luminescence spectra of synthesized terbium complexes at 298 K.

The IR spectra of thermal decomposition products are similar to the lanthanide polyphosphate spectra.

Photoluminescence studies

Fig. 3 presents europium complexes' luminescence spectra recorded upon ligand excitation at maxima of luminescence excita-

Table 3

The spectroscopic characteristic of synthesized lanthanide complexes.

Compound	τ, ms	$\frac{\Delta E(E_{\rm T} \rightarrow {}^5{\rm D}_0)}{{\rm cm}^{-1}},$	Compound	τ, ms	$\begin{array}{l} \Delta E(E_{\rm T} \rightarrow {}^{5}{\rm D}_{4}),\\ {\rm cm}^{-1} \end{array}$
EuL₃· <i>i</i> PrOH	0.86	8810	TbL₃·iPrOH	1.11	5610
EuL₃Dipy	1.24	5583	TbL₃Dipy	1.44	2383
EuL₃Phen	1.55	4252	TbL₃Phen	1.37	1052

tion spectra: $\lambda_{exc} = 275 \text{ nm}$ for EuL₃·iPrOH, $\lambda_{exc} = 320 \text{ nm}$ for EuL₃Dipy and $\lambda_{exc} = 345 \text{ nm}$ for EuL₃Phen. An intensive emission of these compounds points to an effective energy transfer from the ligands to the emitting lanthanide levels. The ${}^{5}D_{0}$ emission spectra of europium complexes consist of five ${}^{5}D_{0} \rightarrow {}^{7}F_{j}$ transitions (j = 0-4). Also two transitions from ${}^{5}D_{1}$ level are registered.

The high intensity of ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transitions compared to the allowed magnetic ${}^{5}D_{0}-{}^{7}F_{1}$ transition suggests relatively low symmetry of Eu(III) surroundings in complexes.

The singlet in the region of ${}^{5}D_{0}-{}^{7}F_{0}$ transition (Fig. 3a) testifies the presence of one luminescent center in each of the complexes under study.

The terbium complexes emission spectra ($\lambda_{exc} = 276$ nm for TbL₃·*i*PrOH, $\lambda_{exc} = 320$ nm for TbL₃Dipy and $\lambda_{exc} = 330$ nm for TbL₃Phen) are presented on Fig. 4. All complexes show strong green emission. In the luminescence spectra recorded at 298 K only four f–f transitions (${}^{5}D_{4}-{}^{7}F_{j}$, *j* = 6–3) from seven possible are clearly observed.

The lowest ligand triplet states for the complexes GdL₃·*i*-PrOH, LaL₃Dipy and LaL₃Phen ($E_{\rm T} \approx 26,110 \mbox{ cm}^{-1}$, 22,883 cm⁻¹ and 21,552 cm⁻¹ respectively) were localized based on the phosphorescence spectra at 77 K.

Table 3 lists luminescence lifetimes, energy gaps between ligand triplet states and lanthanide emissive levels (ΔE) for europium and terbium complexes under study.

Comparing the energies of the lowest ligand triplet state for the complexes with lanthanide emissive levels one can evaluate the possibility of back (from lanthanide ion to ligand) energy transfer. As the named energy gaps values in all studied europium complexes and in two terbium complexes exceed the limit level 1850 cm⁻¹ established by M. Latva and coworkers [18] we can exclude any back energy transfer from lanthanide to ligands in these complexes and expect effective energy transfer for them. For TbL₃Phen the ΔE value is under limit level that presages ⁵D₄ $\rightarrow E_T$ energy transfer as possible process and, as a result, low quantum yield is expected.

Conclusions

X-ray diffraction investigation of the HL compound have shown that N-(diphenylphosphoryl)benzamide molecules in the crystal state are linked by the N—H…Ó and C—H… π hydrogen bonds forming infinite chains along [100] crystallographic axis. Neighboring chains are connected by C—H… π interactions.

The coordination compounds of general formula LnL_3 ·*i*PrOH, LnL_3 Dipy, LnL_3 Phen (Ln = La, Nd, Eu, Gd, Tb, Dipy = 2,2' – dipyridyl, Phen = 1,10-phenanthroline) have been synthesized and studied by TG analysis, IR, NMR ¹H, UV–Vis absorption and luminescence spectroscopy.

High intensity f–f-luminescence at 298 K and 77 K was found for europium and terbium complexes. The luminescence decay curves obtained at 298 K are monoexponential and show rather high luminescence decay time values of studied complexes (0.86–1.55 ms for europium complexes and 1.11–1.44 ms for terbium ones).

The highest luminescence decay times values were registered for EuL₃Phen and TbL₃Dipy complexes with the smallest 'ligand triplet level – lanthanide emissive level' energy gaps thus exceeding 1850 cm⁻¹.

Supplementary material

CCDC 964373 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http:// www.ccdc.cam.ac.uk/data_request/cif or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

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