

Trinitrato-tris-N-(diphenylphosphoryl)-2-methoxybenzamido lanthanides (III); Synthesis and Spectral Studies

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Received March 30, 2024

N-(diphenylphosphoryl)-2-methoxybenzamide (HL) was approbated as a ligand towards lanthanides and new complexes $\text{Ln}(\text{HL})_3(\text{NO}_3)_3$ (Ln= La, Nd, Eu, Gd, Tb, Lu) were obtained and characterized. It was shown that the intramolecular hydrogen bond N-H \cdots O in the N-(diphenylphosphoryl)-2-methoxybenzamide molecule prevents its deprotonation and leads to monodentate coordination towards lanthanide via a phosphoryl group oxygen atom, while the nitrate anions are coordinated in a bidentate manner. The influence of the methoxy group of the aromatic substituent of the ligand on the spectral properties of the obtained compounds is discussed. The complexes $\text{Nd}(\text{HL})_3(\text{NO}_3)_3$, $\text{Eu}(\text{HL})_3(\text{NO}_3)_3$ and $\text{Tb}(\text{HL})_3(\text{NO}_3)_3$ exhibit intense f-f emission, sensitized by N-(diphenylphosphoryl)-2-methoxybenzamide with an emission lifetime for Eu^{III} and Tb^{III} of about 1.3 ms and an intrinsic quantum yield for Eu^{III} of 62 %.

Keywords: lanthanide, luminescence, coordination compounds, carbacylamidophosphates

Тринітрато-трис-N-(дифенілфосфорил)-2-метоксибензамідо лантаноїди (III). Синтез і спектральні властивості. *Н.С. Каряка, В.О. Труш, С.С. Смола, Н.В. Русакова, Т.Ю. Слива, В.М. Амірханов*

N-(дифенілфосфорил)-2-метоксибензамід (HL) був апробований як ліганд по відношенню до іонів лантаноїдів. В результаті одержані та охарактеризовані нові комплекси складу $\text{Ln}(\text{HL})_3(\text{NO}_3)_3$ (Ln= La, Nd, Eu, Gd, Tb, Lu). Показано, що внутрішньомолекулярний водневий зв'язок N-H \cdots O в N-(дифенілфосфорил)-2-метоксибензаміді ускладнює депротонування молекули і призводить до монодентатної координації ліганду до лантаноїдів через атом оксигену фосфорильної групи, тоді як нітрат-аніони координуються бідентатно. Обговорюється вплив метокси-групи ароматичного замісника ліганду на спектральні властивості одержаних сполук. Комплекси $\text{Nd}(\text{HL})_3(\text{NO}_3)_3$, $\text{Eu}(\text{HL})_3(\text{NO}_3)_3$ і $\text{Tb}(\text{HL})_3(\text{NO}_3)_3$ демонструють інтенсивну f-f люмінесценцію, сенсбілізовану N-(дифенілфосфорил)-2-метоксибензамідом, яка характеризується часом життя 1.3 мс (Eu^{III} and Tb^{III}) та внутрішнім квантовим виходом європію 62 %.

1. Introduction

Extensive use of luminescent lanthanide compounds in lighting, OLED devices, telecommunications, solar cells, biology, and medicine as luminescence labels and probes, security

inks, pressure sensors, etc. [1, 2] provokes research on new lanthanide compounds. The basic approach in designing highly luminescent lanthanide coordination compounds is the use of effectively absorbing organic ligands with an

optimal triplet state level for efficient energy transfer to the lanthanide ion. Another important point is the minimization of nonradiative deactivation of the excited state of Ln^{III} [3]. Among the ligands satisfying these criteria, there are phenyl-containing carbacylamidophosphates – organic ligands with a functional fragment -C(O)N(H)P(O)= (CAPH) [4, 5]. The bulky highly absorbing phenyl groups provide shielding of the lanthanide ion from solvent molecules as well as accumulating UV light for further sensitization of lanthanide emission. The phosphoryl group present in CAPH ligands has a high affinity to lanthanides. Changing the substituents near the chelating fragment in CAPHs allows changing the properties of lanthanide complexes, including luminescence properties, thermal stability and stability upon storage, solubility, etc., which determines the prospects for the practical use of the compounds. That is why, the synthesis of new compounds and study of their properties is an important step in the search for compounds valuable for practical use.

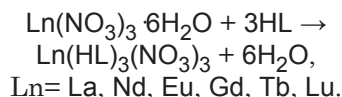
Herein we have used CAPH N-(diphenylphosphoryl)-2-methoxybenzamide (HL, Figure 1) [6] as a ligand towards lanthanide ions for the first time to obtain complexes of general formula Ln(HL)₃(NO₃)₃. The complexes have been studied by IR, NMR, absorption, and luminescence spectroscopy.

2. Experimental

2.1. Synthesis

N-(diphenylphosphoryl)-2-methoxybenzamide (HL) was obtained and identified according to the previously described method [6].

The attempts to synthesize coordination compounds of lanthanides with a deprotonated form of the ligand [L]⁻ have been unsuccessful. The coordination compounds of lanthanides with the neutral ligand (molecular form of ligand) have been obtained according to the following scheme:



Hydrated Ln^{III} nitrate (1 mmol) was dissolved in isopropanol (15 ml) and added to the solution of HL (3 mmol) in 15 ml of acetone and heated to the boiling point. After cooling for ~10 minutes, the precipitate of the target complexes appeared. The precipitate was filtered off,

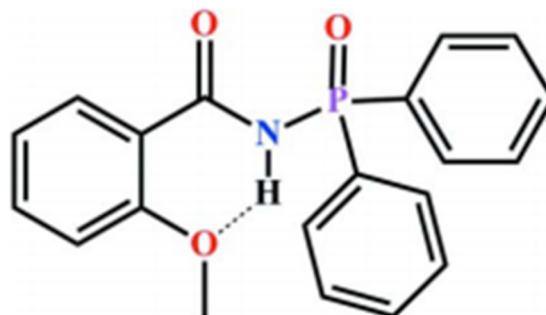


Fig. 1. Structural formula of HL

washed with hexane, and dried in a desiccator over anhydrous CaCl₂. Yields equal 70-75%. The obtained compounds are soluble in acetone, acetonitrile, dichloromethane, and methanol, poorly soluble in isopropanol and toluene, and insoluble in hexane and water. The compounds are stable in air for about a year, after which the complexes slowly degrade, which can be seen in the IR spectra. The melting points of the complexes are in the range 120-135 °C. The content of lanthanides in the complexes found by titrimetric method is consistent with the calculated values. ¹H NMR (DMSO-d₆) for La(HL)₃(NO₃)₃: C—H 3.98 (s, 9H), 7.04 (t, 3H), 7.17 (d, 3H), 7.51 (m, 21H), 7.78 (d, 3H), 7.85 (m, 12H), N—H 9.56 (d, 3H) ppm; for Lu(HL)₃(NO₃)₃: C—H 3.98 (s, 9H), 7.04 (t, 3H), 7.17 (d, 3H), 7.51 (m, 21H), 7.78 (d, 3H), 7.85 (m, 12H), N—H 9.56 (d, 3H) ppm.

2.2 Methods

IR measurements were performed on a Perkin–Elmer Spectrum BX spectrometer on samples in the form of KBr pellets. ¹H NMR spectra in DMSO-d₆ solutions were obtained on an AVANCE 400 Bruker NMR spectrometer at room temperature. The diffuse reflection spectra are recorded on a UV VIS spectrophotometer Specord M 40 Carl Zeiss for the pressed powdered samples at room temperature. Emission and excitation spectra of the solid complexes were measured on an «Fluorolog FL 3-22» spectrofluorimeter at 298 and 77 K. The energy of the lowest triplet state of ligands in the complexes was determined on the base of the phosphorescence spectrum registered for a solid Gd(III) complex at 77 K. The f-f-luminescence lifetime was measured using a FL-1040 “Horiba Jobin Yvon” phosphorimeter attachment with a Fluorolog 3-22 instrument (pulsed Xe–Hg arc lamp, 3 μs bandwidth). The decay time values were estimated with an error of 10 %.

3. Results and discussion

Infrared spectroscopy

The IR spectra of the obtained Ln^{III} complexes are almost identical. The selected band positions for HL and the complexes are given in Table 1. It should be noted that the $\nu(\text{NH})$ band for HL is located at relatively high wavenumbers. This is due to the intramolecular hydrogen bond $\text{N-H}\cdots\text{O}$ (Figure 1). During complexation, the position of this band does not change significantly, which indicates the preservation of hydrogen bonds in the complexes. In our previous work, we have shown that the intramolecular hydrogen bond $\text{N-H}\cdots\text{O}$ in the CAPH molecule prevents its deprotonation and leads to the monodentate coordination towards lanthanide via phosphoryl group oxygen [7]. The position of the $\nu(\text{CO})$ band in the IR spectra of the obtained complexes remains virtually unchanged compared to the IR spectrum of HL. Thus, the carbonyl group does not participate in coordination with the metal ion. In turn, the $\nu(\text{PO})$ band in the IR spectra of the complexes is shifted to lower wavenumbers by approximately 60 cm^{-1} . This shift of the $\nu(\text{PO})$ band is due to the coordination of HL with the lanthanide ion via the oxygen atom of the phosphoryl group. The positions of bands associated with nitrate anion vibrations are characteristic of the bidentate type of coordination [8, 9].

Absorption and luminescence spectroscopy

To understand the absorption region of the ligands, the diffuse reflectance spectrum of the neodymium complex was measured in the UV and visible regions (Figure 2). It is known, that the neodymium absorption in the visible region is also of interest in studying the interactions of lanthanides and ligands [10-13]. The broad band in the UV region of the diffuse reflectance spectrum of $\text{Nd}(\text{HL})_3(\text{NO}_3)_3$ is due to absorption in the ligands. The assignment of narrow bands of the $f-f$ transitions of Nd^{III} ion was made on the basis of Carnall's publication [14]. The bands belonging to the hypersensitive transitions $^4\text{I}_{9/2} \rightarrow ^4\text{G}_{5/2}$, $^2\text{G}_{7/2}$ are broadened, which

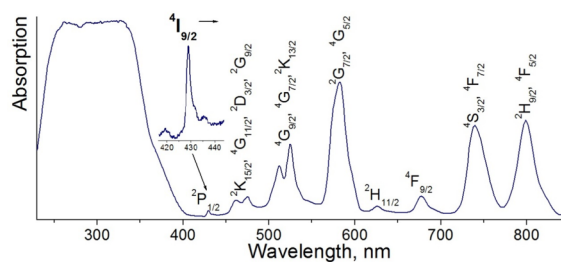


Fig. 2. Diffuse reflectance spectrum of $\text{Nd}(\text{HL})_3(\text{NO}_3)_3$ in the UV-Vis region at 298 K

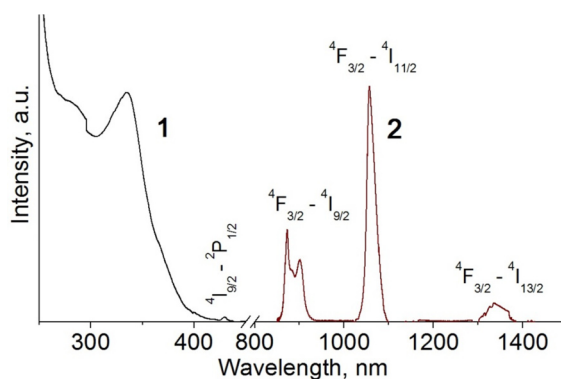


Fig. 3. Excitation (1) and emission (2) spectra of $\text{Nd}(\text{HL})_3(\text{NO}_3)_3$

does not allow analyzing the number of electron components. For the transition $^4\text{I}_{9/2} \rightarrow ^2\text{P}_{1/2}$, the narrow single band is observed at 429 nm, which implies the presence of a single optical center in the complex. The shift of the bands to the red region of the spectrum of $\text{Nd}(\text{HL})_3(\text{NO}_3)_3$ compared with neodymium aqua ion [14] can be considered as evidence of a higher degree of covalence in the complex than that existing in aqua compounds [10], but it is not significant. This indicates a small covalent contribution to the Nd-O bonds and is consistent with literature data for similar Nd^{III} CAPH-based complexes $\text{Nd}(\text{CAPH})_3(\text{NO}_3)_3$ [15].

The ligand absorption bands in the excitation spectra of the solid neodymium, europium and terbium complexes (Figures 3-5) coincide with the diffuse reflectance spectra. The ligand absorption bands in the excitation spectra are much more intense than the bands of $f-f$ transitions; this indicates efficient sensitization of the lanthanide luminescence by the CAPH ligand. The lowest ligand triplet state

Table 1. Selected band positions in the IR spectra of HL and $\text{Ln}(\text{HL})_3(\text{NO}_3)_3$ (cm^{-1})

	$\nu(\text{NH})$	$\nu(\text{CO})$	$\nu(\text{PO})$	$\nu(\text{N=O})$	$\nu_{\text{as}}(\text{NO}_2)$	$\nu_{\text{s}}(\text{NO}_2)$
HL	3270	1671	1225	-	-	-
$\text{Ln}(\text{HL})_3(\text{NO}_3)_3$	3265-3267	1664-1666	1167-1168	1487-1488	1294-1296	1028-1031

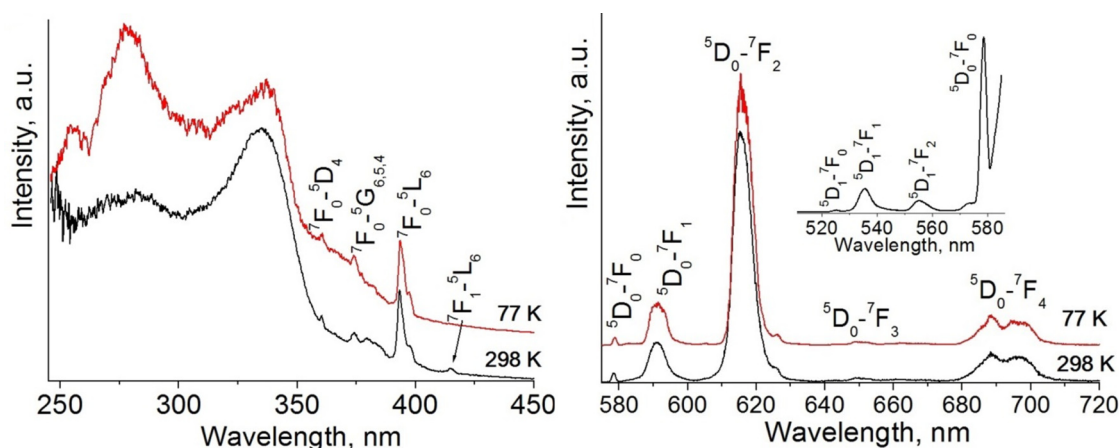


Fig. 4. Excitation (left panel) and emission (right panel) spectra of $\text{Eu}(\text{HL})_3(\text{NO}_3)_3$

(LLTS) in the complexes ($\approx 24\,900\text{ cm}^{-1}$) was localized based on the phosphorescence spectrum of $\text{Gd}(\text{HL})_3(\text{NO}_3)_3$ at 77 K. It is high enough to provide efficient energy transfer from ligands to the excited levels of Nd^{III} ($^4\text{F}_{3/2}$), Eu^{III} ($^5\text{D}_0$, $^5\text{D}_1$) and Tb^{III} ($^5\text{D}_4$) ions and to exclude back energy transfer. Compared with N-(diphenylphosphoryl)-benzamide [16, 17], the HL absorption band is broader, has an additional maximum at 340 nm and a band shoulder in the visible region of 350–400 nm. The lowest ligand triplet state of HL is more than 1000 cm^{-1} lower, compared to N-(diphenylphosphoryl)-benzamide. Thus, the introduction of the OCH_3 group in the ortho-position of the aromatic substituent of the CAPH ligand causes significant changes in the spectral properties of the ligand and its complexes.

When the neodymium complex is excited into the absorption band of the ligand, the characteristic f-f luminescence of Nd^{III} ion is observed in the NIR region (Figure 3). The spectrum is dominated by the band of the transition $^4\text{F}_{3/2} \rightarrow ^4\text{I}_{11/2}$, which is typical for majority of neodymium compounds.

During excitation of the europium complex into the absorption band of the ligand, the intense red Eu^{III} -centered luminescence is observed (Figure 4, right panel). There are narrow bands of Eu^{III} f-f transitions from $^5\text{D}_0$ and $^5\text{D}_1$ levels in the luminescence spectrum of $\text{Eu}(\text{HL})_3(\text{NO}_3)_3$. The ligand fluorescence or phosphorescence bands are absent in the spectra. The bands of the f-f transitions are sufficiently broadened both at room temperature and at 77 K, which does not allow the analysis of Stark components. The transition band $^5\text{D}_0 \rightarrow ^7\text{F}_0$ is singlet, which corresponds to one optical center. In the luminescence spectra of $\text{Eu}(\text{HL})_3(\text{NO}_3)_3$,

the band of hypersensitive electric dipole transition $^5\text{D}_0 \rightarrow ^7\text{F}_2$ dominates, which is also observed for most emission spectra of the europium(III) ion [18,19]. At room temperature, the red/orange ratio $I(^5\text{D}_0 \rightarrow ^7\text{F}_2)/I(^5\text{D}_0 \rightarrow ^7\text{F}_1)$ is 6.4. The luminescence lifetime (τ_{obs}) for $\text{Eu}(\text{HL})_3(\text{NO}_3)_3$ is independent on temperature and slightly dependent on the excitation wavelength. At room temperature, τ_{obs} is 1.18 ms for excitation at 280 and 330 nm, and τ_{obs} is 1.32 ms for excitation at 254 nm; this is one of the lowest values known for europium complexes based on phenyl-containing carbacylamidophosphates, but higher than most europium β -diketonates [4]. The radiative luminescence lifetime of the europium ion in the complex ($\tau_{\text{RAD}} = 2.13\text{ ms}$) was calculated from the measured luminescence spectrum by the following equation [20]: $1/\tau_{\text{RAD}} = A_{\text{MD},0} n^3 \cdot (I_{\text{tot}}/I_{\text{MD}})$, where n is the refractive index of the crystals (1.5); $A_{\text{MD},0}$ is the spontaneous emission probability for the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition in vacuum (14.65 s^{-1}); and $I_{\text{tot}}/I_{\text{MD}}$ is the ratio of the total area of the corrected Eu^{III} emission spectrum to the area of the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ band. The intrinsic quantum yield of the europium ion in the complex $\text{Eu}(\text{HL})_3(\text{NO}_3)_3$ was calculated from lifetimes at $\lambda_{\text{exc}} = 254\text{ nm}$ ($Q_{\text{Ln}}^{\text{Ln}} = \tau_{\text{obs}}/\tau_{\text{RAD}} = 62\%$) and was found to be somewhat lower compared to most previously studied europium complexes based on phenyl containing carbacylamidophosphates [4]. The greater quenching of Eu^{III} luminescence in $\text{Eu}(\text{HL})_3(\text{NO}_3)_3$ compared to the similar complex based on N-(diphenylphosphoryl)-benzamide [17] may be due to a less rigid coordination environment of the europium ion in $\text{Eu}(\text{HL})_3(\text{NO}_3)_3$: in HL, there is an intramolecular hydrogen bond $\text{N-H}\cdots\text{O}$, whereas in the complex based on N-(diphenylphosphoryl)-benzamide, the in-

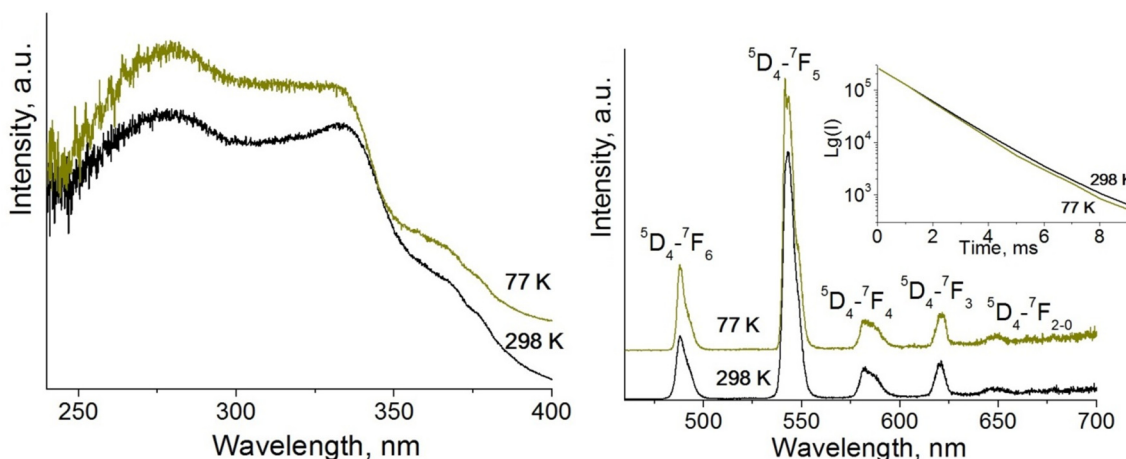


Fig. 5. Excitation (left panel) and emission (right panel) spectra of $\text{Tb}(\text{HL})_3(\text{NO}_3)_3$

tramolecular hydrogen bond $\text{N-H}\cdots\text{O}$ exists between CAPHs and nitrate anions.

During excitation of the terbium complex into the ligand absorption band, the intense green Tb^{III} -centered luminescence is observed both at room temperature and at 77 K (Figure 5, right panel). The narrow bands in the luminescence spectra of $\text{Tb}(\text{HL})_3(\text{NO}_3)_3$ are due to $^5\text{D}_4 \rightarrow ^7\text{F}_{6-0}$ transitions of the terbium ion. The ligand fluorescence or phosphorescence bands are absent in the spectra of the terbium complex. The band of the $^5\text{D}_4 \rightarrow ^7\text{F}_5$ transition dominates in the luminescence spectrum of $\text{Tb}(\text{HL})_3(\text{NO}_3)_3$, which is typical for terbium complexes [4, 21]. Similar to the europium complex, the f-f luminescence intensity of Tb^{III} decreases monoexponentially (inset in Figure 4, right panel), which is further evidence of the existence of one optical center in the complexes under consideration. The τ_{obs} does not depend on temperature and is 1.31 ms at 298 K and 1.35 ms at 77 K, which is within the experimental error.

4. Conclusions

The N-(diphenylphosphoryl)-2-methoxybenzamide has been tested as a ligand for lanthanides and as a sensitizer for Nd^{III} , Eu^{III} and Tb^{III} emission. By means of IR and NMR spectroscopy, it was established that N-(diphenylphosphoryl)-2-methoxybenzamide is coordinated towards lanthanide ions in a monodentate way in neutral (molecular) form, while the nitrate anions are coordinated in a bidentate manner. The complexes $\text{Nd}(\text{HL})_3(\text{NO}_3)_3$, $\text{Eu}(\text{HL})_3(\text{NO}_3)_3$ and $\text{Tb}(\text{HL})_3(\text{NO}_3)_3$ exhibit strong f-f emission sensitized by CAPH ligands with the emission lifetime about 1.3 ms for Eu^{III} and Tb^{III} , and the intrinsic quantum yield for Eu^{III} is 62 %. It was shown, that the introduc-

tion of the OCH_3 group into the ortho-position of the aromatic substituent of the CAPH ligand leads to significant changes in the spectral properties of the ligand and its complexes such as a decrease in the LLTS energy and broadening of the absorption band in the UV region.

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