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LUMINESCENT PROPERTIES OF Nd(III) COMPLEXES WITH ETHYLENEDIAMINE-N,N'-DISUCCINIC AND N,N-BIS(PHOSPHONO-METHYL)-2-AMINOPROPIONIC ACIDS.

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An analysis of the fluorescent characteristics of ethylenediamine-N,N'-disuccinic and N,N-bis(phosphonomethyl)-2-aminopropionic acids was carried out depending on the pH of the solutions. It was established that the change in fluorescence intensity and lifetime is associated with the formation of variously protonated forms of acids in which stable H-cycles are formed with the participation of hydrogen bonds. The energies of the singlet and triplet levels of the ligands were experimentally determined, the values of which are higher than the energy of the radiative level of the Nd(III) ion, which indicates the possibility of intramolecular transfer of the excitation energy to the resonance level of the lanthanide ion. It was established that both homo- and heteronuclear complexes of Nd(III) exhibit 4*f*-luminescence in the near-IR region. It was found that for phosphorus-containing complexes there is an increase in luminescence intensity and relative quantum yields in comparison with aminocarboxylate analogs. In heterometallic complexes based on aminopolycarboxylic acids, the intramolecular transfer of energy from the excited level of Co(II) to the resonance level of the f-metal leads to sensitization of the 4*f*-luminescence of the neodymium ion.

Key words: complexes, neodymium, aminopolycarboxylic acids, aminocarboxyphosphonates, synthesis, luminescence.

INTRODUCTION. The synthesis and research of complex compounds with ligands that have several donor centers are of increased interest due to the possibility of using them as primary molecular blocks to create more complex polynuclear systems with a given structure and predicted properties. The stability and solubility of the complex, as well as the efficiency of *4f*-luminescence, depend on the selected ligand. Effective energy transfer from the triplet level of the ligand to the resonance level of the lanthanide ion is a necessary condition for realizing *4f*-luminescence in lanthanide compounds. Moreover, the effectiveness

of this process and the luminescence yield will be influenced by such factors as the energy of the triplet level of the ligand, the structure of the ligand (the presence of electron-donating and electron-accepting substituents and their mutual location in the ligand molecule), quenching mechanisms, etc. In addition, for selective binding to various metal ions, ligands must have a heterodentate nature and an unsaturated character [1, 2]. These requirements are met by polydentate acyclic ligands, such as aminopolycarboxylic (APC) or aminocarboxyphosphonic (ACPh) acids, which form highly stable metal complexes with lanthanide ions [3–8]. Complexes of lanthanides with APC or ACPh that exhibit luminescence in the IR region (Nd, Pr, Er, Yb) can be used as precursors for luminescent diagnostics, for fluorescent immunoassays, for creating amplifiers in laser systems, etc. [9–13]. In the latter case, factors such as the minimal background signal of bioobjects (high in measurements in the visible region), the possibility of luminescence excitation in a wide range, including non-rigid irradiation with visible light, determine the prospects for the practical use of these compounds.

Work on the enhancement of IR luminescence of Ln(III) ions is mainly divided into two directions: targeted selection of ligands in complexes with which *4f*-luminescence is realized and synthesis of heteronuclear, in particular, d-f-metal complexes. In the latter, 3-d metal complexes can be used as energy transfer "antennas" for the sensitization of the *4f*-luminescence of Ln(III) ions, as well as "energy gaps" between the triplet level of the ligand and the emission level of the lanthanide ion, thus facilitating the sensitization of its luminescence, especially in the near-IR region. This is due to the fact that the absorption bands ($L \rightarrow L^*$ or $L \rightarrow M$) of transition metal complexes lie in the near-ultraviolet, visible, or near long-wavelength region, compared to the $\pi \rightarrow \pi^*$ absorption bands of common ligands [14–16].

The studies of the spectral-luminescent properties of aminopolycarboxylate complexes of lanthanides (both mono- and heterometallic) cover mainly compounds with the most common APC: EDTA and DTPA [17–23]. There are almost no studies of the luminescent properties of Ln(III) complexes with ethylenediaminedi-succinic acid (H_4EDDS), although it is known that heterometallic neodymium complexes can be used as drugs for cancer diseases, immunodeficiency, and blood diseases [24, 25]. In [5], new heterometallic complexes of neodymium and zinc with ethylenediaminedisuccinic acid were synthesized for the first time. It was shown that the monometallic complex of zinc, which is less stable than the corresponding neodymium complex, acts as a "building block" for obtaining a heterobinuclear compound by the exocoordination of additional metal ions. It was found that in the heterometallic complex, the Nd^{3+} ion is bound to the oxygen atoms of two α-carboxyl groups and one β-carboxyl group and to the nitrogen atom of the ligand, and the coordination sphere of the Zn^{2+} ion is formed by the oxygen atoms of the β-carboxyl group of the EDDS molecule, which performs the bridging function, and water molecules. It was shown that both homonuclear and heteronuclear complexes exhibit *4f*-luminescence of neodymium ions, but the intensity and quantum yield of luminescence in the heterometallic system decreases due to the overlap of the luminescence spectra of the zinc-containing fragment with the absorption bands of Nd(III) ions.

To date, in the literature, only a small number of works are devoted to complexes of lanthanides with aminocarboxyphosphonic acids, their structural features and physicochemical properties [26–31], and there is limited information on the luminescent properties of the compounds. The work [26] describes the synthesis of complexes of lanthanides with phosphonomethylglycine (NPMG) of the general formula $LnC_3H_5NO_5P{\cdot}nH_2O$ (Ln(III)= La, Ce, Nd, Er; n= 1; 1.5; 2). It was established that the lanthanide ion coordinates NPMG through the oxygen atoms of the carboxyl and phosphonium groups and the nitrogen atom. The stability constants of phosphonomethylglycinate complexes of Pr(III), Nd(III), and Ga(III) were determined in [27, 28]. However, in none of the cited works, data on the spectral-luminescent characteristics of synthesized compounds were obtained.

Using N-(phosphonomethyl)iminodiacetic acid (H_4PMIDA), the authors of [29–31] obtained a number of isostructural chiral lanthanoid carboxylate-phosphonates Ln(HPMIDA)$(H_2O)_2{\cdot}H_2O$ (Ln(III) = Gd, Tb, Dy, Y, Er, Yb, Lu). It was established that the Ln(III) ion has an 8-coordinate environment and chelates one HPMIDA anion in a tetradentate manner (1N+3O) and two other HPMIDA anions through one carboxylate and one phosphonate oxygen atom. The lanthanide coordination sphere is complemented by two aqua ligands. Luminescence studies of the synthesized compounds showed that the terbium complex exhibits four very strong characteristic emission bands $^5D_4 \rightarrow {}^7F_j$ (j=6;5;4;3) at 490 nm, 547 nm, 582 nm, and 622 nm, respectively. The lifetime of Tb ($^5D_4$) for $\lambda_{ex,em}$ = 380, 488 nm is about 1 ms. In the spectra of the Er complex, there is only a very broad emission band in the visible region at 406 nm. The authors explain the absence of emission bands in the near IR region for the Er(III) compound by the effect of quenching of the luminescent state by high-frequency oscillating water molecules.

The study of Ln(III) (Pr, Nd, Gd, Ho, Er) complexes with phosphonomethylaminosuccinic acid showed that f-metals coordinate to the ligand through a nitrogen atom and three oxygen atoms of the phosphonic group and α- and β-carboxyl groups with the formation of complexes of the composition 1:1 for Pr(III) and Er(III) and dimers for Nd(III) and Gd(III). It has been established that molecular fluorescence is observed for phosphonomethylaminosuccinic acid in a wide pH range. Nd(III) complexes exhibit *4f*-luminescence in solid form and in solution in the near IR region [4].

The survey of scientific literature shows that the synthesis of new aminopolycarboxylates and aminocarboxyphosphonates of lanthanides remains in the circle of interests of modern coordination chemistry, since these compounds can exhibit useful luminescent properties both in the visible and in the near IR region.

EXPERIMENT AND RESULTS DISCUSSION. The synthesis of monometallic complexes was carried out by the interaction of aqueous solutions of neodymium nitrate $Nd(NO_3)_3{\cdot}6H_2O$ with aqueous solutions of complexons at a molar ratio of reagents of 1:1 at pH ~6 and a temperature of 50°C. After cooling the reaction mixture, the formed complexes were precipitated with absolute ethyl alcohol, filtered off and washed with ethanol to remove inorganic impurities.

Ethylenediaminedisuccinic acid was obtained by the condensation reaction of maleic acid with ethylenediamine [32].

The synthesis of N,N-bis(phosphonomethyl)-2-aminopropionic acid (H_5PMAP) (Fig. 1) was carried out in a three-component system using phosphorous acid (hydrophosphoryl component), paraformaldehyde (ketone component) and β-alanine (amine component):

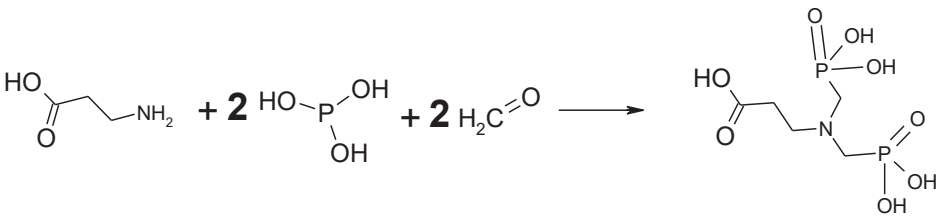

Fig. 1 - Synthesis scheme of N,N-bis(phosphonomethyl)-2-aminopropionic acid.

Synthesis method of N,N-bis(phosphonomethyl)-2-aminopropionic acid. A mixture of 12.07 g (147 mmol) of phosphorous acid and 9.91 g (74.46 mmol) was dissolved in 40 ml of 1:1 hydrochloric acid. A two-fold excess of paraformaldehyde was added in small portions to the resulting solution heated to 100 °C, adding the next portion after dissolving the sediment of the previous one. After that, the reaction mixture was heated for 8–16 hours, controlling the course of the reaction according to the data of ^{31}P NMR spectroscopy until the doublet signal of phosphorous acid ($^1J_{PH}$=670 Hz) completely disappeared. After that, the reaction mixture was heated for another 2 hours and evaporated in vacuo to a thick glue-like consistency. The light viscous oil was additionally evaporated three times under vacuum with isopropanol to remove residual water. A white fine-crystalline precipitate of the target product (H_5PMAP) was formed during long-term grinding of the crushed glassy mass with methanol, it was quickly filtered off, washed twice with methanol, diethyl ester and dried in a vacuum. The product yield of N,N-bis(phosphonomethyl)-2-aminopropionic acid is 9.08 g (28.29 mmol, 38%).

The purity of the final product was determined by elemental analysis and the ^{31}P NMR method. The content of C, H, N was determined on a CHN analyzer Perkin Elmer - 2400. The content of phosphorus was determined by the method of gravimetry. **H_5PMAP**: $C_4H_{11}NO_8P_2$ (M= 263). Anal. calc.(%): C, 18.26; H, 4.14; N, 5.37; P, 23.64. Found (%): C, 18.25; H, 4.18; N, 5.32; P, 23.57. ^{31}P NMR (D_2O; δ, ppm): 10.360, t, $^2J_{HP}$ = 12,4 Hz. FT-IR (KBr, cm^{-1}): 1737 [ν(COOH)]; 1635 [ν_{as}(COO^-)]; 1465 [ν_s(COO^-)]; 1166 [ν_{as}(PO_3)]; 1009 [ν_s(P=O)]; 943 [ν_{as}(POH)]; 3007–2926 [ν(CH)]; 3434 [ν(H_2O)].

The synthesis of the heterometallic complexes NdCoEDDS and NdCoEDTA was carried out by the block method by the interaction of monoprotonated ethylenediaminedisuccinate complex of Co(II) with neodymium nitrate [8].

The excitation, fluorescence, and *4f*-luminescence spectra were recorded on a Fluorolog FL 3–22 spectrofluorimeter (Horiba Jobin Yvon, Xe-450 W ozone-free lamp), equipped with an R928P photoelectric power supply unit (Hamamatsu, Japan) for the visible spectral region and cooled to 77 K (Optical Systems Inc., USA) for the IR region.

In aqueous solutions, depending on the pH, ethylenediaminedisuccinic acid exists in several stable anionic forms, which are characterized by the formation of chelate cycles with the

participation of a proton due to cross hydrogen bonds [33, 34]. At the same time, the presence of intra- and intermolecular hydrogen bonds will affect the fluorescent properties of complexons, since it is known that fluorescence spectra are sensitive to the influence of the latter. From this point of view, it was interesting to study the fluorescence of H_4EDDS at different pH values. Figure 2 shows fluorescence spectra of ethylenediaminedisuccinic acid at different pH values of the solution. At 77 K, the fluorescence spectrum of ethylenediaminedisuccinic acid solutions in the pH range 1–2 (Fig. 2 a, curve 1) is a broad unstructured band with a maximum at 443.6 nm, (integral intensity (I_{fl}) is $97 \cdot 10^6$ a.u.). At these pH values, the emission spectrum of the acid is blurred, which can be attributed to the formation of a network of hydrogen bonds between the molecules of the ligand and the solvent.

The fluorescence lifetime at pH 0.55 is 5.8 ns (Table 1) and has a monoexponential character, which may indicate the predominant existence of betaine cations $(H_6L)^{2+}$ and $(H_5L)^{+}$ in the solution. When carboxyl groups are ionized in the pH range 2–5 (Fig. 2, curve 2), in which H_4L, $(H_3L)^{1-}$ and $(H_2L)^{2-}$ particles are formed, the fluorescence intensity decreases slightly, and the fluorescence maximum bathochromically shifts by 5–8 nm. The lifetimes fluorescence were determined (τ_{fl} (pH 2.2) = 5.6 ns and 2.4 ns; τ_{fl} (pH 4.1) = 6.4 ns and 3.1 ns), the decay curves of which have a multiexponential character and indicate the existence of several forms in the solution.

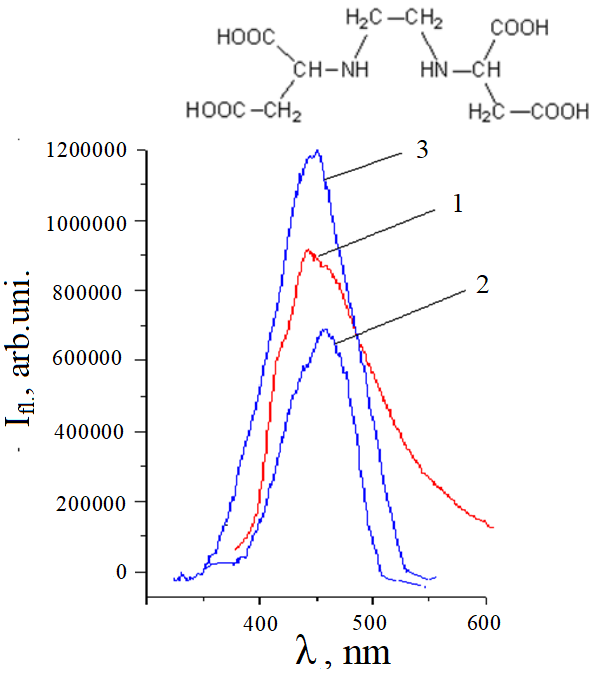

Fig. 2 – Fluorescence spectra of H_4EDDS at different pH values of the solution: 1 – 0.55–0.80; 2 – 2–5; 3 – 9.1; λ_{ex}=340–360 nm, T 77K.

Table 1.

Characteristics of the fluorescence spectra for the variously protonated forms of H_4EDDS and H_5PMAP depending on the pH of the solutions.

pH	Predominant form of the ligand		λ_{fl}, nm		τ_{fl}, ns	
	H_4EDDS	H_5PMAP	H_4EDDS	H_5PMAP	H_4EDDS	H_5PMAP
0,55 - 1 (HCl)	H_6L^{2+}, H_5L^{+}	H_6L^{+}, H_5L,	444	433	5.8	12.6
2.5 (acetate buffer)	H_4L, H_3L;	H_4L^{-}, H_3L^{2-}	449	437	5.6; 2.4	10.8
5 (KOH)	H_2L^{2};	H_2L^{3-}	452	422	6.4; 3.1	12.3
7 (KOH)	HL^{3};	HL^{4-}	-	430	12.3; 4,8	12,6
9-10 (ammonia buffer)	HL^{3-};L^{4-}	HL^{4-}, L^{5-}	454	429	7,3; 1,8	11.7

It can be assumed that, for example, for the form $(H_2L)^{2-}$ (pH ≈ 5.3 – 5.5; I_{fl}=63·10^6 a.u.; τ_{fl}= 12.3 and 4.8 ns) two methyleneaminodiacetate fragments, which make up 50% of the mass of the molecule, rotate freely, causing a non-radiative loss of excitation energy, which explains the weak fluorescence of this form of the ligand. It should be noted that, despite the significant advantage of the presence of the $(H_2L)^{2-}$ form in the solution, the value of the second τ_{fl}=4.8 ns indicates the presence of other protoned forms of EDDS in this pH region [35]. At pH>8 (Fig. 2, curve 3), there is a significant increase in fluorescence with a small shift in λ_{fl}. to the short-wave region. Since the $(H_2L)^{2-}$ and $(HL)^{1-}$ forms of the ligand dominate in the pH range 5–10, the increase in fluorescence intensity can be attributed to the dissociation of the first betaine proton and the formation of a hydrogen bond between nitrogen atoms and α-carboxyl groups, and, therefore, to a change in the symmetry of the ligand. Probably, during the transition to the $(HL)^{3-}$ and $(L)^{4-}$ forms, the formation of hydrogen bonds limits the free rotation of the groups, causing a sharp jump in the fluorescence intensity. The analysis of the data on the fluorescence attenuation of the form $(L)^{4-}$ (pH≈11) made it possible to determine two values of τ_{fl} = 7.3 and 1.8 ns, which can probably be associated with the formation of "short-lived" H-cycles in solutions.

To obtain information on the possibility of realizing *4f*-luminescence in lanthanide-containing compounds based on N,N-bis(phosphonomethyl)-2-aminopropionic acid, its luminescent properties were investigated. Figure 3 shows fluorescence spectra of H_5PMAP aqueous solutions at different pH levels.

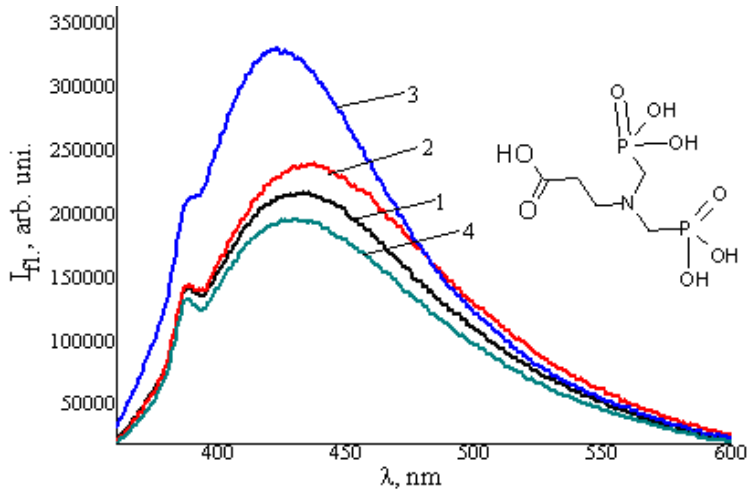

Fig. 3 – Fluorescence spectra of H_5PMAP aqueous solutions at different pH values of the medium: 1– pH 1; 2 – pH 2.5; 3 – pH 5; 4 – pH 7.5 (λ_{ex}=340 nm, T 298 K).

Upon excitation into the absorption band of the ligand at 290 nm at room temperature, a broad structureless band is observed in the region of 370–600 nm, the position of the maximum of which depends on the pH. At pH 1, the maximum of the fluorescence band is at 433 nm and at pH 2 at 437 nm. In a strongly acidic environment, the acid molecule is in the cationic form H_6L^+ as a result of protonation of the amino group and realization of a zwitterionic structure with a positive charge on

the ammonium nitrogen atom and a negative center on one of the phosphonic groups. At pH 5, the maximum of the fluorescence band is at 422 nm, which corresponds to the presence in the solution of a mixture of ligand forms of various degrees of protonation with the predominant form H_3L^{2-}. It should be noted that the fluorescence spectrum of H_5PMAP in solid form consists of a band with a maximum at 420 nm, which is probably caused by the presence of both zwitterionic and deprotonated forms. The fluorescence lifetime at the maximum of this band is 12.61±0.26 ns. With a further increase in pH, the HL_4 and L^{5-} forms prevail in the solution, which is reflected in the fluorescence spectra by a long-wavelength shift of the band maximum: 429 nm at pH 7 and 430 nm at pH 9. At the same time, stable H-cycles are formed in the anions: two 5-membered aminophosphonic cycles and one 6-membered β-alanine cycle.

At a temperature of 77 K, a band with oscillatory structure is observed in the luminescence spectrum of the ligand, the maximum of which is at 449 nm.

For the effective transfer of excitation energy from the triplet level of the ligand to the resonance (radiating) level of lanthanide ions, it is necessary that the difference between these states (energy gap) is within 2500–3500 cm^{-1} [36]. To experimentally determine the energy of the singlet and triplet levels of ethylenediaminedisuccinic and bis(phosphonomethyl)-2-aminopropionic acids, the fluorescence spectra of Gd(III) and Lu(III) complexes were studied. It was established that for gadolinium ethylenediaminedisuccinate, the energy values of the singlet S_1 (E_S) and triplet T_1 (E_T) levels are 22650 cm^{-1} and 19420 cm^{-1}, respectively. The singlet and triplet levels of Lu(III) complexes with H_5PMAP are 22780 cm^{-1} and 21740 cm^{-1}, respectively. The calculated energy values of the triplet levels of the ligands are above the emitting $^4F_{3/2}$ level of the Nd(III) ion, the energy of which is approximately 11460 cm^{-1}, which indicates the possibility of intramolecular transfer of excitation energy from the lower triplet levels of the ligands to the resonance level of the neodymium ion.

All synthesized Nd(III) complexes exhibit *4f*-luminescence in the near IR region. Figure 4 shows excitation (a) and luminescence (b) spectra of the Nd(III) complex with H_4EDDS. The excitation spectrum of NdEDDS contains an intense broad band in the interval 330–380 nm with a maximum at 353 nm, which refers to the π-π* transitions of the ligand. A low-intensity and weak band at 332 nm is the result of the overlap of the excitation spectra of an organic molecule and the Nd(III) ions themselves, and the shoulder at 379 nm corresponds to the transitions $^4I_{9/2}\rightarrow{}^4D_{3/2}$, $^4D_{5/2}$, $^4I_{11/2}$, $^4D_{1/2}$, $^2L_{15/2}$, $^4D_{7/2}$ of the Nd(III) ion. This relationship between the band intensities indicates luminescence sensitization due to intramolecular energy transfer from the aminocarboxylate fragment to the lanthanide ion.

In the spectra of *4f*-luminescence of neodymium ethylenediaminedisuccinate, three bands of intrinsic luminescence of Nd(III) are observed, which correspond to transitions from the excited level $^4F_{3/2}$ to the multiplets of the ground level ^4I_j: $^4I_{9/2}$ (λ_{max} =871/905 nm), $^4I_{11/2}$ (λ_{max} = 1063 nm) and $^4I_{13/2}$ (λ_{max} = 1337/1359 nm) (Fig. 4, b). The most intense emission band, the integral area of which is ~75% of the total intensity, is at 1063 nm, which is characteristic of the so-called «laser» transition $^4F_{3/2}\rightarrow{}^4I_{11/2}$. The relative contributions

of the integral intensities of the $^4I_{9/2}$ and $^4I_{13/2}$ bands to the total intensity are approximately 13.5% and 11.5%, respectively. In this case, the splitting of the $^4F_{3/2} \rightarrow {}^4I_{9/2}$ band into two components at 871, 905 nm is observed. The transition $^4F_{3/2} \rightarrow {}^4I_{13/2}$ is less intense, but is also split into two components, one of which manifests itself in a longer wavelength region (λ_{max} = 1359 nm).

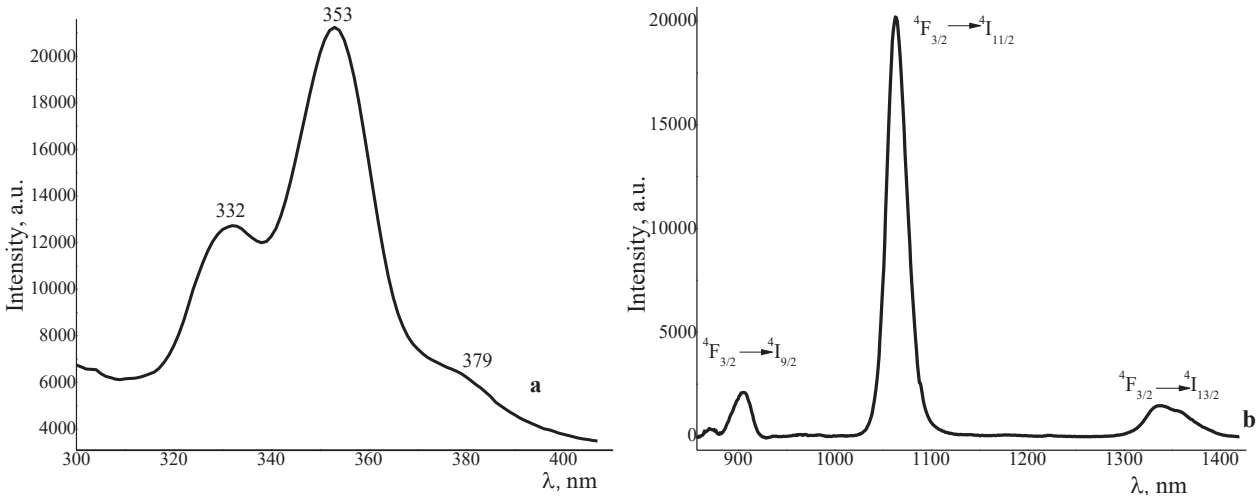

Fig. 4 – Excitation spectrum (a) and *4f*-luminescence spectrum (b) of NdEDDS in the solid state ($\lambda_{exc.}$ = 353 nm, T=298 K).

The structure of the *4f*-luminescence spectra of the neodymium complex based on H_5PMAP is identical to the luminescence spectra of the NdEDDS complex (Fig. 5). However, it should be noted that in the phosphonate complex, in comparison with the ethylenediaminedisuccinate complex, there is a hypsochromic shift of both components of the $^4F_{3/2} \rightarrow {}^4I_{9/2}$ transition by 4-7 nm and the transition band $^4F_{3/2} \rightarrow {}^4I_{13/2}$ by 5 nm. The maximum of the most intense transition $^4F_{3/2} \rightarrow {}^4I_{11/2}$ which is at 1062 nm in the case of NdPMAP and at 1063 nm in the case of NdEDDS, almost does not change its position. The absence of splitting of this band for both complexes indicates the presence of one emitting center.

It should be noted that the luminescence intensity of the NdPMAP complex in solutions is much lower than in the solid state, because in solutions there is a more significant deactivation of the excited state of the lanthanide ion on the O–H oscillators of coordinated water molecules, which is manifested in a low luminescence signal. But when passing from aqueous solutions of complexes to solid samples, the structure of the luminescence spectra and the position of the maxima of the spectral lines does not change, which is a consequence of the absence of significant structural changes in the immediate environment of the lanthanide in both aggregate states.

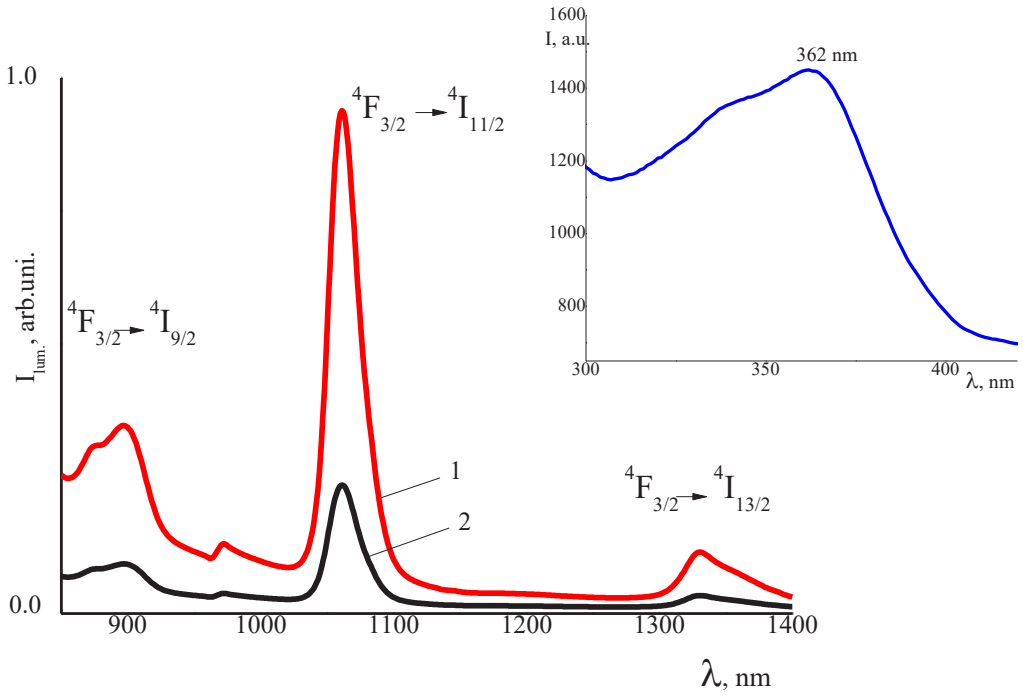

Fig. 5 – Excitation (inset) and *4f*-luminescence spectra of the NdPMAP complex in the solid state (1) and in solution (2) ($\lambda_{exc.}$ = 362 nm, T=298 K; $C_{Nd} = 1 \cdot 10^{-3}$M).

A relatively small increase in luminescence intensity for the NdPMAP complex compared to NdEDDS may be due to the different structure of the complexes, which differ in the size and number of chelate cycles. During complexation, EDDS forms three 5-membered (one ethylenediamine and two glycine) and two 6-membered β-alanine cycles [7, 8]. Two 5-membered metallocycles aminophosphonic and one 6-membered β-alanine metallocycle are formed in the NdPMAP complex. The arrangement of the cycles according to the 5–6–5 system is energetically more attractive than 6–5–6. That is, in the neodymium aminocarboxyphosphonate, a less rigid structure is realized than in the EDDS-based complex, and in the latter, the neodymium ion is more coordinatively saturated.

As it was indicated, recently the interest in heterobinuclear coordination compounds of lanthanides has increased significantly, which is connected with the variety of their properties and the expansion of the field of practical application. There are almost no reports on luminescent Co-Nd aminocarboxylate complexes. Some Co(II) coordination compounds are characterized by fluorescence in the blue or green region and can be used to sensitize the luminescence of Ln(III) ions in the IR region. Therefore, it was of interest to investigate the luminescence of heterometallic complexes CoEDDSNd and CoEDTANd.

For CoGdEDDS solutions, upon excitation in the region of 300–390 nm at room temperature, a broad band of molecular fluorescence in the region of 420–490 nm is observed. At

77K, a structured band was recorded, which is characterized by a maximum in the region of 435–450 nm and a shoulder in the region of 465–480 nm, which is probably a superposition of singlet and triplet states in heteronuclear complexes. The application of a time delay (50 μs) and freezing of the solutions allowed to record the phosphorescence of the complexes understudy, the maxima of which lie in the region of 495–535 nm. Thus, the introduction of Co(II) ions into the composition of neodymium complexes leads, in comparison with monocomplexes, to a decrease in the energy of singlet (ΔE_S ~ 2100–2300 cm^{-1}) and triplet (ΔE_T ~ 2100–2400 cm^{-1}) levels, the latter are located in the region of 18750–20300 cm^{-1}. For all complexes, the position of the fluorescence maximum within the experimental error does not depend on the excitation wavelength. It can be assumed that the influence of Co(II) ions on the S_1 and T_1 states is associated with the enhancement of the spin-orbital interaction in the molecule. The position of the triplet levels accounts for the presence of the *4f*-luminescence signal of the neodymium ion in heteronuclear complexes. It is also necessary to take into account the energy of the excited level of the cobalt ion itself (18500–20000 cm^{-1}). It can be assumed that intramolecular d → f energy transfer leads to sensitization of *4f*-luminescence in the IR region in the case of Nd(III) complexes, the luminescence spectra of which are shown in Fig. 6.

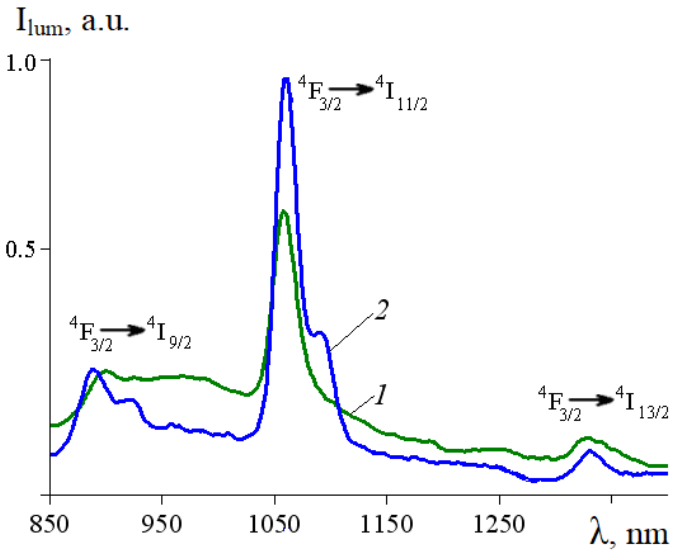

Fig. 6 – *4f*-Luminescence spectra of NdCoEDTA (1) complexes ($\lambda_{exc.}$ = 365 nm) and NdCoEDDS (2) ($\lambda_{exc.}$ = 345 nm).

The *4f*-luminescence spectra of both complexes are identical have the appearance characteristic of the neodymium ion and consist of three transitions: $^4F_{3/2} \rightarrow {}^4I_{9/2}$ (875–902 nm), $^4F_{3/2} \rightarrow {}^4I_{11/2}$ (1062–1065 nm), $^4F_{3/2} \rightarrow {}^4I_{13/2}$ (1330–1335 nm). But in the spectrum of the complex with EDDS, a splitting of the $^4F_{3/2} \rightarrow {}^4I_{9/2}$ and $^4F_{3/2} \rightarrow {}^4I_{13/2}$ transition bands into three components (878, 893, and 905 nm and 1340, 1357, and 1381 nm, respectively) is observed. The $^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition has a pronounced splitting into two components, one of which

manifests itself in the longer wavelength region (1063 and 1078 nm). It is obvious that there are two emission centers in the ethylenediaminedisuccinate complex. A similar set of splittings of the corresponding bands is probably a consequence of the distortion of the configuration of the Nd(III) ion in NdCoEDDS and a decrease in the symmetry of the coordination polyhedron compared to the NdCoEDTA complex.

Taking into account the energy of the excited level of Co(II) ($^4T_1(P)$ ~ 520 nm [37, 38]), it can be assumed that intramolecular d → f energy transfer leads to sensitization of the *4f*-luminescence of the neodymium ion, which is provided both by the overlapping of the luminescence spectra of Co(II) with the excitation bands of neodymium-containing compounds, which correspond to the transitions $^4I_{9/2} \rightarrow {}^4D_{3/2}$ (354 nm), $^4I_{9/2} \rightarrow {}^2P_{1/2}$ (432 nm), and by the low-lying emitting $^4F_{3/2}$ level of the ion neodymium (Fig. 7).

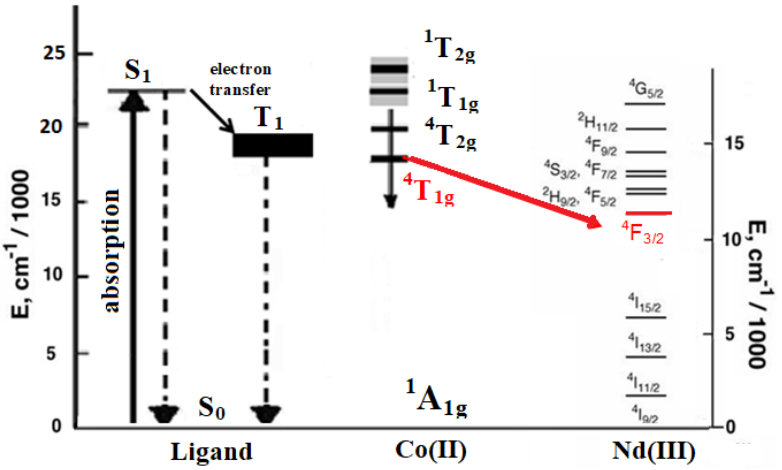

Fig. 7 – Scheme of sensitization of Nd(III) ion luminescence by Co(II) ions.

The increase in the luminescence intensity of Nd(III) ions in cobalt-containing heteronuclear complexes is probably associated with the non-radiative transfer of energy between two metal centers, in which the Co(III) ion acts as a donor, and the Nd(III) ion acts as an acceptor .

Comparison of the structure of the luminescence spectra of NdCoEDDS and NdCoEDTA indicates a different coordination environment of Nd(III) in these complexes. Obviously, in heterometallic ethylenediaminedisuccinate, the Nd^{3+} coordination environment is formed due to the 5-dentate coordination (2N+3O) of one EDDS ion and 3 water molecules. The cobalt ion is bound monodentately to the bridging β-carboxyl group and bidentately to the oxygen atoms of two α-carboxyl groups of the EDDS molecule [8]. The Nd(III) ion in the NdCoEDTA complex, similarly to $Gd_2Co_3(EDTA)_3(H_2O)_{11}$ [39], is in the coordination environment of NdO_{10} (bent bicapped tetragonal antiprism) and is monodentately bound to six carboxylate oxygen atoms from three different EDTA molecules and to four oxygen atoms of water molecules. The Co(II) ion is in a distorted octahedral environment and is coordinated by two nitrogen atoms, four oxygen atoms of EDTA and one oxygen atom of a water molecule. Thus,

a more rigid structure is achieved in the ethylenediaminetetraacetate heterocomplex than in the heteronuclear complex based on EDDS, due to which the radiation intensity decreases. In addition, a larger number of water molecules in the NdCoEDTA complex also contributes to a decrease in luminescence.

But it should be noted that in going from monometallic complexes based on aminopolycarboxylates to their heterometallic analogues, the positions of the most intense transition $^4F_{3/2} \rightarrow {}^4I_{11/2}$ almost do not change, and the components of the transition $^4F_{3/2} \rightarrow {}^4I_{9/2}$ shift by ~1–3 nm, which is evidence of the preservation of the neodymium coordination site in both types of compounds.

When determining the luminescence intensity of Nd(III) ions, as a rule, its «laser» most intense transition $^4F_{3/2} \rightarrow {}^4I_{11/2}$, which corresponds to the band with a maximum at 1060–1065 nm, is used. When calculating the quantum yield of luminescence of Nd(III) ions, the $^4F_{3/2} \rightarrow {}^4I_{9/2}$ transition is also taken into account, the intensity of which is usually 20–40% of the «laser» intensity. Due to the low intensity of the $^4F_{3/2} \rightarrow {}^4I_{13/2}$ transition ($\lambda_{max} \cong$ 1345–1350 nm; emission 5–10%), it is not taken into account in the calculations (Table 2).

Table 2.

Characteristics of the luminescence spectra of Nd(III) complexes with aminopolycarboxylic and aminocarboxyphosphonic acids.

Complex	$\lambda_{ex.}$, nm	$\lambda_{4f\text{-lum.}}$, nm	$I_{lum.} \cdot 10^{-4}$, a.u.	$\varphi_{4\text{-}f} \cdot 10^{-3}$, a.u.
NdEDDS	353	905/871; 1063; 1359/1337	10.65	0.11
NdZnEDDS	365 [4]	902/874; 1064; 1365	4.26	0.06
NdCoEDDS	365	878/893/905; 1064/1077; 1340/1357/1381	14.27	0.29
NdEDTA	365	903/872;1062; 1358	4.04	0.025
NdZnEDTA	365 [4]	905/876; 1062; 1360	3.27	0.021
NdCoEDTA	345	902/867;1064; 1359/1338	8.92	0.17
NdPMAP	362	898/875; 1062; 1332	14.21	0.28

As can be seen from the data in the table. 2, the heterometallic complex NdCoEDDS has the largest integrated intensity of 4f-luminescence among the investigated compounds. The intensity of *4f*-luminescence of NdCoEDTA is 1.72 times lower than the intensity of NdCoEDDS, but 2.2 times greater than NdEDTA. In general, the trend of decreasing $I_{lum.}$ should be noted. of ethylenediaminetetraacetates compared to their ethylenediaminedisuccinate analogues. Obviously, this is related to the structure of the complexes. Complexes based on EDTA are characterized by the formation of net 2D polymers [39], which obviously causes the shielding of the emitting centers of the Nd^{3+} ion, and is the reason for the low intensity and efficiency of luminescence.

The intensity of *4f*-luminescence of the NdPMAP complex is approximately the same as that of $I_{lum.}$ NdCoEDDS, which is probably due to the proximity of the energies of their triplet levels.

The quantum yield of *4f*-luminescence ($\varphi_{4\text{-}f}$) for cobalt-containing heterometallic complex-

es is greater than for monometallic compounds regardless of the complexon, while for ethylene diamine disuccinates $\varphi_{4\text{-}f}$ is greater than for ethylene diamine tetraacetates by a factor of 4.4 in the case of homonuclear complexes and by a factor of 1.6 and – in the case of heteronuclear.

According to the values of *4f*-luminescence intensity and the calculated $\varphi_{4\text{-}f}$, the Nd(III) complexes can be placed in the following order: NdCoEDDS ≥ NdPHMAP > NdCoEDTA > NdEDDS > NdEDTA > NdZnEDTA > NdZnEDDS.

CONCLUSIONS. The fluorescence of ethylenediaminedisuccinic and N,N-bis(phosphonomethyl)-2-aminopropionic acids in solution at different pH values was investigated. It was shown that depending on the pH, the intensity and lifetime of fluorescence of variously protonated forms of acids change, which is due to the formation of stable H-cycles with the participation of hydrogen bonds. The energies of the singlet and triplet levels of the ligands were experimentally determined, the values of which are higher than the energy of the radiative level of the Nd(III) ion, which indicates the possibility of intramolecular transfer of excitation energy to the resonance level of the lanthanide ion.

The luminescent properties of homo- and heteronuclear complexes of Nd(III) with H_4EDDS and H_5PMAP were studied. It was found that intense 4*f*-luminescence in the near IR region is observed for all synthesized compounds upon excitation in the absorption region of the ligand. It was shown that the luminescence intensity depends on the coordination environment of the lanthanide ion. The highest intensity of luminescence is exhibited by the NdCoEDDS and NdPHMAR complexes, which are also characterized by a higher quantum yield. In heterometallic complexes based on aminopolycarboxylic acids, the intramolecular transfer of energy from the excited level of Co(II) to the resonance level of the f-metal leads to sensitization of the 4f-luminescence of the neodymium ion.

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ЛЮМІНЕСЦЕНТНІ ВЛАСТИВОСТІ КОМПЛЕКСІВ Nd(III) З ЕТИЛЕНДІАМІН-N,N'-ДИЯНТАРНОЮ ТА N,N-БІС(ФОСФОНОМЕТИЛ)-2-АМІНОПРОПІОНОВОЮ КИСЛОТАМИ

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Досліджено флуоресценцію етилендиамін-**N,N'**-диянтарної та N,N-біс(фосфонометил)-2-амінопропіонової кислот у розчині за різних значень pH. Показано, що залежно від pH змінюються інтенсивність та час життя флуоресценції різнопротонованих форм кислот, що зумовлено утворенням

стійких Н-циклів за участю водневих зв'язків. Експериментально визначено енергії синглетних та триплетних рівнів лігандів (E_S= 22650 см$^{-1}$, E_T= 21420 см$^{-1}$ для H_4EDDS; E_S= 22780 см$^{-1}$, E_T= 20740 см$^{-1}$ для H_5PMAP), значення яких є вищим енергії випромінювального рівня іона Nd(III) (11 460 см$^{-1}$), що свідчить про можливість внутрішньо-молекулярного перенесення енергії збудження на резонансний рівень іона лантаноїду.

Досліджено люмінесцентні властивості гомо- і гетероядерних комплексів Nd(III) з H_4EDDS та H_5PMAP. Виявлено, що при збудженні в області поглинання ліганду для всіх синтезованих сполук спостерігається інтенсивна 4*f*-люмінесценція в ближній ІЧ-області. Показано, що інтенсивність люмінесценції залежить від координаційного оточення іона лантаноїду. Найбільшу інтенсивність люмінесценції проявляють комплекси NdCoEDDS та NdPHMAP, для яких характерний і більш високий квантовий вихід. У гетерометалічних комплексах на основі амінополікарбонових кислот внутрішньомолекулярне перенесення енергії зі збудженого рівня Co(II) на резонансний рівень f-металу призводить до сенсибілізації *4f*-люмінесценції іона неодиму.

Ключові слова: комплекси, неодим, амінополікарбонові кислоти, амінокарбоксифосфонати, синтез, люмінесценція.

REFERENCES

1. Korovin Y., Rusakova N. Near-infrared luminescence of Yb^{3+}, Nd^{3+} and Er^{3+} in complexes with organic dyes. *Journal of alloys and compounds*. 2004. **374** (1–2): 311–314. https://doi.org/10.1016/j.jallcom.2003.11.097.
2. Liu J.-X., Mei S.-L., Chen X.-H., Yao C.-J. Recent Advances of Near-Infrared (NIR) Emissive Metal Complexes Bridged by Ligands with N- and/or O-Donor Sites. *Crystals* 2021. **11**(2): 155. https://doi.org/10.3390/cryst11020155.
3. Ptaszynski B., Zwolinska A. Synthesis and properties of solid complexes of lanthanum, cerium, neodymium and erbium with N-phosphonomethylglycine. *Polish Journal of Environmental Studies*. 2001. **10** (4): 257–262.
4. Trunova E.K., Rusakova N.V., Berezhnitskaya A.S., Smola S.S., Snurnikova O.V., Makotrik T.A. Synthesis and spectral-luminescent properties of complexes of lanthanides with phosphonomethyl-aminosuccinic acid. *Ukr. Chem. J.* 2011. **77** (12):71–77. [in Russian].
5. Trunova O.K., Rusakova N.V., Shovkova G.V., Gayday Y.M., Korovin O.Yu., Malinka O.V. Synthesis and research of heterometallic complexes of Nd(III) and Zn(II) with ethylenediamine-disuccinic acid *Ukr. Chem. J.* 2014. **80**(3): 3–9. [in Ukrainian].
6. Li X., Zhang Z., Liu B., Mu W., Yang Y., Martin L.R., ... & Rao L. Complexation of Light Trivalent Lanthanides with N-(2-Hydroxyethyl) ethylenediamine-N,N′, N′-triacetic Acid in Aqueous Solutions: Thermodynamic Analysis and Coordination Modes. *Inorganic Chemistry*. 2019. **58** (22): 15618–15628 https://doi.org/10.1021/acs.inorgchem.9b02706.
7. Trunova O.K., Mishchenko A.M., Makotryk T.O. Synthesis and spectral characteristics of heterometallic complexes Pr(III) with Zn(II), Co(II) based on ethylenediaminetetraacetic and ethylenediaminediansuccinic acids. *Ukr. Chem. J.* 2021.**87** (3):3–17. https://doi:10.33609/2708-129X.87.03.2021.3-17.
8. Trunova O.K., Mishchenko A.M., Makotryk T.O. Synthesis, spectral characterization and stability of the Nd(III) and Co(II) heterometallic complexes with aminopolycarboxylic acids. *Ukr.Chem. J.* 2022. **88** (2):116–130. https://doi.org/10.33609/2708-129X.88.02.2022.116-130.

9. Hänninen P., Härmä H. (Eds.). *Lanthanide luminescence: photophysical, analytical and biological aspects*. 2011. Springer Science & Business Media, V. 7. 2011.
10. Armelao L., Quici S., Barigelletti F., Accorsi G., Bottaro G., Cavazzini, M., Tondello E. Design of luminescent lanthanide complexes: From molecules to highly efficient photo-emitting materials. *Coordination Chemistry Reviews*. 2010. **254** (56): 487–505 <https://doi.org/10.1016/j.ccr.2009.07.025 3.3>.
11. Gordon J.W., Fain S.B., Rowland I.J. Effect of lanthanide ions on dynamic nuclear polarization enhancement and liquid-state T_1 relaxation. *Magn. Reson. Med.* 2012. **68**: 1949–1954. https://doi.org/10.1002/mrm.24207.
12. Yang S., Feng W., Feng G. Development of a near-infrared fluorescent sensor with a large Stokes shift for sensing pyrophosphate in living cells and animals. *Analytica Chimica Acta*. 2018. **1034**: 119–127. https://doi.org/10.1016/j.aca.2018.05.076
13. Zapolotsky E.N., Qu Y., Babailov S.P. Lanthanide complexes with polyaminopolycarboxylates as prospective NMR/MRI diagnostic probes: Peculiarities of molecular structure, dynamics and paramagnetic properties. *J. Inclusion Phenomena and Macrocyclic Chemistry*. 2022. **102** (1–2): 1–33. https://doi.org10.1007/s10847-021-01112-34 4.
14. Natrajan L.S., Timmins P.L., Lunn M., Heath S.L. Luminescent Dinuclear Lanthanide Complexes of 5-Me-HXTA. *Inor. Chem.* 2007. **46** (25): 10877–10886. https://doi.org/10.1021/ic701366f.
15. Rusakova N., Smola S., Martsinko E., Seifullina I., Ermilov E., Korovin Yu. The first observation of 4f-luminescence in new heteronuclear lanthanide-germanium complexes. *J. Fluorescence*. 2008. **18** (2): 247–251. https://doi.org/10.1007/s10895-007-0224-y.
16. Liu J.-X., Mei S.-L., Chen X.-H., Yao C.-J. Recent Advances of Near-Infrared (NIR) Emissive Metal Complexes Bridged by Ligands with N- and/or O-Donor Sites. *Crystals*. 2021. (11): 155. https://doi.org/10.3390/ cryst11020155.
17. Hagan A.K., Zuchner T. Lanthanide-based time-resolved luminescence immunoassays. *Analytical and bioanalytical chemistry.* 2011. **400**: 2847–2864. https://doi.org/10.1007/s00216-011-5047-7.
18. Yang F., Yu Z., Li X., Ren P., Liu G., Song Y., Wang J. Design and synthesis of a novel lanthanide fluorescent probe (TbIII-dtpa-bis (2, 6-diaminopurine)) and its application to the detection of uric acid in urine sample. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*. 2018. **203**: 461–471. https://doi.org/10.1016/j.saa.2018.06.011.
19. Hasegawa M., Ohmagari H., Tanaka H., Machida K. Luminescence of lanthanide complexes: From fundamental to prospective approaches related to water-and molecular-stimuli. J. *Photochemistry and Photobiology C: Photochemistry Reviews*. 2022. **50**: 100484. https://doi.org/10.1016/j.jphotochemrev.2022.100484.
20. Mieda E., Morishima Y., Watanabe T., Miyake H., Shinoda S. Synthesis and luminescence properties of self-assembled lanthanide complexes with an EDTA-type chelating ligand in aqueous ethanol solution. *Bulletin of the Chemical Society of Japan*. 2023. **96** (6): 538–544 https://doi.org/10.1246/bcsj.20230069.
21. Costa I.F., Pires G.P., Espínola J.G.P., Brito H.F., Felinto M.C.F., Faustino W.M., Teotonio E.E. Luminescence properties of the Ln–EDTA complexes covalently linked to the chitosan biopolymers containing β-diketonate as antenna ligands. *Luminescence*. 2020. **35** (3): 365–372. https://doi.org/10.1002/bio.3735.
22. Smola S.S., Vitulskaya V.K., Rusakova N.V., Korovin, Y.V. Heteronuclear aminopolycarboxylates of lanthanides (III) and bismuth (III). *Bulletin of the Odessa National University. Chemistry*. 2009. **14** (3–4): 11–21.
23. Smola S.S., Rusakova N.V., Martsinko E.E., Seifullina I.I., Korovin Yu.V. Spectroscopic

properties of heteronuclear Ln(III)-Ge(IV) complexes with ethylenediamine-N,N,N',N'-tetraacetic and diethylenetriamine-N,N,N',-N',N''-pentaacetic acids. *Ukrainian Chemistry Journal*. 2009. **75** (4): 75–79.

24. Petrik V.I. *Anti-Stokes compounds and materials based on them*. (Irkutsk: Regional Printing House №1. 2012: 400) ISBN 978-5-4337-0001-09. [in Russian].
25. Zherdeva V.V., Savitsky A.P. Application of lanthanide inductive resonance energy transfer in the study of biological processes *in vitro* and *in vivo*. *Biological chemistry reviews.* 2012. **52**: 315–362. [in Russian].
26. Ptaszynski B., Zwolinska A. Synthesis and properties of solid complexes of lanthanum, cerium, neodymium and erbium with N-phosphonomethylglycine. *Polish Journal of Environmental Studies,* 2001. **10** (4): 257–262.
27. R. Pangunoori, K. Ram Rare Earth Metal Complexes of N-Phosphonomethyl Glycin. *Asian J. Chem*. 1995. **7** (1): 223–229.
28. Legendziewicz J., Gawryszewska P., Gałdecka E., Gałdecki Z. Novel polynuclear compound of europium with N-phosphonomethylglycine: spectroscopy and structure. *Journal of alloys and compounds*. 199). **275**: 356–360.
29. Mao J.G. Structures and luminescent properties of lanthanide phosphonates. *Coordination chemistry reviews*. 2007. **251** (11–12): 1493–1520. https://doi.org/10.1016/j.ccr.2007.02.008.
30. Tang S.F., Song J.L., Mao J.G. Syntheses, Crystal Structures, and Characterizations of a Series of New Layered Lanthanide Carboxylate-Phosphonates. *Eur. J. Inorg. Chem*. 2006.
31. Tang S.F., Song J.L., Li X.L., Mao J.G. Luminescent lanthanide (III) carboxylate– phosphonates with helical tunnels. *Crystal growth & design*. 2006. **6** (10): 2322–2326.
32. Trunova O.K., Mazurenko E.A., Rogovtsov A.A., Makotryk T.A. Technological basis forthe synthesis of biologically active complexone based on succinic acid. *Voprosy Khimii i Khimicheskoi Tekhnologii.* 2001. (4): 28.
33. Kostromina N.A. Intramolecular hydrogen bonds in complexones and their role in the formation of complexes with metals. *Theoretical and Experimental Chemistry*. 1991. (3): 280–285.
34. Shkolnikova L.M., Poray-Koshits M.A., Dyatlova N.M. Investigation on coordination number and geometrical conformation of rare earth complexes with catenulate aminopolycarboxylic acid ligands. The role of hydrogen bonds. *Problems of Crystal Chemistry*. 1986. M.: Science, 32–87). [in Russian].
35. Trunova O.K. Biologically active complexes of ethylenediaminedisuccinic acid with 3d-metals. (Synthesis, structure, properties). Doctoral (Chem.) Thesis. 2012. Kyiv. [in Ukrainian].
36. Bünzli J.-C., Eliseeva S. Lanthanide NIR luminescence for telecommunications, bioanalyses and solar energy conversion. *J. Rare Earths.* 2010. **28** (6): 824–842. https://www.sciencedirect.com/science/article/abs/pii/S1002072109602088.
37. Kang U., Dymshits O.S., Zhilin A.A., Chuvaeva T.I., Petrovsky G.T. Structural states of Co (II) in β-eucryptite-based glass-ceramics nucleated with ZrO_2. *Journal of non-crystalline solids*. 1996. **204** (2): 151–157. https://doi.org/10.1016/S0022-3093(96)00411-5
38. Gruzdev N.B., Sokolov V.I., Yemelchenko G.A. Donor exciton of cobalt and its interaction with lattice vibrations in ZnO:Co semiconductor crystals. *Fizyka Nyzkykh Temperatur*. 2009. **35** (1): 109–115. https://doi.org/10.1063/1.3064915. [in Russian].
39. Trunova O.K., Sliusarchuk L.I., Shtokvysh O.O., Makotryk T.O. Crystal structure and spectral properties of the heterometallic 3d-4f complex of gadolinium(III) – cobalt(II) with ethylenediamine-N,N,N′,N′-tetraacetic acid. *J. Molecular Structure.* 2023. **1285:** 135302. https://doi.org/10.1016/j.molstruc.2023.135302.

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