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SYNTHESIS, CHARACTERIZATION, AND LUMINESCENT PROPERTIES OF EUROPIUM(III) COMPLEXES WITH SALEN-TYPE LIGANDS CONTAINING 1,2,4-TRIAZOLE MOIETIES.

Valeriia S. Halushchenko[1,2*], Oleksandr Yu. Korovin[1], Serhii S. Smola[1], Yurii S. Bibik[3], Dmytro M. Khomenko[3,4], Roman O. Doroshchuk[3,4], Rostyslav D. Lampeka[3], Natalya V. Rusakova[1]

[1]A.V.Bogatsky Physico-Chemical Institute of the NAS of Ukraine,
86 Lyustdorfska doroga, 65080 Odesa, Ukraine;
[2]Faculty of Chemistry and Pharmacy, Odesa I.I. Mechnikov National University,
2 Dvoryans'ka St, 65082 Odessa, Ukraine;
[3]Department of Chemistry, Taras Shevchenko National University of Kyiv,
64 Volodymyrska st., 01601 Kyiv, Ukraine;
[4]Enamine Ltd. (www.enamine.net),
78 Winston Churchill Street, 02094 Kyiv, Ukraine
[*]e-mail: valeriia.halushchenko@gmail.com

The study presents the synthesis, characterization, and photophysical investigation of novel Ln(III) complexes with 1,2,4-triazole-based Salen-type ligands, focusing on europium-centered optical properties. An optimized synthetic method for Ln(III) complex formation was developed with the use of various salts, solvents, and deprotonating agents, with methanol, triethylamine, and triethyl orthoformate yielding the best results. This approach produced light-yellow crystalline products with a 65–70% yield. Structural characterization through IR spectroscopy and mass spectrometry confirmed coordination by nitrogen and oxygen atoms, as evidenced by shifts in vibrational bands indicative of Eu–N bonds and alterationsin phenolic OH and CO stretching modes. UV-Vis absorption spectra revealed bathochromic shifts, indicating changes in electron density and increased conjugation resulting from complex formation. Upon excitation, the complexes exhibited fluorescence in the 400–500 nm range and phosphorescence in the 450–550 nm range, demonstrating effective energy transfer within the system. The CIE chromaticity coordinates for **EuL1** (x=0,631, y=0,368) and **EuL2** (x=0,603, y=0,396) denote a deep red emission with color purity and correlated color temperature (CCT) values of 2017,94 K and 1720,92 K, respectively, indicating their potential for high-purity red emissions in optoelectronic applications. Lifetime measurements (0,544 ms at 298 K and 0,706 ms at 77 K) indicate non-radiative relaxation processes that may be modulated by local symmetry, as suggested by the distinctive emission splitting in Eu(III) transitions. Emission spectra revealed prominent transitions typical of Eu(III) ions, with extensive splitting indicative of a low-symmetry environment, likely within C_{2v} or C_s point groups. Structural analysis supports a coordination number of 8, suggesting polyhedral arrangements like a bicapped trigonal prism. This synthetic route effectively produces Ln(III) complexes with tunable luminescent properties, revealing key structure-property relationships and enabling tailored red emissions, making these complexes promising precursors for display and lighting technologies.

Keywords: Europium(III), Schiff bases, Salen-type ligands, Complexes, Luminescence.

INTRODUCTION. The unique properties of lanthanide (III) compounds, such as characteristic narrow emission peaks, large Stokes shifts, high luminescence intensity, long lifetimes, and others, provide them advantages over other light emitters. These benefits make the study of Ln(III) complexes increasingly promising with substantial growth in research over recent decades [1–3].

Developers of highly luminescent lanthanide-containing compounds often face the challenge of optimizing sensitization efficiency while minimizing quenching processes. For the first aspect, it is crucial to carefully consider the energy levels of ligand states, charge transfer, and the kinetics of energy migration among these states. Regarding the second aspect, it is essential to avoid energetic vibrations from groups that are either directly associated with the emission ion (the inner coordination sphere) or interact with it at a greater distance through weak interactions (the outer coordination sphere). Although suchweak interactions have long often been overlooked, they constitute a significant portion of all binding interactions and strongly influence energy transfer/quenching processes. Applying these principles is relatively straight forward for lanthanide ions that emit visible light (i.e. Eu(III), Tb(III)), which can exhibit quantum yields exceeding 70%, even in coordination compounds. However, adhering to these principles in coordination compound design is challenging, as organic ligands contain not only O–H and N–H groups, whose vibrations are effective quenchers, but also C–H, C=O, and C=C groups which contribute significantly to the quenching [4–6].

The design of organic ligands is crucial in creating luminescent coordination compounds of Ln(III) with specific topology and desired properties. Research on lanthanide complexes with Schiff bases is motivated by their applications in luminescent probes [7], magnetic resonance imaging [8], and magnetic materials [9]. Among the various types of reagents classified as Schiff bases, compounds of the Salen-group are of particular interest. By condensing (1:2) salicylaldehyde or its derivatives with various diamines, tetradentate N_2O_2 donor Schiff bases are obtained. Consequently, many other N_2O_2 donor ligands based on Schiff bases belonging to the Salen family have been synthesized and characterized, often referred to as Salen-type ligands [10]. The use of polydentate ligands, including Schiff bases prevents the coordination of labile ligand molecules and solvents, while promoting the saturation of the high coordination numbers of lanthanide ions. A new wave of research on Salen complexes is associated with their potential applications in photonics, medical diagnostics and treatment, as well as the development of new functional materials [9–14]. These complexes are often immobilized on inorganic or organic polymer carriers, combined with other materials to enhance or complement their properties, or used as building blocks for creating new supramolecular systems [11–14].

Among organic compounds that serve as N-donor linkers, 1,2,4-triazole and its derivatives attract significant interest due to their functional properties, including various bridging modes, the ability to exhibit intrinsic luminescence, and ease of modification. The introduction of rigid substituents, such as pyridyl and its derivatives with additional donor atoms, creates bi- or tridentate binding sites, enhancing the stability of the resulting complexes through the chelate effect. One of the simplest

and most widely used substituents for this purpose is the 2-pyridyl group, while derivatives of 3- and/or 4-pyridyl have gained researchers' attention only in the past decade [15, 16].

The aim of this work was to establish conditions for the formation of new luminescent lanthanide complexes with a series of functionalized Schiff bases – Salen-type ligands, containing 1,2,4-triazole, and to study their luminescent properties.

EXPERIMENT OF DISCUSSION OF THE RESULTS. Samples for physicochemical studies were prepared by grinding the precipitates of the corresponding compounds, which were aged at a temperature of 90–95°C until a constant mass was achieved.

Electrospray ionization (ESI) mass spectra were recorded using a TSQ Fortis triple quadrupole mass spectrometer (Thermo Fisher Scientific, USA). All spectra were measured for methanol solutions with a complex concentration of approximately 10 μg/cm^3. Isotope distribution patterns were calculated using the online tool at https://www.sisweb.com/mstools/isotope.htm

IR absorption spectra (400–4000 cm^{-1}) of samples pressed with KBr were recorded using a Spectrum BX II FT-IR System spectrophotometer (Perkin – Elmer).

The NMR spectra of the obtained compounds were recorded on a Varian "Mercury 400" instrument in DMSO-d_6 solutions.

Elemental analysis was performed using Perkin – Elmer 2400 CHN Analyzer.

The absorption spectra of the studied complexes were recordedon a ULAB spectrophotometer in the wavelength range of 200–400 nm.

Photoluminescence measurements at room temperature and liquid nitrogen temperature were carried out using a Fluorolog 3–22 spectrofluorometer (Horiba JobinYvon) with a 450 W Xe lamp excitation source. The visible region detector used was a PMT R928P (Hamamatsu, Japan). The excitation and luminescence spectra were corrected to account for the emission distribution of the xenon lamp and the sensitivity of the detectors. The integral luminescence intensity (I_l) was calculated using the Origin Pro 8.5.1 software package.

Oxalohydrazide and salicylic acid imido ester hydrochloride were synthesized as described in [17, 18].

N,N'-dimethyloxalohydrazide was obtained according to the following procedure (Fig. 1):

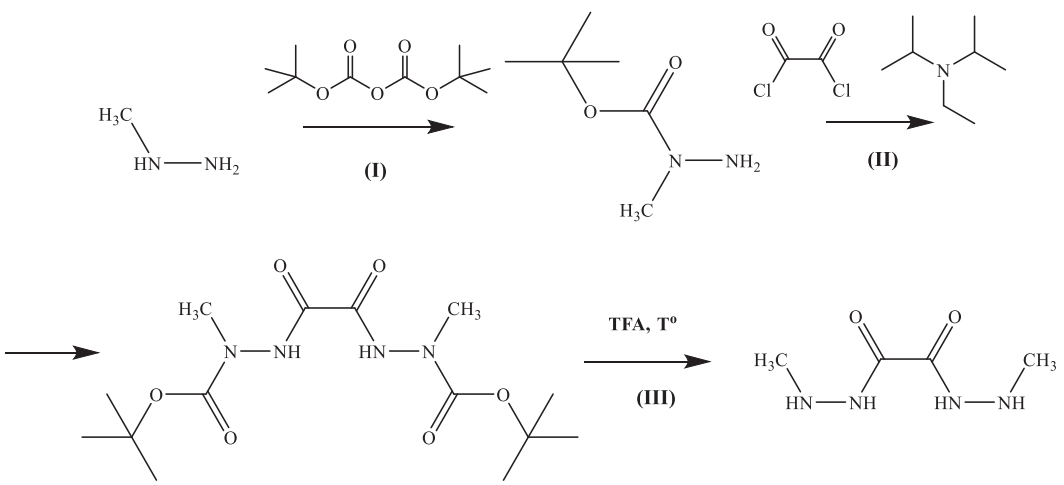


Fig. 1. – Synthesis of N, N'-dimethyloxalohydrazide.

(I) To a cooled (0°C) solution of methylhydrazine (0.1 mol) in dichloromethane (100 ml), a solution of di-tert-butyl dicarbonate (Boc anhydride) (0.1 mol) in dichloromethane (100 ml) was added dropwise. The mixture was stirred for 3 hours at room temperature, the solvent was evaporated, and the residue was distilled (boiling point = 90°C, 20 mm Hg). Yield: 68%.

(II) In a 500 ml three-neck round-bottom flask equipped with a reflux condenser and thermometer, 200 ml of dry dichloromethane was added. Then, 0,5 mol of N-BOC-N-methylhydrazine and 0,5 mol of N,N-diisopropylethylamine (DIPEA, Hunig's base) were added. The mixture was cooled to 0–5°C. To the mixture, 19 ml (0,22 mol) of freshly distilled oxalyl chloride solution in 50 ml of dichloromethane was added dropwise while maintaining the temperature below 5°C. After the addition of oxalyl chloride, the mixture was stirred for 24 hours at room temperature. The solvent was then evaporated, yielding a colorless oil, which crystallized upon stirring with water (1 liter). The white crystalline precipitate was filtered, then refluxed in hexane using a Dean-Stark apparatus for 4 hours and filtered again. Yield: 75%.

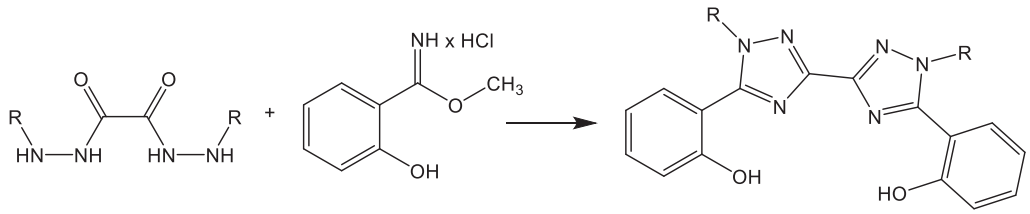
(III) To a solution of disubstituted oxalic acid dihydrazide (0,165 mol, 1 eq.) in dichloromethane, 1,65 mol (10 eq.) of trifluoroacetic acid was added, and the mixture was stirred and refluxed for 24 hours. After cooling, the precipitate formed was filtered, then refluxed in ethanol for 4 hours, and filtered again. Yield: 77%.

1,2,4-triazole-based Salen-type compounds, namely $H_4L^1$2,2'-(1H,1'H-[3,3'-bi(1,2,4-triazole)]-5,5'-diyl)diphenol (**1**) and H_2L^2, 2,2'-(1,1'-dimethyl-1H,1'H-[3,3'-bi(1,2,4-triazole)]-5,5'-diyl)diphenol (**2**) were synthesized using a following method (Fig. 2):

In a 100 ml round-bottom flask, 10 mmol (1 eq.) of grinded oxalohydrazide were placed with 50 ml of methanol. To the resulting suspension, 50 mmol (5 eq.) of salicylic acid imido ester hydrochloride and 50mmol (5 eq.) of triethylamine were added. The reaction mixture was refluxed with stirring for 36 hours. The resulting precipitate of the ligand was filtered and washed with methanol.

For $\mathbf{H_4L^1}$, yield 55%; ^{1}HNMR: (400 MHz, DMSO-d_6), δ 14,52 (br, 2H); 11,24 (br, 2H); 8,04 (d, 2H); 7,39 (t, 2H); 7,06 (d, 2H); 7,02 (t, 2H). For $\mathbf{C_{16}H_{12}N_6O_2}$ (MW = 320,31 g/mol): Anal. calc.(%):C60,00, H3,78, N26,24. Found (%): C59,36, H3,89, N27,2. Melting point = 286 °C with decomposition; white powder, soluble in DMF, poorly soluble in MeOH, insoluble in most organic solvents.

For $\mathbf{H_2L^2}$, yield 46%; ^{1}H NMR: (400 MHz, DMSO-d_6), δ 10,48 (s, 2H); 7,47 (d, 2H); 7,41 (t, 2H); 7,06 (d, 2H); 6,99 (t, 2H); 3,85 (s, 6H). For $\mathbf{C_{18}H_{16}N_6O_2}$(MW = 348,36 g/mol): Anal. calc.(%): C62,06, H4,63, N24,12. Found (%): C61,74, H4,29, N23,99. Melting point> 255 °C with decomposition; white powder, soluble in DMF, poorly soluble in MeOH, insoluble in most organic solvents.



R = H for H_4L^1; CH_3 for H_2L^2

Fig. 2. – General route for the synthesis of the ligands.

A method for the synthesis of Ln(III) complexes was developed, testing various Ln(III) salts (acetates, nitrates, and chlorides), different solvents (alcohols, DMF, DMSO), conditions such as temperature, reagent ratios, deprotonating agents (triethylamine, ammonia). It was determined that the complexes are formed effectively through the reaction of lanthanide acetates in methanol in the presence of triethylamine and triethyl orthoformate. Typically, 0,5 mmol of Ln(III) acetate and 0,5 mmol of H_4L^1 (or H_2L^2) were placed in a 250 cm^3 round-bottom flask with approximately 100 cm^3 of MeOH. Then, about 1 cm^3 of triethylamine and a few drops of triethyl orthoformate were added. The mixture was refluxed until the reagents were fully dissolved (3–4 hours). Next, the solution was filtered through filter paper, evaporated to 1/3 of its volume, and left to cool in air. The following day, a light-yellow fine crystalline precipitate was observed, which was separated from the mother liquor by decantation. Yield was in the range of 65–70%. Thus, **Ln1** and **Ln2** (Ln = Eu, Lu) were synthesized.

The isolated compounds were characterized by means of elemental analysis, FTIR spectroscopy and mass spectrometry methods. In the mass spectrum of the Eu(III) complex with H_4L^1 (Fig. 3), signals for fragmented ion with m/z 563,23 and 561,22 were observed, identified as $[Eu(H_2L^1)(AcO)(MeOH)]$; signals with m/z 490,17 and 488,18 were identified as $[Eu(H_2L^1)(H_2O)]$. The 2,0 m/z difference between the described peaks can be attributed to the presence of Eu(III) isotopes with m = 151 and 153.

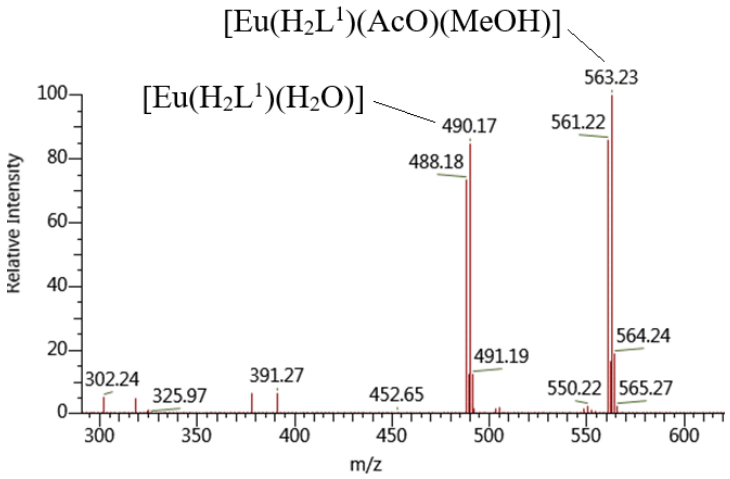


Fig. 3 – ESI mass spectra of Eu(III) complex with H_4L^1.

The IR spectra analysis for both Eu(III) complexes (Fig. 4) reveals consistent coordination features and shifts compared to their respective free ligands, providing insights into complexation behavior. In the spectrum of H_4L^1, a broad band at 3419 cm^{-1} is observed corresponding to O–H stretching of phenolic groups, involved in hydrogen bonding. In the spectrum of **Eu1** multiple bands appear in the 3500–3400 cm^{-1} region, suggesting interactions between Eu(III) ion and coordinated water/methanol molecules. The bands around 1603 cm^{-1}, 1569 cm^{-1}, and 1537 cm^{-1} in the spectrum of **Eu1** are strong, indicating coordination interactions af-

fecting the C=O/C=N vibrations and possibly involving acetate. Specifically, the 1569 cm^{-1} and 1537 cm^{-1} bands suggest asymmetric stretching of the C=O groups in the acetate. The presence of these bands close to 1569 cm^{-1} supports bidentate coordination of the acetate to Eu(III) [19]. Strong bands at 1603 cm^{-1} (complex) and 1622 cm^{-1} (free H_4L^1) region are likely due to C=N stretches of the triazole and aromatic groups. This slight shift upon complexation indicates Eu(III) coordination affects electron density in the ligand, altering C=N bonding character. The bands at 1413 cm^{-1} and 1398 cm^{-1} in the spectrum of **Eu1** suggest the C–O stretch of the phenolic group, shifting slightly compared to the free ligand (1410 cm^{-1}, 1399 cm^{-1}). The shift and retention of the intensity suggest the Eu(III) complexation impacts these bonds, potentially involving O-phenolic coordination.

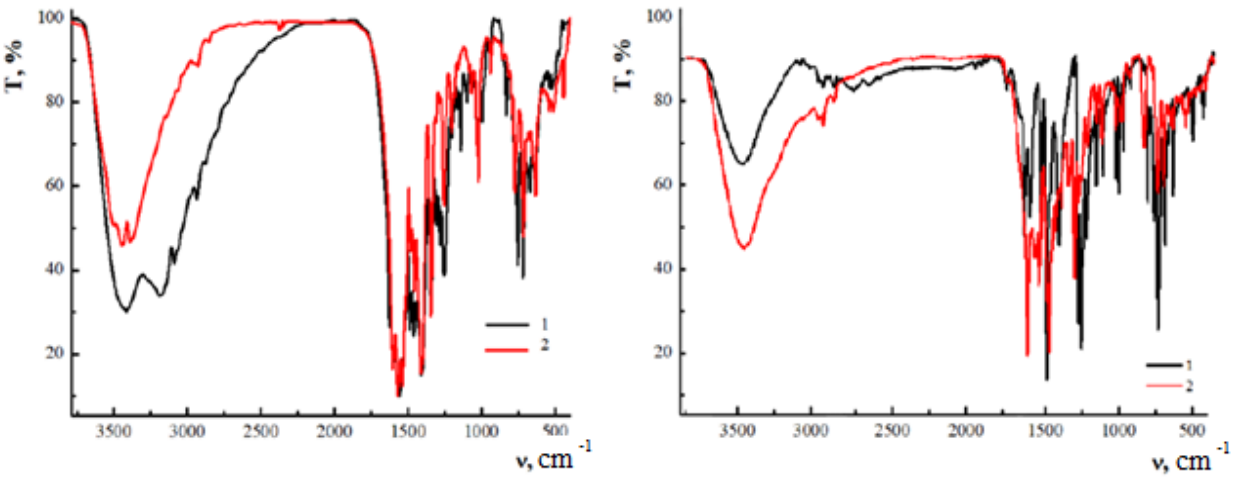


Fig. 4. – IR spectra of compounds (a: 1 – H_4L^1, 2 – **EuL**^{1}, b: 1 – H_2L^2, 2 – **EuL**^{2}) in comparison with the corresponding free ligands.

Bands around 1481 cm^{-1} (**Eu1**) and 1456 cm^{-1} in both spectra correspond to C=C stretches of aromatic rings, with no significant shifts, indicating limited Eu(III) influence on these bonds. The complex's additional bands (e.g., at 512 cm^{-1} and 444 cm^{-1}) can be attributed to Eu–O and Eu–N coordination, which are absent in the free ligand.

In the spectrum of H_2L^2, a medium band at 3448 cm^{-1} indicates O–H stretching, likely from hydrogen-bonded phenolic groups. In the spectrum of **Eu2** complex, a strong band appears at 3442 cm^{-1}, indicating the presence of coordinated water and methanol as in the case of **Eu1**.

A medium band at 1624 cm^{-1} in the spectrum of H_2L^2 can be attributed to C=N stretching in the triazole or aromatic system. In the spectrum of the complex, this band shifts to 1604 cm^{-1} and increases in intensity, suggesting coordination between Eu(III) ion and nitrogen atoms, possibly altering the electron density and stretching mode. In the spectrum of **Eu2** complex, the bands at 1558 cm^{-1} and 1548 cm^{-1} represent the C=O stretching modes of acetate-ion. The appearance of these two bands

points to a bidentate coordination of the acetate to Eu (III) ion, as the two C=O bonds are now involved in binding, altering their stretching behavior. Additionally, a strong band at 1462 cm^{-1} in the complex further indicates asymmetric stretching in the C–O of acetate, reinforcing the bidentate mode.

The bands in the 1590–1580 cm^{-1} range of medium intensity for H_2L^2 shift to 1558–1548 cm^{-1} in the complex. This shift suggests that C=N in the triazole ring are impacted by Eu(III) coordination. A strong band at 1480 cm^{-1} in both spectra represents C=C stretching in the aromatic rings, which remains strong, indicating that Eu(III) does not significantly impact these aromatic bonds.

A medium band at 1403 cm^{-1} in H_2L^2 shifts to 1420 cm^{-1} in the complex, suggesting a C–O stretch, likely from phenolic groups, indicating involvement in coordination with Eu(III). Bands around 1277 cm^{-1} and 1257 cm^{-1} in H_2L^2 also shift to 1299 cm^{-1} and 1274 cm^{-1} in the complex, suggesting C–O vibrations affected by complexation. The complex introduces weak bands at 451 cm^{-1} and 580 cm^{-1}, likely representing Eu–O and Eu–N vibrations, which do not appear in the free ligand, as in the case of **Eu1.** Thus, the detailed analysis of the IR spectra indicate the formation of stable Eu(III) complexes with bidentate acetate coordination, and coordination via triazole nitrogen and phenolic oxygen atoms, complemented by coordinated water and methanol molecules.

Based on the obtained experimental data and considering similar complexes described in the literature, the structure of the synthesized Eu(III) complexes was proposed (Fig. 5).

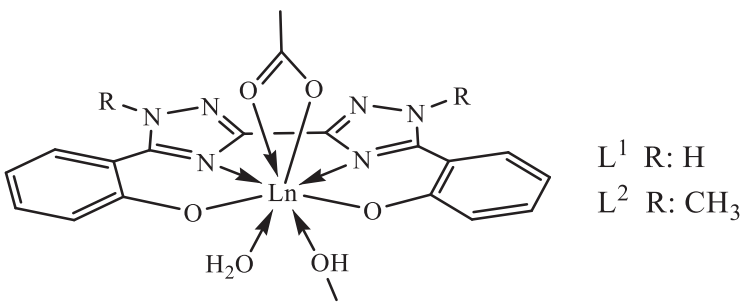


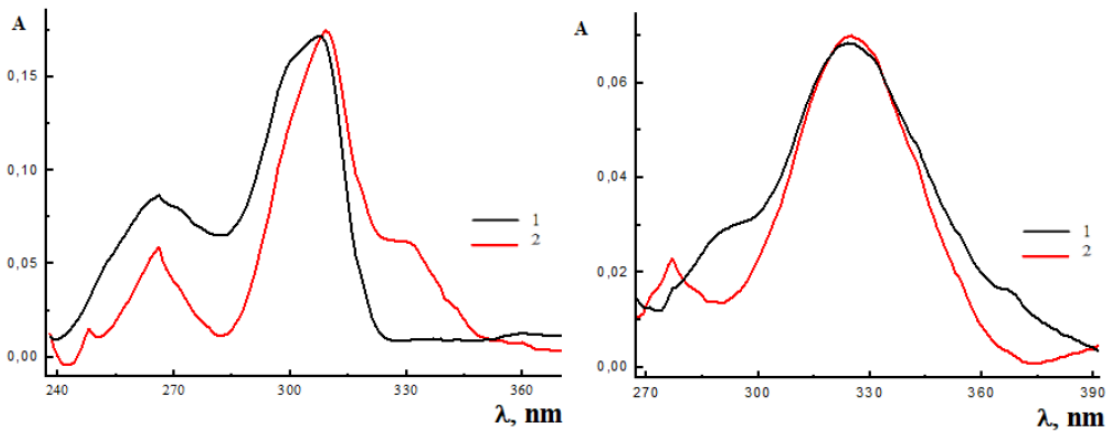
Fig. 5. – Schematic structure of synthetized complexes (Ln = Eu(III), Lu(III)).

In the complex **Ln1**, the coordination polyhedron of the central atom includes two nitrogen atoms from the 1,2,4-triazole groups, two oxygen atoms from the phenolic groups of the ligand, and one oxygen atom from the acetate ion. The structure of the complexes **Ln2** is similar to that of **Ln1**. It should be noted that the exact number of coordinated solvent molecules has not been precisely determined; however, according to mass spectrometry data, one or two labile molecules appear to be coordinated, which exchange occurring between MeOH and H_2O.

The absorption spectra of the compounds H_4L^1 and H_2L^2 (Fig. 6) were analyzed in methanol solutions at concentrations ranging from 1×10^{-4} to 10^{-5} M. These compounds are characterized by broad double bands with maxima in the range of 265–270 nm and 300–330 nm, resulting from the overlap of $\pi\rightarrow\pi^*$

and n→π* transitions within the conjugated systems of the benzene and 1,2,4-triazole rings [20]. Methylation of the nitrogen atom in the 1,2,4-triazole rings results in a bathochromic shift (Δλ = 20 nm) of the maxima of the first absorption band with minimal change in its intensity, which may indicate the involvement of the phenolic rings in the formation of intramolecular hydrogen bonds, specifically -O-H···N. These hydrogen bonds restrict the rotation of the phenolic rings [21]. Furthermore, the compound H_2L^2 exhibits higher extinction than H_4L^1.

The complexation of Ln(III) with the H_4L^1 and H_2L^2 ligands leads to a slight bathochromic shift (Δλ = 2–7 nm) of the absorption band maxima in the 300–330 nm region, which can indeed indicate coordination of the nitrogen atoms in the 1,2,4-triazole groups and the oxygen atoms in the phenolic groups of the ligand. Such a bathochromic shift is typical for processes associated with increased conjugation efficiency or changes in electron density within the system, which often occur during the coordination of metals with nitrogen- and oxygen-containing donors. This effect can be explained by shifts in the energy levels of the ligand's electronic orbitals upon coordination, leading to a change in the position of the absorption bands in the spectrum [20–24].



a b

Fig. 6. – Absorption spectra of the compounds
(a: 1 – H_4L^1 2 – **Eu1**; b: 1 – H_2L^2 2 – **Eu2**, DMF, C = 1×10^{-4}M).

The molecular luminescence spectral profile of Lu(III) complexes is similar across all ligands and features a broad band in the 400–550 nm range, likely attributed to π-π* transitions with in the ligand structure. Similar bands with a slight blue shift are observed in solutions (Fig. 7).

The alignment of the energy levels of the ligand (singlet S_1 and triplet T_1) and the excited states of Ln(III) ions is a key factor in ensuring the efficiency of luminescence in lanthanide complexes [1, 2]. In these complexes the energy level of the singlet state of the ligands is 22124 cm^{-1} for **Lu1** and 24510 cm^{-1} for **Lu2**. According to the provided data, the energy of the lowest lying triplet state for both **Lu1** and **Lu2** is 21008 cm^{-1}, as determined from the maximum wavelength of the phosphorescence band (Fig. 7).

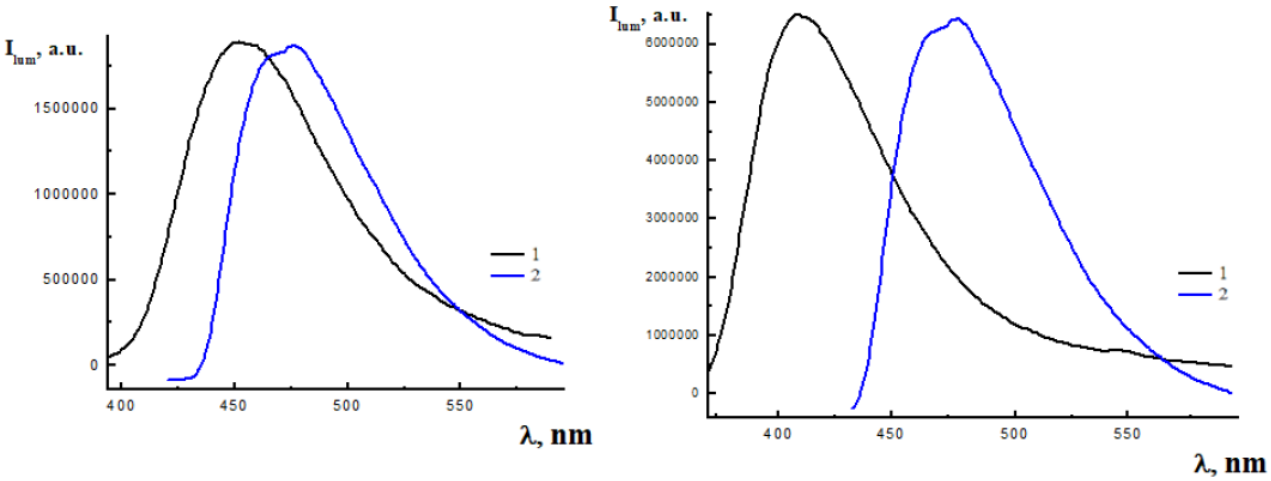


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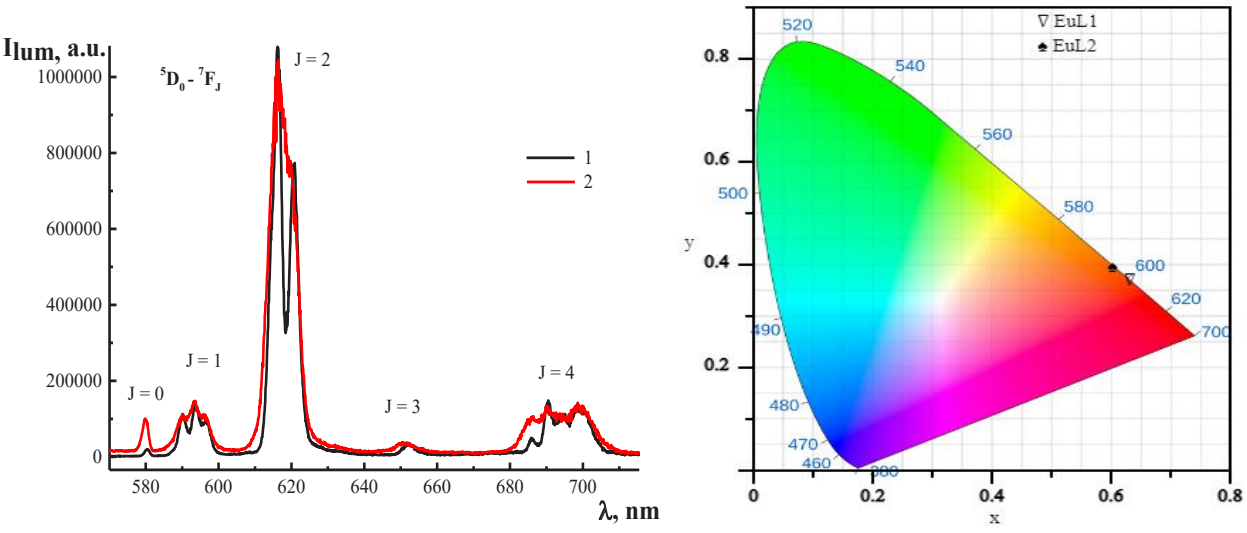
Fig. 7. – Fluorescence (1) and phosphorescence (2) spectra of **Lu1** (a) and **Lu2** (b).

Luminescence of the europium complexes was observed in DMF solutions and in crystalline samples at both room temperature and liquid nitrogen temperature (Fig. 8). Previous studies indicate that the absorption and excitation spectra of 4f-luminescence coincide, which is supports the presence of intramolecular energy transfer from the excited electronic levels of the ligands to the emitting level of the Eu(III) ion.



a b

Fig. 8. – 4f-Luminescence spectra of the complex **Eu1** at 298 K
(for crystalline samples – 1 and solutions in DMF – 2)(a) and CIE chromaticity diagram 1931 (b).

The CIE coordinates for the Eu-centered emission were calculated, placing both **Eu1** and **Eu2** in the red region of the CIE 1931 chromaticity diagram [25]. For **Eu1,** coordinates x=0,631 and y= 0,368 indicate a deep red emission, representing a rich, saturated red light. The coordinates for **Eu2** are 6x = 0,603 and y = 0,396, also fall within the red region but are slightly shifted toward a warmer hue compared to **Eu1**. This shift may result from differences in the ligand field or subtle variations in coordination symmetry, affecting the precise emission profile of the Eu(III) ion and slightly altering the hue.

The correlated color temperature (CCT) values provide additional context on the warmth of the emitted light. For **Eu1, a** CCT of 2017,94 K indicates a warm, intense red light with low color temperature, consistent with deep red region. Such a CCT is typical for narrow red emissions, often desirable in applications like red phosphors for LEDs that require pure red chromaticity. **Eu2,** with a slightly lower CCT of 1720,92 K, produces a warmer and deeper red emission than **Eu1**. The lower CCT aligns with the slight shift in CIE coordinates, indicating that emission of **Eu2** is perceptibly warmer, likely due to subtle structural differences that influence the Eu(III) electronic environment.

Table 1.

Luminescent characteristics of Eu(III) complexes.

Complex	η $(^5D_0\text{-}^7F_2)/(^5D_0\text{-}^7F_1)$		τ, ms				φ_{em},	Φ, %
			DMF		solid			
	DMF	solid	298K	77K	298K	77K	DMF	solid
Eu1	7,6	7,1	0,533	0,549	0,544	0,706	0,023	29,7
Eu2	7,9	7,5	0,563	0,584	0,575	0,685	0,019	26,7

The luminescence decay curves of the complexes were analyzed and fitted with single exponential decay law (Table 1). The shorter lifetime at room temperature (0,544 ms) suggests the presence of non-radiative decay pathways, consistent with a coordination environment that facilitates vibrational relaxation processes. The increase in lifetime at low temperatures (0,706 ms at 77K) is typical, as non-radiative processes are suppressed at lower temperatures. This behavior suggests a somewhat open coordination structure with lower symmetry, allowing for more vibrational coupling and therefore non-radiative decay at higher temperatures [26].

The emission spectrum of the Eu(III) complex provides insight into its coordination environment, revealing information on local symmetry, coordination number, and the point symmetry group of the Eu(III) center [27]. The luminescent profile of the Eu(III) complex in the solid state at 77K (Table 2) shows characteristic emissions in the visible region, with well-resolved transitions from the excited $^5D_0$ state to various ^7F_J ground-state levels. Key observed transitions include the following: $^5D_0 \rightarrow {}^7F_0$ as a single, sharp peak at 580,0 nm; $^5D_0 \rightarrow {}^7F_1$ as three peaks at 590,0, 593,2, and 595,8 nm, indicating splitting due to lower symmetry around the Eu(III) center;

$^5D_0 \rightarrow ^7F_2$ as four distinct peaks at 614,7, 615,4, 616,2, and 619,8 nm, corresponding to the hypersensitive electric dipole transition and suggesting a non-centrosymmetric environment. Higher-order transitions $^5D_0 \rightarrow ^7F_3$ and $^5D_0 \rightarrow ^7F_4$ exhibit even more splitting: the $^5D_0 \rightarrow ^7F_3$ transition shows five peaks (647,7, 649,6, 650,8, 651,7, and 653,6 nm), and the $^5D_0 \rightarrow ^7F_4$ transition shows seven peaks (684,8, 686,1, 690,0, 692,6, 694,2, 698,5, and 700,0 nm), indicating a high degree of asymmetry in the ligand field. It should be noted that in DMF solutions, the profile of band splitting is consistent with that observed in solid state, indicating structural identity in both crystalline and solution phases.

Table 2.

Splitting of bands in the emission spectrum of Eu1 complex.

Measurement conditions		λ_{max}, nm				
		$^5D_0 \rightarrow ^7F_0$	$^5D_0 \rightarrow ^7F_1$	$^5D_0 \rightarrow ^7F_2$	$^5D_0 \rightarrow ^7F_3$	$^5D_0 \rightarrow ^7F_4$
solution (DMF)	298K	580,0	590,8 593,9	616,0 620,0	651,0 657,0	687,0 691,1 699,0
	77K	579,8	590,0 593,2 595,8	614,7 615,4 616,2 619,8	647,7 649,6 650,8 651,7 653,6	684,8 686,1 690,0 692,6 694,2 698,5 700,0
crystal	298K	580,2	590,0 593,5 596,4	614,3 616,1 620,4	651,0 652,3	685,9 690,5 694,6 698,5 700,2
	77K	580,3	590,1 593,6 596,5	614,5 616,2 620,2 620,8	649,1 650,4 651,8 652,4 653,3	685,8 690,5 693,9 694,5 697,1 698,5 700,4

Given the observed high asymmetry and distinctive splitting patterns, the coordination polyhedron around Eu(III) likely has a coordination number (CN) of 8 or 9. This CN is typical for polyhedra with low symmetry such as a bicapped trigonal prism (CN=8) or tricapped trigonal prism (CN=9). The symmetry type appears to be low, likely C_s or C_{2v}, based on the pronouncedsplitting and high η intensity ratio $(^5D_0\text{-}^7F_2)/(^5D_0\text{-}^7F_1)$. These point groups lack a center of inversion, which explains the enhanced electric dipole transitions.

CONCLUSIONS. An optimized synthesis protocol was developed for Ln(III) complexes with 1,2,4-triazole-based Salen-type ligands using various salts, solvents, and deprotonating agents. Through the use of lanthanide acetates in methanol with triethylamine and triethyl orthoformate, crystalline Ln(III) complexes were obtained with high yields (65-70%). Characterization by IR and mass spectrometry confirmed the formation of specific coordination structures, including Eu(III)-centered complexes with triazole and phenolic groups, involving coordination of multiple N and O donor atoms from the ligand and acetate groups. The IR and absorption spectra revealed substantial shifts upon complex formation, consistent with effective coordination of Eu(III) by nitrogen and oxygen donors, and indicating changes in electronic conjugation. Eu(III) complexes exhibited luminescence with intense red emission. The luminescence lifetimes indicated the presence of non-radiative pathways at higher temperatures, which aligns with an open, lower symmetry coordination environment. Emission spectra analysis at low temperatures revealed significant splitting in the Eu(III) transitions, consistent with a low-symmetry coordination polyhedron, likely in a bicapped or tricapped trigonal prismatic arrangement with C_s or C_{2v} point group symmetry. This is supported by the intensity ratio and emission profile. The study establishes a foundation for further exploration of these complexes in applications requiring controlled luminescence properties. The CIE coordinates and CCT values highlight their potential as high-purity red-emitting complexes with desirable color characteristics for optoelectronic and photonic applications, with **Eu2** exhibiting a slightly redder and warmer tone than **Eu1**.

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СИНТЕЗ, ХАРАКТЕРИСТИКА ТА ЛЮМІНЕСЦЕНТНІ ВЛАСТИВОСТІ КОМПЛЕКСІВ ЄВРОПІЮ (III) З ЛІГАНДАМИ SALEN-ТИПУ, ЩО МІСТЯТЬ 1,2,4-ТРИАЗОЛЬНІ ФРАГМЕНТИ

Валерія С. Галущенко[1,2], Олександр Ю. Коровін[1], Сергій С. Смола[1], Юрій С. Бібік[3], Дмитро М. Хоменко[3,4], Роман О. Дорощук[3,4], Ростислав Д. Лампека[3], Наталя В. Русакова[1]

[1]Фізико-хімічний інститут ім. О. В. Богатського НАН України,
Люстдорфська дорога, 86, 65080 Одеса, Україна;
[2]Факультет хімії та фармації Одеського національного університету ім. І. І. Мечникова, вул. Дворянська, 2, Одеса 65026, Україна;
[3]Хімічний факультет Київського національного університету імені Тараса Шевченка, вул. Володимирська, 60, Київ 01601, Україна;
[4]ТОВ «НВП «Єнамін»(www.enamine.net), вул. Вінстона Черчилля, 78, Київ 02094, Україна
[*]e-mail: valeriia.halushchenko@gmail.com

У роботі представлено синтез, характеристику та фотофізичне дослідження нових комплексів Ln(III)з лігандами Salen-типу на основі 1,2,4-триазолу, зокрема оптич-

ні властивості комплексів з європієм. Було оптимізовано метод синтезу для утворення комплексів Ln(III) з використанням різних солей, розчинників та депротонуючих агентів, серед яких найефективнішими виявилися метанол, триетиламін та триетилортоформіат. Це дозволило отримати світло-жовті кристалічні продукти з виходами 65–70%. За допомогою ІЧ-спектроскопії та мас-спектрометрії охарактеризовано координацію через атоми азоту та кисню, що підтримується зсувами в коливальних смугах, які вказують на зв'язки Eu–N та зміни в коливаннях фенольних груп OH і C=O. Спектри поглинання в УФ-видимій області продемонстрували батохромний зсув, вказуючи на змінену густину електронів і підвищену кон'югацію через комплексоутворення. Під час збудження комплекси проявляли флуоресценцію в діапазоні 400–450 нм і фосфоресценцію в діапазоні 450–550нм, що вказує на ефективну передачу енергії в системі. Кольорові координати CIE для **Eu1** (x=0,631, y=0,368) та **Eu2** (x=0,603, y=0,396) вказують на насичене червоне випромінювання з високою чистотою кольору та значеннями корельованої колірної температури (CCT) 2017,94K та 1720,92K відповідно, що робить їх придатними для чисто-червоного випромінювання в оптоелектронних засобах. Вимірювання часу життя (0,544 мс при 298 K та 0,706 мс при 77 K) вказують на наявність безвипромінювальних релаксаційних процесів, які потенційно модулюються локальною симетрією, що підтверджується характерним розщепленням ліній випромінювання переходів Eu(III). Спектри випромінювання продемонстрували виразні переходи, типові для іонів Eu(III), з інтенсивним розщепленням, що вказує на низькосиметричне середовище, ймовірно, у точкових групах C_{2v} або C_s. Структурний аналіз вказує на координаційне число 8, припускаючи поліедральні конфігурації, такі як дво- або тришапкову тригональну призму. Цей метод синтезу ефективно дозволяє отримати комплекси Ln(III) з керованими люмінесцентними властивостями, виявляючи ключові залежності структура – властивість і забезпечуючи спрямоване червоне випромінювання, що робить ці комплекси перспективними для застосування в дисплеях та освітлювальних технологіях.

Ключові слова: європій(III), основи Шиффа, ліганди Salen-типу, комплекси, люмінесценція.

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