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**SYNTHESIS OF Pr(III), Sm(III) AND Eu(III) COMPLEXES WITH 3-METHYL-4-(5-METHYL-1-PHENYL-1H-1,2,3-TRIAZOLE-4-CARBONYL)-1-PHENYL-1H-PYRAZOL-5(4H)-ONE AND THEIR LUMINESCENCE PROPERTIES**

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The formation conditions and the spectral-luminescent properties of Pr(III), Sm(III) and Eu(III) complexes with 3-methyl-4-(5-methyl-1-phenyl-1H-1,2,3-triazole-4-carbonyl)-1-phenyl-1H-pyrazol-5(4H)-one (L), as well as the properties of the mixed-ligand complexes containing neutral ligands, such as 1,10-phenanthroline, trioctylphosphine oxide and triphenylphosphine oxide, have been studied.

*Key words:* lanthanides, 4-carbonylpyrazolones, 1H-1,2,3-triazole, photoluminescence.

Lanthanide (Ln) complexes with 4-acyl-pyrazole-5-ones, which are heterocyclic analogs of  $\beta$ -diketones, have aroused a great interest recently due to their ability of using them mainly as fluorescent materials. Moreover, some of Nd(III), Yb(III) and Er(III) complexes irradiate in the infrared range of the spectrum [1–5].

The 4-acyl-pyrazole-5-ones as well as  $\beta$ -diketones are characterized by keto-enol tautomerism. The value of  $pK_a$  of the enol form is different for the known  $\beta$ -diketones (acetylacetone, benzoylacetone, trifluoroacetylacetone, etc.) and such ligands are weaker. Thus, if the  $pK_a$  value is 13.75 for dibenzoylmethane, then  $pK_a$  for 1-phenyl-3-methyl-4-benzoylpyrazole-5-one equals 2.95 [6].

In the known complex compounds acylpyrazolones are bidentate ligands for Ln(III) and coordinate with the central metal atom by two oxygen atoms. Typically, the coordination number of the Ln(III) ion with acylpyrazolone is 8, but it may be 7, depending on the volume of substituent near the coordination centre. The Ln(III) ion is coordination unsaturated and can also attach a water molecule or an organic solvent (for example, ethanol, tributyl phosphate) or the second ligand – 1,10-phenanthroline (Phen), triphenylphosphine oxide (TPPO), trioctylphosphine oxide (TOPO), etc. Neutral ligands stabilize the complex structure, and depending on the energy of the triplet level they may participate in the intramolecular excitation energy transfer to the ion Ln(III). It is known [7], that the luminescence intensity of the mixed ligand complexes (MLC) containing, except the acylpyrazolone, an additional ligand increases by several times.

In this work, we have studied the conditions of the synthesis and spectral-luminescent properties of Pr(III), Sm(III) and Eu(III) complexes with the synthesized acylpyrazolone, as well as the possibility of their luminescence intensity increasing by introduction of additional (neutral) ligands.

Acylpyrazolones as structural analogs of  $\beta$ -diketones, in the deprotonated form of the enol, form stable complexes with Ln(III) ions [7, 8]. Moreover, by the intensity of the bands, corresponding to hypersensitive transitions (HST) –  $^5D_0 \rightarrow ^7F_2$  (Eu),  $^4G_{5/2} \rightarrow ^6H_{9/2}$  (Sm) and  $^3P_0 \rightarrow ^3H_6$  (Pr), the optimal pH of formation of Ln(III) complexes, the ratio of the components in complexes and other characteristics were determined.

Using acetate-ammonia buffer solutions, the optimal pH values for the formation of lanthanide complexes with acylpyrazolone (L) were established. For Pr(III) complexes solution pH value is 4.5, for Sm(III) – pH 7.0 and Eu(III) – pH 8.0 correspondingly. The ratio of the components in the complex is Ln:L = 1:1. The determined values of the lower energy singlet  $E_{S1} = 19050 \text{ cm}^{-1}$  and triplet  $E_{T1} = 18180 \text{ cm}^{-1}$  ligand L states indicate the possibility of using it to observe the luminescence in the visible range for the complexes with only those lanthanides (III), which irradiating energy levels are below the  $E_{T1}$  (L), that was shown on Figure 1.

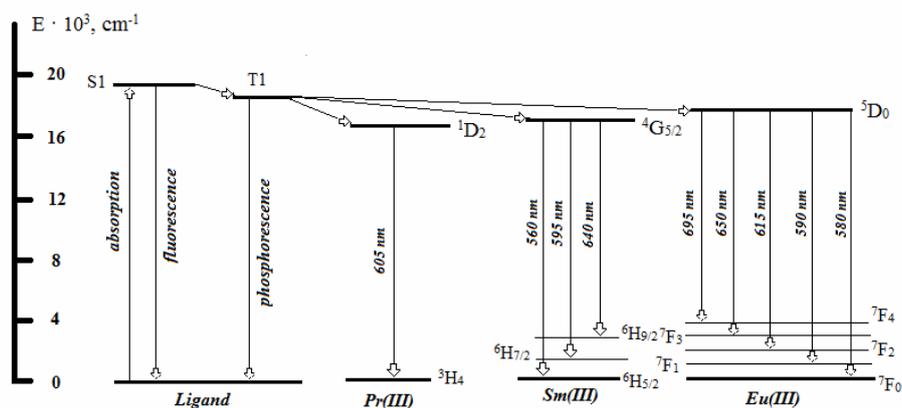


Fig. 1. Energy transfer mechanism between organic donor and lanthanide (III) ions.

For Pr(III) energy  $E(^1D_2)$  equals  $17337 \text{ cm}^{-1}$  ( $\lambda_{lum.} = 605 \text{ nm}$ ), Sm(III) –  $E(^4G_{5/2}) = 17924 \text{ cm}^{-1}$  ( $\lambda_{lum.} = 645 \text{ nm}$ ) and Eu(III) –  $E(^5D_0) = 17264 \text{ cm}^{-1}$  ( $\lambda_{lum.} = 615 \text{ nm}$ ), to which intramolecular energy transfer from the excited  $T_1$  ligand level is possible. The proximity of emitting levels of Ln(III) and  $T_1$  of the ligand presumes not only the possibility of direct  $L \rightarrow Ln(III)$ , but also inverse  $Ln(III) \rightarrow L$  energy transfer, which leads to non-radiative losses of energy and decrease of the luminescence intensity[9]. Excitation and luminescence spectra of Eu(III) acylpyrazolonate at two wavelengths of the exciting radiation are presented in Fig. 2.

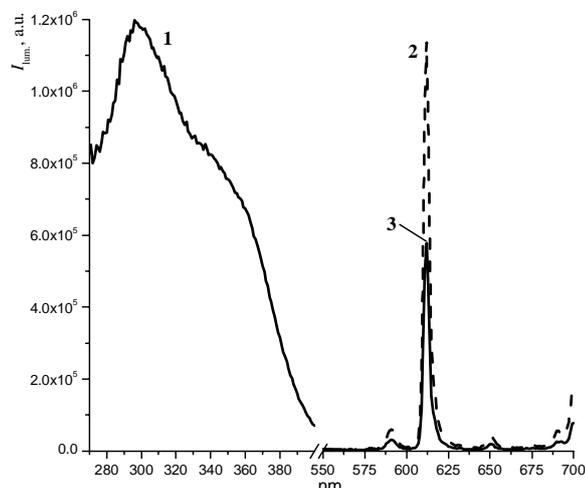


Fig. 2. Excitation ( $\lambda_{lum.} = 612$  nm) - 1 and luminescence spectra - 2 ( $\lambda_{ex.} = 298$  nm) and 3 ( $\lambda_{ex.} = 365$  nm) of the EuL complex in solution.

As a result of the coordination unsaturation, Ln(III) ions in most cases attach to the metal ion water molecules (“OH-oscillators”) which are strong luminescence quenchers. To eliminate such influence the introduction of organic solvents or second ligands was used [7]. The study of solvents influence – THF,  $C_2H_5OH$ , acetonitrile, DMF, and DMSO showed that only in the presence of 10% vol. DMF complex the EuL radiation intensity increases by 1.5 times (Table 1). Increase of solvent concentration in all cases caused the decrease of luminescence intensity of complexes in consequence of their destruction.

Table 1

Influence of the organic solvents on the luminescence intensity of Pr(III), Sm(III) and Eu(III) complexes.

| Complex | $I_0$ , a.u. without solvent | Solvent    |      |      |          |      |      |      |      |      |      |      |      |
|---------|------------------------------|------------|------|------|----------|------|------|------|------|------|------|------|------|
|         |                              | $C_2H_5OH$ |      |      | $CH_3CN$ |      |      | DMSO |      |      | DMF  |      |      |
|         |                              | 10 %       | 30 % | 70 % | 10 %     | 30 % | 70 % | 10 % | 30 % | 70 % | 10 % | 30 % | 70 % |
| PrL     | 80                           | 20         | 3    | 1    | 10       | 4    | 7    | 43   | 10   | -    | 22   | 0    | 0    |
| SmL     | 451                          | 374        | 154  | 22   | 171      | 11   | 6    | 462  | 88   | 28   | 127  | 11   | 11   |
| EuL     | 2625                         | 2100       | 425  | 175  | 325      | 100  | 100  | 2125 | 575  | 25   | 3700 | 50   | 75   |

Note:  $C_{compl.} = 1 \cdot 10^{-4}$  mol/l, the spectra registration conditions are identical.

The luminescence intensity of Ln(III) increases to a greater extent when the second ligand is introduced into the complex – the ligands containing highly hydrophobic alkyl substituents (TOPO, etc.), or multiple cycles (“antenna effect”) such as Phen and TPPO. In Table 2, all second ligands doubly increase only weak luminescence acylpyrazolonate Pr(III), in comparison with Sm(III) and Eu(III).

Table 2.

The luminescence intensity of solutions of Pr(III), Sm(III) and Eu(III) complexes with acylpyrazolone L in the absence ( $I_0$ ) and in the presence of second ligands ( $I$ ) and its relative variation  $I/I_0$  (n, times).

| Ln(III) | $I_{lum.}$ , a.u. |      |      |      | $I/I_0$ , times |      |      |
|---------|-------------------|------|------|------|-----------------|------|------|
|         | $I_0$             | TOPO | TPPO | Phen | TOPO            | TPPO | Phen |
| Pr      | 25                | 47   | 51   | 46   | 1.88            | 2.04 | 1.84 |
| Sm      | 625               | 212  | 781  | 581  | 0.34            | 1.25 | 0.93 |
| Eu      | 2960              | 1603 | 3700 | 4174 | 0.54            | 1.25 | 1.41 |

Note:  $I_{lum.}$  maxima bands recorded in HST: Pr(III) – 605 nm, Sm(III) – 645 nm, Eu(III) – 612 nm ( $C_{compl.} = 1 \cdot 10^{-5}$  mol/L).  $I_{lum.}$  values are given to the same experimental conditions.

On Figure 3 spectra of Pr(III) complexes are presented. From comparison they follow the addition of the second ligand TOPO increases the luminescence intensity, and causes split of Pr(III) band, corresponding the transfer  ${}^1D_2 - {}^3H_6$ .

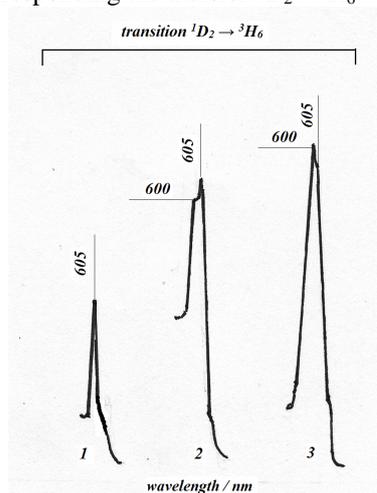


Fig. 3. Luinescence spectra ( $\lambda_{ex} = 365$  nm) of complexes: PrL – 1, PrL-TOPO – 2 and PrL-TPPO – 3. ( $C_{compl.} = 1 \cdot 10^{-5}$  mol/l).

Comparing the infrared spectra of acylpyrazolone (L) with its EuL and Eu(TTA)<sub>3</sub>L complexes, we found weakening of the intensity of the bands with maximum at 1690 and 1668  $\text{cm}^{-1}$ , corresponding valent oscillations of aldehyde group in different ligand molecular forms. Besides, the intensity of the band with maximum at 1330-1350  $\text{cm}^{-1}$  increases significantly, it corresponds to valent oscillations of carbonyl group in deprotonated enol form of the ligand. In the spectra of Eu(TTA)<sub>3</sub> and Eu(TTA)<sub>3</sub>L complexes in the 3000–3600  $\text{cm}^{-1}$  an intensive band is observed, corresponding to the vibrations of water molecules [9].

In the mass spectrum of the  $\text{Eu}(\text{TТА})_3\text{L}$  mixed-ligand complex, there are peaks corresponding to  $[\text{Eu}\cdot\text{TТА}]^{2+}$ ,  $[\text{Eu}\cdot\text{TТА}\cdot\text{L}]^+$ ,  $\text{Eu}(\text{TТА})_3\text{L}\cdot 2\text{H}_2\text{O}$  and splinter fragments (Fig. 4).

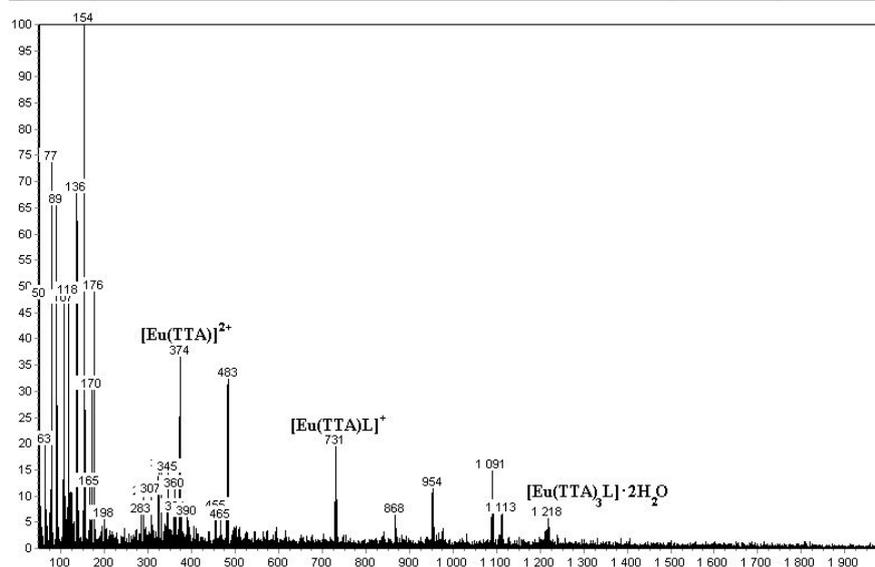


Fig. 4. Mass spectrum of the  $\text{Eu}(\text{TТА})_3\text{L}$  complex.

The  $\text{Eu}(\text{TТА})_3\text{L}$  mixed-ligand complex is also characterized by a high photoluminescence, what allows to recommend its application in electroluminescent devices irradiating in the visible region of the spectrum.

In this study we found that emission intensities of the electric dipole transition of lanthanide complexes with synthesized acylpyrazolone increases in row

$\text{PrL-SmL-EuL}$ . The further increase of luminescence intensity was observed by addition of the neutral ligands with formation of mixed-ligand complexes. In complexes  $\text{EuLTPPO}$  and  $\text{EuLPhen}$  quite intensive monochromatic red luminescence was observed.

### Experimental section

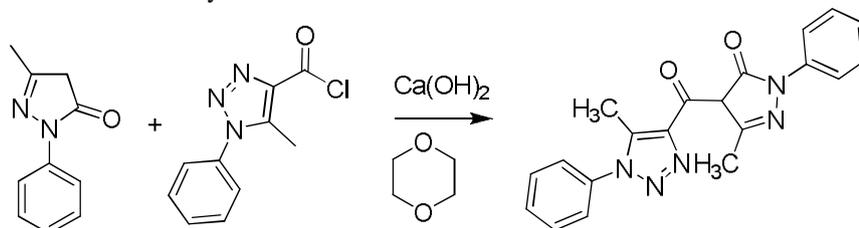
#### Materials and general methods

All reagents and solvents were commercially available and used as received without further purification.  $^1\text{H}$  NMR spectra were recorded on a Varian Mercury 400 instrument (400 MHz for  $^1\text{H}$ ) with TMS or deuterated solvent as an internal reference. Elemental analysis was performed on a PerkinElmer 240 C analyzer. Satisfactory elemental analyses were obtained for new compounds. IR spectra were recorded on a FTIR-8400 Spectrophotometer S "Shimadzu" (Japan) spectrometer by KBr pellet in the range of 400–4000  $\text{cm}^{-1}$ . Photo-luminescence was measured with an Fluorolog FL3-22 (Horiba Jobin Yvon) with a xenon lamp (450 W), and the spectrometer SDL-1 (LOMO, Russia) with Hg-lamp DRSh-250 and photomultiplier PEM-79 at room temperature (23 °C). The luminescence spectra of  $\text{Eu}(\text{III})$  ions were recorded in the range 560–650 nm,  $\lambda_{\text{max}} = 580, 590$  and 612 nm, corresponding to the following transitions:  $^5\text{D}_0 \rightarrow ^7\text{F}_0, ^5\text{D}_0 \rightarrow ^7\text{F}_1$  and  $^5\text{D}_0 \rightarrow ^7\text{F}_2$ ; spectra of  $\text{Sm}(\text{III})$  – in interval 620–670 nm,  $\lambda_{\text{max}} = 562, 595$  and 645 nm

corresponding to transitions  ${}^4G_{5/2} \rightarrow {}^6H_{5/2}$ ,  ${}^4G_{5/2} \rightarrow {}^6H_{7/2}$  and  ${}^4G_{5/2} \rightarrow {}^6H_{9/2}$  and Pr(III) spectra – from 580 to 650 nm. In contrast to the Eu(III) and Sm(III), the observation of Pr(III) luminescence is possible from two emitting levels:  ${}^1D_2$  ( $E = 17337 \text{ cm}^{-1}$ , the transition  ${}^1D_2 \rightarrow {}^3H_4$ ,  $\lambda_{\text{lum.}} = 605 \text{ nm}$ ) and  ${}^3P_0$  ( $E = 21390 \text{ cm}^{-1}$ , the transition  ${}^3P_0 \rightarrow {}^3H_6$ ). The value of the triplet energy levels of ligands was calculated from the phosphorescence spectra of Gd(III) complex with L at 77K [10]. TOPO, TPPO and Phen – reagents produced by Ferak, Aldrich and Sigma were used as second ligands.

#### Synthesis of 3-methyl-4-(5-methyl-1-phenyl-1*H*-1,2,3-triazole-4-carbonyl)-1-phenyl-1*H*-pyrazol-5(4*H*)-one (L)

Ligand (L) was obtained by the next scheme. 5-Methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one reacted with 5-methyl-1-phenyl-1*H*-1,2,3-triazole-4-carbonyl chloride (previously prepared by the method described in [11]) under the base catalysis of  $\text{Ca}(\text{OH})_2$  to form L in excellent yield.



Scheme 1

To a hot solution of 3-methyl-1-phenyl-5-one (1.75 g, 0.01 mol) in dioxane (15 mL)  $\text{Ca}(\text{OH})_2$  (1.40 g, 0.0185 mol) was added and the resulting mixture was heated under reflux with stirring for 30 minutes. 5-Methyl-1-phenyl-1*H*-1,2,3-triazole-4-carbonyl chloride (2.22 g, 0.01 mol) was added to the resulting suspension and the reaction mixture was heated under reflux with stirring for 24–36 hours. Dioxane was distilled off under vacuum. The residue was treated with 40 mL of 2M HCl, the precipitate was filtered off and recrystallized from methanol. Yield: 91 %; m.p.: 182–183°C;  ${}^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ )  $\delta$  7.84 (d,  $J = 8.0 \text{ Hz}$ , 2H,  $\text{H}_{\text{Ph-2,6}}$ ), 7.66 (br.s, 5H,  $\text{H}_{\text{Ph}}$ ), 7.45 (t,  $J = 7.7 \text{ Hz}$ , 2H,  $\text{H}_{\text{Ph-3,5}}$ ), 7.28 (t,  $J = 7.1 \text{ Hz}$ , 1H,  $\text{H}_{\text{Ph-4}}$ ), 3.58 (s, 1H,  $\text{H}_{\text{pyrazole}}$ ), 2.70 (s, 3H,  $\text{H}_{\text{Me}}$ ), 2.47 (s, 3H,  $\text{H}_{\text{Me}}$ ). MS ( $m/z$ ): 360 ( $\text{M}^+ + 1$ ); anal. calcd. for  $\text{C}_{20}\text{H}_{17}\text{N}_5\text{O}_2$ : C 66.84, H 4.77, N 19.49; found: C 66.92, H 4.71, N 19.44.

#### Synthesis of lanthanide complexes

The solution of (1,2,3-triazole-4-carbonyl)-1-phenyl-1*H*-pyrazol-5(4*H*)-one (L) (0.01 mol/L) was prepared by dissolving the compound in THF. The 0.01 mol/L solutions of other reagents were prepared by dissolving their precise weight in ethanol. Initial 0.1 mol/L solutions of chlorides Pr(III), Sm(III) and Eu(III) were prepared by dissolving their oxide (99.99 % pure) in hydrochloric acid (1:1) with subsequent evaporation of the water excess and dissolving the residue in double-distilled water. Solutions of lower concentration were prepared by diluting the initial solutions. While preparing the solutions of complexes, the solution of  $\text{LnCl}_3$  was mixed with a solution L in the presence of a buffer that supported the optimum pH under control at pH-meter OP-211/1 (Hungary) equipped with a glass electrode. To create the desired pH the ammonium acetate-buffered solutions (pH 3.0–8.0) were used.

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**СИНТЕЗ І ЛЮМІНЕСЦЕНТНІ ВЛАСТИВОСТІ КОМПЛЕКСІВ Pr (III),  
Sm (III) І Eu (III) ІЗ 5-МЕТИЛ-4-(5-МЕТИЛ-1-ФЕНІЛ-1H-[1,2,3] ТРИАЗОЛ-4-  
КАРБОН) -2-ФЕНІЛ-2,4 -ДІГІДРО-ПІРАЗОЛ-3-ОНОМ**

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Вивчено умови утворення і спектрально-люмінесцентні властивості комплексів Pr (III), Sm (III) і Eu (III) з 5-метил-4(5-метил-1-феніл-1H-[1,2,3]триазол-4-карбонил)-2-феніл-2,4 дигідро-піразол-3-оном (L), а також різнолігандних, що включають нейтральні ліганди – Фен, ТОФО і ТФФО. З'ясовано, що в комплексі з L, що включає в якості екстра-ліганду ТТА, простежується найвища інтенсивність люмінесценції. Утворення комплексу Eu(ТТА)<sub>3</sub>•L підтверджено методами ІЧ, мас-спектроскопії та люмінесценції.

*Ключові слова:* лантаніди, ацилпіразолонати, фотолюмінесценція.

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