



## Anionic lanthanide complexes with 3-methyl-1-phenyl-4-formylpyrazole-5-one and hydroxonium as counter ion



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### ARTICLE INFO

#### Article history:

Received 20 March 2013

Accepted 28 March 2013

Available online 6 April 2013

#### Keywords:

4-Formyl-pyrazol-5-one

Lanthanide complexes

Crystal structure

Luminescence

### ABSTRACT

A series of  $[H_3O]^+[LnL_4]^- \cdot nH_2O$  complexes ( $n = 1-3$ , Ln = Nd, (1), Sm (2), Eu (3), Tb (4); HL = 3-methyl-1-phenyl-4-formylpyrazole-5-one) were synthesized and characterized. The structures of the Sm<sup>III</sup> and Eu<sup>III</sup> complexes were investigated by X-ray diffraction. The isostructural crystals 2 and 3 consist the tetrakis  $[LnL_4]^-$  anions which are linked by H-bonding with the hydroxonium counter-ion and water molecules. The lanthanide ion is situated in the center of distorted tetragonal antiprism formed by eight oxygen atoms of 4-formyl-5-hydroxypyrazolonate anions. The Tb<sup>III</sup> and Sm<sup>III</sup> complexes show strong luminescence in solid state, whereas the Eu<sup>III</sup> and Nd<sup>III</sup> complexes show low luminescence activity.

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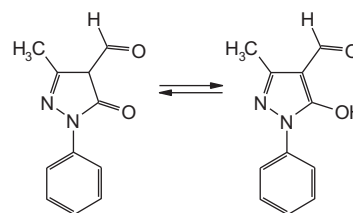
### 1. Introduction

Investigation of coordination compounds of lanthanide ions has been attracted significant attention, that are focuses on several potential applications of its luminescence: application in the lighting industry for the engineering of lamps, ability to provide electroluminescent material for organic light emitting diodes (OLEDs) and optical fibers for telecommunications, a capacity to yield functional complexes for biological assays and medical imaging purposes [1–3].

Among lanthanides coordination compounds, which exhibit strong luminescence in visible range, the Eu<sup>III</sup> and Tb<sup>III</sup> complexes are most studied. Characteristic red and green intensive luminescence, respectively, due to structure of their energy levels are typical for them. However, there are also Ln compounds that emit light in other spectral regions such as near infrared (Nd<sup>III</sup>, Yb<sup>III</sup> and Er<sup>III</sup>), visible (orange for Sm<sup>III</sup>, yellow for Dy<sup>III</sup>, blue for Tm<sup>III</sup>) and near-UV (Ce<sup>III</sup> and Gd<sup>III</sup>) range.

Some types of organic ligands are convenient for the molecular design of luminescent lanthanides complexes, among them are  $\beta$ -diketones, carboxylic acids and acylpyrazolones [4]. 4-Acyl-5-pyrazolones are an interesting class of  $\beta$ -diketones, containing a

pyrazole fused to a chelating arm. The results of acylpyrazolones complexes study are summarizes in some reviews for example [5]. However, coordination compounds of some ligands of this type have not investigated till now. Recently we described the peculiarities of molecular structure and luminescent properties of lanthanides complexes with 3-methyl-1-phenyl-4-formylpyrazole-5-one (HL) of the general formula  $LnL_3 \cdot nSolv$  (Solv = H<sub>2</sub>O, EtOH, Ln = La, Nd, Sm, Eu, Gd, Tb, Dy, Yb) [6].



It was found that solvent molecules in the inner coordination sphere are able to effectively quench luminescence of lanthanides due to the transfer of excitation energy to their oscillating levels. The replacement of OH-oscillators in the coordination sphere via formation of anionic complexes  $[Na(H_2O)][LnL_4]$  and  $[NBu_4][LnL_4]$  yields to a considerable increasing of luminescence intensity [7]. The high stability of the  $[LnL_4]^-$  anions allowed us to synthesize

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the complexes of the composition  $[\text{H}_3\text{O}]^+[\text{LnL}_4]^-$  ( $\text{Ln} = \text{Nd}, \text{Sm}, \text{Eu}, \text{Tb}$ ), which belong to the rare type of lanthanides coordination compounds. The first structurally characterized  $\beta$ -diketonate acid stabilized by hydrogen bonding are described only 10 years ago [8].

## 2. Results and discussion

### 2.1. Synthesis and characterization

3-Methyl-1-phenyl-4-formylpyrazole-5-one is a structural analog of  $\beta$ -diketonates and easily forms coordination compounds in deprotonated enol form. The reaction of sodium salt of 3-methyl-1-phenyl-4-formylpyrazole-5-one and lanthanides salts in molar ratio 4:1 leads to the complex salts  $[\text{Na}(\text{H}_2\text{O})]^+[\text{LnL}_4]^-$  [7]. The synthesis of complexes  $[\text{H}_3\text{O}]^+[\text{LnL}_4]^-$  with hydroxonium as a counterion with high yields was realized by molar ratio of  $\text{HL}:\text{NaOH}:\text{Ln}^{\text{III}}$  as 4:3:1.

The presence of the ligand in a coordinating sphere in a deprotonated form is confirmed by the IR-spectroscopy data. Thus, the formation of complexes **1–4** result in disappearance of bands with maxima absorption in range of 1690 and 1668  $\text{cm}^{-1}$ , corresponding the stretching oscillation of aldehyde group of different molecular forms of 3-methyl-1-phenyl-4-formylpyrazole-5-one. Moreover considerable intensity of absorption band with a maximum at 1633–1635  $\text{cm}^{-1}$  caused by the stretching oscillation of double carbon–nitrogen bond increases and new intensive duplicate line with a maximum of absorption in range of 1364–1367  $\text{cm}^{-1}$ , that is absent in the spectrum of free acylpyrazolone, appeared. These lines are usually attributed to the stretching oscillation of exo- and endo-cyclic carbonyl groups of 4-acyl-pyrazole-5-one [5].

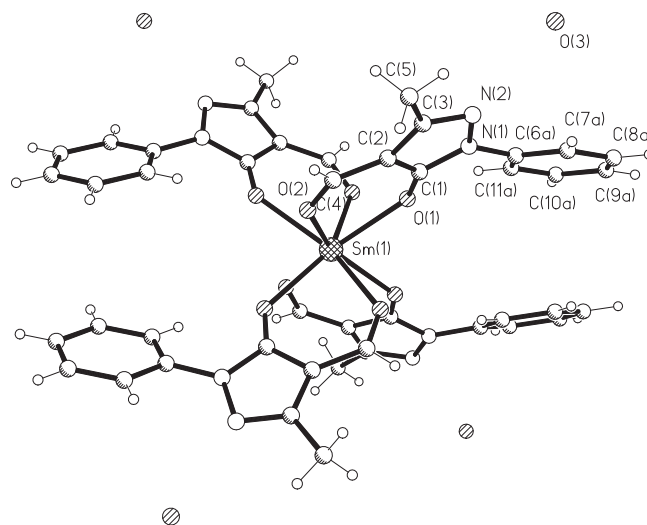
The stretching oscillation of OH-bonds of the water molecules show up in IR-spectra of compounds **1–4** as wide poorly resolved line with maximum of absorption in range 3342–3429 and 3229–3266  $\text{cm}^{-1}$ .

According to the thermal analysis data it was found that the dehydration of **1–4** complexes take place in a range of 100–200 °C. It is accompanied with a strong endothermic effect with a minimum on the DTA curve at 170 °C. Besides 210–260 °C on the curve of TGA there is another endoeffect which is not accompanied by changing of mass and, presumably, it is caused by the process of sample melting. Increasing of temperature up to 280–300 °C results in thermo-oxidative destruction of ligand. The process is accompanied by series of insignificant thermal effects and passes onto the process of burning down of organic residuum with a powerful maximum on the curve of DTA at 540–600 °C. The thermal decomposition process of samples accomplishes at 700–720 °C.

### 2.2. Crystal structure descriptions

X-ray diffraction analysis of crystals than were obtained by the crystallization of complex **2** and **3** from methanol, was performed. It was found that the complex **2** loses part of water and in result  $[\text{H}_3\text{O}][\text{SmL}_4]\cdot\text{H}_2\text{O}$  (compound **2,a**) formed. In the crystal structures of **2,a** and isostructural **3**, the Ln ion is eight-coordinate (Fig. 1). It is situated in the center of distorted tetragonal antiprism formed by eight oxygen atoms of ligands.

Chelate cycles are practically planare, deviations of  $\text{Sm}^{\text{III}}$  and  $\text{Eu}^{\text{III}}$  cation from a chelate planes are 0.014 and 0.006 Å, respectively. The chelating ligands are structurally equivalent. Bonds lengths of Samarium cation and endo- and exocyclic oxygen atoms differs considerably (2.377(5) and 2.464(5) Å, respectively), that is caused by asymmetric coordination of ligand. Bond lengths of Europium cation and oxygen atoms has similar values (2.382(3)



**Fig. 1.** Structure of complex  $[\text{H}_3\text{O}]^+[\text{SmL}_4]^- \cdot \text{H}_2\text{O}$  (compound **2,a**). Four positions of the disorientated water molecules are shown. Selected bond lengths (Å) and bond angles (°): Sm(1)–O(1) 2.378(5), Sm(1)–O(2) 2.464(5), N(1)–N(2) 1.422(8), O(1)–C(1) 1.271(8), O(2)–C(4) 1.234(8), C(1)–C(2) 1.414(8), C(2)–C(4) 1.416(9); O(1)Sm(1)O(1) 80.6(2), O(1)Sm(1)O(1) 111.6(2), O(1)Sm(1)O(1) 142.6(2), O(1)Sm(1)O(2) 75.01(15), O(1)Sm(1)O(2) 144.22(17), O(1)Sm(1)O(2) 72.03(18), O(1)Sm(1)O(2) 75.86(16), O(2)Sm(1)O(2) 137.5(2), O(2)Sm(1)O(2) 119.4(2), O(2)Sm(1)O(2) 76.8(3). Selected bond lengths (Å) for  $[\text{H}_3\text{O}]^+[\text{EuL}_4]^- \cdot \text{H}_2\text{O}$  (compound **3**): Eu(1)–O(1) 2.381(4), Eu(1)–O(2) 2.445(5), N(1)–N(2) 1.422(7), O(1)–C(1) 1.254(7), O(2)–C(4) 1.242(7), C(1)–C(2) 1.421(8), C(2)–C(4) 1.417(8).

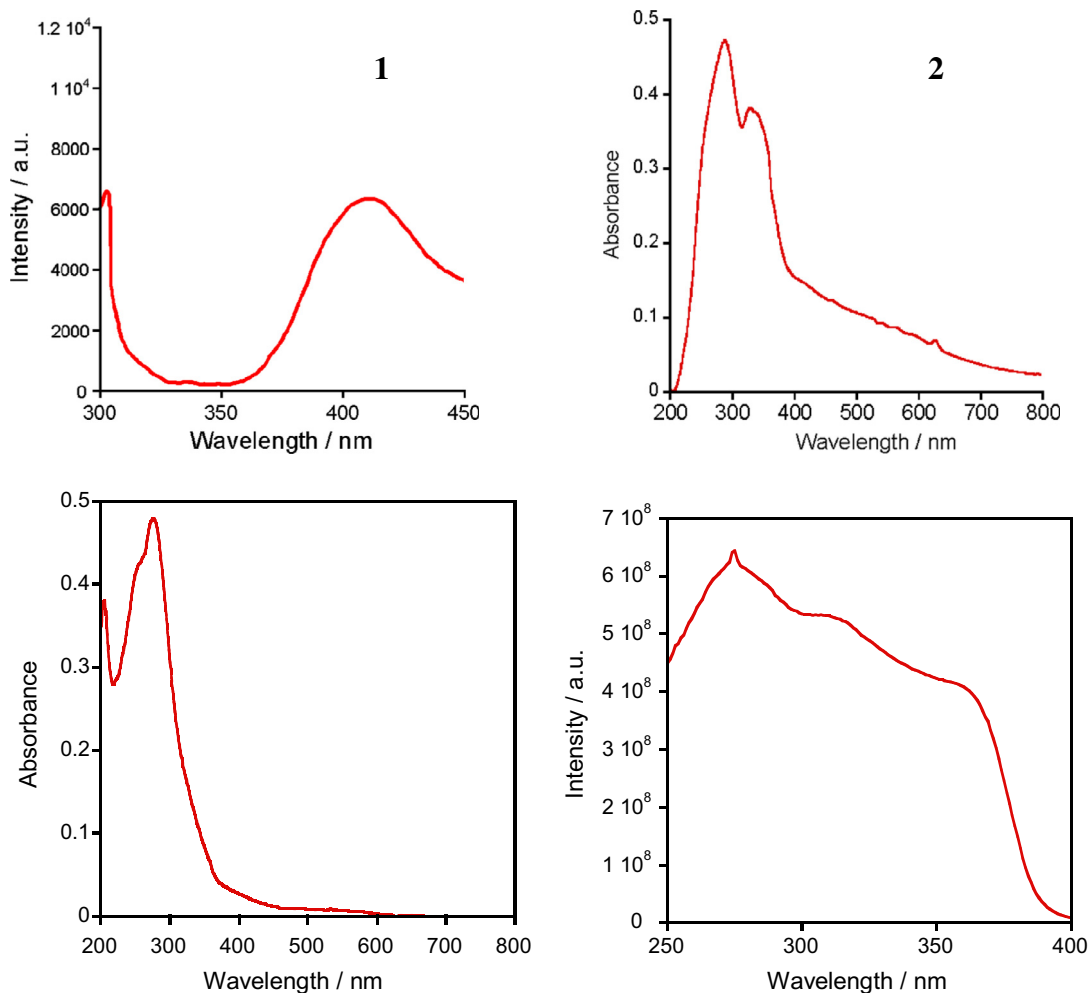
and 2.464(5) Å, respectively). At the same time comparison of lengths of carbon–oxygen bonds (C(1)–O(1) 1.270(8), 1.253(7) Å, and C(4)–O(2) 1.234(8), 1.242(8) Å for  $\text{Sm}^{\text{III}}$  and  $\text{Eu}^{\text{III}}$  complexes, respectively) testifies to the high degree of double bonds delocalization, that are typical for  $\beta$ -diketonates. Bonds lengths and valency angles in the organic ligands are near to the ordinary volumes [9].

Two molecules of water are located in an external sphere and are diffused up on four positions with equal population. In all positions water molecules are connected by H-bonds with the nitrogen atoms of pyrazole heterocycles ( $\text{O}(3) \cdots \text{N}(2)$ , 2.706 Å). Strictly localization of hydrogen cation was not successful. Most probably, that one are dislocated between the molecules of water in all four positions. Being involved in H-bonding hydroxonium ion and water molecule stabilized the crystal structures.

### 2.3. Luminescent properties

It is well known that the luminescence of trivalent lanthanide ions is realized as a result of the energy transfer from the excited organic moiety of the complex molecule [1]. The formation of the stable complexes compound is a necessary but insufficient condition; it is important that the energy of the lower triplet level of the ligand should be equal or higher than the energy of the excited level of the lanthanide ion. Experimentally found values of singlet ( $E_{S_1}$ ) and triplet ( $E_{T_1}$ ) energy levels of 3-methyl-4-formyl-1-phenylpyrazole-5-one are 24 150 and 20 700  $\text{cm}^{-1}$ , respectively. High value of  $E_{T_1}$  of ligand makes possible energy transfer both on the highly located irradiative levels of Terbium<sup>III</sup> ( $E(^5D_4) = 20\,500 - \text{cm}^{-1}$ ) and Samarium<sup>III</sup> ( $E(^4G_{5/2}) = 17\,920 - \text{cm}^{-1}$ ) and the below located level of Europium<sup>III</sup> ( $E(^5D_0) = 17\,250 - \text{cm}^{-1}$ ) and Neodymium<sup>III</sup> ( $E(^4F_{3/2}) = 11\,500 - \text{cm}^{-1}$ ).

The intensive band of absorption with maximum at 300 nm was detected in the electronic spectra of complexes **1–4**. The excitation spectra a quite similar for all complexes and contain a broad band in the region 250–350 nm. Fig. 2 shows the fluorescence spectrum



**Fig. 2.** Fluorescence spectrum ( $\lambda_{\text{exc}} = 270$  nm) of ligand – 1, absorption spectra of complexes  $[\text{H}_3\text{O}][\text{TbL}_4]\cdot\text{H}_2\text{O}$  – 2 and  $[\text{H}_3\text{O}][\text{EuL}_4]\cdot\text{H}_2\text{O}$  – 3 and excitation spectrum of  $[\text{H}_3\text{O}][\text{TbL}_4]\cdot\text{H}_2\text{O}$  – 4.

of ligand and absorption spectra of  $\text{Tb}^{\text{III}}$  and  $\text{Eu}^{\text{III}}$  complexes and excitation spectrum of  $\text{Tb}^{\text{III}}$  complex as example.

According to the luminescence spectra the excitation energy transfer from ligand to ion  $\text{Ln}^{\text{III}}$  occurs more effectively in case of  $\text{Tb}^{\text{III}}$  and  $\text{Sm}^{\text{III}}$ , less – to  $\text{Eu}^{\text{III}}$  and least of all – to  $\text{Nd}^{\text{III}}$  (Fig. 3). Values of the luminescence intensity and quantum yields of complexes are presented in the Table 1.

The luminescence spectrum of Neodymium complex contains three bands: the first with maximum at 896 nm, the second – at 1060 nm, and the third – at 1320 nm, corresponding to the transitions from the irradiative level  ${}^4\text{F}_{3/2}$  on sublevels of the basic level  ${}^4\text{I}_{9/2}$ ,  ${}^4\text{I}_{11/2}$  and  ${}^4\text{I}_{15/2}$ , respectively, that are also observed in the spectra of complexes of  $\text{Nd}^{\text{III}}$  with  $\beta$ -diketones and other reagents [2].

In the spectrum of  $\text{Sm}^{\text{III}}$  complex in range 550–660 nm three bands corresponding to the transitions from the irradiative level  ${}^4\text{G}_{5/2}$  on the sublevels of basic level  ${}^6\text{H}_{5/2,7/2,9/2}$  ( $\lambda_{\text{max}} = 560, 600, 645$  nm respectively) are observed. The transition  ${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{9/2}$  (electric-dipole transition) at around 645 nm the most dominated.  $\text{Tb}^{\text{III}}$  complex displays a typical emission spectrum with emission peaks centered at 489, 546, 590, 621 and 650 nm corresponding to the  ${}^5\text{D}_4 \rightarrow {}^7\text{F}_j$  ( $J = 6, 5, 4, 3, 2$ ) transitions respectively. The  ${}^5\text{D}_4 \rightarrow {}^7\text{F}_6$  band is the most dominate one.

In all cases the strong Stark's splitting of bands corresponding to the hypersensitive transitions (HST) is observed:  ${}^4\text{F}_{3/2} \rightarrow {}^4\text{I}_{9/2}$  of Nd

( $\lambda_{\text{max}} = 872, 896$  nm),  ${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{5/2}$  of Sm ( $\lambda = 640, 645$  nm) and  ${}^5\text{D}_4 \rightarrow {}^7\text{F}_5$  of Tb ( $\lambda = 542, 546, 550$  nm) due to of distortion of the coordinating polyhedron geometry (Fig. 4).

As it was expected the IR-luminescence of  $\text{Nd}^{\text{III}}$  is far weaker in comparison with the complexes of  $\text{Sm}^{\text{III}}$  and  $\text{Tb}^{\text{III}}$  radiating in visible range of spectrum. Thus, the high quantum yield of luminescence of  $\text{Tb}^{\text{III}}$  (28%) is near to previously observed quantum yield for the complex with 6-[(benzylamino)carbonyl]-2-pyridinecarboxylic acid (34%), for example [10]. The discovered high-efficiency luminescence of  $\text{Tb}^{\text{III}}$  and high quantum yield of luminescence its anionic complex with 3-methyl-4-formyl-1-phenylpyrazole-5-one provides a basis to suppose that this compound can be used as irradiative material in OLEDs.

The  $\text{Eu}^{\text{III}}$  complex is isomorphic to the complex of  $\text{Sm}^{\text{III}}$  but does not show the expected strong red luminescence. The luminescence spectra of  $\text{Eu}^{\text{III}}$  complex display typical pattern of europium  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_j$  transitions ( $J = 0-4$ ) emissive transitions with the most prominent band at 610–612 nm assigned to the  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  dominating transition. Usually  $\text{Eu}^{\text{III}}$  complexes show a more intense luminescence, as in  $\text{Sm}^{\text{III}}$  complexes is dissipation of excitation energy in the high-lying ground state sublevels. According to the literature data for an efficient energy transfer to the emitting level of the  $\text{Eu}^{\text{III}}$  the difference between the triplet level of the organic ligand and the resonance level of the lanthanide should be in the range of  $2500\text{--}3500\text{ cm}^{-1}$  [11]. In the europium complexes with the

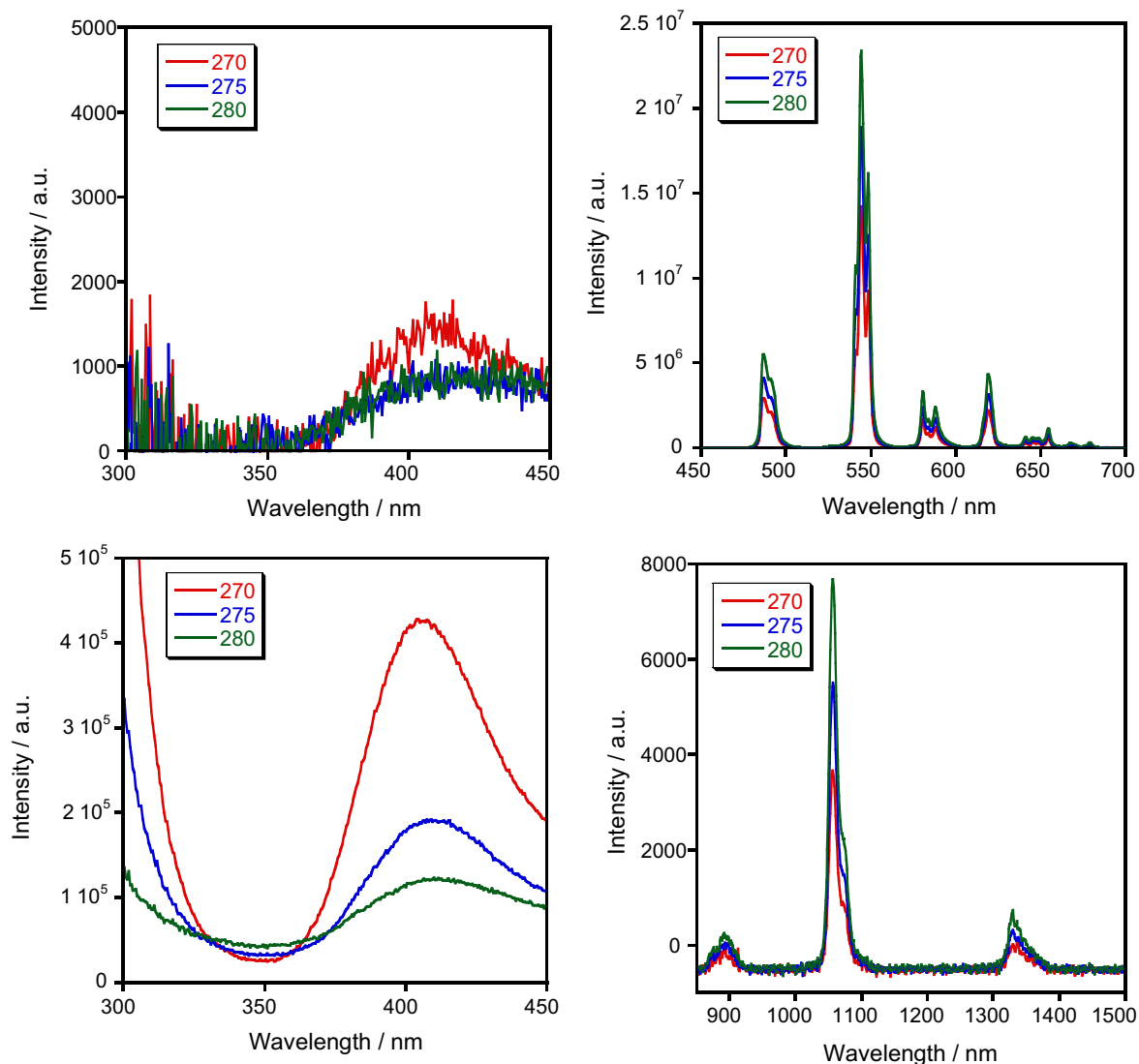


Fig. 3. Luminescence spectra of solid complexes:  $[\text{H}_3\text{O}][\text{TbL}_4]\cdot\text{H}_2\text{O}$  (top) and  $[\text{H}_3\text{O}][\text{NdL}_4]\cdot 2\text{H}_2\text{O}$  (bottom) at different excitation energies.

Table 1

Characteristics of luminescence of lanthanides complexes with 3-methyl-1-phenyl-4-formyl-pyrazole-5-one ( $\lambda_{\text{exc}} = 365 \text{ nm}$ ).

Complex	f-f transition	$\lambda_{\text{max}}$ (nm)	$I_{\text{lum}}$ , a.u. <sup>a</sup>	Quantum yield of luminescence (%)
$[\text{H}_3\text{O}][\text{NdL}_4]\cdot 2\text{H}_2\text{O}$	$^4\text{F}_{3/2} \rightarrow ^4\text{I}_{11/2}$	1060	7.6	–
$[\text{H}_3\text{O}][\text{SmL}_4]\cdot 3\text{H}_2\text{O}$	$^4\text{G}_{5/2} \rightarrow ^6\text{H}_{5/2}$	560	340	0.75
	$^4\text{G}_{5/2} \rightarrow ^6\text{H}_{7/2}$	605	960	
	$^4\text{G}_{5/2} \rightarrow ^6\text{H}_{9/2}$	645	1500	
$[\text{H}_3\text{O}][\text{EuL}_4]\cdot \text{H}_2\text{O}$	$^5\text{D}_0 \rightarrow ^7\text{F}_2$	611	36.5	0.08
	$^5\text{D}_0 \rightarrow ^7\text{F}_4$	700	5.0	
$[\text{H}_3\text{O}][\text{TbL}_4]\cdot \text{H}_2\text{O}$	$^5\text{D}_4 \rightarrow ^7\text{F}_6$	488	6500	27.9
	$^5\text{D}_4 \rightarrow ^7\text{F}_5$	546	21200	

<sup>a</sup> Value  $I_{\text{lum}}$  are corrected to the identical conditions of experiment.

3-methyl-4-formyl-1-phenylpyrazole-5-one energy gap between the triplet level of the ligand and the emitting level of the central atom ( $3450 \text{ cm}^{-1}$ ) is at the upper limit of the optimal range making the transfer of excitation energy inefficient, and molecular phosphorescence of ligand is observed instead of the expected lanthanide ion luminescence. At the same time, the energy gap between the triplet level of the ligand and the resonance level of the  $\text{Sm}^{\text{III}}$  cation ( $2900 \text{ cm}^{-1}$ ) falls in the middle of the optimal

range, making an efficient energy transfer to the resonance level, and the luminescence intensity is higher than that of the europium complex.

It should be noted that the authors of work [12] also discovered that the quantum yield of luminescence of  $\text{Sm}^{\text{III}}$  complex with 1-phenyl-3-methyl-4-phenylacetylpyrazole-5-one is six times more than for analogical  $\text{Eu}^{\text{III}}$  complex, although its luminescence in similar europium complexes is usually 10–100 times higher [1,2]. A same situation was described for the anionic complexes of  $\text{Eu}^{\text{III}}$  and  $\text{Sm}^{\text{III}}$  with the ligands obtained by condensation of salicylic acid hydrazide and 1-phenyl-3-methyl-4-propionylpyrazole-5-one [13].

### 3. Conclusion and perspectives

Summarizing, we have successfully synthesized new anionic lanthanide(III) complexes based on 3-methyl-1-phenyl-4-formylpyrazol-5-one (HL) and the hydroxonium cation as a counter ion. High efficiency luminescence and high luminescence quantum yield of the complex  $[\text{H}_3\text{O}][\text{TbL}_4]\cdot \text{H}_2\text{O}$  uniquely exhibits that this compound can be used as irradiative material in OLEDs.

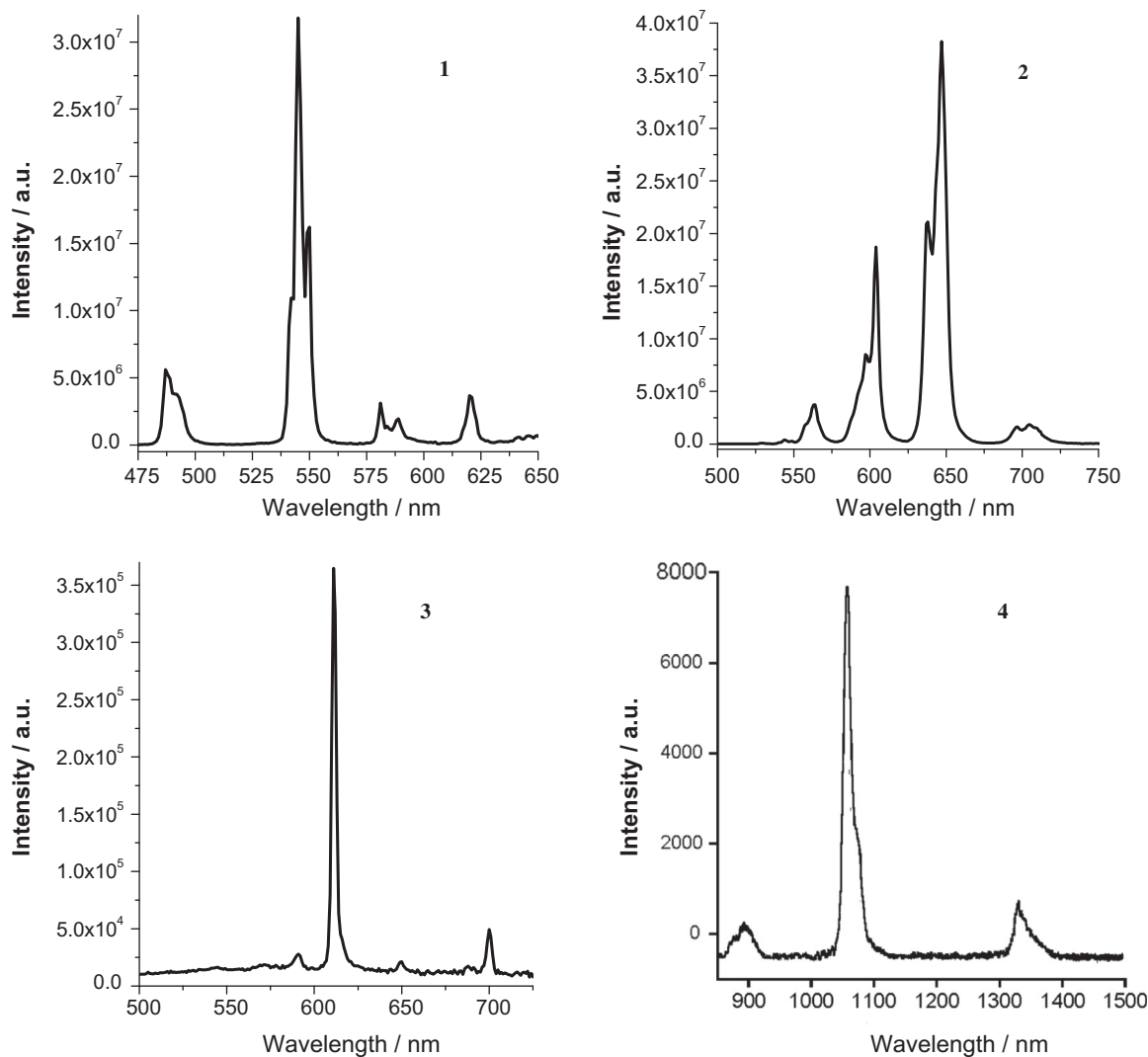


Fig. 4. Luminescence spectra of solid complexes:  $[\text{H}_3\text{O}][\text{TbL}_4]\cdot\text{H}_2\text{O}$  ( $\lambda_{\text{exc}} = 345 \text{ nm}$ ) – 1,  $[\text{H}_3\text{O}][\text{SmL}_4]\cdot 3\text{H}_2\text{O}$  ( $\lambda_{\text{exc}} = 345 \text{ nm}$ ) – 2,  $[\text{H}_3\text{O}][\text{EuL}_4]\cdot\text{H}_2\text{O}$  ( $\lambda_{\text{exc}} = 371 \text{ nm}$ ) – 3,  $[\text{H}_3\text{O}][\text{NdL}_4]\cdot 2\text{H}_2\text{O}$  ( $\lambda_{\text{exc}} = 280 \text{ nm}$ ) – 4.

## 4. Experimental

### 4.1. Materials and methods

Commercially available solvents and lanthanides salts were used without further purification. 3-Methyl-1-phenyl-4-formylpyrazole-5-one was prepared according to the literature procedure [14].

IR spectra were recorded for KBr pellets in the range of  $4000\text{--}400 \text{ cm}^{-1}$  on a Nicolet Nexus 470 FT IR-spectrometer. Thermal analysis experiments were performed on a Paulik–Paulik–Erdy Q-derivatograph under static air atmosphere and calcinated alumina as standard. Luminescence and excitation spectra of solid samples were recorded on Horiba Jobin–Yvon Fluorolog FL3-22 spectrometer equipped with a 450 W Xe-lamp and LOMO SDL-1 spectrometer equipped with a FEU-79 (visible) and FEU-62 (IR range) photomultiplier. The energy of the ligand triplet state ( $E_{T1}$ ) was determined on the basis of a low temperature (77 K) phosphorescence spectrum of  $\text{Gd}^{\text{III}}$  complex in DMSO solution. Quantum yield for solid samples was determined via a direct method using the home-modified integrating sphere [15]. Estimated errors of the values of quantum yields are 10%.

### 4.2. Synthesis of $[\text{H}_3\text{O}][\text{Ln}(\text{L})_4]\cdot n\text{H}_2\text{O}$ (1–4), general procedure

3-Methyl-1-phenyl-4-formylpyrazole-5-one (0.808 g, 4 mmol) was added to a solution of 0.12 g (3 mmol) sodium hydroxide in 25 ml 96% ethanol. The mixture was stirred at ambient temperature until complete dissolution of the precipitate (20–30 min). Then a solution of 1 mmol lanthanide chloride in 10 ml of ethanol was added and again stirred for half an hour. The resulting mixture was filtered off and left for the crystallization. The obtained crystals residue, which appeared after 24 h, was separated by filtration, washed on a filter with a small amount of ethanol and then dried in the air. The yields were 50–80%. Elemental analyses data and characteristic IR-absorption bands of the synthesized compounds are given below:

$[\text{H}_3\text{O}][\text{NdL}_4]\cdot 2\text{H}_2\text{O}$  (1). *Anal. Calc.* for  $\text{C}_{44}\text{H}_{43}\text{N}_8\text{O}_{11}\text{Nd}$ : C, 52.63; H, 4.32; N, 11.16. *Found:* C, 53.03; H, 4.65; N, 10.64%. IR (KBr,  $\text{cm}^{-1}$ ):  $\nu = 3365, 3231 \nu(\text{OH}); 1633, 1364 \nu(\text{CO})$ .

$[\text{H}_3\text{O}][\text{SmL}_4]\cdot 3\text{H}_2\text{O}$  (2). *Anal. Calc.* for  $\text{C}_{44}\text{H}_{45}\text{N}_8\text{O}_{12}\text{Sm}$ : C, 51.40; H, 4.41; N, 10.89. *Found:* C, 51.70; H, 4.51; N, 10.52%. IR (KBr,  $\text{cm}^{-1}$ ):  $\nu = 3429, 3266 \nu(\text{OH}); 1635, 1366 \nu(\text{CO})$ .

$[\text{H}_3\text{O}][\text{EuL}_4]\cdot\text{H}_2\text{O}$  (3). *Anal. Calc.* for  $\text{C}_{44}\text{H}_{41}\text{N}_8\text{O}_{10}\text{Eu}$ : C, 53.18; H, 4.16; N, 11.27. *Found:* C, 53.04; H, 4.57; N, 10.69%. IR (KBr,  $\text{cm}^{-1}$ ):  $\nu = 3377, 3229 \nu(\text{OH}); 1634, 1366 \nu(\text{CO})$ .



**Table 2**  
Crystal data and structure refinement statistics for **2a** and **3**.

Parameter	<b>2a</b>	<b>3</b>
Formula	C <sub>44</sub> H <sub>41</sub> N <sub>8</sub> O <sub>10</sub> Sm	C <sub>44</sub> H <sub>41</sub> N <sub>8</sub> O <sub>10</sub> Eu
Formula weight (g mol <sup>-1</sup> )	992.20	993.81
Crystal dimensions (mm)	0.08 × 0.09 × 0.17	0.10 × 0.10 × 0.32
T (K)	296	296
Crystal system	tetragonal	tetragonal
Space group	I4c2	I4c2
<i>Unit cell parameters</i>		
a (Å)	16.2701(4)	16.3271(3)
b (Å)	16.2701(4)	16.3271(3)
c (Å)	16.1315(6)	16.1084(8)
V (Å <sup>3</sup> )	4270.3(2)	4294.1(2)
Z	4	4
D <sub>calc</sub> (g cm <sup>-3</sup> )	1.543	1.537
μ (mm <sup>-1</sup> )	1.444	1.529
F(000)	2012	2016
θ <sub>max</sub> (°)	28.14	28.30
Index ranges	-21 ≤ h ≤ 21 -21 ≤ k ≤ 20 -21 ≤ l ≤ 21	-21 ≤ h ≤ 21 -20 ≤ k ≤ 21 -21 ≤ l ≤ 21
Reflections measured/reflections independent/reflections with I > 2(σ)	26 102/2616/1822	33 086/2666/1883
R <sub>int</sub>	0.1090	0.0883
R (all data)	0.0857	0.0783
R <sub>1</sub> (I > 2σ(I))	0.0488	0.0452
wR <sub>2</sub>	0.1147	0.0992
Goodness-of-fit (GOF) on F <sup>2</sup>	1.078	1.024
Residual electron density (max/min) (e/Å <sup>3</sup> )	1.881/-1.242	1.671/-1.104

[H<sub>3</sub>O][TbL<sub>4</sub>]·H<sub>2</sub>O (**4**). *Anal. Calc.* for C<sub>44</sub>H<sub>41</sub>N<sub>8</sub>O<sub>10</sub>Tb: C, 52.81; H, 4.13; N, 11.20. *Found*: C, 52.65; H, 4.24; N, 10.84%. IR (KBr, cm<sup>-1</sup>): ν = 3342, 3240 ν(OH); 1635, 1367 ν(CO).

#### 4.3. X-ray crystallography study

Single crystal structures determination of **2a** and **3** by X-ray diffraction was performed on a Bruker Apex-II CCD diffractometer (Mo Kα radiation, graphite monochromator, λ = 0.71073 Å) at 296 K following standard procedure [16]. The structures were solved by direct methods and were refined by the full-matrix least square fits with anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms of the carbon-containing ligands were positioned geometrically and refined using the 'riding' model. All calculations were carried out using the SHELXTL program package [17]. The crystallographic parameters are given in Table 2.

#### Acknowledgements

This study was financially supported by the Ministry of Education and Science, Youth and Sports of the Ukraine (Order Ng447, 16.05.11) by Grant-in-Aid for Scientific Research (No. 23107528) on the Innovative Areas: "Fusion Materials" (Area No. 2206) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan and the Austrian Science Foundation FWF (Project 19335-N17).

#### Appendix A. Supplementary data

CCDC 881782 and 928160 contain the supplementary crystallographic data for compounds **2a** and **3**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif). Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.ica.2013.03.044>.

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