ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2014, Vol. 40, No. 1, pp. 28–33. © Pleiades Publishing, Ltd., 2014.
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Heteroligand Complexes of Lanthanides with 4-Formyl-3-Methyl-1-Phenylpyrazol-5-one and 1,10-Phenanthroline

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Received January 30, 2013

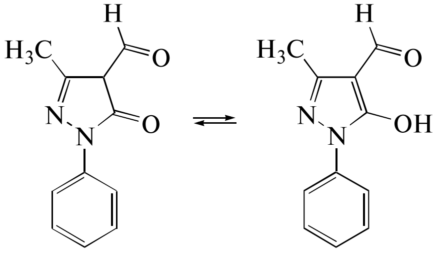
Abstract—Complexes of the general formula $LnL_3 \cdot Phen$ (Ln = Nd, Sm, Eu, Gd, Tb, Dy, and Yb; HL = 4-formyl-3-methyl-1-phenylpyrazol-5-one, Phen = 1,10-phenanthroline) were obtained and examined by IR spectroscopy and thermogravimetry. The structure of the complex $TbL_3 \cdot Phen$ was studied by X-ray diffraction. The coordination polyhedron of terbium is a distorted square antiprism made up of six O atoms of three 4-formylpyrazol-5-one anions and two N atoms of the 1,10-phenanthroline molecule. Polycrystalline samples of the complexes studied show emission in the spectral ranges characteristic of Ln(III).

DOI: 10.1134/S1070328414010035

INTRODUCTION

Considerable attention to lanthanide complexes with 4-acylpyrazol-5-ones is due to their structural similarity to β-diketones [1]. As a rule, the Ln(III) ion in such complexes is coordinatively unsaturated, its vacant coordination sites being usually occupied by molecules of water or a lower alcohol. They quench the emission of the lanthanide by transferring the excitation energy to the vibrational levels of the OH group. This effect of the OH oscillators can be eliminated by introduction of additional ligands that will displace solvent molecules from the coordination sphere of the complex [2].

Earlier, we have described a series of lanthanide complexes with the enolate anion of 4-formyl-3-methyl-1-phenylpyrazol-5-one (HL) with the general formula $LnL_3 \cdot nSolv$ (Solv = H_2O, MeOH, and EtOH).



Examination of emission spectra shows that water and (or) ethanol molecules present in the coordination sphere efficiently quench the photoluminescence of lanthanide cations [3]. We found it interesting to study the possibility of eliminating their quenching effect by substitution of another ligand. In this work, we discuss the data obtained for lanthanide complexes with the anion L^- (basic ligands) and 1,10-phenanthroline (Phen).

EXPERIMENTAL

The ligand HL was prepared as described in [4].

Synthesis of $LnL_3 \cdot Phen$ (Ln = Nd, Sm, Eu, Gd, Tb, Dy, and Yb). 1,10-Phenanthroline monohydrate (0.198 g, 1 mmol) was added to a solution of $LnL_3 \cdot nSolv$ (1 mmol) in chloroform (10 mL). The mixture was refluxed with stirring for 30–40 min to complete homogenization. The resulting solution was filtered and evaporated to dryness. The oily residue was triturated with isooctane (10 mL) for crystallization. After 2 h, the fine crystalline solid that formed was filtered off, washed with isooctane, and dried in air. The yields of tris(4-formyl-5-hydroxy-3-methyl-1-phenylpyrazolato)(1,10-phenanthroline)lanthanides(III) **I**–**VII** were 53–74% (Ln = Nd (**I**), Sm (**II**), Eu (**III**), Gd (**IV**), Tb (**V**), Dy (**VI**), and Yb (**VII**)). All the complexes but **I** and **VII** were isolated as dihydrates.

Elemental analysis data for complexes **I**–**VII** and the positions of the absorption peaks due to the CO stretching vibrations in their IR spectra are given in Table 1. TGA curves were recorded on a Paulik–Paulik–Erdey Q-derivatograph (static air atmosphere, heating rate 10°C/min, an open ceramic crucible as a

Table 1. Elemental analysis data and the IR spectra of complexes **I–VII**

Complex (empirical formula)	Content (found/calculated), %		ν(CO), cm^{-1}
	C	H	
I ($C_{45}H_{35}N_8O_6Nd$)	58.92/58.24	4.52/3.81	1632, 1348
II ($C_{45}H_{39}N_8O_8Sm$)	56.12/55.70	3.93/4.05	1632, 1346
III ($C_{45}H_{39}N_8O_8Eu$)	56.00/55.62	3.97/4.05	1632, 1346
IV ($C_{45}H_{39}N_8O_8Gd$)	55.29/55.31	3.68/4.02	1632, 1346
V ($C_{45}H_{39}N_8O_8Tb$)	55.77/55.22	3.84/4.02	1632, 1348
VI ($C_{45}H_{39}N_8O_8Dy$)	55.56/55.02	4.49/4.00	1634, 1348
VII ($C_{45}H_{39}N_8O_8Yb$)	56.98/56.49	4.45/3.69	1634, 1348

sample holder). Calcined alumina was used as a standard. IR spectra (KBr pellets) were recorded on a PerkinElmer Spectrum BX FTIR spectrophotometer in the 4000–400 cm^{-1} range. Emission spectra of polycrystalline samples were recorded on an SDL-1 (LOMO) diffraction spectrometer with FEU-62 (for the Nd and Yb complexes, IR range) and FEU-79 photomultipliers (for the complexes of the other lanthanides, visible range). Luminescence was excited with a DRSh-250 mercury lamp at λ = 365 nm; this most intense line of mercury was isolated by passing the light beam through a UFS-2 filter.

X-ray diffraction study of complex **Va** was carried out on a Bruker Smart APEX II diffractometer equipped with a CCD detector and a monochromatic radiation source at 296 K (MoK_α radiation, λ = 0.71073 Å, graphite monochromator) according to a standard procedure [5]. The structure was solved by the direct methods and refined in the full-matrix anisotropic approximation for all the non-hydrogen atoms. The hydrogen atoms were located geometrically and refined using a riding model. The calculations were performed with the SHELXL97 program package [6]. Crystallographic parameters and the data collection and refinement statistics for structure **Va** are given in Table 2. The comprehensive crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (no. 919695; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

According to elemental analysis data, the reactions of the complexes $LnL_3 \cdot n$Solv with 1,10-phenanthroline yield the adducts of the formula $[LnL_3 \cdot \text{Phen}] \cdot nH_2O$. The displacement of the water molecules to the outer sphere was confirmed by TGA data. Dehydration of complexes **II–VI** occurs in steps over a wide temperature range (60–200°C), the DTA curve being virtually featureless. Thermooxidative decomposition of the ligands begins above 200°C and is followed by burn-up of the organic residue (with a series of strong

Table 2. Crystallographic parameters and the data collection and refinement statistics for structure **Va**

Parameter	Value
Crystal dimensions, mm	0.19 × 0.15 × 0.10
Empirical formula	$C_{45}H_{35}N_8O_6Tb$
M	942.73
Crystal system	Triclinic
Space group	$P\bar{1}$
a, Å	11.2024(2)
b, Å	19.4206(4)
c, Å	19.9162(3)
α, deg	83.3930(10)
β, deg	75.9400(10)
γ, deg	84.9110(10)
Z	4
V, Å^3	4166.89(13)
μ, cm^{-1}	1.503
ρ_{calcd}, g/cm^3	1.539
θ scan range, deg	3.05–30.37
Ranges of h, k, and l indices	$-14 \le h \le 14$, $-22 \le k \le 24$, $-24 \le l \le 24$
Number of measured reflections	69185
Number of unique reflections (R_{int})	17127 (0.0545)
Number of reflections with $I > 2\sigma(I)$	10900
T_{min}/T_{max}	0.7314/0.8440
Number of parameters refined	1081
R ($I > 2\sigma(I)$)	R_1 = 0.0375, wR_2 = 0.0817
GOOF	0.809
$\Delta\rho_{min}/\Delta\rho_{max}$, e Å^{-3}	−0.420/0.848

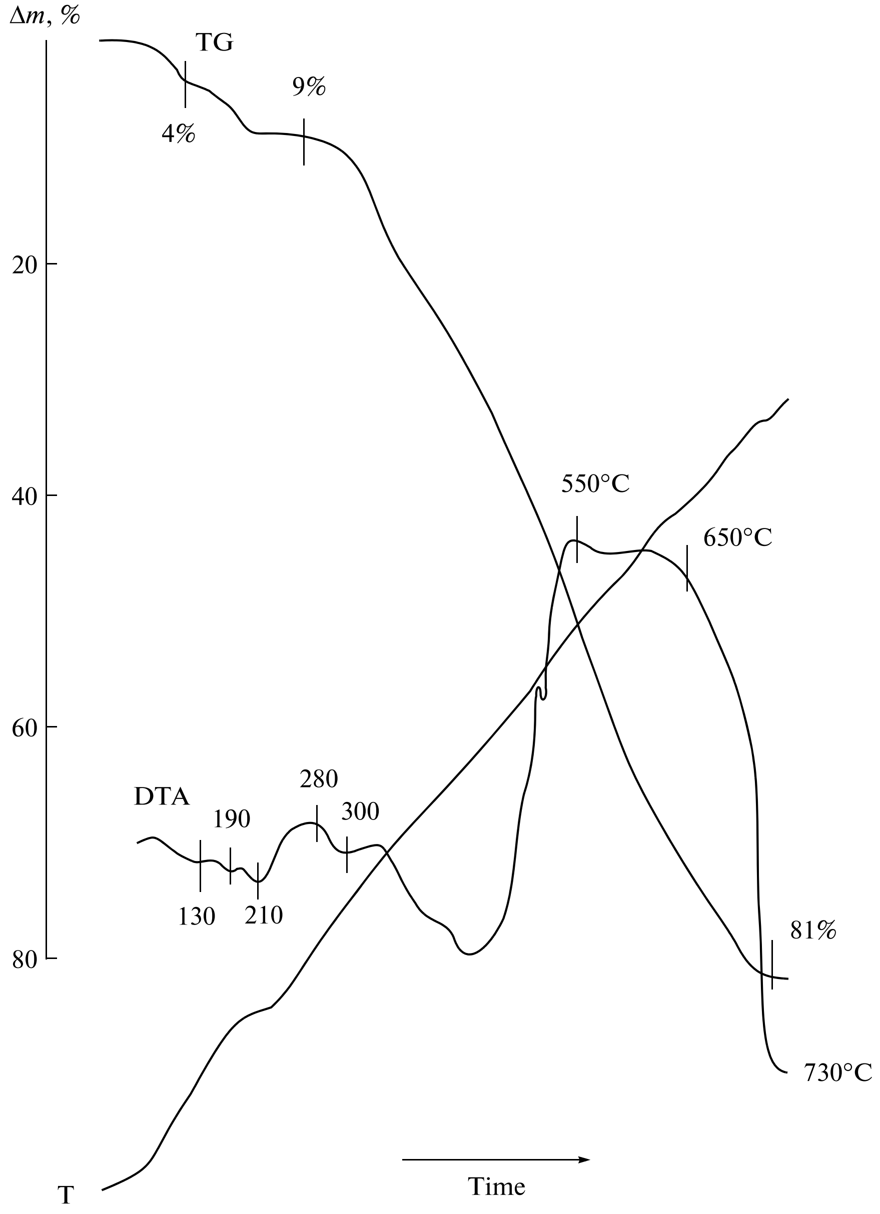


Fig. 1. TGA curves of the complex of terbium(III) 4-formyl-5-hydroxy-3-methyl-1-phenylpyrazolate with 1,10-phenanthroline (**Va**).

exothermic peaks at 500–650°C). The thermolysis becomes completed at 650–750°C (Fig. 1).

Comparison of the IR spectra of phenanthroline adducts **I–VII** reveals their structural similarity. The wide band with a maximum at 3400 cm^{-1} is due to the stretching vibrations of water molecules (complexes **II–VI**). The stretching vibrations of the exocyclic and endocyclic CO groups are manifested as intense absorption bands at 1632–1634 and 1344–1348 cm^{-1}, respectively [1, 3].

To determine the actual structures of the complexes under study, complex **V** was recrystallized from methanol and the resulting single crystals of the formula $TbL_3 \cdot$ Phen (**Va**) were examined by X-ray diffraction.

In complex **Va**, the terbium(III) cation is coordinated to three deprotonated 4-formylpyrazol-5-one residues (L^-) through the O atoms of the carbonyl and deprotonated OH groups and to the phenanthroline molecule through its two N atoms. The unit cell contains two crystallographically independent molecules with different degrees of bending of the chelate rings. The general view of the complex molecule with selected bond lengths is shown in Fig. 2. The coordination polyhedron of the Tb atom is a distorted square antiprism with the bases N(7)N(8)O(1)O(2) and O(3)O(4)O(5)O(6). The chelate rings involving the oxygen atoms are strongly bent. The Tb(1) atom deviates by 0.406–0.541 Å from the mean-square planes

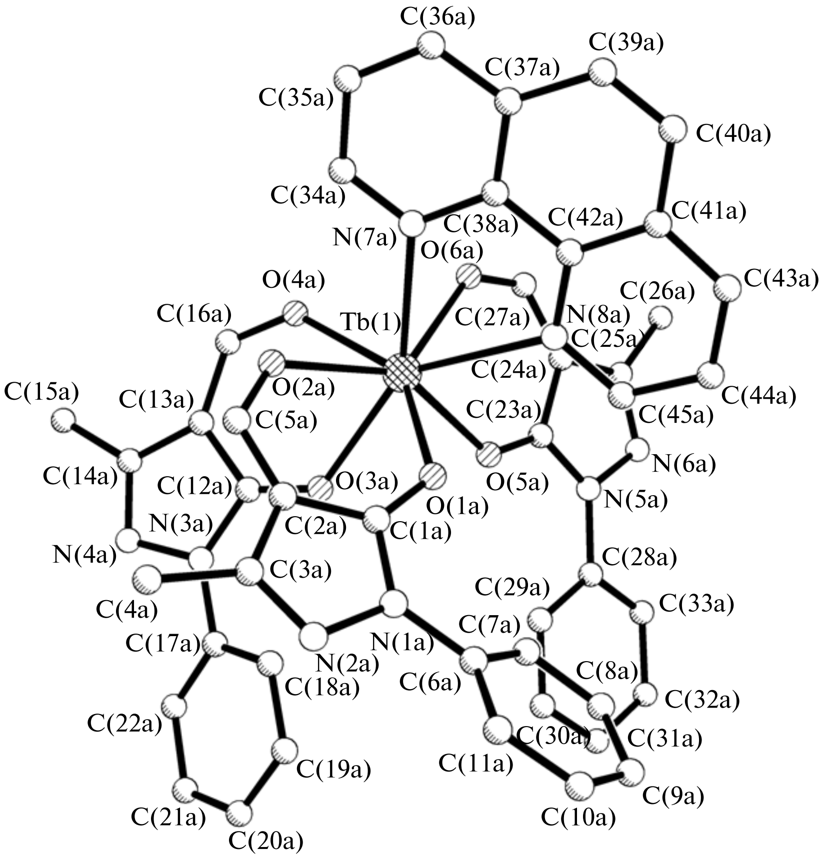


Fig. 2. General view of structure **Va** ($TbL_3 \cdot Phen$) with atomic numbering. Selected bond lengths: Tb(1)–O(1a), 2.302(4) Å; Tb(1)–O(2a), 2.391(4) Å; Tb(1)–O(3a), 2.316(3) Å; Tb(1)–O(4a), 2.374(4) Å; Tb(1)–O(5a), 2.314(3) Å; Tb(1)–O(6a), 2.421(3) Å; Tb(1)–N(7a), 2.552(4) Å; Tb(1)–N(8a), 2.575(5) Å; C(1a)–O(1a), 1.262(6) Å; C(5a)–O(2a), 1.259(7) Å; C(12a)–O(3a), 1.253(6) Å; C(16a)–O(4a), 1.259(6) Å; C(23a)–O(5a), 1.254(6) Å; C(27a)–O(6a), 1.242(6) Å.

made by the atoms of the chelatophore groups. The deviations of the Tb(2) atom from the mean-square planes of the chelate rings are 0.767–0.980 Å. The distortions of the chelate rings involving the nitrogen atoms of the phenanthroline molecule are substantially smaller: the Tb(2) and Tb(1) atoms deviate from the mean-square planes of the corresponding chelate rings by 0.183 and 0.302 Å, respectively.

The Tb–O bond lengths vary in a wide range (2.300–2.445 Å), being close to the upper bound of the range characteristic of mononuclear lanthanide phenoxides (2.00–2.46 Å) [7]. The Tb–N bond lengths lie in a narrow range (2.552–2.584 Å). The C–O bond lengths (1.242–1.259 Å for the formyl oxygen and 1.253–1.274 Å for the hydroxyl oxygen) are nearly equal both within the chelate rings of the same molecule and in nonequivalent molecules. This suggests equalization of the formally single and double carbon–oxygen bonds and a high degree of electron density delocalization in the chelate rings, which is characteristic of metal β-diketonates. The bond lengths and bond angles in the organic ligands have standard values [8].

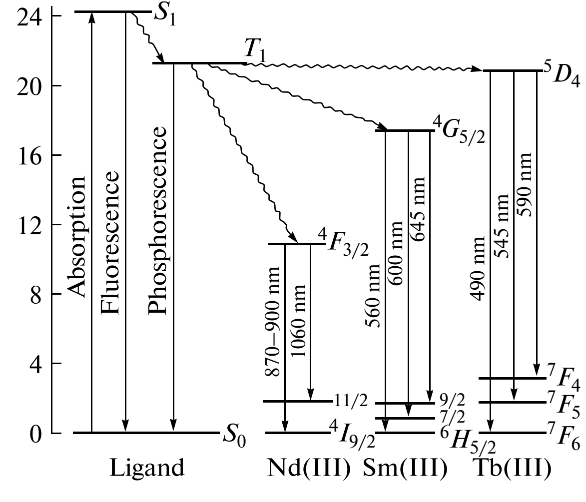


Fig. 3. Schematic representation of energy transfer from the ligand to the Ln^{3+} ions.

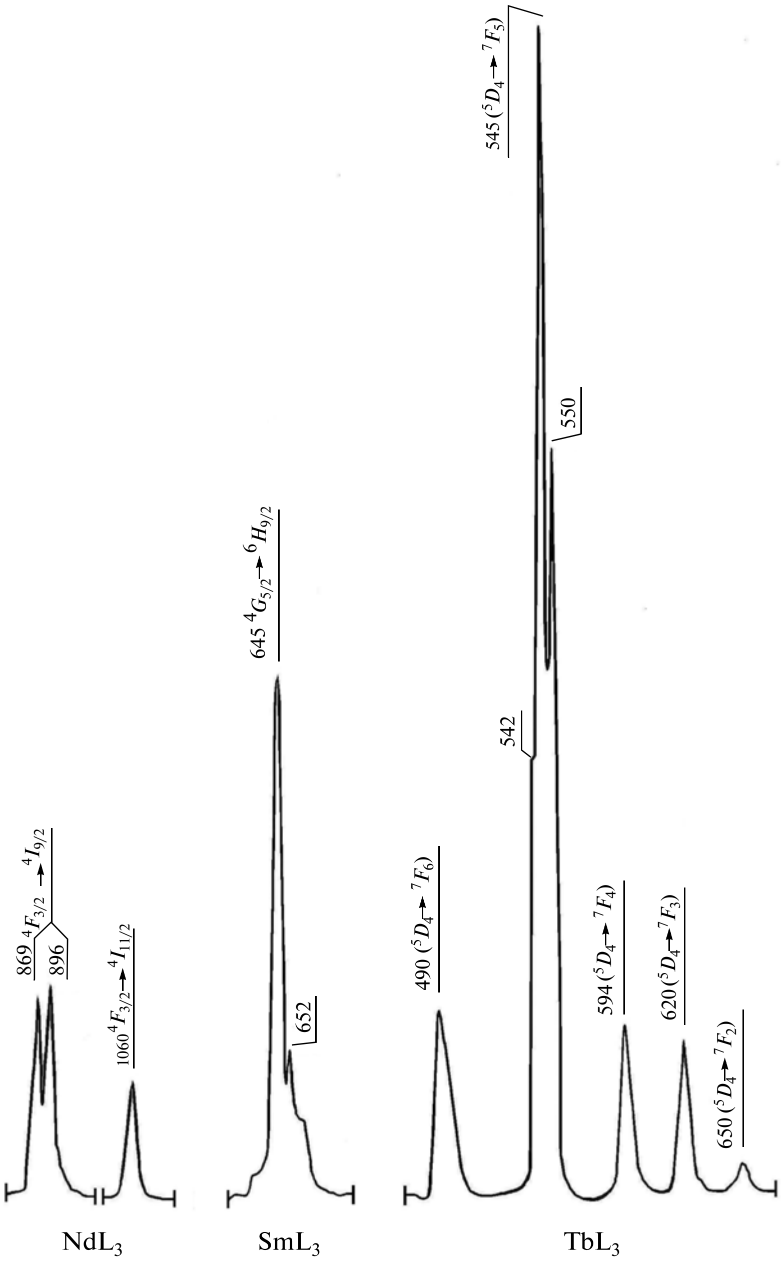


Fig. 4. Emission spectra of Nd(III), Sm(III), and Tb(III) complexes with 4-formyl-3-methyl-1-phenylpyrazol-5-one and Phen (the spectra were recorded at different slit widths of the spectrometer).

Lanthanide(III) complexes show emission due to energy transfer from the organic moiety of the complex molecule in the excited state to the Ln atom (Fig. 3). Luminescence in the visible spectral range is observed for the Sm(III), Eu(III), Tb(III), and Dy(III) complexes, while the Nd(III) and Yb(III) complexes luminesce in the near-IR range (Fig. 4).

The low symmetry of the coordination polyhedron allows observation of the split bands due to the supersensitive transitions: $^4F_{3/2} \rightarrow {}^4I_{9/2}$ for Nd(III), $^5D_0 \rightarrow {}^7F_2$ for Eu(III), and $^5D_4 \rightarrow {}^7F_5$ for Tb(III). Introduction of Phen into a complex molecule does not change the structures of the bands, yet making them much more intense because of displacement of water molecules (“OH oscillators”) from the inner coordination sphere of the complex.

As noted in [9, 10], aromatic diimines such as 2,2'-dipyridine as well as 1,10-phenanthroline and its derivatives most considerably enhance the emission of Eu(III) and Sm(III) β-diketonates, with retention of the general pattern of the emission spectra of trischelates and Phen-containing heteroligand complexes. This is also the case of the complexes under study.

Table 3. Emission peak intensities of the solid-state lanthanide complexes with 4-formyl-3-methyl-1-phenylpyrazol-5-one in the absence and in the presence of 1,10-phenanthroline

Complex	λ_{max}, nm	I_{lum}, rel. units*
$NdL_3 \cdot 4H_2O$	869, 896, 1060	1
$NdL_3 \cdot$ Phen (I)		7
$SmL_3 \cdot 2H_2O$	645	35
$SmL_3 \cdot$ Phen $\cdot 2H_2O$ (**II**)		70
$EuL_3 \cdot 2H_2O$	613	7
$EuL_3 \cdot$ Phen $\cdot 2H_2O$ (**III**)		107
$TbL_3 \cdot 2H_2O$	546	14
$TbL_3 \cdot$ Phen $\cdot 2H_2O$ (**V**)		238
$DyL_3 \cdot 2H_2O$	577	5
$DyL_3 \cdot$ Phen $\cdot 2H_2O$ (**VI**)		16
$YbL_3 \cdot C_2H_5OH \cdot H_2O$	980, 1005	21
$YbL_3 \cdot$ Phen (**VII**)		52

* The emission intensities are given for identical experimental conditions (the slit widths of the SDL-1 spectrometer are 0.1–0.1).

The intensities of the emission bands of Ln(III) due to their supersensitive transitions are given in Table 3 for trischelates and Phen-containing heteroligand complexes in the solid state. Analysis of the relative emission intensities shows that the replacement of the solvent molecules by Phen differently influences the luminescence of the complexes. The emission of the Tb(III) and Eu(III) complexes is enhanced most strongly; these elements have the largest energy gaps between the excited level and the sublevels of the ground-state level. Their emission intensities in Phen-containing heteroligand complexes are more than ten times greater than those in trischelates. In the case of Dy(III) and Sm(III), the associated elements of Tb(III) and Eu(III), the enhancing effect on the emission is smaller, as would be expected by analogy with other complexes.

In the IR emission spectra of the complexes with the ligand under study, the emission intensities of Nd(III) and Yb(III) are substantially lower than those of Ln(III) that produce luminescence in the visible range.

To sum up, we found that introduction of phenanthroline as an additional ligand into Tb(III) and Eu(III) complexes with 4-formyl-5-hydroxy-3-methyl-1-phenylpyrazole increases their emission by more than an order of magnitude, which makes it possible to use these complexes as emitting layers in OLED devices.

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Translated by D. Tolkachev