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Mono- and Mixed Metal Complexes of Eu\(^{3+}\), Gd\(^{3+}\), and Tb\(^{3+}\) with a Diketone, Bearing Pyrazole Moiety and CHF\(_2\)-Group: Structure, Color Tuning, and Kinetics of Energy Transfer between Lanthanide Ions

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Abstract: Three novel lanthanide complexes with the ligand 4,4-difluoro-1-(1,5-dimethyl-1H-pyrazol-4-yl)butane-1,3-dione (HL), namely [LnL\(_2\)(H\(_2\)O)\(_2\)], Ln = Eu, Gd, and Tb, were synthesized, and, according to single-crystal X-ray diffraction, are isostructural. The photoluminescent properties of these compounds, as well as of three series of mixed metal complexes [Eu\(_x\)Tb\(_{1-x}\)L\(_3\)(H\(_2\)O)\(_2\)] (Eu\(_x\)Tb\(_{1-x}\)L\(_3\)), [EuxGd\(_{1-x}\)L\(_3\)(H\(_2\)O)\(_2\)] (EuxGd\(_{1-x}\)L\(_3\)), and [Gd\(_x\)Tb\(_{1-x}\)L\(_3\)(H\(_2\)O)\(_2\)] (Gd\(_x\)Tb\(_{1-x}\)L\(_3\)), were studied. The Eu\(_x\)Tb\(_{1-x}\)L\(_3\) complexes exhibit the simultaneous emission of both Eu\(^{3+}\) and Tb\(^{3+}\) ions, and the luminescence color rapidly changes from green to red upon introducing even a small fraction of Eu\(^{3+}\). A detailed analysis of the luminescence decay made it possible to determine the observed radiative lifetimes of Tb\(^{3+}\) and Eu\(^{3+}\) and estimate the rate of excitation energy transfer between these ions. For this task, a simple approximation function was proposed. The values of the energy transfer rates determined independently from the luminescence decays of terbium(III) and europium(III) ions show a good correlation.

Keywords: pyrazoles; diketones; lanthanides; luminescence; europium; terbium; gadolinium; energy transfer; color tuning

1. Introduction

The unique luminescent properties of lanthanide ions are actively studied due to the possibility of their use in emitting materials [1–3], biovisualization [4–7], banknote protection [8] and in creating sensing materials [9–11].

The sensitization of the luminescence of lanthanide ions with an organic ligand has been studied since Weissman in 1942 [12] discovered sensitization of the luminescence of europium(III) ions in various chelates. This phenomenon, called the “antenna effect”, underlies the modern approach to creating Ln-based luminescent materials and allows one to avoid the problem of low-efficiency of direct excitation due to low absorption coefficients of rare-earth ions [5,13]. Various conjugated ligands, such as aromatic carboxylic acids [14–16], Schiff bases [17] and related compounds [18], as well as various diketones [19–21], have been proposed as antennae.
Among all possible chelating O,O-bidentate ligands, no doubt, 1,3-diketones are the most important and the most studied up to date.

Lanthanide (III) diketones have been proposed as emitting layers in OLED [22,23], as NMR shifting and discriminating agents [24], luminescent thermometers [25] and sensor materials [26]. Diketones, bearing both aromatic and perfluorinated substitutions, are widely used in coordination chemistry, chemical technology and as intermediates in organic and heterocyclic chemistry. Much less attention was paid to 1,3-diketones, which contain partially fluorinated substitutions, e.g., CHF₂– group. Some derivatives of 4,4-difluoro-1-phenylbutane-1,3-dione (1) were described mainly in patents and in medicinal chemistry journals since they are important building blocks in the synthesis of Celecoxib analogs a potent cyclooxygenase-2 (COX-2) inhibitors [27–29]. In coordination chemistry utilizing diketones with CHF₂–, the group is very limited. In fact, only two compounds were used as a ligands, namely, fore mentioned 4,4-difluoro-1-phenylbutane-1,3-dione (1), and 4,4-difluoro-1-(thiophen-2-yl)butane-1,3-dione (2). Complexes with Al³⁺ [30], Zr⁴⁺ [31], Mn²⁺ [32], Co²⁺ [33], Ni²⁺ [34] and Pd²⁺ [35] were reported up to date.

In the lanthanide series, only diketone 1 was tested as a ligand for the synthesis of Sc³⁺ [36], Tb³⁺ [37] and Eu³⁺ [38] complexes with a small set of ancillary diimine ligands.

We have recently reported unusual structural peculiarities and superb luminescent properties of lanthanide complexes with pyrazole-based 1,3-diketones, bearing perfluorinated chains of various lengths [23,39–43]. However, 1,3-diketones with pyrazole moieties and CHF₂– groups have never been studied as ligands before. Here we want to report on our first results on synthesis and luminescent properties of Tb³⁺, Eu³⁺ and Gd³⁺ complexes with 1-[(1,5-dimethyl-1H-pyrazol-4-yl)-4,4-difluorobutane-1,3-dione (3).

Among the many works devoted to luminescent lanthanide coordination compounds in recent years, researchers are attracted by works devoted to mixed-metal lanthanide complexes (MMLC) containing various emission centers, usually Eu³⁺ and Tb³⁺. This is facilitated by both a profound understanding of the luminescence physics of monometallic compounds and diverse applications of MMLC. Such compounds exhibit properties of “luminescent thermometers” [44,45] and also can act as chemical sensors [10,46,47] and color-tunable emitting materials [48–50]. The relative proximity of the excited state energies of Eu³⁺ (~17,240 cm⁻¹) and Tb³⁺ (~20,400 cm⁻¹) and the relatively small metal-to-metal distances in most common structures [51] cannot only provide two independent luminescence processes for each of the ions but also allow the transfer of excitation energy from Tb³⁺ ions to Eu³⁺. The thermal dependence of the efficiency of such transfer mainly determines the working mechanism of “luminescent thermometers” [52].

The existence of energy transfer in MMLC can be confirmed by the following evidence. Firstly, to provide approximately equal luminescence intensity of Eu³⁺ and Tb³⁺, the terbium(III) content in MMLC usually should exceed 90%. Second, quite often, the luminescence excitation spectra of Eu³⁺ contain peaks corresponding to the excitation of Tb³⁺ ions [10,51]. Third, introducing Eu³⁺ ions reduces the lifetimes of the excited state of terbium(III) ions significantly [52]. Finally, in a number of cases, decay curves of Eu³⁺ are not described satisfactorily by usual single- or biexponential models but contain the initial growth period [10]. Unfortunately, a detailed analysis of such kinetic curves, which can be used to determine the constant energy transfer process from Tb³⁺ to Eu³⁺ is scarcely presented in the literature.

Compounds [LnL₃(H₂O)₂], Ln = Eu, Gd, Tb, which were synthesized in this work, turned out to be convenient model objects for studying the dependence of kET on the Eu:Tb ratio in mixed-metal complexes [Euₓ,TbₓL₃(H₂O)₂].
2. Results

2.1. Synthesis

The compounds were synthesized according to the common reaction of lanthanide hydroxide with an alcoholic solution of the ligand. This procedure excludes the ingress of foreign ions into the reaction mixture [20]. The composition of the compounds was confirmed by elemental analysis data (Table S1), almost complete coincidence of the IR spectra (Figures S1–S3). XRD powder patterns of all complexes coincide with the theoretical ones calculated for the europium(III), gadolinium(III) and terbium(III) complexes (Figures S4–S7).

Thermogravimetric Analysis

The decomposition of the Eu and Tb complexes occurs in three stages, corresponding to the peaks of the thermal effect.

At 140–165 °C, a 4% mass loss occurs for TbL₃ with an endothermic effect, which corresponds to eliminating two water molecules from the coordination environment of lanthanide. Then, at the temperature of 200–290 °C, a loss of 29% of the sample mass with an exothermic effect is observed, which may indicate partial thermal decomposition of the ligand with water formation. Upon further heating at 300–600 °C, the mass of the sample decreases by 38.5% with intense heat release, which is explained by the ligand decomposition with the formation of water and carbon dioxide. Further heating of the sample to 700 °C does not lead to mass loss. Thus, the complex completely decomposes at 600 °C with the formation of TbF₃ (experimental weight loss 71.5%, theoretical weight loss taking into account the formation of TbF₃ 74.3%) and some amount of carbon (Supplementary Materials Figure S8).

The decomposition behavior of EuL₃ is similar to the decomposition of the terbium(III) complex. However, there is a difference in the temperatures of the stages. The first stage of decomposition is observed at 160–190 °C; the second at 190–300 °C; the third at 300–560 °C. At the third stage, EuF₃ is formed (experimental weight loss 25.7%, theoretical weight loss 25.1% (Figure S9). Thus, the TbL₃ complex is more thermally stable.

2.2. Crystal Description

The complexes LnL₃ (Ln = Eu, Gd, Tb) are isostructural (Table 1). The molecules of LnL₃ are formed by lanthanide atom, three chelate ligands L and two water molecules (Figure 1; selected distances and angles are given in Table 2). The geometry of polyhedrons LnO₈ corresponds to a square antiprism (see Table S2), which are formed by two planes, O1O6O8O4 and O2O5O3O7. The angles between planes of pyrazole and organometallic chelate ring (LnO₂C₃) are 6.5(2), 7.4(2) and 40.0(2) for EuL₃, 6.4(2), 7.6(2) and 39.9(2) for GdL₃, 6.3(2), 7.8(2) and 39.9(2) for TbL₃. The crystal packing is due to intermolecular H-bonds, C–H … O, C–H … F, and π–π stacking (between pyrazole moieties) interactions (Figure 2, Tables S3 and S4).

| Parameter | EuL₃ | GdL₃ | TbL₃ |
|-----------|------|------|------|
| Empirical formula | C₂₇H₃₁EuF₂N₄O₈ | C₂₇H₃₁F₂GdN₄O₈ | C₂₇H₃₁F₂TbN₄O₈ |
| Formula weight | 833.54 | 838.83 | 840.50 |
| T (K) | 100(2) | 120(2) | 100(2) |
| Crystal system | triclinic | triclinic | triclinic |
| Space group | P-1 | | |
| Crystal size (mm) | 0.05 × 0.05 × 0.03 | 0.05 × 0.05 × 0.03 | 0.05 × 0.05 × 0.03 |
| a (Å) | 11.084(5) | 11.066(2) | 11.054(2) |
| b (Å) | 11.968(4) | 11.928(2) | 11.920(2) |
| c (Å) | 13.711(8) | 13.673(2) | 13.652(3) |
| α (°) | 64.189(15) | 64.208(3) | 64.197(5) |
| β (°) | 86.98(2) | 77.956(4) | 86.896(8) |
| γ (°) | 72.669(14) | 72.477(4) | 72.426(5) |
Table 1. Cont.

| Parameter          | EuL₂₃ | GdL₃   | TbL₃   |
|--------------------|-------|--------|--------|
| V (Å³)             | 1556.8(13) | 1543.2(5) | 1537.6(5) |
| Z                  | 2     | 2      | 2      |
| D<sub>calc</sub> (g cm<sup>-3</sup>) | 1.778 | 1.805  | 1.815  |
| µ (mm<sup>-1</sup>) | 2.109 | 2.244  | 2.395  |
| θ range (°)        | 1.95–28.28 | 1.95–28.0 | 1.94–27.48 |
| θ range (°)        | −14→14 | −14→14 | −13→14 |
| Range of h, k and l| −15→15 | −13→15 | −15→14 |
| θ range (°)        | −18→16 | 0→18   | −17→17 |
| θ min/θ max        | 0.6579/0.7461 | 0.1806/0.3401 | - |
| F(000)             | 832   | 834    | 836    |
| Number of parameters | 461  | 460    | 461    |
| Reflections collected | 14,998 | 13,219 | 22,779 |
| Unique reflections  | 7658  | 7254   | 7041   |
| Reflections with I > 2σ(I) | 6931  | 6354   | 6311   |
| R<sub>int</sub>     | 0.0304 | 0.0548 | 0.1272 |
| GooF                | 1.062 | 1.077  | 1.014  |
| R₁(I > 2σ(I))      | 0.0325 | 0.0546 | 0.0350 |
| wR²(I > 2σ(I))     | 0.0679 | 0.1075 | 0.0857 |

Figure 1. Molecular structure of EuL₃ (H atoms at C atoms of ligands are omitted; the inset shows the EuO₈ polyhedron).

Table 2. Selected distances and angles for LnL₃.

|          | EuL₂₃        | GdL₃         | TbL₃         |
|----------|--------------|--------------|--------------|
| Ln-O(L)  | 2.345 (2)-2.420 (3) | 2.337 (4)-2.407 (4) | 2.317 (2)-2.389 (2) |
| Ln-O(H₂O)| 2.445 (2), 2.536 (2) | 2.419 (5)-2.518 (4) | 2.412 (3), 2.510 (3) |
| C-O      | 1.299 (4)-1.278 (4) | 1.258 (7)-1.272 (7) | 1.261 (4)-1.279 (4) |
| O(L)-Eu-O(L) | 71.91 (8), 72.89 (8), 73.54 (8) | 72.01 (1), 73.10 (1), 73.57 (2) | 72.72 (8), 73.66 (8), 74.24 (9) |
Figure 2. Crystal packing of EuL₃ (dashed lines indicate H-bonds and distances between ring centroids (Cg1-Cg9) (for details see Table S3)).

2.3. Luminescent Properties of EuL₃, TbL₃ and Ln₁ₓLn₂₁ₓL₃, Ln = Eu, Gd, Tb

The optical excitation spectra of luminescence consist of several broad spectral bands in the range of 260–300 nm and 310–370 nm, corresponding to π-π* transitions of the ligand, as well as narrow spectral bands, which are characterized by 4f⁴ intraconfigurational transitions of ion. A band at 480–490 nm is present in the spectra of both compounds and can be attributed to 7F₂→5D₂ transition in the case of EuL₃ and 7F₆→5D₄ transition—in the case of TbL₃. Figure 3 demonstrates the excitation spectra together with the characterization of spectral components as the f-f* transitions of the ions. The excitation spectrum of TbL₃ scarcely contains bands associated with intraconfigurational transitions of Tb³⁺, which indicates efficient sensitization of the ionic luminescence upon excitation through the ligand. On the contrary, due to the lower energy of the 5D₀ europium (III) ion resonant level compared to the 5D₄ level of the Tb³⁺ ion, luminescence sensitization efficiency is less for complex EuL₃ than for complex TbL₃ under optical excitation through ligand environment. This follows from a comparison of the emission intensities at 619 nm upon excitation through the ligand excitation bands and through the 7F₀→5D₂ transition of Eu³⁺. Thus, the excitation of Eu³⁺ through its ligand environment in the mixed compound will be less efficient than the excitation of Tb³⁺.

In addition, the spectra exhibit a broad band in the range of 380–450 nm, which can be attributed to the states of charge transfer between ligand molecules (LLCT), within ligand molecules (ILCT), or between the ligand and the ion (ligand to metal charge transfer, LMCT). The latter appears due to the low reduction potential of Eu³⁺ ion. Since this spectral feature is manifested for the Tb complex, which has a relatively high reduction potential, it cannot be attributed to the LMCT state.

The luminescence spectra of the complexes (Figure 4) contain spectral bands that are characteristic of f-f* transitions of the Eu³⁺ ion: ⁵D₀→⁷F₀ (580 nm), ⁵D₀→⁷F₁ (585–590 nm), ⁵D₀→⁷F₂ (610–620 nm), ⁵D₀→⁷F₃ (650–660 nm), ⁵D₀→⁷F₄ (690–710 nm); as well as f-f* transitions of Tb³⁺ ion: ⁵D₁→⁷F₅ (480–500 nm), ⁵D₄→⁷F₅ (535–555 nm), ⁵D₄→⁷F₄ (575–595 nm), ⁵D₄→⁷F₃ (610–630 nm), ⁵D₄→⁷F₂ (640–660 nm), ⁵D₄→⁷F₁ (660–675 nm), ⁵D₄→⁷F₀ (675–685 nm). Upon dissolving EuL₃ and TbL₃ in CH₃CN no significant shifts in luminescence spectra occur (see Figure S10).
Figure 3. Luminescence excitation spectra recorded for complexes, with registration at 545 nm for Tb$^{3+}$ emission (curve 1) and 617 nm for Eu$^{3+}$ emission (curve 2).

Figure 4. Photoluminescence spectra recorded for the investigated compounds.

As shown in Figure 4, with the increase in Eu concentration, the ratio of the spectral contribution Tb/Eu changes. Table 3 demonstrates that the ratio of the integrals ($I_{700}/I_{545}$) of the luminescence bands of Eu $5D_0 \rightarrow 7F_4$ (680–720 nm) and Tb $5D_4 \rightarrow 7F_5$ (535–555 nm) slightly increases from 0.10 for Eu$_{0.05}$Tb$_{0.95}$L$_3$ to 0.18 in the case of Eu$_{0.125}$Tb$_{0.875}$L$_3$. Then, the ratio of the integrals increases significantly with the increasing percentage of Eu up to almost 30 in the case of Eu$_{0.5}$Tb$_{0.5}$L$_3$ and Eu$_{0.75}$Tb$_{0.25}$L$_3$. The spectral bands associated
with the Eu and Tb emission have an equal number of Stark components with the same relative intensities, which indicates identical symmetry of the coordination polyhedron. Compounds Eu$_{0.25}$Tb$_{0.975}$L$_3$-Eu$_{0.125}$Tb$_{0.875}$L$_3$ are characterized by a more complex band shape in the spectral region 610–630 nm due to the contributions from the $^5$D$_4$→$^7$F$_5$ luminescence band of Tb$^{3+}$ and $^5$D$_0$→$^7$F$_2$ of the Eu$^{3+}$ ion. For the studied complexes, the chromaticity coordinates CIE were calculated (see Figure 5).

Table 3. Calculated ratios of integrated intensities of the $^5$D$_0$→$^7$F$_4$ Eu$^{3+}$ transition and $^5$D$_4$→$^7$F$_5$ Tb$^{3+}$ transition ($I_{700}/I_{545}$) and CIE coordinates for the investigated complexes.

|       | 2.5 | 5   | 7.5 | 10  | 12.5 | 15  | 25  | 50  | 75  |
|-------|-----|-----|-----|-----|------|-----|-----|-----|-----|
| $I_{700}/I_{545}$ | 0.02 | 0.10 | 0.14 | 0.18 | 0.40 | 3.09 | 9.02 | 29.46 | 28.07 |
| CIE   | 0.37, 0.58 | 0.45, 0.51 | 0.56, 0.42 | 0.49, 0.48 | 0.48, 0.48 | 0.52, 0.46 | 0.66, 0.34 | 0.67, 0.33 | 0.68, 0.32 |

Figure 5. CIE chromaticity diagram.

2.4. Description of Luminescence Decays

In the simplest case, luminescence decay is caused by the relaxation of the sole excited state and obeys the single-exponential law:

$$I = I_o e^{-\frac{t}{\tau_{obs}}},$$  (1)

where:

$$\tau_{obs} = \frac{1}{k_{obs}} = \frac{1}{k_{rad} + k_{nr}},$$  (2)

$k_{rad}$ and $k_{nr}$—rate constants of radiative and nonradiative processes of excited state relaxation. In some cases, a deviation from single-exponential law is observed; and biexponential decay is the most common. The biexponential decay is usually explained by the presence of two independent luminescent centers.

The luminescence decay of Eu$L_3$, Tb$L_3$ as well as Eu$_{1-x}$Gd$_x$L$_3$ and Gd$_x$Tb$_{1-x}$L$_3$ can be successfully described with single-exponential curves. Rate constants $k_{obs}$ calculated this way are shown in Table 4.
Table 4. Decay constants for Eu$_x$Gd$_{1-x}$L$_3$ and Gd$_x$Tb$_{1-x}$L$_3$.

| Compound         | $k_{Eu}$ (Eu$^{3+}$ Decay) | Compound         | $k_{Tb}$ (Tb$^{3+}$ Decay) |
|------------------|---------------------------|------------------|-----------------------------|
| Eu$_{0.01}$Gd$_{0.99}$L$_3$ | 3.51                      | Tb$_3$           | 2.91                        |
| Eu$_{0.025}$Gd$_{0.975}$L$_3$ | 3.60                      | Gd$_{0.01}$Tb$_{0.99}$L$_3$ | 2.66                        |
| Eu$_{0.005}$Gd$_{0.95}$L$_3$ | 3.60                      | Gd$_{0.025}$Tb$_{0.975}$L$_3$ | 2.63                        |
| Eu$_{0.075}$Gd$_{0.925}$L$_3$ | 3.60                      | Gd$_{0.05}$Tb$_{0.95}$L$_3$ | 2.75                        |
| Eu$_{0.1}$Gd$_{0.9}$L$_3$ | 3.60                      | Gd$_{0.25}$Tb$_{0.75}$L$_3$ | 2.72                        |
| Eu$_{0.125}$Gd$_{0.875}$L$_3$ | 3.53                      | Gd$_{0.125}$Tb$_{0.875}$L$_3$ | 2.86                        |
| Eu$_{0.15}$Gd$_{0.85}$L$_3$ | 3.57                      | Gd$_{0.15}$Tb$_{0.85}$L$_3$ | 2.64                        |
| Eu$_{0.2}$Gd$_{0.8}$L$_3$ | 3.52                      | Gd$_{0.2}$Tb$_{0.8}$L$_3$ | 2.65                        |
| Eu$_{0.25}$Gd$_{0.75}$L$_3$ | 3.41                      | Gd$_{0.25}$Tb$_{0.75}$L$_3$ | 2.77                        |

The luminescence decays of [Eu$_x$Tb$_{1-x}$L$_3$(H$_2$O)$_2$] registered at 545 nm (Tb$^{3+}$ emission) can be well fitted by single-exponential decay. Estimated $\tau_{obs}$ of Tb$^{3+}$ emission sharply decrease with increased Eu$^{3+}$ concentration. It can be explained by the nonradiative energy transfer from Tb$^{3+}$ ions to Eu$^{3+}$ ions since the resonance energy state ($^5$D$_0$) of Eu$^{3+}$ ion lies lower than the $^5$D$_4$ state for Tb$^{3+}$ ion [53].

The typical luminescence decay curve of europium(III) emission in [Eu$_x$Tb$_{1-x}$L$_3$(H$_2$O)$_2$] ($x < 0.25$) has an uncharacteristic behavior at short times, in which increased emission intensity is observed (see Figure 6).

Figure 6. Luminescence decay of Eu$^{3+}$ (red crosses) emission, Tb$^{3+}$ (green bubbles) emission, and their fitting curves. Compound Eu$_{0.075}$Tb$_{0.925}$L$_3$, $\lambda_{EX}$ 350 nm.

Europium(III) luminescence decays can be described by the following model, hereinafter nonradiative relaxation of excited states of Tb$^{3+}$ and Eu$^{3+}$ is omitted:

$$ Eu^* \xrightarrow{k_{Eu}} Eu + h\nu_{Eu} $$

$$ Tb^* \xrightarrow{k_{Tb}} Tb + h\nu_{Tb} $$

$$ Tb^* \xrightarrow{k_{Tb}} Eu^* $$
The decay rate of luminescence can be expressed by the following differential equations:

\[
\begin{align*}
\frac{\partial C_{\text{Eu}^*}}{\partial t} &= -k_{\text{Eu}} C_{\text{Eu}^*} + k_{\text{ET}} C_{\text{Tb}^*} \\
\frac{\partial C_{\text{Tb}^*}}{\partial t} &= -(k_{\text{Tb}} + k_{\text{ET}}) C_{\text{Tb}^*}
\end{align*}
\]

the solution of these equations allows one to obtain the form of the dependence of the Eu\(^{3+}\) and Tb\(^{3+}\) ions luminescence on time:

\[
C_{\text{Eu}^*} = C_1 e^{-k_{\text{Eu}} t} + C_2 e^{-k_1 t}, \quad (8)
\]

\[
S_{\text{Tb}^*} = C_{\text{Tb}^*}^0 e^{-k_1 t}, \quad (9)
\]

where:

\[
k_1 = k_{\text{ET}} + k_{\text{Tb}}, \quad (10)
\]

\[
C_2 = -S_{\text{Tb}^*}^0 \frac{k_{\text{ET}}}{k_1 - k_{\text{Eu}}}, \quad (11)
\]

\[
C_1 = S_{\text{Eu}^*}^0 - C_2. \quad (12)
\]

Notably, the decay of europium(III) luminescence is described by the biexponential law with a negative pre-exponential factor \((C_2)\) of the second exponential component.

As the europium(III) concentration increases, the probability of energy transfer from Tb to Eu increases, reflected in an increased \(k_{\text{Eu}}\) constant (Table 5). At high Eu concentrations, the luminescence of terbium(III) cannot be detected because nonradiative relaxation occurs.

### Table 5. Europium(III) decay and constants, calculated for Eu\(_x\)Tb\(_{1-x}\)L\(_3\) compounds.

| Compound         | \(k_{\text{Eu}}\) (Eu\(^{3+}\) Decay) | \(k_1 = k_{\text{ET}} + k_{\text{Tb}}\) Calculated from Eu\(^{3+}\) Decay | \(k_1 = k_{\text{ET}} + k_{\text{Tb}}\) Calculated from Tb\(^{3+}\) Decay |
|------------------|-------------------------------------|--------------------------------------------------------------------------|--------------------------------------------------------------------------|
| Eu\(_{0.01}\)Tb\(_{0.99}\) L\(_3\) | 2.95                                | 3.03                                                                      | 2.84                                                                      |
| Eu\(_{0.025}\)Tb\(_{0.975}\) L\(_3\) | 2.82                                | 5.58                                                                      | 3.58                                                                      |
| Eu\(_{0.05}\)Tb\(_{0.95}\) L\(_3\) | 3.01                                | 5.85                                                                      | 4.07                                                                      |
| Eu\(_{0.075}\)Tb\(_{0.925}\) L\(_3\) | 3.23                                | 7.29                                                                      | 5.79                                                                      |
| Eu\(_{0.1}\)Tb\(_{0.9}\) L\(_3\) | 3.40                                | 8.15                                                                      | 7.03                                                                      |
| Eu\(_{0.125}\)Tb\(_{0.875}\) L\(_3\) | 3.39                                | 8.99                                                                      | 7.96                                                                      |
| Eu\(_{0.15}\)Tb\(_{0.85}\) L\(_3\) | 3.35                                | 8.73                                                                      | 7.38                                                                      |
| Eu\(_{0.175}\)Tb\(_{0.825}\) L\(_3\) | 3.47                                | 12.40                                                                     | 10.87                                                                     |
| Eu\(_{0.2}\)Tb\(_{0.8}\) L\(_3\) | 3.40                                | 14.84                                                                     | n/a                                                                       |

Observed rate constants \(k_{\text{Tb}}^{\text{obs}}\) and \(k_{\text{Eu}}^{\text{obs}}\) also include nonradiative relaxation processes:

\[
k_{\text{Tb}}^{\text{obs}} = k_{\text{Tb}}' + k_{\text{Tb}}^{nr} \quad (13)
\]

\[
k_{\text{Eu}}^{\text{obs}} = k_{\text{Eu}}' + k_{\text{Eu}}^{nr}. \quad (14)
\]

The energy transfer rate constant can be estimated by subtracting the \(k_{\text{Tb}}\) determined for the corresponding complex by the formula from \(k_1\) (Table S9).

### 3. Materials and Methods

Lanthanide nitrates, hexahydrates (99.99%) and other reagents were purchased from Aldrich and used without additional purification. Elemental analyses were performed on the Elemental Vario MicroCube CHNO(S) analyzer. Metal content was determined by complexometric titration with Trilon B solution in the presence of Xylenol Orange as an indicator. Complexes were decomposed before analysis by heating with concentrated HNO\(_3\). \(^1\)H and \(^{19}\)F NMR spectra were recorded on Bruker AC-300 instrument (300 and 283 MHz, respectively) at 300 K for solutions in CDCl\(_3\). TMS was used as an internal standard for \(^1\)H NMR spectra and CFCl\(_3\) for \(^{19}\)F NMR spectra (\(\delta = 0.00\)). \(^{13}\)C NMR
spectra were recorded on a Bruker DXR-500 instrument operated at 125.8 MHz with TMS as internal standard. Mass spectra were recorded on a Thermo DSQ II/Thermo Trace instrument; the ionization energy was 70 eV (direct sample injection).

To determine the lanthanide content in mixed metal complexes, a weighted amount of the complex (about 100 mg, exact weight) was destructed in a volumetric flask with a hot concentrated nitric acid. The solution was brought to volume with double distilled water, diluted as necessary, and analyzed by ICP MS using PerkinElmer ELAN DRC-II mass spectrometer.

Photoluminescence spectra and luminescence excitation spectra were recorded at ambient temperature in the crystalline phase. For this task, a Horiba Jobin Yvon Fluorolog FL3-22 spectrofluorometer equipped with a 450 W xenon lamp emitting within the 250–900 nm spectral range was employed. The luminescence of the samples was detected with a Hamamatsu R928 photomultiplier operating within 200–850 nm. The decay kinetics of europium(III) luminescence was observed by the $^5D_0-^7F_4$ transition (maximum at 700 nm) and not by the more usual intense $^5D_0-^7F_2$ transition. This choice of the band for detecting luminescence is associated with the overlap of the $^5D_0-^7F_2$ transition (maximum at 617 nm) with the $^5D_4-^7F_3$ minor transition of terbium(III) (with a maximum at 611 nm).

Single crystal X-ray studies of crystals were carried out on a Bruker D8 Venture (for $[\text{Ln}(\text{L})_3(\text{H}_2\text{O})]$ (Ln = Eu (EuL$_3$), Tb (TbL$_3$)) and Bruker D8 Quest (for $[\text{Gd}(\text{L})_3(\text{H}_2\text{O})]$ (GdL$_3$)) diffractometers equipped with a CCD detector (MoK$_{\alpha}$, $\lambda = 0.71073 \text{ Å}$, graphite monochromator) [54]. A semiempirical adjustment for absorption was introduced for EuL$_3$ and GdL$_3$ [55]. Using Olex2 [56], the structures were solved with the ShelXT [57] structure solution program using Intrinsic Phasing and refined with the olex2.refine [58] refinement package using Least-Squares minimization against $F^2$ in anisotropic approximation for non-hydrogen atoms. The hydrogen atoms in the ligands were calculated geometrically and refined in the “riding” model. The crystallographic parameters and the structure refinement statistics are shown in Table 1. Supplementary crystallographic data for the compounds synthesized are given in CCDC numbers 2074491 (for EuL$_3$), 2074616 (for GdL$_3$), 2074492 (for TbL$_3$). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif, accessed on 24 April 2021 (CCDC: Cambridge, UK).

3.1. Synthesis
3.1.1. Synthesis of 4,4-Difluoro-1-(1,5-dimethyl-1H-pyrazol-4-yl)butane-1,3-dione (HL)

The ligand was obtained by a modified procedure described earlier [59].

Briefly, sodium hydride (4.0 g, 100 mmol, 60% dispersion in mineral oil) was placed in a 500 mL round-bottom flask under Ar blanket, and 150 mL of dry THF was added with vigorous stirring. Anhydrous EtOH (0.5 mL) was added in one portion at 0 °C, followed by the dropwise addition of a solution of 1-(1,5-dimethyl-1H-pyrazol-4-yl)ethan-1-one [60] (6.9 g, 50 mmol) and ethyl difluoroacetate (6.4 g, 51 mmol) in 30 mL of THF. When gas evolution was ceased, the cooling bath was removed, and the reaction mixture was stirred at room temperature for 15 h. After this, the dark brown solution with a small amount of precipitate was re-cooled to 0 °C, 10 mL of anhydrous EtOH was added slowly to decompose traces of NaH. The resulting solution was stirred for 30 min. The solvent was removed by evaporation under reduced pressure (100 Torr, bath temperature 40 °C), then EtOAc (40 mL) and subsequently a mixture of conc. HCl (20 mL) and crushed ice (80 mL) was added to the residue. The organic phase was separated, and the aqueous phase was then extracted with EtOAc (3 × 80 mL). The combined organic fractions were washed with brine (50 mL), dried over MgSO$_4$ and evaporated to dryness. The resulting brown oil was distilled under diminished pressure. The yield was 8.76 g (81%). Yellow oil, which solidified upon standing; bp 178–180 °C (9 torr).

$^1$H NMR (300 MHz CDCl$_3$) δ 7.54 (s, 1H, CH=); 6.10 (s, 1H, CH); 5.91 (t, 1H, $J = 54.5 \text{ Hz}$, CHF$_2$); 3.83 (s, 3H, CH$_3$); 2.52 (s, 3H, CH$_3$). $^{13}$C NMR (128 Hz, CDCl$_3$) δ 185.83; 175.31; 142.91; 139.45; 116.66; 109.40 (t, $J = 245.0 \text{ Hz}$); 94.10 (t, $J = 3.9 \text{ Hz}$); 36.12; 10.91. $^{19}$F NMR
3.1.2. Synthesis of Complexes

Preparation of $\text{EuL}_3$: 137.8 mg (0.309 mmol) of $\text{Eu(NO}_3)_3\cdot6\text{H}_2\text{O}$ was dissolved in a plastic centrifuge tube with 1.5 mL of water at vigorous shaking; to precipitate Eu(OH)$_3$, 200.0 µL (20% excess) of concentrated ammonia solution (25%) was added. To isolate pure Eu(OH)$_3$, the solution with the precipitate was centrifuged for 2 min (8000 rpm), the solution was decanted, and the precipitate was washed with water. Centrifugation and subsequent washing of the precipitate were carried out until the smell of ammonia disappeared. Then the obtained Eu(OH)$_3$ was suspended in 3 mL of EtOH and added to a solution of 200.0 mg (0.926 mmol) of the ligand and 140.0 mg (0.309 mmol) Tb(NO$_3$)$_3\cdot6\text{H}_2\text{O}$ were used. The yield was 83%.

Preparation of $\text{TbL}_3$: the procedure is the same as for the synthesis of EuL$_3$. A total of 200 mg (0.926 mmol) ligand and 140.0 mg (0.309 mmol) Tb(NO$_3$)$_3\cdot6\text{H}_2\text{O}$ were used. The yield was 82%.

Preparation of $\text{GdL}_3$: The procedure is the same as for the synthesis of EuL$_3$. A total of 200.0 mg (0.926 mmol) ligand and 139.4 mg (0.309 mmol) Gd(NO$_3$)$_3\cdot6\text{H}_2\text{O}$ were used. The yield was 78%.

The synthesis of mixed metal complexes was carried out according to the same procedure as for monometallic complexes. Weighed portions of $\text{Eu(NO}_3)_3\cdot6\text{H}_2\text{O}$, $\text{Tb(NO}_3)_3\cdot6\text{H}_2\text{O}$, and Gd(NO$_3$)$_3\cdot6\text{H}_2\text{O}$ were taken in such a molar ratio as planned in the target compound, $x = 0.01, 0.025, 0.05, 0.075, 0.10, 0.125, 0.15, 0.25, 0.5, 0.75$.

The isostructurality of the compounds is confirmed by matching PXRD patterns. The Ln$^1$:Ln$^2$ ratio in synthesized compounds was verified by the EDX method. Thus, in Ln$^1$Ln$^2$(1−$x$)L$_3$ compounds, various REE ions are statistically distributed. Analytical data (IR and elemental analysis data are given in the SI)

4. Conclusions

The molecular complexes of the HL ligand obtained in the present work demonstrate a bright luminescence of both europium (III) and terbium (III) ions. The isostructurality of europium (III), terbium (III), and gadolinium(III) compounds makes it possible to obtain mixed metal complexes with a statistical distribution of rare-earth ions, which opens up possibilities for obtaining phosphors with a tunable emission color. The use of these complexes, including mixed metal terbium–europium systems in OLED is of interest.

The proposed methodology for estimating the energy transfer constant between terbium (III) and europium (III) ions will make it possible to better describe the luminescent properties of mixed metal complexes used as luminescent thermometers and chemical sensors.

The methodology for studying the kinetics of energy transfer to the terbium-europium bimetallic complexes includes a detailed analysis (Figures S11–S14, Tables S5–S8) of the decay curve of europium (III) in the initial region where the rise to an exponential decay was proposed.

Supplementary Materials: The following are available online: Table S1. CHN data and Ln1:Ln2 ratios for a mixed metal complexes Ln$^1$:Ln$^2$·L$_3$. Ln$^1$, Ln$^2$ = Eu, Gd, Tb; Figure S11. IR spectra of Eu$_x$Gd$_{1−x}$L$_3$ complexes; Figure S12. IR spectra of Gd$_x$Tb$_{1−x}$L$_3$ complexes; Figure S13. IR spectra of Eu$_x$Tb$_{1−x}$L$_3$ complexes; Figure S14. PXRD patterns of EuL$_3$, GdL$_3$ TbL$_3$ and simulated from single crystal data of ones; Figure S15. PXRD patterns of Eu$_x$Gd$_{1−x}$L$_3$ compounds; Figure S16. PXRD patterns of Gd$_x$Tb$_{1−x}$L$_3$ compounds; Figure S17. PXRD patterns of Eu$_x$Tb$_{1−x}$L$_3$ compounds; Figure S18. Mass loss (TG) and DTA curves (left) and signals from the mass spectro-metric detector of the thermal decomposition products for [TbL$_3$(H$_2$O)$_2$] (right); Figure S19. Mass loss (TG) and DTA curves
Zinna, F.; Pasini, M.; Galeotti, F.; Botta, C.; Di Bari, L.; Giovanella, U. Design of Lanthanide-Based OLEDs with Remarkable

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(Left) and signals from the mass spectro-metric detector of the thermal decomposition products for [Eu(L(H₂O)₂)] (right); Table S2. SHAPE analysis for compounds LnL₃; Table S3. Selected parameters of intermolecular π–π interactions in LnL₃ (CgI/J is plane of 5-membered ring, CgI-CgJ is distance between ring centroids, α is dihedral angle between planes I and J, CgI–Perp is perpendicular distance of CgI on ring J, CgJ–Perp is perpendicular distance of CgJ on ring I, Slippage is distance between CgI and perpendicular projection of CgJ on ring I); Table S4. Selected parameters of O-H...O, O-H...N, C-H...O, and C-H...F interactions in LnL₃; Figure S10. Emission spectra of EuL₃ and TbL₃ in CH₃CN solution; λₓₓ = 350 nm; Figure S11. Eu³⁺ luminescence fitting curves for for EuₓGd₁₋ₓL₃; λₓₓ = 350 nm, λₓᵧ = 700 nm; Table S15. Eu³⁺ luminescence fitting parameters for EuₓGd₁₋ₓL₃; Figure S12. Tb³⁺ luminescence fitting curves for for GdₓTb₁₋ₓL₃; λₓₓ = 350 nm, λₓᵧ = 545 nm; Table S16. Tb³⁺ luminescence fitting parameters for GdₓTb₁₋ₓL₃; Figure S13. Eu³⁺ luminescence fitting curves for for EuₓTb₁₋ₓL₃; λₓₓ = 350 nm, λₓᵧ = 700 nm; Table S17. Eu³⁺ luminescence fitting parameters for EuₓTb₁₋ₓL₃; Figure S14. Tb³⁺ luminescence fitting curves for for EuₓTb₁₋ₓL₃; Table S18. Tb³⁺ luminescence fitting parameters for EuₓTb₁₋ₓL₃; Table S19. Calculated Tb³⁺ to Eu³⁺ energy transfer rate constants for EuₓTb₁₋ₓL₃ compounds.

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