

Microwave-assisted Preparation, Structures, and Photoluminescent Properties of $[\text{Ln}(\text{NO}_3)_2(\text{H}_2\text{O})_3(\text{L})_2](\text{NO}_3)(\text{H}_2\text{O})$ $\{\text{Ln} = \text{Tb}, \text{Eu}; \text{L} = 2\text{-}(4\text{-pyridylium})\text{ethanesulfonate}, (4\text{-pyH})^+\text{-CH}_2\text{CH}_2\text{-SO}_3^-\}$

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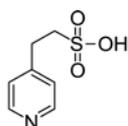
Two lanthanide complexes, $[\text{Ln}(\text{NO}_3)_2(\text{H}_2\text{O})_3(\text{L})_2](\text{NO}_3)(\text{H}_2\text{O})$ $\{\text{Ln} = \text{Eu}$ (**1**), **Tb** (**2**); $\text{L} = 2\text{-}(4\text{-pyridylium})\text{-ethanesulfonate}, (4\text{-pyH})^+\text{-CH}_2\text{CH}_2\text{-SO}_3^-\}$, were prepared from lanthanide nitrate and 4-pyridineethanesulfonic acid in H_2O under microwave-heating conditions. Complexes **1** and **2** are isostructural, and the lanthanide metal in both complexes is coordinated to nine oxygen atoms. The pyridyl nitrogen in the ligand is protonated to give a zwitter ion that possesses an NH^+ (pyridyl) positive end and an SO_3^- negative end. All O–H and N–H hydrogen atoms participate in hydrogen bonds to generate a two-dimensional (complex **1**) or a three-dimensional network (complex **2**). Complex **1** exhibits an intense red emission, whereas complex **2** exhibits an intense green emission in the solid state at room temperature.

Key Words : Lanthanide complex, Crystal structure, Microwave heating, Zwitter ion, Emission

Introduction

The design and synthesis of metal-organic frameworks (MOFs) have received considerable attention recent years not only because of their potential applications in ion exchange, separation, catalysis, molecular magnetism, and electrical conductivity, but also because of their intriguing multidimensional frameworks.¹⁻⁵ Dipyridyl- and multi-carboxylate-type linking ligands are commonly used for the preparation of MOFs. In particular, MOFs of *f*-block metals are typically prepared by utilizing multi-carboxylates, including pyridine carboxylic acid, pyridine dicarboxylic acid, benzene dicarboxylic acid, sulfonic acid, bipyridine carboxylic acid, and benzimidazole carboxylic acid.⁶⁻¹²

4-Pyridineethanesulfonic acid is a rather long and flexible multifunctional ligand that contains a terminal pyridyl (*N*-donor) and a terminal sulfate (*O*-donor) groups. According to the hard-soft acid-base (HSAB) concept, the softer nitrogen atoms of the pyridyl group may coordinate to *d*-block metals, and the harder oxygen atoms of the sulfate group may coordinate to *f*-block metals. Several complexes of 4-pyridineethanesulfonic acid of *d*-block metals were reported.¹³⁻¹⁵ However, *f*-block metal counterparts have not been reported yet.



4-pyridineethanesulfonic acid

MOFs are typically prepared by hydrothermal, hydro-(solvo)thermal, or solvothermal methods.⁴ These methods

typically require long reaction times and high temperatures. To overcome such vigorous conditions, microwave was recently employed, which creates high heating effects in short times.¹⁶⁻²² We performed our work under microwave-heating conditions, and report herein the preparation, structures, and thermal and photoluminescent properties of two lanthanide complexes, $[\text{Ln}(\text{NO}_3)_2(\text{H}_2\text{O})_3(\text{L})_2](\text{NO}_3)(\text{H}_2\text{O})$ $\{\text{Ln} = \text{Eu}$ (**1**), **Tb** (**2**); $\text{L} = 2\text{-}(4\text{-pyridylium})\text{-ethanesulfonate}, (4\text{-pyH})^+\text{-CH}_2\text{CH}_2\text{-SO}_3^-\}$.

Experimental Section

Ethanol was vacuum-distilled over magnesium grain. 4-Pyridineethanesulfonic acid and lanthanide nitrates were purified by recrystallization. IR spectra were obtained in the range of 400-4000 cm^{-1} on a Nicolet 320 FTIR spectrophotometer. Thermogravimetric analysis (TGA) was performed on a TA4000/SDT 2960 instrument at the Cooperative Center for Research Facilities (CCRF) in Sungkyunkwan University. Elemental analyses were carried out by the Analytical Laboratory at Kangneung-Wonju National University. Solid-state luminescent spectra were obtained with an Aminco-Bowman Series2 (Xenon lamp, 150 W).

Preparation of $[\text{Eu}(\text{NO}_3)_2(\text{H}_2\text{O})_3(\text{L})_2](\text{NO}_3)(\text{H}_2\text{O})$ (1**).** 4-Pyridineethanesulfonic acid (44 mg, 0.235 mmol), $[\text{Eu}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}]$ (50 mg, 0.117 mmol), and H_2O (3 mL) were added to a 25 mL Teflon-lined autoclave vessel. The colorless solution was heated by microwave (700 W) for 40 s. The resulting solution was air-cooled slowly, concentrated to one-third its original volume with a rotary evaporator, and then allowed to stand for 5 days. The resulting colorless crystals were separated by filtration, washed with ethanol (10 mL \times 3), and then air-dried (46 mg, 0.058 mmol, 51%

yield). mp 99–101 °C. IR (KBr, cm^{-1}): 3566, 3511, 3399, 3257 (N–H), 3163, 3098, 2937, 2876, 1709, 1644, 1470, 1419, 1300, 1172, 1096, 1062, 908, 806, 747, 698. Anal. Calc. for $\text{C}_{14}\text{H}_{26}\text{N}_5\text{O}_{19}\text{S}_2\text{Eu}$: C 21.43; H 3.34; N 8.93. Found: C 20.85; H 2.95; N 9.05.

Preparation of $[\text{Tb}(\text{NO}_3)_2(\text{H}_2\text{O})_3(\text{L})_2](\text{NO}_3)(\text{H}_2\text{O})_2$. Complex **2** was prepared analogously to complex **1**. Yield: 57%. mp 113–115 °C. IR (KBr, cm^{-1}): 3598, 3537, 3500, 3420, 3251 (N–H), 3154, 3095, 2968, 2938, 2867, 1709, 1644, 1511, 1470, 1303, 1173, 1062, 904, 807, 750, 697. Anal. Calc. for $\text{C}_{14}\text{H}_{26}\text{N}_5\text{O}_{19}\text{S}_2\text{Tb}$: C 21.25; H 3.31; N 8.85. Found: C 21.46; H 2.93; N 8.82.

X-ray Structure Determination. All X-ray data were collected with a Bruker Smart APEX2 diffractometer equipped with a Mo X-ray tube (CCRF). Collected data were corrected for absorption with SADABS based upon the Laue symmetry by using equivalent reflections.²³ All calculations were carried out with SHELXTL programs.²⁴

A colorless crystal of complex **1** of approximate dimensions $0.26 \times 0.24 \times 0.22 \text{ mm}^3$, shaped as a block, was used for crystal- and intensity-data collection. A colorless crystal of complex **2** (block, $0.30 \times 0.18 \times 0.16 \text{ mm}^3$) was used. All non-hydrogen atoms were refined anisotropically. The ethyl groups in the ligands of complex **1** were extremely disordered, and the best fit was obtained by considering these atoms to be distributed over two positions with the site occupation factors of 0.52:0.48 {(C1 and C2):(C1A and C2A)}. The N–H and O–H hydrogen atoms in both complexes could be located and refined freely, and the C–H hydrogen atoms were generated in idealized positions and refined in a riding mode. Details on crystal data, intensity collection, and refinement details are given in Table 1. Selected bond lengths and angles are given in Table 2.

Crystallographic data for the structural analysis have been deposited at the Cambridge Crystallographic Data Center: 816050 (**1**) and 816051 (**2**). Copies of this information may be obtained free of charge from: The director, CCDC, 12 Union Road, Cambridge, CB21EZ, UK (Fax: +44-1223-336-033; email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Results and Discussion

Preparation. In this work, we initially attempted to

Table 1. X-ray data collection and structure refinement

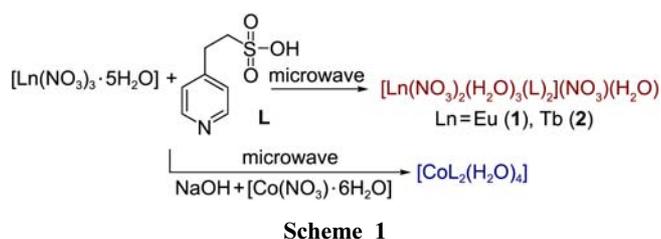
	Complex 1	Complex 2
Empirical formula	$\text{C}_{14}\text{H}_{26}\text{EuN}_5\text{O}_{19}\text{S}_2$	$\text{C}_{14}\text{H}_{26}\text{TbN}_5\text{O}_{19}\text{S}_2$
Formula weight	784.48	791.44
Temperature, K	296(2)	296(2)
Crystal system	orthorhombic	orthorhombic
Space group	Pnma	$P2_12_12_1$
<i>a</i> , Å	17.347(1)	10.793(1)
<i>b</i> , Å	14.296(1)	14.167(2)
<i>c</i> , Å	10.885(1)	17.324(2)
<i>V</i> , Å ³	2699.4(4)	2648.8 (6)
<i>Z</i>	4	4
<i>D</i> _{calc} , g cm ⁻³	1.930	1.985
μ , mm	2.572	2.923
<i>F</i> (000)	1568	1576
θ range (°)	2.21–28.39	1.86–28.28
<i>T</i> _{min}	0.6015	0.6520
<i>T</i> _{max}	0.5544	0.4742
No. of reflections measured	92558	17890
No. of reflections unique	3516	6185
No. of reflections with $I > 2\sigma(I)$	3277	5875
No. of parameters	246	411
Max., in $\Delta\rho$ (e Å ⁻³)	1.066	1.228
Min., in $\Delta\rho$ (e Å ⁻³)	–0.662	–0.515
Absolute structure parameter		0.228(6)
GOF on <i>F</i> ²	1.080	1.013
<i>R</i> 1 ^a	0.0277	0.0223
<i>wR</i> 2 ^b	0.0695	0.0476

$$^a R_1 = \sum |F_o| - |F| / \sum |F_o|, \quad ^b wR_2 = \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]^{1/2}$$

prepare *3d-4f* MOFs by using the title ligand (4-pyridine-ethanesulfonic acid), which possesses the softer *N*-donor and the harder *O*-donor atoms. With this goal in mind, a reaction mixture containing the ligand, $[\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$, $[\text{Ln}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}]$ (Ln = Eu or Tb), and NaOH was microwave-heated (700 W). In this reaction, the Co^{2+} ion was expected to coordinate to the pyridyl N atom, and the Ln^{3+} ion to the sulfate O atom. However, inconsistent with our expectation, the orange crystalline product turned out to be a molecular species, $[\text{CoL}_2(\text{H}_2\text{O})_4]$, which was reported previously (Scheme 1).¹⁴ In this cobalt complex, the Co^{2+} ion is coordinated to the pyridyl N atom. The experimental results indicate that the Co–L formation dominates the reaction

Table 2. Selected bond lengths (Å) and bond angles (°)

Complex 1					
Eu1–O1	2.365(3)	Eu1–O4	2.501(3)	Eu1–O5	2.491(3)
Eu1–O7	2.496(2)	Eu1–O9	2.467(2)	N1–HN1	0.94(6)
O1–Eu1–O1A	144.7(2)	O1–Eu1–O9	71.1(1)	O1–Eu1–O10	86.5(1)
Complex 2					
Tb1–O1	2.341(2)	Tb1–O4	2.369(2)	Tb1–O7	2.485(2)
Tb1–O8	2.466(2)	Tb1–O10	2.487(2)	Tb1–O11	2.454(2)
Tb1–O16	2.328(2)	Tb1–O17	2.476(2)	Tb1–O18	2.427(2)
N1–HN1	0.68(4)	O1–Tb1–O4	143.72(8)	O1–Tb1–O7	76.76(8)
O1–Tb1–O18	69.87(9)				



when the reaction mixture is treated under microwave-heating conditions.

We examined the reaction between the ligand and $[\text{Ln}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}]$ in the absence of $[\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$ and NaOH. A colorless aqueous solution containing the ligand and $[\text{Ln}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}]$ in a Teflon-lined autoclave vessel was heated by microwave. The reaction is complete in 40 s because of high microwave power (700 W). Although the reaction time is very short, the preparation is reproducible. Colorless single crystals formed after five days. The product were characterized by IR spectroscopy, elemental analysis, and X-ray diffraction, and identified to have the chemical formula $[\text{Ln}(\text{NO}_3)_2(\text{H}_2\text{O})_3(\text{L})_2](\text{NO}_3)(\text{H}_2\text{O})$ ($\text{Ln} = \text{Eu}$ (1), Tb (2)). Complexes 1 and 2 are the first examples of *f*-block metal complexes of 4-pyridineethanesulfonic acid. These are molecular species and have the Ln–O bonds as expected (Scheme 1). In the IR spectra, the N–H stretches of complexes 1 and 2 appear at 3257 and 3251 cm^{-1} , respectively.

Crystal Structures. Complexes 1 and 2 crystallized in the orthorhombic centrosymmetric (*Pnma*) and noncentrosymmetric (*P2₁2₁2₁*) space groups, respectively. Nevertheless, both complexes are isostructural, and therefore the structural description is focused on complex 1. The structure of complex 1 is shown in Figure 1, in which the Eu^{3+} ion is

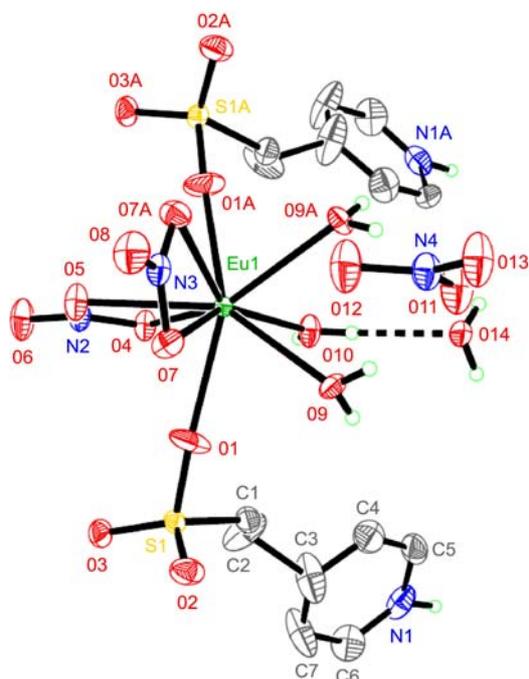


Figure 1. ORTEP drawing of complex 1.

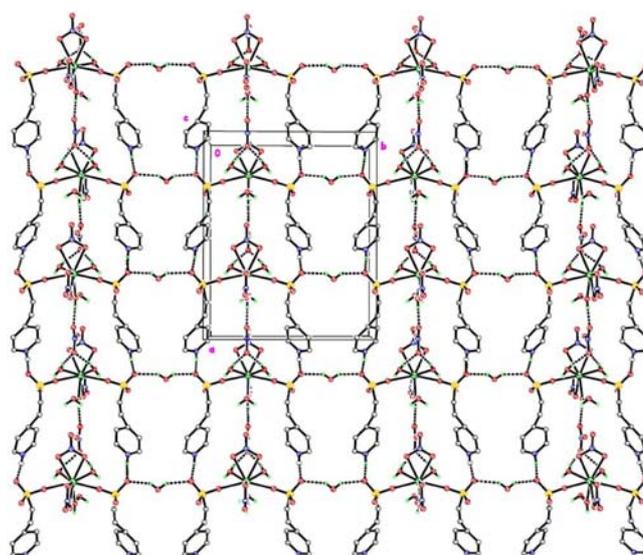


Figure 2. A 2-D network formed by hydrogen bonds in complex 1.

coordinated by nine oxygen atoms. An asymmetric unit, $[\text{Eu}_{0.5}(\text{NO}_3)(\text{H}_2\text{O})_{1.5}(\text{L})](\text{NO}_3)_{0.5}(\text{H}_2\text{O})_{0.5}$, consists of only half the formula unit. The other half is generated by the crystallographic reflection. The central metal (Eu1), two NO_3^- ligands (N2, O4–O6; N3, O8), one aqua ligand (O10), the NO_3^- (N4, O11–O13) counterion, and one crystalline water (O14) molecule, a total of 13 atoms, lie on the crystallographic mirror plane. The pyridyl nitrogen (N1) is protonated, and therefore the ligand acts as a zwitter ion that possesses an NH^+ (pyridyl) positive end and an SO_3^- negative end. As a result, the ligand has a net charge of zero. The Eu–O bond lengths fall in the range of 2.365(3)–2.501(3) Å, which agree well with those found for other europium complexes.^{25–27}

The crystalline water and the NO_3^- counterion are attracted to the first coordination sphere by the O–H \cdots O hydrogen bonds. The crystalline water O–H and the pyridyl N–H hydrogen atoms participate in the intermolecular hydrogen bonds, which connect the complexes to a 2-dimensional network (Fig. 2). In fact, all O–H and N–H hydrogen atoms in complexes 1 and 2 participate in hydrogen bonds (Tables 3 and 4).

The structure of complex 2 is practically the same as that of complex 1, as shown in Figure 3. The Tb^{3+} ion is nine-coordinate with the Tb–O bond lengths in the range of 2.328(2)–2.487(2) Å, which are similar to those found in other related terbium complexes.^{26,28,29} Unlike atoms in

Table 3. Hydrogen bonds in complex 1 (Å and °)

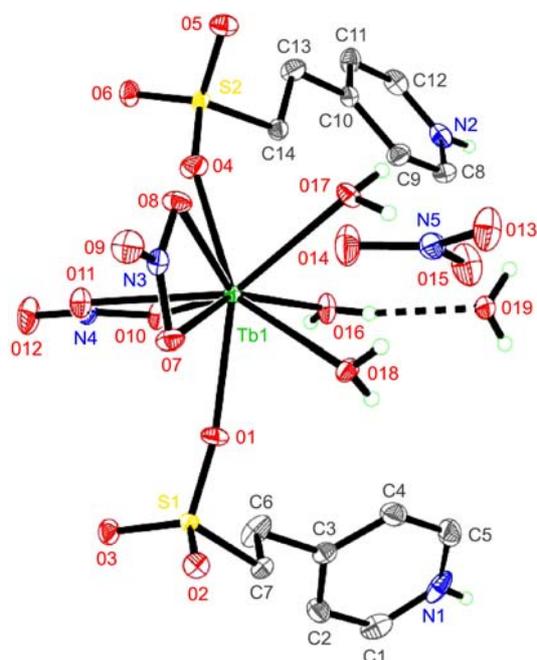
D–H \cdots A	D–H	H \cdots A	D \cdots A	D–H–A
O9–H9A \cdots O3#2	0.73(4)	2.08(4)	2.781(3)	163(4)
O10–H10A \cdots O13#3	0.78(6)	1.93(6)	2.705(5)	172(6)
O14–H14 \cdots O2#2	0.83(6)	2.17(7)	2.909(3)	149(6)
N1–HN1 \cdots O2#3	0.94(6)	1.86(6)	2.792(4)	175(5)

Symmetry transformations used to generate equivalent atoms: #1 = $x, -y + 1/2, z$; #2 = $-x + 1/2, -y, z + 1/2$; #3 = $x + 1/2, y, -z + 3/2$.

Table 4. Hydrogen bonds in complex 2 (Å and °)

D–H···A	D–H	H···A	D···A	D–H–A
O18–HO5···O3#1	0.77(4)	2.04(4)	2.753(3)	155(3)
O17–HO3···O6#2	0.82(4)	2.01(4)	2.826(3)	173(4)
O19–HO7···O2#1	0.70(4)	2.25(4)	2.920(4)	161(6)
O16–HO1···O13#3	0.87(4)	1.84(4)	2.700(3)	172(4)
O19–HO8···O5#2	0.88(4)	1.99(4)	2.861(4)	166(3)
N2–HN2···O2#3	0.93(5)	1.90(5)	2.788(4)	159(5)
N1–HN1···O5#3	0.68(4)	2.13(4)	2.808(5)	171(5)

Symmetry transformations used to generate equivalent atoms: #1 = $x-1/2, -y+3/2, -z+2$; #2 = $x-1/2, -y+5/2, -z+2$; #3 = $-x+1/2, -y+2, z+1/2$.

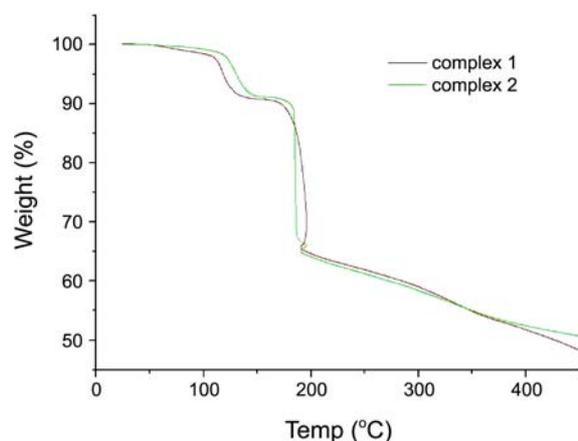
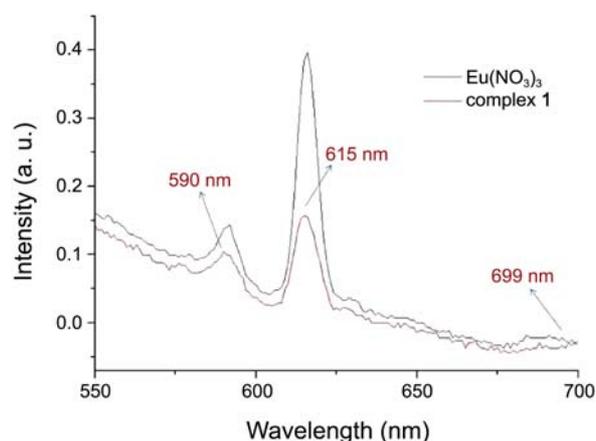
**Figure 3.** ORTEP drawing of complex 2.

complex 1, those in complex 2 all occupy general positions. The O–H···O hydrogen bonds connect the complexes in the [110] direction and the N–H···O hydrogen bonds connect them in the [010] direction to form a 3-D network.

Thermogravimetric Analysis. The TGA curves of complexes 1 and 2 display practically the same pattern, that is, a well-defined two-step weight loss (Fig. 4). Complex 1 is stable up to 102 °C, and the first weight loss occurs at 102–147 °C, which corresponds to the loss of the counterion NO₃[−] (observed: 7.5%, calculated: 7.9%). The second weight loss in the range of 168–190 °C can be attributed to the loss of two NO₃[−] ligands, three aqua ligands, and the crystalline water (observed: 24.7%, calculated: 25.0%). Above 190 °C, complex 1 decomposes gradually.

Complex 2 is stable up to 104 °C, and the first weight loss at 105–148 °C corresponds to the loss of counterion NO₃[−] (observed: 7.8%, calculated: 7.8%). Two NO₃[−] ligands, three aqua ligands, and the crystalline water are eliminated in the second step at 178–189 °C (observed: 24.9%, calculated: 24.8%). Above 189 °C, complex 2 decomposes gradually.

Solid-state Photoluminescence. The absorption and

**Figure 4.** TGA curves of complexes 1 and 2.**Figure 5.** Solid-state emission spectra of complex 1 and [Eu(NO₃)₃·5H₂O] at room temperature.

emission spectra of lanthanides consist of sharp and narrow bands arising from the Laporte-forbidden $f-f$ transitions and are characteristic of the metal ion. In particular, Eu³⁺ and Tb³⁺ ions are the most emissive lanthanide ions. The Eu³⁺ ion has an electronic configuration of [Xe]4f⁶, the ⁷F₀ ground state, and the long-lived ⁵D₀ excited state. On the other hand, the Tb³⁺ ion has an electronic configuration of [Xe]4f⁸, the ⁷F₆ ground state, and the long-lived ⁵D₄ excited state.³⁰ Because complexes 1 and 2 contain Eu³⁺ and Tb³⁺ ions, respectively, their luminescence was examined in the solid state at room temperature.

Figure 5 shows the emission spectra of complex 1 and [Eu(NO₃)₃·5H₂O] upon excitation at 450 nm. Both complexes exhibit practically the same emission pattern, that is, an intense red luminescence. The emission spectrum of complex 1 displays the characteristic transitions of ⁵D₀ → ⁷F_{*n*} ($n = 1-4$) at 590, 615, 650, and 699 nm, which can be explained on the basis of the Eu³⁺ energy-level structure.³¹⁻³⁴ The fact that no emission peaks other than the characteristic emission peaks of Eu³⁺ ions appear in the emission spectrum indicates that a ligand-to-europium energy transfer is inefficient.

The ⁵D₀ → ⁷F₁ emission peak at 590 nm corresponds to a magnetic dipole transition, and its intensity should vary

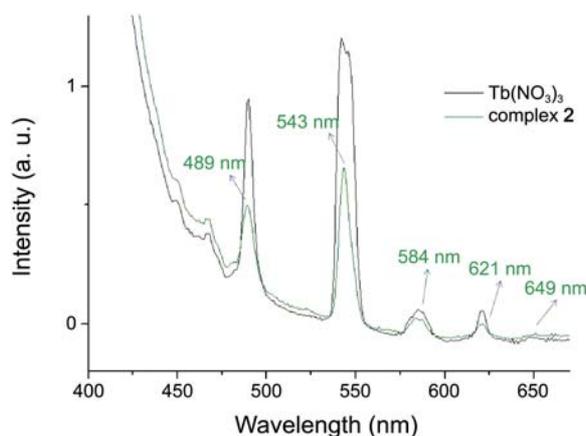


Figure 6. Solid-state emission spectra of complex **2** and $[\text{Tb}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}]$ at room temperature.

with the crystal-field strength acting on the Eu^{3+} ion. The strongest band at 615 nm can be assigned to an electric-dipolar ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition, and it is supposed to be absent if the Eu^{3+} ion lies on an inversion center. The ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition has intensity much higher than that of ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ transition, which suggests the acentric coordination environment of Eu^{3+} ions in complex **1**.³⁵⁻³⁸

Figure 6 shows the emission spectra of complex **2** and $[\text{Tb}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}]$. Both complexes exhibit practically the same intense green luminescence. These results indicate the ligand does not sensitize the emission of the Tb^{3+} ion. Complex **2** emits green light when excited at 370 nm and exhibits the characteristic transitions of ${}^5\text{D}_4 \rightarrow {}^7\text{F}_J$ ($J = 2-6$) of the Tb^{3+} ion at 489, 543, 584, 621 and 649 nm.³⁹ Two intense emission bands at 489 and 543 nm correspond to ${}^5\text{D}_4 \rightarrow {}^7\text{F}_6$ and ${}^5\text{D}_4 \rightarrow {}^7\text{F}_5$, respectively, whereas the weaker emission band at 584 nm originates from ${}^5\text{D}_4 \rightarrow {}^7\text{F}_4$.

Conclusion

In summary, two lanthanide complexes, $[\text{Ln}(\text{NO}_3)_2(\text{H}_2\text{O})_3(\text{L})_2](\text{NO}_3)(\text{H}_2\text{O})$ $\{\text{Ln} = \text{Eu}$ (**1**), Tb (**2**); $\text{L} = (4\text{-pyH})^+\text{-CH}_2\text{CH}_2\text{-SO}_3^-\}$, were prepared from lanthanide nitrate and 4-pyridineethanesulfonic acid in water under microwave-heating (700 W) conditions. The reactions are complete in 40 s and reproducible. Complexes **1** and **2** are the first f -block metal complexes of this ligand and are isostructural. In both complexes, the pyridyl nitrogen in the ligand is protonated to give a zwitter ion that possesses an NH^+ (pyridyl) positive end and an SO_3^- negative end. Complexes **1** and **2** exhibit characteristic emission spectra arising from the f - f transitions in the solid state at room temperature. Complex **1** exhibits an intense red emission, whereas complex **2** exhibits an intense green emission. The ligand does not sensitize the emission of the metal ion in both complexes.

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