

# Syntheses, crystal structures and luminescent properties of two novel lanthanide/4-pya complexes: $[\text{Ln}(4\text{-pya})_3(\text{H}_2\text{O})_2]_2$ (Ln = Eu, La; 4-pya = *trans*-4-pyridylacrylate)

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## Abstract

Reactions of  $\text{Ln}_2\text{O}_3$  and *trans*-4-pyridylacrylic acid (4-Hpya) in EtOH/H<sub>2</sub>O or MeOH/H<sub>2</sub>O produced two new lanthanide/4-pya complexes  $[\text{Ln}(4\text{-pya})_3(\text{H}_2\text{O})_2]_2$  (**1**: Ln = Eu; **2**: Ln = La) in low yields. However, reactions of  $\text{LnCl}_3 \cdot 6\text{H}_2\text{O}$  with 4-Hpya/aqueous ammonia in EtOH/H<sub>2</sub>O or MeOH/H<sub>2</sub>O gave rise to **1** or **2** in higher yields. Both compounds were structurally characterized by elemental analysis, IR spectroscopy and X-ray analysis. Compounds **1** · 2EtOH · 2H<sub>2</sub>O and **2** · 2MeOH · 2H<sub>2</sub>O were confirmed to possess one-dimensional polymeric chain structures. In the structure of **1**, each Eu(III) adopts a monocapped square-antiprism coordination geometry and each dimer  $[\text{Eu}(4\text{-pya})_3(\text{H}_2\text{O})_2]_2$  within the chain is interconnected by two pairs of different bridging 4-pya ligands. On the other hand, each La(III) of **2** takes a bicapped square-antiprism coordination geometry and each dimer  $[\text{La}(4\text{-pya})_3(\text{H}_2\text{O})_2]_2$  within the chain is linked by two pairs of tridentate bridging 4-pya ligands. The luminescent properties of **1** and **2** in the solid state were investigated.

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**Keywords:** *trans*-4-Pyridylacrylic acid; Lanthanide; Crystal structure; Luminescence; Coordination polymer

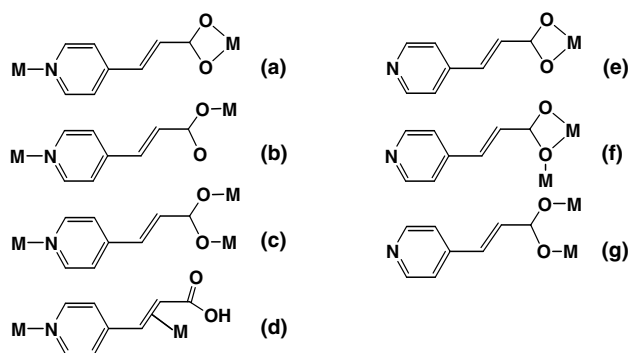
## 1. Introduction

Lanthanide coordination compounds are the subject of intense research efforts owing to their unique structures and their potential applications in advanced materials such as Ln-doped semiconductors [1], magnetic [2], catalytic [3], fluorescent [4,5], and non-linear optical materials [6,7]. It has been proved that ligands containing both nitrogen and oxygen donor atoms are good

building blocks for the formation of various lanthanide coordination compounds [8–12]. *trans*-4-Pyridylacrylic acid (4-Hpya) [13] is one of such interesting ligands. According to the analysis of a limited number of the crystal structures of transition metal complexes with 4-Hpya or 4-pya, four types of coordination modes of 4-pya ((a)–(d)) showed in Scheme 1 are observed [14]. However, the chemistry of lanthanide complexes of 4-pya is less explored [15]. In light of the large radii and the strong oxophilicity of Ln(III) ions, we anticipate that coordination of 4-Hpya or 4-pya at Ln(III) metals may lead to the formation of new compounds with different coordination modes. In this context, we carried

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Scheme 1. The coordination modes of the 4-Hpya ligand.

out the reactions of  $\text{Ln}_2\text{O}_3$  ( $\text{Ln} = \text{Eu}, \text{La}$ ) or  $\text{LnCl}_3 \cdot 6\text{H}_2\text{O}$  with 4-Hpya and isolated two interesting lanthanide/4-pya complexes  $[\text{Ln}(\text{4-pya})_3(\text{H}_2\text{O})_2]_2$  (**1**:  $\text{Ln} = \text{Eu}$ ; **2**:  $\text{Ln} = \text{La}$ ). Results showed that the 4-pya ligands in **1** and **2** exhibited three other different coordination modes, and that **1** showed strong red fluorescence in the solid state. Herein, we report their syntheses, crystal structures and luminescent properties.

## 2. Experimental

### 2.1. General

*trans*-4-Pyridylacrylic acid (4-Hpya) was prepared as reported previously [13]. Other reagents were obtained from commercial sources and used as received. Elemental analyses for C, H, and N were performed on an EA1110-CHNS elemental analyzer. IR spectra were recorded as KBr disks on a Nicolet Magna-IR 550 spectrophotometer. The photoluminescent spectra were performed by Perkin-Elmer LS55 spectrofluorometer.

### 2.2. Synthesis

#### 2.2.1. Preparation of **1**

*Method 1.* To a 25 ml flask containing 3 ml  $\text{H}_2\text{O}$  and 5 ml EtOH was added  $\text{Eu}_2\text{O}_3$  (0.058 g, 0.17 mmol) and 4-Hpya (0.15 g, 1 mmol). The mixture was refluxed at 80 °C for 5 h and then filtered. Colorless block crystals of  $[\text{Eu}(\text{4-pya})_3(\text{H}_2\text{O})_2]_2 \cdot 2\text{EtOH} \cdot 2\text{H}_2\text{O}$  (**1** · 2EtOH · 2H<sub>2</sub>O) were obtained by slow evaporation of EtOH and/or H<sub>2</sub>O in the filtrate at room temperature two days later. The crystals were collected by filtration, washed by EtOH and Et<sub>2</sub>O and dried in vacuo. Yield: 0.075 g (35%). Anal. Calc. for  $\text{C}_{24}\text{H}_{22}\text{EuN}_3\text{O}_8$ : C, 45.58; H, 3.51; N, 6.64. Found: C, 45.70; H, 3.48; N, 6.35%. IR (KBr disk,  $\text{cm}^{-1}$ ): 3242 (m), 2960 (m), 1646 (s), 1601 (s), 1549 (s), 1404 (s), 1256 (m), 990 (m), 822 (m), 744 (m), 593 (m).

*Method 2.* To a suspension containing 4-Hpya (0.050 g, 0.33 mmol) in  $\text{H}_2\text{O}$  (5 ml) was added 0.25 ml of aqueous ammonia. The resulting colorless solution was then treated with a solution of  $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$  (0.040 g, 0.11 mmol) in 5 ml EtOH. A large amount of white precipitate of **1** was observed to form within seconds and stirred for 10 min. The white solid was filtered and washed with EtOH and Et<sub>2</sub>O and dried in vacuo. Yield: 0.061 g (88%).

#### 2.2.2. Preparation of **2**

*Method 1.* To a 25 ml flask containing 3 ml  $\text{H}_2\text{O}$  and 5 ml MeOH was loaded  $\text{La}_2\text{O}_3$  (0.055 g, 0.17 mmol) and 4-Hpya (0.15 g, 1 mmol). Workup similar to that used in the isolation of **1** afforded a small amount of colorless plates of  $[\text{La}(\text{pya})_3(\text{H}_2\text{O})_2]_2 \cdot 2\text{MeOH} \cdot 2\text{H}_2\text{O}$  (**2** · 2MeOH · 2H<sub>2</sub>O) (<1% yield).

*Method 2.* Compound **2** was prepared as above starting from  $\text{LaCl}_3 \cdot 6\text{H}_2\text{O}$  (0.039 g, 0.11 mmol) in 5 ml MeOH and 4-Hpya (0.050 g, 0.33 mmol)/aqueous ammonia (0.25 ml) in MeOH (5 ml). Yield: 0.063 g (92%). Anal. Calc. for  $\text{C}_{24}\text{H}_{22}\text{LaN}_3\text{O}_8$ : C, 46.54; H, 3.58; N, 6.78. Found: C, 46.80; H, 3.65; N, 6.92%. IR (KBr disk  $\text{cm}^{-1}$ ): 3232 (m), 3048 (m), 1647 (s), 1603 (s), 1539 (s), 1403 (s), 1254 (m), 991 (m), 822 (m), 742 (m), 589 (m).

### 2.3. X-ray crystallography

X-ray quality crystals of **1** · 2EtOH · 2H<sub>2</sub>O and **2** · 2MeOH · 2H<sub>2</sub>O were obtained directly from the above preparation. All measurements were made on a Rigaku Mercury CCD X-ray diffractometer (3 kV, sealed tube) at 193 K by using graphite monochromated Mo K $\alpha$  ( $\lambda = 0.71070$  Å). A colorless block of **1** · 2EtOH · 2H<sub>2</sub>O with dimensions 0.30 × 0.13 × 0.10 mm and a colorless plate of **2** · 2MeOH · 2H<sub>2</sub>O with dimensions 0.35 × 0.30 × 0.24 mm were mounted at the top of a glass fiber, and cooled at 193 K in a liquid nitrogen stream. Diffraction data were collected at  $\omega$  mode with a detector distance of 34.52 mm (**1** · 2EtOH · 2H<sub>2</sub>O) and 34.50 mm (**2** · 2MeOH · 2H<sub>2</sub>O) to the crystal, respectively. Indexing was performed from 6 images, each of which was exposed for 12 s. Cell parameters were refined by using the program Crystalclear (Rigaku and MSc, Ver. 1.3, 2001) on 5399 (**1** · 2EtOH · 2H<sub>2</sub>O) or 5977 (**2** · 2MeOH · 2H<sub>2</sub>O) observed reflections between  $\theta$  of 3.0° and 25.3° (**1** · 2EtOH · 2H<sub>2</sub>O) or 3.1° and 25.3° (**2** · 2MeOH · 2H<sub>2</sub>O). A total of 720 oscillation images were collected in the range  $6.00^\circ < 2\theta < 50.60^\circ$  for **1** · 2EtOH · 2H<sub>2</sub>O and  $6.20^\circ < 2\theta < 50.60^\circ$  for **2** · 2MeOH · 2H<sub>2</sub>O. The collected data were reduced by using the program CrystalClear (Rigaku and MSC, Ver. 3.60, 2004), and an absorption correction (multiscan) was applied which resulted in transmission factors ranging from 0.542 to 0.801 for **1** · 2EtOH · 2H<sub>2</sub>O and from

0.530 to 0.685 for  $2 \cdot 2\text{MeOH} \cdot 2\text{H}_2\text{O}$ . The reflection data were also corrected for Lorentz and polarization effects.

The structures of  $1 \cdot 2\text{EtOH} \cdot 2\text{H}_2\text{O}$  and  $2 \cdot 2\text{MeOH} \cdot 2\text{H}_2\text{O}$  were solved by direct methods [16] and were refined on  $F^2$  by full-matrix least-squares using anisotropic displacement parameters for all non-hydrogen atoms [17]. All hydrogen atoms were placed in geometrically idealized positions (C–H = 0.98 Å for methyl groups; C–H = 0.99 Å for methylene groups, C–H = 0.95 Å for phenyl groups and O–H = 0.85 Å for water molecules) and constrained to ride on their parent atoms with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C or O})$ . In the case of  $1 \cdot 2\text{EtOH} \cdot 2\text{H}_2\text{O}$ , the final difference Fourier map had two peaks of 2.08 and 1.81 e/Å<sup>3</sup>, which are 0.96 and 0.94 Å from C10 and C13, respectively. Neutral atom scattering factors were taken from Cromer and Waber [18]. Anomalous dispersion effects were included in  $F_{\text{calc}}$  [19]. All the calculations were performed on a Dell workstation using the CrystalStructure crystallographic software package (Rigaku and MSC, Ver.3.60, 2004). The crystal data along with the structure refinement parameters for  $1 \cdot 2\text{EtOH} \cdot 2\text{H}_2\text{O}$  and  $2 \cdot 2\text{MeOH} \cdot 2\text{H}_2\text{O}$  is summarized in Table 1.

Table 1

Crystallographic data for  $[\text{Eu}(4\text{-pya})_3(\text{H}_2\text{O})_2]_2 \cdot 2\text{EtOH} \cdot 2\text{H}_2\text{O}$  ( $1 \cdot 2\text{EtOH} \cdot 2\text{H}_2\text{O}$ ) and  $[\text{La}(4\text{-pya})_3(\text{H}_2\text{O})_2]_2 \cdot 2\text{EtOH} \cdot 2\text{H}_2\text{O}$  ( $2 \cdot 2\text{MeOH} \cdot 2\text{H}_2\text{O}$ )

Complex	$1 \cdot 2\text{EtOH} \cdot 2\text{H}_2\text{O}$	$2 \cdot 2\text{MeOH} \cdot 2\text{H}_2\text{O}$
Empirical formula	C <sub>26</sub> H <sub>30</sub> EuN <sub>3</sub> O <sub>10</sub>	C <sub>25</sub> H <sub>28</sub> LaN <sub>3</sub> O <sub>10</sub>
Formula weight	696.49	669.41
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
<i>a</i> (Å)	8.6928(8)	8.3944(8)
<i>b</i> (Å)	12.5682(12)	12.8134(13)
<i>c</i> (Å)	14.0904(14)	14.4304(14)
$\alpha$ (°)	108.736(2)	110.186(2)
$\beta$ (°)	101.665(2)	98.626(2)
$\gamma$ (°)	99.205(2)	99.674(2)
<i>V</i> (Å <sup>3</sup> )	1385.1(2)	1399.3(2)
<i>Z</i>	2	2
<i>T</i> (K)	193	193
<i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )	1.670	1.56
$\lambda$ (Mo K $\alpha$ ) (Å)	0.71070	0.71070
$\mu$ (cm <sup>-1</sup> )	23.25	15.77
$2\theta_{\text{max}}$ (°)	50.70	50.70
Reflections collected	13817	13888
Unique reflections ( <i>R</i> <sub>int</sub> )	5036 (0.030)	5090 (0.020)
Number of observations [ <i>I</i> > 2.00 $\sigma$ ( <i>I</i> )]	4303	4666
Number of parameters	380	374
<i>R</i> <sup>a</sup>	0.0397	0.0245
<i>wR</i> <sup>b</sup>	0.0911	0.0584
Goodness-of-fit	1.061	1.071
Largest residual peaks and holes (e Å <sup>-3</sup> )	2.079 and -1.624	0.951 and -0.549

$$^a R = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}$$

$$^b wR = \left\{ \frac{\sum w(|F_o|^2 - |F_c|^2)^2}{\sum w|F_o|^2} \right\}^{1/2}$$

### 3. Results and discussion

#### 3.1. Preparation and characterization of **1** and **2**

Refluxing a mixture containing Eu<sub>2</sub>O<sub>3</sub> and 4-Hpya in EtOH/H<sub>2</sub>O at 80 °C for 5 h afforded complex **1** as colorless block crystals in 35% yield. The relatively low yield of **1** may be ascribed to the low solubility of both Eu<sub>2</sub>O<sub>3</sub> and 4-Hpya in ethanol and water. The analogous reaction of La<sub>2</sub>O<sub>3</sub> and 4-Hpya in MeOH/H<sub>2</sub>O produced complex **2** even in a much lower yield (<1%). The low yields of both compounds drove us to search for a better synthetic route to **1** or **2**. Therefore, we dissolved 4-Hpya in aqueous ammonia to form a colorless solution, to which was added a solution of EuCl<sub>3</sub> · 6H<sub>2</sub>O in EtOH. A large amount of white precipitate was observed to form immediately. Filtration followed by washing with EtOH and H<sub>2</sub>O and drying in vacuo afforded **1** in 88% yield. Similar reactions of LaCl<sub>3</sub> · 6H<sub>2</sub>O with 4-Hpya/aqueous ammonia in MeOH/H<sub>2</sub>O led to the formation of **2** in 92% yield. The high yields of **1** and **2** in the later method may be ascribed to the deprotonation of 4-Hpya in aqueous ammonia. Both compounds are relatively air stable and virtually insoluble in common organic solvents. X-ray fluorescence analysis of solids **1** and **2** showed that there was no Cl in both samples. Their elemental analyses are consistent with the chemical formula of **1** and **2**. In the IR spectra of **1** and **2**, the  $\nu_{\text{as}}(\text{OCO})$  stretching vibration is red-shifted from 1612 cm<sup>-1</sup> (4-Hpya) to 1601 (**1**) or 1603 cm<sup>-1</sup> (**2**) while the  $\nu_{\text{s}}(\text{OCO})$  stretching vibration is also red-shifted from 1420 cm<sup>-1</sup> (4-Hpya) to 1404 (**1**) or 1403 cm<sup>-1</sup> (**2**). These results indicate that the carboxyl groups of 4-pya are bound to the Eu(III) or La(III) ions [13,20]. The identities of **1** and **2** were finally confirmed by X-ray crystallography.

#### 3.2. Molecular structure of $1 \cdot 2\text{EtOH} \cdot 2\text{H}_2\text{O}$

Crystals of  $1 \cdot 2\text{EtOH} \cdot 2\text{H}_2\text{O}$  crystallize in the triclinic space group  $P\bar{1}$  and the asymmetric unit contains one-half of the dimer  $[\text{Eu}(4\text{-pya})_3(\text{H}_2\text{O})_2]_2$ , and one ethanol and one water solvated molecules. According to X-ray analysis, **1** has the one-dimensional chain structure extended along *a*-axis as shown in Fig. 1. Each repeating dimeric unit  $[\text{Eu}(4\text{-pya})_3(\text{H}_2\text{O})_2]_2$  within the chain is interconnected by two bidentate 4-pya and two tridentate 4-pya anions.  $\{[\text{Eu}(4\text{-pya})_3(\text{H}_2\text{O})_2]_2\}_n$  chains are 14 Å apart and are separated by NC<sub>5</sub>H<sub>4</sub>C=C groups and EtOH and H<sub>2</sub>O solvated molecules. For the unit  $[\text{Eu}(4\text{-pya})_3(\text{H}_2\text{O})_2]_2$  (Fig. 2), there is a crystallographic center of symmetry at the midpoint of Eu(1) ···Eu(1A) contact. Each Eu(III) center is nine-coordinated by seven O atoms of 4-pya ligands and two O atoms of coordinated water molecules, forming a monocapped square-antiprism coordination geometry (Fig. 3). The

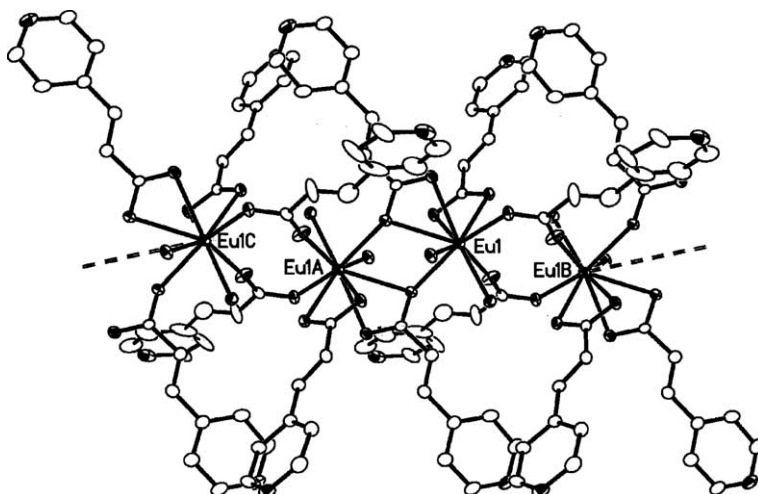


Fig. 1. Perspective view of a section of the 1D polymeric chain of **1** extended along *a*-axis. Hydrogen atoms are omitted for clarity.

Eu(1)···Eu(1A) contact within each dimer is 4.280 Å, shorter than the Eu(1)···Eu(1B) separation (4.789 Å) between dimers. However, these two Eu···Eu contacts are too long to include metal–metal interactions. Interestingly, the 4-pya ligands in **1** show three other different coordination modes ((e)–(g)) relative to those modes ((a)–(d)) shown in Scheme 1. In these three modes, the N atom of each pyridyl group remains intact. For mode (e), one 4-pya chelates the Eu(III) ion via O(1) and O(2) to form a EuO<sub>2</sub>C four-membered ring. On the other hand, the 4-pya (mode (f)) acts as a tridentate ligand, which chelates the Eu(1) ion via O(5A) and O(6A) and links the Eu(1A) via O(5A) atom. As the distance from Eu(1) to O(3A) is 5.507 Å which is much longer than the sum of the van der Waals radii of Eu and O (2.66 Å), the coordination of O(3A) to Eu(1) is thus excluded. The 4-pya ligand (e.g., that carrying O(3) and O(4) atoms) (mode (g)) can serve as a bidentate bridging one to interconnect the dimeric units to form a one-dimensional chain. Because of the existence of the different coordination modes of 4-pya ligands, the Eu(1)–O bond distances vary from 2.365(3) to 2.647(3) Å (Table 2). The Eu(1)–O(1) bond length of 2.573(3) Å is 0.1 Å longer than that of the Eu(1)–O(2) bond (2.470(3) Å), implying that O(1) and O(2) atoms of this 4-pya ligand is not symmetrically bound to Eu(1). On the other hand, as the Eu(1)–O(3) bond length (2.373(4) Å) is comparable to that of Eu(1B)–O(4) bond (2.365(3) Å), the 4-pya with O(3) and O(4) atoms may be considered to symmetrically bridge the Eu(1) atom of one dimeric unit and the Eu(1B) atom of the other. The 4-pya ligand carrying O(5A) and O(6A) also binds to Eu(1) in an unsymmetric way as the Eu(1)–O(5A) bond length is 0.13 Å longer than that of Eu(1)–O(6A) bond. It is noted that the Eu(1)–O(5A) bond length is the longest among all other Eu(1)–O bonds. This may be due to the fact that the O(5A) atom strongly binds to Eu(1A) of the same dimer

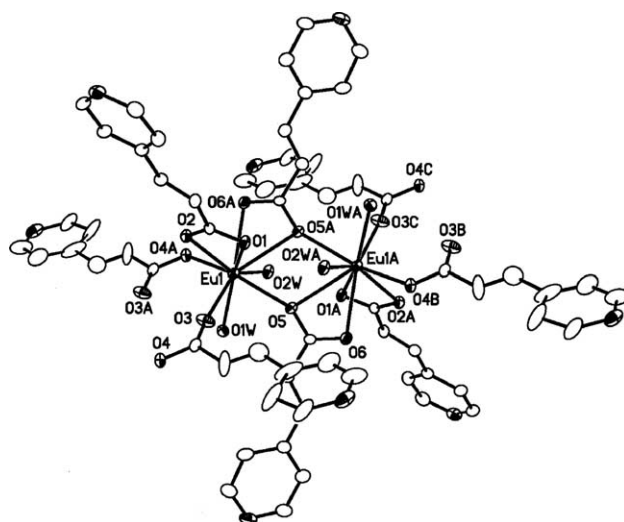


Fig. 2. Perspective view of the dimer [Eu(pya)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub>]<sub>2</sub> with 50% thermal ellipsoids. Hydrogen atoms are omitted for clarity.

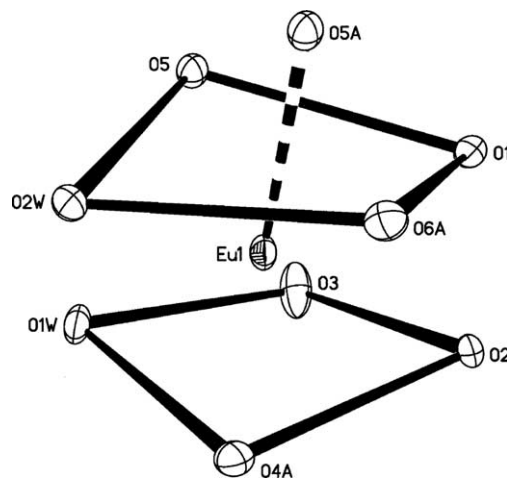


Fig. 3. The monocapped square-antiprismatic coordination geometry about Eu(III).



Table 2  
Selected bond lengths (Å) and bond angles (°) for [Eu(4-pya)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub>]<sub>2</sub> (**1**)

Eu(1)–O(4A)	2.365(3)	Eu(1)–O(3)	2.373(4)
Eu(1)–O(5)	2.388(3)	Eu(1)–O(1W)	2.420(3)
Eu(1)–O(2)	2.470(3)	Eu(1)–O(2W)	2.487(3)
Eu(1)–O(6A)	2.517(4)	Eu(1)–O(1)	2.573(3)
Eu(1)–O(5A)	2.647(3)		
O(4B)–Eu(1)–O(3)	107.49(15)	O(4B)–Eu(1)–O(5)	153.34(12)
O(3)–Eu(1)–O(5)	80.65(14)	O(4B)–Eu(1)–O(1W)	77.62(13)
O(3)–Eu(1)–O(1W)	72.82(13)	O(5)–Eu(1)–O(1W)	80.91(12)
O(4)–Eu(1)–O(2)	75.49(11)	O(3)–Eu(1)–O(2)	74.37(13)
O(5)–Eu(1)–O(2)	130.88(11)	O(1W)–Eu(1)–O(2)	128.25(11)
O(4B)–Eu(1)–O(2W)	78.22(11)	O(3)–Eu(1)–O(2W)	139.51(13)
O(5)–Eu(1)–O(2W)	79.57(11)	O(1W)–Eu(1)–O(2W)	69.40(12)
O(2)–Eu(1)–O(2W)	142.79(12)	O(4B)–Eu(1)–O(6A)	75.50(12)
O(3)–Eu(1)–O(6A)	143.00(12)	O(5)–Eu(1)–O(6A)	113.63(11)
O(1W)–Eu(1)–O(6A)	140.76(12)	O(2)–Eu(1)–O(6A)	70.79(12)
O(2W)–Eu(1)–O(6A)	77.49(12)	O(4)–Eu(1)–O(1)	124.96(11)
O(3)–Eu(1)–O(1)	75.32(13)	O(5)–Eu(1)–O(1)	81.47(11)
O(1W)–Eu(1)–O(1)	145.60(13)	O(2)–Eu(1)–O(1)	51.73(11)
O(2W)–Eu(1)–O(1)	135.10(11)	O(6)–Eu(1)–O(1)	73.60(12)
O(4B)–Eu(1)–O(5A)	119.70(11)	O(3)–Eu(1)–O(5A)	130.86(13)
O(5)–Eu(1)–O(5A)	63.66(13)	O(2)–Eu(1)–O(5A)	103.69(11)
O(2W)–Eu(1)–O(5A)	67.83(11)	O(6)–Eu(1)–O(5A)	49.99(11)
O(1)–Eu(1)–O(5A)	67.28(11)		

with Eu(1A)–O(5A) = 2.388(3) Å. The average Eu(1)–O (carboxylate) bond length (2.491(3) Å) is longer than those reported in [Eu(L)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub>]<sub>n</sub> · 4*n*H<sub>2</sub>O (2.352(4) Å) (HL = nicotinic acid N-oxide) [21] and [Eu<sub>2</sub>(Hpdc)<sub>3</sub>(H<sub>2</sub>O)<sub>6</sub>] (2.395(2) Å) (H<sub>3</sub>pdc = 3,5-pyrazoledicarboxylic acid) [9a]. The Eu(1)–μ-O(5A) length is 2.647(3) Å, which is 0.27 and 0.22 Å longer than those of the corresponding ones of [Eu(*p*-MOBA)<sub>3</sub>(2,2'-bipy)] · 1/2EtOH (*p*-MOBA = *p*-methoxybenzoate) [22] and {[Eu<sub>2</sub>(pzdc)<sub>3</sub>(H<sub>2</sub>O)] · 2H<sub>2</sub>O}<sub>n</sub> (pzdc = 2,3-pyrazinedicarboxylate) [23], respectively. The two Eu(1)–O (water) bond distances are 2.420(3) and 2.487(3) Å, which are comparable to those found in {[Eu<sub>2</sub>(pzdc)<sub>3</sub>(H<sub>2</sub>O)] · 2H<sub>2</sub>O}<sub>n</sub> (2.419(2) Å) and [Eu<sub>2</sub>(2,2'-dpdc)<sub>3</sub>(phen)(H<sub>2</sub>O)<sub>2</sub>]<sub>n</sub> (2.435(3) and 2.497(3) Å) (2,2'-dpdc = 2,2'-diphenyldicarboxylate, phen = 1,10-phenanthroline) [24]. As shown in Table 3, it is noted that, in the unit cell of **1** · 2EtOH · 2H<sub>2</sub>O, the coordinated water molecules interact with the O atoms of 4-pya ligands of the same chain to form intramolecular hydrogen bonds (O(2W)–H(2W1)···O(1A) (2 – *x*,

Table 3  
Hydrogen-bonding geometry (Å, °) for **1** · 2EtOH · 2H<sub>2</sub>O

D–H···A	D–H	H···A	D–A	D–H···A
O(2W)–H(2W2)···N(2)#1	0.85(5)	2.02(5)	2.861(6)	176(5)
O(2W)–H(2W1)···O(1)#2	0.85(5)	1.99(5)	2.803(5)	161(4)
O(1W)–H(1W2)···N(1)#3	0.85(4)	1.97(4)	2.812(6)	176(6)
O(2W)–H(2W1)···O(2)#4	0.84(4)	1.892(17)	2.722(5)	166(6)

Symmetry codes: #1, *x*, 1 + *y*, *z*; #2, 2 – *x*, 1 – *y*, 1 – *z*; #3, *x*, *y*, –1 + *z*; #4, 1 – *x*, 1 – *y*, 1 – *z*.

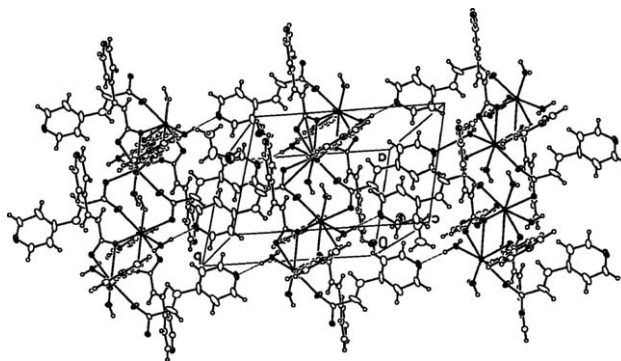


Fig. 4. Cell packing diagrams of **1** looking down the *b*-axis.

1 – *y*, 1 – *z*); O(1W)–H(1W1)···O(2B) (1 – *x*, 1 – *y*, 1 – *z*). On the other hand, these coordinated water molecules are in contact with the N atoms of 4-pya ligands from the adjacent chain to afford intermolecular hydrogen bonds (O(1W)–H(1W2)···N(1B) (*x*, *y*, –1 + *z*), O(2W)–H(2W2)···N(2B) (*x*, 1 + *y*, *z*)), thereby forming a two-dimensional network extended along *ab* plane (Fig. 4).

### 3.3. Molecular structure of **2** · 2MeOH · 2H<sub>2</sub>O

Crystals of **2** · 2MeOH · 2H<sub>2</sub>O crystallize in the triclinic space group *P* $\bar{1}$  and the asymmetric unit has one-half of the dimer [La(4-pya)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub>]<sub>2</sub> and one methanol and one water solvent molecules. As shown in Fig. 5, **2** also has a one-dimensional chain extended along *a*-axis. Unlike **1**, the repeating [La(4-pya)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub>]<sub>2</sub> dimeric units within the chain of **2** are interconnected by four tridentate bridging 4-pya anions. {[La(4-pya)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub>]<sub>2</sub>}<sub>n</sub> chains are 12.8 Å apart and are separated by NC<sub>5</sub>H<sub>4</sub>C=C groups and MeOH and H<sub>2</sub>O solvated molecules. For the [La(4-pya)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub>]<sub>2</sub> dimer (Fig. 6), there is a crystallographic center of symmetry at the midpoint of La(1)···La(1A) contact. The local

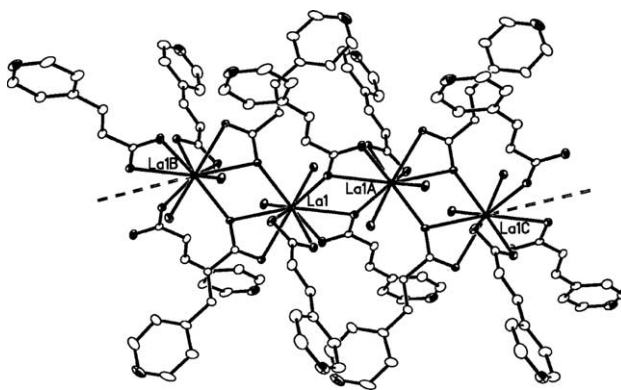


Fig. 5. Perspective view of a section of the 1D polymeric chain of **2** extended along *a*-axis. Hydrogen atoms are omitted for clarity.

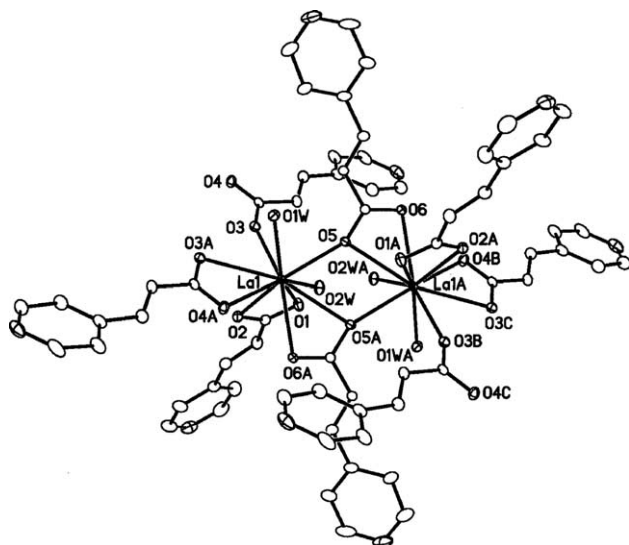


Fig. 6. Perspective view of the  $[\text{La}(\text{pya})_3(\text{H}_2\text{O})_2]_2$  dimer with 50% thermal ellipsoids. Hydrogen atoms are omitted for clarity.

coordination geometry around La(1) can be viewed as a bicapped square-antiprism (Fig. 7). The La(1) center coordinates to eight O atoms of 4-pya ligands and two O atoms of water molecules. The La(1)···La(1A) and the La(1)···La(1B) separations are 4.526 and 4.427 Å, which exclude any metal–metal interactions. In the dimer  $[\text{La}(\text{4-pya})_3(\text{H}_2\text{O})_2]_2$ , the 4-pya ligand only exhibits two coordination modes e and f (Scheme 1). The La(1)–O (carboxylate) bond distances vary from 2.503(18) to 2.753(19) Å (Table 4). Like **1**, the chelating 4-pya ligand with O(1) and O(2) atoms (mode (e)) is not symmetri-

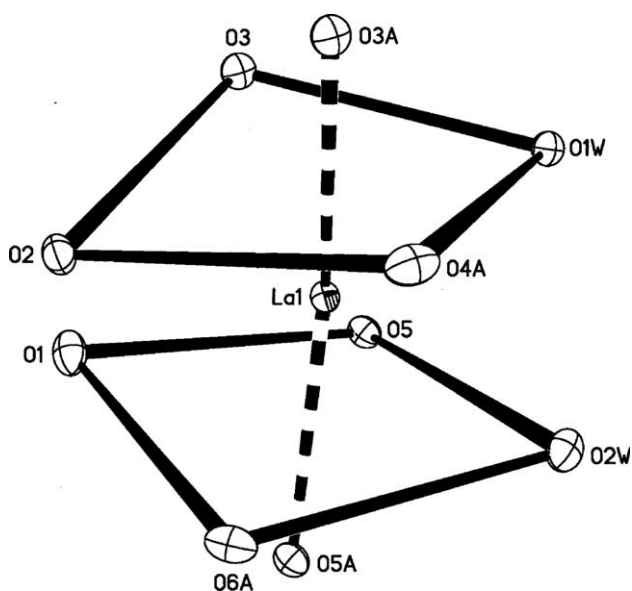


Fig. 7. The bicapped square-antiprismatic coordination geometry about La.

cally bound to La(1) because the La(1)–O(1) bond length (2.672(18) Å) is 0.1 Å longer than that of La(1)–O(2) (2.574(19) Å). The 4-pya with O(5A) and O(6A) (mode (f)) acts as a tridentate ligand in which it chelates the La(1) ion via O(5A) and O(6A) and bridges the La(1A) via O(5A) atom. However, the 4-pya ligand (e.g., that carrying O(3) and O(4) atoms) of **2** behaves somewhat different from the corresponding one of **1** and serves as a triply-bridging one to link the dimers to form one-dimensional chain. This difference may be due to the so-called “lanthanide contraction”. As the radii of La(III) ion is larger than that of Eu(III) ion, the larger La(III) could accept more donor atoms to become 10-coordinated while the smaller Eu(III) is nine-coordinated when the same pya ligand coordinates at Eu(III) and La(III) centers. The La(1)–O(3A) bond distance (2.753(18) Å) is much longer than those of La(1)–O(3) (2.540(19) Å) and La(1)–O(4A) (2.544(19) Å) bonds. The mean La(1)–O (carboxylate) bond distance is 2.645(19) Å, 0.14 Å longer than those of the corresponding ones of  $[\text{La}_2(\text{pdc})_3(\text{H}_2\text{O})_3]$  (av. 2.504(3) Å; pdc = 2,6-pyridinedicarboxylate) [25]. The mean La(1)–μ-O bond distance of 2.522(19) Å is comparable to that observed in  $[\text{La}_2(\text{H}_2\text{O})(1,2\text{-bdc})_2(1,4\text{-bdc})]$  (av. La–μ-O = 2.519 Å) (1,2-bdc and 1,4-bdc = 1,2- or 1,4-benzenedicarboxylate) [26], but 0.09 Å shorter than those of the corresponding ones of  $[\text{La}(\text{nta})(\text{H}_2\text{O})_n]$  (av. 2.611 Å) ( $\text{H}_3\text{nat}$  = nitrolotriacetic acid) [27]. The mean La–O (water) bond distance of 2.569(3) Å, is 0.157 Å shorter than that found in  $[\text{La}_2(2,2'\text{-dpdc})_3(\text{phen})(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$  [24]. As indicated in Table 5, in the unit cell of  $\mathbf{2} \cdot 2\text{MeOH} \cdot 2\text{H}_2\text{O}$ , there are also two hydrogen-bonding interactions among the coordinated water molecules and the N and O atoms of the pya ligands (O(2W)–H(2W2)···N(2B) ( $x, 1+y, z$ ); O(2W)–H(2W1)···O(1B) ( $2-x, 1-y, 1-z$ ); O(1W)–H(1W2)···N(1B) ( $x, y, -1+z$ ); O(1W)–H(1W1)···O(2A) ( $1-x, 1-y, 1-z$ )), thereby forming a two-dimensional network (Fig. 8).

### 3.4. Luminescent properties

Complex **1** emits intense red fluorescence when it is irradiated by UV light. The excitation spectrum of  $\text{Eu}^{3+}$  complex, obtained at room temperature, shows a strong absorption band at 278 nm (Fig. 9). The emission spectra (Fig. 10) shows characteristic transitions of  $\text{Eu}^{3+}$  ions, from  $^5\text{D}_0$  level to  $^7\text{F}_J$  ( $J=0-4$ ) manifolds. The characteristic ‘europium red’ luminescence indicates that the surrounding aromatic ligands absorbed energy and transferred energy efficiently to the europium ions. The  $^5\text{D}_0 \rightarrow ^7\text{F}_0$  transition observed as a weak single peak at 581 nm demonstrates the presence of only one site for the Eu(III) ion [28]. The strong band appearing at ca 615 nm, assigned to the  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  transition, is sharp, showing high

Table 4  
Selected bond lengths (Å) and bond angles (°) for [La(4-pya)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub>]<sub>2</sub> (**2**)

La(1)–O(5)	2.503(18)	La(1)–O(1W)	2.528(19)
La(1)–O(3)	2.540(19)	La(1)–O(4A)	2.544(19)
La(1)–O(2)	2.574(19)	La(1)–O(6A)	2.605(19)
La(1)–O(2W)	2.609(2)	La(1)–O(1)	2.672(19)
La(1)–O(5A)	2.721(18)	La(1)–O(3A)	2.753(18)
O(5)–La(1)–O(1W)	77.86(6)	O(5)–La(1)–O(3)	79.02(6)
O(1W)–La(1)–O(3)	74.64(6)	O(5)–La(1)–O(4A)	154.62(7)
O(1W)–La(1)–O(4A)	82.81(7)	O(3)–La(1)–O(4A)	111.57(6)
O(5)–La(1)–O(2)	125.31(6)	O(1W)–La(1)–O(2)	136.23(6)
O(3)–La(1)–O(2)	74.85(6)	O(4A)–La(1)–O(2)	80.08(6)
O(5)–La(1)–O(6A)	112.70(6)	O(1W)–La(1)–O(6A)	141.42(7)
O(3)–La(1)–O(6A)	142.44(6)	O(4A)–La(1)–O(6A)	73.63(6)
O(2)–La(1)–O(6A)	69.44(6)	O(5)–La(1)–O(2W)	81.46(6)
O(1W)–La(1)–O(2W)	67.81(6)	O(3)–La(1)–O(2W)	140.47(6)
O(4A)–La(1)–O(2W)	76.05(6)	O(2)–La(1)–O(2W)	143.08(6)
O(6A)–La(1)–O(2W)	76.99(7)	O(5)–La(1)–O(1)	77.49(6)
O(1W)–La(1)–O(1)	143.87(7)	O(3)–La(1)–O(1)	75.04(6)
O(4A)–La(1)–O(1)	126.92(6)	O(2)–La(1)–O(1)	49.76(6)
O(6A)–La(1)–O(1)	73.28(7)	O(2W)–La(1)–O(1)	132.92(6)
O(5A)–La(1)–O(5)	64.19(7)	O(1W)–La(1)–O(5A)	123.87(6)
O(3)–La(1)–O(5A)	130.55(6)	O(4A)–La(1)–O(5A)	115.81(6)
O(2)–La(1)–O(5A)	99.83(6)	O(6B)–La(1)–O(5A)	48.63(6)
O(2W)–La(1)–O(5A)	66.99(6)	O(1)–La(1)–O(5A)	65.95(6)
O(5)–La(1)–O(3A)	134.18(6)	O(1W)–La(1)–O(3A)	69.06(6)
O(3)–La(1)–O(3A)	62.50(7)	O(4A)–La(1)–O(3A)	49.09(6)
O(2)–La(1)–O(3A)	69.27(6)	O(6A)–La(1)–O(3A)	112.97(6)
O(2W)–La(1)–O(3A)	112.40(6)	O(5A)–La(1)–O(3A)	161.59(5)
O(1)–La(1)–O(3A)	112.50(6)		

Table 5  
Hydrogen-bonding geometry (Å, °) for **2** · 2MeOH · 2H<sub>2</sub>O

D–H···A	D–H	H···A	D–A	D–H···A
O(2W)–H(2W2)···N(2)#1	0.85(5)	2.01(3)	2.856(3)	172(3)
O(2W)–H(2W1)···O(1)#2	0.84(3)	1.96(3)	2.782(3)	165(3)
O(1W)–H(1W2)···N(1)#3	0.849(10)	1.967(13)	2.799(3)	167(3)
O(2W)–H(2W1)···O(2)#4	0.855(10)	1.855(11)	2.701(3)	170(3)

Symmetry codes: #1,  $x, 1+y, z$ ; #2,  $2-x, 1-y, 1-z$ ; #3,  $x, y, -1+z$ ; #4,  $1-x, 1-y, 1-z$ .

color purity for **1**. This fact implies that **1** may be used as an excellent fluorescent material. The  $^5D_0 \rightarrow ^7F_2$  transition is the induced electric dipole transition, which is greatly affected by the coordination environment, while the  $^5D_0 \rightarrow ^7F_1$  transition (590 nm) is the magnetic dipole transition, which is much less sensitive to the environment [29]. The  $^5D_0 \rightarrow ^7F_2$  transition is clearly stronger than the  $^5D_0 \rightarrow ^7F_1$  transition, which indicates the absence of

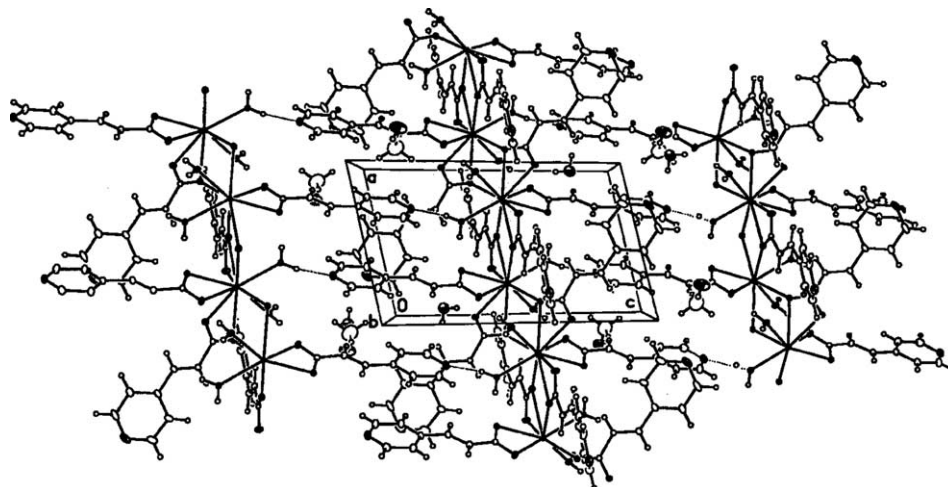


Fig. 8. Cell packing diagrams of **2** looking down the  $b$ -axis.

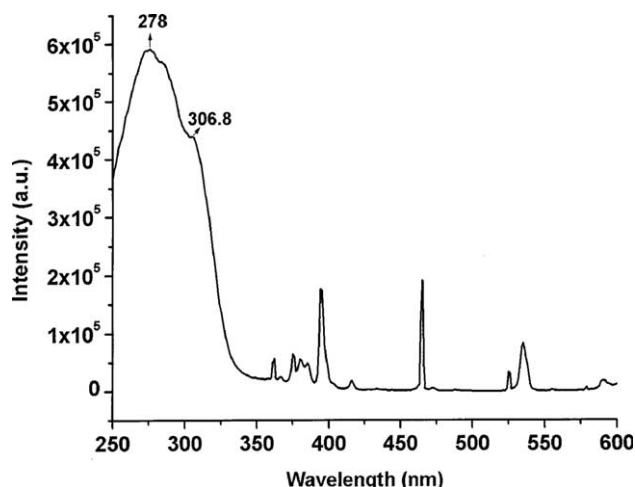


Fig. 9. The excitation ( $\lambda_{em} = 615$  nm) spectrum of complex **1** in the solid state at ambient temperature. The sharp peaks besides the main broad one may be attributed to the f–f transitions of  $\text{Eu}^{3+}$  ions.

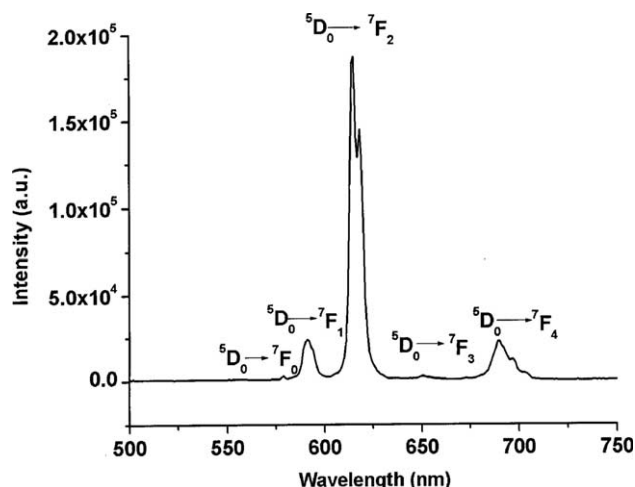


Fig. 10. The emission ( $\lambda_{ex} = 312$  nm) spectrum of complex **1** in the solid state at ambient temperature.

inversion symmetry at  $\text{Eu}(\text{III})$  site [23]. It is noticed that the bands originated from the  $^5\text{D}_0 \rightarrow ^7\text{F}_3$  transition is of low intensity and may be taken as forbidden. The decay curves for  $\text{Eu}(\text{III})$   $^5\text{D}_0 \rightarrow ^7\text{F}_2$  emission of **1** was measured by time-resolved spectroscopy at room temperature (Fig. 11). The lifetime is calculated to be  $0.354 \pm 0.001$  ms through the mono-exponential decay method. This value is comparable to that of  $[\text{Eu}_2(\text{bpc})_3] \cdot n\text{H}_2\text{O}$  ( $0.37 \pm 0.01$  ms,  $\text{bpc} = 2,2'$ -bipyridine-4,4'-dicarboxylic acid) [30a], but smaller than that of  $[\text{Eu}(\text{p-CAP})_3]$  ( $1.94 \pm 0.01$  ms,  $\text{p-CAP} = 6$ -parachloroaniline carbonyl-2-pyridine carboxylate) [30b]. In the emission spectrum of **2** (Fig. 12), it has a broad band at ca. 460 nm, which is quite similar to that of the free ligand 4-Hpya and may be attributable to the  $\pi^* \rightarrow n$  transition.

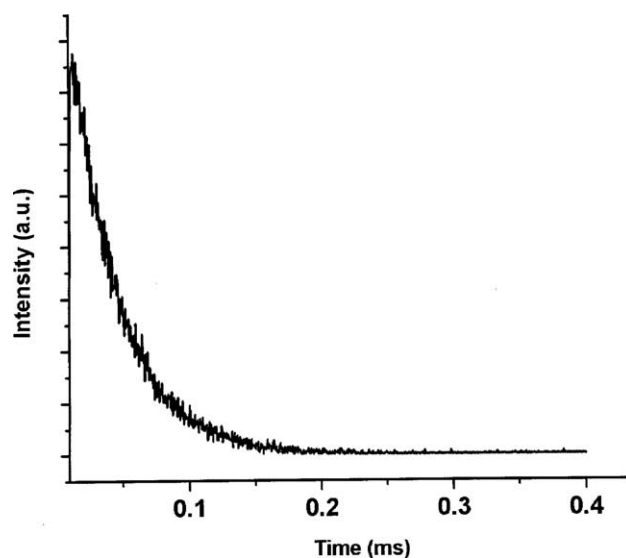


Fig. 11. The decay curve ( $\lambda_{ex} = 309$  nm,  $\lambda_{em} = 615$  nm) for complex **1** in the solid state at ambient temperature.

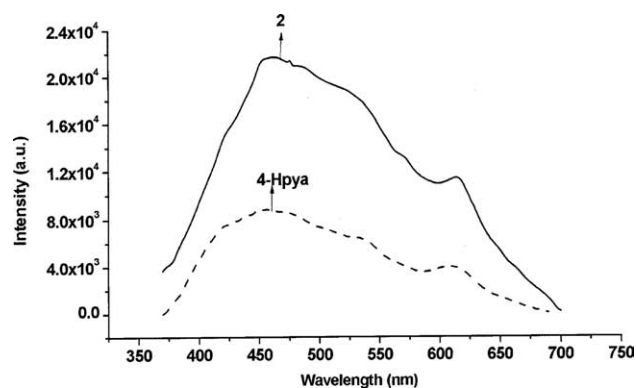


Fig. 12. The emission spectra of complex **2** ( $\lambda_{ex} = 360$  nm, solid line) and 4-Hpya ligand ( $\lambda_{ex} = 350$  nm, dashed line) in the solid state at ambient temperature.

#### 4. Conclusions

Two interesting lanthanide/4-pya complexes  $[\text{Ln}(4\text{-pya})_3(\text{H}_2\text{O})_2]_2$  (**1**:  $\text{Ln} = \text{Eu}$ ; **2**:  $\text{Ln} = \text{La}$ ) were isolated either from reactions of  $\text{Ln}_2\text{O}_3$  and *trans*-4-pyridylacrylic acid (4-Hpya) or from reactions of  $\text{LnCl}_3 \cdot 6\text{H}_2\text{O}$  with 4-Hpya/aqueous ammonia in  $\text{EtOH}/\text{H}_2\text{O}$  or in  $\text{MeOH}/\text{H}_2\text{O}$ . Both compounds were structurally characterized by elemental analysis, IR spectroscopy and X-ray analysis. X-ray analysis revealed that compounds **1**·2EtOH·2H<sub>2</sub>O and **2**·2MeOH·2H<sub>2</sub>O possess somewhat different 1D polymeric chain structures. In the structure of **1**, each  $\text{Eu}(\text{III})$  is nine-coordinated and each dimer  $[\text{Eu}(4\text{-pya})_3(\text{H}_2\text{O})_2]_2$  within the chain is interconnected by two pairs of different bridging 4-pya ligands. On the other hand, each  $\text{La}(\text{III})$  is 10-coordinated and each dimer  $[\text{La}(4\text{-pya})_3(\text{H}_2\text{O})_2]_2$  within the chain is linked by two pairs of tridentate bridging 4-pya ligands. The lumi-



nescent properties of **1** and **2** in the solid state were investigated. Compound **1** showed strong sharp red luminescence in the solid state at room temperature, showing a potential application in organic light-emitting devices (OLED) with the complex as emitter. The preparations and luminescent properties of other lanthanide/pya complexes are currently under way in this laboratory.

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### Appendix A. Supplementary data

Crystallographic data for the structural analyses have been deposited with Cambridge Crystallographic Data Centre, CCDC Nos. 259960 (**1**) and 259961 (**2**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1E2, UK (fax: +44 1223 336 033; deposit@ccdc.cam.ac.uk or www: [www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk)). Supplementary data associated with this article can be found, in the online version at doi:10.1016/j.jorganchem.2005.04.041.

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