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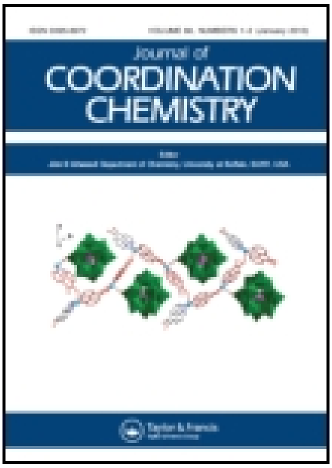

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Hongsheng Wang[ab], Jun Xia[b], Bin Zhai[b] & Xiaoqing Zhao[b]
[a] School of Chemistry and Chemical Engineering, Xuchang University, Xuchang, PR China
[b] Department of Chemistry, Nankai University, Tianjin, PR China

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Structures and luminescent properties of two heterotrimetallic Ln(III)–Sr(II)–K(I) complexes

HONGSHENG WANG*†‡, JUN XIA‡, BIN ZHAI‡ and XIAOQING ZHAO‡

†School of Chemistry and Chemical Engineering, Xuchang University, Xuchang, PR China
‡Department of Chemistry, Nankai University, Tianjin, PR China

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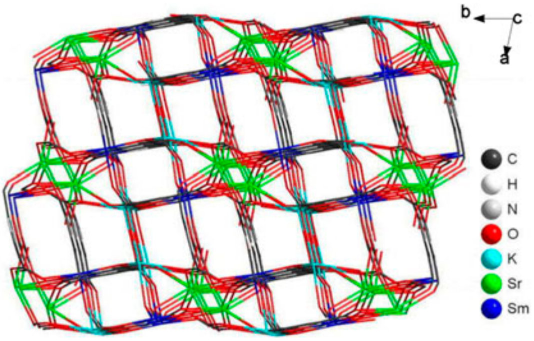

Eu(III)–Sr(II)–K(I) and Tb(III)–Sr(II)–K(I) heterotrimetallic metal-organic frameworks with 2,4,6-pyridinetricarboxylic acid have been synthesized under hydrothermal conditions. The complexes are isomorphic and both in triclinic space group *P-1*. The ligands bond with three metal ions with two coordination modes. One connects seven metal ions and the other connects eight metal ions. IR spectra, thermal analysis, and photoluminescent properties have been studied. The results display strong characteristic emissions of Eu(III) or Tb(III) ions with excitation of ultraviolet radiation.

Keywords: Heterometallic; Luminescence; Lanthanide; Strontium; Potassium

1. Introduction

The synthesis of metal-organic frameworks (MOFs) with lanthanides has attracted much attention due to potential applications such as luminescent materials for fluorescence probes, laser, photo- and electro-luminescence [1–8]. In the research, 3d–4f heterometallic MOFs are the key issue of the active area [9–15]. However, MOFs of lanthanide and main group elements are less studied. A few researchers have studied lanthanide–alkaline metals and

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*Corresponding author. Email: wanghs@mail.nankai.edu.cn lanthanide–alkaline metal complexes [16–18]. Only few examples of heterotrimetallic coordination polymers containing lanthanide have been reported [19–23]. None of them has good luminescent properties because the lanthanide ions employed in the complexes are Pr(III), Gd(III) or Dy(III). Organic ligands play an important role in the structure and properties of MOFs. Recently, we have studied lanthanide photoluminescent complexes, especially for mixed-metal complexes in order to partly substitute relatively expensive Eu and Tb. In this contribution, a stable aromatic acid, 2,4,6-pyridinetricarboxylic acid (H_3pta), was used (m.p. > 300 °C) as the organic linker and two heterotrimetallic (lanthanide alkaline, earth alkaline metals) 3-D MOFs were synthesized $[LnSrK(pta)_2(H_2O)]_n$ (Ln = Eu (**1**) and Tb (**2**)) under hydrothermal conditions. The Eu(III)–Sr(II)–K(I) and Tb(III)–Sr(II)–K(I) with H_3pta heterotrimetallic systems show intense photoluminescence.

2. Experimental

2.1. *Synthesis of 2,4,6-pyridinetricarboxylic acid*

2,4,6-Pyridinetricarboxylic acid (H_3pta) was synthesized by oxidization of 2,4,6-trimethylpyridine with potassium permanganate according to the literature [24]. Anal. Calcd for $C_8H_5NO_6$ (%): C, 45.51; H, 2.39; N, 6.63. Found: C, 45.74; H, 2.08; N, 6.49. IR spectra (KBr pellets, cm^{-1}): 3544m, 3421m, 2502m, 1719s, 1591s, 1555s, 1431m, 1402m, 1280s, 1197s, 1088s, 926w, 722m, 758m, 706s, 685s, 626s, 563w. Rare earth chlorides were prepared with hydrochloric acid and rare earth oxides. Other chemicals purchased commercially were of reagent grade and were used without purification.

2.2. *Syntheses of the heterotrimetallic complexes*

Colorless block crystals of $[EuSrK(pta)_2(H_2O)]_n$ (**1**) and $[TbSrK(pta)_2(H_2O)]$ (**2**) were obtained by hydrothermal reaction of $EuCl_3{\cdot}6H_2O$ (0.2 mM, 0.0732 g), $SrCO_3$ (0.2 mM, 0.0296 g), KNO_3 (0.2 mM, 0.0202 g), and H_3pta (0.4 mM, 0.0844 g) for **1** (yield: 55%) and $TbCl_3{\cdot}6H_2O$ (0.2 mM, 0.0747 g), $SrCO_3$ (0.2 mM, 0.0296 g), KOH (0.2 mM, 0.0112 g), and H_3pta (0.4 mM, 0.0844 g) for **2** (yield: 63%) at 180 °C. Anal. Calcd for $C_{16}H_6N_2O_{13}EuSrK$ (%): C, 26.96; H, 0.85; N, 3.93. Found: C, 26.05; H, 1.69; N, 4.17. IR spectra (KBr pellets, cm^{-1}): 3475sb, 1627s, 1596s, 1455s, 1370s, 1339s, 1267m, 1229m, 1106w, 1017w, 945w, 859w, 786m, 740m, 715s, 621w, 590w, 537w, 467w, 422w. $C_{16}H_6N_2O_{13}TbSrK$ (%): C, 26.70; H, 0.84; N, 3.89. Found: C, 26.21; H, 1.43; N, 3.75. IR spectra (KBr pellets, cm^{-1}): 3383sb, 3089w, 1628s, 1596s, 1441s, 1370s, 1340s, 1268m, 1230m, 1106w, 1019m, 945w, 920w, 859w, 789m, 741m, 715s, 621w, 590w, 539w, 467w, 426w.

2.3. *X-ray data collection and structure refinement*

Crystallographic data of the two complexes were collected with a Bruker SMART1000 CCD area detector which is equipped with graphite monochromated Mo Kα radiation. Structures were solved by direct methods with the SHELXTL-97 programs and refined by full-matrix least-squares against F^2 with the SHELXTL-97 program package [25, 26]. All non-hydrogen atoms were refined anisotropically and hydrogens were located and refined isotropically. Crystal data for the two complexes are listed in tables S1 and S2 (see online supplemental material at http://dx.doi.org/10.1080/00958972.2014.964226).

3. Results and discussion

3.1. *Structural description of 1 and 2*

The structures of the two complexes are isomorphic and **2** is taken as an example to be described in detailed. As shown in figure 1(a), Tb(III) is eight coordinate with six oxygens from six carboxyl groups and two nitrogens from two pyridyl rings. Sr(II) is also eight coordinate with all oxygens from one water and six carboxyl groups. Each Tb(III) is chelated by two pta ligands with 2-, 6-carboxyl groups and pyridyl nitrogen. Both Tb(III) and Sr(II) ions lie in distorted square anti-prisms. Five oxygens from five carboxyl groups coordinate to one K(I) and form a distorted tetragonal pyramid. The pta ligands exhibit two different coordination modes (scheme 1). One bonds seven metal ions, two Tb(III), three Sr (II), and two K(I) ions, while the other bonds eight metal ions, two Tb(III), three Sr(II), and three K(I) ions. Figure 1(b) shows the 3-D network of **2**. The topological approach is used to indicate the frameworks, as shown in figure 2. There are two kinds of 16-member rings (the rings connected by red rods) formed with eight metal ions connected by eight oxygens (the red rods) in each layer. With the eight oxygens, one ring is comprised of two Tb(III) ions, two Sr(II) ions, and four K(I) ions; the other ring is comprised of two Tb(III) ions, four Sr(II) ions, and two K(I) ions. In each ring, the Tb(III) ions and Sr(II) ions as well as Tb(III) ions and K(I) ions are connected by carboxyl groups (the blue rods). The 3-D frameworks are constructed by the connections of carboxyl groups between Tb(III) and K(I) ions as well as Tb(III) and Sr(II) ions in the adjacent 2-D-layers.

3.2. *Thermal analyses and phase purities of complexes*

Thermal analyses of **1** and **2** were tested under N_2 atmosphere. The results are consistent with the molecular formula, as shown in figures 3 and 4. The weight losses at 115.6 °C and 140 °C correspond to water on Sr(II) ion (calcd 2.52%; found 2.31% for **1** and calcd 2.50%; found 2.17% for **2**). The two complexes further lose weight and decompose at

Table 1. Crystal data for **1** and **2**.

	1	**2**
Empirical formula	$C_{16}H_6N_2O_{13}EuSrK$	$C_{16}H_6N_2O_{13}TbSrK$
Crystal system	Triclinic	Triclinic
Space group	*P*-1	*P*-1
a/ Å	8.054(2)	8.034(3)
b/ Å	10.764(3)	10.729(4)
c/ Å	12.051(3)	11.984(4)
α/°	76.002(4)	75.828(5)
β/°	71.351(4)	71.354(5)
γ/°	74.435(5)	74.178(5)
V/ Å^3	939.5(5)	927.4(5)
Z	2	2
μ/ mm^{-1}	6.450	6.965
F (0 0 0)	680	684
GOF on F^2	1.020	1.007
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0386$, $wR_2 = 0.0897$	$R_1 = 0.0324$, $wR_2 = 0.0753$
R indices (all data)	$R_1 = 0.0535$, $wR_2 = 0.0976$	$R_1 = 0.0417$, $wR_2 = 0.0802$

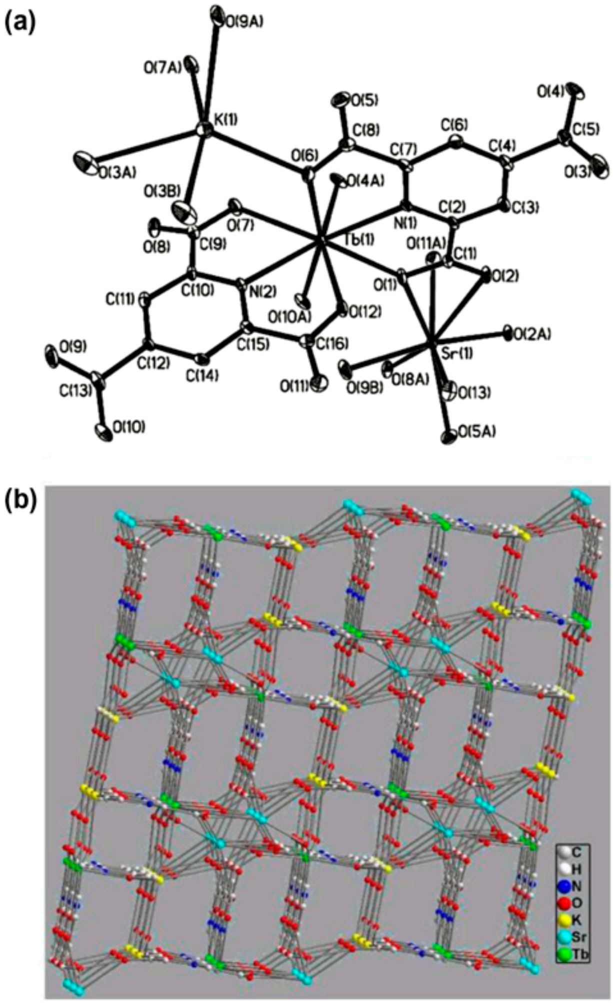


Figure 1. (a) The coordination sphere of Tb(III), Sr(II), and K(I) ions in **2** with ORTEP representation. Thermal ellipsoids were drawn with 30% probability. (b) The 3-D network of **2**. All hydrogens were omitted for clarity.

400 °C. Similar studies on thermal stabilities for lanthanide complexes have been reported [27–29]. The Pr(III) complex with analogous thermal stability reported by Sharif [28] is also coordinated with 2,4,6-pyridinetricarboxylate.

The phase purity was confirmed by comparisons between the powder X-ray diffraction (PXRD) of **1** and **2** and the simulation PXRD with their crystallographic data. Figures 5 and 6 are the experimental results and the simulated results for **1** and **2**, respectively. All major peaks of the tested PXRD of the two complexes match to the corresponding simulated PXRD. The results show that the samples of the two complexes have good crystalline phase purity.

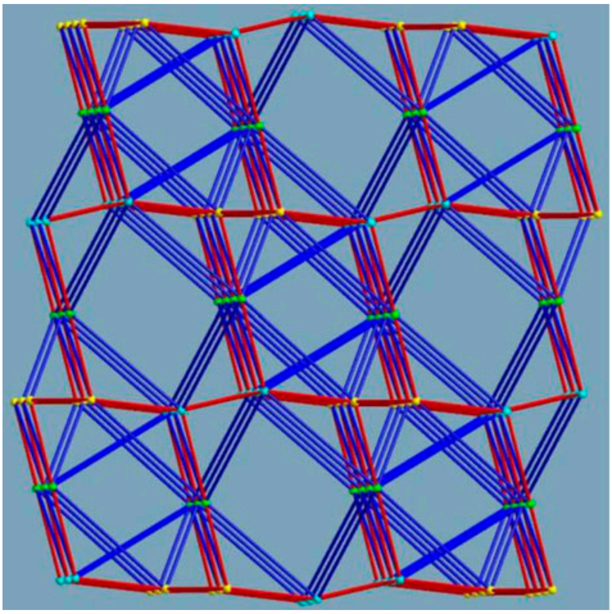


Figure 2. The topological graph of **1** and **2**: the yellow balls are K(I), the azury ones are Sr(II), green ones are Tb (III) or Eu(III) ions, the red rods are oxygens, and blue rods are μ-carboxyl groups (–O–C–O–) (see http://dx.doi.org/10.1080/00958972.2014.964226 for color version).

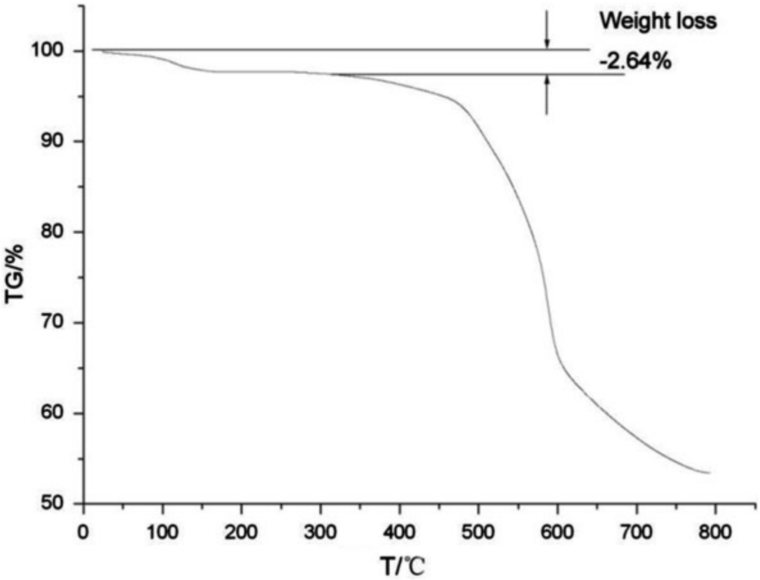


Figure 3. The TG graph of **1** (Eu(III)–Sr(II)–K(I)–pta).

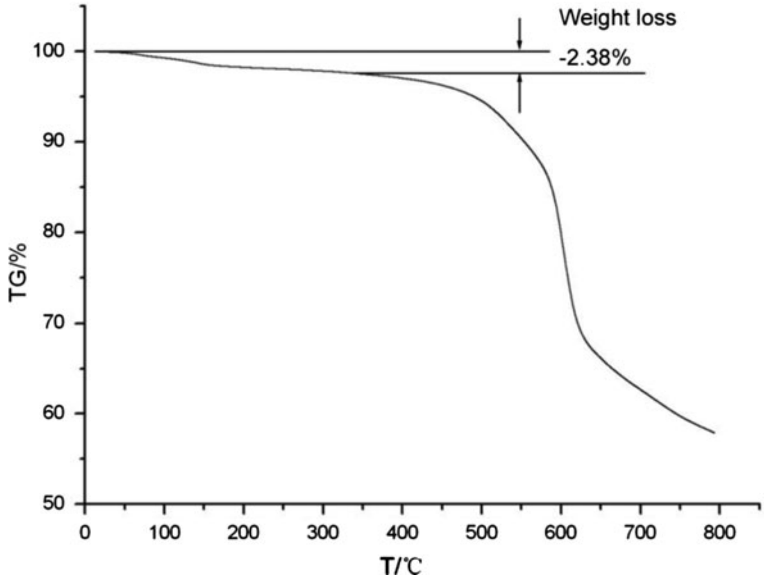


Figure 4. The TG graph of **2** (Tb(III)–Sr(II)–K(I)–pta).

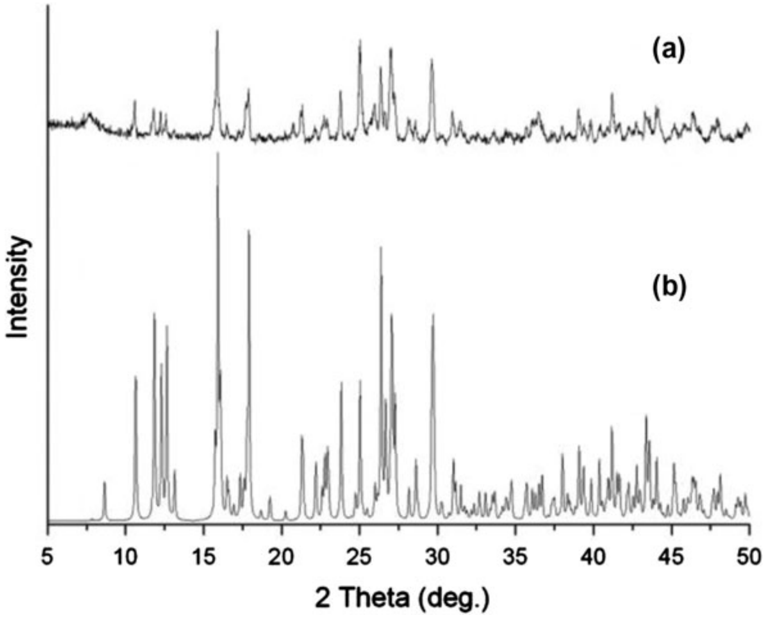


Figure 5. The phase purity for **1** [(a) the tested PXRD pattern with solid sample of **1**; (b) the simulated XRD pattern of **1** with X-ray single-crystal diffraction data].

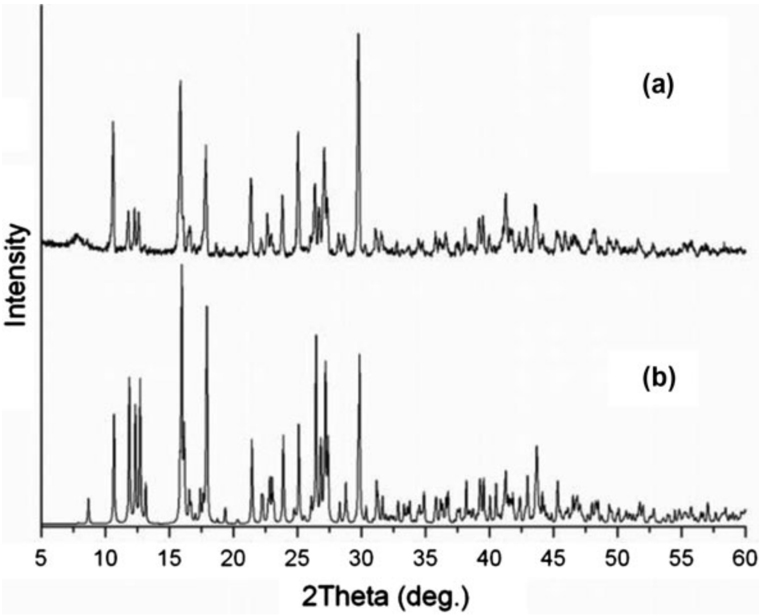


Figure 6. The phase purity for **2** [(a) the tested PXRD pattern with solid sample of **2**; (b) the simulated XRD pattern of **2** with X-ray single-crystal diffraction data].

3.3. *Photoluminescent properties of the two complexes*

Emission spectra were determined with solid samples for the two complexes with excitation at 300 nm under ambient temperature. The excitation and emission slit widths were both regulated at 5 nm.

Both complexes display strong characteristic emission. In emission spectra of **1**, not only the $^5D_0 \rightarrow {}^7F_J$ transitions [$J = 0$ (581 nm), 1 (592 nm), 2 (617 nm), 3 (652 nm), 4 (690 nm)] for Eu(III) ions, but also that of $^5D_1$ to ^7F_J [$J = 1$ (536 nm), 2 (557 nm)] can be observed clearly, as shown in figure 7(a). The ratio of transition intensities of $^5D_0 \rightarrow {}^7F_2$ (electric dipole transition) to $^5D_0 \rightarrow {}^7F_1$ (magnetic dipole transition) is 2.7. The results indicate that the Eu(III) ions lie in coordination environment with low symmetry in the complex [30, 31], which also accords with the result of single-crystal X-ray diffraction. The four emission bands of **2** at 490, 546, 585, and 622 nm are assigned to the $^5D_4 \rightarrow {}^7F_J$ transition ($J = 6$, 5, 4, 3) for Tb(III) ions, as shown in figure 7(b).

According to theories of energy transfer [32, 33], the emission intensity of rare earth ions may be influenced by the structure of the complex, the coordination molecules, efficiency of the energy transfer from ligands to central ions, and the energy absorption efficiency of the ligands. For **1** and **2**, small coordination molecules do not bond to the central luminescent Eu (III) and Tb(III). The photons absorbed by pta ligands are not transferred to the crystal lattice by thermo-vibration of small coordination molecules. Secondly, the introduction of two main group metal ions increases the number of positive charges, which results in increase of pta coordinated to the central luminescent ions to balance the positive charges. According to the antenna effect [34], more energy may be absorbed and effectively transferred to the central ions. As a result, the two trimetallic complexes display strong emission, showing Sr(II) and K(I) ions in **1** and **2** do not quench the emission of Eu(III) or Tb(III) ions.

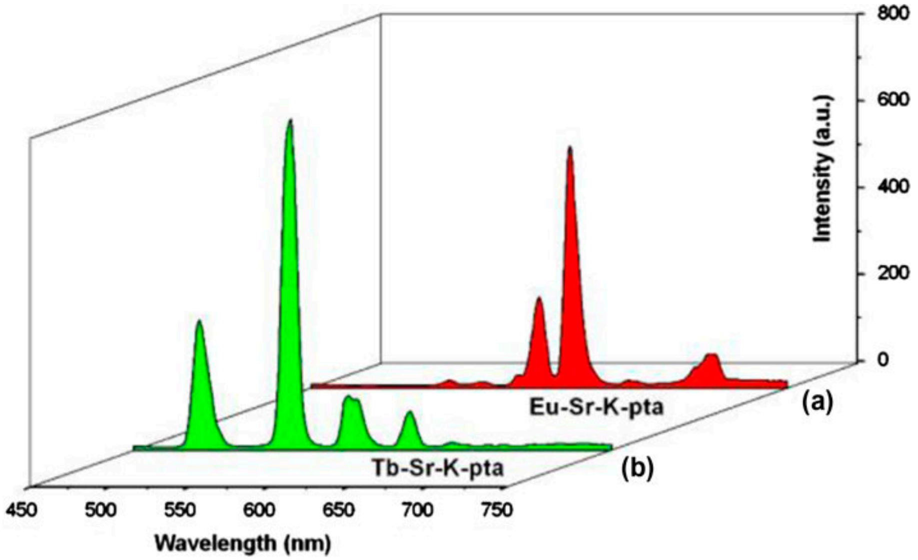
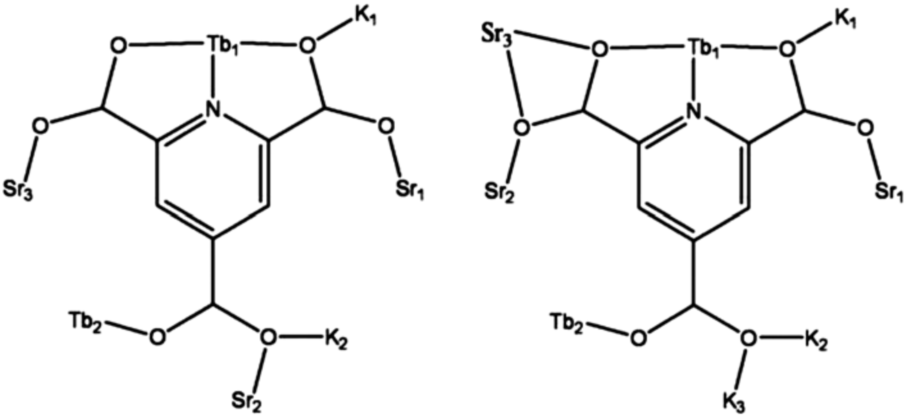


Figure 7. Emission spectra of Eu(III)–Sr(II)–K(I)–pta (a) and Tb(III)–Sr(II)–K(I)–pta (b) in solid samples excited at 300 nm.



Scheme 1. Coordination modes of pta ligands in 1 and 2.

4. Conclusion

We synthesized trimetallic luminescent complexes of Eu(III)–Sr(II)–K(I) and Tb(III)–Sr(II)–K(I) with 2,4,6-pyridinetricarboxylic acid. The highly luminescent complexes make them promising as new luminescent materials and supply a new way to synthesize photo- or electro-luminescent materials.

Supplementary material

Crystallographic data for the two complexes have been deposited at the Cambridge Crystallographic Data Center (CCDC); CCDC Nos. are 625198 for **1** and 621819 for **2**. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB21EZ, UK; Fax: (+44) 1223 336 033; or E-mail: deposit@ccdc.cam.ac.uk).

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