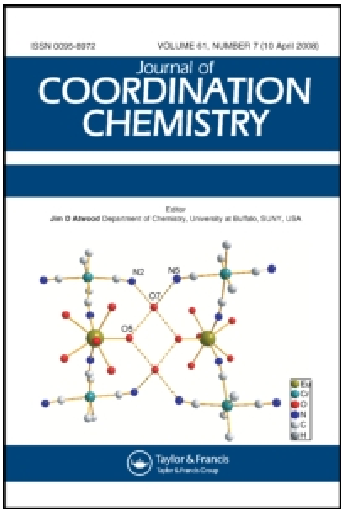

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Structures and luminescent properties of Sm(III) and Dy(III) coordination polymers with 2,4,6-pyridinetricarboxylic acid

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Structures and luminescent properties of Sm(III) and Dy(III) coordination polymers with 2,4,6-pyridinetricarboxylic acid

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Two rare earth coordination compounds with 2,4,6-pyridinetricarboxylic acid (H_3pta) have been synthesized by the hydrothermal method; the formula is $\{[RE(pta)(H_2O)_3]\cdot H_2O\}_n$ [RE = Sm (**1**) and Dy (**2**)]. Complexes **1** and **2** are crystallized in the monoclinic crystal system with *P2₁/c* space group. X-ray structure analyses show the two complexes have the same structure. Each pta^{3-} connects three rare earth ions. Both the Sm(III) and Dy(III) complexes exhibit characteristic luminescence in the visible region upon excitation with UV-rays.

Keywords: 2,4,6-Pyridinetricarboxylic acid; Photoluminescence; Samarium; Dysprosium; Lanthanide

1. Introduction

Design and synthesis of metal organic frameworks (MOFs) with trivalent lanthanide cations and carboxylic acids have attracted much attention due to their luminescent properties and potential applications in luminescent materials [1–4]. Multicarboxylic acids containing phenyl have been widely used as organic linkers in the syntheses of MOFs because they have two or more carboxyl groups and are inclined to forming multidimensional structure [5–10]. The pyridine- and tri-carboxylic acids are also important organic ligands for constructing MOFs as the nitrogen can also coordinate with metal ions in addition to oxygens of carboxyl groups. Much attention has been paid to this field [11–14]. The structures and photoluminescent properties of nine rare earth complexes with 2,4,6-pyridinetricarboxylic acid have been reported by us [15]. They were all synthesized at room temperature and showed three different 1-D chain structures. Furthermore, seven 3-D lanthanide coordination polymers were reported, synthesized mostly with rare earth oxide and 2,4,6-pyridinetricarboxylic acid by the hydrothermal method [16]. New coordination polymers containing three metal ions with 2,4,6-pyridinetricarboxylic acid were also reported [17]. These show that the ligand is a good connector for rare earth ions to construct coordination polymers.

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In this article, we report two new rare earth complexes synthesized with rare earth perchlorate or rare earth chloride and 2,4,6-pyridinetricarboxylic acid at hydrothermal conditions. The two complexes obtained have the same structure. Their photoluminescent properties show that the two complexes display strong characteristic emission in visible region with excitation of UV radiation.

2. Experimental

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

2,4,6-Pyridinetricarboxylic acid was synthesized by oxidization of 2,4,6-trimethylpyridine with potassium permanganate [18]. 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. The rare earth salts were obtained by reacting hydrochloric acid with the corresponding rare earth oxides ($\geq$99.95%) purchased from Grirem Advanced Materials Co. Ltd., Beijing.

2.2. *Preparation of $[Sm(pta)_3(H_2O)]_n$ (1)*

A mixture of 2,4,6-pyridinetricarboxylic acid (0.0422 g, 0.2 mmol), $SmCl_3 \cdot 6H_2O$ (0.0728 g, 0.2 mmol), and 15 mL deionized water was placed in a 25 mL Teflon-lined bomb, which was heated to 180°C for 96 h. After the mixture was cooled to room temperature at a rate of $1.5^\circ C\,h^{-1}$, the products were filtered, washed by ethanol, and dried in air. Yellow block crystals of **2** were obtained in 52% yield. Anal. Calcd for $C_8H_{10}NO_{10}Sm$ (%): C, 22.32; H, 2.34; N, 3.25. Found (%): C, 22.25; H, 2.33; N, 3.28. IR bands (KBr pellets, cm^{-1}): 3603s, 3388sb, 1631s, 1607s, 1580s, 1548s, 1453s, 1393s, 1351s, 1276m, 1235w, 1110w, 1024w, 930w, 818w, 790w, 739s, 623w, 586w, 479w, 434w.

2.3. *Preparation of $[Dy(pta)_3(H_2O)]_n$ (2)*

Synthesis of **2** was similar to **1**. The products were filtered and washed by ethanol, then dried in air. Colorless block crystals of **3** were obtained in 65% yield. Anal. Calcd for $C_8H_{10}NO_{10}Dy$ (%): C, 21.71; H, 2.28; N, 3.16. Found (%): C, 21.44; H, 2.37; N, 3.14. IR bands (KBr pellets, cm^{-1}): 3609s, 3383sb, 1632s, 1609s, 1583s, 1551s, 1446s, 1396s, 1352s, 1278m, 1236w, 1110w, 1025w, 931w, 819w, 791w, 740s, 671w, 622w, 586w, 545w, 478w, 436w.

2.4. *General characterization*

Elemental analyses were performed in a Perkin-Elmer 240 analyzer. IR spectra were recorded with a Tensor 27 FTIR spectrophotometer (KBr pellets, 4000–400 cm^{-1}). Emission spectra in the visible region were tested on a Cary Eclipse fluorescence spectrophotometer.

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

	1	**2**
Empirical formula	$C_8H_{10}NO_{10}Sm$	$C_8H_{10}NO_{10}Dy$
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
Unit cell dimensions (Å, °)		
a	11.959(6)	11.826(4)
b	7.337(4)	7.245(3)
c	13.526(7)	13.462(5)
α	90	90
β	96.593(7)	96.175(5)
γ	90	90
Z	4	4
μ (mm^{-1})	5.036	6.564
$F(000)$	828	844
Goodness-of-fit on F^2	1.089	0.982
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0361$, $wR_2 = 0.1171$	$R_1 = 0.0184$, $wR_2 = 0.0445$
R indices (all data)	$R_1 = 0.0411$, $wR_2 = 0.1207$	$R_1 = 0.0213$, $wR_2 = 0.0450$

2.5. *X-ray diffraction analysis*

Crystallographic data of **1** were collected with a Bruker SMART 1000 CCD diffractometer and the data of **2** with a Rigaku Saturn diffractometer. The two diffractometers were equipped with a graphite monochromator, and Mo-Kα radiation ($\lambda = 0.71073$ Å) was used. The two structures were solved by the direct method and refined with the full-matrix least-squares technique using the SHELXS-97 and SHELXL-97 programs [19]. All non-hydrogen atoms were refined anisotropically and hydrogens located and refined isotropically. Crystallographic data for the two compounds are listed in table 1 and selected bond lengths and angles are listed in tables 2 and 3.

3. Results and discussion

3.1. *Structures of the two complexes*

Complexes **1** and **2** are isostructural and **1** is taken as an example to describe the structure in detail, as shown in figure 1. The coordination number of Sm(III) is nine, with three oxygens (O(7), O(8), and O(9)) from water having Sm–O bond lengths of 2.442(6), 2.474(5), and 2.472(5) Å, respectively; the other five oxygens (O(1), O(6), O(2A), O(3A), and O(4A)) are from carboxylate groups and the Sm–O bond lengths are 2.465(5), 2.400(5), 2.335(5), 2.538(5), and 2.528(5) Å, respectively; the nitrogen N(1) is from the pyridyl ring with a Sm–N bond length of 2.499(5) Å. The bond angles of O–Sm–O range between 71.06(16)° and 150.29(18)° and that of O–Sm–N between 64.03(17)° and 128.67(19)°. The coordination mode of pta^{3-} is shown in scheme 1. The O(1), O(6), and N(1) chelate one Sm(III) through tridentate coordination. O(3) and O(4) of the 4-carboxyl group are bonded to one Sm(III) and O(2) connects another Sm(III), while O(5) does not coordinate with Sm(III) ion. So the ligand in the complex

Table 2. Selected bond lengths (Å) and angles (°) for **1**.

Sm(1)–O(2)#1	2.335(5)	Sm(1)–O(8)	2.474(5)
Sm(1)–O(6)	2.400(5)	Sm(1)–N(1)	2.499(5)
Sm(1)–O(7)	2.442(6)	Sm(1)–O(4)#2	2.528(5)
Sm(1)–O(1)	2.465(5)	Sm(1)–O(3)#2	2.538(5)
Sm(1)–O(9)	2.472(5)		
O(2)#1–Sm(1)–O(6)	150.29(18)	O(1)–Sm(1)–N(1)	64.11(16)
O(2)#1–Sm(1)–O(7)	98.26(19)	O(9)–Sm(1)–N(1)	70.32(18)
O(6)–Sm(1)–O(7)	74.24(19)	O(8)–Sm(1)–N(1)	119.63(18)
O(2)#1–Sm(1)–O(1)	75.36(16)	O(2)#1–Sm(1)–O(4)#2	124.80(16)
O(6)–Sm(1)–O(1)	128.01(16)	O(6)–Sm(1)–O(4)#2	82.13(18)
O(7)–Sm(1)–O(1)	141.95(18)	O(7)–Sm(1)–O(4)#2	76.51(19)
O(2)#1–Sm(1)–O(9)	74.96(17)	O(1)–Sm(1)–O(4)#2	77.07(17)
O(6)–Sm(1)–O(9)	93.82(18)	O(9)–Sm(1)–O(4)#2	137.13(18)
O(7)–Sm(1)–O(9)	143.39(19)	O(8)–Sm(1)–O(4)#2	144.63(17)
O(1)–Sm(1)–O(9)	72.20(17)	N(1)–Sm(1)–O(4)#2	69.65(17)
O(2)#1–Sm(1)–O(8)	76.25(17)	O(2)#1–Sm(1)–O(3)#2	74.44(16)
O(6)–Sm(1)–O(8)	74.09(18)	O(6)–Sm(1)–O(3)#2	126.87(17)
O(7)–Sm(1)–O(8)	72.10(18)	O(7)–Sm(1)–O(3)#2	71.11(18)
O(1)–Sm(1)–O(8)	138.30(17)	O(1)–Sm(1)–O(3)#2	71.06(16)
O(9)–Sm(1)–O(8)	71.34(18)	O(9)–Sm(1)–O(3)#2	136.79(17)
O(2)#1–Sm(1)–N(1)	132.67(17)	O(8)–Sm(1)–O(3)#2	128.24(17)
O(6)–Sm(1)–N(1)	64.03(17)	N(1)–Sm(1)–O(3)#2	111.65(17)
O(7)–Sm(1)–N(1)	128.67(19)	O(4)#2–Sm(1)–O(3)#2	51.56(15)

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

Table 3. Selected bond lengths (Å) and angles (°) for **2**.

Dy(1)–O(2)#1	2.3030(19)	Dy(1)–O(8)	2.459(3)
Dy(1)–O(5)	2.356(2)	Dy(1)–O(4)#2	2.503(2)
Dy(1)–O(9)	2.406(2)	Dy(1)–N(1)	2.462(2)
Dy(1)–O(1)	2.425(2)	Dy(1)–O(3)#2	2.5146(19)
Dy(1)–O(7)	2.452(2)		
O(2)#1–Dy(1)–O(5)	149.52(7)	O(1)–Dy(1)–N(1)	65.01(7)
O(2)#1–Dy(1)–O(9)	96.39(8)	O(7)–Dy(1)–N(1)	69.75(8)
O(5)–Dy(1)–O(9)	73.95(8)	O(8)–Dy(1)–N(1)	117.30(8)
O(2)#1–Dy(1)–O(1)	75.45(7)	O(2)#1–Dy(1)–O(4)#2	125.71(7)
O(5)–Dy(1)–O(1)	129.88(7)	O(5)–Dy(1)–O(4)#2	81.16(7)
O(9)–Dy(1)–O(1)	140.96(7)	O(9)–Dy(1)–O(4)#2	77.32(7)
O(2)#1–Dy(1)–O(7)	75.15(7)	O(1)–Dy(1)–O(4)#2	77.26(7)
O(5)–Dy(1)–O(7)	95.25(7)	O(7)–Dy(1)–O(4)#2	136.59(7)
O(9)–Dy(1)–O(7)	143.41(8)	O(8)–Dy(1)–O(4)#2	144.70(8)
O(1)–Dy(1)–O(7)	72.30(7)	N(1)–Dy(1)–O(4)#2	69.63(7)
O(2)#1–Dy(1)–O(8)	76.87(7)	O(2)#1–Dy(1)–O(3)#2	74.45(7)
O(5)–Dy(1)–O(8)	72.66(8)	O(5)–Dy(1)–O(3)#2	125.82(7)
O(9)–Dy(1)–O(8)	73.01(8)	O(9)–Dy(1)–O(3)#2	70.28(7)
O(1)–Dy(1)–O(8)	137.96(7)	O(1)–Dy(1)–O(3)#2	70.77(6)
O(7)–Dy(1)–O(8)	70.40(8)	O(7)–Dy(1)–O(3)#2	136.74(7)
O(2)#1–Dy(1)–N(1)	133.11(7)	O(8)–Dy(1)–O(3)#2	129.75(7)
O(5)–Dy(1)–N(1)	65.15(7)	N(1)–Dy(1)–O(3)#2	112.48(7)
O(9)–Dy(1)–N(1)	130.19(9)	O(4)#2–Dy(1)–O(3)#2	52.41(6)

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

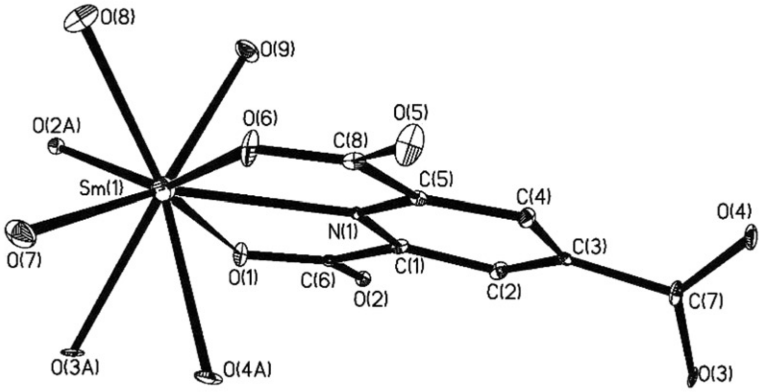
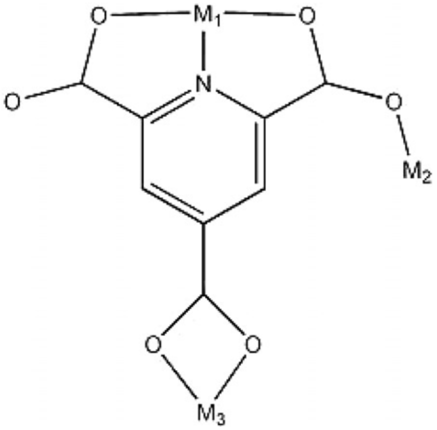


Figure 1. The ORTEP representation of **1** showing the coordination environment of Sm(III) with 30% probability thermal ellipsoids. All hydrogens were omitted for clarity.



Scheme 1. The coordination modes of pta^{3-} in **1** and **2**.

bonds only three metal ions. By connection of pta^{3-} and Sm(III) 2-D layered framework is formed, as shown in figure 2. The 2-D layers are connected by hydrogen bonds formed among coordinated water molecules and carboxyl groups to form a 3-D network (figure 3).

Nine coordination atoms of the central ions form a polyhedron of distorted monocapped square anti-prism, as shown in figure 4. The average bond lengths of RE–O (RE = Sm(III) and Dy(III)) are 2.457 and 2.427 Å, respectively. They become shorter with increasing atomic number, ascribed to lanthanide contraction because they have the same crystal structure.

3.2. *Photoluminescent properties of 1 and 2*

Luminescent materials containing europium and terbium ions have been deeply studied and some of them have been applied [20–22]. Both Sm(III) and Dy(III) can form

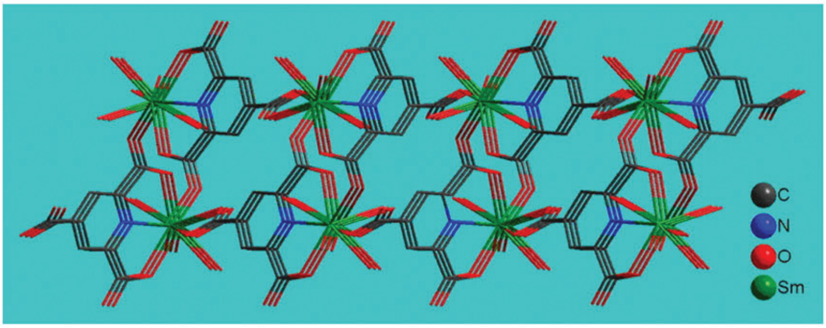


Figure 2. 2-D layered structure formed by pta^{3-} and Sm(III) in **1**.

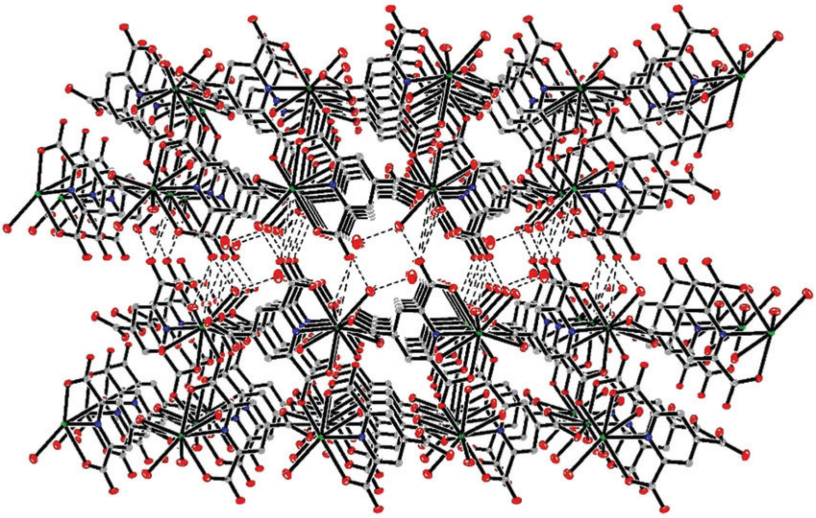


Figure 3. 3-D structure constructed by 2-D layers with hydrogen bonds formed among coordinated water molecules and carboxylates.

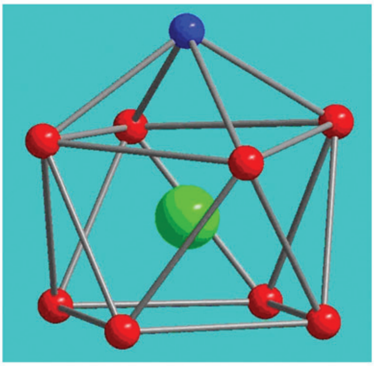


Figure 4. The distorted monocapped tetragonal anti-prism formed by coordinating oxygen and nitrogen.

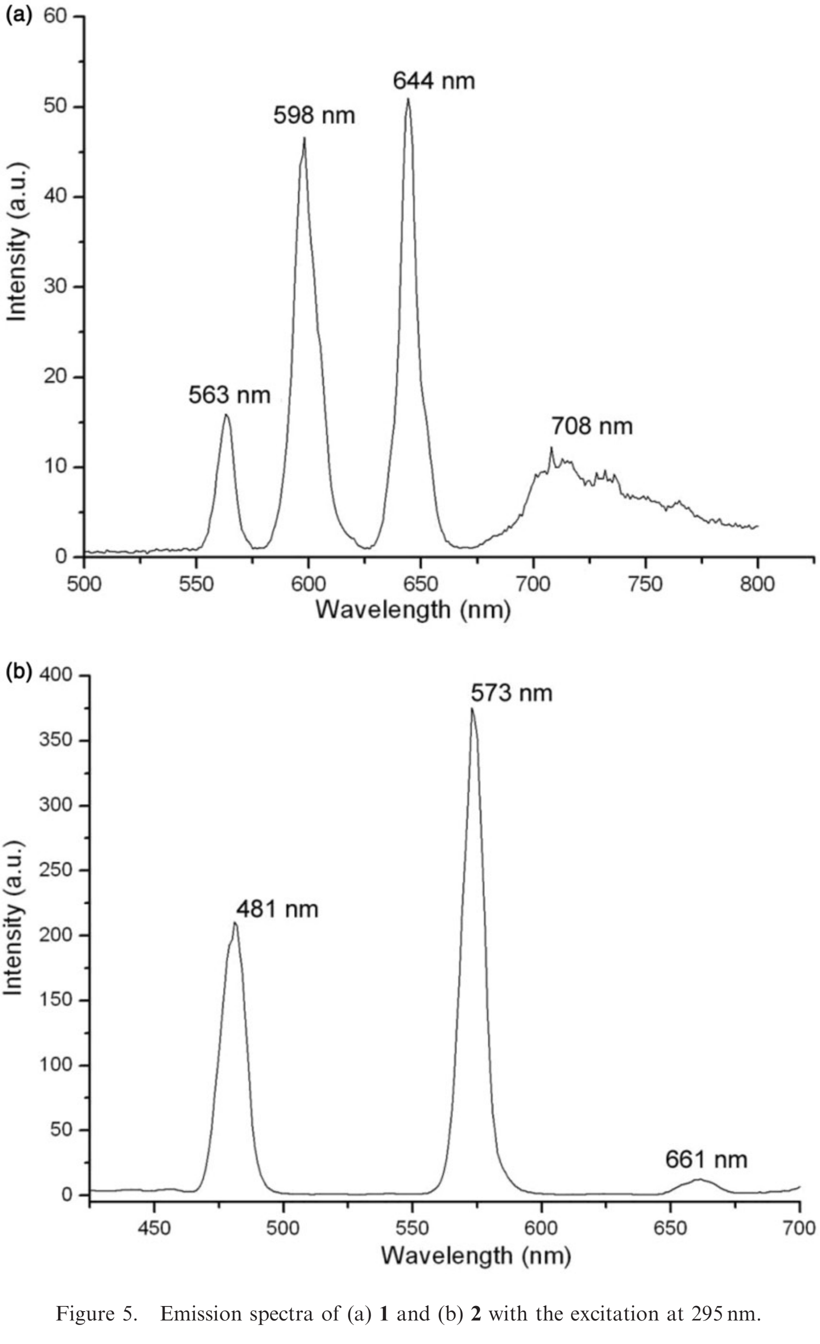


Figure 5. Emission spectra of (a) **1** and (b) **2** with the excitation at 295 nm.

analogous luminescent materials, but they are not used widely due to the weak emission. Here the solid-state photoluminescent spectra of **1** and **2** at ambient temperature were recorded under the excitation at 295 nm. The emission bands of **1** are shown in figure 5(a). The four peaks at 563, 598, 644, and 708 nm corresponded to transitions of Sm(III) from $^4G_{5/2}$ to ^6H_J ($J = 5/2, 7/2, 9/2, 11/2$), respectively [23–26]. In the luminescence spectra of **2**, as shown in figure 5(b), three emitting peaks of Dy(III) complex at 481, 573, and 661 nm are assigned to the transitions $^4F_{9/2} \rightarrow {}^6H_{15/2}$, $^4F_{9/2} \rightarrow {}^6H_{13/2}$, and $^4F_{9/2} \rightarrow {}^6H_{11/2}$, respectively [27–29]. The transitions of $^4G_{5/2}$ to $^6H_{11/2}$ of Sm(III) ion and $^4F_{9/2}$ to $^6H_{11/2}$ of Dy(III) ion are usually weak, rarely seen in the corresponding luminescence spectra. Fortunately the two emission bands are clearly shown in emission spectra of **1** and **2**. The two complexes have relatively strong emission intensity in the visible region probably due to [30–35] the pta^{3-} ligands absorbing excitation energy by pyridyl rings and transferring energy to Sm(III) or Dy(III) and the double-layered 2-D structure is a rigid structure and less energy was lost with the vibrations of the crystal lattice.

In summary, we have synthesized two new coordination polymers of samarium and dysprosium using pta^{3-} as the organic linker. The two complexes are isostructural. The ligand connects three lanthanides. Both complexes show strong characteristic emissions in the visible region.

Supplementary material

Crystallographic data for the two complexes with CCDC Nos. are 705528 and 705529, respectively, in this article have been deposited at the Cambridge Crystallographic Data Center. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (+44) 1223-336-033; or E-mail: deposit@ccdc.cam.ac.uk).

Acknowledgments

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