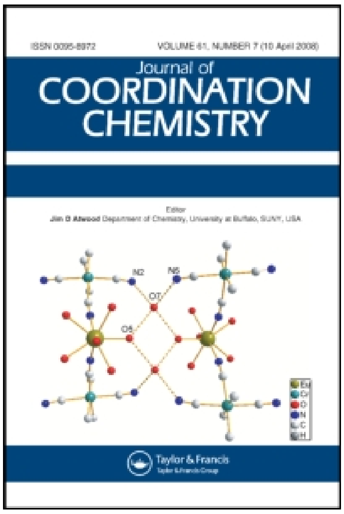

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

1-D Ln-Ag (Ln = Eu; Tb) heterometallic coordination polymers with pyridine-2,6-dicarboxylate as the single ligand: Synthesis, crystal structures, and luminescence

De-Yun Ma[a]; Wei-Xia Wang[a]; Ying-Wei Li[a]
[a] School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, P.R. China

To cite this Article Ma, De-Yun , Wang, Wei-Xia and Li, Ying-Wei(2010) '1-D Ln-Ag (Ln = Eu; Tb) heterometallic coordination polymers with pyridine-2,6-dicarboxylate as the single ligand: Synthesis, crystal structures, and luminescence', Journal of Coordination Chemistry, 63: 3, 448 — 456, First published on: 10 December 2009 (iFirst)
To link to this Article: DOI: 10.1080/00958970903469696
URL: http://dx.doi.org/10.1080/00958970903469696

Journal of Coordination Chemistry
Vol. 63, No. 3, 10 February 2010, 448–456

1-D Ln–Ag (Ln = Eu; Tb) heterometallic coordination polymers with pyridine-2,6-dicarboxylate as the single ligand: Synthesis, crystal structures, and luminescence

DE-YUN MA, WEI-XIA WANG and YING-WEI LI*

School of Chemistry and Chemical Engineering, South China University of Technology,
Guangzhou 510640, P.R. China

(*Received 14 December 2008; in final form 17 August 2009*)

Two new 4d–4f heterometallic coordination polymers $[AgLn(pydc)_2(H_2O)_3] \cdot x(H_2O)$ [Ln = Eu, $x = 1.25$ (**1**); Ln = Tb, $x = 1.25$ (**2**); pydc = 2,6-pyridinedicarboxylate] have been synthesized and characterized by elemental analysis, IR spectroscopy, and single crystal X-ray diffraction. Both structures display the same unusual 1-D heterometallic coordination polymer based on Ln building blocks and Ag ions. Thermal stabilities and luminescent properties of **1** and **2** are presented.

Keywords: Ln(III)–Ag heterometallic complexes; 2,6-Pyridinedicarboxylic acid; Hydrothermal synthesis; Crystal structure; Luminescence

1. Introduction

Lanthanide–transition metal complexes have attracted considerable interest because of their intriguing topological structures [1–3] and unique properties such as magnetism [4, 5], conductivity [6, 7], photoluminescence [8], nonlinear optics [9], and bimetallic catalysis [10]. However, the construction of open heterometallic coordination frameworks is still a formidable task because of the variable and versatile coordination numbers of the lanthanide ions, their low stereochemical preference, and competitive reactions between lanthanide and transition metals coordinated by a ligand. Therefore, metal organic networks containing both lanthanide and transition metal cations have been relatively less reported. In general, there are two approaches for preparing the heterometallic coordination frameworks: (1) self-assembly from solutions containing the different metal ions and ligands and (2) metal-in-ligand strategy [11], where one type of metal ion is first assembled with ligands leaving one or more ligand sites open for subsequent binding to the second type of metal ion. Both approaches are facilitated by utilizing multifunctional ligands that have bonding sites with different affinities to discriminate between metal ions based on their electronic configurations, sizes, and charges.

---

*Corresponding author. Email: liyw@scut.edu.cn

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online
DOI: 10.1080/00958970903469696

Pyridine-2,6-dicarboxylic acid (H_2pydc) is one such multifunctional ligand, in which the carboxylates can chelate lanthanide ions and the nitrogens may bind with alkali, alkaline earth, or transition metal cations. Mononuclear and 3-D networks have been observed in many compounds containing H_2pydc, trivalent lanthanide ion, and Na^+ [12]. Fully bridged infinite chains were constructed from pydc, lanthanide, and transition metal or alkaline earth ions, for example, $[M(pydcH_2)(H_2O)_3][Ce(pydc)_3] \cdot nH_2O$ ($M = Ca$, $n = 5$; $M = Sr$, $n = 6$) or $Ag[Gd(pydc)_2(H_2O)_3] \cdot 3H_2O$ [13]. More recently, Zhao *et al.* [14] employed H_2pydc as a linker between lanthanide and transition metal cations to construct two new coordination polymers $Nd_2(pydc)_6Co_3(H_2O)_6 \cdot 7H_2O$ and $Gd_2(pydc)_6Co_3(H_2O)_6 \cdot 3.25H_2O$.

In this article, we also chose H_2pydc as a potential linker between lanthanide and transition metal ions to construct two new isostructural 4d–4f coordination polymers $[AgLn(pydc)_2(H_2O)_3] \cdot x(H_2O)$ [$Ln = Eu$, $x = 1.25$ (**1**); $Ln = Tb$, $x = 1.25$ (**2**)] by hydrothermal synthesis. The two complexes exhibit the same 1-D heterometallic coordination polymer based on Ln building blocks and Ag ions, as reported by Goodgame *et al.* [13c]. The structures of the new iso-structural bimetallic coordination polymers were thoroughly characterized and thermal stabilities and photoluminescence of **1** and **2** are also reported in this article.

2. Experimental

2.1. *Materials and physical measurements*

All chemicals were commercially available and used as received. Elemental analyses for C, H, and N were carried out using a Vario EL III Elemental Analyzer. Infrared (IR) spectra were recorded (4000–400 cm^{-1}) as KBr disks on a Bruker 1600 FTIR spectrometer. Luminescence spectra for crystal solid samples were recorded at room temperature on a Hitachi F-4500 fluorescence spectrophotometer. Thermogravimetric analyses (TGA) were performed on a simultaneous SDT thermal analyzer (STA449C, Netzsch, PA, USA) under a flow of N_2 at a heating rate of $10^\circ C\,min^{-1}$ between ambient temperature and 800°C.

2.2. *Synthesis of 1 and 2*

A mixture of $AgNO_3$ (0.849 g, 0.5 mmol), $Ln(NO_3)_3 \cdot 6H_2O$ (0.223 g, 0.5 mmol for **1**; 0.226 g, 0.5 mmol for **2**), H_2pydc (0.0835 g, 0.5 mmol), and H_2O (10 mL) was stirred for 30 min in air and then sealed in a 23 mL Teflon reactor and kept under autogenous pressure at 150°C for 72 h. The mixture was cooled to room temperature at a rate of $5^\circ C\,h^{-1}$ and colorless plate crystals were obtained in a yield of 42% based on Eu for **1** [40% based on Tb for **2**]. Calcd for $C_{14}H_{15}AgEuN_2O_{12}$ (**1**): C, 24.83; H, 2.22; N, 4.14. Found: C, 24.86; H, 2.19; N, 4.12. IR bands (KBr pellets, cm^{-1}): $\nu = 3456$(s), 1720(s), 1620(vs), 1377(vs), 1074(s). Calcd for $C_{14}H_{14}AgTbN_2O_{12}$ (**2**): C, 25.02; H, 2.09; N, 4.17. Found: C, 25.05; H, 2.07; N, 4.20. IR bands (KBr pellets, cm^{-1}): $\nu = 3238$(s), 1728(s), 1616(vs), 1380(vs), 728(s).

2.3. *X-ray crystallography*

X-ray diffractions for **1** and **2** were performed on a Bruker Apex II CCD diffractometer operating at 50 kV and 30 mA using Mo-Kα radiation ($\lambda = 0.71073$ Å) at room temperature. Data collection and reduction were performed using APEX II [15]. Multiscan absorption corrections were applied for the datasets using APEX II [15]. Both structures were solved by direct methods and refined by least squares on F^2 using the SHELXTL program package [15]. Both uncoordinated water and Ag ions showed significantly elongated thermal ellipsoids, indicating that there is a high degree of disorder. Thus, one uncoordinated water molecule and the Ag ion were refined as being disordered over two positions. The ADPs of the disordered atoms were constrained to be close to isotropic and those of equivalent atoms were set to be identical. The other uncoordinated water is disordered over two positions with site-occupancy factors of 0.75(2) and 0.25(2). All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogens attached to carbon were placed in geometrically idealized positions and refined using a riding model. Water hydrogens were tentatively located in difference Fourier maps and refined with distance restraints of O–H = 0.84 Å and H $\cdots$ H = 1.39 Å, each within a SD of 0.01 Å, and with $U_{iso}(H) = 1.5\, U_{eq}(O)$. Crystallographic data for **1** and **2** are listed in table 1, and selected bond lengths and angles are given in table 2.

3. Results and discussion

3.1. *Synthesis and characterization*

The hydrothermal reaction of $Ln(NO_3)_3 \cdot 6H_2O$ [Ln = Eu (**1**); Ln = Tb (**2**)], $AgNO_3$, and H_2pydc at a molar ratio of 1 : 1 : 1 in aqueous solution at 150°C for 72 h produced colorless plate crystals of **1** and **2**. The crystals are insoluble in water and common organic solvents. IR spectra of **1** and **2** show broad bands in the region 3300–3500 cm^{-1}, assigned to ν(O–H) stretching vibrations of water. Features at about 1720, 1620, and 1380 cm^{-1} are attributed to asymmetric and symmetric stretching vibrations for carboxylate.

3.2. *Crystal structures*

Single crystal X-ray diffraction studies revealed that **1** and **2** are isostructural, and the structure of **1** is described in detail here. The structure exhibits a 1-D heterometallic coordination polymer constructed by luminescent Ln building blocks and Ag ions. A thermal ellipsoid plot of **1** is shown in figure 1. In the asymmetric unit of **1**, there are one Eu(III), one Ag(I), two crystallographically identical pydc ligands, three coordinated waters, and 1.25 uncoordinated waters. Each pydc exhibits the same coordination mode with one carboxylate monodentate to one Eu(III), the other carboxylate bridging one Eu(III), and one Ag(I) (figure 2). The Eu(III) is surrounded by seven oxygens and two nitrogens in a slightly distorted tricapped trigonal prismatic coordination geometry. Four oxygens and two nitrogens are from two different pydc ligands, while the other three oxygens are from water. The Eu–O bond lengths and O–Eu–O angles, all of which are within the range of those observed for other Ln complexes [16], range from 2.417(6) to 2.523(5) Å and 66.28(17) to 150.57(19)°, respectively. Four coordination around

Table 1. Crystal data and structure refinement details of **1** and **2**.

	1	**2**
Empirical formula	$C_{14}H_{14.5}AgN_2O_{12.25}Eu$	$C_{14}H_{14.5}AgN_2O_{12.25}Tb$
Formula weight	666.61	673.57
Crystal system	Monoclinic	Monoclinic
Space group	*P2₁/c*	*P2₁/c*
Unit cell dimensions (Å, °)		
a	13.751(5)	13.751(5)
b	7.432(3)	7.432(3)
c	21.087(6)	21.087(6)
α	90.00	90.00
β	116.5791(17)	116.579(17)
γ	90.00	90.00
Volume ($Å^3$), *Z*	1927.3(12), 4	1927.3(12), 4
Calculated density ($mg\,cm^{-3}$)	2.297	2.321
Absorption coefficient (mm^{-1})	4.310	4.725
F(000)	1282	1290
Crystal size (mm^3)	0.20 × 0.18 × 0.15	0.20 × 0.18 × 0.15
θ range for data collection (°)	1.6–25.20	1.66–25.20
Limiting indices	$-16 \le h \le 15$; $-8 \le k \le 8$; $-17 \le l \le 25$	$-16 \le h \le 15$; $-8 \le k \le 8$; $-17 \le l \le 25$
Reflections collected/unique	9007/3435	9007/3435
Completeness to $\theta = 26.99$ (%)	99.0	99.0
Data/restraints/parameters	3435/300	3435/300
Goodness-of-fit on F^2	1.059	1.037
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0431$, $wR_2 = 0.0997$	$R_1 = 0.0434$, $wR_2 = 0.0986$
R indices (all data)	$R_1 = 0.0688$, $wR_2 = 0.1121$	$R_1 = 0.0692$, $wR_2 = 0.1111$

$R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$; $wR = [\Sigma w(F_o^2 - F_c^2)2/\Sigma w(F_o)2]^{1/2}$.

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

1			
Ag(1)–O(6)^i	2.246(11)	O(1)^i–Ag(1)–O(6)	161.4(4)
Ag(1)–O(1)	2.217(10)	O(2W)–Eu(1)–O(1)	135.33(19)
Eu(1)–O(3W)	2.524(5)	O(3)–Eu(1)–O(2W)	74.26(18)
Eu(1)–O(3)	2.417(6)	O(3)–Eu(1)–O(7)	150.57(19)
Eu(1)–O(2W)	2.435(5)	O(2W)–Eu(1)–O(7)	76.43(18)
Eu(1)–O(7)	2.438(6)	O(3)–Eu(1)–O(5)	76.04(19)
Eu(1)–O(5)	2.457(6)	O(7)–Eu(1)–O(5)	126.46(17)
Eu(1)–O(1)	2.476(5)	O(3)–Eu(1)–O(1)	126.17(18)
Eu(1)–N(2)	2.537(6)	O(3)–Eu(1)–N(2)	134.8(2)
Eu(1)–N(1)	2.539(6)	O(3)–Eu(1)–N(1)	63.83(19)
2			
Ag(1)–O(1)	2.223(10)	O(1)–Ag(1)–O(6)^i	161.8(3)
Ag(1)–O(6)^i	2.242(11)	O(3)–Tb(1)–O(2W)	74.19(19)
Tb(1)–O(2W)	2.433(6)	O(3)–Tb(1)–O(7)	150.6(2)
Tb(1)–O(3)	2.420(6)	O(1W)–Tb(1)–O(7)	76.6(2)
Tb(1)–O(7)	2.439(6)	O(3)–Tb(1)–O(5)	75.9(2)
Tb(1)–O(1)	2.472(6)	O(7)–Tb(1)–O(5)	126.43(19)
Tb(1)–O(3W)	2.519(6)	O(3)–Tb(1)–O(1)	126.29(19)
Tb(1)–N(2)	2.538(6)	O(3)–Tb(1)–N(2)	134.8(2)
Tb(1)–N(1)	2.539(6)	O(3)–Tb(1)–N(1)	63.9(2)

Symmetry codes: i = *x*, −1 + *y*, *z*.

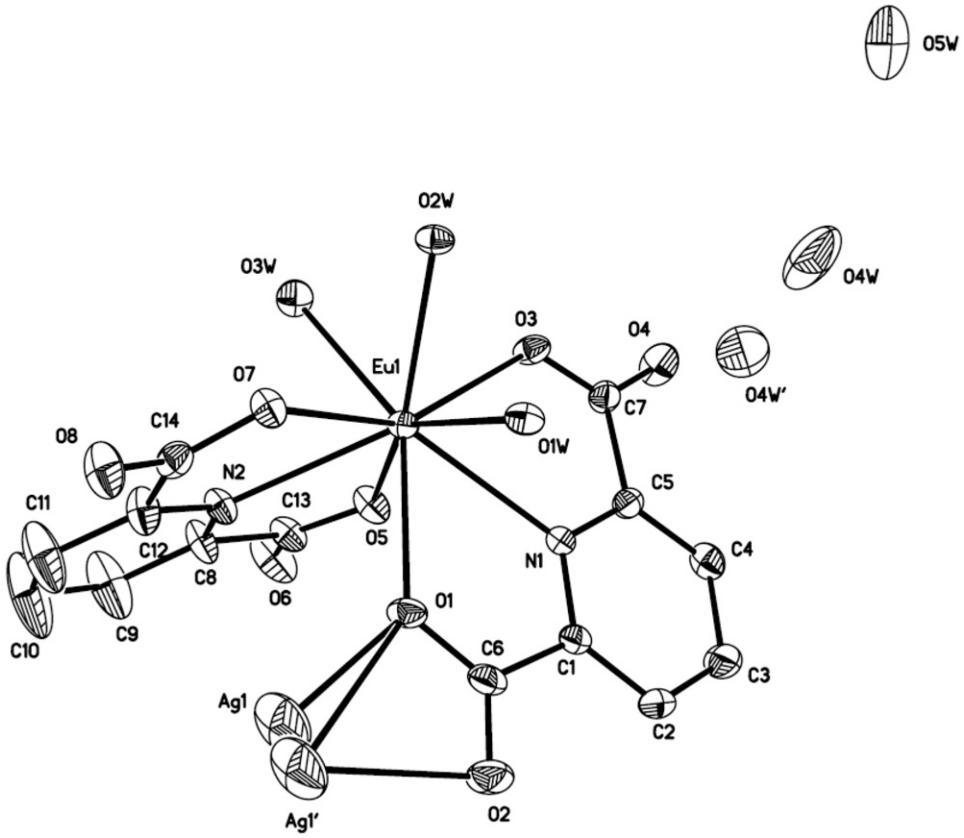

Figure 1. Thermal ellipsoid plot of the asymmetric unit of **1** (30% probability ellipsoids). All H atoms were omitted for clarity.

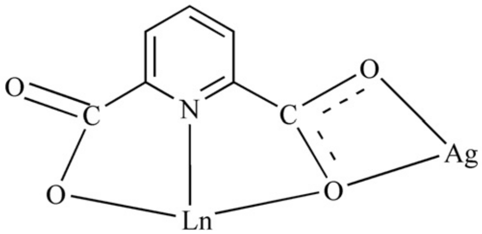

Figure 2. The coordination mode of pydc in **1**.

Ag(I) is achieved by sharing carboxylate oxygens from two $pydc^{2-}$ ligands of adjacent $[Eu(pydc)_2]^-$ units, resulting in a tetrahedral conformation. As expected, Ag–O bond lengths are in the range from 2.246(11) to 2.474(10) Å, which is in agreement with the value reported by Zhao *et al.* [17].

Two $pydc^{2-}$ ligands on Eu(III) with bridging carboxylates link two Ag ions in opposite directions, resulting in a linear chain (figure 3). The Eu–Ag distance is 4.319(3) Å along the chain. The chains are further linked through weak inter/intramolecular hydrogen bonds and $\pi \cdots \pi$ stacking interactions to give a 3-D

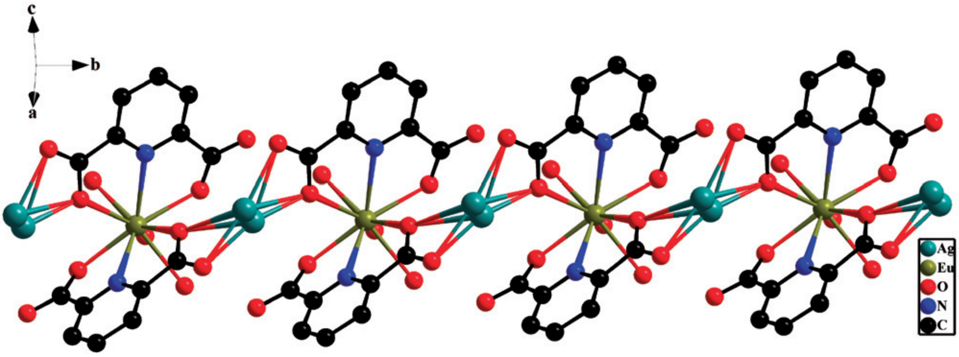

Figure 3. View of the 1-D Ln–pydc–Ag chain.

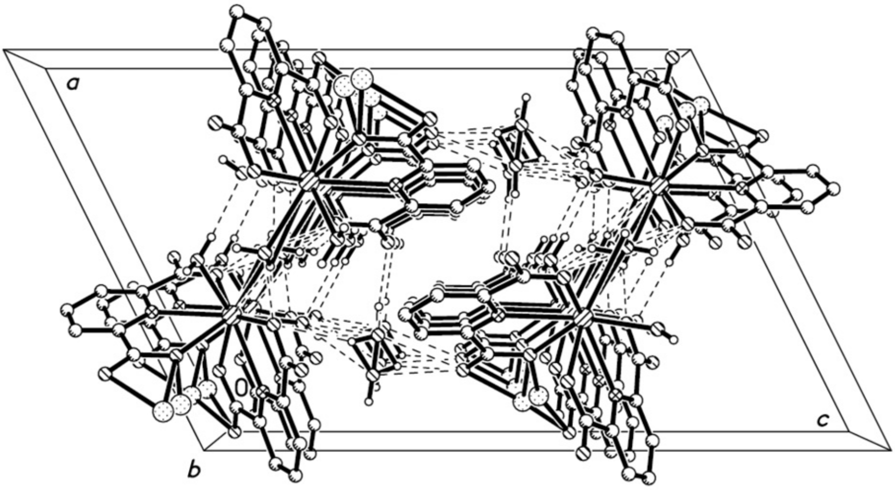

Figure 4. Supramolecular network in **1** through O–H · · · O hydrogen bonding interactions.

supramolecular structure (figure 4). As the crystal structures of **1** and **2** are isostructural, there is no significant difference in the M–L distances between **1** and **2**. For example, as shown in table 2, the Eu–O bond lengths in **1** range from 2.417(6) to 2.523(6) Å, very similar to Tb–O distances in **2** [2.420(6)–2.519(6) Å].

3.3. *Thermal and luminescent properties*

The TGA of **1** and **2** were performed in a N_2 atmosphere when the sample was heated to 800°C at 10°C min^{-1}. For **1**, the TGA trace (Supplementary material) showed a gradual weight-loss step of 10.1% (25–202°C) corresponding to uncoordinated and coordinated water (4.25 H_2O, Calcd 11.5%), followed by a plateau (202–266°C). Weight loss above 266°C corresponds to decomposition of the framework structure. The TGA curve of **2** showed that it has a similar thermal stability to **1**, further indicating their isostructural architectures.

The solid-state luminescence of **1** and **2** were investigated at room temperature under excitation wavelength of 395 nm for **1** and 270 nm for **2**. As shown in figure 5, emission

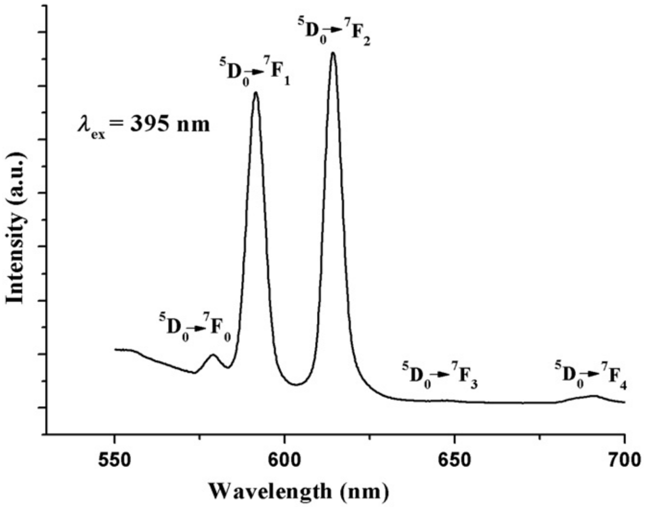

Figure 5. Solid-state emission spectrum of **1** at room temperature.

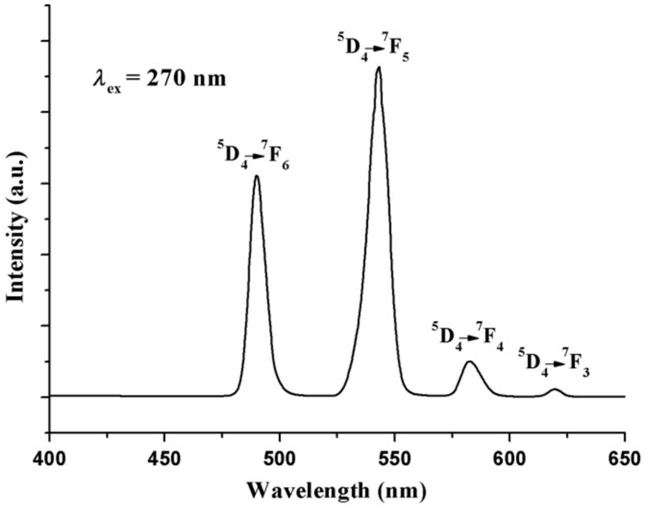

Figure 6. Solid-state emission spectrum of **2** at room temperature.

peaks of **1** at 579, 591, 614, 651, and 690 nm correspond to $^5D_0 \rightarrow ^7F_n$ ($n = 0 \rightarrow 4$) transitions of the Eu(III), indicating a moderately efficient ligand-to-metal (europium) charge transfer (LMCT) [18]. The emission band at 614 nm ($^5D_0 \rightarrow ^7F_2$) is the strongest emission, and the intensity increases as the site symmetry of Eu(III) decreases. The emission peak $^5D_0 \rightarrow ^7F_1$ at 591 nm is a magnetic dipole transition and its intensity should vary with the crystal field strength acting on Eu(III). The symmetry-forbidden weak emission peak $^5D_0 \rightarrow ^7F_0$ at 579 nm indicates that the Eu(III) ions are located on a low-symmetry site [19]. The intensity ratio I($^5D_0 \rightarrow ^7F_2$)/($^5D_0 \rightarrow ^7F_1$) is equal to *ca* 1.2, further confirming that Eu(III) ions have a low-symmetry coordination environment [20], consistent with the single-crystal X-ray analysis. As shown in figure 6, there are four main emission peaks in the emission spectrum of **2**, ascribed to the characteristic emissions of Tb(III) corresponding to electronic transitions from the emitting level $^5D_4$ to the ground multiplet ^7F_n ($n = 6 \rightarrow 3$) [19]. The most intense emission at 543 nm corresponds to $^5D_4 \rightarrow {}^7F_5$ transition. The second intense emission at 490 nm corresponds to $^5D_4 \rightarrow {}^7F_6$ transition. The bands at 582 and 619 nm correspond to $^5D_4 \rightarrow {}^7F_4$ and $^5D_4 \rightarrow {}^7F_3$ transitions of Tb(III), respectively.

4. Conclusion

Two new isostructural 4d–4f heterometallic coordination polymers have been synthesized by a simple hydrothermal reaction of $AgNO_3$, $Ln(NO_3)_3$, and pyridine-2,6-dicarboxylic acid. Both **1** and **2** feature the same 1-D heterometallic coordination frameworks, unusual among the reported heterometallic coordination polymers constructed from lanthanide, transition metals, and pydc ligands [21]. The complexes exhibit strong photoluminescence of Eu(III) for **1** and Tb(III) for **2** and may be used as luminescent materials. This synthetic idea provides new opportunities for preparing other low-dimensional 4d–4f heterometallic coordination polymers with particular properties.

Supplementary material

CCDC 725670 and 725671 contain the supplementary crystallographic data for this article. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

We thank the National Natural Science Foundation of China (No. 20803024) and Guangdong Natural Science Foundation (SN. 8151064101000094) for financial support.

References

[1] (a) M.J. Zaworotko. *Chem. Commun.*, 1 (2001); (b) M.A. Withersby, A.J. Blake, N.R. Champness, P. Hubberstey, W.S. Li, M. Schröder. *Angew. Chem. Int. Ed.*, **39**, 2327 (1997); (c) L. Yi, B. Din, B. Zhao, P. Cheng, D.Z. Liao, S.P. Yan, Z.H. Jiang. *Inorg. Chem.*, **43**, 33 (2004).

[2] M.A. Withersby, A.J. Blake, N.R. Champness, P.A. Cooke, P. Hubberstey, W.S. Li, M. Schröder. *Inorg. Chem.*, **38**, 2259 (1999).

[3] (a) D.M. Shin, I.S. Lee, Y.K. Chung, M.S. Lah. *Inorg. Chem.*, **42**, 5459 (2003); (b) C.D. Wu, C.Z. Lu, H.H. Zhuang, J.S. Huang. *J. Am. Chem. Soc.*, **124**, 3836 (2002).

[4] (a) H.Z. Kou, B.C. Zhou, S. Gao, R.J. Wang. *Angew. Chem. Int. Ed.*, **42**, 3288 (2003); (b) B. Penc, D. Kaczorowski, A. Szytula, A. Winiarski, A. Zarzycki. *Intermetallics*, **15**, 1489 (2007).

[5] (a) A. Szytula, Y. Tyvanchuk, Y. Kalychak, A. Winiarski, B. Penc, A. Zarzycki. *J. Alloys Compd.*, **442**, 279 (2007); (b) H.Z. Kou, Y.B. Jiang, A.L. Cui. *Cryst. Growth Des.*, **5**, 77 (2005).

[6] Y. Pei, P. Bergerat, O. Kahn. *J. Am. Chem. Soc.*, **116**, 3866 (1994).

[7] S. Singh, S.K. Dhar, P. Manfrinetti, A. Palenzona. *J. Magn. Mater.*, **250**, 190 (2002).

[8] (a) B. Zhao, X.Y. Chen, W.Z. Wang, P. Cheng, B. Ding. *Inorg. Chem. Commun.*, **8**, 178 (2005); (b) M.C. Yin, X.F. Lei, M. Li, L.J. Yuan, J. Sun. *J. Phys. Chem. Solids*, **67**, 1372 (2006); (c) B. Zhao, H.L. Gao, X.Y. Chen, P. Cheng, W. Shi, D.A. Liao, S.P. Yan, Z.H. Jiang. *Chem. Eur. J.*, **12**, 149 (2006).

[9] O. Margeat, P.G. Lacroix, J.P. Costes, B. Donnadieu, C. Lepetit, K.N. Akatani. *Inorg. Chem.*, **43**, 4743 (2004).

[10] (a) H. Deng, S. Chun, P. Florian, P.J. Grandinetti, S.G. Sore. *Inorg. Chem.*, **35**, 3891 (1996); (b) S.Y. Yang, L.S. Long, Y.B. Jiang, R.B. Huang, L.S. Zheng. *Chem. Mater.*, **14**, 3229 (2002); (c) Y.P. Ren, L.S. Long, B.W. Mao, Y.Z. Yuan, R.B. Huang, L.S. Zheng. *Angew. Chem. Int. Ed.*, **42**, 532 (2003).

[11] Y.B. Dong, M.D. Smith, H.C.Z. Loye. *Inorg. Chem.*, **39**, 1943 (2000).

[12] (a) J. Albertson. *Acta Chem. Scand.*, **24**, 1213 (1970); (b) J. Albertson. *Acta Chem. Scand.*, **26**, 985 (1972); (c) J. Albertson. *Acta Chem. Scand.*, **26**, 1005 (1972); (d) J. Albertson. *Acta Chem. Scand.*, **26**, 1023 (1972).

[13] (a) G. Swarnabala, M.V. Rajasekharan. *Inorg. Chem.*, **37**, 1483 (1998); (b) S. Sailaja, M.V. Rajasekharan. *Acta Crystallogr., Sect. E*, **57**, m341 (2001); (c) D.M.L. Goodgame, T.E. Müeller, D.J. Williams. *Polyhedron*, **11**, 1513 (1992).

[14] X.Q. Zhao, B. Zhao, Y. Ma, W. Shi, P. Cheng, Z.H. Jiang, D.Z. Liao, S.P. Yan. *Inorg. Chem.*, **46**, 5832 (2007).

[15] (a) Bruker. *APEXII Software (Version 6.3.1)*, Bruker AXS Inc., Madison, Wisconsin, USA (2004); (b) G.M. Sheldrick. *Acta Cryst.*, **A64**, 112 (2008).

[16] (a) B. Zhao, P. Cheng, Y. Dai, C. Cheng, D.Z. Liao, S.P. Yan, Z.H. Jiang, G.L. Wang. *Angew. Chem. Int. Ed.*, **42**, 934 (2003); (b) T.K. Prasad, S. Sailaja, M.V. Rajasekharan. *Polyhedron*, **24**, 1487 (2005).

[17] B. Zhao, L. Yi, P. Cheng, D.Z. Liao, S.P. Yan, Z.H. Jiang. *Inorg. Chem. Commun.*, **7**, 971 (2004).

[18] A. De Betterncount Dias, S. Viswanathan. *Chem. Commun.*, 1024 (2004).

[19] B. Zhao, X.Y. Chen, P. Cheng, D.Z. Liao, S.P. Yan, Z.H. Jiang. *J. Am. Chem. Soc.*, **126**, 15394 (2004).

[20] J.C.G. Bünzli. In *Lanthanide Probes in Life, Chemical and Earth Sciences, Theory and Practice*, J.C.G. Bünzli, G.R. Choppin (Eds), Chap. 7, pp. 219–290, Elsevier Scientific Publishers, Amsterdam, The Netherlands (1989).

[21] (a) J.L. Yi, Z.Y. Fu, S.J. Liao. *J. Coord. Chem.*, **62**, 2290 (2009); (b) X.F. Guo, M.L. Feng, Z.L. Xie, J.R. Li, X.Y. Huang. *Dalton Trans.*, 3101 (2008); (c) Y.K. He, J. Li, P. Zhang, X. Chen, Y. Ma, Z.B. Han. *J. Coord. Chem.*, **61**, 2876 (2008).