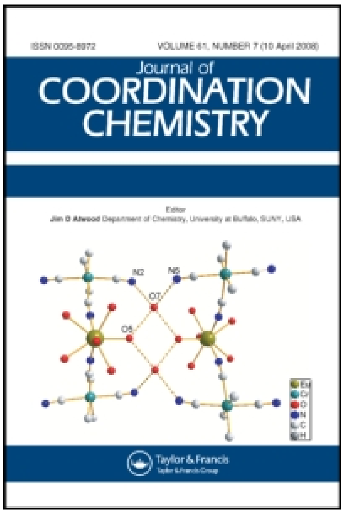
This article was downloaded by:
On: *23 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Coordination Chemistry

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

Syntheses and characterization of three lanthanide(III) complexes containing pyridine-3,5-dicarboxylic acid and oxalic acid ligands

Xiao-Ming Lin[a]; Xiu-Xia Zhou[a]; Hua-Cai Fang[a]; Rong-Hua Zeng[a]; Xin Xiao[a]; Yue-Peng Cai[a]
[a] Key Lab of Technology on Electrochemical Energy Storage and Power Generation in Guangdong Universities, School of Chemistry and Environment, South China Normal University, Guangzhou, China

To cite this Article Lin, Xiao-Ming , Zhou, Xiu-Xia , Fang, Hua-Cai , Zeng, Rong-Hua , Xiao, Xin and Cai, Yue-Peng(2009) 'Syntheses and characterization of three lanthanide(III) complexes containing pyridine-3,5-dicarboxylic acid and oxalic acid ligands', Journal of Coordination Chemistry, 62: 17, 2796 — 2803

To link to this Article: DOI: 10.1080/00958970902898036

URL: http://dx.doi.org/10.1080/00958970902898036

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Journal of Coordination Chemistry
Vol. 62, No. 17, 10 September 2009, 2796–2803

Syntheses and characterization of three lanthanide(III) complexes containing pyridine-3,5-dicarboxylic acid and oxalic acid ligands

XIAO-MING LIN, XIU-XIA ZHOU, HUA-CAI FANG, RONG-HUA ZENG, XIN XIAO and YUE-PENG CAI*

Key Lab of Technology on Electrochemical Energy Storage and Power Generation in Guangdong Universities, School of Chemistry and Environment, South China Normal University, Guangzhou, 510006, China

(*Received 10 October 2008; in final form 7 January 2009*)

Direct reaction of pyridine-3,5-dicarboxylic acid (H_2PDA) and oxalic acid (H_2ox) with $Ln(ClO_4)_3 \cdot nH_2O$ under hydrothermal conditions gave three 3-D coordination networks, $[Ln(PDA)(ox)_{0.5}(H_2O)_2] \cdot H_2O$ [Ln = La(**1**), Nd(**2**), and Eu(**3**)]. The complexes were characterized by elemental analysis (EA), X-ray single-crystal diffraction, infrared spectroscopy (IR), and thermogravimetric analysis (TGA). Single crystal X-ray diffractions shows that the compounds are isomorphous and have 3-D framework structures, in which pyridine-3, 5-dicarboxylates (PDA^{2-}) link lanthanides to give 2-D layers, which are further fabricated into a 3-D network *via bis*-bidentate oxalate bridging. Luminescence of **3** is investigated.

Keywords: Lanthanide compounds; Pyridine-3,5-dicarboxylic acid and oxalic acid; Hydrothermal synthesis and crystal structures; Luminescence

1. Introduction

Synthesis and characterization of rare-earth organic frameworks (REOF) is of interest in crystal engineering and supramolecular chemistry [1] because of their intrinsic aesthetic appeal and exploitable properties in catalysis, molecular adsorption, fluorescence, and magnetism [2]. In principle, rational design of polymeric structures with a wide variety of topologies can be achieved by careful selection of the metal and organic bridging ligands. Pyridinedicarboxylates as excellent building blocks with charge and multifunctional linking groups are well suited for construction of high-dimensionality networks [3–6]. However, REOF built from two different carboxylate bridging ligands have received less attention [7]. Here, three new Ln-based coordination complexes, ($[La(PDA)(ox)_{0.5}(H_2O)_2] \cdot H_2O$ (La = La, Nd, and Eu) (PDA^{2-} = pyridine-3, 5-dicarboxylate, ox^{2-} = oxalate), were synthesized under hydrothermal conditions and characterized by elemental analyses, IR, TGA, fluorescence, and single-crystal X-ray diffraction analyses.

---

*Corresponding author. Email: ypcai8@yahoo.com

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2009 Taylor & Francis
DOI: 10.1080/00958970902898036

2. Experimental

$[Ln(PDA)(ox)_{0.5}(H_2O)_2] \cdot H_2O$ [Ln = La(**1**), Nd(**2**), and Eu(**3**)] were prepared by a similar procedure. Hot aqueous solutions, one containing 1 mmol of pyrazine-3, 5-dicarboxylic acid, 2 mmol oxalic acid (Aldrich), and 1 mmol $Ln(ClO_4)_3 \cdot 6H_2O$, were mixed and refluxed with stirring for 1 h. After evaporation at room temperature, the deposited crystalline material was dissolved in warm methanol. Colorless (for **1** and **3**)/pink (for **2**) rectangular single crystals formed overnight. The dimensions of a single crystal selected for X-ray diffraction data collection are given in table 1.

Diffraction intensities for **1**, **2**, and **3** were collected at 298 K on a computer-controlled Bruker APEX II single-crystal diffractometer equipped with graphite monochromated Mo-Kα radiation (0.71073 Å) using the ω-scan technique. Lorentz polarization and absorption corrections were applied. The structures were solved by direct methods and refined with full-matrix least-squares using SHELXS-97 and SHELXL-97 [8]. Anisotropic thermal parameters were assigned to all non-hydrogen atoms. The organic hydrogen atoms were set in calculated positions and refined as riding atoms with a common fixed isotropic thermal parameter; hydrogens of water were located from difference maps and refined with isotropic temperature factors. Details of the crystal parameters, data collections and refinement for **1**–**3** are listed in table 1. Selected bond lengths and angles are listed in table 2. Further details are provided as "Supplementary material".

3. Discussion

Compounds **1**, **2**, and **3** are isomorphous; we choose **3** to represent the detailed structures. Single crystal X-ray diffractions show that **3** is a 3-D network. The Eu^{3+} centers (figure 1) are eight-coordinate in a distorted bicapped trigonal prism with four oxygens from four different PDA^{2-} ligands, two oxygens come from the bridging ox^{2-} and the remaining two sites water molecules. The Eu–O bond lengths are in the range 2.335(3)–2.502(3) Å (average 2.423(3) Å) (table 2), and the longest Eu–O distance is associated with one carboxylate oxygen of coordinated oxalate (2.502 Å). Oxalate is *bis*-bidentate chelated to two Eu^{III} ions with Eu···Eu separation of 6.399 Å. Each PDA^{2-} links four Eu centers by carboxylate with $\mu_2(\eta^1: \eta^1)$-O coordination (one oxygen binds to one Eu^{III} and each carboxylate coordinates to two Eu^{III} ions) (figure 1). The O–Eu–O bond angles range from 65.30(9) to 149.94(11)°.

Four connections between Eu^{3+} and PDA^{2-}, each Eu^{3+} connects four different PDA^{2-} ligands and each ligand bridges four Eu^{3+} ions, result in 2-D layers, as indicated in figure 2(a). 2-D layers are further linked to a 3-D REOF by bridging ox^{2-} with 1-D channels along *b*-axis direction (figure 2b), in which the guest water molecules are hydrogen bonded with uncoordinated pyridine nitrogens. The nearest face-to-face distance between two neighboring pyridine rings is 3.577 Å, indicating the existence of weak $\pi \cdots \pi$ stacking interactions [9], contributing to the stability of the structure [10]. Compounds **1** and **2** are isomorphous of **3**, and selected distances are listed in table 2. The structures of **1**, **2**, and **3** show the effect of lanthanide contraction: Ln–O bond lengths and Ln $\cdots$ Ln separations decrease along with the decrease of ionic radii from La(**1**), Nd(**2**), to Eu(**3**).

Table 1. Crystal data and structure refinement for **1**–**3**.*

Complexes	**1**	**2**	**3**
Empirical formula	$C_8H_9LaNO_9$	$C_8H_9NdNO_9$	$C_8H_9EuNO_9$
Formula weight	402.07	407.40	415.12
Temperature (K)	298(2)	298(2)	298(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
Unit cell dimensions (Å, °)			
a	7.7648(2)	7.7008(2)	7.6799(3)
b	9.9827(2)	9.9155(3)	9.8742(5)
c	15.1515(4)	14.9899(5)	14.8930(6)
β	98.5910(10)	98.4660(10)	98.364(2)
V (Å^3)	1161.27(5)	1132.12(6)	1117.37(8)
Z	4	4	4
D_{Calcd} (g cm^{-3})	2.300	2.390	2.468
μ (mm^{-1})	3.723	4.632	5.660
$F(000)$	772	784	796
θ range (°)	2.45–27.60	2.47–27.57	2.48–27.50
Measured reflections	7314	6615	6688
Unique reflections	2667 ($R_{int} = 0.0147$)	2602 ($R_{int} = 0.0186$)	2538 ($R_{int} = 0.0265$)
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Parameters refined	191	191	191
Goodness-of-fit on F^2	1.089	1.090	1.083
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0147$, $wR_2 = 0.0366$	$R_1 = 0.0193$, $wR_2 = 0.0512$	$R_1 = 0.0257$, $wR_2 = 0.0659$
R indices (all data)	$R_1 = 0.0158$, $wR_2 = 0.0370$	$R_1 = 0.0210$, $wR_2 = 0.0521$	$R_1 = 0.0279$, $wR_2 = 0.0669$
Largest difference peak and hole (e Å^{-3})	0.605 and 0.367	0.703 and −0.490	1.573 and −1.359

*$R = \Sigma||F_o| - |F_c|/S|F_o|$. $wR = [\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w(F_o^2)^2]^{1/2}$. $w = 1/[\sigma^2(F_o^2) + (0.0169P)^2 + 0.6984P]$ for **1**. $w = 1/[\sigma^2(F_o^2) + (0.0279P)^2 + 0.8632P]$ for **2**. $w = 1/[\sigma^2(F_o^2) + (0.0322P)^2 + 2.4734P]$ for **3**. $P = (F_o^2 + 2F_c^2)/3$.

Table 2. Selected bond distances (Å) for **1**–**3**.[a]

1			
La(1)–O(2)#1	2.4247(14)	La(1)–O(5)	2.5383(15)
La(1)–O(1)	2.4286(14)	La(1)–O(6)	2.5674(14)
La(1)–O(3)#2	2.4387(14)	La(1)–O(7)	2.5766(16)
La(1)–O(4)#3	2.4854(14)	La(1)–O(8)	2.5880(15)
2			
Nd(1)–O(4)#4	2.369(2)	Nd(1)–O(5)	2.490(2)
Nd(1)–O(3)#5	2.371(2)	Nd(1)–O(7)	2.520(2)
Nd(1)–O(2)#6	2.388(2)	Nd(1)–O(6)#8	2.521(2)
Nd(1)–O(1)#7	2.4255(19)	Nd(1)–O(8)	2.526(2)
3			
Eu(1)–O(3)#9	2.335(3)	Eu(1)–O(5)	2.464(3)
Eu(1)–O(4)#10	2.337(3)	Eu(1)–O(8)	2.493(3)
Eu(1)–O(1)	2.356(3)	Eu(1)–O(7)	2.499(3)
Eu(1)–O(2)#11	2.397(3)	Eu(1)–O(6)#12	2.502(3)

[a] Symmetry transformations used to generate equivalent atoms: #1: $-x, -y+1, -z+1$; #2: $-x+1/2, y-1/2, -z+1/2$; #3: $x, y-1, z$; #4: $-x, -y, -z+1$; #5: $x, y+1, z$; #6: $-x+1/2, y+1/2, -z+1/2$; #7: x, y, z; #8: $-x+1, -y+1, -z+1$; #9: $-x+1/2, y+1/2, -z+3/2$; #10: $x-1/2, -y+1/2, z+1/2$; #11: $-x+1/2, y-1/2, -z+3/2$; #12: $-x+1, -y+1, -z+2$.

Compound **1** was selected for the TGA to examine the thermal stability of the three compounds. The TGA curve was obtained in a N_2 atmosphere for a crystalline sample of **1** from 20 to 850°C (Supplementary material). The TG curve shows loss of two coordinated and one free water molecule between 120 and 383°C (found 13.62%; Calcd 13.43%), in agreement with the single crystal X-ray structures. Above 383°C, the weight loss is due to loss of all the organic components and the collapse of the framework.

Figure 3 shows the emission spectrum of **3** in solid state at room temperature. Excitation at 276 nm into the lowest energy ligand-centered absorption band results in luminescence characteristic of Eu^{3+}. The emission spectra of **3** show four characteristic emission bands under the excitation at 276, 593, 617, 652, and 702 nm, attributed to be the $^5D_0$–^7F_J ($J = 1$–4) transitions of Eu(III) [11–13]. The $^5D_0$–$^7F_2$ transition induced by the electric dipole moment is hypersensitive to the environment of the Eu^{3+}, while the $^5D_0$–$^7F_1$ transition is a magnetic dipole transition, which is fairly insensitive to the coordination environment of Eu^{3+}. In spectra of the Eu^{3+} complex, the relative intensity of $^5D_0$–$^7F_2$ is stronger than that of $^5D_0$–$^7F_1$, showing that Eu(III) does not lie in a centro-symmetric coordination site [14]. The room-temperature solid-state fluorescence lifetime of **3** was determined, 238 µs, shorter than that commonly observed for aromatic ligands in aqueous solutions suggesting one or more non-radiative pathways assist in deactivation of the excited state and shorten the observed lifetime. From X-ray structural data PDA^{2-} and ox^{2-} do not encapsulate the entire metal as only one/two monodentate/bidentate ligands surround each metal leaving two sites ligated with water. Earlier work has established that weak vibronic coupling between lanthanides and OH oscillators of coordinated water provides a facile path for radiationless deexcitation of the metal ion [15]. Thus, the lifetimes observed are expected to be shorter due to the coordination of water on the lanthanide. These strong emission bands indicate that the ligand-to-metal energy transfer is moderately efficient under the experimental conditions [16].

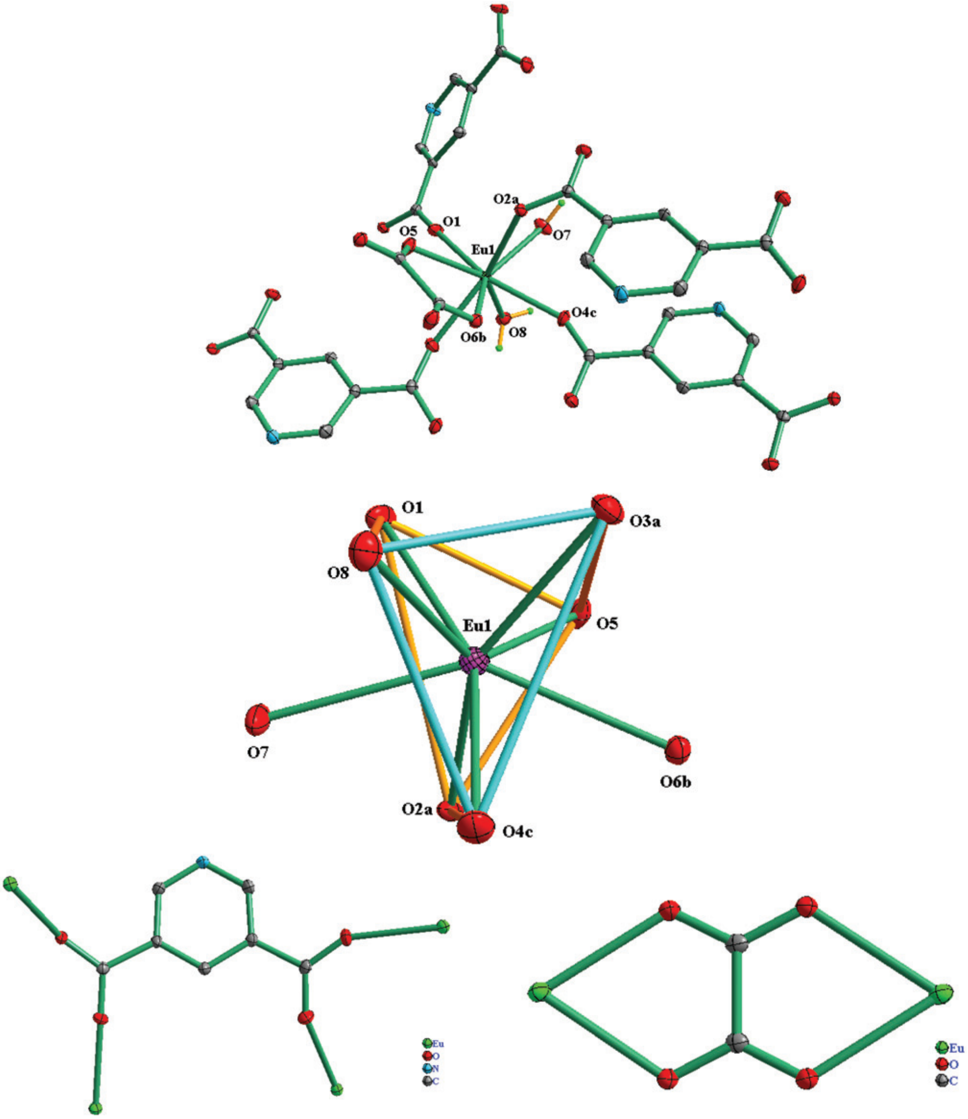


Figure 1. (Top) ORTEP drawing showing coordination environment of Eu^{3+} in **3**. Hydrogen atoms except for two coordinated water molecules are not shown for clarity; (middle) distorted dicapped trigonal prism geometry of Eu^{3+} in **3**; (bottom) coordination modes of PDA^{2-} and ox^{2-} anions in **3**. Symmetry code a: $0.5-x$, $-0.5+y$, $1.5-z$; b: $1-x$, $1-y$, $2-z$; *c*: $-0.5+x$, $0.5-y$, $0.5+z$.

To further understand the observed fluorescence, MO calculations are employed on **3**. The lowest unoccupied (LUMO) and the highest occupied (HOMO) frontier orbital of the investigated compound are shown in ‘‘Supplementary material’’. The HOMO in **3** is located on oxalate and PDA^{2-}, whereas the LUMO is largely on Eu^{3+}. Hence, their emission bands can be assigned to ligand-to-metal charge transfer (LMCT) [17, 18], consistent with the experimental result.

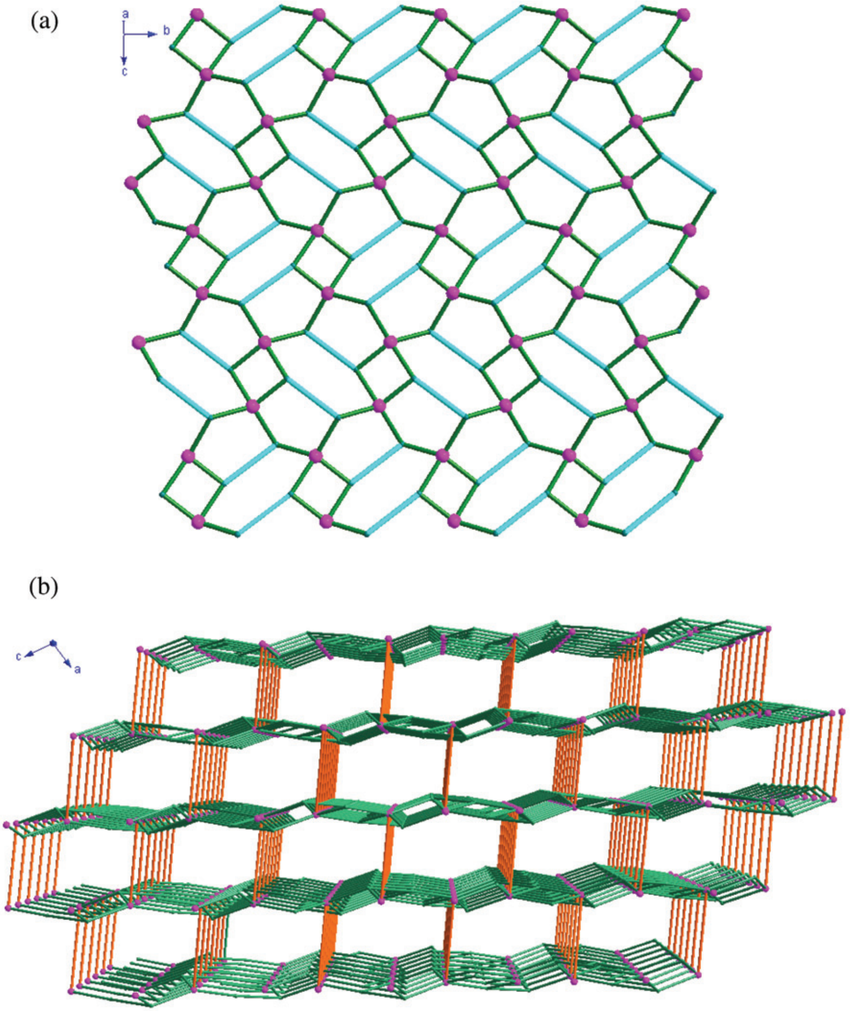


Figure 2. (a) 2-D layer linked by Eu^{3+} (purple) and PDA^{2-} (blue + green) ions viewed in *bc* plane; (b) 3-D rare-earth organic framework (REOF) with 1-D channel along *b*-axis direction constructed by ox^{2-} (yellow) anions bridging 2-D layers (green + purple).

In summary, three new 3-D Ln-based complexes containing PDA^{2-} and ox^{2-} have been synthesized and characterized. X-ray crystallography revealed the three organic lanthanide polymers are isomorphous with 3-D framework structures containing 1-D channels. Furthermore, compound **3** exhibits strong lanthanide-centered luminescence, showing energy transfer from the H_2PDA and H_2ox ligands to Eu^{3+} is effective.

Supplementary material

Observed and calculated structure factors and anisotropic thermal parameters can be obtained from the authors on request. Detailed data on the structure reported in

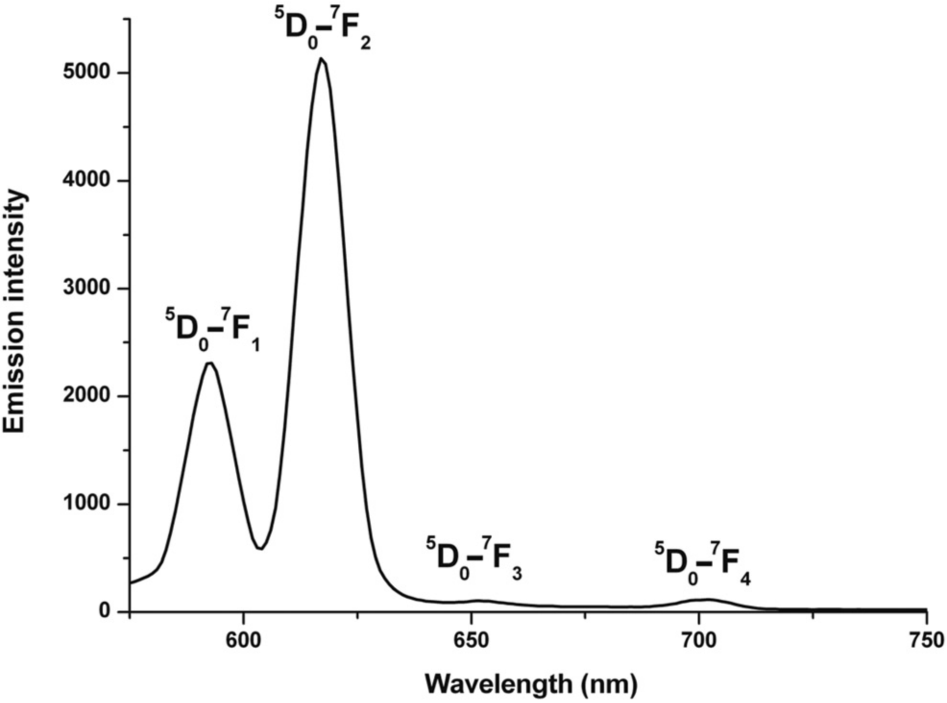


Figure 3. Emission spectrum of **3** in solid state at room temperature (excited at 276 nm).

this article have been deposited with the Cambridge Crystallographic Data Centre under code numbers CCDC 688455, 688456, and 688457 for **1**, **2**, and **3**, respectively.

Acknowledgments

The authors are grateful for financial aid from the National Natural Science Foundation of P.R. China (Grant No. 20772037), Science and Technology Planning Project of Guangdong Province (Grant No. 2006A10902002), and the N.S.F. of Guangdong Province (Grant No. 06025033).

References

[1] F. Schuth. *Annu. Rev. Mater. Res.*, **35**, 209 (2005).
[2] B. Moulton, M.J. Zaworotko. *Chem. Rev.*, **101**, 1629 (2001).
[3] D. Min, S.S. Yong, J.H. Lee, M. Suh, S.W. Lee. *Inorg. Chem. Commun.*, **4**, 297 (2001).
[4] Y.C. Liang, R. Cao, W.P. Su, M.C. Hong, W.J. Zhang. *Angew. Chem., Int. Ed.*, **39**, 3304 (2000).
[5] S.K. Ghosh, P.K. Bharadeaj. *Inorg. Chem.*, **42**, 8250 (2003).
[6] J.F. Eubank, R.D. Walsh, P. Poddar, H. Srikanth, R.W. Larsen, M. Eddaoudi. *Cryst. Growth Des.*, **5**, 1453 (2006).

[7] D. Min, S.W. Lee. *Inorg. Chem. Commun.*, **5**, 978 (2002).

[8] G.M. Sheldrick. *SHELXL-97, Program for the Refinement of Crystal Structure*, University of Göttingen, Germany (1997).

[9] S. Sain, T.K. Maji, G. Mostafa. *Inorg. Chim. Acta*, **351**, 12 (2003).

[10] Y.-L. Shen, J.-G. Mao. *Inorg. Chem.*, **44**, 5328 (2005).

[11] V. Patroniak, P.N.W. Baxter, J.-M. Lehn, Z. Hnatejko, M. Kubicki. *Eur. J. Inorg. Chem.*, 2379 (2004).

[12] C. Tedeschi, J. Azéma, H. Gornitzka, P. Tisnes, C. Picard. *Dalton Trans.*, 1738 (2003).

[13] K.A. Thiakou, V. Bekiari, C.P. Raptopoulou, V. Psycharis, P. Lianos, S.P. Perlepes. *Polyhedron*, **25**, 2869 (2006).

[14] Y.B. Wang, X.J. Zheng, W.J. Zhang, L.P. Jin. *Eur. J. Inorg. Chem.*, 1355 (2003).

[15] M. Latva. *J. Lumin.*, **75**, 149 (1997).

[16] A.B. Dias, S. Viswanathan. *Chem. Commun.*, **4**, 1024 (2004).

[17] B. Xiao, H.-W. Hou, Y.-T. Fan, M.-S. Tang. *Inorg. Chem. Commun.*, **10**, 376 (2007).

[18] X.-M. Lin, H.-C. Fang, Z.-Y. Zhou, L. Chen, J.-W. Zhao, Z.-S. Zhu, Y.-P. Cai. Cryst. Eng. Comm., DOI: 10.1039/B819800D (2009).