

两个基于 2,2'-联吡啶-3,3'-二羧酸的稀土配合物的晶体结构和荧光性质

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摘要: 采用水热法合成了 2 个具有二维结构的吡啶羧酸类稀土配位聚合物 $\{[\text{Ln}_2(\text{bpdc})_3(\text{H}_2\text{O})_2] \cdot 5\text{H}_2\text{O}\}_n$, ($\text{Ln}=\text{Nd}(\mathbf{1}), \text{Eu}(\mathbf{2})$; bpdc=2,2'-Bipyridyl-3,3'-dicarboxylic acid)。单晶衍射分析显示 **1**、**2** 结构相似, 均属于单斜晶系, $P2_1/c$ 空间群。**1**、**2** 的晶胞参数分别为 $a=1.241\ 00(19)\ \text{nm}$, $b=0.748\ 35(59)\ \text{nm}$, $c=2.060\ 50(20)\ \text{nm}$, $\beta=94.84(1)^\circ$; $a=1.241\ 00(19)\ \text{nm}$, $b=0.743\ 01(20)\ \text{nm}$, $c=2.052\ 50(30)\ \text{nm}$, $\beta=94.95(2)^\circ$ 。配合物是由之字形一维链构成的二维网络结构, 其拓扑符号为 $\{3^9; 4^8; 5\}$ 。热重测试结果表明 **1**、**2** 热稳定性较好。配合物 **2** 显示出很好的荧光性能。

关键词: 稀土; 2,2'-联吡啶-3,3'-二羧酸; 晶体结构; 荧光性能

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Synthesis, Structure, Properties of Two Rare Earth Complexes Based on 2,2'-Bipyridine-3,3'-dicarboxylic Acid

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Abstract: Two rare earth coordination polymers $\{[\text{Ln}_2(\text{bpdc})_3(\text{H}_2\text{O})_2] \cdot 5\text{H}_2\text{O}\}_n$, ($\text{Ln}=\text{Nd}(\mathbf{1}), \text{Eu}(\mathbf{2})$; bpdc=2,2'-Bipyridyl-3,3'-dicarboxylic acid) were hydrothermally synthesized. Single-crystal X-ray diffraction shows that **1** and **2** are isomorphic and in the monoclinic system with $P2_1/c$ group. Crystal unit parameters are $a=1.241\ 00(19)\ \text{nm}$, $b=0.748\ 35(59)\ \text{nm}$, $c=2.060\ 50(20)\ \text{nm}$, $\beta=94.84(1)^\circ$ and $a=1.241\ 00(19)\ \text{nm}$, $b=0.743\ 01(20)\ \text{nm}$, $c=2.052\ 50(30)\ \text{nm}$, $\beta=94.95(2)^\circ$ respectively. In addition, the complexes afforded a two-dimensional (2D) structure based on the zigzag chains (1D) linked by bpdc ligands and appear 8-coordinated single network structure with topology symbol $\{3^9; 4^8; 5\}$ as well. Interestingly, pentameric water rings were founded between lattice water molecules in **1** and **2**. Thermo-gravimetric analyses of **1** and **2** display considerable thermal stability. The complex **2** displays good fluorescence property. CCDC: 925994, **1**; 925995, **2**.

Key words: rare earth; 2,2'-bipyridyl-3,3'-dicarboxylic acid; crystal structure; fluorescence property

0 Introduction

The design and synthesis of metal-organic coordination polymers (MOFs) have attracted much attention in recent years for their potential as a new

class of solid materials applied in magnetism^[1-4], luminescence^[5-7], spectroscopic^[8-11], gas adsorption^[12], and catalysis^[13-14], and so on. These MOFs can be obtained from relatively simple subunits, where the metal ions with plastic coordination geometry and

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organic ligands with certain features are crucial to the self-assembly processes. Compared with the predicted coordination geometry of transition metals, lanthanide ions have high coordination numbers and flexible coordination sphere, which play a crucial role in controlling the overall frameworks of lanthanide-based coordination polymers.

The 2,2'-Bipyridyl-3,3'-dicarboxylate (H_2bpdc) is a potential bridging ligand for constructions of MOFs. Precisely because of its diversified coordination modes and flexible conformation, a few transition metal coordination polymers based on H_2bpdc have been reported recently^[15-19].

In fact, according to the hard-soft acid base theory, H_2bpdc with both 2,2'-bipyridyl and dicarboxylate functional groups displays higher reactivity to Ln^{III} ions. In addition, Ln^{III} ions which have larger radii and higher coordination numbers can provide opportunity for the construction of fascinating topologies as well as crystal packing motifs. Combining the merits of lanthanide ions together with H_2bpdc , a few lanthanide coordination polymers bridged by $bpdc$ have been studied so far^[20-24]. However, there was no an article specifically researching the syntheses, structures and properties of those compound. Herein, we report two lanthanide coordination polymers assembled by Nd, Eu and $bpdc$: $[Ln_2(bpdc)_3(H_2O)_2] \cdot 5H_2O$, ($Ln = Nd$ (**1**), Eu (**2**)). In addition, we systematically described the syntheses, structures, XRD, and the thermal stabilities in details, and also the luminescent property of **2** was discussed.

1 Experimental

1.1 Materials and measurements

H_2bpdc was synthesized by literature method^[25]. All other materials and reagents were of analytical grade and used without further purification. Ultra-pure water was used for all solutions preparation. Thermogravimetric analyses were performed on a TGAQ50 instrument with a heating rate of $10\text{ }^\circ\text{C} \cdot \text{min}^{-1}$ in air atmosphere. IR spectra were recorded with MAGNA-IR 750 (Nicolet) spectrophotometer with KBr pellet in the range of $400\sim 4\,000\text{ cm}^{-1}$. Powder X-ray diffraction

(XRD) measurements were performed on a Rigaku XRD-6000 diffractometer, using Cu $K\alpha$ radiation ($\lambda = 0.154\,18\text{ nm}$, Ni-filter) at 40 kV, 30 mA. Fluorescence spectra were measured with Japan's Hitachi F-4500 FL fluorescence spectrophotometer.

1.2 Synthesis of complexes

1.2.1 $[Nd_2(bpdc)_3(H_2O)_2] \cdot 5H_2O$ (**1**)

0.1465 g H_2bpdc was dissolved in 10 mL H_2O by adjusting pH to 3.2 by using $1\text{ mol} \cdot \text{L}^{-1}$ NaOH. To this solution, Nd_2O_3 (0.0673 g) was added. The mixture was transferred to a Teflon bag, sealed and heated in an oven at $160\text{ }^\circ\text{C}$ for 96 h. Then cooled to room temperature at the rate of $2\text{ }^\circ\text{C} \cdot \text{h}^{-1}$. The Lavender tubular crystal of **1** was filtered (yield 68.2%, based on Nd). IR spectrum (KBr, cm^{-1}): 3 413(m), 1 614(s), 1 592 (s), 1 558 (s), 1 446(m), 1 381(s), 1 254(m), 1 090(m), 769(m).

1.2.2 $[Eu_2(bpdc)_3(H_2O)_2] \cdot 5H_2O$ (**2**)

Complex **2** was prepared using a similar method from a mixture of Eu_2O_3 (0.070 4 g), H_2bpdc (0.146 5 g). The pH of the resulting mixture was adjusted with $1\text{ mol} \cdot \text{L}^{-1}$ NaOH to 3.2. The reaction mixtures were heated in an oven at $160\text{ }^\circ\text{C}$ for 96 h. Then cooled to room temperature at the rate of $2\text{ }^\circ\text{C} \cdot \text{h}^{-1}$. The colorless transparent sheet crystals were filtered (yield 70.1%, based on Eu). IR spectrum (KBr, cm^{-1}): 3 436(m), 1 610 (m), 1 592 (s), 1 556 (s), 1 444 (m), 1 387(s), 1 284(m), 1 090(m), 771(m).

1.3 Crystal structure determination

Single crystals of complexes **1**, **2** were taken directly from their mother liquor and immediately mounted on a glass fiber, respectively. The measurement was performed on a Bruker SMART CCD diffractometer at $150(2)\text{ K}$ with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.071\,073\text{ nm}$). The structures were solved by direct methods and refined by full-matrix least squares on F^2 using the SHELXL-97 software. The crystal data and structure refinements are summarized in Table 1. Selected bond distances and angles for complexes **1**, **2** are listed in Table 2.

CCDC: 925994, **1**; 925995, **2**.

Table 1 Crystal data and structure refinements for compounds **1**, **2**

	1	2
Empirical formula	C ₁₈ H ₁₆ NdN ₃ O _{9.5}	C ₁₈ H ₁₆ EuN ₃ O _{9.5}
Formula weight	570.58	578.3
Temperature / K	293(2)	293(2)
Wavelength / nm	0.071 073	0.071 073
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2/ <i>c</i>	<i>P</i> 2/ <i>c</i>
<i>a</i> / nm	1.241 22(4)	1.241 00(19)
<i>b</i> / nm	0.748 35(6)	0.743 01(2)
<i>c</i> / nm	2.060 6(2)	2.052 5(3)
β / (°)	94.844(7)	94.951(19)
<i>V</i> / nm ³	1.907 2(3)	1.885 5(4)
<i>Z</i>	4	4
<i>D_c</i> / (g·cm ⁻³)	1.987	2.037
<i>F</i> (000)	1 124	1 136
Reflns collected / unique	8 023/3 738	8 458/3 695
Goodness-of-fit on <i>F</i> ²	1.150	1.085
<i>R_{int}</i>	0.024 9	0.026 7
<i>R</i> ₁ (<i>wR</i> ₂)(<i>I</i> >2σ(<i>I</i>))	0.033 8(0.073 7)	0.027 6(0.053 1)
<i>R</i> ₁ (<i>wR</i> ₂) (all data)	0.038 4(0.075 8)	0.033 4(0.055 4)
Largest diff. peak and hole / (e·nm ⁻³)	679 and -1 083	475 and -703

Table 2 Selected bond lengths (nm) for **1** and **2**

Compound 1					
Nd(1)-O(3)	0.253 4(3)	O(2)-Nd(1) ⁱ	0.240 6(3)	Nd(1)-O(3) ⁱⁱ	0.260 6(3)
O(3)-Nd(1) ⁱⁱ	0.260 6(3)	Nd(1)-O(4) ⁱⁱ	0.252 6(3)	O(4)-Nd(1) ⁱⁱ	0.252 6(3)
Nd(1)-O(5)	0.251 4(3)	O(6)-Nd(1) ⁱ	0.240 5(3)	Nd(1)-O(6)	0.272 1(3)
Nd(1)-C(12) ⁱⁱ	0.294 0(4)	Nd(1)-O(6) ⁱ	0.240 5(3)	Nd(1)-O(7)	0.252 4(3)
Nd(1)-O(1)	0.241 9(3)				
Compound 2					
Eu(1)-O(5)	0.246 2(2)	O(4)-Eu(1) ⁱ	0.248 1(2)	Eu(1)-C(13)	0.296 2(3)
Eu(1)-O(1) ⁱⁱ	0.257 5(2)	Eu(1)-O(6)	0.271 4(2)	Eu(1)-O(2) ⁱⁱ	0.236 6(2)
Eu(1)-O(6) ⁱ	0.235 5(2)	O(2)-Eu(1) ⁱⁱ	0.236 6(2)	Eu(1)-O(3)	0.249 9(2)
O(6)-Eu(1) ⁱ	0.235 5(2)	Eu(1)-O(4) ⁱ	0.248 1(2)	Eu(1)-O(1)	0.237 0(3)
Eu(1)-O(7)	0.248 1(2)				

Symmetry code: ⁱ 1-*x*, 2-*y*, 1-*z*; ⁱⁱ 1-*x*, 3-*y*, 1-*z*.

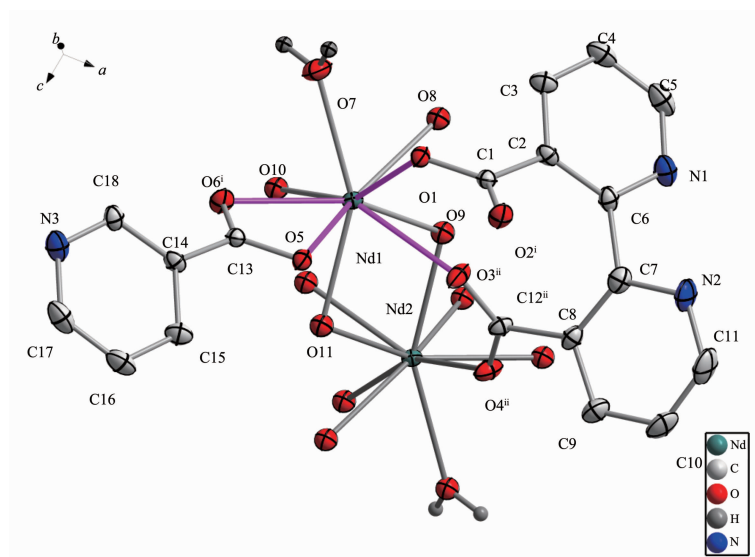
2 Results and discussion

2.1 Crystal structure of complexes

Single crystal X-ray diffraction clarifies that both of complexes **1** and **2** have C₁₈H₁₆LnN₃O_{9.5} as formulas in monoclinic system, *P*2/*c* group, So the structure of

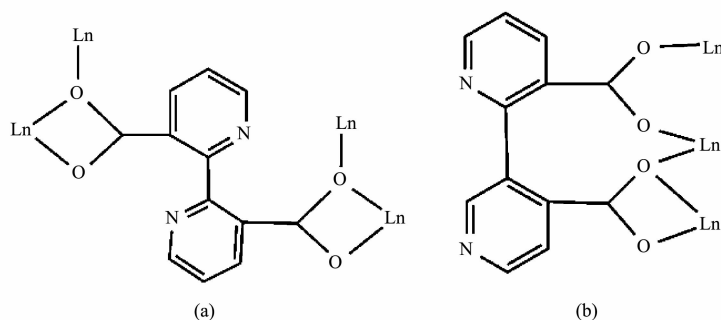
complex **1** is described typically. As shown in Fig.1, the structure unit of **1** consists of [Nd(bpdc)_{1.5}(H₂O)] · 3H₂O as the building block.

The bpdc ligands display two types of coordination modes as shown in Scheme 1: (a) Two carboxylate groups adopt identical chelating-bridging



Symmetry code: ⁱ1-x, 2-y, 1-z; ⁱⁱ1-x, 3-y, 1-z; 50% probability ellipsoids

Fig.1 Structure unit of $[\text{Nd}_2(\text{bpdc})_3(\text{H}_2\text{O})_2] \cdot 5\text{H}_2\text{O}$



Scheme 1 Two coordination modes of bpdc in **1** and **2**

tridentate mode linking four Nd^{III} ions in *anti*-bpdc ligand. (b) The bpdc linked three Nd^{III} ions by bridging bidentate and chelating-bridging tridentate mode in *syn*-conformation. Each Nd^{III} ion is coordinated by nine oxygen atoms and exhibits hendecahedron coordination geometry, with oxygen atoms $\text{O}2^{\text{i}}$, $\text{O}1$, $\text{O}4^{\text{ii}}$ from carboxylate groups of *anti*-bpdc ligands and the other oxygen atoms $\text{O}3$, $\text{O}5$, $\text{O}6^{\text{i}}$ from carboxylate groups of *syn*-bpdc ligands, while $\text{O}7$ is from a coordinated water molecule. The mean Nd-O bond distance is 0.223 7 nm and the O-Nd-O bond angles range from 49.52° to 156.53° in the compound.

Complex **1** is consisted of a 2D network structure based on the zigzag chains as shown in Fig.2 (a). Nd^{III} ions are linked by *syn*-bpdc ligands forming a 1D infinite extension zigzag chain, in which the mean

distance of adjacent $\text{Nd}^{\text{III}}\text{-Nd}^{\text{III}}$ is 0.703 9 nm and the two pyridyl rings of *syn*-bpdc are distorted with dihedral angle of 56.821° . The two adjacent zigzag chains were linked by *anti*-bpdc ligands via Nd^{III} ions forming a 2D plane, in which the shortest distance of $\text{Nd}^{\text{III}}\text{-Nd}^{\text{III}}$ between adjacent zigzag chains is 0.925 6 nm and the two pyridyl rings of *anti*-bpdc are also distorted with dihedral angle of 40.810° . It is noteworthy that with the arraying form of $\cdots\text{ABAB}\cdots$, and the two-dimensional planar structure appears as 8-coordinated net single network structure with the topology symbol is $\{3^9;4^{18};5\}$ as shown in Fig.2(b). In the two-dimensional structure of the compound, the hydrogen bonds were found among ligand water ($\text{O}7$), N-atom on the ligand pyridine ($\text{N}1$, $\text{N}2$), and crystallization H_2O . The distance of $\text{O}9\cdots\text{N}2$, $\text{O}8\cdots$

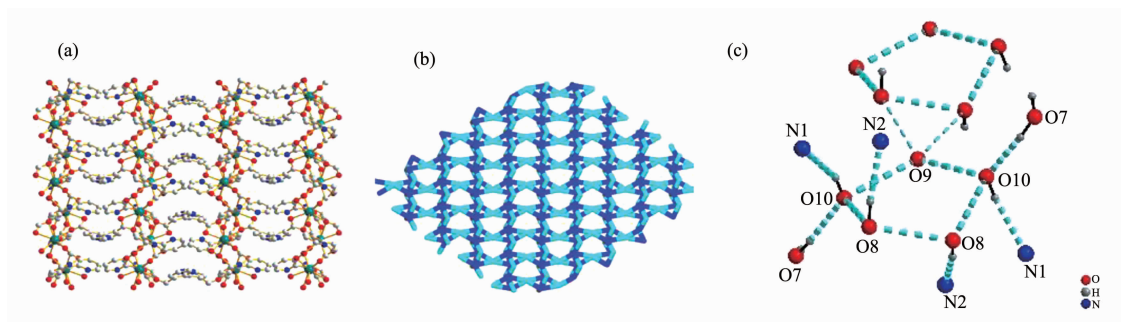


Fig.2 (a) 2D network structure based on zigzag chains in **1** at bc surface; (b) Topology structure of compound **1**; (c) A pentameric water ring in **1**

O9, O8...N1, O7...O8 are 0.279 2, 0.290 9, 0.284 2, 0.281 8 nm respectively. Interestingly, a pentameric water ring formed with coordinated water molecules (two O8 atoms, a O9 atom and two O10 atoms) by hydrogen bond has been found at the a-axis direction, as seen in Fig.2 (c). A motive H atom exists between two O atoms. The distance of hydrogen bonds are 0.287 4 nm (O9...H...O10), 0.290 9 nm (O10...H...O8), 0.275 2 nm (O8...H...O8) respectively. There is a symmetrical axis across O9 direction. Hydrogen bonds also exist between O10 (O8) atom and N1(N2) atoms on pyridine outside the pentameric ring. The distance of O10...H...N1 bond is 0.284 3 nm.

2.2 XRD

The powder XRD patterns of complexes **1** and **2** are essentially in agreement with these simulated from X-ray single-crystal data, which indicate the homogeneous phases of the final products. No other peaks can be found in the pattern, revealing that there is no impurity in the products. This indicates the

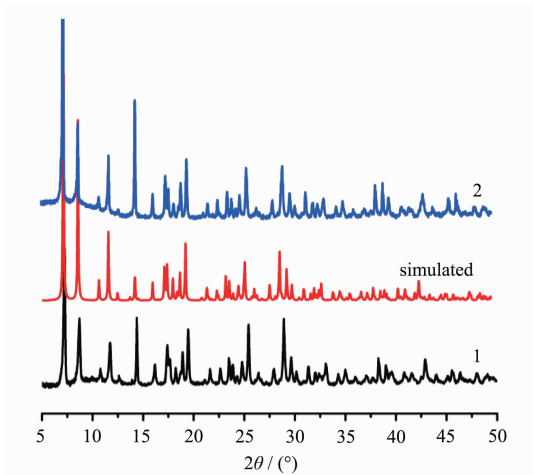


Fig.3 XRD patterns of complexes **1**, **2**

homogeneous phases of the final product as shown in Fig.3.

2.3 Thermal stability

The TGA curve of complexes **1** and **2** are shown in Fig.4. The weight loss process of compounds can be divided into three steps. Complex **1** loses of 7.23% in weight from 35 to 93 °C corresponding to loss of five lattice water molecules (Calcd. 7.90%). The experimental data have big error comparing with theoretical data due to the easily loss of lattice water in the crystal. The second step from 93 to 333 °C with weight loss of 3.21% corresponding to loss of two coordinated water molecules (Calcd. 3.21%). The last step from 333 to 733 °C with weight loss of 64.54% corresponding to loss of three bpdc ligands (Calcd. 63.70%). The complex **2** loses of 6.86% in weight corresponding to loss of five lattice water molecules (Calcd. 6.86%) from 35 to 93 °C, and the second step from 93 to 390 °C with weight loss of 2.95% corresponding to loss of two coordinated water molecules (Calcd. 3.11%), and the last step from 390 to 705 °C with weight to loss of 59.59% corresponding

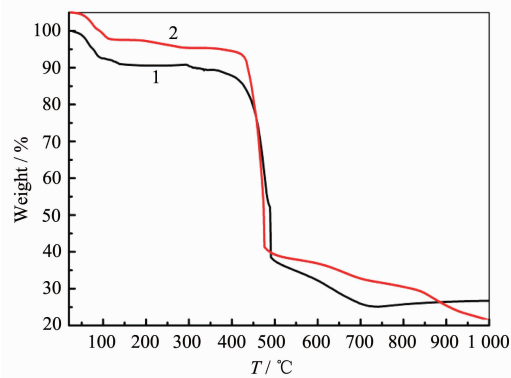


Fig.4 TG curves of the complexes **1**, **2**

to loss of three bpdc ligands (Calcd. 62.83%). These results are consistent with the given formulas of compound **1** and **2**.

2.4 Photoluminescence property

Owing to the excellent luminescent properties of Eu^{III} ions, the luminescence of **2** was studied. The emission spectrum of **2** (Fig.5) at room temperature upon excitation at 394 nm exhibits red luminescence and shows the characteristic transition of $^5D_0 \rightarrow ^7F_J$ ($J=0\sim4$) of Eu^{III} ions, which indicate the effective transfer of energy from ligand to Eu^{III} ions. The transition $^5D_0 \rightarrow ^7F_0$ at 580 nm displays that Eu^{III} ions in **2** possess the noncentrosymmetric coordination environment^[26]. It is known that the $^5D_0 \rightarrow ^7F_1$ transition is a magnetic dipole transition and the $^5D_0 \rightarrow ^7F_2$ transition is an electric dipole transition. The intensity ratio $I(^5D_0 \rightarrow ^7F_2)/I(^5D_0 \rightarrow ^7F_1)$ is equal to 1.1, which further proves that Eu^{III} ions in **2** occupy sites with low symmetry and without an inversion center. The red emission of the $^5D_0 \rightarrow ^7F_2$ transition is the most intense, indicating that the bpdc ligands are suitable for the sensitization of red luminescence for the Eu^{III} ion^[27].

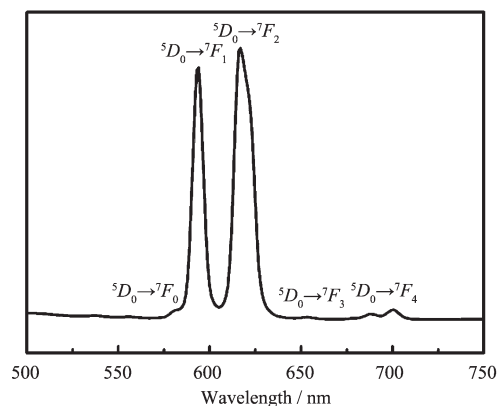


Fig.5 Solid-state photoluminescence spectrum of complex **2**

3 Conclusions

Two binary lanthanide coordination polymers with H_2bpdc were self-assembled by hydrothermal method. The bpdc ligands adopt two types of coordination mode, connecting Ln^{3+} ions to form similar 2D network structure with symmetrical zigzag chains in mirror images, and the compounds appear 8-coordinated net single network structure with topology symbol $\{3^9;4^18;5\}$. The thermal stability of **1** and **2**

were investigated. Complexes **2** reveals intense luminescence property.

References:

- [1] Strzelecki A R, Timinski P A, Helsel B A, et al. *J. Am. Chem. Soc.*, **1992**,**114**:3159-3160
- [2] Stefania T, Marilena F, Fanica C. *Inorg. Chem.*, **2011**,**50**(19): 9678-9687
- [3] Zhuang G L, Chen W L, Zheng J, et al. *Solid. State. Chem.*, **2012**,**192**:284-288
- [4] Wu M F, Wang M S, Guo S P, et al. *Cryst. Growth Des.*, **2011**,**11**:372-381
- [5] Yin M, Sun J. *J. Alloys Compd.*, **2004**,**381**:50-57
- [6] Rybak J C, Meyer L V, Wagenhofer J, et al. *Inorg. Chem.*, **2012**,**51**:13204-13213
- [7] Ramya A R, Sharma D, Natarajan S, et al. *Inorg. Chem.*, **2012**,**51**:8818-8826
- [8] Moynihan S, Van Deun R, Binnemans K, et al. *Opt. Mater.*, **2007**,**29**:1821-1830
- [9] Hou H W, Wei Y L, Song Y L, et al. *Inorg. Chem.*, **2004**,**43**: 1323-1327
- [10] HUANG De-Qian(黄德乾), ZHANG Hong(张宏), SHENG Liang-Quan(盛良全), et al. *Chinese J. Inorg. Chem.(无机化学学报)*, **2013**,**29**(5):1065-1071
- [11] XIANG Hua(向华), JIANG Long(姜隆), LI Huan-Yong(李焕勇), et al. *Chinese J. Inorg. Chem.(无机化学学报)*, **2013**,**29**(5):1084-1088
- [12] Pan L, Adams K M, Hernandez H E, et al. *J. Am. Chem. Soc.*, **2003**,**125**:3062-3067
- [13] Zhang J, Qiu J S, Yao Y M, et al. *Organometallics*, **2012**,**31**: 3138-3148
- [14] Luo Y J, Li W Y, Lin D, et al. *Organometallics*, **2010**,**29**: 3507-3514
- [15] Chen X L, Yao Y J, Hu H M, et al. *J. Coord. Chem.*, **2009**,**62**(13):2147-2154
- [16] Kwak O K, Min K S, Kim B G. *Inorg. Chim. Acta*, **2007**, **360**:1678-1683
- [17] Wu J. *J. Cryst. Res. Technol.*, **2009**,**44**(4):453-456
- [18] Chen X L, Yao Y J, Hu H M, et al. *Inorg. Chim. Acta*, **2009**,**362**:2686-2697
- [19] Sun J Y, Wang W, Wang L, et al. *J. Mol. Struct.*, **2011**,**990**: 204-308
- [20] Xu X X, Liu X X, Sun T, et al. *J. Coord. Chem.*, **2009**,**62** (17):2755-2763
- [21] Hu M, Li H F, Yao J Y, et al. *Inorg. Chim. Acta*, **2010**,**363** (2):368-374

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- [22]Lu W G, Yang K, Jiang L, et al. *Inorg. Chim. Acta*, **2009**, **362**:5259-5264
- [23]Hu M, Wang Q L, Xu G F, et al. *Inorg. Chim. Acta*, **2007**, **360**:1684-1690
- [24]Hu M, Wang Q L, Xu G F, et al. *Inorg. Chem. Commun.*, **2007**,**10**:381-384
- [25]Wamy G Y S K S, Chandramohan K, Lakshmi N V, et al. *Z. Kristallogr.*, **1998**,**213**(3):191-194
- [26]Zhao B, Chen X Y, Cheng P, et al. *J. Am. Chem. Soc.*, **2004**,**126**:15394-15403
- [27]de Betterncourt-Dias A, Viswanathan S. *Chem. Commun.*, **2004**:1024-1025