

以 2,4'-联苯二羧酸及咪唑并[4,5-f][1,10]邻菲咯啉为配体的钴(II)、锰(II)配合物的水热合成及晶体结构

刘春波^{2,3} 赵 晗³ 王珊珊³ 查小林³ 李秀颖^{2,3} 车广波^{*,1,2}

(¹ 吉林师范大学环境科学与工程学院, 四平 136000)

(² 环境友好材料制备与应用教育部重点实验室, 四平 136000)

(³ 吉林师范大学化学学院, 四平 136000)

摘要: 在水热条件下, 以 2,4'-联苯二羧酸(2,4'-H₂bpdca)和咪唑并[4,5-f][1,10]邻菲咯啉(L)为配体构筑了两种配合物[[Co(2,4'-bpdca)(L)(H₂O)]·H₂O]_n (**1**)和[Mn(2,4'-bpdca)(L)(H₂O)]_n (**2**), 并利用元素分析、X-射线单晶衍射和热重分析对其结构进行了表征。配合物 **1** 具有一维链状结构, 配合物 **2** 展示了一维双链结构, 两个配合物都通过分子间氢键和 π - π 相互作用形成三维网状结构。

关键词: 钴(II)配合物; 锰(II)配合物; 2,4'-联苯二羧酸; 咪唑并[4,5-f][1,10]邻菲咯啉; 晶体结构

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Syntheses and Crystal Structures of Co(II) and Mn(II) Complexes with 2,4'-Biphenyldicarboxylic Acid and Imidazo[4,5-f][1,10]phenanthroline Ligands

LIU Chun-Bo^{2,3} ZHAO Han³ WANG Shan-Shan³ ZHA Xiao-Lin³ LI Xiu-Ying^{2,3} CHE Guang-Bo^{*,1,2}

(¹ College of Environmental Science and Engineering, Jilin Normal University, Siping, Jilin 136000, China)

(² Key Laboratory of Preparation and Applications of Environmental Friendly Materials,
Chinese Ministry of Education, Siping, Jilin 136000, China)

(³ College of Chemistry, Jilin Normal University, Siping, Jilin 136000, China)

Abstract: Two complexes constructed with 2,4'-biphenyldicarboxylic acid (2,4'-H₂bpdca), 1,10-phenanthroline derivative ligands and metallic salts, namely, [[Co(2,4'-bpdca)(L)(H₂O)]·H₂O]_n (**1**), [Mn(2,4'-bpdca)(L)(H₂O)]_n (**2**) (L=imidazo [4,5-f][1,10]phenanthroline) were synthesized under hydrothermal reaction. The complexes are characterized by elemental analysis, single crystal X-ray diffraction and thermogravimetric analysis. Complex **1** has a 1D chain structure. Complex **2** forms a one-dimensional double-chain structure. They both further linked into a three-dimensional net structure via the intermolecular hydrogen bonds and aromatic π - π interactions. CCDC: 934719, **1**; 934720, **2**.

Key words: cobalt(II) complex; manganese(II) complex; 2,4'-biphenyldicarboxylic acid; imidazo[4,5-f][1,10]phenanthroline; crystal structure

In recent years, because of the potential applications in many aspects, design and synthesis of novel metal organic frameworks (MOFs) constructed by

metal centers with multidentate nitrogen ligands and organic carboxylic acid ligands have received much more attention than ever before^[1-8]. To obtain desired

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*通讯联系人。E-mail: guangbochejl@yahoo.com

MOFs, hydrogen bonds, π - π interactions and van der Waals interactions must be carefully considered^[9-10]. Also the appropriate use of the well-designed multidentate nitrogen ligands and organic carboxylic acid ligands plays an important role in synthesis of MOFs^[11-14]. As important multidentate nitrogen ligands, 1,10-phenanthroline (phen) and its derivatives have been widely used, we selected imidazo[4,5-f][1,10]phenanthroline (L), which has been less utilized in the construction of MOFs^[15-17]. Identically, 2,4'-biphenyldicarboxylic acid (2,4'-H₂bpdC) was used as bridging ligand, which possesses multiple coordination modes^[18] and can construct complexes with conjugate chelating nitrogen ligands^[19-22]. Complex combination of the same ligands with good structure and characteristics has been reported^[23]. Under hydrothermal reaction, two novel complexes: {[Co(2,4'-bpdC)(L)(H₂O)]·H₂O}_n (**1**) and [Mn(2,4'-bpdC)(L)(H₂O)]_n (**2**) were synthesized and characterized by elemental analysis, single crystal X-ray diffraction. And their thermal stability were also studied.

1 Experimental

1.1 Materials

The ligand L was synthesized according to literature method^[24] and all other analytical grade chemicals and solvent were purchased commercially and used without further purification.

1.2 Syntheses

Synthesis of complex 1. A mixture of Co(NO₃)₂·6H₂O (0.146 g, 0.5 mmol), 2,4'-H₂bpdC (0.121 g, 0.5 mmol), L (0.110 g, 0.5 mmol) and water (15 mL) was sealed in a 23 mL Teflon-lined stainless autoclave and heated at 413 K for 3 d under autogenous pressure and followed by slow cooling to room temperature. Yellow single crystals of complex **1** suitable for X-ray single-crystal diffraction analysis were obtained (yield 63% based on Co). Anal. Calcd. for **1** C₂₇H₂₀N₄O₆Co(%): C, 58.39; H, 3.63; N, 10.09. Found(%): C, 58.34; H, 3.88; N, 10.16.

Synthesis of Complex 2. An identical procedure with **2** was followed to prepare **1** except Co(NO₃)₂·6H₂O was replaced by Mn(NO₃)₂·4H₂O. Yellow

crystals of complex **2** suitable for X-ray single-crystal diffraction analysis were obtained (yield 65% based on Mn). Anal. Calcd. for **2** C₂₇H₁₈N₄O₅Mn (%): C, 60.80; H, 3.40; N, 10.50. Found (%): C, 60.75; H, 3.53; N, 10.38.

1.3 Structure determination

Crystallographic data of two complexes were collected at room temperature on a Bruker SMART APEX CCD diffractometer equipped with a normal-focus, 2.4 kW X-ray source (graphite-monochromated Mo K α radiation with λ =0.071 073 nm) operating at 50 kV and 40 mA with increasing ω (width of 0.3 and exposure time 30 s per frame). All the structures were solved by direct methods using the program SHELXS-97^[25] and refined by full-matrix least-squares techniques against F^2 using the the SHELXTL-97 crystallographic software package^[26]. All non-hydrogen atoms were found from different Fourier map and refined anisotropically, and the hydrogen atoms were placed by geometrical considerations and were added to the structure factor calculation. In complex **1**, the hydrogen atoms attached to water molecule O (2W) could not be positioned reliably. The crystallographic data of the complexes are summarized in Table 1, and selected bond lengths and angles of complex **1**, **2** are listed in Table 2.

CCDC: 934719, **1**; 934720, **2**.

2 Results and discussion

2.1 Description of the crystal structure

The single-crystal X-ray diffraction analysis revealed that complex **1** is a 1D chain. The asymmetric unit of **1** contains one Co(II) ion, one 2,4'-bpdC²⁻ anion, one chelating L ligand, one coordinated water molecule and one free water molecule. As illustrated in Fig.1, the Co(II) ion is six-coordinated with two nitrogen atoms of one L ligand (Co1-N1 0.210 74(18) nm, Co1-N2 0.215 50(18) nm), three oxygen atoms from two 2,4'-bpdC²⁻ ligands (Co1-O1 0.214 53(18) nm, Co1-O2 0.217 51(16) nm, Co1-O3 0.202 19(16) nm) and one water molecule (Co1-O1W 0.209 45(19) nm) in a distorted slightly octahedral coordination. Adjacent Co(II) atoms are bridged by 2,4'-bpdC²⁻ ligands to form a chain with the Co-Co distance of

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

Complex	1	2
Formula	C ₂₇ H ₂₀ N ₄ O ₆ Co	C ₂₇ H ₁₈ N ₄ O ₅ Mn
Formula weight	555.40	533.39
Crystal system	Monoclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> $\bar{1}$
Crystal size / mm	0.421×0.305×0.184	0.361×0.290×0.254
<i>a</i> / nm	0.714 28(13)	1.020 9(6)
<i>b</i> / nm	1.861 8(3)	1.145 4(7)
<i>c</i> / nm	1.759 8(3)	1.190 8(7)
α / (°)	90	116.586(8)
β / (°)	91.293(3)	105.833(9)
γ / (°)	90	100.470(9)
<i>V</i> / nm ³	2.339 7(7)	1.120 8(12)
<i>Z</i>	4	2
μ / mm ⁻¹	0.788	0.639
Goodness-of-fit on <i>F</i> ²	1.089	1.025
Reflns collected/unique	12 873 / 4 561	6 257 / 4 268
<i>D</i> _c / (Mg·m ⁻³)	1.577	1.580
θ range / (°)	1.59 to 25.99	2.05 to 26.05
<i>R</i> (<i>I</i> > 2 σ (<i>I</i>))	<i>R</i> ₁ =0.035 7, <i>wR</i> ₂ =0.093 3	<i>R</i> ₁ =0.042 0, <i>wR</i> ₂ =0.101 1
<i>R</i> (all data)	<i>R</i> ₁ =0.044 5, <i>wR</i> ₂ =0.098 6	<i>R</i> ₁ =0.050 0, <i>wR</i> ₂ =0.107 1

Table 2 Selected bond lengths (nm) and bond angles (°)

Complex 1					
N1-Co1	0.210 74(18)	N2-Co1	0.215 50(18)	O1-Co1	0.214 53(18)
O2-Co1	0.217 51(16)	O1W-Co1	0.209 45(19)	O3-Co1	0.202 19(16)
N1-Co1-N2	77.29(6)	N2-Co1-O1	89.20(7)	O1-Co1-O1W	156.83(7)
N1-Co1-O1	108.56(7)	N2-Co1-O2	95.03(6)	O1-Co1-O3	90.64(7)
Complex 2					
N1-Mn1	0.230 2(2)	N2-Mn1	0.229 4(2)	O1-Mn1	0.213 1(2)
O2-Mn1	0.214 9(2)	O3-Mn1	0.219 4(2)	O1W-Mn1	0.225 4(2)
N1-Mn1-N2	72.13(8)	N2-Mn1-O1	90.22(8)	O1-Mn1-O3	96.32(8)
N1-Mn1-O1	83.28(8)	N2-Mn1-O2	88.25(9)	O1-Mn1-O1W	168.28(8)

1.011 8 nm along the *c* axis (Fig.2a). Two carboxylic group of each 2,4'-bpdc ligand show monodentate bridging and bidentate chelating coordination mode, respectively. Notably, the L ligands are attached on both sides of the chain, and the adjacent chains are linked into a two-dimensional plane structure through aromatic π - π interactions between L and L ligand (bond distances of 0.375 0 and 0.350 7 nm, Table 4) (Fig.2b). In addition, the O-H \cdots O, O-H \cdots N and N-

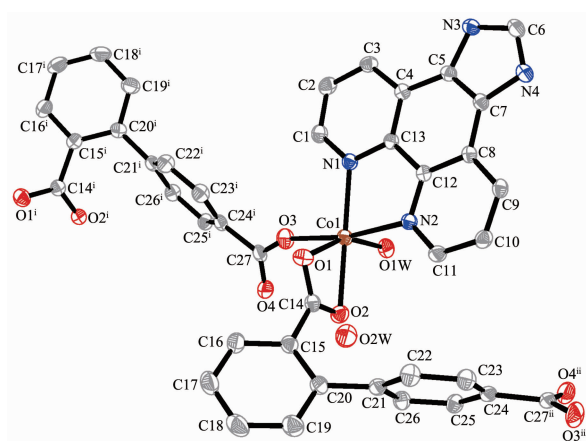
H \cdots O hydrogen bonds (Table 3) involving the water molecules, the carboxylic groups of 2,4'-bpdc²⁻ anions and L ligands further extend the 2D supramolecular arrays into an interesting 3D network structure.

The single-crystal X-ray diffraction analysis revealed that complex **2** displays a one-dimensional double-chain structure. As is shown in Fig.3, each Mn atom is coordinated with two nitrogen atoms of one L ligand (Mn1-N1 0.230 2 (2) nm, Mn1-N2 0.229 4(2)

Table 3 Hydrogen bond lengths and bond angles

D-H...A	<i>d</i> (D-H) / nm	<i>d</i> (H...A) / nm	<i>d</i> (D...A) / nm	∠DHA / (°)
Complex 1				
O1W-H1WB...O2W	0.088(3)	0.199(3)	0.284 4(3)	162(3)
N3-H4...O4 ⁱ	0.086	0.194	0.277 3(2)	162.9
O1W-H1WA...N4 ⁱⁱ	0.079(3)	0.198(3)	0.275 9(3)	167(3)
Complex 2				
O1W-H1B...O4	0.086(4)	0.181(4)	0.263 6(3)	159(4)
N3-H3...O4 ⁱ	0.086	0.199	0.278 0(3)	152.3
O1W-H1A...N4 ⁱⁱ	0.088(3)	0.195(3)	0.282 1(3)	167(3)

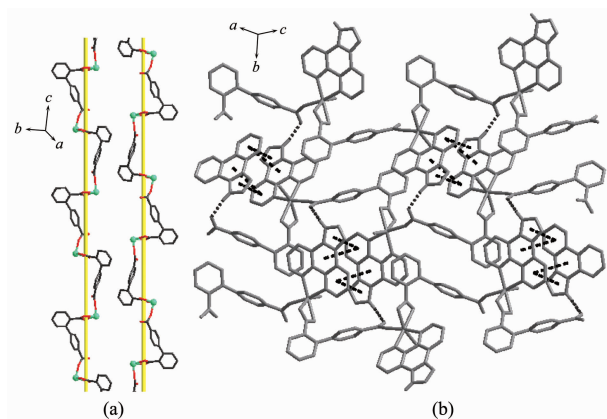
Symmetry codes: **1**: ⁱ $-x+1/2, y-1/2, -z+1/2$; ⁱⁱ $1-x, -y, -z$; **2**: ⁱ $x, y+1, z$; ⁱⁱ $1-x, 1-y, 1-z$.



Hydrogen atoms were omitted for clarity, symmetry codes:

ⁱ $-1/2+x, 1/2-y, 1/2+z$; ⁱⁱ $1/2+x, 1/2-y, -1/2+z$

Fig.1 Coordination environment of Co(II) in complex **1** with 20% probability displacement ellipsoids

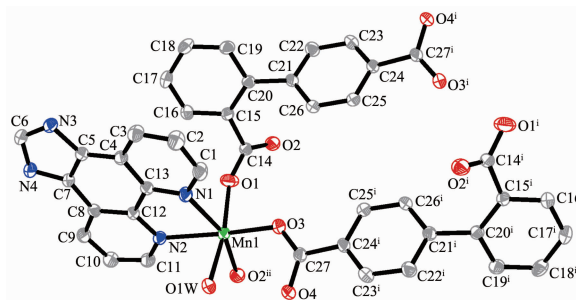


Some of atoms are omitted for clarity

Fig.2 (a) One-dimensional chain structure of **1**; (b) Two-dimensional plane structure constructed by hydrogen bonds and π - π stacking interactions

nm), three oxygen atoms from three different 2,4'-bpdcc²⁻ ligands (Mn1-O1 0.213 1(2) nm, Mn1-O2 0.214 9(2) nm, Mn1-O3 0.219 4(2) nm) and one water molecule

(Mn1-O1W 0.225 4(2) nm). Two adjacent Mn atoms linked together by two 2,4'-bpdcc²⁻ ligands. Neighboring two asymmetric units are bridged by 2,4'-bpdcc²⁻ ligands to form a one-dimensional double chain structure (Fig.4). Interestingly, the chain can be viewed as a series of alternating grids containing a 8-membered ring (Mn₂O₄C₂) and a 22-membered ring (Mn₂O₄C₁₆), respectively. Within the (Mn₂O₄C₂) ring, the distance between the two Mn(II) atoms is 0.438 9 nm, while in the (Mn₂O₄C₁₆) ring, the Mn...Mn distance is 1.082 0 nm. Furthermore, adjacent chains are further interconnected via intermolecular hydrogen-bonding interactions (O1W-H1A...N4ⁱⁱ, N3-H3...O4ⁱ, Table 3) and π - π stacking interactions between L and L/2,4'-bpdcc²⁻ (centroid-to-centroid distances of 0.372 5 and 0.367 6 nm, respectively, Table 4). Nevertheless, intramolecular hydrogen bonds (O1W...O4 0.2636(3) nm,



Hydrogen atoms were omitted for clarity, symmetry codes: ⁱ $2-x, -y, -z$; ⁱⁱ $1-x, -y, -z$

Fig.3 Coordination environment of Mn(II) in complex **2** with 20% probability displacement ellipsoids

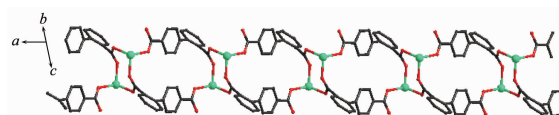


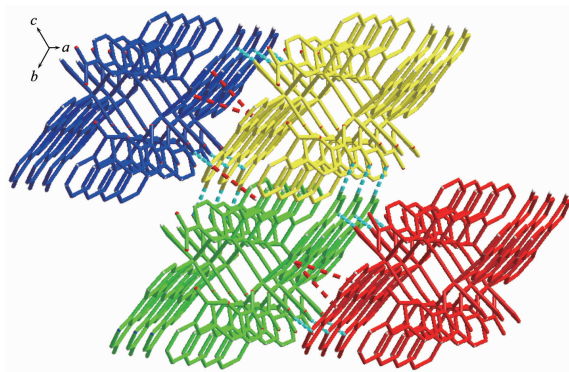
Fig.4 One-dimensional double-chain structure of **2**

159(4)°) are also observed in this complex, as shown in Fig.5. Therefore, such chains are linked by each other to form a 3D supramolecular structure (Fig.5).

Table 4 π - π bond lengths (nm)

Complex 1	
Ring	Dist.
Cg1→Cg3 ⁱ	0.368 03(14)
Cg1→Cg3 ⁱⁱ	0.350 70(13)
Cg1→Cg4 ⁱ	0.354 89(14)
Cg3→Cg4 ⁱⁱ	0.375 02(14)
Cg4→Cg4 ⁱ	0.350 63(14)
Complex 2	
Ring	Dist.
Cg2→Cg6 ⁱ	0.367 6(3)
Cg4→Cg4 ⁱⁱ	0.372 2(3)
Cg4→Cg5 ⁱⁱ	0.372 6(3)

1: Ring: Cg1: 5-Membered Ring (1)N3→C5→C7→N4→C6; Cg3: 6-Membered Ring(3)N2→C11→C10→C9→C8→C12; Cg4: 6-Membered Ring (4)C4→C5→C7→C8→C12→C13; Symmetry codes: ⁱ 1-x, -y, -z; ⁱⁱ 1-x, -y, -z. **2:** Ring: Cg2: 5-Membered Ring (2)N3→C5→C7→N4→C6; Cg4: 6-Membered Ring(4)N2→C11→C10→C9→C8→C12; Cg5: 6-Membered Ring (5)C4→C5→C7→C8→C12→C13; Cg6: 6-Membered Ring (6)C15→C16→C17→C18→C19→C20; Symmetry codes: ⁱ 1-x, 1-y, -z; ⁱⁱ 1-x, 1-y, 1-z.

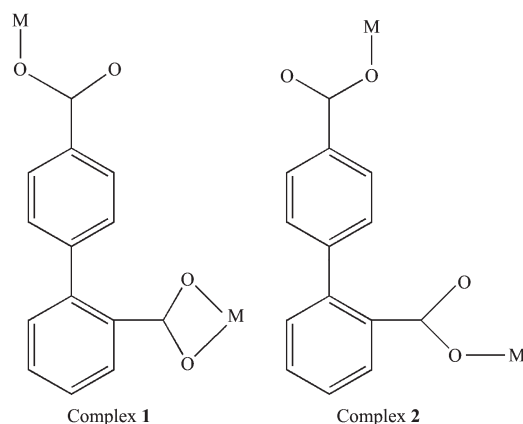


Some of atoms are omitted for clarity

Fig.5 Three-dimensional supramolecular structure constructed by hydrogen bonds and π - π stacking interactions

The effects of the metal center on structures of **1** and **2** have been clearly demonstrated according to X-ray single crystal diffraction analyses. By a comparison of complexes **1** and **2**, when the Co(II) ion was replaced by Mn(II) ion with different coordination modes of 2,4'-bpdc ligands (Scheme 1), structurally

different complex was obtained. In addition, the noncovalent interactions such as hydrogen bonding and π - π stacking interactions, which guide the formation and stabilize the extended network structures.



Scheme 1 Different coordination modes of 2,4'-bpdc ligands

2.2 TGA

The thermal stability of **1** and **2** was investigated by TGA, four distinct weight losses were observed for **1** and three for **2** (Fig.6). For **1** the first weight loss of 3.87% is in the range 90~120 °C, assigned to the decomposition of the free water molecules (Calcd. 3.24%). The second weight loss of 3.40% is in the range 160~190 °C, assigned to the loss of the coordinated water molecules (Calcd. 3.24%). The third weight loss of 38.88% is ascribable to the loss of L ligand (Calcd. 39.65%) from 270 °C to 350 °C. The last weight loss of 42.97% is in the temperature range of 350~540 °C, which corresponding to the release of 2,4'-bpdc²⁻ ligand (Calcd. 43.25%). The final product may be CoO. The reasons of the weight losses for **2**

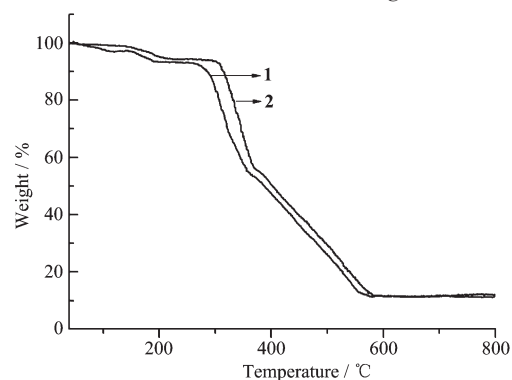


Fig.6 TG curves of complexes **1** and **2**

are similar to **1** from the second step to the end, whereas the losses are 3.60% in the temperature range 140~210 °C for the first (Calcd. 3.38%), 40.90% from 300 to 365 °C for the second (Calcd. 41.29%), and 44.81% in the range of 380~570 °C for the last (Calcd. 45.03%), respectively. And MnO could be the final product.

References:

- [1] Jing X M, Meng H, Li G H, et al. *Cryst. Growth Des.*, **2010**, **10**:3489-3495
- [2] Yang E C, Zhao H K, Ding B, et al. *Cryst. Growth Des.*, **2007**, **7**:2009-2015
- [3] Xu Z L, Li X Y, Che G B, et al. *Chinese J. Struc. Chem.*, **2008**, **27**:593-597
- [4] Pachfule P, Dey C, Panda T, et al. *Cryst. Growth Des.*, **2010**, **10**:1351-1363
- [5] Pachfule P, Das R, Poddar P, et al. *Cryst. Growth Des.*, **2011**, **11**:1215-1222
- [6] Ma L F, Wang Y Y, Wang L Y, et al. *Cryst. Growth Des.*, **2009**, **9**:2036-2038
- [7] Liu T F, Zhang W J, Sun W H, et al. *Inorg. Chem.*, **2011**, **50**:5242-5248
- [8] Chang Z, Zhang D S, Hu T L, et al. *Cryst. Growth Des.*, **2011**, **11**:2050-2053
- [9] Che G B, Liu C B, Liu B, et al. *CrystEngComm*, **2008**, **10**:184-191
- [10] Liu C B, Wang J, Zha X L, et al. *J. Coord. Chem.*, **2011**, **64**:232-243
- [11] CHE Guang-Bo(车广波), LI Xiu-Ying(李秀颖), XU Zhan-Lin(徐占林), et al. *Chinese J. Inorg. Chem.(Wuji Huaxue Xuebao)*, **2009**, **25**(3):556-559
- [12] Cui R H, Xu Y H, Jiang Z H. *Z. Anorg. Allg. Chem.*, **2010**, **636**:605-609
- [13] Wang W, Fu D W, Xu X B, et al. *Z. Anorg. Allg. Chem.*, **2011**, **637**:467-471
- [14] Cui R H, Xu Y H, Jiang Z H. *Inorg. Chem. Commun.*, **2009**, **12**:933-936
- [15] Yu F S, Zhang L L, Tan J T, et al. *Chem. Pap.*, **2011**, **65**:23-28
- [16] Wang F M. *Acta Crystallogr. Sect. E*, **2010**, **66**:m1677
- [17] Li C X, Zha X L, Liu C B, et al. *Acta Crystallogr. Sect. E*, **2009**, **65**:m54
- [18] Yi X Y, Ying Y, Fang H C, et al. *Inorg. Chem. Commun.*, **2011**, **14**:453-457
- [19] Wang A D, Li W B, Guo F, et al. *Asian J. Chem.*, **2010**, **22**:6616-6618
- [20] Guo F, Xu J K, Zhang X L, et al. *Inorg. Chim. Acta*, **2010**, **363**:3790-3797
- [21] Guo F, Zhang X L, Zhu B Y, et al. *J. Inorg. Organomet. Polym. Mater.*, **2010**, **20**:38-45
- [22] Guo F, Zhu B Y, Song Y L, et al. *J. Coord. Chem.*, **2010**, **63**:1304-1312
- [23] Gong Y, Wu T, Li J H, et al. *Z. Anorg. Allg. Chem.*, **2012**, **638**:473-481
- [24] Che G B, Li W L, Kong Z G, et al. *Synth. Commun.*, **2006**, **36**:2519-2524
- [25] Sheldrick G M. *SHELXS-97, Program for Crystal Structure Solution*, University of Göttingen, Germany, **1997**.
- [26] Sheldrick G M. *SHELXL-97, Program for Crystal Structure Refinement*, University of Göttingen, Germany, **1997**.