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基于 3,5-二((4′-羧基苄基)氧)苯甲酸和 4′-(4-吡啶基)-2,2′:6′,2″-三联吡啶为混合配体的两个配合物的水热合成与晶体结构

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摘要:在水热条件下,以 3,5-二((4′-羧基苄基)氧)苯甲酸(H_3bcb)和 4′-(4-吡啶基)-2,2′:6′,2″-三联吡啶(PYTPY)为混合配体构筑了 2 个过渡金属配合物$[Co(H_2bcb)_2(PYTPY)]_n$ (**1**)和$[Mn(H_2bcb)_2(PYTPY)]_n$ (**2**),利用元素分析、红外光谱以及单晶 X 射线衍射表征其结构。分析表明配合物 **1** 和 **2** 为一维链状结构。此外,2 个配合物展示了优良的热稳定性。磁化率的测试结果表明,配合物 **1** 和 **2** 在 2 K 和 8 K 以下时展示了反铁磁相互作用。

关键词:过渡金属配合物;3,5-二((4′-羧基苄基)氧)苯甲酸;4′-(4-吡啶基)-2,2′:6′,2″-三联吡啶;晶体结构;磁性

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Hydrothermal Syntheses and Crystal Structures of Two Complexes Constructed from 3,5-Bis((4′-carboxylbenzyl)oxy)benzoic Acid and 4′-(4-Pyridyl)-2,2′:6′,2″-terpyridine Mixed Ligands

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Abstract: Two transition metal complexes based on 3,5-bis((4′-carboxylbenzyl)oxy)benzoic acid (H_3bcb) and 4′-(4-pyridyl)-2,2′:6′,2″-terpyridine (PYTPY) mixed ligands, namely, $[Co(H_2bcb)_2(PYTPY)]_n$ (**1**) and $[Mn(H_2bcb)_2(PYTPY)]_n$ (**2**), have been synthesized under hydrothermal conditions and characterized by elemental analysis, infrared spectrum and single-crystal X-ray diffraction. Complexes **1** and **2** exhibit one-dimensional chain structures, respectively. Furthermore, these two complexes exhibit excellent thermal stabilities. They also display antiferromagnetic interaction below 2 K and 8 K confirmed through magnetic susceptibility measurements. CCDC: 1439250, **1**; 1439249, **2**.

Keywords: transition metal complex; 3,5-bis((4′-carboxylbenzyl)oxy)benzoic acid; 4′-(4-pyridyl)-2,2′:6′,2″-terpyridine; crystal structure; magnetic property

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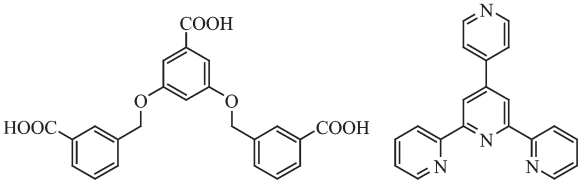
In recent years, rational design and synthesis of the complexes have been extensively studied not only for their fascinating architectures[1], but also for their potential applications in magnetism[2], catalysis[3], luminescence[4-5], adsorption[6] and separation[7]. To the best of our knowledge, the construction of molecular architectures greatly depends on the coordination geometry of central metal and organic ligands. In this regard, the design or selection of suitable organic ligands is one of the keys for the construction of the complexes. Organic aromatic polycarboxylic acids and polypyridyl ligands have been extensively employed in the preparation of the complexes with novel structural motifs and interesting properties because of their versatile bridging or chelating coordination modes[8-10]. 3,5-bis((4′-carboxylbenzyl)oxy)benzoic acid (H_3bcb) has both two twisty benzyloxy carboxylic acid moiety and a rigid benzoic acid moiety. The flexible moiety can freely twist around the C-C bond to meet the requirements of the coordination geometries, and the rigid moiety can help to construct and stabilize certain complexes architectures. Up to now, only a handful of complexes based on H_3bcb ligand have been described[11-13]. As an important polypyridyl ligand, 4′-(4-pyridyl)-2,2′:6′,2″-terpyridine (PYTPY) is excellent ligand to construct supramolecular architectures not only because it can coordinate to the metals easily, but also because the large conjugated aromatic rings system can easily form π-π interactions[14]. Considering all of these above-mentioned, we consider that the simultaneous employment of H_3bcb and PYTPY mixed ligands (Scheme 1) will contribute to the formation of various architectures and help researchers understand the process of self-assembly. Herein, we successfully apply this strategy and obtain two complexes, $[Co(H_2bcb)_2(PYTPY)]_n$ (**1**) and $[Mn(H_2bcb)_2(PYTPY)]_n$ (**2**). In this paper, we report the preparation, crystal structures, thermal stabilities and magnetic properties of complexes **1** and **2**.



Scheme 1 Molecular structure of H_3bcb and PYTPY ligands

1 Experimental

1.1 Materials and instruments

All reagents were used as purchased without further purification. Elemental analyses of carbon, hydrogen and nitrogen were performed on a Perkin-Elmer 240C elemental analyzer. IR spectra were obtained on a Perkin-Elmer 2400LS Ⅱ spectrometer within the 4 000 ~400 cm^{-1} region. Powder X-ray diffraction (PXRD) patterns of the samples were collected on a D/MAX-3C diffractometer with the Cu $K\alpha$ radiation (λ=0.154 06 nm) at room temperature and 2θ ranging from 5° to 50°. Thermogravimetric analysis (TGA) was performed on a NETZSCH STA 449C analyzer under air atmosphere. Magnetic analysis was performed on a SQUID MPMS3 analyzer under liquid helium refrigeration.

1.2 Preparation of the complexes

1.2.1 Synthesis of $[Co(H_2bcb)_2(PYTPY)]_n$ (**1**)

The complex **1** was prepared under hydrothermal condition. A mixture of $Co(NO_3)_2\cdot 6H_2O$ (0.029 1 g, 0.1 mmol), H_3bcb (0.084 g, 0.2 mmol), PYTPY (0.031 g, 0.1 mmol) and distilled water (15 mL) was mixed in a 50 mL beaker. In the process of stirring, NaOH (0.1 $mol\cdot L^{-1}$) was dripped into the system until pH =4. After stirring for 0.5 h, the mixture was sealed in a 25 mL Teflon-lined stainless steel autoclave and heated at 428 K for 72 h, then cooled at a rate of 5 $K\cdot h^{-1}$ to room temperature. After filtration, the product was washed with distilled water and then dried at room temperature. Red block crystals were obtained with a yield of about 48% based on Co. Anal. Calcd. for $C_{66}H_{48}N_4O_{16}Co$ (%):C, 65.40; H, 3.99; N, 4.62. Found (%): C, 65.35; H, 4.06; N, 4.60. IR spectrum (KBr, cm^{-1}): 3 431 (m), 1 709 (s), 1 682 (s), 1 577 (m), 1 541 (s), 1 472 (m), 1 357 (m), 1 278(s), 1 199 (m), 1 164 (s), 1 041 (m), 909 (m), 821 (m), 786(s), 751 (w), 707 (m), 646 (m), 505 (m).

1.2.2 Synthesis of $[Mn(H_2bcb)_2(PYTPY)]_n$ (**2**)

An identical procedure with **1** was followed to prepare **2** except $Co(NO_3)_2\cdot 6H_2O$ was replaced by $MnCl_2$

·$4H_2O$. Brown block crystals were obtained with a yield of about 53% based on Mn. Anal. Calcd. for $C_{66}H_{48}N_4O_{16}Mn$ (%):C, 65.62; H, 4.00; N, 4.64. Found (%): C, 65.56; H, 4.06; N, 4.63. IR spectrum (KBr, cm^{-1}): 3 440 (m), 1 708 (s), 1 618 (s), 1 569 (m), 1 378 (m), 1 297 (s), 1 158 (s), 1 041(s), 903 (m), 827 (m), 787 (s), 753 (w), 698 (m), 623(m), 508 (m).

1.3 Single-crystal X-ray diffraction

Suitable single crystals of complexes **1** and **2** with dimensions of 0.331 mm×0.264 mm×0.202 mm and 0.295 mm×0.246 mm×0.197 mm were mounted on glass fibers for X-ray measurement, respectively. Reflection data were collected at room temperature on a Bruker SMART APEX Ⅱ CCD diffractometer, equipped with graphite-monochromatized Mo $K\alpha$ radiation (λ= 0.071 073 nm) using the φ-ω scan technique. All absorption corrections were performed using the SADABS program[15]. All the structures were solved by direct methods with SHELXS-97 program[16] and refined by full-matrix least-squares techniques on F^2 with SHELXL 97[17]. All of the non-hydrogen atoms were easily found from the different Fourier map and refined anisotropically, whereas the hydrogen atoms of the complexes were placed by geometrical considerations and were added to the structure factor calculation. Detailed crystallographic data and structure refinement parameters of complexes **1** and **2** are given in Table 1, and the selected bond distances and bond angles are listed in Table 2.

CCDC: 1439250, **1**; 1439249, **2**.

Table 1　Crystal data and structure refinements for complexes 1 and 2

Complex	**1**	**2**
Formula	$C_{66}H_{48}CoN_4O_{16}$	$C_{66}H_{48}MnN_4O_{16}$
Formula weight	1 212.01	1 208.02
Crystal system	Orthorhombic	Orthorhombic
Space group	*Pccn*	*Pccn*
a / nm	2.883 5(3)	2.908 4(4)
b / nm	0.861 29(8)	0.853 58(11)
c / nm	2.247 8(2)	2.294 4(3)
V / nm^3	5.582 4(9)	5.695 9(13)
Z	4	4
Goodness-of-fit on F^2	1.019	1.009
Reflections collected, unique	28 939, 5 493	29 325, 5 586
θ range / (°)	1.81~26.01	1.78~25.97
R ($I>2\sigma(I)$)	R_1=0.045 6, wR_2=0.116 6	R_1=0.050 1, wR_2=0.107 9
R (all data)	R_1=0.071 7, wR_2=0.131 9	R_1=0.116 1, wR_2=0.133 4

Table 2　Selected bond lengths (nm) and bond angles (°) for complexes 1 and 2

		Complex **1**			
Co-N3#1	0.205 2(2)	Co-O2#2	0.209 10(17)	Co-O2	0.209 10(17)
Co-N2	0.214 8(3)	Co-N1	0.216 9(2)	Co-N1#2	0.216 9(2)
N3#1-Co-O2	96.85(5)	N3#1-Co-N2	180.0	N3#1-Co-N1	76.44(5)
O2-Co-N1	93.09(8)	O2-Co-N1#2	90.12(8)	N2-Co-N1	103.56(5)
		Complex **2**			
Mn-O2	0.215 0(19)	Mn-O2#1	0.215 0(19)	Mn-N3#2	0.219 2(3)
Mn-N2	0.224 7(3)	Mn-N1#1	0.226 4(2)	Mn-N1	0.226 4(2)
N3#2-Mn-N2	180.0	N3#2-Mn-N1#1	72.58(6)	O2-Mn-N3#2	97.76(5)
O2#1-Mn-N1	91.25(8)	O2-Mn-N1	93.38(8)	N2-Mn-N1#1	107.42(6)

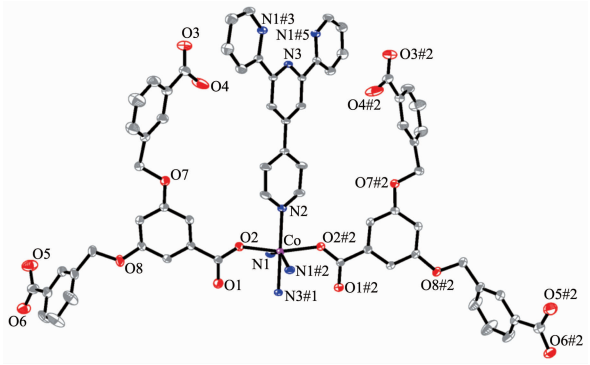
Symmetry codes: #1: $-x+1/2$, y, $z-1/2$; #2: $-x+1/2$, $-y+1/2$, z for **1**; #1: $-x+1/2$, $-y+1/2$, z, #2: $-x+1/2$, y, $z-1/2$ for **2**.

2 Results and discussion

2.1 Description of the crystal structure

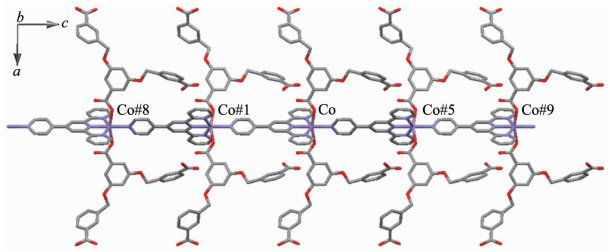
Similar cell parameters with the same space group (Table 1) and the results of crystallographic analysis confirm that **1** and **2** are isostructural. Thus, only the structure of **1** is described in detail as the typical example.

The single-crystal X-ray diffraction analysis reveals that complex **1** exhibits a one-dimensional chain structure, crystallizing in Orthorhombic space group *Pccn*. An asymmetric unit $[Co(H_2bcb)_2(PYTPY)]$ contains one six-coordinated Co^{2+} ion, two H_2bcb^- ligands and one PYTPY ligand. The coordination mode of Co^{2+} is shown in Fig.1. The central Co^{2+} is coordinated with two oxygen atoms (O2 and O2#1, symmetry codes: #1: $-x+1/2$, $-y+1/2$, z) from two monodentate bridging carboxyl group of two different H_2bcb^- ligands, four N atoms (N1, N1#1, N2, N3, symmetry codes: #1: $-x+1/2$, $-y+1/2$, z) from two different PYTPY ligands in a slightly distorted octahedral coordination. The average distances of Co-$O_{H_2bcb^-}$ and Co-N_{PYTPY} are 0.209 14(17) and 0.213 45(3) nm, respectively, all of which are comparable to those reported for other Co^{2+} complexes[18]. The adjacent metal center Co^{2+} ions were bridged by PYTPY ligands, generating an infinite one dimensional (1D) fishbone-like chain along the *c*-axis (Fig.2), in which the PYTPY ligands and Co^{2+} ions form the main skeleton, whereas H_2bcb^- ligands play the roles of the side bones. In complex **1**, the larger conjugated system of PYTPY ligand plays a vital role in further extending and consolidating the molecular structure via $\pi\cdots\pi$ interactions. The neighboring 1D chains interact through $\pi\cdots\pi$ stacking between pyridine rings of PYTPY ligands to yield a two-dimensional (2D) layer structure. The centroid-to-centroid distance is 0.369 2 nm and dihedral angel is 3° between Cg(1) and Cg(1)#6 rings (Cg(1): N1→C30→C31→C32→C33→C34, symmetry codes: #6: $-x+1/2$, $-y+3/2$, z, Fig.3). It is worth mentioning that the intramolecular hydrogen bonds (O4–H4···O1#3 0.253 3 nm, 163.65°, symmetry codes: #3: x, $-y+1/2$, $z+1/2$) and intermolecular hydrogen bonds (O6–H6A···O6#7 0.264 1 nm, 161.03°, symmetry codes: #7: $-x+3/2$, $-y+1/2$, z) involving the carboxylic groups of H_2bcb^- ligands further consolidate 2D supramolecular structure of complex **1**.



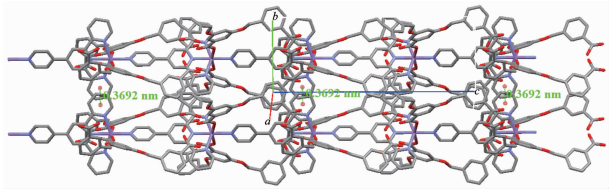
Hydrogen atoms have been removed for clarity; Symmetry codes: #1: $-x+1/2$, y, $z-1/2$; #2: $-x+1/2$, $-y+1/2$, z; #3: x, $-y+1/2$, $z+1/2$; #5: $-x+1/2$, y, $z+1/2$

Fig.1 ORTEP drawing of complex **1** showing Co^{2+} coordination environment with thermal ellipsoids at 30% probability



Symmetry codes: #1: $-x+1/2$, y, $z-1/2$; #5: $-x+1/2$, y, $z+1/2$; #8: x, y, $z-1$; #9: x, y, $z+1$

Fig.2 1D chain structure of complex **1** with hydrogen atoms omitted for clarity



Hydrogen atoms have been omitted for clarity

Fig.3 2D layer structure of complex **1** constructed by the $\pi\cdots\pi$ stacking interactions

2.2 Powder XRD

The experimental PXRD patterns of complexes **1** and **2** match with their simulated ones, indicating the phase purity of the bulk materials. The variation in reflection intensities among the simulated and experimental patterns is due to the superior

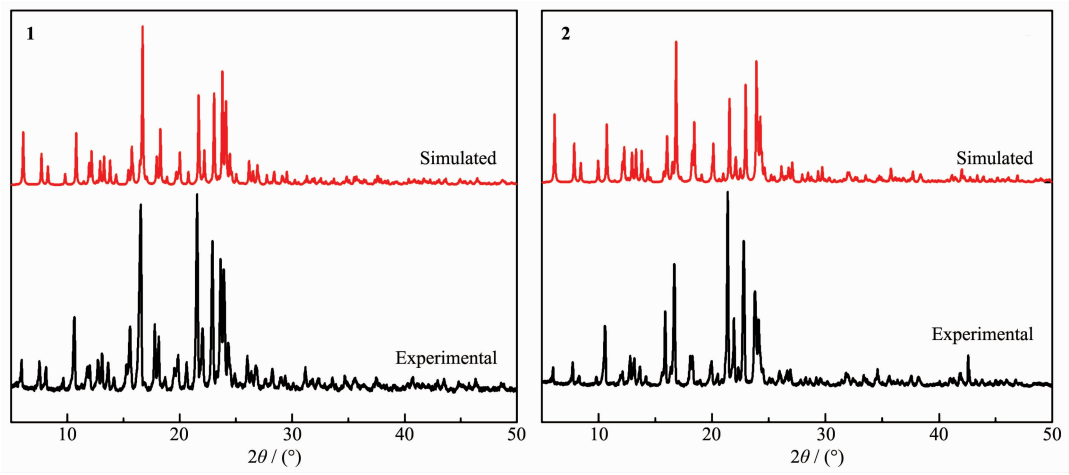


Fig.4　PXRD patterns of simulated and experimental of complexes **1** and **2**

orientation of the powder sample during collection of the experimental PXRD data (Fig.4).

2.3　TG analysis

The thermal stabilities of **1** and **2** are similar, so the TGA of **1** is described as the typical example. The thermal stability of complex **1** in air was examined by the TG techniques in the temperature range of 40~1 000 ℃. As shown in Fig.5, the complex **1** is thermally stable upon heating to 260 ℃. Then the main weight loss happened from 260 to 915 ℃ corresponding to the release of H_2bcb^- and PYTPY ligands with a weight loss of 94.90% (Calcd. 95.14%: H_2bcb^- 69.53%, PYTPY 25.61%).

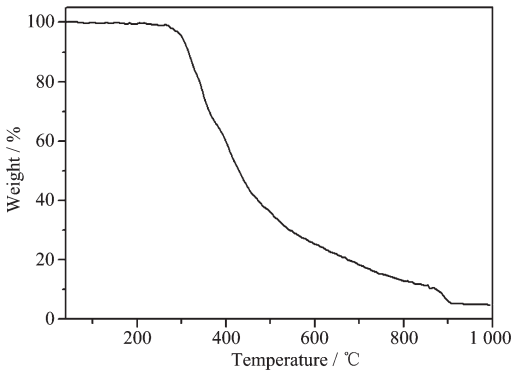
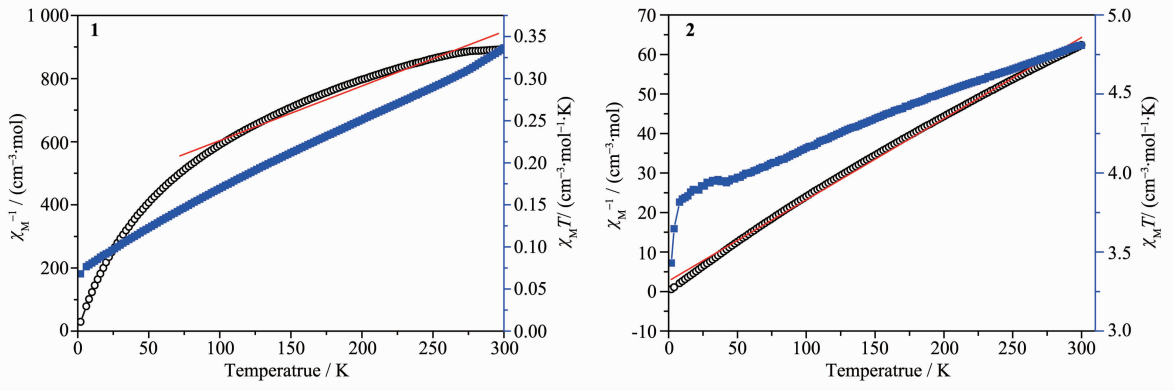


Fig.5　TG curve of complex **1**

2.4　Magnetic properties

Temperature dependence of the molar magnetic susceptibility χ_M of complexes **1** and **2** were measured in the temperature range of 2~300 K at 0.1 T and are shown as χ_M^{-1} vs T and $\chi_M T$ vs T plots in Fig.6.

For complex **1**, as the temperature decreases from room temperature, $\chi_M T$ is 0.34 $cm^3 \cdot mol^{-1} \cdot K$, after which the value decreases until a value of 0.08 $cm^3 \cdot mol^{-1} \cdot K$ is reached at ~2 K. The decline in the $\chi_M T$ value from 300 K is due to an antiferromagnetic (AFM)



Solid line shows the best theoretical fit

Fig.6 Plots of χ_M^{-1} vs T (○) and $\chi_M T$ vs T (■) for **1** and **2**

interaction between the neighboring Co^{2+} centers[19]. The temperature dependence of the reciprocal susceptibility (χ_M^{-1}) is fitted according to the Curie-Weiss law, $\chi_M T = C/(T-\theta)$, affording a Curie constant C=0.578 7 $cm^3 \cdot mol^{-1} \cdot K$ and Weiss temperature θ= −249.2 K. The negative θ value can be attributed to both AFM and exchange coupling.

For complex **2**, the $\chi_M T$ product has values of 4.82 $cm^3 \cdot mol^{-1} \cdot K$ at 300 K, and undergoes a gradual decrease down to 3.8 $cm^3 \cdot mol^{-1} \cdot K$ at 8 K, due to the Boltzmann depopulation of the excited states and simultaneous population of the antiferromagnetically coupled ground state. Upon further cooling, $\chi_M T$ drops sharply, suggesting AFM interactions between the chains or the saturation effect[20]. The molar susceptibilities of Mn obey the Curie-Weiss law perfectly, with C=4.8 $cm^3 \cdot mol^{-1} \cdot K$ and θ=−12.97 K. The negative θ value can be attributed to both AFM and exchange coupling.

3 Conclusions

In this work, two new complexes based on H_3bcb and PYTPY ligands were achieved under hydrothermal conditions. Complexes **1** and **2** possess 1D chain structures. It is worth noting that in this system $\pi\cdots\pi$ stacking has an important influence in linking the low-dimensional (1D) entities into a high dimensional (2D) structure. Moreover, the intramolecular and intermolecular hydrogen bonding interactions consolidated the 2D supramolecular network. In addition, magnetic measurements on complexes **1** and **2** confirm a strong AFM behavior below 2 K and 8 K, respectively. In summary, our research demonstrates further that the ligands H_3bcb and PYTPY could be a potential building block to construct novel coordination compounds with unusual architectures and interesting physical properties.

References:

[1] Tranchemontagne D J, O′Keeffe M, Yaghi O M, et al. *Chem. Soc. Rev.*, **2009**,**38**:1257-1283

[2] Liu J W, Chen L F, Cui H, et al. *Chem. Soc. Rev.*, **2014**,**43**: 6011-6061

[3] Sun Q F, Iwasa J, Ogawa D, et al. *Science*, **2010**,**328**:1144-1147

[4] Desiraju G R. *J. Am. Chem. Soc.*, **2013**,**135**:9952-9967

[5] Zhang C L, Zhang M D, Qin L, et al. *Cryst. Growth Des.*, **2014**,**14**:491-499

[6] Qin L, Ju Z M, Wang Z J, et al. *Cryst. Growth Des.*, **2014**, **14**:2742-2746

[7] Sun C Y, Wang X L, Qin C, et al. *Chem. Eur. J.*, **2013**,**19**: 3639-3643

[8] Pan Z R, Zheng H G, Wang T W, et al. *Inorg. Chem.*, **2008**, **47**:9528-9536

[9] QIAO Yu(乔宇), MA Bo-Nan(马博男), LI Xiu-Ying(李秀颖), et al. *Chinese J. Inorg. Chem.*(无机化学学报), **2015**,**31**(6): 1245-1251

[10]Sun Y C, Wang Y F, Li Z, et al. *J. Mol. Struct.*, **2014**,**1074**: 416-421

[11]Liu J J, Lin Y J, Jin G X, et al. *Organometallics*, **2014**,**33**: 1283-1290

[12]Figgemeier E, Merz L, Hermann B A, et al. *J. Phys. Chem. B*, **2003**,**107**:1157-1162

[13]Leandro M O, Lourenco, Filipe A, et al. *Acta Crystallogr. Sect. E*, **2015**,**71**:330-335

[14]Hiroki K, Toshi N. *Inorg. Chem.*, **2009**,**48**:8593-8602

[15]*SADABS*, Bruker AXS Inc., Madison, Wisconsin, USA, **1997**.

[16]Sheldrick G M. *SHELXS*-97, *Program for the Solution of Crystal Structure*, University of Göttingen, Germany, **1997**.

[17]Sheldrick G M. *SHELXS*-97, *Program for the Refinement of Crystal Structure*, University of Göttingen, Germany, **1997**.

[18]LI Xiu-Ying(李秀颖), HU Bo(胡波), CHE Guang-Bo(车广波), et al. *Chinese J. Inorg. Chem.*(无机化学学报), **2014**,**30** (12):2818-2824

[19]Ganguly S, Mondal R. *Cryst. Growth Des.*, **2015**,**15**:2211-2222

[20]Zeng M H, Zhou Y L, Wu M C, et al. *Inorg. Chem.*, **2010**, **49**:6436-6442