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基于 2-苯基-4-喹啉酸及双咪唑类配体的钴(Ⅱ)配合物的合成、表征、磁性和电化学性质

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摘要: 利用 2-苯基-4-喹啉酸、苯-1,4-双(咪唑基-1-甲基)和乙酸钴在二甲基甲酰胺和水的混合溶剂中反应,得到配合物[Co(pqba)$_2$(biyb)](**1**) (Hpqba=2-苯基-4-喹啉酸,biyb=苯-1,4-双(咪唑基-1-甲基))。采用元素分析、红外光谱、X 单晶衍射结构分析、热重分析等方法对配合物进行了表征和结构测定。配合物 **1** 属单斜晶系,*C*2/*c* 空间群。配合物 **1** 中的 biyb 配体采用双齿桥链模式连接金属钴离子首先形成一维"之"字链,通过 $\pi\cdots\pi$ 堆积作用,进一步拓展为二维超分子结构。循环伏安法测试结果说明配合物 **1** 的电解过程为准可逆过程。磁化率测量表明,配合物 **1** 具有反铁磁性质。

关键词: 钴配合物; 晶体结构; 磁性质; 电化学性质
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Syntheses, Characterizations, Magnetic Susceptibility, and Electrochemical Property of Cobalt Complex Based on 2-Phenyl-4-quinolinecarboxylic Acid and Imidazol-Based Linker

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Abstract: One new metal-organic framework, namely, [Co(pqba)$_2$(biyb)](**1**) (2-phenyl-4-quinolinecarboxylic acid=Hpqba, 1,4-bis (imidazol-1-ylmethyl)benzene =biyb), has been synthesized under hydrothermal conditions. The compound **1** was characterized by elemental analysis, IR spectroscopy, and X-ray single-crystal diffraction. Complex **1** crystallizes in the Monoclinic system, *C*2/*c* space group. In **1**, the biyb act as bidentate ligands assembling with Co(Ⅱ) ions to a one-dimensional framework, which is further expanded to form a 2D supramolecular structure by $\pi\cdots\pi$ stacking interactions with biyb molecules between 1D chains. Thermogravimetric analyses for **1** is discussed. Furthermore, electrochemical property of the **1** shows that electron transfer of Co(Ⅱ) between Co(Ⅲ) in electrolysis is quasi-reversible process, and magnetic susceptibility measurements indicate that compound **1** has dominating antiferromagnetic couplings between metal ions. CCDC: 919474.

Key words: cobalt complex; crystal structure; magnetic susceptibility; electrochemical property

0 Introduction

The design and synthesis of metal -organic frameworks (MOFs) are of great interest not only for their intriguing variety of structures[1-4], but also for their potential applications in magnetism, catalysis,

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adsorption, and fluorescence properties, etc[5-8]. So far, a number of O and N-donor multifunction ligands such as 9-acridinecarboxylic acid, 4-quinolinecarboxylic acid, quinoline-based carboxylic acid, 2-methylquinoline-3, 4-dicarboxylate acid, 2-methylquinoline-2, 4-dicarboxylate acid have been widely employed to construct MOFs[9-11]. In contrast, the use of 2-phenyl-4-quinolinecarboxylic acid ligands (Hpqba) to construct functional MOFs has been less investigated to date[12-15]. In this regard, our synthetic strategy was to select Hpqba and introduce N-donor bridging ligand of biyb with different rigidity as co-ligands into the reaction system, based on the following considerations: (1) The Hpqba can adopts various coordination modes when it coordinates to metals and it have larger conjugated π-systems (three benzene rings), π-π stacking interactions may play important roles in the formation of their complexes; (2) The carboxylic groups can propagate magnetic super exchange between metal centers, and rigid ligands containing multi benzene rings and suitable metal ion form complexes having fluorescence properties; (3)The introduction of flexible long-chain N-donor bridging biyb ligand as co-ligands may helps us to assemble and explore their impact on MOFs.

Herein, to design complexes showing interesting architectures and magnetic behavior, we have chosen the Co(Ⅱ), ion, Hpqba and biyb (1,4-bis(imidazol-1-ylmethyl)benzene) ligands as co-ligands to react. Then, one new complex is obtained, namely, [Co (pqba)$_2$ (biyb)] (1), and the details of their syntheses, structures, and magnetic properties are reported below.

1 Experimental

1.1 Materials and methods

Reagents and solvents employed were commercially available and without further purification. Elemental analysis (C, H, N) was determined on a Perkin-Elmer 2400 type elemental analyzer. IR absorption spectra of the compound was recorded in a Bruker EQUINOX-55 spectrophotometer with the range 400~4 000 cm^{-1} using KBr disks (6 mg of sample in 500 mg of KBr). Thermogravimetric analyses was recorded on a NETZSCH STA 449C thermal analyzer from room temperature up to 900 ℃ using a heating rate of 10 ℃·min^{-1} under an air atmosphere. Magnetic measurement was performed of **1** using a MPMS-XL-7 magnetometer under an applied field of 1000 Oe over the temperature range of 1.8~300 K.

1.2 Syntheses of [Co(pqba)$_2$(biyb)](1)

Compound **1** was prepared as follows: a mixture of Hpqba (0.049 6 g, 0.2 mmol), biyb (0.0477 g, 0.2 mmol), cobalt acetate (0.074 7 g, 0.3 mmol), NaOH (0.0080 g, 0.2 mmol), deionised water (12 mL) and DMF (3 mL)was stirred for 30 min in air, then transferred and sealed in a 25 mL Teon reactor, which was heated at 110 ℃ for 48 h. The solution was then cooled to room temperature at rate of 4 ℃·h^{-1}, a very ne deep red crystalline product 1 in 65% yield based on Co. $C_{46}H_{34}O_4N_6Co$ (793.72): Calcd. (%): C 69.61, H 4.32, N 10.59; Found (%): C 69.57, H 4.44, N 10.62.

1.3 Crystal structure determination

X-ray crystallographic data for the compound **1** were collected at room temperature using Bruker Smart-1000CCD diffractometer. Graphite monochromated Mo $K\alpha$ (λ=0.071 073 nm) radiation was used. Empirical absorption corrections were applied using the SADABS program [16]. The structures of compounds **1~3** was solved by direct methods using the SHELXS-97[17] and refined on F^2 by the full-matrix least-squares methods using the SHELXL-97 program package [18], Atoms were located from iterative examination of difference F-maps following least-squares renements of the earlier models. Hydrogen atoms were placed in calculated positions and included as riding atoms with isotropic displacement parameters 1.2 times U_{eq} of the attached C atoms. The final R=0.055 6, w_R=0.136 9 (ω=1/[$\sigma^2(F_o^2)$+(0.056 0P)^2+10.752 0P], where P=(F_o^2+2F_c^2)/3), $(\Delta\rho)_{max}$=1 495 e·nm^{-3} and $(\Delta\rho)_{min}$=−1 281 e·nm^{-3}. The crystal data and refinement details of the compound are summarized in Table 1, and the selected interatomic distances are given in Table 2.

CCDC: 919474.

Table 1 Crystal data for the compound 1

Measurement temperature	296(2)	V / nm^3	3.775 5
Empirical formula	$C_{46}H_{34}CoN_6O_4$	D_c / (g·cm^{-3})	1.396
Formula weight	793.72	θ range for data collection/(°)	2.11 to 28.32
Crystal system	Monoclinic	Indices range(h, k, l)	$-22\leqslant h\leqslant 36$,$-13\leqslant k\leqslant 14$, $-21\leqslant l\leqslant 16$
Space group	$C2/c$	λ(Mo $K\alpha$) / nm	0.071 073
a / nm	2.719 7	Reflections collected	11 539
b / nm	1.069 0	Data/restraints/parameters	4 557/0/246
c / nm	1.578 9	F(000)	1 644
α / (°)	90.00	Final R	R_1=0.055 6,wR_2=0.136 9
β / (°)	124.67	R indices (all data)	R_1=0.067 4, wR_2=0.146 0
γ / (°)	90.00	Z	4

Table 2 Selected bond lengths (nm) and angles (°) the compound 1

Co1-O1	0.2229(2)	Co1-N2	0.2067(2)	Co1-O2	0.2174(2)
O1i-Co1-O1	162.50(13)	O2-Co1-O1	58.09(9)	N2-Co1-O1	92.41(9)
N2i-Co1-O2i	92.62(10)	O2-Co1-O2i	85.67(15)	O2i-Co1-O1i	58.09(9)

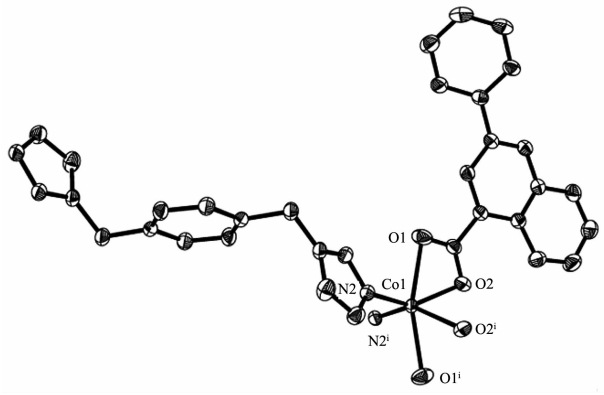
2 Results and discussion

2.1 Crystal Structure of [Co(pqba)$_2$(biyb)](1)

X-ray single crystal diffraction reveals that complex **1** crystallizes in monoclinic $C2/c$ space group. complex **1** is a 1D coordination polymer, and which expand 2D supramolecules via strong $\pi\cdots\pi$ stacking interactions. As shown in Fig.1, the asymmetric unit contains consists of one Co(Ⅱ) ion, two pqba anionics, and one biyb ligand.

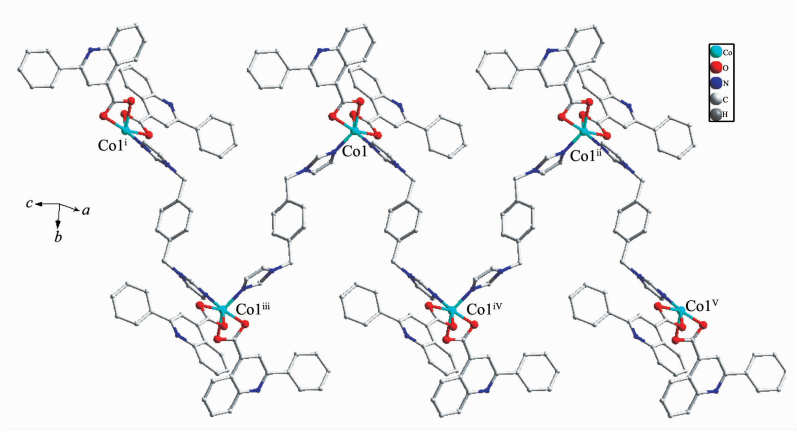
The six-coordinated Co1(Ⅱ) adopts slight distorted [CoO_4N_2] octahedron geometry, where four carboxylate oxygen atoms from two pqba ligands (Co1-O1 0.222 9 (2) nm, Co1-O1^i 0.222 9 (2) nm, Co1-O2 0.217 4(2) nm, and Co1-O2^i 0.217 4 (2) nm), and two N atoms from two biyb ligands(Co1-N2 0.2067(2) nm, and Co1-N2^i 0.206 7 (2) nm). The O1 and O1^i atoms lie at the both sides of the plane, and occupy the vertexes of the octahedral geometry. The selected interatomic distances and angles are given in Table 2. All the bond distances and angles are comparable to those observed in other Co(Ⅱ) compounds[19].

In compound **1**, each deprotonated pqba ligand adopts a μ_2-chelating fashion, and merely contribute to



Hydrogen atoms are omitted for clarity. Symmetry codes: i: 1−x, y, 1.5−z

Fig.1 Coordination environment of the Co(Ⅱ) ion in **1** at 30 % probability level



Symmetry codes: i: x, y, 1+z, ii: x, y, −1+z, iii: 1−x, −y, 2−z, iv: 1−x, −y, 1−z, v: 1−x, −y, −z

Fig.2 View of 1D chain constructed by biyb ligand along the c axis

coordination number around each Co1 ions. As shown in Fig.2, the Co1 ions were bridged by nitrogen atoms of biyb ligands to form a one-dimensional zigzag chain structure along the c axis with the neighboring Co1 distance of 1.476 9 (3) nm. Where, the pqba ligands seem to act as "wings", whereas the biyb and Zn(Ⅱ) acts as "trunk", thus, they compose a butter-fly-like structure (Fig.2). In complex **1**, the $\pi\cdots\pi$ stacking interaction change the framework from one-dimensional zigzag chain structure to 2D supramolecules in bc plane (Fig.3), and there are $\pi\cdots\pi$ stacking interactions (centroid …centroid distances: 0.401 3 nm, centroid …plane distances: 0.3552 nm) between imidazol of biyb ligand in one-dimensional zigzag chains.

2.2 IR spectra

The IR spectra of complex **1** show the characteristic vibration of carboxylic acids. The strong peaks of aromatic rings span over the range 1 330~1 620 cm^{-1} for **1**.

The presence of the characteristic bands at around 1 550~1 570 cm^{-1} in complex **1** that attributed to the protonated carboxylic group. The vibration absorption peak of C=N at 1 540~1 570 cm^{-1} for complex **1**, compared with the IR spectra of bipy ligand the peak upfield shift. Which shows that the nitrogen atoms of bipy ligand coordinated with zinc ions. These spectral information of complex **1** is consistent with the results of the single-crystal X-ray diffraction analyses.

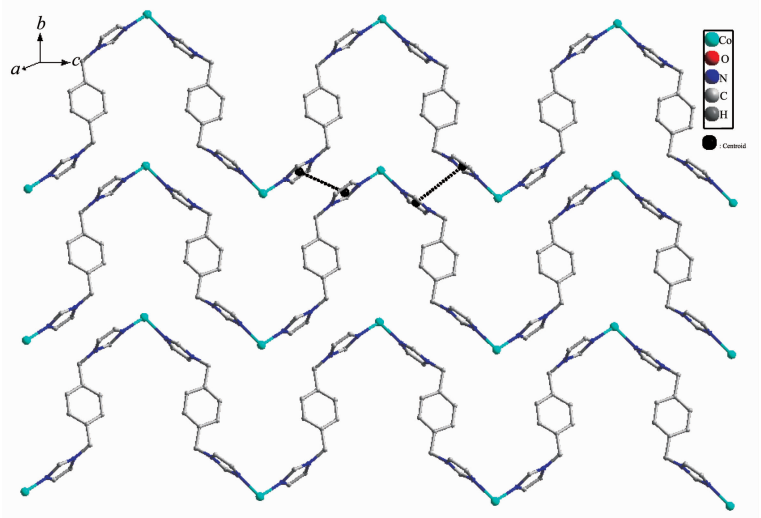


Fig.3 View of 2D supramolecular structure by-stacking interactions along the b axis of **1**

2.3 Thermogravimetric analyses

To characterize the complex **1** more fully in terms of thermal stability, the thermal behaviors were studied by thermogravimetric analyses (Fig.4). For **1**, a weight loss is observed from 140 to 490 ℃, which is attributed to the loss of the pqba anionic, with a weight loss of 62.1% (Calcd. 62.6%); then, the ligands of bipy are removed, and a plateau of 9.2% at 790 ℃ is observed, which may be a CoO (Calcd. 9.4%) residue.

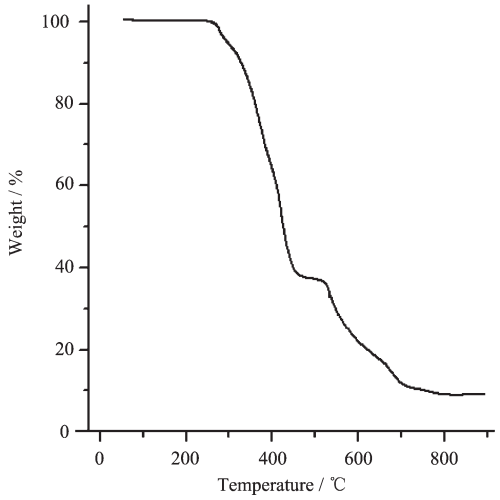


Fig.4 TGA trace of complex **1**

2.4 Electrochemical property

The cyclic voltammetry of **1** (Fig.5) was measured with a three electrode cell in aqueous solution with complex of 6.6×10^{-6} mol·L^{-1}, which with scanning range of −1.500~1.500 and scanning rate of 100 mv·s^{-1} at room temperature. The cyclic voltammogram curve of **1** have one pair of oxidation-reduction peak, which corresponds to Co(Ⅱ)/Co(Ⅲ) redox process. E_{pa}=−0.69 V, E_{pc}=−0.83 V, E=0.14 V, $E_{1/2}$=0.76 V, I_{pa}/I_{pc}=0.10. The

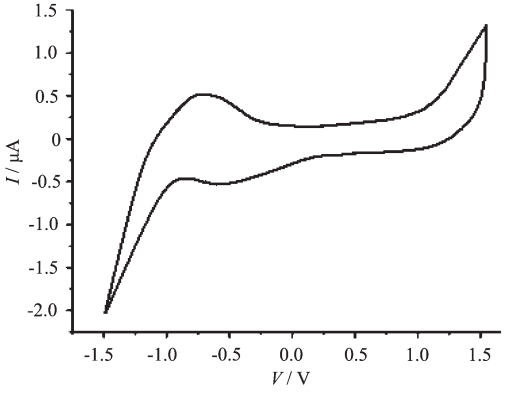


Fig.5 Cyclic volatmmetric of complex **1**

results show that electron transfer of Co(Ⅱ) between Co(Ⅲ) in electrolvsis is quasi-reversible process[20].

2.5 Magnetic property of 1

The magnetic measurement was performed on polycrystalline samples of **1** using a MPMS-XL-7 magnetometer under an applied field of 1 000 Oe over the temperature range of 1.8~300 K. The temperature dependence of the magnetic susceptibility of **1** in the form of χ_M and $\chi_M T$ versus T are displayed in Fig.5. At room temperature, $\chi_M T$ is equal to 2.71 cm^3·mol^{-1}·K, which is much higher than the spin-only value of 1.87 cm^3·mol^{-1} K based on single Co(Ⅱ) ions. Upon lowering the temperature, $\chi_M T$ continuously decreases and reaches 1.45 at 1.99 K. Above 140 K, the magnetic properties of **1** obey the Curie-Weiss law and give C= 2.71 cm^3·mol^{-1}·K, and θ=−5.35. Which indicates an intracluster antiferromagnetic interaction between the Co(Ⅱ) ions[21]. While the distance among Co ions was bridged through the long biyb ligands, it should exclude an efficient direct exchange between Co ions; the overall antiferromagnetic interaction should be attributed to the significant spin-orbit coupling, which is remarkable for the $^4T_{1g}$ ground term of Co in an octahedral ligand field, according to the preceding structure description of **1**, no appropriate model could be used for tting the magnetic properties of such a system[22].

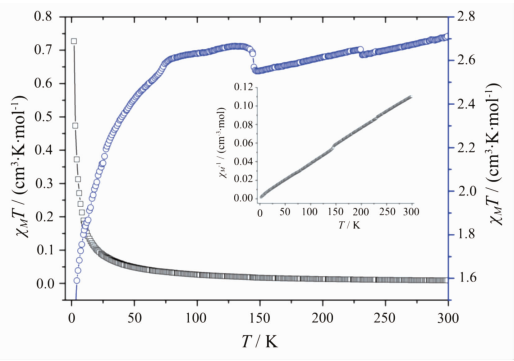


Fig.6 Temperature dependence of of magnetic susceptibility in the form $\chi_M T$, χ_M and $1/\chi_M T$ (inset) for complex **3**

References:

[1] Zhao T T, Jing X M, Wang J, et al. *Cryst. Growth Des.*, **2012**,**12**:5456-5461

[2] Yang W T, Guo M, Sun Z M, et al. *Cryst. Growth Des.*, **2012**, **12**:5529-5534

[3] Zhao F H, Che Y X, Zheng J M. *Inorg.Chem.Commun.*, **2012**,**16**:5560

[4] Zhang Z M, Li Y G , Wang E B, et al. *Angew. Chem. Int. Ed.*, **2009**,**48**:1581-1584

[5] CHEN Man-Sheng(陈满生), ZENG Ju-Lan(曾巨澜), ZHANG Chun-Hua(张春华), et al. *Chinese J. Inorg. Chem.* (*Wuji Huaxue Xuebao*), **2012**,**28**:1775-1778

[6] Wang X Y, Wang Z M, Gao S. *Chem. Commun.*, **2008**: 281294

[7] Maspoch D, Ruiz-Molina D, Veciana J. *Chem. Soc., Rev.*, **2007**, **36**:770-818

[8] Ji W J, Zhai Q G, Hu M C, et al. *Chem. Commun.*, **2011**,**47**: 3834-3836;

[9] Bu X H, Tong M L, Chang H C, et al. *Inorg. Chem.*, **2005**, **44**:,9837-9846

[10]Bu X H, Tong M L, Chang H C, et al. *Ange.Chem. Int. Ed. Engl.*, **2004**,**43**:192-195

[11]Yuan G, Shao K Z, Wang X L, et al. *Inorg. Chem. Commun.*, **2008**,**11**,1246-1249

[12]Zha M Q, Li X, Bing Y. *J. Coord. Chem.*, **2011**,**64**:473-482

[13]Wang J J, Chang Z, Zhang A S, et al. *Inorg. Chim. Acta*, **2010**,**363**:13771385

[14]Qin Z Q, Jennings M C, Puddephatt R J, et al. *Inorg. Chem.*, **2002**,**41**:5174-5186.

[15]Shen Y C, Li Z J, Cheng J K, et al. *Inorg. Chem. Commun.*, **2007**,**10**:888-890

[16]Sheldrick G M. *SADABS*, *A Program for Empirical Absorption Correction of Area detector Data* University of Göttingen, Germany, **1997**.

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

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

[19]HAN Wei(韩伟), CHENG Mei-Lin(程美令), LIU Qi(刘琦), et al. *Chinese J. Inorg. Chem.* (*Wuji Huaxue Xuebao*), **2012**,**28**:1997-2004.

[20]LEI Jing-Bin(雷静彬), HUANG Fu-Ping(黄富平), YU Qing(于青), et al. *Chinese J. Inorg. Chem.* (*Wuji Huaxue Xuebao*), **2012**,**28**:572-578

[21]Cheng X N, Zhang W X, Chen X M. *J. Am. Chem. Soc.*, **2007**,**129**:15738-15739

[22]Cui J H, Li Y Z, Guo Z J, et al. *Cryst. Growth Des.*, **2012**, **12**:3610-3618