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# 一个由 2,4-吡啶二甲酸和 1,4-双(咪唑基-1-甲基)苯构筑的钴配位聚合物的水热合成和晶体结构

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**摘要**:通过水热法合成了一个金属-有机配位聚合物[Co(PDC)(bix)($H_2O$)]$_n$($H_2$PDC=2,4-吡啶二甲酸,bix=1,4-双(咪唑基-1-甲基)苯)。并对其进行了元素分析、热重、红外光谱、紫外光谱和 X-射线单晶衍射测定。该配合物属于单斜晶系,*C*2/*c* 空间群。晶体学数据:*a*=2.525 5(4),*b*=1.318 98(19),*c*=1.441 5(2) nm,*β*=118.656(2)°,*V*=4.213 5(11) nm$^3$,$C_{21}H_{19}CoN_5O_5$,$M_r$=480.34,$D_c$=1.514 g·cm$^{-3}$,*μ*(Mo *Kα*)=0.857 9 mm$^{-1}$,*F*(000)=1 976,*Z*=8,残差因子 *R*=0.030 5,*wR*=0.067 4。在晶体结构中,钴原子为六配位与来自 2 个不同的 PDC 配体上的 2 个羧基氧原子和来自 2 个 bix 配体上的 2 个氮原子、来自 PDC 配体上的 1 个氮原子以及 1 个配位水分子配位,呈现畸变的八面体几何构型。而且该配合物通过氢键作用扩展成三维超分子网状结构。

**关键词**:水热合成;晶体结构;配位聚合物
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# Hydrothermal Synthesis and Crystal Structure of a Co(Ⅱ) Coordination Polymer Assembled by 2,4-Pyridinedicarboxylic Acid and 1,4-Bis(imidazol-1-ylmethyl)-benzene) Ligands

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**Abstract:** A metal-organic coordination polymer [Co(PDC)(bix)($H_2O$)]$_n$ ($H_2$PDC=2,4-pyridinedicarboxyic acid, bix = 1,4-bis (imidazol-1-ylmethyl)-benzene) **1** has been hydrothermally synthesized and structurally characterized by elemental analyses, TG, IR, UV and single-crystal X-ray diffraction. The complex crystallizes in monoclinic, space group *C*2/*c* with *a*=2.525 5(4), *b*=1.318 98(19), *c*=1.441 5(2) nm, *β*=118.656(2)°, *V*=4.213 5(11) nm$^3$, $C_{21}H_{19}CoN_5O_5$, $M_r$=480.34, $D_c$=1.514 g·cm$^{-3}$, *μ*(Mo *Kα*)=0.857 9 mm$^{-1}$, *F*(000)=1 976, *Z*=8, *R*=0.030 5 and *wR*=0.067 4. In the crystalstructure, the cobalt atom is six-coordinated with two carboxylate oxygen atoms from two different PDC ligands and two nitrogen atoms from two bix ligands, one nitrogen atom from PDC ligand and one coordinated water moleculore, showing a distorted octahedral geometry. Furthermore, it exhibits a 3D supramolecular network through hydrogen bonding interactions. CCDC: 878877.

**Key words:** hydrothermal synthesis; crystal structure; coordination polymer

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Recently, there has been much interest in the construction of metal-organic frameworks (MOFs) due to their versatile structures and interesting topologies[1-4] as well as their potential applications as functional materials in the fields of molecular magnetism, catalysis, gas sorption and optoelectronic devices[5-9]. The most useful building blocks for constructing organic-inorganic hybrid MOFs are carboxylate and N-donor ligands. Aromatic carboxylate ligands have been extensively employed in the construction of various dimensional MOFs because of their abundant coordination modes and high structural stability for functional materials applications[10-16]. Bix (1,4-bis(imidazole-1-ylmethyl) benzene), a highly flexible N-containing ligand, has been used as a auxiliary ligand because of the free rotation of the two imidazole planes, which results in *trans* or *cis* conformations as required by the metal coordination geometry in the assembly process[17-20]. In this study, we introduce aromatic carboxylate ligand together with the bix ligand in order to assemble cobalt (Ⅱ) coordination polymers under hydrothermal conditions.

## 1 Experimental

### 1.1 General procedures

All materials were commercially purchased and used without further purification. Infrared spectra (KBr pellets) were taken on a Perkin-Elmer 2400LS Ⅱ spectrometer and elemental analyses for C, H and N were performed on a Perkin-Elmer 240C analyzer. TG studies were performed on a Perkin-Elmer TGA7 analyzer. The UV spectrum was obtained on a Shimzu UV-250 spectrometer in the 200~400 nm range.

### 1.2 Synthesis of $[Co(PDC)(bix)(H_2O)]_n$

The title compound was prepared from a mixture of $Co(OAc)_2\cdot 4H_2O$ (0.10 g, 0.4 mmol), $H_2PDC$ (0.053 g, 0.2 mmol), bix (0.048 g, 0.2 mmol) and $H_2O$ (18 mL) in a 30 mL Teflon-lined autoclave under autogenous pressure at 150 ℃ for 7 d. After cooling to room temperature, pink block crystals were collected by filtration and washed with distilled water in 35% yield (based on Co). Anal. Calcd. (%) for $C_{21}H_{19}CoN_5O_5$: C, 52.54; H, 3.99; N, 14.59. Found(%): C, 52.52; H, 3.96; N, 14.56. IR (KBr, $cm^{-1}$): 3 107w, 2 969w, 2 361w, 1 633 m, 1 598m, 1 545w, 1 520m, 1 471w, 1 456w, 1 426w, 1 388 m, 1 371m, 1 288w, 1 234w, 1 226w, 1 200w, 1 108 w, 1 095w, 1 082w, 1 015w, 943w, 912w, 887w, 849w, 823 m, 777m, 749w, 731w, 717w, 685m, 660m, 629w, 437w.

### 1.3 Structure determination

A single crystal of the title compound with dimensions of 0.338 mm×0.230 mm×0.170 mm was mounted on a Bruker CCD diffractometer equipped with a graphite-monochromatic Mo $K\alpha$ ($\lambda$=0.071 073 nm) radiation using an $\omega$ scan mode at 292(2) K. In the range of $3.60°<2\theta<52.06°$, a total of 11 348 reflections were collected and 4133 were independent with $R_{int}$=0.027 5, of which 3 377 were observed with $I>2\sigma(I)$. The correction for Lp factors was applied. The structure was solved by direct methods with SHELX-97 program[21] and refined by full-matrix least-squares techniques on $F^2$ with SHELXL-97[22]. The non-hydrogen atoms were refined anisotropically, and all the hydrogen atoms were determined with theoretical calculations and included in the final refinement in the riding model approximation with displacement parameters derived from the parent atoms to which they were bonded. The final $R$=0.030 5 and $wR$=0.067 4 ($w=1/[\sigma^2(F_o^2)+(0.029\,6P)^2+2.776\,4P]$, where $P=(F_o^2+2F_c^2)/3$). $S$=1.023, $(\Delta\rho)_{max}$=274 e·nm$^{-3}$, $(\Delta\rho)_{min}$=−314 e·nm$^{-3}$ and $(\Delta/\sigma)_{max}$=0.001. The selected important bond parameters are given in Table 1.

CCDC: 878877.

**Table 1　Selected bond lengths (nm) and bond angles (°)**

| | | | | | |
|---|---|---|---|---|---|
| Co(1)-O(1) | 0.207 49(13) | Co(1)-O(3A) | 0.207 92(13) | Co(1)-N(2) | 0.210 91(16) |
| Co(1)-N(4) | 0.214 02(18) | Co(1)-N(1) | 0.214 89(15) | Co(1)-O(5) | 0.216 13(16) |
| O(1)-Co(1)-N(2) | 94.74(6) | O(1)-Co(1)-N(4) | 92.52(7) | N(2)-Co(1)-N(4) | 88.86(6) |
| O(1)-Co(1)-N(1) | 77.80(5) | N(2)-Co(1)-N(1) | 172.05(6) | N(4)-Co(1)-N(1) | 94.15(6) |
| O(1)-Co(1)-O(5) | 89.51(6) | N(2)-Co(1)-O(5) | 82.81(6) | N(4)-Co(1)-O(5) | 171.56(6) |
| N(1)-Co(1)-O(5) | 94.28(6) | | | | |

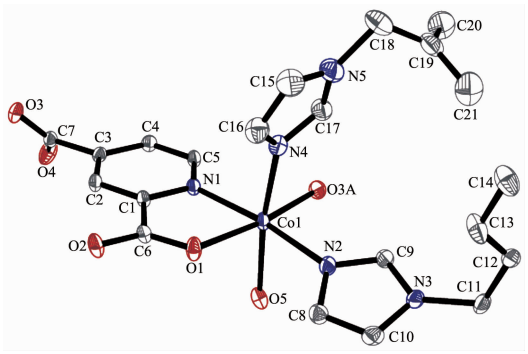
## 2 Results and discussion

### 2.1 IR spectrum

The $COO^-$ is coordinated with its asymmetric and symmetric stretching appearing at 1 598 ($\nu(OCO)_{assym}$) and 1 388 $cm^{-1}$ ($\nu(OCO)_{sym}$)[23], respectively. The $\Delta\nu(\nu(OCO)_{assym}-\nu(OCO)_{sym})$ is 210 $cm^{-1}$ (>200), showing the presence of monodentate linkage of carboxylates in the dianions. Thus the carboxylates coordinate to the metal as monodentate ligands via the carboxylate groups[24]. The absence of the characteristic bands at about 1 722 $cm^{-1}$ in compound **1** attributed to the protonated carboxylic group indicates that the absence protonation of PDC ligand. In addition, X-ray diffraction analysis further indicates the existence of monodentate manners of the carboxylate groups and absence protonation of PDC ligands.

### 2.2 Description of the structure

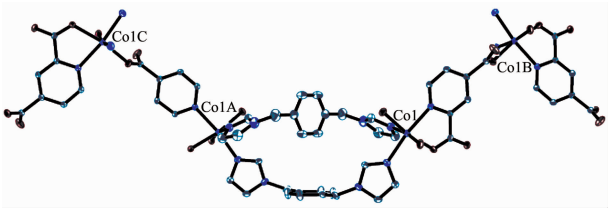
Single-crystal X-ray diffraction analysis reveals that compound $[Co(PDC)(bix)(H_2O)]_n$ (**1**) crystallizes in *C*2/*c* space group. There are one Co(Ⅱ) atom, one PDC ligand, one bix ligand and one coordinated water molecule in the asymmetric unit (Fig.1). The Co(1) ion is coordinated by two carboxylate oxygen atoms (Co(1)-O(1) 0.207 49(13), Co(1)-O(3A) 0.207 92(13) nm) from two different PDC ligands, one nitrogen atom (Co(1)-N(1) 0.214 89(15) nm) from PDC ligand and one nitrogen atom from bix ligand (Co(1)-N(2) 0.210 91(16) nm) in the equatorial plane, one nitrogen atom from the other bix ligand (Co(1)-N(4) 0.214 02(18) nm) and one coordinated water molecule (Co(1)-O(5) 0.216 13(16) nm) at the axial site. Each cobalt(Ⅱ) displays a slightly distorted octahedral geometry. The N(O)-Co-O(N) angles range from 77.80(5)° to 172.05(6)°.




Hydrogen atoms are omitted for clarity; Symmetry code: A: −*x*, −*y*, −*z*

Fig.1 ORTEP drawing of **1** showing the local coordination environment of Co(Ⅱ) with thermal ellipsoids at 30% probability

One coordination mode of the PDC ligand is present in the structure of compound **1**, namely $\mu_3$ bridging mode. The bix ligand also exhibits classic bridging mode, based on this, two Co(Ⅱ) ions are linked by bix ligands to yield one-dimensional chain-like structure, as depicted in Fig.2. The Co⋯Co distance linked by bix ligand along the chain direction is 1.210 1 nm.




Symmetry code: A: −*x*, −*y*, −*z*; B: −*x*+1/2, −*y*+1/2, 1−*z*; C: *x*+1/2, *y*+1/2, *z*

Fig.2 View of the 1D chain in **1**

Hydrogen bonding interactions are usually important in the synthesis of supramolecular architecture[25]. There are persistent O−H⋯O hydrogen bonding interactions between carboxylate oxygen atom and coordinated water molecule (O5⋯O4 0.272 0 nm, O5⋯O2 0.271 1 nm) in the complex, which play an important role in stabilizing the network structure. Therefore, through hydrogen bonding interactions, the one-dimensional chains are further extended into a three-dimensional supramolecular framework (Fig.3).

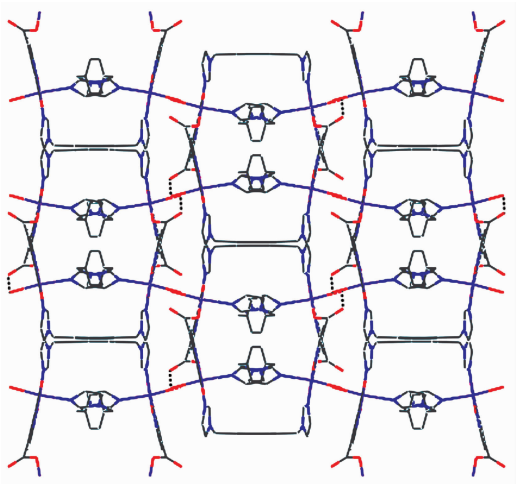


Fig.3 3D Supramolecular network viewed along the *c* axis in **1**

### 2.3 Thermal analysis

TG curve (Fig.4) of 1 show that the first weight loss of 51.5% from 27 to 420 ℃ corresponds to the removal of coordinated water molecule and bix ligands (calcd. 53.3%). Upon further heating, an obvious weight loss (32.2%) occurs in the temperature range of 420~640 ℃, corresponding to the release of PDC ligands (calcd. 34.4%). After 640 ℃ no weight loss is observed, which means the complete decomposition of **1**. The residual weight should be CoO.

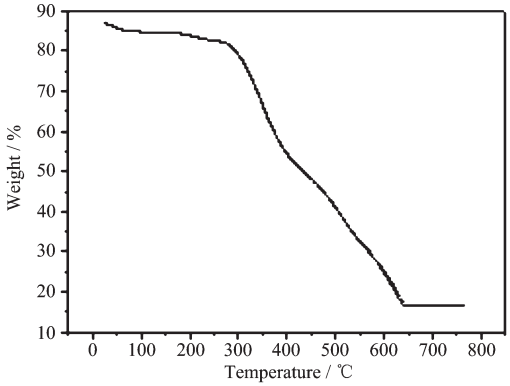



Fig.4　TG curve of the title compound

### 2.4 UV spectrum

The UV spectra (Fig.5) for the title compound, $H_2PDC$ and bix ligands have been investigated in the solid state. For bix ligand, there is no absorption band, while both the title compound and $H_2PDC$ have one absorption band at about 294 nm, which should be assigned to the $n\rightarrow\pi^*$[26] transition of $H_2PDC$. However, after $H_2PDC$ coordinating to the $Co^{2+}$ ion, the absorption intensity slightly increases. It is clearly that the absorption band in $H_2PDC$ remains in the same position with that in the title compound, showing that they are not affected basically by the metal coordination.

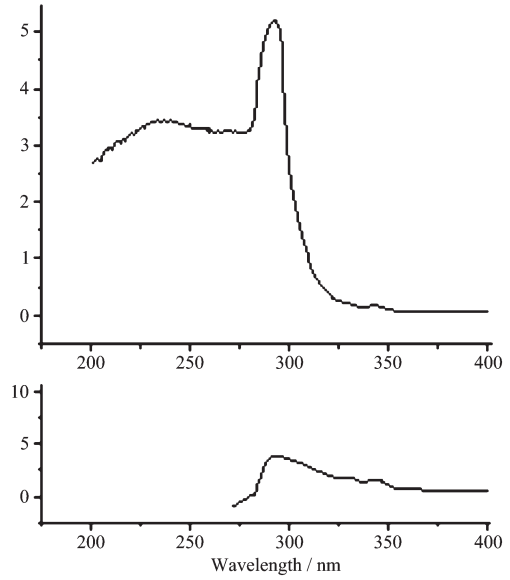



Fig.5　UV spectrum of the title compound and $H_2PDC$ ligand

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