

基于 3,5-双(4-吡啶基)-吡啶的两个钴(II)配合物的合成与晶体结构

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摘要: 用 3,5-双(4-吡啶基)-吡啶(BPYPY)分别与反式-1,4-环己烷二甲酸(*trans*-H₂chdc)和 4,4'-联苯醚二甲酸(H₂oba)组成混合配合物,用温和的溶剂热法与 Co(NO₃)₂·6H₂O 合成了 2 个配合物[Co(BPYPY)₂(H₂O)₄]·(*trans*-chdc)·4H₂O (**1**)和[[Co(BPYPY)(H₂O)₄]·(oba)]_n (**2**),利用 X 射线单晶衍射、元素分析对它们进行了表征。结果显示,配合物 **1** 为单核结构,属于单斜晶系, *P2₁/n* 空间群;配位聚合物 **2** 是一维链通过 O-H···O 氢键形成的三维超分子结构,属于正交晶系, *Pccn* 空间群。

关键词: 晶体结构; 合成; 钴(II)配合物; 含氮配体

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Syntheses and Crystal Structures of Two Cobalt(II) Compounds Based on 3,5-Bis(4-pyridyl)-pyridine

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Abstract: Two compounds [Co(BPYPY)₂(H₂O)₄]·(*trans*-chdc)·4H₂O (**1**) and [[Co(BPYPY)(H₂O)₄]·(oba)]_n (**2**) were synthesized by mild hydrothermal method using two mixed-ligands consisting of 3,5-bis(4-pyridyl)-pyridine (BPYPY), *trans*-1,4'-cyclohexanedicarboxylic acid (*trans*-H₂chdc), 4,4'-oxydibenzoic acid (H₂oba) and Co(NO₃)₂·6H₂O. The complexes were characterized by elemental analysis and their crystal structures were determined by single-crystal X-ray diffraction. Structural analyses show that compound **1** is mononuclear complex, and crystallizes in the monoclinic system, space group *P2₁/n*; compound **2** is a 1D chain and further extended via O-H···O interaction to generate infinite 3D supramolecular structure, and crystallizes in the orthorhombic system, space group *Pccn*. CCDC: 1437803, **1**; 1401543, **2**.

Keywords: crystal structure; synthesis; Co(II) compound; N-containing ligands

Crystal engineering of coordination polymers has attracted intensive attention due to their variable architectures and potential applications in optical materials^[1-3], catalysis^[4-5], gas adsorption^[6], magnetism^[7-8], etc. A large

number of coordination polymers (CPs) of N-containing ligands and carboxylic acids have been reported^[9-12], not only because they can incorporate virtues of different functional groups and it is easier to

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get architecture controlled by changing one of the above two kinds of ligands, but also due to allowing free rotation of the imidazole ring to meet the requirement of coordination geometries of metal ions^[13-14]. To date, however, how to rationally design and synthesize the desired architectures and properties is still a great challenge because the formation of CPs may be easily affected by many factors.

Considering that mixed-ligand of N-containing ligands and carboxylic acids offers greater tunability of the structural framework, two carboxylate ligands of *trans*-1,4-cyclohexanedicarboxylic acid (*trans*-H₂chdc) and 4,4'-oxydibenzoic acid (H₂oba) were introduced to react with 3,5-bis(4-pyridyl)-pyridine (BPYPY) of V-shaped flexible polypyridyl ligand and cobalt nitrate. Then two new compounds [Co(BPYPY)₂(H₂O)₄]·(*trans*-chdc)·4H₂O (**1**) and {[Co(BPYPY)(H₂O)₄]·(oba)}_n (**2**) were obtained. Further, we described their syntheses and crystal structures in detail.

1 Experimental

1.1 Materials and measurement

All the chemicals were commercially purchased and used without further purification. Elemental analyses were performed on an Elementar Vario MICRO Elemental Analyzer. Single crystal X-ray diffraction measurements were carried out on a Bruker Smart APEX II CCD diffraction.

1.2 Synthesis of compounds

[Co(BPYPY)₂(H₂O)₄]·(*trans*-chdc)·4H₂O (**1**): A mixture of Co(NO₃)₂·6H₂O (29.1 mg, 0.1 mmol), *trans*-H₂chdc (17.2 mg, 0.1 mmol) and BPYPY (23.3 mg,

0.1 mmol) were dissolved in 6 mL of H₂O/DMF (2:4, V/V). The final mixture was placed in a Parr Teflon-lined stainless steel vessel (15 mL) and heated at 90 °C for 3 days. After being cooled to room temperature, orange block crystals were obtained. The yield was *ca.* 63% based on BPYPY ligand. Anal. Calcd. for C₃₈H₄₈CoN₆O₁₂(%): C, 54.30; H, 5.72; N, 10.00. Found (%): C, 54.27; H, 5.74; N, 9.88.

{[Co(BPYPY)(H₂O)₄]·(oba)}_n (**2**): A mixture of Co(NO₃)₂·6H₂O (29.1 mg, 0.1 mmol), H₂oba (25.8 mg, 0.1 mmol) and BPYPY (23.3 mg, 0.1 mmol) were dissolved in 6 mL of H₂O/DMF (2:4, V/V). The final mixture was placed in a Parr Teflon-lined stainless steel vessel (15 mL) and heated at 95 °C for 3 days. Orange block crystals were collected. The yield was *ca.* 60% based on BPYPY ligand. Anal. Calcd. for C₂₉H₂₇CoN₃O₉ (%): C, 56.09; H, 4.35; N, 6.77. Found (%): C, 56.07; H, 4.33; N, 6.79.

1.3 Structure determination of Single Crystals

The regular crystals of compounds **1** and **2** were mounted on a Bruker Smart APEX II CCD diffraction (λ=0.071 073 nm). In all cases, empirical absorption corrections by SADABS were applied to the intensity data^[15]. The structures were solved by direct methods, and non-hydrogen atoms were refined anisotropically on *F*² by the full-matrix least-squares techniques using SHELXL-97 program package^[16]. Crystallographic data and structure refinements of compounds **1** and **2** are listed in Table 1. The selected bond lengths and bond angles of compounds are listed in Table 2.

CCDC: 1437803, **1**; 1401543, **2**.

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

Compound	1	2
Empirical formula	C ₃₈ H ₄₈ CoN ₆ O ₁₂	C ₂₉ H ₂₇ CoN ₃ O ₉
Formula weight	839.75	620.47
Crystal system	Monoclinic	Orthorhombic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>Pccn</i>
<i>a</i> / nm	1.479 47(6)	0.800 81(2)
<i>b</i> / nm	0.692 80(3)	2.700 75(7)
<i>c</i> / nm	1.954 89(8)	1.230 98(3)
β / (°)	99.280 0(10)	
<i>V</i> / nm ³	1.977 49(14)	2.662 35(12)

Continued Table 1

<i>Z</i>	2	4
<i>D_c</i> / (g·cm ⁻³)	1.410	1.548
Size / mm	0.28×0.26×0.22	0.30×0.28×0.26
μ / mm ⁻¹	0.504	0.708
<i>F</i> (000)	882	1284
θ_{\min} , θ_{\max} / (°)	2.71, 30.67	2.65, 27.56
Goodness of fit on <i>F</i> ²	1.033	1.058
Reflections collected	13 752	13 759
Independent reflections(<i>R</i> _{int})	4 892(0.021 1)	3048(0.017 7)
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> >2σ(<i>I</i>)]	0.033 7, 0.086 8	0.030 7, 0.084 9
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.045 2, 0.093 8	0.035 7, 0.088 5
(Δρ) _{max} , (Δρ) _{min} / (e·nm ⁻³)	413, -298	272, -349

Table 2 Selected bond lengths(nm) and bond angles (°) of compounds 1 and 2

Compound 1					
Co(1)-O(1)	0.207 40(11)	Co(1)-N(1)	0.218 06(12)	Co(1)-O(2)	0.208 54(11)
O(1)-Co(1)-O(1)#1	180.00(7)	O(1)-Co(1)-O(2)	88.61(5)	O(1)#1-Co(1)-O(2)	91.39(5)
O(1)-Co(1)-O(2)#1	91.39(5)	O(2)-Co(1)-O(2)#1	180.00(8)	O(2)-Co(1)-N(1)#1	91.04(4)
O(1)-Co(1)-N(1)#1	87.54(5)	O(1)-Co(1)-N(1)	92.46(5)	O(1)#1-Co(1)-N(1)	87.54(5)
N(1)-Co(1)-O(2)	88.96(4)	O(2)#1-Co(1)-N(1)	91.04(4)	N(1)#1-Co(1)-N(1)	180.00(16)
Compound 2					
Co(1)-N(1)	0.216 16(11)	Co(1)-O(1)	0.209 37(11)	Co(1)-O(2)	0.213 65(11)
O(2)-Co(1)-N(1)	89.77(4)	O(1)-Co(1)-O(2)#2	93.38(4)	O(2)-Co(1)-O(2)#2	180
O(1)#2-Co(1)-O(1)	180	O(1)-Co(1)-O(2)	86.62(4)	N(1)#2-Co(1)-N(1)	180.00(3)
O(1)-Co(1)-N(1)	87.11(4)	O(2)#2-Co(1)-N(1)	90.23(4)	O(1)#2-Co(1)-N(1)	92.89(4)

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

2 Result and discussion

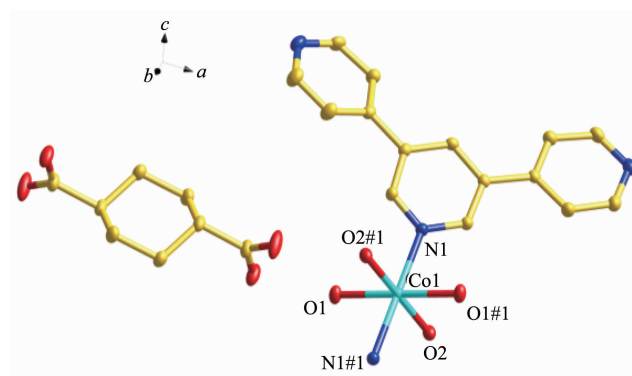
2.1 Crystal structure of compound 1

Compound **1** crystallizes in the monoclinic crystal system with *P2₁/n* space group. The asymmetric unit consists of half of a Co atom, one BPYPY ligand, two coordinated water molecules and half of a free *trans*-chdc²⁻, two free water molecules. As shown in Fig.1, each Co(II) atom is six coordinated by two nitrogen atoms from two BPYPY ligands and four oxygen atoms from four coordinated water molecules, to form the nuclear of [Co(BPYPY)₂(H₂O)₄]. The bond distances

of Co-N are 0.218 06(12) nm. The Co-O(1) bond length is 0.207 40(11) nm, and Co-O(2) bond length is 0.208 54(11) nm. It is noteworthy that [Co(BPYPY)₂(H₂O)₄] cross-link *trans*-chdc²⁻ by O-H···O hydrogen bonds generating the 2D network (Fig.2).

2.2 Crystal structure of compound 2

Compound **2** crystallizes in the orthorhombic crystal system with the space group of *Pccn*, and the asymmetric unit consists of half of a Co atom, half of a BPYPY ligand, two coordinated water molecules, half of a free completely deprotonated oba²⁻ ligand. Each Co(II) atom is surrounded by two nitrogen atoms



Thermal ellipsoids were drawn at the 30% level, and the hydrogen atoms were omitted for clarity; Symmetry codes: #1: $-x+1, -y+1, -z$

Fig.1 Coordination environment of the Co(II) cation in compound **1**

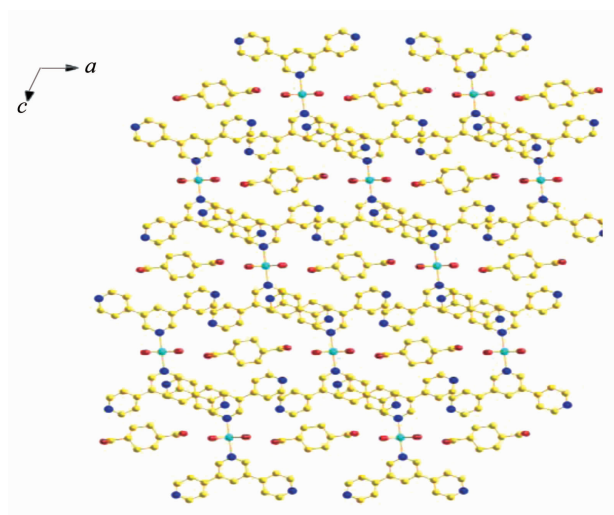
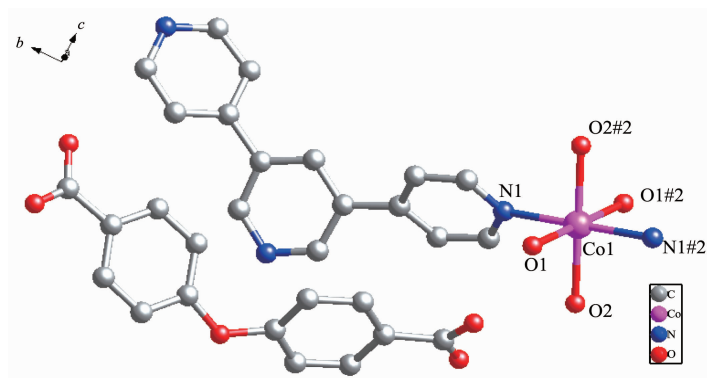


Fig.2 2D network of compound **1**

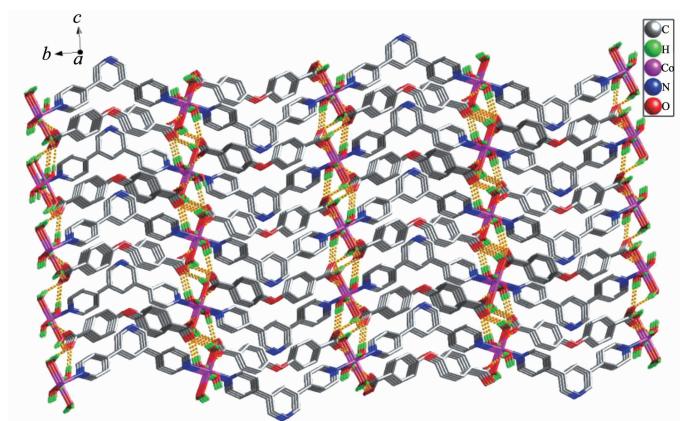


All hydrogen atoms were omitted for clarity; Symmetry codes: #2: $-x+1, -y, -z+1$

Fig.3 Coordination environment of the Co(II) cation in compound **2**

from two BPYPY ligands, and four oxygen atoms from four coordinated water molecules, adopting an octahedral geometry (Fig.3). The bond distance of Co-N is 0.216 16(11) nm. The Co-O bond lengths are 0.209 37(11) and 0.213 65(11) nm, respectively. The

1D linear chain with a Co \cdots Co distance of 1.408 49 nm and a Co \cdots Co \cdots Co angle of 180.00° is generated by BPYPY ligands and the Co(II) cations. Then, the 1D linear chains are held together via O-H \cdots O interaction to generate an infinite 3D network (Fig.4).



The O-H...O hydrogen bonds are shown as dashed lines

Fig.4 3D infinite network of compound 2

3 Conclusions

In summary, by using the V-shaped ligand, 3, 5-bis (4-pyridyl)-pyridine (BPYPY), and two kinds of dicarboxylates, *trans*-1,4'-cyclohexanedicarboxylic acid (*trans*-chdc) and 4,4'-oxydibenzoic acid (H₂oba), we have synthesized two new compounds in mild hydrothermal method. Compound 1 has a 2D network generated by hydrogen bond cross-linked [Co(BPYPY)₂(H₂O)₄] and *trans*-chdc²⁻. Compound 2 is a 1D chain and further extended via O-H...O interaction to generate infinite 3D supramolecular structure.

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