

## 1,3-二吡啶基苯和 4,4'-二羧基二苯砷构筑的钴(II) 配合物合成、结构和性质

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**摘要:** 以两种 V 型的配体 4,4'-二吡啶基苯(1,3-dpb)和 4,4'-二羧基二苯砷(H<sub>2</sub>sdb), 和钴(II)通过溶剂热反应合成了 1 个配位聚合物 {[Co(dpb)(sdb)(H<sub>2</sub>O)<sub>2</sub>]·2H<sub>2</sub>O·DMF}<sub>n</sub> (**1**)。对其进行了红外、热重、粉晶衍射、单晶衍射等表征, 配合物属于三斜晶系, 空间群  $P\bar{1}$ 。其中 Co(II) 的 2 个顶点被水分子占据, 相邻的钴(II)离子连接着 1,3-二吡啶基苯和 4,4'-二羧基二苯砷形成一维的双绳链, 相邻的链之间通过羧基-配位水和配位水-配位水间的氢键相互连接形成二维的层状结构, 层状结构之间通过砷基-配位水间的氢键又相互连接形成三维结构。此外, 还研究了配合物的固体紫外-可见光谱。

**关键词:** 配位聚合物; V-型配体; 固体紫外-可见光谱

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## Synthesis, Structure and Property of Cobalt(II) Complex Constructed by 1,3-Dipyridyl Benzene and 4,4'-Bulfonyldibenzoic Acid

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**Abstract:** A coordination polymer {[Co (dpb)(sdb)(H<sub>2</sub>O)<sub>2</sub>]·2H<sub>2</sub>O·DMF}<sub>n</sub> (**1**) was prepared under hydrothermal conditions based on two types of V-shaped ligand 1,3-dipyridyl benzene (1,3-dpb) with 4,4'-sulfonyldibenzoic acid (H<sub>2</sub>sdb). The complex was characterized by IR spectroscopy, TGA, X-ray powder and single-crystal diffraction. It crystallizes in the triclinic system, space group  $P\bar{1}$ . The neighboring Co(II) ions are linked by dpb and sdb<sup>2-</sup> anions to form infinitely 1D double-strand chain. The apical positions of Co(II) ions are defined by two coordinated water. The adjacent chains were connected by strong hydrogen bonds (coordinated water-carboxyl groups and coordinated water-coordinated water) to form 2D layer. The adjacent layers were also connected by strong hydrogen bonds (coordinated water-sulfonyl groups) to generate 3D network. In addition, the solid-state UV-Vis of complex **1** was also studied. CCDC: 959114.

**Keyword:** coordination polymer; V-shaped ligand; UV-Vis

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The designed construction of metal-organic framework from various V-shaped molecular building blocks connected by coordination bond, supramolecular contacts, is currently a flourishing research field due to their intriguing aesthetic structures<sup>[1-2]</sup>, as well as their promising applications in photochemistry<sup>[3-4]</sup>, molecular magnetism<sup>[5-6]</sup>, and molecular sorption<sup>[7-8]</sup>. Recently, more and more V-shaped ligands have been widely employed to construct coordination polymer with fascinating architectures and interesting properties<sup>[9-10]</sup>. 4,4'-sulfonyldibenzoic acid ( $H_2sdb$ ) presents a V-shaped linker, it has irregular orientations when it coordinates to metals, which may give rise to various structures. In mixed multicomponent complex, the use of this ligand may have a crucial effect on their frameworks and topologies, and gives us additional options to tune the structures<sup>[11]</sup>. To test the ability of this ligand to give new architectures and topologies,  $H_2sdb$ , 1,3-dipyridyl benzene (1,3-dpb) and bivalent cobalt salt were selected to solvothermally synthesize a new coordination polymer with intriguing structure, namely,  $\{[Co(dpb)(sdb)(H_2O)_2] \cdot 2H_2O \cdot DMF\}_n$ .

## 1 Experimental Section

### 1.1 Materials and Methods

The reagents and solvents employed were commercially available and used as received. IR absorption spectrum of **1** was recorded in the range of 400~4000  $cm^{-1}$  on a Nicolet (Impact 410) spectrometer with KBr pellet. C, H, and N analyses were carried out with a Perkin-Elmer 240C elemental analyzer. Powder X-ray diffraction (PXRD) measurements were performed on a Bruker D8 Advance X-ray diffractometer using Cu  $K\alpha$  radiation (0.154 18 nm), in which the X-ray tube was operated at 40 kV and 40 mA. Solid-state UV-Vis diffuse reflectance spectra was performed at room temperature using Shimadzu UV-3600 double monochromator spectrophotometer,  $BaSO_4$  was used as a 100% reflectance standard for all materials. The as-synthesized sample was characterized by thermogravimetric analysis (TGA) on a Perkin Elmer thermogravimetric analyzer Pyris 1

TGA up to 1 023 K using heating rate of 10  $K \cdot min^{-1}$  under  $N_2$  atmosphere.

### 1.2 Synthesis of the compound

A mixture of  $Co(NO_3)_2 \cdot 6H_2O$  (0.2 mmol), dpb (0.1 mmol) and  $H_2sdb$  (0.1 mmol) was dispersed in 8 mL  $DMF/H_2O/C_2H_5OH$  (1:2:1, V/V/V), the final mixture was placed in a Parr Teflon-lined stainless steel vessel (15 mL) and heated at 100  $^{\circ}C$  for 3 d. Purple crystals were obtained and the crystals were filtered off, washed with mother liquid, and dried under ambient condition. (Yield: 56% based on dpb). Anal. Calcd. for  $C_{33}H_{35}CoN_3O_{11}S$  (%): C, 53.51, H, 4.76, N, 5.67; Found(%): C, 53.37, H, 4.86, N, 5.75. IR (KBr,  $cm^{-1}$ ): 3 485(w), 3 062(w), 2 360(m), 1 667(s), 1 604(s), 1 549(s), 1 383(s), 1 298(w), 1 160(m), 1 093(m), 1 010(w), 844(w), 793(m), 734(s), 616(m).

### 1.3 Crystal structure determination

X-ray crystallographic data of **1** was collected at room temperature using epoxy-coated crystal mounted on glass fiber. All measurements were made on a Bruker Smart Apex CCD diffractometer with graphite-monochromated Mo  $K\alpha$  radiation ( $\lambda=0.071\ 073$  nm). The structure of complex **1** was solved by direct methods, and the non-hydrogen atoms were located from the trial structure and then refined anisotropically with SHELXTL using a full-matrix least-squares procedure based on  $F^2$  values<sup>[12]</sup>. The distribution of peaks in the channels of **1** were chemically featureless to refine using conventional discrete-atom models. To resolve these issues, the contribution of the electron density by the remaining solvents was removed by the SQUEEZE routine in PLATON<sup>[13]</sup>. The numbers of solvent molecules were obtained by element analyses and TGA. The hydrogen atoms positions were fixed geometrically at calculated distances and allowed to ride on the parent atoms. The crystallographic data are summarized in Table 1, while the selected bond lengths and angles are given in Table 2.

CCDC: 959114.

## 2 Results and discussion

### 2.1 Crystal structure

The asymmetric unit of **1** contains two indepen-

Table 1 Crystal data and structure refinement for complex 1

Formula	C <sub>33</sub> H <sub>35</sub> CoN <sub>3</sub> O <sub>11</sub> S	$\mu / \text{mm}^{-1}$	0.692
Formula Weight	740.63	$F(000)$	650
Crystal System	Triclinic	Crystal size / mm	0.28×0.20×0.17
Space group	$P\bar{1}$	Temperature / K	296
$a / \text{nm}$	1.155 7(2)	Tot., Uniq. Data	10 582, 5 293
$b / \text{nm}$	1.257 7(3)	$R_{\text{int}}$	0.052
$c / \text{nm}$	1.282 9(3)	Observed data ( $I > 2\sigma(I)$ )	3 469
$\alpha / (^{\circ})$	61.263(2)	$N_{\text{ref}}, N_{\text{par}}$	5 223, 382
$\beta / (^{\circ})$	79.229(2)	$\theta_{\text{min}}, \theta_{\text{max}} / (^{\circ})$	1.8, 25.0
$\gamma / (^{\circ})$	66.854(2)	$R, wR_2$ (all data)	0.051 9, 0.143 4
$V / \text{nm}^3$	1.503 4(6)	$S$ (all data)	0.959
$Z$	2	Max. and Av. Shift / Error	0.000, 0.000
$D_c / (\text{g} \cdot \text{cm}^{-3})$	1.395	$(\Delta\rho)_{\text{min}}, (\Delta\rho)_{\text{max}} / (\text{e} \cdot \text{nm}^{-3})$	-310, 350

Table 2 Selected bond lengths (nm) and angles ( $^{\circ}$ ) for the complex 1

Co1-O5	0.206 5(2)	Co1-O8	0.216 1(2)	Co1-N1	0.216 2(3)
Co2-O7	0.207 5(2)	Co2-O2	0.209 6(3)	Co2-N2	0.218 3(3)
O5-Co1-O5a	179.999(1)	O5-Co1-O8	98.13(10)	O5a-Co1-O8	81.87(10)
O8-Co1-O8	180.0	O5-Co1-N1	88.99(11)	O5-Co1-N1a	91.01(11)
O8-Co1-N1	89.19(11)	O8-Co1-N1a	90.81(11)	N1-Co1-N1a	180.00(16)
O7-Co2-O7b	179.999(1)	O7-Co2-O2	89.19(10)	O7-Co2-O2b	90.81(10)
O7-Co2-N2b	89.29(11)	O2b-Co2-N2	89.00(11)	O2-Co2-N2	91.00(11)
N2-Co2-N2b	180.00(17)				

Symmetry codes: a:  $3-x, 0.5+y, 1.5-z$ ; b:  $1-x, -0.5+y, 1-z$ .

dent Co(II) cations (two Co(II) are on general special position), one dpb ligand, one  $\text{sdb}^{2-}$  anion and two coordinated water molecules. As shown in Fig.1, two types of Co(II) are all located in octahedral coordination environment with two N atoms from two dpb, four O atoms from two  $\text{sdb}^{2-}$  and two coordinated water. The Co-N lengths are 0.216 6(4) and 0.217 9(4) nm,

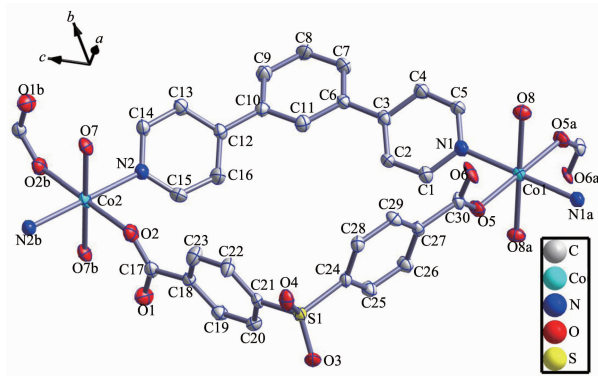
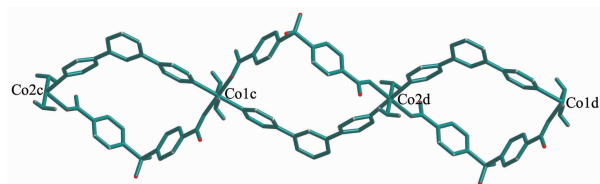
Hydrogen atoms are omitted for clarity; Symmetry code: a:  $1-x, 1-y, -z$ ; b:  $-x, 1-y, 2-z$ 

Fig.1 Coordination environment of complex 1

and the Co-O lengths are in the range of 0.206 7(3)~0.215 2(4) nm, which are similar to those found in other Co(II) complexes. The dihedral angle between two pyridyl rings is  $40.197^{\circ}$ , the dihedral angle between two benzene rings of  $\text{sdb}^{2-}$  is  $73.245^{\circ}$ .

The neighboring Co(II) ions linked V-shaped dpb and  $\text{sdb}^{2-}$  into an infinitely double-strand chain containing  $[\text{Co}_2(\text{dpb})(\text{sdb})]_n$  ring, and the adjacent Co1...Co2 distance is 1.304 9 nm (Fig.2). The formation of the ring benefit not only from the shape of the two V-shaped ligands but also from the match of the two ligands in length. There are strong (O-H...O) hydrogen bonds (O...O distance is 0.263 0~0.294 2 nm) between the adjacent chains, which involve the coordinated water and the carboxyl groups from adjacent chains (Fig.3), the hydrogen bonds extend the structure from infinitely chains to 2D layer. Similarly, these identical layers also exist strong hydrogen bonds (O...O distance is 0.295 8 nm) formed by

coordinated water and sulfonyl groups (green). These hydrogen bonds change the framework from 2D layer to 3D network (Fig.4). Obviously, which suggests that sulfonyl group and coordinated water play an important role in increasing the dimension and sustaining the stabilizing the whole structure, as it does not decompose till 370 °C.



Adjacent distance of Co...Co is 1.304 9 nm; Symmetry code: c:  $x, y, 1+z$ ; d:  $1+x, y, -1+z$

Fig.2  $[\text{Co}_2(\text{dpb})(\text{sdb})]$  metallocyclic ring

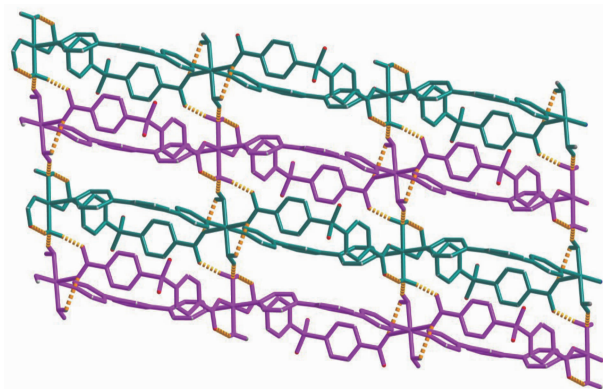


Fig.3 View of 2D sheet induced by hydrogen bonds from coordinated water and carboxyl groups

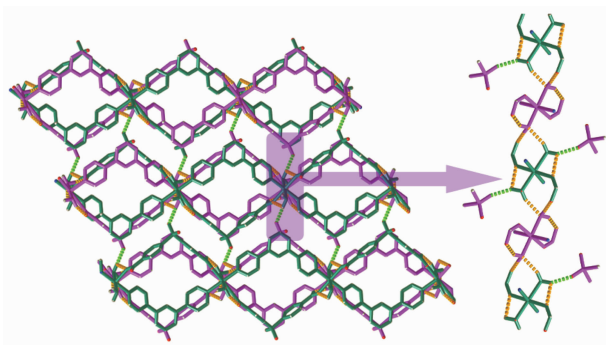


Fig.4 View of 3D framework induced by hydrogen bonds from coordinated water and sulfonyl groups

## 2.2 XRD and thermal analysis results

The PXRD experimental and computer-simulated patterns of complex **1** are shown in Fig.5. The results demonstrate that the experimental PXRD pattern perfectly match the simulated one based on the single-crystal X-ray data. To characterize compound **1**

more fully in terms of thermal stability, its thermal behavior was studied by TGA (Fig.5). A rapid weight loss of 6.41% (Calcd. 6.56%) is observed from 30 to 80 °C, which is attributed to the loss of the two lattice water molecules. And then a weight of 4.21% (Calcd. 4.12%) from 150 to 250 °C, which belongs to the loss of two coordinated water and one DMF molecules, the framework collapses starting at 370 °C (Fig.6).

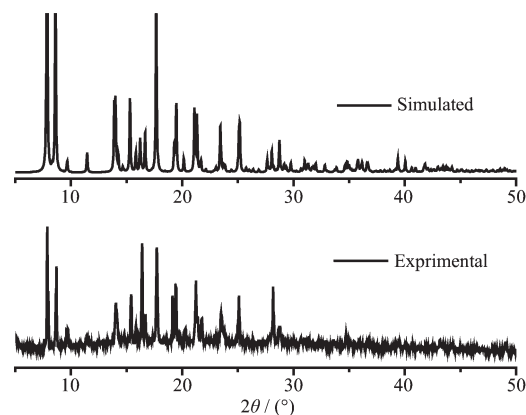


Fig.5 Powder X-ray diffraction pattern of **1**

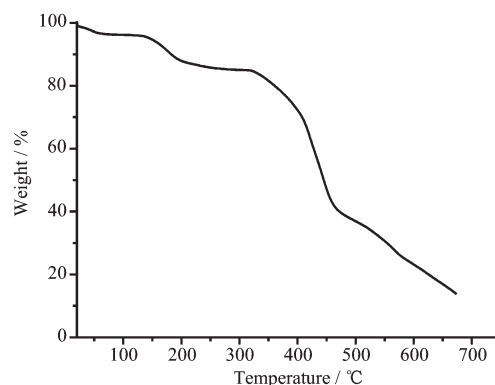


Fig.6 TGA curve of complex **1**

## 2.3 UV-Vis Absorption Spectrum

The UV-Vis absorption spectrum of complex **1** shows intense wide absorption peaks at 450~550 nm,

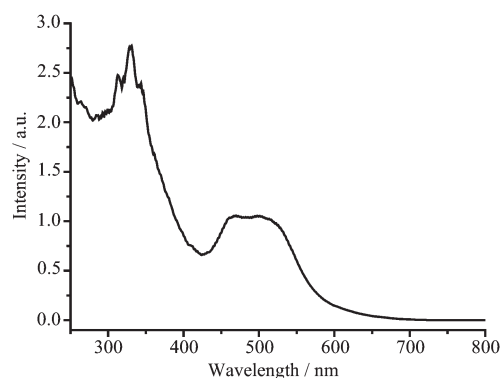


Fig.7 UV-Vis spectrum of complex **1**

which can be assigned as *d-d* transitions of Co(II), the probably reason of wide absorption peaks is that Co(II) was resided in CoN<sub>2</sub>O<sub>4</sub> coordination environment, and generated a distortion octahedron. While lower energy bands from 330 to 370 nm are assigned as ligand-to-metal charge-transfer (LMCT) transitions<sup>[14]</sup> (Fig.7).

### 3 Conclusion

In summary, complex **1** is an infinitely double-strand chain, which further generated 3D network by two type hydrogen bonds. The results demonstrate that the V-shaped ligands can be well used as the structure-directing tool in the synthesis of unusual coordination polymers. Further study about these ligands are in progress.

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