

Synthesis and Crystal Structure of 1D Coordination Polymer of *N,N'*-Bis(3-pyridylmethyl)-1,4-benzenedicarboxamide and Cobalt(II) Nitrate

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A novel cobalt(II) coordination polymer, $\{[\text{Co}(\text{bpmb})(\text{H}_2\text{O})_2(\text{C}_2\text{H}_5\text{OH})_2] \cdot (\text{NO}_3)_2\}_\infty$ (**1**), where bpmb = *N,N'*-bis(3-pyridylmethyl)-1,4-benzenedicarboxamide, was synthesized by self-assembly of the two topic ligands with cobalt nitrate in ethanol solution, and characterized structurally by X-ray crystallography analysis. The crystal data belong to triclinic, space group *P*1 with cell parameters $a=0.8911(3)$ nm, $b=0.9042(3)$ nm, $c=1.0068(3)$ nm, $\alpha=73.083(5)^\circ$, $\beta=81.069(5)^\circ$, $\gamma=76.210(5)^\circ$, $R_1=0.0518$, $wR_2=0.0947$. The results of structure analysis indicate that each bpmb ligand coordinates two Co(II) atoms and each metal atom is in octahedral coordination geometry with four oxygen atoms of two ethanol and two water molecules, two nitrogen atoms from two different bpmb ligands in *trans* position forming an infinite 1D chain-like structure. There are hydrogen bonding and π - π stacking interaction among these chains, leading to supramolecular formation with 3D net structure.

Keywords Co(II) complex, crystal structure, hydrogen bonding, π - π stacking, coordination polymer

Introduction

The research on architecture of coordination polymers has been mushrooming recently for their interesting structural properties and potential applications to magnetism, NLO material, electrical conductivity, ion exchange, *etc.*¹⁻⁵ Coordination polymer is a family which is composed of 1D chains, 2D sheets, and 3D framework of building blocks connected via metal-ligand coordination. Hydrogen bonding and π - π stacking interaction are often further utilized to generate those coordination polymers into multidimensional supramolecular networks.⁶⁻¹¹ In this paper the results of synthesis and crystal structure determination of a novel 1D coordination polymer of Co(II) with *N,N'*-bis(3-pyridylmethyl)-1,4-benzenedicarboxamide are reported. The 1D coordination polymer, $\{[\text{Co}(\text{bpmb})(\text{H}_2\text{O})_2(\text{C}_2\text{H}_5\text{OH})_2] \cdot (\text{NO}_3)_2\}_\infty$ (**1**) contains bpmb (bpmb = *N,N'*-bis(3-pyridylmethyl)-1,4-benzenedicarboxamide) acting as bridging ligand. For bpmb, pyridine pendant ring can perform π - π stacking interaction, amido group can perform hydrogen bonding, methylene is flexible part and phenylene is rigid part. These characters of the ligand make it easy to construct novel supramolecular structure.

Experimental

All reagents were obtained from a commercial source and used without further purification. Bpmb (*N,N'*-bis(3-pyridylmethyl)-1,4-benzenedicarboxamide) was prepared according to the reported method.¹²

Preparation

Cobalt nitrate hexahydrate (0.492 g, 0.003 mmol) was added into one arm of H-shape tube, and bpmb (1.030 g, 0.003 mmol) was added into the other one, then ethanol was added carefully. After about one month, red block-shape single crystal of **1** suitable for X-ray diffraction was obtained by the diffusion method. IR ν : 3390 (s), 3305 (s), 2982 (m), 1645 (s), 1610 (m), 1584 (m), 1020 (s), 878 (m), 815 (m), 792 (m), 710 (m) cm^{-1} . Anal. calcd for $\text{C}_{24}\text{H}_{34}\text{CoN}_6\text{O}_{12}$: C 43.84, H 5.21, N 12.78; found C 43.51, H 5.73, N 12.39.

X-ray structure determination

A single crystal of **1** was selected for data collection on a Bruker Smart CCD area detector with graphite monochromated Mo $K\alpha$ radiation ($\lambda=0.071073$ nm). The structure was solved by direct methods using SHELXL-97 program.¹³ A summary of the crystallographic information is given in Table 1, and selected bond distances and angles are listed in Table 2.

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Table 1 Summary of crystallographic data for **1**

Empirical formula	C ₂₄ H ₃₄ CoN ₆ O ₁₂
Formula weight	657.50
Temperature/K	293(2)
Wavelength/nm	0.071073
Crystal system, space group	Triclinic, $P\bar{1}$
Unit cell dimensions	
<i>a</i> /nm	0.8911(3)
<i>b</i> /nm	0.9042(3)
<i>c</i> /nm	1.0068(3)
α /°	73.083(5)
β /°	81.069(5)
γ /°	76.210(5)
<i>V</i> /nm ³	0.7505(4)
<i>Z</i>	1
Calculated density/(g · cm ⁻³)	1.455
Absorption coefficient/mm ⁻¹	0.642
<i>F</i> (000)	343
Crystal size/mm ³	0.30 × 0.25 × 0.20
θ range for data collection/°	2.36 to 26.41
Limiting indices	-9 ≤ <i>h</i> ≤ 11, -11 ≤ <i>k</i> ≤ 11, -10 ≤ <i>l</i> ≤ 12
Reflections collected/unique	3679/2832 [<i>R</i> _{int} = 0.0251]
Completeness to θ = 26.41/°	91.7%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.000000 and 0.818760
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	2832/0/199
Goodness-of-fit on <i>F</i> ²	1.011
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0518, <i>wR</i> ₂ = 0.0947
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0973, <i>wR</i> ₂ = 0.1100
Largest diff. peak and hole/(e · nm ⁻³)	395 and -242

Table 2 Selected bond distances (nm) and angles (°) for **1**

Co(1)—O(2)	0.2076(3)	Co(1)—O(1W)	0.2109(2)
Co(1)—N(1)	0.2148(3)	N(1)—C(5)	0.1339(4)
N(1)—C(1)	0.1343(4)	N(2)—C(7)	0.1333(4)
N(2)—C(6)	0.1453(4)	O(1)—C(7)	0.1223(4)
C(1)—C(2)	0.1379(4)	C(2)—C(3)	0.1371(5)
C(2)—C(6)	0.1513(4)	C(3)—C(4)	0.1378(5)
C(4)—C(5)	0.1375(5)	C(7)—C(8)	0.1507(5)
C(8)—C(9)	0.1387(4)	C(9)—C(10)	0.1375(5)
O(2)—C(11)	0.1423(5)	C(11)—C(12)	0.1400(7)
O(2)-Co(1)-O(2)#1	180.00(18)	O(2)#1-Co(1)-O(1W)	87.40(10)
O(2)-Co(1)-O(1W)	92.60(10)	O(2)-Co(1)-N(1)	90.43(10)
O(2)#1-Co(1)-N(1)	89.57(10)	O(1W)-Co(1)-N(1)	90.15(10)
O(1W)#1-Co(1)-N(1)	89.85(10)	C(5)-N(1)-C(1)	116.7(3)
C(5)-N(1)-Co(1)	123.5(2)	C(1)-N(1)-Co(1)	119.2(2)
O(1)-C(7)-N(2)	122.1(3)	O(1)-C(7)-C(8)	121.1(3)
N(2)-C(7)-C(8)	116.8(3)	C(9)-C(8)-C(10)#2	118.4(3)
C(9)-C(10)-C(8)#2	121.0(3)		

Symmetry transformations used to generate equivalent atoms: #1 -*x*, -*y*, -*z*; #2 -*x*+1, -*y*+1, -*z*+1.

Results and discussion

The coordination environment of the metal atom in **1** is shown in Figure 1. The Co(II) atom lies at the crystallographic center and has a slightly distorted octahedral coordination. Two nitrogen atoms [N(1) and N(1a)] are from the two symmetry-related bpmb ligands [Co(1)—N(1), 0.2148(3) nm], two oxygen atoms [O(1W) and O(1Wa)] are from the two symmetry-related water molecules [Co(1)—O(1W), 0.2109(2) nm], the other two positions are occupied by two oxygen atoms [O(2) and O(2a)] from the two symmetry-related ethanol molecules [Co(1)—O(2), 0.2076(3) nm] with coordination angles [O(2)—Co(1)—O(1W) 92.60(10)°, O(2)#1—Co(1)—O(1W) 87.40(10)°]. These and other important bond lengths and angles are listed in Tables 1 and 2. Every two Cobalt atoms are bridged by the bpmb, the Co(II)···Co(II) intra-chain distance is 1.9539 nm. In **1**

the flexible ligand exhibits zigzag-like shape while **1** is viewed from different direction (Figure 2).]

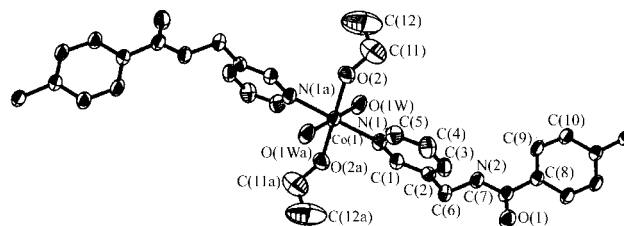


Figure 1 Coordination environment of Co(II) in the polymer with atom 50% probability ellipsoids (H atoms and anions are omitted for clarity).

It is interesting to note that hydrogen bond is formed between the water ligand and the oxygen from neighboring chains [O(1W)···O(1) (symmetry code:

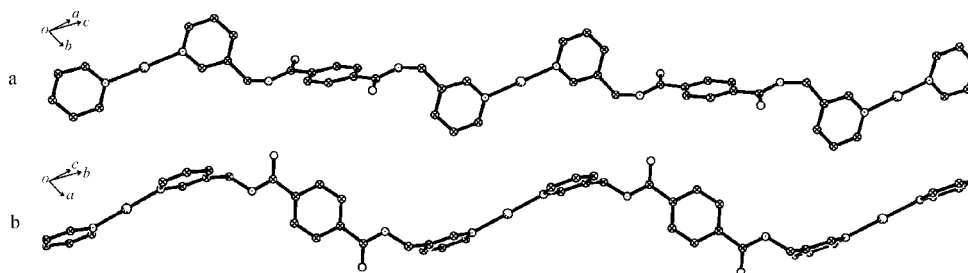


Figure 2 1-D zigzag-like chain viewed from different directions (a) and (b) (waters, ethanols and anions are omitted for clarity).

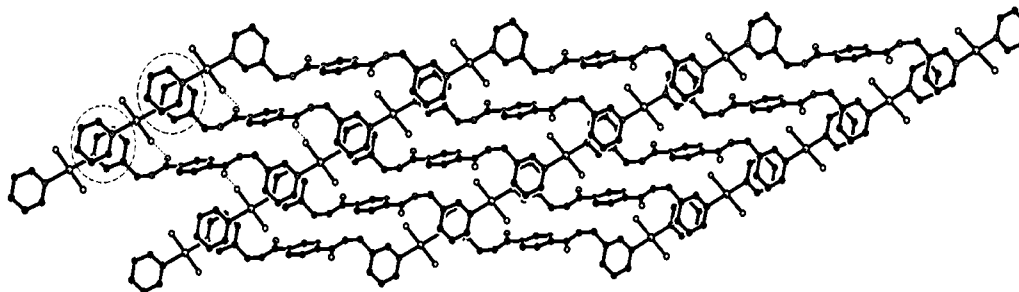


Figure 3 Extended 2D structure of **1** (the interchain offset face-to-face π - π interactions are indicated as dotted circles and hydrogen bonds are indicated as dotted lines).

$-x, -y, 1-z$) 0.27647 nm, O(1W)—H(1B)···O(1) 170.64°]. In combination with the hydrogen bond, aromatic π - π stacking interactions are also apparent in **1**, as shown in Figure 3. It can be depicted by both centroid-centroid and plane-to-plane distances. In **1**, all lateral pyridyl planes of ligands from adjacent zigzag-like chains are parallel-placed, the centroid-centroid distance is 0.4176 nm and plane-to-plane distance is 0.3610 nm. Those interactions link 1-D chains into 2-D layer. The arrangement and stacking of those layers were further extended into a three-dimensional supramolecular network featuring one-dimensional channels running along the a -axis. Nitrate anions as the guest reside in the channels (Figure 4).

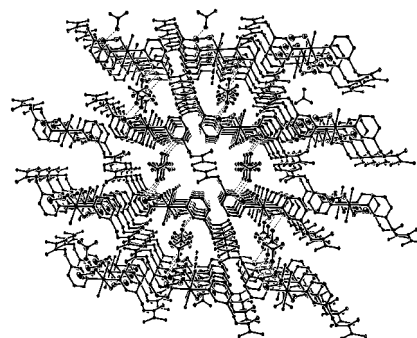


Figure 4 Stacking of the 1-D zigzag-like chain showing 1-D channel in which anions are trapped.

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