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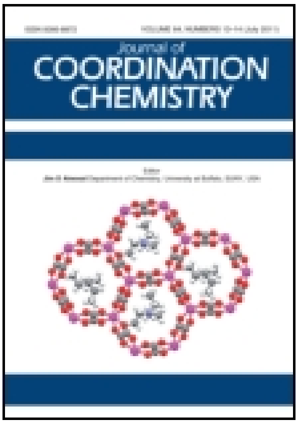

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3-D Coordination polymer containing a 1-D tunnel filled with 4,4′-bpy: synthesis, crystal structure, and characterization

Fan Guang [a] [b] , Yang Zu-Pei [a] , Zhang Yin-Li [b] , Sun Jia-Juan [b] , Zheng Min-Yan [b] & Yu Zhan-Jiang [b]
[a] College of Chemistry and Material Science, Shaanxi Normal University , Xi′an, Shaanxi 710062, China
[b] College of Chemistry and Chemical Engineering, Xianyang Normal University , Xianyang, Shaanxi 712000, China
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3-D Coordination polymer containing a 1-D tunnel filled with 4,4′-bpy: synthesis, crystal structure, and characterization

FAN GUANG†‡, YANG ZU-PEI*†, ZHANG YIN-LI‡, SUN JIA-JUAN‡,
ZHENG MIN-YAN‡ and YU ZHAN-JIANG‡

†College of Chemistry and Material Science, Shaanxi Normal University, Xi'an,
Shaanxi 710062, China
‡College of Chemistry and Chemical Engineering, Xianyang Normal University, Xianyang,
Shaanxi 712000, China

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A coordination polymer, $[Co(2\text{-mpac})_2(4,4'\text{-bpy})\cdot(4,4'\text{-bpy})]_n$ (2-mpac: 5-methyl-2-pyrazinecarboxylic acid; 4,4′-bpy: 4,4′-bipyridine), has been synthesized through hydrothermal synthesis and structurally characterized by X-ray single crystal diffraction. Single crystal X-ray diffraction analysis reveals a 3-D network featuring a 1-D tunnel filled with 4,4′-bpy molecules. Elemental analysis, IR, thermogravimetric analysis, and magnetic properties are presented.

Keywords: Coordination polymer; Crystal structure; 5-Methyl-2-pyrazinecarboxylic acid

1. Introduction

Construction of coordination polymers by self-assembly of polydentate ligands and transition metal ions have attracted considerable interest because of their potential applications in molecular recognition, catalysis, optical, and magnetic materials [1–5]. Rational control over topologies and applications is still a great challenge [6–11].

Large numbers of polynuclear or heteronuclear supramolecular coordination polymers have been successfully prepared by logical choice of ligand such as $M(2\text{-mpac})_2(H_2O)_2$ (M = Mn, Co, Ni, Cu; 2-mpac = 5-methyl-2-pyrazinecarboxylic acid) acting as bridges through their uncoordinated terminal atoms [12–19]. Weak terminal ligands such as methanol or water in the complex ligand may be replaced by ones with stronger coordination such as 4,4′-bipyridine (abbreviated 4,4′-bpy), which is a good bridging ligand to synthesize coordination polymers as linker [20–24], affording new 1-D, 2-D, or 3-D coordination polymers. Complex ligands can be considered as molecular building blocks to construct various coordination polymers.

In a previous work, we designed and synthesized a coordination polymer $[Co_2(2\text{-mpac})_4(4,4'\text{-bpy})\cdot 2H_2O]_n$ with 1 : 1 ratio of $Co(2\text{-mpac})_2(H_2O)_2$ and 4,4′-bpy, featuring neutral 1-D $Co(2\text{-mpac})_2$ chains bridged by 4,4′-bpy to form a 2-D layer [17].

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*Corresponding author. Email: yangzp@snnu.edu.cn

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As part of our ongoing investigations, we changed the ratio of complex ligand and 4,4′-bpy from 1 : 1 to 1 : 2 and obtained a coordination polymer with the formula of [Co(2-mpac)$_2$(4,4′-bpy) · (4,4′-bpy)]$_n$, which has a 1-D tunnel filled with 4,4′-bpy molecules. In this article, we reported the crystal structure and properties of [Co(2-mpac)$_2$(4,4′-bpy) · (4,4′-bpy)]$_n$.

2. Experimental

2.1. *Instruments and reagents*

5-Methyl-2-pyrazinecarboxylic acid and 4,4′-bipyridine were purchased from Acros. All other starting materials were of analytical grade and purchased commercially. C, H, and N elemental analyses were performed on a Vario EL III analyzer. IR spectra were recorded on a BEQ VZNDX 550 FTIR instrument with KBr pellets from 4000 to 400 cm^{-1}. Thermogravimetric analysis (TG-DTG) was performed on a NETZSCH STA 449C thermogravimetric instrument from 25°C to 600°C at a heating rate of 10°C · min^{-1} under static air. Variable temperature magnetic susceptibility data were measured with a polycrystalline sample from 300 to 2 K with a magnetic field of 5 K Oe on a SQUID magnetometer. Diamagnetic corrections were estimated from Pascal's constants.

2.2. *Synthesis of Co(2-mpac)$_2$(H$_2$O)$_2$*

Co(2-mpac)$_2$(H$_2$O)$_2$ was synthesized according to the literature [16] and further proved by elemental analysis and the X-ray single crystal diffraction method.

2.3. *Synthesis of [Co(2-mpac)$_2$(4,4′-bpy) • (4,4′-bpy)]$_n$*

The orange coordination polymer was obtained by hydrothermal synthesis of a mixture of Co(2-mpac)$_2$(H$_2$O)$_2$ (0.1854 g, 0.5 mmol) and 4,4′-bpy (0.1562 g, 1.0 mmol) in 6 mL H$_2$O, sealed in a Teflon-lined stainless container, heated at 140°C for 72 h and slowly cooled to room temperature at 5°C h^{-1}. Yield: 64%. Anal. Calcd for $C_{32}H_{26}CoN_8O_4$ (%): C, 59.59; H, 4.02; N, 17.31%. Found (%): C, 59.54; H, 4.06; N, 17.36. IR (KBr, cm^{-1}) 1647(s), 1595(s), 1518(w), 1465(w), 1415(s), 1344(s), 1165(s), 1063(m), 995(w), 869(m), 794(w).

2.4. *Structure determination*

An orange crystal with dimensions 0.09 × 0.08 × 0.05 mm^3 was mounted on a glass fiber. Diffraction measurements were made on a Rigaku Mercury area-detector diffractometer equipped with a graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 296(2) K. A total of 8640 reflections were collected by using an ω–φ scan mode, of which 3140 were unique with $R_{\text{int}} = 0.0307$ and used in the succeeding structure calculations. Data intensities were corrected by Lorentz-polarization factors and empirical absorption. The structure was solved by

Table 1. Crystal data and structure refinement parameters.

Empirical formula	$C_{32}H_{26}CoN_8O_4$
Formula weight	645.54
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions (Å, °)	
a	9.059(6)
b	9.564(6)
c	9.712(6)
α	107.196(8)
β	90.178(8)
γ	113.405(5)
Volume (Å^3), Z	730.7(8), 1
$F(000)$	333
Calculated density (g cm^{-3})	1.467
Absorption coefficient (mm^{-1})	0.641
Reflections collected	3636
T_{max}/T_{min}	0.9687/0.9371
Data/restraint/parameter	2541/0/206
Goodness-of-fit on F^2	1.080
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0837$, $wR_2 = 0.1147$
R indices (all data)	$R_1 = 0.0917$, $wR_2 = 0.1313$
Largest peak and hole (e Å^{-3})	0.375 and −0.549

Table 2. Selected bond lengths (Å) and angles (°).

Co(1)–O(1)	2.051(4)	Co(1)–N(1)	2.063(4)
Co(1)–N(3)	2.140(4)	O(1)–C(5)	1.279(6)
O(2)–C(5)	1.241(6)	N(1)–C(1)	1.325(6)
N(1)–C(4)	1.341(6)	N(2)–C(2)	1.333(8)
N(2)–C(3)	1.346(7)		
O(1)–Co(1)–N(1)	80.64(14)	O(1)–Co(1)–O(1)#1	180.0(1)
O(1)–Co(1)–N(1)#1	99.36(14)	N(1)–Co(1)–N(3)	90.14(15)
N(1)–Co(1)–N(1)#1	180.0(1)	O(1)–Co(1)–N(3)#1	90.56(14)
N(3)–Co(1)–N(3)#1	180.0(1)	O(2)–C(5)–O(1)	126.7(5)

Symmetry transformations: #1 $-x+3/2$, $y-1/2$, $-z+1/2$.

direct methods by SHELXS-97 [25] and expanded with difference Fourier techniques. All non-H atoms were refined anisotropically by SHELXL-97 [26]. Other details of crystal data, data collection parameters, and refinement statistics are given in table 1. Selected bond distances and angles are given in table 2.

3. Results and discussion

3.1. *Crystal structure*

Single crystal analysis has revealed that the coordination polymer crystallizes in triclinic, space group $P\bar{1}$, and in a 3-D network containing a 1-D tunnel filled with uncoordinated 4,4′-bpy.

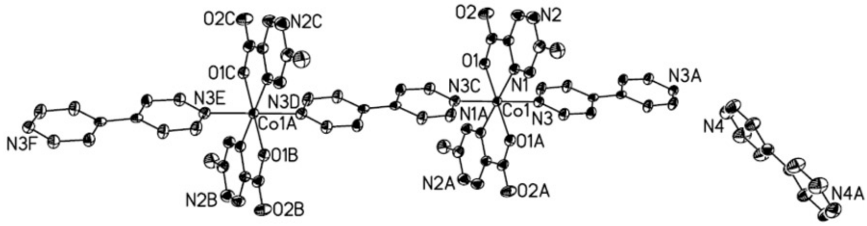

Figure 1. 1-D chain structure of the coordination polymer; hydrogen atoms are omitted for clarity.

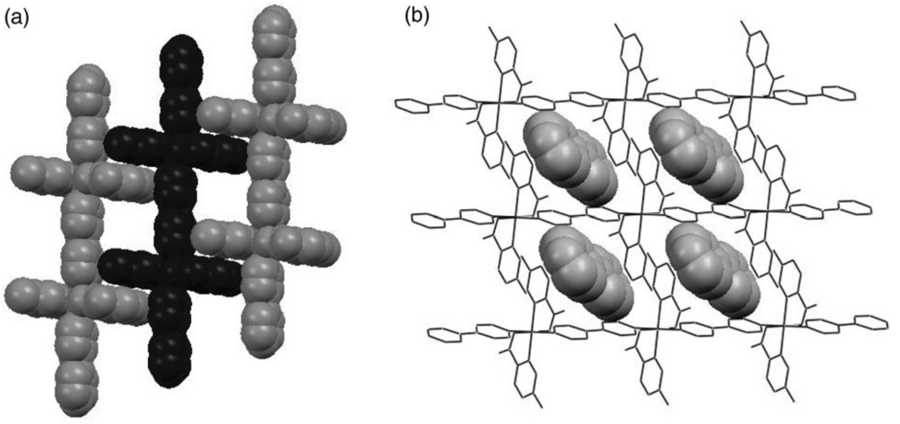

Figure 2. (a) 3-D porous network including 1-D tunnel running along the *b*-axis and (b) 1-D tunnel filled with uncoordinated 4,4′-bpy ligands.

As can be seen from figure 1, the coordination sphere of Co(1) is distorted octahedral. The equatorial plane is constructed with two crystallographically distinguishable nitrogen atoms and two oxygen atoms from two 5-methyl-2-pyrazinecarboxylates with Co(1)–N(1) = 2.063(4) Å and Co(1)–O(1) = 2.051(3) Å. The remaining two axial coordination sites are occupied by two nitrogen atoms from two different 4,4′-bpy ligands with Co(1)–N(3) = 2.140(4) Å. The 4,4′-bpy ligands bridge the Co(2-mpac)$_2$ moieties to form a 1–D chain, shown in figure 1.

Each pair of adjacent chains are packed through π–π stacking interaction of the aromatic ring from 2-mpac ligands in a zipper-like, offset face-to-face fashion with a distance of 3.772 Å [27], constructing a grid-like, 2-D layer (figure 2a). The remarkable feature in the coordination polymer is that the grid-like, 2-D layer is connected into a porous 3-D supramolecular structure containing a 1-D tunnel filled with uncoordinated 4,4′-bpy ligands (figure 2b). Among the free 4,4′-bpy ligands and uncoordinated oxygen atoms of carboxylate from 2-mpac, hydrogen bonds exist with 3.474 Å for C(12)–H(12) $\cdots$ O(1), 3.408 Å for C(7)–H(7) $\cdots$ N(4) and 3.431 Å for C(16)–H(16) $\cdots$ O(2), showing the contribution of the hydrogen-bonding interactions to the stability of the crystal structure.

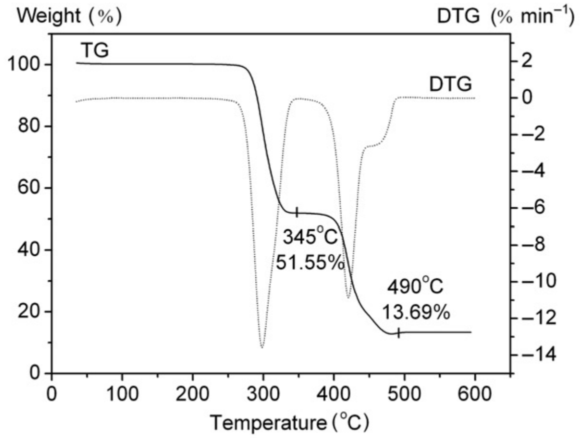

Figure 3. TG analysis curves.

With comparison of $[Co_2(2\text{-mpac})_4(4,4'\text{-bpy}) \cdot 2H_2O]_n$ [17], the 1 : 1 ratio of $Co(2\text{-mpac})_2(H_2O)_2$ and 4,4′-bpy resulted in a 2-D structure featuring *cis*-$Co(2\text{-mpac})_2$ chains bridged by 4,4′-bpy ligands, while the 1 : 2 ratio of $Co(2\text{-mpac})_2(H_2O)_2$ and 4,4′-bpy in $[Co(2\text{-mpac})_2(4,4'\text{-bpy}) \cdot (4,4'\text{-bpy})]_n$ led to a 3-D network containing a 1-D tunnel filled with uncoordinated 4,4′-bpy ligands, showing the influence of reactant ratio on the crystal structure.

3.2. *TG analysis*

The TG analysis (figure 3) shows one well-separated weight loss of 48.45% occurring at 250–345°C, corresponding to the removal of two 4,4′-bpy molecules (Calcd value: 48.39%). No weight loss is observed from 25 to 250°C. Finally, the coordination polymer rapidly decomposed to Co_2O_3 with residue of 13.69%, which accords well with the calculated value of 13.62%.

From the result of TG-DTG analysis, we can draw a conclusion that the 1-D tunnel is a pseudotunnel because the tunnel collapses with loss of 4,4′-bpy.

3.3. *Magnetic properties*

The $\chi_M T$ *versus* T in the 300–2 K range is plotted in figure 4; the $\chi_M T$ value at room temperature equals $2.50\,\text{emu} \cdot \text{mol}^{-1} \cdot \text{K}$, slightly higher than the spin-only value of $1.875\,\text{emu} \cdot \text{mol}^{-1} \cdot \text{K}$ expected for an isolated high spin Co ion with $S = 3/2$ and $g = 2.0$ owing to the orbital contribution of the Co ion [28, 29]. As the temperature is lowered, the $\chi_M T$ value remains almost constant from 300 to 100 K and then abruptly decreases to $0.75\,\text{emu} \cdot \text{mol}^{-1} \cdot \text{K}$ at 2 K. The shape of the curve is characteristic of the presence of an antiferromagnetic interaction. The magnetic susceptibility follows the Curie–Weiss law $\chi_M = C/(T - \theta)$, with $C = 2.55\,\text{emu} \cdot \text{mol}^{-1} \cdot \text{K}$ and $\theta = -3.1\,\text{K}$, and the negative Weiss constant also suggests weak antiferromagnetic interaction between the Co centers from the 1-D chain bridged by 4,4′-bpy with a distance of 11.44 Å, because a C–C single

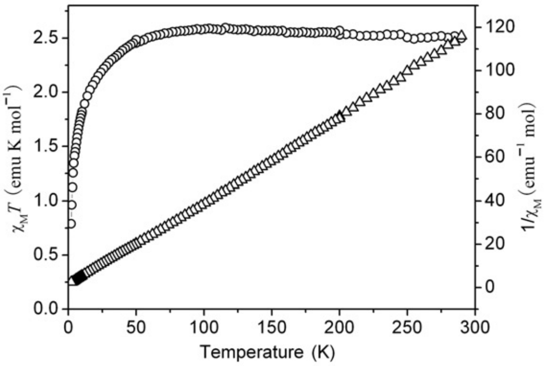

Figure 4. $\chi_M T$ *vs.* T (O) and $1/\chi_M$ *vs.* T (Δ) curves.

bond between two pyridyl groups cannot complete ferromagnetic exchange interactions.

3.4. *Other physical data*

In the IR spectrum of coordination polymer, compared with the spectrum of free 2-mpac and 4,4′-bpy ligands, the appearance of peaks at 1647 and 1415 cm^{-1} can be attributed to asymmetric and symmetric vibrations of carboxyl groups [30]. The separations (Δ) between $\nu_{asym}(COO^-)$ and $\nu_{sym}(COO^-)$ is 232 cm^{-1}, which can be assigned to monodentate carboxylate, consistent with the crystal structure [31, 32].

The X-ray powder diffraction patterns of the simulated and actual measurement agree fairly well, indicating coordination polymer is pure phase, shown in Supplementary material.

4. Conclusions

We report the hydrothermal synthesis, crystal structure, and properties of $[Co(2\text{-mpac})_2(4,4'\text{-bpy}) \cdot (4,4'\text{-bpy})]_n$, which has a 1-D tunnel filled with 4,4′-bpy molecules. The TG-DTG analysis reveals that the 1-D tunnel is a pseudotunnel because the tunnel collapses with loss of 4,4′-bpy. Magnetic properties suggest weak antiferromagnetic interactions between Co centers.

Supplementary material

Crystallographic data for the title compound has been deposited with the Cambridge Crystallographic Data Center as supplementary publications, CCDC No. 818108. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB21EZ, UK; Fax: +44 1223 336 033; E-mail: deposit@ccdc.cam.ac.uk

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