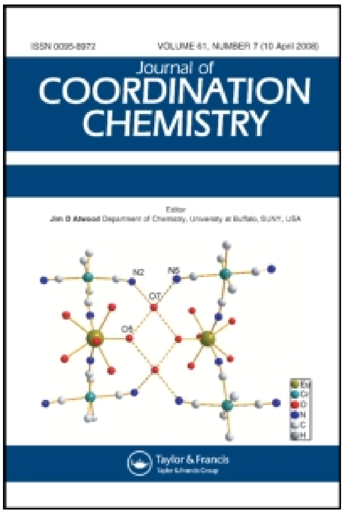

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Synthesis, crystal structure, and magnetism properties of coordination polymer: $Co(2\text{-}mpac)_2(H_2O)_2$ as molecular building block

Fan Guang[ab]; Zhang Yin-Li[a]; Sun Jia-Juan[a]; Zheng Min-Yan[a]; Chen San-Ping[b]; Gao Sheng-Li[b]
[a] College of Chemistry and Chemical Engineering, Xianyang Normal University, Xianyang, Shaanxi 712000, P.R. China [b] Key Laboratory of Synthetic and Natural Functional Molecule Chemistry of Ministry of Education, College of Chemistry and Materials Science, Northwest University, Xi'an, Shaanxi 710069, P.R. China

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Synthesis, crystal structure, and magnetism properties of coordination polymer: $Co(2\text{-}mpac)_2(H_2O)_2$ as molecular building block

FAN GUANG†‡, ZHANG YIN-LI†, SUN JIA-JUAN†, ZHENG MIN-YAN†,
CHEN SAN-PING‡ and GAO SHENG-LI*‡

†College of Chemistry and Chemical Engineering, Xianyang Normal University,
Xianyang, Shaanxi 712000, P.R. China
‡Key Laboratory of Synthetic and Natural Functional Molecule Chemistry of
Ministry of Education, College of Chemistry and Materials Science, Northwest University,
Xi'an, Shaanxi 710069, P.R. China

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Utilizing $Co(2\text{-}mpac)_2(H_2O)_2$ as molecular building block, a coordination polymer, $[Co_2(2\text{-}mpac)_4(4,4'\text{-}bpy)\cdot 2H_2O]_n$ (**1**) (2-mpac = 5-methyl-2-pyrazinecarboxylic acid; 4,4′-bpy = 4,4′-bipyridine), was synthesized and structurally characterized by X-ray single crystal diffraction. Elemental analysis, infrared, and magnetism are presented. Variable temperature magnetic susceptibility measurements exhibit weak antiferromagnetic interaction between Co centers in **1**.

Keywords: Coordination polymer; Crystal structure; Thermogravimetric analysis; Magnetic properties

1. Introduction

Coordination polymers have received much attention because of their potential applications [1–9]. In principle, by choosing the favored geometry of ligands and metal ions, we could design and control the structure of the resultant polymeric network and potential function [10–22]. Since Sinn came out with a series of articles of taking metal complex as ligand to synthesize complexes from 1967 [23–33], a large number of polynuclear or heteronuclear supramolecular coordination polymers have been prepared by the choice of ligand, $M(2,4\text{-}pydc)_2$ (M = Pt, Pd, Cu, 2,4-pydc = 2,4-pyridinedicarboxylic acid), $M(2\text{-}pac)_2(H_2O)_2$ (M = Co, Ni, Cu, 2-pac = 2-pyrazinecarboxylic acid), and $Mn(2\text{-}mpac)_2(H_2O)_2$ (2-mpac = 5-methyl-2-pyrazinecarboxylic acid) as bridge with uncoordinated terminal atoms [34–40].

The complex ligand is also an excellent connector for the propagation of coordination networks as well as the neutral secondary building block units (SBUs)

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*Corresponding author. Email: gaoshli@nwu.edu.cn

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because of the following features: (1) it possesses a rigid structure, which will help in the predictability of network geometry; (2) the metal center facilitates in the design and synthesis of the polynuclear or heteronuclear supramolecular coordination polymers; (3) weak terminal ligands such as methanol or water in the complex ligand which may be replaced by ones with strong coordination, affording new 1-D, 2-D, or 3-D coordination polymers. So, the complex ligand can be considered as a molecular building block to construct various coordination polymers.

Recently, we reported $Co(2\text{-mpac})_2(H_2O)_2$ [41], which is similar to $Mn(2\text{-mpac})_2(H_2O)_2$ [40], possesses two coordinated waters and could be replaced by the N-heterocycle bridging ligands such as 4,4′-bipyridine and pyrazine under appropriate conditions. In this article, we design and synthesize a coordination polymer based on $Co(2\text{-mpac})_2(H_2O)_2$ as a molecular building block. In addition, its magnetic properties are characterized.

2. Experimental

2.1. *Instruments and reagents*

5-methyl-2-pyrazinecarboxylic acid, pyrazine, and 4,4′-bipyridine were purchased from Acros. All other starting materials were of analytical grade and purchased commercially. Elemental analyses, C, H, and N, were performed on a Vario EL III analyzer. Infrared (IR) spectra were recorded on a BEQ VZNDX 550 FTIR instrument with KBr pellets from 4000 to 400 cm^{-1}. Variable temperature magnetic susceptibility data were measured with a polycrystalline sample from 300 to 2 K with a magnetic field of 5 kOe on a superconducting quantum interference device (SQUID) magnetometer. Diamagnetic corrections were estimated from Pascal's constants.

2.2. *Synthesis of $Co(2\text{-mpac})_2(H_2O)_2$*

$Co(2\text{-mpac})_2(H_2O)_2$ was synthesized according to the literature [41] and proved by elemental analysis and X-ray single crystal diffraction.

2.3. *Synthesis of $[Co_2(2\text{-mpac})_4(4,4'\text{-bpy})\cdot 2H_2O]_n$ (1)*

Yellow **1** was obtained by the hydrothermal synthesis of a mixture of $Co(2\text{-mpac})_2(H_2O)_2$ (0.185 g, 0.5 mmol) and 4,4′-bipyridine (0.078 g, 0.5 mmol) in 6 mL H_2O, sealed in a Teflon-lined stainless container, heated at 130°C for 72 h, and slowly cooled to room temperature 5°C per hour. Yield: 19%. Anal. Calcd for **1**, $C_{34}H_{32}Co_2N_{10}$ (%): C, 58.46; H, 4.62; N, 20.05. Found (%): C, 58.42; H, 4.58; N, 20.01.

2.4. *X-ray crystallography*

All single crystal X-ray experiments were performed on a Bruker Smart Apex CCD diffractometer equipped with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) using ω and φ scan mode. The single-crystal structure of **1** was solved

Table 1. Crystal data and structure refinement parameters for **1**.

Empirical formula	$C_{34}H_{32}Co_2N_{10}O_{10}O_{10}$
Formula weight	858.56
Crystal system	Monoclinic
Space group	*C2/c*
Unit cell dimensions (Å, °)	
a	24.174(2)
b	9.8552(8)
c	19.165(2)
α	90.00
β	127.893(1)
γ	90.00
Volume (Å^3), *Z*	3603.1(6), 4
Calculated density (g cm^{-3})	1.583
Absorption coefficient (mm^{-1})	0.994
F(000)	1760
Reflections collected	8849
Independent reflection	3192
Max. and min. transmission	0.9520 and 0.9072
Data/restraints/parameters	3192/2/263
Goodness-of-fit on F^2	1.061
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0409$, $wR_2 = 0.0950$
R indices (all data)	$R_1 = 0.0585$, $wR_2 = 0.1057$
Largest difference peak and hole (e Å^{-3})	0.579 and −0.295

Table 2. Selected bond lengths (Å) and angles (°) for **1**.

Co(1)–N(1)	2.196(3)	Co(1)–N(3)	2.148(3)
Co(1)–N(5)	2.105(3)	Co(1)–O(1)	2.098(2)
Co(1)–O(2)$^{\#1}$	2.074(2)	Co(1)–O(3)	2.051(2)
N(3)–Co(1)–N(1)	90.98(9)	N(5)–Co(1)–N(1)	91.94(10)
O(1)–Co(1)–N(1)	76.26(9)	O(2)$^{\#1}$–Co(1)–N(1)	164.35(9)
O(3)–Co(1)–N(1)	91.34(9)	N(5)–Co(1)–N(3)	172.68(10)
O(1)–Co(1)–N(3)	91.36(9)	O(2)$^{\#1}$–Co(1)–N(3)	87.56(9)
O(3)–Co(1)–N(3)	78.12(9)	O(1)–Co(1)–N(5)	95.86(10)
O(2)$^{\#1}$–Co(1)–N(5)	91.42(10)	O(3)–Co(1)–N(5)	95.09(10)
O(2)$^{\#1}$–Co(1)–O(1)	88.19(8)	O(3)–Co(1)–O(1)	163.70(9)
O(3)–Co(1)–O(2)$^{\#1}$	103.58(9)		

Symmetry transformations: $^{\#1}-x+1/2$, $y-1/2$, $-z+1/2$.

by direct methods (SHELXS-97 [42]) and refined with full-matrix least-squares refinements based on F^2 using SHELXL-97 [43]. Hydrogens of organic ligands were generated geometrically and those of water were located from different maps. 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. *Description of structure*

The X-ray structural determination for **1** reveals that it crystallizes in monoclinic, space group *C2/c*, featuring neutral 1-D Co(2-mpac)$_2$ chains bridged by 4,4′-bpy ligands to

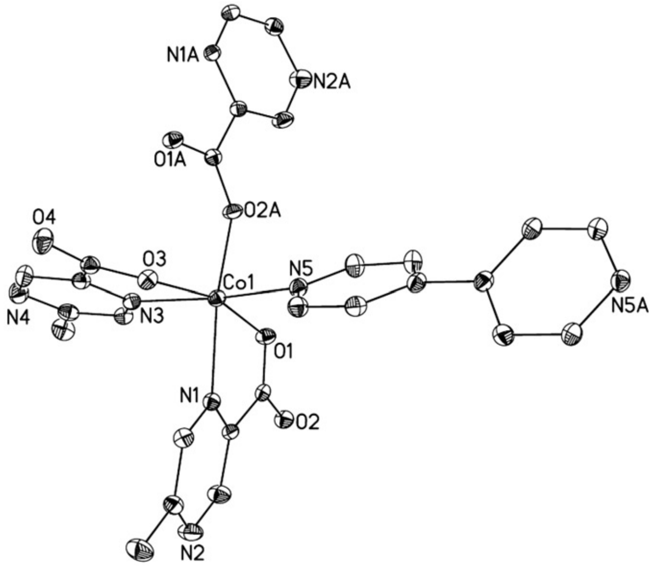

Figure 1. Illustration of molecular structure for **1**; crystal lattice water and hydrogen atoms are omitted for clarity.

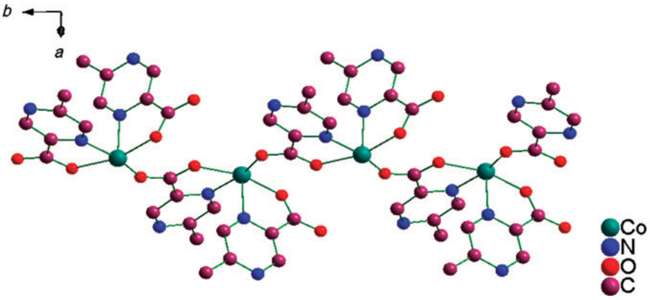

Figure 2. 1-D chain of Co(2-mpac)$_2$; hydrogen atoms are omitted for clarity.

form a 2-D layer. As shown in figure 1, Co(1) is in a distorted octahedral configuration, bonding to three oxygens and two nitrogens from three different 2-mpac ligands and one nitrogen from bpy. Under hydrothermal conditions, the Co(2-mpac)$_2$ unit transformed from *trans* to *cis* and O(1) of carboxylate from one 2-mpac adopted syn-anti bridging mode to link Co(2-mpac)$_2$ units to construct a 1-D chain, as shown in figure 2. Finally, 4,4′-bpy linked neighboring chains to build a 2-D layer. The two pyridine rings of 4,4′-bpy are not coplanar but twist about the C–C bond forming a diplanar angle of 37.1°. In lattice water molecules, the hydrogen bonds with 2.823(4) Å for O5–H5A $\cdots$ O3 and 3.207(4) Å for O5–H5B $\cdots$ O2, shown in figure 3. Furthermore, there are π–π stacking interactions between adjacent layers: Cg(1)–Cg(1)* = 3.648 Å, Cg(2)–Cg(2)* = 4.151 Å [44] (Cg(1) is the centroid of aromatic ring N(1), C(2), C(3), N(2), C(4), C(5), and Cg(1)* is the centroid symmetric aromatic ring; Cg(2) is the centroid of aromatic ring N(3), C(8),

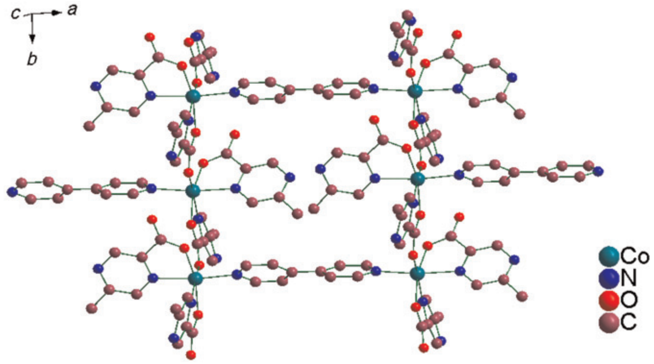

Figure 3. 2-D layer from 1-D chain by $Co(2\text{-mpac})_2$ chains bridged by 4,4′-bpy; hydrogen atoms are omitted for clarity.

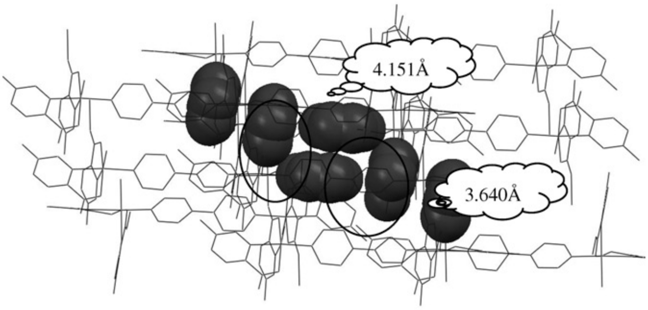

Figure 4. Perspective view of the self-assembled, 3-D supramolecular structure of **1**.

C(9), N(4), C(10), C(11), and Cg(2)* is the centroid symmetric aromatic ring), giving a 3-D supramolecular network, as depicted in figure 4.

3.2. *Thermalgravimetric analysis*

Thermalgravimetric–differential thermogravimetric (TG–DTG) analysis for **1** was performed on a NETZSCH STA 449C thermogravimetric instrument from 25 to 800°C at a heating rate of $10^{\circ}\mathrm{C\,min^{-1}}$ under static air.

The thermalgravimetric analysis curve (Supplementary material) for **1** shows one well-separated weight loss of 4.75% occurring at 150–225°C, corresponding to the removal of crystal water (calculated value: 5.16%). No weight loss was observed from 220°C to 340°C, indicating the formation of a stable phase with $[Co_2(2\text{-mpac})_4(4,4'\text{-bpy})]$; then the complex dramatically decomposed to Co_2O_3 with the residue of 23.32%, which accords well with the calculated value of 23.74%.

3.3. *Magnetic properties*

The temperature dependence of the molar magnetic susceptibility, χ_M of **1** was investigated using a SQUID magnetometer from 300 to 2 K under magnetic fields

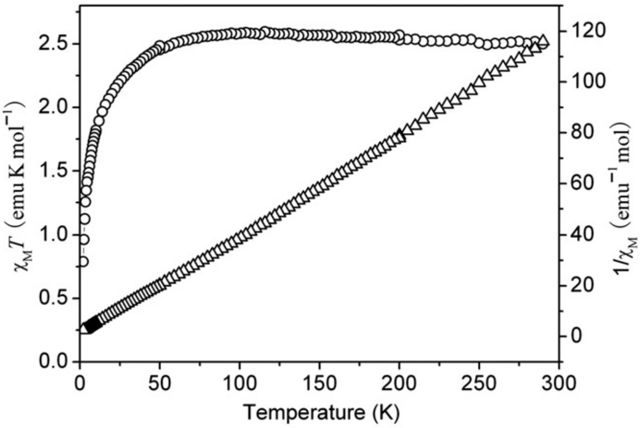

Figure 5. $\chi_M T$ *vs.* T (O) and $1/\chi_M$ *vs.* T (Δ) curves for **1**.

of 5 kOe. The $\chi_M T$ *versus* T in the 300–2 K range for **1** is plotted in figure 5; the $\chi_M T$ value at room temperature equals to 2.50 emu mol^{-1} K^{-1}, slightly higher than the spin-only value of 1.875 emu mol^{-1} K^{-1} 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 [45, 46]. As the temperature is lowered, the $\chi_M T$ value remains almost constant in the range 300–75 K and then abruptly decreases to a value of 0.79 emu mol^{-1} K^{-1} at 2 K. The shape of the curve is characteristic of antiferromagnetic interaction. The magnetic susceptibility follows the Curie–Weiss Law $\chi_M = C/(T - \theta)$, with $C = 2.57$ emu mol^{-1} K^{-1} and $\theta = -2.4$ K, and the negative Weiss constant also suggests weak antiferromagnetic interaction between Co centers [47], from 1-D chain bridged by carboxyl group with a distance of 5.542 Å, because C–C single bond between two pyridyl groups of 4,4′-bpy cannot complete ferromagnetic or antiferromagnetic exchange interactions.

3.4. *Other physical data*

In the IR spectrum for **1**, the strong and broad peak at 3339 cm^{-1} is assigned to the stretching of hydroxyl, indicating the presence of water. The appearance of striking peaks at 1596 and 1411 cm^{-1} can be attributed to asymmetric and symmetric vibrations of carboxyl, evidence of carboxylate binding to cobalt with chelating-bridging mode [48]. The X-ray powder diffraction patterns of the simulated and actual measurement for **1** agree fairly well, indicating coordination polymer **1** is pure phase, shown in the “Supplementary material”.

4. Conclusion

We synthesized a coordination polymer $\{[Co_2(2\text{-mpac})_4(4,4'\text{-bpy})] \cdot 2H_2O\}_n$ based on $Co(2\text{-mpac})_2(H_2O)_2$ as molecular building block, which is further inter-connected by 4,4′-bipyridine to afford a new 2-D network. Furthermore, the 2-D network structures are linked through π–π stacking interactions giving a 3-D supramolecular structure. Temperature dependence of the molar magnetic susceptibility suggests weak antiferromagnetic interaction between Co centers from 1-D chain bridged by carboxylate.

Supplementary material

Crystallographic data for the title compound has been deposited at the Cambridge Crystallographic Data Center as supplementary publications, CCDC no. 634805. 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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