# Two new coordination polymers based on a flexible bib ligand: Structures and magnetic properties 

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#### Abstract

Two new coordination polymers, $\left\{\left[\mathrm{Co}(\mathrm{bib})_{0.5}\left(\mathrm{bdc}^{\left.\left.\left.-\mathrm{Br}_{2}\right)\right] \cdot \mathrm{CH}_{3} \mathrm{OH}\right\}_{\mathrm{n}}(\mathbf{1}) \text { and }\left\{[\mathrm{Co}(\mathrm{bib})(1,4-\mathrm{ndc})] \cdot 0.5 \mathrm{H}_{2} \mathrm{O}\right\}_{\mathrm{n}}}\right.\right.\right.$ (2) have been synthesized. The results of X-ray crystallographic analysis show that compound $\mathbf{1}$ exhibits a 6-connected three-dimensional (3D) 2-fold interpenetrated architectures with the point symbol of $4^{12} .6^{3}, \mathbf{2}$ displays a 4-connected 3D 4-fold [ $2+2$ ] interpenetrated structures with the point symbol of $6^{6}$. The formulas of $\mathbf{1}$ and $\mathbf{2}$ were determined by X-ray crystallography, elemental analysis, and thermogravimetric analysis (TGA). In addition, the compounds $\mathbf{1}$ and $\mathbf{2}$ reveal antiferromagnetic interactions.


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## 1. Introduction

The studies on the synthesis and design of coordination polymers (CPs) have been extensively developed in recent years for their crystallographic diversity and potential applications [1], such as gas storage or separation, heterogeneous catalysis, magnetic, ion exchange and so on $[2,3]$. However, the rationally synthesis and controlled design of CPs with an unique structure and function are influenced by many factors, such as the geometry configuration of organic ligands, the coordination geometry of metal ions, the metal-to-ligand molar ratio, the presence of solvent molecules, reaction temperature, counter ion, and pH value of the solution [4,5]. One of the foregoing factors may lead to a drastic change in the dimensionality and topology. The rigid $p$-phthalic acid and its derivatives with special conformations and diversiform coordination modes have been widely utilized to construct coordination polymers with predetermined networks. The results show that a subtle difference of $p$-phthalic acid may significantly influence the resulting CPs $[6,7]$.

Compared to $p$-phthalic acid, coexistent non-carboxylic groups could effects on the molecular symmetry, of which not only guide

[^0]the formation of the resulting frameworks but also bring new functionalities into CPs. On the other hand, the long flexible ligands with nitrogen donors are another important spacers in construction of CPs with interesting topologies and attractive properties, because the long flexible ligands have variable spatial pattern, and can adopt a variety of conformations according to the coordination geometry of the metal ions [8]. According to previous studies, the bis-imidazole ligands are very useful organic building blocks with special abilities on the assembly systems of multi-carboxylate ligands and metal centers [9]. With the aim of studying the influence of the final crystal structures and properties for the different derivatives of $p$-phthalic acid, we used $\mathrm{Co}(\mathrm{OAc})_{2} \cdot 2 \mathrm{H}_{2} \mathrm{O}$, the long flexible bis-imidazole bib, and $\mathrm{H}_{2} \mathrm{bdc}-\mathrm{Br}_{2}$ or $1,4-\mathrm{H}_{2}$ ndc (Scheme 1 ), respectively, to construct new metal CPs under the same reaction conditions.

In this paper, we report two novel 3D CPs, namely, $\left\{\left[\mathrm{Co}(\mathrm{bib})_{0.5}\left(\mathrm{bdc}-\mathrm{Br}_{2}\right)\right] \cdot \mathrm{CH}_{3} \mathrm{OH}\right\}_{\mathrm{n}} \quad$ (1) and $\quad\{[\mathrm{Co}(\mathrm{bib})(1,4-\mathrm{ndc})] \cdot$ $\left.0.5 \mathrm{H}_{2} \mathrm{O}\right\}_{\mathrm{n}}(2)$, (bib = 1,4-bis(2-methylimidazol-1-yl) butane, bdc-$\mathrm{Br}_{2}=2,5$-bromobenzene-1,4-dicarboxylic acid and 1,4-ndc $=1,4-$ naphthalenedicarboxylic acid). 1 exhibits a three-dimensional (3D) 2-fold interpenetrated structures with the point symbol of $4^{12} .6^{3}, \mathbf{2}$ displays a 3D 4 -fold $[2+2]$ interpenetrated structures with the point symbol of $6^{6}$. Furthermore, thermal stability and the magnetic behaviors for $\mathbf{1}$ and $\mathbf{2}$ were also investigated.


Scheme 1. Structures of ligands, (a) bib, (b) $\mathrm{H}_{2}$ bdc- $\mathrm{Br}_{2}$, (c) $1,4-\mathrm{H}_{2}$ ndc.

## 2. Experimental section

### 2.1. Materials and methods

The ligand bib was synthesized according to the literature's method [10]. All the other chemicals were purchased commercially and used without further purification. Infrared spectra were determined on a Nicolet Avatar 360 FTIR spectrometer in the range of $4000-400 \mathrm{~cm}^{-1}$ using KBr pellets. The elemental analysis of $\mathrm{C}, \mathrm{H}$ and N were recorded by a Perkin-Elmer 2400C Elemental Analyzer. Powder X-ray diffraction (PXRD) was carried out on a Bruker D8 ADVANCE X-ray powder diffractometer (CuK, 1.5418 Å). Thermogravimetric analysis (TGA) were measured using a Seiko Extar 6000 TG/DTA equipment with a heating rate of $10^{\circ} \mathrm{C} / \mathrm{min}$ in $\mathrm{N}_{2}$ stream. Variable temperature magnetic susceptibilities were performed on a Quantum Design SQUID MPMS XL-7 instrument (2-300 K) in the magnetic field of 1 kOe .

### 2.2. Synthesis of the complexes

### 2.2.1. Synthesis of $\left\{\left[\mathrm{Co}(\mathrm{bib})_{0.5}\left(b d c-\mathrm{Br}_{2}\right)\right] \cdot \mathrm{CH}_{3} \mathrm{OH}\right\}_{n}$ (1)

A mixture of $\mathrm{Co}(\mathrm{OAc})_{2} \cdot 2 \mathrm{H}_{2} \mathrm{O}(0.049 \mathrm{~g}, 0.2 \mathrm{mmol}), \mathrm{H}_{2} \mathrm{bdc}-\mathrm{Br}_{2}$ ( $0.064 \mathrm{~g}, 0.2 \mathrm{mmol}$ ) and bib ( $0.044 \mathrm{~g}, 0.2 \mathrm{mmol}$ ) was dissolved in 10 mL of the component solvent $\left(\mathrm{H}_{2} \mathrm{O} / \mathrm{CH}_{3} \mathrm{OH}=1: 1\right)$ and stirred for 30 min . The pH of the reaction mixture was adjusted to 7 by adding $\mathrm{NH}_{3} \cdot \mathrm{H}_{2} \mathrm{O}(w=1 \%)$. Then the reaction mixture was transferred to a 25 mL stainless steel Teflon lined autoclave and sealed followed by heating at $160^{\circ} \mathrm{C}$ for 3 days. The resulted purple block crystals were collected by filtration and characterized. Yield: 35.67\% (based on Co). Anal. Calcd for $\mathrm{C}_{15} \mathrm{H}_{15} \mathrm{Br}_{2} \mathrm{~N}_{2} \mathrm{O}_{5} \mathrm{Co}$ : C, $34.51 \%$; $\mathrm{H}, 2.90 \%$; N , 5.37\%. Found: C, $34.47 \%$; $\mathrm{H}, 2.86 \%$; N, $5.43 \%$. IR ( $\mathrm{KBr}, \mathrm{cm}-1$ ) : 3457s, 3220s, $2941 \mathrm{~m}, 2677 \mathrm{w}, 1890 \mathrm{w}, 1600 \mathrm{w}, 1421 \mathrm{~m}, 1331 \mathrm{w}$, $1200 \mathrm{~m}, 1004 \mathrm{~m}, 933 \mathrm{~m}, 894 \mathrm{~m}, 809 \mathrm{w}, 770 \mathrm{w}, 668 \mathrm{~m}, 517 \mathrm{~m}$.

### 2.2.2. Synthesis of $\left\{[\mathrm{Co}(\mathrm{bib})(1,4-n d c)] \cdot 0.5 \mathrm{H}_{2} \mathrm{O}\right\}_{n}$ (2)

The same synthetic procedure was followed to synthesize 2 as that of 1 except $\mathrm{H}_{2}$ bdc- $\mathrm{Br}_{2}$ was replaced by $1,4-\mathrm{H}_{2}$ ndc $(0.044 \mathrm{~g}$, 0.2 mmol ). The purple sheet crystals were obtained after cooling to room temperature. Yield: $76.55 \%$ (based on Co). Anal. Calcd for $\mathrm{C}_{48} \mathrm{H}_{48} \mathrm{~N}_{8} \mathrm{O}_{9} \mathrm{Co}_{2}$ : C, $57.67 \%$; H, $4.81 \%$; N, $11.21 \%$. Found: C, $57.50 \%$; $\mathrm{H}, 4.90 \%$; N, 11.13\%. IR (KBr , cm-1):3400s, $3009 \mathrm{~m}, 2644 \mathrm{w}, 1900 \mathrm{w}$, 1611w, $1463 \mathrm{~m}, 1368 \mathrm{~m}, 1009 \mathrm{~m}, 930 \mathrm{~m}, 880 \mathrm{~m}, 809 \mathrm{w}, 768 \mathrm{w}, 669 \mathrm{~m}$, 496 m.

### 2.3. Crystallographic data collection and refinement

X-ray Crystallographic Measurements for 1 and 2: The diffraction data of the complexes were carried out on a Bruker SMART APEX II CCD diffractometer equipped with a graphite monochromated Mo-K $\alpha$ radiation $(\lambda=0.71073 \mathrm{~A}$ ) at 296 K . The data reduction were performed by the CrystalClear software package [11]. Absorption corrections were performed by utilizing the SADABS program [12]. The all structures were solved by direct
methods and refined with full-matrix least-squares technique using SHELXTL-97 [13]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at geometrically ideal positions by using a riding model. The detailed crystallograp-hic data and structure refinement parameters are summarized in Table 1. In addition, Selected bond lengths and angles are listed in Table S1-S2.

## 3. Results and discussion

### 3.1. Crystal structure of compounds

### 3.1.1. Structure description of $\mathbf{1}$

Single-crystal X-ray diffraction analysis reveals that complex 1 crystallizes in the triclinic system, space group $P-1$. The crystal structure of 1 with the coordination environment of Co (II) centers is depicted in Fig. 1. The asymmetric unit of 1 consists of one Co (II) ion and one-half of bib ligand, two one-half of bdc- $\mathrm{Br}_{2}$, one $\mathrm{CH}_{3} \mathrm{OH}$ molecule. Each $\mathrm{Co}(\mathrm{II})$ center is penta-coordinated by one N atoms from one bib ligand and four O atoms from other four $\mathrm{bdc}-\mathrm{Br}_{2} \mathrm{li}-$ gands, respectively, showing a distorted rectangular pyramid coordination geometry. Two adjacent Co (II) ions are bridged by four bridging carboxylate groups from four different bdc- $\mathrm{Br}_{2}$ ligands, forming a $\left[\mathrm{Co}_{2}\left(\mathrm{CO}_{2}\right)_{4}\right]$ paddlewheel unit (Fig. 2). The binuclear Co (II) unit can be regarded as a secondary building units (SBUs) with Co-Co distance of $3.010(24) \AA$. The SBU can be simplified as a six-connected node, and the overall structure of 1 shows a pcu topology with the point symbol of $4^{12} .6^{3}$ (Fig. 3). Two identical 3D networks are interpenetrated, resulting in a 3D 2-fold interpenetrated structures (Fig. 4).

Table 1
Crystallographic data and structure refinements for complexes 1-2.

| Complexes | 1 | 2 |
| :---: | :---: | :---: |
| Formula | $\mathrm{C}_{15} \mathrm{H}_{15} \mathrm{Br}_{2} \mathrm{~N}_{2} \mathrm{O}_{5} \mathrm{Co}$ | $\mathrm{C}_{48} \mathrm{H}_{48} \mathrm{~N}_{8} \mathrm{O}_{9} \mathrm{Co}_{2}$ |
| Mr | 522.04 | 998.80 |
| Crystal system | triclinic | monoclinic |
| Space group | P-1 | C2/c |
| $a(\AA)$ | 9.496(3) | 20.207(7) |
| $b(\AA)$ | 9.626(3) | 17.691(7) |
| $c(\AA)$ | 10.958(3) | 16.075(6) |
| $\alpha\left({ }^{\circ}\right)$ | 81.564(5) | 90 |
| $\beta\left({ }^{\circ}\right)$ | 69.191(5) | 125.551(5) |
| $\gamma\left({ }^{\circ}\right)$ | 68.992(5) | 90 |
| $V(\AA ̊ 3)$ | 873.9(4) | 4675(3) |
| Z | 2 | 4 |
| Dcalcd $\left(\mathrm{g} \cdot \mathrm{cm}^{-3}\right)$ | 1.980 | 1.419 |
| $\mu\left(\mathrm{mm}^{-1}\right)$ | 5.583 | 0.774 |
| GOF | 1.005 | 1.207 |
| $R_{1}[\mathrm{I}>2 \sigma(\mathrm{I})] \mathrm{a}$ | 0.0691 | 0.1213 |
| $\mathrm{w} R_{2}[\mathrm{I}>2 \sigma(\mathrm{I})] \mathrm{b}$ | 0.1871 | 0.2210 |
| $R_{1}{ }^{\text {a }}$ (all data) | 0.1276 | 0.1673 |
| $w R_{2}{ }^{\text {b }}$ (all data) | 0.2487 | 0.2429 |
| $R_{\text {int }}$ | 0.0397 | 0.0987 |
| ${ }^{\text {a }} R_{1}=\sum\| \| F_{o}\left\|-\left\|F_{c}\right\|\right\| / \sum\| \| F_{o}\| \| .$ |  |  |
| ${ }^{\mathrm{b}} w R_{2}=\left\|\sum\right\| w\left(\left\|F_{o}\right\|^{2}-\left\|F_{c}\right\|^{2}\right)\| \| / \sum\left\|w\left(F_{o}^{2}\right)^{2}\right\|^{1 / 2}$ |  |  |

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