

Generalized Synthesis of Magnetic Cobalt(II) Coordination Polymers with Halide and N-heterocycle Ligands

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Recent advances in spintronics call for novel magnetic materials. And magnetic coordination polymers (MCPs) have emerged as promising candidates.^{1,2} This is because their magnetism can be fine-tuned by chemical synthesis. MCPs are composed of diverse metals and ligands. So, the interaction between the metals and the ligands has a large degree of freedom. For example, the metal—ligand—metal angle is critical for determining the magnetic order. When the angle is near 90°, the metals exhibit ferromagnetic coupling within the metal-ligand chain, such as in Co(meso-2,3-dmsucc).³ In contrast, another Co(II)-based metal organic framework (MOF), IPF-5, shows antiferromagnetism. In this case, the angle is near 120°.⁴ So, a group of MCPs with the same metal centers and different ligands can offer a way to fine-tune the magnetic properties.

Among various magnetic metal ions, Co(II), as shown in the examples above, often comprises magnetic coordination complexes.^{1,5,6} And N-heterocycles and halides are widely used as ligands binding to Co(II). On the one hand, N-heterocycles form stable coordination bonds. The nitrogen atoms in N-heterocycles act as σ electron donors to the metal centers.⁷⁻⁹ And the π - π interaction of the N-heterocycles further stabilizes the crystal structure.^{10,11} On the other hand, halides are very small ligands that interconnect two nearby metal centers. So, the way the halides bind to the metal centers affects the magnetism of MCPs.¹²

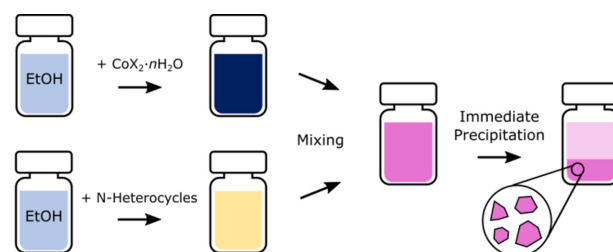
Therefore, $[\text{CoX}_2\text{L}]_n$ ($X = \text{Cl}, \text{Br}$; $L = (\text{pyz})_2, 4,4'$ -bipy; $\text{pyz} = \text{pyrazine}$, $\text{bipy} = \text{bipyridine}$) comprises a group of air-stable coordination polymers with magnetic centers.^{10,12-14} Regarding the structures, Co(II) in $[\text{CoCl}_2(\text{pyz})_2]_n$ and $[\text{CoBr}_2(\text{pyz})_2]_n$ are bridged by pyrazine, whereas those in $[\text{CoCl}_2(4,4'\text{-bipy})]_n$ and $[\text{CoBr}_2(4,4'\text{-bipy})]_n$ are connected via both Cl and 4,4'-bipy. In terms of magnetism, $[\text{CoCl}_2(\text{pyz})_2]_n$,^{12,13} $[\text{CoBr}_2(\text{pyz})_2]_n$,¹³ and $[\text{CoCl}_2(4,4'\text{-bipy})]_n$ ¹⁰

shows antiferromagnetic ordering. The Néel temperature of each product is 0.85 K, 0.65 K and 5 K, respectively.

Despite the similarity in composition, they are prepared by different synthesis methods. For example, $[\text{CoBr}_2(\text{pyz})_2]_n$ is synthesized by precipitation after dripping precursor solution.¹³ $[\text{CoCl}_2(4,4'\text{-bipy})]_n$ is synthesized by hydrothermal synthesis.¹⁰ And $[\text{CoBr}_2(4,4'\text{-bipy})]_n$ is prepared by mechanochemical process.¹⁴ Developing a universal synthesis method is crucial for the study of similar MCP. And it would unveil possibility toward new MCPs having other ligands.

Herein, we report the synthesis of $[\text{CoX}_2\text{L}]_n$ ($X = \text{Cl}, \text{Br}$; $L = (\text{pyz})_2, 4,4'\text{-bipy}$) by a single, versatile process. This process uses ethanol as a common solvent. Metal and ligand precursors are individually dissolved in ethanol, and mixing both solutions instantly precipitates the product. The successful synthesis was confirmed by optical microscopy (OM) and powder X-ray diffraction (PXRD) studies.

The reaction process is summarized in Scheme 1. In a 20 ml vial, 1 mmol of $\text{CoX}_2 \cdot n\text{H}_2\text{O}$ (Alfa aesar, ACS, 98.0-102.0%) or $\text{CoBr}_2 \cdot x\text{H}_2\text{O}$ (Alfa aesar) was dissolved in 6 ml of ethanol. And in another 20 ml vial, 2 mmol of pyrazine (Alfa aesar, 98%) or 1 mmol of 4,4'-bipyridyl (Acros organics, 98%) was dissolved in 6 ml of ethanol



Scheme 1. The overall reaction steps. X of $\text{CoX}_2 \cdot n\text{H}_2\text{O}$ is Cl or Br. N-Heterocycles stand for pyrazine (pyz) or 4,4'-bipyridine (bipy).

(Samchun, anhydrous, 99.9%). Ethanol was used without further dehydration. When each solute was thoroughly dissolved in the solvent, each solution was mixed together. The mixed solution then immediately precipitates powdery product. The product was filtered through a nylon membrane filter with a pore size of 0.45 μm . Note that the product was rinsed with ethanol to remove remaining reagents. The final product was then dried before further analysis.

The product was analyzed by an optical microscope (Eclipse LV150NL, Nikon) and a powder X-ray diffractometer (Ultima IV). The sample was analyzed in air at room temperature. Photographs of as-received products are shown in Fig. 1. All products are obtained as powder and have unique colors. The different colors of each product imply the different strength of the ligand fields. The estimated yields of each product were 88.2% for $[\text{CoCl}_2(\text{pyz})_2]_n$, 85.8% for $[\text{CoCl}_2(4,4'\text{-bipy})]_n$, 97% for $[\text{CoBr}_2(\text{pyz})_2]_n$,

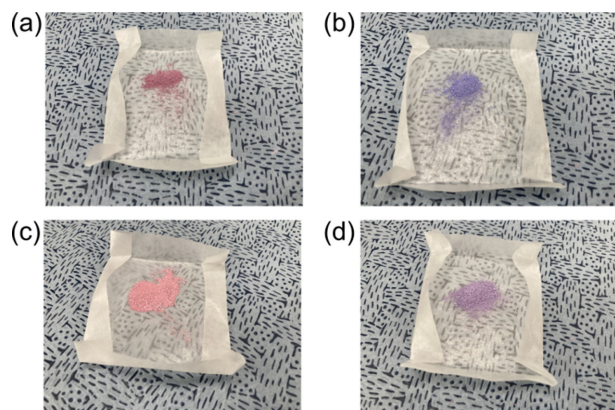


Figure 1. Photographs of obtained products: (a) $[\text{CoCl}_2(\text{pyz})_2]_n$, (b) $[\text{CoCl}_2(4,4'\text{-bipy})]_n$, (c) $[\text{CoBr}_2(\text{pyz})_2]_n$, and (d) $[\text{CoBr}_2(4,4'\text{-bipy})]_n$.

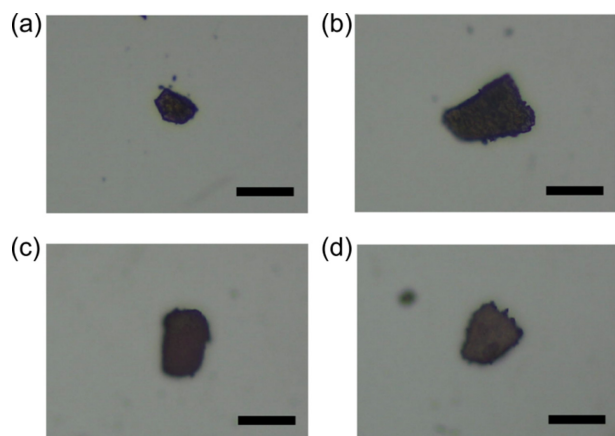


Figure 2. Optical microscope images of obtained powder of (a) $[\text{CoCl}_2(\text{pyz})_2]_n$, (b) $[\text{CoCl}_2(4,4'\text{-bipy})]_n$, (c) $[\text{CoBr}_2(\text{pyz})_2]_n$, and (d) $[\text{CoBr}_2(4,4'\text{-bipy})]_n$. All scale bars represent 50 μm .

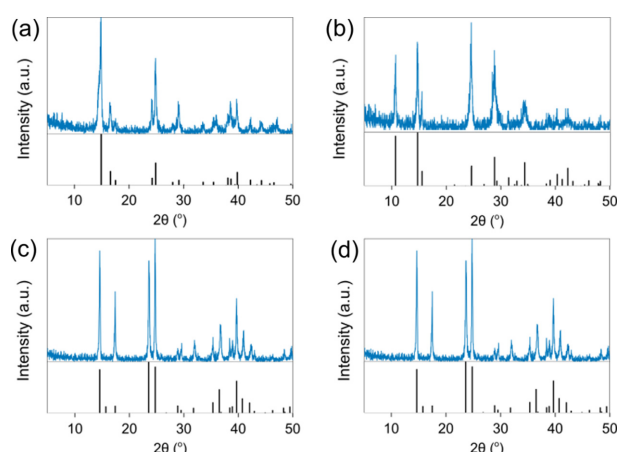


Figure 3. Powder X-ray diffraction patterns of (a) $[\text{CoCl}_2(\text{pyz})_2]_n$, (b) $[\text{CoCl}_2(4,4'\text{-bipy})]_n$, (c) $[\text{CoBr}_2(\text{pyz})_2]_n$, and (d) $[\text{CoBr}_2(4,4'\text{-bipy})]_n$. The upper blue graphs are the measured patterns, and the lower black lines are the patterns calculated from single-crystal data: (a) CPYZCO02, (b) QEJCOX, (c) QQQDJG01, and (d) XAJGUM.

and 92.6% for $[\text{CoBr}_2(4,4'\text{-bipy})]_n$. The high yield of the reaction shows that most of the immediately react. The samples were stable in the air; the samples stored in air for 5 days still did not show any changes in the diffraction patterns. The detailed image of each product was analyzed by optical microscopy (Fig. 2). The size of each crystal was approximately 50 μm in diameter.

The successful synthesis of the products was confirmed by powder X-ray diffraction studies (Fig. 3). The diffraction patterns of each product well match with the diffraction patterns calculated from corresponding single-crystal diffraction data retrieved from Cambridge Structural Database (CSD). And no signs of the byproducts or unreacted reagents were found. Possible remnants of the byproducts would have been washed during rinsing after filtration.

The results show that $[\text{CoX}_2\text{L}]_n$ ($X = \text{Cl}, \text{Br}$; $L = (\text{pyz})_2, (4,4'\text{-bipy})$) are successfully synthesized by simply mixing the precursor solutions. This is attributed to the high solubility of the precursors in ethanol. The polarity of ethanol allows the dissolution of both ionic and non-polar solutes. In addition, ethanol is not included in the product crystals. Many solvents are included in the crystals as ligands or solvates.¹⁵ For example, dissolving chromium (II) acetate ($\text{Cr}_2(\text{OAc})_4$) in solvent L always result in the coordination of the L.⁷⁻⁹ The solute therefore becomes $\text{Cr}_2(\text{OAc})_4\text{L}_2$. Therefore, it is impossible to obtain anhydrous (i.e., non-coordinated) $\text{Cr}_2(\text{OAc})_4$ by solution-based crystallization. Ethanol, however, is a very weak neutral base. So, it does not effectively bind to Co(II) centers as

ligands. The tight structure of MCPs also prevents the insertion of ethanol as solvates.

In conclusion, a series of CPs, i.e., $\text{CoCl}_2(\text{pyz})_2$, $\text{CoBr}_2(\text{pyz})_2$, $\text{CoCl}_2(4,4'\text{-bipy})$, and $\text{CoBr}_2(4,4'\text{-bipy})$, were successfully synthesized by mixing the ethanol solution of cobalt halide and N-heterocycles. The mixed solution immediately precipitates the products without further treatment. Despite the differences in structures or compositions, all CPs were successfully synthesized by a single method. This new method would suggest a possibility of other MCPs by changing the ligand precursors.

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