

Synthesis, characterization, magnetic properties of cobalt coordination polymer based on 4,4'-Oxybisbenzoic acid and 1,4-bis(pyrid-4-yl)benzene

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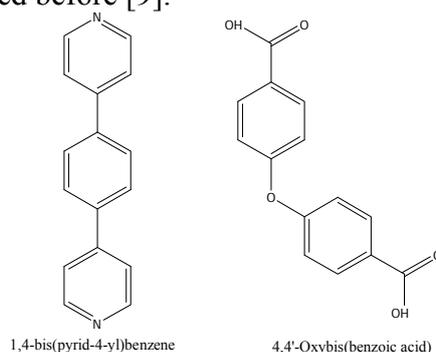
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Abstract. A compound with cation chains and monomers, $[\text{Co}_{1/2}(\text{bpbenz})_{1/2}]^+ [\text{Co}_{1/2}(\text{oba})]^-$ (**1**) (bpbenz = 1,4-bis(pyrid-4-yl)benzene and H_2oba = 4,4'-Oxybisbenzoic acid) has been synthesized under hydrothermal condition. Single crystal X-ray diffraction analyses reveal that in compound **1**, the monomer $[\text{Co}_{1/2}(\text{oba})]^-$ anions stack in three orientations to generate a 1D pseudo channels encapsulation of cationic chains $[\text{Co}_{1/2}(\text{bpbenz})_{1/2}]^+$. Magnetic studies indicate that compound **1** exhibit weak antiferromagnetic interactions.

1. Introduction

Coordination polymers have been widely studied in material science because of their potential applications in luminescence, magnetism, catalysis, drug delivery and molecule storage [1-5]. However, the achievements of these applications require careful design of structures. As is known, ligand and metal ion are two necessary components leading to extended supramolecular multi-metallic assemblies. Among all the ligands, *exo*-bidentate ligands such as 4, 4'-bipyridine or pyrazine are regarded as excellent ancillary ligands for constructing novel structures [6]. As the bidentate bridge with different conformations may leading to the formation of different motifs like 1D chain, 2D layer and 3D network [7]. Besides ligand, the choice of metal ions is also important as different metal have their own preferred properties. For example, nickel-based complexes have owned considerable interest as pre-catalysts, fluorescent emission and the identification of coordination environments in biological nickel centers [8]. Another transition metal of Co-based complexes is also identified with excellent magnetism properties.

Based on these research backgrounds, herein, we choose the *exo*-bidentate ligands 1,4-bis(pyrid-4-yl) benzene (bpbenz) as bridging ligands in combination with 4,4'-Oxybisbenzoic acid (H_2oba) (Scheme 1) to build new coordination polymers. A one-dimensional polymer $[\text{Co}_{1/2}(\text{bpbenz})_{1/2}]^+ [\text{Co}_{1/2}(\text{oba})]^-$ (**1**) has been constructed successfully. We report herein the synthesis, crystal structure, and magnetic properties of it. Magnetic data reveal weak antiferromagnetic coupling for compound **1**. It's worth noting that complex **1** has been reported recently but its magnetic properties have never been studied before [9].



Scheme 1 Structural formulas of all ligands

2. Experimental

2.1 Synthesis of $[\text{Co}_{1/2}(\text{bpbenz})_{1/2}]^{+}[\text{Co}_{1/2}(\text{oba})]^{-}$ (1)

The mixture of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.0476 g, 0.2 mmol), 4,4'-Oxybisbenzoic acid (0.0516 g, 0.2 mmol), 1,4-bis(pyrid-4-yl)benzene (0.0465 g, 0.2 mmol) and 10 mL distilled water were sealed in a 25 mL Teflon-lined stainless steel vessel. The mixture was heated at 160°C for 70 h and cooled to room temperature at a rate of $10^{\circ}\text{C}/\text{h}$. Subsequently, red block-shaped crystals were obtained by filtration, washed with distilled water and dried in air. Anal. Yield 40.2 % (based on $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$). Calcd. for $\text{C}_{22}\text{H}_{22}\text{CoNO}_9$ (Mr = 503.34): C 52.50, H 4.41, N 2.76 %; found: C 52.91, H 4.23, N 2.60 %. IR (KBr pellet, cm^{-1}): 3239 s, 2928 s, 2378 s, 1663 m, 1604 s, 1543 s, 1365 s, 1227 s, 1157 m, 1007 m, 888 m, 799 s, 710 m, 492 m.

2.2 X-ray Crystallography

The single crystal structure data for compound **1** was collected on a Bruker SMART1000 CCD with graphite monochromatic Mo/K α radiation ($\lambda = 0.71073 \text{ \AA}$) at room temperature. The structure was solved by direct method with SHELXS-97 program and refined by full-matrix least-squares on F^2 with SHELXL-97 package. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were located and included at their calculated positions. CCDC No. 1524320

3. Results and Discussion

3.1 X-ray diffraction of compound 1

As shown in Fig. 1, compound **1** crystallizes in the $P-1$ space group, the asymmetric units of **1** are composed of one $[\text{Co}_{1/2}(\text{bpbenz})_{1/2}]^{+}$ cationic chain and one $[\text{Co}_{1/2}(\text{oba})]^{-}$ anion. Both two Co^{2+} anions are six-coordinated in octahedral geometry. $\text{Co}1$ connect to four O atoms from water molecules in the basal plane (O8, O9 and O8#1, O9#1) and two N atoms from two bpbenz ligands in the axial position (N1, N1#1); the other Co^{2+} anion connect to four O atoms from water molecules in the basal plane (O6, O7, O6#2, O7#2) and two O atoms from oba^{2-} ligands in the axial position (O4, O4#2) The bond lengths of Co-O in the range 2.067 (1)- 2.124 (1) Å while bond lengths of Co1-N1 is 2.181(1) Å . The bpbenz ligand connects two symmetry-related $\text{Co}1(\text{II})$ ions and each $\text{Co}1(\text{II})$ ion is connects to two different bpbenz ligands, thus generating a 1D chain (Fig. 1).

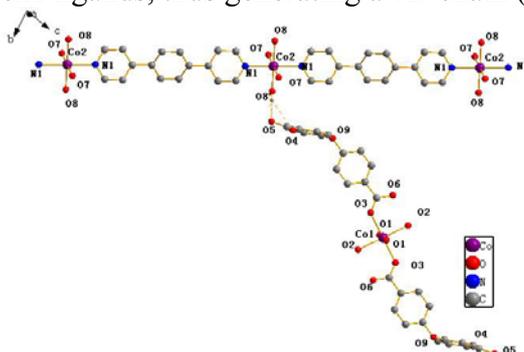


Fig. 1 Molecular structure of compound 1, all hydrogen atoms are omitted for clarity.

3.2 Powder X-ray diffraction and Thermogravimetric analysis of compound 1

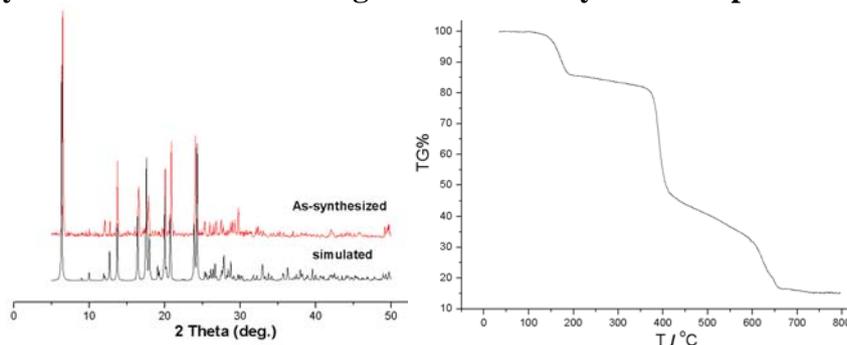


Fig. 2 PXRD patterns (left) and TGA trace (right) of compound 1

To check the crystallinity and purity, compound **1** was measured by X-ray powder diffraction at room temperature (Fig.2 left). XRD results show that this compound is of high crystallinity with sharp Bragg reflections. The diffraction peaks agree well with simulated pattern.

In order to characterize the thermal stability of compound **1**, we performed the thermogravimetric analysis (TGA). The relevant experiments for the crystalline samples of compound **1** was performed in a N₂ atmosphere wherein the sample was heated from room temperature to 800 °C at a rate of 10°C/min. The TG curve of it is shown in Fig.2 (right). The TG curve show a weight loss in the temperature range of 120-190 °C corresponds to the removal of four lattice water molecules (calcd. 14.3%, obsd. 14.2%). Upon further heating, a sharp weight loss was observed from 360 °C to 410°C corresponds to the removal of four oba ligands (calcd. 50.9%, obsd. 51.3%). Finally, compound **1** was completely degraded into CoO with total loss of 84.9 wt% (calcd. 85.1 wt%).

3.3 Magnetic properties of compound **1**

The temperature dependence of the molar magnetic susceptibilities of compound **1** was measured from 300 to 2.0 K in an applied field of 2 kOe. As shown in Fig. 3, the χ_{MT} value at room temperature is 2.91 cm³·K·mol⁻¹, which is higher than expected for the uncoupling value for a high-spin Co(II) center ($\chi_{MT} = 1.87$ cm³·K·mol⁻¹) due to orbital angular momentum. Upon cooling, χ_{MT} decreases continuously to reach 0.032 cm³·K·mol⁻¹ at 2.0 K. The decreasing trend of χ_{MT} value with the temperature suggests the presence of antiferromagnetic interactions.

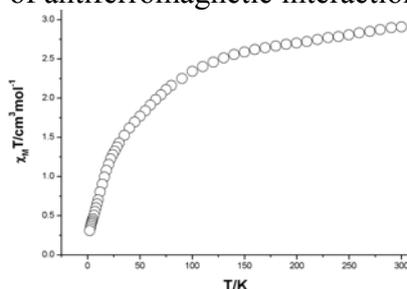


Fig. 3 Temperature dependence of the χ_{MT} product of compound **1**.

4. Summary

In summary, A compound of Co based 1,4-bis(pyrid-4-yl)benzene and 4,4'-Oxybisbenzoic acid has been successfully synthesized and characterized. The crystal structural analyses indicate that monomer anions stack in three orientations to generate a 1D pseudo channels encapsulation of one-dimensional cationic chains. The magnetic studies indicate that compound **1** shows antiferromagnetic coupling between Co (II) ions.

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