A New Copper Coordination Polymer with Magnetic Property Based on 3-(1,2,4-Triazol-1-yl)benzoic Acid (Postprint)

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Abstract

A copper coordination polymer, namely [CuL2(H2O)2] · H2O 1 (HL = 3-(1,2,4-triazol-1-yl)benzoic acid) has been synthesized by the hydrothermal reaction under 140 ºC. The structure of 1 was characterized by single-crystal X-ray diffraction analysis, elemental analyses, powder X-ray diffraction, IR spectroscopy, and thermogravimetric analysis. Single-crystal X-ray diffraction analysis reveals that 1 crystallizes in P21/n space group with a = 12.374(5), b = 12.730(5), c = 12.561(5) Å, = 91.105(9)º, V = 1978.2(14) Å3, Z = 4, Dc = 1.618 g/cm3, = 1.160 mm-1, F(000) = 964, the final R = 0.0449 and wR = 0.1443 with I > 2 (I). Magnetic measurements show that 1 exhibits antiferromagnetic interactions by the analysis of magnetic test data.

Full Text

Preamble

A New Copper Coordination Polymer with Magnetic Property Based on 3-(1,2,4-Triazol-1-yl)benzoic Acid

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ABSTRACT

A copper coordination polymer, namely [CuL (H O)] · H O (HL = 3-(1,2,4-triazol-1-yl)benzoic acid), has been synthesized by hydrothermal reaction at 140

°C. The structure of **1** was characterized by single-crystal X-ray diffraction analysis, elemental analyses, powder X-ray diffraction, IR spectroscopy, and thermogravimetric analysis. Single-crystal X-ray diffraction analysis reveals that **1** crystallizes in the P2 /n space group with a = 12.374(5), b = 12.730(5), c = 12.561(5) Å,   = 91.105(9)°, V = 1978.2(14) Å^3, Z = 4, Dc = 1.618 g/cm^3,   = 1.160 mm ^{1}, F(000) = 964, with final R = 0.0449 and wR = 0.1443 for I > 2 (I). Magnetic measurements show that **1** exhibits antiferromagnetic interactions based on analysis of the magnetic test data.

Keywords: copper coordination polymer; hydrothermal reaction; crystal structure; magnetic property
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1 INTRODUCTION

In recent years, coordination polymers have attracted considerable attention due to their potential applications in luminescence, gas adsorption, gas capture and separation, chemical catalysis, magnetic behavior, electrical conductivity, drug delivery, and other areas [1-7]. Numerous coordination polymers with interesting structures and desired functions have been synthesized through the deliberate selection of metal ions and ligands, yielding well-defined and designable structures [8-12]. Most of these materials were synthesized via self-assembly approaches using inorganic and organic building units [13]. In this process, the primary challenge is selecting appropriate metal-connecting nodes and bridging ligands to obtain desired structures and functions [14]. Among organic ligands, multidentate N- and O-donor bridging ligands containing multicarboxylate groups are often employed as multifunctional organic linkers [15-17]. These ligands construct novel frameworks due to their abundant coordination modes to metal ions, which allow for various structural topologies, as well as their ability to act as hydrogen-bond acceptors and donors.

In this study, the multidentate organic linker 3-(1,2,4-triazol-1-yl)benzoic acid (HL) and Cu^2 ions were selected to synthesize novel coordination polymers with interesting magnetic properties. A new 2D supramolecular coordination polymer [CuL (H O)] · H O (**1**) has been successfully synthesized via hydrothermal synthesis. The structure of **1** has been comprehensively investigated through single-crystal analysis and various characterization techniques. Meanwhile, magnetic measurements demonstrate that **1** shows antiferromagnetic interactions.

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2 EXPERIMENTAL

2.1 Materials and Instruments

All reagents were commercially available and used as received without further purification. Powder X-ray diffraction (PXRD) patterns at room temperature were collected on a Rigaku Miniflex II diffractometer using CuK radiation (= 1.540598 Å) at 40 kV and 40 mA in the range of 5 2 85°. Simulated patterns were derived using Mercury Version software (http://www.ccdc.cam.ac.uk/products/mercury). Elemental analyses of C, H, and N were performed on an Elementar Vario EL III micro-analyzer. Thermogravimetric analysis (TGA) experiments were conducted on a TGA/NETZSCH STA449F3 thermogravimetric analyzer in N atmosphere with the sample heated in an Al O crucible at a rate of 10 K/min. FT-IR spectra were obtained on a Perkin-Elmer Spectrum One Spectrometer using KBr pellets in the 4000–400 cm^{1} range. Magnetic measurements were performed using a SQUID magnetometer (MPMS, Quantum Design) and a commercial Quantum Design Physical Property Measurement System (PPMS). Powder samples of [CuL (H O)] · H O were placed in a gel capsule sample holder that was suspended in a plastic drinking straw. Magnetic susceptibility was measured at 0.1 T from 300 to 2 K (temperature scan rate of 5 K/min), and magnetization was measured at 2 K with applied fields from -8 to 8 T (field scan rate of 0.1 T/step).

2.2 Synthesis of [CuL (H O)] · H O (1)

A mixture of Cu(NO) · 3H O (90.60 mg, 0.38 mmol) and 3-(1,2,4-triazol-1-yl)benzoic acid (HL) (47 mg, 0.25 mmol) in 10.0 mL of distilled water was sealed in a 25 mL Teflon-lined stainless-steel vessel under autogenous pressure, then heated to 140 °C, maintained at this temperature for 2 days, and finally cooled to room temperature. Blue block crystals suitable for X-ray analysis were obtained, washed with distilled water, and dried in air. Yield: 68% (based on Cu) for **1**. Anal. Calcd. for C H CuN O **1**: C, 43.77; H, 3.67; N, 17.02%. Found: C, 44.03; H, 3.71; N, 16.91%. IR (KBr pellet, cm^{1}): 3446 b, 3139 m, 3028 w, 1667 w, 1568 vs, 1527 s, 1444 w, 1392 vs, 1360 vs, 1283 s, 1215 s, 1148 vs, 1065 m, 987 s, 899 m, 831 w, 780 s, 728 w, 671 s, 603 w, 526 w, 485 w, 433 w.

2.3 Structure Determination

The single crystal of **1** was mounted on glass fibers with dimensions of 0.25 mm × 0.10 mm × 0.09 mm. Single-crystal X-ray diffraction measurement was performed on a Saturn 724 CCD for **1**, which was equipped with a graphite-monochromated MoK radiation source (= 0.71073 Å) using an scan mode. The structure was solved by direct methods using the SHELXS-97 version 5 package [18]. Subsequent successive difference Fourier syntheses yielded the remaining non-hydrogen atoms. The final structures were refined using full-matrix least-squares refinement on F^2. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms of the ligands were added geometrically and refined using the riding model. All calculations were carried out using the SHELXL-97 program package of crystallographic software [19]. A total of 16660 reflections were collected, of which 4506 were independent (Rint = 0.0310). All non-H atoms were refined anisotropically. The hydrogen atoms of organic ligands were placed in calculated positions and refined using a riding mode on the attached atoms with isotropic thermal parameters 1.2 times those of their carrier atoms. The lattice water molecule is disordered over two positions with site occupancy factors of 0.54/0.46. The positions of hydrogen atoms attached to carbon atoms were generated geometrically. The title compound crystallizes in the monoclinic system, space group P2 /n. Selected bond distances and bond angles for **1** are listed in Table 1 , and hydrogen bonds are listed in Table 2 .

3 RESULTS AND DISCUSSION

3.1 Description of the Crystal Structure

Structural analyses reveal that **1** crystallizes in the monoclinic space group P2 /n and features a 1D framework constructed by L ligands, coordinated H O molecules, and Cu(II) ions. There exists one Cu(II) atom, two L ligands, two coordinated H O molecules, and one lattice water molecule in an asymmetric unit (Fig. 1 [Figure 1: see original paper]). All crystallographically unique Cu(II) ions are six-coordinated in a distorted octahedral coordination geometry, with Cu-O and Cu-N distances falling in the normal range of 1.946(2)-2.647(2) Å, which is comparable to other related reported compounds [20]. Adjacent Cu(II) atoms are bound together through the L linker with a distance of 8.901(2) Å, resulting in negligible interaction between adjacent Cu(II) atoms. Two L ligands adopt their N and O atoms to chelate two Cu(II) atoms, forming a dinuclear [Cu L] cluster, and the [Cu L] clusters connect with each other to fabricate a 1D chained structure. The 2D supramolecular framework is constructed through hydrogen bonding interactions between adjacent 1D chains (dotted lines in Fig. 2 [Figure 2: see original paper], hydrogen bonds: O(1W)-H(1WA) · · · O(12), O(1W)-H(1WB) · · · O(22), O(2W)-H(2WA) · · · N(12), O(3W)-H(3WA) · · · O(2W), O(3W)-H(3WA) ··· O(2W), O(2W)-H(2WB) ··· O(22)), which shows – interaction in the layer with a centroid-to-centroid distance of 3.962(2) Å and a vertical distance of 3.768(2) Å.

3.2 Powder X-ray Diffraction Patterns and Thermal Stability

Thermogravimetric analysis (TGA) shows that **1** has a weight loss of 10.6% up to 170 °C, corresponding to the release of one lattice water molecule and two coordinated water molecules (calcd. 10.58%). No weight loss occurred until heating to approximately 260 °C, indicating that **1** has high thermal stability (Fig. 3a [Figure 3: see original paper]), after which the framework began to decompose upon continued heating. The PXRD measurement and elemental analysis confirm the phase purity of **1**. The experimental PXRD pattern of **1** is in good agreement with the simulated pattern from the single-crystal X-ray data, and when the temperature increased to 100 °C, the molecular framework of **1** remained stable, with continuous heating leading to framework collapse, presumably due to decomposition of the organic ligand (Fig. 3b). The IR spectrum of the compound exhibits broad absorption centered at 3446 cm ^{1}, which belongs to the O–H stretching vibrations of water molecules. The strong bands at 1563 and 1526 cm ^{1}, and 1390 cm ^{1} are characteristic of the asymmetric and symmetric stretching vibrations of carboxylate groups for the compound, respectively.

3.3 Magnetic Properties of 1

The variable-temperature magnetic susceptibilities of **1** were measured under 1 kOe over the 2–300 K temperature range (Fig. 4a [Figure 4: see original paper]). The measured T value at 300 K is 0.756 cm^{3} · K · mol ^{1}, which is higher than the expected spin-only value of 0.375 cm^{3} · K · mol ^{1} for an isolated Cu^{2} ion with g = 2.0 (Fig. 5a [Figure 5: see original paper]) [21]. Upon cooling, the T value increases to a maximum of 0.801 cm^{3} · K · mol ^{1} at 31 K, then decreases to a minimum of 0.79 cm^{3} · K · mol ^{1} at 2 K. This indicates the existence of antiferromagnetic interaction in **1**. The magnetic susceptibility above 50 K follows the Curie-Weiss law well. Fitting of the experimental data for the plot of vs. T over the temperature range of 5–300 K yielded the Curie constant C = 0.795 cm^{3}·K·mol ^{1} and Weiss constant = -0.12 K, suggesting antiferromagnetic interactions among Cu^{2} ions. Fig. 4b shows the field-dependent magnetization at 2 K to further confirm the magnetic interactions in **1**. The magnetization increases rapidly as the field is lifted from zero, then slowly increases to 0.92 B at 800 kOe, which approaches the saturation value (1.0 B), supporting the antiferromagnetic ground state.

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4 CONCLUSION

In summary, a new 2D supramolecular coordination polymer [CuL (H O)] · H O (**1**) has been successfully fabricated by hydrothermal synthesis. The structure of compound **1** has been investigated using single-crystal X-ray diffraction analysis, elemental analyses, powder X-ray diffraction, IR spectroscopy, and thermogravimetric analysis. The 2D supramolecular framework is constructed through hydrogen bonding interactions between adjacent 1D chains. Magnetic measurements demonstrate that compound **1** shows interesting antiferromagnetic interactions. This work provides an effective approach to construct new supramolecular coordination polymers and explore interesting properties using N- and O-donor bridging ligands.

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Table 1. Bond Lengths (Å) and Bond Angles (°) for 1

Dist.		Dist.	
Cu(1)-O(1W)	2.440(2)	Cu(1)-O(21)	1.9743(19)
Cu(1)-N(13)#2	2.005(2)	Cu(1)-O(11)	1.9495(19)
Cu(1)-N(23)#1	2.002(2)	Cu(1)-O(2W)	2.6470(19)
Angle		**Angle**	
O(11)-Cu(1)-O(21)	174.68(8)	N(23)#1-Cu(1)-N(13)#2	179.29(8)
N(13)#2-Cu(1)-O(1W)	89.08(9)	O(11)-Cu(1)-N(23)#1	88.55(8)
O(11)-Cu(1)-O(1W)	98.86(8)	N(13)#2-Cu(1)-O(2W)	93.239(58)
O(21)-Cu(1)-N(23)#1	92.23(8)	O(11)-Cu(1)-O(2W)	81.065(56)
N(23)#1-Cu(1)-O(2W)	86.017(57)	O(11)-Cu(1)-N(13)#2	91.27(8)
O(21)-Cu(1)-O(1W)	86.38(8)	O(21)-Cu(1)-O(2W)	93.687(57)
O(21)-Cu(1)-N(13)#2	87.89(8)	N(23)#1-Cu(1)-O(1W)	91.63(8)
O(11)-Cu(1)-O(2W)	81.065(56)	O(1W)-Cu(1)-O(2W)	177.697(52)

Symmetry transformations used to generate equivalent atoms: #1: x -1/2, -y + 1/2, z + 1/2; #2: x + 1/2, -y + 1/2, z -1/2

Table 2. Hydrogen Bonds for Compound 1 (Å and º)

D—H ··· A	d(D—H)	d(H ··· A)	d(D ··· A)	<(DHA)
O(1W)—H(1WA)··· O(12)#1	0.841(17)	2.189(16)	2.881(2)	139.7(19)
O(1W)—H(1WA)··· O(12)	0.841(17)	2.56(2)	3.171(2)	130.3(18)
O(1W)—H(1WB)··· O(22)#4	0.839(18)	1.842(11)	2.701(2)	168(2)
O(2W)—H(2WA)··· N(12)#3	0.87(2)	2.32(4)	3.111(3)	156(3)
O(2W)—H(2WB)··· O(22)	0.872(12)	2.137(18)	2.974(2)	175(2)
O(3W)—H(3WA)··· O(2W)	0.84(3)	2.25(2)	3.107(3)	178(2)
O(3W)—H(3WB)··· O(1W)#2	0.84(3)	2.48(3)	3.229(3)	149(3)

Symmetry transformations used to generate equivalent atoms: #1: 1 -x, 1 -y, 2 -z; #2: 1/2 + x, 1/2 -y, -1/2 + z; #3: 3/2 -x, -1/2 + y, 3/2 -z; #4: 1/2 -x, 1/2 + y, 3/2 -z

Fig. 1. Coordination environment around the Cu(II) atoms, L ligand and coordinated water molecules in **1**, with hydrogen atoms omitted for clarity. Symmetry codes: #1: x -1/2, -y + 1/2, z + 1/2; #2: x + 1/2, -y + 1/2, z -1/2

Fig. 2. 2D supramolecular structure with dotted lines representing hydrogen bonds

Fig. 3. (a) TGA curve of **1**. (b) Comparison of experimental PXRD patterns for compound **1** with its simulated patterns from single-crystal X-ray data

Fig. 4. (a) Magnetic susceptibility of **1** plotted as vs. T and T vs. T curves; the red solid line represents the fit to the Curie-Weiss law. (b) Field-dependent magnetization of **1** at 2 K

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