



Two novel two-dimensional copper(II) coordination polymers with 1-(4-aminobenzyl)-1,2,4-triazole: Synthesis, crystal structure, magnetic characterization and absorption of anion pollutants



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ABSTRACT

In this work a flexible multi-dentate 1-(4-aminobenzyl)-1,2,4-triazole (abtz) ligand has been employed, two novel triazole-Cu(II) coordination polymers $\{[\text{Cu}(\text{abtz})_2(\text{Br})_2] \cdot (\text{H}_2\text{O})_2\}_n$ (**1**) and $\{[\text{Cu}(\text{abtz})_2] \cdot (\text{SiF}_6) \cdot (\text{H}_2\text{O})_2\}_n$ (**2**) have been isolated under solvo-thermal conditions. **1** is a 2D neutral Cu^{II} coordination polymer while **2** is 2D cation micro-porous Cu^{II} coordination polymer with the channel dimensionalities of 11.852(1) Å × 11.852(1) Å (metal-metal distances). Variable-temperature magnetic susceptibility data of **1** and **2** have been recorded in the 2–300 K temperature range indicating weak anti-ferromagnetic interactions. Further absorption properties of anion pollutants for **2** also have been investigated. **2** presents the novel example of cationic triazole-copper(II) coordination framework for effectively capturing anion pollutants Cr₂O₇²⁻ in the water solutions and selectively capturing Congo Red in the methanol solutions.

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1. Introduction

In recent years, much interest is focused on the design and construction of coordination polymers with interesting properties such as optics, redox activity and magnetism, these materials can be used as special functional materials such as optical, photonic, and magnetic materials [1,2]. The appropriate design of organic ligands is undoubtedly a key element in assembling coordination polymers with fantastic topologies [3,4]. Although a variety of metal coordination frameworks with beautiful topology (such as Complex Molecular Knots, Links, and Entanglements) [5] and interesting properties have been synthesized to date, rational control in the construction of polymeric networks remains a great challenge in crystal engineering [6].

With the development of modern industry, anion pollutants have become a more and more severe problem. Among common anion pollutants, heavy-metal pollutants, normally in their oxo-/

hydroxo anionic forms, such as Cr₂O₇²⁻, have been a focus of concern because it causes serious damage to human health and environment. These anion pollutants have become a worldwide problem that is listed as a priority by the U.S. Environmental Protection Agency [7]. However these anion pollutants have been widely used in the field of metallurgy, pigment manufacturing, leather tanning, and wood preservation [8]. The exploration of new materials for the efficient capture and separation of anion pollutants from industrial waste water is also highly important [9].

On the other hand, it has been extensively recognized that dye molecules have found an increasingly wide utilization in many industrial fields, including paper, printing, plastics, textiles, cosmetics, pharmaceuticals and so on [10,11]. As a large amount of industrial byproducts, dye molecules including electrically neutral, positively, and negatively charged ones, molecules, as widely used chemicals in many industries, have caused serious environmental pollution due to their poor biodegradability [12]. Recently, Metal-organic frameworks (MOFs) with nano-sized pores have been applied in the field of selective adsorption and separation of dye molecules. Compared with other traditional techniques, such as chemical degradation and membrane filtration technologies, the adsorption method adopted by these coordination polymers

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possesses incomparable advantages in user-friendly control and low energy-cost [13,14].

Generally, in the construction of metal organic frameworks, one of the most fruitful choices is taking advantage of neutral nitrogen-containing ligands that can bridge between transition-metal ions. It has been well-known that five-membered heterocycles, such as imidazole, triazole, pyrazole and tetrazole, are good candidate ligands in the construction of functional coordination compounds. Among them, 1,2,4-triazole and its derivatives have received more interest as ligands to bridge different metal ions to form functional coordination polymers because of their potential bridging fashions and intriguing functional properties [15]. We are also interested in exploiting the coordination chemistry and application of 1,2,4-triazole and its derivatives [16]. To further explore this attractive topic, in this work a flexible multi-dentate 1-(4-aminobenzyl)-1,2,4-triazole (abtz) ligand has been employed, two novel triazole-Cu(II) coordination polymers $\{[\text{Cu}(\text{abtz})_2(\text{Br})_2] \cdot (\text{H}_2\text{O})_2\}_n$ (**1**) and $\{[\text{Cu}(\text{abtz})_2(\text{H}_2\text{O})_2] \cdot \text{SiF}_6\}_n$ (**2**) has been isolated under solvothermal conditions. **1** is a 2D neutral Cu^{II} coordination framework while **2** is 2D cation micro-porous Cu^{II} coordination framework with the channel dimensionalities of 11.852(1) Å × 11.852(1) Å (metal-metal distances). Variable-temperature magnetic susceptibility data of **1** and **2** in the 2–300 K temperature range have been recorded indicating weak anti-ferromagnetic interactions. Further absorption properties of anion pollutants for **2** also have been investigated. **2** presents the novel example of cationic triazole-copper(II) coordination framework for effectively capturing anion pollutants Cr₂O₇²⁻ in the water solutions and selectively capturing Congo Red in the methanol solutions.

2. Experimental

2.1. General

Ligand 1-(4-aminobenzyl)-1,2,4-triazole (abtz) was prepared by literature methods [17]. All the other reagents were purchased commercially and used without further purification. Deionized water was used as solvent in this work. C, H, and N microanalyses were carried out with a Perkin-Elmer 240 elemental analyzer. Powder X-ray diffraction analysis has been determined on a D/Max-2500 X-ray diffractometer using Cu-K α radiation. FT-IR spectra were recorded from KBr pellets in the range 4000–400 cm⁻¹ on a Bio-Rad FTS 135 spectrometer. Variable-temperature magnetic susceptibilities were measured on a Quantum Design MPMS-7 SQUID magnetometer. Ultraviolet–visible (UV–vis) adsorption spectra were collected on a PerkinElmer Lambda 35 spectrophotometer.

Preparation of Coordination Polymers 1–2:
 $\{[\text{Cu}(\text{abtz})_2(\text{Br})_2] \cdot (\text{H}_2\text{O})_2\}_n$ (1**)** A mixture of CuBr₂ (11.1 mg, 0.05 mmol) and abtz (17.4 mg, 0.1 mmol) was stirred for 0.5 h in H₂O (5 mL) and CH₃OH (5 mL). Then the mixed solutions were placed in a Teflon vessel in a steel autoclave, heated at 160 °C for 12 h and then cooled to room temperature over the period of 72 h. The resulting green block-shaped crystals of **1** can be obtained and washed several times by water and diethyl ether. Yield: 43% based on abtz. Elemental analysis calcd (%) for C₁₈H₂₄Br₂CuN₈O₂: C 35.57, H 3.98, N 18.44; found: C 35.76, H 4.06, N 18.59. FT-IR data (cm⁻¹): 3300 (m), 1600 (m), 1510 (m), 1430(m), 1250 (m), 1120 (m), 1012 (m), 831 (m), 760 (m), 630 (m), 535 (m).

$\{[\text{Cu}(\text{abtz})_2(\text{H}_2\text{O})_2] \cdot \text{SiF}_6\}_n$ (2**)** **2** was synthesized by the similar methods as **1** only using CuSiF₆·6H₂O (15.68 mg, 0.05 mmol) instead of CuBr₂. The resulting green block-shaped crystals of **2** were washed several times by water and diethyl ether. Yield: 49% based on abtz. Elemental analysis calcd (%) for C₁₈H₂₄CuF₆N₈O₂Si: C 36.64, H 4.10, N 18.99; found: C 36.86, H 4.36, N 19.21. FT-IR data

(cm⁻¹): 3350 (m), 1610 (m), 1515 (m), 1431 (m), 1280 (m), 860 (m), 768 (m), 690 (m), 633 (m), 540 (m).

Absorption of anion pollutants Cr₂O₇²⁻ and Congo Red by **2.** As-synthesized **2** (29.5 mg, 0.05 mmol) was immersed in aqueous solution (10 mL) of K₂Cr₂O₇ (0.0050 mol L⁻¹). On the other hand, as-synthesized **2** (10 mg) was added into the 10 mL methanol solutions containing Congo Red molecules (1 mg mL⁻¹). Then the corresponding mixture was shaken at room temperature for 24 h. The absorption process was monitored by liquid UV–vis spectroscopy based on typical absorption of Cr₂O₇²⁻ at 350 nm, Congo Red at 500 nm, respectively [18]. A 0.1 mL aliquot solution was pipetted at different time intervals and was diluted using deionized water or methanol to measure the UV–vis adsorption intensity. Absorption properties were evaluated by measuring the decolonization rate of anion pollutants Cr₂O₇²⁻ and Congo Red, which was calculated by the following formula

$$D = \frac{C_0 - C_1}{C_0} \times 100\% = \frac{A_0 - A_1}{A_0} \times 100\%$$

where D is exchange capacity, and C₀, A₀ and C₁, A₁ are the concentration and absorbency of Cr₂O₇²⁻ in the water solutions and Congo Red in the methanol solutions before and after absorption process, respectively.

X-ray Crystallography. Diffraction intensities for **1–2** were collected on a Bruker SMART 1000 CCD diffractometer with graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) by using the ω - ϕ scan technique. Lorentz polarization and absorption corrections were applied. The structures were solved by direct methods and refined with the full-matrix least-squares technique using the SHELXS-97 and SHELXL-97 programs [19,20]. Anisotropic thermal parameters were assigned to all non-hydrogen atoms. The organic hydrogen atoms were generated geometrically; the hydrogen atoms of the water molecules were located from difference maps and refined with isotropic temperature factors. Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated. The crystallographic data and details of refinements for **1–2** are summarized in Table 1, selected bond lengths and angles are listed in Table 2, selected hydrogen bonds lengths [Å] and angles [°] are listed in Table S1. CCDC-1031674 (**1**), and CCDC-1031675 (**2**) contain the supplementary crystallographic data for this paper.

Table 1
Crystal data and structure refinement information for compounds **1–2**.

	1	2
Empirical formula	C ₁₈ H ₂₄ Br ₂ CuN ₈ O ₂	C ₁₈ H ₂₄ CuF ₆ N ₈ O ₂ Si
Fw	607.81	590.08
crystal system	Monoclinic	Monoclinic
Space group	P2 ₁ /c	P2 ₁ /c
a (Å)	10.9995(12)	10.4169(9)
b (Å)	8.8942(10)	21.292(2)
c (Å)	11.9732(14)	10.4629(9)
α (°)	90	90
β (°)	108.727(2)	90.216(2)
γ (°)	90	90
V (Å ³)	1109.3(2)	2320.6(4)
Z	2	4
F(000)	606	1204
ρ (Mg/m ³)	1.820	1.689
abs coeff (mm ⁻¹)	4.620	1.076
Data/restraints/params	1946/0/150	4071/0/331
GOF	1.075	1.046
R1 ^a (I = 2 σ (I))	0.0426	0.0829
WR2 ^a (all data)	0.0918	0.1865

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$, $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$.

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