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Anion-Dependent Copper(II) Coordination Polymers Based on 1,3-Di-(1,2,4-Triazole-4-yl)benzene: Syntheses and Crystal Structures[1]

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Abstract—Three Cu(II) coordination polymers, namely $\{[Cu(Dtb)(H_2O)](SO_4)(H_2O)\}_n$ (**I**), $\{[Cu(Dtb)(C_2O_4)(H_2O)](H_2O)_2\}_n$ (**II**), and $\{[Cu(Dtb)(NO_3)](NO_3)(H_2O)_2\}_n$ (**III**) (Dtb = 1,3-di-(1,2,4-triazole-4-yl)benzene), have been synthesized under hydrothermal conditions and characterized by elemental analyses, IR spectra, and single-crystal X-ray diffraction (CIF file CCDC nos. 1001347 (**I**); 1001348 (**II**); 1001349 (**III**)). Complex **I** is a 1D double-chain structure, Dtb acts as $\mu_{1,1'}$-bridging ligand and SO_4^{2-} does not participate in coordination. In contrast, complex **II** shows a 1D single-chain, in which Dtb shows $\mu_{1,2'}$-bridges mode and $C_2O_4^{2-}$ occupies two coordination positions. In complex **III**, NO_3^- shortens the distance of two Cu(II) centers by bridging coordination interaction, so Dtb becomes $\mu_{1,1',2,2'}$-bridges linker to extend the Cu(II) centers to the resulting 2D layer.

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INTRODUCTION

Coordination polymers (CPs) have attracted considerable research interest in the past two decades, not only because of their intriguing variety of structures but also owing to their potential applications as functional materials [1–4]. It is well known that the structures and properties of the CPs are mainly dependent on two facts, organic ligands and metal atoms, which are main constructing elements of CPs. The reaction conditions used such as the temperature, solvent, pH, also usually result in completely different framework structures in the assemble process of CPs [5–7]. Moreover, counter anions in the crystal can also significantly influence the final structure by coordination or intermolecular interactions [8–10]. 1,2,4-Triazole and its derivatives are of particular interest in coordination chemistry [11–15], since they are effective bridging ligands combing the coordination modes of imidazoles and pyrazoles. As a double 1,2,4-triazole ligand, 1,3-di-(1,2,4-triazole-4-yl)benzene (Dtb) has been paid attention due to its multiple coordination modes [16–18]. In this work, we have chosen SO_4^{2-}, $C_2O_4^{2-}$, and NO_3^- as the anions to construct different coordination polymers with Dtb. As a result, three Cu(II) coordination polymers, $\{[Cu(Dtb)(H_2O)](SO_4)(H_2O)\}_n$ (**I**), $\{[Cu(Dtb)(C_2O_4)(H_2O)](H_2O)_2\}_n$ (**II**), and $\{[Cu(Dtb)(NO_3)](NO_3)(H_2O)_2\}_n$ (**III**), have been synthesized and characterized.

[1] The article is published in the original.

EXPERIMENTAL

Materials and methods. Dtb was prepared according to the literature method [18]. The other reagents for syntheses and analyses were obtained from commercial sources and used without further purification. IR spectra were recorded on a Nicolet Avatar-360 spectrometer. ^{1}H NMR spectrum was measured using a Bruker DPX-400 spectrometer. Elemental analyses were carried out on a Flash 1112 analyzer.

Synthesis of I. A mixture of $CuSO_4 \cdot 5H_2O$ (49.9 mg, 0.2 mmol), Dtb (21.2 mg, 0.1 mmol), and 10 mL water was sealed in a 25 mL Teflon-lined stainless steel vessel, which was heated at 120°C for 72 h and then cooled to room temperature at a rate of 5°C h^{-1}. The blue block crystals of **I** were obtained with yield of 33%.

IR (KBr; ν, cm^{-1}): 3089, 2989, 1650, 1534, 1236, 1104, 968, 799, 681.

For $C_{20}H_{24}N_{12}O_8SCu$

anal. calcd., %:	C, 36.61;	H, 3.69;	N, 25.62.
Found, %:	C, 36.43;	H, 3.75;	N, 25.38.

Table 1. Crystallographic data and structure refinement for complexes **I**–**III**

Parameter	Value		
	I	**II**	**III**
Formula weight	656.11	417.83	435.82
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$C2/c$	$P\bar{1}$	$P2_1/c$
a, Å	12.5018(17)	7.5775(10)	11.023(3)
b, Å	14.629(2)	9.9701(13)	7.039(2)
c, Å	15.259(2)	10.8440(14)	20.662(6)
α, deg	90	88.4030(10)	90
β, deg	93.077(2)	78.7990(10)	101.707(4)
γ, deg	90	77.0810(10)	90
V, Å^3	2786.7(7)	783.20(18)	1569.8(8)
Z	4	2	4
ρ_{calcd}, mg/m^3	1.564	1.772	1.844
μ, mm^{-1}	0.926	1.448	1.457
F(000)	1348	426	884
θ Range, deg	2.48–25.50	2.81–25.50	2.46–25.00
Reflections collected	9278	5880	5225
Independent reflections (R_{int})	2572 (0.0343)	2901 (0.0152)	2700 (0.0468)
Goodness of fit on F^2	1.055	1.061	1.068
R_1, wR_2 ($I > 2\sigma(I)$)	0.0403, 0.1015	0.0307, 0.0816	0.0768, 0.2258
R_1, wR_2 (all data)	0.0570, 0.1086	0.0363, 0.0858	0.1088, 0.2467
$\Delta\rho_{max}/\Delta\rho_{min}$, e Å^{-3}	0.417/–0.357	0.366/–0.330	1.742/–1.986

Synthesis of II was carried out by the same procedure as **I**, except adding $Na_2C_2O_4$ (13.4 mg, 0.1 mmol) in the reaction mixture. The blue block crystals of **II** were obtained with yield of 21%.

IR (KBr; ν, cm^{-1}): 3100, 2987, 1674, 1605, 1402, 1240, 1058, 788, 686.

For $C_{12}H_{14}N_6O_7Cu$

anal. calcd., %:	C, 34.50;	H, 3.38;	N, 20.11.
Found, %:	C, 34.33;	H, 3.52;	N, 19.93.

Synthesis of III was carried out by the same procedure as **I**, except using of $Cu(NO_3)_2 \cdot 3H_2O$ (48.2 mg, 0.2 mmol) instead of $CuSO_4 \cdot 5H_2O$. The blue block crystals of **III** were obtained with yield of 25%.

IR (KBr; ν, cm^{-1}): 3146, 3065, 1617, 1504, 1424, 1367, 1293, 1056, 887, 685.

For $C_{10}H_{12}N_8O_8Cu$

anal. calcd., %:	C, 27.56;	H, 2.78;	N, 25.71.
Found, %:	C, 27.33;	H, 2.85;	N, 25.91.

X-ray diffraction analysis. Diffraction data for **I**–**III** were collected on a Bruker SMART APEX II CCD diffractometer equipped with a graphite-monochromated MoK_α radiation (λ = 0.71073 Å). The structures were solved by direct methods with SHELXS-97 [19] and refined by the least-squared method with SHELXL-97 program [20]. Most hydrogen atoms were assigned with common isotropic displacement factors and included in the final refinement by use of geometrical restrains. The crystallographic data for compound **I**–**III** are listed in Table 1, and the selected bond lengths and bond angles are given in Table 2.

Supplementary material for structures **I**–**III** has been deposited with the Cambridge Crystallographic Data Centre (nos. 1001347 (**I**); 1001348 (**II**); 1001349 (**III**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

Three Cu(II) coordination polymers based on 1,3-di-(1,2,4-triazole-4-yl)benzene (Dtb) with different counter anions have been synthesized through hydrothermal reactions of the similar precursors. Complexes **I**–**III** exhibit different 1D, 1D, and 2D structures, respectively. The structures depend on the nature of the anions (SO_4^{2-}, $C_2O_2^{2-}$, and NO_3^-), which

Table 2. Selected bond distances (Å) and angles (deg) for complexes **I**–**III**

I

Bond	*d*, Å	Bond	*d*, Å
Cu(1)–N(2)	2.022(3)	Cu(1)–O(1)	2.339(3)
Cu(1)–N(5*B*)$^{\#1}$	2.031(3)		
Angle	**ω, deg**	**Angle**	**ω, deg**
N(2)Cu(1)N(5*B*)$^{\#1}$	89.30(14)	N(5*B*)$^{\#1}$Cu(1)O(1)	90.69(15)
N(2)Cu(1)O(1)	87.91(13)		

II

Bond	*d*, Å	Bond	*d*, Å
Cu(1)–O(3)	1.9297(18)	Cu(1)–N(6*A*)$^{\#2}$	2.000(2)
Cu(1)–O(1)	1.9690(18)	Cu(1)–O(5)	2.311(2)
Cu(1)–N(2)	1.9752(19)		
Angle	**ω, deg**	**Angle**	**ω, deg**
O(3)Cu(1)O(1)	83.33(8)	N(2)Cu(1)N(6*A*)$^{\#2}$	96.87(8)
O(3)Cu(1)N(2)	168.75(10)	O(3)Cu(1)O(5)	100.45(10)
O(1)Cu(1)N(2)	91.15(8)	O(1)Cu(1)O(5)	95.96(9)
O(3)Cu(1)N(6*A*)$^{\#2}$	87.24(8)	N(2)Cu(1)O(5)	89.84(9)
O(1)Cu(1)N(6*A*)$^{\#2}$	168.16(8)	N(6*A*)$^{\#2}$Cu(1)O(5)	92.78(9)

III

Bond	*d*, Å	Bond	*d*, Å
Cu(1)–N(6*C*)$^{\#3}$	1.986(7)	Cu(1)–N(3*A*)$^{\#4}$	2.015(7)
Cu(1)–N(5*B*)$^{\#4}$	1.997(7)	Cu(1)–O(1')$^{\#4}$	2.39(3)
Cu(1)–N(2)	2.007(7)	Cu(1)–O(1)	2.299(16)
Angle	**ω, deg**	**Angle**	**ω, deg**
N(6*C*)$^{\#3}$Cu(1)N(5*B*)$^{\#4}$	176.8(3)	N(5*B*)$^{\#4}$Cu(1)O(1')	99.8(8)
N(6*C*)$^{\#3}$Cu(1)N(2)	88.5(3)	N(2)Cu(1)O(1')	86.7(8)
N(5*B*)$^{\#4}$Cu(1)N(2)	90.2(3)	N(3*A*)$^{\#5}$Cu(1)O(1')	97.6(8)
N(6*C*)$^{\#3}$Cu(1)N(3*A*)$^{\#5}$	91.0(3)	O(1)Cu(1)O(1')	11.6(9)
N(5*B*)$^{\#4}$Cu(1)N(3*A*)$^{\#5}$	90.0(3)	N(6C)$^{\#3}$Cu(1)O(1')$^{\#5}$	93.5(8)
N(2)Cu(1)N(3*A*)$^{\#5}$	175.6(3)	N(5*B*)$^{\#4}$Cu(1)O(1')$^{\#5}$	83.5(9)
N(6*C*)$^{\#3}$Cu(1)O(1)	91.7(4)	N(2)Cu(1)O(1')$^{\#5}$	89.2(7)
N(5*B*)$^{\#4}$Cu(1)O(1)	90.9(4)	N(3*A*)$^{\#5}$Cu(1)O(1')$^{\#5}$	86.5(7)
N(2)Cu(1)O(1)	79.3(4)	O(1)Cu(1)O(1')$^{\#5}$	167.2(8)
N(3*A*)$^{\#5}$Cu(1)O(1)	105.1(4)	O(1')Cu(1)O(1')$^{\#5}$	174.7(11)
N(6*C*)$^{\#3}$Cu(1)O(1')	83.0(8)		

* Symmetry codes: $^{\#1}\,x-1/2,-y+1/2,z+1/2$; $^{\#2}\,x+1,y-1,z$; $^{\#3}\,x+1,y,z$; $^{\#4}\,-x+1,y-1/2,-z+1/2$; $^{\#5}\,-x+2,y-1/2,-z+1/2$.

present during the synthesis. In complex **III**, the bridging NO_3^- shorten the distance between Cu^{2+} ions, so Dtb can bridging four Cu^{2+} ions as $\mu_{1,1',2,2'}$ mode to generate the final 2D layer. As far as complexes **I** and **II**, uncoordinated SO_4^{2-} or terminal ligand $C_2O_2^{2-}$ can not help Dtb to generate higher dimensional structures. Moreover, the geometry of Dtb in **I**, **II**, and **III** are greatly different, which can be seen from the dihedral angles between triazole ring and benzene ring.

The asymmetric unit of **I** contains one Cu^{2+} ion, two Dtb ligands, two coordinated water molecules, two

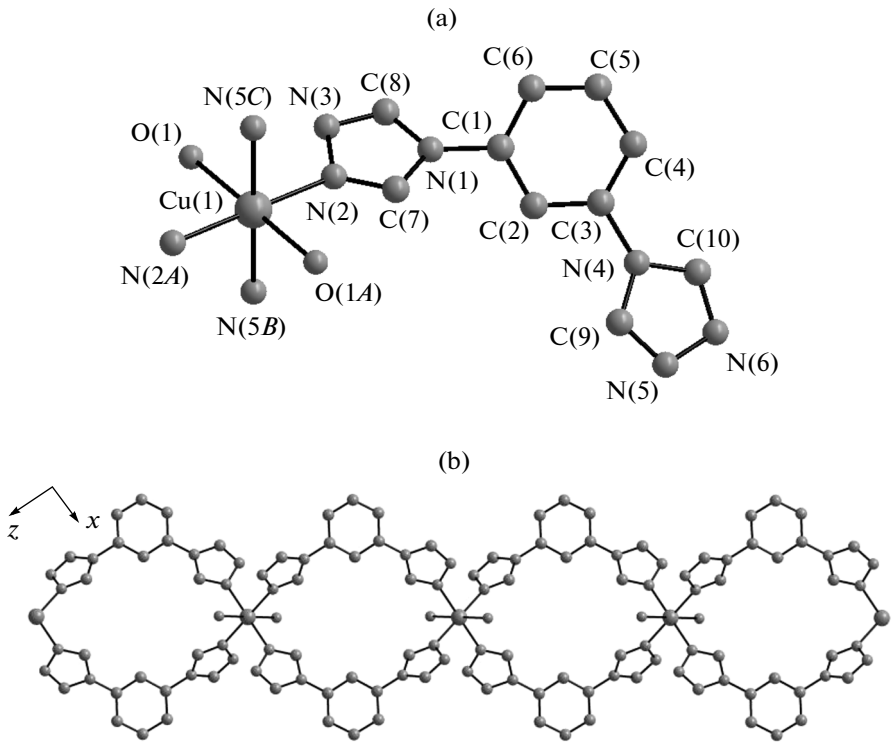

Fig. 1. Coordination environment of Cu(II) atom (a) and the view of 1D double chain (b) in crystal of **I**.

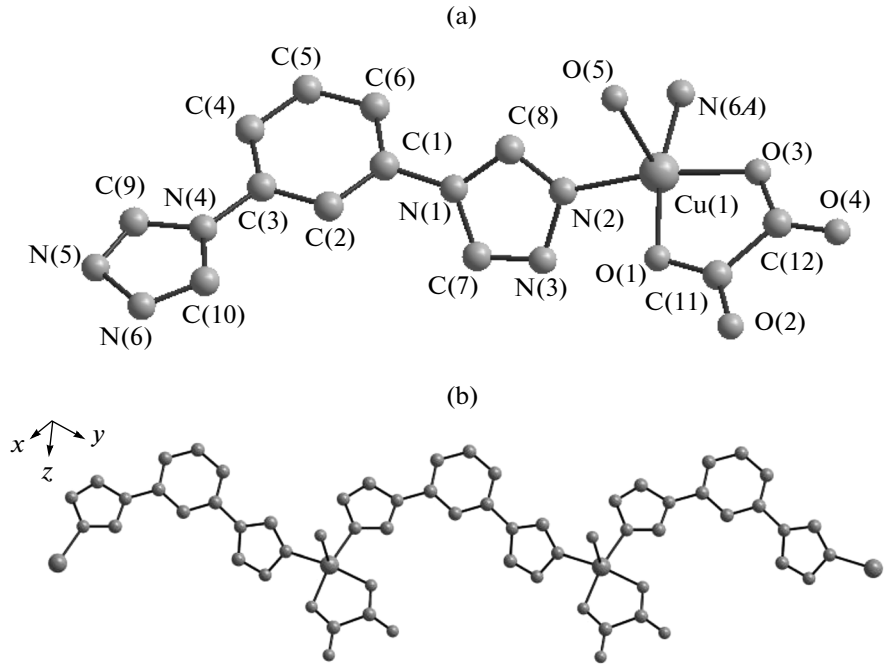

Fig. 2. Coordination environment of Cu(II) atom (a) and the view of 1D single chain (b) in crystal of **II**.

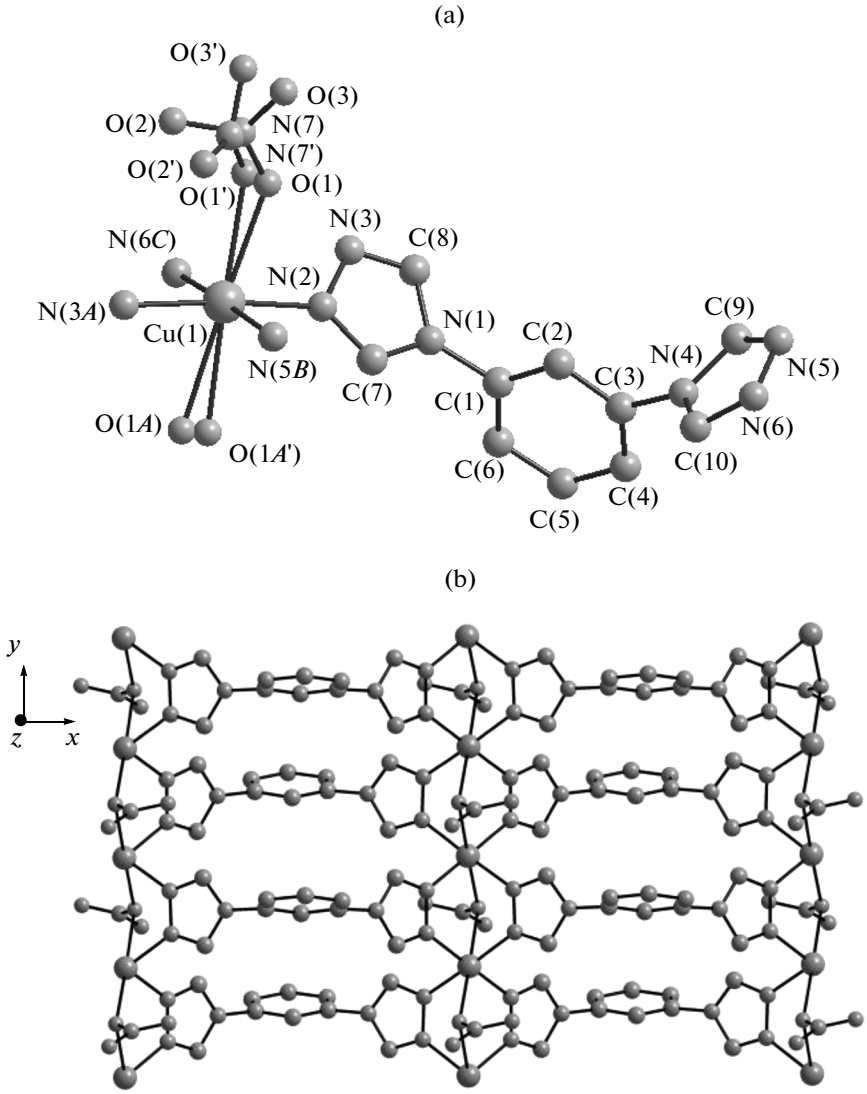

Fig. 3. Coordination environment of Cu(II) atom (a) and the view of 2D layer (b) in crystal of **III**.

lattice water molecules, and one SO_4^{2-} anion (Fig. 1). The Cu(1) center is six-coordinated and has an alongated tetragonal bipyramid (4 + 2) coordination environment. The equatorial plane is completed by four nitrogen atoms (N(2), N(2*A*), N(5*B*), and N(5*C*)) from four Dtb ligands, while the axial positions are occupied by two oxygen atoms (O(1) and O(1*A*)) from two water molecules. All Cu–N bond distances of Cu(1) (Table 2) are similar to those reported values for the Cu(II)/triazole complexes [21, 22]. In complex **I**, Dtb acts as $\mu_{1,1'}$-bridging ligand, and the dihedral angles between triazole ring and benzene ring are 19.98(8)° and 42.17(5)°, respectively. Each Cu(II) center connects with four Dtb ligands and each Dtb ligand connects with two Cu(II) centers, and therefore the 1D double-chains are formed with a Cu···Cu distance of 10.119(1) Å (Fig. 1). It should be pointed out that the 1D chain is centrosymmetric with Cu atom as its inversion center.

The asymmetric unit of **II** contains one Cu^{2+} ion, one Dtb ligand, one coordinated $C_2O_4^{2-}$ anion, one coordinated water molecule, and two lattice water molecules (Fig. 2). Each Cu^{2+} ion shows a distorted tetragonal pyramidal geometry (4 + 1), two nitrogen atoms (N(2) and N(6*A*)) from two Dtb ligands and two oxygen atoms (O(1) and O(3)) from a $C_2O_4^{2-}$ anion form the basal plane, and the apical position is occupied by one water oxygen atom (O(5)). All Cu–N bond distances of Cu(1) (Table 2) are in accord with those reported values for the Cu(II)/triazole complexes [23, 24]. In complex **II**, each Dtb ligand shows $\mu_{1,2'}$-bridges mode, and the dihedral angles between triazole ring and benzene ring are 6.39(9)° and 41.30(8)°, respec-

tively. Adjacent Cu^{2+} ions are linked into 1D chain by Dtb, and the $C_2O_4^{2-}$ anion only acts as terminal ligand (Fig. 2). The Cu···Cu distance is 11.092(1) Å.

The asymmetric unit of **III** contains one Cu^{2+} ion, one Dtb ligand, one disorder coordinated NO_3^- anion, one uncoordinated NO_3^- anion, and two lattice water molecules (Fig. 3). The Cu(1) center is six-coordinated in an alongated tetragonal bipyramid (4 + 2) by four nitrogen atoms (N(2), N(3*A*), N(5*B*), and N(6*C*)) from four Dtb ligands and two oxygen atoms (O(1) and O(1*A*)) from two NO_3^- anions. All Cu–N bond distances of Cu(1) (Table 2) are comparable to those observed in other Cu(II)/triazole complexes [25, 26]. In complex **III**, each Dtb ligand adopts $\mu_{1,1',2,2'}$-bridges mode to connect four Cu^{2+} ions, leading to the formation of a 2D layered structure (Fig. 3). The dihedral angles between triazole ring and benzene ring are 79.65(9)° and 82.46(3)°, respectively. The NO_3^- acts as an auxiliary ligand in a monodentate coordination mode to bridge two Cu^{2+} ions. The Cu···Cu distance is 3.525(1) Å.

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