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Influence of the Size of Aromatic Chelate Ligands on the One-Dimensional Chains of Copper(II) Dicarboxylate Coordination Polymers[1]

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Abstract—To investigate the influence of the size of aromatic chelate ligands on the frameworks of metal dicarboxylate polymers, two one-dimensional coordination compounds $[Cu(BDC)(TATP)(H_2O)]_n$ (**I**) and $[Cu(BDC)(DPPZ)]_n$ (**II**), (BDC = 1.4-benzenedicarboxylate, TATP = 1,4,8,9-tetranitrogentrisphene, DPPZ = dipyrido[3,2-a:2',3'-c]phenazine) were synthesized under similar conditions and structurally characterized by X-ray crystallography. Compounds **I** and **II** have the similar zigzag chain structure, but the substitution of TATP with DPPZ results in the difference of the degree of bending of the chain, indicating that the sizes of the rigid aromatic chelate ligands have important effect on the structures of their complexes.

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INTRODUCTION

The design and synthesis of organometallic framework coordination polymers have provoked significant interest mainly because of their potential properties as materials ranging from catalysis, gas absorption, molecular recognition, and optics, as well as their fascinating framework structures [1–4]. In order to control the topology structure and geometry of the networks to produce useful functional materials, a great interest has been devoted to the theoretical forecast and practical approaches. However, the design of synthetic pathways to obtain systems with desired properties continues to be a challenge for inorganic chemists, because the self-assembly progress is highly influenced by several factors, such as the metal/ligand nature [5], solvent [6–8], templates [9–11], and counterions [12]. In this respect, the influence of ligand spacers of flexible bridging ligands on the framework formation of their coordination polymers has widely been documented [13, 14]. However, the studies on the effect of the size of the N-donor chelate ligand on the framework formation of their complexes have rarely been reported [15–17]. In this paper, we report two metal dicarboxylate complexes with an N-donor chelate ligand TATP and its large analog DPPZ and studied the effects of the size of the aromatic chelate ligands and the coordinating water molecules on the framework structures of their coordination polymers, namely, $[Cu(BDC)(TATP)(H_2O)]_n$ (**I**) and $[Cu(BDC)(DPPZ)]_n$ (**II**) (BDC = 1,4-benzenedicarboxylate, TATP = 1,4,8,9-tetranitrogentrisphene, DPPZ = dipyrido[3,2-a:2',3'-c]phenazine).

EXPERIMENTAL

The aromatic chelate ligand TATP and DPPZ were synthesized according to the literature method [18, 19], all other reagents and solvents employed were commercially available and used without further purification. The C, H, and N microanalyses were carried out with Perkin–Elmer 240 elemental analyzer.

Synthesis I. A mixture of $Cu(NO_3)_2 \cdot 3H_2O$ (0.120 g, 0.5 mmol), TATP (0.118 g, 0.5 mmol), H_2BDC (0.041 g, 0.25 mmol), NaOH (0.02 g, 0.5 mmol), and H_2O (10 ml) was mixed in a 23-ml Teflon reactor, which was heated at 160°C for 6 days and then cooled to room temperature at a rate of 5°C/h. Blue block crystals of **I** were obtained in 58% yield after being washed with water and dried in air. The yield was ~58%.

For $C_{22}H_{14}CuN_4O_5$			
anal. calcd, %:	C, 55.29;	H, 2.95;	N, 11.72.
Found, %:	C, 55.24;	H, 2.90;	N, 11.75.

Syntheses II. A mixture of $Cu(NO_3)_2 \cdot 3H_2O$ (0.120 g, 0.5 mmol), DPPZ (0.144 g, 0.5 mmol), H_2BDC (0.041 g, 0.25 mmol), NaOH (0.02 g, 0.5 mmol), and H_2O (10 ml) was mixed in a 23-ml Teflon reactor, which was heated at 160°C for 6 days and then cooled to room temperature at a rate of 5°C/h. Blue block crystals **II** were

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[1] The article is published in the original.

Table 1. Crystallographic parameters and summary of data collection for structure **I** and **II**

Formula weight	477.91	509.95
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$
Unit cell dimensions:		
a, Å	11.450(2)	9.783(1)
b, Å	15.009(3)	10.472(1)
c, Å	12.175(2)	11.413(1)
α, deg	90	115.66(1)
β, deg	116.396(3)	95.560(1)
γ, deg	90	104.489 (1)
V, Å^3	1874.2(6)	991.85(2)
Z	4	2
ρ_c, g/cm^3	1.694	1.708
μ, mm	1.213	1.149
$F(000)$	972	518
Crystal size, mm	0.37 × 0.32 × 0.25	0.51 × 0.36 × 0.12
θ Range, deg	2.03–26.00	2.04–26.00
Reflections collected (all data)	10038	5484
Independent reflections (R_{int})	3678 (0.0247)	3822 (0.0141)
Goodness-of-fit on F^2	1.041	1.071
Parameters	289	316
Final R indices ($I > 2\sigma(I)$)[a]	$R_1 = 0.0383$, $wR_2 = 0.1049$	$R_1 = 0.0364$, $wR_2 = 0.0983$
R indices (all data)	$R_1 = 0.0463$, $wR_2 = 0.1120$	$R_1 = 0.0404$, $wR_2 = 0.1016$
Largest diff. peak and hole, e Å^{-3}	0.612, –0.646	0.639, –0.334

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

obtained in 35% yield after being washed with water and dried in air. The yield was ~35%.

For $C_{26}H_{14}CuN_4O_4$			
anal. calcd, %:	C, 61.24;	H, 2.77;	N, 10.99.
Found, %:	C, 61.29;	H, 2.80;	N, 11.05.

X-ray crystallography. Crystallographic data for **I** and **II** were collected at room temperature (293(2) K) on a Bruker P4 diffractometer with MoK_α radiation ($\lambda = 0.71073$ Å) and a graphite monochromator using the ω scan mode. The structures were solved by direct methods and refined on F^2 by full-matrix least squares using SHELXTL [20]. All non-hydrogen atoms were treated anisotropically. The positions of hydrogen atoms were generated geometrically. Crystallographic data and experimental details for structural analyses are summarized in Table 1. Selected bond lengths and

Table 2. Selected bond distances (Å) and angles (deg) for **I** and **II***

Bond	*d*, Å	Bond	*d*, Å
I		**II**	
Cu(1)–O(1*w*)	1.937(2)	Cu(1)–O(2)	1.940(2)
Cu(1)–N(1)	1.994(2)	Cu(1)–N(2)	1.996(2)
Cu(1)–O(3)	2.226(2)	Cu(1)–O(6)	1.954(2)
Cu(1)–O(2)^i	1.959(2)	Cu(1)–N(1)	2.025(2)
Cu(1)–N(2)	2.042(2)		
Angle	ω, deg	Angle	ω, deg
I		**II**	
O(1*w*)Cu(1)O(2)^i	94.63(8)	O(2)Cu(1)O(1)	88.58(1)
O(2)^{i}Cu(1)N(1)	91.05(8)	O(6)Cu(1)N(2)	94.69(1)
N(1)Cu(1)N(2)	81.44(9)	O(6)Cu(1)N(1)	160.83(1)
O(1*w*)Cu(1)O(3)	92.44(7)	O(2)Cu(1)N(2)	167.43(1)
N(1)Cu(1)O(3)	99.24(8)	O(2)Cu(1)N(1)	99.43(1)
O(1*w*)Cu(1)N(1)	166.16(9)	N(2)Cu(1)O(1)	81.27(1)
O(2)^{i}Cu(1)N(2)	166.69(9)		
O(1*w*)Cu(1)N(2)	90.44(8)		
O(2)^{i}Cu(1)O(3)	98.26(8)		
N(2)Cu(1)O(3)	93.81(8)		

* Symmetry transformations used to generate equivalent atoms for **I**: ^{i} –*x* + 3/2, *y* – 1, –*z* + 5/2.

angles are listed in Table 2. Supplementary material for structure **I** and **II** has been deposited with the Cambridge Crystallographic Data Centre (no. 700831 (**I**) and 700832 (**II**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

In the crystal structure of **I**, there is one Cu(II) atom, one bis(monodentate) BDC ligand, one TATP ligand, and one aqua ligand in an independent crystallographic unit. The Cu(II) atom in **I** is five-coordinated by two nitrogen atoms from one TATP ligand (Cu(1)–N(1) 1.994(2), Cu(1)–N(2) 2.041(3) Å), three oxygen atoms from two individual BDC ligands (Cu(1)–O(2) 1.959(1), Cu–O(3B) 2.225(2) Å) and one coordination water molecule (Cu(1)–O(5) 1.937(3) Å). Thus, the Cu(II) center displays a square-pyramidal coordination geometry. The TATP ligand binds to one Cu(II) atom in a chelate mode and the BDC group adopts only one coordination mode, both of the carboxyl groups binding to two individual Cu(II) ions monodentately (Fig. 1a). The pair of Cu(II) atoms are bridged by a BDC ligand to form a infinite zigzag chain, where the CuCuCu angles, defined by the orientation of the BDC ligand are 83.05°. The Cu–Cu distance within the chain is 11.319(3) Å. The TATP ligands decorate two sides of the chain alternately (Fig. 1b). The lateral TATP ligands from adjacent chains are paired to furnish π–π stacking interactions [21, 22]. It is observed that π–π stacking between the adjacent TATP ligands (*x* + 1/2, *y* + 1/2, *z* + 1/2) with perpendicular separation of 3.409(2) Å, a centroid-to-centroid distance of 3.836 Å, and slip angle (the angle between the centroid vector normal to the plane) of 27.29°. These values are typical of aromatic π–π stacking interactions [23]. The C(20) atom of BDC ligand also has C–H···π interactions with a the TATP aromatic ring (C(1), C(2), C(3), C(4), C(12), N(1)) at (–*x* + 1, –*y*, –*z*) of an adjacent chain (C(20) atom–ring centroid distance ~3.250(2) Å). The adjacent chains are further linked *via* π–π stacking interactions to construct a two-dimensional wave-like layer (Fig. 2). Strong O···H···O hydrogen bonds exist between carboxylate oxygen atoms of BDC ligands and oxygen atoms of coordination water molecules (Table 3). The hydrogen bonds linked the two-dimensional wave-like layer into a three-dimensional supromulecular network. The hydrogen bonds and π–π and C–H···π stacking interactions enhance the stability of the complex (Fig. 2).

When DPPZ, an aromatic chelate ligand of a larger size, was used instead of TATP, analogous zigzag chain of **II** is formed under similar reaction conditions. However, unlike compound **I**, Cu(II) atoms in **II** adopt different coordination patterns. As shown in Fig. 3a, the Cu(II) center is coordinated by two oxygen atoms from two bis(monodentate) BDC ligands (Cu(1)–O(2) 1.940(2), Cu(1)–O(6) 1.954(1) Å) and two nitrogen atoms from the chelate DPPZ (Cu(1)–N(1) 2.025(2),

Table 3. Geometric parameters of hydrogen bonds in cristal structure **I***

D–H···A	Distance, Å			Angle D–H···A, deg
	D–H	H···A	D···A	
O(1*w*)–H(1*wB*)···O(4)	0.85	1.86	2.577 (3)	141
O(1*w*)–(1*wA*)···O(1*w*)^{ii}	0.85	2.45	2.965 (4)	120

* Symmetry codes: ^{ii} *x* + 2, –*y*, –*z* + 2.

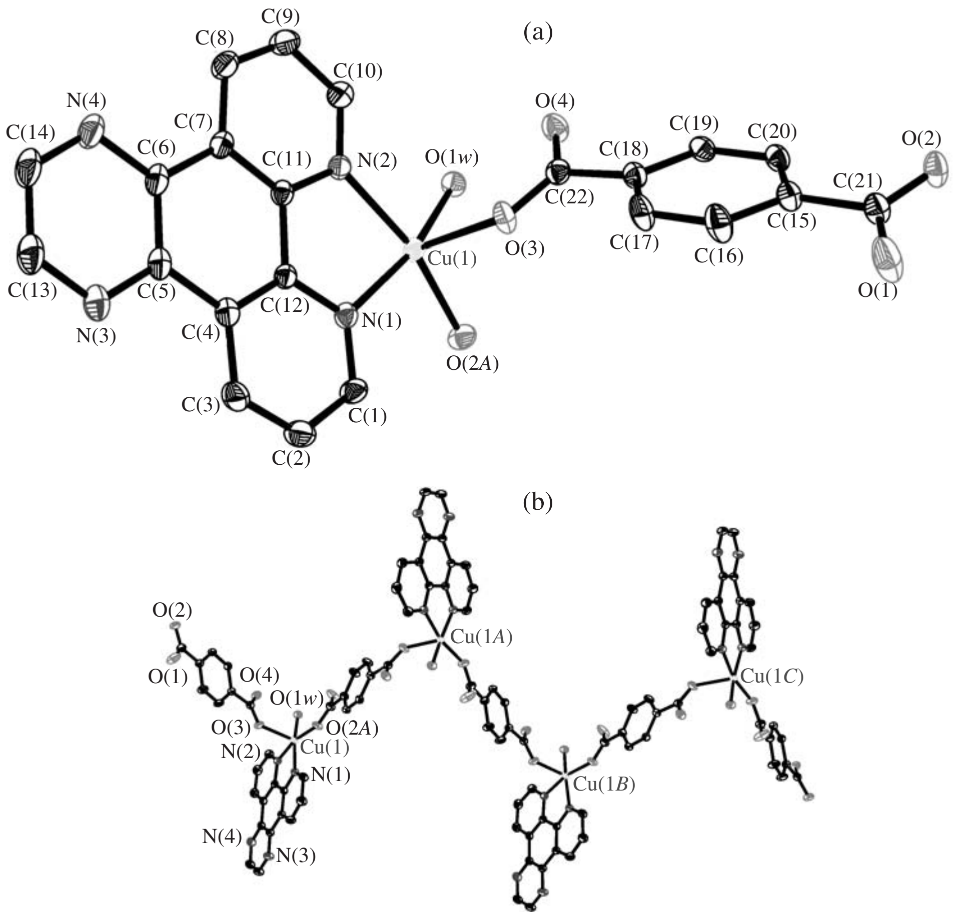

Fig. 1. Coordination environment of the copper atom and a fragment of the zigzag chain in **I**.

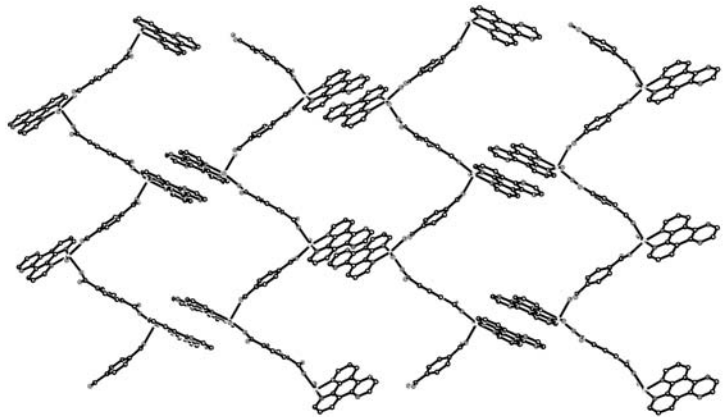

Fig. 2. Two-dimensional wave-like layer constructed by π–π stacking interactions.

Cu(1)–N(2) 1.996(2) Å) to furnish a distorted square-planar coordination geometry. Similarly to **I**, the BDC ligands bridge each pair of adjacent Cu(II) atoms into a zigzag chain running along the *x* axis and the DPPZ ligands are alternately attached to both sides of the zigzag chains (Fig. 3b). It is noted that compared to the chain in **I**, the substitution of TATP with larger DPPZ in **II** causes a decrease in the CuCuCu angle, leading to a more bent chain. The observed CuCuCu angle within the chain is 65.65° in **II**. The Cu–Cu distances for cop-

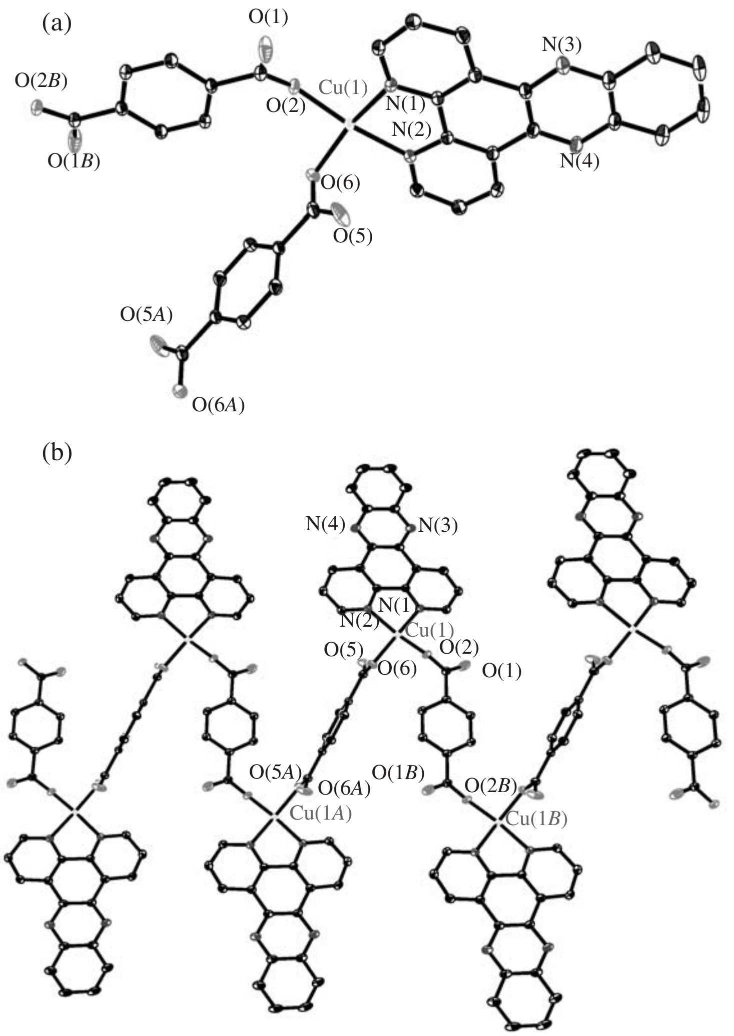

Fig. 3. Coordination environment of the copper atom and a fragment of the zigzag chain in **II**.

per atoms bridged by bis(monodentate) BDC ligand (10.617(5) and 10.925 Å) in **II** are similar to those in **I**.

The presence of chelate ligands in transition metal dicarboxylate systems usually results in the formation of low-dimensional coordination polymers with the metal ions acting as nodes and the dicarboxylate ligands as connectors, especially 1D chains. The sizes of the chelate ligands and the incorporation of the coordinating water molecule, play a major role in determining the coordination modes of mental centers and the degrees of bending of the chains. As shown above, compounds **I** and **II** have the similar structures, where the copper centers chelated by amine ligands are bridged by BDC ligands bismonodenatly to form an infinite zigzag chain. The major structural difference between **I** and **II** lies in the incorporation of the coordinating water molecules in the lattice, which results in the different coordination environment of Cu^{2+} ions and, hence, causes variation of the bending angle of CuCuCu. In this context, we may conclude that the substitution of TATP with DPPZ, an aromatic chelate ligand of a larger size, resulted in the loss of a coordinating water molecule. Furthermore, affecting the degree of bending of the chain indicates that the size of the rigid aromatic chelate ligands have an important effect on the structures of their complexes.

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