ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2009, Vol. 35, No. 6, pp. 468–472. © Pleiades Publishing, Ltd., 2009.

Influence of the Size of Aromatic Chelate Ligands on the One-Dimensional Structures of Copper(II) 4,4'-Oxy-bis(benzoate) Coordination Polymers[1]

Y. J. Song and Z. B. Han*

College of Chemistry, Liaoning University, Shenyang 110036, P.R. China

**e-mail: ceshzb@lnu.edu.cn*

Received September 24, 2008

Abstract—Two one-dimensional coordination polymers, $[Cu(Oba)(TATP)]_n \cdot nH_2O$ (I) and $[Cu(Oba)(DPPZ)(H_2O)]_n \cdot nH_2O$ (II) (Oba is 4.4'-oxy-bis(benzoate), TATP is 1,4,8,9-tetranitrogen-tris(phene), DPPZ is dipyrido[3,2-a:2',3'-c]phenazine), have been synthesized under similar conditions and structurally characterized by elemental analysis, IR spectra, and X-ray crystal structure. Compounds I and II are based on topologically identical chains, where the copper centers chelated by the amine ligands are linked by the Oba bridges, as well as the coordination modes of the Oba ligands. However, the angles between the individual links and the environment of the copper centers are substantially different between the two compounds and were found to be primarily influenced by the sizes of the rigid aromatic chelate ligands.

DOI: 10.1134/S1070328409060141

Current interest in metal-organic frameworks is rapidly expanding for their fascinating structures and potential applications as adsorption [1–3], separation, and catalysis [4, 5]. Additionally, the ability to incorporate almost all the elements of the periodic table along with the possibility of introducing functionality through the organic linkers provide the added impetus for the continuing interest [6, 7]. On the one hand, the metal clusters may introduce their inherent extraordinary physical properties to the polymeric frameworks [8–11]. On the other hand, the exceptional stability of polymerized products makes them more promising in potential applications than the metallic clusters themselves [12, 13]. As is known, the self-assembling process involving metal ions and organic ligands has attracted increasing attention for the development of novel functional materials with desired properties [14–17]. However, in most cases, it is still difficult to predict the exact structures and compositions of the assembling products by the mixed ligands [18], because the self-assembling progress is highly influenced by several factors, such as the geometric preference of metal ions, the sizes and shapes of the organic building blocks, templates, solvent systems, and counterions [19–21]. So, it is a challenge for inorganic chemists to design the synthetic pathways to obtain systems with desired properties. Despite this challenge, some notable successes have achieved in the area, such as the discovery of the influence of ligand spacers of flexible bridging ligands on the framework formation of their coordination polymers [22]. 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 [23]. Accordingly, in the copper(II)–4,4'-oxy-bis(benzoate) (**Oba**) system, two copper(II) complexes were synthesized by using different amine ligands – 1,4,8,9-tetranitrogen-tris(phene) (**TATP)** and dipyrido[3,2-a:2',3'-c]phenazine (**DPPZ**). The aim of this study is to analyze the influence of the size of the N-donor chelate ligand on the framework formation of their complexes.

EXPERIMENTAL

The aromatic chelate ligand TATP was synthesized according to the literature method [24]. All other reagents and solvents employed were commercially available and used without further purification. The C, H, and N microanalyses were carried out with a Perkin-Elmer 240 elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the range 4000–400 cm^{-1} on a Nicolet 5DX spectrometer.

Synthesis $[Cu(Oba)(TATP)]_n \cdot nH_2O$ (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_2Oba (0.129 g, 0. 5 mmol), NaOH(0.02 g, 0.5 mmol), and H_2O (10 ml) were 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. Green block crystals of **I** were obtained in 45% yield

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Table 1. Crystallographic data for **I** and **II**

Parameter	Value	
	I	**II**
Formula weight	570.00	640.09
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
Unit cell dimensions:		
a, Å	5.8058(7)	5.6229(8)
b, Å	14.6212(2)	14.7298(2)
c, Å	27.578(3)	32.997(4)
β, deg	91.842	93.466
V, Å^3	2339.8(5)	2727.9(6)
Z	4	4
ρ_c, g/cm^3	1.618	1.559
μ, mm	0.989	0.861
$F(000)$	1164	1316
θ Range, deg	1.48–26.00	1.24–28.32
Reflections collected (all data)	12605	16120
Independent reflections ($R_{\rm int}$)	4570 (0.0436)	6177 (0.0533)
Max, min transmission	0.6797, 0.8001	0.7424, 0.8234
Goodness-of-fit on F^2	1.148	1.156
Refined parameters	352	392
Final R indices ($I > 2\sigma(I)$)*	$R_1 = 0.0621$ $wR_2 = 0.1370$	$R_1 = 0.0766$ $wR_2 = 0.1794$
R indices (all data)	$R_1 = 0.0838$ $wR_2 = 0.1570$	$R_1 = 0.1073$ $wR_2 = 0.2010$
Largest diff. peak and hole, e Å^{-3}	0.508, –0.528	0.560, –0.793

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

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

Bond	d, Å	Angle	ω, deg
		I	
Cu(1)–O(5)	1.914(3)	O(5)Cu(1)O(1A)	90.47(1)
Cu(1)–N(1)	2.001(3)	O(1A)Cu(1)N(1)	175.59(1)
Cu(1)–O(1A)	1.930(3)	O(1A)Cu(1)N(2)	93.79(1)
Cu(1)–N(2)	2.002(3)	O(5)Cu(1)N(1)	93.87(1)
		O(5)Cu(1)N(2)	175.73(1)
		N(1)Cu(1)N(2)	81.88(1)
		II	
Cu(1)–O(5)	1.943(3)	O(5)Cu(1)O(2A)	90.36(14)
Cu(1)–N(2)	2.023(4)	O(2A)Cu(1)N(2)	95.66(14)
Cu(1)–O(1w)	2.287(3)	O(2A)Cu(1)N(1)	174.91(14)
Cu(1)–O(2A)	1.968(3)	O(5)Cu(1)O(1w)	95.36(13)
Cu(1)–N(1)	2.024(4)	N(2)Cu(1)O(1w)	91.92(13)
		O(5)Cu(1)N(2)	169.88(14)
		O(5)Cu(1)N(1)	92.29(15)
		N(2)Cu(1)N(1)	81.11(15)
		O(2A)Cu(1)O(1w)	97.39(12)
		N(1)Cu(1)O(1w)	86.69(14)

* Symmetry transformations used to generate equivalent atoms for **I** and **II**: (A) $-x + 1/2$, $y + 1/2$, $-z + 1/2$ for I; $-x + 1/2$, $y + 1/2$, $-z + 1/2$ for II.

after being washed with water and dried in air. The yield was ~45%.

For $C_{28}H_{18}CuN_4O_6$			
anal. calcd, %:	C, 59.00;	H, 3.18;	N, 9.83.
Found, %:	C, 59.05;	H, 3.20;	N, 9.80.

IR spectrum (KBr; ν, cm^{-1}): 3462 (H_2O), 1607 $\nu_{as}(COO^-)$, 1570 $\nu_{as}(COO^-)$, 1483 $\nu s(COO^-)$.

Synthesis $[Cu(Oba)(DPPZ)(H_2O)]_n \cdot nH_2O$ (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_2Oba (0.129 g, 0. 5 mmol), NaOH (0.02 g, 0.5 mmol), and H_2O (15 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. Red block crystals of **II** were obtained after being washed with distilled water and dried in air. The yield was ~56%.

For $C_{32}H_{24}CuN_4O_7$:			
anal. calcd, % :	C, 60.04;	H, 3.78;	N, 8.75.
Found, %:	C, 60.09;	H, 3.75;	N, 8.70.

IR spectrum (KBr; ν, cm^{-1}): 3448 (H_2O), 1599 $\nu_{as}(COO^-)$, 1560 $\nu_{as}(COO^-)$, 1496 $\nu_s(COO^-)$.

X-ray diffraction analysis. Single-crystal X-ray diffraction measurements were carried out on a Bruker Smart Apex CCD diffractometer at room temperature (293 K). The data collections were performed with MoK_α radiation ($\lambda = 0.71073$ Å). Unit cell dimensions were obtained with least-squares refinements, and structures **I** and **II** were solved by a direct method. The non-hydrogen atoms were located in the successive dif-

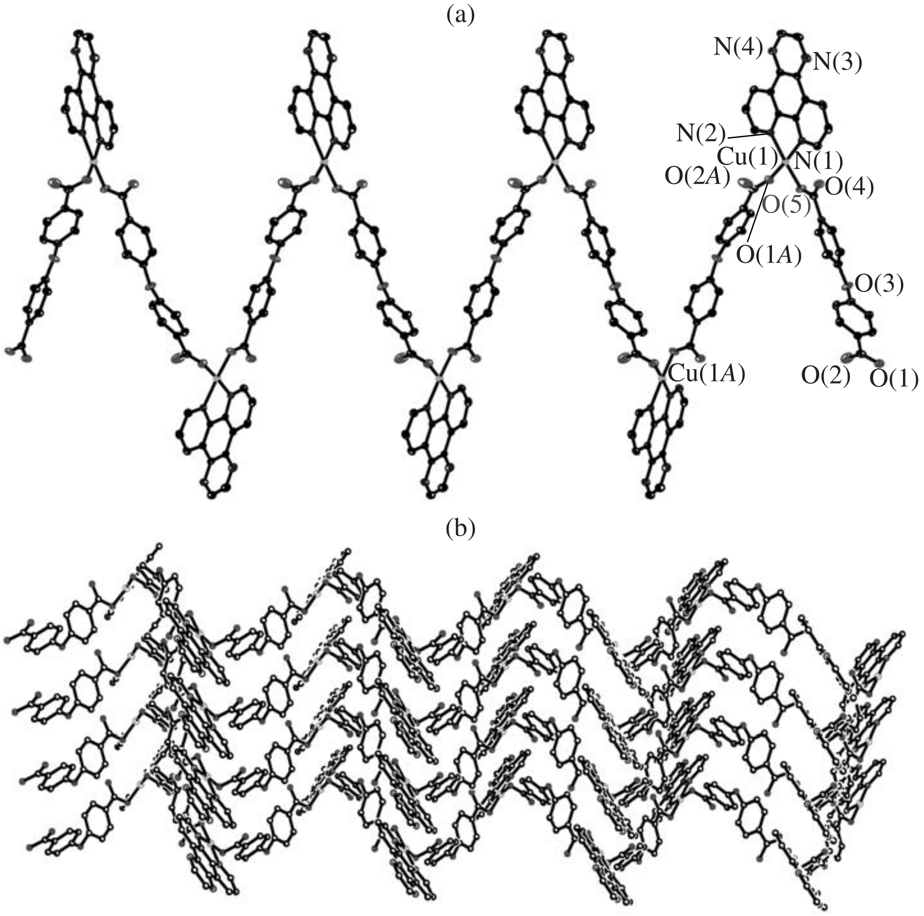

Fig. 1. The coordination environment of the copper atom: fragment of the zigzag chain in **I** (a), 2D wave like layers constructed π–π stacking interactions in **I** (b).

ference Fourier syntheses. The final refinement was performed by full-matrix least-squares methods with anisotropic thermal parameters for non-hydrogen atoms on F^2 [25]. Hydrogen atoms were added theoretically and were riding on their parent atoms. Crystallographic data and experimental details for structural analyses are summarized in Table 1, and the selected bond lengths and bond angles are listed in Table 2.

RESULTS AND DISCUSSION

In the crystal structure of I, there is one Cu atom, one bismonodentate Oba ligand, and one TATP ligand in each independent crystallographic unit. The Cu atom in **I** is primarily coordinated by two oxygen atoms from two individual Oba ligands (Cu(1)–O(5) 1.914(3), Cu(1)–O(1*A*) 1.930(3) Å) and two nitrogen atoms from the chelate TATP ligand (Cu(1)–N(1) 2.001(3), Cu(1)–N(2) 2.002(3) Å) to furnish a distorted square planar coordination geometry (Fig. 1a). First, the Cu atom is chelated by the TATP ligand and then each pair of Cu atoms are bridged by a Oba ligand bismonodenatly to form a infinite zigzag chain, where the CuCuCu angle defined by the orientation of the Oba ligands is 57.53. The Cu–Cu distance within the chain is 14.621 Å. The TATP ligands decorate two sides of the chain alternately (Fig. 1b).

Compound **II** has the similar chain structure with **I**, where the copper centers chelated by amine ligands are linked by Oba bridges bismonodentately. However, the coordination environment of the Cu(II) centers, as well as the angles between the individual links are substantially different among the two compounds. Figure 2a shows the Cu(II) coordination environment in **II**. The Cu(II) center is coordinated by two nitrogen atoms from a chelate DPPZ ligand (Cu(1)–N(1) 2.024(4), Cu(1)–N(2) 2.023(4) Å), three oxygen atoms from two bismonodentate Oba ligands (Cu(1)–O(5) 1.943(3), Cu(1)–O(2A) 1.968(3) Å), and one coordination water molecule (Cu(1)–O(1w) 2.287(3) Å) to furnish a distorted tetrahedral geometry. The bismonodenate Oba ligands bridge each pair of Cu(II) atoms into an infinite zigzag chain, where the CuCuCu angle, defined by the orientation of the Oba ligands is 58.10° and the Cu–Cu distances within the chain are 14.730 Å. Similarly to **I**, the DPPZ ligands are alternately attached to both sides

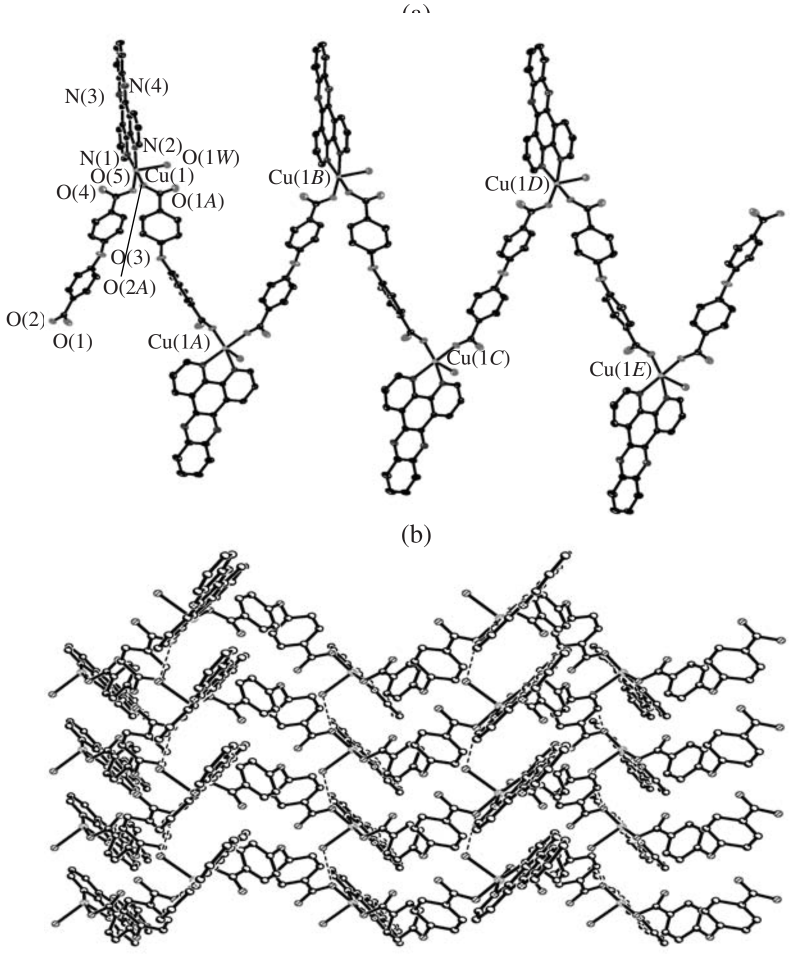

Fig. 2. The coordination environment of copper the atom: fragment of the zigzag chainin **II** (a), 2D wavelike layer showing π–π stacking interactions in **II** (b).

of the zigzag chain. In contrast to **I**, the incorporation of the water molecule in **II** causes an increase in the CuCuCu angle to 58.10°, leading to a less bent chain.

The IR spectrum of **I** shows that the characteristic bands of carboxyl groups at 1607 and 1570 cm^{-1} for the antisymmetric stretching and at 1483 cm^{-1} for symmetric stretching. The IR spectrum of **II** shows that the characteristic bands of carboxyl groups at 1599 and 1560 cm^{-1} for antisymmetric stretching and at 1496 cm^{-1} for symmetric stretching. The separations between $\nu_{as}(CO_2)$ and $\nu_s(CO_2)$ indicate the presence of the monodentate coordination mode [26]. The absence of strong characteristic peaks around 1720 cm^{-1} indicates that all carboxylic groups are completely deprotonated [27], which is consistent with the results of the X-ray analysis.

In summary, we successfully synthesized two new coordination polymers $[Cu(Oba)(TATP)]_n \cdot nH_2O$ and $[Cu(Oba)(DPPZ)(H_2O)]_n \cdot nH_2O$ under similar reaction conditions. Compounds **I** and **II** have the identical 1D zigzag chain, and the coordination mode of Oba ligands. 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, and the employment of a V-shaped dicarboxylate may generate helical chains. The incorporation of the coordinating water molecule, which plays a major role in determining the coordination mode of dicarboxylate ligands and the degree of bending of the chain, is primarily influenced by the size of chelate ligands. As shown for **I** and **II**, the DPPZ (the chelate aromatic ligand of a larger size) was used instead of TATP resulted in the incorporation of the coordinating water molecule and caused an increase in the CuCuCu angle, leading to less bent chains. The observed CuCuCu angles within the chains are 57.53° in **I** and 58.10° in **II**. In this context, we may conclude that the bending degree of the chains decreases with a larger chelate ligand or incorporation of coordinating water molecule.

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