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# Hydrothermal syntheses and crystal structures of two 4,4'biphenyldicarboxylate copper(II) complexes with 1,10-phenanthroline

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### Abstract

Two structurally diverse compounds,  $[Cu(Hbpdc)_2(phen)]$  (1) and  $[Cu(bpdc)(phen)(H_2O)]_n$  (2)  $(H_2bpdc = 4,4'$ -biphenyldicarboxylic acid, phen = 1,10-phenanthroline), were synthesized under hydrothermal conditions. Copper atom in 1 is four-coordinated to one bidentate phen ligand and two monodentate partly deprotonated 4,4'-biphenyldicarboxylates. As expected, the structure of 1 is a monomeric species and affords an extended two-dimensional hydrogen bonding architecture. Each copper atom in 2 is five-coordinated to one phen, one water molecule, and two bis-monodentate fully deprotonated 4,4'-biphenyldicarboxylates. Therefore, the structure of 2 is a one-dimensional chain. © 2004 Elsevier B.V. All rights reserved.

Keywords: Hydrogen bonding; Crystal structure; Copper complex; Diversity; Polymer

#### 1. Introduction

Structural or framework diversity of coordination polymers is currently under intensive studies due to the important relationship between structures and properties [1-3]. Many successful examples of structural diversity have been achieved in the syntheses of benzenedicarboxylate complexes [4-8]. Recently, 4,4'-biphenyldicarboxylic acid (H<sub>2</sub>bpdc), which is a longer rigid spacer, has attracted attention to construct novel coordination polymers with potential applications as functional materials [9-13]. Here, we represent two copper complexes of 4,4'-biphenyldicarboxylate complexes with partly and fully deprotonated ligands, namely [Cu(Hbpdc)<sub>2</sub>(phen)] (1) and [Cu(bpdc)(phen)(H<sub>2</sub>O)]<sub>n</sub> (2).

## 2. Experimental

#### 2.1. Synthesis and IR spectra

For the preparation of compound **1**, a mixture of Cu(CH<sub>3</sub> COO)<sub>2</sub>· H<sub>2</sub>O (0.040 g, 0.2 mmol), 4,4'-biphenyldicarboxylic

acid (0.048 g, 0.2 mmol), and 1,10-phenanthroline (0.080 g, 0.4 mmol) in an aqueous solution (8 ml) was sealed in a 25 ml stainless-steel reactor with Teflon liner, then heated to 120 °C and kept at this temperature for 24 h. Blue block crystals were obtained after being cooled to room temperature. Anal. Calc. For  $C_{40}H_{26}CuN_2O_8$ : C, 66.16; H, 3.61; N, 3.86%. Found: C, 66.32; H, 3.57; N, 3.94%.

A similar procedure was used for preparation of compound **2**. A mixture of Cu(CH<sub>3</sub>COO)<sub>2</sub>·H<sub>2</sub>O (0.040 g, 0.2 mmol), 4,4'-biphenyldicarboxylic acid (0.048 g, 0.2 mmol), and 1,10-phenanthroline (0.040 g, 0.2 mmol), sodium hydroxide (0.012 g, 0.3 mmol), and water (8 ml) was sealed in a 25 ml stainless-steel reactor with Teflon liner and heated at 140 °C for 24 h. After cooling, blue block crystals of compound **2** were filtrated and dried in vacuum. Anal. Calc. For C<sub>26</sub>H<sub>18</sub>CuN<sub>2</sub>O<sub>5</sub>: C, 62.21; H, 3.61; N, 5.58%. Found: C, 61.97; H, 3.70; N, 5.68%.

The two carboxylic protons of  $H_2$ bpdc have different acidity values. The unprecedented compound **1** involves the first deprotonated state of Hbpdc<sup>-</sup>. Under hydrothermal condition using aqueous NaOH solution, we expect the proton on Hbpdc<sup>-</sup> to be easily deprotonated and thus compound **2** was synthesized. This strategy allows us to create different structure topologies.

The IR spectra of compounds 1 and 2 display the asymmetric and symmetric stretching vibrations of the carboxylate groups at 1546, 1426, and  $1389 \text{ cm}^{-1}$  for

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Table 1 Crystal data and details of structural determination of compounds 1 and 2

Formula	$\mathrm{C}_{40}\mathrm{H}_{26}\mathrm{CuN}_{2}\mathrm{O}_{6}$	$\mathrm{C_{26}H_{18}CuN_2O_5}$	
Fw	726.17	501.965	
Crystal color, shape	Blue, block	Blue, block	
Crystal size $(mm^3)$	$0.26 \times 0.25 \times 0.19$	$0.50 \times 0.18 \times 0.14$	
Space group	Monoclinic (C2/c)	Monoclinic (P21/n)	
a (Å)	12.9262(5)	14.599(4)	
b (Å)	24.4718(10)	9.764(2)	
c (Å)	10.0004(4)	16.936(4)	
$\alpha$ (deg)	90	90	
$\beta$ (deg)	90.443(2)	95.581(5)	
$\gamma$ (deg)	90	90	
$V(Å^3)$	3163.3(2)	2402.6(10)	
$D (Mg/cm^{-3})$	1.525	1.388	
T (K)	$293 \pm 2$	$293 \pm 2$	
$\mu (\mathrm{mm}^{-1})$	0.753	0.953	
Measured reflections	8420	13387	
Independent reflections	2859	5073	
Observed reflections	2859	5073	
R1 and wR2 $(I > 2\sigma(I))$	0.055, 0.130	0.069, 0.185	
R1 and wR2 (all data)	0.059, 0.132	0.121, 0.202	
Number of variables	231	325	
Goodness-of-fit (GOF)	1.133	0.982	
Largest difference peak and hole (e $Å^{-3}$ )	0.470, -0.355	0.980, -0.484	

compound **1** and 1543, 1426, and  $1382 \text{ cm}^{-1}$  for compound **2**, respectively. The strong absorption at 1708 cm<sup>-1</sup> in compound **1** is in agreement with a carboxylic group, while in compound **2** no absorption peak of any protonated ligand (1680–1730 cm<sup>-1</sup>) confirms completely deprotonation of H<sub>2</sub>bpdc by sodium hydroxide.

#### 2.2. Single crystal structure determination

Crystals with dimensions of 0.26 mm × 0.25 mm × 0.19 mm for compound **1** and 0.50 mm × 0.18 mm × 0.14 mm for compound **2** were carefully selected and mounted on a Bruker Smart CCD area detector with graphite monochromatized Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). An empirical absorption correction was applied using the SADABS program [14]. The structures were solved by direct methods using SHELXS-97 [15] and refined by least-squares procedures on  $F_0^2$  with SHELXL-97 [16] in the WinGX environment [17]. Crystal data and structure refinements are given in Table 1.

#### 3. Results and discussion

Compound **1** consists of a mononuclear Cu<sup>II</sup> complex and has two-fold symmetry (Fig. 1). The molecule displays a square planar geometry and atom Cu1 is coordinated by two oxygen atoms of two monodentate carboxylate groups and two nitrogen atoms of one 1,10-phenanthroline ligand. Distances associated with the coordination sphere are



Fig. 1. ORTEP view of compound [Cu(Hbpdc)<sub>2</sub>(phen)] (1).

1.922(2) Å for Cu-O and 1.989(2) Å for Cu-N (Table 2). Atoms of N1, O2, N1\* (symmetry code: 2 - x, y, 1/2 - z), and O2\* consist of a square planar geometry with the rms = 0.1646, indicating some deviations from perfect square plane. Each Hbpdc<sup>-</sup> ligand affords one deprotonated carboxylate and one carboxylic group, leading to a single negative charge on the ligand. The coordination behavior of the deprotonated carboxylate group results in a larger dihedral angle [22.73(39)°] between deprotonated carboxylate group and its connected benzene ring as compared with the smaller dihedral angle  $[8.94(11)^{\circ}]$ between the carboxylic group and its attached benzene ring. The dihedral angles of two benzene rings and between deprotonated carboxylate group and carboxylic group for one Hbpdc<sup>-</sup> ligand are 47.29(10)° and 77.44(28)°, respectively, indicating some flexible nature of the Hbpdc<sup>-</sup> ligand.

It is worth noting that the hydroxyl group forms hydrogen bond with uncoordinated oxygen atom (O1) and the hydrogen bond length of  $O1 \cdots O4^*$  distance is 2.6260 (34) Å, thus the structure is assembled into 2D hydrogen bonding network (Fig. 2). The hydrogen bonding interaction made the structure more stable.

Table 2Selected bond lengths and angles for compound 1

Cu1–O2	1.922(2)	Cu1-N1	1.989(2)
O2–Cu1–N1	93.0(1)	O2-Cu1-N1*	169.2(1)
O2–Cu1–O2*	92.7(2)	N1-Cu1-N1*	83.0(1)

Symmetry code: \*, 2 - x, y, 1/2 - z.

102



Fig. 2. Two-dimensional hydrogen bonding network view of (1). Phenanthroline ligands and H atoms were deleted for clarity.



Fig. 3. ORTEP view of  $[Cu(bpdc)(phen)(H_2O)]_n$  (2).

Table 3 Selected bond lengths and angles for compound **2** 

Cu1-O1	1.931(4)	Cu1-O4#	2.267(4)
Cu1-O5	1.963(3)	Cu1-N1	2.015(4)
Cu1-N2	2.025(5)		
O1-Cu1-O4#	100.3(2)	O1-Cu1-O5	95.1(2)
O1-Cu1-N1	89.9(2)	O1-Cu1-N2	166.0(2)
O5-Cu1-O4#	90.4(2)	O5-Cu1-N1	166.8(2)
O5-Cu1-N2	91.7(2)	N1-Cu1-O4#	100.8(2)
N1-Cu1-N2	81.0(2)	N2-Cu1-O4#	91.9(2)

Symmetry code: #, 1 - 2 + x, -1/2 + y, z.

In compound 2, the copper center is five-coordinated and is a square pyramidal geometry (Fig. 3). Atoms of O1, O5, N1, and N2 are sitting in the basal plane, while the atom O4# (symmetry code: 1/2 + x, -1/2 + y, z) occupies the apical position. The copper center coordinates to two monodentate oxygen atoms of two  $bpdc^{2-}$ ligands in the cis positions with Cu-O distances of 1.931(4) and 2.267(4) Å (Table 3). The other three sites are occupied by one terminal water with a Cu-O distance of 1.963(3) Å and by 1,10-phenanthroline with Cu-N distances of 2.015(4) and 2.025(5) Å. The  $bpdc^{2-}$ in compound 2 is coordinated to metal ions as bismonodentate mode, so that the structure is extended into one-dimensioanl zig-zag chain with the Cu-.-Cu separation of 15.473(2) Å by  $bpdc^{2-}$  linkage (Fig. 4). The dihedral angle between two rings of  $bpdc^{2-}$  is 24.76(39)°, indicating some torsion, while the carboxylate has a nearly co-planar with the benzene ring.

Framework diversity in the system of Cu<sup>2+</sup>/bpdc/phen is interesting. Besides above two compounds, a tetranuclear compound,  $[Cu_4(bpdc)_4(phen)_4(H_2O)_2](2H_2O)$  (3), with fully deprotonated ligand based on the system of Cu<sup>2+</sup>/bpdc/phen, was synthesized [18]. The synthetic strategy of compound 3 is similar to that of 2 except triethylamine used in the synthesis of 3. A close look at the crystal structures of 1, 2, and 3 reveals some important feature regarding their structure formations. In compound 1, Hbpdc<sup>-</sup> is partly deprotonated and coordinated as a monodentate ligand, in compound 2, bpdc<sup>2-</sup> is fully deprotonated and coordinated as bismonodentate mode, while in compound 3 the  $bpdc^{2-}$  is in monodentate-bidentate mode. Therefore, compound 1 is a monomer, compound 2 is a one-dimensional chain, and compound 3 is a rhombic species.

In summary, the syntheses and structures of two compounds,  $[Cu(Hbpdc)_2(phen)]$  (1) and  $[Cu(bpdc) (phen)(H_2O)]_n$  (2), have been accomplished. The framework diversity associated with compounds 1 and 2 shows monomer and one-dimensional chain. The exploration of the nature of framework diversity will be benefit for the design of new functional compounds.



104

#### 4. Supplementary materials

Crystallographic data (excluding structure factors) for the structural analysis have been deposited with the Cambridge Crystallographic Data Center as supplementary publication No. 235941 and 235942 for compounds **1** and **2**, respectively. Copies of the data can be obtained free of charge via www.ccdc.ac.uk/conts/retrieving.html (or from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, fax: +44-1223-336-033. E-mail: deposit@ccdc.cam. ac.uk).

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