

Two-dimensional Copper Coordination Polymers Based on Paddle-Wheel Type Secondary Building Units of $\text{Cu}_2(\text{CO}_2\text{R})_4$: $[\text{Cu}(1,3\text{-BDC})(\text{H}_2\text{O})]\cdot 2\text{H}_2\text{O}$ and $[\text{Cu}_2(\text{OBC})_2(\text{H}_2\text{O})_2]\cdot \text{H}_2\text{O}$ (1,3-BDC = 1,3-benzenedicarboxylate; OBC = 4,4'-oxybis(benzoate))

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Received August 31, 2004

Key Words : CuBDC, CuOBC, 2-D coordination polymer, Paddle wheels, SBU

Coordination polymers with a variety of cavities or channels have got continuous attraction due to their useful zeolite-like properties and potential applications as functional materials.¹⁻⁵ In designing extended porous coordination polymers, the selection of appropriate ligands is crucial to determining the structural outcome of target polymers. In this context, the concept of "node-spacer", in which the node corresponds to a metal (or a metal complex) and the spacer to a linking ligand, has become a fundamental tool in the rational design of crystalline architectures.⁶

Secondary building units (SBUs) are molecular complexes or clusters, in which ligand-coordination modes and metal-coordination environments are utilized to incorporate these fragments into extended networks through multidentate ligands.⁷ The SBUs have long been fundamental concepts in zeolite chemistry,⁸⁻¹⁰ and now draw considerable attention as a firm basis of synthetic strategies for constructing high-dimensional coordination polymers. For example, Yaghi and co-workers used the paddle-wheel cluster of the type $[\text{M}_2(\text{CO}_2\text{R})_4]$ (M = Cu or Zn) as a square-planar SBU to prepare porous polymers with large voids and channels.⁷

We recently prepared several coordination polymers based on a mixed-ligand system possessing dicarboxylates and bipyridyls by hydrothermal or hydro(solvo)thermal reactions.¹¹⁻¹⁷ As a continuation of our work, we set out to prepare copper coordination polymers based only on dicarboxylates, 1,3-benzenedicarboxylate (1,3-BDC) and OBC (OBC = 4,4'-oxybis(benzoate)). The 1,3-BDC ligand has a coordination angle of 120° , and the OBC ligand has a flexible coordination angle due to the central oxygen atom in the ligand backbone. Hydro(solvo)thermal treatments of copper(II) nitrate ($\text{Cu}(\text{NO}_3)_2\cdot 2.5\text{H}_2\text{O}$) with 1,3-BDC and OBCH₂ gave 2-dimensional networks. In this contribution,

we report 2-D copper coordination polymers, $[\text{Cu}(1,3\text{-BDC})(\text{H}_2\text{O})]\cdot 2\text{H}_2\text{O}$ (1) and $[\text{Cu}_2(\text{OBC})_2(\text{H}_2\text{O})_2]\cdot \text{H}_2\text{O}$ (2), which are based on paddle-wheel type SBUs of $[\text{Cu}_2(\text{CO}_2\text{R})_4]$.

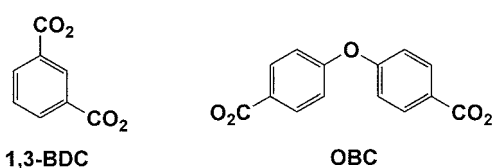
Experimental Section

$\text{Cu}(\text{NO}_3)_2\cdot 2.5\text{H}_2\text{O}$, 1,3-BDCH₂, and OBCH₂ were purchased. IR spectra were recorded with a Nicolet 320 FTIR spectrophotometer. Elemental analyses were performed with EA1110 (CE instrument, Italy) at the Korea Basic Science Institute.

Preparation of $[\text{Cu}(1,3\text{-BDC})(\text{H}_2\text{O})]\cdot 2\text{H}_2\text{O}$ (1). A mixture of $\text{Cu}(\text{NO}_3)_2\cdot 2.5\text{H}_2\text{O}$ (0.233 g, 1.00 mmol), 1,3-BDCH₂ (0.166 g, 0.999 mmol), benzene (3 mL, 0.0337 mol), and H₂O (5.0 mL, 0.277 mol) in the mole ratio of 1 : 1 : 34 : 277 was heated in a 23-mL Teflon-lined vessel at 180 °C for 3 days, and then cooled to room temperature. The green crystalline product was collected by filtration, washed with H₂O (2 × 5 mL), ethanol (3 × 5 mL), and acetone (2 × 5 mL), and then air-dried to give 0.220 g (0.781 mmol, 78.1%) of $[\text{Cu}(1,3\text{-BDC})(\text{H}_2\text{O})]\cdot 2\text{H}_2\text{O}$. mp: 307-309 °C (decom). IR (KBr): 3385, 3088, 1620, 1449, 1387, 1276, 1169, 1092, 750, 728, 671, 492 cm⁻¹. Anal. Calcd for C₈H₁₀O₇Cu: C, 34.11; H, 3.58. Found: C, 33.98; H, 3.75.

Preparation of $[\text{Cu}_2(\text{OBC})_2(\text{H}_2\text{O})_2]\cdot \text{H}_2\text{O}$ (2). This compound was prepared analogously. A mixture of $\text{Cu}(\text{NO}_3)_2\cdot 2.5\text{H}_2\text{O}$ (0.233 g, 1.00 mmol), OBCH₂ (0.258 g, 1.00 mmol), benzene (3 mL, 0.0337 mol), and H₂O (5.0 mL, 0.277 mol) was heated at 180 °C for 3 days to give 0.070 g (0.103 mmol, 20.6%) of $[\text{Cu}_2(\text{OBC})_2(\text{H}_2\text{O})_2]\cdot \text{H}_2\text{O}$. mp: 299-301 °C (decom). IR (KBr): 3385, 1611, 1496, 1398, 1249, 1159, 877, 775, 667, 475 cm⁻¹. Anal. Calcd for C₂₈H₂₁Cu₂O_{21.5}: C, 49.13; H, 3.09. Found: C, 49.27; H, 3.01.

X-ray structure determination. All X-ray data were collected with a Siemens P4 diffractometer equipped with a Mo X-ray tube. Intensity data were empirically corrected for absorption with ψ -scan data. All structures were solved by direct methods, and all non-hydrogen atoms were refined anisotropically. Unless otherwise stated, hydrogen atoms were generated in ideal positions and refined in a riding mode. All calculations were carried out with SHELXTL



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Table 1. X-ray data collection and structure refinement

	1	2
empirical formula	C ₈ H ₁₀ CuO ₇	C ₂₈ H ₂₁ Cu ₂ O _{12.5}
fw	281.70	684.53
temperature, K	293(2)	293(2)
crystal system	tetragonal	tetragonal
space group	<i>P4/n</i>	<i>I-4</i>
<i>a</i> , Å	19.106(2)	17.837(2)
<i>c</i> , Å	6.7812(6)	17.010(3)
<i>V</i> , Å ³	2475.5(4)	5412(1)
<i>Z</i>	8	8
<i>d</i> _{calc} , g cm ⁻³	1.512	1.680
<i>μ</i> , mm ⁻¹	1.779	1.641
<i>F</i> (000)	1144	2776
<i>T</i> _{min}	0.1919	0.6483
<i>T</i> _{max}	0.3663	0.8973
2θ range (°)	3.5–50	3.5–50
scan type	<i>ω</i>	<i>ω</i>
scan speed	variable	variable
No. of reflns measured	1188	2638
No. of reflns unique	1188	2628
No. of reflns with <i>I</i> > 2σ(<i>I</i>)	1087	2442
No. of params refined	146	396
Max., in Δρ (e Å ⁻³)	0.826	0.328
Min., in Δρ (e Å ⁻³)	-0.392	-0.331
<i>GOF</i> on <i>F</i> ²	1.063	1.074
<i>R</i>	0.0452	0.0320
<i>wR</i> ₂ ^a	0.1292	0.0771

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

programs.¹⁸

A green crystal of **1**, shaped as a plate of approximate dimensions 0.56 × 0.40 × 0.20 mm³, was used. The unit-cell parameters and systematic absences indicated two possible space groups: *P4/n* and *P4/nmm*. The structure analysis converged only in *P4/n*. The hydrogen atoms in the aqua ligand and guest water molecules could not be located.

A green crystal of **2**, shaped as a block of approximate dimensions 0.40 × 0.24 × 0.20 mm³, was used. The unit-cell parameters and systematic absences indicated three possible space groups: *I-4*, *I4/m*, and *I4*. The structure analysis converged only in *I-4*. Details on crystal data, intensity collection, and refinement details are given in Table 1. Selected bond lengths and bond angles are given in Tables 2

Table 2. Selected bond lengths (Å) and bond angles (°) in **1**

Cu1-Cu1#1	2.610(1)	Cu1-O1	1.956(4)	Cu1-O4#1	1.959(4)
Cu1-O2#1	1.962(4)	Cu1-O3	1.966(4)	Cu1-O5	2.130(4)
O1-Cu1-O4#1	89.8(2)	O1-Cu1-O2#1	167.8(2)	O4#1-Cu1-O2#1	87.9(2)
O1-Cu1-O3	90.4(2)	O4#1-Cu1-O3	168.1(2)	O2#1-Cu1-O3	89.4(2)
O1-Cu1-O5	98.6(2)	O4#1-Cu1-O5	93.8(2)	O2#1-Cu1-O5	93.6(2)
O3-Cu1-O5	97.9(2)	O1-Cu1-Cu1#1	86.2(1)	O4#1-Cu1-Cu1#1	81.7(1)
O2#1-Cu1-Cu1#1	81.6(1)	O3-Cu1-Cu1#1	86.5(1)	O5-Cu1-Cu1#1	173.5(1)

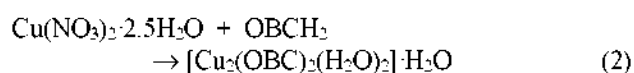
Symmetry transformations used to generate equivalent atoms: #1 = -x, -y + 1, -z + 1

and 3.

Crystallographic data for the structural analysis have been deposited at the Cambridge Crystallographic Data Center: CCDC No. 247686 for polymer **1** and 247687 for polymer **2**. Copies of this information may be obtained free of charge from: The director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Results and Discussion

Preparation. Two 2-dimensional copper(II) coordination polymers, [Cu(1,3-BDC)(H₂O)]·2H₂O (**1**) and [Cu₂(OBC)₂(H₂O)₂]·H₂O (**2**), were prepared from Cu(NO₃)₂·2.5H₂O and dicarboxylates (1,3-BDCH₂ for **1** and OBCH₂ for **2**) under hydro(solvo)thermal conditions (eqs 1 and 2). Both polymers are based on the paddle-wheel SBUs. When Cu(NO₃)₂·2.5H₂O was treated with a 1 : 1 mixture of 1,3-BDCH₂ and OBCH₂ under the same condition, polymer **2** was a sole product. This observation indicates that OBC has a greater coordinating ability than 1,3-BDC.



The preparation of polymer **1** deserves some considerations. With an attempt to prepare guest-containing open frameworks, we carried out solvothermal reactions of Cu(NO₃)₂·2.5H₂O with 1,3-BDCH₂ in the presence or absence of an organic base (pyridine or Bu₄NOH) under various conditions: (i) DMF/EtOH at 25 °C for 1 day, (ii) DMF/EtOH at 70–100 °C for 1–3 days, or (iii) DMF/EtOH/pyridine or Bu₄NOH at 70 °C for 3 days. Unfortunately, all these reactions failed to produce X-ray quality crystals. Only hydro(solvo)thermal reactions in the presence of benzene

Table 3. Selected bond lengths (Å) and bond angles (°) in **2**

Cu1-Cu2	2.6038(9)	Cu1-O1	1.958(4)	Cu1-O5	1.963(4)
Cu1-O10	1.978(4)	Cu1-O7	1.980(4)	Cu1-O11	2.196(5)
Cu2-O6	1.937(4)	Cu2-O2	1.954(4)	Cu2-O4	1.968(4)
Cu2-O9	1.973(5)	Cu2-O12	2.170(5)		
O11-Cu1-Cu2	175.9(1)	O12-Cu2-Cu1	168.7(2)		

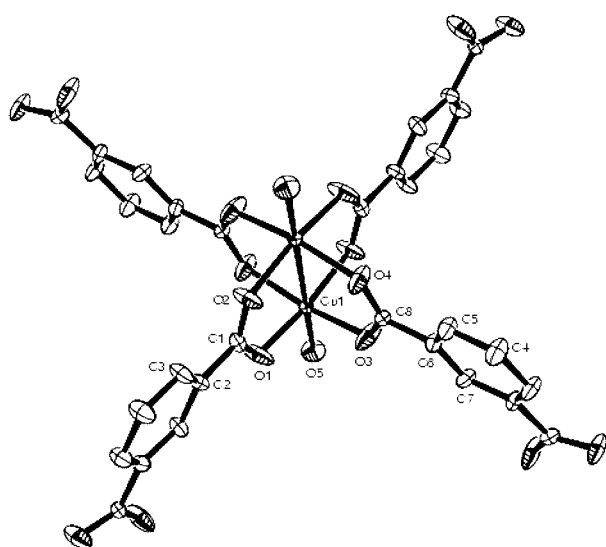


Figure 1. ORTEP drawing of a paddle-wheel unit of polymer 1.

led to the formation of single crystalline products. Although we do not know the exact function of benzene in our reaction system, benzene appears to have promoted the formation of good crystals. A similar approach was previously employed in the preparations of $\text{Cu}_3(\text{C}_6\text{H}_8\text{O}_4)_3(\text{H}_2\text{O})_2 \cdot (\text{C}_6\text{H}_{11}\text{OH})^{19}$ and $[\text{M}_3(2,6\text{-NDC})_3(\text{bipy})_{1.5}]^{17}$ (Ni or Co; NDC = 2,6-naphthalenedicarboxylate; bipy = 4,4'-bipyridine).

Structure. Figure 1 illustrates a paddle-wheel SBU of the type $[\text{M}_2(\text{OOCR})_4]$ in polymer 1, which comprises two copper metals and four di(monodentate) bridging carboxylates. A monomer unit consists of one 1,3-BDC ligand, one aqua ligand, and one copper(II) metal. The copper paddle-wheel $[\text{Cu}_2(\text{OOCR})_4]$ has been observed in several copper coordination polymers.^{7,20,21} The Cu-O (carboxylate) bond lengths lie in the range of 1.956(4)–1.966(4) Å, and the Cu-Cu bond length of 2.610(1) Å indicates a Cu-Cu single bond. Each copper metal has a pseudo-octahedral geometry, whose equatorial plane consists of four oxygen atoms from four 1,3-BDC. In addition, the axial positions are occupied by one copper atom and one aqua ligand. Two copper metals and four 1,3-BDC ligands form the paddle-wheel SBUs, which are linked by BDC ligands to give a 2-D network. The packing diagram of polymer 1 along the *c*-axis is shown in

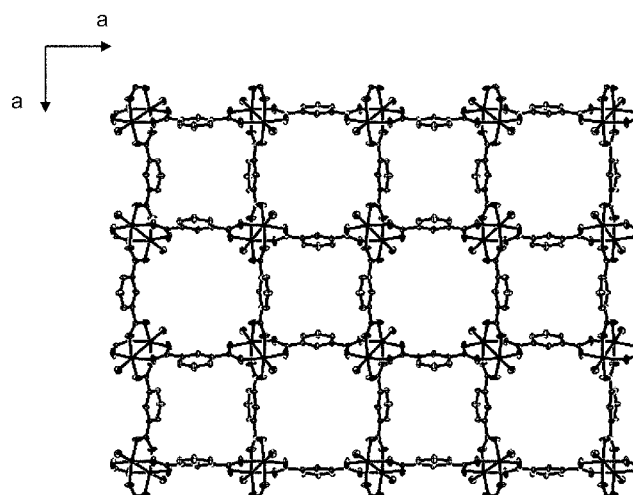


Figure 2. Packing diagram of polymer 1 along the *c*-axis.

Figure 2, which demonstrates a 2-dimensional square-grid network in the [110] direction. Each square grid has approximate dimensions of 9.6×9.6 Å based on Cu metals.

Polymer 2 has essentially the same framework as polymer 1. Figure 3 shows a paddle-wheel SBU of the type $[\text{Cu}_2(\text{OOCR})_4]$ in polymer 2. A monomer unit consists of two OBC ligands, two aqua ligands, and two copper(II) metals. The Cu-O (carboxylate) bond lengths are 1.937(4)–1.980(4) Å, and the Cu-Cu bond length is 2.6038(9) Å. The paddle-wheel SBUs, which consist of two copper metals and four carboxylates, are linked by OBC ligands to give a 2-D network (Figure 4). The packing diagram of polymer 2 along the *c*-axis (Figure 5) shows a 2-dimensional square-grid network, in which the constituent square grid has approximate dimensions of 14.8×14.8 Å, which are quite larger than those in polymer 1 as expected.

Recently, a very closely related coordination polymer $[\text{Cu}(1,3\text{-BDC})(\text{H}_2\text{O})](\text{H}_2\text{O})$ (**1'**), which is blue and has one less water molecule than polymer 1, was reported.²¹ This blue polymer was prepared from $\text{Cu}(\text{OAc})_2 \cdot (\text{H}_2\text{O})$, 1,3-BDC, H_2O , imidazole, and *n*-propyl alcohol at 160 °C. Despite only one water difference between **1** and **1'**, these two polymers have different colors (green for **1** versus blue for **1'**), space groups ($P4/n$ for **1** versus $P4/mmm$ for **1'**), and unit-cell parameters ($a = 19.106(2)$, $c = 6.7812(6)$ Å for **1**; a

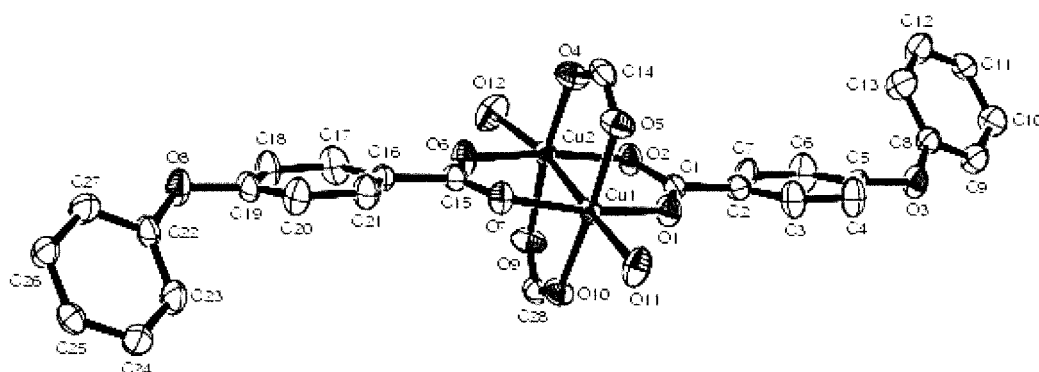


Figure 3. ORTEP drawing of a monomer unit of polymer 2.

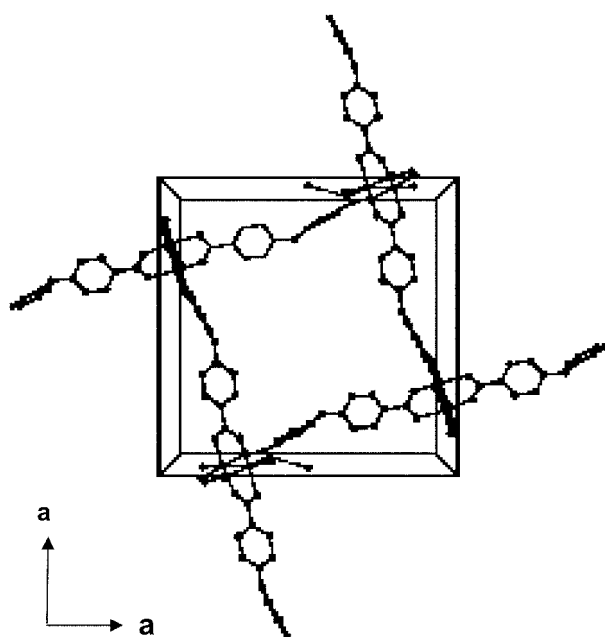


Figure 4. Combination of paddle-wheel units of polymer **2** per unit cell.

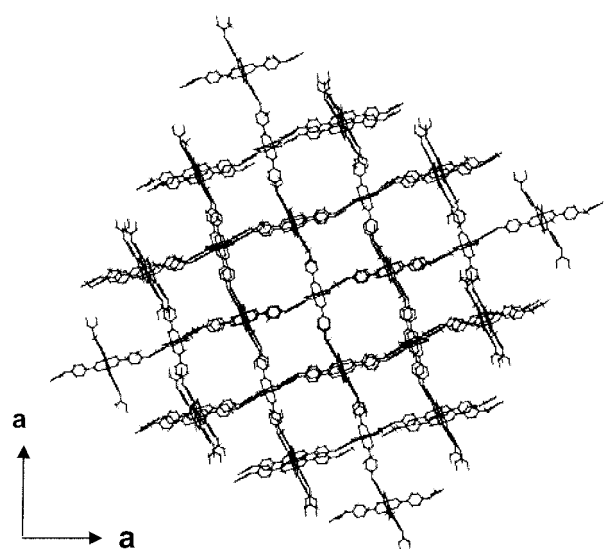


Figure 5. Packing diagram of polymer **2** along the *c*-axis.

= 19.1411(5), $c = 6.7881(2)$ Å for **1**). Both polymers, however, have essentially the same framework, a 2-dimensional open structure, although polymer **1** has somewhat larger cavities due to the presence of two water guests.

In summary, hydro(solvo)thermal reactions of $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ and 1,3-BDCH₂ produced a 2-dimensional copper coordination polymer, $[\text{Cu}(1,3\text{-BDC})(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$ (**1**), which is based on the paddle-wheel SBUs ($[\text{Cu}_2(\text{CO}_2\text{R})_4]$). An OBC analogue, $[\text{Cu}_2(\text{OBC})_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ (**2**), could also be prepared in the same way. Benzene was required to produce high-quality crystals of both polymers. These results indicate that a solvent composition can exert a great influence on the structural outcome of the resulting coordination polymer. A competitive experiment revealed that OBC has a greater coordinating ability than 1,3-BDC.

Acknowledgements. This work was supported by Korea Research Foundation Grant (KRF-2003-015-C00309).

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