

2차원 격자 형태의 구리 배위 고분자: Bromo(pyrazine)copper(I), [CuBr(pyz)]의 합성 및 구조

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A Two-dimensional Grid of Copper (I) Coordination Polymer: Preparation and Structure of Bromo(pyrazine)copper(I), [CuBr(pyz)]

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요 약

Copper(I) bromide(CuBr)와 pyrazine($C_4H_4N_2$, pyz)의 수열 반응으로 2차원 배위 고분자 [CuBr(pyz)] (1)이 얻어졌다. X-ray 구조 결정 결과, 고분자 1은 $4.0 \times 5.7 \text{ \AA}$ 크기를 갖는 직사각형 격자들을 토대로 한 2차원 그물 망 구조를 갖고 있었다. 고분자 1은 *b*-축 방향으로 통로(channel)를 갖고 있다.

Abstract

The hydrothermal reaction of copper(I) bromide (CuBr) and pyrazine ($C_4H_4N_2$, pyz) gave a 2-D coordination polymer [CuBr(pyz)] (1). X-ray structure determination revealed that polymer 1 has a 2-D network based on rectangular grids, each of which has the dimensions of $4.0 \times 5.7 \text{ \AA}$. Polymer 1 has channels along the *b*-axis.

1. Introduction

Metal-organic coordination networks (or polymers) with cavities of suitable sizes, shapes, and ultimately functions have got continuous attractions because of their useful properties such as chemical separations, sorption, and catalysis, as well as potential applications in functional materials.¹⁻⁵⁾ In designing 1-, 2-, and 3-D extended porous coordination polymers, the selection of appropriate ligands is crucial to determining the structural outcome of target polymers. For example, carboxylates^{6,7)} and pyridyls⁸⁾ frequently provide rigid frameworks although the carboxylates tend to form relatively more rigid frameworks due to the potential bidentate coordination of their carboxylate groups. Recently, the mixed-linker systems of both carboxylates

and pyridyls have proved effective for the preparation of novel coordination polymers.⁹⁻¹⁴⁾

We have been continually interested in preparing coordination polymers based on carboxylates, pyridyls, or both by hydrothermal reactions.¹⁵⁻²⁶⁾ Yaghi and co-workers recently reported the self-assembly of copper(I) chloride (CuCl) and 4,4'-bipyridine (4,4'-bpy) to give a 2-D copper polymer [Cu(4,4'-bpy)Cl], which exhibit mutually interpenetrating sheets and channels.²⁷⁾ These results prompted us to carry out hydrothermal reactions of copper(I) bromide and pyrazine ($C_4H_4N_2$), which has two potential coordinating nitrogen sites and therefore can act as a connector in resulting coordination polymers. Herein, we report the preparation and structure of a copper(I) coordination polymer with the empirical formula of [CuBr($C_4H_4N_2$)] (1).

2. Experimental Section

Copper(I), bromide (CuBr) and pyrazine (C₄H₄N₂, pyz) were purchased from Aldrich company. IR spectra were recorded with a Nicolet 320 FTIR spectrophotometer. Elemental analyses were performed by the Korea Basic Science Institute.

Preparation of [CuBr(C₄H₄N₂)] (1). A mixture of CuBr (0.18 g, 1.25 mmol), pyz (0.10 g, 1.25 mmol), and H₂O (6 ml) was heated in a 23-ml Teflon-lined autoclave at 150°C for 2 days, and then cooled to room temperature. The orange product was filtered, washed with H₂O (2 × 5 ml) and ethanol (2 × 5 ml), and air-dried to give crystalline [CuBr(pyz)] (0.039 g, 0.174 mmol, 14% yield). Anal. Calcd for C₄H₄BrN₂Cu: C, 21.49; H, 1.80; N, 5.09. Found: C, 21.68; H, 1.95; N, 5.02. IR (KBr, cm⁻¹): 1628, 1472, 1409, 1152, 1108, 1045, 800, 449 cm⁻¹.

Structure determination. All X-ray data were collected with the use of a Siemens P4 diffractometer equipped with a Mo X-ray tube and a graphite monochromator. The orientation matrix and unit-cell parameters were determined by the least-squares analyses of the setting angles of 10 reflections in the range of 10.0° < 2θ < 25.0°. Three check-reflections were measured every 100 reflections throughout data collection. Intensity data were empirically corrected for absorption with ψ-scan data. Decay corrections were also made. All calculations were carried out with the use of SHELXTL programs.²⁸⁾

An orange crystal of **1**, shaped as a block of approximate dimensions 0.16 × 0.14 × 0.12 mm³, was used for crystal- and intensity-data collection. The unit-cell parameters and systematic absences,

Table 1. X-ray data collection and structure refinement for 1

empirical formula	C ₄ H ₄ BrCuN ₂
fw	223.54
temperature, K	293(2)
crystal system	monoclinic
space group	<i>P2/c</i>
<i>a</i> , Å	4.017(3)
<i>b</i> , Å	6.563(2)
<i>c</i> , Å	11.376(4)
<i>β</i> , deg	96.65(4)
<i>V</i> , Å ³	297.9(3)
<i>Z</i>	2
<i>d</i> _{calc} , g cm ⁻³	2.492
<i>μ</i> , mm ⁻¹	10.250
<i>F</i> (000)	212
<i>T</i> _{min}	0.1667
<i>T</i> _{max}	0.6390
2θ range (°)	3.5–50
scan type	ω
scan speed	variable
No. of reflns measured	596
No. of reflns unique	520
No. of reflns with <i>I</i> > 2σ(<i>I</i>)	470
No. of params refined	47
Max., in Δρ (e Å ⁻³)	0.504
Min., in Δρ (e Å ⁻³)	-0.443
<i>GOF</i> on <i>F</i> ²	1.055
<i>R</i>	0.0295
<i>wR</i> ₂ ^a	0.0724

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

h0l (*l* = 2*n* + 1), indicated two possible space groups: *Pc* (acentric) and *P2/c* (centric). Although the statistical analysis of reflection intensities suggested an acentric space group, and the structure analysis converged reasonably only in *P2/c*. The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located in the difference Fourier maps and refined isotropically.

Details on crystal data and refinement details are

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

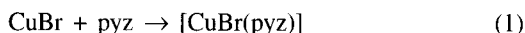
Cu1-N1	2.047(3)	Cu1-Br1	2.477(1)		
N1#1-Cu1-N1	111.3(2)	N1#1-Cu1-Br1	105.0(1)	N1-Cu1-Br1	113.7(1)
N1#1-Cu1-Br1#2	113.7(1)	N1-Cu1-Br1#2	105.0(1)	Br1-Cu1-Br1#2	108.34(6)
Cu1-Br1-Cu1#3	108.34(6)				

Symmetry transformations used to generate equivalent atoms: #1 = -*x*, *y*, -*z* + 1/2; #2 = *x* - 1, *y*, *z*; #3 = *x* + 1, *y*, *z*; #4 = -*x*, -*y*, *z* + 1

given in Table 1. Selected bond lengths and bond angles for **1** are given in Table 2.

3. Results and Discussion

Preparation. The title compound was prepared by hydrothermal reactions. CuBr reacts with pyrazine ($C_4H_4N_2$, pyz) in the mole ratio of 1 : 1 at 150°C for 2 days to give a 2-D copper coordination polymer with an empirical formula of $[\text{CuBr}(\text{pyz})]$ (**1**) (eq 1). Orange crystalline polymer **1** is stable in air and insoluble in common organic solvents.



Structure. The local coordination geometry about the copper metal is shown in Fig. 1. The coordination sphere of Cu can be described as a tetrahedron, composed of two nitrogen atoms from two pyrazine ligands and two bromo ligands. In this context, the monomeric unit of this compound can be written as $[\text{CuBr}(\text{pyz})]$, and the formal oxidation state of the copper metal is +1 (d^{10}). The Cu-N and Cu-Br bond lengths are usual, and the X-Cu-Y (X and Y = N or Br) bond angles fall in the range of $105.0(1)$ - $113.7(1)^\circ$.

The packing diagram of this polymer is shown in Fig. 2, which clearly demonstrates a 2-D polymeric structure. The bromo ligand behaves a symmetrical bridging ligand for the Cu-Br-Cu linkage to give a 1-D unit along the *a*-axis. The pyrazine ligand also behaves as a bridging ligand for the N-Cu-N link-

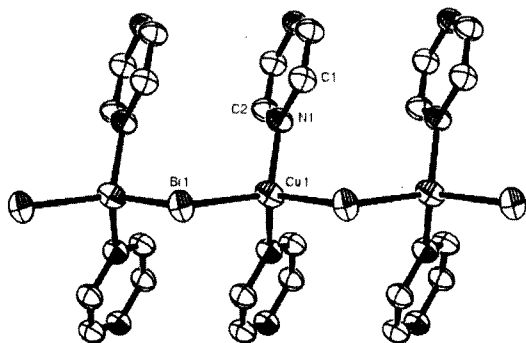


Fig. 1. ORTEP drawing of the local coordination environment of copper, showing the atom-labeling scheme and 50% probability thermal ellipsoids.

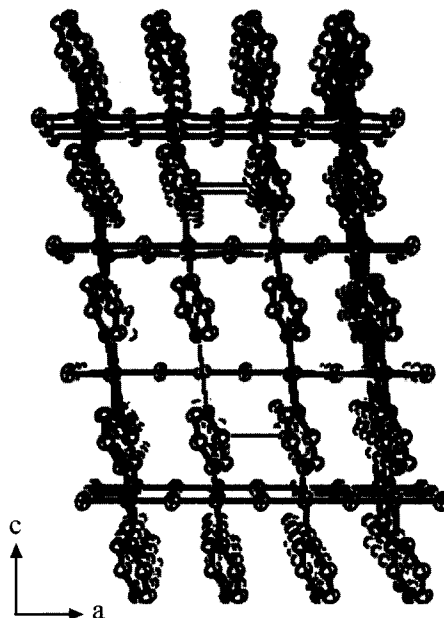


Fig. 2. A perspective view along the *b*-axis.

age along the *c*-axis to complete an overall 2-D network. The entire network can be thought of as a collection of rectangular grids, each of which has approximate dimensions of the *a*-axis length and one half of the *c*-axis length ($4.0 \times 5.7 \text{ \AA}$). As a consequence of the arrangement of those grids; this polymer has channels along the *b*-axis.

In general, coordination polymers from the combination of copper(I) halide (CuX) and bidentate bridging ligands (B) exhibit two structural types, 1-D chains based on Cu_2X_2 rings and 2-D sheet networks based on $(\text{CuX})_\infty$ chains, both of which are linked by the large bridging ligands.²⁹⁾ Polymer **1** belongs to the family of the 2-D sheet networks. This type of 2-D polymers has also been known for $[\text{CuBr}(\text{cng})]$ (cng = 1-cyanoguanidine) and $[\text{CuCl}(\text{pyz})]$.^{30,31)}

In summary, we prepared a 2-D copper(I) coordination polymer $[\text{CuBr}(\text{pyz})]$ (**1**) from CuBr and pyrazine by the hydrothermal reaction. Polymer **1** has a sheet-like 2-D network with a channel ($4.0 \times 5.7 \text{ \AA}$) along the *b*-axis.

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