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Two-dimensional Cu Coordination Polymer: $[Cu_2Cl_2(4,4'\text{-dipyen})]$

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2차원 구리 배위 고분자: $[Cu_2Cl_2(4,4'\text{-dipyen})]$

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Abstract

Under hydrothermal conditions, a 2-dimensional copper(I) coordination polymer $[Cu_2Cl_2(4,4'\text{-dipyen})]$ (**1**) was prepared from $[Cu(OAc)_2]\cdot H_2O$, 4,4'-dipyen, and KCl. In polymer **1**, copper atoms are linked by the 4,4'-dipyen ligands approximately along the *b*-axis and are also linked by the chloro ligands approximately along the *a*-axis to form a 2-D layer, a network of rectangles.

요 약

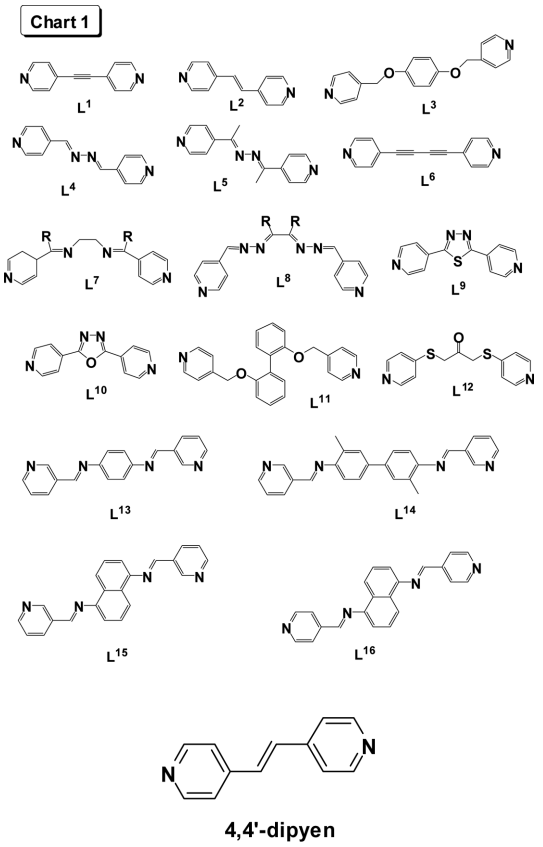
수열 반응 조건 하에서, $[Cu(OAc)_2]\cdot H_2O$, 4,4-dipyen, 그리고 KCl로부터 2차원 구리 배위 고분자 $Cu_2Cl_2(4,4'\text{-dipyen})]$ (**1**)이 합성되었다. 고분자 **1** 내에서, 구리 원자들이 4,4-dipyen 리간드들로 대략 *b*-축 방향으로 연결되고, 또한 Cl 리간드들로 대략 *a*-축 방향으로 연결되어 직사각형 그물 망 형태의 2차원 층이 형성된다.

1. Introduction

Coordination polymers with various topologies are currently under intensive study because of their remarkable properties applicable to catalysis, chirality, conductivity, luminescence, magnetism, adsorption, porosity, and gas storage.[1-10] In preparing these polymers, multi-functional carboxylates or dipyridyl derivatives are typically used. For example, Yaghi and co-workers have reported many intriguing coordination polymers by employing di- or multicarboxylato ligands.[11-15] For the past few years, our research group has reported on the preparation of several coordination polymers based on dicarboxylates or dipyridyls under hydrothermal or solvothermal conditions.[16-20]

Several types of 4,4'-dipyridyl-type linking ligands are now known (Chart 1): $\mathbf{L^1}$, $\mathbf{L^2}$,[21] $\mathbf{L^3}$,[22] $\mathbf{L^4}$, $\mathbf{L^5}$,[23] $\mathbf{L^6}$,[24] $\mathbf{L^7}$, $\mathbf{L^8}$,[25] $\mathbf{L^9}$, $\mathbf{L^{10}}$,[26] $\mathbf{L^{11}}$,[27] and $\mathbf{L^{12}}$.[28] Very recently, we also prepared several long dipyridyl-type ligands $\mathbf{L^{13}}$~$\mathbf{L^{16}}$ and their coordination polymers: $[Zn(H_2O)_4\mathbf{L^{13}}]\cdot(MeOH)$, $[Zn(NO_3)(H_2O)_2\mathbf{L^{13}}]\cdot(NO_3)\cdot(H_2O)_2$, $[Zn\mathbf{L^{14}}(NO_3)_2]$, $[Co\mathbf{L^{14}}_{1.5}(NO_3)_2]$, $[Co\mathbf{L^{14}}_2(NO_3)_2]\cdot X$ (X = benzene or toluene), $[Zn\mathbf{L^{15}}(NO_3)_2]$, $[Zn\mathbf{L^{16}}(NO_3)_2]$, $[Cd\mathbf{L^{16}}_{1.5}(NO_3)_2]$, and $[Co\mathbf{L^{16}}(bpdc)]\cdot(EtOH)$ ($bpdcH_2$ = biphenyl-4,4'-dicarboxylic acid) (Chart 2).[29-32] Among them, eight ligands ($\mathbf{L^2}$, $\mathbf{L^4}$, $\mathbf{L^7}$, $\mathbf{L^8}$, and $\mathbf{L^{13}}$~$\mathbf{L^{16}}$) were prepared by Schiff-base condensation.

As a continuation of our research, we set out to prepare novel copper coordination polymers by employing the dipyridyl-type ligands. When $Cu(OAc)_2\cdot H_2O$ (copper(II) acetate monohydrate) was treated with 4,4'-dipyen [1,2-di(4-pyridyl)ethylene] in the presence of KCl under hydrothermal conditions, a 2-D copper(I) coordination polymer $[Cu_2Cl_2(4,4'\text{-dipyen})]$ (**1**) was produced. We report herein the preparation and structure of this polymer.



2. Experimental Section

All solid chemicals were purified by recrystallization, and all solvents were distilled and stored over molecular sieves. IR spectra were recorded with a Nicolet 320 FTIR spectrophotometer.

Preparation of [Cu_2Cl_2(4,4'-dipyen)] (1) A mixture of [$Cu(OAc)_2$]·H_2O (0.100 g, 0.500 mmol), 4,4'-dipyen (0.050 g, 0.274 mmol), KCl (0.050 g, 0.670 mmol), and H_2O (6.0 ml) was heated in a 23-ml Teflon-lined vessel at 180°C for three days and then air-cooled to room temperature. The orange crystalline product was collected by filtration, washed with H_2O (2 × 5 ml) and ethanol (2 × 5 ml), and then air-dried to give polymer **1** (67% yield). IR (KBr, cm^{-1}): 3424 (br), 2954 (m), 1462 (m), 1411 (m), 1271 (m), 1150 (s), 1076 (s), 779 (m), 533 (m).

X-ray structure determination. All X-ray data were collected with use of a Siemens P4 diffractometer equipped with a Mo X-ray tube. Details on crystal data and intensity data are given in Table 1. The orientation matrix and unit-cell parameters were determined by least-squares analyses of the setting angles of 22 reflections in the range $15.0° < 2\theta < 25.0°$. The intensity data were empirically corrected for absorption with y-scan data. All calculations were carried out with the use of the SHELXTL programs.[33]

Table 1. X-ray data collection and structure refinement

formula	$C_{12}H_{10}N_2Cl_2Cu_2$
fw	380.20
temperature, K	293(2)
crystal system	monoclinic
space group	$P2_1/c$
a, Å	3.765(2)
b, Å	14.971(3)
c, Å	10.818(3)
β, deg	96.42(2)
V, $Å^3$	606.0(4)
Z	2
d_{cal}, g cm^{-3}	2.084
μ, mm^{-1}	3.927
T_{min}	0.1301
T_{max}	0.1728
F(000)	376
No. of reflections measured	1253
No. of reflections unique	1066
No. of reflections with $I > 2\sigma(I)$	906
No. of parameters refined	82
2θ range (°)	3.5~50.0
GOF (goodness-of-fit on F^2)	1.080
Max., min. in Δρ (e $Å^{-3}$)	0.394 , −0.543
$R1$[a]	0.0344
$wR2$[b]	0.0859

[a] $R1 = \Sigma||F_o| - |F||/\Sigma|F_o|$, [b] $wR2 = \Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]^{1/2}$

Table 2. Atomic (× 10^4) and equivalent isotropic displacement parameters ($Å^2$ × 10^4)

Cu(1)	2312(2)	5625(1)	4402(1)	53(1)
Cl(1)	3114(2)	4990(1)	6581(1)	36(1)
N(1)	1877(8)	6925(2)	4694(3)	32(1)
C(1)	3284(10)	7312(2)	5742(3)	37(1)
C(2)	3023(10)	8206(2)	5972(3)	35(1)
C(3)	1234(9)	8761(2)	5093(3)	30(1)
C(4)	−208(10)	8362(2)	3989(3)	35(1)
C(5)	165(10)	7461(2)	3840(3)	36(1)
C(6)	881(9)	9706(2)	5364(3)	32(1)

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

Cu1-N1	1.981(3)	Cu1-Cl1#1	2.314(1)	Cu1-Cl1#2	2.381(2)
Cu1-Cl1	2.528(1)	Cu1-Cu1#1	2.947(1)	Cu1-Cu1#2	2.952(1)
N1-Cu1-Cl1#1	122.92(9)	N1-Cu1-Cl1#2	111.66(9)	Cl1#1-Cu1-Cl1#2	106.65(5)
N1-Cu1-Cl1	102.22(9)	Cl1#1-Cu1-Cl1	105.15(4)	Cl1#2-Cu1-Cl1	106.14(4)

Symmetry transformations used to generate equivalent atoms: #1 = $-x+1$, $-y+1$, $-z+1$; #2 = $-x$, $-y+1$, $-z+1$

An orange crystal of **1** of approximate dimensions 0.24 × 0.18 × 0.16 mm, shaped as a block, was used for crystal and intensity data collection. The unit-cell parameters and systematic absences [$h0l$ ($l = 2n + 1$) and $0k0$ ($k = 2n + 1$)] unambiguously indicated $P2_1/c$ as a space group. The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were generated in idealized positions and refined in a riding model. Final atomic coordinates for **1** are given in Table 2. Selected bond lengths and angles are given in Table 3.

3. Results and Discussion

Preparation. A 2-dimensional copper(I) coordination polymer [Cu_2Cl_2(4,4'-dipyen)] (**1**) was prepared in 67% yield from [$Cu(OAc)_2$]·H_2O, 4,4'-dipyen, and KCl under hydrothermal conditions. The formal oxidation state of polymer **1** indicates that the copper metal in the starting compound was reduced from +2 to +1 during the reaction.

Structure. A monomer unit of polymer **1** with the atom-numbering scheme is shown in Fig. 1, in which an asymmetric unit consists of one half 4,4'-dipyen ligand, one chloro ligand, and one copper atom. The copper atom is bonded to one nitrogen atom (4,4'-dipyen), three chlorine atoms, and other two copper atoms, leading to a 6-coordinate copper. The Cu···Cu distances (2.947(2) and 2.952(2) Å) indicate weak Cu-Cu single bonds (the covalent radius of Cu is 1.28 Å). Each chlorine atom is bonded asymmetrically to three copper atoms (Cu1-Cl = 2.314(1)-2.528(1) Å). Polymer **1** is isostructural with [Cu_2Cl_2(4,4'-dipyrine)].[34] In contrast, the structure of polymer **1** is essentially different from that of [CuCl(4,4'-dipyrine)], a 3-D structure constructed on the basis of mutually interpenetrating sheets and channels.[35]

A projection along the c-axis is presented in Fig. 2. Copper atoms are linked by the 4,4'-dipyen ligands approximately along the b-axis and are linked by the chloro ligands approximately along the a-axis to form a 2-D layer, which can be described as a network of rectangles. In particular, the [CuCl] units form a stair-like conformation in the [010] direction.

In summary, we prepared a 2-D copper(I) coordination polymer [Cu_2Cl_2(4,4'-dipyen)] from [$Cu(OAc)_2$]·H_2O, 4,4'-dipyen, and KCl under hydrothermal conditions. X-ray structural study of this polymer revealed that it has a 2-D network of rectangles.

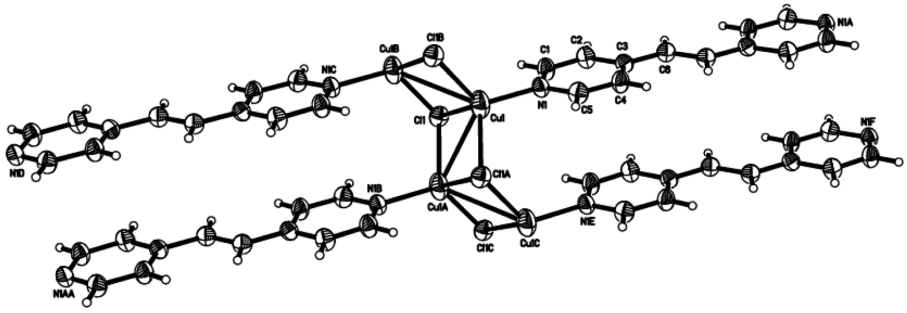


Fig. 1. Local coordination environments of Cu metals in polymer 1. Unlabeled atoms are related to the labeled ones by the crystallographic inversion.

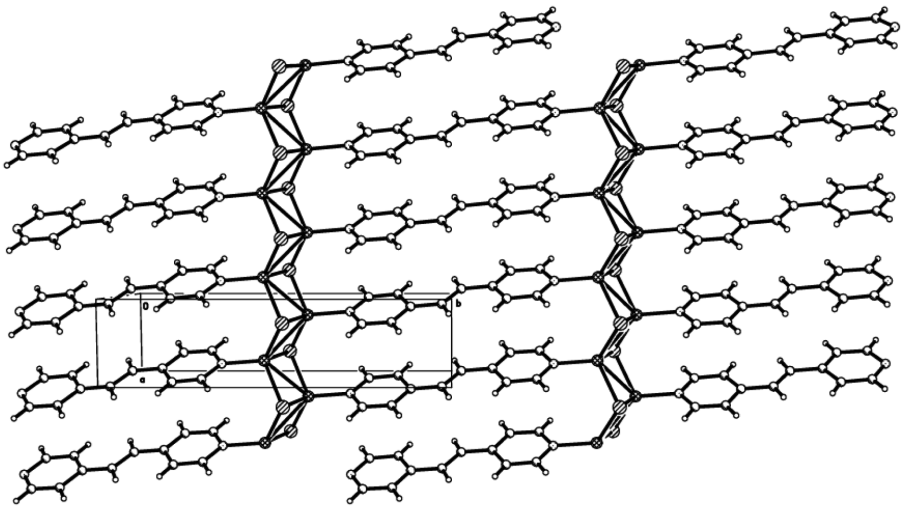


Fig. 2. Packing of polymer 1 along the *c*-axis.

References

1) Swiergers, G. F. and Malefetse, T. J., *Chem. Rev.*, **100**, 3483 (2000).
2) Moulton, B. and Zaworotko, M. J., *Chem. Rev.*, **101**, 1629 (2001).
3) Eddaoudi, M., Moler, D. B., Li, H., Chen, B., Reineke, T. M., O'Keeffe, M. and Yaghi, O. M., *Acc. Chem. Res.*, **319**, 34 (2001).
4) Eddaoudi, M., Kim, J., Rosi, N., Vodak, D., Wachter, J., O'Keeffe, M. and Yaghi, O. M., *Science*, **295**, 469 (2002).
5) Janiak, C., *Dalton Trans.*, 2781 (2003).
6) Kesanli, B. and Lin, W., *Coord. Chem. Rev.*, **246**, 305 (2003).
7) Barnett, S. A. and Chanmpness, N. R., *Coord. Chem. Rev.*, **246**, 145 (2003).
8) Rowsell, J. L. C. and Yaghi, O. M., *Micropor. Mesopor. Mater.*, **73**, 3 (2004).
9) Ockwig, N. W., Friedrichs, O. D., O'Keeffe, M. and Yaghi, O. M., *Acc. Chem. Res.*, **38**, 176 (2005).
10) Robin, A. Y. and Fromm, K. M., *Coord. Chem. Rev.*, **250**, 2127 (2006).
11) Chae, H. K., Kim, J., Friedrichs, O. D., O'Keeffe, M. and Yaghi, O. M., *Angew. Chem. Int. Ed.*, **42**, 3907 (2003).
12) Chae, H. K., Siverio-Perez, D. Y., Kim, J., Go, Y. B., Eddaoudi, M., Matzger, A. J., O'Keeffe, M. and O. M., Yaghi, *Nature*, **427**, 523 (2004).
13) Chen, B., Ockwig, N. W., Fronczek, F. R., Contreas, D. S. and Yaghi, O. M., *Inorg. Chem.*, **44**, 181 (2005).
14) Rosi, N. L., Kim, J., Eddaoudi, M., Chen, B., O'Keeffe, M. and Yaghi, O. M., *J. Am. Chem. Soc.*, **127**, 1504 (2005).
15) Sudik, A. C., Millward, A. R., Ockwig, N. W., Cote, A. P., Kim, J. and Yaghi, O. M., *J. Am. Chem. Soc.*, **127**, 7110 (2005).
16) Baeg, J.-Y. and Lee, S. W., *Inorg. Chem. Commun.*, **6**, 313 (2003).
17) Lee, Y. K. and Lee, S. W., *Bull. Korean Chem. Soc.*, **24**, 7 (2003).
18) Kim, H. J., Lee, Y. K., Park, K., Son, J. H., Kwon, Y.-U. and Lee, S. W., *Inorg. Chim. Acta*, **353**, 151 (2003).
19) Lee, H. K., Min, D., Cho, B.-Y. and Lee, S. W., *Bull. Korean Chem. Soc.*, **25**, 1955 (2004).
20) Choi, E.-Y., Park, K., Yang, C.-M., Kim, H. J., Son, J.-H., Lee, S. W., Lee, Y. H., Min, D. and Kwon, Y.-U., *Chem. Eur. J.*, **10**, 5535 (2004).
21) Dong, Y.-B., Smith, M. D. and zur Loye, H.-C., *Inorg. Chem.*, **39**, 4927 (2000).
22) Hou, H., Fan, Y., Zhang, L., Du, C. and Zhu, Y., *Inorg. Chem. Commun.*, **4**, 168 (2001).
23) Curtin, D. M., Dong, Y.-B., Smith, M. D., Barclay, T. and zur Loye, H.-C., *Inorg. Chem.*, **40**, 2825 (2001).

24) Zaman, M. B., Smith, M. D. and zur Loye, H.-C., *Chem. Mater.*, **13**, 3534 (2001).
25) Patra, G. K. and Goldberg, I., *J. Chem. Soc., Dalton Trans.*, 1051 (2002).
26) Huang, Z., Song, H.-B., Du, M., Chen, S.-T. and Bu, X.-H., *Inorg. Chem.*, **43**, 931 (2004).
27) Gong, Y.-Q., Wang, R.-H., Zhou, Y.-F., Lin, Z.-Z. and Hong, M.-C., *J. Mol. Struct.*, **751**, 121 (2005).
28) Chen, C.-L., Goforth, A. M., Smith, M. D., Su, C.-Y. and zur Loye, H.-C., *Inorg. Chem.*, **44**, 8762 (2005).
29) Kim, H. N., Lee, H. K. and Lee, S. W., *Bull. Korean Chem. Soc.*, **26**, 6 (2005).
30) Min, D., Cho, Y.-B., Lee, H. K. and Lee, S. W., *Inorg. Chim. Acta*, **359**, 577, (2006).
31) Cho, Y.-B., Min, D., Lee, H. K. and Lee, S. W., *Cryst. Growth Des.*, **6**, 342 (2006).
32) Kim, S. H., Huh, H. S. and Lee, S. W., *J. Mol. Struct.*, **841**, 78 (2007).
33) Bruker, SHELXTL, Structure Determination Software Programs, Bruker Analytical X-ray Instruments Inc., Madison, Wisconsin, USA (1997).
34) Lu, J. Y., Cabrera, B. R., Wang, R.-J. and Li, J., *Inorg. Chem.*, **38**, 4608 (1999).
35) Yaghi, O. M. and Li, G., *Angew. Chem. Int. Ed.*, **34**, 207 (1995).