

## Crystal Structure of Three-Dimensional Copper(II) Macrocyclic Complex Linked by Hydrogen-Bonds

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## 水素 결합에 의한 三次元の Copper(II) 巨大고리 錯物の 結晶構造

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### Abstract

The complex  $[\text{Cu}(\text{L})(\text{H}_2\text{O})_2](\text{PDC})$  (**1**) ( $\text{L} = 2,5,9,12$ -tetramethyl-1,4,8,11-tetraazacyclotetradecane; PDC = 1,4-pyridinedicarboxylate) has been synthesized and characterized by X-ray crystallography. The compound **1** crystallizes in the triclinic space group  $P1$ , with  $a = 7.553(1)$  Å,  $b = 9.619(2)$  Å,  $c = 10.692(2)$  Å,  $\alpha = 74.22(1)^\circ$ ,  $\beta = 73.32(1)^\circ$ ,  $\gamma = 78.70(1)^\circ$ ,  $V = 710.1(2)$  Å<sup>3</sup>,  $Z = 1$ ,  $R_1(wR_2)$  for 2634 observed reflections of  $[I > 2\sigma(I)]$  was 0.0854 (0.2242). The compound **1** is interconnected to give a three-dimensional network through weak hydrogen-bonding interactions.

### 要約

$[\text{Cu}(\text{L})(\text{H}_2\text{O})_2](\text{PDC})$  (**1**) ( $\text{L} = 2,5,9,12$ -tetramethyl-1,4,8,11-tetraazacyclotetradecane; PDC = 1,4-pyridinedicarboxylate) 錯物を合成하고 構造를 糾明하였다. 이 錯物は 三斜晶系, 空間群  $P1$ ,  $a = 7.553(1)$  Å,  $b = 9.619(2)$  Å,  $c = 10.692(2)$  Å,  $\alpha = 74.22(1)^\circ$ ,  $\beta = 73.32(1)^\circ$ ,  $\gamma = 78.70(1)^\circ$ ,  $V = 710.1(2)$  Å<sup>3</sup>,  $Z = 1$ 로 決定化 되었다. 이 錯物の 構造는 最小自乘法으로 精密化하였으며, 最終 信賴度  $R_1(wR_2)$  값은 2634개의 回折斑點에 대하여 0.0854 및 0.2242이었다. 化合物 **1**은 水素結合들로 연결된 三次元の 網格構造를 갖는다.

### 1. Introduction

The rational self-assembly of ordered supramolecular arrays in the solid state using covalent<sup>1)</sup> and noncovalent forces such as hydrogen bonding<sup>2-4)</sup> and  $\pi$ - $\pi$  stacking<sup>5)</sup> is a rapidly expanding field. Recently, there are a rapidly growing number of noncovalently linked multidimensional networks containing channels or cavities of various sizes and shapes.<sup>6-8)</sup> However, macrocyclic complexes have seldom been employed as building blocks in the constructions of the

multidimensional networks.<sup>9)</sup> Terephthalate dianion and 4,4'-bipyridine are good candidates for molecular building blocks because of their rodlike rigidity and length. The  $\text{Cu}^{2+}$  cation is normally octahedrally coordinated and forms square two-dimensional networks with pyrazine and substituted pyrazine<sup>10)</sup> or interpenetrated two-dimensional networks with 4,4'-bipyridine.<sup>11)</sup> In the present work, we report on the one-dimensional complex  $[\text{Cu}(\text{L})(\text{H}_2\text{O})_2](\text{PDC})$  (**1**) ( $\text{L} = 2,5,9,12$ -tetramethyl-1,4,8,11-tetraazacyclotetradecane; PDC = 1,4-pyridinedicarboxylate), which

solid-state structure spreads out via hydrogen bonds of Cu(II) macrocyclic complex and PDC ligand.

## 2. Experimental

**Materials and Physical Measurements.** All chemicals and solvents used in the synthesis were of reagent-grade and were used without further purification. The macrocyclic ligand L was prepared as described previously.<sup>12)</sup> IR spectra were recorded with a Perkin-Elmer Paragon 1000 FT-IR spectrophotometer. High-resolution fast-atom bombardment mass spectrometry (FAB mass) was performed by using a Jeol JMS-HA 100A/100A instrument. Elemental analyses were performed by the Korea Research Institute of Chemical Technology, Taejon, Korea.

**Preparation of [Cu(L)(H<sub>2</sub>O)<sub>2</sub>](PDC) (1).** To a methanol solution (20 ml) of CuCl<sub>2</sub>·2H<sub>2</sub>O (170 mg, 1 mmol) was added L (256 mg, 1 mmol), and then the mixture was heated at reflux for 1 h. An aque-

ous solution (5 ml) of sodium 1,4-pyridinedicarboxylate (374 mg, 2 mmol) was then added consecutively. When the mixture was allowed to stand at room temperature for several days, violet crystals were precipitated. These were filtered out, and one of them was subjected to X-ray analysis. IR (KBr, cm<sup>-1</sup>): 3259, 3178, 2966, 1590, 1457, 1388, 1348, 1154, 1112, 1068, 1018, 996, 950, 902, 815, 764, 502. Found: C, 42.60; H, 7.91; N, 11.76. Calc. for C<sub>21</sub>H<sub>47</sub>CuN<sub>5</sub>O<sub>10</sub>: C, 42.52; H, 7.99; N, 11.81%. FAB mass (CH<sub>2</sub>Cl<sub>2</sub>, m/z): 593 (M<sup>+</sup>).

**X-ray Crystallography.** The crystal was mounted on an Enraf-Nonius CAD4 diffractometer. X-ray data were collected with graphite-monochromated MoK $\alpha$  radiation ( $\lambda = 0.71069 \text{ \AA}$ ), with the  $\omega$ -2 $\theta$  scan technique. Unit cell parameters were determined from automatic centering of 25 reflections and refined by least-squares methods. Intensity data were corrected for Lorentz and polarization effects. An empirical absorption correction based on  $\phi$ -scan was applied.

Table 1. Crystal Data and Structure Refinement for 1

Empirical formula	C <sub>21</sub> H <sub>47</sub> CuN <sub>5</sub> O <sub>10</sub>
Formula weight	593.18
Temperature	293(2) K
Crystal system	Triclinic
Space group	P1
Unit cell dimensions	$a = 7.553(1) \text{ \AA}$ $\alpha = 74.22(1)^\circ$ $b = 9.619(2) \text{ \AA}$ $\beta = 73.32(1)^\circ$ $c = 10.692(2) \text{ \AA}$ $\gamma = 78.70(1)^\circ$
Volume	710.1(2) $\text{\AA}^3$
Z	1
Density (calculated)	1.387 Mg/m <sup>3</sup>
Absorption coefficient	0.827 mm <sup>-1</sup>
Diffractometer	Enraf-Nonius CAD4
Radiation/wavelength	MoK $\alpha$ (graphite monochrom.)/0.71069 $\text{\AA}$
F(000)	317
Crystal size	0.30 $\times$ 0.17 $\times$ 0.13 mm <sup>3</sup>
$\theta$ range for data collection	2.04 to 24.97 $^\circ$
Index ranges	-8 $\leq h \leq$ 8, -10 $\leq k \leq$ 11, 0 $\leq l \leq$ 12
Reflection collected/unique	2634/2634 ( $R_{\text{int}} = 0.0000$ )
Absorption correction ( $\phi$ -scan)	$T_{\text{max}} = 0.8987$ , $T_{\text{min}} = 0.7912$
Refinement method	Full-matrix least-squares on $F^2$
Data/restraints/parameters	2634/3/259
Goodness-of-fit on $F^2$	1.005
Final R indices [ $I > 2\sigma(I)$ ]	$R_1^a = 0.0854$ , $wR_2^b = 0.2242$
R indices (all data)	$R_1^a = 0.0995$ , $wR_2^b = 0.2496$
Absolute structure parameter	-0.02(4)
Largest diff. peak and hole	1.642 and -0.597 e $\text{\AA}^{-3}$

<sup>a</sup> $R_1 = \sum |F_o| - |F_c| / \sum |F_o|$ .

<sup>b</sup> $wR_2 = [\sum (w(F_o^2 - F_c^2))^2 / \sum (w(F_o^2))^2]^{1/2}$ .

The crystallographic data, conditions used for the intensity data collection, and some features of the structure refinement are listed in Table 1. The structure was solved by direct methods and refined by full-matrix least-squares on  $F^2$  with anisotropic factors for all non-hydrogen atoms<sup>13,14</sup> except for C(2) and Ow(5) atoms, which were refined isotropically in order to avoid their disorderings. All hydrogen atoms except for the water hydrogen atoms were placed in calculated positions with isotropic displaced parameters. Final atomic coordinates and equivalent isotropic displacement parameters are given in Table 2.

### 3. Results and Discussion

An ORTEP drawing of  $[\text{Cu}(\text{L})(\text{H}_2\text{O})_2](\text{PDC})$  (**1**) with the atomic numbering scheme is shown in Figure 1, and the selected bond distances and angles are listed in Table 3. Apparently the structure of **1** seems to be centric. In order to be centric, both Cu atom in the center of pseudooctahedron and the centroid of the pyridine ring should be located at the special positions. According to our calculation, however, the centroid does not sit at the special position, and if it does, it leads to a difficulty for the identification of the N(5) atom. Therefore the only space group for **1** is  $P1$ . The ligand skeleton of the title compound takes up the most stable *trans*-III conformation. The copper(II) center lies in a  $4+2$  pseudooctahedral environment ( $\text{N}(1)\text{-Cu-N}(2) = 88.4(6)^\circ$ ,  $\text{N}(1)\text{-Cu-N}(3) = 174.0(7)^\circ$ ,  $\text{N}(2)\text{-Cu-N}(4) = 177.9(7)^\circ$ ,  $\text{N}(2)\text{-Cu-N}(3) = 95.0(5)^\circ$ ,  $\text{N}(1)\text{-Cu-Ow}(1) = 91.3(5)^\circ$ ,  $\text{Ow}(1)\text{-Cu-Ow}(2) = 179.7(4)^\circ$ ), which consists of two oxygen atoms from two water molecules and four nitrogen atoms from the macrocyclic ligand. The average Cu-N bond distance in the compound **1** is  $2.03(1)$  Å, which is very similar to that ( $2.028(2)$  Å) found in  $[\text{Cu}(\text{DTAD})(\text{H}_2\text{O})_2]\cdot\text{Cl}_2$  (DTAD = 3,14-dimethyl-2,6,13,17-tetraazatricyclo[14,4,0,1<sup>8</sup>,0<sup>7,12</sup>]docosane).<sup>15</sup> The Cu-Ow bond distances in the compound **1** are  $2.50(1)$  Å and  $2.51(1)$  Å, slightly longer than that ( $2.484(6)$  Å) in  $[\text{Cu}(\text{cyclam})(\text{H}_2\text{O})_2]\cdot\text{F}_2\cdot 4\text{H}_2\text{O}$  (cyclam = 1,4,8,11-tetraazacyclotetradecane).<sup>16</sup> This fact may be due to the steric repulsion by four methyl groups. The Cu-Ow bonds are bent slightly

**Table 2. Atomic Coordinates ( $\times 10^4$ ) and Equivalent Isotropic Displacement Parameters ( $\text{\AA}^2 \times 10^3$ ) for **1****

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq)
Cu	234(1)	8274(1)	2637(1)	26(1)
N(1)	158(16)	6612(14)	1967(13)	24(3)
N(2)	400(20)	9545(16)	723(16)	37(4)
N(3)	553(19)	9944(15)	3439(13)	30(3)
N(4)	114(17)	7070(13)	4542(12)	24(3)
N(5)	5683(16)	3990(14)	5861(13)	46(3)
C(1)	450(30)	7040(18)	483(15)	43(4)
C(2)	-320(40)	6120(30)	-180(30)	88(7)
C(3)	-73(19)	8569(14)	-3(14)	29(3)
C(4)	-550(30)	11003(19)	581(18)	41(4)
C(5)	-160(20)	11800(18)	-942(17)	40(4)
C(6)	-50(30)	11861(19)	1337(19)	44(5)
C(7)	-670(20)	11258(17)	2889(15)	38(4)
C(8)	-340(20)	9483(19)	4922(17)	38(4)
C(9)	150(20)	10495(16)	5622(15)	43(3)
C(10)	810(20)	7871(19)	5229(19)	46(5)
C(11)	1110(20)	5527(16)	4763(15)	27(3)
C(12)	850(30)	4700(20)	6189(19)	49(5)
C(13)	540(20)	4670(20)	3930(17)	34(4)
C(14)	1080(30)	5130(17)	2470(20)	45(5)
C(15)	5741(16)	4213(14)	3495(13)	36(3)
C(16)	5484(15)	3281(14)	4969(12)	32(2)
C(17)	5480(20)	3182(14)	7118(13)	43(3)
C(18)	5117(17)	1761(14)	7559(13)	37(3)
C(19)	4896(19)	950(16)	9062(13)	41(3)
C(20)	4973(18)	1073(14)	6627(13)	38(3)
C(21)	5030(30)	1930(20)	5328(17)	48(5)
O(1)	6169(19)	5380(11)	3134(18)	68(5)
O(2)	5477(15)	3556(11)	2660(12)	55(3)
O(3)	4890(18)	1823(15)	9792(14)	70(3)
O(4)	4581(16)	-286(14)	9463(14)	49(3)
Ow(1)	-3250(14)	8747(14)	3277(14)	56(4)
Ow(2)	3724(16)	7794(12)	2006(12)	44(3)
Ow(3)	5520(20)	4614(14)	9(13)	63(4)
Ow(4)	4232(17)	1080(14)	2350(14)	57(4)
Ow(5)	5570(30)	7310(20)	8190(20)	123(6)
Ow(6)	5700(30)	6956(13)	5774(16)	76(5)

$U(\text{eq})$  is defined as one-third of the trace of the orthogonalized  $U_{ij}$  tensor

off from the perpendicular axis to the  $\text{CuN}_4$  plane by  $1.2\text{-}3.5^\circ$ . The basal plane is slightly distorted [deviation: N(1)  $-0.047(8)$ , N(2)  $0.024(8)$ , N(3)  $-0.044(8)$ , N(4)  $0.027(9)$  Å from the least-squares plane through these basal donor atoms], whereas the copper(II) ion is  $0.040(6)$  Å apart from this plane. Import hydrogen-bonding interactions in the compound **1** play a significant role in aligning the mol-

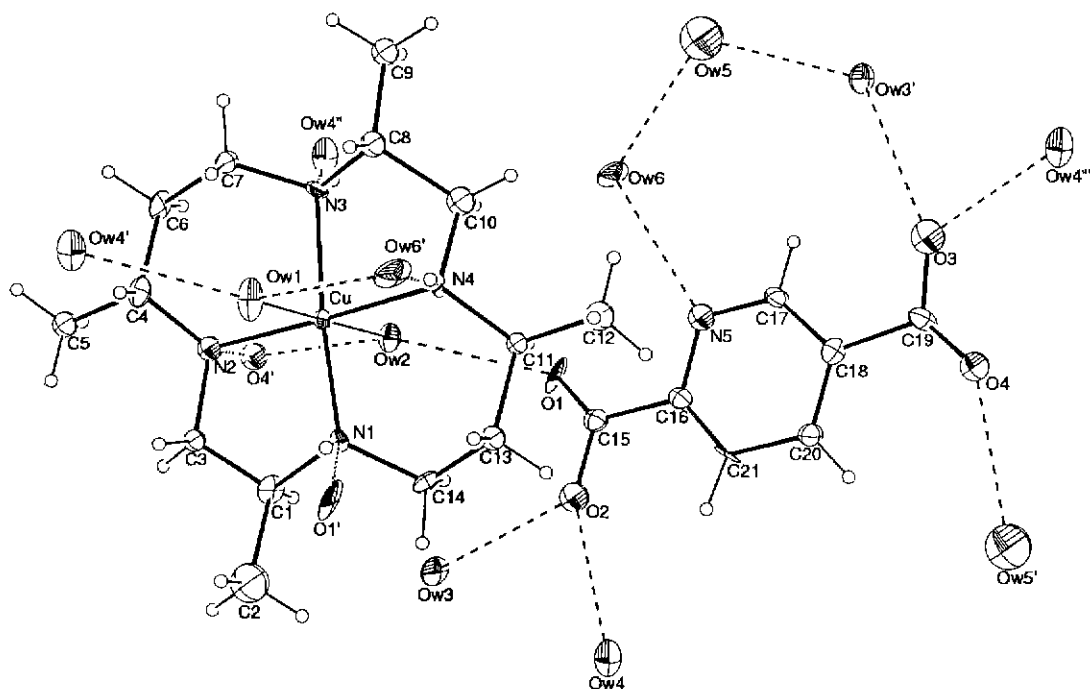


Fig. 1. An ORTEP drawing of 1 with the atomic numbering scheme. Thermal ellipsoids are drawn at 20% probability.

Table 3. Selected Bond Distances (Å) and Angles (°) for 1

Cu-N(1)	1.94(1)	Cu-N(2)	2.06(2)
Cu-N(3)	2.10(1)	Cu-N(4)	2.04(1)
Cu-Ow(1)	2.50(1)	Cu-Ow(2)	2.51(1)
N(5)-C(16)	1.37(2)	N(5)-C(17)	1.34(2)
C(15)-C(16)	1.57(2)	C(15)-O(1)	1.16(2)
C(15)-O(2)	1.30(2)	C(18)-C(19)	1.56(2)
C(19)-O(3)	1.29(2)	C(19)-O(4)	1.20(2)
N(1)-Cu-N(2)	88.4(6)	N(1)-Cu-N(3)	174.0(7)
N(1)-Cu-N(4)	93.5(5)	N(2)-Cu-N(3)	95.0(5)
N(2)-Cu-N(4)	177.9(7)	N(3)-Cu-N(4)	83.0(5)
Ow(1)-Cu-N(1)	91.3(5)	Ow(1)-Cu-N(2)	92.8(5)
Ow(1)-Cu-N(3)	93.5(5)	Ow(1)-Cu-N(4)	88.0(5)
Ow(2)-Cu-N(1)	88.8(5)	Ow(2)-Cu-N(2)	87.5(5)
Ow(2)-Cu-N(3)	86.5(5)	Ow(2)-Cu-N(4)	91.7(4)
Ow(1)-Cu-Ow(2)	179.7(4)		

ecules in the crystalline solid. The molecules are interconnected to give a three-dimensional network through weak hydrogen-bonding interactions involving the secondary amines of macrocycle, coordinated and free water molecules, and free oxygen

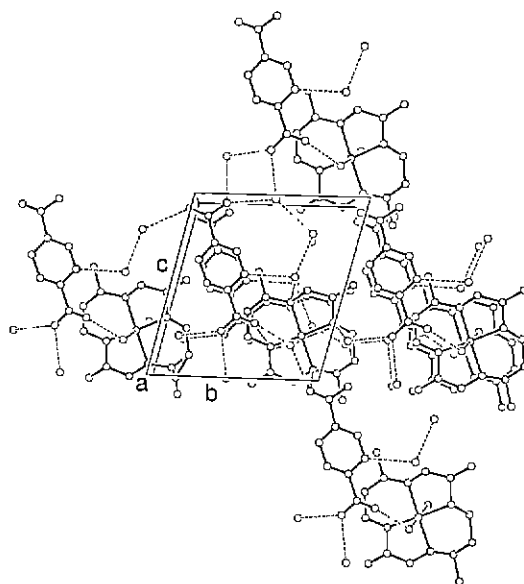


Fig. 2. Packing diagram of 1, showing the hydrogen bonds as dotted lines.

atoms of PDC ligand (Figure 2 and Table 4).

**Table 4. Hydrogen Bonding Parameters (Å, °) for 1**

D-H...A	D-H (Å)	H...A (Å)	D...A (Å)	D-H...A (°)
N(1)-H(1)O(1) <sup>ii</sup>	0.91	2.36	3.24(2)	161.1
N(2)-H(2)O(4) <sup>i</sup>	0.91	2.16	3.07(2)	176.3
N(3)-H(3)Ow(4) <sup>iv</sup>	0.91	2.12	2.99(2)	159.7
N(4)-H(4)Ow(6) <sup>ii</sup>	0.91	2.32	3.22(2)	173.3
N(5)Ow(6)			2.83(2)	
O(1)Ow(2)			2.89(2)	
O(2)Ow(3)			2.73(2)	
O(2)Ow(4)			2.86(2)	
O(3)Ow(3) <sup>v</sup>			2.90(2)	
O(3)Ow(4) <sup>v</sup>			2.56(2)	
O(4)Ow(5) <sup>vi</sup>			2.87(3)	
Ow(1)Ow(4) <sup>iii</sup>			2.80(2)	
Ow(1)Ow(6) <sup>ii</sup>			2.75(2)	
Ow(2)O(4) <sup>i</sup>			2.82(2)	
Ow(5)Ow(3) <sup>v</sup>			2.79(2)	
Ow(5)Ow(6)			2.66(3)	

Symmetry codes: (i) x, y+1, z-1; (ii) x-1, y, z; (iii) x-1, y+1, z; (iv) x, y+1, z; (v) x, y, z+1; (vi) x, y-1, z.

#### 4. Supplementary Material

Atomic coordinates, bond lengths and angles, and thermal parameters are available from author K.-Y. Choi on request.

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