

Synthesis and Crystal Structure of Syn-Anti Carboxylate-Bridged Dinuclear Copper(II) Complex

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對稱-反對稱 Carboxylate 다리로 連結된 이핵 구리(II) 錯物の 合成 및 結晶構造

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Abstract

The dinuclear copper(II) complex $\{[\text{Cu}(\text{pmea})\text{Cl}][\text{Cu}(\text{H}_2\text{O})_3]\}_2\text{Cl}_2 \cdot \text{H}_2\text{O}$ (**1**) (Hpmea=bis(2-pyridylmethyl)amino-2-ethanoic acid) has been synthesized and characterized. It crystallizes in the monoclinic system $P2_1/c$, $a=9.0008(6)$ Å, $b=28.0171(19)$ Å, $c=8.5590(6)$ Å, $\beta=104.2280(10)^\circ$, $V=2092.2(2)$ Å³, $Z=4$. Crystal structure of **1** reveals a syn-anti carboxylate-bridged dinuclear complex, in which the coordination environment around each copper atom exhibits a distorted square-pyramid and a distorted square plane, respectively.

要 約

이핵 구리 錯物 $\{[\text{Cu}(\text{pmea})\text{Cl}][\text{Cu}(\text{H}_2\text{O})_3]\}_2\text{Cl}_2 \cdot \text{H}_2\text{O}$ (**1**) (Hpmea=bis(2-pyridylmethyl)amino-2-ethanoic acid)을 合成하고 構造를 糾明하였다. 이 錯物은 單斜晶系, 空間群 $P2_1/c$, $a=9.0008(6)$ Å, $b=28.0171(19)$ Å, $c=8.5590(6)$ Å, $\beta=104.2280(10)^\circ$, $V=2092.2(2)$ Å³, $Z=4$ 로 決定化 되었다. 錯物 **1**의 結晶構造는 對稱-反對稱 carboxylate 다리로 連結된 이핵 錯物로서, 各各 구리원자의 配位環境은 若干 일그러진 사각뿔構造와 若干 일그러진 사각평면構造를 갖는다.

1. Introduction

Self-assembled coordination polymers of transition metal(II) ions and Schiff-base carboxylate ligands have attracted considerable attention because of their structural and magnetic properties.¹⁻⁷ It is well known that the structures and chemical properties of these compounds can be influenced by the metal ion, the structure of Schiff-base ligands, the possible counterion and solvent effects. For example, the self-assembly of copper(II) perchlorate with bis(2-pyridylmethyl)amino-4-butyric acid (Hpmba) leads to the carboxylate bridged one-dimensional chain com-

plex $\{[\text{Cu}(\mu\text{-pmba})(\text{H}_2\text{O})](\text{ClO}_4) \cdot 3\text{H}_2\text{O}\}_n$, which exhibits a distorted square-pyramidal geometry with a N_3O basal plane and a water molecule in the axial position.⁶ However, the reaction of copper(II) chloride with Hpmba ligand leads to the mononuclear square-pyramidal complex $[\text{Cu}(\text{Hpmba})\text{Cl}_2] \cdot \text{H}_2\text{O}$ ⁷ in which the presence of chloride ions in the reaction mixture prevents any dimer and chain formation. In order to better understand some aspects of different molecular topologies, we prepared the dinuclear copper(II) complex $\{[\text{Cu}(\text{pmea})\text{Cl}][\text{Cu}(\text{H}_2\text{O})_3]\}_2\text{Cl}_2 \cdot \text{H}_2\text{O}$ (**1**) (Hpmea=bis(2-pyridylmethyl)amino-2-ethanoic acid).

2. Experimental

Materials and Physical Measurements. All chemicals and solvents used in the synthesis were of reagent-grade and used without further purification. The bis(2-pyridylmethyl)amino-2-ethanoic acid (Hpmea) was prepared according to the literature method.⁶⁾ IR spectra were recorded with a Perkin-Elmer Paragon 1000 FT-IR spectrometer. Elemental analysis (C, H, N) were performed on a Perkin Elmer CHN-2400 analyzer.

Synthesis of $\{[\text{Cu}(\text{pmea})\text{Cl}][\text{Cu}(\text{H}_2\text{O})_3]\text{Cl}_2 \cdot \text{H}_2\text{O}$ (1). A mixture of Hpmea (129 mg, 0.5 mmol), $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (82 mg, 0.5 mmol), and disodium 1,3-benzenedicarboxylate (105 mg, 0.5 mmol) in H_2O solution (20 mL) was heated to reflux for 1 h and then cooled to room temperature. The solution was filtered and left at room temperature until the blue

crystals formed. These were filtered out, and one of them was subjected to X-ray analysis. IR (KBr, cm^{-1}): 3420(m), 3341(m), 3195(m), 1614(s), 1572(m), 1482(m), 1436(s), 1397(m), 1325(m), 1281(m), 1164(w), 1097(w), 1021(w), 983(w), 825(w), 778(m), 730(m), 651(w), 557(w), 492(w). Found: C, 29.84; H, 3.87; N, 7.56%. Calc. for $\text{C}_{14}\text{H}_{22}\text{N}_3\text{Cl}_3\text{Cu}_2\text{O}_6$: C, 29.93; H, 3.95; N, 7.48%.

X-ray Crystallography. A blue crystal was mounted on a Bruker Smart 1000 CCD diffractometer. Intensities were collected with a graphite-monochromated Mo $\text{K}\alpha$ radiation ($\lambda=0.71073 \text{ \AA}$), using the $\omega/2\theta$ scan technique at 293 K. A total of 5214 independent reflections were measured in the range $2<\theta<25^\circ$. Absorption correction was applied by SADABS.⁸⁾ The crystallographic data, conditions used for the intensity collection, and some features of the structure refinement are listed in Table 1. The

Table 1. Crystal data and structure refinement for 1

Empirical formula	$\text{C}_{14}\text{H}_{22}\text{N}_3\text{Cl}_3\text{Cu}_2\text{O}_6$
Formula weight	561.78
Temperature	293(2) K
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	$a=9.0008(6) \text{ \AA}$ $b=28.0171(19) \text{ \AA}$ $c=8.5590(6) \text{ \AA}$ $\beta=104.2280(10)^\circ$
Volume	$2092.2(2) \text{ \AA}^3$
Z	4
Density (calculated)	1.784 Mg/m^3
Absorption coefficient	2.452 mm^{-1}
Diffractometer	Bruker SMART 1000 CCD/ ω -2 θ
Radiation/wavelength	Mo $\text{K}\alpha$ (graphite monochrom.)/ 0.71073 \AA
$F(000)$	1136
Crystal size	$0.22 \times 0.16 \times 0.07 \text{ mm}^3$
θ range for data collection	1.45 to 28.34°
Index ranges	$-11 \leq h \leq 12$, $-37 \leq k \leq 37$, $-11 \leq l \leq 11$
Reflection collected/unique	21126/5214 ($R_{int}=0.0449$)
Absorption correction	$T_{max}=0.8485$ and $T_{min}=0.6425$
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5214/0/271
Goodness-of-fit on F^2	1.048
Final R indices [$I > 2\sigma(I)$]	$R_1^a=0.0415$, $wR_2^b=0.0941$
R indices (all data)	$R_1^a=0.0729$, $wR_2^b=0.1081$
Largest diff. peak and hole	0.689 and -0.578 e\AA^{-3}

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$.

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

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) ^a
Cu(1)	4183(1)	673(1)	9272(1)	30(1)
Cu(2)	1454(1)	2069(1)	5825(1)	27(1)
Cl(1)	2942(1)	35(1)	7967(1)	51(1)
Cl(2)	828(1)	2032(1)	10640(1)	43(1)
Cl(3)	6346(1)	1897(1)	6342(2)	52(1)
O(1)	3076(3)	1286(1)	7735(3)	36(1)
O(2)	3017(3)	2078(1)	7862(3)	27(1)
N(1)	3039(4)	695(1)	11011(4)	32(1)
N(2)	5389(3)	1224(1)	10628(3)	27(1)
N(3)	5938(4)	675(1)	8238(4)	31(1)
C(1)	1664(5)	513(2)	10953(5)	43(1)
C(2)	976(6)	552(2)	12228(6)	52(1)
C(3)	1729(6)	785(2)	13593(6)	53(1)
C(4)	3151(5)	978(2)	13659(5)	44(1)
C(5)	3776(5)	931(1)	12339(4)	34(1)
C(6)	5326(5)	1117(1)	12320(4)	36(1)
C(7)	6981(4)	1214(2)	10461(5)	39(1)
C(8)	7130(4)	946(1)	8975(4)	32(1)
C(9)	8444(5)	980(2)	8420(5)	42(1)
C(10)	8524(6)	738(2)	7049(6)	51(1)
C(11)	7291(6)	470(2)	6276(5)	50(1)
C(12)	6022(5)	441(2)	6889(4)	39(1)
C(13)	4603(5)	1679(1)	10070(4)	36(1)
C(14)	3502(4)	1665(1)	8422(4)	27(1)
Ow(1)	-67(4)	1897(1)	7009(3)	44(1)
Ow(2)	26(4)	1847(1)	3845(3)	42(1)
Ow(3)	3047(3)	2112(1)	4632(3)	32(1)
Ow(4)	7176(4)	2154(1)	3171(4)	58(1)

^a*U*(eq) is defined as one-third of the trace of the orthogonalized *U*_{ij} tensor.

structure was solved by direct methods⁹⁾ and the least-squares refinements of the structure were performed by the program SHELXL97.¹⁰⁾ All atoms except for all hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions allowing to ride on their parent C atoms with $U_{iso}(H)=1.2U_{eq}(C \text{ or } N)$. The hydrogen atoms of Ow(4) were not found. Final atomic coordinates and equivalent isotropic displacement parameters are given in Table 2.

3. Results and Discussion

An ORTEP drawing¹¹⁾ of $\{[\text{Cu}(\text{pmea})\text{Cl}][\text{Cu}(\text{H}_2\text{O})_3]\text{Cl}_2 \cdot \text{H}_2\text{O}$ (1) with the atomic numbering scheme is shown in Fig. 1. The selected bond distances and angles are listed in Table 3. The dinuclear entity

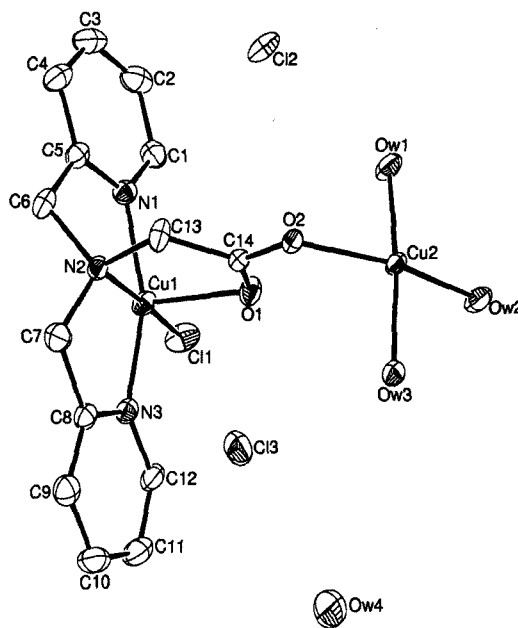


Fig. 1. An ORTEP drawing of 1 with the atomic numbering scheme. Thermal ellipsoids are drawn at 30% probability. The hydrogen atoms are omitted for clarity.

Table 3. Selected bond distances (\AA) and angles ($^\circ$) for 1

Bond lengths			
Cu(1)-N(1)	2.008(3)	Cu(1)-N(2)	2.071(3)
Cu(1)-N(3)	1.991(3)	Cu(1)-O(1)	2.242(3)
Cu(1)-Cl(1)	2.253(1)	Cu(2)-O(2)	1.953(2)
Cu(2)-Ow(1)	1.953(3)	Cu(2)-Ow(2)	1.960(3)
Cu(2)-Ow(3)	1.958(3)	O(1)-C(14)	1.228(4)
O(2)-C(14)	1.288(4)	Cu...Cu#3	5.145(1)
Cu...Cu#2	4.129(1)		
Bond angles			
N(1)-Cu(1)-N(2)	81.7(1)	N(1)-Cu(1)-N(3)	159.5(1)
N(2)-Cu(1)-N(3)	83.3(1)	N(1)-Cu(1)-O(1)	100.2(1)
N(2)-Cu(1)-O(1)	81.6(1)	N(1)-Cu(1)-Cl(1)	96.3(1)
N(3)-Cu(1)-O(1)	91.4(1)	N(2)-Cu(1)-Cl(1)	175.4(1)
O(1)-Cu(1)-Cl(1)	102.8(1)	N(3)-Cu(1)-Cl(1)	97.6(1)
O(2)-Cu(2)-Ow(1)	89.0(1)	O(2)-Cu(2)-Ow(2)	162.1(1)
O(2)-Cu(2)-Ow(3)	90.3(1)	Ow(1)-Cu(2)-Ow(2)	88.7(1)
Ow(1)-Cu(2)-Ow(3)	169.2(1)	Ow(2)-Cu(2)-Ow(3)	88.7(1)
Cu(1)-O(1)-C(14)	109.8(2)	Cu(2)-O(2)-C(14)	115.1(2)
O(1)-C(14)-O(2)	124.2(3)		

Symmetry codes: (#2) *x*-1, *y*, *z*; (#3) *x*, *y*, *z*-1.

consists of the two copper(II) ions connected through a carboxylate group displaying a syn-anti bridging mode. Each syn-anti carboxylate group bridges two

Table 4. Hydrogen bonding parameters (Å, °) for 1

D-H...A	D-H (Å)	H...A (Å)	D...A (Å)	D-H...A (°)
Ow(1)-H(15B)...Cl(2)#1	0.73(5)	2.31(5)	3.036(3)	176(5)
Ow(2)-H(16A)...Ow(4)#2	0.86(5)	1.77(5)	2.633(5)	174(5)
Ow(2)-H(16B)...Cl(2)#3	0.68(5)	2.39(5)	3.048(3)	163(6)
Ow(3)-H(17A)...Cl(3)#1	0.81(5)	2.24(5)	3.031(3)	166(4)
Ow(3)-H(17B)...O(2)#4	0.66(5)	2.08(5)	2.724(4)	169(6)

Symmetry codes: (#1) x, y, z ; (#2) $x-1, y, z$; (#3) $x, y, z-1$; (#4) $x, -y+1/2, z-1/2$.

copper(II) atoms through O(1) and O(2) oxygen atoms involving axial and equatorial positions on the copper(II) coordination polyhedra, respectively. The Cu(1) atom exhibits a CuN_3ClO coordination environment with the three nitrogen atoms of the pmea ligand and one chloride anion occupying the basal plane [Cu(1)-N(1) 2.008(3) Å, Cu(1)-N(2) 2.071(3) Å, Cu(1)-N(3) 1.991(3) Å, Cu(1)-Cl(1) 2.253(1) Å] and an oxygen atom from the carboxylate group according the axial position [Cu(1)-O(1) 2.242(3) Å], which can be described as a distorted square pyramidal ($\tau=0.27$). The structure index is defined as $\tau=(\beta-\alpha)/60$ (where, β and α are the largest coordination angles; the τ has values of 1 and 0 for trigonal-bipyramidal (D_{3h}) and square-pyramidal (C_{4v}) geometries, respectively).¹² However, the coordination environment around the Cu(2) atom shows a slightly distorted square-plane with the three water molecules and the bridging carboxylate O(2) atom of the pmea ligand [Cu(2)-Ow(1) 1.953(3) Å, Cu(2)-Ow(2) 1.960(3) Å, Cu(2)-Ow(3) 1.958(3) Å, Cu(2)-O(2) 1.953(2) Å]. The intramolecular Cu...Cu separation is 5.145(1) Å, whereas the closest intermolecular Cu...Cu distance is 4.129(1) Å. The Cu(1) atoms lies 0.166(1) Å above the N_3ClO basal planes toward the carboxylate oxygen atom O(1). The axial Cu(1)-O(1) linkage is not perfectly perpendicular to the CuN_3Cl plane with N-Cu(1)-O(1) and Cl(1)-Cu(1)-O(1) angles ranging from 81.6(1) to 102.8(1)°. The N(1)-Cu(1)-N(2) and N(2)-Cu(1)-N(3) bite angles of the five-membered chelate rings are 81.7(1) and 83.3(1)°, respectively. The average Cu(1)- N_{py} (secondary) and tertiary Cu(1)-N(2) bond distances [2.000(2) and 2.071(3) Å] are comparable to those found in $[\text{Cu}(\text{dpa})\text{Cl}_2]$ (dpa=di-(2-picoly)amine) [2.006(2) and 2.075(2) Å]¹³ and $\{[\text{Cu}(\mu\text{-pmea})](\text{ClO}_4)_n \cdot \text{H}_2\text{O}\}_n$ [1.990(4) and 2.060(8) Å],⁹ which reveals

the distorted square pyramidal geometry ($\tau=0.12$ and 0.25). Furthermore, the average N(2)-C [1.483(3) Å] distance involving the tertiary amine is approximately 0.14 Å longer than the average N(1)-C [1.335(4) Å] and N(3)-C [1.343(4) Å] distance involving the secondary amines. This fact may be attributed to the sp^3 hybridization of the coordinated tertiary nitrogen atom. The water molecules form hydrogen-bonds with the uncoordinated chloride ions [Ow(1)...Cl(2)#1 3.036(3) Å, 176(5)°; Ow(2)...Cl(2)#3 3.048(3) Å, 163(6)°; Ow(3)...Cl(3)#1 3.031(3) Å, 166(4)°; symmetry codes (#1): x, y, z (#3): $x, y, z-1$]. Furthermore, the water molecules Ow(2) and Ow(3) are linked to the lattice water molecule Ow(4) and the bridging carboxylate oxygen atom O(2) [Ow(2)...Ow(4)#2 2.633(5) Å, 174(5)°; Ow(3)...O(2)#4 2.724(4) Å, 169(6)°; symmetry codes (#2):

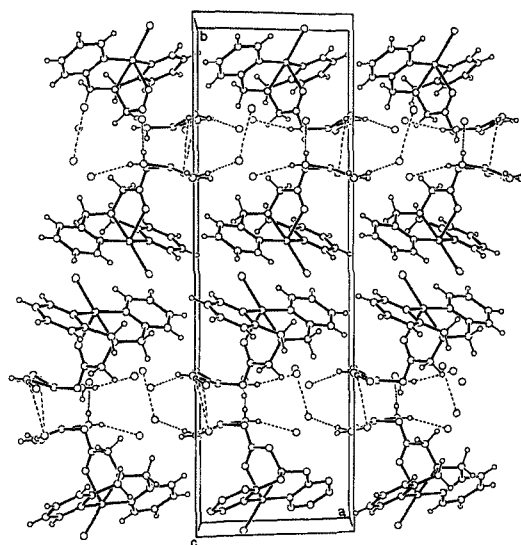


Fig. 2. Packing diagram of 1, showing the hydrogen bonds as dotted lines.

$x-1, y, z$ (#4): $x, -y+1/2, z-1/2$] (Table 4 and Fig. 2).

The IR spectrum of complex **1** shows $\nu_{\text{as}}(\text{COO})$ stretching frequency at 1614 and $\nu_{\text{sym}}(\text{COO})$ at 1436 cm^{-1} . Their difference, $\Delta\nu=178 \text{ cm}^{-1}$, is characteristic of the syn-anti coordination mode of the bridging carboxylate group.¹⁴⁾ The absorption for **1** reveals bands at 1482 and 1572 cm^{-1} , associated with pyridine skeleton.

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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