

Bis[(2-pyridyl)methyl]-2-(2-pyridyl)ethylamine 구리(II) 착물의 합성, 성질 및 X-ray 결정구조

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Synthesis, Properties, and X-ray Crystal Structure of Copper(II) Complex with Bis[(2-pyridyl)methyl]-2-(2-pyridyl)ethylamine

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요 약. 트리포달 구리(II) 착물 $[\text{Cu}(\text{pmea})(\text{H}_2\text{O})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (**1**) ($\text{pmea} = \text{bis}[(2\text{-pyridyl)methyl}]-2\text{-}(2\text{-pyridyl})\text{-ethylamine}$)을 합성하고 X-선 회절법으로 구조를 규명하였다. 이 착물은 삼사정계, 공간군 $P-1$, $a = 9.9362(9)$ Å, $b = 15.7299(17)$ Å, $c = 18.0562(11)$ Å, $\alpha = 68.760(8)^\circ$, $\beta = 76.331(6)^\circ$, $\gamma = 77.092(9)^\circ$, $V = 2526.2(4)$ Å³, $Z = 2$ 로 결정화 되었다. 각각의 구리 원자는 약간 일그러진 사각뿔 구조를 갖는데, 바탕 면은 pmea 리간드에 있는 세 개의 질소 원자와 물 분자가 포함되어 있으며 축 방향에는 피리딘 고리의 질소 원자가 포함되어 있다. 착물 **1**의 순환 전압전류 그림은 가역 일-전자 산화 Cu^{II} 및 환원 Cu^{I} 과정으로 진행됨을 보여주었다.

주제어: 결정구조, 구리(II) 착물, 트리포달 리간드, 일그러진 사각뿔구조, Bis[(2-pyridyl)methyl]-2-(2-pyridyl)-ethylamine

ABSTRACT. The tripodal copper(II) complex $[\text{Cu}(\text{pmea})(\text{H}_2\text{O})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (**1**) ($\text{pmea} = \text{bis}[(2\text{-pyridyl)methyl}]-2\text{-}(2\text{-pyridyl})\text{-ethylamine}$) has been synthesized and structurally characterized by X-ray diffraction method. It crystallizes in the triclinic system $P-1$ with $a = 9.9362(9)$, $b = 15.7299(17)$, $c = 18.0562(11)$ Å, $\alpha = 68.760(8)^\circ$, $\beta = 76.331(6)^\circ$, $\gamma = 77.092(9)^\circ$, $V = 2526.2(4)$ Å³, $Z = 2$. Each copper atom reveals a distorted square pyramidal with three nitrogen atoms of the pmea ligand and water molecule occupying the basal plane and one nitrogen atom from the pyridine ring according the axial position. The cyclic voltammogram of **1** undergoes reversible one-electron oxidation to the Cu^{II} and reversible one-electron reduction to the Cu^{I} .

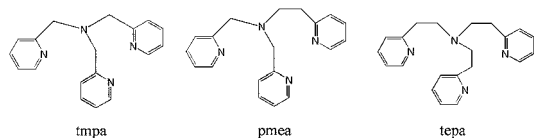
Keywords: Crystal Structure, Copper(II) Complex, Tripodal Ligand, Distorted Square Pyramidal Geometry, Bis[(2-pyridyl)methyl]-2-(2-pyridyl)ethylamine

INTRODUCTION

Copper complexes with tripodal ligands have attracted considerable interest due to their importance in a variety of synthetic, industrial, and biological processes.¹⁻³ Several authors have systematically investigated copper complexes of tripodal ligands

by appropriate ligand design and use of low temperature synthesis, handling and characterization to provide insight into the kinetics and thermodynamics of their formation, possible structures and spectroscopy and physicochemical properties.^{4,12} For example, the tripodal copper(II) complexes $[\text{Cu}(\text{tmpa})\text{Cl}]\text{PF}_6$ ($\text{tmpa} = \text{tris}(2\text{-pyridyl)methylamine}$) and

[Cu(tepa)Cl]PF₆ (tepa = tris[2-(2-pyridyl)ethyl]amine) exhibit a distorted square-pyramidal geometry, with N₃Cl basal plane and one nitrogen atom of the axial pyridyl group.⁸ In a previous paper, Karlin *et al.*⁹ report the synthesis and characterization of [Cu(pmea)]PF₆ (pmea = bis[(2-pyridyl)methyl]-2-(2-pyridyl)ethylamine) in which the geometry about copper atom is best described as pyramidal with the amine nitrogen occupying the axial position and three pyridyl nitrogens in the trigonal plane. In contrast, the crystal structure of [Cu(pmea)Cl]ClO₄·H₂O reveals a five coordinate distorted square pyramidal CuN₃Cl environment.⁹ It seems that the chlorine anion could play a role here to stabilize the copper(II)-pmea complex. In order to better understand some aspects of the different molecular topologies, we report the synthesis and crystal structure of tripodal copper(II) complex [Cu(pmea)(H₂O)](ClO₄)₂·H₂O (**1**). By metathesis of uncoordinated chloride with perchlorate anions, we could obtain the single crystals of title complex, in which this complex exhibits some uncommon feature.



EXPERIMENTAL

Materials and physical measurements. The bis[(2-pyridyl)methyl]-2-(2-pyridyl)ethylamine (pmea) was synthesized according to the literature method.¹⁵ IR spectra were recorded as KBr pellets on a Perkin-Elmer Paragon 1000 FT-IR spectrometer. Solution and solid state electronic spectra were obtained on a Jasco Uvidec-610 spectrophotometer. Elemental analysis (C, H, N) were performed on a Perkin Elmer CHN-2400 analyzer. Electrochemical measurements were accomplished with a three electrode potentiostat BAS-100BW system. A 3-mm Pt disk was used as the working electrode. The counter electrode was a coiled Pt wire and a Ag/AgCl electrode was used as a reference elec-

trode. Cyclic voltametric data were obtained in DMSO solution using 0.10 M tetraethylammonium perchlorate (TEAP) as supporting electrolyte at 20.0±0.1 °C. The solution was degassed with high purity N₂ prior to carrying out the electrochemical measurements.

Synthesis of [Cu(pmea)(H₂O)](ClO₄)₂·H₂O (1**).** To a methanol solution (20 mL) of Cu(ClO₄)₂·6H₂O (185 mg, 0.5 mmol) was added pmea (152 mg, 0.5 mmol). The mixture was heated to reflux for 1 h and then cooled to room temperature. The solution was filtered and left at room temperature until blue crystals formed. The product was filtered out and one of them was subjected to the X-ray analysis. Yield: 72%. Calc. (found) for C₃₈H₄₈Cl₂Cu₂N₈O₂₀: C, 37.85 (37.76); H, 4.01 (4.11); N, 9.29 (9.17)%. IR (KBr; cm⁻¹): 3484(m), 3422(m), 3064(w), 1608(m), 1568(m), 1482(m), 1443(m), 1309(w), 1289(w), 1144(s), 1116(s), 1088(s), 1029(w), 1004(w), 942(w), 808(w), 766(m), 629(m), 545(w), 422(w). UV-Vis in DMSO [λ_{max} , nm (ϵ , M⁻¹cm⁻¹)] 261(1.43×10⁴), 641(134); in diffuse reflectance spectrum (λ_{max} , nm): 261, 645.

X-ray crystallography. Intensity data for the compounds were measured on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo-K α radiation in the ω -2 θ scan mode. Accurate cell parameters and an orientation matrix were determined by least-squares fit of 25 reflections. The intensity data were collected for Lorentz and polarization effects. An empirical absorption correction based on ϕ -scan was applied. The structure was solved direct methods¹⁴ and the least-squares refinement of the structure was performed by the program SHELXL-97.¹⁵ All atoms except all hydrogen atoms, O(1), O(4), O(6), O(9), O(11), O(12), O(16), Ow(4), C(10), C(11), C(13), and C(17) were refined anisotropically. The 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(1), Ow(2), Ow(3), and Ow(4) were not found. The rather higher R_1 and wR_2 values may be attributed mainly to the bad quality of the sample compound. Crystal parameters and details of the data collections and refinement are listed in Table 1.

Table 1. Crystallographic Data

Chemical formula	C ₃₃ H ₃₃ Cl ₂ Cu ₂ N ₅ O ₂
Formula weight	1205.72
Temperature	293(2) K
Crystal system	Triclinic
Space group	<i>P</i> -1
Unit cell dimensions	
<i>a</i> (Å)	9.9362(9)
<i>b</i> (Å)	15.7299(17)
<i>c</i> (Å)	18.0562(11)
α (°)	68.760(8)
β (°)	76.331(6)
γ (°)	77.092(9)
Volume (Å ³)	2526.2(4)
<i>Z</i>	2
Density (calculated, mg/m ³)	1.585
Absorption coefficient (mm ⁻¹)	1.136
Diffractionmeter/scan	Enraf-Nonius/ ω -2 θ
Radiation/wavelength	Mo-K α /0.71073
<i>F</i> (000)	1236
Crystal size (mm ³)	0.40 × 0.30 × 0.20
θ range for data collection (°)	1.23 to 24.96
Index ranges	-11 ≤ <i>h</i> ≤ 11, -17 ≤ <i>k</i> ≤ 18, 0 ≤ <i>l</i> ≤ 21
Reflections collected/unique	8915/8613 (<i>R</i> _{int} = 0.0320)
Absorption correction	ψ -scan
Maximum and minimum transmission	0.8047 and 0.6594
Refinement method	full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	8613/0/589
Goodness of fit on <i>F</i> ²	1.038
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	
<i>R</i> ₁	0.0902
<i>wR</i> ₂	0.2398
<i>R</i> indices (all data)	
<i>R</i> ₁	0.1950
<i>wR</i> ₂	0.2981
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.1630P)^2 + 3.0031P]$ with $P = (F_o^2 + 2F_c^2)/3$
Largest difference peak and hole	1.397 and -0.858 eÅ ⁻³

Note. $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$, $wR_2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$.

RESULTS AND DISCUSSION

Structural description. An ORTEP drawing¹⁶ of **1** with the atomic numbering scheme is shown in Fig. 1. Selected bond distances and angles are listed in Table 2. Two crystallographically independent but chemically identical [Cu(pmea)(H₂O)]⁺ cations exist in the asymmetric unit. Each copper(II) atom in the cations is pentacoordinated structure with three pyridyl nitrogens, one aliphatic amine nitrogen and

a water molecule. The Cu(1) atom reveals a CuN₃O coordination environment with three nitrogen atoms of the pmea ligand and water molecule occupying the basal plane [Cu(1)-N(1) 1.997(8), Cu(1)-N(2) 2.100(9), Cu(1)-N(4) 2.010(8), Cu(1)-Ow(1) 2.087(7) Å] and one nitrogen atom from the pyridine ring according the axial position [Cu(1)-N(3) 2.226(8) Å], which can be described as a distorted square pyramidal with a τ value of 0.18 (values of 0 and 1 are indicative of idealized square-pyramidal and

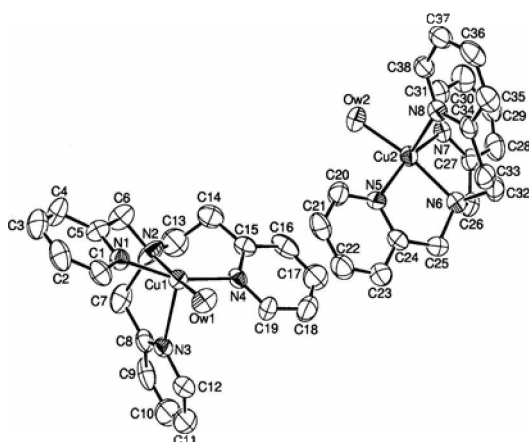


Fig. 1. An ORTEP drawing of 1 showing the atomic numbering scheme (30% probability ellipsoids). The hydrogen atoms and perchlorate anions are omitted for clarity.

trigonal bipyramidal geometries, respectively).¹⁷ The Cu(2) atom presents a similar coordination environment [Cu(2)-N(5) 2.021(8), Cu(2)-N(6) 2.015(9), Cu(2)-N(7) 2.012(9), Cu(2)-Ow(2) 2.036(7), Cu(2)-N(8) 2.246(8) Å], but in this case, the τ value is 0.05. The Cu(1) and Cu(2) atoms are displaced

0.188(5) and 0.274(4) Å from the least-squares plane defined by the N₃O basal plane toward the pyridyl nitrogen atoms N(3) and N(8). The axial Cu-N_{py} bond distances of Cu(1)-N(3) and Cu(2)-N(8) are ca. 0.22 Å longer than the equatorial Cu-N_{py} bond distances. Similar results are reported on the related complexes [Cu(tepa)Cl]PF₆ and [Cu(tmpa)Cl]PF₆, which indicates the distorted square-pyramidal geometry.⁵ The average Cu-N_{py} and Cu-N_{amine} bond distances are similar to those found in the chloride derivative [Cu(pmea)Cl]ClO₄·H₂O (2.092(2) Å and 2.055(2) Å),⁹ which exhibits a distorted square pyramidal geometry ($\tau = 0.12$ and 0.14) with N₃Cl basal plane and one of the pyridines in the axial position. The N(1)-Cu(1)-N(2), N(2)-Cu(1)-N(3), N(5)-Cu(2)-N(6) and N(6)-Cu(2)-N(7) bite angles of the five-membered chelate rings [81.4(4)°, 87.2(4)°, 83.3(4)° and 84.6(4)°] are larger than the N(2)-Cu(1)-N(4) and N(6)-Cu(2)-N(8) bite angles of the six-membered chelate rings [90.9(4)° and 96.1(4)°]. The axial Cu(1)-N(3) and Cu(2)-N(8) linkages are bent slightly off the perpendicular to CuN₃O basal plane by 2.1-13.4° and 6.1-9.0°, respectively.

Table 2. Selected Bond Lengths (Å) and Angles (°)

Bond lengths			
Cu(1)-N(1)	1.997(8)	Cu(1)-N(2)	2.100(9)
Cu(1)-N(3)	2.226(8)	Cu(1)-N(4)	2.010(8)
Cu(1)-Ow(1)	2.087(7)	Cu(2)-N(5)	2.021(8)
Cu(2)-N(6)	2.015(9)	Cu(2)-N(7)	2.012(9)
Cu(2)-N(8)	2.246(8)	Cu(2)-Ow(2)	2.036(7)
Bond angles			
N(1)-Cu(1)-N(2)	81.4(4)	N(1)-Cu(1)-N(3)	103.4(3)
N(1)-Cu(1)-N(4)	162.2(3)	N(2)-Cu(1)-N(3)	87.2(4)
N(2)-Cu(1)-N(4)	90.9(4)	N(3)-Cu(1)-N(4)	92.1(3)
N(1)-Cu(1)-Ow(1)	94.4(3)	N(2)-Cu(1)-Ow(1)	173.8(3)
N(3)-Cu(1)-Ow(1)	98.2(3)	N(4)-Cu(1)-Ow(1)	92.0(3)
N(5)-Cu(2)-N(6)	83.3(4)	N(5)-Cu(2)-N(7)	161.0(4)
N(5)-Cu(2)-N(8)	97.9(3)	N(6)-Cu(2)-N(7)	84.6(4)
N(6)-Cu(2)-N(8)	96.1(4)	N(7)-Cu(2)-N(8)	98.0(3)
N(5)-Cu(2)-Ow(2)	96.3(3)	N(6)-Cu(2)-Ow(2)	164.8(4)
N(7)-Cu(2)-Ow(2)	91.6(3)	N(8)-Cu(2)-Ow(2)	99.0(3)
C(1)-N(1)-C(5)	119.8(10)	C(6)-N(2)-C(7)	110.3(10)
C(6)-N(2)-C(13)	113.5(11)	C(7)-N(2)-C(13)	100.9(11)
C(8)-N(3)-C(12)	119.9(9)	C(15)-N(4)-C(19)	121.0(9)
C(20)-N(5)-C(24)	118.2(10)	C(25)-N(6)-C(26)	112.1(9)
C(25)-N(6)-C(32)	110.5(10)	C(26)-N(6)-C(32)	109.7(9)
C(27)-N(7)-C(31)	119.7(10)	C(34)-N(8)-C(38)	119.8(10)

Table 3. Cyclic Voltammetric Data^a

Complex	Potentials (V) versus Ag/AgCl	
	Cu(II)/Cu(III)	Cu(II)/Cu(I)
[Cu(Hdpa)]Cl ₂ ^b	+0.25	-0.17
[Cu(pnea)(H ₂ O)](ClO ₄) ₂ ·H ₂ O(1)	-0.23	-0.22

^aMeasured in 0.10 M TEAP-DMSO solution at 20.0±0.1 °C.
^bRef. 19.

Chemical properties. The infrared spectrum of complex **1** exhibits bands at 1443-1608 cm⁻¹ associated with pyridine skeleton. The strong bands at 1088 cm⁻¹ was also assigned to the ν(Cl-O). The visible spectra of **1** in DMSO solution and the solid state show d-d transition bands at 641 and 645 nm, which is typical of a square pyramidal Cu(II) complex.¹⁸ Similar absorption bands (approximately 650 nm) were also found in other Cu(II) complexes of tripodal ligands.^{8,9} Cyclic voltammetric data for the copper(II) complexes in 0.10 M TEAP-DMSO solution are listed in Table 3. The cyclic voltammogram of **1** is shown in Fig. 2. The oxidation and reduction potentials of **1** gives the reversible one-electron processes at +0.23 V and -0.22 V vs the Ag/AgCl reference electrode, assigned to the Cu^{II}/Cu^{III} and Cu^{II}/Cu^I couples, respectively. The redox potential for **1** is slightly more negative than that of the square-pyramidal complex[Cu(Hdpa)]Cl₂.¹⁹ This can be attributed the more severe steric crowding caused by the presence of the N-coordinated pyridine group in which the complex **1** makes the oxidation of Cu(II)

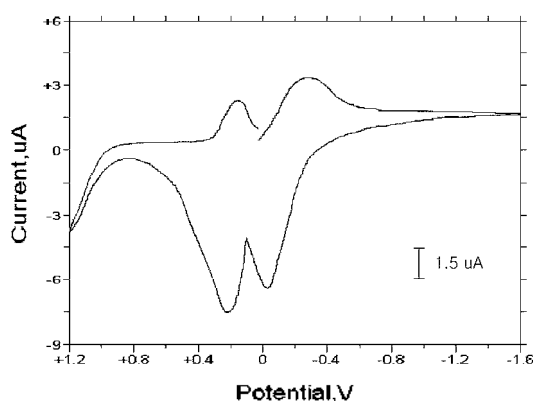


Fig. 2. Cyclic voltammogram of **1** in 0.10 M TEAP-DMSO solution at 20.0±0.1°C. The scan rate is 50 mV/s.

to Cu(III) easier and the reduction to Cu(I) difficult.

Supplementary Material. Atomic coordinates, bond lengths and angles, and thermal parameters for **1** are available from author K.-Y. Choi on request.

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