

Template Synthesis, Structure, and Properties of a New Five-Coordinate Copper(II) Complex of an Unsaturated Pentadentate Ligand

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Synthesis and characterization of new copper(II) complexes are important to develop models for copper proteins and to understand the factors affecting the distortions from regular coordination geometry observed in various copper(II) complexes.^{1,2} The coordination geometry of most five-coordinate copper(II) complexes ranges between trigonal bipyramidal (TBP) and square-pyramidal (SP) structures, but copper(II) complexes with regular TBP or SP geometry are not common.¹⁻¹⁰ It has been also observed that copper(II) complexes with SP geometry are more common than those with TBP one.¹ For example, the five coordinate complexes $[\text{Cu}(\mathbf{3})]^{2+}$ and $[\text{Cu}(\mathbf{4})]^{2+}$ have somewhat distorted SP coordination geometry in the solid state.^{3,4,11} In the case of $[\text{Cu}(\mathbf{4})]^{2+}$, the coordination geometry shifts toward TBP in various solvents.⁴ Until now, the factors affecting such behaviors are not clearly understood. Although many five-coordinate copper(II) complexes have been prepared, those with pentadentate ligands are relatively few.¹⁻⁴

contrast to the cases for $[\text{Cu}(\mathbf{3})]^{2+}$ and $[\text{Cu}(\mathbf{4})]^{2+}$. Preparation, crystal structure, and properties of $[\text{Cu}(\mathbf{2})](\text{ClO}_4)_2$ are reported.

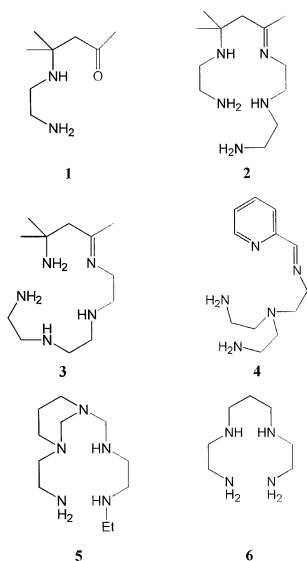
Experimental

Measurements. Infrared spectra were recorded with a Shimadzu IR-440 spectrophotometer, electronic absorption spectra with a Shimadzu UV-160 spectrophotometer, and conductance measurements with a Metrohm Herisau Conductometer E518. Elemental analyses and FAB mass spectral analysis were performed at the Korea Basic Science Institute, Seoul, Korea.

Preparation. *Safety Note:* Perchlorate salts of transition metal complexes with organic ligands are often explosive and should be handled with caution.

$[\text{H}_2\mathbf{1}](\text{ClO}_4)_2$. The procedure for preparation of this compound was adapted from a literature method.¹² The white solid $[\text{H}_2\text{en}](\text{ClO}_4)_2$ (H_2en = diprotonated form of ethylenediamine) was prepared by the addition of 60% perchloric acid (33 mL, 0.15 mol) to a cold methanol (*ca.* 20 mL) solution of en (5.0 mL, 0.7 mol). An acetone suspension (*ca.* 30 mL) of $[\text{H}_2\text{en}](\text{ClO}_4)_2$ (5.0 g) was stirred for 3 hr at room temperature. The reactant slowly went into the solution, and then new white solid was precipitated. The product was filtered, washed with cold acetone, and dried in air. Yield: >80% based on $[\text{H}_2\text{en}](\text{ClO}_4)_2$. Anal. Calcd for $\text{C}_8\text{H}_{20}\text{N}_2\text{Cl}_2\text{O}_9$: C, 26.75; H, 5.61; N, 7.84. Found: C, 26.66; H, 5.11; N, 8.10%. IR (Nujol mull, cm^{-1}): 3360 ($\nu\text{N-H}$), 3250 ($\nu\text{N-H}$), 3020 ($\nu\text{N-H}$), 1695 ($\nu\text{C=O}$), and 1600 (δNH_2).

$[\text{Cu}(\mathbf{2})](\text{ClO}_4)_2$. To a warm methanol solution (50 mL) of $\text{Cu}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (1.2 g, 5.5 mmol) and $[\text{H}_2\mathbf{1}](\text{ClO}_4)_2$ (2.0 g, 5.5 mmol) was added a methanol solution (*ca.* 10 mL) of dien (0.6 mL, 5.5 mol) during the period of 30 min. The mixture was stirred for *ca.* 20 h at room temperature and then an excess of $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ was added to produce blue solids. The product was filtered, washed with cold methanol, and dried in air. The crude product contains a considerable amount (~50%) of copper(II) complex with dien as a by-product. The solubility of $[\text{Cu}(\mathbf{2})](\text{ClO}_4)_2$ in methanol is considerably higher than that of the by-product. The pure product was obtained by fractional recrystallizations of the crude product from hot water and then hot methanol. Yield: ~30%. Anal. Calcd for $\text{C}_{12}\text{H}_{29}\text{N}_5\text{CuCl}_2\text{O}_8$: C, 28.49; H, 5.77; N, 13.84. Found: C, 28.12; H, 5.57; N, 13.48%. FAB Mass (*m*



We prepared a new unsaturated copper(II) complex $[\text{Cu}(\mathbf{2})](\text{ClO}_4)_2$ ($\mathbf{2}$ = 5,5,7-trimethyl-1,4,8,11,14-pentaazatetradec-7-ene) from the metal template condensation of 1,4,7-triazaheptane (dien) and 7-amino-4,4-dimethyl-5-azahaptan-2-one ($\mathbf{1}$) to investigate the effects of the ligand structure on the coordination geometry of the complex and its geometrically change in solutions. Interestingly, it was found that the coordination geometry of the complex is a distorted TBP in the solid state but shifts toward SP in various solvents, in

z): 405 ([M-ClO₄]⁺) and 306 ([M-2ClO₄-H]). IR (Nujol mull, cm⁻¹): 3360 (N-H), 3330 (νN-H), 3270 (νN-H), 3250 (νN-H), 3230 (νN-H), 1670 (νC=N), and 1600 (δNH₂).

[Cu(H₂)](ClO₄)₃. The blue complex [Cu(2)](ClO₄)₂ (1.5 g, 3.0 mmol) was dissolved in minimum volume of warm water. A methanol solution of 1.0 M HClO₄ (3.0 mL, 3.0 mmol) and an excess of NaClO₄ · H₂O were added to the blue solution. The resulting purple solution was evaporated to dryness, and then methanol (ca. 10 mL) was added to the residue. The red solid was isolated by filtration, washed with cold methanol, and dried in air. Yield: ~50%. Anal. Calcd for C₁₂H₃₀N₅CuCl₃O₁₂: C, 23.80; H, 5.01; N, 11.58. Found: C, 23.95; H, 4.90; N, 11.47%. IR (Nujol mull, cm⁻¹): 3320 (νN-H), 3290 (νN-H), 3220 (νN-H), 3150 (νN-H), 1680 (νC=N), and 1600 (δNH₂).

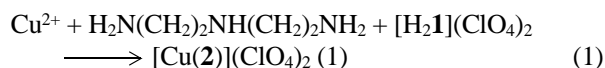
Crystal Structure Analysis. A single crystal in a sealed thin walled glass capillary was mounted on an Enraf-Nonius CAD4 diffractometer. Unit cell parameters and orientation matrix were obtained by least-squares refinement using 25 reflections in the range of 10° < θ < 13°. A summary of the crystal and structure refinement data is tabulated in Table 1. Mo K_α radiation (λ = 0.71073 Å) was used for data collection using ω-2θ scan mode. Two standard reflections (-2 -5 -5, -2 -4 -6) were monitored every one hour during data collection. The intensity data were corrected for Lorentz and polarization effects, and decay (less than 0.2%). An empirical absorption correction based on scans was applied to the

data (correction coefficients, 0.9704 to 0.9997).¹³

The structure was determined by direct methods with the SHELXS-97 program.¹⁴ Subsequent Fourier syntheses yielded the remaining non-H atoms. Full-matrix refinement on F² was carried out with SHELXL-97 program¹⁵ using anisotropic thermal parameters for non-H atoms except the disordered C(1) and C(2) atoms which were refined isotropically with occupancies at 0.5s. All hydrogen atoms were calculated geometrically using a riding model from the attached carbon atoms except hydrogen atoms on nitrogen atoms that were refined isotropically. No parameter shifted more than 0.01% of its estimated standard deviation during the last least-squares refinement.

Results and Discussion

Synthesis. The salt [H₂1](ClO₄)₂ can be obtained in high yield by the reaction of [enH₂](ClO₄)₂ with acetone. The reaction (Eq. (1)) of copper(II) ion, dien, and [H₂1](ClO₄) at room temperature produces the blue complex [Cu(2)](ClO₄)₂.



The red complex [Cu(H₂)](ClO₄)₃, in which one primary amino group of the ligand is protonated, was prepared by addition of a molar equivalent of HClO₄ to an aqueous solution of [Cu(2)](ClO₄)₂. The protonation reaction is reversible, and it is possible to generate the blue solid of [Cu(2)](ClO₄)₂ by addition of NaOH to the solution of [Cu(H₂)](ClO₄)₃. The complexes are quite stable in the solid states. The values of molar conductance of [Cu(2)](ClO₄)₂ measured in water (230 Ω⁻¹mol⁻¹cm²) and acetonitrile (245 Ω⁻¹mol⁻¹cm²) indicate that the complex is a 1 : 2 electrolyte. In the case of [Cu(H₂)](ClO₄)₃, the values measured in water (410 Ω⁻¹mol⁻¹cm²) and acetonitrile (430 Ω⁻¹mol⁻¹cm²) are corresponding to a 1 : 3 electrolyte. Infrared spectra of the copper(II) complexes show νN-H of the secondary and primary amino groups at 3150-3360 cm⁻¹, together with δ(NH₂) at 1600 cm⁻¹. The band for C=N was also observed at ca. 1670 cm⁻¹. The FAB mass spectrum of [Cu(2)](ClO₄)₂ shows two peaks corresponding to the fragments [M-ClO₄]⁺ and [M-2ClO₄-H]⁺ at m/z 405 and 306, respectively. The structure of [Cu(2)](ClO₄)₂ was confirmed by its crystal structure.

Description of the Crystal Structure. ORTEP drawing¹⁶ of the complex cation [Cu(2)]²⁺ with atomic numbering is shown in Figure 1. The coordination geometry about the central copper atom is best described as distorted TBP; the two primary amino groups and the imino group of the ligand form the equatorial plane, and the two secondary amino groups of the ligand occupy the axial positions. (see below).

The C(5)-N(3) bond distance (1.271(6) Å), together with the angles about these atoms, is corresponding to the C=N double bond. The five Cu-N bond distances range from 2.009(5) to 2.146(5) Å. Although the Cu-N(5) distance is somewhat longer than the other four Cu-N distances, the

Table 1. Crystal data and structure refinement for [Cu(2)](ClO₄)₂

Formula	C ₁₂ H ₂₉ Cl ₂ CuN ₅ O ₈
Fw	505.84
T, K	293(2)
Wavelength, Å	0.71073
Crystal size, mm	0.50 × 0.40 × 0.35
Crystal system	Monoclinic,
Space group	P2 ₁ /c
a, Å	7.8709(6)
b, Å	17.3934(8)
c, Å	15.1093(7)
β, deg	91.950(5)
V, Å ³	2067.3(2)
Z	4
D _{calc} , g cm ⁻³	1.63(1)
μ, cm ⁻¹	13.6
F(000)	1052
range, deg	1.79 - 25.46
Index ranges	-9 < h < 9, 0 < k < 21, 0 < l < 18
Reflections collected / unique	4134 / 3421 [R(int) = 0.0108]
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3421 / 0 / 268
Goodness-of-fit on F ²	1.079
Final R indices [I > 2σ(I)] ^a	R = 0.0523, wR = 0.1516
R indices (all data) ^a	R = 0.0663, wR = 0.1598
Largest diff. peak and hole, eÅ ⁻³	0.743 and -0.723

^aR = Σ||F_o - F_c|| / Σ|F_o|, wR = [Σw (|F_o - F_c|)² / ΣwF_o²]^{1/2}, where w = 1 / [σ²(F_o²) + (0.0994 × P)² + 3.10 × P] in which P = [Max (F_o², 0) + 2 × F_c²] / 3.

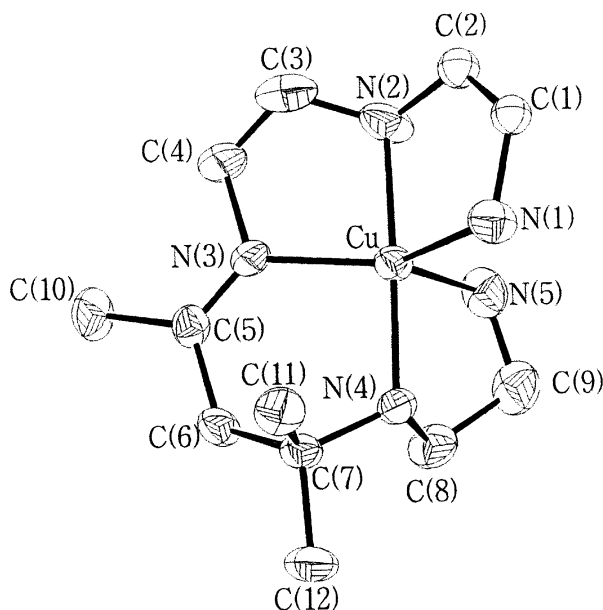


Figure 1. ORTEX drawing of $[\text{Cu}(\mathbf{2})]^{2+}$ in $[\text{Cu}(\mathbf{2})](\text{ClO}_4)_2$.

distances are in the normal range for Cu-N distances of copper(II) complexes with TBP coordination geometry. The N-Cu-N angles of the trigonal plane ($\text{N}(1)\text{-Cu-N}(3)$, $136.3(2)^\circ$; $\text{N}(1)\text{-Cu-N}(5)$, $104.2(2)^\circ$; $\text{N}(3)\text{-Cu-N}(5)$, $118.6(2)^\circ$) are somewhat deviated from ideal trigonal angle. However, the $\text{N}(2)\text{-Cu-N}(4)$ angle ($177.5(2)^\circ$) is close to that of regular TBP geometry. The other N-Cu-N angles range from $83.1(2)$ to $99.2(2)^\circ$. The axial Cu-N(2) and Cu-N(4) distances are somewhat shorter than the equatorial Cu-N distances, typical of copper(II) complexes with TBP coordination geometry.^{1,9,10} The copper atom lies at $0.113(3)$ Å out of the N(1)-N(3)-N(5) plane.

In a five-coordinated copper(II) complex in which one Cu-N bond distance is longer than the others, a method for quantitative description of the degree of geometrical distortion has been developed.^{4,17} According to the method, the longer Cu-N bond is assumed as the apical bond in a SP structure, and the percentage trigonal distortion from square-pyramidal geometry is defined as $\tau = [(\theta - \pi)/60] \times 100$, where θ and π are two basal angles; τ is 100 for an ideal TBP but is 0 for an ideal SP geometry. In the case of $[\text{Cu}(\mathbf{2})]^{2+}$, the θ and

Table 2. Selected Bond Distances [Å] and angles [deg] for $[\text{Cu}(\mathbf{2})](\text{ClO}_4)_2$

Cu-N(1)	2.086(4)	Cu-N(2)	2.009(5)
Cu-N(3)	2.018(4)	Cu-N(4)	2.015(4)
Cu-N(5)	2.146(5)	N(3)-C(4)	1.476(6)
N(3)-C(5)	1.271(6)		
N(1)-Cu-N(2)	83.1(2)	N(1)-Cu-N(3)	136.3(2)
N(1)-Cu-N(4)	99.2(2)	N(1)-Cu-N(5)	104.2(2)
N(2)-Cu-N(3)	83.8(2)	N(2)-Cu-N(4)	177.5(2)
N(2)-Cu-N(5)	96.2(2)	N(3)-Cu-N(4)	93.9(2)
N(3)-Cu-N(5)	118.6(2)	N(4)-Cu-N(5)	84.1(2)
N(3)-C(5)-C(6)	120.9(4)	N(3)-C(5)-C(10)	124.2(5)

π values are $177.5(2)$ ($\text{N}(2)\text{-Cu-N}(4)$) and $136.3(2)$ ($\text{N}(1)\text{-Cu-N}(3)$), respectively. The τ value for the complex is calculated as *ca.* 69%. This and above crystallographic results strongly indicate that the coordination geometry of $[\text{Cu}(\mathbf{2})]^{2+}$ is close to TBP. The coordination geometry is quite different from those of the unsaturated complexes $[\text{Cu}(\mathbf{3})]^{2+}$ and $[\text{Cu}(\mathbf{4})]^{2+}$,^{3,4} indicating that the geometry of a five-coordinate copper(II) complex is strongly affected by the ligand structure.

Electronic Absorption Spectra and Solution Behaviors.

It has been widely observed that regular and distorted SP copper(II) complexes have an absorption band in the region 550-670 nm, whereas TBP complexes exhibit a maximum absorption at > 670 nm.^{4,9,10,18,19} The spectrum (Table 3) of $[\text{Cu}(\mathbf{2})](\text{ClO}_4)_2$ measured as Nujol mull shows a band centered at 690 nm which is *ca.* 80 nm longer than that for the distorted SP complex $[\text{Cu}(\mathbf{4})](\text{ClO}_4)_2$.⁴ This result corresponds to the crystallographic result that the complex has a distorted TBP structure in the solid state. Interestingly, the wavelength (610-620 nm) of the band for $[\text{Cu}(\mathbf{2})](\text{ClO}_4)_2$ measured in MeNO_2 , MeCN, or H_2O is > 70 nm shorter than that in Nujol mull. The wavelength is even shorter than that for the square-pyramidal complex $[\text{Cu}(\mathbf{4})](\text{ClO}_4)_2$ measured in MeNO_2 or MeCN, in contrast to the case in Nujol mull. This strongly indicates that in the solutions the coordination polyhedron of $[\text{Cu}(\mathbf{2})](\text{ClO}_4)_2$ shifts toward SP geometry. Present result is in contrast to the reported result that the geometry of $[\text{Cu}(\mathbf{4})](\text{ClO}_4)_2$ shifts toward the TBP in solutions; in the case of $[\text{Cu}(\mathbf{4})](\text{ClO}_4)_2$, the wavelength of the band in MeCN or H_2O is *ca.* 40 nm longer than that in Nujol mull (Table 3).⁴ The reasons for such geometrical change in the solutions are not clearly understood at this time. However, solvation of the complex may be correlated with the geometrical change. The spectrum of $[\text{Cu}(\mathbf{H2})](\text{ClO}_4)_3$ measured in Nujol mull or MeNO_2 shows a *d-d* band at 520 or 515 nm, respectively, and is comparable with those of square-planar copper(II) complexes of **5** and other related tetradentate ligands,¹⁹⁻²² indicating that the protonated com-

Table 3. Electronic Absorption Spectral Data of $[\text{Cu}(\mathbf{2})](\text{ClO}_4)_2$ at 25 °C

Compound	λ_{max} , nm (ϵ , $\text{M}^{-1}\text{cm}^{-1}$)	Solvent or Condition
$[\text{Cu}(\mathbf{2})](\text{ClO}_4)_2$	690	Nujol mull
	618(103)	MeNO_2
	612(142)	MeCN
	620(124)	H_2O
$[\text{Cu}(\mathbf{H2})](\text{ClO}_4)_3$	520	Nujol mull
	515(75)	MeNO_2
	536(90)	MeCN
$[\text{Cu}(\mathbf{4})](\text{ClO}_4)_2^a$	547(90)	H_2O
	610	Nujol mull
	647(162)	MeCN
$[\text{Cu}(\mathbf{5})](\text{ClO}_4)_2^b$	650(149)	H_2O
	530(98)	MeNO_2
	544(104)	H_2O

^aRef. 4. ^bRef. 20.

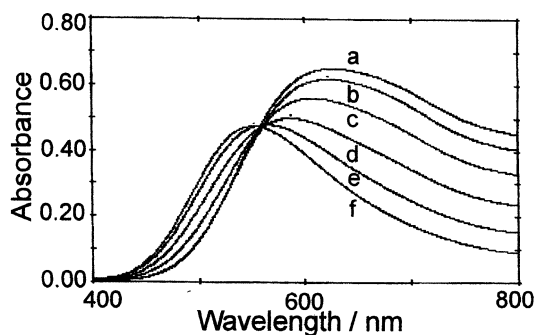


Figure 2. Electronic absorption spectra of $\text{Cu(2)}](\text{ClO}_4)_2$ (5.0×10^{-3} M) in aqueous solutions containing HClO_4 , $[\text{HClO}_4] = 0.0$ (a), 1.0×10^{-3} (b), 2.0×10^{-3} (c), 3.0×10^{-3} (d), 4.0×10^{-3} (e), and 5.0×10^{-3} M (f).

plex has a square-planar coordination geometry. The band of the complex measured in H_2O is observed at *ca.* 30 nm longer wavelength than that in MeNO_2 or Nujol mull. This may be resulted from the axial coordination of water molecule.^{19-21,23}

Figure 2 shows that the addition of HClO_4 ($\leq 5.0 \times 10^{-3}$ M) to an aqueous solution of $[\text{Cu(2)}](\text{ClO}_4)_2$ (5.0×10^{-3} M) decreases the absorption at *ca.* 620 nm. On the other hand, the absorption at *ca.* 550 nm increases as the concentration of the acid is increased; the spectrum (curve f) of $[\text{Cu(2)}](\text{ClO}_4)_2$ measured in 5.0×10^{-3} M HClO_4 solution is quite similar to that of $[\text{Cu(H2)}](\text{ClO}_4)_3$ measured in pure water, indicating the formation of the protonated complex. The protonation reaction rate is too fast to measure with ordinary methods. However, the resulting protonated complex $[\text{Cu(H2)}]^{3+}$ was decomposed relatively slowly even in concentrated HClO_4 solutions. Pseudo first-order rate constant (*k*) for the decomposition reaction of $[\text{Cu(H2)}]^{3+}$ (2.0×10^{-3} M) measured in 0.1 M HClO_4 solution was found to be *ca.* $4.4 \times 10^{-2} \text{ s}^{-1}$. It is obvious that the reaction rate is distinctly slower than those reported for $[\text{Cu(5)}]^{2+}$ ($k > 0.1 \text{ s}^{-1}$ in 0.1 M HClO_4)²⁰ and $[\text{Cu(6)}]^{2+}$ ($k = 0.16 \text{ s}^{-1}$ in 0.1 M HNO_3).²⁴ The slower decomposition of $[\text{Cu(H2)}]^{3+}$, compared to $[\text{Cu(5)}]^{2+}$, may be related to the more rigid structure of the ligand containing one imine bond. Unfortunately, direct comparison of the protonation behaviors of $[\text{Cu(2)}]^{2+}$ with those of the unsaturated complexes $[\text{Cu(3)}]^{2+}$ and $[\text{Cu(4)}]^{2+}$ cannot be made at this time, because the data of the latter complexes are not available.

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