

## Synthesis and Structure of [Cu(L)](ClO<sub>4</sub>)<sub>2</sub> (L: 3,5,10,12-Tetramethyl-1,4,8,11-tetraazacyclotetradecane)

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## [Cu(L)](ClO<sub>4</sub>)<sub>2</sub> (L: 3,5,10,12-Tetramethyl-1,4,8,11-tetraazacyclotetradecane) 錯物の合成 및 構造

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### Abstract

The complex [Cu(L)](ClO<sub>4</sub>)<sub>2</sub> (**1**) (L: 3,5,10,12-Tetramethyl-1,4,8,11-tetraazacyclotetradecane) has been synthesized and structurally characterized. The complex **1** crystallizes in the monoclinic system, space group P2<sub>1</sub>/n with cell parameters a=8.208(2) Å, b=13.339(6) Å, c=10.752(5) Å, β=111.02(4)°, Z=2. Least-squares refinement of **1** led to a R (R<sub>w</sub>) factor of 0.073 (0.142) for 617 observed reflections of F<sub>o</sub>>4σ(F<sub>o</sub>). The crystal structure of **1** has a square-planar geometry and adopts the *trans*-III conformation.

### 要 約

[Cu(L)](ClO<sub>4</sub>)<sub>2</sub> (**1**) (L: 3,5,10,12-Tetramethyl-1,4,8,11-tetraazacyclotetradecane) 錯물을 合成하고 構造를 糾明하였다. 이 錯물은 單結晶系, 空間群 P2<sub>1</sub>/n, a=8.208(2) Å, b=13.339(6) Å, c=10.752(5) Å, β=111.02(4)°, Z=2로 結晶化되었다. 이 錯물의 構造는 最小自乘法으로 精密化하였으며, 最終 信賴度 R(R<sub>w</sub>)값은 617個의 回折班點에 대하여 0.073 및 0.142이었다. 이 錯물의 結晶構造는 平面四角構造와 *trans*-III 形態를 갖는다.

### 1. Introduction

Transition metal complexes of C-alkyl substituted tetraaza macrocycles show specific stabilization, redox and catalytic properties.<sup>1</sup> Recently, a number of copper (II) complexes of C-alkyl substituted ligands have been synthesized.<sup>2-7</sup> The coordination environments around copper (II) ion in these complexes are known to be a

square-planar or octahedral geometry. In a previous paper, we reported the synthesis and X-ray crystal structure of [Cu(DTAD)(H<sub>2</sub>O)<sub>2</sub>]Cl<sub>2</sub> (DTAD: 3,14-dimethyl-2,6,13,17-tetraazatricyclo [14,4,0,1,18,0,7,12]docosane), in which the copper (II) ion adopts a tetragonally elongated octahedral geometry with two apical water oxygen atoms.<sup>5</sup> However, it may act as tetradentate when complexed with low-spin nickel

(II) ion which prefer a square-planar geometry.<sup>8</sup> Therefore, we have been interested in further investigation of the effects of the C-alkyl group on the properties of the macrocyclic transition metal (II) complexes.

In this paper, we report the synthesis and crystal structure of a copper (II) complex of 3,5,10,12-tetramethyl-1,4,8,11-tetraazacyclotetradecane (L).

## 2. Experimental Section

**Materials and Physical Measurements.** All solvents were reagent grade and purified according to the literature.<sup>9</sup> Chemicals used were of reagent grade and were used without further purification. The ligand L and [Cu(L)(H<sub>2</sub>O)<sub>2</sub>]Cl<sub>2</sub> were prepared by the literature methods.<sup>10,7</sup> High-resolution fast atom bombardment mass spectrometry (FAB mass) were performed by using a Jeol JMS-HA 110A/110A instrument. Elemental analyses were carried out by the Korea Basic Science Institute, Seoul, Korea.

**Synthesis of [Cu(L)](ClO<sub>4</sub>)<sub>2</sub> (1).** To a methanol solution (20 ml) of [Cu(L)(H<sub>2</sub>O)<sub>2</sub>]Cl<sub>2</sub> (427 mg, 1 mmol) was added excess NaClO<sub>4</sub> and the mixture refluxed for 1 hr. When this solution was allowed to stand for a few days, a quantity of pink crystals were precipitated. These were filtered off, washed with diethyl ether and desiccated until dry (Yield 389 mg, 75%). Anal. Calcd for CuC<sub>14</sub>H<sub>32</sub>N<sub>4</sub>Cl<sub>2</sub>O<sub>8</sub>: C, 32.4; H, 6.2; N, 10.8. Found: C, 32.3; H, 6.1; N, 10.9%. FAB mass (CH<sub>2</sub>Cl<sub>2</sub>, m/z): 518.9 (M)<sup>+</sup>.

**X-ray Structural Determination.** A pink crystal of **1** (0.26×0.20×0.05 mm<sup>3</sup>) was mounted on an Enraf-Nonius CAD4 diffractometer with graphite monochromated Mo-Kα(λ=0.71069 Å) radiation. Accurate cell parameters and an orientation matrix were determined from the least-squares fit of 25 accurately centered reflections

with 2θ range of 19.38 to 28.06°. Intensity data were collected in the ω/2θ scan mode to a maximum 2θ of 48°. Data were corrected for Lorentz and polarization effects. No absorption correction was applied. A total of 2914 unique reflections were measured, of which 617 with (F<sub>0</sub>>4σ(F<sub>0</sub>)) were used in the structural analysis. The structure was solved by use of direct methods<sup>11</sup> and successive cycles of difference Fourier map followed by least-squares refinement.<sup>12</sup> All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions and allowed to ride upon the appropriate carbon or nitrogen atoms. The refinement gave R (R<sub>w</sub>)=0.073 (0.142) and (Δ/σ)<sub>max</sub> was 0.000. The highest and deepest peaks in the last difference map were 0.456 and -0.623e Å<sup>-3</sup>, respectively. Crystallographic data and refinement details are summarized in Table 1. Atomic coordinates and bond distances and angles are listed in Table 2 and 3.

**Table 1. Crystallographic Data for [Cu(L)](ClO<sub>4</sub>)<sub>2</sub> (1)**

Formula	CuC <sub>14</sub> H <sub>32</sub> N <sub>4</sub> Cl <sub>2</sub> O <sub>8</sub>
Formula weight	518.88
Crystal system	Monoclinic
Space group	P2 <sub>1</sub> /n
a (Å)	8.208(2)
b (Å)	13.339(6)
c (Å)	10.752(5)
β (Å)	111.02(4)
V (Å <sup>3</sup> )	1098.8(8)
Z	2
F (000)	542
D <sub>c</sub> (Mg m <sup>-3</sup> )	1.568
Diffractometer	Mo-Kα
λ (Mo-Kα) (Å)	0.71069
μ (mm <sup>-1</sup> )	1.284
2θ range (°)	48
Data collection method	Enraf-Nonius CAD4
Scan width	0.8+0.34 tanθ
h, k, l range	-10 10, 0 17, 0 14
No. of unique reflections	2914
No. of observed reflections	617
[F <sub>o</sub> >4σ(F <sub>o</sub> )]	
R <sup>a</sup>	0.073
R <sub>w</sub> <sup>b</sup>	0.142
G <sub>o</sub> F <sup>c</sup>	0.989

<sup>a</sup>R=Σ(F<sub>o</sub>-F<sub>c</sub>)/Σ(F<sub>o</sub>).

<sup>b</sup>R<sub>w</sub>=[Σw(F<sub>o</sub>-F<sub>c</sub>)<sup>2</sup>/Σ(wF<sub>o</sub><sup>2</sup>)]<sup>1/2</sup>.

<sup>c</sup>GoF=[Σw(F<sub>o</sub>-F<sub>c</sub>)<sup>2</sup>/(no. of rflns-no. of params)]<sup>1/2</sup>.

**Table 2. Atomic Coordinates ( $\times 10^4$ ) and Equivalent Isotropic Displacement Parameters ( $\text{\AA}^2 \times 10^3$ ) for [Cu(L)](ClO<sub>4</sub>)<sub>2</sub> (1)**

	x	y	z	U (eq)
Cu	0	0	0	94(1)
Cl	-2418(3)	-2403(2)	-203(3)	50(1)
O(1)	-3746(8)	-3056(5)	-173(6)	78(2)
O(2)	-2360(10)	-2468(6)	-1451(8)	115(3)
O(3)	-2611(9)	-1431(5)	-9(7)	90(2)
O(4)	-971(8)	-2770(5)	583(6)	83(2)
N(1)	-1942(7)	871(5)	-1032(7)	45(2)
N(2)	243(7)	657(5)	1769(5)	44(2)
C(1)	-2740(10)	379(6)	-2263(9)	54(3)
C(2)	-3146(10)	1269(7)	-448(10)	70(3)
C(3)	-2225(11)	1792(7)	922(10)	63(3)
C(4)	-1256(12)	1155(7)	2015(10)	73(3)
C(5)	-2255(10)	336(7)	2363(8)	69(3)
C(6)	1474(10)	30(7)	2818(7)	48(2)
C(7)	2285(12)	579(8)	4166(9)	95(4)

U (eq) is defined as one third of the trace of the orthogonalized U<sub>ij</sub> tensor.

### 3. Results and Discussion

An ORTEP drawing of [Cu(L)](ClO<sub>4</sub>)<sub>2</sub> (1) with the atomic numbering scheme is shown in Fig. 1. An inversion center of this complex exists on the central copper (II) ion. The structure of the complex **1** contains of [Cu(L)]<sup>2+</sup> cation and two ClO<sub>4</sub><sup>-</sup> anions. The four secondary amine nitrogen atoms are bound to the copper ion in a square-planar geometry and adopt a *trans*-III conformation. Two perchlorate oxygen atoms are located 2.867(1) Å from the copper (II) ion. The coordination geometry around the Cl atom is a pseudotetrahedral, in which Cl-O bond distances are in the range 1.283(6)<sup>o</sup> to 1.405(6) Å with O-Cl-O angles of 105.3(5) to 117.6(4)<sup>o</sup>, respectively. The Cu-N bond distances are 1.963(6) and 2.038(6) Å and lie in the range expected for the square-planar copper (II) complexes.<sup>13,14</sup> The N-Cu-N angles of the six-memb-

**Table 3. Bond Distances (Å) and Angles (°) for [Cu(L)](ClO<sub>4</sub>)<sub>2</sub> (1)**

Cu-N(1)	1.963(6)	N(2)-C(6)	1.474(8)
Cu-N(1)i	1.963(6)	C(1)-C(6)i	1.476(10)
Cu-N(2)	2.038(6)	C(2)-C(3)	1.558(11)
Cu-N(2)i	2.038(6)	C(3)-C(4)	1.437(11)
Cu-O(3)	2.867(1)	C(4)-C(5)	1.492(10)
Cu-O(3)i	2.867(1)	C(6)-C(1)i	1.476(10)
Cu-Cl	3.735(1)	C(6)-C(7)	1.546(11)
Cu-Cl <i>i</i>	3.735(1)	Cl-O(1)	1.405(6)
N(1)-C(1)	1.411(9)	Cl-O(2)	1.363(7)
N(1)-C(2)	1.449(9)	Cl-O(3)	1.331(6)
N(2)-C(4)	1.503(10)	Cl-O(4)	1.283(6)
N(1)-Cu-N(2)	93.5(3)	N(2)-C(6)-C(7)	113.3(7)
N(1)-Cu-N(2)i	86.5(3)	N(2)-C(4)-C(3)	114.7(6)
N(1)i-Cu-N(2)	93.5(3)	N(2)-C(4)-C(5)	119.7(6)
N(1)i-Cu-N(2)	86.5(3)	C(1)-N(1)-C(2)	116.6(8)
N(1)i-Cu-N(1)	180.0	C(4)-N(2)-C(6)	116.4(8)
N(2)-Cu-N(2)i	180.0	C(2)-C(3)-C(4)	115.2(7)
O(3)-Cu-O(3)i	179.9	C(3)-C(4)-C(5)	111.4(7)
Cl-Cu-Cl <i>i</i>	179.9	C(1)i-C(6)-C(7)	106.2(8)
Cu-N(1)-C(1)	105.3(5)	O(1)-Cl-O(2)	106.5(4)
Cu-N(1)-C(2)	120.9(5)	O(1)-Cl-O(3)	117.6(4)
Cu-N(2)-C(4)	122.8(5)	O(1)-Cl-O(4)	106.9(4)
Cu-N(2)-C(6)	106.3(5)	O(2)-Cl-O(3)	105.3(5)
N(1)-C(1)-C(6)i	113.2(7)	O(2)-Cl-O(4)	105.8(5)
N(1)-C(2)-C(3)	113.5(7)	O(3)-Cl-O(4)	113.8(5)
N(1)-C(6)-C(1)i	106.8(6)		

Symmetry code: (i) -x, -y, -z.

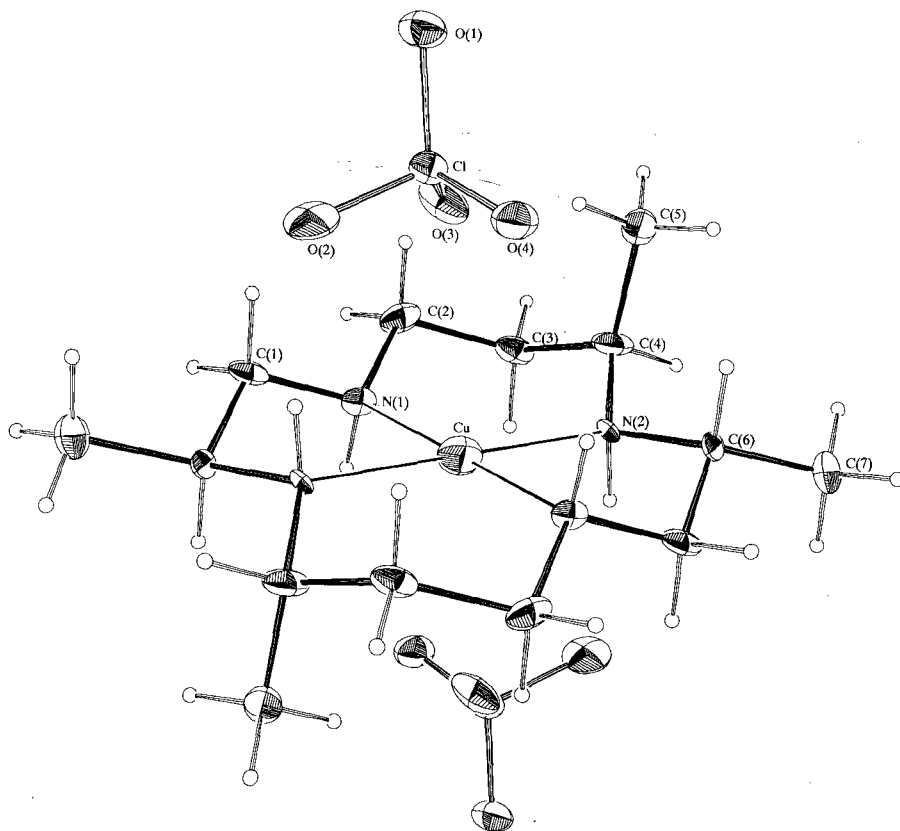


Fig. 1. An ORTEP drawing of [Cu(L)](ClO<sub>4</sub>)<sub>2</sub> (1) with the atomic numbering scheme. The displacement ellipsoids are drawn at the 40% probability level. H atoms are drawn as small circles of arbitrary radii.

ered chelate rings (93.5(3)°) are larger than those of the five-membered chelate ring (86.5(3)°). Both six-membered chelate rings adopt a chair conformation and five-membered rings are gauche. Four methyl groups on both five- and six-membered chelate rings are *anti* with respect to the CuN<sub>4</sub> plane.

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