

## Copper(II) Complex of a Di-N-hydroxyethylated Tetraaza Macrocycle

Ki-Young Choi<sup>a\*</sup>, Yong-Son Kim<sup>a</sup>, Hailil Ryu<sup>b</sup>, Il-Hwan Suh<sup>c</sup>,  
Geum-Hong Choo<sup>c</sup>, Jin-Gyu Kim<sup>c</sup> and Moon-Jip Kim<sup>d</sup>

<sup>a</sup>Department of Cultural Heritage Conservation Science, Kongju National University, Kongju 314-701, Korea

<sup>b</sup>Department of Chemical Education, Kongju National University, Kongju 314-701, Korea

<sup>c</sup>Department of Physics, Chungnam National University, Taejon 305-764, Korea

<sup>d</sup>Department of Physics, Soonchunhyang University, Onyang 336-600, Korea

## Di-N-hydroxyethylated Tetraaza 巨大고리 Copper(II) 錯物

崔琪泳<sup>a\*</sup> · 金容善<sup>a</sup> · 柳海日<sup>b</sup> · 徐日煥<sup>c</sup> · 秋錦洪<sup>c</sup> · 金珍圭<sup>c</sup> · 金文執<sup>d</sup>

<sup>a</sup>公州大學校 文化財保存科學科, <sup>b</sup>公州大學校 化學教育科

<sup>c</sup>忠南大學校 物理學科, <sup>d</sup>順天鄉大學校 物理學科

### Abstract

The complex  $[\text{CuL}]\text{Cl}_2 \cdot 3\text{H}_2\text{O}$  (**1**) (L=2,13-bis(2-hydroxyethyl)-5,16-dimethyl-2,6,13,17-tetraazatricyclo[14,4,0<sup>1,18</sup>,0<sup>7,12</sup>]docosane) has been synthesized and characterized by X-ray crystallography. **1** crystallized in the monoclinic, space group  $C2/c$ , with  $a=21.647(6)$  Å,  $b=8.549(1)$  Å,  $c=18.132(5)$  Å,  $\beta=118.58(2)^\circ$ ,  $V=2946.8(12)$  Å<sup>3</sup>,  $Z=4$ ,  $R_1(wR_2)$  for 2374 observed reflections of  $[I > 2\sigma(I)]$  was 0.052(0.187). The centrosymmetric complex **1** has an axially elongated octahedral geometry with four secondary and tertiary amines of the macrocycle and two oxygen atoms of the pendant hydroxyethyl groups

### 要約

$[\text{CuL}]\text{Cl}_2 \cdot 3\text{H}_2\text{O}$  (**1**) (L=2,13-bis(2-hydroxyethyl)-5,16-dimethyl-2,6,13,17-tetraazatricyclo[14,4,0<sup>1,18</sup>,0<sup>7,12</sup>]docosane) 錯物を合成하고 X-ray 회折法을 이용하여 構造를 糾明하였다. 이 錯物은 單斜晶系, 空間群  $C2/c$ ,  $a=21.647(6)$  Å,  $b=8.549(1)$  Å,  $c=18.132(5)$  Å,  $\beta=118.58(2)^\circ$ ,  $V=2946.8(12)$  Å<sup>3</sup>,  $Z=4$ 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 2374個의 回折班點에 대하여 0.052 및 0.187이었다. 中心 對稱을 갖는 錯物 **1**의 構造는 巨大고리 리간드의 二次 및 三次 아민과 hydroxyethyl 基의 두 個 酸素 原子에 의하여 結合된 軸方向으로 늘어난 六配位 八面體 構造를 갖는다.

### 1. Introduction

Successful applications of several cyclam (1,4,8,11-tetraazacyclotetradecane) derived mainly from their use as models for protein-metal binding sites in biological systems<sup>1-3)</sup> and as selective reagents of metallic ions.<sup>4-6)</sup> We have been interested in the synthesis of the macrocyclic ligands through the functionalization of 5,16-dimethyl-2,6,13,17-tetraazatricyclo[14,4,0<sup>1,18</sup>,0<sup>7,12</sup>]docosane (DTTD) with pendant donor

groups of different nature, in order to improve the selectivity of the ligands and the stability of the complexes.<sup>7,8)</sup> To that purpose, di-functionalized derivatives of DTTD have to be readily available in high yields. However, partially N-functionalized tetraazamacrocycles are relatively rare.<sup>9-11)</sup> This may be due to the difficulties encountered for the attachment of only one or two pendant groups to the tetraazamacrocyclic according to several steps in low yields. The purpose of this work is to investigate

the coordination behaviors of the di-*N*-hydroxyethylated macrocycle.

In this paper, we report the synthesis and crystal structure of  $[\text{CuL}]\text{Cl}_2 \cdot 3\text{H}_2\text{O}$  (**1**) (L=2,13-bis(2-hydroxyethyl)-5,16-dimethyl-2,6,13,17-tetraazatricyclo [14,4,0<sup>1,18</sup>,0<sup>7,12</sup>]docosane)

## 2. Experimental Section

**Materials and physical methods.** The di-*N*-hydroxyethylated tetraazamacrocyclic L was prepared as described previously.<sup>12)</sup> IR spectra were recorded with a Perkin-Elmer Paragon 1000 FT-IR spectrophotometer. Electronic spectra were obtained with a Jasco Uvidec-610 spectrometer. Elemental analyses and FAB mass spectra were performed by the Korea Basic Science Institute, Taejeon, Korea.

**Synthesis of  $[\text{CuL}]\text{Cl}_2 \cdot 3\text{H}_2\text{O}$  (**1**).** A methanol solution (20 ml) of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (85 mg, 0.5 mmol) and L (212 mg, 0.5 mmol) was heated at reflux for 1 h and then cooled to room temperature. The solution was filtered and left at room temperature until dark violet crystals formed. The product was filtered and recrystallized from a hot water-acetonitrile (1 : 1, 10 ml) mixture. Yield: 248 mg (81%). Found: C, 47.12; H, 8.82; N, 9.06. Calc. for  $\text{C}_{24}\text{H}_{54}\text{Cl}_2\text{CuN}_4\text{O}_5$ : C, 47.01; H, 8.88; N, 9.14%. IR (KBr,  $\text{cm}^{-1}$ ): 3238 [ν(N-H)] and 3358 [ν(O-H)]. Electronic spectra ( $\text{H}_2\text{O}$ ):  $\lambda_{\text{max}}$ , nm ( $\epsilon$ ,  $\text{M}^{-1} \text{cm}^{-1}$ ): 566 (76). FAB mass ( $\text{CH}_2\text{Cl}_2$ ,  $m/z$ ): 613 ( $\text{M}^+$ ).

**X-ray Crystallography.** Dark violet crystals of **1** were grown from water-acetonitrile. A crystal was mounted on an Enraf-Nonius CAD4 diffractometer. X-ray data were collected using graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda=0.71069 \text{ \AA}$ ), by the  $\omega$ - $2\theta$  scan technique. The accurate unit-cell parameters and an orientation matrix for data collection were obtained by least-squares refinement of the setting angles of 25 reflections. The intensity data were corrected for Lorentz and polarization effects. An empirical absorption correction based on  $\phi$ -scan was applied. 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> All hydrogen atoms except for the water hydrogen atoms were placed in calculated positions with iso-

**Table 1. Crystal Data and Structure Refinement for **1****

Color/shape	Dark violet/block
Empirical formula	$\text{C}_{24}\text{H}_{54}\text{Cl}_2\text{CuN}_4\text{O}_5$
Formula weight	613.15
Temperature	293(2) K
Wavelength	0.71069 $\text{ \AA}$
Crystal system	Monoclinic
Space group	$C2/c$
Unit cell dimensions	$a=21.647(6) \text{ \AA}$ $\alpha=90^\circ$ $b=8.549(1) \text{ \AA}$ $\beta=118.58(2)^\circ$ $c=18.132(5) \text{ \AA}$ $\gamma=90^\circ$
Volume	$2946.8(12) \text{ \AA}^3$
Z	4
Density (calculated)	$1.382 \text{ Mg/m}^3$
Absorption coefficient	$0.962 \text{ mm}^{-1}$
$F(000)$	1316
Crystal size	$0.50 \times 0.46 \times 0.30 \text{ mm}$
$\theta$ range for data collection	2.14 to $24.97^\circ$
Index ranges	$-25 \leq h \leq 25$ , $-10 \leq k \leq 8$ , $-21 \leq l \leq 12$
Reflection collected/unique	2442/2374 ( $R_{\text{int}}=0.0360$ )
Absorption correction	Empirical ( $\phi$ -scan)
Max. and min. transmission	0.999 and 0.571
Refinement method	Full-matrix least-squares on $F^2$
Data/restraints/parameters	2374/0/166
Goodness-of-fit on $F^2$	1.027
Final $R$ indices [ $I > 2\sigma(I)$ ]	$R_1^a=0.0524$ , $wR_2^b=0.1874$
$R$ indices (all data)	$R_1^a=0.0668$ , $wR_2^b=0.1970$
Weight	$w=1/[\sigma^2(F_o^2)+(0.1356P)^2+0.0000P]$ where $P=(F_o^2+2F_c^2)/3$
Largest diff. peak and hole	$0.842$ and $-0.479 \text{ e \AA}^{-3}$

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

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

tropic displaced parameters. A summary of the data collection and details of the structure refinement is listed in Table 1. Final atomic coordinates and equivalent isotropic displacement parameters are given in Table 2.

## 3. Results and Discussion

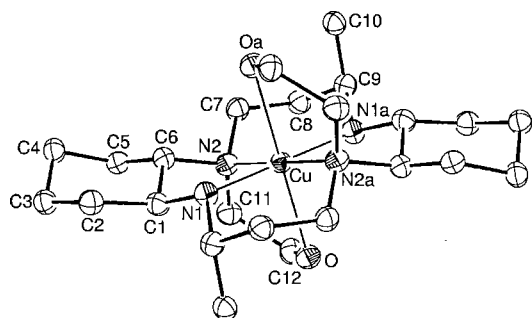
An ORTEP diagram of **1** with the atomic label-

**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	2500	7500	5000	37(1)
Cl	1223(1)	11687(2)	5776(1)	57(1)
N(1)	3523(2)	7879(5)	5303(3)	46(1)
N(2)	2310(3)	8263(5)	3894(3)	49(1)
O	2188(2)	10238(4)	5057(2)	51(1)
C(1)	3538(3)	8597(7)	4569(4)	50(1)
C(2)	4327(3)	8242(7)	4659(4)	52(2)
C(3)	4192(3)	8849(7)	3718(4)	50(1)
C(4)	3628(3)	7995(7)	3006(4)	49(1)
C(5)	2965(3)	8498(6)	3077(4)	50(2)
C(6)	2953(3)	7960(7)	3804(4)	45(1)
C(7)	1740(3)	7242(7)	3235(4)	49(1)
C(8)	981(3)	7297(7)	3158(4)	52(2)
C(9)	971(3)	6429(7)	3861(4)	49(1)
C(10)	1021(3)	4737(7)	3712(4)	49(1)
C(11)	2074(3)	9902(7)	3630(4)	52(2)
C(12)	1800(3)	10709(7)	4251(4)	53(2)
Ow(1)	0	11570(9)	2500	87(2)
Ow(2)	143(3)	9881(6)	3914(3)	79(1)

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

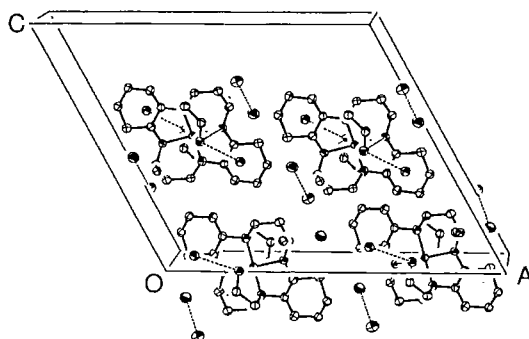
ling scheme is shown in Fig. 1, and the selected bond lengths and angles are presented in Table 3. The molecule is centrosymmetrical. The complex shows that the two hydroxyethyl groups are attached to the sterically less hindered nitrogen atoms of the macrocycle. The structure of 1 reveals an axially elongated octahedral geometry with bonds from the copper(II) ion to the secondary and tertiary amines of the macrocycle and two oxygen atoms of the pendant hydroxyethyl groups. The Cu atom and the four nitrogen atoms [N(1), N(2), N(1a), N(2a)] are

**Fig. 1.** An ORTEP drawing (30% probability ellipsoids) of 1 with the atomic numbering scheme.**Table 3. Selected Bond Distances ( $\text{\AA}$ ) and Angles ( $^\circ$ ) for 1**

Cu-N(1)	2.037(5)	Cu-N(2)	1.956(5)
Cu-O	2.452(4)	N(2)-C(11)	1.490(7)
C(11)-C(12)	1.654(8)	O-C(12)	1.352(7)
N(1)-Cu-N(2)	83.8(2)	N(1)-Cu-N(2) <sup>i</sup>	96.2(2)
N(1)-Cu-N(1) <sup>i</sup>	180.0	O-Cu-N(1)	97.0(2)
O-Cu-N(1) <sup>i</sup>	83.0(2)	O-Cu-N(2)	78.3(2)
O-Cu-N(2) <sup>i</sup>	101.7(2)	O-Cu-O <sup>i</sup>	180.0
Cu-O-C(12)	106.2(3)	N(2)-C(11)-C(12)	110.6(5)
O-C(12)-C(11)	111.9(5)		

Symmetry code: (i)  $-x+1/2, -y+3/2, -z+1$ .

exactly on the same plane. The Cu-N(1) (secondary amine) distance of 2.037(5)  $\text{\AA}$  is slightly longer than that of Cu-N(2) (tertiary amine) [1.956(5)  $\text{\AA}$ ]. As expected from the Jahn-Teller effect, the axial Cu-O distance (hydroxyethyl group) of 2.452(4)  $\text{\AA}$  is considerably longer than the average Cu-N distance. Interestingly, the axial Cu-O distance is longer than the axial Cu-O (carboxylate group) distance (2.369(3)  $\text{\AA}$ ) of  $[\text{CuL}^1][\text{ClO}_4]_2 \cdot 2\text{H}_2\text{O}$  ( $\text{L}^1=1,8$ -bis(carboxymethyl)-4,11-dimethyl-1,4,8,11-tetraazacyclotetradecane).<sup>15</sup> The long Cu-O distance may be due to the steric hindrance between the oxygen atom and methyl group at the six-membered chelate ring. The N-Cu-N angles of the six-membered chelate rings are larger than those of the five-membered chelate rings. Also, the Cu-O (hydroxyethyl group) bond is not perpendicular to the square plane as the  $\text{O}_{\text{axial}}\text{-Cu-N}_{\text{basal}}$  angles range from 78.3(2)-101.7(2) $^\circ$ . The oxygen atom of the hydroxyethyl group forms

**Fig. 2.** Packing diagram of 1, showing the hydrogen bonds as dotted lines. The hydrogen atoms are omitted for clarity.

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

D-H...A	D-H (Å)	H...A (Å)	D...A (Å)	D-H...A (°)
O-HO...Cl	0.98(1)	2.25(1)	3.193(4)	161.5(2)
N(1)-HN(1)...O <sup>i</sup>	0.91(1)	2.49(1)	2.990(6)	114.8(2)
Ow(1)...Ow(2)			2.828(7)	
Ow(1)...Ow(2) <sup>ii</sup>			2.828(7)	

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

hydrogen bonds with the chloride ion and secondary amine N(1) of the macrocycle (Fig. 2 and Table 4).

The infrared spectra of the complex shows  $\nu(\text{N-H})$  of the coordinated secondary amines and  $\nu(\text{O-H})$  of the pendant arms at ca. 3238 and 3358  $\text{cm}^{-1}$ , respectively. The visible spectrum of **1** in water appears at 566 nm, which is ca. 80 nm longer compared with that of the square-planar  $[\text{Cu}(\text{DTTD})](\text{ClO}_4)_2$ .<sup>16)</sup> This is attributed to the coordination of the pendant hydroxyethyl groups to the copper(II) ion.

#### 4. Supplementary Material

All spectral data and X-ray crystallographic file in CIF format for **1** are available from author K.-Y. Choi on request.

#### Acknowledgment

This research is supported by the Ministry of Science and Technology of Korea, the National Research Lab. Program grant to NRLCP (Nondestructive Research Lab. of Cultural Property) of Kongju National University, 2000.

#### References

- 1) Kimura, E. and Koike, T., *Advances in Inorganic Chemistry*, Vol. 44, Academic Press (1996).
- 2) Kimura, E., Koike, T. and Shionoya, M., *Struct. Bonding*, **89**, 1 (1997).
- 3) Kimura, E. and Koike, T., *Chem. Commun.*, 1495 (1998).
- 4) Blain, S., Appriou, P., Chaumeil, H. and Handel, H., *Anal. Chim. Acta*, **232**, 331 (1990).
- 5) Tsubuke, H., Yoden, T., Iwachido, T. and Zenki, M., *J. Chem. Soc., Chem. Commun.*, **1069** (1991).
- 6) Kimura, E. and Koike, T., *Chem. Soc. Rev.*, **27**, 179 (1998).
- 7) Choi, K.-Y., Suh, I.-H., Kim, J.-G., Park, Y.-S., Jeong, S.-I., Kim, I.-K., Hong, C. P. and Choi, S. N., *Polyhedron*, **18**, 3013 (1999).
- 8) Choi, K.-Y. and Suh, I.-H., *Inorg. Chim. Acta*, **299**, 128 (2000).
- 9) Jide, X., Shisheng, N. and Yuguan, L., *Inorg. Chem.*, **27**, 4651 (1988).
- 10) Pallavicini, P. S., Perotti, A., Poggi, A., Seghi, B. and Fabbri, L., *J. Am. Chem. Soc.*, **109**, 5139 (1987).
- 11) Belsky, V. S., Streltsova, N. R., Kuzmina, E. N. and Nazarenko, A. Y., *Polyhedron*, **12**, 831 (1993).
- 12) Kang, S.-G., Kim, M.-S., Choi, J.-S., Whang, D. and Kim, K., *J. Chem. Soc., Dalton Trans.*, 363 (1995).
- 13) Sheldrick, G. M., *Acta Crystallogr., Sect. A*, **A46**, 467 (1990).
- 14) Sheldrick, G. M., *SHELXL-97, Program for the Refinement of Crystal Structures*, University of Gttingen, Germany (1997).
- 15) Chapman, J., Ferguson, G., Gallagher, J. F., Jennings, M. C. and Parker, D., *J. Chem. Soc., Dalton Trans.*, 345 (1992).
- 16) Kang, S.-G., Kweon, J. K. and Jung, S.-K., *Bull. Korean Chem. Soc.*, **12**, 483 (1991).