

Crystal Structure of Copper(II) Complex with 3,5,10,12-Tetramethyl-1,4,8,11-tetraazacyclotetradecane

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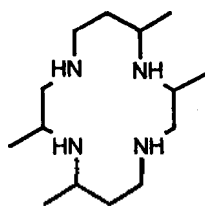
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Macrocyclic polyamine complexes with N-pendant arms and C-alkyl substituents in the macrocyclic ring have been attracted considerable attention due to their structural and chemical properties, which are often quite different from those of the unsubstituted macrocyclic ligands.¹⁻¹¹ Some of these ligands coordinate metal ions at the axial position and dramatically alter the properties of the complexes. Typically, the pendant-arm macrocycle 6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane-6,13-diamine has been shown to be a versatile polyamine ligand when coordinates to transition metal ions. It has become clear that the pendant amine groups will generally coordinate metal ion above and below the macrocyclic plane in the octahedral complexes of cobalt(III),³ rhodium(III),⁴ and nickel(II),⁶ but remain uncoordinated in the complex of copper(II).⁵ In the previous paper, we reported the synthesis and X-ray crystal structure of [Cu(DTAD)](H₂O)₂Cl²⁷ (DTAD=3,14-dimethyl-2,6,13,17-tetraazatricyclo[14,4,0^{1,6},0^{7,12}]docosane), in which the copper(II) is coordinated by the secondary amines of the macrocycle and two water molecules.

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



L

Experimental

General. All solvents were reagent grade and purified according to the literature.¹² All chemicals used in synthesis were of reagent grade. Distilled water was used for all reactions. Elemental analyses were carried out by the Korea Research Institute of Chemical Technology, Taejeon, Korea.

Physical Measurements. Infrared spectra were recorded as KBr pellets on a Perkin-Elmer Paragon 1000 FT-IR spectrophotometer. Electronic absorption spectra were obtained on a Jasco Uvidec-610 spectrophotometer. High-resolution fast atom bombardment mass spectrometry (FAB MS) was performed by using a Jeol JMS-HA 100A/100A in-

strument.

Preparation of Ligand (L). The ligand L was prepared according to the previously published procedures.^{13,14} Anal. Calcd for C₁₄H₃₂N₄: C, 65.57; H, 12.58; N, 21.85%. Found: C, 65.71; H, 12.64; N, 21.65%. FAB MS: m/z 255.4 (M)⁺.

Preparation of [Cu(L)(H₂O)₂]Cl₂ (1). A methanol solution (20 mL) of L (256 mg, 1 mmol) and CuCl₂·2H₂O (170 mg, 1 mmol) was refluxed for 1 h. The solution was cooled to room temperature and the solvent was removed under reduced pressure. The crude product was dissolved in water/acetonitrile (1:1, 10 mL). When this mixture was allowed to stand for a few days, light-red crystals were precipitated, which were filtered off, washed with diethyl ether, and dried *in vacuo*. Yield: 307 mg (72% based on L). Anal. Calcd for CuC₁₄H₃₆N₄O₂Cl₂: C, 39.38; H, 8.50; N, 13.13%. Found: C, 39.45; H, 8.43; N, 13.21%. FAB MS: m/z 425.9 (M)⁺. IR (KBr, cm⁻¹): 3363 (νOH), 3266 (νOH), 3130 (νNH), 1641 (νHOH), 1458, 1386, 1309, 1122, 1046, 1005, 953, 905, 841, 796, 670. Electronic spectra (H₂O) λ_{max}, nm (ε, M⁻¹ cm⁻¹): 508 (158), 264 (9440).

X-ray Crystallography. A light-red single crystal of 1 (0.25 × 0.20 × 0.43 mm³) 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 24.00 to 31.10°. Intensity data were collected in the ω/2θ scan mode to a maximum 2θ of 52°. Data were corrected for Lorentz and polarization effects. No absorption correction was applied. A total of 1937 unique reflections were measured, of which 1713 with (F_o>3σ(F_o)) were used in the structural analysis. The structure was solved by use of heavy atom methods. All remaining non-hydrogen atoms were found by iterative cycles of full matrix least-squares refinement and difference-Fourier synthesis using NRCVAX.¹⁵ All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included at calculated positions (d_{C-H}=1.08 Å) and refined isotropically at the final cycle. In the final refinement cycles a unit weight was employed. The maximum and minimum residual were 0.77 and -0.42 e/Å³, respectively. Crystallographic data and refinement details are summarized in Table 1.

Results and Discussion

Crystal Structure of [Cu(L)(H₂O)₂]Cl₂ (1). The ligand skeleton of the complex contains two gauche five-membered and two chair six-membered chelate rings with

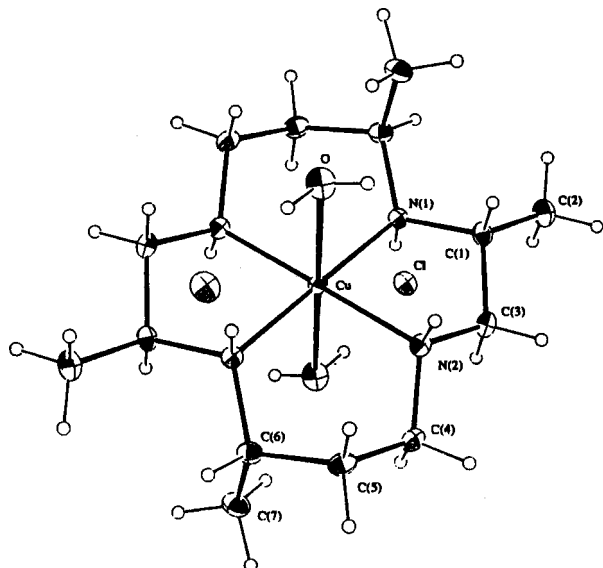
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Table 1. Crystallographic data for $[\text{Cu}(\text{L})(\text{H}_2\text{O})_2]\text{Cl}_2$ (**1**)

formula	$\text{CuC}_{14}\text{H}_{36}\text{N}_4\text{O}_2\text{Cl}_2$
formula weight	426.92
crystal system	Triclinic
space group	$P1$
a, Å	7.767(2)
b, Å	9.267(1)
c, Å	7.616(2)
α , deg	82.29(1)
β , deg	71.15(1)
γ , deg	71.42(1)
V, Å ³	491.5(2)
Z	2
F(000)	228
D _c , Mg m ⁻³	1.443
diffractometer	Enraf-Nonius CAD 4
λ (Mo-K α), Å	0.71069
μ , mm ⁻¹	1.40
data collection method	$\omega/2\theta$
scan width	0.8+0.34 tan θ
h, k, l range	-8 9, 0 11, -9 9
2 θ range, deg	52
no. of unique reflections	1937
no. of observed reflections	1713
$[F_o > 3\sigma(F_o)]$	
R ^a	0.023
R _w ^b	0.025
GOF	0.64

^a $R = \Sigma (F_o - F_c) / \Sigma (F_o)$. ^b $R_w = [\Sigma w(F_o - F_c)^2 / \Sigma (wF_o^2)]^{1/2}$. ^cGOF = $[\Sigma w(F_o - F_c)^2 / (\text{no. of rflns} - \text{no. params})]^{1/2}$.

the most stable *trans*-III conformation. Four methyl groups on both five- and six-membered chelate rings are anti with respect to the N₄ plane. An ORTEP diagram of **1** with the atomic numbering scheme is shown in Figure 1. Selected bond distances and angles are listed in Table 2. The crystal structure of **1** shows that the copper(II) is coordinated by

**Figure 1.** ORTEP diagram of **1** with the atomic numbering scheme.**Table 2.** Interatomic bond distances (Å) and angles (deg) for $[\text{Cu}(\text{L})(\text{H}_2\text{O})_2]\text{Cl}_2$ (**1**)

Cu-N(1)	2.051(2)	Cu-N(2)	1.996(2)
Cu-O	2.666(2)	N(1)-C(1)	1.495(3)
N(1)-C(6)	1.499(3)	N(2)-C(3)	1.477(3)
N(2)-C(4)	1.479(3)	C(1)-C(2)	1.523(3)
C(1)-C(3)	1.515(3)	C(4)-C(5)	1.514(3)
C(5)-C(6)	1.524(3)	C(6)-C(7)	1.517(3)
N(1)-Cu-N(1) ⁱ	180.0	N(1)-Cu-N(2)	85.2(1)
N(1)-Cu-N(2) ⁱ	94.8(1)	N(2)-Cu-N(2) ⁱ	179.9
O-Cu-O ⁱ	179.9	N(1)-Cu-O	84.1(1)
N(1)-Cu-O ⁱ	95.9(1)	N(2)-Cu-O	91.7(1)
N(2)-Cu-O ⁱ	88.3(1)	Cu-N(1)-C(1)	107.6(1)
Cu-N(1)-C(6) ⁱ	120.8(1)	C(1)-N(1)-C(6) ⁱ	114.9(2)
Cu-N(2)-C(3)	107.3(1)	Cu-N(2)-C(4)	116.5(1)
C(3)-N(2)-C(4)	112.4(2)	N(1)-C(1)-C(2)	113.6(2)
N(1)-C(1)-C(3)	106.1(2)	C(2)-C(1)-C(3)	111.6(2)
N(2)-C(3)-C(1)	108.7(2)	N(2)-C(4)-C(5)	111.9(2)
C(4)-C(5)-C(6)	115.9(2)	N(1)-C(6)-C(5)	109.1(2)
N(1)-C(6)-C(7)	112.4(2)	C(5)-C(6)-C(7)	112.9(2)

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

the four nitrogen atoms of the macrocyclic ligand and two oxygen atoms of water molecules. The structure of **1** is very similar to that of $[\text{Cu}(\text{DTAD})](\text{H}_2\text{O})_2\text{Cl}_2$ ⁷ which has an essentially square-planar arrangement. The average Cu-N distance (2.024(2) Å) of **1** is comparable to those found in $[\text{Cu}(\text{DTAD})](\text{H}_2\text{O})_2\text{Cl}_2$ (2.028(2) Å)⁷ and $[\text{Cu}(\text{DBTT})](\text{H}_2\text{O})_2\text{Cl}_2$ (DBTT=*trans*-6,13-dimethyl-6,13-bis(dimethylamino)-1,4,8,11-tetraazacyclotetradecane) (2.018(8) Å).⁵ The axial Cu-O distance of 2.666(2) Å is longer than that 2.484(6) Å in $[\text{Cu}(\text{cyclam})(\text{H}_2\text{O})_2]\text{F}_2 \cdot 4\text{H}_2\text{O}$ (cyclam=1,4,8,11-tetraazacyclotetradecane),¹⁶ which may be attributable to steric repulsion by four axial methyl groups.¹⁷ This long distance may be stabilized by the four hydrogen-bonding with chelate rings involving the chlorides, water molecules, secondary amines of macrocycle, and the central Cu(II) ion (Table 3). The Cu-O bondings are bent slightly off from the perpendicular axis to the CuN₄ plane by 1.7-5.9°. The N-Cu-N angles of the six-membered chelate rings (94.8(1)°) are larger than those (85.2(1)°) of the five-membered chelate rings.

Spectroscopic Studies. The crystalline solid **1** is stable to air for several months and is soluble in water, nitromethane, methylene chloride, and chloroform. The infrared bands at 3363 and 3266 cm⁻¹ in **1** were assigned to antisymmetric and symmetric OH stretchings and a band at 1641 cm⁻¹ was assigned to HOH bending vibration of the coordinated water. The N-H stretching of coordinated secondary amines in **1** appears at 3130 cm⁻¹. Generally, antisym-

Table 3. Hydrogen-bond parameters (Å, deg) for $[\text{Cu}(\text{L})(\text{H}_2\text{O})_2]\text{Cl}_2$ (**1**)

D-H...A	D-H	H...A	D...A	D-A...H
N(1)-HN(1)···Cl	0.91(2)Å	2.73(3)Å	3.439(2)Å	165(2)°
N(2)-HN(2)···Cl ⁱ	0.93(3)Å	2.44(3)Å	3.334(2)Å	162(2)°
O-HO(1)···Cl ⁱ	0.73(3)Å	2.48(3)Å	3.188(2)Å	161(3)°
O-HO(2)···Cl	0.86(4)Å	2.28(4)Å	3.133(2)Å	174(3)°

Symmetry code: (i) 1-x, -y, -z

metric and symmetric OH stretchings and HOH bending of lattice water lie in the range of 3550-3200 and 1630-1600 cm^{-1} , respectively. Although water molecules in inorganic solids are classified as the lattice or the coordinated, the distinction between the two from the infrared spectra is usually hard due to the high sensitivity to their surroundings.¹⁷ The electronic spectrum of **1** in aqueous solution shows two bands at ca 264 and 508 nm, which are similar to those of the related copper(II) macrocyclic tetraamine complexes.^{14,18-20} The lower energy *d-d* transition (508 nm) in the visible region is believed to be the transitions $dx_y, dx_z, dy_z \rightarrow dx^2-y^2$.²⁰ Possibly, the lowest energy absorption, $dz^2 \rightarrow dx^2-y^2$ transition, was not observed in the visible region. The higher energy band (264 nm) is tentatively assigned to ligand-metal charge-transfer transitions associated with the nitrogen and oxygen donors.²⁰ The visible spectrum of **1** in aqueous solution is similar to those of square-planar copper(II) complexes of macrocyclic tetraamines such as cyclam and its analogs measured in aqueous solution.^{14,18-20}

Conclusion

C-methyl substituent of macrocyclic complex $[\text{Cu}(\text{L})(\text{H}_2\text{O})_2]\text{Cl}_2$ (**1**) lead to six-coordinated complex in the solid state. Although the crystal structure of **1** has a tetragonally elongated octahedral geometry, the electronic spectrum of **1** in aqueous solution is similar to those of the square-planar Cu(II) complexes.

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Supporting Information Available. Tables of crystallographic details, atomic coordinates, interatomic distance and angles, hydrogen atom coordinates, anisotropic displacement parameters, and structure factors for **1** (23 pages) are available. Supplementary materials are available from K.-Y. Choi.

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