

Template Synthesis and Characterization of Four- and Five-Coordinate Copper(II) Complexes with Hexaaza Macrotricyclic Ligands 1,3,6,9,11,14-Hexaazatricyclo[12.2.1.1^{6,9}]octadecane(L₁) and 1,3,6,10,12,15-Hexaazatricyclo[13.3.1.1^{6,10}]eicosane(L₂)

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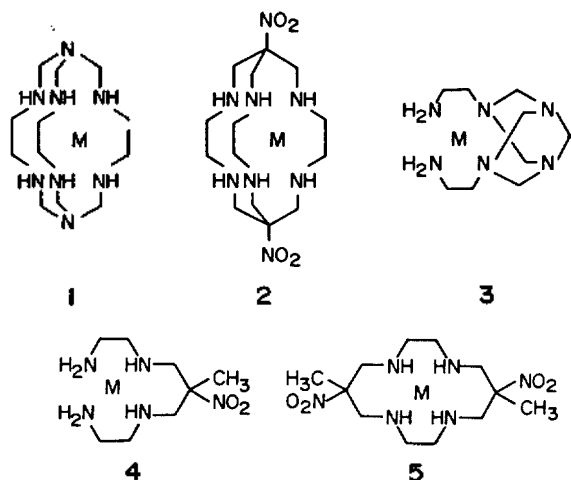
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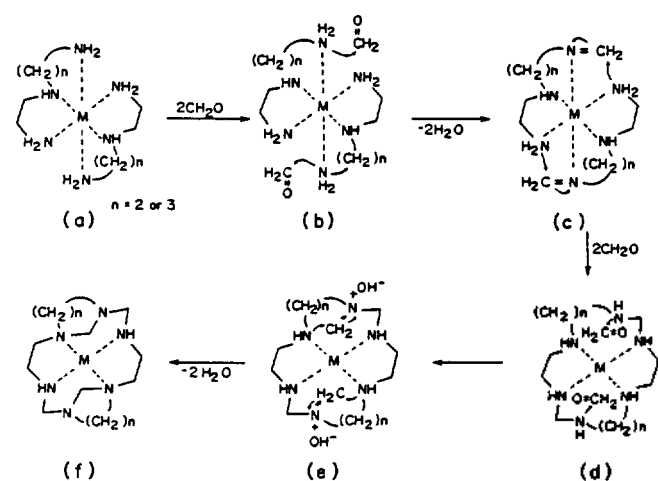
Cu(II) hexaazamacrotricyclic complexes [Cu(L)](ClO₄)₂ and [Cu(L)Cl]ClO₄, where L = 1,3,6,9,11,14-hexaazatricyclo[12.2.1.1^{6,9}]octadecane(L₁) or 1,3,6,10,12,15-hexaazatricyclo[13.3.1.1^{6,10}]eicosane(L₂), have been prepared by the simple template condensation reactions of triamines, diethylenetriamine for L₁ and N-(2-aminoethyl)-1,3-propanediamine for L₂, with formaldehyde in the presence of Cu(OAc)₂ or CuCl₂. The Cu(II) complexes of L₁ contain two 1,3-diazacyclopentane ring moieties and those of L₂ contain two 1,3-diazacyclohexane ring moieties that are fused to the 14-membered macrocyclic framework. Spectra indicate that complexes [Cu(L)](ClO₄)₂ and [Cu(L)Cl]ClO₄ have square-planar and square-pyramidal chromophores, respectively. Square-planar [Cu(L)Cl]ClO₄ are remarkably stable against ligand dissociation in acidic aqueous solutions. Square-pyramidal [Cu(L)Cl]ClO₄ complexes dissociate their axial Cl⁻ ligands easily in aqueous solutions to form [Cu(L)H₂O]²⁺ species. Infrared and UV/vis absorption spectra of the Cu(II) complexes reveal that Cu-N interactions and the ligand field strengths are significantly weaker in the complexes of L₂ than in the complexes of L₁.

Introduction

Macrocyclic complexes show enhanced thermodynamic and kinetic stabilities and the characteristic properties inaccessible to the complexes of non-cyclic chelate ligands. Macrocyclic complexes are often prepared by the metal template reactions because metal template syntheses provide selective and high yielding routes to the complexes of new ligands. For example, reactions of simple inert [M(en)₃]ⁿ⁺ ions (en = ethylenediamine; M = Co³⁺, Rh³⁺, Ir³⁺, Pt⁴⁺), formaldehyde, and ammonia or carbon acids such as nitromethane resulted in the formation of macrobicyclic complexes



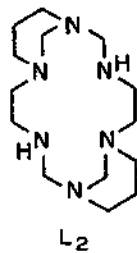
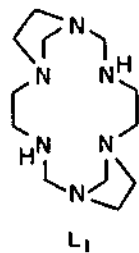
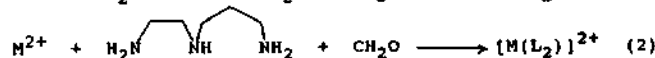
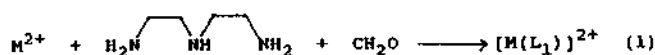
such as **1** or **2**.¹⁻³ In these reactions, each open octahedral faces of [M(en)₃]ⁿ⁺ complexes are condensed with formaldehyde and ammonia or carbon acid. However, the same condensation reactions with the labile metal ions such as Ni(II) and Cu(II) result in primarily the square planar complexes of **3**, **4**, or **5**.⁴⁻¹⁰ For example, the condensation reaction of [Ni(en)₃]²⁺ with formaldehyde and ammonia resulted mostly in square planar complex **3**, and only ca. 1% of octahedral



complex **1**.^{4,5} Especially, Cu(II) ion has been known to be an ineffective template for the reactions involving octahedral precursor complexes because of Jahn-Teller distortions.⁶⁻¹⁰

Recently, we have reported the Ni(II) complexes of macrotricyclic ligands L₁ and L₂. The complexes were synthesized from the template condensation reaction of triamines and formaldehyde as described in Eq. (1) and (2).¹¹ The ligands L₁ and L₂ are highly interesting because they contain six nitrogen atoms in the macrocyclic framework but acting as tetradentates. Moreover, they also contain rarely occurring 1,3-diazacyclopentane or 1,3-diazacyclohexane small ring moieties. These macrocycles are formed through the reactions that each two cis coordinated nitrogen atoms of octahedral [Ni(triamine)₂]²⁺ are linked by formaldehyde as described in Scheme 1. We tried the same reactions by using Cu(II) ion as template metal source to see if Cu(II) ion is able to template this type of macrocyclization reactions. As a result, we obtained Cu(II) complexes of macrotricyclic ligands L₁ and L₂ in high yield.

In this report, we will describe the synthesis and char-



acterization of the square-planar $[\text{Cu}(L)(\text{ClO}_4)_2]$ and five-coordinate $[\text{Cu}(L)\text{Cl}]\text{ClO}_4$ complexes with macrotricyclic ligands (L), 1,3,6,9,11,14-hexaazatricyclo[12.2.1]^{6,9}octadecane (L_1) and 1,3,6,10,12,15-hexaazatricyclo[13.3.1]^{6,10}eicosane (L_2).

Experimental Section

Materials. All solvents and chemicals used in synthesis were of reagent grade and were used without further purification. Solvents used for the measurement of spectra were purified according to the literature.¹²

Instrumentation. Conductance measurements were performed by using an TOA conductivity meter CM-30ET in conjunction with a conductivity cell with the cell constant of 1.0 cm^{-1} . Infrared spectra were measured with a JASCO IR-810 spectrophotometer. Electronic absorption spectra were recorded with a Shimadzu UV-260 spectrophotometer. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN., U.S.A.

Synthesis. Caution! Some of the compounds containing perchlorate anions must be regarded as potentially explosive and should be handled with caution.

$[\text{Cu}(L_1)](\text{ClO}_4)_2$. To a stirred methanol (30 ml) solution of $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (10 g) were added diethylenetriamine (10.3 g) and 36% formaldehyde (24.3 ml), and the mixture was heated at reflux for 4 h. The solution was cooled to room temperature, and excess LiClO_4 dissolved in methanol was added. The solutions were allowed to stand in refrigerator until red crystals were formed, which were mixed with a small amount of blue five-coordinated complexes. The crystals were filtered, washed with methanol, and dried. The crystals were fractionally recrystallized from hot water, and the red crystals free of blue solids were obtained. The same complexes were synthesized when $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (12 g) were employed as the template metal source. Yield: $\approx 50\%$. Anal. Calcd. for $\text{CuC}_{12}\text{H}_{26}\text{N}_6\text{Cl}_2\text{O}_8$: C, 27.89; H, 5.07; N, 16.26. Found: C, 27.84; H, 5.08; N, 16.29.

$[\text{Cu}(L_1)\text{Cl}]\text{ClO}_4$. When $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ was utilized as the template metal source instead of $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ or $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, and the same reaction procedures as for the synthesis of $[\text{Cu}(L_1)](\text{ClO}_4)_2$ were followed, blue crystals were resulted. The crystals were filtered, washed with methanol, and recrystallized from hot water. The compound can be prepared by the addition of methanol solutions of excess LiCl to the acetonitrile solution of $[\text{Cu}(L_1)](\text{ClO}_4)_2$. Yield: $\approx 60\%$. Anal. Calcd. for $\text{CuC}_{12}\text{H}_{26}\text{N}_6\text{Cl}_2\text{O}_4$: C, 31.86; H, 5.73; N, 18.49. Found: C, 31.83; H, 5.78; N, 18.56.

$[\text{Cu}(L_2)](\text{ClO}_4)_2$. To a 1:1 mixture of water and methanol (100 ml) solutions of $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (10 g) were added N-(2-aminoethyl)-1,3-propanediamine (12.1 g) and 36% formaldehyde (31 ml) with stirring. The mixture was heated at reflux for 5 h. The solution was cooled to room temperature and then filtered to remove insoluble hydroxide. A saturated aqueous solution of excess LiClO_4 was added to the filtrate, and the solutions were allowed to stand in the refrigerator until red crystals formed, which were mixed with small amount of blue crystals. The products were recrystallized from hot water. Red crystals were filtered, washed with methanol, and dried in vacuo. Yield: $\approx 60\%$. Anal. Calcd. for $\text{CuC}_{14}\text{H}_{30}\text{N}_6\text{Cl}_2\text{O}_8$: C, 30.86; H, 5.55; N, 15.42. Found: C, 30.85; H, 5.56; N, 15.61.

$[\text{Cu}(L_2)\text{Cl}]\text{ClO}_4 \cdot \text{CH}_3\text{OH}$. The compounds were synthesized by the procedure similar to that of $[\text{Cu}(L_2)](\text{ClO}_4)_2$, but $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (8.5 g) was utilized as template source instead of $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$. Yield: $\approx 40\%$. Anal. Calcd. for $\text{CuC}_{15}\text{H}_{34}\text{N}_6\text{Cl}_2\text{O}_5$: C, 35.12; H, 6.69; N, 16.39. Found: C, 35.21; H, 7.00; N, 16.39.

Results and Discussion

Template condensation reactions of triamines, diethylenetriamine for L_1 and N-(2-aminoethyl)-1,3-propanediamine for L_2 , with formaldehyde in the presence of $\text{Cu}(\text{II})$ ions with the mole ratio of triamine: $\text{CH}_2\text{O}:\text{Cu}^{2+} = 2:4:1$ in methanol solutions produced the $\text{Cu}(\text{II})$ macrotricyclic complexes of L_1 and L_2 with the yield of 40–60%. When $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ or $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ was employed as the template source and then the product was precipitated with LiClO_4 , square-planar red complexes $[\text{Cu}(L)](\text{ClO}_4)_2$ were obtained as major product. On the other hand, as $\text{CuCl}_2 \cdot \text{H}_2\text{O}$ was used for the template, five-coordinate blue complexes $[\text{Cu}(L)\text{Cl}]\text{ClO}_4$ were resulted. The easy and high yielding synthesis of these $\text{Cu}(\text{II})$ macrotricyclic complexes demonstrates that the $\text{Cu}(\text{II})$ ion is able to template the condensation reactions even though the reactions involve the octahedral precursors.

Square-planar complexes $[\text{Cu}(L_1)]^{2+}$ and $[\text{Cu}(L_2)]^{2+}$ exhibit remarkable stability against ligand dissociation in acidic solutions. The spectra of $[\text{Cu}(L_1)](\text{ClO}_4)_2$ ($7.4 \times 10^{-3} \text{ M}$) indicated that 30% of the $\text{Cu}(\text{II})$ complexes was decomposed in acidic aqueous solutions (0.15M HClO_4) in 17 h, while those ($2.9 \times 10^{-3} \text{ M}$) of $[\text{Cu}(L_2)](\text{ClO}_4)_2$ indicated that almost no complex was decomposed in 0.15 M HClO_4 in 24 h. Usually, $\text{Cu}(\text{II})$ macrocyclic complexes are known to be inert in acidic aqueous solutions.

The spectra and conductance data are summarized in Table 1. The values of molar conductance indicate that $[\text{Cu}(L_1)](\text{ClO}_4)_2$ and $[\text{Cu}(L_2)](\text{ClO}_4)_2$ are 1:2 electrolytes in aqueous solutions and $[\text{Cu}(L_1)\text{Cl}]\text{ClO}_4$ and $[\text{Cu}(L_2)\text{Cl}]\text{ClO}_4$ are 1:1 electrolytes in MeNO_2 solutions.¹³ However, molar conductance values of the five-coordinate $[\text{Cu}(L)\text{Cl}]\text{ClO}_4$ complexes fall in the range of 1:2 electrolytes in aqueous solutions and the blue color of the complex turns to red. This indicates that the coordinated Cl^- ions are readily dissociated from the complexes in aqueous solutions.

The infrared spectra of $\text{Cu}(\text{II})$ complexes show ν_{NH} bands at around $3210\text{--}3275 \text{ cm}^{-1}$ for the coordinated secondary amines. The ν_{NH} values for both square-planar and five-coordinate $\text{Cu}(\text{II})$ complexes of L_2 are much higher than those

Table 1. Spectral and Conductance Data for Copper(II) Macrotricyclic Complexes

Complex	IR ^a , cm ⁻¹	Electronic spectra ^b , λ_{max} , nm(ϵ , M ⁻¹ cm ⁻¹)	Λ_M^c (Ω^{-1} cm ⁻² M ⁻¹)
[Cu(L ₁)](ClO ₄) ₂	ν_{NH} 3212	486(151) ^b , 535(185) ^c	259 ^c
[Cu(L ₂)](ClO ₄) ₂	ν_{NH} 3268	505(122) ^b , 529(142) ^c	207 ^c
[Cu(L ₁ Cl)]ClO ₄	ν_{NH} 3220	618(292) ^b , 550(191) ^c , 616(201) ^d	107 ^b , 217 ^c
[Cu(L ₂ Cl)]ClO ₄ ·CH ₃ OH	ν_{NH} 3275, 3246	637(178) ^b , 563(160) ^c , 612(217) ^e	85 ^b , 196 ^c

^a Measured with Nujol mulls. ^b Measured in MeNO₂ solutions. ^c Measured in aqueous solutions at 20 °C. ^d Measured in Me₂SO solutions. ^e Measured in MeCN solutions.

for the complexes of L₁. This indicates that Cu-N interaction is much weaker in the complexes of L₂ containing 1,3-diazacyclohexane ring moieties than in the complexes of L₁ containing 1,3-diazacyclopentane ring moieties.

The ClO₄⁻ bands of square pyramidal complexes [Cu(L₁Cl)]ClO₄ and [Cu(L₂Cl)]ClO₄ are splitted in 1200–900 cm⁻¹ region, suggesting that there are interactions of ClO₄⁻ anions with the complex cations in the solid state. The X-ray structure of [Cu(L₁Cl)]ClO₄ reveals that the oxygen atom of ClO₄⁻ ion is hydrogen-bonded to the secondary amine of the macrocyclic ligand.¹⁴

The electronic spectra (Table 1) of Cu(II) complexes with hexaaza macrotricyclic ligands exhibit a *d-d* transition band in the visible region, around 480–620 nm. The spectra depend not only on the coordination number and the type of macrocyclic ligand but also on the solvent. The square-planar Cu(II) complexes of L₁ and L₂ show maximum absorptions that are about 130 nm shorter wavelengths than the five-coordinate Cu(II) complexes of corresponding ligands in noncoordinating MeNO₂ solvent. The electronic spectra of Cu(II) complexes in this study as well as the X-ray structure analysis¹⁴ reveal that complexes [Cu(L₁)](ClO₄)₂ and [Cu(L₂)](ClO₄)₂ have square-planar geometries and complexes [Cu(L₁Cl)]ClO₄ and [Cu(L₂Cl)]ClO₄ have square-pyramidal structures. It has been reported that the square-planar Cu(II) complexes with tetraaza macrocyclic ligands exhibit a broad *d-d* band containing both ²A_{1g} ← ²B_{1g} and ²E_g ← ²B_{1g} transitions at approximately 500–520 nm in H₂O, and those of five- or six-coordinate Cu(II) complexes show lower energy *d-d* bands.^{15–19} In addition, the spectra of the Cu(II) macrocyclic complexes were often observed to be solvent-dependent.^{15–18}

The values of λ_{max} measured in MeNO₂ solutions show that Cu(II) complexes of L₂ absorb at much longer wavelengths than Cu(II) complexes of L₁. This indicates that the macrotricyclic ligand containing six-membered 1,3-diazacyclohexane ring moieties exerts a much weaker ligand field than the one containing five-membered 1,3-diazacyclopentane ring moieties.

Significant differences between the spectra measured in non-coordinating solvent CH₃NO₂ and those measured in water suggest that square-planar [Cu(L)]²⁺ complexes as well as five-coordinate [Cu(LCl)]⁺ complexes coordinate water considerably in aqueous solutions to form [Cu(L)(H₂O)]²⁺ species.¹⁹ Furthermore, the differences between the aqueous solution spectra of square-planar [Cu(L)]²⁺ and those of five-coordinated [Cu(LCl)]⁺ having same L suggest that [Cu(L)]²⁺ and [Cu(LCl)]⁺ coordinate water to different extents.

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