

## Synthesis and Characterization of Various Di-N-Functionalized Tetraaza Macrocyclic Copper(II) Complexes

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Two copper(II) complexes,  $[\text{CuL}^3](\text{ClO}_4)_2$  bearing one  $N\text{-CH}_2\text{CH}_2\text{CONH}_2$  group as well as one  $N\text{-CH}_2\text{CH}_2\text{CN}$  group and  $[\text{CuL}^4](\text{ClO}_4)_2$  bearing two  $N\text{-CH}_2\text{CH}_2\text{CONH}_2$  groups, have been prepared by the selective hydrolysis of  $[\text{CuL}^2](\text{ClO}_4)_2$  ( $\text{L}^2 = C\text{-meso-1,8-bis(cyanoethyl)-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraaza-cyclotetradecane}$ ). The complex  $[\text{CuL}^5](\text{ClO}_4)_2$  bearing one  $N\text{-CH}_2\text{CH}_2\text{C(=NH)OCH}_3$  and one  $N\text{-CH}_2\text{CH}_2\text{CN}$  groups has been prepared as the major product from the reaction of  $[\text{CuL}^2](\text{ClO}_4)_2$  with methanol in the presence of triethylamine. In acidic aqueous solution, the  $N\text{-CH}_2\text{CH}_2\text{C(=NH)OCH}_3$  group of  $[\text{CuL}^5](\text{ClO}_4)_2$  undergoes hydrolysis to yield  $[\text{CuL}^6](\text{ClO}_4)_2$  bearing both  $N\text{-CH}_2\text{CH}_2\text{COOCH}_3$  and  $N\text{-CH}_2\text{CH}_2\text{CN}$  groups. The crystal structure of  $[\text{CuL}^5](\text{ClO}_4)_2$  shows that the complex has a slightly distorted square-pyramidal coordination polyhedron with an apical Cu-N ( $N\text{-CH}_2\text{CH}_2\text{C(=NH)OCH}_3$  group) bond. The apical Cu-N bond distance (2.269(3) Å) is *ca.* 0.06 Å longer than the apical Cu-O ( $N\text{-CH}_2\text{CH}_2\text{CONH}_2$  group) bond of  $[\text{CuL}^4](\text{ClO}_4)_2$ . The pendant amide group of  $[\text{CuL}^3](\text{ClO}_4)_2$  is involved in coordination. The carboxylic ester group of  $[\text{CuL}^6](\text{ClO}_4)_2$  is also coordinated to the metal ion in various solvents but is removed from the coordination sphere in the solid state.

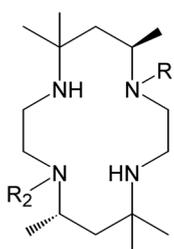
**Key Words :** Macrocyclic compounds, Functional pendant arm, Hydrolysis, Methanolysis, X-ray structure

### Introduction

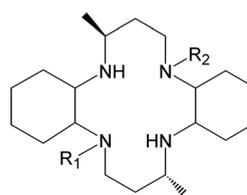
Polyaza macrocyclic compounds bearing additional functional group(s) has received much attention because of their interesting chemical properties and potential applications in various fields.<sup>1-13</sup> It has been revealed that coordination polyhedron and chemical properties of such compounds are influenced by various factors, such as the number and type of the functional pendant arms. The majority of functionalized macrocyclic compounds reported so far contain a single type of pendent arm. However, examples of polyaza macrocyclic compounds bearing two different functional groups are relatively few.<sup>9-11</sup> One of the problems in the synthesis of hetero-functionalized macrocyclic compounds is that attaching two different functional groups to a macrocycle is difficult or requires several steps.

Recently, some triaza and tetraaza macrocyclic complexes with  $N\text{-(CH}_2)_n\text{CN}$  ( $n = 1$  or  $2$ ) pendant arms have been used as precursors to prepare macrocyclic derivatives bearing other types of functional groups, such as  $N\text{-(CH}_2)_n\text{CONH}_2$  or  $N\text{-(CH}_2)_n\text{C(=NH)OCH}_3$  group.<sup>6-10</sup> For instance,  $[\text{CuL}^7]^{2+}$  bearing two  $N\text{-CH}_2\text{CN}$  groups readily reacts with water or methanol in the presence a base to yield  $[\text{CuL}^8]^{2+}$  bearing two  $N\text{-CH}_2\text{CONH}_2$  groups or  $[\text{CuL}^9]^{2+}$  bearing two  $N\text{-CH}_2\text{C(=NH)OCH}_3$  groups; the reaction is promoted by the metal ion.<sup>7</sup> On the other hand, the di- $N$ -cyanoethylated complex  $[\text{CuL}^{12}]^{2+}$  does not undergo such hydrolysis or methanolysis under similar conditions;  $\text{L}^{12}$  is rapidly removed from the coordination sphere in basic aqueous solution or in non-aqueous solutions containing a base like triethylamine or ethylenediamine.<sup>5</sup> Literature up to date shows that

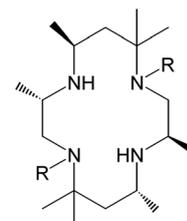
the reactivity of macrocyclic complexes bearing  $N\text{-(CH}_2)_n\text{CN}$  group(s) is dependent on various factors, such as the length of the  $N$ -cyanoalkyl groups and the structure of the macrocycles. We have been interested in the synthesis of various types of hetero-functionalized macrocyclic compounds by utilizing the reactivity of  $N$ -cyanoalkylated macrocyclic complexes.



- $\text{L}^1$ :  $\text{R}_1 = \text{R}_2 = \text{H}$   
 $\text{L}^2$ :  $\text{R}_1 = \text{R}_2 = \text{CH}_2\text{CH}_2\text{CN}$   
 $\text{L}^3$ :  $\text{R}_1 = \text{CH}_2\text{CH}_2\text{CONH}_2$   
 $\text{R}_2 = \text{CH}_2\text{CH}_2\text{CN}$   
 $\text{L}^4$ :  $\text{R}_1 = \text{R}_2 = \text{CH}_2\text{CH}_2\text{CONH}_2$   
 $\text{L}^5$ :  $\text{R}_1 = \text{CH}_2\text{CH}_2\text{C(=NH)OCH}_3$   
 $\text{R}_2 = \text{CH}_2\text{CH}_2\text{CN}$   
 $\text{L}^6$ :  $\text{R}_1 = \text{CH}_2\text{CH}_2\text{COOCH}_3$   
 $\text{R}_2 = \text{CH}_2\text{CH}_2\text{CN}$



- $\text{L}^7$ :  $\text{R}_1 = \text{R}_2 = \text{CH}_2\text{CN}$   
 $\text{L}^8$ :  $\text{R}_1 = \text{R}_2 = \text{CH}_2\text{CONH}_2$   
 $\text{L}^9$ :  $\text{R}_1 = \text{R}_2 = \text{CH}_2\text{C(=NH)OCH}_3$   
 $\text{L}^{10}$ :  $\text{R}_1 = \text{H}$ ;  $\text{R}_2 = \text{CH}_2\text{CH}_2\text{COOCH}_3$   
 $\text{L}^{11}$ :  $\text{R}_1 = \text{R}_2 = \text{CH}_2\text{CH}_2\text{COOCH}_3$



- $\text{L}^{12}$ :  $\text{R} = \text{CH}_2\text{CH}_2\text{CN}$   
 $\text{L}^{13}$ :  $\text{R}_1 = \text{R}_2 = \text{CH}_2\text{CH}_2\text{COOCH}_3$

In this work, we examined the reaction of  $[\text{CuL}^2]^{2+}$  ( $\text{L}^2 = C\text{-meso-1,8-bis}(N\text{-cyanoethyl})\text{-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane}$ ) with water or methanol under various experimental conditions and prepared new copper(II) complexes  $[\text{CuL}^3](\text{ClO}_4)_2$  and  $[\text{CuL}^5](\text{ClO}_4)_2$  bearing two different functional pendant arms. The complexes  $[\text{CuL}^4](\text{ClO}_4)_2$  and  $[\text{CuL}^6](\text{ClO}_4)_2$  were also prepared by the hydrolysis of  $[\text{CuL}^3](\text{ClO}_4)_2$  and  $[\text{CuL}^5](\text{ClO}_4)_2$ , respectively. Synthesis, characterization, and chemical properties of the copper(II) complexes of  $\text{L}^3\text{-L}^6$  are reported, along with the crystal structure of  $[\text{CuL}^5](\text{ClO}_4)_2$ .

### Experimental

**Measurements.** Electronic absorption spectra were recorded with an Analytikjena Specord 200 UV/Vis spectrophotometer, infrared spectra with a Genesis II FT-IR spectrometer,  $^1\text{H}$  and  $^{13}\text{C}$ -NMR spectra with a Varian Mercury 300 NMR spectrometer, and conductance measurements with a Metrohm Herisau Conductometer E518. Elemental analyses were performed at the Research Center for Instrumental Analysis, Daegu University, Gyeongsan, Korea. FAB-mass analysis was performed at the Korea Basic Science Institute, Daegu, Korea.

**Preparation of  $[\text{CuL}^3](\text{ClO}_4)_2\cdot 2\text{H}_2\text{O}$  ( $\text{L}^3 = C\text{-meso-1-(Carbamoyl ethyl)-8-(cyanoethyl)-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane}$ ).** The macrocycle  $\text{L}^2$  was prepared by the reaction of  $\text{L}^1$  with acrylonitrile at room temperature.<sup>14</sup> The complex  $[\text{CuL}^2](\text{ClO}_4)_2$  was prepared by the reaction of  $\text{L}^2$  with  $\text{Cu}(\text{OAc})_2\cdot\text{H}_2\text{O}$  in acetonitrile.<sup>14</sup> The copper(II) complex was dissolved in a minimum volume of a warm ( $\sim 50^\circ\text{C}$ ) water-acetonitrile ( $v/v = 1:3$ ) and then pH of the solution was adjusted to *ca.* 9 through the addition of 0.1 M NaOH solution. The color of the solution changed from red to purple as soon as the NaOH solution was added. After the addition of an excess amount of  $\text{HClO}_4$  dissolved in water, the resulting solution ( $\text{pH} < 3$ ) was evaporated at room temperature to produce a purple solid. The product was filtered, washed with ethanol, and recrystallized from acetonitrile-water ( $v/v = 1:1$ ) mixture. Yield:  $\sim 70\%$ . Anal. Calcd for  $\text{C}_{22}\text{H}_{48}\text{N}_6\text{CuCl}_2\text{O}_{11}$ : C, 37.34; H, 6.79; N, 11.88%. Found: C, 37.65; H, 7.08; N, 11.86%. FAB Mass ( $m/z$ ): 570.2 ( $[\text{CuL}^3 + \text{ClO}_4]^+$ ) and 471.2 ( $[\text{CuL}^3 - \text{H}]^+$ ). IR ( $\text{cm}^{-1}$ ): 3510 ( $\nu\text{O-H}$ ), 3440 ( $\nu\text{N-H}$ ), 3340 ( $\nu\text{N-H}$ ), 3290 ( $\nu\text{N-H}$ ), 3220 ( $\nu\text{N-H}$ ), 2250 ( $\nu\text{CN}$ ), 1660 ( $\nu\text{CO}$ ), 1590 ( $\delta\text{NH}_2$ ), and 1100 ( $\nu\text{ClO}_4$ ).

**Preparation of  $[\text{CuL}^4](\text{ClO}_4)_2$  ( $\text{L}^4 = C\text{-meso-1,8-Bis(carbamoyl ethyl)-8-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane}$ ).** The pH of a warm ( $\sim 50^\circ\text{C}$ ) water-acetonitrile ( $v/v = 1:3$ ) solution (10 mL) of  $[\text{CuL}^3](\text{ClO}_4)_2$  (0.5 g) (or  $[\text{CuL}^2](\text{ClO}_4)_2$  (0.5 g)) was adjusted to  $> 13$  through the addition of 1.0 M NaOH solution. The color of the solution changed from purple to blue within 10 min. The solution was cooled to room temperature and then an excess amount of  $\text{HClO}_4$  was added to the solution. The resulting solution ( $\text{pH} < 3$ ) was evaporated at room temperature to produce a blue-purple solid. The product was

filtered, washed with ethanol, and recrystallized from acetonitrile-water ( $v/v = 1:2$ ) mixture. Yield:  $\sim 80\%$ . Anal. Calcd for  $\text{C}_{22}\text{H}_{46}\text{N}_6\text{CuCl}_2\text{O}_{10}$ : C, 38.35; H, 6.73; N, 12.20%. Found: C, 38.05; H, 6.70; N, 12.00%. FAB mass ( $m/z$ ): 588.2 ( $[\text{CuL}^4 + \text{ClO}_4]^+$ ) and 489.2 ( $[\text{CuL}^4 - \text{H}]^+$ ). IR ( $\text{cm}^{-1}$ ): 3355 ( $\nu\text{N-H}$ ), 3305 ( $\nu\text{N-H}$ ), 3225 ( $\nu\text{N-H}$ ), 3210 ( $\nu\text{N-H}$ ), 1695 ( $\nu\text{C=O}$ ), 1660 ( $\nu\text{C=O}$ ), 1600 ( $\delta\text{N-H}$ ), and 1100 ( $\nu\text{ClO}_4$ ).

**Preparation of  $[\text{CuL}^5](\text{ClO}_4)_2\cdot 2\text{H}_2\text{O}$ .** To a methanol-acetonitrile ( $v/v = 6:1$ ) suspension (*ca.* 20 mL) of  $[\text{CuL}^2](\text{ClO}_4)_2$  (0.5 g) was added triethylamine (*ca.* 1.0 mL). The mixture was stirred at *ca.*  $60^\circ\text{C}$  for 1 h. During which time, the red solid ( $[\text{CuL}^2](\text{ClO}_4)_2$ ) went into the solution and a blue solid was precipitated. After the addition of excess amount of  $\text{NaClO}_4$  dissolved in methanol, the mixture was stored in a refrigerator for *ca.* 5 h. The product was filtered, washed with methanol, and dried in air. The product was recrystallized by the addition of excess amount of  $\text{NaClO}_4$  dissolved in methanol to a hot  $\text{Me}_2\text{SO}$  solution of the crude product. Yield:  $\sim 70\%$ . Anal. Calcd for  $\text{C}_{23}\text{H}_{46}\text{N}_6\text{CuCl}_2\text{O}_9$ : C, 40.32; H, 6.77; N, 12.27%. Found: C, 39.98; H, 7.01; N, 11.98%. FAB mass ( $m/z$ ): 584.5 ( $[\text{CuL}^5 - \text{H}]^+$ ) and 485.5 ( $[\text{CuL}^5 + \text{ClO}_4]^+$ ). IR ( $\text{cm}^{-1}$ ): 3280 ( $\nu\text{N-H}$ ), 3220 ( $\nu\text{N-H}$ ), 3210 ( $\nu\text{N-H}$ ), 2250 ( $\nu\text{CN}$ ), 1640 ( $\nu\text{C=N}$ ), and 1100 ( $\nu\text{ClO}_4$ ).

**Preparation of  $[\text{CuL}^6](\text{ClO}_4)_2\cdot 2\text{H}_2\text{O}$  ( $\text{L}^6 = C\text{-meso-1,8-Bis(2-carbomethoxyethyl)-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane}$ ).** To a warm ( $\sim 50^\circ\text{C}$ ) water-acetonitrile ( $v/v = 2:1$ ) solution (20 mL) of  $[\text{CuL}^5](\text{ClO}_4)_2$  (0.5 g) was added 2-3 drops of concentrated  $\text{HClO}_4$ . The color of the solution changed from blue to purple as soon as the acid was added. After the addition of an excess of  $\text{NaClO}_4$ , the resulting solution was evaporated at room temperature to produce a red solid. The product was filtered, washed with methanol, dried in air. It was recrystallized by the addition of excess amount of  $\text{NaClO}_4$  dissolved in methanol to a hot acetonitrile solution of the crude product. Yield:  $\sim 80\%$ . Anal. Calcd for  $\text{C}_{23}\text{H}_{45}\text{N}_5\text{CuCl}_2\text{O}_{10}$ : C, 40.26; H, 6.61; N, 10.21%. Found: C, 40.28; H, 6.80; N, 10.42%. FAB mass ( $m/z$ ): 585.5 ( $[\text{CuL}^6 - \text{H}]^+$ ) and 486.5 ( $[\text{CuL}^6 + \text{ClO}_4]^+$ ). IR (Nujol mull,  $\text{cm}^{-1}$ ): 3170 ( $\nu\text{N-H}$ , *br*), 2250 ( $\nu\text{CN}$ ), 1740 ( $\nu\text{C=O}$ ), and 1100 ( $\nu\text{ClO}_4$ ).

**Crystal Structure Determination.** A single crystal of  $[\text{CuL}^5](\text{ClO}_4)_2$  suitable for X-ray analysis was sealed in a thin walled glass capillary and mounted on CAD-4 diffractometer with  $\text{MoK}_\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). Unit cell parameters were determined by least-squares using 25 well-centered reflections in the range of  $10.28\text{-}13.05^\circ$ . A total 6373 reflections were collected and corrected for Lorenpolarization effects and applied empirical absorption correction based on  $\psi$  scans. Crystal data, data collection, and refinement for the complex are shown in Table 1. The structure was solved by direct methods and refined by full-matrix least-squares using SHELXS-97 and SHELXL-97 program packages using reflections with  $I > 2\sigma(I)$ .<sup>15</sup> All non-hydrogen atoms were refined anisotropically except disordered oxygen atoms on perchlorate ions which were refined isotropically with 0.6 and 0.4 occupancies.

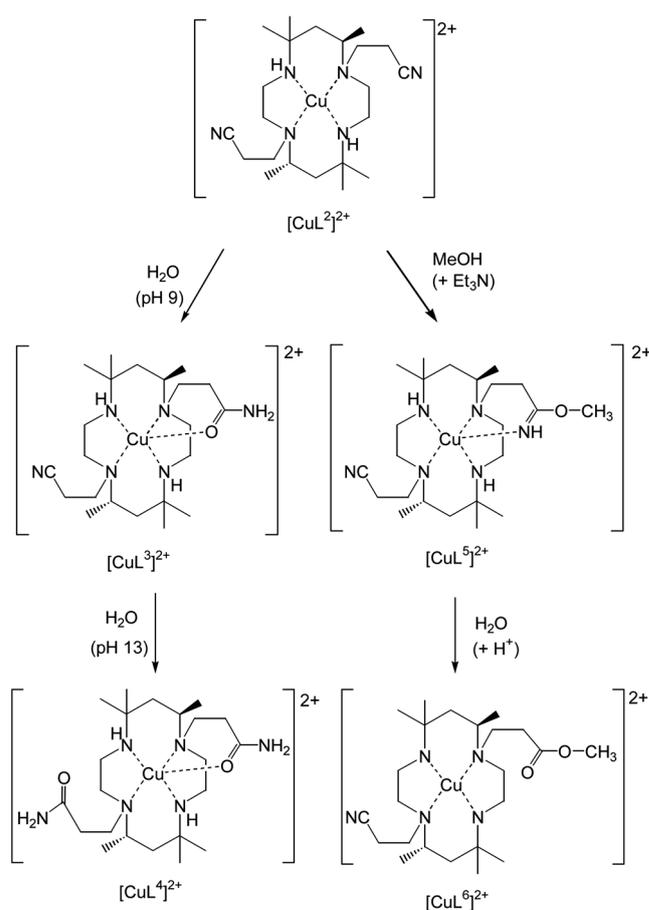
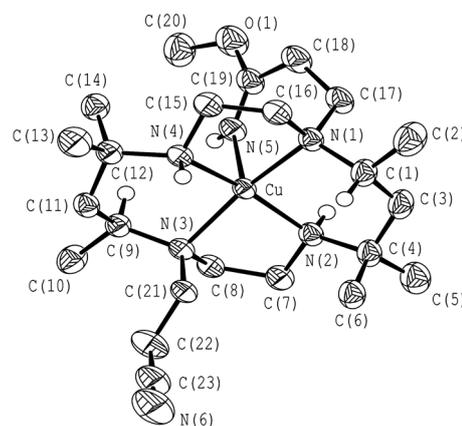
**Table 1.** Crystal data and structure refinement for  $[\text{CuL}^5](\text{ClO}_4)_2$ 

Empirical formula ( <i>M</i> )	$\text{C}_{23}\text{H}_{46}\text{Cl}_2\text{N}_6\text{CuO}_9$ (685.10)
Crystal system (space group)	monoclinic ( $P2_1/c$ )
<i>a</i> / <i>b</i> / <i>c</i> (Å)	19.1909(16) / 9.4056(6) / 17.874(2)
$\beta$ (°)	97.511(8)
<i>V</i> (Å <sup>3</sup> )	3198.7(5)
<i>Z</i>	4
<i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )	1.423
$\mu$ (cm <sup>-1</sup> )	9.05
<i>F</i> (000)	1444
$\theta$ range for data collection (°)	2.14–25.47
Index ranges	$-23 \leq h \leq 23, -11 \leq k \leq 0, 0 \leq l \leq 21$
Reflections collected	6373
Independent reflections	5952 [R(int) = 0.0101]
Reflections observed (>2 $\sigma$ )	4262
Data Completeness	1.000
Data / restraints / parameters	5952 / 0 / 356
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.157
Final R indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.058 <i>wR</i> <sub>2</sub> = 0.185
R indices (all data)	<i>R</i> <sub>1</sub> = 0.086 <i>wR</i> <sub>2</sub> = 0.196
Largest diff. peak and hole (eÅ <sup>-3</sup> )	01.164 and -0.676

## Results and Discussion

**Synthesis.** The copper(II) complex of  $\text{L}^2$  was found to be inert against hydrolysis in acidic aqueous solution. Electronic absorption spectra of  $[\text{CuL}^2](\text{ClO}_4)_2$  ( $3.0 \times 10^{-3}$  M) measured in 0.1 M  $\text{HClO}_4$  solution indicated that no apparent hydrolysis or decomposition takes place in 3 h at 40 °C. However, the *N*- $\text{CH}_2\text{CH}_2\text{CN}$  group in  $[\text{CuL}^2](\text{ClO}_4)_2$  is readily hydrolyzed in basic aqueous solution. The complex  $[\text{CuL}^3](\text{ClO}_4)_2$  bearing one *N*- $\text{CH}_2\text{CH}_2\text{CONH}_2$  and one *N*- $\text{CH}_2\text{CH}_2\text{CN}$  groups was prepared by the selective hydrolysis of  $[\text{CuL}^2](\text{ClO}_4)_2$  at pH 9. As described in the Experimental section,  $[\text{CuL}^3](\text{ClO}_4)_2$  as well as  $[\text{CuL}^2](\text{ClO}_4)_2$  is also hydrolyzed to yield  $[\text{CuL}^4](\text{ClO}_4)_2$  bearing two *N*- $\text{CH}_2\text{CH}_2\text{CONH}_2$  groups at pH > 13. The complex  $[\text{CuL}^2](\text{ClO}_4)_2$  reacts with methanol in the presence of triethylamine to yield  $[\text{CuL}^5](\text{ClO}_4)_2$  bearing one *N*- $\text{CH}_2\text{CH}_2\text{C}(=\text{NH})\text{OCH}_3$  and one *N*- $\text{CH}_2\text{CH}_2\text{CN}$  groups; further methanolysis of the *N*- $\text{CH}_2\text{CH}_2\text{CN}$  group in  $[\text{CuL}^5](\text{ClO}_4)_2$  was attempted under various experimental conditions, but failed. Above results shows that the reactivity of  $[\text{CuL}^2](\text{ClO}_4)_2$  is quite different from that reported for  $[\text{CuL}^7](\text{ClO}_4)_2$  or  $[\text{CuL}^{12}](\text{ClO}_4)_2$  (see Introduction).<sup>5,7</sup> It can be suggested that the *N*-( $\text{CH}_2$ )<sub>*n*</sub>CN groups attached to 14-membered tetraaza macrocyclic copper(II) complexes are strongly influenced by the length of the *N*-( $\text{CH}_2$ )<sub>*n*</sub>CN groups and by the number and/or type of *C*-alkyl substituents. The complex  $[\text{CuL}^6](\text{ClO}_4)_2$  bearing *N*- $\text{CH}_2\text{CH}_2\text{COOCH}_3$  and *N*- $\text{CH}_2\text{CH}_2\text{CN}$  groups was also prepared by the hydrolysis of the *N*- $\text{CH}_2\text{CH}_2\text{C}(=\text{NH})\text{OCH}_3$  group of  $[\text{CuL}^5](\text{ClO}_4)_2$  in acidic aqueous solution. The synthetic procedures for the copper(II) complexes of  $\text{L}^3$ - $\text{L}^6$  are shown in Scheme 1.

**Crystal Structure of  $[\text{CuL}^5](\text{ClO}_4)_2$ .** The ORTEP draw-

**Scheme 1**

**Figure 1.** An ORTEP drawing of  $[\text{CuL}^5]^{2+}$  in  $[\text{CuL}^5](\text{ClO}_4)_2$ . Displacement ellipsoids are shown at the 40% probability level. H-atoms attached to the carbon atoms are omitted for clarity.

ing (Fig. 1) of  $[\text{CuL}^5]^{2+}$  shows that both *N*- $\text{CH}_2\text{CH}_2\text{C}(=\text{NH})\text{OCH}_3$  and *N*- $\text{CH}_2\text{CH}_2\text{CN}$  groups are attached to the less sterically hindered nitrogen atoms of the macrocycle. The nitrogen atom of the pendant imidate group is coordinated to the metal ion, and the complex has somewhat distorted square-pyramidal coordination geometry. The macrocyclic ligand adopts the *trans*-III stereochemistry.

Selected bond distances and angles of the complex are listed in Table 2. The in-plane Cu-N distances (2.044(3)-

**Table 2.** Selected Bond Distances (Å) and Angles (°) for [CuL<sup>5</sup>](ClO<sub>4</sub>)<sub>2</sub>

Cu-N(1)	2.084(3)	Cu-N(2)	2.044(3)
Cu-N(3)	2.098(3)	Cu-N(4)	2.055(3)
Cu-N(5)	2.269(3)	C(16)-N(1)	1.472(6)
C(19)-N(5)	1.262(6)	C(23)-N(6)	1.128(7)
C(19)-O(1)	1.342(5)	C(20)-O(1)	1.446(6)
C(21)-C(22)	1.543(6)	C(22)-C(23)	1.450(7)
N(1)-Cu-N(2)	93.0(2)	N(1)-Cu-N(3)	168.0(2)
N(1)-Cu-N(4)	86.8(2)	N(2)-Cu-N(3)	85.0(2)
N(2)-Cu-N(4)	166.0(2)	N(3)-Cu-N(4)	92.2(2)
N(1)-Cu-N(5)	90.8(2)	N(2)-Cu-N(5)	95.7(2)
N(3)-Cu-N(5)	101.1(2)	N(4)-Cu-N(5)	98.4(2)
N(5)-C(19)-O(1)	128.3(4)	N(5)-C(19)-C(18)	123.8(4)
O(1)-C(19)-C(18)	107.9(4)	N(6)-C(23)-C(22)	176.2(8)

2.098(3) Å) are comparable with those of other related macrocyclic copper(II) complexes, such as [CuL<sup>4</sup>](ClO<sub>4</sub>)<sub>2</sub>.<sup>13</sup> The apical Cu-N(5) (*N*-CH<sub>2</sub>CH<sub>2</sub>C(=NH)OCH<sub>3</sub>) distance (2.269(3) Å) is distinctly longer than the in-plane Cu-N distances and is *ca.* 0.06 Å longer than the apical Cu-O (*N*-CH<sub>2</sub>CH<sub>2</sub>CONH<sub>2</sub> group) distance (2.207(3) Å) of [CuL<sup>4</sup>](ClO<sub>4</sub>)<sub>2</sub>,<sup>13</sup> indicating that the coordination bond is relatively weak. The C(19)-N(5) and C(23)-N(6) distances (1.262(6) and 1.128(7) Å, respectively) are corresponding to the C=N bond of the imidate ester group and CN bond of the nitrile group, respectively. The C(19)-O(1) distance (1.342(5) Å) is shorter than the C(20)-O(1) distance (1.446(6) Å, as usual). The N(1)-Cu-N(3) and N(2)-Cu-N(4) angles (168.0(2) and 166.0(2)°, respectively) are distorted from 180°. The angles are somewhat smaller than the *trans*-N-Cu-N angles (172.9(2) and 169.3(2)°) of [CuL<sup>4</sup>](ClO<sub>4</sub>)<sub>2</sub>.<sup>13</sup> The metal ion lies 0.233(2) Å above the mean N<sub>4</sub> (N(1)-N(4)) plane toward the N(5) atom and, therefore, the Cu-N(5) bond is not perpendicular to the in-plane Cu-N bonds with the N-Cu-N(5) angles 90.8(2)-101.1(2)°. The C(18)-C(19)-N(5) and N(5)-C(19)-O(1) angles (123.8(4) and 128.3(4)°, respectively) are considerably larger than the O(1)-C(19)-C(18) angle (107.9(4)°).

**Spectra and Properties of [CuL<sup>3</sup>](ClO<sub>4</sub>)<sub>2</sub> and [CuL<sup>4</sup>](ClO<sub>4</sub>)<sub>2</sub>.** The electronic absorption spectra (Table 3) of [CuL<sup>4</sup>](ClO<sub>4</sub>)<sub>2</sub> prepared in the present work as well as the infrared and FAB mass spectra (see Experimental) are identical with those reported for the complex that prepared from direct reaction between Cu<sup>2+</sup> ion and L<sup>4</sup>.<sup>13</sup> The complex, in which only one *N*-CH<sub>2</sub>CH<sub>2</sub>CONH<sub>2</sub> group is involved in coordination, has square-pyramidal coordination geometry.<sup>13</sup>

The infrared spectrum of [CuL<sup>3</sup>](ClO<sub>4</sub>)<sub>2</sub> shows  $\nu$ (N-H) of the pendant amide and the secondary amine groups at 3450, 3340, 3290, and 3220 cm<sup>-1</sup>. Bands corresponding to  $\nu$ (C=O) of the coordinated amide group and  $\nu$ (CN) of the nitrile group are observed at 1660 and 2250 cm<sup>-1</sup>, respectively. These data and the FAB mass spectrum (see Experimental) indicate that the complex contains both *N*-CH<sub>2</sub>CH<sub>2</sub>CN and

**Table 3.** Electronic Absorption Spectral Data<sup>a</sup>

Complex	$\lambda_{\max}$ , nm ( $\epsilon$ , M <sup>-1</sup> cm <sup>-1</sup> )			
[CuL <sup>2</sup> ](ClO <sub>4</sub> ) <sub>2</sub>	502(186)	545(212) <sup>b</sup>	547(190) <sup>c</sup>	490 <sup>d</sup>
[CuL <sup>3</sup> ](ClO <sub>4</sub> ) <sub>2</sub>	563(178)	568(184) <sup>b</sup>	564(190) <sup>e</sup>	570 <sup>d</sup>
[CuL <sup>4</sup> ](ClO <sub>4</sub> ) <sub>2</sub>	563(180)	565(185) <sup>b</sup>	563(193) <sup>e</sup>	570 <sup>d</sup>
[CuL <sup>5</sup> ](ClO <sub>4</sub> ) <sub>2</sub>	593(278)	596(272) <sup>b</sup>	583(216) <sup>e</sup>	591 <sup>d</sup>
[CuL <sup>6</sup> ](ClO <sub>4</sub> ) <sub>2</sub>	548(169)	550(166) <sup>b</sup>	549(163) <sup>e</sup>	490 <sup>d</sup>
[CuL <sup>7</sup> ](ClO <sub>4</sub> ) <sub>2</sub> <sup>f</sup>		535(230) <sup>b</sup>		500 <sup>d</sup>
[CuL <sup>12</sup> ](ClO <sub>4</sub> ) <sub>2</sub> <sup>g</sup>	495(333)	502(335) <sup>b</sup>		

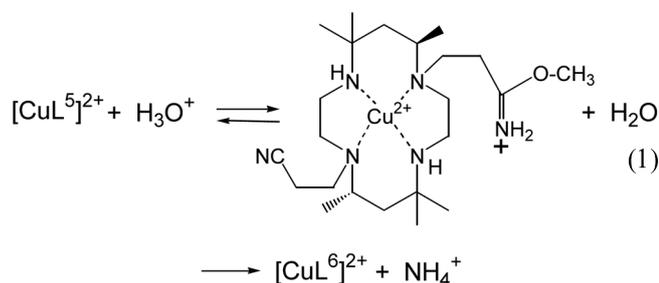
<sup>a</sup>In nitromethane at 20 °C unless otherwise specified. <sup>b</sup>In acetonitrile. <sup>c</sup>In DMSO. <sup>d</sup>In Nujol mull. <sup>e</sup>In water. <sup>f</sup>Ref. 7. <sup>g</sup>Ref. 5.

*N*-CH<sub>2</sub>CH<sub>2</sub>CONH<sub>2</sub> groups. The molar conductance values for the complex measured in water and acetonitrile are 195 and 280 Ω<sup>-1</sup>mol<sup>-1</sup>cm<sup>2</sup>, respectively, indicative of a 1:2 electrolyte. The electronic absorption spectra (Table 3) of [CuL<sup>3</sup>](ClO<sub>4</sub>)<sub>2</sub> measured in various solvents show a d-d transition band at 560-570 nm ( $\epsilon$  = 178-190 M<sup>-1</sup>cm<sup>-1</sup>). The spectra are comparable with those of other square-pyramidal copper(II) complexes, such as [CuL<sup>4</sup>](ClO<sub>4</sub>)<sub>2</sub>. Although [CuL<sup>3</sup>](ClO<sub>4</sub>)<sub>2</sub> is hydrolyzed to [CuL<sup>4</sup>](ClO<sub>4</sub>)<sub>2</sub> at pH > 13, the complex is quite stable in acidic aqueous solution; no apparent hydrolysis was observed in the solution (pH: 2-7) during 5 h even at an elevated temperature (~50 °C).

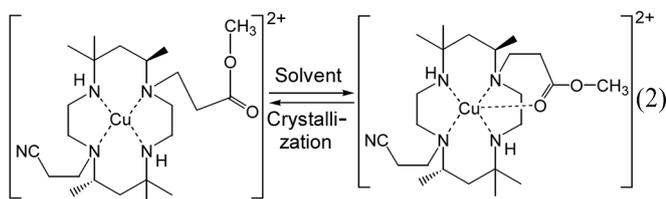
**Spectra and Properties of [CuL<sup>5</sup>](ClO<sub>4</sub>)<sub>2</sub>.** As expected from the crystal structure, the infrared spectrum of [CuL<sup>5</sup>](ClO<sub>4</sub>)<sub>2</sub> shows  $\nu$ C=N of the coordinated *N*-CH<sub>2</sub>CH<sub>2</sub>C(=NH)OCH<sub>3</sub> group and  $\nu$ CN of the *N*-CH<sub>2</sub>CH<sub>2</sub>CN group at 1640 and 2250 cm<sup>-1</sup>, respectively. Bands corresponding to  $\nu$ N-H of the secondary amino groups and the *N*-CH<sub>2</sub>CH<sub>2</sub>C(=NH)OCH<sub>3</sub> group are observed at 3280, 3220, and 3210 cm<sup>-1</sup>. The values of molar conductance for [CuL<sup>5</sup>](ClO<sub>4</sub>)<sub>2</sub> measured in acetonitrile (260 Ω<sup>-1</sup>mol<sup>-1</sup>cm<sup>2</sup>) and nitromethane (140 Ω<sup>-1</sup>mol<sup>-1</sup>cm<sup>2</sup>) indicate that the complex is a 1:2 electrolyte. The electronic absorption spectra (Table 3) of [CuL<sup>5</sup>](ClO<sub>4</sub>)<sub>2</sub> measured in nitromethane and acetonitrile show a d-d transition band at 593 ( $\epsilon$  = 278 M<sup>-1</sup>cm<sup>-1</sup>) and 596 nm ( $\epsilon$  = 272 M<sup>-1</sup>cm<sup>-1</sup>), respectively. The wavelengths are quite similar to that measured in Nujol mull (590 nm). This implicates that the coordination geometry (square pyramid) of the complex in the solvents is nearly identical to that in the solid state. It is seen that the wavelength for [CuL<sup>5</sup>](ClO<sub>4</sub>)<sub>2</sub> in each solvent is *ca.* 30 nm longer than that of [CuL<sup>4</sup>](ClO<sub>4</sub>)<sub>2</sub>.<sup>13</sup> One of the reasons for the red-shift may be the severer distortion of the coordination geometry from regular square-pyramid.<sup>13</sup>

As described above, [CuL<sup>5</sup>](ClO<sub>4</sub>)<sub>2</sub> is hydrolyzed to [CuL<sup>6</sup>](ClO<sub>4</sub>)<sub>2</sub> in acidic aqueous solution. Quantitative measurements of the reaction rate were not carried out in the present work. However, visible absorption spectra of the complex (2.0 × 10<sup>-3</sup> M) measured in aqueous solutions at 20 °C indicated that the half-life (*t*<sub>1/2</sub>) of the reaction in 5.0 × 10<sup>-3</sup> M HClO<sub>4</sub> solution (*ca.* 130 sec) is considerably shorter than that in 1.0 × 10<sup>-3</sup> M HClO<sub>4</sub> (*ca.* 330 sec) or in neutral aqueous solution (> 24 h). This observation corresponds to the suggestion that the hydrolysis reaction begins with the

protonation of the imidate group (Eq. (1)).<sup>16</sup> The protonated form does not bind the metal ion and readily undergoes hydrolysis to form the carboxylic ester group.



**Spectra and Coordination Behavior of  $[\text{CuL}^6](\text{ClO}_4)_2$ .** The FAB mass spectrum of the red complex  $[\text{CuL}^6](\text{ClO}_4)_2$  as well as the elemental analysis is corresponding to the formula of the complex. The value of molar conductance for  $[\text{CuL}^6](\text{ClO}_4)_2$  measured in acetonitrile ( $255 \Omega^{-1}\text{mol}^{-1}\text{cm}^2$ ) corresponds to the fact that the complex is a 1:2 electrolyte. The infrared spectrum of  $[\text{CuL}^6](\text{ClO}_4)_2$  measured in Nujol mull shows  $\nu\text{C}=\text{O}$  at  $1740 \text{ cm}^{-1}$ , indicating that the oxygen atom of the  $N\text{-CH}_2\text{CH}_2\text{COOCH}_3$  group is not involved in coordination. Bands corresponding to  $\nu\text{N-H}$  and  $\nu\text{CN}$  are observed at  $3170$  and  $2250 \text{ cm}^{-1}$ , respectively. The electronic absorption spectrum of  $[\text{CuL}^6](\text{ClO}_4)_2$  measured in Nujol mull shows a d-d transition band at *ca.*  $490 \text{ nm}$ . The wavelength is quite similar to that for  $[\text{CuL}^2](\text{ClO}_4)_2$ ,  $[\text{CuL}^7](\text{ClO}_4)_2$ , or  $[\text{CuL}^{12}](\text{ClO}_4)_2$  in Nujol mull or nitromethane and is comparable with those for other related square-planar copper(II) complexes.<sup>7,12</sup> This result, together with the infrared spectrum, clearly shows that the  $N\text{-CH}_2\text{CH}_2\text{COOCH}_3$  group of  $[\text{CuL}^6](\text{ClO}_4)_2$  as well as the  $N\text{-CH}_2\text{CH}_2\text{CN}$  group is not coordinated to the metal ion in the solid state. However, the wavelength ( $548\text{-}550 \text{ nm}$ ) measured in various solvents, such as nitromethane, acetonitrile, and DMSO, is *ca.*  $60 \text{ nm}$  longer than that measured in Nujol mull and is quite similar to those for  $[\text{CuL}^3](\text{ClO}_4)_2$  and  $[\text{CuL}^4](\text{ClO}_4)_2$ . It is also seen that the wavelength and molar absorption coefficient for  $[\text{CuL}^6](\text{ClO}_4)_2$  measured in nitromethane, a very poorly coordinating solvent, is nearly the same as those in the coordinating solvents (acetonitrile and DMSO). Furthermore, the infrared spectra of  $[\text{CuL}^6](\text{ClO}_4)_2$  dissolved in nitromethane and acetonitrile showed  $\nu\text{C}=\text{O}$  at  $1685 \text{ cm}^{-1}$  (no peak at  $> 1700 \text{ cm}^{-1}$  corresponding to  $\nu\text{C}=\text{O}$  of uncoordinated carboxylic ester group was observed). Therefore, it can be concluded that the  $N\text{-CH}_2\text{CH}_2\text{COOCH}_3$  group of  $[\text{CuL}^6](\text{ClO}_4)_2$  is not involved in coordination in the solid state but is coordinated to the metal ion in the solvents (Eq. (2)). This may be closely related to the relatively weak



coordination ability of the carboxylic ester group.<sup>12</sup>

Interestingly, the coordination behavior of  $[\text{CuL}^6](\text{ClO}_4)_2$  is quite different from that observed for  $[\text{CuL}^{10}](\text{ClO}_4)_2$  or  $[\text{CuL}^{11}](\text{ClO}_4)_2$ , in which the  $N\text{-CH}_2\text{CH}_2\text{COOCH}_3$  group is coordinated to the metal ion in the solid state and in various solvents.<sup>12</sup> In the case of  $[\text{CuL}^{13}](\text{ClO}_4)_2$ , both a square-pyramidal isomer (only one  $N\text{-CH}_2\text{CH}_2\text{COOCH}_3$  group is coordinated to the metal ion) and a square-planar isomer (the  $N\text{-CH}_2\text{CH}_2\text{COOCH}_3$  groups are not involved in coordination) can be prepared selectively by controlling ionic strength of its methanol solution.<sup>5</sup> However, all our efforts to obtain a square-pyramidal isomer of  $[\text{CuL}^6](\text{ClO}_4)_2$  as a solid were unsuccessful.

## Conclusion

The copper(II) complexes of  $L^3\text{-}L^5$  bearing various types of functional pendant arms can be prepared by selective hydrolysis or methanolysis of the  $N\text{-CH}_2\text{CH}_2\text{CN}$  groups in  $[\text{CuL}^2]^{2+}$ . The reactivity of  $[\text{CuL}^2]^{2+}$  is quite different from that of  $[\text{CuL}^7]^{2+}$  or  $[\text{CuL}^{12}]^{2+}$ . This work also shows that the coordinated  $N\text{-CH}_2\text{CH}_2\text{C(=NH)OCH}_3$  group of  $[\text{CuL}^5](\text{ClO}_4)_2$  readily undergoes acid hydrolysis to yield  $[\text{CuL}^6](\text{ClO}_4)_2$ . The  $N\text{-CH}_2\text{CH}_2\text{CONH}_2$  group of  $[\text{CuL}^3](\text{ClO}_4)_2$  or the  $N\text{-CH}_2\text{CH}_2\text{C(=NH)OCH}_3$  group of  $[\text{CuL}^5](\text{ClO}_4)_2$  is coordinated to the metal ion in the solid state and in various solvents. Interestingly, the  $N\text{-CH}_2\text{CH}_2\text{COOCH}_3$  group of  $[\text{CuL}^6](\text{ClO}_4)_2$  is not involved in coordination in the solid state but binds the metal ion in various solvents.

**Supplementary Material.** Crystallographic data for  $[\text{CuL}^5](\text{ClO}_4)_2$  have been deposited with the Cambridge Crystallographic Data Center (CCDC number 653063). Copies of the data may be obtained free of charge, on application to the director, CCDC, 12 Union Road, Cambridge CB2 IEZ, UK (<http://www.ccdc.cam.ac.uk>, fax: +44-1233-336-033, or e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

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