

Template Synthesis of Copper(II) Complexes of N₃O-Donor Macrotricycles Containing N-CH₂-N and N-CH₂-O Linkages

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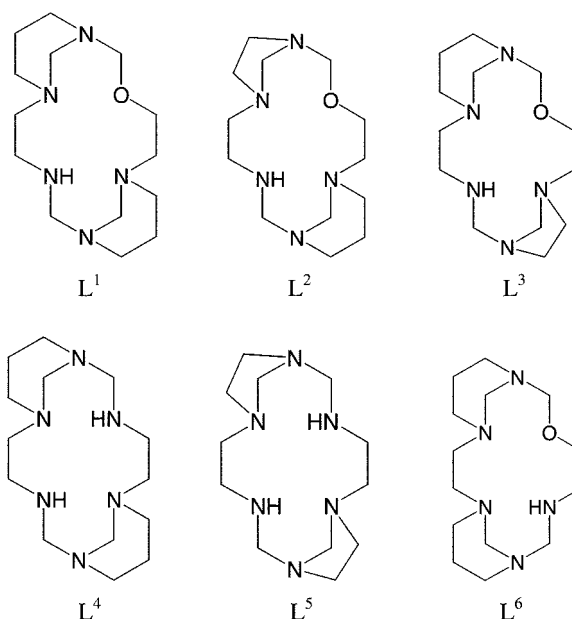
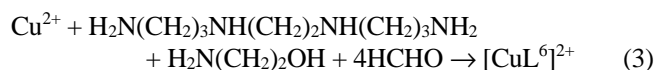
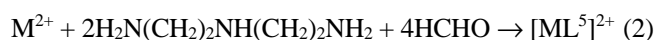
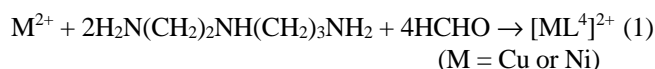
Received September 1, 2004

Key Words : Mixed donor macrocycles, N₃O-Donor macrotricycles, Metal template synthesis, Copper(II) complexes

Various types of macrocyclic compounds containing mixed donors of nitrogen and oxygen have been prepared and investigated.¹⁻⁹ Much of this activity has been associated with the synthesis of macrocyclic ligands that exhibit high selectivity for specific metal ions. In most cases, the preparation of mixed donor macrocyclic compounds requires several steps and/or results in low yield.

Metal directed condensation reactions involving coordinated polyamines and formaldehyde have been utilized for the preparation of various types of saturated polyaza macrocyclic compounds that could not be prepared by other methods.⁹⁻¹⁶ For example, the nickel(II) and copper(II) complexes of L⁴ and L⁵ containing N-CH₂-N linkages have been prepared by the one-pot reactions of Eqs. (1) and (2).^{14,15} Some macrocyclic compounds containing N-CH₂-O linkages have been also prepared by metal-directed condensations involving amines, formaldehyde, and/or alcohols.^{9,16,17} The preparation of [CuL⁶]²⁺ containing both N-CH₂-N and N-CH₂-O linkages in the macrotricyclic skeleton was reported for the first time by Lawrance *et al.*, who prepared the complex from the reaction (Eq. (3)) of formaldehyde with a tetraamine and ethanolamine.⁹ It has been revealed that the coordination geometry of [CuL⁶]²⁺ is similar to that of [CuL⁴]²⁺ or [CuL⁵]²⁺, except that L⁶ acts as a N₃O-donor; the Cu-O distance (2.008(3) Å) of [CuL⁶]²⁺ is comparable with the Cu-N distances (2.020-1.976 Å).⁹ However, reports on the formation of such mixed donor macrocyclic compounds containing both N-CH₂-O and N-CH₂-N linkages are limited in number, and their chemical properties are not thoroughly understood.⁹

Herein, we report the synthesis and chemical properties of new copper(II) complexes of L¹-L³ incorporating N₃O-donor sets. The complexes were prepared by the one-pot reactions (Eqs. (4)-(6)) of appropriate triamines, diaminoalcohols, and formaldehyde in the presence of the metal ion.



Experimental Section

Measurements. Infrared spectra were recorded with a Shimadzu IR-440 spectrophotometer, electronic absorption spectra with a Analytikjena Specord 200 UV/Vis spectrophotometer, and conductance measurements with a Metrohm Herisau Conductometer E518. FAB-mass spectra and elemental analyses were performed at the Korea Basic Science Institute, Daegu, Korea. Cyclic voltammograms were recorded using a BAS-100 B/W auto cyclic volt/ampere meter. The working and counter electrodes were platinum, and the reference electrode was saturated calomel electrode (SCE). The electrochemical measurements were conducted in 0.1 M (*n*-Bu)₄NClO₄ acetonitrile solutions at 20 °C.

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Safety Note: Perchlorate salts of transition metal complexes with organic ligands are often explosive and should be handled with caution.

Preparation of $[\text{CuL}^1](\text{ClO}_4)_2$ ($\text{L}^1 = 3\text{-oxa-1,6,10,12,15-pentaazatricyclo[13.3.1.1}^{6,10}\text{]eicosane}$). A methanol solution (*ca.* 40 mL) of $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (3.0 g, 15 mmol), 1,4,8-triazaoctane (1.9 mL, 15 mmol), 2-(3-aminopropylamino)ethanol (1.8 mL, 15 mmol), and 35% formaldehyde (9.0 mL) was stirred for > 24 h at room temperature. An excess NaClO_4 was added to the solution, and a deep purple-red solid was precipitated. The crude product often contains small amount (< 5%) of $[\text{CuL}^4](\text{ClO}_4)_2$ as a by-product. The pure product was obtained by fractional recrystallizations of the crude product from hot water-acetonitrile (1 : 3). The product was collected by filtration, washed with methanol, and dried in air. Yield: > 80%. *Anal.* Found: C, 30.84; H, 5.68; N, 12.89. Calc. for $\text{C}_{14}\text{H}_{29}\text{N}_5\text{CuCl}_2\text{O}_5$: C, 30.81; H, 5.37; N, 12.84%. FAB mass (m/z): 446 ($[\text{M}-\text{ClO}_4]^+$), 346 ($[\text{M}-2\text{ClO}_4-\text{H}]^+$). IR (Nujol mull, cm^{-1}): 3260 ($\nu(\text{N-H})$).

Preparation of $[\text{CuL}^1(\text{Cl})]\text{ClO}_4 \cdot 2\text{H}_2\text{O}$. The synthetic procedure of this complex was similar to that of $[\text{CuL}^1](\text{ClO}_4)_2$, except that $\text{CuCl}_2 \cdot 4\text{H}_2\text{O}$ (2.6 g, 15 mmol) was reacted instead of $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$. The blue-purple solid was recrystallized from hot water-acetonitrile (2 : 1), washed with methanol, and dried in air. Yield: > 80%. *Anal.* Found: C, 32.30; H, 6.28; N, 13.45. Calc. for $\text{C}_{14}\text{H}_{33}\text{N}_5\text{CuCl}_2\text{O}_7$: C, 32.48; H, 6.43; N, 13.53%. FAB mass (m/z): 482 ($[\text{M}-2\text{H}_2\text{O}]^+$), 446 ($[\text{M}-2\text{H}_2\text{O}-\text{Cl}]^+$), 382 ($[\text{M}-2\text{H}_2\text{O}-\text{ClO}_4]^+$), 346 ($[\text{M}-2\text{H}_2\text{O}-\text{H}^+-\text{Cl}-\text{ClO}_4]^+$). IR (Nujol mull, cm^{-1}): 3500 ($\nu(\text{O-H})$), 3180 ($\nu(\text{N-H})$), 1620 ($\delta(\text{H}_2\text{O})$).

Preparation of $[\text{CuL}^2(\text{Cl})]\text{ClO}_4$ ($\text{L}^2 = 11\text{-oxa-1,3,6,9,14-pentaazatricyclo[12.3.1.1}^{6,9}\text{]nonadecane}$). A methanol solution (*ca.* 30 mL) of $\text{CuCl}_2 \cdot 4\text{H}_2\text{O}$ (2.6 g, 15 mmol), diethylenetriamine (1.6 mL, 15 mmol), 2-(3-aminopropylamino)ethanol (1.8 mL, 15 mmol), and 35% formaldehyde (9.0 mL) was stirred for > 48 h at room temperature. An excess NaClO_4 was added to the solution, and a sky-blue solid was precipitated. The crude product was dissolved in minimum volume of hot acetonitrile. Addition of excess NaClO_4 dissolved in methanol (*ca.* 30 mL) to the solution produced the sky-blue solid. The product was filtered, washed with methanol, and dried in air. Yield: > 70%. *Anal.* Found: C, 33.03; H, 5.77; N, 14.85. Calc. for $\text{C}_{13}\text{H}_{27}\text{N}_5\text{CuCl}_2\text{O}_5$: C, 33.38; H, 5.83; N, 14.98%. FAB mass (m/z): 431 ($[\text{M}-\text{Cl}]^+$), 367 ($[\text{M}-\text{ClO}_4]^+$), 332 ($[\text{M}-\text{Cl}-\text{ClO}_4-\text{H}]^+$). IR (Nujol mull, cm^{-1}): 3220 ($\nu(\text{N-H})$).

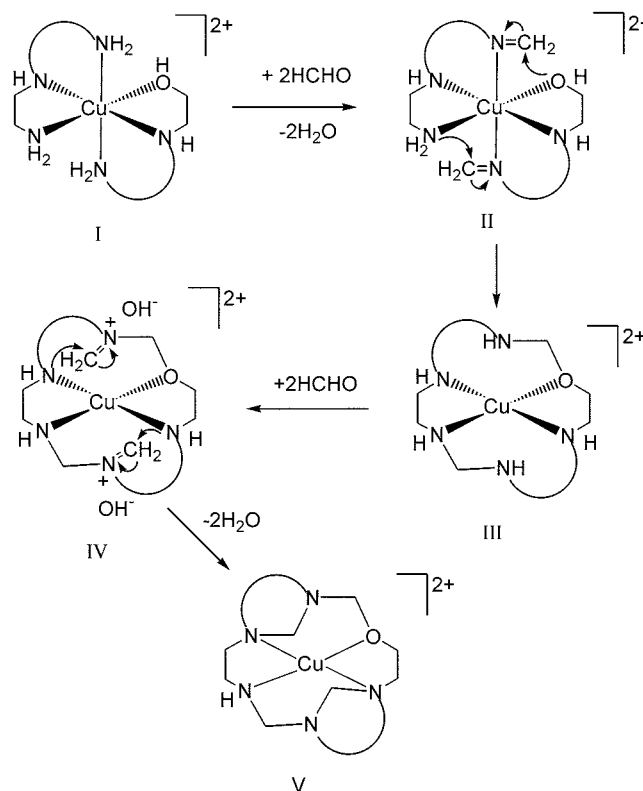
Preparation of $[\text{CuL}^3(\text{Cl})]\text{ClO}_4$ ($\text{L}^3 = 3\text{-oxa-1,6,9,11,14-pentaazatricyclo[12.3.1.1}^{6,9}\text{]nonadecane}$). This complex was prepared by a method similar to that of $[\text{CuL}^1(\text{Cl})]\text{ClO}_4$, except that *N*-(2-aminoethyl)ethanolamine (1.5 mL, 15 mmol) was reacted instead of 2-(3-aminopropylamino)ethanol. The crude product was dissolved in minimum volume of DMSO-acetonitrile, and excess NaClO_4 dissolved in methanol (*ca.* 30 mL) was added to the solution to produce the blue-green solid. The product was filtered, washed with methanol, and dried in air. Yield: > 70%. *Anal.* Found: C, 33.41; H, 5.98; N, 15.00. Calc. for $\text{C}_{13}\text{H}_{27}\text{N}_5$ -

CuCl_2O_5 : C, 33.38; H, 5.83; N, 14.98%. FAB mass (m/z): 431 ($[\text{M}-\text{Cl}]^+$), 367 ($[\text{M}-\text{ClO}_4]^+$), 332 ($[\text{M}-\text{Cl}-\text{ClO}_4-\text{H}]^+$). IR (Nujol mull, cm^{-1}): 3200 ($\nu(\text{N-H})$).

Results and Discussion

Synthesis. The reaction of excess formaldehyde with a 1 : 1 : 1 molar mixture of $\text{CuCl}_2 \cdot 4\text{H}_2\text{O}$, 1,4,8-triazaoctane, and 2-(3-aminopropylamino)ethanol at room temperature, followed by addition of an excess of NaClO_4 , produced $[\text{CuL}^1(\text{Cl})]\text{ClO}_4$. When $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ was reacted instead of $\text{CuCl}_2 \cdot 4\text{H}_2\text{O}$, the product was $[\text{CuL}^1](\text{ClO}_4)_2$. The complexes $[\text{CuL}^2(\text{Cl})]\text{ClO}_4$ and $[\text{CuL}^3(\text{Cl})]\text{ClO}_4$ were also prepared by similar one-pot reactions (*see* Experimental Section). The proposed routes to give the complexes of L^1 - L^3 are shown in Scheme 1, which is corresponding to those reported for other related macrocyclic complexes.¹³⁻¹⁵ The complex **I** initially reacts with formaldehyde to yield **II**. The $-\text{N}=\text{CH}_2$ groups of **II** react with neighboring primary amino or hydroxyalkyl groups to form **III**. The $-\text{NH}-\text{CH}_2-\text{NH}-$ and $-\text{HN}-\text{CH}_2-\text{O}-$ linkages of **III** react with additional formaldehyde to produce **IV** containing iminium groups. The reaction of each iminium group with neighboring secondary amino group yields the complexes (**V**) containing 1,3-diazacyclohexane and/or 1,3-diazacyclopentane rings.

As described in the Experimental Section, the copper(II) complexes of L^1 - L^3 were prepared in high yield (> 70%) by the one-pot reactions at room temperature. However, unexpectedly, the main product prepared by refluxing the reaction solutions was $[\text{CuL}^4](\text{ClO}_4)_2$ or $[\text{CuL}^5](\text{ClO}_4)_2$; the



Scheme 1

Table 1. Molar conductance and electronic spectral data of the complexes^a

Complex	λ_{\max} , nm (ϵ , M ⁻¹ cm ⁻¹)	Λ_M , $\Omega^{-1}\text{mol}^{-1}\text{cm}^2$
[CuL ¹](ClO ₄) ₂	530(140) 550(150) ^b 580(91) ^c 525 ^d	140 270 ^b 210 ^c
[CuL ¹ (Cl)]ClO ₄ ·2H ₂ O	615(133) 615(117) ^b 580(92) ^c 560 ^d	105 170 ^b 210 ^c
[CuL ² (Cl)]ClO ₄	665(186) 670(180) ^b 585(101) ^c 650 ^d	102 165 ^b 216 ^c
[CuL ³ (Cl)]ClO ₄	760(216) 775(215) ^b 580(100) ^c 740 ^d	104 160 ^b 230 ^c
[CuL ⁴](ClO ₄) ₂ ^e	505(122) 529(142) ^c	
[CuL ⁴ (Cl)]ClO ₄ ^e	612(217) ^b 563(160) ^c	
[CuL ⁵](ClO ₄) ₂ ^e	486(151) 535(185) ^c	
[CuL ⁵ (Cl)]ClO ₄ ^e	616(201) ^b 550(191) ^c	
[CuL ⁶](ClO ₄) ₂ ^f	600(120) ^c	

^aMeasured in nitromethane at 20 °C unless otherwise specified. ^bIn acetonitrile. ^cIn water. ^dIn Nujol mull. ^eRef. 15. ^fRef. 9.

complexes of L¹-L³ could not be isolated. This indicates that the reaction temperature is an important factor for the formation of the mixed donor macrocyclic compounds. All our efforts to prepare nickel(II) complexes of L¹-L³ under various experimental conditions were also unsuccessful. The only macrocyclic complex prepared from the attempts was [NiL⁴](ClO₄)₂ or [NiL⁵](ClO₄)₂.¹⁴ The easy formation of the copper(II) complexes of L¹-L³ may be attributed to the relatively strong Lewis acidity of the metal ion that can stabilize the N-CH₂-O linkage through strong Cu-O bond.

Spectra and properties. The formula of the copper(II) complexes of L¹-L³ prepared in the present work were confirmed by their FAB mass spectra and elemental analyses (see Experimental Section). In the infrared spectrum of each complex, ν (N-H) of the coordinated secondary amino group is observed at *ca.* 3200 cm⁻¹. The molar conductance values (Table 1) of [CuL¹](ClO₄)₂ measured in various solvents indicate that the complex is a 1 : 2 electrolyte. The values of [CuL¹(Cl)]ClO₄, [CuL²(Cl)]ClO₄, and [CuL³(Cl)]ClO₄ measured in nitromethane (102-105 $\Omega^{-1}\text{mol}^{-1}\text{cm}^2$) and acetonitrile (160-170 $\Omega^{-1}\text{mol}^{-1}\text{cm}^2$) correspond to 1 : 1 electrolytes. However, those (210-230 $\Omega^{-1}\text{mol}^{-1}\text{cm}^2$) measured in water correspond to 1 : 2 electrolytes, showing that the chloride ion of each complex is removed from coordination sphere.

The electronic absorption spectra (Table 1) of [CuL¹](ClO₄)₂ measured in nitromethane, a non-coordinating solvent, and Nujol mull show a *d-d* transition band at *ca.* 530 nm, indicating that the complex has a square-planar coordination geometry.^{9,15,18,19} The wavelength is *ca.* 30 nm longer than that of [CuL⁴](ClO₄)₂. This corresponds to the suggestion that [CuL¹](ClO₄)₂ with N₃O-donor set exhibits weaker ligand field strength than [CuL⁴](ClO₄)₂ with N₄-donor set does. The spectrum of [CuL¹(Cl)]ClO₄ measured in nitromethane shows the band at 615 nm (ϵ , 133 M⁻¹cm⁻¹). The wavelength is *ca.* 80 nm longer than that of [CuL¹]-

(ClO₄)₂ and is comparable with those of the square-pyramidal complexes [CuL⁴(Cl)]ClO₄ and [CuL⁵(Cl)]ClO₄.¹⁵ Interestingly, the wavelengths and molar absorption coefficients of [CuL²(Cl)]ClO₄ {665 nm (ϵ , 186 M⁻¹cm⁻¹)} and [CuL³(Cl)]ClO₄ {760 nm (ϵ , 216 M⁻¹cm⁻¹)} measured in nitromethane are much longer and larger, respectively, than those of [CuL¹(Cl)]ClO₄. Both values vary with the ligand in the order of L¹ < L² < L³. The five coordinate complexes can exist as various structures such as a regular square-pyramid, a regular trigonal bipyramid, a distorted square-pyramid, and a trigonal bipyramid.²⁰ In many cases, the energy differences between these structures are small, and the structural conversion occurs easily.¹⁸⁻²¹ It has been also observed that regular and distorted square-pyramidal copper(II) complexes exhibit a *d-d* transition band in the region 550-670 nm, whereas trigonal bipyramidal ones show a maximum absorption at > 670 nm.^{18,19,21-23} Unfortunately, we could not obtain single crystals of the copper(II) complexes suitable for X-ray work, and their crystal structures have not been investigated. However, the longer wavelengths and the larger molar absorption coefficients for [CuL²(Cl)]ClO₄ and [CuL³(Cl)]ClO₄ in nitromethane or in the solid state, compared to those for [CuL¹(Cl)]ClO₄, strongly indicate that their coordination geometry is more severely distorted from a regular square-pyramid.

In the electronic spectrum of [CuL¹](ClO₄)₂ measured in water, the wavelength (580 nm) of the *d-d* band is ~50 nm longer than that in Nujol mull or nitromethane. This can be attributed to the coordination of water molecule(s) to the metal ion. The wavelengths and/or molar absorption coefficients of [CuL¹(Cl)]ClO₄, [CuL²(Cl)]ClO₄, and [CuL³(Cl)]ClO₄ measured in water are nearly independent on the ligand structure and are quite similar to those of [CuL¹](ClO₄). This trend is in sharp contrast to that observed in Nujol mull, nitromethane, or acetonitrile. The electronic spectra, together with the molar conductance values, clearly show that the chloride ion of [CuL(Cl)]ClO₄ (L = L¹-L³) is substituted by water molecule to give [CuL(H₂O)]²⁺ (or [CuL(H₂O)₂]²⁺) in aqueous solution, though the anion is involved in coordination in the solid state and in nitromethane or acetonitrile. The spectra measured in water also show that the coordination geometry of [CuL(H₂O)]²⁺ (or [CuL(H₂O)₂]²⁺) is not affected significantly by the ligand structure, in contrast to the case of [CuL(Cl)]ClO₄.

Cyclic voltammograms of [CuL(Cl)]ClO₄ measured in acetonitrile showed one electron oxidation and reduction peaks corresponding to Cu(II)/Cu(III) and Cu(II)/Cu(I) proc-

Table 2. Cyclic voltammetric data

Compound	Potential (V vs. SCE) ^a	
	Cu(II)/Cu(III)	Cu(II)/Cu(I)
[CuL ¹ (Cl)]ClO ₄	+1.33(i) ^b	-0.51
[CuL ² (Cl)]ClO ₄	+1.41(i)	-0.49
[CuL ³ (Cl)]ClO ₄	+1.37(i)	-0.47

^aMeasured in 0.1 M (*n*-Bu)₄NClO₄ acetonitrile solution at 20 °C; scan rate = 200 mV/s. ^bi = irreversible.

esses, respectively. Interestingly, the redox potentials (Table 2) of $[\text{CuL}(\text{Cl})]\text{ClO}_4$ are not influenced significantly by the ligand structure, unlike their electronic absorption spectra measured in acetonitrile. This means that the electron density on the metal ion of the copper(II) complexes is nearly independent on the structure.

The copper(II) complexes of $\text{L}^1\text{-L}^3$ are extremely stable in nitromethane, acetonitrile, and DMSO. They are rapidly decomposed in acidic aqueous solutions. The kinetics of the decomposition of the complexes (2.0×10^{-3} M) in 0.01 M HClO_4 solution were carried out spectrophotometrically by recording the decrease in absorbance at 580 nm. The pseudo first-order rate constant for $[\text{CuL}^1(\text{Cl})]\text{ClO}_4$ measured at 20 °C was found to be $4.1 \times 10^{-2} \text{ sec}^{-1}$ ($t_{1/2} = 17$ sec). In the cases of $[\text{CuL}^2(\text{Cl})]\text{ClO}_4$ and $[\text{CuL}^3(\text{Cl})]\text{ClO}_4$, the decomposition rate was too fast to measure with ordinary methods under similar conditions. Although $[\text{CuL}^1(\text{Cl})]\text{ClO}_4$ and $[\text{CuL}^2(\text{Cl})]\text{ClO}_4$ are stable in neutral aqueous solutions, $[\text{CuL}^3(\text{Cl})]\text{ClO}_4$ is completely decomposed in boiling water within 10 min. Factors affecting their stability in aqueous solutions are not clearly understood at this time. However, it is obvious that the copper(II) complexes of $\text{L}^1\text{-L}^3$ (N_3O -donor) are much less stable than the complexes of L^4 and L^5 (N_4 -donor).^{14,15} The latter complexes are relatively inert against decomposition even in 0.1 M HClO_4 aqueous solution.^{14,15} The free macrocycles $\text{L}^1\text{-L}^3$ containing $\text{N-CH}_2\text{-N}$ and $\text{N-CH}_2\text{-O}$ linkages could not be isolated as solids because of their instability in aqueous solutions.^{10,13} Direct comparison of the solution behaviors of the copper(II) complexes of $\text{L}^1\text{-L}^3$ with those of $[\text{CuL}^6](\text{ClO}_4)_2$ cannot be made at this time, since the data of the latter complex are not available.

Concluding Remarks

New copper(II) complexes of the N_3O -donor macrotricycles $\text{L}^1\text{-L}^3$, containing both $\text{N-CH}_2\text{-N}$ and $\text{N-CH}_2\text{-O}$ linkages, were prepared in high yield by the one-pot reactions at room temperature. The electronic spectra of $[\text{CuL}(\text{Cl})]^{2+}$ are strongly influenced by the ligand structure, whereas their redox potentials are nearly independent on the structure. The copper(II) complexes of $\text{L}^1\text{-L}^3$ are rapidly decomposed in acid solutions, unlike $[\text{CuL}^4](\text{ClO}_4)_2$ and $[\text{CuL}^5](\text{ClO}_4)_2$ with N_4 -donor sets. The complex $[\text{CuL}^3(\text{Cl})]\text{-ClO}_4$ is unstable even in neutral aqueous solution.

Acknowledgments. This work was supported by the Research Grant of Daegu University.

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