One-Pot Reaction Involving Two Different Amines and Formaldehyde Leading to the Formation of Poly(Macrocyclic) Cu(II) Complexes

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New polynuclear poly(hexaaza macrocyclic) copper(II) complexes [**1**]$(ClO_4)_{2n} \cdot (H_2O)_{2n}$, [**2**]$(ClO_4)_{2n} \cdot (H_2O)_{2n}$, and [**3**]$(ClO_4)_{2n} \cdot (H_2O)_{2n}$ have been prepared by the one-pot reaction of formaldehyde with ethylenediamine and 1,2-bis(2-aminoethoxy)ethane, 1,3-diaminopropane, or 1,6-diaminohexane in the presence of the metal ion. The polymer complexes contain fully saturated 14-membered hexaaza macrocyclic units (1,3,6,8,10,13-hexa-azacyclotetradecane) that are linked by N-$(CH_2)_2$-O-$(CH_2)_2$-O-$(CH_2)_2$-N, N-$(CH_2)_3$-N, or N-$(CH_2)_6$-N chains. The mononuclear complex $[Cu(H_2L^5)](ClO_4)_4$ (H_2L^5 = a protonated form of L^5) bearing two N-$(CH_2)_2$-O-$(CH_2)_2$-O-$(CH_2)_2$-NH_2 pendant arms has also been prepared by the metal-directed reaction of ethylenediamine, 1,2-bis(2-aminoethoxy)ethane, and formaldehyde. The polymer complexes were characterized employing elemental analyses, FT-IR and electronic absorption spectra, molar conductance, X-ray diffraction (XRD), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and scanning electron micrograph (SEM). Electronic absorption spectra of the complexes show that each macrocyclic unit of them has square-planar coordination geometry with a 5-6-5-6 chelate ring sequence. The polymer complexes as well as $[Cu(H_2L^5)]^{4+}$ are quite stable even in concentrated $HClO_4$ solutions. Synthesis and characterization of the polynuclear and mononuclear copper(II) complexes are reported.
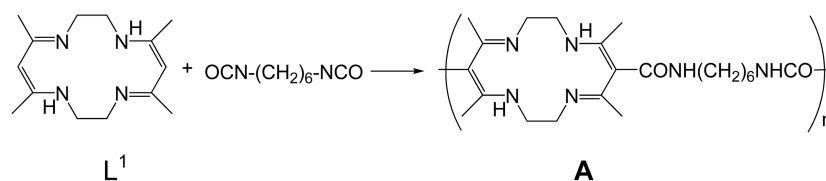
Key Words : Polynuclear complex, Poly(macrocyclic) complex, Polymer complex, Copper(II) complex, Functional pendant arm
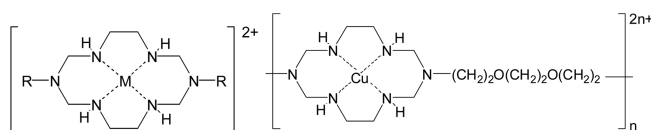
Introduction

Transition metal complexes of polymers are attracting considerable attention because of their potential applications in various fields, such as catalysts, organic synthesis, magnetic materials, and solid electrolytes.[1-12] Most polymer complexes are known to be insoluble in water, though water-soluble macromolecules or polymers are of importance for many industrial and technological applications.

Some polymers containing polyaza macrocyclic units have been prepared and investigated.[8-12] The preparation of such compounds generally starts with a pre-formed polyaza macrocycle that can react with polymer bearing reactive functional groups or with α,ω-difunctionalized reagents. For instance, the unsaturated poly(tetraaza macrocycle) **A** (Scheme 1) has been prepared by the reaction of L^1 with the diisocyanate OCN-$(CH_2)_6$-NCO.[9] Until now, however, relatively few studies have been reported for polymer complexes containing polyaza macrocyclic units.[9,11]

Formaldehyde is a good reagent to link two amine moieties and, therefore, metal-directed reaction of coordinated amines and formaldehyde is useful for the preparation of various types of fully saturated polyaza macrocyclic complexes containing N-CH_2-N linkages.[13-18] For example, the 14-membered hexaaza macrocyclic complex $[ML^2]^{2+}$ (M = Cu(II) or Ni(II)) can be prepared by the one-pot reaction (Eq. (1)) of formaldehyde with ethylenediamine and methylamine in the presence of the metal ion.[13] Such reaction has been extended to the synthesis of $[ML^3]^{2+}$ and $[ML^4]^{2+}$ bearing two N-functional pendant arms (Eq. (1)).[17,18] It has been revealed that the reactions are simple and selective synthetic routes toward saturated polyaza macrocyclic complexes that could not be prepared by other methods. We have been interested in the preparation of various types of polynuclear poly(macrocyclic) complexes containing N-CH_2-N linkages from the one-pot metal-directed reaction of amines and formaldehyde.

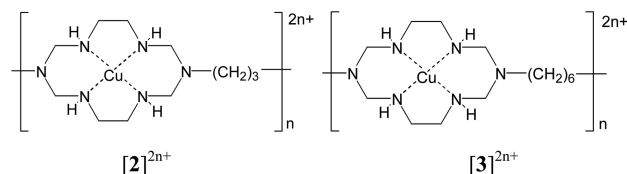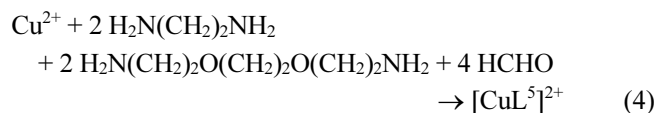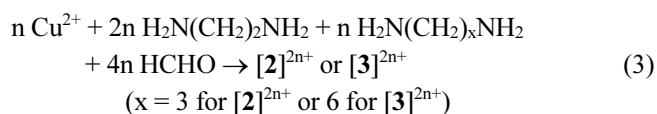**Scheme 1.** Synthetic scheme of **1**.

[ML²]²⁺: R = Me

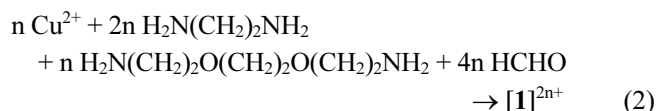[ML³]²⁺: R = (CH₂)₂NH₂

[ML⁴]²⁺: R = (CH₂)₂OH

[ML⁵]²⁺: R = (CH₂)₂O(CH₂)₂O(CH₂)₂NH₂

[1]²ⁿ⁺

[2]²ⁿ⁺   **[3]²ⁿ⁺**

$$M^{2+} + 2\ H_2N(CH_2)_2NH_2 + 2\ R\text{-}NH_2 + 4HCHO \rightarrow [ML]^{2+} \quad (1)$$

$$R = Me\ for\ L^2 \quad (M = Cu(II)\ or\ Ni(II);\ L = L^2,\ L^3,\ or\ L^4)$$
$$(CH_2)_2NH_2\ for\ L^3$$
$$(CH_2)_2OH\ for\ L^4$$

$$n\ Cu^{2+} + 2n\ H_2N(CH_2)_2NH_2$$
$$+\ n\ H_2N(CH_2)_2O(CH_2)_2O(CH_2)_2NH_2 + 4n\ HCHO$$
$$\rightarrow [1]^{2n+} \quad (2)$$

$$n\ Cu^{2+} + 2n\ H_2N(CH_2)_2NH_2 + n\ H_2N(CH_2)_xNH_2$$
$$+\ 4n\ HCHO \rightarrow [2]^{2n+}\ or\ [3]^{2n+} \quad (3)$$
$$(x = 3\ for\ [2]^{2n+}\ or\ 6\ for\ [3]^{2n+})$$

$$Cu^{2+} + 2\ H_2N(CH_2)_2NH_2$$
$$+\ 2\ H_2N(CH_2)_2O(CH_2)_2O(CH_2)_2NH_2 + 4\ HCHO$$
$$\rightarrow [CuL^5]^{2+} \quad (4)$$

In this work, we successfully prepared the poly(hexaaza macrocyclic) copper(II) complexes [**1**]²ⁿ⁺, [**2**]²ⁿ⁺, and [**3**]²ⁿ⁺ from the one-pot reaction of Eqs. (2) and (3). Interestingly, the polymer complexes contain fully saturated 14-membered hexaaza macrocyclic units (1,3,6,8,10,13-hexaazacyclotetradecane) that are linked by the *N*-(CH₂)₂O(CH₂)₂O(CH₂)₂-*N*, *N*-(CH₂)₃-*N*, or *N*-(CH₂)₆-*N* linkages. Each macrocyclic unit binds one copper(II) ion, and the polymer complexes possess cationic charges. The mononuclear complex [Cu(H₂L⁵)]⁴⁺ bearing two *N*-(CH₂)₂O(CH₂)₂O(CH₂)₂NH₂ pendant arms was also prepared by the reaction of Eq. (4).

There has been considerable interest in the preparation of polyelectrolytes which possess cationic or anionic charges along the polymer chains because of their potential industrial and technological applications.[19] However, most of them reported are organic macromolecules. As far as we know, inorganic polyelectrolytes containing 14-membered hexaaza macrocyclic units as integral parts of the polymer backbone are not reported to date.

Experimental

Measurements. Infrared spectra were recorded with a

Genesis II FT-IR spectrometer, electronic absorption spectra with an Analytik Jena Specord 200 UV/vis spectrophotometer, and conductance measurements with a Z18 Oyster Conductivity/Temperature meter. Microanalyses 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. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were carried out using SDT Q600 system under air at a heating rate of 10 °C/min. X-ray diffraction (XRD) patterns were recorded on a D/MAX-2500/PC X-ray diffractometer in the 2θ range 5-80° with a scanning rate 1°/min. Scanning electron micrograph (SEM) images were recorded with a Hitachi S-4300 field emission scanning electron microscope.

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

Preparation of [1](ClO₄)₂ₙ·(H₂O)₂ₙ. To a methanol (30 mL) solution of Cu(OAc)₂·H₂O (2.0 g, 10 mmol) were added 99% ethylenediamine (1.4 mL, 20 mmol), 1,2-bis(2-aminoethoxy)ethane (2.2 mL, 10 mmol), and 40% formaldehyde solution (4.8 mL, 60 mmol). The mixture was refluxed for *ca.* 15 h and then cooled to room temperature. The addition of HClO₄ (2.0 mL) and NaClO₄ (1.0 g) to the solution produces a red-purple solid. The product was collected by filtration, washed with methanol, and dried in air. It was recrystallized from hot acetonitrile-water (1:3). Yield: ~30%. *Anal.* Calc. for (C₁₄H₃₆N₆CuCl₂O₁₂)ₙ: C, 27.35; H, 5.24, N, 13.67%. Found: C, 27.29; H, 5.48; N, 13.44%. IR (Nujol mull, cm⁻¹): 3500 (ν_{O-H}, H₂O), 3237 (ν_{N-H}), 1640 (δH₂O, *br*), 1100 (ν_{Cl-O}, ClO₄).

Preparation of [Cu(H₂L⁵)](ClO₄)₄·H₂O. To a methanol (30 mL) solution of Cu(OAc)₂·H₂O (2.0 g, 10 mmol) were added 99% ethylenediamine (1.4 mL, 20 mmol), 1,2-bis(2-aminoethoxy)ethane (3.8 mL, 25 mmol), and 40% formaldehyde solution (4.8 mL, 60 mmol). The mixture was refluxed for *ca.* 15 h and then cooled to room temperature. After the addition of HClO₄ (2.0 mL) and NaClO₄ (1.0 g), the mixture was filtered to remove any solid. The filtrate was slowly evaporated at room temperature to form a red-purple solid. The crude product often contains small amount of by-product ([**1**](ClO₄)₂ₙ·(H₂O)₂ₙ) that is poorly soluble in water at room temperature. The pure product was obtained by fractional recrystallization of the crude product from 0.1 M HClO₄ aqueous solution. The product collected by filtration was washed with methanol and dried in air. Yield: ~10%. *Anal.* Calc. for C₂₀H₅₂N₈CuCl₄O₂₁: C, 25.39; H, 5.54, N, 11.84. Found: C, 25.37; H, 5.37; N, 11.72%. FAB-MS (*m/z*): 828.5 for [Cu(H₂L⁵) + 3ClO₄]⁺, 728.7 for [Cu(HL⁵) + 2ClO₄]⁺, 626.6 for [CuL⁵ + ClO₄]⁺. IR (Nujol mull, cm⁻¹): 3500 (ν_{O-H}, H₂O), 3251 (ν_{N-H}), 3200 (ν_{N-H}), 3168 (ν_{N-H}, *br*), 1605 (δNH₂), 1100 (ν_{Cl-O}, ClO₄).

Preparation of [2](ClO₄)₂ₙ·(H₂O)₂ₙ. To a methanol (30 mL) solution of Cu(OAc)₂·H₂O (2.0 g, 10 mmol) were added 99% ethylenediamine (1.4 mL, 20 mmol), 1,3-diaminopropane (0.9 mL, 10 mmol), and 40% formaldehyde solu-

tion (4.8 mL, 60 mmol). The mixture was refluxed for *ca.* 15 h and then cooled to room temperature. After the addition of HClO$_4$ (2.0 mL) and NaClO$_4$ (1.0 g), the mixture was slowly evaporated at room temperature to form a red-purple solid. The product was collected by filtration, washed with methanol, and dried in air. It was recrystallized from hot acetonitrile-water (1:1). Yield: ~20%. *Anal.* Calc. for (C$_{11}$H$_{30}$N$_6$CuCl$_2$O$_{10}$)$_n$: C, 24.43; H, 5.59, N, 15.54%. Found: C, 23.99; H, 5.31; N, 15.55%. IR (Nujol mull, cm^{-1}): 3500 (ν_{O-H}, H$_2$O), 1645 (δH$_2$O, *br*), 3240 (ν_{N-H}), 1100 (ν_{Cl-O}, ClO$_4$).

Preparation of [3](ClO$_4$)$_{2n}$·(H$_2$O)$_{2n}$. To a methanol (30 mL) solution of Cu(OAc)$_2$·H$_2$O (2.0 g, 10 mmol) were added 99% ethylenediamine (1.4 mL, 20 mmol), 1,6-diaminohexane (1.2 g, 10 mmol), and 40% formaldehyde solution (4.8 mL, 60 mmol). The mixture was refluxed for *ca.* 15 h and then cooled to room temperature. After the addition of HClO$_4$ (2.0 mL) and NaClO$_4$ (1.0 g), the mixture was slowly evaporated at room temperature to precipitate a red-purple solid. The product was collected by filtration, washed with methanol, and dried in air. It was recrystallized from hot acetonitrile-water (3:1). Yield: ~20%. *Anal.* Calc. for (C$_{14}$H$_{36}$N$_6$CuCl$_2$O$_{10}$)$_n$: C, 28.85; H, 6.22, N, 14.42%. Found: C, 29.25; H, 5.90; N, 14.39%. IR (Nujol mull, cm^{-1}): 3500 (ν_{O-H}, H$_2$O), 3240 (ν_{N-H}), 1640 (δH$_2$O, *br*), 1100 (ν_{Cl-O}, ClO$_4$).

Preparation of [Cu(H$_2$L^5)](PF$_6$)$_4$·H$_2$O, [1](PF$_6$)$_{2n}$·(H$_2$O)$_{2n}$, [2](PF$_6$)$_{2n}$·(H$_2$O)$_{2n}$, and [3](PF$_6$)$_{2n}$·(H$_2$O)$_{2n}$. To a warm acetonitrile solution (10 mL) of [Cu(H$_2$L^5)](ClO$_4$)$_4$·H$_2$O, [1](ClO$_4$)$_{2n}$·(H$_2$O)$_{2n}$, [2](ClO$_4$)$_{2n}$·(H$_2$O)$_{2n}$, or [3](ClO$_4$)$_{2n}$·(H$_2$O)$_{2n}$ (*ca.* 0.5 g) was added NH$_4$PF$_6$ (1.0 g). After filtering the mixture, water (10 mL) was added to the filtrate. The resulting solution was slowly evaporated at room temperature to precipitate a red-purple solid. The solid was collected by filtration, washed with cold water, and dried in air.

[Cu(H$_2$L^5)](PF$_6$)$_4$·2H$_2$O: *Anal.* Calc. for C$_{20}$H$_{52}$N$_8$CuF$_{24}$P$_4$O$_6$: C, 21.00; H, 4.58, N, 9.79. Found: C, 20.51; H, 4.58; N, 10.33%. IR (Nujol mull, cm^{-1}): 3200-3350 (ν_{N-H}, *br*), 1600 (δNH$_2$), 850 (ν_{P-F}, PF$_6$).

[1](PF$_6$)$_{2n}$·(H$_2$O)$_{2n}$: *Anal.* Calc. for C$_{14}$H$_{36}$N$_6$CuP$_2$F$_{12}$O$_4$: C, 23.82; H, 5.14, N, 11.90. Found: C, 23.74; H, 4.79; N, 11.79%. IR (Nujol mull, cm^{-1}): 3500 (ν_{O-H}, H$_2$O), 3280 (ν_{N-H}), 850 (ν_{P-F}, PF$_6$).

[2](PF$_6$)$_{2n}$·(H$_2$O)$_{2n}$: *Anal.* Calc. for C$_{11}$H$_{30}$N$_6$CuP$_2$F$_{12}$O$_2$: C, 20.91; H, 4.79, N, 13.30. Found: C, 20.93; H, 4.69; N, 13.43%. IR (Nujol mull, cm^{-1}): 3500 (ν_{O-H}, H$_2$O), 3275 (ν_{N-H}), 850 (ν_{P-F}, PF$_6$).

[3](PF$_6$)$_{2n}$·(H$_2$O)$_{2n}$: *Anal.* Calc. for C$_{14}$H$_{36}$N$_6$CuP$_2$F$_{12}$O$_2$: C, 25.64; H, 5.22, N, 12.81. Found: C, 25.99; H, 4.92; N, 11.73%. IR (Nujol mull, cm^{-1}): 3500 (ν_{O-H}, H$_2$O), 3273 (ν_{N-H}), 850 (ν_{P-F}, PF$_6$).

Results and Discussion

Synthesis. Both [1](ClO$_4$)$_{2n}$·(H$_2$O)$_{2n}$ and [Cu(H$_2$L^5)]-(ClO$_4$)$_4$·H$_2$O (H$_2$L^5 = a protonated form of L^5) can be prepared selectively by the one-pot reaction of ethylenediamine, 1,2-bis(2-aminoethoxy)ethane, and formaldehyde in

the presence of Cu^{2+} ion. The reaction of excess formaldehyde with the metal ion, ethylenediamine, and 1,2-bis(2-aminoethoxy)ethane in a 1:2:1 molar ratio, followed by the addition of HClO$_4$ and/or NaClO$_4$, produces [1](ClO$_4$)$_{2n}$·(H$_2$O)$_{2n}$ in high yield. On the other hand, [Cu(H$_2$L^5)](ClO$_4$)$_4$·H$_2$O bearing two *N*-(CH$_2$)$_2$O(CH$_2$)$_2$O(CH$_2$)$_2$NH$_3^+$ pendant arms can be prepared as the major product by the reaction of excess formaldehyde with the metal ion, ethylenediamine, and 1,2-bis(2-aminoethoxy)ethane in a 1:2:2.5 molar ratio. Both reactions often produce a mixture of [1](ClO$_4$)$_{2n}$·(H$_2$O)$_{2n}$ and [Cu(H$_2$L^5)](ClO$_4$)$_4$·H$_2$O. However, each complex can be isolated by fractional recrystallizations of the crude product from water, since the solubility of [Cu(H$_2$L^5)](ClO$_4$)$_4$·H$_2$O in water is much higher than that of [1](ClO$_4$)$_{2n}$·(H$_2$O)$_{2n}$. The poly(macrocyclic) complexes [2](ClO$_4$)$_{2n}$·(H$_2$O)$_{2n}$ and [3]-(ClO$_4$)$_{2n}$·(H$_2$O)$_{2n}$ were also prepared by a method similar to that for [1](ClO$_4$)$_{2n}$·(H$_2$O)$_{2n}$, except that 1,3-diaminopropane or 1,6-diaminohexane was reacted instead of 1,2-bis(2-aminoethoxy)ethane. The synthetic routes for the polymer complexes must be similar to those for the complexes of L^2 and L^3.[13,17] The present synthetic procedure is interesting because the formation and linking of the fully saturated macrocyclic subunits can be achieved by one-pot reaction involving simple starting materials.

Characterization of [Cu(H$_2$L^5)](ClO$_4$)$_4$·H$_2$O. The red-purple complex [Cu(H$_2$L^5)](ClO$_4$)$_4$·H$_2$O readily dissolves in water and various polar organic solvents, such as nitromethane and acetonitrile. It is extremely stable in the solid state and is inert against decomposition even in low pH; no apparent decomposition of the complex (1.0 × 10^{-3} M) was observed in 0.1 M HClO$_4$ aqueous solution in 2 h at room temperature. This behavior is quite similar to the reported behaviors of various other square-planar copper(II) complexes of 14-membered hexaaza macrocycles, such as [CuL^2]$^{2+}$.[13,14,17]

Unfortunately, we were unable to obtain single crystals of the complex suitable for X-ray crystallography. However, the formation of [Cu(H$_2$L^5)](ClO$_4$)$_4$·H$_2$O could be confirmed by its FAB mass spectrum as well as the elemental analysis and the infrared and electronic absorption spectra. The FAB mass spectrum of [Cu(H$_2$L^5)](ClO$_4$)$_4$·H$_2$O shows three groups of peaks at *m/z* 828.5 {[Cu(H$_2$L^1) + 3ClO$_4^-$]$^+$}, 728.7

Figure 1. FT-IR Spectra of [Cu(H$_2$L^5)](ClO$_4$)$_4$·H$_2$O (a), [1](ClO$_4$)$_{2n}$·(H$_2$O)$_{2n}$ (b), [2](ClO$_4$)$_{2n}$·(H$_2$O)$_{2n}$ (c), and [3](ClO$_4$)$_{2n}$·(H$_2$O)$_{2n}$ (d) measured in Nujol mull.

Table 1. Molar conductance and electronic absorption spectral data for the Copper(II) complexes[a]

Complex	Empirical formula	λ_{max}, nm (ε, $M^{-1}cm^{-1}$)[b]		Λ_M, $\Omega^{-1}cm^2mol^{-1}$ [b]
$[CuL^2](ClO_4)_4 \cdot H_2O$ [c]		486(73)	495(70)[d]	240[e]
$[Cu(H_2L^5)](ClO_4)_4 \cdot H_2O$		490(75)	503(80)[d]	460[e]
		510(80)[e]	490[f]	
$[1](ClO_4)_{2n} \cdot (H_2O)_{2n}$	$C_{14}H_{36}N_6CuCl_2O_{12}$	493(75)	502(85)[d]	220[e]
		511(80)[e]	500[f]	
$[2](ClO_4)_{2n} \cdot (H_2O)_{2n}$	$C_{11}H_{30}N_6CuCl_2O_{10}$	498(80)	497(90)[d]	215[e]
		500(77)[e]	495[f]	
$[3](ClO_4)_{2n} \cdot (H_2O)_{2n}$	$C_{14}H_{36}N_6CuCl_2O_{10}$	500(84)	495(70)[d]	240[d]
		490[f]		

[a]Measured in nitromethane at 25 °C unless otherwise specied. [b]Values per empirical formula. [c]Ref. 13. [d]In acetonitrile. [e]In water. [f]In Nujol mull.

$\{[Cu(HL^1) + 2ClO_4^-]^+\}$, and 626.6 $\{[CuL^1 + ClO_4^-]^+\}$. In the infrared spectrum (Fig. 1(a)) of the complex, several peaks corresponding to ν_{N-H} of the coordinated secondary amino groups and the pendant ammonium groups are observed at 3300-3100 cm^{-1}. A peak corresponding to $\delta(NH_2)$ of the pendant primary amino groups was also observed at *ca.* 1610 cm^{-1}. The molar conductance value (460 $\Omega^{-1}mol^{-1}cm^2$) of the complex measured in water indicates that the complex is a 1:4 electrolyte. The electronic absorption spectrum (Table 1) of $[Cu(H_2L^5)](ClO_4)_4 \cdot H_2O$ measured in nitromethane shows a *d-d* transition band at 490 nm ($\varepsilon = 75$ $M^{-1}cm^{-1}$), which is quite similar to that measured in Nujol mull. The wavelength and/or molar absorption coefficient are comparable with those of $[CuL^2]^{2+}$ and other related copper(II) complexes of 14-membered hexaaza macrocyclic ligands,[13,14] indicating that the complex has square-planar coordination geometry with a 5-6-5-6 chelate ring sequence; the functional pendant arms are not involved in coordination. The wavelengths measured in the coordinating solvents, such as acetonitrile and water, are longer than that in nitromethane or Nujol mull. This is attributed to the coordination of the solvent molecule(s).

Characterization of the Poly(Macrocyclic) Complexes. The polynuclear poly(macrocyclic) complexes $[1](ClO_4)_{2n} \cdot (H_2O)_{2n}$, $[2](ClO_4)_{2n} \cdot (H_2O)_{2n}$, and $[3](ClO_4)_{2n} \cdot (H_2O)_{2n}$ are soluble in various polar organic solvents, such as nitromethane and acetonitrile. Both $[1](ClO_4)_{2n} \cdot (H_2O)_{2n}$ and $[2](ClO_4)_{2n} \cdot (H_2O)_{2n}$ are also soluble in water. All of them are extremely stable in the solid state and in various solvents. Elemental analysis values (*see* Experimental) of the polynuclear complexes are in good agreement with the theoretical values. In the FAB mass spectra of the polymer complexes measured up to *m/z* 2000, no peak corresponding to their molecular ions was observed. This indicates that their molecular weights are fairly high. However, all our efforts to measure the molecular weights by using various other methods, such as gel permeation chromatography (GPC) and matrix-assisted laser desorption ionization mass spectrometer (MALDI-TOP), were also unsuccessful. This failure may be ascribed to the fact that the complexes are highly charged cationic polymers.

The FT-IR spectra of $[1](ClO_4)_{2n} \cdot (H_2O)_{2n}$, $[2](ClO_4)_{2n} \cdot (H_2O)_{2n}$, and $[3](ClO_4)_{2n} \cdot (H_2O)_{2n}$ were found to be quite similar to that of $[CuL^2](ClO_4)_2$.[13] The spectrum (Fig. 1(b)) of $[1](ClO_4)_{2n} \cdot (H_2O)_{2n}$ shows a sharp peak corresponding to ν_{N-H} of the coordinated secondary amino groups at 3237 cm^{-1}. The spectrum also shows peaks corresponding to ClO_4^- anions and lattice water molecules at *ca.* 1100 and 3500 cm^{-1}, respectively. In the spectra of $[2](ClO_4)_{2n} \cdot (H_2O)_{2n}$ (Fig. 1(c)) and $[3](ClO_4)_{2n} \cdot (H_2O)_{2n}$ (Fig. 1(d)), a sharp peak corresponding to ν_{N-H} of the secondary amino groups is observed at *ca.* 3240 cm^{-1}. In all cases, no peak assignable to primary amino groups was observed. The FT-IR spectra strongly support the chain structure of the complexes. The electronic absorption spectra (Table 1) of the polymer complexes measured in various solvents show a *d-d* transition band around 493-511 nm. The wavelengths are quite similar to those of $[CuL^2](ClO_4)_4$ and $[Cu(H_2L^5)](ClO_4)_4 \cdot H_2O$. Furthermore, the molar absorption coefficients (75-90 $M^{-1}cm^{-1}$) per each unit (empirical formula) of the polymer complexes are also comparable with those of $[CuL^2](ClO_4)_4$ and $[Cu(H_2L^5)](ClO_4)_4 \cdot H_2O$, indicating that each macrocyclic unit of the polymer complexes also has square-planar coordination geometry with a 5-6-5-6 chelate ring sequence. The molar conductance values per empirical formula of the poly(macrocyclic) complexes were calculated to be 215-240 $\Omega^{-1}mol^{-1}cm^2$ in water or water-acetonitrile, showing that they are 1:2n electrolytes. All of the polynuclear complexes were found to be quite inert against decomposition even in concentrated strong acid solutions; electronic absorption spectra of the complexes (1.0×10^{-3} M) measured in 0.1 M $HClO_4$ aqueous solutions show that only less than 5% of them are decomposed in 24 h at room temperature. This behavior is quite similar to those for $[CuL^2]^{2+}$ and $[Cu(H_2L^5)]^{4+}$. The spectral and chemical properties of the polymer complexes described above as well as the elemental analyzes clearly support the suggestion that they, like $[CuL^2]^{2+}$ and $[Cu(H_2L^5)]^{4+}$, contain fully saturated 14-membered hexaaza macrocyclic units (1,3,6,8,10,13-hexaazacyclotetradecane). It is obvious that the polymer complexes consist of one highly charged poly(macrocyclic) cation ($[1]^{2n+}$, $[2]^{2n+}$, or $[3]^{2n+}$), in which each macrocyclic unit has square-planar coordination geometry, and uncoordinated ClO_4^- ions. Each complex ionizes into the cation and anions when it dissolves in solvents.

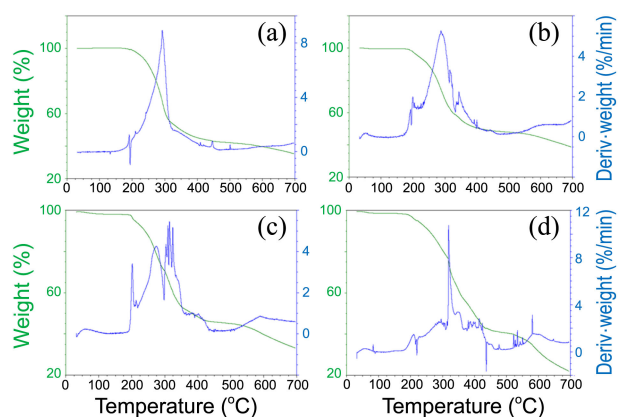The thermal behaviors of the polymer complexes were

Figure 2. TGA and DTGA curves of $[Cu(H_2L^5)](PF_6)_4 \cdot H_2O$ (a), $[\mathbf{1}]$ $(PF_6)_{2n} \cdot (H_2O)_{2n}$ (b), $[\mathbf{2}](PF_6)_{2n} \cdot (H_2O)_{2n}$ (c), and $[\mathbf{3}](PF_6)_{2n} \cdot (H_2O)_{2n}$ (d).

studied by using thermogravimetric techniques in the range of 30-700 °C. The TGA curve (Fig. 2(b)) of $[\mathbf{1}](PF_6)_{2n} \cdot (H_2O)_{2n}$ shows a multi-step decomposition of the complex. Although the curve of $[\mathbf{1}](PF_6)_{2n} \cdot (H_2O)_{2n}$ is similar to that of $[Cu(H_2L^5)]$-$(PF_6)_4 \cdot 2H_2O$ (Fig. 2(a)), its decomposition process is some-what more complicated. The weight loss below 195 °C can be attributed to the evaporation of the lattice water mole-cules. Initial thermal decomposition temperature (IDT) of the complex is found to be *ca.* 195 °C. The second weight loss about 50% occurs between 195 and 370 °C; the temperature of maximum rate decomposition (T_{max}) is *ca.* 287 °C. This is corresponding to the departure of the ligand (47%). Continued heating to 700 °C gives a further gradual weight loss. The identification of the decomposition products has not been attempted. However, relatively high fraction (*ca.* 35%) of residue at 700 °C may be associated with the presence of the PF_6^- anion. The curves of $[\mathbf{2}](PF_6)_{2n} \cdot (H_2O)_{2n}$ (Fig. 2(c)) and $[\mathbf{3}](PF_6)_{2n} \cdot (H_2O)_{2n}$ (Fig. 2(d)) are not quite different from that of $[\mathbf{1}](PF_6)_{2n} \cdot (H_2O)_{2n}$, though their de-composition processes are more complicated; the second weight loss of $[\mathbf{2}](PF_6)_{2n} \cdot (H_2O)_{2n}$ (*ca.* 40%) or $[\mathbf{3}](PF_6)_{2n} \cdot (H_2O)_{2n}$ (*ca.* 42%) also corresponds to the departure of the ligand part of each complex (38 or 42%, respectively).

In the DSC curve for $[\mathbf{1}](PF_6)_{2n} \cdot (H_2O)_{2n}$, the glass transi-tion temperatures (T_g) were found to be 198, 270, 349, 448, 550, and 600 °C. The DSC curves for $[\mathbf{2}](PF_6)_{2n} \cdot (H_2O)_{2n}$ and $[\mathbf{3}](PF_6)_{2n} \cdot (H_2O)_{2n}$ are different from that for $[\mathbf{1}](PF_6)_{2n} \cdot (H_2O)_{2n}$. For example, the lowest T_g values of the former complexes are higher than that for the latter (Table 2). The differences in transition may be due to the crystallinity of the polymer complexes and the nature of the bridging groups.

The XRD pattern (Fig. 3(a)) of $[Cu(H_2L^5)](ClO_4)_4 \cdot H_2O$ shows two intense sharp peaks ($2\theta = 11$ and $22°$) and several

Table 2. Glass transition temperature (T_g) the Copper(II) complexes

Complex	Temp. (°C)
$[Cu(H_2L^5)](PF_6)_4 \cdot H_2O$	199 306 325 452
$[\mathbf{1}](PF_6)_{2n} \cdot (H_2O)_{2n}$	198 270 349 448 550 600
$[\mathbf{2}](PF_6)_{2n} \cdot (H_2O)_{2n}$	219 270 365 427 589
$[\mathbf{3}](PF_6)_{2n} \cdot (H_2O)_{2n}$	220 295 420 459 587

Figure 3. XRD patterns for $[Cu(H_2L^5)](ClO_4)_4 \cdot H_2O$ (a), $[\mathbf{1}](ClO_4)_{2n} \cdot (H_2O)_{2n}$ (b), $[\mathbf{2}](ClO_4)_{2n} \cdot (H_2O)_{2n}$ (c), and $[\mathbf{3}](ClO_4)_{2n} \cdot (H_2O)_{2n}$ (d).

Figure 4. Scanning Electron Micrographs for $[Cu(H_2L^5)](ClO_4)_4 \cdot$ H_2O (× 3000) (a), $[\mathbf{1}](ClO_4)_{2n} \cdot (H_2O)_{2n}$ (× 5000) (b), $[\mathbf{2}](ClO_4)_{2n} \cdot$ $(H_2O)_{2n}$ (× 5000) (c), and $[\mathbf{3}](ClO_4)_{2n} \cdot (H_2O)_{2n}$ (× 5000) (d).

relatively weak sharp peaks, indicating the crystalline nature of the mononuclear complex.[5] The patterns of the polymer complexes exhibit much broader peaks. The pattern (Fig. 3(c)) of $[\mathbf{2}](ClO_4)_{2n} \cdot (H_2O)_{2n}$ shows relatively sharp peaks at $2\theta = 13, 17, 23, 26,$ and $29°$. In the patterns of $[\mathbf{1}](ClO_4)_{2n} \cdot$ $(H_2O)_{2n}$ (Fig. 3(b)) and $[\mathbf{3}](ClO_4)_{2n} \cdot (H_2O)_{2n}$ (Fig. 3(d)), the peaks have shoulders and are somewhat broader than those of $[\mathbf{2}](ClO_4)_{2n} \cdot (H_2O)_{2n}$. This strongly indicates that $[\mathbf{1}](ClO_4)_{2n} \cdot (H_2O)_{2n}$ and $[\mathbf{3}](ClO_4)_{2n} \cdot (H_2O)_{2n}$ containing longer bridging chains are more amorphous than $[\mathbf{2}](ClO_4)_{2n} \cdot (H_2O)_{2n}$.

The SEM images of the complexes are shown in Figure 4. The particles of the polymer complexes are agglomerated (Fig. 4(b)-4(d)), and their shapes are distinctly different from that of $[Cu(H_2L^5)](ClO_4)_4 \cdot H_2O$ (Fig. 4(a)). It is also seen that $[\mathbf{1}](ClO_4)_{2n} \cdot (H_2O)_{2n}$ and $[\mathbf{3}](ClO_4)_{2n} \cdot (H_2O)_{2n}$ are more amorphous than $[\mathbf{2}](ClO_4)_{2n} \cdot (H_2O)_{2n}$.

Concluding Remarks

This work shows that various poly(14-membered hexaaza

macrocyclic) copper(II) complexes, such as [**1**](ClO$_4$)$_{2n}$·(H$_2$O)$_{2n}$, [**2**](ClO$_4$)$_{2n}$·(H$_2$O)$_{2n}$, and [**3**](ClO$_4$)$_{2n}$·(H$_2$O)$_{2n}$, can be prepared by the one-pot reaction involving two different amines and formaldehyde. To our knowledge, they are rare examples of poly(macrocyclic) complexes that have been prepared by the simple metal-template condensation involving amines and formaldehyde. Interestingly, the polymer complexes possess cationic charges along the polymer chains and are quite inert against decomposition even in concentrated strong acid solutions. Furthermore, [**1**](ClO$_4$)$_{2n}$·(H$_2$O)$_{2n}$ and [**2**](ClO$_4$)$_{2n}$·(H$_2$O)$_{2n}$ are soluble in water. The crystallinity of the complexes as well as the solubility in water is influenced by the nature of the bridging groups that link the macro-cyclic units.

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