Polyaza Non-Macrocyclic and Bis(macrocyclic) Complexes

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Template Synthesis and Characterization of Copper(II) Complexes of a Polyaza Non-Macrocyclic or a Bis(macrocyclic) Ligand

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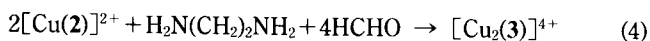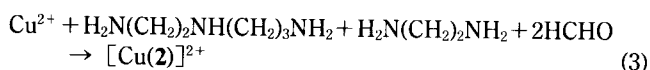[†]*Department of Chemistry Education, Taegu University, Kyungsan 713-714, Korea*
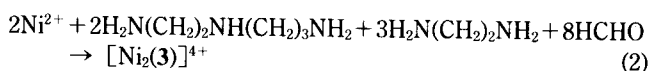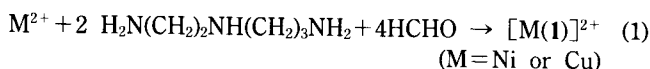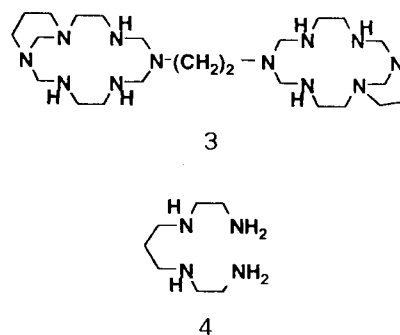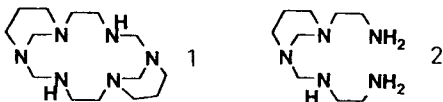
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New copper(II) complex of the pentaaza non-macrocyclic ligand 1-(2-aminoethyl)-3-(N-{2-aminoethyl}aminomethyl)-1,3-diazacyclohexane (2) and a dinuclear copper(II) compex of the bis(macrocyclic) ligand 3, in which two 1,5,8,10,12,15-hexaazabicyclo[11.3.1^{1,5}]heptadecane subunits are linked together by an ethylene chain through the uncoordinated nitrogen (N^{10}) atoms, have been prepared selectively by the reaction of the metal ion, 1,4,8-triazaoctane, ethylenediamine, and formaldehyde. The dinuclear complex [Cu$_2$(3)]$^{4+}$ has been also prepared by the reaction of [Cu(2)]$^{2+}$ with ethylenediamine and formaldehyde. The reaction products largely depend on the molar ratio of the reactants employed. The mononuclear complex or each macrocyclic subunit of the dinuclear complex contains one 1,3-diazacyclohexane ring and has a square-planar geometry with a 5-6-5 or 5-6-5-6 chelate ring sequence. In acidic solution, the copper(II) complex of **2** dissociates more slowly than those of other related non-cyclic polyamines.

Introduction

Metal template condensation of coordinated amines with formaldehyde is useful for the syntheses of saturated polyaza macrocyclic complexes containing N-CH$_2$-N linkages.[1~11] For example, the nickel(II) and copper(II) complexes of the hexaaza macrocyclic ligand **1** have been synthesized by the reaction as described in eq. (1).[3,8] Some dinuclear complexes of bis(macrocyclic) ligands have been also prepared by one-pot metal template condensation reactions of amines and formaldehyde.[12~16] Recently, the dinuclear nickel(II) complex of bis(macrocyclic) ligand **3** was prepared in our group by the one-pot reaction (eq. (2)) of formaldehyde with 1,4,8-triazaoctane and ethylenediamine in the presence of Ni(II) ion.[13] However, transition metal complexes of the non-macrocyclic ligand **2** was not prepared. Until now, the synthesis of non-macrocyclic complexes containing N-CH$_2$-N linkages is rarely reported.[17,18]

In this work, the syntheses of a new copper(II) complex of the pentaaza non-macrocyclic ligand **2** containing one 1,3-diazacyclohexane ring and a dinuclear copper(II) complex of the bis(macrocyclic) ligand **3** were attempted from the metal template condensation of 1,4,8-triazaoctane, ethylenediamine, and formaldehyde. The major aim in this study is to investigate the effects of metal ion on the reaction and the properties of the non-macrocyclic copper(II) complex. Interestingly, it was found that the products obtained from the reaction are strongly affected by the molar ratio of the reactants. The non-macrocyclic copper(II) complex thus formed dissociates in acidic solutions more slowly than copper (II) complexes of **4** and other related non-cyclic tetraamines. Syntheses, spectra, and chemical properties of the copper(II) complexes of **2** as well as the dinuclear copper(II) complex of **3** are described.

3

4

$$M^{2+} + 2\ H_2N(CH_2)_2NH(CH_2)_3NH_2 + 4HCHO \rightarrow [M(1)]^{2+} \quad (1)$$
$$(M = Ni\ or\ Cu)$$

$$2Ni^{2+} + 2H_2N(CH_2)_2NH(CH_2)_3NH_2 + 3H_2N(CH_2)_2NH_2 + 8HCHO \rightarrow [Ni_2(3)]^{4+} \quad (2)$$

$$Cu^{2+} + H_2N(CH_2)_2NH(CH_2)_3NH_2 + H_2N(CH_2)_2NH_2 + 2HCHO \rightarrow [Cu(2)]^{2+} \quad (3)$$

$$2[Cu(2)]^{2+} + H_2N(CH_2)_2NH_2 + 4HCHO \rightarrow [Cu_2(3)]^{4+} \quad (4)$$

Experimental

Measurements. Infrared spectra were obtained with a Shimadzu IR-440 spectrophotometer and electronic absorption spectra with Shimadzu UV-160 spectrophotometer. Conductance measurements were made using a Metrohm Herisau Conductometer E518. Elemental analyses and FAB mass spectra were performed at the Korea Basic Science Institute, Seoul, Korea. Cyclic voltammograms were obtained using a Yanaco Voltammetric Analyzer p-1000 equipped with a FG-121B function generator and a Watanabe X-Y recorder. The working and reference electrode were platinum and SCE, respectively. The measurements were conducted in oxygen free 0.1 M (n-Bu)$_4$NClO$_4$ acetonitrile solutions at 20 ℃.

The kinetics of dissociation rates of the copper(II) comple-

1

2

xes in acidic solutions were studied by the spectrophotometric method. Pseudo first order conditions were maintained by reacting 1.5×10^{-3} M of the complex and at least 60-fold excess acid ($[HClO_4] = 0.1\text{-}1.5$ M). $NaClO_4$ was used to maintain constant ionic strength at $\mu = 2.5$ M in all solutions. The temperature of the sample solutions was maintained within ± 0.1 °C by using a thermostated cell holder connected to a Haake D_3 circulating bath. Each reaction was monitored using the absorption decrease at 535 ($[Cu(2)]^{2+}$) or 512 nm ($[Cu_2(3)]^{4+}$).

Caution!. Perchlorate salts of metal complexes with organic ligands are explosive and should be handled with great caution.

Synthesis of $[Cu(2)](ClO_4)_2$. To a methanol (20 mL) suspension of $Cu(OAc)_2 \cdot H_2O$ (3.0 g, 15 mmol) was added 97% 1,4,8-triazaoctane (2.0 mL, 15 mmol), 99% ethylenediamine (2.0 mL, 30 mmol), and paraformaldehyde (1.4 g, 45 mmol). The mixture was heated at reflux for 12 h and then cooled to room temperature. An exccess amount of sodium perchlorate was added to the blue-purple solution, and the resulting solution was stored in a refrigerator until purple solids were precipitated. The solids collected by filtration contain a small amount (<5%) of red-purple $[Cu_2(3)](ClO_4)_4$ as a by-product. The pure product was obtained by fractional recrystallizations of the product from hot water. Yield: ~50 %. Anal. Calcd for $C_9H_{23}N_5CuCl_2O_8$: C, 23.30; H, 5.00, N, 15.10 %. Found: C, 23.20; H, 5.24; N, 14.96%. FAB Mass (m/z): 363 ($[M-ClO_4]^+$), 264 ($[M-2ClO_4-H]^+$). IR (Nujol mull, cm^{-1}): 3340 (vN-H), 3280 (vN-H), 3220 (vN-H), 3160 (vN-H), and 1610 (δNH_2).

Synthesis of $[Cu_2(3)](ClO_4)_4$. Method I. To a water-methanol (1 : 1) solution (20 mL) of $[Cu(2)](ClO_4)_2$ (2.0 g, 4.4 mmol) was added 99% ethylenediamine (0.24 mL, 3.4 mmol) and paraformaldehyde (1.2 g, 12.8 mmol). The mixture was heated at reflux for 20 h and then cooled to room temperature. After an excess of perchloric acid was added, the resulting mixture was stored in a refrigerator. The red-purple solid formed was filtered, washed with methanol, and recrystallized from hot water-acetonitrile (3 : 1) mixture. Yield: ~30%. Anal. Calcd for $C_{24}H_{54}N_{12}Cu_2Cl_4O_{16}$: C, 27.83; H, 5.26; N, 16.23%. Found: C, 28.02; H, 5.23; N, 16.20%. FAB Mass (m/z): 935 ($[M-ClO_4]^+$), 836 ($[M-2ClO_4-H]^+$), 735 ($[M-3ClO_4-2H]^+$). IR (Nujol mull, cm^{-1}): 3240 (vN-H).

Method II. The dinuclear copper(II) complex was also synthesized by the one-pot condensation of $Cu(OAc)_2 \cdot H_2O$ (6.0 g, 30 mmol), 97% 1,4,8-triazaoctane (4.2 mL, 24 mmol), 99% ethylenediamine (4.1 mL, 48 mmol), and paraformaldehyde (4.0 g). The experimental methods for the preparation and isolation of the complex were quite similar to those for the dinuclear nickel(II) complex $[Ni_2(3)](ClO_4)_4$,[13] except that $CuCl_2 \cdot H_2O$ was reacted instead of $NiCl_2 \cdot 6H_2O$. Yield: ~30%. The elemental analyses data and the FAB mass, infrared, and electronic spectra of the product were identical with those of the dinuclear complex obtained from the above method.

Results and Discussion

Synthesis. The products obtained by the reaction of copper(II) ion, 1,4,8-triazaoctane, ethylenediamine, and formaldehyde were largely affected by the molar ratio of the reac-

tants. The reaction of a 1 : 1 : 1 : 2 molar mixture of the reactants, followed by the addition of an excess sodium perchlorate, yields a mixture of the non-macrocyclic complex $[Cu(2)](ClO_4)_2$ and relatively small amount of $[Cu(1)](ClO_4)_2$ and/or $[Cu_2(3)](ClO_4)_4$ as by-products. However, the proportion of the by-products in the crude product can be readily reduced to less than 5% by employing a 1 : 1 : 2 : 3 molar ratio of the reactants (see Experimental section). The non-macrocyclic complex was easily isolated by fractional recrystallizations of the crude product from hot water. When a 2 : 1.6 : 3.2 : 8 molar mixture of the reactants was reacted, the major product was the dinuclear bis(macrocyclic) complex $[Cu_2(3)](ClO_4)_4$, which can be easily isolated (see Experimental section). The dinuclear complex was also synthesized by the reaction (eq. (4)) of excess formaldehyde with a 2 : 1 molar mixture of $[Cu(2)]^{2+}$ and ethylenediamine. The routes to give the copper(II) complexes of **2** and **3** may be similar to those reported for copper(II) and nickel(II) complexes of other related macrocyclic and bis(macrocyclic) ligands.[1~13] Strangely, the reaction of $[Cu(2)]^{2+}$ with formaldehyde in the presence or absence of 1,4,8-triazaoctane produced the macrocyclic complex $[Cu(1)]^{2+}$, together with other uncharacterized species.

Somewhat unexpectedly, we could not isolate nickel(II) complex of **2** as a solid from the reaction similar to that for $[Cu(2)]^{2+}$.

Spectra and Properties. The non-macrocyclic complex $[Cu(2)](ClO_4)_2$ and the bis(macrocyclic) complex $[Cu_2(3)]$ $(ClO_4)_4$ are soluble in polar solvents such as water, acetonitrile, and nitromethane. However, the solubility of the bis(macrocyclic) complex in each solvent is somewhat lower than that of the non-macrocyclic complex.

The formulation of new copper(II) complexes can be established by their fast atom bombardment (FAB) mass spectra,[15,19,20] together with elemental analyses. Although peaks of molecular ions of the copper(II) complexes are not observed in the FAB mass spectra, the observed fragments are consistent with the loss of perchlorate groups from the molecular ions. In the spectrum of $[Cu(2)](ClO_4)_2$ ($M^+ = 463$), the two groups of peaks due to the fragments formed by the stepwise liberations of the perchlorates were observed at m/z 363 ($[M-ClO_4]^+$) and 264 ($[M-2ClO_4-H]^+$). The spectrum of $[Cu_2(3)](ClO_4)_4$ ($M^+ = 1035$) showed three groups of peaks at m/z 935, 836, and 735 corresponding to the fragments $[M-ClO_4]^+$, $[M-2ClO_4-H]^+$, and $[M-3ClO_4-2H]^+$, respectively. The infrared spectrum of $[Cu(2)](ClO_4)_2$ shows strong absorptions at 3340, 3280, 3220, and 3160 cm^{-1}, which is attributed to N-H stretching vibrations of the coordinated secondary and primary amino groups. One strong peak at 1610 cm^{-1} is assigned to N-H bending of the primary amino groups. In the spectrum of $[Cu_2(3)](ClO_4)_4$, one peak at 3240 cm^{-1} is assigned to vN-H of the coordinated secondary amino groups.

The electronic absorption spectra and molar conductance data of the complexes are listed in Table 1. The values of molar conductance of $[Cu(2)](ClO_4)_2$ (2.0×10^{-3} M) measured in various solvents indicate that the complex is a 1 : 2 electrolyte. The value of $[Cu_2(3)](ClO_4)_4$ measured in each solution corresponds to a 1 : 4 electrolyte. Electronic absorption spectrum of $[Cu(2)](ClO_4)_2$ measured in nitromethane shows a single *d-d* transition band at 523 nm ($\varepsilon = 79$ M^{-1} cm^{-1}).

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Table 1. Electronic Spectra and Molar Conductance Data of the Copper(II) Complexes at 20 ℃

Complex	λ_{max}, nm (ε, $M^{-1}cm^{-1}$)			Λ_M, $\Omega^{-1}cm^2mol^{-1}$	
	$MeNO_2$	H_2O	MeCN	H_2O	MeCN
[Cu(1)](ClO$_4$)$_2$^{a}	505(122)	529(142)			
[Cu(2)](ClO$_4$)$_2$	523(79)	535(72)	535(70)	245	268
[Cu$_2$(3)](ClO$_4$)$_4$	486(182)	512(213)	505(220)	435	454
[Cu(4)](ClO$_4$)$_2$		526^b			

^{a}Ref. 8. ^{b}Ref. 31.
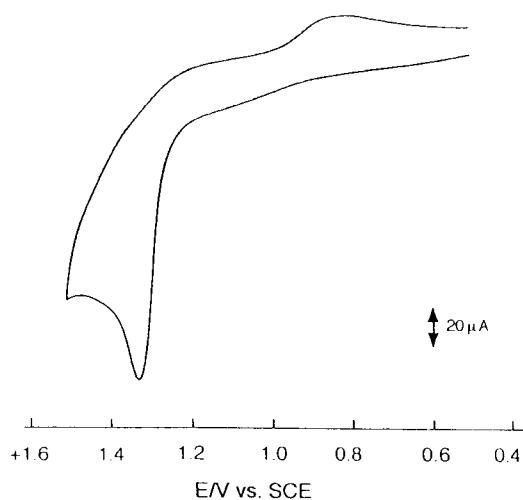
Figure 1. Cyclic Voltammogram of [Cu(2)](ClO$_4$)$_2$ in MeCN (0.1 M (n-Bu)$_4$NClO$_4$) at 20 ℃.

The wavelength and the molar absorption coefficient are similar to those of the square-planar copper(II) complexes of **4** and other related non-macrocyclic tetradentate ligands,[21~23] indicating that the complex has a square-planar geometry with a 5-6-5 chelate ring sequence. The spectrum of [Cu$_2$(3)] (ClO$_4$)$_4$ measured in nitromethane solution shows the d-d transition band at 486 nm (ε=182 $M^{-1}cm^{-1}$). This means that each metal ion of the complex is in a square-planar Cu(II)-N$_4$ environment.[1,8,12,15,23] However, the wavelength for [Cu$_2$(3)]$^{4+}$ is *ca.* 20 and 35 nm shorter than those for [Cu (1)]$^{2+}$ and [Cu(2)]$^{2+}$, respectively. The stronger ligand field strength of **3**, compared to that of **1**, parallels with the general observation that the secondary nitrogen donors of a macrocyclic complex result in shorter M-N (M=metal atom) bond distance and stronger ligand field strength than the tertiary nitrogen donors.[3~8,24~27] The occurrence of the band at a longer wavelength for [Cu(2)]$^{2+}$, compared to those for [Cu(1)]$^{2+}$ and [Cu$_2$(3)]$^{4+}$, is attributed to the weaker ligand field of the non-macrocyclic ligand. The wavelengths of the d-d bands of the copper(II) complexes measured in coordinating solvents such as water and acetonitrile are somewhat longer than those in nitromethane. This is attributed to the axial coordination of the solvent molecules.[28]

The cyclic voltammogram (Figure 1) of [Cu$_2$(3)](ClO$_4$)$_4$ measured in 0.1 M (n-Bu)$_4$NClO$_4$ acetonitrile solution showed one irreversible peak centered at +1.34 V *vs.* SCE at 20 ℃ corresponding to a Cu(II)/Cu(III) process. It is likely that each metal ion releases one electron at the same poten-

tials.[12~14]

Solution Behaviors. The copper(II) complexes [Cu(2)] (ClO$_4$)$_2$ and [Cu$_2$(3)](ClO$_4$)$_4$ are extremely stable in the solid states. The dinuclear complex is relatively stable even in concentrated acidic solutions; electronic spectra of [Cu$_2$(3)]$^{4+}$ (1.5×10^{-3} M) in 1.0 M HClO$_4$ solution indicated that less than 5% of the complex was decomposed in 15 h at 25 ℃. This behavior is similar to those for other square-planar copper(II) complexes of 14-membered polyaza macrocyclic and bis(macrocyclic) ligands.[1,8,12~14] However, the complex of **2** is unstable under acidic conditions; the dissociation reaction of the complex was found to proceed to completion within 3 min under the similar condition. The rapid dissociation of [Cu(2)]$^{2+}$, in contrast to the bis(macrocyclic) complex, can be attributed to the greater flexibility of the non-macrocyclic ligand. The kinetics of dissociation reaction of [Cu(2)]$^{2+}$ were studied in 0.1-1.5 M HClO$_4$ aqueous solutions at 25 ℃ to see the effect of ligand structure on the reaction rate. The pseudo first-order rate constant (k_{obs}) of the complex dissolved in 0.1 M HClO$_4$ solution is 3.6×10^{-2} s^{-1}. Interestingly, the reaction rate is nearly independent on the concentration of the acid (0.1-2.0 M); the value of the k_{obs} measured in 1.0 or 1.5 M HClO$_4$ solution is 3.5×10^{-2} s^{-1}. This result is different from that reported for [Cu(4)]$^{2+}$.[29] In the case for the complex of **4**, the dissociation rate is steadily increased as the concentration of the acid increases.[29] Furthermore, the reaction rate of [Cu(2)]$^{2+}$ is much slower than that of [Cu(4)]$^{2+}$ (k_{obs}=0.16 s^{-1} in 0.1 M HNO$_3$ solution at 25 ℃)[29] under the similar condition. The reasons for the differences in the kinetic behaviors between the complexes of **2** and **4** are not clearly understood at this point. However, the slower dissociation of [Cu(2)]$^{2+}$, compared to [Cu(4)]$^{2+}$, may be related to the more rigid structure of the ligand containing one 1,3-diazacyclohexane ring.

In organic compounds, the diaminomethane group (R$_2$N-CH$_2$-NR$_2$) is known to be unstable unless both of the nitrogen atoms are tertiary.[17,30] In the complexes of **2** and **3**, each diaminomethane linkage containing one secondary nitrogen atom is stabilized by the coordination of the secondary nitrogen to the metal ion.[1,17] Therefore, it is expected that the protonated form of free ligand 2 must be unstable and is decomposed to several fragments. This was confirmed by the the the electronic spectrum of the blue neutral or basic solution (*ca.* pH 8-11), which was obtained by the addition of NaOH to 1.0 M HClO4 solution of [Cu(2)](ClO$_4$)$_2$; the spectrum of the blue solution exhibited the d-d transition band near 580 nm, which is *ca.* 50 nm longer than that observed for [Cu(2)]$^{2+}$. However, the solution slowly turned purple at an elevated temperature (*ca.* 40 ℃) and the electronic spectrum obtained after *ca.* 24 h was nearly identical with that of [Cu(2)]$^{2+}$. Furthermore, the evaporation of the resulting solution reproduced the purple solid [Cu(2)](ClO$_4$)$_2$.

Summary. The copper(II) complexes of the non-macrocycle **2** and bis(macrocycle) **3** were prepared selectively by the reaction of the metal ion, 1,4,8-triazaoctane, ethylenediamine, and formaldehyde in different molar ratios. The dissociation rate of [Cu(2)]$^{2+}$ in HClO$_4$ solution is much slower than that of [Cu(4)]$^{2+}$.

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Formation of Tetra-Chlorinated Dibenzo-p-dioxins and Their Thermal Decomposition Products from Pyrolysis Reactions of Tri-Chlorophenates

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Tetra-chlorodibenzo-p-dioxins (tetra-CDDs) were prepared by microscale pyrolysis of trichlorophenates. During the pyrolysis reaction, tri-, di-, and mono-CDDs were also formed by the thermolysis of tetra-CDDs. The dechlorination pathways of tetra-CDDs were suggested for this reaction. The identification of these products was performed with capillary column gas chromatography-mass spectrometry.

Introduction

Chlorophenols can be precursors in the formation of polychlorinated dibenzo-p-dioxins (PCDDs) during the industrial production processes. Tetra-chlorinated dibenzo-p-dioxins (tetra-CDDs) usually exist as impurities in technical chlorophenols and in other chloro compounds.[1,2] In particular, 2,3,7,8-tetra-CDD is formed as a byproduct[3] during the high temperature hydrolysis of tetrachlorobenzene to 2,4,5-trichlorophenoxy acid. In addition, tetra-CDDs are also found in emit-