A hint the possibility of ZnO formation in the alpha cage. Since the size and number of beta cage are same in both zeolite Y and A, they would lead to the same size of ZnO cluster. Then it is difficult to explain the above experimental observation without guessing the ZnO formation in the alpha cage. Therefore, we expect some Zn vapor absorption, which would lead to ZnO formation in the alpha cage of zeolites.

Further studies are in progress to confirm the existence of nano clusters in zeolite and to investigate the nature of the cluster. We are also studying the size and configuration of ZnO nano clusters in zeolites by theoretical approach. We will continue to investigate the electronic properties of ZnO nano interfaces, once we secure the uniform ZnO cluster distribution in zeolite pores.

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Synthesis of Copper(II) Complexes of Pentaamine Ligands Containing One 1,3-Diazacyclohexane Ring

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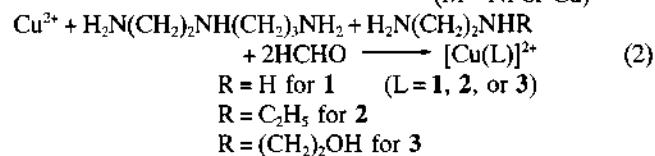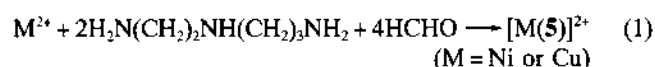*Department of Chemistry, Taegu University, Kyungsan 712-714, Korea*
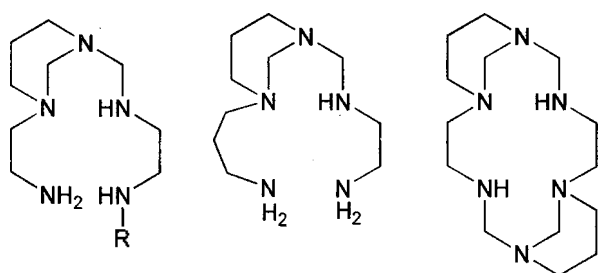*[†]Department of Chemistry, Kongju National University, Kongju 314-701, Korea*
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Various types of polyaza macrocyclic copper(II) and nickel (II) complexes containing N-CH$_2$-N linkages have been prepared by one-pot metal template condensation of amines and formaldehyde (for example, see Eq. (1)[6,7]).[1-13] However, examples of non-macrocyclic polyamine complexes containing N-CH$_2$-N linkages are relatively rare.[12-14] Recently, the copper(II) complex of the non-macrocyclic pentaamine ligand 1 containing one 1,3-diazacyclohexane ring was prepared in our group by the reaction of Eq. (2).[12] The complex [Cu(1)]$^{2+}$ has a square-planar coordination geometry with a 5-6-5 chelate ring sequence, likewise the tetraamine complex [Cu(6)]$^{2+}$. However, chemical properties of [Cu(1)]$^{2+}$ such as kinetic behaviors in acidic solutions are different from those of the copper(II) complexes of 6 and other related tetraamine ligands.[12] Therefore, we have been interested in the synthesis of various types of such non-macrocyclic complexes to further investigate the effects of the structural characteristics on their properties.
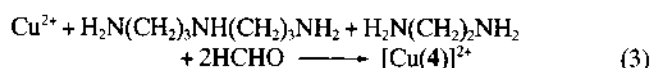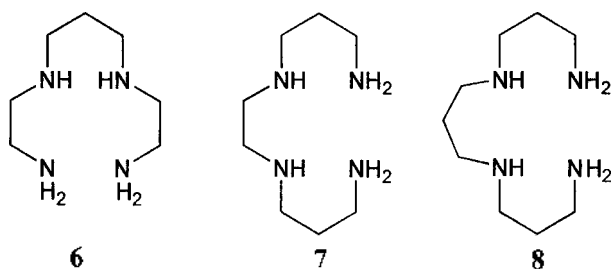
In this work we prepared new copper(II) complexes of 2-4

from the reactions of Eqs. (2) and (3). The crystal structure of [Cu(3)](ClO$_4$)$_2$ was also determined to investigate the coordination behaviors of the hydroxyethyl group. To our knowledge, [Cu(4)]$^{2+}$ is a rarely prepared polyamine complex in which four nitrogen atoms are coordinated with a 5-6-6 chelate ring sequence. Although various polyamine complexes with a symmetrical 5-6-5 or 6-5-6 chelate ring sequence have been prepared, those with an asymmetrical 5-6-6 chelate ring sequence have not been widely investigated because of synthetic difficulties.[15]

$$M^{2+} + 2H_2N(CH_2)_2NH(CH_2)_3NH_2 + 4HCHO \longrightarrow [M(5)]^{2+} \quad (1)$$
$$(M = Ni \text{ or } Cu)$$

$$Cu^{2+} + H_2N(CH_2)_2NH(CH_2)_3NH_2 + H_2N(CH_2)_2NHR$$
$$+ 2HCHO \longrightarrow [Cu(L)]^{2+} \quad (2)$$
$$R = H \text{ for } 1 \quad (L = 1, 2, \text{ or } 3)$$
$$R = C_2H_5 \text{ for } 2$$
$$R = (CH_2)_2OH \text{ for } 3$$

1: R = H   4   5
2: R = C₂H₅
3: R = (CH₂)₂OH

6   7   8

$$Cu^{2+} + H_2N(CH_2)_3NH(CH_2)_3NH_2 + H_2N(CH_2)_2NH_2$$
$$+ 2HCHO \longrightarrow [Cu(4)]^{2+} \qquad (3)$$

Experimental

Materials and Measurements. The complex [Cu(1)] (ClO₄)₂ was prepared as described previously.[12] *Safety Note*: Perchlorate salts of transition metal complexes with organic ligands are often explosive and should be handled with caution.

Electronic absorption spectra were obtained with a Shimadzu UV-160 spectrophotometer, infrared spectra with a Shimadzu IR-440 spectrophotometer, and conductance measurements with a Metrohm Herisau Conductometer E518. Elemental analyses and FAB mass spectral analysis were performed at the Korea Basic Science Institute, Seoul, Korea.

Preparation of [Cu(2)](ClO₄)₂. To a methanol (30 mL) suspension of Cu(OAc)₂ · H₂O (3.0 g, 15 mmol) were added 97% 1,4,8-triazaoctane (2.0 mL, 15 mmol), 99% 2-ethylaminoethylamine (3.2 mL, 30 mmol), and paraformaldehyde (1.4 g, 45 mmol). The mixture was refluxed for 12 h and then cooled to room temperature. To the blue-purple solution was added an excess amount of sodium perchlorate. The resulting solution was stored in a refrigerator until purple solids were precipitated. The crude product collected by filtration contains a small amount (10% <) of the red complex [Cu(5)](ClO₄)₂ as a by-product. The pure product was obtained by recrystallizations of the crude product from hot water. Yield: ~30%. *Anal.* Calcd. for C₁₁H₂₇N₅CuCl₂O₈: C, 26.86; H, 5.53; N, 14.24. Found: C, 26.97; H, 5.65; N, 14.15. FAB Mass (*m/z*): 391 ([M-ClO₄]⁺) and 292 ([M-2ClO₄-H]⁺). IR (Nujol mull, cm⁻¹): 3330 (νN-H), 3255 (νN-H), 3230 (νN-H), 3150 (νN-H), 1590 (δNH₂), and 1100 (νClO₄).

Preparation of [Cu(3)](ClO₄)₂. The procedure for the synthesis of the blue-purple complex is similar to that

of [Cu(2)](ClO₄)₂ except that 98% N-(2-hydroxyethyl) ethylenediamine (3.0 mL, 30 mmol) was reacted instead of 2-ethylaminoethylamine. Yield: ~30%. *Anal.* Calcd. for C₁₁H₂₇N₅CuCl₂O₉: C, 26.02; H, 5.36; N, 13.79. Found: C, 26.10; H, 5.42; N, 13.75. FAB Mass (*m/z*): 407 ([M-ClO₄]⁺) and 308 ([M-2ClO₄-H]⁺). IR (Nujol mull, cm⁻¹): 3390 (νO-H), 3335 (νN-H), 3275 (νN-H), 3240 (νN-H), 3150 (νN-H), 1590 (δNH₂), and 1100 (νClO₄).

Preparation of [Cu(4)](ClO₄)₂. A methanol suspension of Cu(OAc)₂ · H₂O (3.0 g, 15 mmol), 1,5,9-triazanonane (2.1 mL, 15 mmol), 99% ethylenediamine (2.0 mL, 30 mmol), and paraformaldehyde (1.4 g, 45 mmol) was refluxed for 12 h. An excess amount of sodium perchlorate was added to the blue-purple solution. The purple solids were collected by filtration, washed with methanol, and recrystallized from hot water. Yield: ~40%. *Anal.* Calc. for C₁₀H₂₅N₅CuCl₂O₈: C, 25.14; H, 5.27; N, 14.66. Found: C, 25.32; H, 5.47; N, 14.80. FAB Mass (*m/z*): 377 ([M-ClO₄]⁺) and 278 ([M-2ClO₄-H]⁺). IR (Nujol mull, cm⁻¹): 3335 (νN-H), 3280 (νN-H), 3260 (νN-H), 3230 (νN-H), 1600 (δNH₂), and 1100 (νClO₄).

Crystal Structure Analysis. A crystal of [Cu(3)](ClO₄)₂ was mounted on a thin glass fiber and intensity data were collected on an Enraf-Nonius CAD4 diffractometer. Unit cell parameters were determined from a least-squares fit of 25 accurately centered reflections (18 < 2θ < 31°). Three intense reflections were monitored every 200 reflections to check stability. Data were collected for Lorentz and polarization effects. The SHELXS-86 program was utilized for the heavy atom method.[16] The structure refinements were performed with the SHELXL-93 program on *F²* data.[17] Heavy atoms were located by use of heavy atom method. Other non-hydrogen atoms were found from successive difference Fourier synthesis. Anisotropic thermal parameters for all nonhydrogen atoms were included in the refinements. All hydrogen atoms bonded to carbon atoms were included in calculated positions. This C-H bond distance was fixed at 1.00 Å and U values were assigned based approximately on the U value of the attached atom. The other hydrogens (N-H) were included in located positions with U = 0.05 Å². The crystal and refinement data are listed in Table 1.

Results and Discussion

Synthesis and Characterization. The reaction (*Eq.* (2)) of copper(II) ion, 1,4,8-triazaoctane, formaldehyde, and appropriate diamine produces the non-macrocyclic complex [Cu(2)]²⁺ or [Cu(3)]²⁺. The complex [Cu(4)]²⁺ was prepared by the similar metal template condensation of 1,5,9-triazanonane, ethylenediamine, and formaldehyde (*Eq.* (3)). However, all efforts to prepare nickel(II) complexes of 2-4 as a solid from the reactions similar to those for the corresponding copper(II) complexes were unsuccessful.

The values of molar conductance of [Cu(L)](ClO₄)₂ (L = 2, 3, or 4) measured in water (210-230 Ω⁻¹mol⁻¹cm²) and acetonitrile (250-280 Ω⁻¹mol⁻¹cm²) indicate that the complexes are 1:2 electrolytes. The FAB mass spectra of the complexes show two groups of peaks corresponding to the fragments [M-ClO₄]⁺ and [M-2ClO₄-H]⁺; peaks of molecular ions of the copper(II) complexes are not observed, as usual.[12,18,19] The mass spectra, together with elemental

Table 1. Crystal and refinement data for $[Cu(3)](ClO_4)_2$

Formula	$C_{11}H_{27}N_5CuCl_2O_9$
Fw	507.82
Crystal system	monoclinic
Space group (No.)	$P2_1/n$ (14)
a (Å)	8.732(1)
b (Å)	17.986(1)
c (Å)	13.139(2)
β (deg)	104.86(1)
V (Å³)	1994.5(4)
Z	4
λ (Å)	0.71073
D_{calc} (g/cm³)	1.691
μ (cm⁻¹)	14.18
T (°C)	20(2)
Crystal size (mm)	$0.4 \times 0.3 \times 0.2$
Scan mode	ω
Measured reflections (unique)	3027
Observed reflections	2334 $(I > 2\sigma(I))$
Maximum 2θ (deg)	50
$R_1{}^a$	0.068
$wR_2{}^b$	0.173
G.O.F.	1.13
No. of parameters	253
$\Delta\rho_{max}$ (eÅ⁻³)	1.166
$\Delta\rho_{min}$ (eÅ⁻³)	-0.571

$^aR_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. $^bwR_2 = [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^2)^2]^{1/2}$, where $w = 1/[\sigma^2(F_o{}^2)+0.1019P]^2 + 5.1705P]$; $P = [max(F_o{}^2, 0) + 2F_c{}^2]/3$.

analyses and the infrared spectra, strongly support the formula of the copper(II) complexes of **2-4** (*see* Experimental). The structure of $[Cu(3)](ClO_4)_2$ was confirmed by its crystal structure (*see* below).

The electronic absorption spectra of the copper(II) complexes are summarized in Table 2. The spectrum of [Cu (2)]²⁺ measured in nitromethane shows a single *d-d* band at 530 nm ($\varepsilon = 98$ M⁻¹cm⁻¹) and is comparable with that of the square-planar copper(II) complex [Cu(1)]²⁺ with a 5-6-5 chelate ring sequence.[12] The wavelength of the band for [Cu(4)]²⁺ is much longer than that for [Cu(7)]²⁺ with a symmetric 6-5-6 chelate ring sequence,[22] and is between those for [Cu(1)]²⁺ (or [Cu(6)]²⁺) and [Cu(8)]²⁺.[20-23] This result agrees with the generally observed trend that the ligand field strength of a non-macrocyclic complex is affected by the chain length of the ligand and by the chelate ring

Table 2. Electronic Absorption Spectral Data of Copper(II) Complexes

Complex	λ_{max}, nm (ε, M⁻¹cm⁻¹)		
	MeNO₂	H₂O	MeCN
$[Cu(1)](ClO_4)_2{}^a$	523(79)	535(72)	535(72)
$[Cu(2)](ClO_4)_2$	530(98)	544(104)	543(90)
$[Cu(3)](ClO_4)_2$	545(80)	549(78)	549(77)
$[Cu(4)](ClO_4)_2$	542(129)	558(115)	554(116)
$[Cu(6)]^{2+\,b}$		526	
$[Cu(7)]^{2+\,c}$		531(151)	
$[Cu(8)]^{2+\,c}$		598(171)	

^{a}Ref. 12. ^{b}Ref. 23. ^{c}Ref. 22.
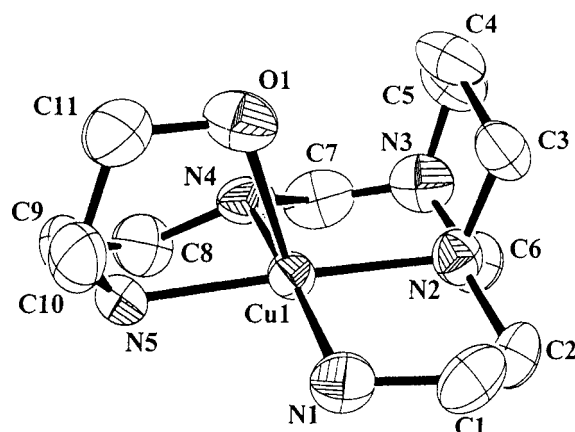
Figure 1. Molecular structure of $[Cu(3)]^{2+}$ with atomic numbering scheme.

sequence.[22,23] The wavelengths for the complexes of **2** and **4** measured in coordinating solvents such as water and acetonitrile are distinctly longer then those in nitromethane. This can be attributed to the apical coordination of the solvent molecules.[12,22] In the case of [Cu(3)]²⁺, the wavelength of the band measured in nitromethane is longer than that of [Cu(2)]²⁺. Furthermore, the spectrum is quite similar to those measured in water and acetonitrile, in contrast to the cases for the complexes of **2** and **4**. This strongly indicates that the hydroxyl group of [Cu(3)]²⁺ is coordinated to the metal ion.

Crystal structure of [Cu(3)](ClO₄)₂. The ORTEP drawing (Figure 1) of the complex cation [Cu(3)]²⁺ shows that the complex has a slightly distorted square-pyramidal coordination geometry with four nitrogen atoms in a plane and one apical oxygen atom of the hydroxyethyl group; the O(1) atom is located at the axial position toward the same direction as the C(3)-C(4)-C(5) part of the 1,3-diazacyclohexane ring moiety. The N(3) atom and the perchlorate anions are not involved in coordination.

Selected bond distances and angles of the complex are listed in Table 3. The four Ni-N bond distances range from 2.012(6) to 2.072(6) Å. The bond distances are in the normal range for Cu-amine distances (1.99-2.08 Å) of square-pyramidal copper(II) complexes.[24,25] The Cu-O(1) bond distance (2.405(6) Å) is *ca.* 0.4 Å longer than the in-

Table 3. Selected bond distances (Å) and angles (deg) and their estimated standard deviations for $[Cu(3)](ClO_4)_2$

Cu-N(1)	2.009(6)	Cu-N(2)	2.072(6)
Cu-N(4)	2.012(6)	Cu-N(5)	2.057(7)
Cu-O(1)	2.405(6)	O(1)-C(11)	1.43(2)
N(2)-C(6)	1.49(2)	N(4)-C(7)	1.50(2)
N(3)-C(6)	1.41(2)	N(3)-C(7)	1.39(2)
N(1)-Cu-N(4)	170.5(3)	N(2)-Cu-N(5)	176.7(3)
N(1)-Cu-N(2)	84.9(3)	N(1)-Cu-N(5)	95.4(3)
N(2)-Cu-N(4)	94.6(3)	N(4)-Cu-N(5)	84.6(3)
O(1)-Cu-N(5)	76.9(2)	O(1)-Cu-N(4)	97.0(2)
O(1)-Cu-N(2)	106.4(2)	O(1)-Cu-N(1)	92.2(3)
C(2)-N(2)-C(6)	109.4(6)	C(5)-N(3)-C(6)	111.5(8)
C(5)-N(3)-C(7)	117.2(8)	C(6)-N(3)-C(7)	115.3(7)

plane Cu-N distances and is typical for apical Cu-O bond distance of square-pyramidal copper(II) complexes.[25]

The Cu atom lies slightly above the N_4 plane toward the apical O(1) atom. Therefore, the bond angles around the metal ion somewhat deviate from ideal square-pyramidal angles; the N(1)-Cu-N(4) and N(2)-Cu-N(5) angles are 170. 5(3) and 176.7(3)°, respectively. The O(1)-Cu-N(5) and O(1)-Cu-N(2) angles are much smaller and larger, respectively, than the rest O(1)-Cu-N angles. However, the N(1)-Cu-N(5) angle is quite similar to N(2)-Cu-N(4) angle in the six-membered chelate ring. One of the remarkable structural features of the complex is that the angles about the uncoordinated N(3) atom are significantly larger than the ideal tetrahedral angles with the C(5)-N(3)-C(7) angle of 117.2(8)°. Furthermore, the N(3)-C(7) and N(3)-C(6) bond distances are 1.39(2) and 1.41(2) Å, respectively, which are distinctly shorter than other N-C distances. These observations strongly support the sp²-like hybridization of the N(3) atom.[6,7,9]

Solution Behaviors. The complexes [Cu(L)](ClO₄)₂ (L = 2, 3, or 4) are readily decomposed in low pH. It has been reported that pseudo first-order rate constant (k) for the decomposition reaction of [Cu(1)]²⁺ in 0.1 M HClO₄ solution at 25 °C is $k = 3.6 \times 10^{-2}$ sec⁻¹.[12] In the cases for [Cu(2)]²⁺, [Cu(3)]²⁺, and [Cu(4)]²⁺ in 0.1 M HClO₄ aqueous solutions, the reaction rate for the complexes is too fast to measure with ordinary methods. However, we could observe that these complexes dissociate more rapidly than [Cu(1)]²⁺; the k values for the complexes of **2-4** were found to be larger than 0.1 sec⁻¹. The more rapid dissociation of the complexes of **2** and **3**, compared to that of **1**, can be attributed to the steric hindrance of the N-substituent and/or the stronger proton affinity of the secondary amino group. The more rapid dissociation of [Cu(4)]²⁺ with a 5-6-6 chelate ring sequence, compared to that of **1**, may be resulted from the larger chelate ring size; the dissociation rate of [Cu(7)]²⁺ in an acid solution is much faster than that of [Cu(6)]²⁺.[23]

The copper(II) complexes of **2-4** are also unstable in aqueous solutions containing 1,4,8-triazaoctane and/or formaldehyde. They readily react with 1,4,8-triazaoctane and formaldehyde to produce the macrocyclic complex [Cu (5)]²⁺. Furthermore, the addition of excess formaldehyde to hot aqueous solutions of [Cu(2)](ClO₄)₂ and [Cu(3)](ClO₄)₂ in the absence of 1,4,8-triazaoctane also produces [Cu(5)] (ClO₄)₂. The similar behavior was also observed for the complex of **1**. This indicates that, in the complexes of **1-4**, the N-CH₂-N linkages are labile.

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