Metal-Directed Condensation of Two Different Triamines with Formaldehyde: Preparation of Asymmetrical Hexaaza Macrotricyclic Copper(II) Complexes with a 5-6-6-6 Chelate Ring Sequence

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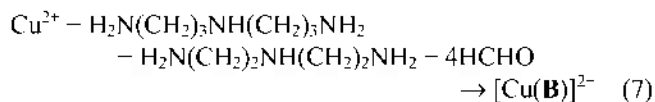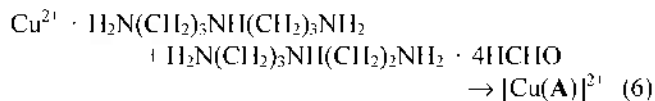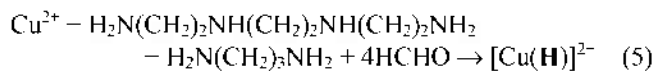*Department of Chemistry, Daegu University, Gyeongsan 712-714, Korea. *E-mail: sgkang@daegu.ac.kr*
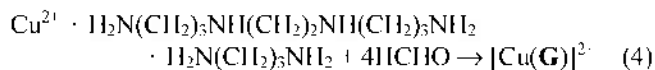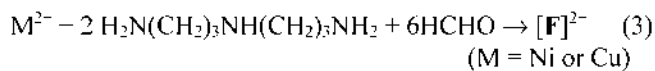†*Department of Chemistry, Kyungpook National University, Daegu 702-701, Korea*
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Metal-directed condensation reactions involving amines and formaldehyde have been utilized for the preparation of various polyaza macrocyclic compounds containing N-CH_2-N linkages.[1-11] For instance, the square-planar complexes $[M(C)]^{2-}$ and $[M(D)]^{2-}$ (M = Cu(II) or Ni(II)) with a 5-6-5-6 chelate ring sequence have been prepared by the reaction (Eq. (1) or (2)) of formaldehyde with one kind of linear triamine (N-(3-aminopropyl)-ethylenediamine or diethylenetriamine) in the presence of the metal ion.[6,7] The hexaaza macrotricyclic ligands **C** and **D** contain two additional -$(CH_2)_3$- or -$(CH_2)_2$- chains that link the nitrogen atoms of the N-CH_2-N linkages. It has been revealed that $[M(C)]^{2+}$ and $[M(D)]^{2-}$ do not react with further formaldehyde and are quite inert against decomposition even in low pH. The reaction of bis(3-aminopropyl)amine with excess formaldehyde in the presence of copper(II) or nickel(II) ion has been known to produce the metal-free macropolycyclic compound $[F]^{2+}$ (Eq. (3)), instead of $[M(E)]^{2+}$.[8] This is attributed to the instability of $[M(E)]^{2-}$ with a 6-6-6-6 chelate ring sequence; although the reaction initially produces $[M(E)]^{2+}$ as an intermediate, the complex reacts with additional formaldehyde to produce $[F]^{2+}$.[8]

In a previous paper, we reported the preparation of two new square-planar complexes $[Cu(G)]^{2-}$ and $[Cu(H)]^{2-}$ with a 5-6-6-6 chelate ring sequence from the reactions of Eqs. (4) and (5).[9] Although the complexes do not react with additional formaldehyde, they are decomposed in low pH. Interestingly, the decomposition rate of $[Cu(H)]^{2-}$ is ~10^4 times faster than that of $[Cu(G)]^{2-}$,[9] showing that their chemical properties are strongly influenced by the length of the -$(CH_2)_n$- chains that link the nitrogen atoms of the N-CH_2-N linkages. Until now, examples of hexaaza macrotricyclic complexes with a 5-6-6-6 chelate ring sequence limited in number and their chemical properties have not been thoroughly investigated; to our knowledge, $[Cu(G)]^{2+}$ and $[Cu(H)]^{2+}$ are rarely prepared hexaaza macrotricyclic complexes with a 5-6-6-6 chelate ring sequence.

$$M^{2+} + 2 \ H_2N(CH_2)_3NH(CH_2)_2NH_2 - 4HCHO \rightarrow [M(C)]^{2-}$$
$$(M = Ni \ or \ Cu) \quad (1)$$

$$M^{2+} + 2 \ H_2N(CH_2)_2NH(CH_2)_2NH_2 \cdot 4HCHO \rightarrow [M(D)]^{2}$$
$$(M - Ni \ or \ Cu) \quad (2)$$

A   B   C   D

E $[F]^{2+}$

G   H   I

$$M^{2-} - 2 \ H_2N(CH_2)_3NH(CH_2)_3NH_2 + 6HCHO \rightarrow [F]^{2-} \quad (3)$$
$$(M = Ni \ or \ Cu)$$

$$Cu^{2+} \cdot H_2N(CH_2)_3NH(CH_2)_2NH(CH_2)_3NH_2$$
$$\cdot H_2N(CH_2)_3NH_2 + 4HCHO \rightarrow [Cu(G)]^{2-} \quad (4)$$

$$Cu^{2+} - H_2N(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH_2$$
$$- H_2N(CH_2)_3NH_2 + 4HCHO \rightarrow [Cu(H)]^{2-} \quad (5)$$

$$Cu^{2+} \cdot H_2N(CH_2)_3NH(CH_2)_3NH_2$$
$$+ H_2N(CH_2)_3NH(CH_2)_2NH_2 \cdot 4HCHO$$
$$\rightarrow [Cu(A)]^{2+} \quad (6)$$

$$Cu^{2+} - H_2N(CH_2)_3NH(CH_2)_3NH_2$$
$$- H_2N(CH_2)_2NH(CH_2)_2NH_2 - 4HCHO$$
$$\rightarrow [Cu(B)]^{2-} \quad (7)$$
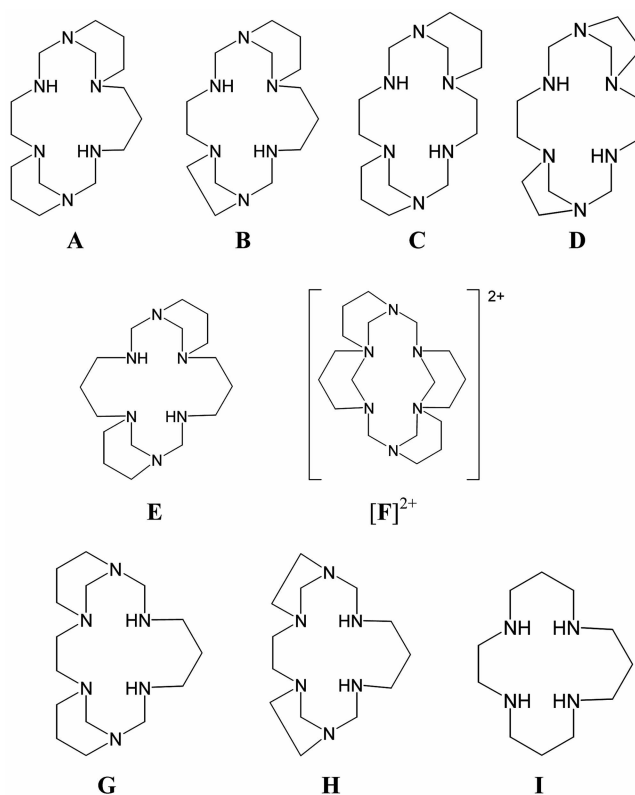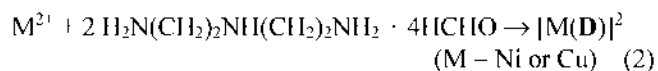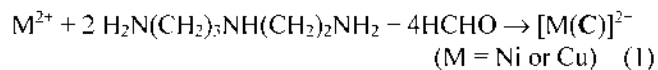
In this work, we attempted the one-pot metal-directed

condensation reactions (Eqs. (6) and (7)) of two different triamines with formaldehyde and successfully prepared new hexaaza macrotricyclic complexes [Cu(**A**)]$^{2+}$ and [Cu(**B**)]$^{2+}$ with a 5-6-6-6 chelate ring sequence as the major products. Although the ligand **A** resembles **G**, the positions of the -(CH$_2$)$_3$- chains are different. The complex [Cu(**B**)]$^{2+}$ is a rare example of hexaaza macrotricyclic complex containing both -(CH$_2$)$_2$- and -(CH$_2$)$_3$- chains. Here synthesis and chemical properties of the copper(II) complexes of **A** and **B** are reported, along with the crystal structure of [Cu(**A**)]$^{2+}$. The spectroscopic and chemical properties of the copper(II) complexes of **A** and **B** are compared with those of **G** and **H**.

Experimental Section

Measurements. Elemental analyses and FAB-mass spectra were performed at the Korea Basic Science Institute, Daegu, Korea. Infrared spectra were recorded with a Shimadzu IR-440 spectrophotometer, electronic absorption spectra with an Analytikjena Specord 200 UV/Vis spectrophotometer, and conductance measurements with a Metrohm Herisau Conductometer E518.

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

Preparation of [Cu(A)](ClO$_4$)$_2$ (A = 1,3,6,10,12,16-Hexa-azatricyclo[14.3.1.1^{6,10}]heneicosane). To a methanol solution (*ca.* 30 mL) of Cu(OAc)$_2$·H$_2$O (2.0 g, 10 mmol) were added 97% *N*-(3-aminopropyl)ethylenediamine (1.8 mL, 12 mmol) and 97% bis(3-aminopropyl)amine (1.0 mL, 7.7 mmol). The solution was stirred at room temperature for 30 min. After the addition of 35% formaldehyde (4.7 mL, 60 mmol), the mixture was stirred for *ca.* 2 h at room temperature. The resulting solution was further stirred at *ca.* 50 °C for 12 h. An excess amount of NaClO$_4$ was added to the solution, and the mixture was stored at room temperature to produce a blue-purple solid. The crude product often contains a small amount (< 5%) of [Cu(C)](ClO$_4$)$_2$ and/or [F](ClO$_4$)$_2$ as by-products. The product was collected by filtration, washed with methanol, and recrystallized from hot acetonitrile-water (1:2). Yield: ~50%. *Anal.* Found: C, 31.98; H, 6.06; N, 14.89. Calc. for C$_{15}$H$_{32}$Cl$_2$CuN$_6$O$_8$: C, 32.23; H, 5.77; N, 15.04 %. FAB mass (*m/z*): 359.3 [Cu(**A**) − H]$^+$, 458.3 [Cu(**A**) + ClO$_4$]$^+$. IR (Nujol mull, cm^{-1}): 3248 (ν(N-H), *br*)).

Preparation of [Cu(B)](ClO$_4$)$_2$ (B = 1,3,6,9,11,15-Hexa-azatricyclo[13.3.1.1^{6,9}]eicosane). To a methanol solution (*ca.* 30 mL) of Cu(OAc)$_2$·H$_2$O (2.0 g, 10 mmol) were added 97% diethylenediamine (1.0 mL, 8.9 mmol) and bis(3-aminopropyl)amine (1.8 mL, 12 mmol). The solution was stirred at room temperature for 20 min. After the addition of 35% formaldehyde (4.7 mL, 60 mmol), the mixture was stirred for *ca.* 2 h at room temperature. The resulting solution was further stirred at *ca.* 50 °C for 12 h. An excess amount of NaClO$_4$ was added to the solution, and the mixture was stored at room temperature to produce a blue-purple solid. The crude product often contains a small

amount (< 3%) of [Cu(D)](ClO$_4$)$_2$ and/or [F](ClO$_4$)$_2$ as by-products. The product was collected by filtration, washed with methanol, and recrystallized from hot acetonitrile-water (1:3). Yield: ~40%. *Anal.* Found: C, 30.37; H, 5.98; N, 15.39. Calc. for C$_{14}$H$_{30}$Cl$_2$CuN$_6$O$_8$: C, 30.86; H, 5.55; N, 15.42%. FAB mass (*m/z*): 444.2 [Cu(**B**) − H]$^+$, 345.2 [Cu(**B**) + ClO$_4$]$^+$. IR (Nujol mull. cm^{-1}): 3243 (ν(N-H), *br*).

Crystal Structure Analysis. Single crystals of [Cu(**A**)]-(ClO$_4$)$_2$ suitable for X-ray diffraction were obtained by evaporating a water-acetonitrile solution of the complex at room temperature. Experimental details for the structure determinations are listed in Table 1. Intensity data were collected with CAD4 diffractometer using monochromated Mo *Kα* radiation (λ = 0.71073 Å). The structures were solved by direct methods and refined by full-matrix least-squares methods based on F^2 using SHELXS-97 and SHELXL-97.[13] Non hydrogen atoms were refined anisotropically except disordered oxygen atoms at ClO$_4$ anions and 2 carbon atoms at the ligand which were refined isotropically. All hydrogen atoms were placed in calculated positions and refined using a riding model.

Results and Discussion

Synthesis. As expected from the reactions of Eqs. (1) and (3), the reaction of excess formaldehyde with a 1:1:1 molar mixture of copper(II) ion, *N*-(3-aminopropyl)ethylene-diamine, and bis(3-aminopropyl)amine in boiling methanol, followed by addition of NaClO$_4$, usually produces a mixture of [Cu(**A**)](ClO$_4$)$_2$, [Cu(**C**)](ClO$_4$)$_2$, and [F](ClO$_4$)$_2$; in most cases, the main products were [Cu(**C**)](ClO$_4$)$_2$ and [F]-(ClO$_4$)$_2$. However, as described in the Experimental section, [Cu(**A**)](ClO$_4$)$_2$ can be prepared as the major product by controlling the reaction conditions, such as the reaction temperature and the molar ratio (1:0.8:1.2) of the reactants.

Table 1. Crystal Data and Structure Refinement for [Cu(**A**)](ClO$_4$)$_2$

Empirical formula (*M*)	C$_{15}$ H$_{32}$ Cl$_2$ Cu N$_6$ O$_8$ (558.91)
Temperature (K)	293(2)
Crystal system/ space group	triclinic/*P*1
a / *b* / *c* (Å)	8.4245(6)/8.8316(7)/15.591(2)
α / *β* / *γ*	79.058(1)/75.794(1)/75.521(1)
V (Å^3)	1078.6(2)
Z · *D*$_{calc}$ (g cm^{-3})	2 / 1.721
μ (cm^{-1})	13.20
F$_{000}$	594
θ range (°)	2.40-28.27
Limiting indices	−11 ≤ *h* ≤ 11, −11 ≤ *k* ≤ 11, −19 ≤ *l* ≤ 19
Reflections collected / unique	9447/8361 [*R*$_{int}$ = 0.0113]
Reflections observed (> 2σ)	7807
Data Completeness	0.908
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8361 / 3 / 571
Goodness-of-fit on F^2	1.035
Final *R* indices [*I* > 2σ(*I*)]	*R*$_1$ = 0.0349, *wR*$_2$ = 0.0847
R indices (all data)	*R*$_1$ = 0.0378, *wR*$_2$ = 0.0867
Largest diff. peak and hole (Å^3)	0.583 and −0.528

Notes

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The macrotricyclic complex [Cu(**B**)](ClO₄)₂ was also prepared as the major product by a similar reaction employing a 1:0.9:1.2 molar mixture of copper(II) ion, diethylenetriamine, and bis(3-aminopropyl)amine. The preparation of nickel(II) complexes of **A** and **B** was also attempted from the similar one-pot reactions in the presence of nickel(II) ion, instead of copper(II) ion, but failed. In each attempt, only [Ni(**C**)](ClO₄)₂ (or [Ni(**D**)](ClO₄)₂) and [**F**](ClO₄)₂ could be isolated. This indicates that the condensation to give **A** or **B** is strongly influenced by the nature of the metal ion. Polyaza macrocyclic nickel(II) and copper(II) complexes with a 5-6-6-6 chelate ring sequence are less stable than those with a 5-6-5-6 chelate ring sequence.[9,11,12,14] One of the factors affecting the formation of [Cu(**A**)]²⁻ and [Cu(**B**)]²⁺ with a 5-6-6-6 chelate ring sequence may be the relatively strong Lewis acidity (Cu(II) > Ni(II)) of the metal ion; the copper(II) ion stabilizes the coordinated secondary nitrogen atoms of N-CH₂-N linkages in the complexes.[9]

Crystal Structure of [Cu(A)](ClO₄)₂. The crystallographic asymmetric unit of [Cu(**A**)](ClO₄)₂ contains two crystallographically independent molecules (**1** and **2**). The ORTEP drawing (Fig. 1) of **1** shows that it contains **A**, which is coordinated to the metal ion with a 5-6-6-6 chelate ring sequence. The axial Cu(1)-O(5) and Cu(1)-O(13) distances (2.577(5) and 2.595(6) Å, respectively) strongly indicate that two ClO₄ anions are coordinated to the metal ion very weakly. The macrotricyclic ligand **A** adopts the *trans*-III type conformation. The -(CH₂)₃- chains involved in the 1,3-diazacyclohexane rings are *anti* with respect to the macrocyclic plane.

Table 2 shows that the Cu(1)-N distances of **1** range from 2.028(5) to 2.101(4) Å. Although the Cu-N distances are comparable with those (2.074(7)-2.120(6) Å) of [Cu(**G**)]²⁻, the average value (2.064 Å) is somewhat shorter than that of [Cu(**G**)]²⁻ (2.088 Å).[9] The N(1)-Cu(1)-N(4) and N(3)-Cu(1)-N(6) angles are 179.0(3) and 178.6(3)°, respectively. One of the most remarkable structural features of the complex is that the N(1)-Cu(1)-N(6) angle (87.8(2)°) of the six-membered chelate ring is considerably smaller than the
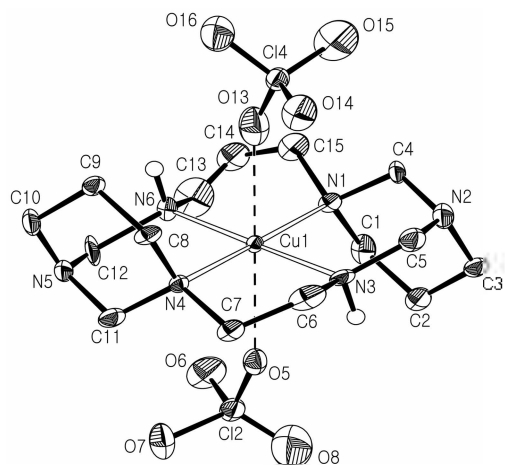

Figure 1. ORTEP drawing of **1** (one of asymmetric units in [Cu(**A**)](ClO₄)₂). Thermal ellipsoids are drawn to include 40% probability. H atoms attached to the carbons are omitted for clarity.

Table 2. Selected Bond Distances [Å] and Angles [°] for **1**

Cu(1)-N(1)	2.101(4)	Cu(1)-N(3)	2.034(5)
Cu(1)-N(4)	2.092(5)	Cu(1)-N(6)	2.028(5)
Cu(1)-O(5)	2.577(5)	Cu(1)-O(13)	2.595(6)
N(1)-Cu(1)-N(4)	179.0(3)	N(3)-Cu(1)-N(6)	178.6(3)
N(1)-Cu(1)-N(3)	92.6(2)	N(1)-Cu(1)-N(6)	87.8(2)
N(3)-Cu(1)-N(4)	87.7(2)	N(4)-Cu(1)-N(6)	92.0(2)
O(5)-Cu(1)-O(13)	179.2(2)	N(1)-Cu(1)-O(5)	97.1(3)
C(1)-N(1)-Cu(1)	114.9(4)	C(15)-N(1)-Cu(1)	108.3(4)
C(4)-N(1)-Cu(1)	109.4(4)	C(5)-N(3)-Cu(1)	119.1(4)
C(13)-N(6)-Cu(1)	110.1(4)	C(12)-N(6)-Cu(1)	117.7(4)

N(1)-Cu(1)-N(3) and N(4)-Cu(1)-N(6) angles (92.6(2) and 92.0(2)°, respectively) but is nearly the same as the N(3)-Cu(1)-N(4) angle (87.7(2)°) of the five-membered chelate ring. Furthermore, the Cu(1)-N(6) (secondary) distance (2.028(5) Å) involved in two six-membered chelate rings is shorter than the Cu(1)-N(3) (secondary) distance (2.034(5) Å) involved in the five- and six-membered ones.

The *trans*-N-Cu(2)-N angles (178.6(3) and 179.0(3)°) and the *cis*-N-Cu(2)-N angles (87.2(2), 89.0(2), 91.8(2), and 92.0(2)°) of **2** as well as the Cu(2)-N distances (2.021(6)-2.121(5) Å) are not quite different from those of **1**. Other structural features of **2** are also similar to those of **1**.

Spectra and Properties. The FAB mass and infrared spectra (*see* Experimental Section) of [Cu(**A**)](ClO₄)₂ and [Cu(**B**)](ClO₄)₂ as well as the elemental analyses correspond to the structure of the complexes. The molar conductance values of the complexes measured in water (200-220 Ω⁻¹ mol⁻¹cm²) indicate that they are 1:2 electrolytes. The electronic absorption spectra (Table 3) of [Cu(**A**)](ClO₄)₂ and [Cu(**B**)](ClO₄)₂ measured in nitromethane show *d-d* transition band at 552 (ε = 158 M⁻¹cm⁻¹) and 566 nm (ε = 235 M⁻¹cm⁻¹), respectively. The wavelengths are > 50 nm longer than those of [Cu(**C**)](ClO₄)₂ and [Cu(**D**)](ClO₄)₂ with a 5-6-5-6 chelate ring sequence and are comparable with those of [Cu(**G**)](ClO₄)₂, [Cu(**H**)](ClO₄)₂, and [Cu(**I**)]²⁻ with a 5-6-6-6 chelate ring sequence.[7,9,15,16] Unexpectedly,

Table 3. Electronic Absorption Spectra and Decomposition Rate Constants (*k*) of the Complexes

Complex	λ$_{max}$, nm (ε, M⁻¹cm⁻¹)^a	*k*, s⁻¹ ^{b}
[Cu(**A**)](ClO₄)₂	552(158) 569(164)^c 579(173)^d	3.4 × 10⁻⁵ (*ca.* 5.6 h)
[Cu(**B**)](ClO₄)₂	566(235) 574(196)^c 596(210)^d	1.2 × 10⁻⁴ (*ca.* 1.5 h)
[Cu(**C**)](ClO₄)₂ ^{e}	505(122)	very slow
[Cu(**D**)](ClO₄)₂ ^{e}	486(151)	very slow
[Cu(**G**)](ClO₄)₂ ^{f}	577(150) 578(150)^c 590(160)^d	2.5 × 10⁻⁶ (*ca.* 77 h)
[Cu(**H**)](ClO₄)₂ ^{f}	553(175) 555(173)^c 555(150)^d	1.4 × 10⁻² (*ca.* 50 sec)

^{a}Measured in nitromethane at 20 °C unless otherwise specified. ^{b}Pseudo first-order rate constant (*k*) for the decomposition of the complex (2.0 × 10⁻³ M) measured in 0.3 M HClO₄ solution; half-life (*t*$_{1/2}$) of the reaction is in parentheses. ^{c}In acetonitrile. ^{d}In water. ^{e}Ref. 7. ^{f}Ref. 9.

[Cu(**A**)](ClO$_4$)$_2$ exhibits the *d-d* band at *ca.* 15 nm shorter wavelength than [Cu(**B**)](ClO$_4$)$_2$. This result is in contrast to the trend that [Cu(**C**)](ClO$_4$)$_2$ and [Cu(**G**)](ClO$_4$)$_2$ with two additional -(CH$_2$)$_3$- chains exhibit weaker ligand field strength than [Cu(**D**)](ClO$_4$)$_2$ and [Cu(**H**)](ClO$_4$)$_2$ containing two -(CH$_2$)$_2$- chains, respectively.[6,7,9] Furthermore, the wavelength for [Cu(**A**)](ClO$_4$)$_2$ is *ca.* 25 nm shorter than that for [Cu(**G**)](ClO$_4$)$_2$ (577 nm), indicating that their ligand field strength is influenced significantly by the position of the -(CH$_2$)$_3$- chains. This trend corresponds to the crystallographic observation that the average Cu-N distance of [Cu(**A**)](ClO$_4$)$_2$ is shorter than that of [Cu(**G**)]$^{2+}$. The *d-d* band of each complex is observed at longer wavelength in acetonitrile or water than in nitromethane, a poorly coordinating solvent. This fact can be explained by the coordination of the solvent molecule in the coordinating solvent.

Solution Behaviors. Although [Cu(**A**)](ClO$_4$)$_2$ and [Cu(**B**)]-(ClO$_4$)$_2$ are extremely stable in the solid state and in neutral aqueous solution, they are decomposed in HClO$_4$ solutions. The decomposition rate of the complexes (2.0 × 10^{-3} M) in 0.3 M HClO$_4$ solution was measured spectrophotometrically at 20 °C. The pseudo first-order rate constants (*k*) for the decomposition reaction are listed in Table 3, along with those for [Cu(**G**)](ClO$_4$)$_2$ and [Cu(**H**)](ClO$_4$)$_2$. The *k* value decreases in the order of [Cu(**H**)](ClO$_4$)$_2$ (1.4 × 10^{-2} s^{-1}) >> [Cu(**B**)](ClO$_4$)$_2$ (1.2 × 10^{-4} s^{-1}) > [Cu(**A**)](ClO$_4$)$_2$ (3.4 × 10^{-5} s^{-1}) > [Cu(**G**)](ClO$_4$)$_2$ (2.5 × 10^{-6} s^{-1}); the rate of [Cu(**B**)]-(ClO$_4$)$_2$ containing one -(CH$_2$)$_3$- and one -(CH$_2$)$_2$- chains is considerably faster than [Cu(**A**)](ClO$_4$)$_2$ and [Cu(**G**)](ClO$_4$)$_2$ containing two -(CH$_2$)$_3$- chains but is *ca.* 100 times slower than that of [Cu(**H**)](ClO$_4$)$_2$ containing two -(CH$_2$)$_2$- chains. It is obvious that the decomposition rate of the macrotricyclic complexes with a 5-6-6-6 chelate ring sequence is strongly influenced by the position of the -(CH$_2$)$_n$- chains as well as their length. The order of the reaction rate is not parallel with the order of ligand field strength ([Cu(**H**)]-(ClO$_4$)$_2$ ~ [Cu(**A**)](ClO$_4$)$_2$ > [Cu(**B**)](ClO$_4$)$_2$ > [Cu(**G**)](ClO$_4$)$_2$) and the average Cu-N distance ([Cu(**A**)](ClO$_4$)$_2$ < [Cu(**G**)]-(ClO$_4$)$_2$), indicating that the rate is not directly influenced by the strength of the Cu-N interactions. Unfortunately, the crystal structures of [Cu(**B**)](ClO$_4$)$_2$ and [Cu(**H**)](ClO$_4$)$_2$ were not available and, therefore, the reasons for such kinetic behaviors of the copper(II) complexes were not thoroughly investigated. However, the relatively slow decomposition of [Cu(**A**)](ClO$_4$)$_2$ and [Cu(**G**)](ClO$_4$)$_2$ supports the suggestion that one of the factors affecting the reaction rate is the "*I*-strain" of the 1,3-diazacycloalkane ring involving the -(CH$_2$)$_n$- chain.[17] According to the "*I*-strain", the proton affinity of the nitrogen atoms in the 1,3-diazacyclohexane ring (**A** and **G**) is expected to be weaker than that in the 1,3-diazacyclopentane ring (**H**).[9,17]

Summary

New hexaaza macrotricyclic copper(II) complexes [Cu(**A**)]$^{2+}$ and [Cu(**B**)]$^{2+}$ with a 5-6-6-6 chelate ring sequence were prepared as the major product by the metal-template

condensation of formaldehyde and two different triamines. The ligand field strength and chemical properties of the copper(II) complexes are strongly influenced by the position and the length of the additional -(CH$_2$)$_n$- linkages. This work also supports the suggestion that the decomposition rate of the copper(II) complexes is not directly influenced by the strength of Cu-N interactions but is intimately related to the "*I*-strain" of the 1,3-diazacycloalkane ring involving the -(CH$_2$)$_2$- or -(CH$_2$)$_3$- chain.

Supplementary material. Crystallographic data of [Cu(**A**)]-(ClO$_4$)$_2$ are available from the Cambridge Structural Database. CCDC reference number 679737. Copies of the data can be obtained free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 IEZ, UK (http://www.ccdc.cam.ac.uk, fax: +44-1223-336-033, or e-mail: deposit@ccdc.cam.ac.uk).

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