

## Synthesis and Characterization of New Reinforced Pentaaza Macrobicyclic and Bis(macrobicyclic) Copper(II) Complexes

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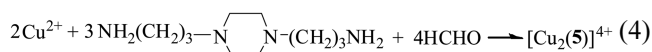
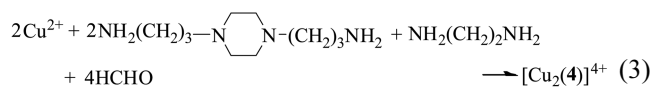
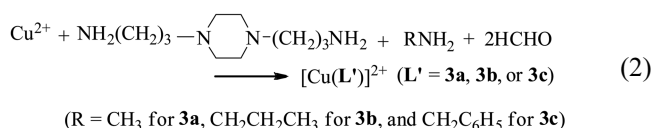
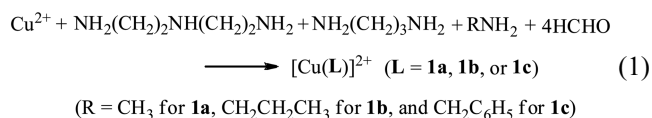
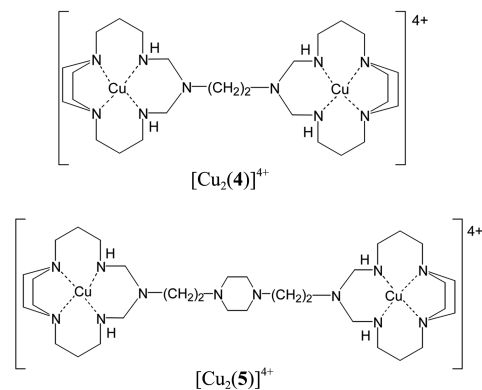
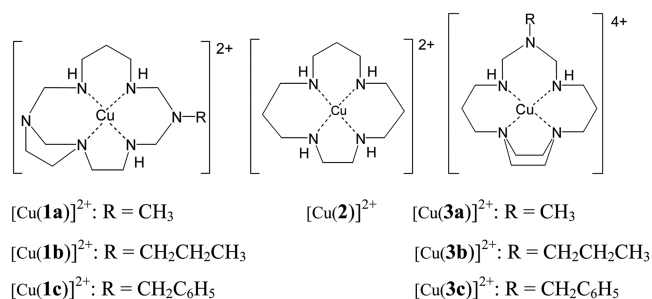
**Key Words** : Template synthesis, Macrocyclic complexes, Copper(II) complexes, Acidic dissociation, Dinuclear complexes

Various types of polyaza macrocyclic complexes have been prepared and investigated. Especially, structurally reinforced polyaza macrocyclic compounds, in which one or two pairs of nitrogen atoms are linked together by an additional  $-(CH_2)_n-$  bridge, have attracted considerable attention because of their wide range of chemical properties.<sup>1-6</sup> In general, chemical properties of such compounds are strongly influenced by the nature, number, and position of the additional bridging group(s).

Metal-template condensation reactions involving amines and formaldehyde have been used for the preparation of polyaza macrocyclic compounds containing  $N-CH_2-N$  linkages.<sup>4-11</sup> Recently, the 15-membered hexaaza macrocyclic complexes  $[Cu(\mathbf{1a})]^{2+}$ ,  $[Cu(\mathbf{1b})]^{2+}$ , and  $[Cu(\mathbf{1c})]^{2+}$  containing one additional  $N-(CH_2)_2-N$  bridge and one  $N$ -alkyl pendant arm have been prepared by the reaction (Eq. (1)) of formaldehyde with three different amines in the presence of the metal ion.<sup>6</sup> The copper(II) complexes are known to be decomposed in low pH, like other 15-membered polyaza macrocyclic copper(II) complexes such as  $[Cu(\mathbf{2})]^{2+}$ .<sup>12</sup> However, interestingly, the decomposition rate of  $[Cu(\mathbf{1a})]^{2+}$  is *ca.*  $10^2$  times slower than that of  $[Cu(\mathbf{2})]^{2+}$ , but is *ca.* 10 times faster than that of  $[Cu(\mathbf{1c})]^{2+}$ .<sup>6</sup> This indicates that chemical properties of such complexes can be affected by the additional  $N-(CH_2)_2-N$  bridge and the nature of  $N$ -alkyl pendant arms. Until now, relatively few examples of structurally reinforced 15-membered polyaza macrocyclic complexes have been prepared and investigated.<sup>4-6</sup> Therefore, we have been interested in the synthesis and chemical properties of various types of 15-membered macrocyclic complexes bearing  $N$ -alkyl pendant arm(s).

In this work, we prepared  $[Cu(\mathbf{3a})]^{2+}$ ,  $[Cu(\mathbf{3b})]^{2+}$ , and  $[Cu(\mathbf{3c})]^{2+}$  from the metal-template condensation of Eq. (2). Although the pentaaza macrobicycles  $\mathbf{3a-3c}$  resemble  $\mathbf{1a-1c}$ , the position of the additional  $-(CH_2)_2-$  bridge is different. In the complexes of  $\mathbf{3a-3c}$ , two coordinated nitrogen atoms are connected by the additional  $-(CH_2)_2-$  bridge. New dinuclear copper(II) complexes  $[Cu_2(\mathbf{4})]^{4+}$  and  $[Cu_2(\mathbf{5})]^{4+}$ , in which two pentaaza macrobicyclic units are linked together by a bridging chain, were also prepared by the one-pot reaction of Eq. (3) or (4). Interestingly, the dinuclear complexes are relatively inert against decomposition even in concentrated

acid solutions. Herein, synthesis and chemical properties of the mononuclear and dinuclear copper(II) complexes are reported.



## Experimental Section

**Measurements.** 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 an Oyster Conductivity/Temperature meter. Elemental analyses were performed at the Research Center for Instrumental Analysis, Daegu University, Gyeongsan, Korea. FAB-mass spectra were performed at the Korea Basic Science Institute, Daegu, Korea.

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

**Preparation of [Cu(3a)](ClO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O (3a = 7-methyl-1,5,7,9,13-pentaazabicyclo[11.2.2]heptadecane).** To a methanol solution (*ca.* 30 mL) of Cu(OAc)<sub>2</sub>·H<sub>2</sub>O (2.0 g, 10 mmol) were added 97% 1,4-bis(3-aminopropyl)piperazine (2.1 mL, 10 mmol) and 40% methylamine (1.3 mL, 15 mmol). After the addition of 35% formaldehyde (2.4 mL, 30 mmol), the mixture was refluxed for *ca.* 15 h. An excess amount of NaClO<sub>4</sub> dissolved in water (10 mL) was added to the reaction solution. The resulting solution was slowly evaporated at room temperature to produce a purple solid. The crude product was filtered, washed with ethanol, and recrystallized from hot water. Yield: ~80% based on the metal salt. *Anal.* Found: C, 28.91; H, 5.64; N, 12.88. Calc. for C<sub>13</sub>H<sub>31</sub>N<sub>5</sub>CuCl<sub>2</sub>O<sub>9</sub>: C, 29.14; H, 5.83; N, 13.07%. FAB mass (*m/z*): 417.2 for [Cu(3a) + ClO<sub>4</sub>]<sup>+</sup>, 318.3 for [Cu(3a) – H]<sup>+</sup>. IR (Nujol mull, cm<sup>-1</sup>): 3241 (ν<sub>N-H</sub>).

**Preparation of [Cu(3b)](ClO<sub>4</sub>)<sub>2</sub> (3b = 7-(*n*-propyl)-1,5,7,9,13-pentaazabicyclo[11.2.2]heptadecane).** This complex was prepared by a method similar to that for [Cu(3a)](ClO<sub>4</sub>)<sub>2</sub>, except that 99% *n*-propylamine (1.3 mL, 15 mmol) was reacted instead of methylamine. The product was recrystallized from hot water-acetonitrile (3:1). Yield: ~80% based on the metal salt. Found: C, 33.56; H, 6.18; N, 13.10. Calc. for C<sub>15</sub>H<sub>33</sub>N<sub>5</sub>CuCl<sub>2</sub>O<sub>8</sub>: C, 33.00; H, 6.09; N, 12.99%. FAB mass (*m/z*): 445.3 for [Cu(3b) + ClO<sub>4</sub>]<sup>+</sup>, 346.3 for [Cu(3b) – H]<sup>+</sup>. IR (Nujol mull, cm<sup>-1</sup>): 3232 (ν<sub>N-H</sub>).

**Preparation of [Cu(3c)](ClO<sub>4</sub>)<sub>2</sub> (3c = 7-phenylmethyl-1,5,7,9,13-pentaazabicyclo[11.2.2]heptadecane).** This complex was prepared by a method similar to that for [Cu(3a)](ClO<sub>4</sub>)<sub>2</sub>, except that 99% benzylamine (1.6 mL, 15 mmol) was reacted instead of methylamine. The product was recrystallized from hot water-acetonitrile (1:1). Yield: ~80% based on the metal salt. Found: C, 38.45; H, 5.77; N, 11.76. Calc. for C<sub>19</sub>H<sub>33</sub>N<sub>5</sub>CuCl<sub>2</sub>O<sub>8</sub>: C, 38.42; H, 5.60; N, 11.94%. FAB mass (*m/z*): 493.3 for [Cu(3c) + ClO<sub>4</sub>]<sup>+</sup>, 394.3 for [Cu(3c) – H]<sup>+</sup>. IR (Nujol mull, cm<sup>-1</sup>): 3228 (ν<sub>N-H</sub>).

**Preparation of [Cu<sub>2</sub>(4)](ClO<sub>4</sub>)<sub>4</sub>·2H<sub>2</sub>O.** A methanol solution (*ca.* 30 mL) of Cu(OAc)<sub>2</sub>·H<sub>2</sub>O (2.0 g, 10 mmol), 97% 1,4-bis(3-aminopropyl)piperazine (2.1 mL, 10 mmol), 99% ethylenediamine (0.35 mL, 5.0 mmol), and 35% formaldehyde (2.4 mL, 30 mmol) was refluxed for *ca.* 15 h and then was cooled to room temperature. After the addition of an excess amount of NaClO<sub>4</sub> dissolved in water (10 mL),

the mixture was slowly evaporated in an open beaker at room temperature to produce a purple solid. The product was filtered, washed with ethanol, and recrystallized from hot water. Yield: ~60% based on the metal salt. Found: C, 28.90; H, 5.60; N, 12.89. Calc. for C<sub>26</sub>H<sub>60</sub>N<sub>10</sub>CuCl<sub>4</sub>O<sub>18</sub>: C, 29.19; H, 5.65; N, 13.09%. FAB mass (*m/z*): 933.0 for [Cu<sub>2</sub>(4) + 3ClO<sub>4</sub>]<sup>+</sup>, 834.1 for [Cu<sub>2</sub>(4) – H + 2ClO<sub>4</sub>]<sup>+</sup>. IR (Nujol mull, cm<sup>-1</sup>): 3240 (ν<sub>N-H</sub>).

**Preparation of [Cu<sub>2</sub>(5)](ClO<sub>4</sub>)<sub>4</sub>·H<sub>2</sub>O.** To a methanol solution (*ca.* 30 mL) of Cu(OAc)<sub>2</sub>·H<sub>2</sub>O (2.0 g, 10 mmol) were added 97% 1,4-bis(3-aminopropyl)piperazine (3.2 mL, 15 mmol) and 35% formaldehyde (2.4 mL, 30 mmol). The solution was refluxed for *ca.* 15 h and then was cooled to room temperature. After the addition of an excess amount of NaClO<sub>4</sub> dissolved in water (10 mL), the mixture was slowly evaporated in an open beaker at room temperature to produce a purple solid. The product was filtered, washed with ethanol, and recrystallized from 0.01 M NaOH aqueous solution. Yield: ~70% based on the metal salt. Found: C, 34.21; H, 6.70; N, 14.06. Calc. for C<sub>34</sub>H<sub>74</sub>N<sub>12</sub>CuCl<sub>4</sub>O<sub>17</sub>: C, 34.26; H, 6.26; N, 14.10%. FAB mass (*m/z*): 1073.4 for [Cu<sub>2</sub>(5) + 3ClO<sub>4</sub>]<sup>+</sup>, 972.6 for [Cu<sub>2</sub>(5) – H + 2ClO<sub>4</sub>]<sup>+</sup>. IR (Nujol mull, cm<sup>-1</sup>): 3230 (ν<sub>N-H</sub>).

**Preparation of [Cu<sub>2</sub>(H<sub>2</sub>5)](ClO<sub>4</sub>)<sub>6</sub>.** To an aqueous solution (10 mL) of [Cu<sub>2</sub>(5)](ClO<sub>4</sub>)<sub>4</sub> (1.0 g) was added concentrated HClO<sub>4</sub> (0.5 mL). After the addition of excess NaClO<sub>4</sub>, the mixture was evaporated in an open beaker at room temperature to produce a purple solid. The product was filtered, washed with ethanol, and dried in air. Yield: ~90%. Found: C, 29.59; H, 5.97; N, 12.07. Calc. for C<sub>34</sub>H<sub>74</sub>N<sub>12</sub>CuCl<sub>6</sub>O<sub>24</sub>: C, 29.70; H, 5.43; N, 12.23%. IR (Nujol mull, cm<sup>-1</sup>): 3239 (ν<sub>N-H</sub>), 3250 (ν<sub>N-H</sub>).

## Results and Discussion

**Synthesis and Characterization.** The 15-membered macrobicyclic complexes [Cu(3a)]<sup>2+</sup>, [Cu(3b)]<sup>2+</sup>, and [Cu(3c)]<sup>2+</sup> were prepared in high yield by the reactions (Eq. (2)) of 1,4-bis(3-aminopropyl)piperazine, formaldehyde, and appropriate primary amines in the presence of the metal ion. The dinuclear complex [Cu<sub>2</sub>(4)]<sup>4+</sup> was prepared by the one-pot reaction (Eq. (3)) of the metal ion, 1,4-bis(3-aminopropyl)piperazine, ethylenediamine, and formaldehyde in a 2:2:1:4 molar ratio. The reaction (Eq. (4)) of Cu<sup>2+</sup> ion, 1,4-bis(3-aminopropyl)piperazine, and formaldehyde in a 2:3:4 molar ratio produces [Cu<sub>2</sub>(5)]<sup>4+</sup>. The addition of an acid to a solution of [Cu<sub>2</sub>(5)]<sup>4+</sup> produces [Cu<sub>2</sub>(H<sub>2</sub>5)]<sup>6+</sup>, in which two tertiary nitrogen atoms of the bridging piperazine group are protonated. The preparation of [Cu<sub>2</sub>(4)]<sup>4+</sup> and [Cu<sub>2</sub>(5)]<sup>4+</sup> in this work is somewhat interesting because the formation and linking of two 15-membered macrobicyclic complexes take place simultaneously. Furthermore, the synthesis of [Cu<sub>2</sub>(5)]<sup>4+</sup> requires only one kind of amine.

Unfortunately, we were unable to obtain any single crystals of the copper(II) complexes suitable for X-ray crystallography. However, the formation of the mononuclear and dinuclear complexes could be confirmed by their FAB mass

spectra as well as the elemental analyses and the infrared spectra (see Experimental Section). The FAB mass spectra of  $[\text{Cu}(\text{L}')](\text{ClO}_4)_2$  ( $\text{L}' = \mathbf{3a}, \mathbf{3b},$  or  $\mathbf{3c}$ ) show two groups of peaks corresponding to the fragments  $[\text{Cu}(\text{L}') + \text{ClO}_4]^+$  and  $[\text{Cu}(\text{L}') - \text{H}]^+$ . The spectrum of  $[\text{Cu}_2(\mathbf{4})](\text{ClO}_4)_4$  shows two groups of peaks corresponding to  $[\text{Cu}_2(\mathbf{4}) + 3\text{ClO}_4]^+$  and  $[\text{Cu}_2(\mathbf{4}) - \text{H} + 2\text{ClO}_4]^+$  at  $m/e$  933.0 and 834.1, respectively. In the spectrum of  $[\text{Cu}_2(\mathbf{5})](\text{ClO}_4)_4$ , peaks corresponding to  $[\text{Cu}_2(\mathbf{5}) + 3\text{ClO}_4]^+$  and  $[\text{Cu}_2(\mathbf{5}) - \text{H} + 2\text{ClO}_4]^+$  are observed at  $m/e$  1073.4 and 972.6, respectively. Infrared spectrum of each complex shows  $\nu_{\text{N-H}}$  of the coordinated secondary amino groups at *ca.* 3230 nm. The molar conductance values of the monuclear complexes  $[\text{Cu}(\text{L}')](\text{ClO}_4)_2$  measured in water (200–220  $\Omega^{-1}\text{mol}^{-1}\text{cm}^2$ ) and acetonitrile (250–260  $\Omega^{-1}\text{mol}^{-1}\text{cm}^2$ ) indicate that they are 1:2 electrolytes. The values of  $[\text{Cu}_2(\mathbf{4})](\text{ClO}_4)_4$  and  $[\text{Cu}_2(\text{H}_2\mathbf{5})](\text{ClO}_4)_6$  measured in water were found to be 440 and 580  $\Omega^{-1}\text{mol}^{-1}\text{cm}^2$ , respectively.

The electronic absorption spectrum (Table 1) of  $[\text{Cu}(\mathbf{3a})]^{2+}$  measured in nitromethane shows a *d-d* transition band at 545 nm ( $\epsilon = 190 \text{ M}^{-1}\text{cm}^{-1}$ ). The wavelength and molar absorption coefficient are comparable with those of other related square-planar copper(II) complexes with a 5-6-6-6 chelate sequences.<sup>4,6</sup> The wavelengths of the *d-d* band for  $[\text{Cu}(\mathbf{3b})]^{2+}$  and  $[\text{Cu}(\mathbf{3c})]^{2+}$  measured in nitromethane are quite similar to that for  $[\text{Cu}(\mathbf{3a})]^{2+}$ , showing that their ligand field strengths are nearly invariant with the nature of the *N*-alkyl pendant arms. However, the molar absorption coefficients of the *d-d* bands are influenced by the structural characteristics of the ligands, showing the order  $\mathbf{3a}$  ( $190 \text{ M}^{-1}\text{cm}^{-1}$ ) <  $\mathbf{3b}$  ( $210 \text{ M}^{-1}\text{cm}^{-1}$ ) <  $\mathbf{3c}$  ( $250 \text{ M}^{-1}\text{cm}^{-1}$ ).

The wavelengths of the *d-d* band for the complexes of  $\mathbf{3a-3c}$  are *ca.* 15 nm longer than those for the complexes of  $\mathbf{1a-1c}$ . This corresponds to the generally observed trend that the stepwise alkylation on coordinated amino groups of a polyaza macrocyclic complex weakens the ligand field strength;<sup>13,14</sup> in the complexes of  $\mathbf{3a-3c}$ , two coordinated nitrogen atoms are linked together by an additional ethylene bridge. It is also seen that the molar absorption coefficients for the complexes of  $\mathbf{3a-3c}$  ( $190\text{--}250 \text{ M}^{-1}\text{cm}^{-1}$ ) are distinctly larger than those for the complexes of  $\mathbf{1a-1c}$  ( $147\text{--}151 \text{ M}^{-1}\text{cm}^{-1}$ ). This may indicate the more distorted structure of

the former complexes containing additional  $-(\text{CH}_2)_2-$  bridge that links two coordinated nitrogen atoms. Table 1 also shows that the wavelengths and molar absorption coefficients of the *d-d* bands for the complexes measured in acetonitrile or water are longer and larger, respectively, than those measured in nitromethane. This can be attributed to the coordination of acetonitrile or water molecule(s).

The spectra of  $[\text{Cu}_2(\mathbf{4})]^{4+}$ ,  $[\text{Cu}_2(\mathbf{5})]^{4+}$  and  $[\text{Cu}_2(\text{H}_2\mathbf{5})]^{6+}$  measured in various solvents show the *d-d* band at 550–575 nm ( $\epsilon = 350\text{--}540 \text{ M}^{-1}\text{cm}^{-1}$ ); the spectra of  $[\text{Cu}_2(\mathbf{5})]^{4+}$  in acetonitrile and water are quite similar to those of  $[\text{Cu}_2(\text{H}_2\mathbf{5})]^{6+}$ . The wavelengths for the dinuclear complexes are quite similar to that for  $[\text{Cu}(\mathbf{3a})]^{2+}$ . Furthermore, the molar absorption coefficients are nearly twice that for  $[\text{Cu}(\mathbf{3a})]^{2+}$  or  $[\text{Cu}(\mathbf{3b})]^{2+}$ . The spectra indicate that each metal of the dinuclear complexes is in a square-planar Cu-N<sub>4</sub> environment.

#### Decomposition Reaction in Acidic Aqueous Solutions.

The copper(II) complexes of  $\mathbf{3a-3c}$ ,  $\mathbf{4}$ , and  $\mathbf{5}$  are extremely stable in the solid states and in neutral aqueous solutions, but are decomposed in acidic aqueous solutions. The decomposition rate of each complex ( $2.0 \times 10^{-3} \text{ M}$ ) in 0.3 M HClO<sub>4</sub> solution was measured spectrophotometrically at 20 °C. The pseudo first-order rate constants (*k*) for the reaction are listed in Table 2, along with those reported for the copper(II) complexes of  $\mathbf{1a-1c}$ .

The *k* value (Table 2) decreases in the order of  $[\text{Cu}(\mathbf{3a})]^{2+}$  ( $3.0 \times 10^{-6} \text{ s}^{-1}$ ) >  $[\text{Cu}(\mathbf{3b})]^{2+}$  ( $2.3 \times 10^{-6} \text{ s}^{-1}$ ) >  $[\text{Cu}(\mathbf{3c})]^{2+}$  ( $4.7 \times 10^{-7} \text{ s}^{-1}$ ), supporting the suggestion that their decomposition rates are strongly influenced by the bulkiness of the *N*-alkyl pendant arm, even though the alkyl group is attached to the uncoordinated nitrogen atom.<sup>6</sup> The decomposition rates of  $[\text{Cu}(\mathbf{3a})]^{2+}$  and  $[\text{Cu}(\mathbf{3c})]^{2+}$  are *ca.* 10 times slower than those of  $[\text{Cu}(\mathbf{1a})]^{2+}$  and  $[\text{Cu}(\mathbf{1c})]^{2+}$ , respectively, in spite of the fact that the former complexes exhibit somewhat weaker ligand field strength than the latter ones. This implicates that the rate is not directly influenced by the strength of the Cu-N interactions, but is largely affected by the position of the additional *N-CH<sub>2</sub>CH<sub>2</sub>-N* linkage. According the “B-strain”,<sup>15</sup> coordinated tertiary amino groups in a macrocyclic complex are expected to exhibit weaker proton affinity than

**Table 1.** Electronic Absorption Spectra of the complexes<sup>a</sup>

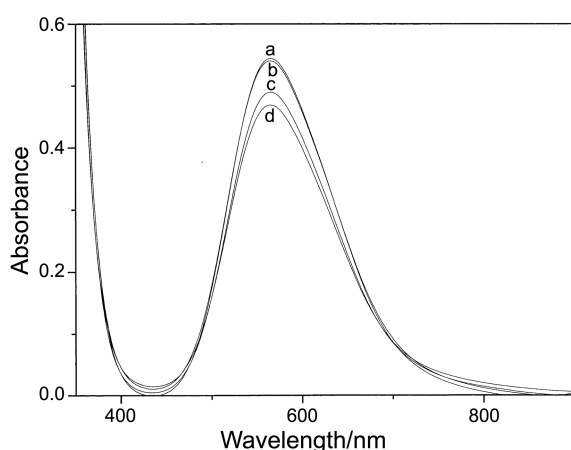
Complex	$\lambda_{\text{max}}$ , nm ( $\epsilon$ , $\text{M}^{-1}\text{cm}^{-1}$ ) <sup>a</sup>			
$[\text{Cu}(\mathbf{1a})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}^b$	532(148)	543(142) <sup>c</sup>		
$[\text{Cu}(\mathbf{1b})](\text{ClO}_4)_2^b$	530(151)	544(147) <sup>c</sup>		
$[\text{Cu}(\mathbf{1c})](\text{ClO}_4)_2^b$	530(147)	544(147) <sup>c</sup>		
$[\text{Cu}(\mathbf{3a})](\text{ClO}_4)_2$	545(190)	560(250) <sup>c</sup>	572(210) <sup>d</sup>	550 <sup>e</sup>
$[\text{Cu}(\mathbf{3b})](\text{ClO}_4)_2$	547(210)	560(280) <sup>c</sup>	570(225) <sup>d</sup>	550 <sup>e</sup>
$[\text{Cu}(\mathbf{3c})](\text{ClO}_4)_2$	545(250)	560(290) <sup>c</sup>	573(260) <sup>d</sup>	560 <sup>e</sup>
$[\text{Cu}_2(\mathbf{4})](\text{ClO}_4)_4 \cdot 2\text{H}_2\text{O}$	550 (350)	564(460) <sup>b</sup>	573(365) <sup>d</sup>	555 <sup>e</sup>
$[\text{Cu}_2(\mathbf{5})](\text{ClO}_4)_4 \cdot \text{H}_2\text{O}$		562(540) <sup>b</sup>	574(485) <sup>d</sup>	560 <sup>e</sup>
$[\text{Cu}_2(\text{H}_2\mathbf{5})](\text{ClO}_4)_6$	550 (408)	563(533) <sup>b</sup>	575(480) <sup>d</sup>	555 <sup>e</sup>

<sup>a</sup>Measured in nitromethane at 20 °C unless otherwise specified. <sup>b</sup>Ref. 6. <sup>c</sup>In acetonitrile. <sup>d</sup>In water. <sup>e</sup>In Nujol mull.

**Table 2.** Decomposition Rate Constants ( $k_{\text{obsd}}$ ) of the Complexes in 0.3 M HClO<sub>4</sub> Solutions at 20 °C<sup>a</sup>

Complex	$k_{\text{obsd}}$ , $\text{s}^{-1}$
$[\text{Cu}(\mathbf{1a})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}^b$	$2.9 \times 10^{-5}$ ( <i>ca.</i> 6.6 h)
$[\text{Cu}(\mathbf{1b})](\text{ClO}_4)_2^b$	$5.4 \times 10^{-6}$ ( <i>ca.</i> 35.5 h)
$[\text{Cu}(\mathbf{1c})](\text{ClO}_4)_2^b$	$2.1 \times 10^{-6}$ ( <i>ca.</i> 91.6 h)
$[\text{Cu}(\mathbf{2})](\text{ClO}_4)_2^c$	$3.3 \times 10^{-3}$ ( <i>ca.</i> 210 s)
$[\text{Cu}(\mathbf{3a})](\text{ClO}_4)_2$	$3.0 \times 10^{-6}$ ( <i>ca.</i> 63.4 h)
$[\text{Cu}(\mathbf{3b})](\text{ClO}_4)_2$	$2.3 \times 10^{-6}$ ( <i>ca.</i> 84.4 h)
$[\text{Cu}(\mathbf{3c})](\text{ClO}_4)_2$	$4.7 \times 10^{-7}$ ( <i>ca.</i> 411 h)
$[\text{Cu}_2(\mathbf{4})](\text{ClO}_4)_4$	$1.3 \times 10^{-7}$ ( <i>ca.</i> 1516 h)
$[\text{Cu}_2(\text{H}_2\mathbf{5})](\text{ClO}_4)_6$	$1.1 \times 10^{-7}$ ( <i>ca.</i> 1740 h)

<sup>a</sup>[Complex] =  $2.0 \times 10^{-3} \text{ M}$ ; half-life ( $t_{1/2}$ ) is in parentheses. <sup>b</sup>Ref. 6. <sup>c</sup>Ref. 12; measured in 0.3 M HNO<sub>3</sub>.



**Figure 1.** Electronic absorption spectra of  $[\text{Cu}_2(\text{H}_2\mathbf{5})](\text{ClO}_4)_6$  ( $2.0 \times 10^{-3}$  M) in 0.3 M  $\text{HClO}_4$  water-acetonitrile (1:1) solution at 20 °C. Curve a is the first spectrum. Curves b, c, and d are the spectra measured after 21, 216, and 360 h, respectively.

coordinated secondary amino groups. Furthermore, the proton affinity of the tertiary nitrogen atoms in the 1,4-diazacyclohexane ring (**3a**) may be weaker than that in the 1,3-diazacyclopentane ring (**1a**).<sup>4,5,15</sup> Therefore, the slow decomposition of the copper(II) complexes of **3a-3c** is attributed in part to the relatively weak proton affinity of two coordinated tertiary amino groups that are linked together by the additional  $-(\text{CH}_2)_2-$  bridge.

Most interestingly, the decomposition rates of the dinuclear bis(macrocyclic) complexes  $[\text{Cu}_2(\mathbf{4})]^{4+}$  ( $k = 1.3 \times 10^{-7} \text{ s}^{-1}$ ;  $t_{1/2} = \text{ca. } 1516 \text{ h}$ ) and  $[\text{Cu}_2(\text{H}_2\mathbf{5})]^{6+}$  ( $k = 1.1 \times 10^{-7} \text{ s}^{-1}$ ;  $t_{1/2} = \text{ca. } 1740 \text{ h}$ ) are extraordinarily slow; the electronic absorption spectra (Fig. 1) of  $[\text{Cu}_2(\text{H}_2\mathbf{5})]^{6+}$  measured in 0.3 M  $\text{HClO}_4$  solution show that only less than 13% of the complex is decomposed during 320 h. The rate of  $[\text{Cu}_2(\text{H}_2\mathbf{5})]^{6+}$  is ca. 30 times slower than that of the mononuclear complex  $[\text{Cu}(\mathbf{3a})]^{2+}$ . This can be attributed to the topologically constrained structure of the ligand and the bulkiness of the *N*-substituent that restrict the protonation of the coordinated amino groups.

### Summary

The dinuclear bis(macrocyclic) complexes  $[\text{Cu}_2(\mathbf{4})]^{4+}$  and  $[\text{Cu}_2(\mathbf{5})]^{4+}$  as well as the mononuclear copper(II) complexes of **3a-3c** can be prepared by the metal-template condensation involving 1,4-bis(3-aminopropyl)piperazine and formaldehyde. This work supports the suggestion that their

decomposition reaction rates in acidic aqueous solutions are strongly influenced by the steric factors of the *N*-alkyl groups, even though the alkyl groups are attached to the uncoordinated nitrogen atoms.<sup>6</sup> This work also shows that the ligand field strength and chemical properties of the copper(II) complexes are strongly influenced by the position of the additional  $-(\text{CH}_2)_2-$  linkage. To our knowledge,  $[\text{Cu}_2(\mathbf{4})]^{4+}$  and  $[\text{Cu}_2(\mathbf{5})]^{4+}$  are very rare examples of 15-membered pentaaza macrocyclic complexes that are relatively inert against decomposition even in concentrated  $\text{HClO}_4$  solutions.

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