Synthesis and Characterization of New Mono-N-functionalized Tetraaza Macrocyclic Nickel(II) and Copper(II) Complexes

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The reaction of bromoacetonitrile with 3,14-dimethyl-2,6,13,17-tetraaza-tricyclo[16.4.1.0,18,0.1.12]tricosane (L) containing a N-CH$_2$-N linkage produces 17-cyanomethyl-3,14-dimethyl-2,6,13,17-tetraaza-tricyclo[16.4.1.0,18,0.1.12]tricosane (L). The mono-N-functionalized macrocyclic complexes [ML]$^{2+}$ (M = Ni(II) or Cu(II)); L = 2-cyanomethyl-5,16-dimethyl-2,6,13,17-tetraaza-tricyclo[16.4.0.0,12]docosane) can be prepared by the reaction of L with nickel(II) or copper(II) ion in acetonitrile. The N-CH$_2$CN group attached to [ML]$^{2+}$ readily reacts with water or methanol to yield the corresponding complexes of HL$^-$ bearing one N-CH$_2$CONH$_2$ pendant arm or L$^-$ bearing one N-CH$_2$C(=NH)OCH$_3$ group. The N-CH$_2$CONH$_2$ or N-CH$_2$C(=NH)OCH$_3$ group of each complex is coordinated to the central metal ion. Both [NiL$^2$($\text{H}_2$O)$_2$] and [CuL$^2$] are quite stable in acidic aqueous solutions, but undergo hydrolysis to yield [Ni(L$^3$)(H$_2$O)$_2$]$^{2+}$ or [Cu(L$^3$)]$^{2+}$ in basic aqueous solutions. In contrast to [Cu(HL$^3$)]$^{2+}$, [NiL$^3$] (H$_2$O)$_2$$^+$ is readily deprotonated to form [NiL$^3$($\text{H}_2$O)]$^+$ (L$^3$ = a deprotonated form of HL$^-$) in basic aqueous solutions.

Key Words: Macro cyclic complexes, Mono-N-functionalized macrocycle, Functional pendant arm, Hydrolysis, Methanolysis

Introduction

Polyaza macrocyclic compounds bearing functional pendant arm(s) have attracted a great attention because of their interesting chemical properties and potential applications in various fields. The introduction of functional pendant arm(s) into polyaza macrocycles often leads to significant changes in chemical properties of the ligands. Chemical properties and coordination behaviors of such compounds are also influenced by the number of the functional group. For example, two N-CH$_2$CH$_2$OH groups of [NiL$^3$] are coordinated to the central metal ion, whereas the functional group of [Ni(HL$^9$)]$^{2+}$ is not involved in coordination in the solid state. The N-CH$_2$CH$_2$OH groups of [NiL$^3$] are known to be quite resistant to deprotonation in basic aqueous solutions. On the other hand, [Ni(HL$^9$)]$^{2+}$ is readily deprotonated to yield [NiL$^3$($\text{H}_2$O)$_2$]$^+$ (L$^9$ = a deprotonated form of HL$^-$). Although a number of functionalized tetraaza macrocycles and their metal complexes have been prepared and investigated to date, those bearing only one functional pendant arm are relatively rare. This may be attributed to the fact that selective substitution to one of the four secondary amino groups in a 14-membered tetraaza macrocycle often requires several steps and/or is difficult. Therefore, we have been interested in the regioselective N-functionalization of 14-membered tetraaza macrocycles.

Polyaza macrocyclic compounds bearing N-(CH$_2$)$_n$CN (n = 1 or 2) pendant arms are useful precursors for the preparation of various types of functionalized macrocyclic complexes. For instance, [ML]$^{2+}$ (M = Ni(II) or Cu(II)) bearing two N-CH$_2$CN groups reacts with water or methanol under relatively mild conditions to yield [ML]$^{2+}$ bearing two N-CH$_2$CONH$_2$ (amide) groups or [ML]$^{2+}$ bearing two N-CH$_2$C(=NH)OCH$_3$ (imidate ester) pendant arms. It has been revealed that the reactivity of the N-CH$_2$CN group attached to a macrocyclic complex is strongly influenced by the nature of the central metal ion. In this work, we prepared [ML]$^{2+}$ bearing only one N-CH$_2$CN pendant arm. The complexes of HL$^-$ and L$^-$ bearing one N-CH$_2$CONH$_2$ or one N-CH$_2$C(=NH)OCH$_3$ pendant arm were also prepared by the reaction of [ML]$^{2+}$ with water or methanol. Interestingly, the N-CH$_2$CONH$_2$ group attached to [Ni(L$^3$)]$^{2+}$ was found to be much more acidic than that of [Cu(L$^3$)]$^{2+}$ or [NiL$^3$]$. Herein we report an efficient synthesis and chemical properties of the nickel(II) and copper(II) complexes of L$^2$.L$^4$.
Experimental

Measurements. Electronic absorption spectra were recorded with an Analytikjena Specord 200 UV-vis spectrophotometer, infrared spectra with a Genesis II FT-IR spectrophotometer, NMR spectra with a Varian Mercury 300 FT NMR spectrometer, and conductance measurements with a Metrohm Herisau Conductometer E518. GC-mass spectra were measured with a Shimadzu GCMS-QP5050 spectrometer. FAB mass spectra were performed at the Korea Basic Science Institute, Daegu, Korea. Elemental analyses were performed at the Research Center for Instrumental Analysis, Daegu University, Gyeongsan, Korea. Magnetic moments were calculated from magnetic susceptibility data obtained at 293 K using a Johnson Matthey MK-1 magnetic susceptibility balance.

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

Preparation of 17-Cyanomethyl-3,14-dimethyl-2,6,13,17-tetraazatetracyclo[16.4.4.03,11.04,10]tricosane (L1) and [NiL3](ClO4)2·H2O. L1 was prepared by the reaction of L1 with formaldehyde. A chloroform solution (20 mL) of L1 (2.0 g, 5.7 mmol) and bromoacetonitrile (0.5 mL, 6.9 mmol) was stirred at 70 °C for 30 min. The resulting solution was evaporated at room temperature to produce a dark purple solid. The product was recrystallized from 1.0 × 10−3 M HClO4 acetonitrile-water (1:2) solution. Yield: ~70%. Found: C, 45.69; H, 7.34; N, 11.92
calc. for C39H37Ni3O11, 40.28; H, 6.61; N, 10.67
calc. for C39H37Ni3O11

Preparation of [Cu(HL2)(H2O)][ClO4]2. This complex was prepared by a method similar to that for [NiL3](ClO4)2·H2O except that Cu(OAc)2·H2O (2.0 g, 10 mmol) was reacted instead of Ni(OAc)2·4H2O. The red-purple solid was recrystallized from 1.0 × 10−3 M HClO4 acetonitrile-water (1:2) solution. Yield: ~40% based on L1. Anal. Found: C, 40.78; H, 6.88; N, 10.40 calc. for C52H46NiCl2CuO6: C, 40.28; H, 6.61; N, 10.67
calc. for C52H46NiCl2CuO6

Preparation of [Ni(HL3)(H2O)][ClO4]2. The pH of a water-acetonitrile (1:2) solution (20 mL) of [NiL3](ClO4)2·H2O (0.5 g) was adjusted to ≥ 8 through the addition of 0.1 M NaOH solution. The solution was stirred at room temperature for 5 min. The resulting pale purple solution was filtered to remove any solid, and then concentrated HClO4 (1.0 mL) was added to the filtrate. The mixture was evaporated at room temperature to produce a pale purple solid. The product was collected by filtration, washed with cold methanol, and dried in air. It was recrystallized by the addition of HClO4 to hot a water-acetonitrile (1:1) solution of the crude product. Yield: ~70%. Found: C, 39.48; H, 6.51; N, 10.56 calc. for C42H44Ni3Cl2NiO11: C, 39.48; H, 6.78; N, 10.46
calc. for C42H44Ni3Cl2NiO11

Preparation of [NiL3](H2O)3[ClO4]2. This complex was also prepared by stirring a warm (~50 °C) solution of [NiL3](ClO4)2·H2O (0.5 g) for 10 min. The resulting solution was filtered, washed with cold water, and dried in air. It was recrystallized by the addition of concentrated HClO4 (1.0 mL) to the resulting solution produced the purple solid.

Preparation of [NiL3](H2O)3[ClO4]2. The pH of a water-acetonitrile (1:1) solution (20 mL) of [NiL3](ClO4)2·H2O (0.5 g) was adjusted to ≥ 8 through the addition of 1.0 M NaOH solution. The solution was evaporated at room temperature to produce a dark purple solid. The product was collected by filtration, washed with cold water, and dried in air. Yield: ~80%. Found: C, 45.69; H, 7.34; N, 11.92 calc. for C42H44Ni3Cl2NiO11: C, 46.46; H, 7.80; N, 12.31
calc. for C42H44Ni3Cl2NiO11

Preparation of [NiL3](H2O)3[ClO4]2. The pH of a water-acetonitrile (1:1) solution (20 mL) of [NiL3](ClO4)2·H2O (0.5 g) was adjusted to ≥ 7 through the addition of 1.0 M NaOH solution. The solution was evaporated at room temperature to produce a dark purple solid. The product was collected by filtration, washed with cold water, and dried in air. Yield: ~70%. Found: C, 45.69; H, 7.34; N, 11.92
calc. for C42H44Ni3Cl2NiO11: C, 45.69; H, 7.34; N, 11.92
calc. for C42H44Ni3Cl2NiO11
IR (cm$^{-1}$): 3501 (ν$\text{O-H}$), 3243 (ν$\text{N-H}$), 3202 (ν$\text{C=O}$), 1680 (ν$\text{C-O}$), and 1600 [δ(\text{NH}_2)].

This complex was also prepared by stirring a warm (~50 °C) basic (pH ≥ 10) water-acetonitrile (1:1) mixture. The resulting solution was refluxed for 5 min. During which time, the addition of concentrated HClO$_4$ (0.5 g) was added triethylamine (0.1 mL). The resulting solution produced the purple solid.

Preparation of [NiL$^4$(H$_2$O)](ClO$_4$)$_2$. To a methanol-acetonitrile (1:3) solution (20 mL) of [NiL$^4$](ClO$_4$)$_2$:H$_2$O (0.5 g) was added triethylamine (0.1 mL). The resulting solution was refluxed for 5 min. During which time, the mixture was evaporated to precipitate a purple solid. The product was collected by filtration, washed with cold methanol, and dried in air. It was recrystallized from hot water-acetonitrile (1:1) mixture. Yield: ~70%. Anal. Found: C, 40.90; H, 7.45; N, 10.09. Calc. for C$_{25}$H$_{24}$N$_4$Cl$_2$NiO$_6$: C, 40.43; H, 6.93; N, 10.25%. FAB Mass (m/z): 564.2 for [NiL$^4$ + ClO$_4$]$^{-}$; 464.3 for [NiL$^4$ – H]$^{-}$. IR (cm$^{-1}$): 3500 (ν$\text{O-H}$, H$_2$O), 3290 (ν$\text{N-H}$), 3200 (ν$\text{C=O}$), 1666 (ν$\text{C-O}$), and 1620 [δ(\text{H}_2\text{O})]: μ$_{\text{eff}}$ = 2.76 μB.

Preparation of [CuL$^4$(ClO$_4$)$_2$. This complex was prepared in a methanol-acetonitrile (1:3) solution (20 mL) by a method similar to that for [NiL$^4$(H$_2$O)](ClO$_4$)$_2$: except that [CuL$^2$](ClO$_4$)$_2$ (0.5 g) was reacted instead of [NiL$^4$](ClO$_4$)$_2$:H$_2$O. The purple solid was recrystallized from hot acetonitrile-water (1:2) solution. Yield: ~70%. Anal. Found: C, 40.25; H, 7.01; N, 9.93. Calc. for C$_{23}$H$_{19}$N$_3$Cl$_2$CuO$_6$: C, 40.15; H, 6.88; N, 10.18%. FAB Mass (m/z): 591.4 for [CuL$^4$ + ClO$_4$]$^{-}$; 470.2 for [CuL$^4$ – H]$^{-}$. IR (cm$^{-1}$): 3500 (ν$\text{O-H}$, H$_2$O), 3300 (ν$\text{N-H}$), 3200 (ν$\text{N-H}$, br), 1665 (ν$\text{C=O}$), and 1620 [δ(\text{H}_2\text{O})]

**Synthesis.** The mono-N-hydroxyethylated macrocycle HL$^3$ has been prepared by the direct reaction of L$^1$ with BrCH$_2$CH$_2$OH. However, unexpectedly, our initial attempts to prepare L$^2$ from the reaction of L$^1$ with BrCH$_2$CN in a 1:1 molar ratio were unsuccessful; the solid isolated from the reaction solution was found to be a mixture of L$^2$ bearing two N-CH$_2$CN pendant arms and the reactant L$^1$. Therefore, the synthesis of L$^2$ begins with the preparation of L$^10$ where two amino groups are protected. The reaction of L$^10$ with BrCH$_2$CN produces the macrocycle L$^{11}$ bearing only one N-CH$_2$CN pendant arm. The macrocycle L$^2$ could be prepared as its nickel(II) or copper(II) complex, [ML$^2$]$^{2+}$ (M = Ni(II) or Cu(II)), by the reaction of L$^{11}$ with the metal ion in acetonitrile. The nickel(II) and copper(II) complexes of HL$^3$ and L$^4$ bearing one N-CH$_2$CONH$_2$ or N-CH$_2$C($\equiv$NH)OMe pendant arm were prepared by the reaction of [ML$^2$]$^{2+}$ with water or methanol. The reactivity of [ML$^2$]$^{2+}$ in water or methanol is not quite different from that reported for [ML$^3$]$^{2+}$: 17,23 The preparation of nickel(II) and copper(II) complexes of HL$^3$ can also be achieved by the hydrolysis of the corresponding complexes of L$^4$ in basic aqueous solutions. The synthetic procedures for the complexes of L$^2$ – L$^4$ are shown in Scheme 1.

In basic aqueous solutions, [Ni(HL$^3$)(H$_2$O)](ClO$_4$)$_2$ readily undergoes deprotonation to yield [NiL$^4$(H$_2$O)]ClO$_4$ (L$^2$ = a deprotonated form of HL$^3$). The isolation of [NiL$^4$(H$_2$O)]ClO$_4$ as a solid in the present work is quite interesting, because such deprotonation is not observed for other related macrocyclic complexes, such as [Cu(HL$^3$)](ClO$_4$)$_2$ and [NiL$^6$](ClO$_4$)$_2$.

In the case of [Cu(HL$^3$)](ClO$_4$)$_2$ or [NiL$^6$](ClO$_4$)$_2$, any

![Scheme 1](image-url)
Table 1. Electronic Absorption Spectra and Molar Conductance Data

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\lambda_{max}$, nm (ε, M$^{-1}$cm$^{-1}$)</th>
<th>$\Lambda$\textsubscript{0} (Ω$^{-1}$cm$^{2}$mol$^{-1}$)</th>
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<tr>
<td>[NiL$^2$]$^1$(ClO$_4$)$_2$</td>
<td>465(66)$^f$</td>
<td>477(100)$^f$</td>
</tr>
<tr>
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<td>478(100)</td>
<td>695(2.6)</td>
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<td><a href="H$_2$O">NiHL$^2$</a>(ClO$_4$)$_2$</td>
<td>523(7.7)</td>
<td>724(2.1)$^f$</td>
</tr>
<tr>
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<td>506(7.4)$^f$</td>
<td>700(2.7)$^f$</td>
</tr>
<tr>
<td><a href="H$_2$O">NiL$^2$</a>$_2$ClO$_4$</td>
<td>532(7.5)$^f$</td>
<td>750(6.7)$^f$</td>
</tr>
<tr>
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<td>537(11.5)</td>
<td>740(3.1)</td>
</tr>
<tr>
<td><a href="H$_2$O">NiL$^3$</a>$_2$ClO$_4$</td>
<td>556(25)$^f$</td>
<td>750(8.0)$^f$</td>
</tr>
<tr>
<td><a href="H$_2$O">NiL$^3$</a>$_2$ClO$_4$</td>
<td>568(40)$^f$</td>
<td>710(4.5)$^f$</td>
</tr>
<tr>
<td><a href="ClO$_4$">NiL$^3$</a>$_2$$^f$</td>
<td>333(13)$^f$</td>
<td>495$^f$</td>
</tr>
<tr>
<td>[CuL$^2$]ClO$_4$ $^b$</td>
<td>492(77)$^f$</td>
<td>532(18)$^f$</td>
</tr>
<tr>
<td><a href="ClO$_4$">CuL$^2$</a>$_2$:H$_2$O</td>
<td>497(137)</td>
<td>553(20)</td>
</tr>
<tr>
<td><a href="ClO$_4$">CuHL$^2$</a>$_2$</td>
<td>527(170)$^f$</td>
<td>710(4.5)$^f$</td>
</tr>
<tr>
<td>[CuHL$^2$]ClO$_4$</td>
<td>532(165)$^f$</td>
<td>130 233 55$^f$</td>
</tr>
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<td>100$^f$</td>
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<td>553(120)</td>
<td>134 235 56$^f$</td>
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<tr>
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<td>552(122)$^f$</td>
<td>130 235 56$^f$</td>
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<td>55$^f$</td>
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<tr>
<td>[CuL$^2$]ClO$_4$</td>
<td>533(13)$^f$</td>
<td>134 235 56$^f$</td>
</tr>
</tbody>
</table>

*Measured in nitromethane at room temperature unless otherwise specified. $^a$Ref. 24. $^b$Measured in acetonitrile. $^c$Measured in DMSO. $^d$Measured in Nujol mull. $^e$Ref. 17.

deprotonated form could not be prepared under similar experimental conditions. It is obvious that the acidity of the N-CH$_2$CONH$_2$ group in [Ni(HL)$_3$(H$_2$O)](ClO$_4$)$_2$ is stronger than that attached to [Cu(HL)$_3$](ClO$_4$)$_2$ or [NiL$^2$](ClO$_4$)$_2$.

Spectra and Properties of [NiL$^2$](ClO$_4$)$_2$:H$_2$O and [CuL$^2$](ClO$_4$)$_2$:H$_2$O. The FAB mass spectrum of [NiL$^2$]-
(ClO$_4$)$_2$:H$_2$O shows two groups of peaks at $m/z$ 531.9 {[NiL$^2$ + ClO$_4$]$^+$} and 431.9 {[NiL$^2$ − H]$^+$}. The spectrum of [CuL$^2$]-
(ClO$_4$)$_2$:H$_2$O also shows two groups of peaks corresponding to [CuL$^2$ + ClO$_4$]$^+$ and {[CuL$^2$ − H]$^+$} fragments at $m/z$ 536.9 and 438.0, respectively. In the infrared spectra of the complexes, peaks corresponding to $\nu_{N-H}$ of the coordinated amino groups are observed at 3120-3220 cm$^{-1}$. The spectra also show $\nu_{C-CON}$ of the pendant arm at ca. 2250 cm$^{-1}$. The nickel(II) complex was found to be a diamagnetic substance.

$^{13}$C-NMR spectrum (see Experimental Section) of the nickel(II) complex also corresponds to the ligand structure of L$_2$, in which one cyanomethyl group is attached to the sterically less hindered nitrogen atom. The electronic absorption spectra (Table 1) of [NiL$^2$]ClO$_4$:H$_2$O measured in Nujol mull and various solvents show a d-d transition band at ca. 477 nm. The wavelength is intermediate between those of the square-planar complexes [NiL$^2$](ClO$_4$)$_2$ (465 nm) and [NiL$^3$](ClO$_4$)$_2$ (492 nm).$^{15,25}$ This corresponds to the general trend that stepwise alkylation to coordinated nitrogen atoms of a 14-membered tetraaza macrocyclic nickel(II) complex weakens the ligand field strength.$^{15,16,26}$ The visible absorption spectra of [CuL$^2$]ClO$_4$:H$_2$O measured in Nujol mull (495 nm) and nitromethane (497 nm) are also corresponding to the square-planar Cu-N$_2$ chromophore.$^{15,25}$ Above results strongly indicate that [NiL$^2$](ClO$_4$)$_2$:H$_2$O has a square-planar coordination geometry. The wavelengths measured in acetonitrile (527 nm) and DMSO (532 nm) are ca. 30 nm longer than those measured in Nujol mull and nitromethane, implicating the coordination of the solvent molecule in the solvents.

The nickel(II) and copper(II) complexes are soluble in acetonitrile, nitromethane, or DMSO, but are nearly insoluble in methanol or water at room temperature. The complexes are quite inert against hydrolysis in acidic aqueous solutions (pH ≤ 6). As described above, however, they are readily hydroyzed to [Ni(HL)$_3$](H$_2$O)$_2$$^2$ or [Cu(HL)$_3$]$$^2$$^+$ in basic aqueous solutions.

Spectra and Properties of [Ni(HL)$_3$(H$_2$O)](ClO$_4$)$_2$, [Cu(HL)$_3$](ClO$_4$)$_2$, and [NiL$^2$(H$_2$O)]ClO$_4$. Infrared spectra of [Ni(HL)$_3$(H$_2$O)](ClO$_4$)$_2$ and [Cu(HL)$_3$](ClO$_4$)$_2$ show several peaks corresponding to $\nu_{N-H}$ of the coordinated amino and the amide groups at 3390-3190 cm$^{-1}$. The spectra also show $\nu_{C=O}$ of the pendant arm at ca. 1670 cm$^{-1}$. In the spectrum of [NiL$^2$(H$_2$O)]ClO$_4$, four peaks of $\nu_{N-H}$ are observed at 3310-3200 cm$^{-1}$. The FAB mass spectra of the nickel(II) and copper(II) complexes show two groups of peaks corresponding to the fragments [M(HL)$_3$] + ClO$_4$]$^+$ and [M(HL)$_3$ − H]$^+$ (see Experimental section). The magnetic moments (μ$_{eff}$) of [Ni(HL)$_3$(H$_2$O)](ClO$_4$)$_2$ and [NiL$^2$(H$_2$O)]ClO$_4$ in the solid states are 2.80 and 2.78 μ$_B$, respectively, at room temperature. This is consistent with a d$^8$ electronic configuration of the complexes in octahedral coordination geometry. The electronic absorption spectrum (Table 1) of [Ni(HL)$_3$(H$_2$O)](ClO$_4$)$_2$ measured in Nujol mull shows three bands at ca. 340 ($^3$B$_{1g}$ → $^1$E$_g$(P)), 510 ($^3$B$_{1g}$ → $^3$E$_b$), and 690 ($^3$B$_{1g}$ → $^3$B$_{2g}$ + $^3$B$_{2g}$ → $^3$A$_{2g}$) nm, indicating that the complex has octahedral coordination geometry in the solid state.$^{10,14,17,27}$ Water molecule as well as the pendant amide group is involved in coordination. The spectra measured in various solvents are similar to that measured in Nujol mull. The spectra of [NiL$^2$(H$_2$O)]ClO$_4$ measured in various solvents are comparable with those of [Ni(HL)$_3$(H$_2$O)](ClO$_4$)$_2$. However, the
wavelength and molar absorption coefficient of each band for [NiL^2(H_2O)][ClO_4]_2 are somewhat longer and larger, respectively, that those for [Ni(L^3)(H_2O)][ClO_4]_2. The electronic absorption spectra of [Cu(HL^3)][ClO_4]_2 measured in Nujol mull and various solvents show a d-d transition band at ca. 540 nm (ε = 125-130 M^(-1) cm^(-1)), supporting the suggestion that the complex has square-pyramidal coordination geometry.

The copper(II) complex, unlike the nickel(II) complexes, is reluctant to form octahedral structure. This may be closely related to Jahn-Teller distortion of octahedral copper(II) complexes. The values of the molar conductance (Table 1) measured in various solvents indicate that [Ni(L^2)(H_2O)][ClO_4]_2 (or [Cu(HL^3)][ClO_4]_2) and [NiL^4(H_2O)][ClO_4]_2 are 1:2 and 1:1 electrolytes, respectively. The deprotonated complex [NiL^4(H_2O)][ClO_4] as well as [Ni(L^2)(H_2O)][ClO_4]_2 and [Cu(HL^3)][ClO_4]_2 is quite stable in the solid state and in pure water, acetonitrile, or DMSO. Both [Ni(L^2)(H_2O)][ClO_4]_2 and [Cu(HL^3)][ClO_4]_2 are also stable in acidic aqueous solutions.

**Spectra and Properties of [NiL^2(H_2O)][ClO_4]_2 and [CuL^4](ClO_4)˭**

The FAB mass spectrum of [NiL^4(H_2O)][ClO_4]_2 shows two groups of peaks at m/z 564.2 ([NiL^4 + ClO_4^-]) and 464.3 ([NiL^4 - H]^+). In the spectrum of [CuL^4](ClO_4)˭, two groups of peaks corresponding to [CuL^4 + ClO_4^-] and [CuL^4 - H]^+ fragments are observed at m/z 569.1 and 470.2, respectively. Infrared spectra of the complexes show several peaks of ν(CH) at 3300-3200 cm^−1. The spectra also show ν(C=N) of the coordinated N-CH_2CONH_2 pendant arm at ca. 1665 cm^−1. The electronic absorption spectra (Table 1) of [NiL^2(H_2O)][ClO_4]_2 measured in various solvents are comparable with those of other octahedral complexes, such as [Ni(L^2)(H_2O)][ClO_4]_2, indicating that the water molecule as well as the pendant imidate ester group is involved in coordination. The magnetic moment (2.76 μB) of [NiL^4(H_2O)][ClO_4]_2 is also consistent with a d^8 electronic configuration in octahedral coordination geometry. The spectra of [CuL^4](ClO_4)˭ measured in various solvents also similar to those of [Cu(L^3)][ClO_4]_2 and other square-pyramidal complexes, indicating that the pendant imidate ester group is coordinated to the metal center. The nickel(II) and copper(II) complexes are quite stable in the solid state and in pure water, acetonitrile, or DMSO.

**Solution Behaviors.** Both [NiL^4(H_2O)]^2^2+ and [CuL^4]^2^2+ readily undergo hydrolysis to give [Ni(HL)^2(H_2O)]^2+ or [Cu(HL)^3]^2+ in basic aqueous solutions (see above). It has been reported that the N-CH_2CONH_2 pendant arms attached to [CuL^4]^2+ are readily hydrolyzed to N-CH_2COOCH_3 groups at pH ≤ 7, though those attached to [NiL^4]^2+ are inert against hydrolysis under similar conditions. However, [CuL^4]^2+ as well as [NiL^4(H_2O)]^2+ was found to be quite inert against hydrolysis in neutral or acidic aqueous solutions (1 ≤ pH ≤ 7); no apparent hydrolysis was observed even after 24 h at room temperature. The stability of [CuL^4]^2+ and [NiL^4(H_2O)]^2+ in acidic aqueous solutions was also confirmed by the recrystallization of the complexes from warm 0.1 M HClO_4 aqueous solutions.

Electronic absorption spectrum of [Ni(L^3)(H_2O)]^2+ or [Cu(L^3)]^2+ measured in 0.1 M HClO_4 solution was found to be nearly the same as that measured in neutral aqueous solution, indicating that the N-CH_2CONH_2 pendant arm is not protonated in the solution. Figure 1 shows that the addition of NaOH to an aqueous solution of [Ni(L^3)(H_2O)]^2+ shifts the absorption bands at 337 and 506 nm to longer wavelengths and increases their molar absorption coefficients. This is attributed to the fact that the complex exists as an equilibrium mixture of [Ni(L^3)(H_2O)]^2+ and [Ni(L^4)(H_2O)]^2+ (Eq. (1)) in basic aqueous solutions. Figure 1 also shows that the majority part of the complex exists as [Ni(L^3)(H_2O)]^2+ at pH ≤ 10, whereas most of the complex is deprotonated to form [NiL^4(H_2O)]^2+ at pH ≥ 11. Although the formation of [NiL^4(H_2O)]^2+ was confirmed by the isolation of [NiL^4(H_2O)][ClO_4], the deprotonation of the coordinated water could not be excluded in the basic aqueous solutions. The spectra (Fig. 2) of [Cu(L^3)]^2+ measured in NaOH aqueous solutions also show that the complex has square-pyramidal coordination geometry. The magnetic moment (2.76 μB) of [NiL^4(H_2O)][ClO_4]_2 is also consistent with a d^8 electronic configuration in octahedral coordination geometry. The spectra of [CuL^4](ClO_4)˭ measured in various solvents also similar to those of [Cu(L^3)][ClO_4]_2 and other square-pyramidal complexes, indicating that the pendant imidate ester group is coordinated to the metal center. The nickel(II) and copper(II) complexes are quite stable in the solid state and in pure water, acetonitrile, or DMSO.

**Solution Behaviors.** Both [NiL^4(H_2O)]^2+ and [CuL^4]^2+ readily undergo hydrolysis to give [Ni(HL)^2(H_2O)]^2+ or [Cu(HL)^3]^2+ in basic aqueous solutions (see above). It has been reported that the N-CH_2CONH_2 pendant arms attached to [CuL^4]^2+ are readily hydrolyzed to N-CH_2COOCH_3 groups at pH ≤ 7, though those attached to [NiL^4]^2+ are inert against hydrolysis under similar conditions. However, [CuL^4]^2+ as well as [NiL^4(H_2O)]^2+ was found to be quite inert against hydrolysis in neutral or acidic aqueous solutions (1 ≤ pH ≤ 7); no apparent hydrolysis was observed even after 24 h at room temperature. The stability of [CuL^4]^2+ and [NiL^4(H_2O)]^2+ in acidic aqueous solutions was also confirmed by the recrystallization of the complexes from warm 0.1 M HClO_4 aqueous solutions.

Electronic absorption spectrum of [Ni(L^3)(H_2O)]^2+ or
show that the addition of NaOH shifts the band to a longer wavelength. This also supports the deprotonation of the copper(II) complex and/or the coordination of water (or hydroxide ion) in basic aqueous solutions. In contrast to the case of $\text{[Ni(HL)\text{\textsubscript{2}}(H\text{\textsubscript{2}}O)\text{\textsuperscript{2+}}]}$, however, the only copper(II) complex isolated as a solid in the basic aqueous solutions was $\text{[Cu(HL)\text{\textsubscript{2}}(H\text{\textsubscript{2}}O)\text{\textsuperscript{2+}}]}$.

The approximate $pK_a$ values of $\text{[Ni(HL)\text{\textsubscript{2}}(H\text{\textsubscript{2}}O)\text{\textsuperscript{2+}}]}$ and $\text{[Cu(HL)\text{\textsubscript{2}}(H\text{\textsubscript{2}}O)\text{\textsuperscript{2+}}]}$ were determined at 25 °C by using a spectrophotometric method. The $pK_a$ value (ca. 10.6) for $\text{[Ni(HL)\text{\textsubscript{2}}(H\text{\textsubscript{2}}O)\text{\textsuperscript{2+}}]}$ was found to be much smaller than that (≥ 12.2) for $\text{[Cu(HL)\text{\textsubscript{2}}(H\text{\textsubscript{2}}O)\text{\textsuperscript{2+}}]}$. One of the reasons for the easier deprotonation of $\text{[Ni(HL)\text{\textsubscript{2}}(H\text{\textsubscript{2}}O)\text{\textsuperscript{2+}}]}$, compared to that of $\text{[Cu(HL)\text{\textsubscript{2}}(H\text{\textsubscript{2}}O)\text{\textsuperscript{2+}}]}$, may be the stronger interaction between the $\text{N-CH\text{\textsubscript{2}}CONH}^+$ group and the central metal ion of the conjugate base ([(NL\text{\textsubscript{2}}(H\text{\textsubscript{2}}O)\text{\textsuperscript{3-}})]$^{13}$). In the case of the copper(II) complex, the interaction between the functional group and the metal ion is expected to be relatively weak because of the Jahn-Teller distortion.

$$\begin{align*}
\text{[Ni(HL)\text{\textsubscript{2}}(H\text{\textsubscript{2}}O)\text{\textsuperscript{2+}}]} & \iff 3\text{[Cu(HL)\text{\textsubscript{2}}(H\text{\textsubscript{2}}O)\text{\textsuperscript{2+}}]} + \text{OH}^- \\
\text{[Ni(HL)\text{\textsubscript{2}}(H\text{\textsubscript{2}}O)\text{\textsuperscript{3-}}]} & \iff 3\text{[Cu(HL)\text{\textsubscript{2}}(H\text{\textsubscript{2}}O)\text{\textsuperscript{2+}}]} + \text{H}_2\text{O} (1)
\end{align*}$$

**Concluding Remarks**

This work shows that the mono-N-cyanomethylated macropolycycle L$^{10}$, which can be prepared by the reaction of bromoacetonitrile with L$^{10}$ containing one N-CH$_2$N linkage, is a useful precursor for the preparation of various types of mono-N-functionalized macrocyclic compounds, such as the nickel(II) and copper(II) complexes of L$^{2}$-$L^{4}$. This work also shows that chemical properties of the N-CH$_2$CONH$_2$ or N-CH$_2$C(=NH)OCH$_3$ group attached to a macrocyclic complex is strongly influenced by the number of the functional pendant arm and by the nature of the central metal ion.

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**References**