

Preparation and Properties of New Di-*N*-alkylated 14-Membered Tetraaza Macrocycles and Their Nickel(II) and Copper(II) Complexes

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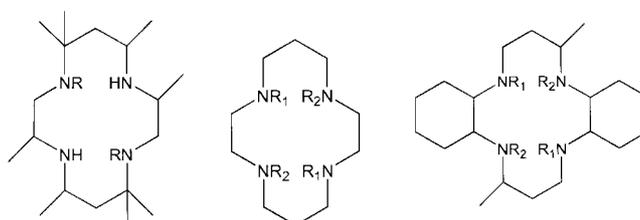
New 14-membered tetraaza macrocycles 1,8-diallyl-3,5,7,7,10,12,14,14-octamethyl-1,4,8,11-tetraazacyclotetradecane (L^2) and 1,8-bis(*n*-propyl)-3,5,7,7,10,12,14,14-octamethyl-1,4,8,11-tetraazacyclotetradecane (L^3) have been prepared by direct reaction of 2,5,5,7,9,12,12,14-octamethyl-1,4,8,11-tetraazacyclotetradecane (L^1) with allyl bromide or *n*-propyl bromide. The nickel(II) and copper(II) complexes of L^2 and L^3 have been prepared. The macrocycles show high copper(II) selectivity against nickel(II) ion in methanol solutions containing water. The wavelengths (*ca.* 505 nm) of the *d-d* bands for the nickel(II) complexes are extraordinarily longer than those for the complexes of L^1 and other related di-*N*-alkylated 14-membered tetraaza macrocycles. Crystal structure of $[\text{NiL}^2](\text{ClO}_4)_2$ shows that the average Ni-N bond distance (1.992 Å) of the complex is distinctly longer than those of other related nickel(II) complexes. Effects of the *N*- and *C*-substituents on the properties of the macrocyclic compounds are discussed.

Introduction

Polyaza macrocyclic compounds containing pendant *N*- and/or *C*-alkyl groups have been of interest for many years.¹⁻¹⁶ It has been well known that chemical properties and structures of fully *N*-alkylated 14-membered tetraaza macrocyclic compounds are distinctly different from those of unalkylated ones. For example, although the macrocycles L^1 , L^4 , and L^7 readily react with copper(II) and nickel(II) ions without showing any considerable selectivity for a particular metal ion, the fully *N*-methylated macrocycles L^6 and L^9 exhibit a high selectivity for copper(II) ion.⁵⁻⁹ The ligand field strengths of $[\text{NiL}^6]^{2+}$ and $[\text{NiL}^9]^{2+}$ are also much weaker than those of $[\text{NiL}^4]^{2+}$ and $[\text{NiL}^7]^{2+}$.^{8,10,11} This has been attributed to the steric effect of the *N*-alkyl groups. In the cases of di-*N*-alkylated macrocyclic compounds, the effects of *N*-alkyl groups are much less significant than those in fully *N*-alkylated ones; chemical properties L^5 and L^8 are not so much different from those of L^4 and L^7 .¹²⁻¹⁶ In most cases, the effects of *C*-alkyl groups upon the properties of polyaza macrocyclic compounds are relatively weak or negligible. However, some recent works show that properties of macrocyclic compounds containing both *N*- and *C*-alkyl groups are affected significantly by the *C*-substituents.^{7-9,15} Until now, the effects of *C*-alkyl groups on the properties of such compounds have been investigated much less extensively than those of the *N*-alkyl groups.

In this work, we prepared new di-*N*-alkylated tetraaza macrocycles L^2 and L^3 containing eight *C*-methyl groups to investigate the effects of the *C*- and *N*-alkyl groups on their chemical properties and coordination behaviors. Interestingly, it was found that L^2 and L^3 readily form their copper(II) complexes but do not react with nickel(II) ion in methanol solutions containing water. Furthermore, the wavelengths of the *d-d* bands for $[\text{NiL}^2]^{2+}$ and $[\text{NiL}^3]^{2+}$ are extraordinarily

longer than those reported for other related nickel(II) complexes. Crystal structure of $[\text{NiL}^2](\text{ClO}_4)_2$ was determined to understand its unusual spectral properties. Synthesis and unexpected properties of the di-*N*-substituted tetraaza macrocycles and their copper(II) and nickel(II) complexes are reported.



L^1 : R = H

L^2 : R = $\text{CH}_2\text{CH}=\text{CH}_2$

L^3 : R = $\text{CH}_2\text{CH}_2\text{CH}_3$

L^4 : $\text{R}_1 = \text{R}_2 = \text{H}$

L^5 : $\text{R}_1 = (\text{CH}_2)_3\text{CH}_3$;

$\text{R}_2 = \text{H}$

L^6 : $\text{R}_1 = \text{R}_2 = \text{CH}_3$

L^7 : $\text{R}_1 = \text{R}_2 = \text{H}$

L^8 : $\text{R}_1 = (\text{CH}_2)_2\text{CH}_3$;

$\text{R}_2 = \text{H}$

L^9 : $\text{R}_1 = \text{R}_2 = \text{CH}_3$

Experimental Section

Materials and Measurements. The macrocyclic ligand L^1 was prepared according to the reported methods.^{17,18} Mass spectra and elemental analyzes were performed at the Korea Basic Science Institute, Seoul, Korea. Electronic spectra were obtained using a Shimadzu UV-160 spectrophotometer. IR spectra were recorded on a Shimadzu IR-440 spectrophotometer, conductance measurements with a Metrohm Herisau Conductometer E518, and NMR spectra with a Bruker WP 300 FT NMR spectrometer.

Synthesis of Compounds. *Caution!* Perchlorate salts of metal complexes with organic ligands are explosive. Although we have had no problems with the perchlorate salts described in this work, such compounds should be handled with great

caution.

L². A toluene (30 mL) suspension of L¹ (3.0 g, 9.6 mmol), 98% allyl bromide (4.4 mL, 50 mmol), and KOH (5.4 g, 94 mmol) was refluxed for 2 days. The reaction mixture was filtered and washed several times with chloroform. The mixture of the filtrate and washings was evaporated on a rotary evaporator. The residue was dissolved in chloroform and then filtered. The filtrate was evaporated until a semi-solid remained. Methanol (*ca.* 20 mL) was added to the resulting residue, and then the white solid formed. The product was filtered off, washed with cold methanol, and dried in air. Yield: ~70%. Anal. Calc. for C₂₄H₄₈N₄: C, 73.41; H, 12.32; N, 14.27%. Found: C, 73.05; H, 12.08; N, 13.98%. Mass (*m/z*): 392. IR (cm⁻¹): 1640 (ν (C=C)) and 3235 (ν (N-H)). ¹H NMR (CDCl₃): δ 0.85 (*d*, Me), 0.90 (*s*, Me), 0.99 (*d*, Me), and 1.15 ppm (*d*, Me). ¹³C NMR (CDCl₃): 18.2 (Me), 20.7 (Me), 23.1 (Me), 27.1, 45.6, 45.9, 47.0, 49.3, 53.6, 113.0 (-CH₂=CH₂), and 140.8 (-CH₂=CH₂) ppm.

L³. This compound was prepared by the method similar to that of L², except that *n*-propyl bromide (4.5 mL, 50 mmol) was reacted instead of allyl bromide. Yield: ~70%. Anal. Calc. for C₂₄H₅₂N₄: C, 72.60; H, 13.21; N, 14.12%. Found: C, 72.85; H, 12.86; N, 13.87. Mass (*m/z*): 396. IR (cm⁻¹): 3240 (ν (N-H)). ¹³C-NMR (CDCl₃): 11.9 (CH₂CH₂CH₃), 18.3 (Me), 20.6 (Me), 22.3, 23.7, 27.1, 45.7, 46.5, 47.0, 49.9, 54.9, 57.0 ppm.

[CuL²](ClO₄)₂. A methanol (*ca.* 20 mL) suspension of Cu(OAc)₂ · H₂O (2.0 g) and L² (1.0 g) was refluxed for 1 h and then cooled to room temperature. Excess NaClO₄ · H₂O or HClO₄ was added to the solution and then stored in a refrigerator to produce red solids. The product was filtered, washed with water, and recrystallized from hot acetonitrile-water (2 : 1). Yield: > 90%. Anal. Calc. for C₂₄H₄₈N₄CuCl₂O₈: C, 44.00; H, 7.39; N, 8.55%. Found: C, 44.07; H, 7.28; N, 8.68%. IR (cm⁻¹): 1640 (ν (C=C)) and 3220 (ν (N-H)).

[CuL³](ClO₄)₂. This complex was prepared by the method similar to that of [CuL²](ClO₄)₂, except that L³ was used instead of L². Yield: >90%. Anal. Calc. for C₂₄H₅₂N₄CuCl₂O₈: C, 43.70; H, 7.94; N, 8.49%. Found: C, 43.55%; H, 8.23; N, 8.75%. IR (cm⁻¹): 3230 (ν (N-H)).

[NiL²](ClO₄)₂. A methanol suspension (25 mL) of Ni(OAc)₂ · 4H₂O (2.0 g) and CH(OEt)₃ (6.0 mL) was heated at reflux for 2 h. After the addition of L² (1.0 g), the resulting mixture was further refluxed for 3h. Excess HClO₄ or NaClO₄ dissolved in water was added to the reaction solution and then red solids formed. The product was filtered, washed with water, and recrystallized from hot acetonitrile-water (2 : 1). Yield: > 80%. Anal. Calc. for C₂₄H₄₈N₄NiCl₂O₈: C, 44.33; H, 7.44; N, 8.62%. Found: C, 43.95; H, 7.37; N, 8.84%. IR (cm⁻¹): 1640 (ν (C=C)) and 3230 (ν (N-H)).

[NiL³](ClO₄)₂. This complex was prepared by the method similar to that of [NiL²](ClO₄)₂, except that L³ was used instead of L². Yield: > 80%. Anal. Calc. for C₂₄H₅₂N₄NiCl₂O₈: C, 44.02; H, 7.94; N, 8.49%. Found: 44.45; H, 8.23; N, 8.24%. IR (cm⁻¹): 3245 (ν (N-H)).

[NiL²](PF₆)₂. Addition of an excess of NH₄PF₆ to a warm acetonitrile (*ca.* 5 mL) suspension of [NiL²](ClO₄)₂ (*ca.* 0.4 g) produces the white solid NH₄ClO₄. After filtration, water

(10 mL) was added to the filtrate. A red solid was filtered, washed with water, and dried in air. Yield: ~90%. Anal. Calc. for C₂₄H₄₈N₄NiP₂F₁₂: C, 38.89; H, 6.53; N, 7.56%. Found: C, 39.05; H, 6.64; N, 7.52%. ¹H NMR(CD₃NO₂): δ 1.20 (*s*, Me), 1.23 (*d*, Me), 1.62 (*d*, Me), and 1.98 ppm (*s*, Me). ¹³C NMR (CDCl₃): 11.7, 19.2, 22.1, 30.2, 45.1, 49.3, 53.1, 56.7, 57.5, 64.1, 122.4 (-CH₂=CH₂), and 131.1 (-CH₂=CH₂) ppm.

[H₂L²](ClO₄)₂. Addition of an excess amount of NaClO₄ dissolved in water was added to a methanol solution of L² produces a white solid. The product was filtered off, washed with methanol, and dried in air. Anal. Calc. for C₂₄H₅₀N₄Cl₂O₈: C, 48.56; H, 8.49; N, 9.44%. Found: C, 48.45; H, 8.27; N, 9.34%.

Determination of Protonation and Formation Constants. Protonation constants of L¹ and L² were determined at 25 ± 0.1 °C and μ = 0.1 M (Me₄NCl) by potentiometric titration of the protonated macrocycles with 0.1 M Me₄NOH. The titrations were performed using a Metrohm 665 Dosimat auto buret and a Metrohm 605 pH meter. Each titration was performed on a 95% (v/v) ethanol-water solution (50 mL) of the ligand (2.5 mM) and HCl (11 mM). The constants were calculated from the potentiometric data with the use of the program PKAS.¹⁹

The formation constants of the copper(II) and nickel(II) complexes with L¹ and L² were determined in 95% ethanol-water by the reported out-of-cell spectrophotometric method,^{8,20} because the complex formation rate is slow. A set of the solutions containing the ligand (1.5 mM), metal ion (0.8 mM), HNO₃ (0.1-50 mM), and NaNO₃ (μ = 0.10 M) was prepared in sealed test tubes and allowed to equilibrate at 25 °C. Electronic spectra of the solutions were recorded during 6 weeks. The spectral change was not observed after 5 weeks, and it was assumed that the equilibrium had been reached. The stability constants were calculated by using the pH-dependent electronic spectra, together with the protonation constants.

X-ray Crystal Structure Determination. Single crystals of [NiL²](ClO₄)₂ suitable for X-ray structural determination were obtained from an acetonitrile-water solution of the complex. A crystal on a glass fiber was mounted on an Enraf-Nonius CAD4 diffractometer equipped with a graphite-monochromated Mo K α (λ = 0.71073 Å) radiation source. Cell parameters and an orientation matrix for data collections were obtained from least squares refinement, using the setting angles of 25 reflections. The crystallographic data and additional details of data collection and refinement are summarized in Table 1. The intensities of 3 standard reflections, recorded every 3h of X-ray exposure, showed no systematic changes. The intensity data were corrected for Lorentz and polarization effects. The structure were solved by patterson methods and subsequent difference Fourier methods.²¹ Empirical absorption corrections were also applied.²² All the non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms were idealized (d (C-H)=0.96 Å) with their thermal parameters of 1.2 times those of attached atoms.

Table 1. Crystal and refinement data for $[\text{NiL}^2](\text{ClO}_4)_2$

Formula	$\text{C}_{24}\text{H}_{48}\text{Cl}_2\text{N}_4\text{NiO}_8$
M	650.27
Crystal system	monoclinic
Space group	$P2_1/n$
a (Å)	9.531(3)
b (Å)	13.119(4)
c (Å)	12.092(2)
β (°)	100.50(2)
V (Å ³)	1486.6(7)
Z	2
D_c (g cm ⁻³)	1.453
μ (cm ⁻¹)	8.84
$F(000)$	692
Crystal size (mm)	$0.45 \times 0.40 \times 0.35$
θ range (°)	2.31-25.96
Index ranges	$-11 \leq h \leq 11, 0 \leq k \leq 16, 0 \leq l \leq 14$
Reflections collected	3228
Independent reflections	2899
Refinement method	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	1.047
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0451, wR2 = 0.1074$
R indices (all data)	$R1 = 0.0606, wR2 = 0.1169$
Largest diff. peak and hole	0.342 and $-0.329 \text{ e} \cdot \text{Å}^{-3}$

$$R1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, WR2 = \frac{[\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]}{1/2}, \text{ where } w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP]; P = (F_o^2 + 2F_c^2) / 3.$$

Results and Discussion

Synthesis of the Ligands and Complexes. All of the four amino groups of L^7 are readily alkylated by the reaction of the macrocycle with an excess of ethyl bromide, *n*-propyl bromide, or allyl bromide.^{9,16} However, the only product prepared from the one-step reaction of L^1 with an excess of allyl bromide or *n*-propyl bromide was the di-*N*-substituted macrocycle L^2 or L^3 ; any fully *N*-substituted macrocycle was not isolated. This indicates that the steric crowding around the nitrogen atoms is more severe for L^1 than for L^7 . The macrocycles L^2 and L^3 readily dissolve in chloroform and slightly dissolve in methanol or ethanol. The infrared, ¹³C NMR, and mass spectra (see Experimental) are consistent with the macrocycles. The structure of L^2 was confirmed by the crystal structure of its nickel(II) complex (see below).

The reaction of L^2 or L^3 with $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ in methanol containing water produces the complex $[\text{CuL}^2]^{2+}$ or $[\text{CuL}^3]^{2+}$. However, unexpectedly, all efforts to prepare nickel(II) complexes of L^2 and L^3 from the reaction of $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ with the ligands in methanol were unsuccessful. After heating at reflux of the reaction mixture for > 48 h, addition of NaClO_4 or HClO_4 to the resulting solution yielded only the white solid $[\text{H}_2\text{L}^2](\text{ClO}_4)_2$ or $[\text{H}_2\text{L}^3](\text{ClO}_4)_2$ instead of its nickel(II) complex. The square-planar complexes $[\text{NiL}^2](\text{ClO}_4)_2$ and $[\text{NiL}^3](\text{ClO}_4)_2$ can be prepared only under dehydrated condition (see Experimental); the reagent $\text{HC}(\text{OEt})_3$ reacts with H_2O to produce HCO_2Et and EtOH .^{9,23} It is clear

that L^2 and L^3 are highly selective for complex formation with copper(II) over nickel(II) ion in aqueous solutions. Such a high copper(II) ion selectivity is not observed for most other di-*N*-alkylated 14-membered tetraaza macrocycles such as L^5 or L^8 .^{11,12,16} The macrocycles L^5 and L^8 readily form their nickel(II) and copper(II) complexes aqueous solutions.

Spectra and Properties of the Complexes. The nickel(II) and copper(II) complexes $[\text{ML}](\text{ClO}_4)_2$ ($\text{M} = \text{Ni}(\text{II})$ or $\text{Cu}(\text{II})$; $\text{L} = \text{L}^2$ or L^3) are extremely stable in the solid states and are decomposed very slowly even at low pH, likewise other 14-membered tetraaza macrocyclic complexes.^{8,9,14} Electronic spectra of the complexes (1.0 mM) in 0.3 M HClO_4 water-acetonitrile (1 : 1) solution show that only less than 3% of each complex is decomposed in 10 h at 20 °C. In 0.1 M NaOH water-acetonitrile (1 : 1) solution, however, the nickel(II) complex $[\text{NiL}^2](\text{ClO}_4)_2$ or $[\text{NiL}^3](\text{ClO}_4)_2$ is completely decomposed to produce the white solid of the free macrocyclic ligand within 10 min at 20 °C. This result is in contrast to the fact that no apparent decomposition is observed for $[\text{NiL}^1]^{2+}$, $[\text{NiL}^7]^{2+}$, and $[\text{NiL}^8]^{2+}$ in a similar basic condition for 10 min. The copper(II) complexes of L^2 and L^3 are also unstable in the basic solutions.

The electronic absorption spectra (Table 2) of $[\text{NiL}^2](\text{ClO}_4)_2$ and $[\text{NiL}^3](\text{ClO}_4)_2$ measured in nitromethane show one *d-d* transition band at ca. 505 nm. As expected from other systems,^{8,10,15,24-26} the wavelength is ca. 40 nm longer than that for $[\text{NiL}^1]^{2+}$. However, to our knowledge, such a large red shift caused by the introduction of only two *N*-alkyl groups has not been reported for other systems. The wavelength for $[\text{NiL}^2]^{2+}$ or $[\text{NiL}^3]^{2+}$ is also ca. 45 and 20 nm longer than those for the di-*N*-alkylated complexes $[\text{NiL}^5]^{2+}$ and $[\text{NiL}^8]^{2+}$, respectively, but is rather similar to those of the fully-*N*-methylated macrocyclic complexes $[\text{NiL}^6]^{2+}$ and $[\text{NiL}^9]^{2+}$ (Table 2).^{8,25} The unusually weak ligand field strength of $[\text{NiL}^2]^{2+}$ or $[\text{NiL}^3]^{2+}$ may be resulted from the weak Ni-N interaction caused by steric repulsion between the *N*- and *C*-alkyl groups. The wavelengths (ca. 490 nm)

Table 2. Electronic spectra of the nickel(II) and copper(II) complexes^a

Complex	λ_{max} , nm ($\epsilon, \text{M}^{-1} \text{cm}^{-1}$)	
$[\text{NiL}^1](\text{ClO}_4)_2$	469(83)	468(78) ^b
$[\text{NiL}^2](\text{ClO}_4)_2$	505(120)	506(118) ^b
$[\text{NiL}^3](\text{ClO}_4)_2$	502(110)	502(112) ^b
$[\text{NiL}^5]^{2+ c}$		461 ^b
$[\text{NiL}^6]^{2+ d}$		512(195) ^b
$[\text{NiL}^8]^{2+ e}$	484(109)	486(103) ^b
$[\text{NiL}^9]^{2+ f}$	501(93)	503(89) ^b
$[\text{CuL}^1](\text{ClO}_4)_2$	482(105)	511(127) ^b
$[\text{CuL}^2](\text{ClO}_4)_2$	487(340)	492(350) ^b
$[\text{CuL}^3](\text{ClO}_4)_2$	485(410)	490(420) ^b
$[\text{CuL}^8]^{2+ g}$		486(234) ^b
$[\text{CuL}^9]^{2+ f}$	473(235)	

^aIn nitromethane solution at 20 °C. ^bIn acetonitrile. ^cRef. 12. ^dRef. 11. ^eRef. 15. ^fRef. 8. ^gRef. 16.

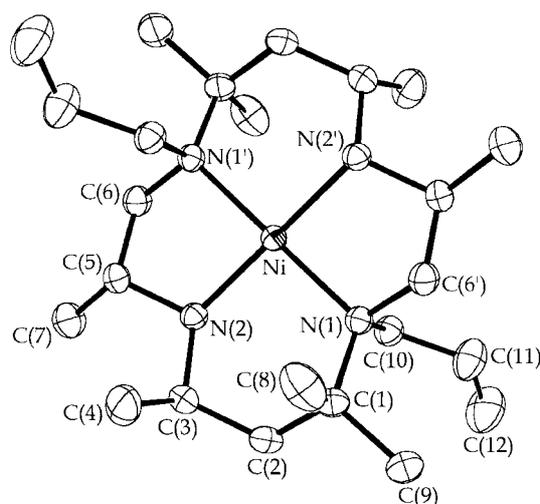


Figure 1. An ORTEP drawing of $[\text{NiL}^2]^{2+}$ in $[\text{NiL}^2](\text{ClO}_4)_2$ with the atomic labeling scheme.

for $[\text{CuL}^2]^{2+}$ and $[\text{CuL}^3]^{2+}$ are comparable with those for the square-planar copper(II) complexes of L^1 , L^8 , L^9 , and other 14-membered polyaza macrocycles.^{8,16,25} This supports that the ligand field strength of the copper(II) complexes is not affected significantly by the *N*- and *C*-alkyl groups. On the other hand, the molar absorption coefficient of $[\text{CuL}^2]^{2+}$ or $[\text{CuL}^3]^{2+}$ is much larger than that for $[\text{CuL}^1]^{2+}$ because of the steric crowding.^{8,9,27,28}

Crystal Structure of the Nickel(II) Complex. The crystal structure (Fig. 1) of $[\text{NiL}^2](\text{ClO}_4)_2$ shows that the complex has a square-planar coordination geometry with an inversion center. The macrocyclic ligand adopts the *trans*-III conformation. The five-membered chelate rings have a *gauche* conformation, and the six-membered chelate rings a chair one. The *N*-allyl and *C*-methyl groups in a same five-membered chelate ring are *anti* with respect to the ring. The methyl groups attached to C(3) and C(5) are also *anti* with respect to the macrocycle.

Table 3 shows that the C(11)-C(12) bond distance (1.270(6) Å) is corresponding to the C=C double bond. The Ni-N(1) (tertiary) and Ni-N(2) (secondary) bond distances are 2.000(2) and 1.984(2) Å, respectively. The Ni-N distances of $[\text{NiL}^2]^{2+}$ are much longer than those of the di-*N*-alkylated complex $[\text{NiL}^5]^{2+}$ (Ni-N(tertiary), 1.970(2) Å; Ni-N(secondary), 1.939(2) Å);¹² the average Ni-N distance of the former (1.992 Å) is *ca.* 0.035 Å longer than that of the latter. The Ni-N distances are comparable with those of $[\text{NiL}^8]^{2+}$ (Ni-N(tertiary), 2.003(2) Å; Ni-N(secondary), 1.957(3) Å).¹⁵ However, the average value of the present complex is *ca.* 0.01 Å longer than that of $[\text{NiL}^8]^{2+}$. The average Ni-N distance of $[\text{NiL}^2]^{2+}$ is also longer than that of the fully *N*-methylated complex $[\text{NiL}^5]^{2+}$ (1.983 Å).²⁹ Interestingly, the N(1)-C(1) bond distance (1.550(4) Å) is extraordinarily longer than the N(1)-C(10), N(1)-C(6), and other N-C bond distances. The C(1)-N(1)-Ni bond angle is also distinctly smaller than the C(3)-N(2)-Ni angle. The crystallographic study reveals that the alkyl substituents attached to carbon atoms next to donor nitrogen atoms of a 14-membered tetra-

Table 3. Bond distances [Å] and angles [deg] for $[\text{NiL}^2](\text{ClO}_4)_2$

Ni-N(1)	2.000(2)	Ni-N(2)	1.984(2)
N(1)-C(1)	1.550(4)	N(1)-C(10)	1.515(4)
N(1)-C(6')	1.493(4)	N(2)-C(5)	1.602(4)
N(2)-C(3)	1.503(4)	C(10)-C(11)	1.503(5)
C(11)-C(12)	1.270(6)		
N(1)-Ni-N(1')	180.0	N(1)-Ni-N(2)	94.3(1)
N(1)-Ni-N(2')	85.7(2)	C(1)-N(1)-Ni	116.7(2)
C(1)-N(1)-C(6')	109.1(2)	C(3)-N(2)-Ni	124.2(3)
C(3)-N(2)-C(5)	111.3(2)	C(1)-C(2)-C(3)	120.1(3)
N(2)-C(3)-C(2)	110.4(2)	C(4)-C(3)-N(2)	113.1(3)
C(11)-C(10)-N(1)	118.2(3)	C(10)-C(11)-C(12)	123.7(4)

Table 4. The equilibrium constants for the reactions of H^+ , Ni^{2+} , and Cu^{2+} ions with the macrocyclic ligands at 25 °C^a

Reaction	log <i>K</i>			
	L ¹	L ²	L ⁴	L ⁶
$\text{L} + \text{H}^+ = \text{LH}^+$	10.45	10.04	11.54 ^b	9.34 ^c
$\text{LH}^+ + \text{H}^+ = \text{LH}_2^{2+}$	8.96	7.90	10.53 ^b	8.99 ^c
$\text{Cu}^{2+} + \text{L} = [\text{CuL}]^{2+}$	19.0(2)	14.5(2)		
$\text{Ni}^{2+} + \text{L} = [\text{NiL}]^{2+}$	11.8(2)	n.c. ^d		

^aObtained in 95% (v/v) ethanol-water mixture. ^bRef. 17. ^cRef. 5. ^dNo evidence of the complex formation even in the high pH at which the nickel(II) hydroxide precipitates.

aza macrocyclic nickel(II) complex have a significant effect on the Ni-N and N-C bond lengths.

Protonation and Stability Constants. The protonation equilibria of L^1 and L^2 were studied by potentiometric titration in 95% ethanol at 25.0 ± 0.1 °C and $\mu = 0.1$ M (Me_4NCl). Although L^1 and L^2 have four basic centers, only two protonation constants of each macrocycle could be determined by the present potentiometric titration. The log *K* values (Table 4) of L^1 containing eight *C*-methyl groups are lower than those of L^4 in each protonation step. The proton affinity of L^2 containing two *N*-allyl groups is weaker than that of L^1 . The formation constants for the nickel(II) and copper(II) complexes of L^1 and L^2 were determined by a spectrophotometric method. Table 4 shows that alkylation of L^1 to give L^2 decreases the stability constant of the copper(II) complex, as usual. For nickel(II) ion, any evidence for the complex formation with L^2 could not be observed even in solutions of high pH at which nickel(II) hydroxide forms. It is clear that the protonation and complexation behaviors of L^2 are strongly affected by the *C*- and *N*-substituents. Another reason for the high selectivity of L^2 in the complex formation with copper(II) over nickel(II) ion may be the acidity difference between the two metal ions; nickel(II) ion is a weaker acid than copper(II) ion.^{9,30,31}

Conclusions

New di-*N*-alkylated macrocycles L^2 and L^3 containing eight *C*-methyl groups were selectively prepared by one-step

reaction of L¹ and appropriate alkyl bromides. To our knowledge, L² and L³ are rarely prepared di-*N*-alkylated 14-membered tetraaza macrocycles that show high copper(II) selectivity against nickel(II) ion in aqueous solutions. Furthermore, their nickel(II) complexes exhibit unusually weak ligand field strength. This work shows that the *C*-alkyl substituents of a macrocyclic compound as well as the *N*-substituents significantly affect the complex formation reaction and the M-N interactions.

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