

e). Reaction of **3** with β -alanine ethyl ester hydrochloride and triethylamine (1.1 mmol) gave **4e** as an oil in 47% yield. IR (chloroform): 1735, 1720, 1665 cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3): δ 1.23 (t, 3H, $J=7.20$ Hz), 1.35 (t, 3H, 7.10 Hz), 2.85 (t, 2H, $J=6.20$ Hz), 4.02-4.42 (m, 6H), 6.53 (d, 1H, $J=9.50$ Hz), 7.87 (dd, 1H, $J=2.40, 9.50$ Hz), 8.31 ppm (d, 1H, $J=2.40$ Hz); $^{13}\text{C-NMR}$ (CDCl_3): δ 14.04, 14.28, 32.79, 47.07, 59.91, 61.00, 109.90, 119.53, 138.94, 143.84, 162.40, 164.27, 170.96 ppm.

Ethyl 4-carbethoxy-5-isopropylamino-2,4-pentadienoate (5a). Reaction of **3** with isopropylamine gave **5a** as an oil in 65% yield. IR (chloroform): 3280, 1700, 1660 cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3): δ 1.07-1.36 (m, 12H), 3.53 (m, 1H), 3.98-4.33 (m, 4H), 6.95 (d, 1H, $J=16.90$), 7.17-7.43 (m, 2H), 8.79-8.90 ppm (brd m, 1H); $^{13}\text{C-NMR}$ (CDCl_3): δ 14.31, 23.45, 50.53, 59.39, 59.54, 94.06, 107.27, 143.42, 155.14, 168.80, 169.05 ppm.

Ethyl 5-*t*-Butylamino-4-carbethoxy-2,4-pentadienoate (5b). Reaction of **3** with *t*-butylamine gave **5b** as an oil in 72% yield. IR (chloroform): 3260, 1700, 1660 cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3): δ 1.31 (s, 9H), 1.13-1.48 (m, 6H), 4.05-4.35 (m, 4H), 6.99 (d, 1H, $J=15.50$ Hz), 9.15-9.30 ppm (brd m, 1H); $^{13}\text{C-NMR}$ (CDCl_3): δ 14.10, 14.37, 29.85, 52.90, 59.48, 59.60, 94.09, 107.15, 143.76, 153.05, 168.96, 169.14 ppm.

Conclusion

An expedient route has been developed for the preparation of *N*-alkyl-5-carbethoxy-2-pyridones from cyclic sulfamides and primary amines, which is a new example of ring transformation.

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References

- (a) C.-H. Lee, Y. H. Lee, W. S. Choi, and B. Y. Chung, *Bull. Korean Chem. Soc.*, **13**, 462 (1992); (b) C.-H. Lee, M. S. Lee, Y. H. Lee, and B. Y. Chung, *Bull. Korean Chem. Soc.*, **13**, 357 (1992); (c) C.-H. Lee, S. Y. Jin, Y. H. Lee, and B. Y. Chung, *Bull. Korean Chem. Soc.*, **13**, 8 (1992); (d) C.-H. Lee and H. Kohn, *J. Heterocyclic Chem.*, **27**, 2107 (1990); (e) C.-H. Lee and H. Kohn, *J. Org. Chem.*, **55**, 6097 (1990); (f) C.-H. Lee and Kohn, *J. Pharm. Sci.*, **79**, 716 (1990); (g) C.-H. Lee, J. D. Korp, and H. Kohn, *J. Org. Chem.*, **54**, 3077 (1989); (h) C.-H. Lee and H. Kohn, *Heterocycles*, **27**, 2581 (1988).
- (a) P. Aeberli, J. Gogerty, and W. Houlihan, *J. Med. Chem.*, **10**, 636 (1967); (b) E. H. Weiseman, J. N. Pereira, K. F. Finger, and R. Pinson, *J. Med. Chem.*, **8**, 777 (1965); (c) H. Stegelmeier, E. Nimers, U. Rosentereter, A. Knorr, and B. Garthoff (Bayer AG), D.O.S. 3309655, Sept. 20, 1984; *Chem. Abstr.*, **102**, 24633 (1985); (d) A. M. Pietruszkiewicz and J. J. Baldwin, *J. Heterocyclic Chem.*, **20**, 821 (1983); (e) A. Zeidler, K. H. Konig, and D. Mangold, *Kem.-Kemi*, **9**, 590 (1974).
- J. Elguero, P. Goya, and A. Martinez, *Heterocycles*, **29**, 245 (1989).

Effects of *N*-and *C*-Substituents on Protonation of 14-Membered Tetraaza Macrocycles and Formation of their Copper(II) and Nickel(II) Complexes

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The protonation constants of the 14-membered tetraaza macrocycles A(3,14-dimethyl-2,6,13,17-tetraazatricyclo[16.4.0^{1,18}.0^{7,12}]docosane) and B(2,3,6,13,14,17-hexamethyl-2,6,13,17-tetraazatricyclo-[16.4.0^{1,18}.0^{7,12}]docosane) were measured by potentiometry. The formation constants of each of these ligands with copper(II) and nickel(II) were determined by an out-of-cell spectrophotometric method. The results indicate that the per-*N*-methylated macrocycle B exhibits much higher selectivity for complex formation with copper(II) over nickel(II) ion than A and other related 14-membered tetraaza macrocycles. The effects of the *N*-and *C*-substituents on the basicity and the metal ion selectivity of the ligands are discussed. The synthesis and properties of copper(II) and nickel(II) complexes of B are also described.

Introduction

There has been considerable interest in the synthesis of macrocyclic ligands which show high selectivity for a particular metal ion in the complex formation,¹⁻¹⁴ since such ligands can be used in the fields of biochemistry, waste treatment,

and hydrometallurgy. Crown ethers often show some size-based selectivity toward IA or IIA metal ions.¹ However, most polyaza macrocyclic ligands form complexes with nickel(II) and copper(II) ions without showing considerable selectivity for one of the two.⁵⁻¹³ Although it has been reported that D in the Chart 1 shows some selectivity for copper(II) over

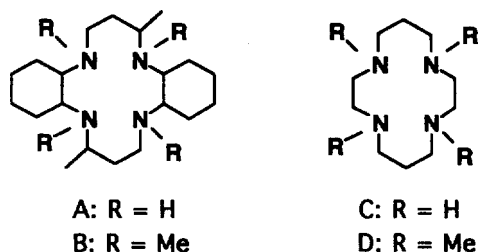


Chart 1

nickel(II) ion, the ligand readily reacts with the two metal ions in methanol solutions to produce the complexes.^{7,11,12}

In a recent communication,¹⁴ we reported the synthesis of the per-N-methylated macrocycle B containing cyclohexane rings. It has been observed that the macrocycle readily reacts with copper(II) ion to form the stable square planar complex but not with nickel(II) ion in methanol solutions containing water. Such a high selectivity for complex formation with copper(II) over nickel(II) ion is not observed for A, C, D, and other related 14-membered tetraaza macrocycles. To understand the effects of the N-methyls and the C-substituents on the extraordinary high selectivity of B, the protonation constants of A and B and the formation constants of their nickel(II) and copper(II) complexes have been determined in 90% (v/v) methanol-water mixture. The synthesis of nickel(II) complex of B has also been attempted in various conditions, and the properties of the nickel(II) and copper(II) complexes are described.

Experimental

Materials. The macrocyclic ligands A¹⁵ and B¹⁴ were prepared and purified as described previously. Chemicals used in spectral, electroanalytical, and potentiometric measurements were of analytical grade.

Instrumentation. Infrared spectra were recorded on a Shimadzu IR-440 spectrophotometer using Nujol mulls. Visible spectra were obtained on either a Kontron Uvikon 860 UV/vis spectrophotometer or a Shimadzu UV-160 spectrophotometer. Conductances were measured using Metrohm Herisau Conductometer E518. NMR spectra were recorded on a Bruker WP 300 FT NMR spectrometer. Elemental analyses were performed at the Kolon R & D Center, Kumi, Korea. Cyclic voltammograms were recorded using a Yanaco Voltammeter Analyzer P-1000 equipped with a FG-121B function generator and a Watanabe X-Y recorder. The working and reference electrodes were platinum and SCE, respectively. Potentiometric titrations were carried out using a Orion Model 701 A/digital Ionanalyzer.

Protonation Constants. Protonation constants for A and B were determined by potentiometric titration of the protonated ligands with 0.1 M Me₃NOH. Each titration was performed on a 90% (v/v) methanol-water solution (50 ml) of the ligand (2.5×10^{-3} M) and HCl (1.1×10^{-2} M) adjusted to 0.1 M ionic strength with Me₄NCl. The speciation curves for A and B are shown in Figures 1 and 2, respectively. The apparent protonation constants were determined using the program BEST.¹⁶

Formation Constants. The equilibration of 90% methanol-water solutions of copper(II) and nickel(II) ions with A

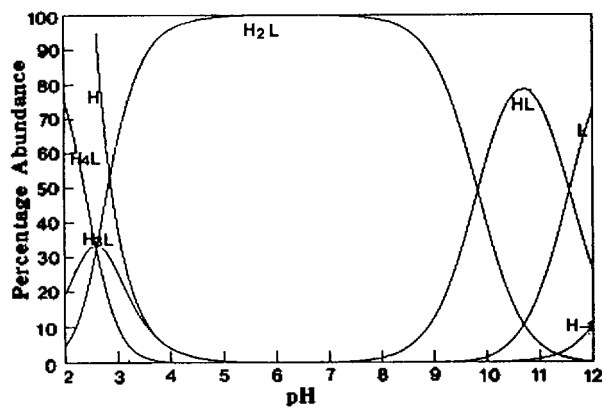


Figure 1. Speciation curves for the protonated forms of A in 90% (v/v) methanol-water mixture at 25°C ($\mu=0.1$ M).

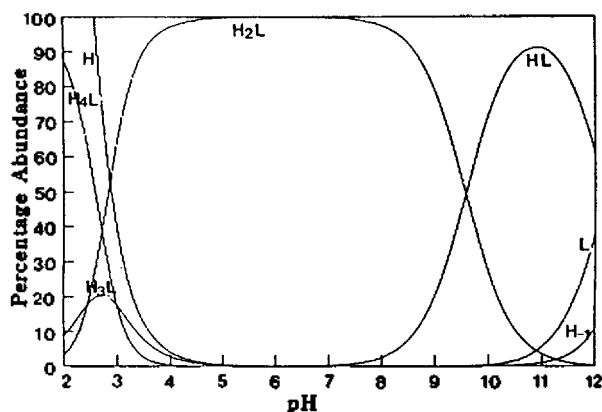


Figure 2. Speciation curves for the protonated forms of B in 90% (v/v) methanol-water mixture at 25°C ($\mu=0.1$ M).

and B was slow, and the formation constants were obtained by an out-of-cell spectrophotometric method similar to that used for C.^{6,17} A set of the solutions containing the metal ion (8.0×10^{-4} M), ligand (1.5×10^{-3} M), HNO₃ (1.0×10^{-3} –0.20 M), and sufficient NaNO₃ ($\mu=0.20$ M) was prepared in sealed volumetric flasks and allowed to equilibrate at 25 °C. Electronic spectra of the solutions were recorded during 16 weeks. Slow spectral changes were observed for 4 weeks. After 8 weeks, the change was rarely observed, and it was assumed that the equilibrium had been reached. The pH of the solutions were calculated by using the protonation constants of the ligands and/or were measured by a pH meter. The variation of the spectra of the solutions of Cu(II) and A as a function of pH is illustrated in Figure 3. The stability constants were calculated by using the pH-dependent spectra.

Synthesis. [Cu(B)](ClO₄)₂·H₂O. A methanol solution (20 ml) of Cu(OAc)₂·H₂O (1.0 g) and B (1.0 g) was heated at reflux for 3 h. Excess NaClO₄ was added to the solution and then the mixture was placed in a refrigerator to complete the crystallization. The red crystals were filtered off, washed with methanol, and dried in air. The product was recrystallized from hot acetonitrile-water (4 : 1) mixture. Yield: >90%. Anal. Calcd for CuC₂₄H₅₀N₄Cl₂O₉: C, 42.8; H, 7.47; N, 8.08%. Found: C, 42.9; H, 7.34; N, 8.08%.

B·2HClO₄. The a methanol solution (20 ml) of B (0.5

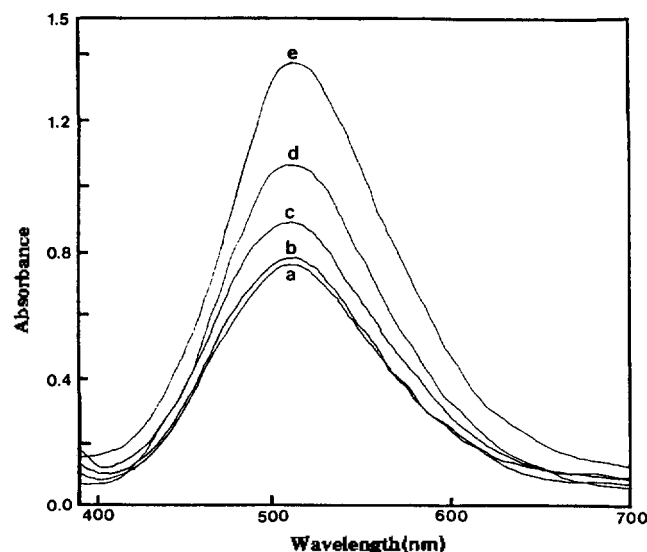


Figure 3. Electronic spectra of 90% (v/v) methanol-water mixtures of Cu^{2+} (8.0×10^{-4} M) and A (1.5×10^{-3} M) at pH 0.708(a), 1.019 (b), 1.336(c), and 2.186(d) after equilibration for 16 weeks at 25°C ($\mu=0.20$ M). The curve e is for $[\text{Cu}(\text{A})](\text{NO}_3)_2$ (8.0×10^{-4} M).

g) was added excess NaClO_4 , and the white solid was precipitated. The product was collected by filtration, washed with methanol, and dried in air. Anal. Calcd for $\text{C}_{24}\text{H}_{50}\text{N}_4\text{Cl}_2\text{O}_9$: C, 47.2; H, 8.20; N, 9.19%. Found: C, 46.8; H, 8.27; N, 9.39%.

The same salt was also obtained in all attempts to prepare the nickel(II) complex of B from the reaction similar to that for $[\text{Cu}(\text{B})](\text{ClO}_4)_2$ using $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ instead of the copper(II) salt.

$[\text{Ni}(\text{B})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$. To an acetonitrile-DMSO (1:1) solution (20 ml) of $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (1.3 g) was added $\text{CH}(\text{OEt})_3$ (4.0 ml), and then the mixture was heated at reflux for 2 h. After B (1.0 g) was added, the resulting solution was further refluxed for 8 h. Excess $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ dissolved in water was added to the solution, and then the mixture was stored in a refrigerator to form the red crystals. The product was filtered off, washed with methanol, and dried in air. Yield: ~80%. Anal. Calcd for $\text{NiC}_{24}\text{H}_{50}\text{N}_4\text{Cl}_2\text{O}_9$: C, 43.1; H, 7.49; N, 8.38%. Found: C, 42.8; H, 7.39; N, 8.36%.

$[\text{Ni}(\text{B})](\text{PF}_6)_2$. To a warm acetonitrile suspension of $[\text{Ni}(\text{B})](\text{ClO}_4)_2$ was added excess NH_4PF_6 , and the compound was penetrated into the solution and white precipitates of NH_4ClO_4 were formed. After the solid was removed by filtration, water was added to the filtrate and then the red precipitate was formed. The product was filtered, washed with methanol, and dried in air. Anal. Calcd for $\text{NiC}_{24}\text{H}_{48}\text{N}_4\text{P}_2\text{F}_{12}$: C, 38.9; H, 6.53; N, 7.56%. Found: C, 39.0; H, 6.74; N, 7.70%. ^{13}C -NMR: δ 19.2 (C-Me), 23.7, 23.8, 24.8, 24.9, 29.0, 40.4 (N-Me), 41.2 (N-Me), 52.5, 56.6, 64.6, 71.4 ppm.

Results and Discussion

Protonation Constants. The macrocycles A and B act as tetraprotic bases, and the protonation equilibria were studied by potentiometric titration at 25°C and $\mu=0.1$ M Me_4NCl . The speciation curves (Figures 1 and 2) show that the proportions of H_4A and H_4B are 76% and 88%, respec-

Table 1. Protonation Constants of the Tetraaza Macrocycles at 25°C

	A ^a	B ^a	C ^a	D ^c
$\log K_1$	11.56	12.21	11.54	9.34
$\log K_2$	9.83	9.58	10.53	8.99
$\log K_3$	2.61	2.43	2.43	2.58
$\log K_4$	2.60	3.00	1.97	2.25
$\log \beta_4$	26.60	27.22	26.47	23.16

^aThis work; in 0.1 M Me_4NCl . ^bRef. 19; in 0.1 M KNO_3 . ^cRef. 20; in 0.1 M NaNO_3 .

tively, of the total macrocycles at pH 2. Furthermore, the proportion of the deprotonated form of B (ca. 3%) at pH 10.7 is much less than that of A (ca. 11%). This indicates that the proton affinity of B is much higher than that of A. Table 1 shows that the stepwise protonation constant $\log K_1$ and the overall protonation constant $\log \beta_4$ values for A are quite similar to those for C,¹⁸⁻²⁰ indicating that the proton affinity is rarely affected by the substituents on the carbons. This strongly indicates that the introduction of the methyls and $-(\text{CH}_2)_4$ -chains to the carbon atoms of C increases the inherent proton affinity of the nitrogens but reduces the extent of the solvation of the resulting ammonium ion produced by protonation. Although the basicity of alkylamines in the gas phase is mainly affected by the inductive effect of the alkyl group(s), the solvation effect is also important in aqueous solutions.²³ Interestingly, the values for B are much higher than those for D²⁰ showing that the proton affinity of the N-methylated macrocycles is significantly affected by the C-substituents, unlike the unmethylated ligands. In the cases of B and D, it is expected that the solvation of the protonated species is rather restricted by the presence of the N-methyls and then the proton affinity is mainly affected by the inductive effect. Therefore, the greater proton affinity of B, compared to that of D, may be attributed to the inductive effect of the C-substituents. Table 1 also shows that the $\log K_1$ and $\log \beta_4$ values for B are much higher than those for A. It is interesting to see that this trend is in sharp contrast to the orders $\text{C} > \text{D}$ and $\text{Me}_2\text{NH} > \text{Me}_3\text{N}$ measured in aqueous solutions but is rather similar to the order $\text{Me}_3\text{N} > \text{Me}_2\text{NH}$ in the gas phase.²³ This may be arisen from the fact that the solvation of the protonated species of A as well as B is much restricted by the hydrophobic substituents.

Above results clearly show that, despite that the proton affinity of A is rarely affected by the C-substituents, the affinity of the per-N-methylated macrocycle B is strongly affected by the substituents and is much greater than that of D.

Complex Formation. The formation constants ($\log K$) for copper(II) and nickel(II) ions with A and B measured in 90% (v/v) methanol-water mixture are listed in Table 2. The $\log K$ values for the complexes of A are quite similar to those of C.^{17,20} This strongly indicates that the stability of the complexes of A are rarely affected by the steric factor of the C-substituents. The N-methylation on A to give B causes a large decrease in $\log K$ for copper(II) ion. This trend is similar to the reported result that the complexes of D are much less stable than those of C.^{11,20} The lower stability

Table 2. Formation Constants ($\log K^f$) for the complexes of Cu(II) and Ni(II) with the Tetraaza Macrocyclic Ligands at 25°C

Metal ion	A ^b	B ^b	C ^c	D ^c
Cu(II)	26.5(1)	18.8(1)	27.2	18.3
Ni(II)	17.2(2)	n.c. ^d	22.2	8.6
			(20.0) ^e	

^aRefers to the equilibria $M^{2+} + L = [M(L)]^{2+}$, where L is the free ligand. ^bThis work; obtained in 90% (v/v) methanol-water mixture ($\mu=0.20$ M). ^cRef. 11. ^dn.c.=No evidence of complex formation even in the high pH at which the nickel(II) hydroxide precipitates. ^eRef. 6.

of the complex of B, compared to A, can be attributed to the higher proton affinity and the more severe steric crowding of the ligand caused by the N-methyl groups. For nickel(II) ion, the destabilization produced by the N-methylation is such that any evidence for the formation of the complex of B can not be observed in the solutions and even in solutions of high pH at which nickel(II) hydroxide forms.

We have also attempted the synthesis of nickel(II) complex of B in various experimental conditions. Although the red-purple complex $[Cu(B)](ClO_4)_2$ was readily prepared by the reaction of $Cu(OAc)_2 \cdot H_2O$ with B in methanol solution followed by addition of $NaClO_4$, all efforts to obtain the nickel(II) complex of B from the reaction of $Ni(OAc)_2 \cdot 4H_2O$ with the ligand in the similar conditions were unsuccessful. Even after prolonged heating (>60 h) at reflux of the mixture, no spectral change of the solution was observed and the addition of $NaClO_4$ produced only the white salt $B \cdot 2HClO_4$ instead of the nickel(II) complex. This result is quite different from the reported results that, in the cases of A, C, and D, the square planar copper(II) and nickel(II) complexes can be readily prepared by the reaction of the hydrated metal ions and the ligands in methanol solutions.^{11,14} However, the red complex $[Ni(B)](ClO_4)_2$ can be prepared by the reaction (see Experimental)^{21,22} of dehydrated nickel(II) ion and the ligand in a dehydrated acetonitrile-DMSO mixture or DMSO solution.

From the above results together with the data of the protonation constants obtained in 90% (v/v) methanol-water mixture, it is clear that the ligand B is more readily protonated than A, C, or D, and the protonated species can react with copper(II) ion to form the complex but not with nickel(II) ion. It has been known that copper(II) ion is stronger acid than nickel(II) ion.^{23,24} In a dehydrated acetonitrile-DMSO mixture or DMSO solution, the ligand is not protonated and reacts with the nickel(II) ion to form the complex. Therefore, it can be suggested that the high selectivity of B for the complex formation with Cu(II) over Ni(II) ion in methanol solutions containing water mainly depends on the large proton affinity of the ligand and the acidity difference between the two metal ions. To our knowledge, the copper(II) ion selectivity of B against nickel(II) ion is one of the highest yet reported for any other polyaza macrocycles.¹⁵⁻¹³

Properties of Complexes. The complexes $[Ni(B)](ClO_4)_2$ and $[Cu(B)](ClO_4)_2$ are soluble in acetonitrile, DMF, and DMSO, but insoluble in water and methanol. The complexes are extremely stable in solid states and in the solutions.

Table 3. Molar Conductance and Electronic Spectral Data of the Nickel(II) and Copper(II) Complexes^a

Complex	λ_{max} , nm (ϵ , $M^{-1} cm^{-1}$)	Λ_M , $\Omega^{-1} M^{-1} cm^{-2}$
$[Ni(A)]^{2+}$	463(73)	
$[Ni(B)](ClO_4)_2$	501(93) 503(89) ^b	289 ^b
$[Ni(D)]^{2+}$	512(195)	
$[Cu(A)]^{2+}$	508(150) ^c	
$[Cu(B)](ClO_4)_2$	563(286) ^c	278 ^b
$[Cu(D)]^{2+}$	583(214)	

^aMeasured in nitromethane solution at 20°C unless otherwise specified. ^bIn acetonitrile solution. ^cRef. 15. ^dRef. 32.

Table 4. Cyclic Voltammetric Data for the Ni(II) and Cu(II) Complexes^a

Complex	Potential, V vs. SCE	
	M(II)→M(III)	M(II)→M(I)
$[Ni(A)]^{2+}$	+1.08	-1.28
$[Ni(B)](ClO_4)_2$	+1.67(i) ^b	-1.07(i)
$[Ni(D)]^{2+}$	+1.46	-1.08
$[Cu(A)]^{2+}$	+1.41	-0.92(i)
$[Cu(B)](ClO_4)_2$	+1.91(i)	-0.26

^aMeasured in 0.1 M (*n*-Bu)₄NClO₄ acetonitrile solution at 20°C. ^bRef. 15. ^cRef. 31. ^di=irreversible.

The copper(II) complex is decomposed very slowly even in low pH, likewise the complexes of A, D, and other 14-membered tetraaza macrocyclic complexes.^{15,25} Electronic spectra of the copper(II) complex (1.0×10^{-3} M) dissolved in 0.3 M HNO₃ acetonitrile-water (1:1) solution shows that only less than 2% of the complex is decomposed in 17 h at 20°C. However, in the same condition, about 30% of the nickel(II) complex is decomposed in 9 h.

The infrared spectra of the nickel(II) and copper(II) complexes of B show no band near 3200 cm^{-1} , indicating that all of the nitrogens of the ligand are methylated. ¹³C-NMR spectrum of $[Ni(B)](PF_6)_2$ shows 12 peaks (see Experimental), indicating that the complex contains 12 pairs of non-equivalent carbon atoms. This is consistent with the ligand structure. The molar conductance and electronic spectral data of the complexes are listed in Table 3. The conductivity data for the nickel(II) and copper(II) complexes in acetonitrile show that the complexes are 1:2 electrolytes. The electronic absorption spectra of $[Ni(B)](ClO_4)_2$ and $[Cu(B)](ClO_4)_2$ measured in acetonitrile show single *d-d* transition bands at 503 nm ($\epsilon=89 M^{-1} cm^{-1}$) and 563 nm ($\epsilon=286 M^{-1} cm^{-1}$), respectively, indicating that the complexes are in square planar M(II)-N₄ environments. It is seen that the bands of the nickel(II) and copper(II) complexes of B are appeared at ca. 50 nm longer wavelengths than those of A. The weaker ligand field strength of B, compared to A, is corresponds to the general trend that the alkylation of the coordinated nitrogen atoms of a macrocyclic complex lengthens the M-N bond length and reduces the interaction between the metal ion and the ligand.²⁵⁻²⁷ The larger values of molar extinction coefficients for the complexes of B, compared to A, may be

attributable to the more distorted structures of the complexes because of the increased steric crowding by the presence of the N-methyls.²⁸⁻³⁰

The oxidation and reduction potentials (Table 4) of the nickel(II) and copper(II) complexes of B were obtained by published methods.¹⁵ The redox potentials of $[M(B)]^{2+}$ ($M = Ni$ (II), Cu (II)) are more anodic than those for the complexes of A.¹⁵ This result is similar to the generally observed trend that N-alkylation of a macrocyclic complex makes the attainment of the M(III) state more difficult and the access to the M(I) easier.²⁸⁻³¹ Although the reduction potential of $[Ni(B)]^{2+}$ is similar to that of $[Ni(D)]^{2+}$, the oxidation potential is more anodic. The more difficult oxidation for the complex of B can be attributed to the presence of the C-substituents, which inhibit the axial ligation and restrict the shortening of the Ni-N distances in the Ni(III) complex.³¹

References

1. Y. Inoue and G. W. Gokel, *Cation Binding by Macrocycles*, Marcel Dekker, Inc., New York, 1990 and references therein.
2. R. M. Izatt and J. J. Christensen, *Synthesis of Macrocycles*, John Wiley & Sons, Inc., New York, 1987 and references therein.
3. K. R. Adam, M. Antolovich, D. S. Baldwin, L. G. Brigden, P. A. Duckworth, L. F. Lindoy, A. Bashall, M. McPartin, and P. A. Tasker, *J. Chem. Soc., Dalton Trans.*, 1869 (1992).
4. K. V. Damu, H. Maumela, R. D. Hancock, J. C. A. Boeyens, and S. M. Dobson, *J. Chem. Soc., Dalton Trans.*, 2717 (1991).
5. H. Tsukube, T. Yoden, T. Iwachido, and M. Zenki, *J. Chem. Soc., Chem. Commun.*, 1069 (1991).
6. R. C. Luckay and R. D. Hancock, *J. Chem. Soc., Dalton Trans.*, 1491 (1991).
7. R. W. Hay, M. P. Pujari, W. Moodie, S. Craig, D. T. Richens, A. Perotti, and L. Ungaretti, *J. Chem. Soc., Dalton Trans.*, 2605 (1987).
8. M. Hujiwara and H. Wakita, *Polyhedron*, **9**, 2491 (1990).
9. E. Kimura, Y. Kurogi, S. Wada, and M. Shionoya, *J. Chem. Soc., Chem. Commun.*, 781 (1989).
10. M. D. Casa, L. Fabbrizzi, A. Perotti, A. Poggi, and P. Tundo, *Inorg. Chem.*, **24**, 1611 (1985).
11. C. M. Madeyski, J. P. Michael, and R. D. Hancock, *Inorg. Chem.*, **23**, 1487 (1984).
12. E. K. Barefield and F. Wagner, *Inorg. Chem.*, **12**, 2435 (1973).
13. E. Kimura, C. A. Dalimunte, A. Yamashita, and R. Machida, *J. Chem. Soc., Chem. Commun.*, 1041 (1985).
14. S.-G. Kang, J. K. Kweon, S.-K. Jung, and M.-S. Kim, *Bull. Korean Chem. Soc.*, **13**, 465 (1992).
15. S.-G. Kang, J. K. Kweon, and S.-K. Jung, *Bull. Korean Chem. Soc.*, **12**, 483 (1991).
16. A. E. Martell and R. J. Motekaitis, *Determination and Use of Stability Constants*, VCH, New York, 1989.
17. V. D. Thom, G. D. Hosken, and R. D. Hancock, *Inorg. Chem.*, **24**, 3378 (1985).
18. E. Suet, A. Laouenan, H. Handel, and R. Guglielmetti, *Helv. Chim. Acta.*, **67**, 441 (1984).
19. R. M. Izatt, K. Pawlak, and J. S. Bradshaw, *Chem. Rev.*, **91**, 1721 (1991).
20. B. S. Nakani, J. J. B. Welsh, and R. D. Hancock, *Inorg. Chem.*, **22**, 2956 (1983).
21. The reagent $HC(OEt)_3$ reacts with H_2O to produce $HCOOEt$ and $EtOH$. See also ref. 22.
22. A. Bakac and J. H. Espenson, *Inorg. Chem.*, **31**, 1108 (1992).
23. J. E. Huheey, *Inorganic Chemistry: Principles of Structure and Reactivity*, 3rd Ed., Harper & Row, Publisher, Cambridge, 1983, pp. 294-302.
24. F. Basolo and R. G. Pearson, *Mechanisms of Inorganic Reactions*, 2nd Ed., John Wiley and Sons, Inc., New York, 1968, p. 32.
25. F. Wagner and E. K. Barefield, *Inorg. Chem.*, **15**, 408 (1976).
26. N. Jubran, G. Ginzburg, H. Cohen, Y. Koresh, and D. Meyerstein, *Inorg. Chem.*, **24**, 251 (1985).
27. F. Wagner, M. T. D. Aniello, A. H. Wang, and E. K. Barefield, *J. Am. Chem. Soc.*, **96**, 2625 (1974).
28. S.-G. Kang and J. K. Kweon, *Bull. Korean Chem. Soc.*, **13**, 256 (1992).
29. M. S. Haltman and S. C. Cumming, *Inorg. Chem.*, **15**, 660 (1976).
30. R. W. Hay and D. P. Piplani, *J. Chem. Soc., Dalton Trans.*, 1956 (1976).
31. E. K. Barefield, G. M. Freeman, and D. G. V. Derveer, *Inorg. Chem.*, **25**, 552 (1986).
32. M. Micheloni, P. Paoletti, S. Burki, and T. A. Kaden, *Helv. Chim. Acta.*, **65**, 587 (1982).