

N-Alkylation of Secondary Amines in Nickel(II) Complexes of Polyaza Macrotricyclic Ligands

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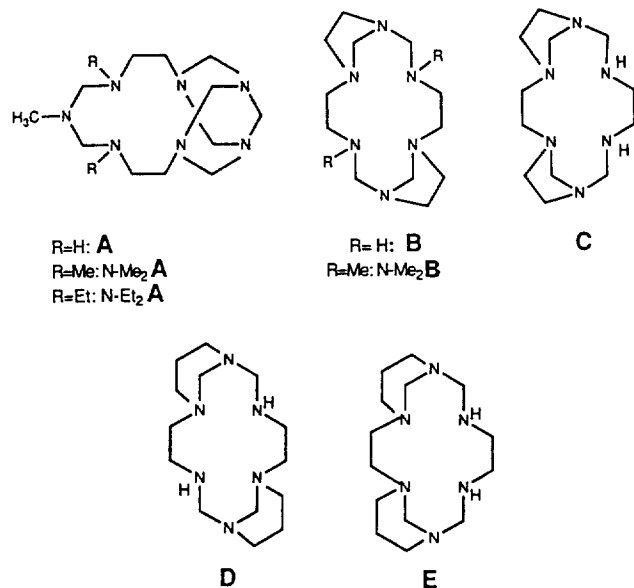
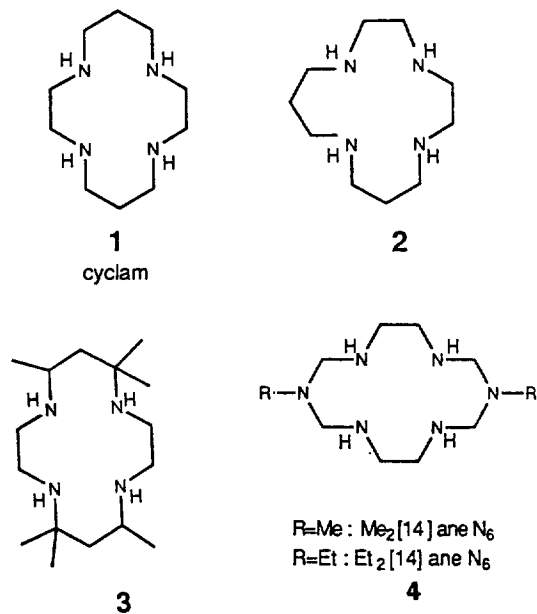
The secondary nitrogen donors of the Ni(II) complexes of macrotricyclic ligands 8-methyl-1,3,6,8,10,13,15-heptaazatricyclo[13.1.1.1^{13,15}]octadecane (**A**) and 1,3,6,9,11,14-hexaazatricyclo[12.2.1.1^{6,9}]octadecane (**B**) are N-alkylated and the Ni(II) complexes of N-Me₂A, N-Et₂A, and N-Me₂B are obtained. The Ni(II) complexes of N-Me₂A and N-Et₂A are stable in acidic aqueous solutions while that of N-Me₂B decomposes relatively rapidly. The N-alkylation leads to the decrease in the ligand field strength as well as an anodic shift in both of the oxidation and the reduction potentials of the Ni(II) complexes.

Introduction

It has been known that redox properties and ligand field strengths of the Ni(II) complexes with neutral tetraaza macrocyclic ligands are affected by the substituents, ligand unsaturation, macrocyclic cavity size, and chelate ring sequences.¹⁻³ In addition, it has been indicated by the limited numbers of reports that the presence of tertiary amine donors in the macrocyclic ligand also alters such properties. For instance, N-methylation of Ni(II) complexes of tetraaza macrocyclic ligands of **1**, **2**, and **3** results in a decrease in the ligand field strength and an anodic shift in both of the oxidation and the reduction potentials.⁴⁻⁸

secondary nitrogen donors only. However, the ligand field strengths of Ni(II) complexes of **A** and **B** are not weaker than that of R₂[14]aneN₆ or cyclam (Table 1).¹² Furthermore, X-ray structures of Ni(II) complexes of **A-E** show that the Ni-N bond distances involving tertiary amine donors are not significantly longer than those involving secondary nitrogen donors.⁹⁻¹² Therefore, it prompted us to N-alkylate the secondary amines of the ligands **A-E** in order to examine the effect of the existence of additional tertiary nitrogen donors on the properties of the Ni(II) complexes.

In this report, we describe the synthesis and properties of the Ni(II) complexes of the N-methyl- and the N-ethyl-substituted **A** and the N-methyl-substituted **B**. Preparation of the N-alkylated Ni(II) complexes of **C-E** has not been successful although various synthetic methods have been employed.



Recently, various square-planar Ni(II) complexes of polyaza macrotricyclic ligands **A-E** have been synthesized by the simple template condensation reactions of amines and formaldehyde.⁹⁻¹¹ The complexes of **A-E** contain two tertiary- and two secondary-nitrogen donors in the ligand. All complexes show more positive oxidation and reduction potentials than the Ni(II) complex of the related 14-membered hexaaza monocyclic ligands R₂[14]aneN₆ (**4**) or cyclam (**1**) that contains

Experimental Section

Instrumentation. Infrared spectra were recorded with a Shimadzu IR-440 spectrophotometer. Conductance measurements were performed by using a Metrohm Herisau E518 conductometer and RC 216B₂ conductivity bridge. ¹H and

Table 1. Properties of Ni(II) Complexes of N-Alkylated Macrotricyclic Ligands

Ligand	$\lambda_{max}^{a,b}$ nm (ϵ , $M^{-1}cm^{-1}$)	$E_{ox}^{c,d}$ Ni ^{II} /Ni ^{III}	$E_{red}^{c,d}$ Ni ^{II} /Ni ^I	Λ_M^a $\Omega^{-1}cm^{-2}M^{-1}$	reference
N-Me ₂ A	447 (75) ^a , 447 (103) ^b	+1.60 (i)	-1.07	209	this work
N-Me ₃ A	454 (134) ^a			401	this work
N-Et ₂ A	455 (118) ^a , 457 (119) ^b	+1.41	-1.12	173	this work
N-Me ₂ B	455 (92) ^a , 466 (102) ^b	+1.64 (i)	-0.94 (qr)	228	this work
A	434 (80) ^a , 439 (83) ^b	+1.32	-1.39		9
B	443 (71) ^a , 447 (80) ^b	+1.50	-1.28		10
C	458 (84) ^a , 456 (89) ^b	+1.43 (i)	-1.25		11
D	468 (58) ^a , 465 (95) ^b	+1.25	-1.14		10
E	477 (50) ^a , 471 (90) ^b	+1.34	-1.20		11
Me ₂ [14]aneN ₆	446 (40) ^a , 449 (56) ^b	+0.93	-1.55		12
Et ₂ [14]aneN ₆	445 (47) ^a , 449 (64) ^b	+0.90	-1.47		12
cyclam	445 (64) ^a , 455 ^b	+0.91	-1.46		4,8
N-Mecyclam	454 (85.2) ^a				5
N-Me ₄ cyclam	511 (71) ^a , 492 ^b				6,8

^a Measured in H₂O at 20°C. ^b Measured in MeNO₂ at 20°C. ^c Measured in acetonitrile solutions; 0.1 M (n-Bu)₄NClO₄; volts vs. SCE.

^d i=irreversible, qr=quasi reversible.

¹³C NMR spectra were recorded on a Bruker WP80 FT NMR spectrometer. The peaks of the ¹³C NMR spectra were assigned with the DEPT program. Electronic absorption spectra were obtained on a Shimadzu 260 UV/vis spectrophotometer. Elemental analyses were performed by Galbraith Laboratories Inc., Knoxville, TN. Gases were analyzed on a Hewlett Packard 5890 A Gas Chromatograph (flame ionization detector) with a 2.4 m Porapak Q column. Peak integrations were performed with a HP 3390 A Integrator. Cyclic voltammetry was carried out with CV-1B cyclic voltammograph coupled with a Hewlett Packard 7015A X-Y recorder. The electrochemical data were obtained in acetonitrile with 0.1 M (n-Bu)₄NClO₄ as supporting electrolyte. The working electrode was a platinum disk, the auxiliary electrode was a coiled platinum wire, and the reference electrode was a SCE.

Synthesis. Safety Note. *Caution!* Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of material should be prepared, and these should be handled with great caution.

All chemicals and solvents used in the syntheses were dried and purified according to the literature methods,¹³ and degassed prior to use. The Ni(II) complexes of macrocyclic ligands A-E were synthesized according to the methods previously reported.⁹⁻¹¹ N-alkylation reactions were performed by using a method similar to that previously reported by Barefield.⁷ All deprotonation and alkylation reactions were conducted under a dry nitrogen atmosphere.

[Ni(N-Me₂A)](ClO₄)₂. [Ni(A)](ClO₄)₂ (2.5 g) were dissolved in Me₂SO (20 ml). Finely pulverized KOH (1.0 g) was added and the mixture was stirred vigorously for 1 h. To the purple solution was added CH₃I (1 ml) and the solution was stirred for additional 3 h. EtOH (10 ml) was added to the resulting yellow solution. The yellow precipitates were filtered, washed with EtOH, and then recrystallized from hot water. The yellow crystals were collected, washed with ethanol, and dried *in vacuo*. Yields: ~20%. Anal. Calcd for NiC₁₄H₃₁N₇Cl₂O₈: C, 30.30; H, 5.63; N, 17.67. Found: C, 30.10; H, 5.54; N, 17.51. ¹H-NMR (Me₂SO-d₆): δ 2.75 (s, Ni-N-CH₃).

¹³C-NMR (CD₃CN) for [Ni(N-Me₂A)](PF₆)₂: δ 41.3, 43.3, 52.4, 57.0, 68.7, 75.1, 75.3, 80.5.

[Ni(N-Me₃A)](ClO₄)₃. When an excess amount of CH₃I (1.5 ml) was added to the Me₂SO solution of the deprotonated Ni(II) complex of A, an extra methyl group was attached to an uncoordinated tertiary nitrogen atom. Anal. Calcd for NiC₁₅H₃₄N₇Cl₃O₁₂: C, 26.91; H, 5.12; N, 14.64. Found: C, 26.59; H, 5.24; N, 14.49.

[Ni(N-Et₂A)](ClO₄)₂. [Ni(A)](ClO₄)₂ (2.8 g) and finely pulverized KOH (0.9 g) were mixed in Me₂SO (20 ml), and the mixture was stirred vigorously for 30 min. To the purple solution was added EtI (1.1 ml). The color of the solution immediately changed to green and then to orange. Ethanol (5 ml) and an excess amount of LiClO₄ dissolved in methanol were added to the solution. The solution was allowed to stand in a refrigerator until orange crystals formed. The crystals were filtered, washed with EtOH, and then recrystallized from the mixture (1 : 2 v/v) of Me₂SO and EtOH. Yield: ~30%. Anal. Calcd for NiC₁₆H₃₅N₇Cl₂O₈: C, 32.96; H, 6.05; N, 16.82. Found: C, 32.60; H, 5.74; N, 16.49. ¹H-NMR (CD₃NO₂): δ 1.16 (t, Ni-N-C-CH₃), 2.61 (q, Ni-N-CH₂-). ¹³C-NMR (Me₂SO-d₆): δ 5.05, 40.47, 42.68, 48.37, 50.63, 66.66, 73.30.

[Ni(N-Me₂B)](ClO₄)₂. The complex was synthesized by a method similar to that described for the synthesis of [Ni(N-Me₂A)](ClO₄)₂. After the deprotonation of the complex, were added CH₃I and then EtOH to the solutions of the complex. The solution was filtered and an excess LiClO₄ dissolved in MeOH was added to the filtrate. The solution was allowed to stand in a refrigerator until orange crystals formed. The crystals were filtered, washed with methanol, and air-dried. When LiClO₄ was not added to the solution, I⁻ salts were obtained. Yield: ~20%. Anal. Calcd for NiC₁₄H₃₀N₆Cl₂O₈: C, 31.12; H, 5.60; N, 15.57. Found: C, 30.41; H, 5.56; N, 15.70. ¹³C-NMR (Me₂SO-d₆): δ 45.9, 47.0, 48.7, 49.8, 53.5, 55.4, 56.1, 57.1, 59.3, 68.7, 75.1, 80.3.

Unsuccessful Attempts for N-alkylation of Ni(II) Complexes of C-E. Method 1. The secondary nitrogens in [Ni(L)](ClO₄)₂ (L=C-E) were deprotonated by KOH in

a Me₂SO solution and then was added CH₃I as described in the syntheses of N-alkylated Ni(II) complexes of **A** and **B**. EtOH was added to induce crystallization. The deep brown crystals formed were filtered and washed with EtOH, which were identified as [Ni(DMSO)₃I₂]₂. N-alkylated complexes were never produced. **Method 2.** An aqueous solution of Ni(II) complex was heated with formic acid and formaldehyde at reflux for 24 h.⁶ The solution was cooled in an ice bath and was added KOH until the solution became slightly basic. The solution was allowed to stand in a refrigerator until the crystals formed. Only the starting Ni(II) complexes were isolated. **Method 3.** Direct template condensation reactions were carried out for the synthesis of N-alkylated complexes of **C** and **E**. To a stirred methanol solution of NiCl₂·6H₂O (12 g) were added N,N'-dimethylethylenediamine (N,N'-Me₂en) and 36% formaldehyde (16 ml). Then, diethylenetriamine was added to the solutions for **C** and N,N'-bis(3-aminopropyl)ethylenediamine was added for **E**. The solutions were heated at reflux for 24 h. The solutions were filtered to remove Ni(OH)₂ and excess LiClO₄ was added to the filtrate. The solutions were kept in a refrigerator until the crystals formed, which were identified as [Ni(N,N'-Me₂en)₂Cl₂].

Results and Discussion

Synthesis. Deprotonation of secondary amines in the Ni(II) macrocyclic complexes of **A** and **B** in Me₂SO solutions followed by alkylation with CH₃I resulted in the N-methylated complexes of **A** and **B**, [Ni(N-Me₂A)](ClO₄)₂ and [Ni(N-Me₂B)](ClO₄)₂. When EtI was used as the alkylating reagent, the N-ethylated Ni(II) complex of **A** [Ni(N-Et₂A)](ClO₄)₂ was formed. However, addition of EtI to the deprotonated Ni(II) complex of **B** produced ethylene gas instead of the N-ethylated complex. It has been noted previously that alkyl halides with β-hydrogen undergo HX elimination rather than S_N2 reaction.⁷ The formation of N-ethylated complex of **A** in this study suggests that HX elimination is slower than S_N2 reaction in the reaction of EtI with the deprotonated Ni(II) complex of **A**.

As for the Ni(II) complexes of **C-E**, all attempts to prepare the N-alkylated complexes were unsuccessful as described in the Experimental Section. In particular, deprotonation-alkylation process for the Ni(II) complexes of **C-E** in Me₂SO solutions resulted in the formation of [Ni(Me₂SO)₃I₂]₂. It is likely that hole size of the N-alkylated ligands of **C-E** are too large to accommodate the Ni(II) ion and thus the Ni(II) ions are dissociated from the macrocyclic ligand. It has been reported that the metal-nitrogen donor distances are increased by the N-alkylation. The average Ni-N distance (1.990 Å) of Ni(II) TMC complex is ca. 0.04 Å longer than Ni(II) cyclam complex.⁴ Furthermore, an average Ni-N distance of Ni(II) perchlorate complex of **E**, that contains six-membered subrings in the macrocycle, is 0.03 Å longer than those of **A** or **B**.^{10,11} Therefore, if the N-alkylated Ni(II) complexes of **D** or **E** existed, their average Ni-N bond distances would be ca. 1.99 Å which is ca. 0.07 Å longer than those of **A** or **B** and is too long for the square-planar Ni(II) complex.

All efforts to obtain the free ligands from the N-methylated Ni(II) complexes by treating them with excess NaCN or H₂S gas in aqueous solution were unsuccessful. The reactions

resulted in the exchange of ClO₄⁻ anions with CN⁻ or S²⁻. In addition, treatment of the N-alkylated complexes of **A** with HCl gas in dry acetonitrile solutions resulted in coordination of Cl⁻ ions at the axial sites of the complex while same reaction with [Ni(N-Me₂B)]²⁺ yielded decomposition products such as ammonium salts and formaldehyde instead of the protonated free ligand.

Properties. The N-methylated- and the N-ethylated- Ni(II) complexes of **A**, [Ni(N-Me₂A)](ClO₄)₂ and [Ni(N-Et₂A)](ClO₄)₂, are stable against ligand dissociation in acidic aqueous solutions. No spectral change was observed for the aqueous solutions of [Ni(N-Me₂A)]²⁺ (4.72 × 10⁻³ M) and [Ni(N-Et₂A)]²⁺ (5.34 × 10⁻³ M) upon the addition of H₂SO₄ (0.1 M) in 24 h.¹⁴ However, spectra of the aqueous solution of [Ni(N-Me₂B)]²⁺ (5.72 × 10⁻³ M) indicated that ca. 50% of the complexes were decomposed in 110 min at 25°C upon the addition of H₂SO₄ (0.1 M).¹⁴ It is also observed for [Ni(N-Me₂B)](ClO₄)₂ in an attempt to exchange ClO₄⁻ ions with PF₆⁻ that either addition of water to the MeCN solution of the complex in the presence of an excess NH₄PF₆ or heating the aqueous solution of the complex resulted in dealkylation.

Electronic absorption spectral data and cyclic voltammetry data as well as conductance data for the N-alkylated Ni(II) complexes of **A** and **B** are summarized in Table 1, and are compared with the data for the parent Ni(II) complexes of **A** and **B**. The spectra of the N-alkylated Ni(II) complexes show typical Ni(II) square-planar chromophores. The introduction of N-alkyl substituents at the secondary nitrogens of the Ni(II) complexes of **A** and **B** results in the shift of λ_{max} to 10-20 nm longer wavelengths, indicating the decrease in the ligand field strength for the N-alkylated complexes. The decrease in the ligand field strength upon N-alkylation of the Ni(II) complex was observed for other macrocyclic ligand systems such as cyclam.⁴⁻⁸ In addition, the average Ni-N distance of square-planar Ni(II) TMC complex was observed to be ca. 0.04 Å longer than that of Ni(II) cyclam.⁴ Therefore, the weaker ligand field strength of the N-alkylated complexes of **A** and **B** in this study may be attributed to the longer Ni-N bond distances of the complexes. The spectra also indicate that N-ethyl substituents weaken the ligand field strength of the complex better than N-methyl substituents. Nitrogen atoms with bulky substituent tend to form sp² hybridization rather than sp³ and thus elongate the Ni-N bonds further.

Infrared spectrum (Nujol mull) of [Ni(N-Et₂A)](ClO₄)₂ shows splitted ClO₄⁻ band around 1150-1000 cm⁻¹, indicating that the complex cation interacts with the ClO₄⁻ anions in the solid state. It was found in the Ni(II) complex of N-alkylated macrocyclic ligand C-meso-1,5,8,12-tetramethyl-1,4,8,11-tetraazacyclotetradecane that the perchlorate ions are weakly coordinated to the Ni(II) ion at the apical sites with the distance of Ni-O being 2.887 (3) Å.¹⁵

¹H and ¹³C-NMR spectra of N-alkylated complexes are summarized in the Experimental Section. ¹³C-NMR spectra of [Ni(N-Me₂A)](PF₆)₂ and [Ni(N-Me₂B)](ClO₄)₂ show the N-methyl carbon peaks of the coordinated nitrogens at δ 43.3 and 45.9 ppm, respectively. The carbon peaks of the N-ethyl groups of the coordinated nitrogens in [Ni(N-Et₂A)](ClO₄)₂ appeared at δ 5.05 and 42.7 ppm. Broadening of NMR spectra was not observed in MeCN-d₃ or Me₂SO-d₆ solutions,

indicating that the N-alkylated complexes maintain the diamagnetic square-planar geometry even in the coordinating solvents.

Cyclic voltammograms for the Ni(II) complexes of N-Me₂A, N-Et₂A, and N-Me₂B indicate that the complexes exhibit two one-electron waves corresponding to Ni(III)/Ni(II) and Ni(II)/Ni(I) processes. The cyclic voltammetry data in Table 1 show that the introduction of N-alkyl substituents results in anodic shifts in both of the oxidation and the reduction potentials compared with the complexes of parent ligand systems. That is, N-alkylation makes attainment of Ni(I) state easier and Ni(III) state more difficult. The methyl and the ethyl groups have similar effects on the redox potentials. This anodic shift of redox potentials may be attributed to the weaker Ni-N interactions in the N-alkylated complexes. The weaker Ni-N interaction for the tertiary amine results in stabilization of antibonding σ -orbitals of the Ni(II) complex, and this makes addition of an electron more favorable while removal of an electron less favorable.^{1,2,4}

The present study shows that introduction of alkyl substituents at the secondary amine donors in the polyaza macrocyclic Ni(II) complexes, which already contain two tertiary nitrogen donors, results in the decrease in the ligand field strength as well as an anodic shift in both of the oxidation and the reduction potentials.

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Conversion of 1,3-Thiazolidines to Dihydro-1,4-thiazine by Chlorinolysis

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The ring expansion of 1,3-thiazolidines **4** derived from β -ketoacid derivatives to the corresponding dihydro-1,4-thiazines **1** by using the action of chlorine on **4** has been achieved. In the chlorinolysis unisolable sulfenyl chlorides **5** may be formed from chlorosulfonium ions **11** by β -elimination involving carbonyl activated methylene hydrogens. Addition of sulfenyl chloride to the internal double bond appears to form probable thiiranium ions **14**, which in turn gave **1** with loss of acidic proton. Imminium ions **15** could be hydrolyzed easily to give enol **8**. As a side reaction, dihydrothiazine that was formed was further chlorinated to produce dichlorides **16** which were rearranged readily to the chloromethyl compounds **10**.

Introduction

Recently we reported the synthesis of dihydro-1,4-thiazines **1** by rearrangement of 1,3-thiazolidine sulfoxides **2** involving

sulfenic acid¹ **3**. As an extension of this work, we now report the synthesis of **1** by chlorinolysis of 1,3-thiazolidines **4** involving sulfenyl chloride **5**.

An important feature of the 1,3-thiazolidines¹ **4** is the pre-