Synthesis and Characterization of 14-Membered Tetraaza Macrocycles with N-Ethyl Groups and their Nickel(II) and Copper(II) Complexes

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The 14-membered tetraaza macrocyclic ligand 1,8-diethyl-5,12-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene(B) can be synthesized as its dihydroperchlorate salt by the one-pot reaction of 2-ethylaminoethylamine, methyl vinyl ketone, and perchloric acid in absolute ethanol. The reaction of Ni(II) or Cu(II) ion and the salt yields $[M(B)]^{2+}$ (M=Ni(II) or Cu(II)), which reacts with $NaBH_4$ to produce $[M(D)]^{2+}$ (D=1,8-diethyl-5,12-dimethyl-1,4,8, 11-tetraazacyclotetradecane). The complexes $[M(L)]^{2+}$ (L=B or D) have planar geometry and contain two ethyl groups at the donor nitrogen atoms of the ligands. The red solids $[Cu(B)](X)_2$ ($X=ClO_4^-$ or PF_6^-) react with water molecules of atmospheric moisture to produce the purple solids in which water molecules are coordinated to the metal ion. Synthesis, characterization, and the properties of the new N-ethylated macrocyclic ligands and their Ni(II) and Cu(II) complexes are reported.

Introduction

Polyaza macrocyclic ligands with alkyl pendant arms at the donor nitrogen atoms and their metal complexes have received much attention because of their structural and chemical properties, which are often quite differ from those for the unalkylated macrocyclic compounds.[1-13] Although various per-N-alkylated tetraaza macrocyclic compounds have been prepared by alkylations on the secondary nitrogens of pre-formed macrocycles, examples of partial-N-alkylated macrocyclic ligands are relatively rare. Moreover, those with more bulky alkyl groups than methyl are even rare. This may be arised from the fact that the selective alkylation is more complicated and requires several steps.[12,13] Therefore, we have been interested in the direct synthesis of free macrocyclic ligands, in which bulky alkyls are partially substituted on the donor nitrogens.

Although some unsaturated macrocycles have been obtained by nontemplate reactions of α,β-unsaturated ketones with diamines,[14-19] most of the ligands have no substituent at the nitrogen atoms. Utilizing the characteristics of the reactions, we have attempted the synthesis of new di-N-ethylated tetraaza macrocycle B by the one-pot reaction Eq. (1) of methyl vinyl ketone, 2-ethylaminoethylamine, and perchloric acid. This paper reports the synthesis and properties of the ligands B·2HClO₄ and D and their Ni(II) and Cu(II) complexes.

Experimental

Measurements. Infrared spectra were obtained using a Shimadzu IR-440 spectrophotometer. Conductance measurements were made by using a Metrohm Herisau Conductometer E518. Visible spectra were recorded using a Perkin-Elmer Lambda 5 UV/vis spectrophotometer. ^1H and ^{13}C-NMR spectra were recorded with a Bruker WP 300FT NMR spectrometer. Elemental analyses were performed at the Kolon R & D Center. Cyclic voltammetric measurements were performed by a reported method.

Synthesis. B·2HClO₄. To a cooled (0-4°C) ethanol (100

m*l*) solution of 98% 2-ethylaminoethylamine (10.7 m*l*) was added dropwise 60% perchloric acid (10.0 m*l*) with stirring. Methyl vinyl ketone (8.3 m*l*) was added over a period of 1 h to the solution, and then the resulting mixture was allowed to warm up to room temperature for 30 min. The white precipitates formed were filtered and washed with methanol. The product is highly hygroscopic and unstable in air. Yield: ~15%. Anal. Calcd for $C_{16}H_{34}N_4Cl_2O_8$: C. 39.9; H. 7.12; N, 11.6%. Found: C, 40.8; H, 7.70; N, 11.6%.

[Ni(B)] (ClO₄)₂·H₂O. A methanol suspension of Ni (OAc)₂·4H₂O (3.5 g) and B·2HClO₄ (6.0 g) was heated at reflux for 30 min, and then yellow solids were precipitated. The product was filtered, recrystallized from hot water, and air-dried. Yield: >90%. Anal. Calcd for $NiC_{16}H_{34}N_4Cl_2O_9$: C, 34.5; H, 6.12; N, 10.1%. Found: C, 34.3; H, 5.85; N, 9.74%.

[Ni(D)] (ClO₄)₂·H₂O. To a cooled (0-4°C) water-acetonitrile(1:2) solution (30 m*l*) of [Ni(B)](ClO₄)₂·H₂O (1.4 g) was slowly added NaBH₄ (0.3 g) over a period of 2 h. The resulting mixture was stirred for 3 h at room temperature, heated to reflux for 20 min, and filtered to remove small amount of metallic nickel. The filterate was acidified by adding HClO₄ and then the orange-red crystals formed. The product was filtered, washed with water, and air-dried. The product was recrystallized from hot water. Yield: ~90%. Anal. Calcd for $NiC_{16}H_{38}N_4Cl_2O_9$: C, 34.3; H, 6.84; N, 10.0%. Found: C, 34.1; H, 6.47; N, 9.94%.

[Cu(B)] (ClO₄)₂. This red complex was prepared by a procedure similar to that for [Ni(B)](ClO₄)₂·H₂O using Cu (OAc)₂·H₂O (3.0 g) in place of Ni(OAc)₂·4H₂O. The product was dried at ~100°C and stored in a tightly sealed tube. Yield:>90%. Anal. Calcd for $CuC_{16}H_{32}N_4Cl_2O_8$: C, 35.4, 5.94; N, 10.3%. Found: C, 35.9; H, 6.03; N, 9.89%.

[Cu(D)] (ClO₄)₂·H₂O. This red compound was prepared by a method similar to that for [Ni(D)](ClO₄)₂ using the Cu(II) complex of B. Yield: 80%. Anal. Calcd for $CuC_{16}H_{38}N_4Cl_2O_9$: C, 34.0; H, 6.78; N, 9.92%. Found: C, 34.5; H, 6.77; N, 9.69%.

D. This compound was prepared by the reaction of [Ni (D)](ClO₄)₂ and NaCN in an acetonitrile-water (1:1) solution. The demetallization and isolation procedures are similar to

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Table 1. Electronic Spectral Data for the N-Ethylated Ni(II) and Cu(II) Complexes

Compound	Electronic Spectra[a] λ_{max}, nm (ε, M^{-1}cm^{-1})		
[Ni(A)]$^{2+d}$	448(82)	446(87)[b]	
[Ni(B)](ClO$_4$)$_2$	457(142)	456(144)[b]	459(143)[c]
[Ni(C)]$^{2+c}$	460(22)	467(64)[b]	
[Ni(D)](ClO$_4$)$_2$	469(101)	473(102)[b]	
[Cu(A)]$^{2+d}$	508(87)		
[Ni(B)](ClO$_4$)$_2$	526(219)	520(239)[c]	
[Cu(C)]$^{2+c}$	508(92)		
[Ni(D)](ClO$_4$)$_2$	525(159)	524(148)[c]	

[a] In aqueous solutions at 25°C unless otherwise specified. [b] In nitromethane solutions. [c] In acetonitrile solutions. [d] Ref. 14. [e] Ref. 24.

those for cyclam from [Ni(cyclam)]$^{2+}$.[20] Yield: ~85%. Mass spectrum: m/e 284(M$^+$).

Results and Discussion

Syntheses. The unsaturated tetraaza macrocycle B is obtained as its dihydroperchlorate salt from the reaction (Eq. (1)) of 2-ethylaminoethylamine with perchloric acid and methyl vinyl ketone (1 : 1 : 1 mole ratio) in absolute ethanol solution. The white salt B·2HClO$_4$ is relatively unstable in atmospheric moisture and decomposed in air at room temperature within a few hours of its isolation. However, the salt can be stored for several monthes in a tightly sealed vessel. The salt is slightly soluble in DMSO but readily decomposed. Infrared spectrum of the salt shows $v_{C=N}$ and $v_{ClO_4^-}$ at 1650 and 1100 cm^{-1}, respectively.

$$2Et-NH \frown NH_2 + 2HClO_4 +$$

$$2CH_2 = CH - CO - CH_3 \rightarrow B \cdot 2HClO_4 \qquad (1)$$

$$[M(B)]^{2+} + NaBH_4 \rightarrow$$

$$[M(D)]^{2+} \quad (M = Ni(II) \text{ or } Cu(II)) \qquad (2)$$
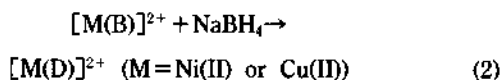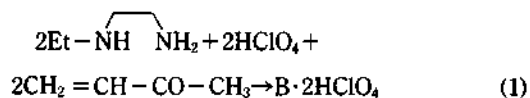
The orange yellow [Ni(B)](ClO$_4$)$_2$ and purple [Cu(B)](ClO$_4$)$_2$ are readily prepared by the reactions of B·2HClO$_4$ with the metal ions. Reductions (Eq. (2)) of the Ni(II) and Cu(II) complexes with NaBH$_4$ give the complexes [Ni(D)](ClO$_4$)$_2$ and [Cu(D)](ClO$_4$)$_2$, respectively. Demetallization of the ligand D can be achieved by the reaction of the complex and NaCN. The free ligand D is very stable in air and readily soluble in chloroform. Infrared spectrum of the ligand shows a v_{N-H} band at 3250 cm^{-1}.

Properties and Spectra of the Complexes. The complexes [M(L)](ClO$_4$)$_2$ (M = Ni(II) or Cu(II); L = B or D) are extremely stable in crystalline states and are highly stable against ligand dissociation even in acidic solutions, likewise various other 14-membered tetraaza macrocyclic complexes.[21] [-23] Visible spectra of the Ni(II) and Cu(II) complexes (2.0 × 10^{-3} M) in 0.3 M HNO$_3$ solutions showed that only 2-5% of the complexes were decomposed in 17 h at 20°C. In the case of the red solids [Cu(B)](X)$_2$ (X = ClO$_4^-$ or PF$_6^-$), the color is converted to purple in air at room temperature but returned to red at high temperature (~90°C). However, the

Table 2. Oxidation and Reduction Potentials (V vs SCE) for the Ni(II) and Cu(II) Complexes[a]

Complex	M$^{2+}\rightarrow$M^{3+}	M$^{2+}\rightarrow$M$^+$
[Ni(B)](ClO$_4$)$_2$	+1.34	−1.06
[Ni(D)](ClO$_4$)$_2$	+1.27	−1.08
[Ni(cyclam)]$^{2+c}$	+0.92	−1.46
[Ni(N-Me$_2$ cyclam)]$^{2+c}$	+1.16	−1.26
[Ni(N-Me$_3$ cyclam)]$^{2+c}$	+1.27	−1.28
[Ni(N-Me$_4$ cyclam)]$^{2+c}$	+1.46	−1.08
[Cu(B)](ClO$_4$)$_2$	+1.63(i)[b]	−0.51
[Cu(D)](ClO$_4$)$_2$	+1.60(i)	−0.74(i)
[Cu(cyclam)]$^{2+d}$	+1.35	−1.10

[a] Measured in 0.1 M (n-Bu)$_4$ NClO$_4$ acetonitrile solutions at 25°C. [b] i = irreversible. [c] Ref. 10; cyclam = 1,4,8,11-tetraazacyclotetradecane; N-Me$_2$ cyclam = 1,4-dimethyl-cyclam; N-Me$_3$ cyclam = 1,4,8-trimethyl-cyclam: N-Me$_4$ cyclam = 1,4,8,11-tetramethyl-cyclam. [d] Ref. 30.

red color of the complexes are maintained for several monthes in tightly sealed tubes. Infrared spectra of the purple complexes showed intense peaks at 3500 and 1620 cm^{-1}, but the peaks were not observed in the spectra of the red complexes. This indicates that water molecules of atmospheric moisture is readly coordinated to the metal ion of the solids at room temperature and removed from the coordination sphere at the high temperature.

Molar conductances of the complexes measusred in aqueous solutions are 202-210 ohm^{-1} mol^{-1} cm^2, indicating that the complexes are 1 : 2 electrolytes. The infrared spectra of the Ni(II) and Cu(II) complexes of B show $v_{C=N}$ at 1665 and 1660 cm^{-1}, respectively. The spectra of the complexes of D show a band at *ca.* 3200 cm^{-1}, which is assigned to v_{N-H} of the coordinated secondary amines. The electronic absorption spectra (Table 1) of the Ni(II) complexes of B and D in various solutions show single d-d transition bands at 456-476 nm ($\varepsilon = 101$-144 M^{-1} cm^{-1}) and the Cu(II) complexes show the bands at 520-534 nm ($\varepsilon = 140$-268 M^{-1} cm^{-1}), indicating that the Ni(II) and Cu(II) complexes have square planar M(II)-N$_4$ chromophores.[14,21,24] The absorption bands of the complexes of B and D are appeared at some longer wavelengths than those of A[14] and C,[24] respectively. This indicates that the ligand field strengths of the tetraaza macrocyclic ligands containing N-ethyl groups are much weaker than those containing secondary nitrogens only. In general, the N-alkylation of a macrocyclic complex lengthens the M-N bond length[25] and reduces the interaction between the

A : R = H
B : R = Et

C : R$_1$ = R$_2$ = H
D : R$_1$ = H ; R$_2$ = Et
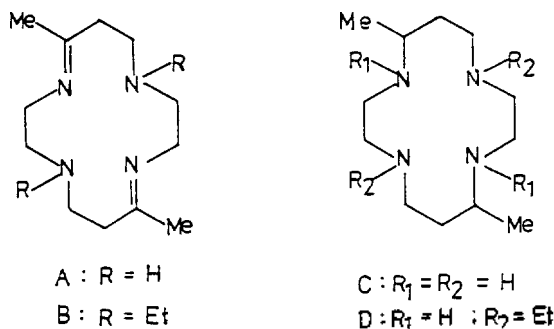
metal ion and the ligand.[8,11,25] The larger values of the molar absorptions for the complexes of B and D, compared to A and C, also indicate the more distorted structures of the complexes because of the increased steric crowding[24,26] by the presence of the N-ethyl groups.

The oxidation and reduction potentials of the Ni(II) and Cu(II) complexes obtained by cyclic voltammograms are as shown in Table 2. The oxidation potential of $[Ni(D)]^{2+}$ is +1.34 V and is more positive than that of $[Ni(B)]^{2+}$ (+1.27 V). The increase in ligand unsaturation increases degree of polarizability of the metal-ligand bond and causes the oxidation to Ni(III) more difficult.[27] It has been reported that methylation on the coordinated nitrogens of tetraaza macrocyclic Ni(II) complexes increases steric repulsions, lengthens the Ni-N bond distances, and makes the oxidation to Ni(III) more difficult and the reduction to Ni(I) more easier.[8,10,11,25] Table 2 shows that the oxidation and reduction potentials of the Ni(II) and/or Cu(II) complexes of D are more anodic than those for cyclam and N-Me$_2$ cyclam. The oxidation and reduction potentials of $[Ni(D)]^{2+}$ are rather similar to those for the complexes of N-Me$_3$ cyclam and N-Me$_4$ cyclam, respectively. This may indicates that the N-ethyl group causes more severe steric effects than the N-Methyl group.

^{1}H-NMR spectrum of $[Ni(B)]^{2+}$ shows two triplets centered at δ1.05 and 1.25 ppm for the methyls of the N-ethyl groups and two singlets at δ2.21 and 2.22 ppm for the imine methyl groups. The ^{13}C-NMR spectrum also shows two types of carbon peaks with unequal intensities. The carbon peaks of the imine bonds and the methyl groups on the bonds are observed near 187 and 24 ppm, respectively. The peaks of methyls at the N-ethyl groups are observed near 7 ppm. Other peaks are observed at 37-56 ppm. The complexes of B contain two chiral nitrogen centers, and the N-racemic and N-meso isomers are possible. The NMR spectra shows that the sample is a mixture of the two isomers and the structure of each isomer has a symmetric arrangement of the carbon atoms. All attempts to separate each isomer from

N-*meso*   N-*racemic*
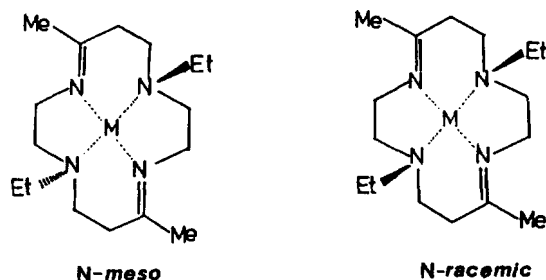
the mixture were unsuccessful. In the attempts, we have only obtained the mixtures with different ratios of the peak intensities of the two isomers in the NMR spectra. The complexes of D contain two chiral carbon and four chiral nitrogen centers, and 20 diastereoisomeric structures[24,28,29] are theoretically possible. In the ^{1}H-NMR spectrum of $[Ni(D)]^{2+}$, one triplet peak for the methyl groups at the N-ethyls and one doublet for the ring methyls are observed at δ1.05 and 1.26 ppm, respectively. Only one doublet at δ1.26 ppm for the two ring-methyls shows that both of the two are in equatorial positions.[17,24] ^{13}C-NMR spectrum of the complex also shows only eight carbon peaks at 6.1, 17.8, 32.2, 45.5, 48.2,

54.3, 56.6, and 57.5 ppm indicating one isomer with the symmetric structure. However, it is difficult to confirm the isomeric structure on the basis of its NMR spectra only.

The above results shows that the ligand field strength and the redox potentials of the 14-membered tetraaza macrocyclic complexes are significantly affected by the ethyl groups at the coordinated nitrogen atoms. The synthesis of B in this study also indicates that the simple nontemplate condensations of mono-N-substituted 1,2-diamines with α,β-unsaturated ketones are useful for the preparation of di-N-substituted 14-membered tetraaza macrocycles.

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Electrochemical Studies of Viologens in Homogeneous Aqueous and Sodium Dodecyl Sulfate Micellar Solutions

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Cyclic voltammetric behavior of symmetric (dimethyl, diheptyl, dioctyl, dibenzyl) and asymmetric (methyloctyl, methyldodecyl, methylbenzyl) viologens was investigated in homogeneous aqueous solution and sodium dodecyl sulfate (SDS) micellar media. In SDS-free 0.1 M NaCl solutions, the reduction potential is less negative as the chain length of alkyl substituent is longer. This is due to the stabilization of the reduced cationic radical and neutral form of viologen by adsorption on electrode surface. The adsorbed species show the "aging-effect". With the exceptions of methyldodecyl viologen and methylbenzyl viologen, the viologens show strong tendency of conproportionation reaction between viologen dications and neutral forms. In cases of methyldodecyl viologen and methylbenzyl viologen, the conproportionation reaction is kinetically disfavored, though it is thermodynamically favorable. SDS micelles dissolve the adsorbed species and the viologens exhibit two reversible redox processes in SDS micellar solutions. The reduction potentials of viologens in SDS micellar solutions depend little on the length of alkyl chain. Benzyl-substituted viologens are more easily reduced than the alkyl substituted viologens, presumably due to electron-withdrawing character of benzyl group.

Introduction

1,1'-Disubstituted-4,4'-bipyridinium salts (viologens) are important class of compounds which show reversible redox character and have been used as herbicides,[1] as electron mediators in experimental schemes aimed at photochemical conversion of solar energy into hydrogen[2-4] and in reduction of organic substrates by variety of means,[5,6] and as materials for electrochromic displays.[7-8] Viologens undergo two successive one-electron reduction as shown below:[9]

$$V^{2+} \underset{}{\overset{E_1}{\rightleftharpoons}} V^{\cdot+} \underset{}{\overset{E_2}{\rightleftharpoons}} V^{\circ} \qquad (1)$$
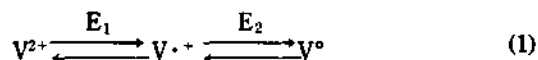
The viologen monocation radical ($V^{\cdot+}$) is deeply blue colored with $\lambda_{max} \simeq 600$ nm, whereas V^{2+} shows its absorption maximum near 260 nm and that of V° is about 400 nm. In solution and at the surface of an electrode, dimerization of $V^{\cdot+}$, disproportionation reaction of $V^{\cdot+}$, and conproportionation reaction between V° and V^{2+} can take place.[9]

Since the reactions of reduced forms of viologen markedly influences the deposition and the color of the reduction products of viologens, understanding of the relative extent of the reactions is important for the use of viologens as active materials of electrochromic display. Also it must be recog-

nized that the reactions can strongly affect the course of reactions in which viologens take part as electron mediators.

Cyclic voltammetry is a major mean for investigation of redox properties and reactivity of the electrogenerated species of viologens.[9] Symmetric dimethyl viologen ($C_1C_1V^{2+}$) and diheptyl viologen ($C_7C_7V^{2+}$) were widely studied. However, a few scattered reports which deal with asymmetric viologens have appeared. Barna and Fish[7d] reported an improved electrochromic display using 1-benzyl-1'-heptyl viologen, instead of $C_7C_7V^{2+}$. Lu et al.[10] showed that the chain length of alkyl substituent of viologens has a large effect on the cyclic voltammetric behavior of the compounds. From a resonance Raman study, they also demonstrated that the extents of dimerization and disproportionation reaction of reduced asymmetric viologens are different from those of symmetric viologens and depend on chain length of the alkyl substituent.[11]

Oxidative quenching reactions of photoexcited tris(2,2'-diimine)ruthenium(II) complexes with viologens in both homogeneous and microheterogeneous media have been studied intensively in relation to solar energy conversion into hydrogen.[2-4] Anionic surfactants such as sodium dodecyl sulfate (SDS),[12-14] polyelectrolytes,[15] and vesicle[16] media were found to give large effects on the electrochemical behavior of viologens, presumably due to hydrophobic and electrostatic