atoms, while that of Mn(pytrien)$^{2+}$ is trigonal prismatic.[1] The UV-vis spectra of M(pytrien)$^{2+}$ (M=Co and Cu) in aqueous solution were measured and their absorption maxima in the visible region are as follows: Co, 471 nm (ε=18 $M^{-1}cm^{-1}$); Cu, 591 nm (ε=94 $M^{-1}cm^{-1}$). It is still uncertain whether M(pytrien)$^{2+}$ (M=Co and Cu) are pseudooctahedral or trigonal prismatic. The crystal structures of M(pytrien)$^{2+}$ (M=Co, Cu, and Zn) are to be determined.

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Oxidative Dehydrogenation of an Octahedral Nickel(II) Complex of Saturated Tetraaza Macrocycle Containing *N*-(2-Hydroxyethyl) Pendant Arms: Synthesis of a Square-Planar Nickel(II) Complex of Unsaturated Macrocycle

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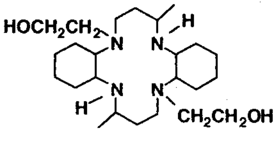
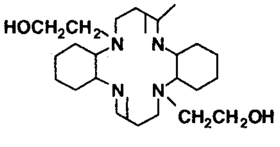
Some transition metal(II) complexes of polyaza macrocyclic ligands containing coordinated secondary amino groups can be chemically oxidized to metal(II) complexes with increased ligand unsaturation.[1~7] It has been suggested that metal(III) state is an intermediate in the oxidative dehydrogenation reaction.[1~6] The reaction is assisted by the central metal ion and is strongly affected by the nature of metal ion, the ligand structure, the oxidizing agent, and the reaction condition such as temperature.[1~7]

The introduction of additional functional pendant arms such as hydroxyl, carboxylato, and amino groups into polyaza macrocyclic compounds often causes a considerable change in chemical properties and structures.[8~20] Recently, we reported the synthesis and crystal structure of the octahedral nickel(II) complex $[Ni(A)]^{2+}$ in which two *N*-(2-hydroxyethyl) pendant arms are coordinated to the central metal ion.[8] The cyclic voltammetric study indicated that the octahedral complex $[Ni(A)]^{2+}$ is more easily oxidized to Ni(III) state than the square-planar complex $[Ni(C)]^{2+}$ containing two *N*-ethyl pendant arms.[8,21] In this work, we attempted the synthesis of the diimine complex $[Ni(B)]^{2+}$ from the oxidative dehydrogenation reaction (eq. (1)) of $[Ni(A)]^{2+}$ to further investigate the effects of the hydroxyethyl groups on the reaction and on the properties of the diimine complex. Interestingly, it was found that the hydroxyl groups of $[Ni(B)]^{2+}$ are not directly involved in coordination. This note reports the synthesis and properties of the new diimine complex.

$$[Ni(A)]^{2+} \xrightarrow{HNO_3} [Ni(B)]^{2+} \qquad (1)$$



A



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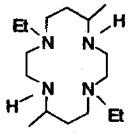

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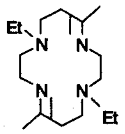

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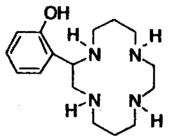


E

Experimental

Measurements. Infrared spectra were recorded as ether KBr pellets or Nujol mulls on a Shimadzu IR-440 spectrophotometer, conductance measurements with a Metrohm Herisau Conductometer E518, visible absorption spectra with a Shimadzu UV-440 spectrophotometer, and NMR spectra with a Bruker WP 300 FT NMR spectrometer. Magnetic susceptibilities were measured with a Johnson Matthey MK-1 magnetic susceptibility balance. Molar susceptibilities were corrected for diamagnetism of the ligand and the anions by use of Pascal's constants. Elemental analyses were performed at the Korea Basic Science Institute, Seoul, Korea. Cyclic voltammograms were recorded using a Yanaco p-1000 voltammetric analyzer equipped with a FG-121B function generator and a Watanabe X-Y recorder.

Materials. All chemicals used in syntheses were of reagent grade and were used without further purification. The complex $[Ni(A)](ClO_4)_2$ was prepared as described previously.[8]

Caution!. Perchlorate salts of metal complexes with organic ligands are explosive and should be handled with great caution.

Synthesis. $[Ni(B)](ClO_4)_2$. To an acetonitrile-water (1 : 1) suspension (20 mL) of $[Ni(A)](ClO_4)_2$ (1.0 g) was added an excess amount of *conc.* HNO_3 (*ca.* 5 mL) with stirring. The mixture was heated on a steam bath (*ca.* 70 ℃) for 1 hr. After the resulting orange solution was cooled to room

Table 1. Electronic Spectra and Oxidation Potentials of Nickel (II) Complexes at 20 ℃

Complex	λmax, nm (ε, $M^{-1}cm^{-1}$)			Oxidation potential,[c] Volt *vs.* SCE
	$MeNO_2$	H_2O	MeCN	
$[Ni(A)](ClO_4)_2$[a]		516(7.2)	520(6.8)	+1.14
		323(18)	335(16)	
$[Ni(B)](ClO_4)_2$	456(76)	450(72)	454(73)	+1.39
$[Ni(C)](ClO_4)_2$[b]	473(102)	469(101)		+1.27
$[Ni(D)](ClO_4)_2$[b]	456(144)		459(143)	+1.34

[a] Ref. 8. [b] Ref. 21. [c] Measured in 0.1 M $(n\text{-}Bu)_4NClO_4$ acetonitrile solution.

temperature, an excess amount of $NaClO_4$ was added and then a yellow solid was precipitated. The product was filtered off, washed with methanol, and recrystallized from hot water. Yield: ~80%. Anal. Calcd for $NiC_{24}H_{44}N_4Cl_2O_{10}$: C, 42.50; H, 6.54; N, 8.26%. Found: C, 42.24; H, 6.85; N, 8.23%. IR spectrum: 3445 (νO-H) and 1645 (νC=N). $\mu_{eff}=0.21$ BM.

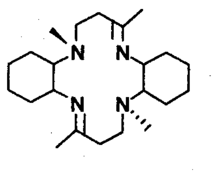
$[Ni(B)](PF_6)_2$. To a hot saturated aqueous solution of the above complex was added excess NH_4PF_6 dissolved in water. The yellow solids formed were filtered off, washed with a cold water-ethanol (1 : 1) mixture, and dried in air. Anal. Calcd for $NiC_{24}H_{44}N_4O_2P_2F_{12}$: C, 37.47; H, 5.77; N, 7.28 %. Found: C, 37.45; H, 6.15; N, 7.22%. ^1H NMR (CD_3NO_2): δ 2.38 (s, Me) and 2.45 ppm (s, Me). ^{13}C NMR (CD_3NO_2): δ 22.0, 22.1, 22.3, 23.0, 23.2, 23.3, 23.5, 23.6, 30.0, 30.2, 35.3, 40.4, 42.2, 49.0, 53.9, 56.0, 65.0, 65.7, 66.1, 67.2, 67.4, 83.3, 185.6 (C=N), and 191.0 (C=N) ppm.

Results and Discussion

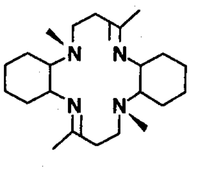
The reaction of the octahedral complex $[Ni(A)]^{2+}$ with conc. HNO_3 in an acetronitrile-water (1 : 1) solution at *ca.* 70 ℃, followed by addition of an excess amount of $NaClO_4$, produced the diimine complex $[Ni(B)](ClO_4)_2$ in high yield (>70%). Keeping the reaction temperature above 50 ℃ is crucial as we found that, at room temperature, any color change of the mixture was not observed even after 20 hr. All efforts to synthesize $[Ni(D)]^{2+}$ from the reaction of $[Ni(C)]^{2+}$ with HNO_3 were unsuccessful; in the attempts only the starting material $[Ni(C)](ClO_4)_2$ was isolated even after prolonged heating (>1 day) at an elevated temperature (~70 ℃) of the reaction mixture. It is expected that the reaction begins with the oxidation of nickel(II) to nickel(III) state which then rapidly oxidizes the ligand through an intramolecular electron transfer and/or disproportionation.[3~7,22,23] However, in this work the nickel(III) state or any other intermediate was not isolated as a solid. Table 1 shows that the oxidation potential (+1.14 V *vs.* SCE) of the nickel(II) complex of A is more cathodic than that of C (+1.27 V *vs.* SCE).[8,21] The oxidation potentials of other related macrocyclic nickel(II) complexes, which undergo oxidative dehydrogenation in conc. HNO_3 solution,[2,6,7] are also lower than that of $[Ni(C)]^{2+}$.[24] Therefore, one of the reasons for the easy metal-ion promoted oxidative dehydrogenation reaction of $[Ni(A)]^{2+}$, in contrast to $[Ni(C)]^{2+}$, can be attributed to the fact that the oxidation to Ni(III) state is easier for the former than for the latter.

The yellow complex $[Ni(B)](ClO_4)_2$ is stable in the solid state and are soluble in polar solvents such as water, nitromethane and acetonitrile. The molar conductance values for the complex measured in water (190 $\Omega^{-1}mol^{-1}cm^2$) and acetonitrile (285 $\Omega^{-1}mol^{-1}cm^2$) show that the complex is a 1 : 2 electrolyte. The observed magnetic moment of $[Ni(B)](ClO_4)_2$ is 0.21 BM at room temperature, which is consistent with a d^8 electronic configuration in a square-planar geometry. The infrared spectrum of the complex shows νC=N of the imine bonds at 1645 cm^{-1}. Any band around 3200 cm^{-1} attributible to secondary amino groups was not observed. Somewhat interestingly, νO-H of the pendant hydroxyl groups was observed at 3445 cm^{-1}, which is *ca.* 85 cm^{-1} higher than that for the complex of A.[8] Visible spectrum (Table 1) of the complex in each solvent shows a single d-d transition band at *ca.* 450 nm. The spectrum is quite different from that of the octahedral $[Ni(A)]^{2+}$ but is rather similar to that of square-planar nickel(II) complexes of di-N-alkylated 14-membered tetraaza macrocycles such as C and D.[21] The oxidation potential (+1.39 V *vs.* SCE) of $[Ni(B)]^{2+}$ measured by cyclic voltammetry is also similar to the value for the square-planar complex $[Ni(D)]^{2+}$ (Table 1). The infrared and electronic spectra, the oxidation potential, and the value of magnetic moment of $[Ni(B)](ClO_4)_2$ clearly support that the complex has a square-planar geometry without coordination of the hydroxyl groups in the solid state and in the solutions. This result is in sharp contrast to that of $[Ni(A)]^{2+}$ in which the hydroxyl groups are coordinated to the metal ion.[8] It has been generally observed that the increase in the degree of unsaturation in a 14-membered polyaza macrocyclic nickel (II) complex shortens the in-plane Ni-N distances and strengthens the Ni-N interactions.[21,25] Therefore, the uncoordination of the hydroxyl groups in the diimine complex can be attributed to the weaker axial Ni-O (hydroxyl group) interaction caused by the stronger in-plane Ni-N interaction. Another factor affecting the weak Ni-O interaction of $[Ni(B)]^{2+}$, compared to $[Ni(A)]^{2+}$, may be the more rigid structure of the ligand. It has been reported that the phenol group of $[Ni(E)]^{2+}$ is easily deprotonated in neutral or basic solutions and the resulting phenolate group is axially coordinated.[16] However, even in >1.0 M NaOH aqueous solutions of $[Ni(B)]^{2+}$, the formation of any complex with a deprotonated form of B was not observed; the addition of excess $NaClO_4$ to the solutions produced only $[Ni(B)](ClO_4)_2$.

The complex of B contains two chiral nitrogen centers. Therefore, both the centrosymmetric N-meso and the assymmetric N-racemic isomers are theoretically possible. ^1H NMR spectrum of $[Ni(B)](PF_6)_2$ measured in CD_3NO_2 shows two singlets centered at δ 2.38 and 2.45 ppm for the methyl groups attached to the imine bonds and the ^{13}C NMR spectrum shows 24 carbon peaks (see Experimental section), indicating an assymmetric arrangement of the carbon atoms.



N-*meso*



N-*racemic*

It is likely that the diimine complex prepared in this work has a N-racemic conformation.

In conclusion, the oxidative dehydrogenation of $[Ni(A)]^{2+}$ in the presence of nitric acid produces the N-racemic isomer of $[Ni(B)]^{2+}$. This work shows that the axial coordination of the hydroxyl group in the complex $[Ni(A)]^{2+}$ makes the oxidation to the nickel(III) state easier and then accelerates the reaction. Most interestingly, the hydroxyl groups of the unsaturated complex $[Ni(B)]^{2+}$ are not involved in coordination.

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Melt Polymerization of Hexachlorocyclotriphosphazene in the Presence of Aluminum Trichloride and Diethyltin(IV) Dichloride

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It is well known that the thermal polymerization of hexachlorocyclotriphosphazene is very sensitive to impurities of reactant and reaction conditions,[1~3] and thus the yield of the linear polyphosphazene and gel formation by cross-linking are unpredictable. Thermal polymerization of hexachlorocyclotriphosphazene is usually stopped when the melted reactant ceases to flow, since cross-linking reaction is accelerated beyond this point.[2] In fact, when polymerization of purified hexachlorocyclotriphosphazene at 250 °C was stopped after 11 h where the reactant ceased to flow, approximately 40% yield of the linear polymer was obtained without gel formation, but extension of the reaction time to 15 h lowered the yield of the linear polymer to 11% with cross-linked gel formation up to more than half of the reactant.[4] To overcome this drawback, various kinds of Lewis acid catalysts were reported to improve both production yield and reaction time, but most catalytic polymerizations result in lower molecular weight polymers.[5~12]

In our previous report, organotin(IV) chlorides were shown to act as inhibitor delaying remarkably the rate of polymerization with prominent improvements in both the molecular weight and the yield of the linear polymer in contrast to most Lewis acids.[4] On the other hand, using excess amounts (>2 wt.%) of aluminum trichloride as catalyst, low molecular weight poly(dichlorophosphazene) ($\bar{M}_w = 10^4$-10^5) was easily prepared in almost quantitative yield.[13]

Herein we report high conversion of hexachlorocyclotriphosphazene to high molecular weight polymers in the presence of mixed catalysts of aluminum trichloride and diethyltin(IV) dichloride.

Experimental

Materials. Hexachlorocyclotriphosphazene, $(NPCl_2)_3$ pur-