Synthesis and Characterization of New Polyaza Non-macrocyclic and Macrocyclic Nickel(II) Complexes Containing One 1,3-Diazacyclohexane Ring

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A new nickel(II) complex $[NiL^1]^{2+}$ (L^1 = 1-(2-aminoethyl)-3-(N-{2-aminoethyl}aminomethyl-1,3-diazacyclo-hexane) containing one 1,3-diazacyclohexane ring has been prepared selectively by the metal-template condensation of formaldehyde with N-(2-aminoethyl)-1,3-propanediamine and ethylenediamine at room temperature. The complex reacts with nitroethane and formaldehyde to yield the pentaaza macrocyclic complex $[NiL^2]^{2+}$ (L^2 = 8-methyl-8-nitro-1,3,6,10,13-pentaazabicyclo[13.3.1]heptadecane) bearing one C-NO_2 pendant arm. The reduction of $[NiL^2]^{2+}$ by using Zn/HCl produces $[NiL^3(H_2O)]^{2+}$ (L^3 = 8-amino-8-methyl-1,3,6,10,13-pentaazabicyclo[13.3.1]heptadecane) bearing one coordinated C-NH_2 pendant arm that is readily protonated in acid solutions. The hexaaza macrocyclic complex $[NiL^4]^{2+}$ (L^4 = 8-phenylmethyl-8-nitro-1,3,6,8,10,13-hexaazabicyclo[13.3.1]heptadecane) bearing one N-$CH_2C_6H_5$ pendant arm has also been prepared by the reaction of $[NiL^1]^{2+}$ with benzylamine and formaldehyde. The nickel(II) complexes of L^1, L^2, and L^4 have square-planar coordination geometry in the solid states and in nitromethane. However, they exist as equilibrium mixtures of the square-planar $[NiL]^{2+}$ ($L = L^1$, L^2, or L^4) and octahedral $[NiL(S)_2]^{2+}$ species in various coordinating solvents (S); the proportion of the octahedral species $[NiL(S)_2]^{2+}$ is strongly influenced by the ligand structure and the nature of the solvent. Synthesis, spectra, and chemical properties of the nickel(II) complexes of L^1-L^4 are described.

Key Words : Macrocyclic complex, Nickel(II) complex, Metal-template condensation, Solution behaviors, Functional pendant arm
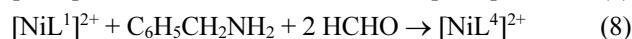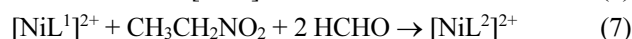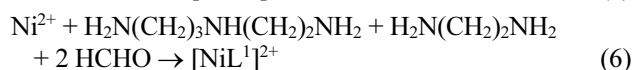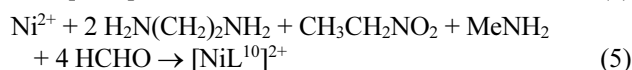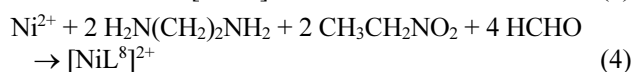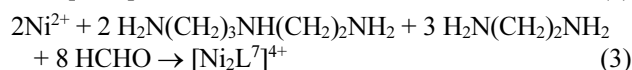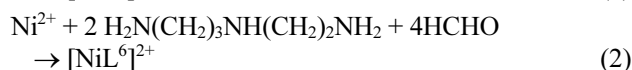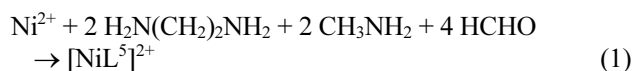
Introduction

There has been considerable interest in the synthesis of polyaza macrocyclic ligands and complexes, since chemical properties of such compounds are closely correlated with their structural characteristics. Metal template condensation reactions involving coordinated amines and formaldehyde are known to be useful for the preparation of various types of polyaza non-macrocyclic and macrocyclic complexes containing N-CH_2-N and/or N-CH_2-C(R)(NO_2)-CH_2-N linkages.[1-12] For instance, the nickel(II) complexes $[NiL^5]^{2+}$, $[NiL^6]^{2+}$, and $[Ni_2L^7]^{4+}$ containing N-CH_2-N linkages have been prepared by the reactions (Eq. (1)-(3)) of formaldehyde and appropriate amines in the presence of the metal ion.[8-10] The complex $[NiL^8]^{2+}$ containing two N-CH_2-C(Me)(NO_2)-CH_2-N linkages can also be prepared by the metal-template condensation (Eq. (4)) of ethylenediamine, nitroethane, and formaldehyde.[11] This type of reaction was extended to the synthesis of $[NiL^{10}]^{2+}$ containing both N-CH_2-N and N-CH_2-C(Me)(NO_2)-CH_2-N linkages (Eq. (5)).[12] It has been revealed that the ligand field strength and chemical properties of $[NiL^{10}]^{2+}$ are quite different from those of $[NiL^5]^{2+}$ and $[NiL^8]^{2+}$. We have been interested in the preparation and chemical properties of various types of polyaza macrocyclic complexes.

In this work, we prepared a new pentaaza non-macrocyclic complex $[NiL^1]^{2+}$ containing one 1,3-diazacyclohexane ring from the reaction of Eq. (6). Two macrocyclic complexes,

L[1]   L[2]: X = O   L[4]   L[5]   L[6]
L[3]: X = H

L[7]

L[8]: X = O   L[10]   L[11]   L[11]
L[9]: X = H
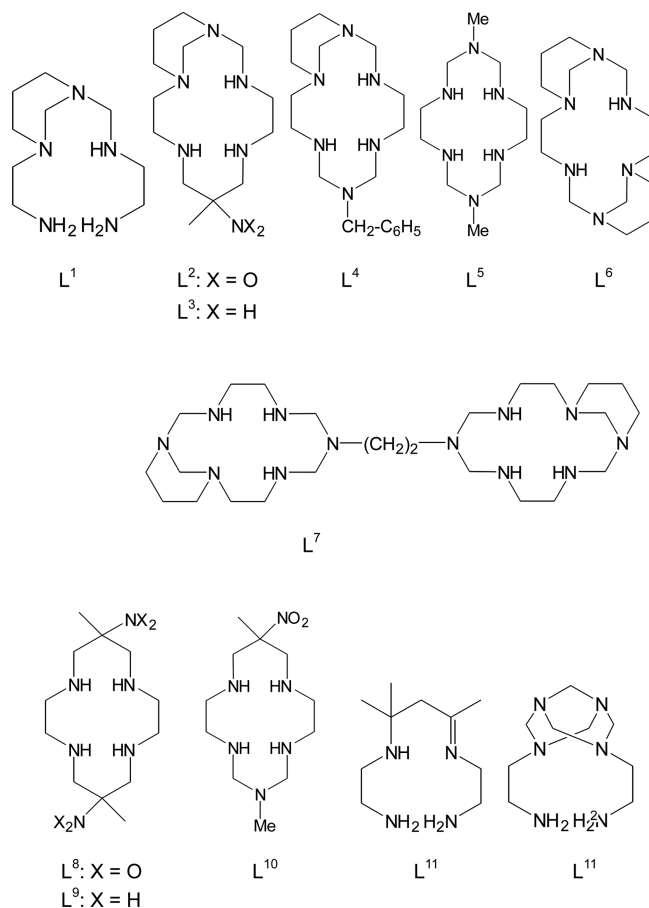
$[NiL^2]^{2+}$ bearing one C-NO$_2$ pendant arm and $[NiL^4]^{2+}$ bearing one N-CH$_2$C$_6$H$_5$ pendant arm, were prepared by the reaction of Eq. (7) or (8). The six-coordinate complex $[NiL^3$-(H$_2$O)]$^{2+}$ bearing one coordinated C-NH$_2$ group was also prepared. This paper reports the synthesis, spectra, and chemical properties of the nickel(II) complexes of L^1-L^4.

$$Ni^{2+} + 2\ H_2N(CH_2)_2NH_2 + 2\ CH_3NH_2 + 4\ HCHO$$
$$\rightarrow [NiL^5]^{2+} \qquad (1)$$

$$Ni^{2+} + 2\ H_2N(CH_2)_3NH(CH_2)_2NH_2 + 4HCHO$$
$$\rightarrow [NiL^6]^{2+} \qquad (2)$$

$$2Ni^{2+} + 2\ H_2N(CH_2)_3NH(CH_2)_2NH_2 + 3\ H_2N(CH_2)_2NH_2$$
$$+ 8\ HCHO \rightarrow [Ni_2L^7]^{4+} \qquad (3)$$

$$Ni^{2+} + 2\ H_2N(CH_2)_2NH_2 + 2\ CH_3CH_2NO_2 + 4\ HCHO$$
$$\rightarrow [NiL^8]^{2+} \qquad (4)$$

$$Ni^{2+} + 2\ H_2N(CH_2)_2NH_2 + CH_3CH_2NO_2 + MeNH_2$$
$$+ 4\ HCHO \rightarrow [NiL^{10}]^{2+} \qquad (5)$$

$$Ni^{2+} + H_2N(CH_2)_3NH(CH_2)_2NH_2 + H_2N(CH_2)_2NH_2$$
$$+ 2\ HCHO \rightarrow [NiL^1]^{2+} \qquad (6)$$

$$[NiL^1]^{2+} + CH_3CH_2NO_2 + 2\ HCHO \rightarrow [NiL^2]^{2+} \qquad (7)$$

$$[NiL^1]^{2+} + C_6H_5CH_2NH_2 + 2\ HCHO \rightarrow [NiL^4]^{2+} \qquad (8)$$

Experimental Section

Measurements. Infrared spectra were recorded with a Genesis II Fourier transform infrared (FTIR) spectrometer, electronic absorption spectra with an Analytik Jena Specord 200 UV/Vis spectrophotometer, nuclear magnetic resonance (NMR) spectra with a Bruker WP 300 FT NMR spectrometer, and conductance measurements with a Z18 Oyster Conductivity/Temperature meter. Elemental analyses were performed at the Research Center for Instrumental Analysis, Daegu University, Gyeongsan, Korea. Fast atom bombardment mass (FAB MS) spectra were performed at the Korea Basic Science Institute, Daegu, Korea. Magnetic moments were calculated from magnetic susceptibility data obtained at 293 K using a Johnson Matthey MK-1 magnetic susceptibility balance. Cyclic voltammograms were recorded using a CH Instrument 1000A. The working, reference, and auxiliary electrodes were glassy carbon, saturated calomel electrode (SCE), and platinum, respectively. The electrochemical measurements were conducted in oxygen free 0.1 M (n-Bu)$_4$NClO$_4$ acetonitrile solutions at 20 °C.

Safety Note: Perchlorate salts of transition metal complexes with organic ligands are often explosive and should be handled with caution.

Materials. The complexes $[NiL^{11}](ClO_4)_2$ (Ref. 13) and $[NiL^{12}](ClO_4)_2$ (Ref. 7) were synthesized as previously described.

Preparation of $[NiL^1](ClO_4)_2$ (L^1 = 1-(2-aminoethyl)-3-(N-{2-aminoethyl}aminomethyl-1,3-diazacyclohexane). To a cold methanol solution (20 mL) of Ni(OAc)$_2$·4H$_2$O (3.7 g, 15 mmol), ethylenediamine (1.6 mL, 23 mmol), and N-(2-aminoethyl)-1,3-propanediamine (2.0 mL, 15 mmol) was added 35% formaldehyde (3.1 mL, 40 mmol). The blue-

purple solution was stirred for *ca.* 24 h at room temperature. After the addition of an excess amount of NaClO$_4$, the resulting purple solution was evaporated in an open beaker at room temperature to precipitate a yellow solid. The product was collected by filtration. The crude product often contains small amount (< 10%) of by-products, such as $[NiL^6](ClO_4)_2$. The product was dissolved in minimum volume of cold acetonitrile and then filtered to remove any solid. The addition of excess NaClO$_4$ dissolved in water (5 mL) to the filtrate produces a yellow solid. It was collected by filtration, washed with cold ethanol, and dried in air. Yield: ~40%. *Anal.* Found: C, 23.64; H, 5.02; N, 15.41. Calc. for C$_9$H$_{23}$N$_5$NiCl$_2$O$_8$: C, 23.56; H, 5.05; N, 15.26%. FAB MS (m/z): 358.2 for $[NiL^1 + ClO_4]^+$; 258.2 for $[NiL^1 -$ H$]^+$. IR (Nujol mull, cm^{-1}): 3313 (ν_{N-H}), 3267 (ν_{N-H}), 3200 (ν_{N-H}, *br*), 3130 (ν_{N-H}) and 1602 (δ (NH$_2$)). ^{13}C NMR (CDCl$_3$) δ 24.9 (N-CH$_2$CH$_2$CH$_2$-N), 38.1, 41.6, 48.1, 50.0, 55.9, 60.4, 70.4 (N-CH_2-N), and 74.1 (N-CH_2-N) ppm

Preparation of $[NiL^2](ClO_4)_2 \cdot H_2O$ (L^2 = 8-methyl-8-nitro-1,3,6,10,13-pentaazabicyclo[13.3.1]heptadecane). To a methanol-water (4:1) solution (20 mL) of $[NiL^1](ClO_4)_2$ (1.0 g, 2.2 mmol) were added nitroethane (0.2 mL, 2.6 mmol), paraformaldehyde (0.2 g, 6.7 mmol), and triethylamine (*ca.* 0.2 mL) at room temperature. The mixture was stirred for *ca.* 15 h at 50-60 °C and then cooled to room temperature. The pH of the solution was adjusted to 4-5 through the addition of 1.0 M HClO$_4$. The resulting orange solution was evaporated in an open beaker at room temperature to precipitate an orange solid. The product was collected by filtration, washed with ethanol, and dried in air. It was recrystallized from hot acetonitrile-water (3:1). Yield: ~30%. *Anal.* Found: C, 27.36; H, 5.14; N, 14.78. Calc. for C$_{13}$H$_{30}$N$_6$NiCl$_2$O$_{11}$: C, 27.11; H, 5.25; N, 14.59%. FAB MS (m/z): 457.3 for $[NiL^2 + ClO_4]^+$; 357.3 for $[NiL^2 - H]^+$. IR (Nujol mull, cm^{-1}): 3251 (ν_{N-H}), 3220 (ν_{N-H}), 3185 (ν_{N-H}), and 1546 (ν_{N-O}, NO$_2$). ^{13}C NMR (CDCl$_3$) δ 23.1 (Me), 24.6 (N-CH$_2$CH$_2$CH$_2$-N), 48.2, 49.4, 52.9 (*d*), 54.9, 55.0, 56.9, 59.0, 71.2 (N-CH_2-N), 74.9 (N-CH_2-N), and 88.6(C(Me)(NO$_2$)) ppm.

Preparation of $[Ni(HL^3)](ClO_4)_3 \cdot H_2O$ (L^3 = 8-amino-8-methyl-1,3,6,10,13-pentaazabicyclo[13.3.1]heptadecane). To a methanol solution (20 mL) of $[NiL^2](ClO_4)_2$ (1.0 g, 1.8 mmol) was added zinc dust (2.0 g, 30 mmol). After the addition of concentrated HCl (8.0 mL, 90 mmol), the mixture was stirred at room temperature until all the zinc dust was dissolved. The resulting orange solution was diluted with methanol (30 mL). The pH of the solution was adjusted to > 10 through the addition of 2.0 M NaOH aqueous solution. The white solid ZnO formed was removed by filtration, and then the purple filtrate was evaporated to dryness. After dissolving the residue in methanol (20 mL), concentrated HClO$_4$ (5.0 mL) was added to the solution. The resulting orange solution was evaporated in an open beaker at room temperature to precipitate an orange solid. The product was collected by filtration, washed with ethanol, and dried in air. It was recrystallized from 1.0 M HClO$_4$ methanol solution. Yield: ~40%. *Anal.* Found: C, 24.48; H, 5.04; N, 13.08.

Calc. for $C_{13}H_{33}N_6NiCl_3O_{13}$: C, 24.15; H, 5.15; N, 13.00%. IR (Nujol mull, cm^{-1}): 3310 (ν_{N-H}), 3249 (ν_{N-H}), 3223 (ν_{N-H}), 3090 (ν_{N-H}, *br*), and 1602 (δ (NH$_2$)).

Preparation of [NiL^3(H$_2$O)](ClO$_4$)$_2$·H$_2$O. To a methanol solution (20 mL) of [Ni(HL^3)](ClO$_4$)$_3$ (0.5 g) were added 1.0 M NaOH aqueous solution (50 mL) and NaClO$_4$ (1.0 g). The solution was evaporated at room temperature to precipitate a purple solid. The product was collected by filtration, washed by ethanol, and dried in air. Yield: ~70%. *Anal.* Found: C, 27.90; H, 6.01; N, 15.02. Calc. for $C_{13}H_{34}N_6NiCl_2O_{10}$: C, 27.68; H, 6.08; N, 14.90%. FAB MS (*m/z*): 427.2 for [NiL^3 + ClO$_4$]$^+$; 327.2 for [NiL^3 – H]$^+$. IR (Nujol mull, cm^{-1}): 3425 (ν_{O-H}, H$_2$O), 3330 (ν_{N-H}), 3323 (ν_{N-H}), 3288 (ν_{N-H}), 3190 (ν_{N-H}, *br*), and 1605 (δ (NH$_2$)). Magnetic moment (μ_{eff}): 2.90 μ_B at room temperature.

Preparation of [NiL^4(ClO$_4$)$_2$·H$_2$O (L^4 = 8-phenylmethyl-8-nitro-1,3,6,8,10,13-hexaazabicyclo[13.3.1]heptadecane). To a methanol-water (4:1) solution (20 mL) of [NiL^1](ClO$_4$)$_2$ (1.0 g, 2.2 mmol) were added 99% benzylamine (0.4 mL, 4.0 mmol), and paraformaldehyde (0.2 g, 6.7 mmol) at room temperature. The mixture was refluxed for *ca.* 20 h and then cooled to room temperature. After the addition of concentrated HClO$_4$ (1.0 mL) and water (10 mL), the resulting orange solution was evaporated in an open beaker at room temperature to precipitate an orange solid. The product was collected by filtration, washed with ethanol, and dried in air. It was recrystallized from hot acetonitrile-water (3:1). Yield: ~40%. *Anal.* Found: C, 35.43; H, 5.33; N, 14.25. Calc. for $C_{18}H_{34}N_6NiCl_2O_9$: C, 35.55; H, 5.64; N, 13.82%. FAB mass (*m/z*): 489.2 for [NiL^4 + ClO$_4$]$^+$; 390.3 for [NiL^4 – H]$^+$. IR (Nujol mull, cm^{-1}): 3218 (ν_{N-H}), 3200 (ν_{N-H}, *br*), 3028 (ν_{C-H}, phenyl), and 1605-1550 ($\nu_{C=C}$, phenyl). ^{13}C NMR (CD$_3$NO$_2$) δ 26.4 (N-CH$_2$CH$_2$CH$_2$-N), 47.0, 50.0, 51.3, 57.3 (*d*), 58.6, 61.2, 70.6 (N-CH$_2$-N), 70.8 (N-CH$_2$-N), 73.3 (N-CH$_2$-N), 76.9 (N-CH$_2$-N), 130.9 (phenyl), 131.3 (phenyl), 131.7 (phenyl), and 140.0 (phenyl) ppm.

Results and Discussion

Synthesis. The reaction of nickel(II) ion, 1,4,8-triazaoctane, ethylenediamine, and formaldehyde is strongly influenced by the molar ratio of the reactants and the reaction temperature. Therefore, the reaction conditions should be carefully controlled for the preparation of [NiL^1]$^{2+}$ as the major product. Our initial attempts to prepare [NiL^1]$^{2+}$ by refluxing a methanol solution of the reactants in a 1:1:2:3 molar ratio were unsuccessful; the major product was found to be [NiL^6]$^{2+}$. However, [NiL^1]$^{2+}$ can be prepared by the reaction at room temperature, though the crude product also contains considerable amount of [NiL^6]$^{2+}$ and/or [Ni$_2$L^7]$^{4+}$. The proportion of the by-products in the crude product could be reduced to less than 10% by reacting 1:1:1.5:2.7 molar mixture of the reactants at room temperature (*see* Experimental Section).

The non-macrocyclic complex [NiL^1](ClO$_4$)$_2$ reacts with nitroethane and formaldehyde in the presence of triethylamine to form [NiL^2](ClO$_4$)$_2$ (Eq. (7)). The reaction (Eq. (8))

of [NiL^1](ClO$_4$)$_2$ with benzyl amine and formaldehyde produces [NiL^4](ClO$_4$)$_2$. The routes to give the nickel(II) complexes of L^1, L^2, and L^4 may be similar to those reported for the complexes of L^5 – L^8.[8-12] The octahedral complex [NiL^3(H$_2$O)](ClO$_4$)$_2$, in which the pendant *C*-NH$_2$ group as well as one water molecule is involved in coordination, could be prepared by the reduction of the *C*-NO$_2$ group of [NiL^2](ClO$_4$)$_2$. The square-planar complex [Ni(HL^3)](ClO$_4$)$_3$ was also isolated by the addition of HClO$_4$ to an aqueous solution of [NiL^3(H$_2$O)](ClO$_4$)$_2$.

Spectra and Properties of [NiL^1](ClO$_4$)$_2$, [NiL^2](ClO$_4$)$_2$, and [NiL^4](ClO$_4$)$_2$·H$_2$O. The FAB MS spectrum of [NiL^1](ClO$_4$)$_2$ shows two groups of peaks at *m/z* 358.2 and 258.2 corresponding to the fragments [NiL^1 + ClO$_4$]$^+$ and [NiL^1 – H]$^+$, respectively. The spectra (*see* Experimental section) of [NiL^2](ClO$_4$)$_2$ and [NiL^4](ClO$_4$)$_2$·H$_2$O as well as the elemental analyses are also corresponding to the formula of the complexes. The infrared spectrum of [NiL^1](ClO$_4$)$_2$ shows several peaks corresponding to ν_{N-H} of the coordinated secondary and primary amino groups at 3313-3130 cm^{-1}. A sharp peak due to the δ (NH$_2$) of the primary amino groups is observed at 1602 cm^{-1}. The spectrum of [NiL^2](ClO$_4$)$_2$ shows ν_{N-H} of the coordinated secondary amino groups at 3185, 3220, and 3251 cm^{-1}. A peak corresponding to ν_{N-O} of the nitro group is also observed at 1546 cm^{-1}. In the spectrum of [NiL^4](ClO$_4$)$_2$·H$_2$O, peaks corresponding to $\nu_{C=C}$ of the phenyl group are observed at 1605-1550 cm^{-1}. The nickel(II) complexes were found to be diamagnetic substances in the solid states. The ^{13}C NMR spectrum of [NiL^1](ClO$_4$)$_2$ measured in CD$_3$NO$_2$, shows two carbon peaks of the N-CH$_2$-N linkages at 70.4 and 74.1 ppm. Seven peaks corresponding to the N-CH$_2$CH$_2$-N and N-CH$_2$CH$_2$CH$_2$-N linkages are observed at 24.9-60.4 ppm. The ^{13}C NMR spectrum (*see* Experimental section) of [NiL^2](ClO$_4$)$_2$ or [NiL^4](ClO$_4$)$_2$·H$_2$O is also consistent with the ligand structure of each complex. The molar conductance values of the nickel(II) complexes measured in acetonitrile (230-250 Ω^{-1}mol^{-1}cm^2) indicate that they are 1:2 electrolytes.

The electronic absorption spectra (Table 1) of [NiL^1](ClO$_4$)$_2$, [NiL^2](ClO$_4$)$_2$, and [NiL^4](ClO$_4$)$_2$·H$_2$O measured in nitromethane show a *d-d* transition band at 460 (ε = 55 M^{-1}cm^{-1}), 465 (ε = 72 M^{-1}cm^{-1}), and 460 nm (ε = 78 M^{-1}cm^{-1}), respectively. The wavelength for each complex is quite similar to that measured in Nujol mull. The spectra are comparable with those of [NiL^5](ClO$_4$)$_2$, [NiL^{10}](ClO$_4$)$_2$, [NiL^{11}](ClO$_4$)$_2$, [NiL^{12}](ClO$_4$)$_2$, and various other related square-planar nickel(II) complexes,[7-12] indicating that they have square-planar coordination geometry in the solid state and in nitromethane. It should be mentioned that the wavelength for [NiL^1](ClO$_4$)$_2$ in each solvent is 17-25 nm shorter than those for [NiL^{11}](ClO$_4$)$_2$ and [NiL^{12}](ClO$_4$)$_2$ (Table 1). This implicates that L^1 exerts much weaker ligand field than L^{11} and L^{12} because of its less rigid structure.

Cyclic voltammograms of [NiL^1](ClO$_4$)$_2$, [NiL^2](ClO$_4$)$_2$, and [NiL^4](ClO$_4$)$_2$·H$_2$O obtained in 0.1 M (*n*-Bu)$_4$NClO$_4$ acetonitrile solution showed one anodic and cathodic peak corresponding to a Ni(II)/Ni(III) process. Their oxidation

Table 1. Electronic Absorption Spectra of the Nickel(II) complexes[a]

| Complex	λ_{max}, nm (ε, M^{-1}cm^{-1})[a]					
$[NiL^1](ClO_4)_2$	460(55)	356(7.9)[b]	343(8.0)[c]	366(8.1)[d]	360(8.9)[e]	460[f]
		558(3.8)[b]	521(4.3)[c]	561(6.2)[d]	570(4.5)[e]	
		808(3.2)[b]	810(3.8)[c]	814(4.1)[d]	810(2.8)[e]	
$[NiL^2](ClO_4)_2$	465(72)	475(14)[c]	464(15)[d]	468(29)[e]	470[f]	
$[NiL^3(H_2O)](ClO_4)_2$		333(8.7)[b]	316(11)[c]	333(12)[d]	340(3.4)[e]	330[f]
		505(5.5)[b]	495(7.5)[c]	510(9.1)[d]	515(6.2)[e]	505[f]
		708(3.0)[b]	720(3.9)[c]	719(4.7)[d]	711(3.0)[e]	700[f]
$[Ni(HL^3)](ClO_4)_3$		334(8.3)[b]	319(14)[c]	334(4.1)[d]	345(8.6)[e]	460[f]
		504(4.9)[b]	473(13)[c]	507(11)[d]	520(5.7)[e]	
		710(2.6)[b]	715(3.4)[c]	720(6.1)[d]	710(2.8)[e]	700[f]
$[NiL^4](ClO_4)_2$	460(78)	465(31)[c]	464(48)[d]	466(64)[e]	465[f]	
$[NiL^5](ClO_4)_2$[g]	449(56)					
$[NiL^6](ClO_4)_2$[h]	465(95)					
$[Ni_2L^7](ClO_4)_4$[i]	455(150)	452(107)[b]				
$[NiL^9](ClO_4)_2$[j]	457(59)					
$[NiL^{10}](ClO_4)_2$[k]	455(69)					
$[NiL^{11}](ClO_4)_2$	443(68)	440(67)[b]	443(53)[c]	440(69)[d]	437(67)[e]	
$[NiL^{12}](ClO_4)_2$	440(77)	437(71)[b]	445(70)[c]	442(70)[d]	440(75)[e]	

[a]Measured in nitromethane at 20 °C unless otherwise specified. [b]In water. [c]In acetonitrile. [d]In DMF. [e]In DMSO. [f]In Nujol mull. [g]Ref. 8. [h]Ref. 9. [i]Ref. 10. [j]Ref. 11. [k]Ref. 12.

potentials (Table 2) vary with the ligand structure, showing the order $[NiL^4]^{2+}$ (+1.16 V) < $[NiL^1]^{2+}$ (+1.24 V) $[NiL^2]^{2+}$ (+1.26 V). It is seen that the addition of the -CH₂C(Me)(NO₂)CH₂- bridge on $[NiL^1]^{2+}$ to give $[NiL^2]^{2+}$ does not change significantly the electron density on the metal ion. On the other hand, the addition of the -CH₂N(CH₂C₆H₅)CH₂- bridge on $[NiL^1]^{2+}$ to give $[NiL^4]^{2+}$ increases the electron density on the metal center and makes the oxidation easier. Table 2 also shows that the potentials of $[NiL^1]^{2+}$, $[NiL^2]^{2+}$, and $[NiL^4]^{2+}$ are lower than that of $[NiL^6]^{2+}$ (+1.34 V) containing two 1,3-diaminocyclohexane rings. This corresponds to the generally observed trend that the stepwise alkylation on the coordinated secondary amino groups of a macrocyclic complex reduces the electron density on the metal ion of the complex and makes the oxidation more difficult process.[10,14]

The non-macrocyclic complex $[NiL^1](ClO_4)_2$ is readily decomposed in 0.1 M HClO₄ aqueous solution; the reaction proceeds to completion within 5 min. On the other hand, both $[NiL^2](ClO_4)_2$ and $[NiL^4](ClO_4)_2 \cdot H_2O$ are quite inert against decomposition even in concentrated HClO₄ solution, in analogy with various other 14-membered polyaza macrocyclic nickel(II) complexes with a 5-6-5-6 chelate ring sequence; [8,9] visible absorption spectra of the complexes (1.0 × 10⁻³ M) in 0.1 M HClO₄ aqueous solution showed that only less than 5% of them are decomposed in 20 h at room temperature.

Coordination of Solvent Molecule. Table 1 shows that the molar absorption coefficients for $[NiL^2](ClO_4)_2$ and $[NiL^4](ClO_4)_2 \cdot H_2O$ measured in coordinating solvents, such as water, acetonitrile, dimethylformaldehyde (DMF), and dimethylsulfoxide (DMSO), at *ca.* 465 nm are considerably smaller than those measured in nitromethane, a non-coordi-nating solvent. This indicates that the complexes exist as equilibrium mixtures (Eq. (9)) of the octahedral $[NiL(S)_2]^{2+}$ (L = L² or L⁴) and square-planar $[NiL]^{2+}$ species in the solvent molecules (S).[8,9,12-18] Percentage of the octahedral species in each solvent was determined from the molar absorption coefficient of the complex at *ca.* 465 nm. (Percentage of octahedral species = $100\{(\varepsilon_N - \varepsilon_S)/\varepsilon_N\}$ where ε_N and ε_S are the molar absorption coefficients measured in nitromethane and in the coordinating solvent, respectively; the absorption coefficients of the complexes measured in nitromethane, a non-coordinating solvent, were assumed to be identical with those of the square-planar species in the coordinating solvents) [8,9,12-18]

$$[NiL]^{2+} + 2S = [NiL(S)_2]^{2+} \qquad (9)$$
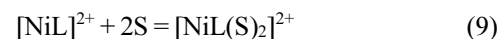
The percentages (Table 2) of the octahedral species for $[NiL^2]^{2+}$ and $[NiL^4]^{2+}$ were found to be CH₃CN (80.6%) ≥ DMF (79.2) > DMSO (59.7%) and CH₃CN (60.3 %) > DMF (38.5%) > DMSO (17.9%), respectively, showing that the equilibrium is strongly influenced by the nature of the solvents. The stronger coordinating ability of CH₃CN, compared

Table 2. Oxidation Potentials ((Volts *vs.* SCE) for the Nickel(II) Complexes[a]

Complex	$[NiL]^{2+} \rightarrow [NiL]^{3+}$
$[NiL^1](ClO_4)_2$	+1.24
$[NiL^2](ClO_4)_2$	+1.26
$[NiL^3](ClO_4)_2$	+1.01
$[NiL^4](ClO_4)_2$	+1.15
$[NiL^6](ClO_4)_2$[b]	+1.34

[a]Measured in 0.1 M (*n*-Bu)₄NClO₄ acetonitrile solution at 20 °C. [b]Ref. 10.
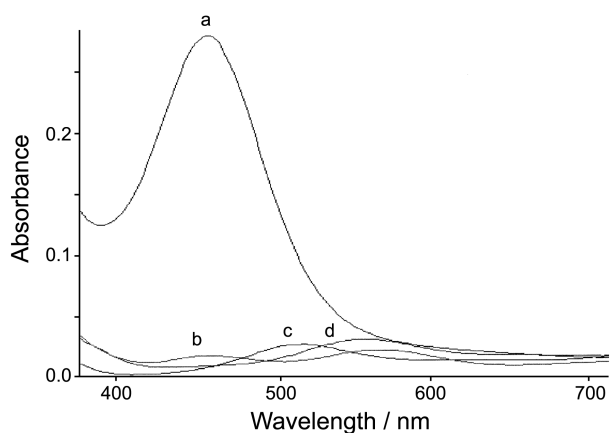
Figure 1. Electronic absorption spectra of $[NiL^1](ClO_4)_2$ (5.0 × 10^{-3} M) measured in nitromethane (a), DMSO (b), acetonitrile (c), and DMF (d).

Table 3. Percentage (%) of Octahedral Species of the Nickel(II) Complexes in Various Solvents at 20 °C

Complex	H_2O	MeCN	DMF	DMSO
$[NiL^1](ClO_4)_2$	95	98	98	95
$[NiL^2](ClO_4)_2$		81	79	60
$[NiL^4](ClO_4)_2$		60	39	18
$[NiL^{11}](ClO_4)_2$	< 1.0	22	< 1.0	< 1.0
$[NiL^{12}](ClO_4)_2$	7.8	9.1	9.1	2.6

to that of DMF or DMSO, may be due to its rod-like geometry and weak self-association ability.[16,17] The relatively weak coordination ability of DMSO is attributed to the severe steric hindrance of the methyl groups.[17,18] In each solvent, the percentage of the octahedral species for $[NiL^2]^{2+}$ is distinctly higher than that for $[NiL^4]^{2+}$. The coordination of the solvent molecules must be strongly influenced by steric repulsion between the square-planar and the axially oriented solvent molecules. The present result shows that the steric effect of *N*-CH$_2$C$_6$H$_5$ group in $[NiL^4]^{2+}$ is more severe than that of the *C*-Me and *C*-NO$_2$ groups in $[NiL^4]^{2+}$ and makes the formation of the octahedral species more difficult.

The electronic absorption spectra of $[NiL^1](ClO_4)_2$ measured in water, acetonitrile, DMF, and DMSO show three bands at 340-370 nm (ε = 7.9-8.9 M^{-1}cm^{-1}), 520-570 nm (ε = 3.8-6.2 M^{-1}cm^{-1}), and 808-814 nm (ε = 2.8-4.1 M^{-1}cm^{-1}). The wavelength and molar absorption coefficients are quite different from those measured in nitromethane and/or Nujol mull. The spectra are similar to those for various other octahedral nickel(II) complexes.[19,20] In the coordinating solvents, the absorption at 460 nm is nearly negligible (Fig. 1). It is obvious that the majority part (at least 95%) of the complex exists as the octahedral species $[NiL^1(S)_2]^{2+}$ in the coordinating solvents (Table 2). This trend is quite different from those for $[NiL^{11}]^{2+}$ and $[NiL^{12}]^{2+}$. The percentage of the octahedral species for $[NiL^{11}]^{2+}$ is less than 5% in water, DMF, and DMSO and is *ca.* 20% in acetonitrile. In the case of $[NiL^{12}]^{2+}$, the percentage was found to be less than 10% in the coordinating solvents. The higher concentration of the octahedral species for $[NiL^1]^{2+}$, compared to that for $[NiL^{11}]^{2+}$ or $[NiL^{12}]^{2+}$, may be attributed to the relatively weak in-plane Ni-N interactions and/or the weak steric repulsion between the ligand and the axially oriented solvent molecule.

Spectra and Properties of $[NiL^3(H_2O)](ClO_4)_2$ and $[Ni(HL^3)](ClO_4)_3$. The FAB mass spectrum of $[NiL^3(H_2O)]$-$(ClO_4)_2$ shows two groups of peaks at *m/z* 427.2 and 327.2 corresponding to the fragments $[NiL^3 + ClO_4]^+$ and $[NiL^3 - H]^+$, respectively. The infrared spectra of $[NiL^3(H_2O)](ClO_4)_2$ and $[Ni(HL^3)](ClO_4)_3$ show ν_{N-H} of the coordinated secondary

and primary amino groups at 3350-3100 cm^{-1}. A sharp peak due to δ (NH$_2$) of the primary amino group is also observed at *ca.* 1605 cm^{-1}. The magnetic moment of $[NiL^3(H_2O)]$-$(ClO_4)_2$ in the solid state is 2.90 μ_B at room temperature, indicating the d^8 electronic configuration of octahedral coordination geometry. On the other hand, $[Ni(HL^3)](ClO_4)_3$ was found to be a diamagnetic substance, supporting the fact that the complex has square-planar coordination geometry in the solid state. The molar conductance value (195 Ω^{-1}mol^{-1} cm^2) for $[NiL^3(H_2O)](ClO_4)_2$ measured in water indicates that the complex is a 1:2 electrolyte. However, the value (480 Ω^{-1}mol^{-1}cm^2) for $[Ni(HL^3)](ClO_4)_3$ in water is somewhat larger than that expected for a 1:3 electrolyte.

The electronic absorption spectra of $[NiL^3(H_2O)](ClO_4)_2$ measured in Nujol mull and various solvents show three bands centered at *ca.* 330, 500, and 710 nm, as expected for a high-spin octahedral chromophore.[19,20] This supports the fact that the pendant amino group and one water molecule of $[NiL^3(H_2O)](ClO_4)_2$ are involved in coordination. The spectrum of $[Ni(HL^3)](ClO_4)_3$ measured in Nujol mull shows a *d-d* transition band at 465 nm, indicating that the complex is in a square-planar Ni-N$_4$ environment in the solid state. However, the spectra measured in water, acetonitrile, DMF, and DMSO are quite similar to those for $[NiL^3(H_2O)]$-$(ClO_4)_2$. The value of pH measured in aqueous solution of $[Ni(HL^3)](ClO_4)_3$ (2.0 × 10^{-3} M) was found to be ~2.9. These observations, together with the molar conductance, support the suggestion that $[Ni(HL^3)]^{3+}$ is readily deprotonated to produce $[NiL^3(S)]^{2+}$ in the solvents (S). The oxidation potential (+1.01 V) of $[NiL^3(H_2O)](ClO_4)_2$ is distinctly lower than those of $[NiL^1]^{2+}$, $[NiL^2]^{2+}$, and $[NiL^4]^{2+}$. This is attributed to the relatively high electron density on the metal center of the six-coordinate complex.

The addition of strong acids, such as HClO$_4$, to an aqueous solution of $[NiL^3(H_2O)]^{2+}$ increases the absorption at *ca.* 465 nm (Fig. 2), indicating the formation of the square-planar form $[Ni(HL^3)]^{3+}$. Figure 2 also shows that the absorption coefficient (47 M^{-1}cm^{-1}) of $[NiL^3(H_2O)]^{2+}$ measured in 2.0 M HClO$_4$ solution is larger than that (43 M^{-1}cm^{-1}) in 1.0 M HClO$_4$ solution. However, the value is distinctly smaller than that (72 M^{-1}cm^{-1}) of $[NiL^2](ClO_4)_2$ measured in nitromethane. This implies that the square-planar complex $[Ni(HL^3)]^{3+}$ is not the only protonated form even in 2.0 M HClO$_4$ solution; the octahedral complex $[Ni(HL^3)(H_2O)_2]^{3+}$ also exists in the solution. It can be suggested that the nickel(II) complex exists as an equilibrium mixture of $[NiL^3(H_2O)_2]^{2+}$, $[Ni(HL^3)]^{3+}$, and $[Ni(HL^3)(H_2O)_2]^{3+}$ in HClO$_4$
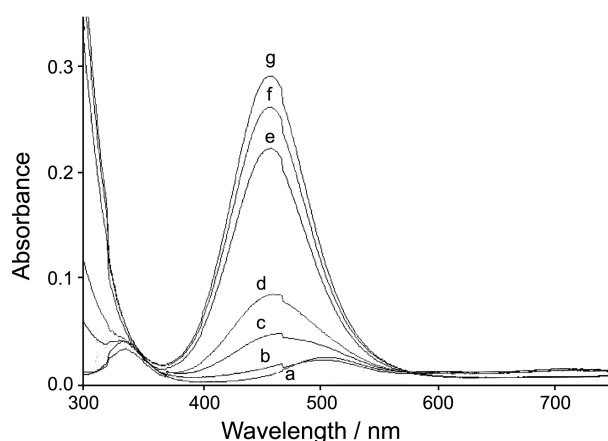
Figure 2. Electronic spectra of [NiL³(H₂O)](ClO₄)₂ (5.0 x 10⁻³ M) measured in aqueous solutions containing various concentration of HClO₄; [HClO₄] = 0.0 (a), 0.01 (b), 0.05 (c), 0.10 (d), 0.50 (e), 1.0 (f), and 2.0 M (g).
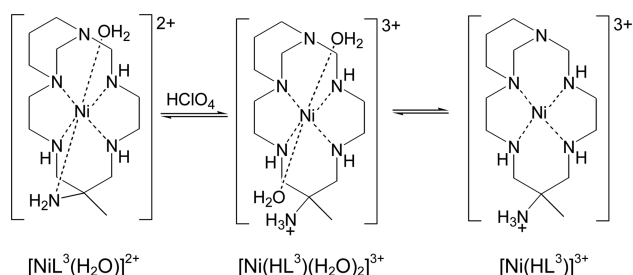
Scheme 1

solutions (Scheme 1).

Concluding Remarks

This work shows that the non-macrocyclic complex [NiL¹]²⁺ can be prepared selectively by the metal-directed reaction of *N*-(2-aminoethyl)-1,3-propanediamine, ethylenediamine, and formaldehyde at room temperature. The complex is a useful starting material for the preparation of various penta-aza and hexaaza macrocyclic complexes, such as [NiL²]²⁺, [NiL³(H₂O)]²⁺, and [NiL⁴]²⁺. The *C*-NH₂ pendant arm of [NiL³(H₂O)]²⁺ is protonated in acid solutions, yielding [Ni(HL³)]³⁺. Chemical properties of the nickel(II) complexes are strongly influenced by the structural characteristics of the ligands.

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