Template Syntheses and Crystal Structures of Nickel(II) Complexes of Hexaaza Macrocyclic Ligands with Pendant Functional Groups: Formation of a Coordination Polymer

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The nickel(II) complexes of hexaaza macrocyclic ligands **1−4**, which incorporate functional groups such as −OH and −CN into the pendant arms attached at the uncoordinated bridgehead nitrogen atoms, are synthesized by the simple template condensation of ethylenediamine, formaldehyde, and primary amines with the appropriate functional groups. The hydroxyl pendant groups in the nickel(II) complex of **1** react with acetic anhydride to produce the Ni(II) complex of **5**. The Ni(II) complexes of **1−5** are in a square-planar geometry in solution. Their UV/vis spectra and electrochemical data are slightly affected by the type of functional group and the length of the pendant chain. The pendant hydroxyl groups in $[Ni(\mathbf{1})]^{2+}$ and $[Ni(\mathbf{2})]^{2+}$ do not coordinate Ni(II) ion in water at pH ≤ 13.0 and an ionic strength 1.0 M ($NaClO_4$) or at pH ≤ 10.0 and an ionic strength 0.1 M ($NaClO_4$). The nickel(II) complex with macrocycle **3** forms a coordination polymer on crystallization. $[Ni(\mathbf{2})](ClO_4)_2$ ($NiC_{14}H_{34}N_6Cl_2O_{10}$) crystallizes in the monoclinic space group $P2_1/c$ with $a = 8.724(2)$ Å, $b = 14.581(2)$ Å, $c = 9.255(2)$ Å, $\beta = 103.84(1)°$, and $Z = 2$. The structure was solved by the direct method and refined to R values of $R = 0.0335$ and $wR(F^2) = 0.0785$ for 1751 observed reflections ($F > 4\sigma(F)$) measured with Mo Kα radiation on an Enraf-Nonius CAD-4 diffractometer. The Ni(II) ion forms a square-planar geometry, coordinated by four secondary nitrogen donors of the macrocycle with the average Ni−N bond distance of 1.929(2) Å. The oxygen atoms of the pendant hydroxyl groups form hydrogen bondings with the secondary NH's of the neighboring macrocyclic ligands. Coordination polymer $[Ni(\mathbf{3})]_n(BF_4)_{2n}$ ($NiC_{14}H_{28}N_8B_2F_8$) crystallizes in the monoclinic space group $P2_1/n$ with $a = 8.269(1)$ Å, $b = 8.559(1)$ Å, $c = 15.814(2)$ Å, $\beta = 101.27(1)°$, and $Z = 2$. The structure was solved by the direct method and refined to R values of $R = 0.0485$ and $wR(F^2) = 0.1395$ for 1509 observed reflections ($F > 6\sigma(F)$) measured with Mo Kα radiation on an Enraf-Nonius CAD-4 diffractometer. In the Ni(II) coordination polymer, each Ni(II) ion in the macrocyclic unit is coordinated by two nitrile groups of the neighboring macrocycles. The Ni(II) atom is virtually in an octahedral geometry with the average Ni−N(macrocycle) bond distance of 2.056(3) Å and the Ni(II)−N(nitrile) bond distance of 2.162(4) Å.

Introduction

Macrocyclic complexes with functional groups have been synthesized in order to investigate how the functional groups affect the properties of the macrocyclic complexes. For instance, amine, hydroxyl, amide, carboxylic, and nitrile functional groups have been attached to the side chains of the coordinated nitrogen donors.[1−4] Some of these donors coordinate metal ions intramolecularly at the axial position and dramatically alter the properties of the complexes. In addition, phenol, pyridyl, catechol, imidazole, and amine have been attached to the carbon atoms of macrocyclic framework and they affect the coordination geometry of the metal ions.[5−7] All these functionalized macrocyclic complexes have been synthesized by inserting the metal ions in the free ligands which were prepared by rather elaborate many-step procedures.

Recently, we have been interested in the macrocyclic complexes containing pendant donors which are capable of intra- or intermolecular coordination and tried to synthesize them by the simple one pot template condensation reaction instead of a many-step procedure.

Over the last few years, various saturated polyaza multidentate, macrocyclic, and macropolycyclic complexes have been prepared by the template condensation reactions involving formaldehyde and amines.[8−17] Especially, we have developed a simple procedure for the preparation of the complexes of hexaaza macrocyclic ligand **A**,[11,12] which resembles 1,4,8,11-tetraazacyclotetradecane (cyclam). By modifying a previous method, we have synthesized the complexes of macrocyclic

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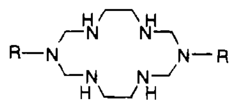

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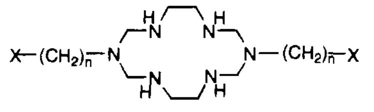


L

1: X = OH, n = 2, **2**: X = OH, n = 3,
3: X = CN, n = 2, **4**: X = CN, n = 5
5: X = OCO-CH_3, n = 2

ligands whose general structure is represented by **L**. The ligands incorporate the pendant chains with hydroxyl or nitrile functional groups onto the bridgehead nitrogen atoms.

In this paper, we describe the template synthesis of Ni(II) complexes of **1**−**4** and the X-ray structures of **2** and **3**.[18] All Ni(II) complexes of **1**−**4** are square-planar in solution. However, the Ni(II) complex of **3** forms a coordination polymer upon crystallization. The coordination polymer contains six-coordinated Ni(II) macrocyclic units, in which Ni(II) ion is coordinated by four nitrogen donors of the macrocycle and by two nitrile groups of the neighboring macrocyclic ligands as shown in Chart 1. The Ni(II) and Cu(II) complexes of tetranitrile derivative of cyclam were previously reported, but none of their nitrile groups were used for the coordination of the metal ion.[4,19,20] Therefore, this study presents the first example of intermolecular coordination of pendant nitrile groups forming a coordination polymer. The pendant hydroxyl groups in the Ni(II) complexes react with acetic anhydride leading to the complex of **5** containing acetyl pendant groups.

Experimental Section

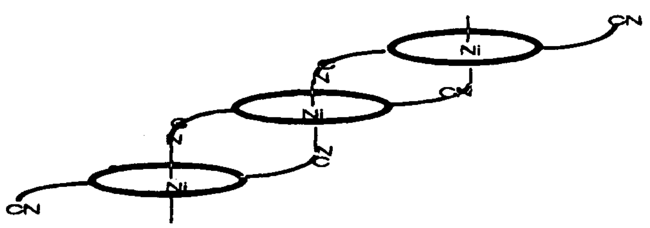
Reagent. All chemicals and solvents used in the synthesis were of reagent grade and were used without further purification. For the spectroscopic measurements, water was distilled and organic solvents were purified according to the literature method.[21]

Measurements. Infrared spectra were recorded with a JASCO IR-810 spectrophotometer. Conductance measurements were performed by using a TOA CM-30ET conductivity meter. ^1H and ^{13}C NMR spectra were recorded on a Bruker AC80 FT NMR spectrometer. Electronic absorption spectra were obtained on a Shimadzu 260 UV/vis spectrophotometer. Magnetic susceptibility was measured with a Faraday type magnetometer. Elemental analyses were performed by the Analytical Laboratory in Seoul National University, Seoul. Cyclic voltammetry was carried out with PARC Model 173 potentiostat coupled with a universal programmer and a Kipp and Zonen X-Y recorder. The electrochemical data were obtained in MeCN with 0.1 M $(n\text{-}Bu)_4NClO_4$ as supporting electrolyte. The working electrode was a platinum disk, the auxiliary electrode was a coiled platinum wire, and the reference electrode was Ag/AgCl. The pH value was measured with a Model DP-135M digital pH/ion meter.

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.

$[Ni(L)](ClO_4)_2$ (L = 1−4). To a stirred methanol solution (75 mL) of $NiCl_2{\cdot}6H_2O$ (12 g) were slowly added ethylenediamine (6.8 mL), paraformaldehyde (10 g), and appropriate primary amines (0.10 mol), ethanolamine for **1**, 3-amino-1-propanol for **2**, β-aminopropionitrile for **3**, and 6-aminocapronitrile for **4**, respectively. The mixture was heated at reflux for 6−30 h (6 h for **1**, 12 h for **2**, 24 h for **3**, and 30 h for **4**). The solution was filtered hot, and the filtrate was allowed to stand at room temperature. Purple precipitate $[Ni(L)Cl_2]$ formed, which was filtered off, washed with methanol, and dried in *vacuo*. $[Ni(L)Cl_2]$ was dissolved in a minimum amount of water to give a yellow solution, and a saturated methanol solution of an excess amount of $LiClO_4$ was added. The solution was allowed to stand at room temperature until yellow crystals formed for L = **1**, **2**, and **4** and a pale green precipitate formed for **3**. The solids were filtered off, washed with methanol, and dried in *vacuo*. The compounds were recrystallized by cooling hot saturated aqueous solutions. Yield: 30% for L = **1**, 60% for L = **2**, 40% for L = **3** and **4**. Anal. Calcd for $[Ni(\mathbf{1})](ClO_4)_2$ ($NiC_{12}H_{30}N_6Cl_2O_8$): C, 26.30; H, 5.52; N, 15.33. Found: C, 26.29; H, 5.72; N, 15.27. Calcd for $[Ni(\mathbf{2})](ClO_4)_2$ ($NiC_{14}H_{34}N_6Cl_2O_8$): C, 29.19; H, 5.95; N, 14.59. Found: C, 29.15; H, 6.22; N, 14.89. Calcd for $[Ni(\mathbf{3})]_n(ClO_4)_{2n}$ ($NiC_{14}H_{28}N_8C_{12}O_8$): C, 29.71; H, 4.98; N, 19.80. Found: C, 28.66; H, 4.93; N, 19.54. Calcd for $[Ni(\mathbf{4})](ClO_4)_2$ ($NiC_{20}H_{40}N_8Cl_2O_8$): C, 36.94; H, 6.20; N, 17.23. Found: C, 36.60; H, 5.92; N, 17.10.

Chart 1



$[Ni(L)](PF_6)_2$ (L = 1, 2, 4). To an MeCN suspension of perchlorate salt of the corresponding Ni(II) complex was added an MeCN solution of an excess of NH_4PF_6. The complex went into the solution, and the white precipitate of NH_4ClO_4 formed. NH_4ClO_4 was filtered off, and then water was added dropwise to the filtrate to induce the crystallization of PF_6^- salts. The crystals were filtered off and washed with a 5:1 mixture of water and MeCN.

$[Ni(\mathbf{3})]_n(BF_4)_{2n}$. $[Ni(\mathbf{3})Cl_2]$ was dissolved in a 1:1 mixture of Me_2SO and water. A saturated aqueous solution of an excess of $NaBF_4$ was added to the solution, and the solution was allowed to stand at room temperature until pale green crystals formed. The crystals were filtered off, washed with EtOH, and dried in *vacuo*. Single crystals were selected for the X-ray crystal structure determination. Anal. Calcd for $NiC_{14}H_{28}N_8B_2F_8$: C, 31.09; H, 5.21; N, 20.72. Found: C, 31.00; H, 5.08; N, 20.46.

$[Ni(\mathbf{5})](ClO_4)_2$. The compound was prepared by using the modified method reported previously.[22] $[Ni(\mathbf{1})](ClO_4)_2$ (0.7 g) was placed in a serum-capped Schlenk bottle which was filled with nitrogen. Dichloromethane (90 mL) which was dried and distilled was added by using a syringe. To a stirred suspension were added acetic anhydride (3.7 mL), triethylamine (3.2 mL), and 4-(dimethylamino)pyridine (0.5 g) as a catalyst. The mixture was stirred at room temperature for 48 h under a nitrogen atmosphere until an orange solution resulted. The solution was stirred additionally in the air for 24 h. The solution was filtered, and the filtrate was concentrated to ca. $^1/_{10}$ of the original volume by the evaporation of the solvent. The solution was allowed to stand in a refrigerator until a yellow precipitate formed. The precipitate was filtered off, washed with MeOH, and dried in *vacuo*. The compound was recrystallized by dissolving it in a minimum amount of hot 1:1 (v/v) MeOH−H_2O mixture and then allowing the solution to stand at room temperature. Yield: ~40%. Anal. Calcd for $NiC_{16}H_{34}N_6Cl_2O_{12}$: C, 30.40; H, 5.42; N, 13.29. Found: C, 29.91; H, 5.25; N, 13.43.

X-ray Diffraction Measurements. All X-ray examination and data collection procedures were performed at room temperature on an Enraf-Nonius CAD-4 diffractometer. Data were collected with graphite-monochromated Mo Kα radiation through the use of the $\omega-2\theta$ scan technique. All data were corrected for Lorentz and polarization effects and for absorption. The crystallographic data collection and refinement details are summarized in Table 1. Complete details of the data collection and refinement process are given in Table S1 of the supplementary material. The structures were solved by direct methods

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Table 1. Crystallographic Data for [Ni(**2**)](ClO_4)$_2$ and [Ni(**3**)]$_n$(BF_4)$_{2n}$

formula	$NiC_{14}H_{34}N_6Cl_2O_{10}$	$NiC_{14}H_{28}N_8B_2F_8$
fw	576.08	540.77
space group	$P2_1/c$	$P2_1/n$
a, Å	8.724(2)	8.269(1)
b, Å	14.581(2)	8.559(1)
c, Å	9.255(2)	15.814(2)
β, deg	103.84(1)	101.27(1)
V, Å^3	1143.1(4)	1097.6(2)
Z	2	2
ϱ_{calc}, g/cm^3	1.674	1.636
T, °C	23	22
λ, Å	0.710 69	0.710 69
cryst size, mm	0.60 × 0.50 × 0.10	0.46 × 0.40 × 0.26
μ, cm^{-1}	11.46	9.71
R_1[a]	0.0335 (4σ data)	0.0485 (6σ data)
R_2[b]	0.0785 (4σ data)	0.1395 (6σ data)

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_2 = [\sum[w(|F_o|^2 - |F_c|^2)^2]/\sum[w(|F_o|)^4]^{1/2}$.

by using SHELXS86.[23] Full-matrix least-squares refinement was carried out by minimizing the function $\sum w(F_o^2 - F_c^2)^2$. All 2009 data were used in the refinement of [Ni(**2**)](ClO_4)$_2$, and 1509 data with $F > 6\sigma(F)$ were used in the refinement of [Ni(**3**)]$_n$(BF_4)$_{2n}$. The positions of all non-hydrogen atoms were refined with anisotropic displacement factors. Both the ClO_4^- anion in [Ni(**2**)](ClO_4)$_2$ and the BF_4^- anion in [Ni(**3**)]$_n$(BF_4)$_{2n}$ suffered from rotational disorder. Calculated positions of all hydrogen atoms were allowed to ride on their bonded atoms with the isotropic displacement factors fixed with values of 1.2 times those of the bonded atoms. All calculations were done by using the program SHELXL93.[24]

Spectral Titration. The spectral titration of the Ni(II) complexes of **1** and **2** was carried out on a Shimadzu 260 UV/vis spectrophotometer. The concentrations of Ni(II) complexes were 1.0 × 10^{-2} M for **1** and 8.0 × 10^{-3} M for **2** and **A**. The pH of the solutions was adjusted to 7.0–12 by using buffer solutions (0.03 M). Buffers used were *N*-(2-hydroxyethyl)piperidine-*N'*-ethanesulfonate (pH 7–8), borate (pH 9–10), and sodium carbonate (pH 11–12). The pH values of the solutions were measured before and after the spectral measurement. The ionic strength was adjusted with 1.5 M $NaClO_4$. Spectral titrations are shown in Figure S2 of the supplementary material.

Results and Discussion

Synthesis. The Ni(II) complexes of macrocyclic ligand **L**, which incorporates the pendant chains with the functional donors on the bridgehead nitrogen atoms, were synthesized by the simple template condensation reactions as described in eq 1. As

$$Ni^{2+} + NH_2CH_2CH_2NH_2 + CH_2O + NH_2{-}(CH_2)_n{-}X \longrightarrow [Ni(\mathbf{L})]^{2+} \quad (1)$$

$$X = OH, CN;\ n = 2{-}5$$

the template condensation reactions were carried out in the presence of $NiCl_2{\cdot}6H_2O$, octahedral [Ni(**L**)Cl_2] (**L** = **1**–**4**) complexes resulted initially. The axial Cl^- ligands in [Ni(**L**)Cl_2] are labile in an aqueous solution, and the complex turns to square-planar Ni(II) species [Ni(**L**)]$^{2+}$, which is precipitated by the addition of appropriate anions such as $LiClO_4$ or $NaBF_4$. In the solid state, Ni(II) complexes with **1**, **2**, and **4** are yellow, and that of **3** is pale green. Unlike most of the perchlorate salts of Ni(II) macrocyclic complexes, [Ni(**1**)](ClO_4)$_2$ and [Ni(**2**)](ClO_4)$_2$ are very soluble in water, which may be attributed to the hydrogen bonding between the hydroxyl groups of the macrocycles and water molecules.

Spectra and Properties. The data of infrared, UV/vis, and ^{13}C NMR spectra as well as the conductance of the Ni(II) complexes were summarized in Table 2. The infrared spectra (Nujol mull) of octahedral [Ni(**1**)Cl_2] and [Ni(**2**)Cl_2] show O–H stretchings of hydroxyl pendant groups at 3375 and 3390 cm^{-1}, respectively, while those of square-planar [Ni(**1**)](ClO_4)$_2$ and [Ni(**2**)](ClO_4)$_2$ show them at 3520 and 3525 cm^{-1}, respectively. The lower ν_{OH} values of hydroxyl groups in octahedral [Ni(**L**)Cl_2] (**L** = **1**, **2**) than in square-planar [Ni(**L**)](ClO_4)$_2$ suggest the existence of hydrogen-bonding between hydroxyl groups and the axial Cl^- ligands in [Ni(**L**)Cl_2]. In [Ni(**2**)](ClO_4)$_2$, N–H stretchings of secondary amines appear at 3150 and 3248 cm^{-1} while that of [Ni(**1**)](ClO_4)$_2$ appears at 3205 cm^{-1}. The low ν_{NH} value of 3150 cm^{-1} implies that some secondary amines are involved in the hydrogen bonding; the crystal structure indicates that a N–H of secondary nitrogen forms a hydrogen bond with the oxygen atom of the hydroxyl group of neighboring macrocycle.

The ν_{CN} value of pendant nitriles in pale green [Ni(**3**)](ClO_4)$_2$ is 2283 cm^{-1} while those of [Ni(**3**)Cl_2], [Ni(**4**)Cl_2], and [Ni(**4**)](ClO_4)$_2$ are 2249–2251 cm^{-1} (Table 2). The higher ν_{CN} value in [Ni(**3**)](ClO_4)$_2$ by ca. 30 cm^{-1} compared to others indicates that the nitrile pendants in **3** coordinate the Ni(II) ion.[25] In addition, the magnetic moment of [Ni(**3**)](ClO_4)$_2$ is μ_{eff} = 3.05 μ_B at room temperature, which also suggests that the Ni(II) ion takes an octahedral geometry through the coordination of nitrile pendants. The Ni(II) and Cu(II) complexes of the tetranitrile derivative of cyclam were previously reported, but none of its nitrile groups were used for the coordination of the metal ion.[4,19,20] Therefore, the present [Ni(**3**)]X_2 (X = ClO_4^- or BF_4^-) is the first example for the coordination of pendant nitrile groups incorporated in the macrocyclic ligand. Moreover, the fact that nitrile groups in **3** coordinate metal ions but not those in **4** suggests that the length of the pendant chain is the important factor to determine whether the nitrile pendant groups are able to coordinate intermolecular metal ions or not.

The electronic absorption spectra for the aqueous solution of [Ni(**L**)](ClO_4)$_2$ (**L** = **1**–**5**) indicate that d–d transitions of the complexes occur at 445–446 nm, which are characteristic chromophores for the square-planar Ni(II) complexes. In addition, the spectra are very similar to that of the Ni(II) cyclam complex. This indicates that the presence of two uncoordinated tertiary nitrogen atoms in the macrocyclic framework, the length of the pendant chain, or the type of the functional group appended at the bridgehead nitrogen slightly affects the ligand field strength of the complexes. It was previously observed also for the Ni(II) complexes with **A** containing various alkyl pendants that the spectra are not affected by the type of alkyl chain.[11,12] Moreover, Fabbrizzi et al. showed that the spectrum of the azacyclam complex with a pyridyl functional group was similar to that of cyclam complex.[16,17] The pale green crystals of [Ni(**3**)]$_n$(BF_4)$_{2n}$ turn to yellow in water and in Me_2SO; the maximum absorptions appear at 445 and 449 nm, respectively. This indicates that the bond between nitrile functional group and the Ni(II) ion is weak and labile and thus easily dissociates in donating solvents to result in square-planar species.

Cyclic voltammogram of [Ni(**1**)]$^{2+}$ show quasi-reversible one-electron oxidation at +1.00 V and one electron reduction at −1.41 V vs the Ag/AgCl reference electrode (Table 2). These are similar to the values of the Ni(II) complexes with **A** reported previously and have only 0.01–0.03 V differences from those

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Table 2. Properties of Ni(II) Macrocyclic Complexes

compd	IR,[a] cm^{-1} ν_{NH}	ν_{OH}	ν_{CN}	UV/vis:[b,c] λ_{Max}, nm (ϵ)	Λ_M,[b,c] $\Omega^{-1}\ cm^{-2}\ M^{-1}$	^{13}C NMR:[e] δ, ppm	E_{ox},[f] V Ni(II)/Ni(III)	E_{red},[f] V Ni(II)/Ni(I)
$[Ni(\mathbf{1})Cl_2]$	3270, 3210	3375						
$[Ni(\mathbf{1})](ClO_4)_2$	3205	3520		446 (56),[b] 448 (82)[c]	204[b]	46.4, 53.1, 60.9, 67.4	+1.00 (qr)	−1.41 (qr)
$[Ni(\mathbf{2})Cl_2]$	3285, 3225	3390						
$[Ni(\mathbf{2})](ClO_4)_2$	3248, 3150	3525		445 (55),[b] 449 (77)[c]	156[c]	31.7, 48.0, 48.5, 60.7, 69.1		
$[Ni(\mathbf{3})Cl_2]$	3285, 3220		2251					
$[Ni(\mathbf{3})](ClO_4)_2$	3275		2283	445 (27),[b] 451 (39)[d]	65[d]			
$[Ni(\mathbf{4})Cl_2]$	3290, 3230		2249					
$[Ni(\mathbf{4})](ClO_4)_2$	3210		2249	445 (57),[b] 449 (63)[c]	180[b]			
$[Ni(\mathbf{5})](ClO_4)_2$	3225	1725 (ν_{CO})		451 (62)[c]	161[c]			
$[Ni(\mathbf{A})](ClO_4)_2$[g]	3220			446 (40),[b] 449 (56)[c]	225[b]		+0.99	−1.49
$[Ni(cyclam)]^{2+}$ [h]				445 (46)[b]			+0.97	−1.40

[a] Measured with Nujol mull. [b] Measured in H_2O. [c] Measured in $MeNO_2$. [d] Measured in Me_2SO. [e] Measured in PF_6^- salt in d_3-$MeNO_2$ because of the insolubility of the ClO_4^- salt. [f] Measured in MeCN with 0.1 M $(n\text{-}Bu)_4NPF_6$, V vs Ag/AgCl reference electrode; qr = quasi-reversible. [g] Reference 11. [h] References 26 and 27.

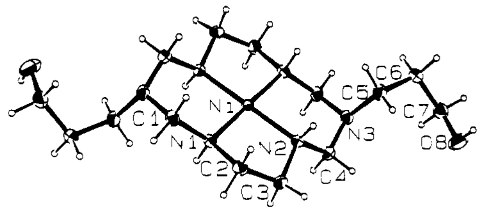
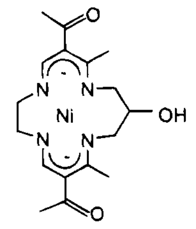


Figure 1. ORTEP drawing of the cation in $[Ni(\mathbf{2})[(ClO_4)_2$ with atomic numbering scheme. Thermal ellipsoids are drawn at the 30% probability level.

of Ni(II) cyclam complex.[11,12,26,27] That is, the presence of extra two nitrogen atoms in the macrocyclic framework and the types of pendant chains do not significantly affect the electrochemical properties of Ni(II) complexes.

Reactivity of Hydroxyl Pendants in $[Ni(\mathbf{1})]^{2+}$ and $[Ni(\mathbf{2})]^{2+}$. It has been reported that the uncoordinated alcoholic OH group has an abnormal absence of reactivity toward electrophiles in a number of chelate complexes.[28,29] However, it has been reported quite recently that the uncoordinated hydroxyl group in macrocyclic complex **B** reacted smoothly with acylating agents.[22]



B

The hydroxyl groups in $[Ni(\mathbf{1})](ClO_4)_2$ also reacted with acetic anhydride to result in $[Ni(\mathbf{5})](ClO_4)_2$. The IR spectrum of the $[Ni(\mathbf{5})](ClO_4)_2$ shows a strong acetyl carbonyl band at 1725 cm^{-1}. UV/vis spectrum of the Ni(II) complex of **5** indicates that the acetyl groups do not coordinate intra- or intermolecular Ni(II) ions and the complex is in a square-planar geometry.

Crystal Structure of $[Ni(\mathbf{2})](ClO_4)_2$. An ORTEP[30] view of cation $[Ni(\mathbf{2})]^{2+}$ is shown in Figure 1. Tables 3 and 4 show the selected fractional coordinates and bond lengths and angles. The Ni(II) ion in the complex is coordinated by the four secondary nitrogen donors of the macrocycle and forms a square-planar geometry. The average Ni−N bond distance is 1.929(2) Å, which is close to 1.92 Å of square-planar $[Ni(cyclam)]^{2+}$.[31] The complex possesses an inversion center at the nickel atom, and thus the nitrogen donors form a perfect plane including the Ni(II) ion. The bite distances of the five-membered and six-membered chelate rings are 2.647(3) and

Table 3. Fractional Atomic Coordinates[a] ($\times 10^4$) and Equivalent Isotropic Displacement Parameters[b] ($Å^2 \times 10^3$) for $[Ni(\mathbf{2})](ClO_4)_2$

atom	*x*	*y*	*z*	U_{eq}
Ni	0	5000	10000	23(1)
N(1)	−2157(3)	4669(2)	9082(2)	27(1)
N(2)	−493(2)	6188(2)	9097(2)	27(1)
N(3)	2230(3)	6751(2)	9508(3)	32(1)
C(1)	−3020(3)	4088(2)	9966(3)	32(1)
C(2)	−3072(3)	5519(2)	8564(3)	34(1)
C(3)	−2005(3)	6125(2)	7935(3)	36(1)
C(4)	757(3)	6623(2)	8454(3)	34(1)
C(5)	2245(4)	7456(2)	10641(3)	36(1)
C(6)	3792(3)	7981(2)	11066(3)	38(1)
C(7)	4196(4)	8487(2)	9779(4)	46(1)
O(8)	2962(4)	9071(2)	9027(3)	66(1)
Cl	1911(1)	3969(1)	6812(1)	44(1)
O(1)	1606(4)	3346(2)	5619(3)	73(1)
O(2a)*	602(11)	4251(10)	7239(16)	126(5)
O(3a)*	2839(12)	4695(6)	6615(10)	91(4)
O(4a)*	2822(18)	3459(5)	8059(9)	125(5)
O(2b)**	933(18)	3867(12)	7722(13)	116(7)
O(3b)**	1528(34)	4825(7)	6080(17)	184(11)
O(4b)**	3438(9)	4005(18)	7570(18)	167(12)

[a] Site occupation factors are 0.569 for atoms marked with an asterisk and 0.431 for atoms marked with two asterisks. [b] U_{eq} is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 4. Bond Lengths (Å) and Angles (deg) for $[Ni(\mathbf{2})](ClO_4)_2$[a]

Ni−N(1)	1.931(2)	Ni−N(2)	1.927(2)
C(1)−N(1)	1.500(3)	N(1)−C(2)	1.490(3)
C(2)−C(3)	1.499(4)	C(3)−N(2)	1.492(3)
N(2)−C(4)	1.502(3)	C(4)−N(3)	1.428(3)
N(3)−C(5)	1.467(4)	N(3)−C(1)′	1.431(4)
C(5)−C(6)	1.519(4)	C(6)−C(7)	1.513(4)
C(7)−O(8)	1.418(4)		

N(2)−Ni−N(1)	86.63(9)	N(1)−Ni−N(2)′	93.37(9)
C(2)−N(1)−C(1)	110.2(2)	C(2)−N(1)−Ni	108.9(2)
C(1)−N(1)−Ni	117.7(2)	C(3)−N(2)−C(4)	109.9(2)
C(3)−N(2)−Ni	108.9(2)	C(4)−N(2)−Ni	116.3(2)
C(4)−N(3)−C(1)′	113.8(2)	C(4)−N(3)−C(5)	115.6(2)
C(1)′−N(3)−C(5)	115.8(2)	N(3)′−C(1)−N(1)	113.9(2)
N(1)−C(2)−C(3)	106.3(2)	N(2)−C(3)−C(2)	106.3(2)
N(3)−C(4)−N(2)	113.8(2)	N(3)−C(5)−C(6)	113.2(2)
C(7)−C(6)−C(5)	113.7(2)	O(8)−C(7)−C(6)	112.8(3)

[a] Symmetry transformations used to generate equivalent atoms: prime, $-x, -y + 1, -z + 2$.

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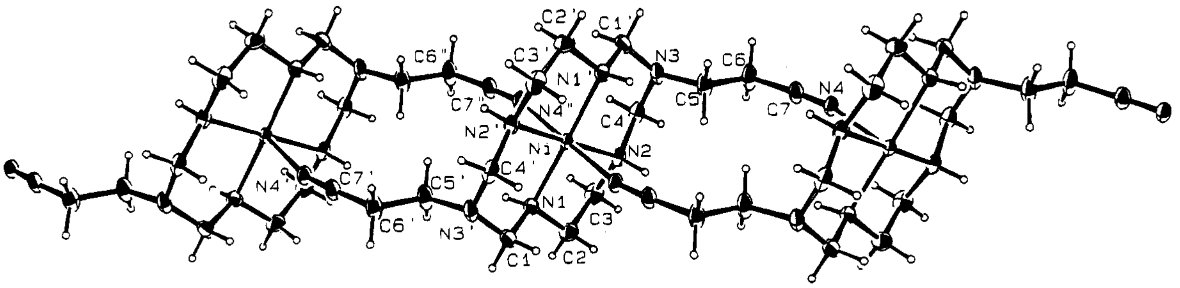

Figure 2. ORTEP drawing of the polymeric cation in $[Ni(\mathbf{3})]_n(BF_4)_{2n}$ with atomic numbering scheme. Thermal ellipsoids are drawn at the 30% probability level.

2.807(3) Å, respectively. The bite angles of five-membered and six-membered chelate rings are 86.63(9) and 93.37(9)°, respectively. These are normally observed values for the bite distances and angles for the five- and six-membered chelate rings in the square-planar Ni(II) complexes with a 14-membered macrocycle.[10,13,14] The macrocyclic ligand adopts a *R,R,S,S* (*trans* III) configuration where the two hydrogens in secondary amines orient to a side opposite to that of the other two, which is the most stable form thermodynamically.[32] The six-membered chelate rings adopt a chair conformation, and thus the alkyl chains on the bridgehead nitrogens are axial. The five-membered chelate rings assume a gauche conformation. The average N−C bond distance involving bridgehead tertiary nitrogen atom N(3) is 1.439(2) Å, which is shorter than the normal C−N single bond distance. Moreover, the C−N−C angles involving N(3) are 114−116°. The similar shortening of the bond and flattening of the bond angle involving the uncoordinated tertiary amine have been observed for other complexes.[8,10−14,16,17,33] The pendant hydroxyl groups of the ligand are not coordinated. However, the oxygen atom of the hydroxyl group forms a hydrogen bond with the secondary H−N of the neighboring macrocycle: O(8)- - -H(1)−N(1), 2.93 Å; <O(8)HN(1), 151°. In addition, the hydrogen atom in the hydroxyl group forms a hydrogen bond with an oxygen atom of perchlorate anion: O(8)−H(8)- - -O(ClO_4), 2.98 Å; <O(8)-H(8)O, 169°. These hydrogen bondings are reflected in the values of ν_{OH} and ν_{NH} of the complex, as discussed previously.

Crystal Structure of $[Ni(3)]_n(BF_4)_{2n}$. An ORTEP[30] plot of the polymeric cation is presented in Figure 2. Tables 5 and 6 show the selected fractional coordinates and bond lengths and angles. The Ni(II) ion in each macrocyclic unit is coordinated by four secondary nitrogen donors of the hexaaza macrocycle and by two nitrile groups contained in the neighboring macrocyclic ligands to form an octahedral geometry. Therefore, macrocyclic ligand **3** acts as a hexadentate ligand which binds three metal ions; four secondary amines bind one metal ion, and two nitriles bind two different metal ions. The average Ni−N bond distance is ca. 2.056(3) Å, which is comparable to 2.067 Å of $[Ni(cyclam)Cl_2]$[34] but is ca. 0.13 Å longer than that of square-planar $[Ni(\mathbf{2})](ClO_4)_2$. The axial Ni−N(nitrile) bond distance of 2.162(4) Å is considerably longer than equatorial Ni−N(macrocycle) bond distances, which explains the lability of the axial bonds in the polar solvents. The axial bonds linking four atoms from Ni to C(6), Ni−N(4″)−C(7″)−C(6″), are almost linear; bond angles of Ni−N(4″)−C(7″) and N(4″)−C(7″)−C(6″) are 166.2(5) and 176.2(6)°, respectively.

Table 5. Fractional Atomic Coordinates[a] ($\times 10^4$) and Equivalent Isotropic Displacement Parameters[b] ($Å^2 \times 10^3$) for $[Ni(\mathbf{3})]_n(BF_4)_{2n}$

atom	*x*	*y*	*z*	U_{eq}
Ni	0	0	5000	24(1)
N(1)	1168(5)	2104(5)	4946(3)	34(1)
N(2)	−1708(5)	815(6)	3970(3)	33(1)
N(3)	−3039(5)	−1750(7)	3674(3)	42(1)
N(4)	−8482(5)	−961(6)	4159(3)	35(1)
C(1)	1886(7)	2772(7)	5806(4)	43(2)
C(2)	−40(8)	3107(7)	4378(5)	48(2)
C(3)	−902(8)	2146(8)	3623(4)	47(2)
C(4)	−2368(7)	−407(8)	3323(3)	42(2)
C(5)	−4526(7)	−1505(10)	4029(4)	55(2)
C(6)	−6055(7)	−1602(10)	3391(5)	58(2)
C(7)	−7463(7)	−1260(8)	3806(4)	43(2)
B	5522(11)	6662(13)	6432(7)	68(3)
F(1)	5160(9)	7475(12)	7185(5)	148(3)
F(2a)*	4323(20)	6909(25)	5774(7)	107(8)
F(3a)*	6901(18)	7077(45)	6370(12)	192(15)
F(4a)*	5473(25)	5390(15)	6882(8)	119(5)
F(2b)*	4161(22)	6313(33)	5947(20)	197(15)
F(3b)*	6234(35)	7843(18)	6179(17)	175(13)
F(4b)*	6553(21)	5500(20)	6310(21)	219(14)

[a] Site occupation factors are 0.5 for atoms marked with an asterisk. [b] Equivalent isotropic U_{eq} is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 6. Bond Lengths (Å) and Angles (deg) for $[Ni(\mathbf{3})]_n(BF_4)_{2n}$[a]

Ni−N(1)	2.053(5)	N(3)−C(1′)	1.430(8)
Ni−N(2)	2.058(4)	N(3)−C(5)	1.463(7)
Ni−N(4″)	2.162(4)	N(3)−C(4)	1.435(8)
N(1)−C(1)	1.488(7)	C(2)−C(3)	1.509(10)
N(1)−C(2)	1.481(8)	C(5)−C(6)	1.457(9)
N(2)−C(3)	1.478(8)	C(6)−C(7)	1.473(8)
N(2)−C(4)	1.490(7)	N(4)−C(7)	1.127(7)
N(1)−Ni−N(2)	85.7(2)	N(1′)−Ni−N(2)	94.3(2)
N(1)−Ni−N(4″)	88.5(2)	N(2)−Ni−N(4″)	91.9(2)
N(2′)−Ni−N(4″)	88.1(2)	N(1′)−Ni−N(4″)	91.5(2)
C(1)−N(1)−Ni	114.0(4)	C(7″)−N(4″)−Ni	166.2(5)
C(2)−N(1)−Ni	105.5(3)	N(3′)−C(1)−N(1)	113.1(5)
C(2)−N(1)−C(1)	115.7(5)	N(1)−C(2)−C(3)	108.8(5)
C(3)−N(2)−Ni	105.4(3)	N(2)−C(3)−C(2)	107.7(5)
C(3)−N(2)−Ni	114.1(4)	N(3)−C(4)−N(2)	114.5(4)
C(3)−N(2)−C(4)	114.6(4)	C(6)−C(5)−N(3)	114.0(5)
C(4)−N(3)−C(5)	116.8(6)	C(5)−C(6)−C(7)	109.6(5)
C(1′)−N(3)−C(5)	112.5(5)	N(4)−C(7)−C(6)	176.2(6)
C(1′)−N(3)−C(4)	116.6(4)		

[a] Symmetry transformations used to generate equivalent atoms: prime, $-x$, $-y$, $-z + 1$; double prime, $x + 1$, y, z.

The bite angle of the five-membered chelate ring is 85.7(2)° and that of six-membered chelate ring is 94.3(2)°, which are similar to those of square-planar $[Ni(\mathbf{2})](ClO_4)_2$. However, the bite distances of five-membered and six-membered chelate rings are 2.797(6) and 3.013(7) Å, respectively, which are ca. 0.2 Å longer than those of four-coordinate $[Ni(\mathbf{2})](ClO_4)_2$. This implies that hexaaza macrocyclic ligands **1**−**4** are flexible enough to enlarge their hole size upon the change in coordination geometry. The six-membered chelate rings adopt a chair conformation and the alkyl groups appended at the bridgehead

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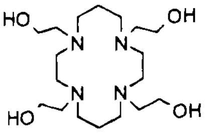
nitrogens are axial, similarly to the observation made with [Ni(**2**)](ClO$_4$)$_2$. The five-membered chelate rings assume a gauche conformation. Each macrocyclic unit adopts thermodynamically the most stable *R,R,S,S* (*trans* III) configuration. The C−N bond distances involving uncoordinated bridgehead tertiary amine N(3) are short [average 1.445(4) Å], ranging from 1.430(8) to 1.463(7) Å, and the bond angles involving N(3) are 113−117°, similarly to the observations made with [Ni(**2**)](ClO$_4$)$_2$. The nearest distance between two nickel centers is 8.269 Å along the *a* axis in an unit cell, and this is too long for the mutual interaction of Ni(II) ions.

Solution Behavior of Ni(II) Complexes of 1 and 2 in Water. Complexes [Ni(**1**)](ClO$_4$)$_2$ and [Ni(**2**)](ClO$_4$)$_2$ show the characteristic chromophore of square-planar Ni(II) macrocyclic complex in water (Table 2). Moreover, both [Ni(**1**)](ClO$_4$)$_2$ and [Ni(**2**)](ClO$_4$)$_2$ do not show any spectral change at pH = 7−13 and ionic strength (*I*) 1.0 M or at pH = 7−10.0 and *I* = 0.1 M. The Ni(II) complex of **A** also shows no spectral change at pH 7−10.0 and *I* = 0.1 M. These stand in contrast with the report for the Ni(II) complex of **C**. It has been reported that the hydroxyl pendants in **C** coordinate the intramolecular Ni(II) ion in water to give a blue solution indicative of an octahedral Ni(II) chromophore, and the octahedral Ni(II) species containing deprotonated hydroxyethyl side arms, [Ni(CH$_{-1}$)]ClO$_4$, was isolated as a blue crystal.[1] The spectral titration of the Ni(II) complex of **C** gave pK_1 = 8.75 at *I* = 0.1 M and 25 °C.[1] In view of the spectral titration results of [Ni(L)](ClO$_4$)$_2$ (**L** = **1**, **2**, and **A**) and the p*K* value reported for the coordinated hydroxyl groups of the Ni(II) complex of **C**, it is assumed that the pendant hydroxyl groups in **1** and **2** do not coordinate intra- or intermolecular Ni(II) ions and are not deprotonated in the solution at pH < 10.0 and *I* = 0.1 M.



C

$$\underset{\text{square, low spin}}{[Ni(\mathbf{L})]^{2+}} + 2H_2O \rightleftharpoons \underset{\text{octahedral, high spin}}{[Ni(\mathbf{L})(H_2O)_2]^{2+}} \qquad (2)$$

It has been reported that some macrocyclic Ni(II) complexes including **A** exist as equilibrium mixtures of square-planar and octahedral species in water.[11,14,35] The equilibrium constant for eq 2 is known to decrease when either the concentration of supporting electrolyte (e.g. NaClO$_4$) or the temperature is raised. In Table 2, it is seen that the extinction coefficients at λ_{max} measured in water are smaller than those measured in nitromethane. This implies that some of the square-planar species are converted into the octahedral species in water. The equilibrium constants for eq 2 can be estimated from $K = (\epsilon_{lim} - \epsilon)/\epsilon$, where ϵ_{lim} and ϵ represent the limiting value of molar extinction coefficient of the square-planar species and the apparent molar extinction coefficient, respectively. By the assumption that ϵ_{lim} is the same as that measured in nitromethane, the *K* values at 25 °C were estimated as 0.46 for [Ni(**1**)]$^{2+}$ and 0.40 for [Ni(**2**)]$^{2+}$. These are comparable to *K* = 0.40 for [Ni(**A**)]$^{2+}$.[11] Therefore, the spectral changes observed with Ni(II) complexes of **1**, **2**, and **A** at pH > 10.0 (*I* = 0.1 M) or at pH > 13 (*I* = 1.0 M) are attributed to the deprotonation (eq 3) of the coordinating axial water instead of pendant hydroxyl groups.

$$[Ni(\mathbf{L})(H_2O)_2]^{2+} \rightleftharpoons [Ni(\mathbf{L})(H_2O)(OH)]^{+} + H^{+} \qquad (3)$$

Conclusion

By our template synthesis, it is shown that two pendant chains containing functional groups can be conveniently appended to the nitrogen atoms at the bridgehead position of a macrocycle. The hydroxyl pendants of the hexaaza macrocycle do not coordinate Ni(II) ion in the basic aqueous solution or in the solid state. With the appropriate chain length, however, the nitrile pendant donors coordinate intermolecular Ni(II) ions to form a coordination polymer. It is expected that various coordination polymers may be designed and synthesized if the functional groups and the chain length are appropriately varied.

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Supplementary Material Available: Figures S1 and S2, showing the stereoview of the unit cell packing of [Ni(**2**)](ClO$_4$)$_2$ and the spectral titrations of [Ni(**1**)]$^{2+}$, [Ni(**2**)]$^{2+}$, and [Ni(**A**)]$^{2+}$, and Tables S1−S5, listing complete crystallographic details, anisotropic displacement parameters, and hydrogen atom positions for [Ni(**2**)](ClO$_4$)$_2$ and [Ni(**3**)]$_n$(BF$_4$)$_{2n}$ (8 pages). Ordering information is given on any current masthead page.

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