

NaCl-type layers of YSe and one atom thick layer of Se. The substructure of $\text{YSe}_{1.83}$ is tetragonal with $P4/nmm$ symmetry with $a=4.011(2)$ and $c=8.261(3)$ Å with final $R/R_w=6.4/6.9\%$. The superstructure with $a_{\text{super}}=2a$, $b_{\text{super}}=6b$ and $c_{\text{super}}=2c$ was found. The complicated superstructure reflections observed in Weissenberg photograph suggested the further ordering within Se layers.

In the powder X-ray diffraction analysis, the superstructure with $a_{\text{super}}=a$, $b_{\text{super}}=b$ and $c_{\text{super}}=2c$ was found and the occupancies in two repeating Se layers in the unit cell appear to be a little different, and also partial occupancies on Y and Se in YSe layers were revealed. The measurements of electronic and magnetic property indicate that this compound is an electronic insulator and diamagnet.

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Supplementary Material Available. Tables of observed and calculated structure factors for $\text{YSe}_{1.83}$ (2 pages) will be sent, when they are requested to the author.

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Template Synthesis of New Nickel(II) Complexes of 14-Membered Pentaaza Macrocyclic Ligands: Effects of C-Alkyl and N-Hydroxyalkyl Pendant Arms on the Solution Behaviors of the Complexes

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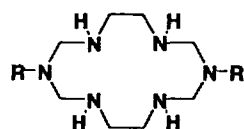
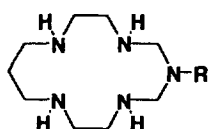
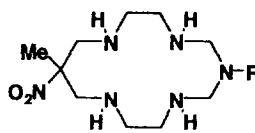
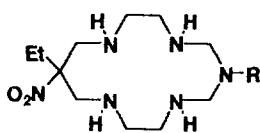
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New square planar nickel(II) complexes with various 1-alkyl (**4a-4c**) and 1-hydroxyalkyl (**4d-4f**) derivatives of the 14-membered pentaaza macrocycle 8-ethyl-8-nitro-1,3,6,10,13-pentaazacyclotetradecane have been synthesized by two-step metal template condensation reactions of ethylenediamine, nitroethane, formaldehyde, and appropriate primary amines. The nitro group and/or hydroxyl group of **4a-4f** are not directly involved in the coordination. The nickel(II) complexes exist in coordinating solvents such as MeCN, Me_2SO , and H_2O as equilibrium mixtures of the square planar $[\text{Ni}(\text{L})]^{2+}$ ($\text{L}=\text{4a-4f}$) and octahedral species $[\text{Ni}(\text{L})_2]^{2+}$ ($\text{S}=\text{solvent molecule}$). Although the ligand field strength and redox potentials of the complexes are not affected by the nature of the substituents, the formation of octahedral species for **4d-4f** in MeCN is strongly restricted by the hydroxyl group. Synthesis, characterization, and solution behaviors of the nickel(II) complexes are described.

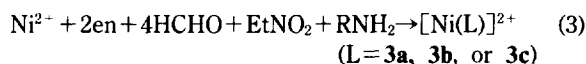
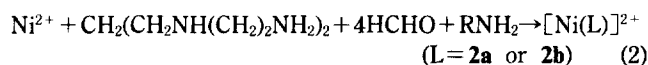
Introduction

Since properties of polyaza macrocyclic ligands and complexes are closely correlated with their structural characteristics, a variety of research has concerned the synthesis of

new types of such compounds. Especially, macrocyclic compounds with functional pendant arms such as hydroxyalkyl group have received much attention, because the introduction of a functional group into a macrocyclic compound often causes a considerable change in chemical properties.¹⁻⁶

1a: R=Me 1b: R=*n*-Pr2a: R=Me 2b: R=*n*-Pr3a: R=*n*-Pr 3b: R=*n*-Bu
3c: R=*iso*-Bu4a: R=*n*-Pr 4b: R=*n*-Bu
4c: R=*iso*-Bu
4d: R=(CH₂)₂OH
4e: R=(CH₂)₃OH
4f: R=CH₂CH(Me)OH

Various polyaza macrocyclic complexes have been prepared by template condensation reactions involving metal ions, formaldehyde, amines, and/or carbon acids.⁷⁻¹⁹ For example, the nickel(II) complexes of the hexaaza macrocycle **1a**¹¹ or **1b**¹² and the pentaaza macrocycle **2a**¹⁷ or **2b**¹⁸ have been synthesized by the reactions of eqs. (1) and (2), respectively. Recently, this type of reaction was extended to the synthesis of nickel(II) complexes of the pentaaza macrocyclic ligands **3a-3c** containing both alkylamino and nitroethane bridging groups (eq. (3)).¹⁹ It has been observed that, although the tertiary nitrogen atom and/or the nitro group of the pentaaza and hexaaza macrocycles are not involved in the coordination, chemical properties of the nickel(II) complexes of **3a-3c** are distinctly different from those of **1a** and **2a**.¹⁷⁻¹⁹



In this work, we prepared new square planar nickel(II) complexes of the pentaaza macrocycles **4a-4f** containing *C*-ethyl and *N*-alkyl or -hydroxyalkyl pendant arms from the reaction of ethylenediamine, nitropropane, formaldehyde, and appropriate primary amines. The major aim in this study is to investigate the effects of the *C*-alkyl and the functional *N*-hydroxyalkyl pendant arms on their spectral and chemical properties, with the aim of synthesis of new macrocyclic complexes. It will be shown that, although the hydroxyl group of **4d-4f** is not directly involved in coordination, solution behaviors of their nickel(II) complexes are strongly affected by the pendant arm.

Experimental

Measurements. Infrared spectra were recorded as either nujol mulls or KBr pellets on a Shimadzu IR-440 spectrophotometer, conductance measurements with a Metrohm Herisau Conductometer E518, and electronic absorption spectra with a Shimadzu UV-160 spectrophotometer. NMR spectra were recorded with a Bruker WP 300 FT NMR spec-

trometer. Elemental analyses were performed at the Korea Basic Science Center, Seoul, Korea. The cyclic voltammetric measurements were performed using a Yanaco Voltammetric Analyzer p-1000 equipped with a FG-121B function generator and a Watanabe X-Y recorder. The cyclic voltammetric data were obtained by published methods.¹¹⁻¹³

Equilibrium constants for the square planar to octahedral conversion (eq. (4)) of the nickel(II) complexes of **4a-4f** in coordinating solvents were determined from visible spectra of the complexes ($[\text{complex}] = \sim 2.0 \times 10^{-3}$ M). The temperature of the sample solution was maintained within ± 0.1 °C by using thermostated cell holder connected to a Haake D₃ circulating bath.

Materials. All chemicals used in synthesis were of reagent grade and were used without further purification. Solvents used in spectroscopic and electrochemical measurements were of spectroscopic and electroanalytical grade, respectively.

Syntheses. **[Ni(4a)](ClO₄)₂.** A methanol solution (30 mL) of Ni(OAc)₂·4H₂O (3.0 g, 0.012 mol), 99.5% ethylenediamine (1.6 mL, 0.024 mol), 97% 1-nitropropane (1.1 mL, 0.012 mol), triethylamine (0.1 mL), and paraformaldehyde (0.7 g, 0.024 mol) was heated to reflux for 15 h. After addition of 99% *n*-propylamine (1.0 mL, 0.012 mol) and paraformaldehyde (1.0 g, 0.034 mol), the resulting mixture was further heated to reflux for 20 h. An excess amount of NaClO₄ was added to the solution at room temperature. The yellow precipitates formed were filtered off, washed with methanol, and dried in air. The crude product may contain small amount of by-products such as [Ni(**1a**)](ClO₄)₂. Therefore, the product was recrystallized more than twice from hot water-acetonitrile (3 : 1) mixture. Yield: ~25%. Anal. Calcd for C₁₄H₃₂N₆NiCl₂O₁₀: C, 29.29; H, 5.62; N, 14.64%. Found: C, 28.70; H, 5.43; N, 14.79%. IR (Nujol mull): 3205 (νN-H) and 1550 cm⁻¹ (νNO₂).

[Ni(4b)](ClO₄)₂. This complex was prepared by a method similar to that for [Ni(**4a**)](ClO₄)₂ except that 99% *n*-butylamine (1.3 mL, 0.012 mol) was reacted instead of *n*-propylamine. Yield: ~25%. Anal. Calcd for C₁₅H₃₄N₆NiCl₂O₁₀: C, 30.64; H, 5.83; N, 14.29%. Found: C, 29.96; H, 5.61; N, 14.39%. IR (Nujol mull): 3200 (νN-H) and 1555 cm⁻¹ (νNO₂).

Ni(4c)](ClO₄)₂. This yellow complex was synthesized by a method similar to that for [Ni(**4a**)](ClO₄)₂ except that 98% *iso*-butylamine (1.3 mL, 0.012 mol) was used instead of *n*-propylamine. The crude product obtained was recrystallized from hot water-acetonitrile (2 : 1) mixture. Yield: ~25%. Anal. Calcd for C₁₅H₃₄N₆NiCl₂O₁₀: C, 30.64; H, 5.83; N, 14.29%. Found: C, 29.90; H, 5.60; N, 14.43%. IR (Nujol mull): 3205 (νN-H) and 1560 cm⁻¹ (νNO₂).

[Ni(4d)](ClO₄)₂. This compound was prepared as a yellow solid by a method similar to that for [Ni(**4a**)](ClO₄)₂ except that 99% 2-hydroxyethylamine (0.7 mL, 0.012 mol) was reacted instead of *n*-propylamine. The yellow product was recrystallized from hot water. Yield: ~25%. Anal. Calcd for C₁₃H₃₀N₆NiCl₂O₁₁: C, 27.11; H, 5.25; N, 14.59%. Found: C, 27.63; H, 5.37; N, 14.80%. IR (Nujol mull): 3400 (νO-H), 3195 (νN-H), and 1560 cm⁻¹ (νNO₂).

[Ni(4e)](ClO₄)₂. This yellow compound was prepared by a method similar to that for [Ni(**4a**)](ClO₄)₂ except that 97% 3-amino-1-propanol (0.9 mL, 0.012 mol) was reacted in-

stead of *n*-propylamine. The product was recrystallized from hot water. Yield: ~25%. Anal. Calcd for C₁₄H₃₂N₆NiCl₂O₁₁: C, 28.50; H, 5.47; N, 14.24%. Found: C, 29.05; H, 5.90; N, 14.52%. IR (Nujol mull): 3390 (νO-H), 3200 (νN-H), and 1560 cm⁻¹ (νNO₂).

[Ni(4f)](ClO₄)₂. This complex was prepared by a method similar to that for [Ni(4a)](ClO₄)₂ except that 93% 1-amino-2-propanol (1.0 mL, 0.012 mol) was reacted instead of *n*-propylamine. The product was recrystallized from hot water. Yield: ~25%. Anal. Calcd for C₁₄H₃₂N₆NiCl₂O₁₁: C, 28.50; H, 5.47; N, 14.24%. Found: C, 29.50; H, 5.61; N, 14.62%. IR (Nujol mull): 3410 (νO-H), 3195 (νN-H) and 1550 cm⁻¹ (νNO₂).

[Ni(L)](PF₆)₂ (L = 4a-4f). To a warm acetonitrile suspension (10 mL) of [Ni(L)](ClO₄)₂ (0.5 g) was added excess NH₄PF₆, and then the white solid NH₄ClO₄ was precipitated. The solid was removed by filtration and then water (15 mL) was added to the filtrate. The yellow solid formed was filtered off, washed with water, and dried in air.

Results and Discussion

Synthesis and Characterization. The two-step condensation reactions (see Experimental Section) of ethylenediamine, nitroethane, formaldehyde, and appropriate primary amines in the presence of nickel(II) ion, followed by addition of excess NaClO₄, produced the 14-membered pentaaza macrocyclic complexes [Ni(4*n*)](ClO₄)₂ (*n* = a-f). The synthetic procedure is similar to that for the complexes of 3a-3c.¹⁹ The yellow nickel(II) complexes [Ni(4*n*)](ClO₄)₂ are soluble in acetonitrile and nitromethane but are insoluble in methanol. The complexes of 4d-4f containing one *N*-hydroxyalkyl group are soluble in water. These complexes are decomposed very slowly even in concentrated acid solutions; electronic spectra of [Ni(4*n*)](ClO₄)₂ (2.0 × 10⁻³ M) in 0.3 M HClO₄ water-acetonitrile (1 : 1) solutions showed that <5% of the complexes was decomposed in 15 h at 25 °C. This result is similar to those observed for the complexes of other related 14-membered polyaza macrocycles.^{11,12,17-19}

The infrared spectra (see Experimental Section) of the complexes [Ni(4*n*)](ClO₄)₂ show both νNO₂ of the nitro group and νN-H of the coordinated secondary amino groups at *ca.* 1555 and 3200 cm⁻¹, respectively. In the cases of 4d-4f, νO-H of the *N*-hydroxyalkyl group is also observed at *ca.* 3400 cm⁻¹. However, no band around 1600 cm⁻¹ corresponding to primary amine group was observed. The values of molar conductances for the nickel(II) complexes measured in acetonitrile (~290 Ω⁻¹mol⁻¹cm²) and nitromethane (~140 Ω⁻¹mol⁻¹cm²) indicate that the complexes are 1 : 2 electrolytes. The ligand structures of the nickel(II) complexes of 4a-4f can be confirmed by their ¹³C NMR spectra (Table 1). Each spectrum is consistent with the corresponding ligand structure. The carbon peaks of the -C(Et)(NO₂)- group in each complex are observed at *ca.* 8, 32, and 93 ppm. The peak of N-C-N linkages is observed at *ca.* 69 ppm. The spectra also show carbon peaks corresponding to the *N*-alkyl (4a-4c) or *N*-hydroxyalkyl group (4d-4f). The electronic absorption spectra (Table 2) of the nickel(II) complexes in nitromethane show *d-d* bands at *ca.* 453 nm (ε = 58-68 M⁻¹cm⁻¹), indicating that each complex has a square planar Ni-N₄ ch-

Table 1. ¹³C NMR Spectral Data of [Ni(L)](PF₆)₂ in CD₃NO₂

L	δ, ppm								
	C(Et)NO ₂		N-C-N		N-R		Others		
4a	7.9	31.4	93.2	69.0	11.2	22.1	48.1	53.1	54.0
					52.6				
4b	7.9	31.9	92.9	69.0	14.0	20.2	48.4	53.1	54.1
					30.9	50.5			
4c	7.9	31.9	92.9	69.1	20.1	28.1	48.1	53.1	54.1
					58.3				
4d	7.9	31.9	93.0	69.1	55.3	61.8	47.9	53.3	53.9
4e	7.9	31.8	93.0	69.2	30.4	48.3	48.2	53.2	54.1
					61.0				
4f	7.8	31.9	93.0	69.5	20.9	60.1	47.9	53.1	53.9
					67.7				

Table 2. Electronic Spectra and Oxidation Potentials of the Nickel(II) Complexes

Complex	λ _{max} ^a	[Ni(L)] ²⁺ → [Ni(L)] ³⁺ ^b
	nm(ε, M ⁻¹ cm ⁻¹)	Volt vs. SCE
[Ni(4a)](ClO ₄) ₂	453(62)	+1.09
[Ni(4b)](ClO ₄) ₂	453(62)	+1.08
[Ni(4c)](ClO ₄) ₂	453(61)	+1.07
[Ni(4d)](ClO ₄) ₂	453(81)	+1.07
[Ni(4e)](ClO ₄) ₂	453(74)	+1.09
[Ni(4f)](ClO ₄) ₂	450(68)	+1.07
[Ni(3a)](ClO ₄) ₂ ^c	455(69)	+1.04

^a Measured in nitromethane at 20 °C. ^b Measured in 0.1 M (*n*-Bu)₄NClO₄ acetonitrile solutions at 20 °C. ^c Ref. 19.

romophore.^{11,12,18,19} The spectra for 4a-4c are not varied significantly with the *N*-alkyl group and are quite similar to those for 3a-3c containing the *C*-methyl group. This indicates that the ligand field strength of the complexes is not affected significantly by the variation of the alkyl groups attached to the carbon and the uncoordinated nitrogen atom. The spectra of the complexes of 4d-4f containing one *N*-hydroxyalkyl pendant arm are also similar to those of 4a-4c, strongly indicating that the hydroxyl group in each complex is not coordinated to the central metal ion. Cyclic voltammograms of the nickel(II) complexes of 4a-4f obtained in 0.1 M (*n*-Bu)₄NClO₄ acetonitrile solutions exhibited one-electron oxidation peaks corresponding to a Ni(II)/Ni(III) process. The oxidation potential of [Ni(4a)]²⁺ is +1.10 V vs. SCE, which is similar to those observed for the complexes of 3a¹⁹ and 4b-4f. This means that the electron density on the metal ion of the complexes is not affected significantly by the *C*- and *N*-substituents. The oxidation potentials, together with the spectral data, also confirm that the oxygen atom of the nickel(II) complexes of 4d-4f is not directly involved in coordination.

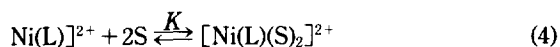
Solution Behaviors. Table 3 shows that the molar absorption coefficients of the nickel(II) complexes of 4a-4f at *ca.* 455 nm measured in coordinating solvents such as MeCN, Me₂SO, and H₂O are much lower than those measured in

Table 3. Equilibrium Constants (*K*) and Thermodynamic Parameters for the $[\text{Ni}(\text{L})]^{2+} + 2\text{S} = [\text{Ni}(\text{L})(\text{S})_2]^{2+}$ System at 25 °C

L	S	$\epsilon, \text{M}^{-1} \text{cm}^{-1a}$	K^b	$\Delta H^\circ, \text{kcal/mol}$	$\Delta S^\circ, \text{cal/K}\cdot\text{mol}$
4a	MeCN	5.5	9.9(91)	-5.0	-12.7
	Me ₂ SO	12.8	3.7(79)	-6.0	-18.0
4b	MeCN	4.0	14.2(93)	-8.7	-24.0
	Me ₂ SO	12.6	3.7(79)	-5.8	-17.1
4c	MeCN	4.0	14.0(93)	-8.5	-23.7
	Me ₂ SO	15.9	2.8(73)	-5.1	-15.5
4d	MeCN	27.8	1.8(67)	+2.8	+10.6
	Me ₂ SO	20.3	2.8(74)	-5.7	-17.4
	H ₂ O	19.7	2.9(74)	-3.4	-9.5
4e	MeCN	22.1	2.2(69)	+3.6	+13.6
	Me ₂ SO	23.1	2.1(67)	-5.3	-16.5
	H ₂ O	20.7	2.4(71)	-2.9	-8.3
4f	MeCN	10.4	4.3(81)	0 ^d	+2.7
	Me ₂ SO	16.2	2.4(70)	-5.3	-16.4
	H ₂ O	20.4	1.7(63)	-3.8	-11.9
3a^c	MeCN		4.2(81)	-3.4	-8.5
	Me ₂ SO		2.3(70)	-7.1	-18.4

^a Molar absorption coefficients at *ca.* 453 nm. ^b $K = (\epsilon_{\text{spt}} - \epsilon_{\text{obsd}}) / (\epsilon_{\text{obsd}})$ where ϵ_{obsd} and ϵ_{spt} are the molar absorption coefficients in coordinating solvent and in nitromethane, respectively; Percentage of octahedral species, $100 (\epsilon_{\text{spt}} - \epsilon_{\text{obsd}}) / \epsilon_{\text{spt}}$, is in parenthesis. ^c Ref. 19. ^d The absorption was not affected by temperature (20-35 °C).

nitromethane (Table 2). This is attributed to the fact that the nickel(II) complexes exist in the coordinating solvents as equilibrium mixtures (eq. (4)) of the square planar $[\text{Ni}(\text{L})]^{2+}$ (L = macrocyclic ligand) and octahedral $[\text{Ni}(\text{L})(\text{S})_2]^{2+}$ (S = solvent molecule) species.^{7-10,18-25} The equilibrium constants ($K = [[\text{Ni}(\text{L})(\text{S})_2]^{2+}] / [[\text{Ni}(\text{L})]^{2+}]$), percentage of octahedral species, and thermodynamic parameters calculated by the reported methods^{8,10,19-23} are also listed in Table 3.

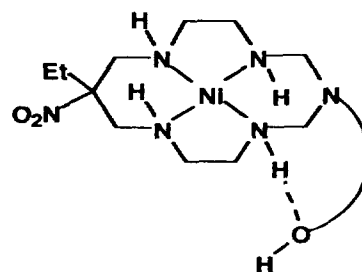


The values of ΔH° and ΔS° for the complexes of **4a-4c** containing one *N*-alkyl pendant arm are negative and are comparable to those observed for the nickel(II) complexes of **1a**, **3a**, and other 14-membered polyaza macrocyclic ligands,^{7-9,11,19-25} indicating that the formation of octahedral species arises as a consequence of a favorable enthalpic contribution. The coordination of solvent molecules to axial positions of a macrocyclic nickel(II) complex makes the in-plane Ni-N bond distances longer. The exothermicity has been attributed to the fact that the endothermic effect of the in-plane Ni-N bond weakening is overwhelmed by the exothermic effect of the Ni-S bond formation. The negative values of ΔS° has been explained by the decrease in mobility due to the formation of the Ni-S bonds.

The *K* values and the percentages of the octahedral species for **4a-4c** show that the equilibrium is not strongly affected by the variation of the *N*-alkyl group. However, interestingly, the concentration of octahedral species for **4a** in

each solution is distinctly higher than that for **3a** containing the *C*-methyl group. The introduction of bulky alkyl pendant arm to a square planar macrocyclic nickel(II) complex causes steric repulsion of the complex with axially oriented solvent molecules and makes the formation of the octahedral species more difficult.^{9,11,27} On the other hand, the alkyl group can also sterically hinder the interactions between coordinated secondary amines and solvent molecules and makes the formation of the octahedral species easier; the weaker the interaction between solvent molecule and the coordinated secondary amine group of a macrocyclic complex, the easier is the axial coordination of the solvent.^{21,26-28} The larger *K* values for **4a**, compared to those for **3a**, may indicate that the steric effect of the *C*-ethyl group on the coordinated secondary amine-solvent interactions is more significant than that on the axial Ni-S bonds. The equilibrium constants for the complexes of **4a-4c** are strongly affected by the solvents (MeCN > Me₂SO). The stronger coordination ability of MeCN, compared to Me₂SO, is generally attributed to its rod-like geometry, relatively weak interactions with the coordinated secondary amine groups, and weak self-association ability.^{19,21,24,29}

The thermodynamic parameters for the nickel(II) complexes of **4d-4f**, which contain one *N*-hydroxyalkyl group, measured in Me₂SO or H₂O are negative and are comparable to those for the complexes of **4a-4c**. However, somewhat surprisingly, the values for **4d** and **4f** in MeCN are positive. The equilibrium constant for **4f** is not affected by temperature (20-35 °C). This result is in sharp contrast to those obtained for **3a** and **4a-4c** in MeCN. It is also seen that the *K* values for **4d-4f** measured in MeCN are much smaller than those for **4a-4c** and decrease in the order of **4f** > **4e** ≥ **4d**. In the case of $[\text{Ni}(\text{4d})]^{2+}$, the axial coordination ability of MeCN is even weaker than that of Me₂SO; the *K* value is smaller in MeCN than in Me₂SO. Although the reasons for the unusual behaviors of the complexes of **4d-4f** in MeCN are not clearly understood at this time, it may be considered that such behaviors are closely correlated with the interactions between the pendant hydroxyl and the coordinated secondary amine groups. In the solution of Me₂SO or H₂O, the hydroxyl group of the complexes of **4d-4f** is readily solvated through hydrogen bonding with the solvent molecules, and therefore any significant interaction between the hydroxyl group with the coordinated amines can not be exerted. However, the interaction of the hydroxyl group with MeCN must be relatively weak; MeCN with sp hybridization is known to act as much weak base toward the interactions with protons of hydroxyl or amine groups.^{21,29,30} Therefore, it can be assumed that in MeCN solution the coordinated secondary amine group could be hydrogen bonded by the pendant hydroxyl group, as shown below.



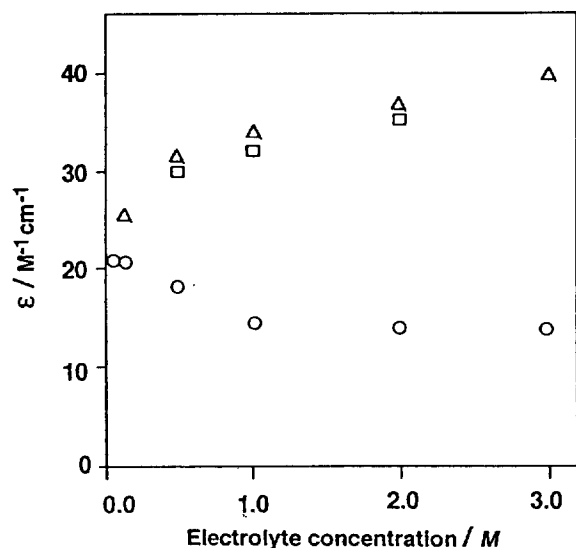


Figure 1. Variation of the absorption at 453 nm for $[\text{Ni}(\mathbf{4d})]^{2+}$ with increasing concentration of HCl(○), HClO_4 (△), and NaCl(□) at 25 °C.

The smaller K values for **4d-4f** in MeCN, compared to that for **4a-4c**, can be attributed in part to the relatively strong hydroxyl-secondary amine interaction, which sterically hinders the axial coordination of the solvent molecules. The order ($\mathbf{4f} \geq \mathbf{4e} > \mathbf{4d}$) of K values also parallels with the expectation that the hydroxyl-amine interaction is weaker for **4f** containing 2-hydroxypropyl group than for **4d** or **4e** because of the more severe steric hindrance of the former. The positive values of ΔH° for **4d** and **4e** in MeCN may indicate that the exothermic effect of the Ni-S bond formation is exceeded by the endothermic effects of the destruction of the hydrogen bonding and of the Ni-N bond weakening. In the case of **4f** ($\Delta H^\circ = 0$) the exothermic effect is counterbalanced by the endothermic effect; the exothermic effect for **4f** is less significant than that for **4d** or **4e** because of its relatively weak hydroxyl-secondary amine interaction. The positive ΔS° values for **4d-4f** in MeCN imply more disorder in the octahedral species. It is likely that the endoentropic contribution of the axial Ni-NMe bond formation is less significant than the exoentropic contribution caused by the destruction of the amine-hydroxyl interactions. To our knowledge, the complexes of **4d-4f** are rare examples that exhibit positive values of ΔH° and/or ΔS° in the equilibrium (eq. (4)).

Effects of Electrolytes. The electronic spectra of $[\text{Ni}(\text{L})]^{2+}$ (L = **4d**, **4e**, or **4f**) were also measured in aqueous solutions containing various concentration of NaX (X = Cl⁻, NO₃⁻, or ClO₄⁻) and HX to investigate the effects of the electrolytes on the solution behaviors. The proportion of the octahedral species $[\text{Ni}(\text{L})(\text{H}_2\text{O})_2]^{2+}$ in water is 63-73% at 25 °C (Table 3). Figure 1 shows that the addition of NaCl to aqueous solution of $[\text{Ni}(\mathbf{4d})]^{2+}$ increases the absorption at 453 nm, indicating the decrease in the concentration of the octahedral species. Similar behaviors were also observed upon the addition of NaNO₃ or NaClO₄ to aqueous solutions of the nickel(II) complexes of **4d-4f**. This result is attributed to the dehydrating effect of the added salts; the salts form their hydrates and reduce the concentration of free water

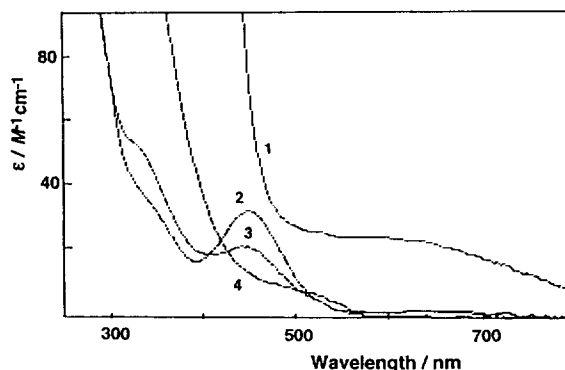
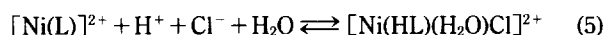


Figure 2. Electronic spectra of $[\text{Ni}(\mathbf{4d})]^{2+}$ in HNO_3 (1), HClO_4 (2), neutral water(3), and HCl(4) solutions ($[\text{complex}] = 2.0 \times 10^{-3}$ M; $[\text{acid}] = 2.0$ M).

and the octahedral species.^{8,17,31}

However, on adding HCl the absorption at 453 nm decreases, whereas two bands at ca. 330 and 520 nm corresponding to the chromophores of octahedral nickel(II) complexes become stronger (Figures 1 and 2). This result is similar to those obtained for the nickel(II) complex of **2a**.¹⁷ It is likely that the addition of HCl favors the formation of octahedral species such as $[\text{Ni}(\text{HL})(\text{H}_2\text{O})\text{Cl}]^{2+}$ (HL = monoprotonated form of L) (eq. (5)); in the solution of HCl, the uncoordinated tertiary nitrogen atom of $[\text{Ni}(\text{L})]^{2+}$ is protonated, and the resulting ammonium group assists the axial coordination of Cl⁻ ion through ion pair formation and/or hydrogen bonding with the anion.^{17,31}



Figures 1 and 2 show that the effect of HClO_4 on the spectrum is in contrast to that of HCl; the amount of the square planar species increases as the concentration of HClO_4 is increased, similarly to the result obtained with NaCl or NaClO₄. This may be related to the poor coordination ability of the anion ClO₄⁻, which is not coordinated to the central metal ion even in the acid solution.¹⁷ It has been observed that in low concentration of HClO_4 (≤ 1.0 M) the octahedral species $[\text{Ni}(\text{H}2\text{a})(\text{H}_2\text{O})_2]^{3+}$ (H2a = monoprotonated form of **2a**) is stabilized by the formation of the hydrogen bonding between the tertiary ammonium group and the axially coordinating water molecule.¹⁷ However, present result shows that the stabilizing effect is exceeded by the dehydrating effect of H⁺ and ClO₄⁻ ions even under the low concentration of the acid (≤ 1.0 M). The addition of HNO_3 (≤ 0.5 M) to the solution of $[\text{Ni}(\text{L})]^{2+}$ induced a slight increase in the absorption at ca. 453 nm. However, on adding an excess HNO_3 (≤ 1.0 M) an abrupt increase in the absorption was observed (Figure 1). This behavior is attributed to the oxidation of the complex in high concentration of HNO_3 .³¹

Conclusion

Above results show that the nickel(II) complexes prepared in this work contain 14-membered pentaaza macrocycles **4a-4f**, which are coordinated to the metal ion with a 5-6-5-6 chelate ring sequence. The nitro group and/or hydroxyl group of the macrocycles are not involved in coordination.

The C- and N-substituents of the nickel(II) complexes scarcely affect the ligand field strength and oxidation potentials. However, the square planar-to-octahedral equilibrium is largely affected by the nature of the substituents and the solvents. It is obvious that the proportion of the octahedral species for the complexes of **4d-4f** in MeCN is remarkably reduced by the formation of hydrogen bonding between the hydroxyl group and the coordinated secondary amine group. The solution behaviors of the nickel(II) complexes in water are also strongly affected by the type of added electrolyte.

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