

# Effect of Uncoordinated Tertiary Nitrogen Atoms in Hexaaza Macrocyclic Nickel(II) Complexes on Axial Binding of Anions and Water in Acidic Solutions

Seong-Jin Kim, Jang-Sik Choi, Shin-Geol Kang\*, Chang-Su Kim†, and Myunghyun Paik Suh‡

Department of Chemistry, Taegu University, Kyungsan 713-714, Korea

†Department of Chemistry Education, Taegu University, Kyungsan 713-714, Korea

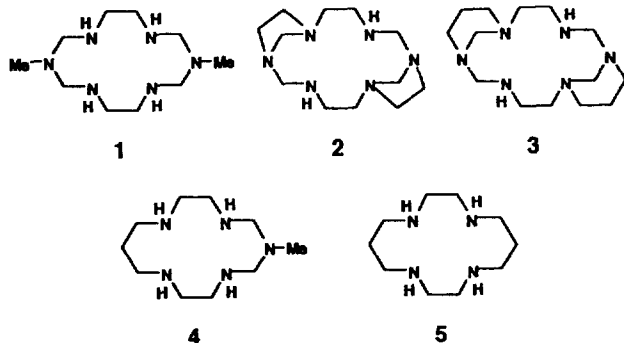
‡Department of Chemistry Education, Seoul National University, Seoul 151-742, Korea

Received October 31, 1994

Axial coordination of anions or water to the square-planar nickel(II) complexes of the hexaaza macrocyclic ligands 1, 2, and 3, which contain two extra uncoordinated tertiary nitrogens, have been investigated in aqueous solutions containing HX (X=Cl<sup>-</sup>, Br<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, or ClO<sub>4</sub><sup>-</sup>) and/or NaX. The nickel(II) complexes exist in the acidic solutions as equilibrium mixtures of the square-planar [Ni(L)]<sup>2+</sup> (L=1, 2, and 3) and octahedral species [Ni(H<sub>2</sub>L)X<sub>2</sub>]<sup>2+</sup> (H<sub>2</sub>L=diprotinated form of L). Some octahedral complexes have been isolated and characterized. The solution behaviors of the complexes indicate that the formation of the octahedral complexes are significantly promoted by the protonation of the uncoordinated tertiary amines. The proportion of the octahedral complexes depends on the type of acid, and increases in the order of HBr<HNO<sub>3</sub><HCl.

## Introduction

Square-planar nickel(II) complexes with various saturated polyaza macrocyclic ligands have been prepared and investigated.<sup>1-6</sup> The ligands 1-4 coordinate nickel(II) ion to form square-planar complexes with a 5-6-5-6 chelate ring sequence,<sup>1-3</sup> similarly to 5.<sup>4,5</sup> Two tertiary amine groups at the bridgehead positions in 1-4 are not involved in the coordination.<sup>1-3</sup> The nickel(II) complexes of 1-5 are known to exist in water as equilibrium mixtures (eq. (1)) of low-spin square-planar [Ni(L)]<sup>2+</sup> (L=1-5) and high-spin octahedral [Ni(L)(H<sub>2</sub>O)<sub>2</sub>]<sup>2+</sup> species and the equilibrium constants (*K* in eq. (1)) are markedly dependant on the structures of the macro-

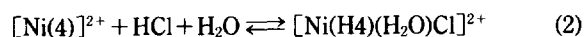


cyclic ligands.<sup>1,3,5-8</sup> The complexes also react with SCN<sup>-</sup> to form octahedral complexes [Ni(L)(SCN)<sub>2</sub>]<sup>2+</sup> but not with weaker ligands Cl<sup>-</sup>, Br<sup>-</sup>, and NO<sub>3</sub><sup>-</sup> in the aqueous solution.<sup>2,9-11</sup>



It has been generally understood that formation of hydrogen bonding between water molecules and the coordinated secondary amine groups of a polyaza macrocyclic nickel(II) complex prevents the axial coordination of water and the anions.<sup>7,8,10-12</sup> Fabbrizzi *et al.*,<sup>3</sup> however, recently reported

that octahedral complex [Ni(H4)(H<sub>2</sub>O)Cl]<sup>2+</sup> (H4=monoprotonated form of 4) formed as the square-planar complex [Ni(4)]<sup>2+</sup> was protonated in concentrated HCl (eq. (2)). The stability of the octahedral complex was explained by the formation of hydrogen bonding between the trialkylammonium function of the uncoordinated tertiary amine and the axial water molecule or Cl<sup>-</sup> ion. However, the effect of the protonation on the axial binding has been investigated only for the nickel(II) complex of 4 and it was observed only in solutions without isolation of the octahedral species.



We have been interested in elucidating the effects of various strong acids such as HCl, HBr, HNO<sub>3</sub>, and HClO<sub>4</sub> on the formation of the octahedral nickel(II) species for hexaaza macrocyclic ligands 1-3 which contain two extra uncoordinated tertiary nitrogens at the bridgehead position. This paper reports solution behaviors of the nickel(II) complexes of hexaaza macrocyclic ligands 1-3, and the isolation and characterization of octahedral nickel(II) complexes [Ni(H<sub>2</sub>L)X<sub>2</sub>]<sup>2+</sup> (H<sub>2</sub>L=diprotinated form of 1, 2, or 3; X=Cl<sup>-</sup>, Br<sup>-</sup>, or NO<sub>3</sub><sup>-</sup>).

## Experimental

**Measurements.** Visible spectra were recorded on a Shimadzu UV-160 spectrophotometer. Infrared spectra were obtained on a Shimadzu IR-440 spectrophotometer using Nujol mulls. Conductance were measured by using a Metrohm Herisau Conductometer E518. Elemental analyses were performed at the Basic Science Center, Seoul, Korea. pH measurements were performed with a Corning pH Meter Model 220.

**Study on the Solution Behavior of Nickel(II) Complexes.** The conversion of square-planar to octahedral species for the nickel(II) complexes of 1-3 were observed with the electronic spectra in aqueous solutions containing various

acids. The temperature of the sample solutions was maintained within  $\pm 0.1$  °C by using a thermostated cell holder connected to a Haake D<sub>3</sub> circulating bath. The concentration of square-planar complex  $[\text{Ni}(\text{L})]^{2+}$  was estimated by the methods reported previously.<sup>1,3,6,13</sup>

**Synthesis.** Nickel(II) complexes  $[\text{Ni}(\text{L})](\text{ClO}_4)_2$  (L = 1, 2, or 3) were prepared by the methods reported previously.<sup>1,2</sup>

**Safety Note.** Caution! Perchlorate salts of metal complexes with organic ligands are explosive. Only small amounts of material should be prepared, and these should be handled with great caution.

**$[\text{Ni}(\text{H}_2\text{1})\text{Cl}_2]\text{Cl}(\text{ClO}_4)$ .** An excess amount of 35% HCl (*ca.* 7.0 mL) was added to an aqueous suspension (10 mL) of  $[\text{Ni}(\text{1})](\text{ClO}_4)_2$  (1.0 g). To the resulting purple solution was added an excess amount (*ca.* 5 mL) of 60% HClO<sub>4</sub>. The mixture was stored at room temperature until the purple precipitates formed. The product was filtered off, washed with ethanol, and dried *in vacuo*. Yield: ~30%. Anal. Calcd for NiC<sub>10</sub>H<sub>28</sub>N<sub>6</sub>Cl<sub>4</sub>O<sub>4</sub>: C, 24.15; H, 5.63; N, 16.90%. Found: C, 24.32; H, 5.46; N, 16.78%. IR (cm<sup>-1</sup>): 3220 (2° amine), 2720 (3° ammonium), and 1100 (br, ClO<sub>4</sub><sup>-</sup>).

**$[\text{Ni}(\text{H}_2\text{2})\text{Cl}_2]\text{Cl}(\text{ClO}_4)$ .** The purple complex was prepared by the method similar to that for  $[\text{Ni}(\text{H}_2\text{1})\text{Cl}_2]\text{Cl}(\text{ClO}_4)$  by using  $[\text{Ni}(\text{2})](\text{ClO}_4)_2$  and 35% HCl. Yield: >40%. Anal. Calcd for NiC<sub>12</sub>H<sub>28</sub>N<sub>6</sub>Cl<sub>4</sub>O<sub>4</sub>: C, 27.67; H, 5.42; N, 16.13%. Found: C, 27.76; H, 6.00; N, 16.08%. IR (cm<sup>-1</sup>): 3245 (2° amine), 2600 (br, 3° ammonium), and 1100 (br, ClO<sub>4</sub><sup>-</sup>).

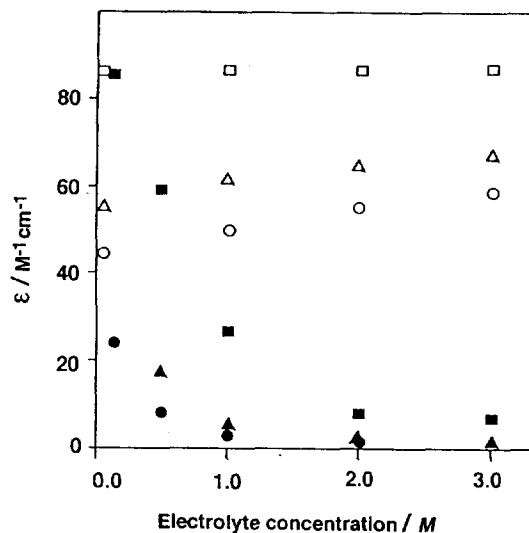
**$[\text{Ni}(\text{H}_2\text{3})\text{Cl}_2](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ .** This complex was prepared by the method similar to that for  $[\text{Ni}(\text{H}_2\text{1})\text{Cl}_2]\text{Cl}(\text{ClO}_4)$  by using  $[\text{Ni}(\text{3})](\text{ClO}_4)_2$  and 35% HCl. Yield: ~50%. Anal. Calcd for NiC<sub>14</sub>H<sub>36</sub>N<sub>6</sub>Cl<sub>4</sub>O<sub>10</sub>: C, 25.91; H, 5.59; N, 12.95%. Found: C, 25.94; H, 6.08; N, 12.92%. IR (cm<sup>-1</sup>): 3450 (H<sub>2</sub>O), 3270 (2° amine), 2720 (br, 3° ammonium), 1640 (H<sub>2</sub>O), and 1100 (br, ClO<sub>4</sub><sup>-</sup>).

**$[\text{Ni}(\text{H}_2\text{1})\text{Br}_2]\text{Br}_2$ .** The addition of an excess amount of 47% HBr to an aqueous suspension of  $[\text{Ni}(\text{1})](\text{ClO}_4)_2$  produced the purple precipitate. The precipitate was filtered off, washed with ethanol, and dried *in vacuo*. Yield: ~50%. Anal. Calcd for NiC<sub>10</sub>H<sub>28</sub>N<sub>6</sub>Br<sub>4</sub>: C, 19.67; H, 4.59; N, 13.77%. Found: C, 19.45; H, 5.04; N, 13.91%. IR (cm<sup>-1</sup>): 3220 (2° amine), and 2500 (br, 3° ammonium).

**$[\text{Ni}(\text{H}_2\text{2})\text{Br}_2](\text{ClO}_4)_2$ .** The purple complex was prepared by the method similar to that for  $[\text{Ni}(\text{H}_2\text{1})\text{Br}_2]\text{Br}_2$  except that  $[\text{Ni}(\text{2})](\text{ClO}_4)_2$  was employed instead of  $[\text{Ni}(\text{1})](\text{ClO}_4)_2$ . Yield: ~40%. Anal. Calcd for NiC<sub>12</sub>H<sub>28</sub>N<sub>6</sub>Br<sub>2</sub>Cl<sub>2</sub>O<sub>8</sub>: C, 21.39; H, 4.19; N, 12.47%. Found: C, 21.74; H, 4.54; N, 12.65%. IR (cm<sup>-1</sup>): 3240 (2° amine), 2500 (br, 3° ammonium), and 1100 (br, ClO<sub>4</sub><sup>-</sup>).

**$[\text{Ni}(\text{H}_2\text{3})\text{Br}_2]\text{Br}_2$ .** The blue-purple complex was prepared by the method similar to that for  $[\text{Ni}(\text{H}_2\text{1})\text{Br}_2]\text{Br}_2$  by using  $[\text{Ni}(\text{3})](\text{ClO}_4)_2$  and 47% HBr. Yield: ~40%. Anal. Calcd for NiC<sub>14</sub>H<sub>32</sub>N<sub>6</sub>Br<sub>4</sub>: C, 25.37; H, 4.87; N, 12.68%. Found: C, 25.57; H, 5.21; N, 12.66%. IR (cm<sup>-1</sup>): 3140 (2° amine) and 2400 (br, 3° ammonium).

**$[\text{Ni}(\text{H}_2\text{2})(\text{NO}_3)_2](\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ .** To an aqueous solution of  $[\text{Ni}(\text{2})](\text{ClO}_4)_2$ , was added 61% HNO<sub>3</sub> and then 60% HClO<sub>4</sub>. The purple solid formed, which was filtered off, washed with ethanol, and dried *in vacuo*. Yield: ~30%. Anal. Calcd for NiC<sub>12</sub>H<sub>36</sub>N<sub>8</sub>Cl<sub>2</sub>O<sub>18</sub>: C, 20.30; H, 5.11; N, 15.78%. Found: C, 20.49; H, 5.83; N, 15.88%. IR (cm<sup>-1</sup>): 3450 (H<sub>2</sub>O), 3180 (2° amine), 2700 (br, 3° ammonium), 1640 (H<sub>2</sub>O), 1385



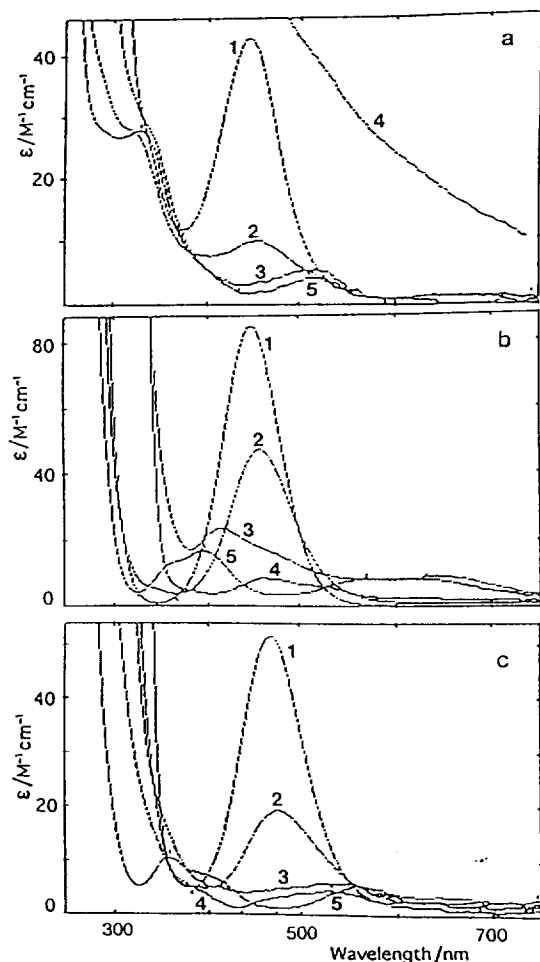
**Figure 1.** Variation of the absorption at  $\lambda_{\text{max}}$  for the square-planar  $[\text{Ni}(\text{L})]^{2+}$  with increasing concentration of NaCl (L=1(○); 2(□); 3(△)) and HCl (L=1(●); 2(■); 3(▲)).

(br, NO<sub>3</sub><sup>-</sup>), and 1100 (br, ClO<sub>4</sub><sup>-</sup>).

## Results and Discussion

**Solution Behaviors.** The electronic spectra were measured with aqueous solutions of the hexaaza macrocyclic nickel(II) complexes containing various concentration of HX and/or NaX (X = Cl<sup>-</sup>, Br<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, or ClO<sub>4</sub><sup>-</sup>). The concentration of the square-planar complex in each solution was estimated from the absorbance at 446 nm for  $[\text{Ni}(\text{1})]^{2+}$ , 445 nm for  $[\text{Ni}(\text{2})]^{2+}$ , and 468 nm for  $[\text{Ni}(\text{3})]^{2+}$  assuming that the molar absorption coefficients in nitromethane were identical with those of the square-planar complexes.<sup>1,6,12,13</sup> Figure 1 shows that the addition of NaCl to the aqueous solutions of  $[\text{Ni}(\text{1})]^{2+}$  and  $[\text{Ni}(\text{3})]^{2+}$  results in an increase in the absorption at 446 and 468 nm, respectively, indicating the increase in the proportion of the square-planar species. The similar behavior was observed upon the addition of NaBr, NaNO<sub>3</sub>, or NaClO<sub>4</sub>. This clearly shows that the added salts behave as inert electrolytes and reduce the concentration of octahedral  $[\text{Ni}(\text{L})(\text{H}_2\text{O})_2]^{2+}$  species in water. It has been known that the salts dissolved in water form their hydrates and reduce the effective concentration of free water. Thus, the proportion of the octahedral species decreases as the concentration of the salt is increased. In the case of  $[\text{Ni}(\text{2})]^{2+}$ , the spectra are rarely affected by the concentration of added NaCl, which indicates that almost all the complex exists in water as the square-planar species in the absence of the salt.<sup>2,6</sup>

Figure 1 also shows that the increase in the concentration of HCl decreases the absorption of  $[\text{Ni}(\text{L})]^{2+}$  (L=1-3). This result is in contrast to the observations made upon the addition of NaCl. For all cases except  $[\text{Ni}(\text{1})]^{2+}$  with HNO<sub>3</sub>, the addition of an excess HBr, HNO<sub>3</sub> or HClO<sub>4</sub> to the aqueous solutions of the nickel(II) complexes also decreases the absorptions at ~450 nm (Figure 2), indicating the decrease in the concentration of the square-planar species. Such behaviors have never been observed for the complexes of tetraaza



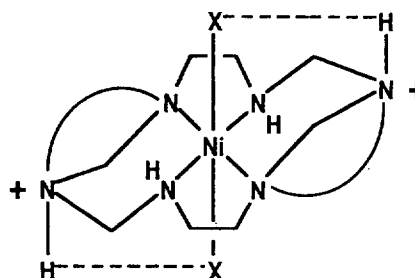
**Figure 2.** Electronic spectra of  $[\text{Ni}(1)]^{2+}$  (a),  $[\text{Ni}(2)]^{2+}$  (b), and  $[\text{Ni}(3)]^{2+}$  (c) in neutral water (1) and in the presence of  $\text{HClO}_4$ (2),  $\text{HBr}$ (3),  $\text{HNO}_3$ (4), and  $\text{HCl}$ (5) solutions ( $[\text{complex}] = 5 \times 10^{-3} \text{ M}$ ;  $[\text{Acid}] = 3.0 \text{ M}$ ).

macrocycles such as 5 which does not contain uncoordinated amine groups; the addition of either  $\text{HCl}$  or  $\text{NaCl}$  to the aqueous solution of  $[\text{Ni}(5)]^{2+}$  increases the concentration of the square-planar species.<sup>3</sup> The decomposition of the complexes in the acidic solutions was not observed during the measurements; the nickel(II) complexes of 1-3 dissociate very slowly in highly acidic solution.<sup>1,2</sup> It is assumed that the hexaaza macrocyclic complexes exist in aqueous solutions with added acid  $\text{HX}$  as the equilibrium mixtures of the square-planar  $[\text{Ni}(\text{L})]^{2+}$  and octahedral species such as  $[\text{Ni}(\text{L})(\text{H}_2\text{O})_2]^{2+}$ ,  $[\text{Ni}(\text{HL})(\text{H}_2\text{O})\text{X}]^{2+}$ ,  $[\text{Ni}(\text{H}_2\text{L})\text{X}_2]^{2+}$ ,  $[\text{Ni}(\text{HL})(\text{H}_2\text{O})_2]^{3+}$ , and  $[\text{Ni}(\text{H}_2\text{L})(\text{H}_2\text{O})_2]^{4+}$ . For all cases except  $[\text{Ni}(1)]^{2+}$  in  $\text{HNO}_3$ , the bands at 300-410 nm and 510-650 nm which correspond to chromophore of the octahedral species appears upon the addition of the acids (Figure 2). In addition, the wavelength of the maximum absorption was strongly affected by the type of the acids. Percentage of the square-planar species of the nickel(II) complexes in aqueous solutions containing various amount of the strong acids is listed in Table 1. In the presence of same concentration of acid the proportion of the square-planar species depends on the type of acid, and decreases in the order of  $\text{HClO}_4 > \text{HBr} >$

**Table 1.** Percentage of the Square-planar Species for  $[\text{Ni}(\text{L})]^{2+}$  ( $\text{ClO}_4$ )<sub>2</sub> in Water Containing Various Acids (HX) at 25 °C<sup>a,b</sup>

L	X	[HX], M							
		0	0.1	0.5	1.0	2.0	3.0	4.0	4.6
1 <sup>d</sup>	$\text{Cl}^-$	70	37	11	6	5	<4	<3	
	$\text{Br}^-$		54	25	16	11	9	<7	<5
	$\text{NO}_3^-$		51	30	<sup>c</sup>	<sup>c</sup>	<sup>c</sup>		
	$\text{ClO}_4^-$		59	32	24	18	19	25	27
2 <sup>e</sup>	$\text{Cl}^-$	96	94	66	29	8	<5		
	$\text{Br}^-$			92	77	39	31	26	20
	$\text{NO}_3^-$			90	66	20	9	<8	<7
	$\text{ClO}_4^-$			93	84	72	52	52	55
3 <sup>f</sup>	$\text{Cl}^-$	63		19	6	<3			
	$\text{Br}^-$			52	38	22	11	<5	
	$\text{NO}_3^-$			28	13	<sup>g</sup>	<3		
	$\text{ClO}_4^-$			58	51	30	24	18	19

<sup>a</sup>Percentage of the square-planar species is defined as  $(\epsilon_{\text{obsd}}/\epsilon_{\text{sqpl}}) \times 100$  where  $\epsilon_{\text{obsd}}$  and  $\epsilon_{\text{sqpl}}$  are the molar absorptivities in acid solution and in nitromethane, respectively. <sup>b</sup>Concentration of complexes:  $1.0 \times 10^{-3} \text{ M}$ . <sup>c</sup>The value could not be obtained because of an abrupt increase in the absorption (see also Figure 2). <sup>d</sup>Measured at 446 nm. <sup>e</sup>Measured at 445 nm. <sup>f</sup>Measured at 468 nm.



**Figure 3.** Proposed structure of the octahedral complex  $[\text{Ni}(\text{H}_2)\text{X}_2]^{2+}$  or  $[\text{Ni}(\text{H}_2\text{3})\text{X}_2]^{2+}$  in an aqueous solution containing excess  $\text{HX}$  ( $\text{X} = \text{Cl}^-$ ,  $\text{Br}^-$ , or  $\text{NO}_3^-$ ).

$\text{HNO}_3 > \text{HCl}$  (Figure 2 and Table 1). The similar trends were observed as  $\text{NaBr}$ ,  $\text{NaNO}_3$ , or  $\text{NaCl}$  was added to 0.1 M  $\text{HClO}_4$  solutions of the complexes. These results indicate that the anions of the added acids coordinate to the nickel(II) complexes to form octahedral species and that the coordinating ability of the anions increases in the order of  $\text{Br}^- < \text{NO}_3^- < \text{Cl}^-$ . Therefore, the formation of the octahedral species in the acidic solutions must be attributed to the protonation of the uncoordinated nitrogen atoms as well as the coordination of the anions. The octahedral species were isolated as  $[\text{Ni}(\text{H}_2\text{L})\text{X}_2]^{2+}$ , which may be stabilized by the hydrogen bonding and/or formation of ion pairs between the trialkylammonium groups of the macrocyclic ligand and the axial anions. X-ray structures of the square-planar complexes of 1-3 indicated that the complexes have *R,R,S,S*-(trans-III) conformation and the partial contribution of  $\text{sp}^2$  hybridization at the bridgehead nitrogen atoms.<sup>2,6,14</sup> The proposed structure of the octahedral complex in acidic solutions is presented in Figure 3.

In a given concentration of any acid, the proportion of the square-planar species depends on the macrocyclic ligand structure and decreases in the order of 2>3>1 (Table 1). This indicates that formation of the octahedral species for the monocyclic ligand 1 is easier than that for the tricyclic ligands 2 and 3. The in-plane Ni-N bond distances are longer in octahedral species than in square-planar species.<sup>15,16</sup> Therefore, the formation of octahedral species should be affected by the Ni-N bond distance of the square-planar complex and the flexibility of the macrocyclic ligand.<sup>5,12</sup> The monocyclic ligand 1 must be more flexible than the macrotricycles 2 and 3. The average Ni-N bond distance of the square-planar nickel(II) complex of 3 are longer than that of 2.<sup>2,6</sup> The easy formation of the octahedral species for [Ni(3)]<sup>2+</sup>, compared to that for [Ni(2)]<sup>2+</sup>, can be attributed to the longer Ni-N bond distance.<sup>6</sup>

Addition of HNO<sub>3</sub> to the solution of [Ni(1)]<sup>2+</sup> results in a decrease in the proportion of the square-planar species in the concentration range [HNO<sub>3</sub>]=0.1-0.5 M (Table 1), indicating the formation of [Ni(H<sub>2</sub>1)(NO<sub>3</sub>)<sub>2</sub>]<sup>2+</sup>. However, at the higher concentration of HNO<sub>3</sub> an abrupt increase in the absorption occurs (Figure 1), which is in contrast to the observations made for the other systems. It has been observed that the oxidation of the nickel(II) complex of 1 (E<sub>ox</sub>=+0.93 V vs. SCE) to nickel(III) species is much easier than those for the nickel(II) complexes of 2 (+1.50 V vs. SCE) and 3 (+1.34 V vs. SCE).<sup>1,6</sup> Therefore, the exceptional behavior of [Ni(1)]<sup>2+</sup> in high concentration of HNO<sub>3</sub> is attributed to the oxidation of the nickel(II) ion.<sup>17,18</sup> The isolation of the oxidized product was not attempted in this work.

Table 1 also shows that the amount of the square-planar species decreases as the concentration of HClO<sub>4</sub> is increased ([HClO<sub>4</sub>]≤3.0 M), similar to the results obtained with HCl, HBr, and HNO<sub>3</sub>. However, further addition of the acid (≥4.0 M) increases the amount of the square-planar species. This can be attributed to the coordination of water molecules instead of the weakly coordinating ClO<sub>4</sub><sup>-</sup> anion.<sup>3</sup> It can be suggested that, at lower concentration of HClO<sub>4</sub>, the ammonium groups can stabilize the octahedral species [Ni(H<sub>2</sub>L)(H<sub>2</sub>O)<sub>2</sub>]<sup>4+</sup> through the hydrogen bonding with the axially coordinating water molecules. At the higher concentration of HClO<sub>4</sub> (≥4.0 M), however, it is exceeded by the dehydrating effect of excess H<sup>+</sup> and ClO<sub>4</sub><sup>-</sup> ions and reduces the amount of the octahedral species.

**Synthesis and Properties of the Octahedral Complexes.** The isolation of octahedral complexes [Ni(H<sub>2</sub>L)X<sub>2</sub>]<sup>2+</sup> (L=1-3; X=Cl<sup>-</sup>, Br<sup>-</sup>, or NO<sub>3</sub><sup>-</sup>) was attempted. The addition of excess HX (X=Cl<sup>-</sup>, Br<sup>-</sup>, or NO<sub>3</sub><sup>-</sup>) and/or HClO<sub>4</sub> to aqueous solutions of the square-planar nickel(II) complexes of 1-3 produced perchlorate or bromide salts of [Ni(H<sub>2</sub>L)X]<sup>2+</sup> in high yield (see Experimental Section). The octahedral complexes were relatively unstable to the atmospheric moisture at room temperature and slowly decomposed to corresponding yellow square-planar complexes. As HClO<sub>4</sub> and HNO<sub>3</sub> were added to an aqueous solution of [Ni(3)]<sup>2+</sup>, purple solid [Ni(H<sub>2</sub>3)(NO<sub>3</sub>)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> was isolated, which was rapidly decomposed to its yellow square-planar form. All attempts to prepare octahedral complexes [Ni(H<sub>2</sub>L)(ClO<sub>4</sub>)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> were unsuccessful.

Infrared spectra (see Experimental Section) of the octahedral complexes show N-H stretchings for the coordinated

**Table 2.** Properties of Octahedral Nickel(II) Complexes

Complex	Color	$\lambda_{max}$ , <sup>a</sup>		$\Lambda_M$ , <sup>a</sup>	
		nm ( $\epsilon$ , M <sup>-1</sup> cm <sup>-1</sup> )		$\Omega^{-1}$ mol <sup>-1</sup> cm <sup>2</sup>	pH <sup>c</sup>
[Ni(1)](ClO <sub>4</sub> ) <sub>2</sub>	yellow		447(44)	225	7.02
[Ni(H <sub>2</sub> 1)Cl <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	purple	510 <sup>b</sup>	448(41)	760	2.95
[Ni(H <sub>2</sub> 1)Br <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	purple	537 <sup>b</sup>	447(44)	820	2.85
[Ni(2)](ClO <sub>4</sub> ) <sub>2</sub>	yellow		450(86)	238	6.91
[Ni(H <sub>2</sub> 2)Cl <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	purple	538 <sup>b</sup>	446(85)	970	2.95
[Ni(H <sub>2</sub> 2)Br <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	purple	517 <sup>b</sup>	445(86)	1206	2.90
[Ni(H <sub>2</sub> 2)(NO <sub>3</sub> ) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub> ·4H <sub>2</sub> O	purple	530 <sup>b</sup>	446(71)	954	2.97
[Ni(3)](ClO <sub>4</sub> ) <sub>2</sub>	yellow		468(55)	198	6.97
[Ni(H <sub>2</sub> 3)Cl <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub> ·2H <sub>2</sub> O	purple	585 <sup>b</sup>	469(26)	535	3.45
[Ni(H <sub>2</sub> 3)Br <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	blue-purple	592 <sup>b</sup>	467(53)	955	3.15

<sup>a</sup>Measured in water at 25 °C otherwise specified; [complex]=1.0×10<sup>-3</sup> M. <sup>b</sup>Measured with Nujol Mull.

secondary amines and the tertiary ammonium groups around 3200 and 2700 cm<sup>-1</sup>, respectively. The electronic absorption spectra (Table 2) of the octahedral complexes (Nujol mulls) show the bands at 510-590 nm, which correspond to the octahedral nickel(II) chromophores.<sup>3,10</sup> However, the spectra measured in aqueous solutions are rather similar to those for the corresponding square-planar complexes, indicating that the protons and coordinated anions are readily removed in the solution. The high molar conductance values and low pH values (Table 2) measured for the aqueous solutions of the octahedral complexes ([complex]=1.0×10<sup>-3</sup> M) confirm the dissociation of the protons and coordinated anions from the complexes. The pH values (2.90-3.45) measured for the octahedral complexes (1.0×10<sup>-3</sup> M) also indicate that the uncoordinated amine groups of the complexes behave as weaker base than the simple trialkylamines.<sup>19</sup> This may be attributed to the back-strain of the tertiary amines in 1-3, which decreases s-character of lone pair electrons of the nitrogens and weakening the basicity of the amines.<sup>19</sup> The partial contribution of sp<sup>2</sup> hybridization on the uncoordinated tertiary nitrogens in 2 and 3 was shown by the X-ray crystal structures.<sup>2,6,14</sup> The weak basicity of the amine groups of the hexaaza macrocyclic complexes makes the coordination of the anions as well as the protonation of the macrocycles only at the high concentration of acid.

For [Ni(H<sub>2</sub>3)Cl<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>·2H<sub>2</sub>O, the observed molar absorption coefficient at 469 nm and molar conductance values in water are much lower than those of [Ni(H<sub>2</sub>3)Br<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>. Furthermore, the pH value (3.45) of the former is higher than that for the latter (3.15). This result indicates that the degree of formation of square-planar species due to the dissociations of the protons and the coordinated chloride is lower in [Ni(H<sub>2</sub>3)Cl<sub>2</sub>]<sup>2+</sup> than in [Ni(H<sub>2</sub>3)Br<sub>2</sub>]<sup>2+</sup>. This may be attributed to the better coordinating ability of Cl<sup>-</sup> than Br<sup>-</sup> ion.

**Summary.** The solution behaviors of [Ni(L)]<sup>2+</sup> (L=1, 2, or 3) and the synthesis of the octahedral species [Ni(H<sub>2</sub>L)X<sub>2</sub>]<sup>2+</sup> clearly show that the coordination of the anions and/or water molecules is assisted by the protonation of the uncoor-

minated trialkylamine groups of the macrocycle. The formation of the octahedral species accompanied by the protonation is also affected by the coordinating ability of the anion.

**Acknowledgment.** This work was supported by the Basic Science Research Program (1994), the Ministry of Education of the Republic of Korea.

### References

1. Suh, M. P.; Kang, S.-G. *Inorg. Chem.* **1988**, *27*, 2544.
2. Suh, M. P.; Shin, W.; Kang, S.-G.; Lah, M. S.; Chung, T. M. *Inorg. Chem.* **1989**, *28*, 1602.
3. Fabbrizzi, L.; Lanfred, A. M. M.; Pallavicini, P.; Perrotti, A.; Taglietti, A.; Ugozzoli, F. *J. Chem. Soc., Dalton Trans.* **1991**, 3263.
4. Bosnich, B.; Tobe, M. L.; Webb, G. A. *Inorg. Chem.* **1965**, *4*, 1109.
5. Melson, G. A. *Coordination Chemistry of Macrocyclic Compounds*; Plenum Press: New York, U. S. A, 1979.
6. Suh, M. P.; Kang, S.-G.; Goedken, V. L.; Park, S.-H. *Inorg. Chem.* **1991**, *30*, 365.
7. Vice, G. S.; Watkins, C. L.; Bowen, H. F. *Inorg. Chim. Acta* **1979**, *35*, 255.
8. Iwamoto, E.; Yokoyama, T.; Yamasaki, S.; Yabe, T.; Kumoramaru, T.; Yamamoto, Y. *T. J. Chem. Soc., Dalton Trans.* **1988**, 1935 and references therein.
9. Kang, S.-G.; Kim, S.-J. Unpublished Results.
10. Mochizuki, K.; Suwabe, M.; Ito, T. *Bull. Chem. Soc. Japan* **1990**, *63*, 3024.
11. Ito, T.; Tsutsumi, K.; Ito, H. *Bull. Chem. Soc. Japan* **1981**, *54*, 1096.
12. Kang, S.-G.; Jung, S.-K. *J. Korean Chem. Soc.* **1991**, *35*, 527.
13. Hay, R. W.; Jeragh, B.; Ferguson, G.; Kaiter, B.; Rule, B. L. *J. Chem. Soc., Dalton Trans.* **1982**, 1531.
14. Suh, M. P.; Shim, B. Y.; Yoon, T. S. *Inorg. Chem.*, In press, 1994.
15. Mochizuki, K.; Fujimoto, M.; Ito, H.; Ito, T. *Bull. Chem. Soc. Japan* **1980**, *53*, 2535.
16. Martin, L. Y.; Sperati, D. R.; Busch, D. H. *J. Am. Chem. Soc.* **1977**, *99*, 2968.
17. McAuley, M.; Palmer, T.; Whitcombe, T. W. *Can. J. Chem.* **1993**, *71*, 1792.
18. Gore, E. S.; Busch, D. H. *Inorg. Chem.* **1973**, *12*, 1.
19. Huheey, J. E.; Keiter, E. A.; Keiter, R. L.; *Inorganic Chemistry: Principles of Structures and Reactivity*, 4th Ed.; Harper Collins College Publisher; New York, U. S. A. 1993; pp 329-344.

## Determination of Nitrate in Chromium Plating Solution with Nitrate-Selective Electrodes

You Ra Kang, Won Lee<sup>1</sup>, Hwang Huh<sup>2</sup>, Geun Sig Cha, and Hakhyun Nam<sup>\*</sup>

Department of Chemistry, Kwang Woon University, Seoul 139-701, Korea

<sup>1</sup>Research Institute for Basic Science and Department of Chemistry, Kyunghee University, Seoul 130-701, Korea

<sup>2</sup>Department of Chemistry, Ulsan University, Ulsan 680-190, Korea

Received November 10, 1994

A method for determining nitrate in post treatment chromium plating solutions with PVC-based nitrate-selective electrodes is described. PVC-based nitrate-selective membranes which contain TDMANO<sub>3</sub> ion-exchanger in PVC/NPOE, PVC/DOA or PVC/DBP matrices, and a commercially available Corning electrode (No. 476134) have been compared in respect of their detection limits, response slopes, selectivities at various pHs, and dynamic response to the hydrochromate ion in basic condition. The PVC/DBP/TDMANO<sub>3</sub> membrane electrode was chosen as the ISE detector for the determination of nitrate in the presence of hydrochromate interference. The amount of nitrate in real post treatment chromium plating solution could be determined successfully with this electrode in both static and flow-injection measurements when the sample was properly diluted with an alkaline buffer.

### Introduction

Nitrate is commonly monitored for environmental, ecological and agricultural investigations, and for the control of some industrial processes.<sup>1,2</sup> The amounts of nitrate in various samples, such as in foods, industrial effluents, wastes, soil and water, have been determined with numerous methods.<sup>1-6</sup> Among many analytical methods developed to date nitrate-selective electrodes have emerged as one of the

most promising tool for those purposes, especially for *in situ* monitoring of industrial samples.<sup>6-15</sup>

Ion-selective electrodes offer many advantages over other analytical techniques in the analysis of industrial samples or in the control of a particular chemical species in a process stream.<sup>2</sup> ISEs have high selectivities over a wide dynamic range (typically from 10<sup>-1</sup> to 10<sup>-5</sup> M), exhibit fast response times (seconds to few minutes) and can be adapted easily to a flow through analysis system. Unlike most photometric