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Syntheses and Properties of New Nickel(II) Complexes of 14-Membered Pentaaza Macrocyclic Ligands with C-Nitro and N-Alkyl Pendant Arms

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Square planar nickel(II) complexes with various 1-alkyl derivatives of the 14-membered pentaaza macrocycle 8-methyl-8-nitro-1,3,6,10,13-pentaazacyclotetradecane can be readily prepared by two-step metal template condensation reactions of ethylenediamine, nitroethane, formaldehyde, and appropriate primary alkylamines. In coordinating solvents the nickel (II) complexes form octahedral species containing two axially coordinated solvent molecules and thus show square planar-octahedral equilibrium. The properties of the pentaaza macrocyclic complexes are considerably different from those of the complexes of analogous hexaaza and tetraaza macrocyclic complexes. Synthesis, characterization, and spectroscopic and chemical properties of the new complexes are described.

Introduction

Many works have been concerned with the synthesis of new types of polyaza macrocyclic ligands and complexes, since the properties of such compounds are closely correlated with their structural characteristics. Various saturated polyaza macrocyclic complexes have been prepared by one-pot reactions of complexed amines with formaldehyde.[1-10] For example, the nickel(II) complexes of the hexaaza macrocycles
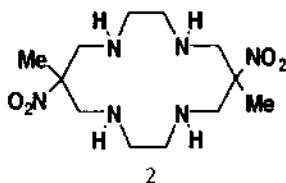
1a-1d,[5,6] which contain two alkylamino bridging groups in the six-membered chelate rings, have been synthesized by the reactions of Eq. (1). It has also been reported that the reaction Eq. (2) of ethylenediamine, formaldehyde, and nitroethane in the presence of nickel(II) ion produces the complex of the tetraaza macrocycle 2 containing the nitroethane bridging groups.[8] The hexaaza and tetraaza macrocycles are known to behave as tetradentate ligands; the two tertiary nitrogen atoms or nitro groups of the ligands are not involv-

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ed in the coordination.[5,6,8,10] Although it has been observed that the ligand field strength and redox potentials of $[Ni(1n)]^{2+}$ ($n = a$-d) are similar to those of $[Ni(cyclam)]^{2+}$ (cyclam = 1,4, 8,11-tetraazacyclotetradecane),[5,6] the effects of the nitroethane bridging group on the properties have not been extensively studied.
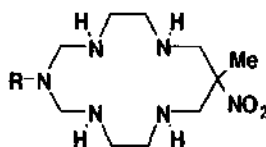
In this work, utilizing the characteristics of the reactions (Eqs. 1 and 2), we designed and prepared new square planar nickel(II) complexes of the pentaaza macrocycles **3a-3d** from the template condensations of ethylenediamine, nitroethane, formaldehyde, and appropriate alkylamines to see the effects
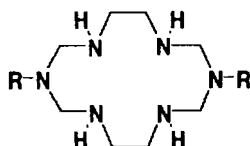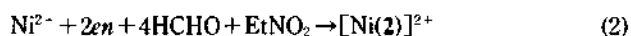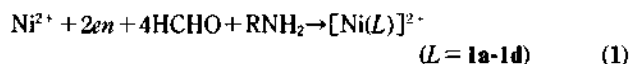

1a: R=Me   1b: R=*n*-Pr
1c: R=*n*-Bu 1d: R=*iso*-Bu

2

3a: R=Me   3b: R=*n*-Pr
3c: R=*n*-Bu 3d: R=*iso*-Bu

$$Ni^{2+} + 2en + 4HCHO + RNH_2 \rightarrow [Ni(L)]^{2+}$$
$$(L = \mathbf{1a\text{-}1d}) \qquad (1)$$

$$Ni^{2+} + 2en + 4HCHO + EtNO_2 \rightarrow [Ni(2)]^{2+} \qquad (2)$$

of the bridging groups on the properties. Interestingly, it was found that the spectroscopic and chemical properties of the new complexes are considerably different from those of the complexes with the hexaaza macrocycles **1a-1d** and the tetraaza macrocycle **2**. This paper reports the synthesis and characterization of the new nickel(II) complexes. The effects of the bridging groups on the properties are also discussed.

Experimental

Measurements. Infrared spectra were obtained on a Shimadzu IR-440 spectrophotometer using Nujol mulls. Conductance measurements were made by using a Metrohm Herisau Conductometer E518. Visible spectra were obtained on a Shimadzu UV-160 spectrophotometer. ^1H- and ^{13}C-NMR spectra were recorded with a Bruker WP 300 FT NMR spectrometer. Elemental analyses were performed at the Kolon R & D Center, Kumi, 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.[5]

Equilibrium constants for the square planar to octahedral conversion of the nickel(II) complexes were determined from visible spectra of the complexes. The temperature of the sample solution was maintained within ±0.1°C by use of a thermostated cell holder, connected to a Haake D_3 circulating bath. The concentration of the complexes was 1.0-2.0× 10^{-3} M in each solution.

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. $[Ni(2)](ClO_4)_2$ was prepared as the reported method.[8]

Syntheses. $[Ni(3a)](ClO_4)_2$. To a methanol solution (30 ml) of $Ni(OAc)_2 \cdot 4H_2O$ (3.0 g, 0.012 mol) were added 99.5% ethylenediamine (1.6 ml, 0.024 mol), 95% nitroethane (1.0 ml, 0.012 mol), triethylamine (0.1 ml), and paraformaldehyde (0.7 g, 0.024 mol). After refluxing the mixture for 12 h, 40% methylamine (1.0 ml, 0.012 mol) and paraformaldehyde (1.0 g, 0.034 mol) were added. The resulting mixture was further heated to reflux for 12 h. After addition of an excess of $NaClO_4$, the solution was stored in a refrigerator to form the yellow precipitates. The product was filtered off, washed with methanol, and dried in air. The crude product may contain small amount of $[Ni(2)](ClO_4)_2$ and/or $[Ni(1a)](ClO_4)_2$ as by-products. Therefore, the product was recrystallized more than twice from hot water. Yield: ~15%. Anal. Calcd for $C_{11}H_{26}N_4NiCl_2O_8$: C, 24.84; H, 4.93; N, 15.80%. Found: C, 24.66; H, 5.03; N, 16.05%.

$[Ni(3b)](ClO_4)_2$. This complex was prepared by a method similar to that for $[Ni(3a)](ClO_4)_2$ except that 99% *n*-propylamine (1.0 ml, 0.012 mol) was reacted instead of methylamine. Yield: ~20%. Anal. Calcd for $C_{13}H_{30}N_4NiCl_2O_8$: C, 27.88; H, 5.39; N, 15.00%. Found: C, 27.46; H, 5.02; N, 14.70 %.

$[Ni(3c)](ClO_4)_2$. This complex was synthesized by a method similar to that for $[Ni(3a)](ClO_4)_2$ except that 99% *n*-butylamine (1.3 ml, 0.012 mol) was used instead of methylamine. The crude product obtained was recrystallized from hot water-acetonitrile (2 : 1) mixture. Yield: ~20%. Anal. Calcd for $C_{14}H_{32}N_4NiCl_2O_8$: C, 29.29; H, 5.62; N, 14.64%. Found: C, 29.53; H, 5.44; N, 14.39%.

$[Ni(3d)](ClO_4)_2$. This compound was prepared by a method similar to that for $[Ni(3c)](ClO_4)_2$ except that 98% *iso*-butylamine (1.3 ml, 0.012 mol) was reacted instead of *n*-butylamine. Yield: ~20%. Anal. Calcd for $C_{14}H_{32}N_4NiCl_2O_8$: C, 29. 29; H, 5.62; N, 14.64%. Found: C, 30.02; H, 5.58; N, 14.49%.

$[Ni(L)](PF_6)_2(L = \mathbf{3a\text{-}3d})$. To a warm acetonitrile suspension (10 ml) of $[Ni(L)](ClO_4)_2$ (0.5 g) was added excess NH_4PF_6, and then the white solid NH_4ClO_4 was precipitated. The solid was removed by filtration and then water (15 ml) was added to the filtrate. The yellow soid formed was filtered, washed with water, and dried in air.

Results and Discussion

Synthesis and Characterization. The two-step condensation reactions (see Experimental) of ethylenediamine, nitroethane, formaldehyde, and appropriate primary alkylamines
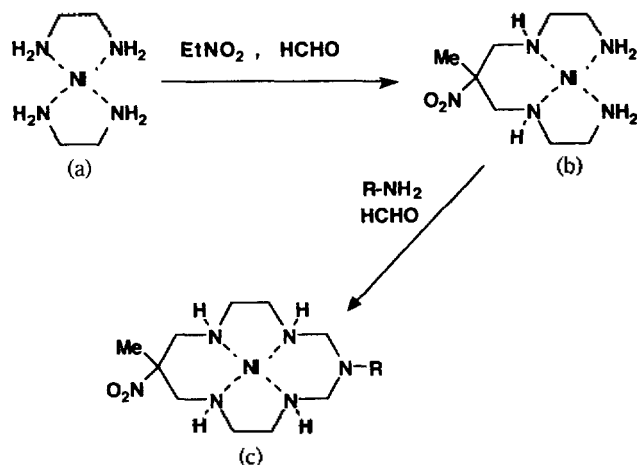
Scheme 1.

Table 1. ^{13}C-NMR Spectral Data of [Ni(L)](PF$_6$)$_2$ in CD$_3$NO$_2$

L	δ, ppm			
	N-C-N	C(Me)NO$_2$	N-R	Others
3a	69.5	89.1 23.5	38.1	47.5 52.0 54.0
3b	68.5	89.0 23.6	11.1 22.0 54.8	47.8 51.9(d)
3c	69.1	89.1 23.6	14.0 20.7 30.9 51.3	48.5 50.5(d)
3d	69.5	89.3 23.5	20.1 28.1 58.4	48.5 51.8(d)

Table 2. Molar Conductance and Spectral Data of the Complexes

Complex	IR, cm^{-1}		λ$_{max}$,	Λ$_M$,
	νN-H	νNO$_2$	nm(ε, M^{-1}cm^{-1})[a]	ohm^{-1}mol^{-1}cm^{2b}
[Ni(3a)](ClO$_4$)$_2$	3200	1555	455(60)	302
[Ni(3b)](ClO$_4$)$_2$	3205	1555	455(69)	281
[Ni(3c)](ClO$_4$)$_2$	3200	1555	454(66)	273
[Ni(3d)](ClO$_4$)$_2$	3210	1555	454(72)	304
[Ni(1a)](ClO$_4$)$_2$[c]	3185		449(56)	
[Ni(1d)](ClO$_4$)$_2$[d]	3190		446(62)	
[Ni(2)](ClO$_4$)$_2$	3230 3140	1550	457(59)	285

[a] In nitromethane at 20°C, [b] In acetonitrile solution at 20°C, [c] Ref. 5. [d] Ref. 6.

Table 3. Oxidation Potentials (Volts *vs.* SCE) for the Nickel(II) Complexes[a]

Complex	[Ni(L)]$^{2+}$→[Ni(L)]$^{3+}$
[Ni(3a)](ClO$_4$)$_2$	+1.06
[Ni(3b)](ClO$_4$)$_2$	+1.04
[Ni(3c)](ClO$_4$)$_2$	+1.05
[Ni(3d)](ClO$_4$)$_2$	+1.06
[Ni(1a)](ClO$_4$)$_2$[b]	+0.93
[Ni(1d)](ClO$_4$)$_2$[c]	+0.95
[Ni(2)](ClO$_4$)$_2$	+1.21

[a] Measured in 0.1 M (*n*-Bu)$_4$NClO$_4$ acetonitrile solutions at 20°C. [b] Ref. 5, [c] Ref. 6.

in the presence of nickel(II) ion and triethylamine, followed by addition of an excess of NaClO$_4$, produce the 14-membered pentaaza macrocyclic complexes [Ni(3*n*)](ClO$_4$)$_2$ (*n* = *a*-*d*). Although the crude product may contain small amounts of [Ni(2)](ClO$_4$)$_2$ and/or [Ni(1*n*)(ClO$_4$)$_2$ as by-products, the pure product is easily isolated by the fractional recrystallizations. Yields of the products are somewhat lower than those for the complexes of 1*n*[5,6] and 2[8] prepared by the reactions of Eqs. 1 and 2, respectively. The proposed synthetic procedure is shown in Scheme 1, which is in accord with those for the complexes of 1*n*[5] and 2.[8] The isolation of the intermidiate (b) in the Scheme as a solid was not achieved. We also attempted the synthesis of the complexes of 3a-3d from the one-step condensation reactions of the reactants. However, the crude products contain large amounts of the by-products, unlike those obtained by the two-step condensations, and therefore it was very difficult to isolate the pure products by the simple fractional recrystallizations.

The nickel(II) complexes [Ni(L)](ClO$_4$)$_2$ (L = 3a-3d) are quite stable in the solid state and dissociate very slowly even in low pH, in analogy with the complexes of 1a-1d[5,6] and 2. Visible spectra showed that, in 0.3 M HNO$_3$ water or water-acetonitrile (1 : 1) solutions, only less than 3% of the complexes are decomposed in 24 h at 20°C.

^{13}C-NMR spectral data (Table 1) of the nickel(II) complexes are consistent with the ligand structures. The carbon peak of the nitrated carbon in each complex is observed near 89 ppm and that of the C-methyl group is near 23 ppm. The peak near 69 ppm is corresponding to the N-C-N linkages. The infrared and electronic spectral data as well as

molar conductance data of the nickel(II) complexes are listed in Table 2. The infrared spectra of the complexes of 3a-3d show a νNO$_2$ near 1555 cm^{-1}. The spectra also show νN-H bands for the coordinated secondary amino groups at 3200-3210 cm^{-1}. The νN-H values are 10-15 cm^{-1} higher than those for the complexes of 1a-1d.[5,6] This indicates that the Ni-N interactions are weaker for the complexes of 3 a-3d than the complexes of 1a-1d. In the case of [Ni(2)](ClO$_4$)$_2$ the peaks are observed at 3230 and 3140 cm^{-1}. The values of molar conductance for the complexes indicate that the complexes are 1 : 2 electrolytes. The electronic spectra of nitromethane solutions of the nickel(II) complexes show the *d-d* bands at *ca.* 455 nm (ε = 54-66 M^{-1}cm^{-1}), indicating that the complexes have square planar Ni-N$_4$ chromophores. The spectra also show that the ligand field strengths of the 14-membered pentaaza macrocyclic complexes are not affected significantly by the variation of the alkyl group attached to the uncoordinated nitrogen atom. However, the wavelengths are somewhat shorter than that observed for [Ni(2)](ClO$_4$)$_2$ but are *ca.* 6 nm longer than those for the nickel(II) complexes of 1a-1d.[5,6] This supports that the ligand field strength is affected by the nature of the bridging group and decreases according to the order 1*n* > 3*n* > 2.

Cyclic voltammograms of the complexes of 2 and 3a-3d obtained in 0.1 M (*n*-Bu)$_4$NClO$_4$ acetonitrile solutions exhibited one-electron oxidation peaks corresponding to a Ni(II) /Ni(III) process. Table 3 shows that the oxidation potentials
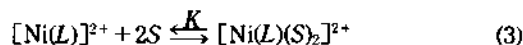
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Table 4. Equilibrium Constants (*K*) and Thermodynamic Parameters for the $[Ni(L)]^{2+}+2S=[Ni(L)(S)_2]^{2+}$ System at 25℃

L	S	ε $M^{-1}cm^{-1a}$	K^b	$-\Delta H^o$ kcal/mol	$-\Delta S^o$ cal/K·mol
2	MeCN	11.3	4.24(80.9)	3.4	8.4
	H$_2$O	11.7	4.05(80.2)	3.9	10.2
	DMSO	11.1	4.34(81.3)	5.6	16.1
3a	MeCN	11.8	4.13(80.5)	4.0	10.3
	H$_2$O	18.0	2.35(70.2)	2.8	7.6
	DMSO	16.3	2.70(73.1)	4.9	14.4
3b	MeCN	13.5	4.15(80.6)	3.4	8.5
	H$_2$O	24.5	1.84(64.8)	8.5	20.3
	DMSO	20.8	2.34(70.1)	7.1	18.4
3c	MeCN	13.0	4.08(80.3)	4.0	10.6
	DMSO	20.8	2.17(68.5)	7.9	18.6
3d	MeCN	19.5	2.70(73.0)	3.6	10.0
	DMSO	23.3	2.11(67.8)	7.9	22.5
1a^{c,d}	MeCN		1.01(50.2)	8.8	22.5
	H$_2$O		0.44(30.4)	4.3	15.2
	DMSO		0.56(35.9)	5.5	19.7
1b^d	MeCN		0.79(44.2)	2.2	8.1
	H$_2$O		0.35(26.1)	5.4	20.2
	DMSO		0.27(21.4)	3.7	14.9

^{a} Molar extinction coefficients at *ca.* 455 nm, ^{b} Percent of octahedral species in parenthesis, ^{c} Ref. 5, ^{d} Ref. 11.

of the complexes of **3a-3d** are not affected by the nature of the *N*-alkyl group. The similar result has also been observed for the complexes of **1a-1d**.[5,6] However, interestingly, the potentials (*ca.* +1.05 V *vs.* SCE) of the pentaaza macrocyclic complexes are somewhat higher than those for the complexes of **1a** and **1d** (*ca.* +0.94 V)[5,6] but are much lower than that of $[Ni(2)](ClO_4)_2$ (+1.21 V), showing that the electron density on the metal ion varies with the ligand structure in the order of **1n**>**3n**>**2**. It is clear that the stepwise substitution of the nitroethane group for the alkylamino groups on **1n** to give **3n** and **2** reduces the electron density on the metal ion of the complex and makes the oxidation a more unfavorable process.

Square Planar-Octahedral Equilibrium. The visible spectra of the nickel(II) complexes of **2** and **3a-3d** showed that the molar absorption coefficients at *ca.* 455 nm measured in coordinating solvents such as H$_2$O, MeCN, and dimethylsulfoxide (DMSO) are much lower than those measured in nitromethane, a non-coordinating solvent. This indicates that the nickel(II) complexes dissolve in the coordinating solvents to give equilibrium mixtures (Eq. 3) of the square planar $[Ni(L)]^{2+}$ (*L* = macrocyclic ligand) and octahedral $[Ni(L)(S)_2]^{2+}$ (*S* = solvent molecule) species.[1-3,5,11-16] For the purpose of determining the equilibrium constant, $K=[[Ni(L)(S)_2]^{2+}]/[[Ni(L)]^{2+}]$, the molar extinction coefficient in nitromethane was assumed to be identical with that of the square planar species in the coordinating solvent. The *K* values and thermodynamic parameters calculated by the reported methods[2,5,11-14] are summerized in Table 4, together with the molar extinction coefficients.

$$[Ni(L)]^{2+}+2S \xrightleftharpoons{K} [Ni(L)(S)_2]^{2+} \qquad (3)$$

As expected, the values of ΔH^o and ΔS^o for the complexes are negative and are comparable to those observed for the nickel(II) complexes of other 14-membered polyaza macrocyclic ligands.[1-3,5,7,11-16] The exothermicity has been attributed to the fact that the endothermic effect of the in-plane Ni-N bond weakening is exceeded by the exothermic effect due to the formation of two axial Ni-S bonds. The negative values of ΔS^o are consistant to the decrease in mobility of the solvent molecules due to the formation of the axial bonds in the octahedral species. The thermodynamic parameters show that the formation of octahedral species arises as a consequence of a favorable enthalpic contribution.

The values of *K* for the nickel(II) complexes are affected by the ligand structure. Although the *K* values for the complexes of **3a-3d** in MeCN are rarely affected by the *N*-alkyl group, the order is found to be **3a**>**3b**>**3c**>**3d** in DMSO or water. This result is in analogy with the trend **1a**>**1b**>**1c**>**1d**[12] and indicates that the presence of bulkier *N*-alkyl group exerts more severe steric repulsion of the square planar complex with the solvent molecules and reduces the proportion of the octahedral species. In all solvents, the values for the complexes of **3a-3d** are much larger than those of **1a-1d** but are smaller than those of **2**; the proportion of the octahedral species for **2** is even more than 80% in all solvents, whereas that for **1b** is less than 50%. This shows that the substitution of the nitroethane group for the alkylamino groups on **1n** to give **3n** and **2** increases the axial ligation ability of the complex. The higher *K* values for the complexes of **3a-3d**, compared to those for **1a-1d**, may be attributed to the weak in-plane Ni-N interactions and/or weak steric repulsion of the pendant arm with the solvent molecules.

Table 4 also shows that the equilibrium constants of the complexes are affected by the nature of the solvents. Furthermore, the relative ligation ability of the solvents depends on the ligand structure; the *K* value for **3a-3d** decrease according to the sequence of MeCN>DMSO>H$_2$O, which is similar to that for **1a** but is different from those for **1b-1d** (MeCN)>H$_2$O>DMSO)[11] and **2** (DMSO>MeCN>H$_2$O). Any correlation of the *K* values with DN (donor number; DMSO>H$_2$O>MeCN) or dielectric constant (H$_2$O>DMSO>MeCN)[17] of the solvents is not observed. However, in all systems, the proportion of the octahedral species in acetonitrile is higher than that in water. The stronger ligation ability of MeCN in spite of its lower DN, compared to H$_2$O, can be attributed to its rod-like geometry and relatively weak base character toward interactions with the protons of the coordinated secondary amino groups.[12,15,18] Somewhat interestingly, it is seen that as one proceeds from **1n**, through **3n** to **2**, the relative coordinating ability of DMSO molecule is increased; the ligation ability of bulky DMSO molecule is weaker than that of water for **1b** and **1c** but is even stronger than that of MeCN for **2**. Furthermore, the *K* values for **2** are less affected by the nature of the solvents than those for **1n** and **3n**. These may indicate that the stepwise substitution of the nitroethane group for the alkylamino groups on **1n** also reduces the steric hindrance of the solvent

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molecules with the pendant arms and that, in the case of **2**, the donor ability (DN) of DMSO molecule plays an important role to the axial coordination.

The equilibrium study clearly shows that not only the proportion of the octahedral species in a given coordinating solvent but also the relative ligation ability of the solvents is strongly affected by the ligand structure.

Summary. Results of the above chemical and spectroscopic properties together with the elemental analyses show that the new nickel(II) complexes prepared from the two-step condensation reactions contain the 14-membered pentaaza macrocycles, **3a-3d**. In each complex, the four secondary nitrogen atoms are coordinated to the metal ion in a square planar geometry with a 5-6-5-6 chelate ring sequence. This work also shows that the stepwise substitution of the nitroethane group for the alkylamino bridging groups on $[Ni(1n)]^{2-}$ to give $[Ni(3n)]^{2+}$ and $[Ni(2)]^{2-}$ weakens the Ni-N interactions, decreases the electron density on the metal ion, increases the proportions of the octahedral species in the coordinating solvents, and enhances the relative ligation ability of DMSO. The reasons for the trends are not clearly understood at this time, because the crystal structures of the complexes are not available. However, the results are corresponding to the suggestion that the Ni-N bond distances of the complexes are considerably affected by the ligand structure and increase according to the sequence of $1n<3n<2$. It has been generally observated that the ligand field strength, redox potentials, and the equilibrium constants of a polyaza macrocyclic nickel(II) complex are largely dependant on the Ni-N bond distances.[2,3,19,20]

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