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Synthesis, Properties, and X-ray Structures of Nickel(I) Complexes of Polyaza Macrotricyclic Ligands

Myunghyun Paik Suh,* Hyun Kyung Kim, Myung Jin Kim, and Kye Young Oh

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

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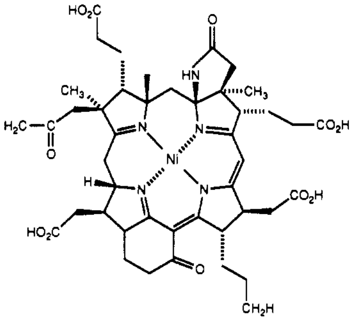
Square-planar Ni(I) complexes of various saturated polyaza macrotricyclic ligands **1–7** have been prepared by the reduction of Ni(II) complexes with Na(Hg) in MeCN solutions, and some Ni(I) complexes [Ni(L)]ClO_4 (L = **1–5**) were isolated as crystals. UV/vis spectra of the Ni(I) complexes show a d–d transition band at 538–600 nm, which is at ca. 100 nm longer wavelength than those of Ni(II) complexes, with relatively large extinction coefficients (ϵ = 250–1000). EPR spectra of the Ni(I) complexes show anisotropic axial $g_{\parallel}$ and $g_{\perp}$ ($g_{\parallel} > g_{\perp}$) values or rhombic g_1, g_2, and g_3 values. [Ni(**1**)]$ClO_4 \cdot CH_3CN$ (**1** = $C_{12}H_{27}N_7$) crystallizes in the triclinic space group $P\bar{1}$ with a = 9.407 (1) Å, b = 9.577 (2) Å, c = 13.216 (4) Å, α = 69.20 (2)°, β = 78.68 (2)°, γ = 61.81 (2)°, and Z = 2. The structure was solved by the heavy-atom method and refined anisotropically to R values of R = 0.049 and R_w = 0.052 for 2659 observed reflections ($F \geq 3\sigma(F)$) measured with Mo Kα radiation on a CAD-4 diffractometer. [Ni(**3**)]ClO_4 (**3** = $C_{12}H_{26}N_6$) crystallizes in the orthorhombic space group $Pna2_1$ with a = 16.239 (1) Å, b = 7.7723 (1) Å, c = 13.460 (2) Å, and Z = 4. The structure was solved by the heavy-atom method and refined anisotropically to R values of R = 0.053 and R_w = 0.057 for 1053 observed reflections measured with Mo Kα radiation on a CAD-4 diffractometer. The X-ray crystal structures of [Ni(**1**)]$ClO_4 \cdot CH_3CN$ and [Ni(**3**)]ClO_4 indicate that the compounds have square-planar geometry. [Ni(**1**)]$ClO_4 \cdot CH_3CN$ shows a square-pyramidal distortion and [Ni(**3**)]ClO_4 shows a tetrahedral distortion of the donor nitrogen atoms. The two 1,3-diazacyclopentane ring moieties in [Ni(**3**)]ClO_4 are located anti and almost perpendicular to the plane of the 14-membered macrocycle. The Ni(I) complexes of **1** and **3** show two sets of Ni–N bond distances, each set consisting of two cis-positioned Ni–N bonds involving a six-membered chelate ring, rather than a simple expansion of macrocyclic hole, average 1.893 (2) and 1.936 (2) Å for [Ni(**1**)]$ClO_4 \cdot CH_3CN$ and average 1.859 (7) and 1.974 (7) Å for [Ni(**3**)]ClO_4.

Introduction

Recently, Ni(I) macrocyclic complexes have been a subject of great interest. This is because Ni(II) tetraaza macrocyclic complexes catalyzed the electrochemical reduction of CO_2[1–3] and alkyl halides,[4–8] and nickel(I) species were proposed to be involved in the reactions. Furthermore, F_{430} (A), a Ni(II) hydrocorphinoid complex is a prosthetic group of methyl coenzyme M reductase that catalyzes the reductive cleavage of *S*-methyl coenzyme M to methane.[9–12] An EPR signal detected in whole cells of *Methanobacterium thermoautotrophicum* was attributed to a Ni(I) form of F_{430} in the intact, active enzyme.[13,14]

Macrocyclic ligands often allow the stabilization of the metal in an unusual oxidation state. And thus, some Ni(I) macrocyclic complexes have been prepared, mostly in situ, and their electronic absorption and EPR spectra have been measured.[15–21] However, there still is a lack of visible spectral data especially for the d–d transitions of the Ni(I) macrocyclic complexes. This is because only limited numbers of Ni(I) complexes have been isolated as



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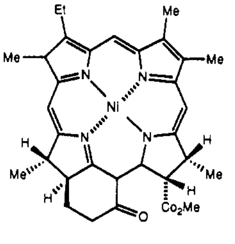

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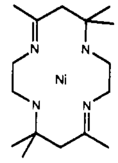

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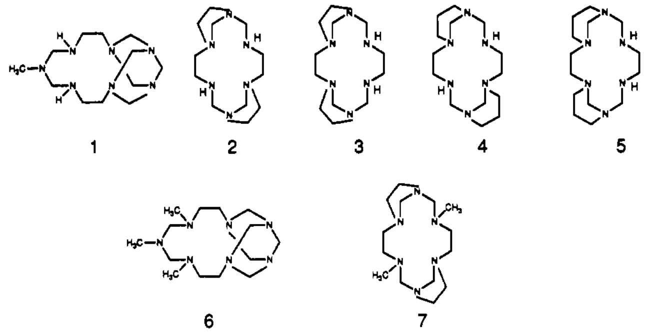
Chart I



solids to afford solutions concentrated enough to measure the d–d transitions and, moreover, most of them contain imine bonds in the ligand that cause charge transfer between metal and ligand in the visible region.

Furthermore, there have been few reports on the X-ray structures of Ni(I) complexes with macrocyclic ligands or porphyrin analogues to date, only one for a Ni(I) azamacrocyclic complex[22] and one for a Ni(I) thiaporphyrin complex,[23] and the structural consequences associated with the reduction of Ni(II) to Ni(I) have not been well documented. It has been suggested by Stolzenberg that the Ni(I) ion should be larger than a high-spin Ni(II) ion and thus the Ni–N bond distances of the Ni^{I}-OEiBC complex may be ca. 2.1 Å, which is ca. 0.2 Å longer than that of Ni(II) complex.[24] Alternatively, recent reports on the EXAFS data analyses on Ni(I) F$_{430}$[25] and the Ni^{I}iBC complex (B)[26] suggested two sets of Ni–N distances rather than a simple expansion of macrocyclic core.[25,26] In addition, the X-ray crystal structure of the Ni(I) tetraazamacrocyclic complex (C) also shows two distinct sets of Ni–N bond distances as well as the expansion of the macrocyclic hole.[22] In the Ni(I) complex of C, Ni–N bond distances involving amine nitrogens are longer than those involving imine nitrogens. This was also observed for the Ni(II) complex although the difference between Ni–N(amine) and Ni–N(imine) bond lengths is greater in the Ni(I) complex.

In the present paper, we describe the synthesis and the spectroscopic properties of square-planar Ni(I) complexes with **1**–**7** (Chart I) as well as the X-ray crystal structures of two different Ni(I) complexes with macrocyclic ligands, 8-methyl-1,3,6,8,10,13,15-heptaazatricyclo[13.1.1.1^{13,15}]octadecane (**1**) and 1,3,6,9,11,14-hexaazamacrotricyclo[12.2.1.1.^{6,9}]octadecane (**3**). Our results show that two cis Ni–N bond distances involving a six-membered chelate ring differ significantly from the other two.

Experimental Section

Reagents. All solvents and reagents were purified according to the literature[27] and were deaerated thoroughly prior to use. Ni(II) complexes of **1**–**5** were prepared according to the literature.[28-30] N-alkylated Ni(II) complexes of **6** and **7** were prepared from the Ni(II) complexes of **1** and **2** by a method similar to that previously reported.[31,32]

Table I. Crystal Data and Data Collection for [Ni(**1**)]$ClO_4 \cdot CH_3CN$ and [Ni(**3**)]ClO_4

emp formula	$NiC_{12}H_{25}N_7ClO_4 \cdot CH_3CN$	$NiC_{12}H_{26}N_6ClO_4$
fw	466.58	412.53
cryst system	triclinic	orthorhombic
space group	$P\bar{1}$	$Pna2_1$
a, Å	9.407 (1)	16.239 (1)
b, Å	9.577 (2)	7.723 (1)
c, Å	13.216 (4)	13.460 (2)
α, deg	69.20 (2)	
β, deg	78.68 (2)	
γ, deg	61.81 (2)	
V, Å^3	980.5 (6)	1687.9 (4)
Z	2	4
d_{calcd}, g cm^{-3}	1.579	1.623
cryst size, mm	0.21 × 0.30 × 0.44	0.36 × 0.39 × 0.42
μ, cm^{-1}	10.96	12.64
scan method	$\omega/2\theta$	$\omega/2\theta$
data collcd	$h,\pm k,\pm l$; $3 < 2\theta < 50$	h,k,l; $3 < 2\theta < 50$
tot. no. of observns	3897	1130
no. of unique data > $3\sigma(I)$	2659	1053
no. of params refined	281	216
gof	0.8477	0.209
R,[a] R_w[b]	0.049, 0.052	0.053, 0.057

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

Measurements. Infrared spectra were recorded with a JASCO IR-810 spectrophotometer. Electronic absorption spectra were obtained on a Shimadzu UV-260 spectrophotometer. Electron spin resonance spectra were recorded on a Bruker ER 200E-SRC instrument with powder samples at room temperature.[33] Elemental analyses were performed by Galbraith Laboratories Inc., Knoxville, TN.

Preparation of Ni(I) Complexes. The Ni(I) complexes were prepared and handled under an atmosphere of nitrogen by using Schlenk techniques. Nitrogen was purified by passing it through a BASF column and a $CaCl_2$ column.

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(II) complex [Ni(L)]$(ClO_4)_2$ (L = **1**–**7**) (3 g) and excess Na(Hg) (20 g) were suspended in MeCN (40 mL) with stirring. The complexes went into solution as the reactions proceeded. The solutions were stirred for 5–30 min until the colors of the solutions changed to purple for **1**, violet for **2** and **3**, blue for **4**–**6**, and green for **7**. If solutions of Ni(II) complexes were contacted with Na(Hg) for a prolonged period of time (longer than 30 min), metallic nickel was produced and the solutions gradually became colorless. The deeply colored solutions were filtered and allowed to stand in a refrigerator until the crystals formed. The crystals were filtered out, washed with MeCN, and dried in vacuo. Anal. Calcd for [Ni(**1**)]$ClO_4 \cdot CH_3CN$ ($NiC_{14}H_{30}N_8ClO_4$): C, 35.88; H, 6.45; N, 23.91. Found: C, 36.09; H, 6.27; N, 24.12. Anal. Calcd for [Ni(**2**)]ClO_4 ($NiC_{12}H_{26}N_6ClO_4$): C, 34.94; H, 6.35; N, 20.37. Found: C, 34.45; H, 6.30; N, 19.40.[34] Anal. Calcd for [Ni(**3**)]ClO_4 ($NiC_{12}H_{26}N_6ClO_4$): C, 34.94; H, 6.35; N, 20.37. Found: C, 34.67; H, 6.25; N, 20.24.

X-ray Diffraction Measurements. Crystals were sealed in glass capillaries under a nitrogen atmosphere, and all X-ray examination and data collection procedures were performed at room temperature on a CAD-4 Enraf Diffractometer. The crystallographic data collection and refinement details for [Ni(**1**)]$ClO_4 \cdot CH_3CN$ and [Ni(**3**)]ClO_4 are summarized in Table I. Absorption corrections were made. The structures

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(33) The frozen acetonitrile solutions showed very weak intensity probably due to the low solubility of the complexes and the precipitation of the complexes at the low temperature.

(34) The compound tended to pick up oxygen during the transit to Galbraith Laboratories, and the analytical data sometimes suggested that the compound was an oxygen adduct [Ni(**2**)O_2]ClO_4. The present analytical data indicate that the ratio of C:H:N is correct even if the absolute numbers are not.

Table II. Electronic Absorption and EPR Spectral Data for Nickel(I) Macrotricyclic Complexes

ligand	color of cryst	$\lambda_{\max}$,[a] nm (ϵ, M^{-1} cm^{-1})	EPR data[b]
1	red	538 (600), 330 (2020), 234 (2670)	$g_{\parallel} = 2.240$, $g_{\perp} = 2.062$
2	violet	560 (330), 338 (1180), 246 (3110)	$g_1 = 2.197$, $g_2 = 2.122$, $g_3 = 2.065$
3	violet	559 (450), 340 (1840), 240 (1990)	$g_{\parallel} = 2.253$, $g_{\perp} = 2.071$
4	blue	596 (250), 354 (810), 252 (2530)	$g_{\parallel} = 2.272$, $g_{\perp} = 2.075$
5	blue	589 (990), 355 (3020), 242 (9503)	$g_{\parallel} = 2.272$, $g_{\perp} = 2.074$
6		572[c]	
7		564, 338[c]	

[a] Measured in MeCN solutions. [b] The spectra are measured with powder samples at room temperature. [c] The crystals are not isolated with analytical purity.

Table III. Positional Parameters and Equivalent Isotropic Thermal Parameters (Å^2) for $[\mathrm{Ni}(\mathbf{1})]\mathrm{ClO_4 \cdot CH_3CN}$[a]

atom	*x*	*y*	*z*	U_{eq}
Ni	−0.0359 (1)	0.6702 (1)	0.3396 (<1)	0.031 (<1)
N(1)	−0.1368 (4)	0.6579 (4)	0.2304 (3)	0.038 (2)
N(2)	−0.2137 (4)	0.6650 (4)	0.4348 (3)	0.036 (2)
N(3)	0.0643 (4)	0.6908 (4)	0.4407 (3)	0.037 (2)
N(4)	0.1350 (4)	0.6872 (4)	0.2349 (3)	0.038 (2)
N(5)	0.1014 (5)	0.5661 (5)	0.1106 (3)	0.054 (2)
N(6)	−0.0546 (4)	0.8576 (4)	0.0881 (3)	0.046 (2)
N(7)	−0.1616 (4)	0.7490 (4)	0.5715 (3)	0.044 (2)
C(1)	−0.2734 (5)	0.6203 (6)	0.2836 (4)	0.056 (3)
C(2)	−0.3465 (5)	0.7051 (6)	0.3690 (4)	0.052 (3)
C(3)	−0.2791 (5)	0.7755 (5)	0.5027 (3)	0.045 (2)
C(4)	−0.0384 (5)	0.7987 (5)	0.5072 (3)	0.045 (2)
C(5)	0.1810 (5)	0.7571 (6)	0.3809 (4)	0.050 (3)
C(6)	0.2621 (5)	0.6774 (6)	0.2924 (4)	0.052 (3)
C(7)	0.2112 (5)	0.5580 (6)	0.1774 (4)	0.049 (3)
C(8)	0.0351 (6)	0.7322 (6)	0.0321 (4)	0.058 (3)
C(9)	0.0532 (5)	0.8561 (5)	0.1532 (3)	0.043 (2)
C(10)	−0.1892 (5)	0.8287 (5)	0.1488 (3)	0.042 (2)
C(11)	−0.0292 (6)	0.5323 (6)	0.1725 (4)	0.053 (3)
C(12)	−0.2457 (6)	0.8583 (6)	0.6410 (4)	0.056 (3)
Cl	−0.6927 (1)	0.7417 (1)	0.7372 (1)	0.048 (1)
O(1)	−0.6281 (5)	0.5980 (5)	0.8278 (3)	0.081 (3)
O(2)	−0.6513 (7)	0.8656 (5)	0.7392 (4)	0.109 (4)
O(3)	−0.6304 (5)	0.6988 (6)	0.6401 (3)	0.088 (3)
O(4)	−0.8633 (4)	0.8037 (6)	0.7419 (4)	0.089 (3)
N(1S)	0.3621 (7)	0.0267 (8)	0.1267 (5)	0.098 (4)
C(1S)	0.4054 (6)	0.1243 (7)	0.0865 (4)	0.061 (3)
C(2S)	0.4611 (8)	0.2512 (7)	0.0318 (5)	0.078 (4)

[a] Equivalent isotropic U_{eq} defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

were solved by the heavy-atom method. All non-hydrogen atoms were refined anisotropically. All calculations were done by using the program SHELX 76.[35]

Results

Reduction of Ni(II) complexes of macrotricyclic ligands **1**–**7** with Na(Hg) in MeCN solutions produced Ni(I) macrotricyclic complexes. Ni(I) complexes of **1**–**5** were isolated as crystals, and those of N-alkylated ligands **6** and **7** were obtained in situ.

The UV/vis spectra of Ni(I) complexes are summarized in Table II. The EPR spectra of Ni(I) complexes were measured with powder samples at room temperature,[33] and the data are summarized also in Table II.

X-ray structure studies for $[\mathrm{Ni}(\mathbf{1})]\mathrm{ClO_4 \cdot CH_3CN}$ and $[\mathrm{Ni}(\mathbf{3})]\mathrm{ClO_4}$ were undertaken, whose results are presented in Tables III–VI. Non-hydrogen atom coordinates are listed in Tables III and IV, and the bond length and angles are listed in Tables V and VI.

Table IV. Positional Parameters and Equivalent Isotropic Thermal Parameters (Å^2) for $[\mathrm{Ni}(\mathbf{3})]\mathrm{ClO_4}$[a]

atom	*x*	*y*	*z*	U_{eq}
Ni	0.3518 (1)	0.2595 (2)	0.5000 (0)	0.043 (1)
Cl	0.3868 (2)	0.0413 (4)	0.0084 (4)	0.068 (2)
O(1)	0.3146 (11)	0.0393 (29)	0.0698 (17)	0.168 (22)
O(2)	0.4112 (15)	0.1818 (30)	−0.0307 (27)	0.261 (57)
O(3)	0.4581 (10)	−0.0004 (28)	0.0715 (20)	0.178 (21)
O(4)	0.3885 (15)	−0.1065 (39)	−0.0457 (32)	0.269 (58)
N(1)	0.3612 (7)	0.2540 (14)	0.3596 (12)	0.055 (8)
C(1)	0.3973 (10)	0.4225 (22)	0.3292 (12)	0.082 (13)
C(2)	0.4680 (10)	0.4645 (22)	0.4025 (11)	0.073 (11)
N(2)	0.4295 (5)	0.4562 (11)	0.5002 (10)	0.052 (7)
C(3)	0.4928 (8)	0.4363 (17)	0.5810 (11)	0.054 (7)
N(3)	0.4505 (6)	0.4753 (14)	0.6711 (8)	0.054 (6)
C(4)	0.4002 (8)	0.6317 (20)	0.6458 (16)	0.082 (15)
C(5)	0.3862 (8)	0.6190 (16)	0.5332 (12)	0.064 (11)
C(6)	0.4032 (9)	0.3320 (23)	0.7098 (12)	0.070 (10)
N(4)	0.3346 (8)	0.2726 (16)	0.6448 (12)	0.057 (8)
C(7)	0.3050 (11)	0.1059 (19)	0.6819 (10)	0.069 (10)
C(8)	0.2440 (14)	0.0436 (24)	0.6008 (14)	0.090 (14)
N(5)	0.2900 (6)	0.0585 (11)	0.5061 (10)	0.059 (7)
C(9)	0.2313 (11)	0.0193 (21)	0.4253 (14)	0.081 (11)
N(6)	0.2687 (8)	0.0344 (14)	0.3261 (9)	0.064 (8)
C(10)	0.3486 (13)	−0.0431 (21)	0.3140 (14)	0.091 (15)
C(11)	0.4160 (10)	0.1042 (21)	0.3262 (14)	0.078 (11)
C(12)	0.2811 (8)	0.2186 (18)	0.3087 (10)	0.067 (8)

[a] Equivalent isotropic U_{eq} defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table V. Bond Distances (Å) and Bond Angles (deg) for $[\mathrm{Ni}(\mathbf{1})]\mathrm{ClO_4 \cdot CH_3CN}$

Ni–N(1)	1.939 (3)	N(5)–C(11)	1.442 (6)
Ni–N(2)	1.896 (3)	N(6)–C(8)	1.459 (6)
Ni–N(3)	1.890 (3)	N(6)–C(9)	1.445 (5)
Ni–N(4)	1.933 (3)	N(6)–C(10)	1.449 (5)
N(1)–C(1)	1.476 (5)	N(7)–C(3)	1.441 (6)
N(1)–C(10)	1.508 (5)	N(7)–C(4)	1.463 (5)
N(1)–C(11)	1.502 (5)	N(7)–C(12)	1.476 (6)
N(2)–C(2)	1.483 (5)	C(1)–C(2)	1.491 (7)
N(2)–C(3)	1.465 (5)	C(5)–C(6)	1.505 (7)
N(3)–C(4)	1.464 (5)	Cl–O(1)	1.422 (4)
N(3)–C(5)	1.481 (5)	Cl–O(2)	1.423 (4)
N(4)–C(6)	1.489 (5)	Cl–O(3)	1.419 (4)
N(4)–C(7)	1.496 (6)	Cl–O(4)	1.421 (4)
N(4)–C(9)	1.512 (5)	N(1S)–C(1S)	1.116 (7)
N(5)–C(7)	1.444 (6)	C(1S)–C(2S)	1.451 (8)
N(5)–C(8)	1.463 (6)		
N(2)–Ni–N(1)	88.4 (1)	C(11)–N(5)–C(8)	109.2 (4)
N(3)–Ni–N(1)	177.1 (1)	C(9)–N(6)–C(8)	109.8 (4)
N(3)–Ni–N(2)	93.6 (1)	C(10)–N(6)–C(8)	108.6 (4)
N(4)–Ni–N(1)	89.0 (1)	C(10)–N(6)–C(9)	114.1 (3)
N(4)–Ni–N(2)	176.1 (1)	C(4)–N(7)–C(3)	110.8 (3)
N(4)–Ni–N(3)	88.9 (1)	C(12)–N(1)–C(3)	107.8 (4)
C(1)–N(1)–Ni	107.6 (2)	C(12)–N(7)–C(4)	106.8 (3)
C(10)–N(1)–Ni	103.3 (2)	C(2)–C(1)–N(1)	108.3 (3)
C(10)–N(1)–C(1)	113.1 (3)	C(1)–C(2)–N(2)	107.6 (4)
C(11)–N(1)–Ni	115.9 (3)	N(7)–C(3)–N(2)	113.4 (3)
C(11)–N(1)–C(1)	108.9 (3)	N(7)–C(4)–N(3)	112.8 (3)
C(11)–N(1)–C(10)	108.1 (3)	C(6)–C(5)–N(3)	108.0 (3)
C(2)–N(2)–Ni	107.9 (2)	C(5)–C(6)–N(4)	108.1 (3)
C(3)–N(2)–Ni	117.8 (2)	N(5)–C(7)–N(4)	113.5 (4)
C(3)–N(2)–C(2)	107.7 (3)	N(6)–C(8)–N(5)	110.2 (3)
C(4)–N(3)–Ni	118.0 (2)	N(6)–C(9)–N(4)	111.4 (3)
C(5)–N(3)–Ni	108.3 (2)	N(6)–C(10)–N(1)	112.8 (3)
C(5)–N(3)–C4	106.2 (3)	N(5)–C(11)–N(1)	113.1 (3)
C(6)–N(4)–Ni	107.8 (3)	O(2)–Cl–O(1)	110.0 (3)
C(7)–N(4)–Ni	115.6 (3)	O(3)–Cl–O(1)	109.6 (3)
C(7)–N(4)–C(6)	108.7 (3)	O(3)–Cl–O(2)	109.6 (3)
C(9)–N(4)–Ni	103.9 (2)	O(4)–Cl–O(1)	108.8 (3)
C(9)–N(4)–C(6)	111.9 (3)	O(4)–Cl–O(2)	109.7 (3)
C(9)–N(4)–C(7)	108.9 (3)	O(4)–Cl–O(3)	109.0 (3)
C(8)–N(5)–C(7)	108.7 (4)	C(2S)–C(1S)–N(1S)	178.6 (6)
C(11)–N(5)–C(7)	112.8 (3)		

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[35] Sheldrick, G. M. *SHELX 76, Program for Crystal Structure Determination*; University of Cambridge: Cambridge, England, 1976.

Table VI. Bond Distances (Å) and Bond Angles (deg) for $[Ni(3)]ClO_4$

Ni–N(1)	1.897 (16)	C(5)–C(4)	1.536 (25)
Ni–N(2)	1.975 (8)	C(4)–N(3)	1.497 (18)
Ni–N(4)	1.972 (16)	N(3)–C(6)	1.444 (19)
Ni–N(5)	1.850 (8)	C(6)–N(4)	1.489 (20)
O(1)–Cl	1.435 (18)	N(4)–C(7)	1.462 (20)
O(2)–Cl	1.269 (18)	C(7)–C(8)	1.550 (23)
O(3)–Cl	1.472 (18)	C(8)–N(5)	1.482 (23)
O(4)–Cl	1.354 (28)	N(5)–C(9)	1.479 (19)
C(1)–N(1)	1.485 (17)	C(9)–N(6)	1.471 (22)
C(1)–C(2)	1.548 (20)	N(6)–C(10)	1.438 (23)
C(2)–N(2)	1.457 (22)	C(10)–C(11)	1.587 (25)
N(2)–C(3)	1.504 (16)	C(11)–N(1)	1.527 (20)
C(3)–N(3)	1.427 (17)	N(6)–C(12)	1.456 (15)
N(2)–C(5)	1.508 (17)	C(12)–N(1)	1.495 (17)

N(2)–Ni–N(1)	88.1 (5)	C(5)–N(2)–Ni	110.1 (7)
N(4)–Ni–N(1)	176.1 (6)	C(5)–N(2)–C(2)	115.4 (11)
N(4)–Ni–N(2)	92.9 (5)	C(5)–N(2)–C(3)	101.0 (10)
N(5)–Ni–N(1)	94.0 (5)	N(3)–C(3)–N(2)	105.3 (10)
N(5)–Ni–N(2)	172.7 (4)	C(4)–N(3)–C(3)	103.9 (11)
N(5)–Ni–N(4)	85.5 (5)	C(6)–N(3)–C(3)	113.7 (12)
O(2)–Cl–O(1)	120.2 (16)	C(6)–N(3)–C(4)	114.2 (10)
O(3)–Cl–O(1)	108.0 (14)	C(5)–C(4)–N(3)	104.7 (12)
O(3)–Cl–O(2)	100.4 (15)	C(4)–C(5)–N(2)	106.0 (10)
O(4)–Cl–O(1)	108.5 (16)	N(4)–C(6)–N(3)	115.0 (13)
O(4)–Cl–O(2)	119.5 (27)	C(6)–N(4)–Ni	119.4 (9)
O(4)–Cl–O(3)	96.3 (16)	C(7)–N(4)–Ni	109.8 (10)
C(1)–N(1)–Ni	106.7 (11)	C(7)–N(4)–C(6)	108.5 (13)
C(11)–N(1)–Ni	110.9 (10)	C(8)–C(7)–N(4)	104.1 (11)
C(11)–N(1)–C(1)	110.7 (14)	N(5)–C(8)–C(7)	105.0 (14)
C(12)–N(1)–Ni	113.0 (9)	C(8)–N(5)–Ni	112.2 (10)
C(12)–N(1)–C(1)	112.2 (12)	C(9)–N(5)–Ni	119.3 (9)
C(12)–N(1)–C(11)	103.5 (12)	C(9)–N(5)–C(8)	107.0 (11)
N(1)–C(1)–Ni	41.8 (8)	N(6)–C(9)–N(5)	112.7 (12)
C(2)–C(1)–Ni	76.1 (8)	C(10)–N(6)–C(9)	116.3 (12)
C(2)–C(1)–N(1)	107.5 (12)	C(12)–N(6)–C(9)	106.3 (12)
N(2)–C(2)–C(1)	104.4 (12)	C(12)–N(6)–C(10)	105.3 (11)
C(2)–N(2)–Ni	107.8 (9)	C(11)–C(10)–N(6)	108.2 (13)
C(3)–N(2)–Ni	111.0 (7)	C(10)–C(11)–N(1)	99.9 (13)
C(3)–N(2)–C(2)	111.4 (10)	N(6)–C(12)–N(1)	103.0 (10)

Table VII. Properties of Nickel(II) Macrotricyclic Complexes

ligand	λ_{max} (ϵ, M^{-1} cm^{-1})	E_{ox}[a,b] Ni(II)/ Ni(III)	E_{red}[a,b] Ni(II)/ Ni(I)	ref
1	438 (83),[c] 442 (80)[d]	+1.32	−1.39	28
2	447 (80),[c] 449 (78)[d]	+1.50 (i)	−1.28	29, 30
3	456 (89),[c] 459 (80)[d]	+1.43 (i)	−1.25	30
4	465 (95),[c] 471 (41)[d]	+1.34	−1.20 (qr)	29, 30
5	471 (90),[c] 480 (28)[d]	+1.25	−1.14	30
6	447 (103)[c]	+1.60	−1.07	31
7	466 (102)[c]	+1.64 (i)	−0.94 (qr)	31
[14]aneN_4[e]		+0.91	−1.46	36
Me_6[14]aneN_4[e]		+1.11	−1.33	36

[a] Measured in acetonitrile solutions, 0.1 M $(n\text{-}Bu)_4NClO_4$, volts vs SCE. [b] i = irreversible; qr = quasi-reversible. [c] Measured in $MeNO_2$. [d] Measured in MeCN. [e] Abbreviations: [14]aneN_4 = 1,4,8,11-tetraazacyclotetradecane; Me_6[14]aneN_4 = 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane.

Discussion

Synthesis. Cyclic voltammetry data for the Ni(II) macrocyclic complexes of **1**–**7** that were previously reported[28-31] are summarized in Table VII. The data indicate that the Ni(II) complexes of saturated polyaza macrotricyclic ligands **1**–**7** are reduced to the Ni(I) state more easily than the [14]aneN_4 (cyclam) or Me_6[14]aneN_4 ligand complexes, whose Ni(I) complexes were prepared.[4,15,16] The reduction potentials for the Ni^{II}/Ni^{I} couples are influenced significantly by the structure of the ligand, the values ranging from −0.94 to −1.39 V vs SCE. The order of ease for the electrochemical attainment of the Ni(I) state is in the order of the ligands **7** > **6** > **5** > **4** > **3** > **2** > **1**, implying that the Ni(I) state is thermodynamically attained more easily for macrocycles with the alkyl substituents at the donor nitrogen atoms or with six-membered 1,3-diazacyclohexane sub-ring moieties.[30-32] The data in Table VII also indicate that there exists a qualitative correlationship between Ni^{II}/Ni^{I} couples and the ligand field strengths of the Ni(II) complexes. The attainment of the Ni(I) state becomes easier as the ligand field strength of the macrocyclic ligand decreases.

All Ni(I) complexes of **1**–**7** are prepared by the reduction of Ni(II) complexes with Na/Hg in MeCN solutions under nitrogen atmosphere. The Ni(I) complexes of **1**–**5** were isolated as crystals, but Ni(I) complexes of N-alkylated ligands **6** and **7** were obtained only in solution because they decomposed before the crystals formed. Although it has been reported that N-alkylation of the macrocyclic ligand [14]aneN_4 or Me_6[14]aneN_4 increases the kinetic stability of Ni(I) complexes in aqueous solutions,[17] the Ni(I) complexes of N-methylated ligands **6** and **7** are less stable than those of parent ligand systems **1** and **2**. Thermodynamic ease of attainment of the Ni(I) state for N-alkylated ligands does not guarantee better kinetic stability of the Ni(I) complexes, and the stabilization of the Ni(I) state by N-alkylation might depend on the type of macrocycle. All Ni(I) complexes are extremely unstable in the air in the crystalline state or in solutions. They are soluble in MeCN, and the MeCN solutions are stable for extended periods of time in an inert atmosphere.

Spectra. The solid samples of Ni(I) complexes show anisotropic axial EPR spectra for ligand systems **1**, **3**, and **5** and rhombic spectra for **2**. The anisotropic axial spectra giving $g_{\parallel}$ values greater than $g_{\perp}$ and the rhombic spectra showing g_1, g_2, and g_3 values indicate that the complexes are in the form of typical d^9 electronic structures with an unpaired electron in the $d_{x^2-y^2}$ orbital of the square-planar Ni(I) complexes.[5,15-21,36] If the powder samples are exposed to the air, the signals become weaker and some extraneous bumps appear.

UV/vis spectra of the MeCN solutions of Ni(I) complexes with **1**–**7** indicate that d–d transitions of the complexes occur at 538–596 nm that are at ca. 100 nm longer wavelengths than those for Ni(II) complexes with the same ligand system (Tables II and VII). This implies that the Ni(I) metal ion exerts a significantly weaker ligand field strength than the Ni(II) ion due to the lower oxidation state. Furthermore, Ni(I) complexes with **4** and **5** containing six-membered 1,3-diazacyclohexane ring moieties in the macrocycle show d–d transitions at longer wavelengths than those with **2** and **3** containing five-membered 1,3-diazacyclopentane ring moieties, which is consistent with the observation made for the Ni(II) complexes. The values of extinction coefficients (ϵ = 250–1000) for the d–d transitions of the Ni(I) complexes are ca. 5–10 times greater than those for the parent square-planar Ni(II) complexes (ϵ = 80–100). This indicates that there is some kind of intensity increasing mechanism, perhaps a tetrahedral distortion such as that revealed by the X-ray structure of $[Ni(3)]ClO_4$. The charge-transfer bands of the Ni(I) complexes appear at 330–355 and 230–250 nm. Similar charge-transfer spectra were observed for other Ni(I) macrocyclic complexes of cyclam, Me_6[14]aneN_4, and their N-methylated ligands.[15-19]

The spectra and the elemental analysis data indicate that Ni(I) complexes of **1**–**5** are four-coordinate. The value of ν_{CN} for $[Ni(1)]ClO_4 \cdot CH_3CN$ is 2250 cm^{-1}, indicating that acetonitrile is not coordinated to the Ni(I) ion.

X-ray Structures of Ni(I) Macrocyclic Complexes. ORTEP plots of the $[Ni(1)]^+$ and $[Ni(3)]^+$ cations with the atomic numbering schemes are presented in Figures 1 and 2. There are large thermal vibrations in the perchlorate anion of $[Ni(3)]ClO_4$. Each structure consists of a square-planar Ni(I) complex of a 14-membered hexaaza macrocyclic framework. In $[Ni(1)]ClO_4 \cdot CH_3CN$ and $[Ni(3)]ClO_4$, the closest contacts of Ni(I) ion with the oxygen atoms of ClO_4^- anions are 3.881 (5) and 3.585 (20) Å, respectively,

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(36) Dietrich-Buchecker, C. O.; Kern, J.; Sauvage, J.-P. *J. Chem. Soc., Chem. Commun.* **1985**, 760.

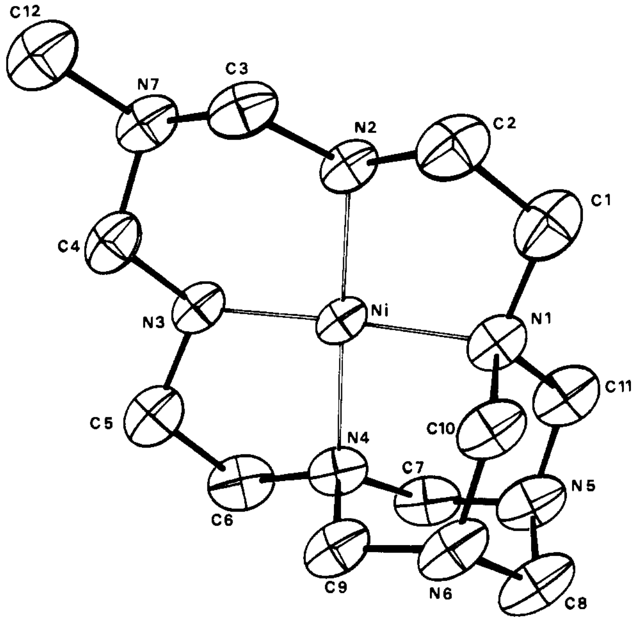

Figure 1. ORTEP drawing and the atomic labeling scheme of [Ni(**1**)]$ClO_4\cdot CH_3CN$.

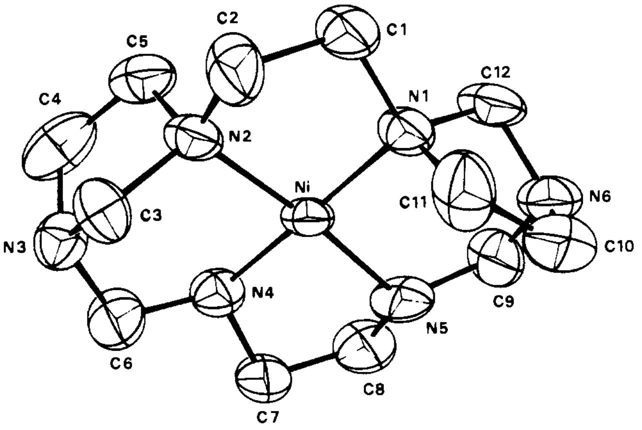

Figure 2. ORTEP drawing and the atomic labeling scheme of [Ni(**3**)]ClO_4.

too far for coordination. Complex [Ni(**1**)]$ClO_4\cdot CH_3CN$ contains a molecule of acetonitrile that is not coordinated to the Ni(I) ion. The distance from the Ni(I) ion to the nitrogen atom of acetonitrile is 5.892 (7) Å. The shortest intermolecular Ni-Ni distance is 4.276 (2) Å for [Ni(**1**)]$ClO_4\cdot CH_3CN$ and 7.723 (2) Å for [Ni(**3**)]ClO_4. In both complexes, there is no hydrogen bonding between secondary nitrogens of the macrocycle and the oxygen atoms of perchlorate anions.

The overall structures of Ni(I) complexes [Ni(**1**)]$ClO_4\cdot CH_3CN$ and [Ni(**3**)]ClO_4 are very much similar to those observed for the nickel(II) perchlorate complexes.[28,30] [Ni(**1**)]$ClO_4\cdot CH_3CN$ contains three six-membered chelate rings, and each ring has an amino function at the bridgehead position. Two six-membered chelate rings involving tertiary nitrogen donors N(1) and N(4) are linked with a carbon, forming a football-shaped bicyclononane ring moiety. The two six-membered rings in the bicyclononane ring assume a stable chair conformation. The two six-membered chelate rings formed between the bicyclononane ring and the nickel ion also assume a chair conformation. However, the six-membered chelate ring formed with secondary nitrogens N(2) and N(3) adopts a conformation intermediate between the normal and the half-chair conformations. The five-membered chelate rings assume a gauche conformation. The lengths of the N–C single bonds in [Ni(**1**)]$ClO_4\cdot CH_3CN$ show systematic variations, as was observed in the Ni(II) complex,[28] depending on the environments of the nitrogen atoms. There are five tertiary nitrogen atoms, N(1), N(4), N(5), N(6), and N(7). The four bonds from N(1) and N(4) to the carbon atoms of the bicyclononane ring are longest with an average length of 1.505 (3) Å. The four N–C bonds involving N(5) and N(6), namely, N(5)–C(7), N(5)–C(11), N(6)–C(9), and N(6)–C(10), have an average length of 1.445 (3) Å, while the N(5)–C(8) and N(6)–C(8) bonds have an average value of 1.461 (4) Å. The N–C bonds involving secondary nitrogen donors N(2) and N(3), N(2)–C(3) and N(3)–C(4), are on average 1.465 (4) Å, which is shorter by 0.039 Å than those in the Ni(II) complex, while N–C bonds around N(7) have an average value of 1.460 (3) Å, which are longer by 0.034 Å than those in the Ni(II) complex.[28] Complex [Ni(**3**)]ClO_4 contains two 1,3-diazacyclopentane ring moieties that are fused to amino functions at the bridgehead position of the six-membered chelate rings. The six- and five-membered chelate rings adopt the chair and gauche conformation, respectively. The two 1,3-diazacyclopentane rings have an envelope conformation, and these are located anti and nearly perpendicular (109°) to the coordination plane. As was observed for the Ni(II) complexes,[30] the C–N(uncoordinated) distances in the six-membered chelate rings are significantly shorter (average of four N–C distances is 1.448 (9) Å) than normal aliphatic N–C distances (~1.52 Å).

The four nitrogen donor atoms of the Ni(I) complexes form a least-squares plane. The maximum deviation of the nitrogen atoms from the least-squares plane is 0.008 (4) Å for [Ni(**1**)]$ClO_4\cdot CH_3CN$ and 0.095 (9) Å for [Ni(**3**)]ClO_4. The nickel atom is displaced from the least-squares plane by 0.042 (1) Å for the former complex and 0.027 (2) Å for the latter. Thus, complex [Ni(**1**)]$^+$ shows a square-pyramidal distortion and [Ni(**3**)]$^+$ shows a tetrahedral distortion. The distortions in the Ni(I) complexes are increased compared with those in the Ni(II) analogs (Table VIII).

The most interesting structural features observed in the Ni(I) complexes of **1** and **3** are the Ni–N bond distances. The size of the Ni(I) ion should be larger than the Ni(II) ion in the square-planar geometry because of an additional electron in the $d_{x^2-y^2}$ orbital, and the UV/vis spectra indicated significantly weaker ligand field strengths for the Ni(I) complexes than for the Ni(II) complexes. Thus, the Ni–N bond distances of the Ni(I) complexes are anticipated to be much longer than those of the Ni(II) complexes. However, the structures of [Ni(**1**)]$ClO_4\cdot CH_3CN$ and [Ni(**3**)]ClO_4 indicate two sets of Ni–N bond distances rather than a simple expansion of the macrocyclic core. In [Ni(**1**)]$ClO_4\cdot CH_3CN$, two Ni–N bonds involving secondary nitrogen donors N(2) and N(3) have an average bond distance of 1.893 (2) Å and the other two Ni–N bonds involving tertiary nitrogens N(1) and N(4) have an average bond distance of 1.936 (2) Å. The nickel(II) perchlorate complex of the corresponding ligand showed an average Ni–N bond distance of 1.918 (3) Å without significant difference in Ni–N bond distances between secondary and tertiary nitrogens.[28] As a consequence of short Ni–N(2) and Ni–N(3) bonds in the Ni(I) complex, the N(2)–Ni–N(3) bite angle of 93.6 (1)° and the N(2)–N(3) bite distance of 2.759 (5) Å are smaller than those (95.4° and 2.836 (6) Å) of the Ni(II) complex. The N(1)–Ni–N(4) bite angle and N(1)–N(4) bite distance are almost the same as those in the Ni(II) complex due to the rigidity of tetraazabicyclononane ring. Thus, there is almost no expansion of the macrocyclic core. In [Ni(**3**)]ClO_4, the two Ni–N bonds involving N(1) and N(5) have an average bond distance of 1.859 (7) Å and the other two Ni–N bonds involving N(2) and N(4) have an average bond distance of 1.974 (7) Å. Here, Ni–N bond distances are not differentiated by the secondary and tertiary amines, contrary to the observation made for [Ni(**1**)]$ClO_4\cdot CH_3CN$. It is not likely that secondary and tertiary amines determine the short or long Ni–N bond distances in the present Ni(I) complexes of **1** and **3**. Instead, it is observed for both of the Ni(I) macrocyclic complexes that the two cis-Ni–N bonds involving a six-membered chelate ring form a set of long

Table VIII. Comparison of Structures between Nickel(I) and Nickel(II) Perchlorate Complexes of Macrotricyclic Ligands

		distortion, Å[a]		five-membered chelate rings		six-membered chelate rings	
complex	av Ni–N, Å	Ni	N	N–N, Å	N–Ni–N, deg	N–N, Å	N–Ni–N, deg
[Ni(**1**)]$^+$	1.893 (2)	0.04	±0.01	2.67 (1)	88.4 (1)	2.76 (1)	93.6 (1)
	1.936 (2)			2.68 (1)	88.9 (1)	2.72 (1)	89.0 (1)
[Ni(**1**)]$^{2+}$	1.918 (3)	0.03	±0.01	2.66 (1)	87.7 (2)	2.84 (1)	95.4 (2)
				2.65 (1)	87.7 (2)	2.69 (1)	89.1 (2)
[Ni(**3**)]$^+$	1.859 (7)	0.03	±0.09	2.69 (2)	88.1 (5)	2.74 (2)	94.0 (5)
	1.974 (7)			2.60 (2)	85.5 (5)	2.86 (2)	92.9 (5)
[Ni(**3**)]$^{2+}$	1.923 (2)	0.02	±0.08	2.66 (1)	87.4 (2)	2.75 (1)	91.3 (2)
				2.64 (1)	86.9 (2)	2.83 (1)	94.7 (2)

[a] The shift from the least-squares plane made by four nitrogen donors.

or short bonds. It is noteworthy that Ni–N(tert) bond distances of the Ni^{II}TMC complex are longer than Ni–N(sec) bond distances of the Ni(II) cyclam complex[37] but no significant difference exists in the Ni–N distances between the secondary and the tertiary amines for the Ni(II) complexes containing both secondary and tertiary nitrogen donors in the macrocyclic ligand.[28,30]

The structures of the Ni(I) and Ni(II) complexes are compared in Table VIII. The N–N bite distances of five- and six-membered chelate rings in Ni(I) complexes of **1** and **3** are not always longer than those of the corresponding Ni(II) complexes. It is evident that reduction of Ni(II) to Ni(I) induces two different sets of Ni–N bonds as well as the increased distortion of the coordination geometry, rather than a simple expansion of the macrocyclic hole. The relatively large extinction coefficient of the d–d transitions in the Ni(I) complexes may be attributed to these distortions and the asymmetric Ni–N bond distances. Although there has been only one X-ray structure of a Ni(I) macrocyclic complex reported so far[22] other than this study, the report as well as the reports on the analyses of EXAFS data for Ni(I) F_{430} (A) and the Ni^{I}iBC derivative (B) also suggested two sets of Ni–N distances.[25,26] In Ni(I) tetraazamacrocyclic complex C, all Ni–N bond lengths are longer than those in the Ni(II) complex and each set is formed by trans-Ni–N bonds, differentiating the imine and amine nitrogens. The different bond lengths of Ni–N(imine) and Ni–N(amine) are also observed in the Ni(II) complex although the difference between two sets of Ni–N bond distances is larger in the Ni(I) complex.[22] The present results for the Ni(I) complexes of macrocyclic ligands **1** and **3**, however, show that cis-Ni–N bonds involving a six-membered chelate ring form a set almost without expansion of the macrocyclic core.

The occurrence of two sets of Ni–N bond distances is common in all of the square-planar Ni(I) compounds studied so far for the synthetic macrocyclic ligands as well as the porphyrin derivatives. In order to draw conclusions, however, for the structural changes associated with the reduction of Ni(II) to Ni(I) in the square-planar macrocyclic complexes, X-ray crystallographic studies on Ni(I) complexes with more symmetric ligands such as cyclam or R_2[14]aneN_6[38] are needed.

Acknowledgment. We thank Professor Hyun-Soo So at Seo-Gang University for helpful discussions about EPR spectra. This work was supported by grants from the Ministry of Education (1990) and the Korea Science and Engineering Foundation (90-03-05) of the Republic of Korea.

Supplementary Material Available: Tables listing anisotropic thermal parameters for [Ni(**1**)]$ClO_4 \cdot CH_3CN$ and [Ni(**3**)]ClO_4 and hydrogen atom positions for [Ni(**1**)]$ClO_4 \cdot CH_3CN$ (Tables S1–S3) and a packing diagram of [Ni(**1**)]$ClO_4 \cdot CH_3CN$ (Figure S1) (5 pages). Ordering information is given on any current masthead page.

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