Selective Synthesis of a New Macropolycycle Containing One N-CH$_2$-N Linkage and Its Reaction with Cu^{2+} and Ni^{2+} Ions in Methanol

Shin-Geol Kang, * **Jae Keun Kweon, Gyeong Rok Jeong, and Uk Lee**[†,*]

*Department of Chemistry, Daegu University, Gyeongsan 712-714, Korea. *E-mail: sgkang@daegu.ac.kr*
*†Department of Chemistry, Pukyong National University, Busan 608-737, Korea. *E-mail: uklee@pknu.ac.kr*
Received July 2, 2008

The reaction of 3,14-dimethyl-2,6,13,17-tetraazatetracyclo[16.4.0$^{1.18}$.0$^{7.12}$]docosane (L^1) with formaldehyde in warm methanol yielded 3,14-dimethyl-2,6,13,17-tetraazatetracyclo[16.4.1$^{2.6}$.0$^{1.18}$.0$^{7.12}$]tricosane (L^7) containing one 1,3-diazacyclohexane subunit. In methanol, L^7 readily reacts with Cu^{2+} ion to form [CuL^7(H$_2$O)]$^{2+}$ which is extremely inert against methanolysis. In the solution containing Ni^{2+} ion, however, L^7 reacts with methanol to yield [NiL^3]$^{2+}$ (L^3 = 2-(methoxymethyl)-5,16-dimethyl-2,6,13,17-tetraazatricyclo[16.4.0$^{1.18}$.0$^{7.12}$]-docosane), in which one *N*-CH$_2$OCH$_3$ pendant arm is appended. The copper(II) complex [CuL^7(H$_2$O)]-(ClO$_4$)$_2$·3H$_2$O (**I·3H$_2$O**) has a severely distorted trigonal bipyramidal coordination geometry with a 4-5-6-5 chelate ring sequence. The crystal structure of [NiL^3](PF$_6$)$_2$·2H$_2$O (**IIb**) shows that the *N*-CH$_2$OCH$_3$ pendant arm is not coordinated to the metal ion in the solid state. In various solvents (S), however, the nickel(II) complex exists as a mixture of [NiL^3(S)]$^{2+}$, in which the *N*-CH$_2$OCH$_3$ group as well as S is coordinated to the metal ion, and [NiL^3]$^{2+}$.

Key Words : Macrocycle, Nickel(II) complex, Copper(II) complex, Crystal structure, Methoxymethyl group

Introduction

The design and preparation of polyaza macrocyclic ligands and complexes bearing additional functional pendant arms have received much attention because of their interesting chemical properties which are influenced by various factors, such as the number, position, and nature of the functional groups.[1-11]
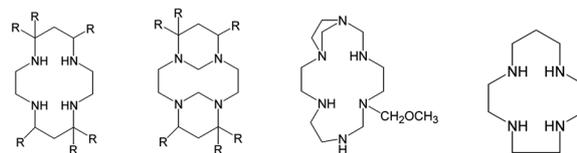
Formaldehyde has been utilized for the preparation of various types of polyaza macrocyclic and macropolycyclic compounds containing N-CH$_2$-N linkages.[12-19] For instance, the reaction of L^9 or L^{10} with two equivalents of formaldehyde yields L^{11} or L^{12} containing two 1,3-diazacyclohexane rings.[12-18] However, the major product prepared from the reaction of L^1 with two equivalents of formaldehyde is L^6 containing two 1,3-diazacyclopentane rings.[19] Interestingly, L^6 readily reacts with methanol in the presence of Cu^{2+} ion to yield [CuL^2]$^{2+}$ bearing two *N*-CH$_2$OCH$_3$ pendant arms (Eq. (1)).[19] It has been revealed that one of the two *N*-CH$_2$OCH$_3$ groups in [CuL^2]$^{2+}$ is coordinated to the metal ion in the solid state and in various solvents.[19] A few other macrocyclic complexes bearing *N*-CH$_2$OCH$_3$ group(s), such as [NiL^{13}(Cl)]$^+$, have also been reported.[10,11] As far as we know, however, [CuL^2]$^{2+}$ is a rarely prepared 14-membered tetraaza macrocyclic complex where the *N*-CH$_2$OCH$_3$ group is involved in coordination. Therefore, we have been interested in the preparation and chemical properties of various types of macrocyclic compounds containing N-CH$_2$-N linkages and those bearing *N*-CH$_2$OCH$_3$ pendant arm(s).

In this work, we attempted the reaction of L^1 with one equivalent of formaldehyde and successfully prepared 3,14-dimethyl-2,6,13,17-tetraazatetracyclo[16.4.1$^{2.6}$.0$^{1.18}$.0$^{7.12}$]tricosane (L^7) containing one 1,3-diazacyclohexane subunit. In methanol, L^7 binds Cu^{2+} ion to form [CuL^7(H$_2$O)]$^{2+}$ which is extremely inert against methanolysis. In the presence of Ni^{2+} ion, however, L^7 reacts with methanol to yield [NiL^3]$^{2+}$ (L^3 = 2-(methoxymethyl)-5,16-dimethyl-2,6,13,17-tetraazatri-cyclo[16.4.0$^{1.18}$.0$^{7.12}$]docosane) bearing one *N*-CH$_2$OCH$_3$ pendant arm. This paper reports the synthesis and chemical properties of L^7, [CuL^7(H$_2$O)]$^{2+}$, and [NiL^3]$^{2+}$. Crystal structures of [CuL^7(H$_2$O)](ClO$_4$)$_2$·3H$_2$O (**I·3H$_2$O**) and [NiL^3](PF$_6$)·2H$_2$O (**IIb**) are also described.
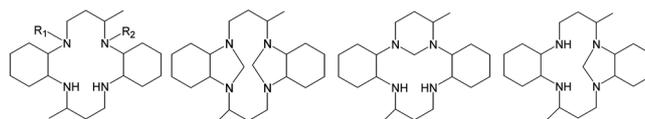
L^1: R$_1$ = R$_2$ = H   L^6 L^7 L^8
L^2: R$_1$ = R$_2$ = CH$_2$OCH$_3$
L^3: R$_1$ = CH$_2$OCH$_3$; R$_2$ = H
L^4: R$_1$ = CH$_2$CH$_2$OH; R$_2$ = H
L^5: R$_1$ = CH$_2$CH$_2$CN; R$_2$ = H

L^9: R = H   L^{11}: R = H   L^{13} L^{14}
L^{10}: R = Me   L^{12}: R = Me

$$Cu^{2+} + L^6 + 2CH_3OH \rightarrow [CuL^2]^{2+} \qquad (1)$$
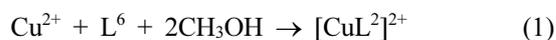
Experimental

Measurements. Electronic absorption spectra were obtain-

ed using an Analytic Jena Specord 200 UV/vis spectro-photometer, infrared spectra with a Genesis II FT-IR spectrometer, and NMR spectra with a Varian Mercury 300 FT NMR spectrometer. GC-mass spectra were measured with a Shimadzu GCMSD-QP5050 spectrometer. Conductance measurements were taken with a Metrohm Herisau Conductometer E518. Magnetic moments were calculated from magnetic susceptibility data obtained at 293 K using a Johnson Matthey MK-1 magnetic susceptibility balance. FAB-mass spectra and elemental analyzes were performed at the Korea Basic Science Institute, Daegu, Korea.

Safety note: Perchlorate salts of transition metal complexes with organic ligands are often explosive and should be handled with caution.

Preparation of $L^7 \cdot H_2O$. The macropolycycle L^1 was prepared as described previously.[20] A methanol solution (30 mL) of L^1 (3.0 g, 9.0 mmol) and 35% formaldehyde (0.92 mL, 11.7 mmol) was stirred in a warm water bath (*ca.* 50 °C) for 1 h. During which time a small amount of white solid (L^6) was precipitated. The solution was filtered at room temperature, and 1.0 M NaOH aqueous solution (*ca.* 20 mL) was added to the filtrate. The mixture was evaporated at room temperature to precipitate a white solid. The crude product was collected by filtration and was dissolved in minimum volume of methanol at room temperature. After the addition of acetonitrile (*ca.* 20 mL), the resulting solution was evaporated at room temperature. The white solid formed was collected by filtration, washed with acetonitrile, and dried in air at room temperature (Yield: ~60%). Anal. Calcd for $C_{21}H_{42}N_4O$: C, 68.80; H, 11.55; N, 15.28. Found: C, 67.96; H, 12.25; N, 15.12%. GC-Mass (*m/z*): 348 (M⁺). IR (Nujol mull, cm⁻¹): 3400 (ν_{O-H}, H_2O), 3287 (ν_{N-H}), 3265 (ν_{N-H}). ¹³C-NMR (CDCl₃): 20.0, 21.4, 23.1, 23.3, 24.7, 25.3 (*d*), 25.9, 31.7 (*d*), 33.2, 35.4 (*d*), 41.9, 46.3, 50.2, 51.4, 52.8, 53.3, 59.2, and 62.2 (N-*CH₂*-N) ppm.

Preparation of $[CuL^7(H_2O)](ClO_4)_2$ (I). A methanol solution (20 mL) of $L^7 \cdot H_2O$ (2.0 g, 5.5 mmol) and Cu(OAc)₂·H₂O (3.0 g, 15 mmol) was stirred for 10 min at room temperature. After the addition of an excess amount of NaClO₄ dissolved in water (20 mL), the solution was slowly evaporated to precipitate a blue solid. The solid was collected by filtration, washed with water, and dried in air. The product was recrystallized from a hot acetonitrile-water (1:2) solution (Yield: ~70%). Anal. Calcd for $C_{21}H_{42}N_4CuCl_2O_9$: C, 40.10; H, 6.73; N, 8.91. Found: C, 40.90; H, 6.68; N, 9.15%. FAB mass (*m/z*): 509.8 $[Ni(L^7) + ClO_4]^+$, 410.1 $[Ni(L^7) - H]^+$. IR (cm⁻¹): 3500 (ν_{O-H}, H_2O), 3230 (ν_{N-H}), 3190 (ν_{N-H}), 1620 (δ_{HOH}). This complex was also prepared as the only product even after refluxing a methanol solution of L^7 and Cu(OAc)₂·H₂O for >24 h.

Preparation of $[NiL^3](ClO_4)_2 \cdot 2H_2O$ (IIa). A methanol suspension (30 mL) of $L^7 \cdot H_2O$ (2.0 g, 5.5 mmol) and Ni(OAc)₂·4H₂O (*ca.* 3.7 g, 15 mmol) was refluxed for *ca.* 1 hr. After the addition of NaClO₄ (> 2.0 g) at room temperature, the mixture was stored in a refrigerator to precipitate an orange-red solid. The solid was collected by filtration, washed with water, and dried in air. The product was

recrystallized from a hot acetonitrile-water (3:1) solution (Yield: ~80%). Anal. Calcd for $C_{22}H_{48}N_4NiCl_2O_{11}$: C, 39.16; H, 7.18; N, 8.31. Found: C, 38.89; H, 7.05; N, 8.22%. FAB mass (*m/z*): 437.0 $[Ni(L^3) - H]^+$, 536.8 $[Ni(L^3) + ClO_4]^+$. IR (cm⁻¹): 3520 (ν_{OH}, H_2O), 3210 (ν_{N-H}), 3150 (ν_{N-H}), 3100 (ν_{N-H}), 1620 (δ_{HOH}). This complex could be prepared as the only product by the reaction of L^6 (2.0 g) with methanol in the presence of Ni(OAc)₂·4H₂O (*ca.* 3.0 g) under similar experimental conditions.

Preparation of $[NiL^3](PF_6)_2 \cdot 2H_2O$ (IIb). Addition of an excess of NH₄PF₆ to a warm acetonitrile (*ca.* 5 mL) suspension of $[NiL^3](ClO_4)_2 \cdot 2H_2O$ (*ca.* 0.4 g) produces the white solid NH₄ClO₄. After filtration, water (10 mL) was added to the filtrate. A red solid was collected by filtration, washed with water, and dried in air. Yield: ~90%. Anal. $C_{22}H_{48}N_4Ni$-$P_2O_3F_{12}$: C, 34.53; H, 6.43; N, 7.32. Found: C, 34.35; H, 6.56; N, 7.37%. IR (cm⁻¹): 3530 (ν_{O-H}, H_2O), 3170 (ν_{N-H}), 3220 (ν_{N-H}), 1620 (δ_{HOH}). ¹³C NMR (CD₃NO₂): 16.3, 16.6, 25.4, 25.5, 25.6, 25.8, 26.6, 30.8, 31.6, 31.7, 33.3, 40.7, 46.0, 47.2, 51.7, 58.1, 58.3, 58.5, 61.0, 66.2, 74.0, and 86.1 ppm.

Crystal Structure Determination. Single-crystals of **I·3H₂O** and **IIb** suitable for X-ray study were grown from water-DMSO and water-acetonitrile, respectively. Data were

Table 1. Crystal and Refinement Data for **I·3H₂O** and **IIb**

Complex	**I·3H₂O**	**IIb**
Formula (*M*)	$C_{21}H_{48}Cl_2CuN_4O_{12}$ (683.07)	$C_{22}H_{48}F_{12}N_4NiO_3P_2$ (765.29)
T (K)	298	173
Crystal system (Space group)	Tetragonal (*I* 41/*a*)	Monoclinic (*P*2₁/*c*)
a / *b* / *c* (Å)	26.268(4)/26.268(4)/ 18.727(5)	9.238(2)/18.534(2)/ 11.581(2)
β (°)	90	127.2(1)
V (Å³)	12922(4)	1578.5(2)
Z	16	2
D_{calc} (g cm⁻³)	1.404	1.610
μ (cm⁻¹)	9.0	8.2
F(000)	5776	796
θ range (°)	1.55 – 25.00	2.3 - 28.3
Limiting indices	$-21 \le h \le 22, 0 \le k \le 31, 0 \le l \le 22$	$-11 \le h \le 11, -23 \le k \le 23, -14 \le l \le 14$
Reflections collected	5695	12860
Independent reflections	5695	3229
Reflections with $I > 2\sigma(I)$	3604	3151
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	1.103	1.296
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0946$, $wR_2 = 0.2251$	$R_1 = 0.0874$, $wR_2 0.2004$
R indices (all data)	$R_1 = 0.1525$, $wR_2 = 0.2918$	$R_1 0.0888$, $wR_2 = 0.2009$
Largest diff. peak and hole (eÅ⁻³)	0.969 and −0.467	

collected at 298 (**I·3H$_2$O**) and 173 K (**IIb**) on a Bruker (**I·3H$_2$O**) or STOE STADI4 (**IIb**) single crystal diffracto-meter equipped with a graphite monochromer (λ = 0.71069 (**I**) or 0.71073 Å (**IIb**). Direct methods were used to solve the structures and to locate the heavy atoms.[21] All H atoms were positioned geometrically and refined using a riding model, with 0.97 Å for methylene and 0.96 Å for methyl H atoms, and with U_{iso}(H) = 1.2U_{eq}(C) for methylene H atoms and U_{iso}(H) = 1.5U_{eq}(C) for methyl H atoms. The hydrogen atoms of water molecules in the complex could not be found on the difference maps. The deepest hole for **IIb** was −1.42 eÅ^{-3} located 1.37 Å from H12C and the largest peak was 0.63 eÅ^{-3} located 1.57 Å from H12C. Absorption corrections were performed using SADABS (for **I·3H$_2$O**) and X-SHAPE (for (**IIb**) programs. Crystallographic data and the result of refinements are summarized in Table 1.

Results and Discussion

Synthesis. The major product prepared from the reaction of L^1 and formaldehyde in a 1:1 molar ratio was L^7 contain-ing one 1,3-diazacyclohexane ring; the isomer L^8 could not be prepared in the present experimental conditions. The mass, infrared, and ^{13}C-NMR spectra of L^7 were listed in the Experimental section. The structure of L^7 was confirmed by the crystal structure of its copper(II) complex (*see* below). The reasons for the predominant formation of L^7 are not clearly understood at this point.

As described in the Experimental section, L^7 rapidly reacts with Cu^{2+} ion in methanol to form the complex **I** as the only product. Unexpectedly, the macrotetracycle does not react with methanol in the presence of the metal ion; any copper(II) complex of L^3 could not be prepared even after refluxing the methanol solution for > 24 h. This means that the copper(II) complex of L^7 is quite inert against methano-lysis. Our attempts to prepare nickel(II) complex of L^7 from the reaction of the macrocycle with the metal ion in meth-anol or acetonitrile at room temperature were unsuccessful. The addition of NaClO$_4$ to the resulting solution produced the white salt L^7·2HClO$_4$, indicating that L^7 did not form

stable nickel(II) complex. In the refluxing methanol solution containing Ni^{2+} ion, however, L^7 readily reacts with meth-anol to yield the complex **IIa** bearing one N-CH$_2$OCH$_3$ pendant arm (*see* the Experimental section). The preparation of the metal-free macrocycle L^3 was attempted from the reaction of **IIa** with NaCN in acetonitrile-water, but failed. The only macrocyclic compound isolated from the reaction solution was found to be L^1. This shows that the pendant N-CH$_2$OCH$_3$ group of L^3 is readily hydrolyzed or decomposed when the macrocycle is removed from the coordination sphere. The synthetic procedures for the copper(II) and nickel(II) complexes are summarized in Scheme 1.

Obviously, the reaction of L^7 with methanol is strongly influenced by the nature of the metal ions. It is likely that the reaction is initiated by the protonation of the tertiary amino group in L^7. Therefore, one of the reasons for the inertness of **I** (or L^7 in the presence of Cu^{2+} ion) against methanolysis may be the relatively strong Cu-N (N-CH$_2$-N linkage) bonds (*see* below); the coordination of L^7 to the metal ion weakens the proton affinity of the amino groups and stabilizes the N-CH$_2$-N linkage. In the methanol solution of Ni^{2+} ion, L^7 can react with methanol because it is not so strongly coordinated to the metal ion. Furthermore, the product (L^3) is stabilized by the formation of its nickel(II) complex. However, the effects of the metal ions on the reaction are not clearly understood at this point.

X-ray Crystal Structure of I·3H$_2$O. The ORTEP draw-ing of [CuL^7(H$_2$O)]$^{2+}$ in **I·3H$_2$O** is shown in Figure 1, and its bond distances and angles are listed in Table 2. The macrotetracyclic ligand contains one 1,3-diazacyclohexane ring. Four nitrogen atoms of L^7 are involved in coordination, along with one water molecule, and the complex has a 4-5-6-5 chelate ring sequence. Figure 1 and Table 2 show that the coordination geometry is severely distorted from regular trigonal bipyramidal structure. The metal ion lies 0.604(3) Å above the mean N$_4$ plane toward the O(1w) atom and, therefore, the N-Cu-O(1w) angles are distinctly larger than 90°. The *trans*-N(1)-Cu-N(3) and N(2)-Cu-N(4) angles are 142.8(3) and 138.2(3)°, respectively. The N(1)-Cu-N(2) angle involved in the four-membered chelate ring (67.4(3)°)
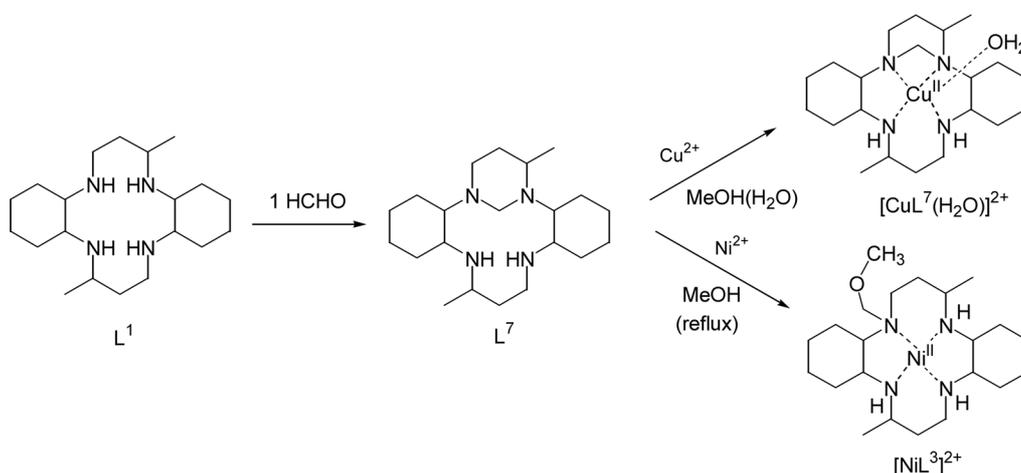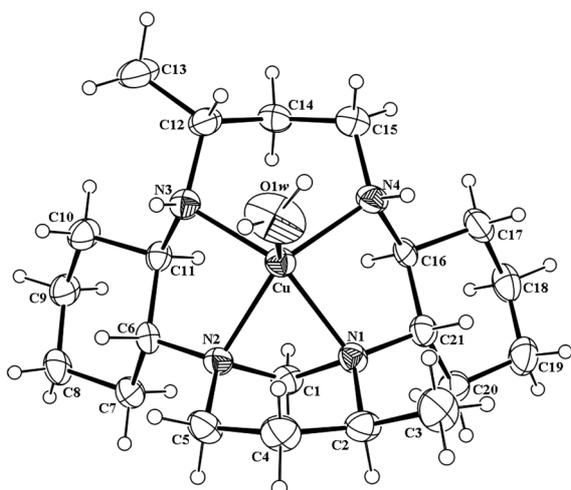
Scheme 1

Figure 1. An ORTEP drawing of $[CuL^7(H_2O)]^{2+}$ cation in **I·2H₂O**.

Table 2. Bond Distances (Å) and Angles (°) for **I·3H₂O**

Cu-N(1)	2.061(7)	Cu-N(2)	2.039(7)
Cu-N(3)	2.031(7)	Cu-N(4)	2.042(7)
Cu-O(1)	2.105(9)		
N(1)-Cu-N(2)	67.4(3)	N(1)-Cu-N(3)	142.8(3)
N(1)-Cu-N(4)	84.0(3)	N(2)-Cu-N(3)	84.8(3)
N(2)-Cu-N(4)	138.2(3)	N(3)-Cu-N(4)	103.2(3)
N(1)-Cu-O(1)	116.4(4)	N(2)-Cu-O(1)	117.7(4)
N(3)-Cu-O(1)	98.0(4)	N(4)-Cu-O(1)	102.0(3)
N(1)-C(1)-N(2)	100.4(6)	C(1)-N(1)-Cu	84.0(4)

Table 3. Hydrogen Bond Geometry (Å, °) for **I·3H₂O**

D-H···A	$d(D$-H)	d(H···A)	$d(D$···A)	<(D-H···A)
O(1w)-HAW···O(11w)	0.9 (1)	2.0 (1)	2.77(2)	137(12)
O(1w)-HBW···O(10w)	0.80(7)	1.97(8)	2.73(2)	161(11)
N(3)-H(3)···O(8^i)	0.91	2.49	3.35(2)	156.7
N(4)-H(4)···O(6)	0.91	2.42	3.30(2)	161.7
C(6)-H(6)···O(6^i)	0.98	2.59	3.55(2)	167.2
C(11)-H(11)···O(2)	0.98	2.50	3.44(3)	160.8

Symmetry code: (i) −y+5/4, x−1/4, z−1/4

is considerably smaller than other N-Cu-N angle involved in the five-membered (84.0(3) or 84.8(3)°) or six-membered chelate (103.2(3)°) ring. The Cu-O(1w) distance (2.105(9) Å) is longer than the Cu-N distances (2.031(7)-2.061(7) Å). Table 3 and Figure 2 show that the coordinated water molecule is hydrogen bonded to the oxygen atoms (O(10w) and O(11w)) of two uncoordinated water molecules. The secondary amino groups involving the N(3) and N(4) atoms are also hydrogen bonded to the oxygen atoms of the perchlorate anions.

X-ray Crystal Structure of IIb. The ORTEP drawing (Fig. 3) of $[NiL^3]^{2+}$ in **IIb** shows that one N-CH₂OCH₃ pendant arm is attached to one of the less sterically hindered nitrogen atoms of the ligand. The atoms of L^3 and two water molecules are located as positional disorder by occupancy 0.5. The N-CH₂OCH₃ group and the C-methyl group at the
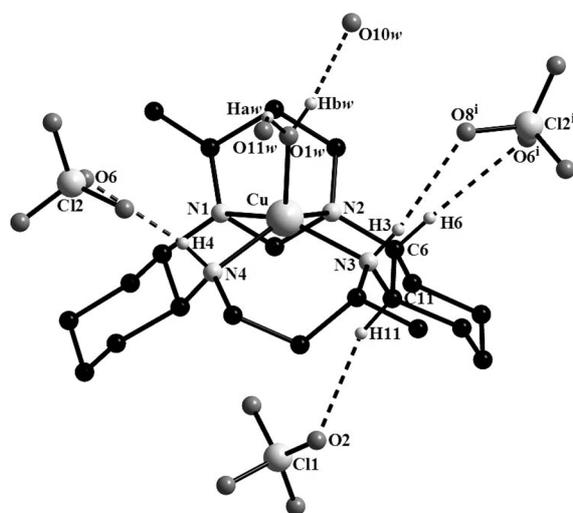

Figure 2. A perspective view of **I·2H₂O** showing hydrogen bonds. The hydrogen bonds are shown as dotted lines. Symmetry code: (i) −y+5/4, x−1/4, z−1/4.
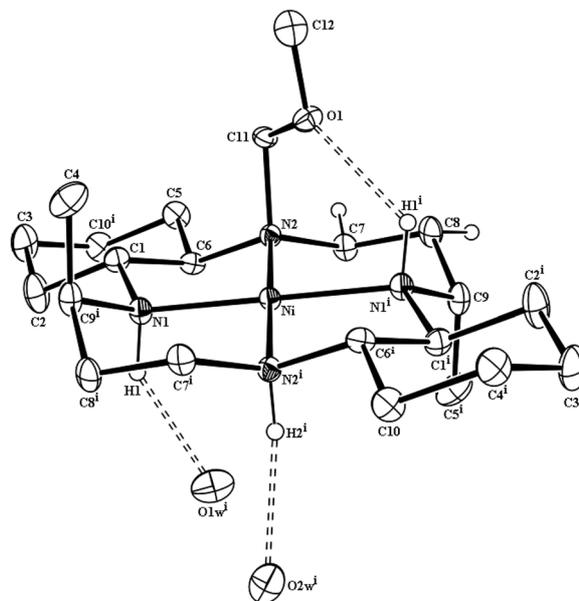
Figure 3. An ORTEP drawing of $[NiL^2]^{2+}$ cation in **IIb**. Symmetry code: (i) 1−x, −y, −z.

six-membered chelate ring are *anti* with respect to the plane. The macrocyclic ligand adopts the *trans*-III stereochemistry.

The Ni-N distances (Table 4) are comparable with those of other related low-spin nickel(II) complexes of 14-membered tetraaza macrocycles. The Ni-N(2) (tertiary) distance (1.976 (5) Å) is longer than the Ni-N (secondary) distance (1.951(5) Å), as usual. The Ni···O(1) distance (2.769(7) Å) is *ca*. 0.3 Å longer than the Cu-O (one of the two N-CH₂OCH₃ groups) distance (2.471(2) Å) of $[CuL^2](ClO_4)_2$·CH₃CN.[19] This strongly shows that, in contrast to the case of $[CuL^2]$-$(ClO_4)_2$·CH₃CN, the metal ion of **IIb** is not directly coordinated by the oxygen atom of the N-CH₂OCH₃ group. When the O(1) atom is not involved in coordination, the complex has a square-planar coordination polyhedron in the solid state. The observed N(1^i)···O(1) distance (2.87(2) Å) shows

Table 4. Bond Distances (Å) and Angles (°) for **IIb**

Ni-N(1)	1.951(5)	Ni-N(2)	1.976(5)
Ni⋯O(1)	2.738(9)	O(1)-C(11)	1.41(1)
O(1)-C(12)	1.41(2)	N(1)-C(1)	1.503(7)
N(2)-C(11)	1.56(1)	N(2)-C(6)	1.511(7)
N(1)-Ni-N(2)	86.0(2)	C(11)-O(1)-C(12)	111(2)
O(1)-C(11)-N(2)	108.0(8)	Ni-N(2)-C(11)	106.1(5)

Table 5. Hydrogen Bond Geometry (Å, °) for **IIb**

D-H⋯A	$d(D\text{-H})$	$d(\text{H}⋯A)$	$d(D⋯A)$	$<(D\text{-H}⋯A)$
N(1^i)-H(1^i)⋯O(1)	0.99(8)	2.23(8)	2.87(2)	121(6)
N(1)-H(1)⋯O(1w^i)	0.99(8)	2.09(8)	2.94(3)	143(6)
N(2^i)-H(2^i)⋯O(2w^i)	0.91	2.16	3.05(2)	167

Symmetry codes: (i) −x+1, −y, −z.

that the secondary amino group involving the N(1^i) atom is hydrogen bonded to the oxygen atom of the pendant N-CH$_2$OCH$_3$ group (Fig. 3 and Table 5). The secondary amino groups involving the N(1) and N(2^i) atoms are also hydrogen bonded to the oxygen atoms of water molecules.

Spectra and Properties of I. The infrared spectrum of **I** shows $\nu_{N\text{-}H}$ of the secondary amino groups at *ca.* 3230 and 3190 cm^{-1}. Visible absorption spectra (Table 6) of the complex measured in various solvents show a *d-d* band at *ca.* 700 nm ($\varepsilon = 400$-450 M^{-1}cm^{-1}), supporting the crystallographic result that the complex has distorted trigonal bipyramidal coordination polyhedron. The molar conductance value (245 Ω^{-1}mol^{-1}cm^2) of the complex measured in acetonitrile indicates that the complex is a 1:2 electrolyte.

As described above, the complex is extremely inert against methanolysis. The complex is also stable in neutral aqueous solution; no evidence of hydrolysis or decomposition of the complex was observed even in boiling aqueous solution during > 5 h. However, the complex is rapidly decomposed in low pH at room temperature. The decomposition rate of the complex (2.0 × 10^{-3} M) in 0.1 M HClO$_4$ solution was measured spectrophotometrically. The pseudo first-order rate constant (k) measured at 20 °C was found to be 1.9 × 10^{-2} sec^{-1} ($t_{1/2} = ca.$ 36 sec). The reaction rate of **I** is much faster than that of the square-planar complex [CuL^{14}](ClO$_4$)$_2$ ($k = 4.5 \times 10^{-4}$ sec^{-1} in 0.3 M HClO$_4$ solution at 20 °C) with a 5-5-5-6 chelate ring sequence.[22]

Spectra and Properties of IIa and IIb. The IR spectrum of **IIa** shows three peaks of $\nu_{N\text{-}H}$ at 3210, 3150, and 3100 cm^{-1}. The molar conductance value (230 Ω^{-1}mol^{-1}cm^2) of **IIa** measured in acetonitrile indicates that the complex is a 1:2 electrolyte. Both **IIa** and **IIb** were found to be diamagnetic compounds. ^{13}C-NMR spectrum (*see* Experimental section) of **IIb** as well as FAB mass spectrum of **IIa** is consistent with the ligand structure. Visible absorption spectra (Table 6) of **IIa** and **IIb** measured in Nujol mull and in nitromethane show a *d-d* band at *ca.* 484 nm. The spectra are comparable with those for [NiL^4]$^{2+}$ and [NiL^5]$^{2+}$, in which the N-CH$_2$CH$_2$OH or N-CH$_2$CH$_2$CN pendant arm is

Table 6. Electronic Absorption Spectral Data^a

Complex	λ_{max}, nm (ε, M^{-1}cm^{-1})			
[NiL^1](ClO$_4$)$_2$ ^{b}	463(73)			
IIa	485(84)	484(64)^c	483(81)^d	485(51)^e
IIb	486(84)	485(63)^c	482(81)^d	485(50)^e
[NiL^4](ClO$_4$)$_2$ ^{f}	485(86)	480(50)^c	480(62)^d	479(48)^e
[NiL^5](ClO$_4$)$_2$ ^{g}	484(95)	483(90)^c	485(87)^d	483(91)^h
I	702(400)	715(405)^c	690(450)^h	

^{a}In nitromethane at 20 °C unless otherwise specified. ^{b}Ref. 20. ^{c}In acetonitrile. ^{d}In dimethylsulfoxide. ^{e}In DMF. ^{f}Ref. 9. ^{g}Ref. 8. ^{h}In water.

not involved in coordination.[8,9] This strongly indicates that the pendant N-CH$_2$OCH$_3$ group in [NiL^3]$^{2+}$ is not directly coordinated to the metal ion in the solid state and in nitromethane. The longer wavelength for **IIa** or **IIb**, compared to that for [NiL^1]$^{2+}$, is corresponding to the generally observed trend that the introduction of an alkyl group into a secondary nitrogen atom of a 14-membered tetraaza macrocyclic nickel(II) complex weakens the ligand field strength.[6,8]

Both **IIa** and **IIb** are soluble in various polar solvents, such as nitromethane and acetonitrile, but are nearly insoluble in water. They are extremely stable in the solid state and are relatively stable even in low or high pH. Visible absorption spectra of the complexes (2.0 × 10^{-3} M) measured in 0.1 M HClO$_4$ or 0.1 M NaOH solutions showed no apparent decomposition during 5 h at room temperature.

$$(2)$$
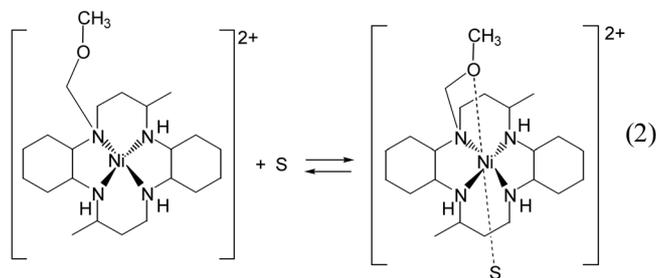
Table 6 shows that the molar absorption coefficients of the *d-d* band (*ca.* 485 nm) for **IIa** measured in Me$_2$SO (81 M^{-1}cm^{-1}), MeCN (64 M^{-1}cm^{-1}), and DMF (51 M^{-1}cm^{-1}) are smaller than that in MeNO$_2$ (84 M^{-1}cm^{-1}), a non-coordinating solvent. This trend is quite similar to that reported for [NiL^4](ClO$_4$)$_2$ bearing one N-CH$_2$CH$_2$OH group, which binds the metal ion in coordinating solvents, but is different from the behavior of [NiL^5](ClO$_4$)$_2$ containing non-coordinating N-CH$_2$CH$_2$CN group (see Table 6).[8,9] Therefore, the relatively small molar absorption coefficients of **IIa** in the coordinating solvents must be closely correlated with the coordination of the pendant N-CH$_2$OCH$_3$ group and the solvent molecule; the coordination of the pendant arm makes the coordination of the solvent molecule easier and *vice versa*.[9] It can be suggested that the nickel(II) complex dissolves in the coordinating solvents (S) to give a mixture (Eq. (2)) of the octahedral [NiL^3(S)]$^{2+}$, in which the oxygen atom of the pendant N-CH$_2$OCH$_3$ group is coordinated to the metal ion, and square-planar [NiL^3]$^{2+}$ species.[9,23-25] Percentage of the octahedral species in each solvent at 20 °C was

determined from the molar absorption coefficient at *ca.* 485 nm. (Percentage of octahedral species = $100\{(\varepsilon_N - \varepsilon_S)/\varepsilon_N\}$ where ε_S and ε_N represent the molar absorption coefficients measured in the coordinating solvent and in nitromethane, respectively.)[9,23,24] The percentage varies with the solvent in the order of Me_2SO (4%) < MeCN (24%) < DMF (39%). This trend is similar to that reported for $[NiL^4]^{2+}$ {Me_2SO (28%) < MeCN (42%) < DMF (45%)}.[9] In each solvent, however, the proportion of the octahedral species for $[NiL^3]^{2+}$ is lower than that for $[NiL^4]^{2+}$. This can be attributed to the relatively weak coordinating ability of the pendant N-CH_2OCH_3 group in $[NiL^3]^{2+}$.

Conclusion

The macrotetracycle L^7 was prepared by the reaction of L^1 with one equivalent of formaldehyde. The macrotetracycle reacts with methanol in the presence of Ni^{2+} ion to yield $[NiL^3]^{2+}$, whereas $[CuL^7(H_2O)]^{2+}$ is prepared as the only product in the presence of Cu^{2+} ion. This work shows that Cu^{2+} ion readily binds L^7 to form the stable complex $[CuL^7(H_2O)]^{2+}$ with a 4-5-6-5 chelate ring sequence and makes the macrotricycle inert against methanolysis. On the other hand, Ni^{2+} ion, which does not bind L^7 so strongly, enables the mathanolysis and stabilize the product L^3 through the formation of the complex $[NiL^3]^{2+}$. The N-CH_2OCH_3 group of $[NiL^3]^{2+}$ is not directly involved in coordination in the solid state. In coordinating solvents (S), the complex exists as a mixture of $[NiL^3(S)]^{2+}$, in which the N-CH_2OCH_3 group as well as S is coordinated to the metal ion, and $[NiL^3]^{2+}$.

References

1. Siegfried, L.; Comparone, A.; Neuburger, M.; Kaden, T. A. *Dalton Trans.* **2005**, 30 and references cited therein.
2. (a) Costamagna, J.; Ferraudi, G.; Matsuhiro, B.; Vampus-Vallette, M.; Canales, J.; Villagran, M.; Vargas, J.; Aguirre, M. J. *Coord. Chem. Rev.* **2000**, *196*, 125. (b) Wainwright, K. P. *Coord. Chem. Rev.* **1997**, *166*, 35 and references cited therein.
3. Lukes, I.; Kotek, J.; Vojtisek, P.; Hermann, P. *Coord. Chem. Rev.* **2001**, *216-217*, 287.
4. Kim, K. J.; Jung, D. S.; Kim, D. S.; Choi, C. K.; Park, K. M.; Byun, J. C. *Bull. Korean Chem. Soc.* **2006**, *27*, 1747.
5. Mayer, M.; Dahaoui-Gindrey, V.; Lecomte, C.; Guilard, R. *Coord. Chem. Rev.* **1998**, *178-180*, 1313.
6. (a) Kang, S.-G.; Kim, M.-S.; Choi, J.-S.; Whang, D.; Kim, K. *J. Chem. Soc., Dalton Trans.* **1995**, 363. (b) Kang, S.-G.; Nam, K.; Jeong, J. H. *Inorg. Chim. Acta* **2008**, in press (doi:10.1016/j.ica.2008.05.016).
7. Kang, S.-G.; Nam, K.; Kweon, J. K.; Jung, S.-K.; Lee, U. *Bull. Korean Chem. Soc.* **2006**, *27*, 577.
8. Kang, S.-G.; Ryu, K. *Bull. Korean Chem. Soc.* **2000**, *21*, 535.
9. Kang, S.-G.; Ryu, K.; Song, J. *Polyhedron* **1999**, *18*, 2193.
10. Suh, M. P.; Choi, J.; Kang, S.-G.; Shin, W. *Inorg. Chem.* **1989**, *28*, 1763.
11. Suh, M. P.; Lee, J.; Han, M. Y.; Yoon, T. S. *Inorg. Chem.* **1997**, *36*, 5651.
12. Tripier, R.; Lagrange, J.-M.; Espinosa, E.; Denat, F.; Guilard, R. *Chem. Commun.* **2001**, 2278 and references cited therein.
13. Alcock, N. W.; Moore, P.; Mok, K. F. *J. Chem. Soc., Perkin Trans. II* **1980**, 1186.
14. Comparone, A.; Kaden, T. A. *Helv. Chim. Acta* **1998**, *81*, 1765.
15. Bucher, C.; Royal, G.; Barbe, J.-M.; Guilard, R. *Tetrahedron Lett.* **1999**, *40*, 2315.
16. Batsanov, A. S.; Goeta, A. E.; Howard, J. A. K.; Maffeo, D.; Puschmann, H.; Williams, J. A. G. *Polyhedron* **2001**, *20*, 981.
17. Royal, G.; Dahaoui-Gindrey, V.; Dahaoui, S.; Tabard, A.; Guilard, R.; Pullumbi, P.; Lecomte, C. *Eur. J. Org. Chem.* **1998**, 1971.
18. Alder, R. W.; Heilbronner, E.; Honegger, E.; McEwen, A. B.; Moss, R. E.; Olefirowicz, E.; Petillo, P. A.; Sessions, R. B.; Weisman, G. R.; White, J. M.; Yang, Z.-Z. *J. Am. Chem. Soc.* **1993**, *115*, 6580.
19. Kang, S.-G.; Kweon, J. K.; Lee, Y. H.; Kim, J.-S.; Lee, U. *Bull. Korean Chem. Soc.* **2007**, *28*, 489.
20. Kang, S.-G.; Kweon, J. K.; Jung, S.-K. *Bull. Korean Chem. Soc.* **1991**, *12*, 483.
21. (a) Sheldrick, G. M. *Acta Cryst.* **2008**, *A64*, 112. (b) Sheldrick, G. M. *SADABS*; University of Göttingen: Germany, 2000.
22. Suh, M. P.; Kang, S.-G. *Inorg. Chem.* **1988**, *27*, 2544.
23. Kang, S.-G.; Jung, S.-K. *J. Korean Chem. Soc.* **1989**, *33*, 510.
24. Iwamoto, E.; Yokoyama, T.; Yamasaki, S.; Yabe, Y.; Kumamaru, T.; Yamamoto, Y. *J. Chem. Soc., Dalton Trans.* **1998**, 1935.
25. Boiocchi, M.; Fabbrizzi, L.; Foti, F.; Vázquez, M. *Dalton Trans.* **2004**, 2616.