

Selective Synthesis of a New Macropolycycle Containing One N-CH₂-N Linkage and Its Reaction with Cu²⁺ and Ni²⁺ 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

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The reaction of 3,14-dimethyl-2,6,13,17-tetraazatetracyclo[16.4.0^{1.18.0^{7.12}}]docosane (L¹) 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 (L⁷) containing one 1,3-diazacyclohexane subunit. In methanol, L⁷ readily reacts with Cu²⁺ ion to form [CuL⁷(H₂O)]²⁺ which is extremely inert against methanolysis. In the solution containing Ni²⁺ ion, however, L⁷ reacts with methanol to yield [NiL³]²⁺ (L³ = 2-(methoxymethyl)-5,16-dimethyl-2,6,13,17-tetraazatri-cyclo[16.4.0^{1.18.0^{7.12}}]docosane), in which one *N*-CH₂OCH₃ pendant arm is appended. The copper(II) complex [CuL⁷(H₂O)](ClO₄)₂·3H₂O (**I-3H₂O**) has a severely distorted trigonal bipyramidal coordination geometry with a 4-5-6-5 chelate ring sequence. The crystal structure of [NiL³](PF₆)₂·2H₂O (**IIb**) shows that the *N*-CH₂OCH₃ 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 [NiL³(S)]²⁺, in which the *N*-CH₂OCH₃ group as well as S is coordinated to the metal ion, and [NiL³]²⁺.

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

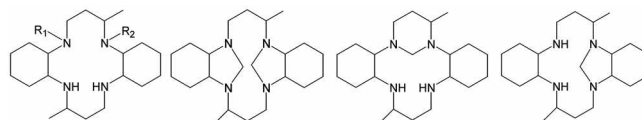
Introduction

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

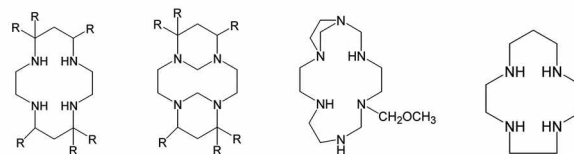
Formaldehyde has been utilized for the preparation of various types of polyaza macrocyclic and macropolycyclic compounds containing N-CH₂-N linkages.¹²⁻¹⁹ For instance, the reaction of L⁹ or L¹⁰ with two equivalents of formaldehyde yields L¹¹ or L¹² containing two 1,3-diazacyclohexane rings.¹²⁻¹⁸ However, the major product prepared from the reaction of L¹ with two equivalents of formaldehyde is L⁶ containing two 1,3-diazacyclopentane rings.¹⁹ Interestingly, L⁶ readily reacts with methanol in the presence of Cu²⁺ ion to yield [CuL²]²⁺ bearing two *N*-CH₂OCH₃ pendant arms (Eq. (1)).¹⁹ It has been revealed that one of the two *N*-CH₂OCH₃ groups in [CuL²]²⁺ is coordinated to the metal ion in the solid state and in various solvents.¹⁹ A few other macrocyclic complexes bearing *N*-CH₂OCH₃ group(s), such as [NiL¹³(Cl)]⁺, have also been reported.^{10,11} As far as we know, however, [CuL²]²⁺ is a rarely prepared 14-membered tetraaza macrocyclic complex where the *N*-CH₂OCH₃ group is involved in coordination. Therefore, we have been interested in the preparation and chemical properties of various types of macrocyclic compounds containing N-CH₂-N linkages and those bearing *N*-CH₂OCH₃ pendant arm(s).

In this work, we attempted the reaction of L¹ 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 (L⁷) containing one 1,3-diazacyclohexane subunit. In

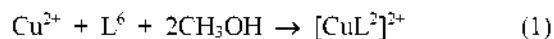
methanol, L⁷ binds Cu²⁺ ion to form [CuL⁷(H₂O)]²⁺ which is extremely inert against methanolysis. In the presence of Ni²⁺ ion, however, L⁷ reacts with methanol to yield [NiL³]²⁺ (L³ = 2-(methoxymethyl)-5,16-dimethyl-2,6,13,17-tetraazatri-cyclo[16.4.0^{1.18.0^{7.12}}]docosane) bearing one *N*-CH₂OCH₃ pendant arm. This paper reports the synthesis and chemical properties of L⁷, [CuL⁷(H₂O)]²⁺, and [NiL³]²⁺. Crystal structures of [CuL⁷(H₂O)](ClO₄)₂·3H₂O (**I-3H₂O**) and [NiL³](PF₆)₂·2H₂O (**IIb**) are also described.



- L¹ : R₁ = R₂ = H
 L² : R₁ = R₂ = CH₂OCH₃
 L³ : R₁ = CH₂OCH₃; R₂ = H
 L⁴ : R₁ = CH₂CH₂OH; R₂ = H
 L⁵ : R₁ = CH₂CH₂CN; R₂ = H



- L⁹ : R = H
 L¹⁰ : R = Me
 L¹¹ : R = H
 L¹² : R = Me



Experimental

Measurements. Electronic absorption spectra were obtain-

ed using an Analytic Jena Specord 200 UV/vis spectrophotometer, 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}). ^{13}C -NMR ($CDCl_3$): 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- CH_2 -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 $Cu(OAc)_2 \cdot H_2O$ (3.0 g, 15 mmol) was stirred for 10 min at room temperature. After the addition of an excess amount of $NaClO_4$ 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 $Cu(OAc)_2 \cdot H_2O$ 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 $Ni(OAc)_2 \cdot 4H_2O$ (ca. 3.7 g, 15 mmol) was refluxed for ca. 1 hr. After the addition of $NaClO_4$ (> 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 $Ni(OAc)_2 \cdot 4H_2O$ (ca. 3.0 g) under similar experimental conditions.

Preparation of $[NiL^3](PF_6)_2 \cdot 2H_2O$ (IIb). Addition of an excess of NH_4PF_6 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 NH_4ClO_4 . 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. $C_{22}H_{48}N_4NiP_2O_3F_{12}$: 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}). ^{13}C NMR (CD_3NO_2): 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**·3 H_2O 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**·3 H_2O and **IIb**

Complex	I ·3 H_2O	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 ($I41/a$)	Monoclinic ($P2_1/c$)
$a/b/c$ (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 (Å ³)	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	$-21 \leq h \leq 22, 0 \leq k \leq 31, 0 \leq l \leq 22$	$-11 \leq h \leq 11, -23 \leq k \leq 23, -14 \leq l \leq 14$
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·3H₂O) and 173 K (IIb) on a Bruker (I·3H₂O) or STOE STADI4 (IIb) single crystal diffractometer equipped with a graphite monochromator ($\lambda = 0.71069$ (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 $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for methylene H atoms and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ 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 $-1.42 \text{ e}\text{\AA}^{-3}$ located 1.37 Å from H12C and the largest peak was $0.63 \text{ e}\text{\AA}^{-3}$ located 1.57 Å from H12C. Absorption corrections were performed using SADABS (for I·3H₂O) and X-SHAPE (for IIb) programs. Crystallographic data and the result of refinements are summarized in Table 1.

Results and Discussion

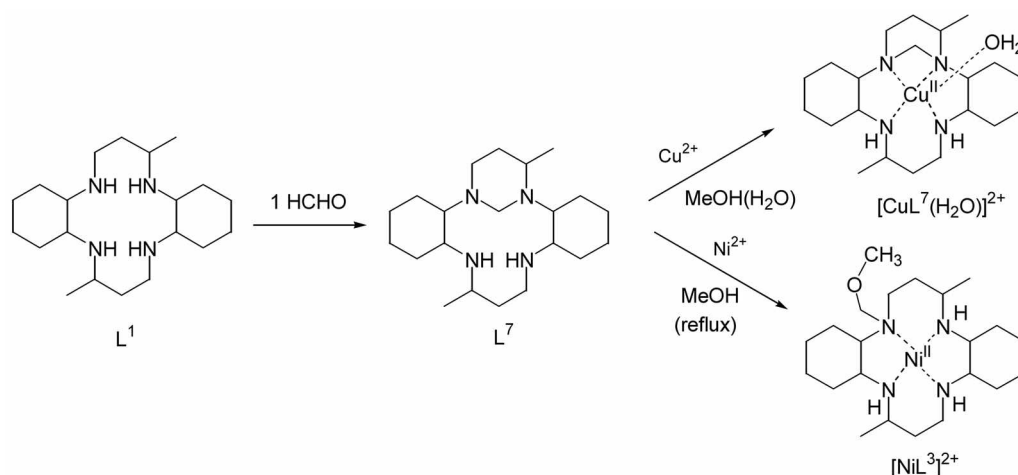
Synthesis. The major product prepared from the reaction of L¹ and formaldehyde in a 1:1 molar ratio was L⁷ containing one 1,3-diazacyclohexane ring; the isomer L⁸ could not be prepared in the present experimental conditions. The mass, infrared, and ¹³C-NMR spectra of L⁷ were listed in the Experimental section. The structure of L⁷ was confirmed by the crystal structure of its copper(II) complex (see below). The reasons for the predominant formation of L⁷ are not clearly understood at this point.

As described in the Experimental section, L⁷ rapidly reacts with Cu²⁺ 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 L³ could not be prepared even after refluxing the methanol solution for > 24 h. This means that the copper(II) complex of L⁷ is quite inert against methanolysis. Our attempts to prepare nickel(II) complex of L⁷ from the reaction of the macrocycle with the metal ion in methanol or acetonitrile at room temperature were unsuccessful. The addition of NaClO₄ to the resulting solution produced the white salt L⁷·2HClO₄, indicating that L⁷ did not form

stable nickel(II) complex. In the refluxing methanol solution containing Ni²⁺ ion, however, L⁷ readily reacts with methanol to yield the complex IIa bearing one N-CH₂OCH₃ pendant arm (see the Experimental section). The preparation of the metal-free macrocycle L³ 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 L¹. This shows that the pendant N-CH₂OCH₃ group of L³ 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 L⁷ 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 L⁷. Therefore, one of the reasons for the inertness of I (or L⁷ in the presence of Cu²⁺ ion) against methanolysis may be the relatively strong Cu-N (N-CH₂-N linkage) bonds (see below); the coordination of L⁷ to the metal ion weakens the proton affinity of the amino groups and stabilizes the N-CH₂-N linkage. In the methanol solution of Ni²⁺ ion, L⁷ can react with methanol because it is not so strongly coordinated to the metal ion. Furthermore, the product (L³) 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·3H₂O. The ORTEP drawing of [CuL⁷(H₂O)]²⁺ in I·3H₂O 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 L⁷ 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 N₄ 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 $138.2(3)^\circ$, respectively. The N(1)-Cu-N(2) angle involved in the four-membered chelate ring ($67.4(3)^\circ$)



Scheme 1

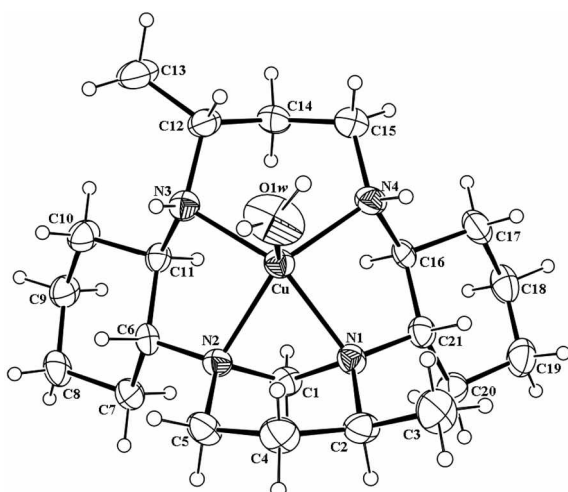


Figure 1. An ORTEP drawing of $[\text{CuL}^7(\text{H}_2\text{O})]^{2+}$ cation in $\text{I}\cdot 2\text{H}_2\text{O}$.

Table 2. Bond Distances (Å) and Angles (°) for $\text{I}\cdot 3\text{H}_2\text{O}$

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 $\text{I}\cdot 3\text{H}_2\text{O}$

$D\text{-H}\cdots A$	$d(D\text{-H})$	$d(\text{H}\cdots A)$	$d(D\cdots A)$	$\angle(D\text{-H}\cdots A)$
O(1w)-HAW \cdots O(11w)	0.9(1)	2.0(1)	2.77(2)	137(12)
O(1w)-HBW \cdots O(10w)	0.80(7)	1.97(8)	2.73(2)	161(11)
N(3)-H(3) \cdots O(8 ⁱ)	0.91	2.49	3.35(2)	156.7
N(4)-H(4) \cdots O(6)	0.91	2.42	3.30(2)	161.7
C(6)-H(6) \cdots O(6 ⁱ)	0.98	2.59	3.55(2)	167.2
C(11)-H(11) \cdots 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)^o) or six-membered chelate (103.2(3)^o) 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 $\text{I}\cdot 2\text{H}_2\text{O}$. The ORTEP drawing (Fig. 3) of $[\text{NiL}^3]^{2+}$ in $\text{I}\cdot 2\text{H}_2\text{O}$ shows that one $N\text{-CH}_2\text{OCH}_3$ 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 $N\text{-CH}_2\text{OCH}_3$ group and the C-methyl group at the

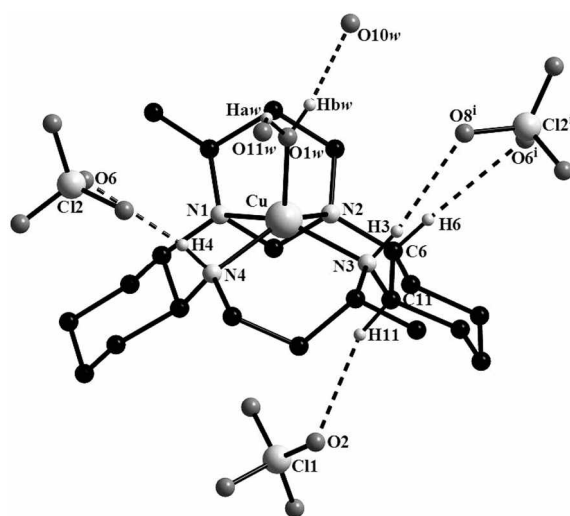


Figure 2. A perspective view of $\text{I}\cdot 2\text{H}_2\text{O}$ showing hydrogen bonds. The hydrogen bonds are shown as dotted lines. Symmetry code: (i) $-y+5/4, x-1/4, z-1/4$.

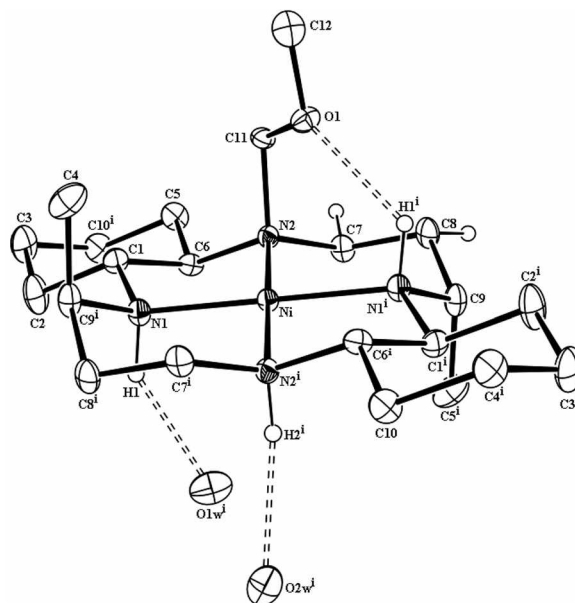


Figure 3. An ORTEP drawing of $[\text{NiL}^3]^{2+}$ cation in $\text{I}\cdot 2\text{H}_2\text{O}$. Symmetry code: (i) $1-x, -y, -z$.

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 \cdots O(1) distance (2.769(7) Å) is *ca.* 0.3 Å longer than the Cu-O (one of the two $N\text{-CH}_2\text{OCH}_3$ groups) distance (2.471(2) Å) of $[\text{CuL}^2](\text{ClO}_4)_2\cdot\text{CH}_3\text{CN}$.¹⁹ This strongly shows that, in contrast to the case of $[\text{CuL}^2](\text{ClO}_4)_2\cdot\text{CH}_3\text{CN}$, the metal ion of $\text{I}\cdot 2\text{H}_2\text{O}$ is not directly coordinated by the oxygen atom of the $N\text{-CH}_2\text{OCH}_3$ 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) \cdots 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**

<i>D</i> -H... <i>A</i>	<i>d</i> (<i>D</i> -H)	<i>d</i> (H... <i>A</i>)	<i>d</i> (<i>D</i> ... <i>A</i>)	∠(<i>D</i> -H... <i>A</i>)
N(1 ^b)-H(1 ^b)...O(1)	0.99(8)	2.23(8)	2.87(2)	121(6)
N(1)-H(1)...O(1w ^b)	0.99(8)	2.09(8)	2.94(3)	143(6)
N(2 ^b)-H(2 ^b)...O(2w ^b)	0.91	2.16	3.05(2)	167

Symmetry codes: (i) -x+1, -y, -z.

that the secondary amino group involving the N(1^b) atom is hydrogen bonded to the oxygen atom of the pendant *N*-CH₂OCH₃ group (Fig. 3 and Table 5). The secondary amino groups involving the N(1) and N(2^b) atoms are also hydrogen bonded to the oxygen atoms of water molecules.

Spectra and Properties of I. The infrared spectrum of **I** shows $\nu_{\text{N-H}}$ 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 ($\epsilon = 400\text{--}450 \text{ M}^{-1}\text{cm}^{-1}$), supporting the crystallographic result that the complex has distorted trigonal bipyramidal coordination polyhedron. The molar conductance value (245 $\Omega^{-1}\text{mol}^{-1}\text{cm}^2$) 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 HClO₄ 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 [CuL¹](ClO₄)₂ (*k* = 4.5 × 10⁻⁴ sec⁻¹ in 0.3 M HClO₄ 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 $\nu_{\text{N-H}}$ at 3210, 3150, and 3100 cm⁻¹. The molar conductance value (230 $\Omega^{-1}\text{mol}^{-1}\text{cm}^2$) of **IIa** measured in acetonitrile indicates that the complex is a 1:2 electrolyte. Both **IIa** and **IIb** were found to be diamagnetic compounds. ¹³C-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 [NiL⁴]²⁺ and [NiL⁵]²⁺, in which the *N*-CH₂CH₂OH or *N*-CH₂CH₂CN 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	

^aIn nitromethane at 20 °C unless otherwise specified. ^bRef. 20. ^cIn acetonitrile. ^dIn dimethylsulfoxide. ^eIn DMF. ^fRef. 9. ^gRef. 8. ^hIn water.

not involved in coordination.^{8,9} This strongly indicates that the pendant *N*-CH₂OCH₃ group in [NiL³]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 [NiL¹]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 HClO₄ or 0.1 M NaOH solutions showed no apparent decomposition during 5 h at room temperature.

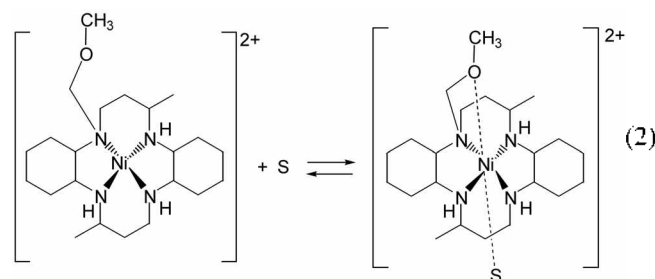


Table 6 shows that the molar absorption coefficients of the *d-d* band (*ca.* 485 nm) for **IIa** measured in Me₂SO (81 M⁻¹cm⁻¹), MeCN (64 M⁻¹cm⁻¹), and DMF (51 M⁻¹cm⁻¹) are smaller than that in MeNO₂ (84 M⁻¹cm⁻¹), a non-coordinating solvent. This trend is quite similar to that reported for [NiL⁴](ClO₄)₂ bearing one *N*-CH₂CH₂OH group, which binds the metal ion in coordinating solvents, but is different from the behavior of [NiL⁵](ClO₄)₂ containing non-coordinating *N*-CH₂CH₂CN 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*-CH₂OCH₃ 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 [NiL³(S)₂]²⁺, in which the oxygen atom of the pendant *N*-CH₂OCH₃ group is coordinated to the metal ion, and square-planar [NiL³]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 = $100 \{(\epsilon_N - \epsilon_S)/\epsilon_N\}$ 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 Me₂SO (4%) < MeCN (24%) < DMF (39%). This trend is similar to that reported for [NiL⁴]²⁻ {Me₂SO (28%) < MeCN (42%) < DMF (45%)}.⁹ In each solvent, however, the proportion of the octahedral species for [NiL³]²⁻ is lower than that for [NiL⁴]²⁻. This can be attributed to the relatively weak coordinating ability of the pendant *N*-CH₂OCH₃ group in [NiL³]²⁺.

Conclusion

The macrotetraycle L⁷ was prepared by the reaction of L¹ with one equivalent of formaldehyde. The macrotetraycle reacts with methanol in the presence of Ni²⁺ ion to yield [NiL³]²⁻, whereas [CuL⁷(H₂O)]²⁻ is prepared as the only product in the presence of Cu²⁺ ion. This work shows that Cu²⁺ ion readily binds L⁷ to form the stable complex [CuL⁷(H₂O)]²⁻ with a 4-5-6-5 chelate ring sequence and makes the macrotricyclic inert against methanolysis. On the other hand, Ni²⁺ ion, which does not bind L⁷ so strongly, enables the methanolysis and stabilize the product L³ through the formation of the complex [NiL³]²⁻. The *N*-CH₂OCH₃ group of [NiL³]²⁺ is not directly involved in coordination in the solid state. In coordinating solvents (S), the complex exists as a mixture of [NiL³(S)]²⁺, in which the *N*-CH₂OCH₃ group as well as S is coordinated to the metal ion, and [NiL³]²⁺.

Supplementary Material. Crystallographic data of **I**·3H₂O and **IIa** are available from the Cambridge Structural Database, CCDC reference numbers and 689785 and 684250, respectively. Copies of the data can be obtained free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (<http://www.ccdc.cam.ac.uk>, fax: +44-1223-336-033, or e-mail: deposit@ccdc.cam.ac.uk).

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