

Synthesis and Characterization of New Tetraaza Macrocycles Bearing Two or Four *N*-Methoxyethyl Pendant Arms and Their Copper(II) and/or Nickel(II) Complexes

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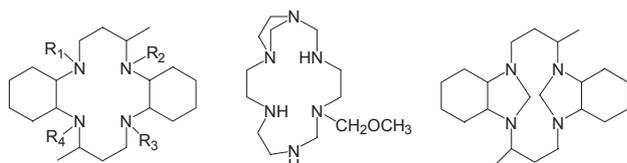
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A variety of work has been concerned with the preparation of polyaza macrocyclic ligands and complexes bearing additional functional pendant arms because of their interesting chemical properties and potential applications.¹⁻¹³ In general, coordination geometry and chemical properties of such compounds are strongly influenced by the nature and number of the functional groups.

Some polyaza macrocyclic complexes bearing pendant ether group(s), such as [CuL^{4,2+}], [NiL^{5,2+}], and [NiL^{10,2+}], have been prepared and investigated.¹⁰⁻¹³ The preparation of [CuL^{4,2+}] and [NiL^{5,2+}] bearing two and one *N*-CH₂OCH₃ groups, respectively, has been achieved by the reaction of L¹¹ with methanol in the presence of the corresponding metal ion.¹⁰⁻¹¹ It has been revealed that one of the two *N*-CH₂OCH₃ groups in [CuL^{4,2+}] is coordinated to the metal ion,¹⁰ whereas the pendant arm of [NiL^{5,2+}] or [NiL^{10,2+}] is not involved in coordination.^{11,12} To our knowledge, they are rare examples of polyaza macrocyclic complexes bearing *N*-(CH₂)_nOCH₃ group(s). Furthermore, the isolation of the metal-free macrocycle L⁴, L⁵, or L¹⁰ could not be achieved;¹⁰⁻¹² both L⁴ and L⁵ are decomposed to L² if they are removed from the coordination sphere. For this reason, chemical properties of polyaza macrocycles bearing *N*-CH₂OCH₃ group(s) have not been intensively investigated. This prompted us to prepare various types of polyaza macrocycles bearing *N*-(CH₂)_nOCH₃ group(s) and their transition metal complexes.

In this work, we prepared L² and L³ bearing two or four *N*-(CH₂)₂OCH₃ groups from the reaction of L¹ with 1-bromo-2-methoxyethane. Their copper(II) and/or nickel(II) complexes were also prepared. Herein, we report the preparation and coordination behaviors of L² and L³, along with the crystal structure of [CuL²](ClO₄)₂.



- L¹: R₁ = R₂ = R₃ = R₄ = H
 L²: R₁ = R₃ = CH₂CH₂OCH₃; R₂ = R₄ = H
 L³: R₁ = R₂ = R₃ = R₄ = CH₂CH₂OCH₃
 L⁴: R₁ = R₂ = CH₂OCH₃; R₃ = R₄ = H
 L⁵: R₁ = CH₂OCH₃; R₂ = R₃ = R₄ = H
 L⁶: R₁ = R₃ = CH₂CH₂OH; R₂ = R₄ = H
 L⁷: R₁ = R₂ = R₃ = R₄ = CH₂CH₂CH₃
 L⁸: R₁ = R₃ = CH₂CH₂CN; R₂ = R₄ = H
 L⁹: R₁ = R₃ = CH₂CH₂CH₃; R₂ = R₄ = H

Experimental Section

Measurements. Infrared spectra were recorded with a Genesis II FT-IR spectrometer, electronic absorption spectra with an Analytic Jena Specord 200 UV-vis spectrophotometer, NMR spectra with a Varian Mercury 300 FT NMR spectrometer, and GC-mass spectra 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 were performed at the Korea Basic Science Institute, Daegu, Korea. Elemental analyses were performed at the Research Center for Instrumental Analysis, Daegu University, Gyeongsan, Korea.

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

Preparation of L². A toluene solution (20 mL) of L¹ (Ref. 14) (2.0 g, 5.9 mmol), 99% 1-bromo-2-methoxyethane (1.4 mL, 14.9 mmol), and KOH (2.0 g, 35 mmol) was refluxed for 48 h. The reaction mixture was filtered at room temperature, and the filtrate was evaporated to leave semi solid. After the addition of acetonitrile (20 mL) to the residue, the mixture was stored at room temperature for 2 h. The white solid formed was collected by filtration. The crude product was redissolved in methanol (20 mL) at room temperature and then filtered to remove any solid. The addition of 0.1 M NaOH aqueous solution (20 mL) produced a white solid. The product was collected by filtration, washed with water, and dried in air (Yield: ~ 50%). Anal. Calcd for C₂₆H₅₂N₄O₂: C, 68.98; H, 11.58; N, 12.38. Found: C, 68.60; H, 12.06; N, 12.31%. GC-Mass (*m/z*) 452 (M⁺). IR (Nujol mull, cm⁻¹) 3258 (ν_{N-H}). ¹³C-NMR (CDCl₃) 20.6, 24.9, 25.4, 25.5, 26.0, 26.5, 47.0, 49.5, 54.5, 58.9(d), 72.8 (-CH₂-O-CH₃), 77.5 (-CH₂-O-CH₃) ppm.

Preparation of L³. A toluene solution (20 mL) of L¹ (2.0 g, 5.9 mmol), 99% 1-bromo-2-methoxyethane (3.4 mL, 35.7 mmol), and KOH (3.3 g, 60 mmol) was refluxed for 50 h. The reaction mixture was filtered at room temperature, and the filtrate was evaporated. After the addition of methanol (20 mL) to the residue, the mixture was stored at room temperature to form a white solid. The product was collected by filtration and dissolved in minimum volume of hot methanol (> 50 °C). The solution was evaporated slowly at room temperature until a

white solid formed. The product was collected by filtration, washed with cold methanol, and dried in air (Yield: ~ 30%). Anal. Calcd for $C_{32}H_{64}N_4O_4$: C, 67.56; H, 11.34; N, 9.85. Found: C, 68.05; H, 12.57; N, 10.00 %. GC-Mass (m/z) 568 (M^+). ^{13}C -NMR ($CDCl_3$) 18.9, 26.4, 26.7, 27.0, 31.2, 38.1, 45.6, 49.5, 50.5, 59.0(*d*), 62.4, 73.7 (-CH₂-O-CH₃), 74.0 (-CH₂-O-CH₃), 77.3 (-CH₂-O-CH₃), 77.5 (-CH₂-O-CH₃) ppm.

Preparation of $[CuL^2](ClO_4)_2$. A methanol solution (25 mL) of L^2 (2.0 g, 4.4 mmol) and $Cu(OAc)_2 \cdot H_2O$ (1.8 g, 8.8 mmol) was refluxed for 1 h. After the addition of an excess amount of $NaClO_4$, the mixture was stored in a refrigerator to precipitate a purple solid. The solid was collected by filtration, washed with methanol, and dried in air. The product was recrystallized from a hot acetonitrile-water (1:2) solution (Yield: ~ 80%). Anal. Calcd for $C_{26}H_{52}N_4CuCl_2O_{10}$: C, 43.67; H, 7.33; N, 7.83. Found: C, 43.63; H, 7.21; N, 7.80 %. IR (cm^{-1}) 3250 (ν_{N-H}), 1100 (ν_{Cl-O} , ClO_4^-). FAB mass (m/z) 614.5 $\{[CuL^2 + ClO_4]^+\}$, 515.5 $\{[CuL^2 - H]^+\}$.

Preparation of $[NiL^2](ClO_4)_2$. This compound was prepared by a method similar to that for $[CuL^2](ClO_4)_2$, except that Ni(OAc)₂·4H₂O (2.2 g, 8.8 mmol) was reacted instead of $Cu(OAc)_2 \cdot H_2O$. The orange compound was recrystallized twice from a hot acetonitrile-water (1:2) solution (Yield: ~ 80%). Anal. Calcd for $C_{26}H_{52}N_4CuCl_2O_{10}$: C, 43.96; H, 7.38; N, 7.89. Found: C, 44.01; H, 7.53; N, 7.88 %. IR (cm^{-1}) 3115 (ν_{N-H}), 1100 (ν_{Cl-O} , ClO_4^-).

Preparation of $[NiL^2](PF_6)_2$. A warm acetonitrile (*ca.* 10 mL) suspension of $[NiL^2](ClO_4)_2$ (*ca.* 0.4 g) and NH_4PF_6 (1.5 g) was stirred for 10 min and then filtered to remove any solid. After the addition of water (20 mL) to the filtrate, the mixture was evaporated to yield an orange solid. The product was collected by filtration, washed with water, and dried in air. Yield: ~ 90%. FAB mass (m/z) 655.6 $\{[NiL^2 + PF_6]^+\}$, 509.5 $\{[NiL^2 - H]^+\}$. IR (cm^{-1}) 3121 (ν_{N-H}), 850 (ν_{P-F} , PF_6^-). ^{13}C -NMR (CD_3NO_2): 19.4, 26.9, 27.4, 35.3, 49.7, 53.9, 55.6(*d*) 59.2, 62.9(*d*), 72.5 (-CH₂-O-CH₃), 78.4 (-CH₂-O-CH₃) ppm.

Preparation of $[Cu(HL^3)](ClO_4)_3 \cdot 2H_2O$. A methanol solution (25 mL) of L^2 (2.0 g, 3.5 mmol) and $Cu(OAc)_2 \cdot H_2O$ (1.4 g, 7.1 mmol) was refluxed for 3 h and then cooled to room temperature. After the addition of an excess amount of $NaClO_4$ and 2 ~ 3 drops of $HClO_4$, the solution was evaporated slowly at room temperature until a green precipitate formed. The solid was collected by filtration, washed with cold methanol, and dried in air. The product was recrystallized from a methanol-water (1:2) solution (Yield: ~ 60%). Anal. Calcd for $C_{32}H_{69}N_4CuCl_3O_{18}$: C, 39.71; H, 7.19; N, 5.79. Found: C, 39.75; H, 7.81; N, 5.87%. FAB mass (m/z) 831.9 $\{[Cu(HL^3) + 2ClO_4]^+\}$, 730.9 $\{[Cu(L^3) + ClO_4]^+\}$, 631.1 $\{[Cu(L^3) - H]^+\}$. IR (cm^{-1}) 3500 - 3300 (ν_{OH} , *br*), 1100 (ν_{Cl-O} , ClO_4^-).

Crystal structure determination. A purple crystal of $[CuL^2](ClO_4)_2$ was obtained from water-acetonitrile. Intensity data were collected on a Rigaku R-AXIS RAPID II-S diffractometer equipped with graphite monochromated Mo $K\alpha$ ($\lambda = 0.71073$ Å) radiation source and imaging plate detector (460 mm × 256 mm). A total of 240 oscillation images were collected at 100 k using widths of 3° in ω . The raw data were processed to give structure factors using the RAPID AUTO program. The structure was solved by direct method and refined by full

matrix least squares against F^2 for all data using SHELXL-97.¹⁵ All non-hydrogen atoms were anisotropically refined. All other hydrogens were included in the calculated position.

Crystal and refinement data: $C_{26}H_{52}N_4CuCl_2O_{10}$, $M = 715.16$, monoclinic, $C2/c$, $a = 17.331(1)$, $b = 11.401(1)$, $c = 17.471(1)$ Å, $\beta = 116.333(1)^\circ$, $V = 3094.0(2)$ Å³, $Z = 4$, $D_{calc} = 1.535$ g cm⁻³, $\mu = 9.40$ cm⁻¹, Goodness-of-fit on $F^2 = 1.075$, Final $R_1 = 0.0353$, $wR_2 = 0.0874$ ($I > 2\sigma(I)$), $R_1 = 0.0433$, $wR_2 = 0.0907$ (all data).

Results and Discussion

Synthesis. The major product prepared from the reaction of L^1 with 1-bromo-2-methoxyethane in a 1:2.5 molar ratio was L^2 bearing two N -CH₂CH₂OCH₃ pendant arms. The fully N -methoxyethylated macrocycle L^3 was also prepared by the reaction of L^1 with an excess 1-bromo-2-methoxyethane. The di- N -substituted macrocycle L^2 readily dissolves in methanol, whereas L^3 is nearly insoluble at room temperature. In contrast to the cases of L^4 and L^5 bearing N -CH₂OCH₃ pendant arm(s),^{10,11} both L^2 and L^3 are extremely stable in the solid state and in various solvents. The mass, infrared, and ^{13}C -NMR spectral data of L^2 and L^3 are listed in the Experimental section. The structure of L^2 was confirmed by the crystal structure of its copper(II) complex (*see below*).

Both $[CuL^2]^{2+}$ and $[NiL^2]^{2+}$ were prepared readily by the reaction of L^2 with the corresponding metal ions. The fully- N -substituted macrocycle L^3 reacts with Cu^{2+} ion to form $[Cu(HL^3)]^{3+}$ where one of the four tertiary nitrogen atoms is protonated. The formation of $[Cu(HL^3)]^{3+}$ in the present work is quite different from the trend that most 14-membered tetraaza macrocycles bearing four N -alkyl pendant arms, such as L^7 bearing four N -propyl groups, form square-planar copper(II) complexes, in which the metal ion is coordinated by all of the four tertiary nitrogen atoms.^{16,17} This can be attributed to the coordination ability of the N -CH₂CH₂OCH₃ groups in L^3 . All efforts to prepare nickel(II) complex of L^3 under various experimental conditions were unsuccessful; the addition of $NaClO_4$ to the reaction mixture produced the white salt $L^3 \cdot 2HClO_4$.

Crystal structure of $[CuL^2](ClO_4)_2$. The ORTEP drawing (Fig. 1) of the cation $[CuL^2]^{2+}$ shows that two methoxyethyl groups are attached to the less sterically hindered nitrogen atoms of the macrocyclic ligand. The macrocycle containing

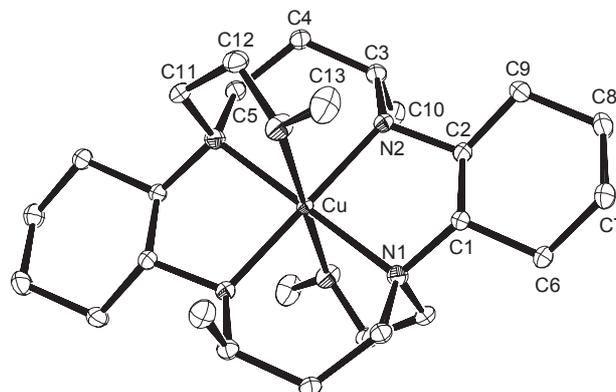


Figure 1. An ORTEP drawing of $[CuL^2]^{2+}$ cation in $[CuL^2](ClO_4)_2$.

Table 1. Bond distances (Å) and angles (°) for [CuL²](ClO₄)₂

Cu-N(1)	2.067(2)	Cu-N(2)	2.043(2)
Cu-O(1)	2.595(2)	C(1)-N(1)	1.518(2)
C(2)-N(2)	1.498(2)	C(12)-O(1)	1.422(3)
C(13)-O(1)	1.422(3)		
N(1)-Cu-N(2)	85.5(2)	N(1)-Cu-N(2')	94.5(2)
N(1)-Cu-N(1')	180.0(1)	N(2)-Cu-N(2')	180.0(1)
C(11)-C(12)-O(1)	108.5(2)	C(12)-O(1)-C(13)	111.7(2)
N(1)-Cu-O(1)	77.1(1)	N(2)-Cu-O(1)	79.9(2)

two *trans*-1,2-diaminocyclohexane subunits adopts *trans*-III stereochemistry. The methoxyethyl group and the methyl group in each six-membered chelate ring are *anti* with respect to the plane.

The selected bond distances and angles of the complex are listed in Table 1. The Cu-N(1) (tertiary) distance (2.067 Å) is longer than the Cu-N(2) (secondary) distance (2.043 Å). The in-plane Cu-N distances are comparable with those of [CuL⁴](ClO₄)₂·CH₃CN and other related macrocyclic complexes.¹⁰ The axial Cu-O(1) distance (2.595 Å) indicates that the oxygen atoms of the pendant *N*-CH₂CH₂OCH₃ groups are coordinated to the metal ion relatively weakly. The Cu-O(1) distance is much longer than the in-plane Cu-N distances and is *ca.* 0.1 Å longer than the Cu-O (one of the two *N*-CH₂OCH₃ groups) distance (2.471 Å) of [CuL⁴](ClO₄)₂·CH₃CN.¹⁰ When the metal ion is directly coordinated by the O(1) atom, the complex has a *trans*-octahedral coordination polyhedron. The *trans*-N-Cu-N angles are 180°. The N(1)-Cu-N(2) angle (85.5(2)°) of the five-membered chelate ring is smaller than the N(1)-Cu-N(2') angle (94.5°) of the six-membered chelate ring. The C(12)-O(1)-C(13) angle (111.7°) is similar to the C-O-C angle (112.8°) involved in the coordinated *N*-CH₂OCH₃ group of [CuL⁴](ClO₄)₂·CH₃CN.¹⁰

Properties of [CuL²](ClO₄)₂ and [NiL²](ClO₄)₂. Both [CuL²](ClO₄)₂ and [NiL²](ClO₄)₂ dissolve in various polar organic solvents, such as nitromethane, acetonitrile and DMSO, but is nearly insoluble in water. They are relatively inert against decomposition even in concentrated acid solutions, in analogy with other related copper(II) and nickel(II) complexes of 14-membered tetraaza macrocycles;^{9,10} the electronic absorption spectra of the complexes measured in 0.1 M HClO₄ acetonitrile-water (1:1) solutions show that only less than 5% of the complexes are decomposed in 24 h at room temperature.

Infrared spectra of [CuL²](ClO₄)₂ and [NiL²](ClO₄)₂ show ν_{N-H} of the secondary amino groups at 3250 and 3115 cm⁻¹, respectively. The values of molar conductance for the complexes measured in nitromethane (130 - 140 Ω⁻¹mol⁻¹cm²) and acetonitrile (220 - 240 Ω⁻¹mol⁻¹cm²) indicate that they are 1:2 electrolytes. ¹³C-NMR spectrum (*see* Experimental section) of the nickel(II) complex corresponds to the structure of the macrocycle. Molar magnetic susceptibility of [NiL²](ClO₄)₂ was found to be a negative value at room temperature, showing that the complex is a diamagnetic substance.

The electronic absorption spectra (Table 2) of [CuL²](ClO₄)₂ measured in Nujol mull and various solvents show a *d-d* transition band at 510 - 520 nm. The wavelengths are similar to

Table 2. Electronic absorption spectral data^a

Complex	λ _{max} , nm (ε, M ⁻¹ cm ⁻¹)			
[NiL ¹](ClO ₄) ₂ ^b	463(73)			
[NiL ²](ClO ₄) ₂	488(82)	490(73) ^c	494(81) ^d	495 ^e
[NiL ³](ClO ₄) ₂ ^f	485(84)	484(64) ^c	485(51) ^d	
[NiL ⁶](ClO ₄) ₂ ^g	520(6.8) ^c	335(16) ^c		
[NiL ⁸](ClO ₄) ₂ ^h	490(117)			
[NiL ⁹](ClO ₄) ₂ ⁱ	484(109)	486(103) ^b		
[CuL ¹](ClO ₄) ₂ ^b	487(113)			
[CuL ²](ClO ₄) ₂	509(134)	511(130) ^c	517(168) ^d	520 ^e
[Cu(HL ³)](ClO ₄) ₃ ·2H ₂ O	715(120)	670(110)	675 ^e	
[CuL ⁶](ClO ₄) ₂ ^g	522(98)	523(98) ^c		
[CuL ⁷](ClO ₄) ₂ ^j	476(440)			
[CuL ⁸](ClO ₄) ₂ ^h	490(189)			

^aIn nitromethane at 20 °C unless otherwise specified. ^bRef. 14. ^cIn acetonitrile. ^dIn DMF. ^eIn Nujol mull. ^fRef. 11. ^gRef. 9. ^hRef. 18. ⁱRef. 19. ^jRef. 16.

those of [CuL⁶](ClO₄)₂ bearing two *N*-CH₂CH₂OH pendant arms and are considerably longer than those of various square-planar copper(II) complexes, such as [CuL¹](ClO₄)₂ and [CuL⁸](ClO₄)₂.^{9,14,18} This corresponds to the crystallographic result that two *N*-CH₂CH₂OCH₃ groups are involved in coordination. The spectra of [NiL²](ClO₄)₂ measured in various solvents, such as nitromethane and acetonitrile, show a *d-d* transition band at *ca.* 490 nm (ε = 73 - 82 M⁻¹cm⁻¹). The spectra are comparable with those of other square-planar nickel(II) complexes with di-*N*-alkylated macrocyclic ligands, such as [NiL⁸](ClO₄)₂ and [NiL⁹](ClO₄)₂,^{18,19} but are quite different from those of the octahedral complex [CuL⁶](ClO₄)₂.⁹ This observation as well as the molar magnetic susceptibility supports the suggestion that the pendant *N*-CH₂CH₂OCH₃ groups of [NiL²]²⁺ are not directly coordinated to the metal ion in the solid state and in various solvents, unlike those in [CuL²]²⁺.

Spectra and properties of [Cu(HL³)](ClO₄)₃·2H₂O. The complex is extremely stable in the solid state and is relatively stable even in low pH. Visible absorption spectra of the complex (6.0 × 10⁻⁴ M) measured in 0.2 M HClO₄ water-acetonitrile (1:1) solution showed no apparent decomposition during 3 h at room temperature.

FAB mass spectrum (*see* Experimental section) of [Cu(HL³)](ClO₄)₃·2H₂O as well as the elemental analysis strongly indicates that one of the four tertiary amino groups of the macrocycle is protonated and is not involved in coordination; two or three oxygen atoms as well as the other three tertiary amino groups of the macrocycle may be involved in coordination. The electronic absorption spectra (Table 2) of the complex show a *d-d* transition band at 670 - 715 nm, which is *ca.* 200 nm longer than that for [CuL²](ClO₄)₂ or [CuL⁷](ClO₄)₂. The spectra strongly support the suggestion that [Cu(HL³)](ClO₄)₃·2H₂O is a complex with a 5-coordination environment.²⁰⁻²³ It has been widely observed that regular and distorted trigonal bipyramidal copper(II) complexes exhibit an absorption band at > 670 nm, whereas square-pyramidal copper(II) complexes show an absorption band at considerably shorter wavelength.²⁰⁻²² Therefore, the coordination geometry may be considered intermediate between TBP and SP in the solid state. Unfortunately, we

were unable to isolate single crystals of the complex suitable for X-ray work. Therefore, the coordination geometry of the copper(II) complex is not thoroughly investigated.

Summary

This work shows that both L^2 and L^3 bearing two and four $N-(CH_2)_2OCH_3$ groups, respectively, can be prepared selectively by the reaction of L^1 with 1-bromo-2-methoxyethane. The di- N -substituted macrocycle L^2 readily forms its copper(II) and nickel(II) complexes. The $N-(CH_2)_2OCH_3$ groups in $[CuL^2]^{2+}$ are coordinated to the metal ion, whereas those in $[NiL^2]^{2+}$ are not involved in coordination. Interestingly, L^3 reacts with Cu^{2+} ion to form $[Cu(HL^3)]^{3+}$, in which one tertiary amino group is not involved in coordination.

Supplementary Material. Crystallographic data of $[CuL^2](ClO_4)_2$ are available from the Cambridge Structural Database, CCDC reference number 771902 (<http://www.ccdc.cam.ac.uk>, fax: +44-1223-336-033, or e-mail: deposit@ccdc.cam.ac.uk).

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