

Synthesis and Properties of New Tetraaza Macrocylic Ligands Containing *N*-Cyanoethyl Pendant Arms and Their Nickel(II) and Copper(II) Complexes

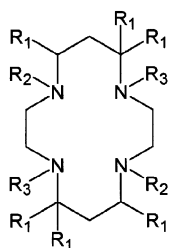
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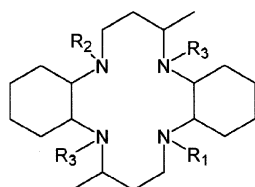
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Polyaza macrocyclic compounds containing functional pendant arms have received much attention, because properties of such compounds are strongly affected by the nature of the functional groups.¹⁻⁸ Some 14-membered tetraaza macrocyclic compounds containing *N*-cyanoethyl groups have been prepared.⁶⁻⁹ For example, the macrocycles L² and L⁴ containing four or two *N*-cyanoethyl groups have been prepared by the reaction of L¹ or L³ with an excess of acrylonitrile.^{6,7} The hydrolysis and decyanoethylation reactions of [NiL²]²⁺ in aqueous solutions have been also reported.^{6,9} The reactivity of *N*-cyanoethylated macrocyclic complexes, however, are not thoroughly understood to date, because only few examples of such compounds have been prepared and investigated.⁶⁻⁸

In this work, we prepared new tetraaza macrocycles L⁶ and L⁷ containing four or two *N*-cyanoethyl pendant arms from the reaction of L⁵ with acrylonitrile. The complexes [NiL⁷]²⁺ and [CuL⁷]²⁺, together with [NiL⁸]²⁺ containing only one *N*-cyanoethyl group, could be prepared. Unexpectedly, the nickel(II) and copper(II) complexes are very rapidly decyanoethylated in basic conditions. Selective synthesis and properties of the macrocyclic ligands and complexes are reported.



- L¹: R₁ = R₂ = R₃ = H
 L²: R₁ = H, R₂ = R₃ = CH₂CH₂CN
 L³: R₁ = Me, R₂ = R₃ = H
 L⁴: R₁ = Me, R₂ = CH₂CH₂CN, R₃ = H



- L⁵: R₁ = R₂ = R₃ = H
 L⁶: R₁ = R₂ = R₃ = CH₂CH₂CN
 L⁷: R₁ = R₂ = CH₂CH₂CN, R₃ = H
 L⁸: R₁ = CH₂CH₂CN, R₂ = R₃ = H
 L⁹: R₁ = R₂ = R₃ = CH₂CH₂CH₃
 L¹⁰: R₁ = R₂ = CH₂CH₂CH₃, R₃ = H
 L¹¹: R₁ = CH₂CH₂OH, R₂ = R₃ = H

Experimental Section

Measurements. ¹³C NMR spectra were obtained with a Varian Mercury 300 NMR spectrometer, infrared spectra with a Shimadzu IR-440 spectrophotometer, electronic absorption spectra with a Shimadzu UV-160 spectrophotometer, and conductance measurements with a Metrohm Herisau Conductometer E518. Elemental analyses and mass spectral analysis were performed at the Korea Basic Science Insti-

tute, Seoul, Korea.

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

Preparation of L⁶. The macrocycle L⁵ was prepared as described before.¹¹ To a methanol solution (10 mL) of L⁵ (2.5 g, 7.5 × 10⁻³ mol) was added an excess of acrylonitrile (4.8 mL, 1.5 × 10⁻¹ mol). The mixture was stirred for ca. 20 h at room temperature and then a white solid formed. The solid was filtered and dissolved in minimum volume of chloroform. After methanol (ca. 10 mL) had been added, the resulting solution was evaporated at room temperature to produce the white solid. The product was filtered, washed with methanol, and dried in air. Yield: ~90%. Anal. Calcd. for C₃₂H₅₂N₈: C, 70.03; H, 9.55, N, 20.42%. Found: C, 69.52; H, 9.28; N, 19.84%. Mass (*m/z*): 548 (M⁺). IR (cm⁻¹): 2240 (νCN). ¹H NMR (CDCl₃): 1.1 ppm (Me, *t*). ¹³C NMR (CDCl₃): δ 19.3, 19.5, 20.1, 26.5, 26.8, 27.0, 35.2, 38.2, 43.8, 47.8, 49.4, 52.5, 63.1, 120.2 (CN), 120.3 (CN) ppm.

Preparation of L⁷. A methanol solution (15 mL) of L⁵ (2.5 g, 7.5 × 10⁻³ mol) and acrylonitrile (0.8 mL, 2.3 × 10⁻² mol) was stirred for 24 h at room temperature. The solution was filtered to remove the white solid L⁶ and then 1.0 M NaOH aqueous solution (ca. 8 mL) was added to the filtrate. The white solid, which had been formed, was filtered, and washed with water, and dried in air. Yield: ~60%. Anal. Calcd for C₂₆H₄₆N₆: C, 70.59; H, 10.41; N, 19.00%. Found: C, 70.94; H, 10.35; N, 18.65%. Mass (*m/z*): 442 (M⁺). IR (cm⁻¹): 2240 (νCN) and 3270 (νN-H).

Preparation of [NiL⁷](ClO₄)₂. A methanol solution (20 mL) of Ni(OAc)₂·4H₂O (1.0 g, 4.0 mmol) and L⁷ (1.7 g, 4.0 mmol) was refluxed for ca. 30 min and then cooled to room temperature. An excess of HClO₄ was added to the solution. The orange-red solid, which had been precipitated, was filtered and washed with methanol. The product was recrystallized from a 1.0 × 10⁻⁴ M HClO₄ Me₂SO-water (2 : 1) mixture. Yield: ~90%. Anal. Calcd for C₂₆H₄₆N₆NiCl₂O₈: C, 44.59; H, 6.62; N, 12.00%. Found: C, 44.54; H, 6.36; N, 11.86%. IR (cm⁻¹): 2240 (νCN) and 3170 (νN-H).

This complex can be also prepared from the reaction of the metal ion with L⁶. A methanol suspension (20 mL) of L⁶ (1.0 g, 4.0 mmol) and Ni(OAc)₂·4H₂O (2.7 g, 5.0 mol) was refluxed for 1 hr and then cooled to room temperature. Addition of an excess HClO₄ to the mixture produced the orange-red complex (yield: >80%).

Preparation of [CuL⁷](ClO₄)₂. The synthetic procedure was similar to that for [NiL⁷](ClO₄)₂, except that Cu(OAc)₂·H₂O was reacted instead of the nickel(II) salt. Yield: ~90%.

Anal. Calcd for $C_{26}H_{46}N_6CuCl_2O_8$: C, 44.29; H, 6.58; N, 11.92%. Found: C, 43.88; H, 6.59; N, 11.71%. IR (cm^{-1}): 2250 (ν_{CN}) and 3200 (ν_{N-H}).

Preparation of $[NiL^8](ClO_4)_2$. An acetonitrile-water (4 : 1) suspension (ca. 50 mL) of $[NiL^7](ClO_4)_2$ (1.0 g) was stirred in a warm water bath (ca. 60 °C) for 30 min. After filtering, addition of an excess $HClO_4$ to the filtrate produces an orange-yellow solid. The product was recrystallized from from a 1.0×10^{-4} M $HClO_4$ acetonitrile-water (3 : 1) solution. Calcd for $C_{23}H_{42}N_5NiCl_2O_8$: C, 42.68; H, 6.54; N, 10.82%. Found: C, 42.63; H, 7.09; N, 10.54%. FAB Mass (m/z): 547 ($[M-ClO_4]^+$) and 447 ($[M-H^+-2ClO_4]^+$). IR (cm^{-1}): 2240 (ν_{CN}), 3160 (ν_{N-H}), and 3180 (ν_{N-H}). This complex can be also prepared by direct reaction of L^6 or L^7 with $Ni(OAc)_2 \cdot 4H_2O$ in acetonitrile-water (2 : 1) mixture; the synthetic procedure was similar to that for $[NiL^7](ClO_4)_2$ except that solvent was acetonitrile-water (2 : 1) mixture instead of methanol.

Preparation of $[NiL](PF_6)_2$ ($L=L^7$ or L^8). To a Me_2SO solution (20 mL) of $[NiL](ClO_4)_2$ (1.0 g) was added an excess of NH_4PF_6 dissolved in water (ca. 20 mL). The solid, which had been formed, was filtered, washed with water, and dried in air. Yield: >80%. $[NiL^7](PF_6)_2$. Anal. Calcd for $C_{26}H_{46}N_6NiP_2F_{12}$: C, 39.46; H, 5.86; N, 10.62%. Found: C, 40.05; H, 5.69; N, 10.86%. ^{13}C NMR (CD_3NO_2): δ 14.1, 16.4, 24.0, 25.5, 26.4, 29.3, 30.0, 43.5, 45.6, 45.9, 56.8, 74.3, 118.3 (CN) ppm. $[NiL^8](PF_6)_2$. Anal. Calcd for $C_{23}H_{42}N_5NiP_2F_{12}$: C, 37.42; H, 5.87; N, 9.49%. Found: C, 37.25; H, 5.95; N, 9.34%. ^{13}C NMR ($CDCl_3$): δ 15.8, 15.9, 16.1, 24.9, 25.0, 25.7, 25.9 (d), 29.7, 30.3, 31.4, 31.5, 32.8, 40.7, 46.7, 47.0, 47.9, 48.9, 59.0, 65.9, 76.9, and 119.4 (CN) ppm.

Preparation of $[H_2L^6](ClO_4)_2$. The addition of $HClO_4$ to a chloroform-methanol (1 : 1) solution of L^6 produced a white solid. The product was filtered, washed with methanol, and dried in air. Anal. Calcd for $C_{32}H_{54}N_8Cl_2O_8$: C, 51.27; H, 7.26; N, 14.95%. Found: C, 50.85; H, 7.57; N, 15.35%. The compound was also obtained by the addition of $HClO_4$ to the reaction mixture of L^6 and $NiCl_2 \cdot 6H_2O$ or $CuCl_2 \cdot 4H_2O$ in methanol.

Results and Discussion

Synthesis. The sterically less hindered nitrogen atoms of L^5 can be selectively alkylated by the reaction of the macrocycle with an alkylating agent in a 1 : 2 molar ratio.^{3,5,12} In some cases, the nitrogen atoms next to the methylated carbons are not alkylated even if an excess amount of alkylating agent is employed.^{3,4,12} In this work, both the two macrocycles L^6 and L^7 can be prepared selectively by the reaction of L^5 with acrylonitrile at room temperature (see Experimental). The ligand L^7 reacts with acrylonitrile to yield L^6 . This result is different from the fact that the only product obtained from the reaction of L^3 with acrylonitrile is the di-*N*-cyanoethylated macrocycle L^4 .⁷ It is likely that the steric effects of the *C*-substituents of L^5 are less severe than those of L^3 .

The macrocycles L^6 and L^7 freely dissolve in chloroform. The solubility of L^6 in methanol is much lower than that of

L^7 . The mass, infrared, and ^{13}C NMR spectra (see Experimental) of L^6 and L^7 support the structure of each compound.

The complexes $[NiL^7](ClO_4)_2$ and $[CuL^7](ClO_4)_2$ were readily prepared by the reaction of the metal ions with L^7 in methanol. The mono-*N*-cyanoalkylated complex $[NiL^8](ClO_4)_2$ can be prepared by the selective decyanoalkylation of $[NiL^7](ClO_4)_2$ in a warm acetonitrile-water (see Experimental). All attempts to prepare nickel(II) or copper(II) complex of L^6 were unsuccessful. As described in Experimental, the reaction of L^6 with $Ni(OAc)_2 \cdot 4H_2O$ or $Cu(OAc)_2 \cdot H_2O$ in methanol or water-acetonitrile solution produced the complex of L^7 or L^8 . This result is different from that reported for L^4 ; nickel(II) complex of L^4 can be prepared by the reaction of $NiCl_2 \cdot 6H_2O$ in ethanol or acetonitrile.^{6,9}

It should be noted that the product obtained by the reaction of $Ni(OAc)_2 \cdot 4H_2O$ or $Cu(OAc)_2 \cdot H_2O$ with L^6 or L^7 is dependent on the reaction time. The reaction time described in Experimental is the condition for the preparation of each complex in high yield. The major compound obtained after refluxing aqueous or non-aqueous solutions of the reactants for more than 5 h was $[ML^7](ClO_4)_2$ ($M=Ni(II)$ or $Cu(II)$). It has been reported that the pendant cyanoethyl groups of L^4 are converted to the corresponding amide groups by refluxing an aqueous solution of the ligand and nickel(II) ion.⁹ However, any complex containing the pendant amide group(s) was not isolated in the present work.⁹

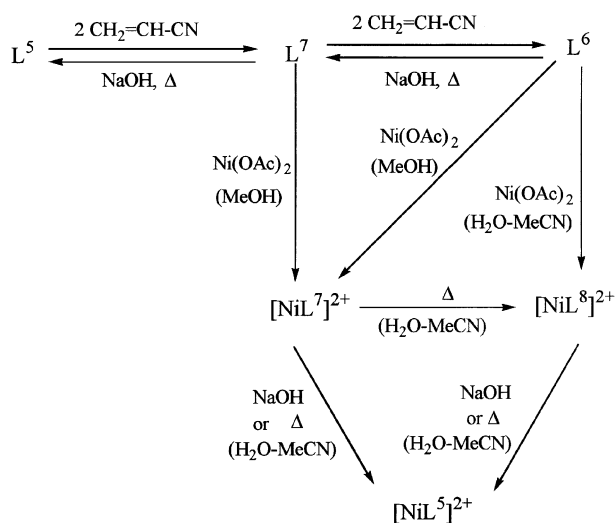
Infrared, ^{13}C NMR, and FAB-mass spectra of $[NiL^7](ClO_4)_2$, $[NiL^8](ClO_4)_2$, and/or $[CuL^7](ClO_4)_2$ are summarized in Experimental. The electronic absorption spectra (Table 1) of $[NiL^7](ClO_4)_2$ and $[NiL^8](ClO_4)_2$ are similar to those of $[NiL^{10}]^{2-}$ and $[NiL^{11}]^{2-}$,^{4,5} supporting that the pendant cyano group is not involved in coordination. The wavelength of the band for the complexes is affected by the ligand structure in the order of $L^5 < L^8 < L^7$. In general, *N*-alkylation of a 14-membered tetraaza macrocyclic nickel(II) complex weakens the ligand field strength.^{4,5,14,15} The spectrum of $[CuL^7](ClO_4)_2$ measured in nitromethane is also similar to those of other square-planar copper(II) complexes.^{11,12,13}

Solution Behaviors. As mentioned above, the macrocyclic compounds prepared in this work undergo decyanoethylation in various solutions. The reactivity of the compounds was examined in various conditions. The macrocycles L^6 and L^7 must be stable in 0.1 M NaOH chloroform-methanol-

Table 1. Electronic Absorption Spectral Data^a

Complex	λ_{max} , nm (ϵ , $M^{-1}cm^{-1}$)		
$[NiL^5](ClO_4)_2$ ^a	463(73)		
$[NiL^7](ClO_4)_2$	490(117)	490(115) ^c	
$[NiL^8](ClO_4)_2$	484(95)	485(87) ^c	483(90) ^d 483(91) ^c
$[NiL^{10}](ClO_4)_2$ ^f	484(109)	486(103) ^d	
$[NiL^{11}](ClO_4)_2$ ^g	485(86)	484(76) ^c	
$[CuL^5](ClO_4)_2$ ^a	487(113)		
$[CuL^7](ClO_4)_2$	490(189)	535(235) ^d	
$[CuL^8](ClO_4)_2$ ^b	476(440)		

^aIn nitromethane at 20 °C unless otherwise specified. ^bRef. 11. ^cIn dimethylsulfoxide. ^dIn acetonitrile. ^eIn water. ^fRef. 4. ^gRef. 5. ^hRef. 13.



Scheme 1

water mixture at room temperature, because the decyanoethylation was not observed even after 24 h. However, L⁶ is slowly decyanoethylated in 0.1 M NaOH chloroform-methanol-water mixture at *ca.* 60 °C. The only product obtained from the solution after 10 h was L⁵. This result is not so much different from the trend that a retro-Michael-type reaction for an organic compound is catalyzed by a base.¹⁶

The complexes [NiL⁷](ClO₄)₂, [CuL⁷](ClO₄)₂, and [NiL⁸](ClO₄)₂ are stable in acidic solutions. Electronic absorption spectra of the complexes (3.0 × 10⁻³ M) measured in 0.1 M HClO₄ solutions indicated that no apparent decyanoethylation takes place in 3 h even at 50 °C.

The nickel(II) and copper(II) complexes are relatively stable in neutral aqueous solutions at room temperature. However, the complexes are completely decyanoethylated within 5 h in boiling aqueous solutions; the only compound isolated from the resulting solution was [ML⁵](ClO₄)₂ (yield >90%). This result is in sharp contrast to the fact that the cyanoethyl groups of [NiL⁷](ClO₄)₂ are slowly hydrolyzed to the corresponding amide groups in boiling aqueous solutions (yield: *ca.* 90%).⁶ Unexpectedly, the addition of NaOH (0.1 M) to a solution of [NiL⁷](ClO₄)₂, [CuL⁷](ClO₄)₂, or [NiL⁸](ClO₄)₂ causes instantaneous color change even at room temperature and produces [ML⁵](ClO₄)₂. The results for the cyanoethylation and decyanoethylation of the macrocyclic compounds are summarized in Scheme 1. Above result shows that the coordinated metal ion promotes the decyanoethylation. The steric effect of the central metal ion as well as the interaction of the cyano group with the metal ion may be important for

the decyanoethylation of the complexes. This work also shows that the properties of the *N*-cyanoethylated macrocyclic compounds are strongly affected by the steric crowding of the *C*-substituents.

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