Unexpected Intramolecular Cyclization of a Tetraaza Macrocyclic Nickel(II) Complex Bearing Two *N*-Alkynyl Pendant Arms

Shin-Geol Kang, * **Hyunja Kim, Ji Young Lee, and Chee-Hun Kwak**[†]

*Department of Chemistry, Daegu University, Gyeongsan 712-714, Korea. *E-mail: sgkang@daegu.ac.kr*
†Department of Chemistry Education, Sunchon National University, Sunchon 540-742, Korea

The reaction of amines with alkynes, which is commonly known as hydroamination, has attracted considerable attention because it can be a useful organic transformation to form biologically important unsaturated heterocycles.[1-8] A large number of studies have examined the hydroamination. To the best of our knowledge, however, there are no reports on intramolecular hydroamination involving alkynyl groups attached to a tetraaza macrocyclic compound.

This paper reports the synthesis of $[NiL^2]^{2+}$ bearing two *N*-$CH_2C\equiv CH$ pendant arms that undergo an unusual intramolecular hydroamination in the presence of a tetraaza macrocycle (Scheme 1). The complex $[NiL^2]^{2+}$ was synthesized by a reaction of Ni^{2+} ion with L^2, which could be prepared by reacting L^1 with propargyl bromide.

The nickel(II) complex is quite stable in DMSO containing triethylamine or diethylamine. However, interestingly, $[NiL^2]^{2+}$ undergoes intramolecular cyclization readily in the presence of L^1 to yield a mixture of $[NiL^3]^{2+}$, $[NiL^4]^{2+}$, and $[NiL^5]^{2+}$, approximately with a mole ratio of 1:1:2 (Scheme 1). The formation of the three complexes in the reaction is strongly supported by the ^{13}C NMR spectrum of the product; for example, the spectrum showed four peaks corresponding to the methyl groups at 18.4, 19.4, 19.9, and 20.5 ppm (one peak for $[NiL^3]^{2+}$, one for $[NiL^4]^{2+}$, and two for $[NiL^5]^{2+}$) and eight peaks corresponding to the -CH=CH- groups at 125.7, 125.8, 126.6, 126.9, 131.6, 131.9, 132.6, and 133.0 ppm (two peaks for $[NiL^3]^{2+}$, two for $[NiL^4]^{2+}$, and four for

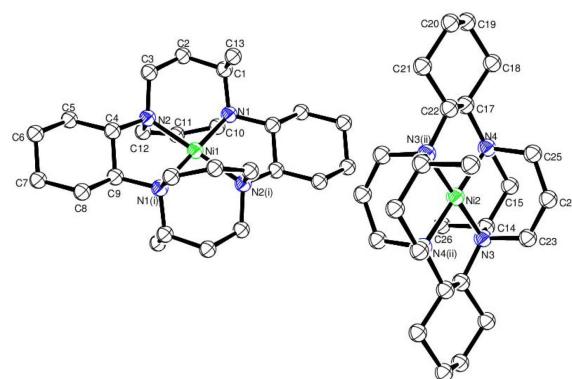**Figure 1.** ORTEP views of the cations $[NiL^3]^{2+}$ (left) and $[NiL^4]^{2+}$ (right). Symmetry transformations used to generate equivalent atoms: i = 1−x, 1−y, −z; ii = −x, 2−y, z.

$[NiL^5]^{2+}$). Unfortunately, our efforts to isolate each isomer separately by fractional crystallization of the mixture were unsuccessful. However, a single cocrystal composed of $[NiL^3](ClO_4)_2$ and $[NiL^4](ClO_4)_2$ could be obtained by evaporating an acetonitrile-water solution of the product; this was confirmed by X-ray structural characterization of the crystal.

Figure 1 shows that the crystallographic asymmetric unit of the crystal contains both $[NiL^3]^{2+}$ and $[NiL^4]^{2+}$. Selected bond distances and angles of the cations are listed in Table 1. The ORTEP drawing of $[NiL^3]^{2+}$ shows that the cation has square-planar coordination geometry with an inversion center at the metal ion. The C(11)-C(12) distance (1.391(6) Å) is distinctly shorter than the C(10)-C(11) distance (1.427(6) Å) and corresponds to a C=C double bond. The Ni(1)-N(1) and Ni(1)-N(2) distances are 1.946(3) and 1.948(3) Å, respectively. The N(1)-Ni(1)-N(2) angle (90.6(2)°) is similar to the N(1)-Ni(1)-N(2)(i) angle (89.4(3)°). This result is quite different from the reported trend that the N-Ni-N angles involved in the six-membered chelate rings (93.6(2)°) of $[NiL^1](ClO_4)$ are significantly larger than those involved in the five-membered chelate rings (85.9(2).[9] The position of the C=C double bonds on $[NiL^4]^{2+}$ is different from that on $[NiL^3]^{2+}$, even though both complexes exhibit similar Ni-N distances and N-Ni-N angles (Table 1); the C(23)-C(24)
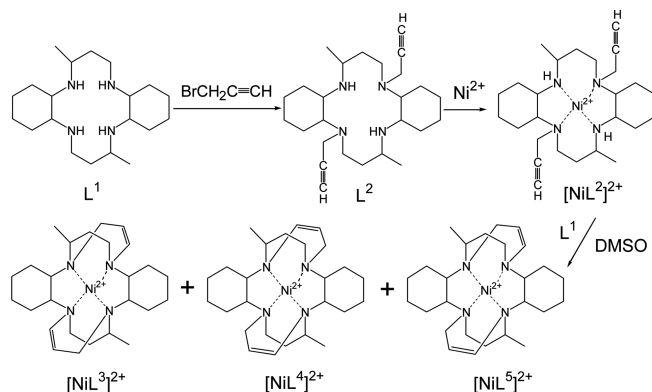
Scheme 1. Synthesis and reaction of L^2 and $[NiL^2]^{2+}$.

Table 1. Selected bond distances (Å) and angles (°) of $[NiL^3]^{2+}$ and $[NiL^4]^{2+}$

|			
Ni(1)-N(1)	1.946(3)	Ni(1)-N(2)	1.948(3)
C(10)-C(11)	1.427(6)	C(11)-C(12)	1.391(6)
N(1)-Ni(1)-N(2)(*i*)	180	N(1)-Ni(1)-N(2)	90.6(2)
N(1)-Ni(1)-N(2)(*i*)	89.4(3)	N(1)-C(10)-C(11)	118.3(4)
C(10)-C(11)-C(12)	131.5(4)	C(11)-C(12)-N(2)	117.9(4)
Ni(2)-N(3)	1.943(3)	Ni(2)-N(4)	1.955(3)
C(23)-C(24)	1.380(6)	C(24)-C(25)	1.440(6)
N(3)-Ni(2)-N(3)(*ii*)	180.0	N(3)-Ni(2)-N(4)	91.1(3)
N(3)-Ni(2)-N(4)(*ii*)	89.9(2)	N(3)-C(23)-C(24)	122.5(3)
C(23)-C(24)-C(25)	130.0(4)	C(24)-C(25)-N(4)	116.1(3)

Symmetry code: i = 1−x, 1−y, −z; ii = −x, 2−y, z.

distance (1.380(6) Å) is shorter than the C(24)-C(25) distance (1.440(6) Å).

The stepwise protonation constants (log K) of L^1 are 11.56, 9.93, 2.61, and 2.60,[10] showing that the macrocycle exhibits stronger proton affinity than triethylamine or diethylamine. The reaction of $[NiL^2]^{2+}$ in the presence of L^1 may begin with the deprotonation of the coordinated secondary amino groups (Scheme 2). Each amido group of the deprotonated form (A) attacks the activated alkyne function to form intermediate B. Hydrogen-atom migration at the N-CH=C⁻-CH$_2$-N linkages of B can produce the intermediate C. The protonation of C yields a mixture of the three isomers. The reaction must be promoted by the Ni-alkyne interaction in the intermediate(s). However, the route to producing a mixture of $[NiL^3]^{2+}$, $[NiL^4]^{2+}$, and/or $[NiL^5]^{2+}$ is unclear at this point.

The electronic absorption spectrum of the product (a mixture of $[NiL^3]^{2+}$, $[NiL^4]^{2+}$, and/or $[NiL^5]^{2+}$) measured in DMSO shows a *d-d* transition band centered at 458 nm. The wavelength is similar to that of $[NiL^1]^{2+}$ (463 nm),[11] indicating that the introduction of two -CH$_2$-CH=CH- chains into $[NiL^1]^{2+}$ to give $[NiL^3]^{2+}$, $[NiL^4]^{2+}$, or $[NiL^5]^{2+}$ does not change the ligand field strength. Each complex is stable, even in a 1.0 M HClO$_4$ or 1.0 M NaOH aqueous solution, like $[NiL^1]^{2+}$.[9] Unlike $[NiL^1]^{2+}$, however, $[NiL^3]^{2+}$, $[NiL^4]^{2+}$, and $[NiL^5]^{2+}$ are inert against ligand substitution with CN⁻ ion; L^3-L^5 of the complexes could not be substituted by CN⁻ ion in boiling (> 8 h) DMSO-water solutions containing an excess of NaCN. This trend is attributed to the topologically constrained structure of L^3-L^5.
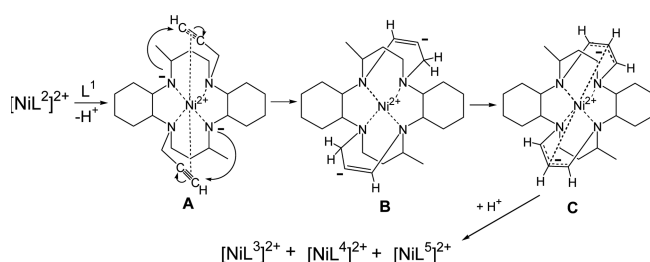
Scheme 2. Proposed route to produce a mixture of the three complexes.

This study shows that, in the presence of L^1, the *N*-CH$_2$C≡CH groups of $[NiL^2]^{2+}$ can react with the coordinated secondary amino groups to provide a mixture of $[NiL^3]^{2+}$, $[NiL^4]^{2+}$, and $[NiL^5]^{2+}$. To our knowledge, $[NiL^2]^{2+}$ is a rare example of polyaza macrocyclic complex that undergoes intramolecular cyclization involving *N*-CH$_2$C≡CH pendant arms and coordinated secondary amino groups. Further studies on the reactions of *N*-(CH$_2$)$_n$C≡CH groups attached to polyaza macrocycles are currently underway.

Experimental

Measurements. Elemental analyses were performed at the Research Center for Instrumental Analysis, Daegu University, Gyeongsan, Korea. FAB MS spectra were performed at the Korea Basic Science Institute, Daegu, Korea. NMR spectra were obtained with a Bruker WP 300 FT NMR spectrometer, Infrared spectra with a Genesis II FT IR spectrometer, and electronic absorption spectra with an Analytik Jena Specord 200 UV/Vis spectrophotometer.

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

Preparation of L^2. A toluene (40 mL) solution of L^1 (Ref. 11) (2.0 g, 6.0 mmol) and propargyl bromide (4.6 g, 18 mmol) was refluxed for *ca.* 48 h and then cooled to room temperature. A white solid (L^2·2HBr) formed was collected by filtration. To a methanol suspension (20 mL) of the solid, 1.0 M NaOH aqueous solution (20 mL) was added. The mixture was stirred for > 5 h at room temperature. During which time, the original solid went into the solution and a new solid was precipitated. After filtration, the solid was dissolved in chloroform and then filtered to remove any solid. The filtrate was evaporated to leave a white solid. The product was collected by filtration, washed with methanol, and dried in air. Yield: ~70%. *Anal*. Calc. for C$_{26}$H$_{44}$N$_4$: C, 75.68; H, 10.75; N, 13.58. Found: C, 74.77; H, 10.50; N, 13.49%. Mass (*m/z*): 412. IR (Nujol mull, cm⁻¹): 2115 ($\nu_{C≡C}$, alkyne), 3267 (ν_{N-H}), and 3298 (ν_{C-H}, alkyne). ^{13}C NMR (CDCl$_3$): 17.9 (Me), 22.4, 24.7, 26.0, 32.2, 33.0, 46.3, 47.3, 54.0, 68.2, 72.6 (-C≡*C*H), 82.2 (-*C*≡CH) ppm.

Preparation of $[NiL^2](ClO_4)_2$·H$_2$O. An acetonitrile suspension (20 mL) of Ni(OAc)$_2$·4H$_2$O (3.0 g) and L^2 (1.0 g) was refluxed for *ca.* 70 min and then cooled to room temperature. Concentrated HClO$_4$ (3.0 mL) dissolved in water (20 mL) was added to the resulting solution to precipitate an orange solid. The solid was collected by filtration, washed with cold acetonitrile, and dried in air. The product was recrystallized from hot DMSO-water (3:1) solution. Yield: ~80%. *Anal*. Calcd for C$_{26}$H$_{46}$N$_4$NiCl$_2$O$_9$: C, 45.37; H, 6.74; N, 8.14. Found: C, 45.82; H, 6.49; N, 8.01%. FAB mass (*m/z*): 569.4 for $[NiL^2 + ClO_4]^+$, 470.4 for $[NiL^2 − H]^+$. IR (Nujol mull, cm⁻¹): 1100 (ν_{Cl-O}, ClO$_4^-$), 2120 ($\nu_{C≡C}$, alkyne), 3198 (ν_{N-H}), and 3268 (ν_{C-H}, alkyne). ^{13}C NMR (DMSO-d_6): 17.1, 24.6, 25.5, 26.0, 29.7, 30.0, 46.0, 47.4, 57.3, 74.3, 76.6 (-C≡*C*H), 80.9 (-*C*≡CH) ppm. UV/Vis spec. (λ_{max}, nm (ε, M⁻¹cm⁻¹)): 485 (109) in DMSO.

Notes

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Preparation of a Mixture of [NiL³](ClO₄)₂, [NiL⁴](ClO₄)₂, and/or [NiL⁵](ClO₄)₂. A DMSO-acetonitrile (1:1) suspension (10 mL) of [NiL²](ClO₄)₂·H₂O (1.0 g) and L¹ (1.0 g) was stirred at *ca.* 60 °C for 2 h and then was allowed to stand at room temperature for > 5 h. After removing a white solid (L¹) by filtration, concentrated HClO₄ (3.0 mL) and water (10 mL) was added to the filtrate to precipitate an orange-red solid. The product was collected by filtration and recrystallized from hot acetonitrile-water (5:1) solution. Yield: ~60%. *Anal*. Calcd for $C_{26}H_{44}N_4NiCl_2O_8$: C, 46.59; H, 6.62; N, 8.36. Found: C, 46.78; H, 6.69; N, 8.38%. FAB mass (*m/z*): 568.9 for $[NiL + ClO_4]^+$, 470.0 for $[NiL - H]^+$. IR (Nujol mull, cm^{-1}): 1100 (ν_{Cl-O}, ClO_4^-), 1650 ($\nu_{C=C}$, alkene). ^{13}C NMR (DMSO-d_6) δ 18.4 (Me), 19.4 (Me), 19.9 (Me), 20.5 (Me), 23.2, 23.6, 23.7, 23.8, 24.0, 24.1, 24.3 (*d*), 24.4, 24.5 (*d*), 24.6 (*d*), 24.7, 25.0, 25.2, 26.9, 27.1, 27.9, 28.1, 48.9, 50.1, 51.0, 51.1, 52.1, 52.2, 52.3, 52.5, 54.0, 54.3, 63.3, 64.0, 64.8, 65.8, 68.2, 69.4, 69.7, 71.1, 125.7 (N-CH=*C*H-CH₂-N), 125.8 (N-CH=*C*H-CH₂-N), 126.6 (N-CH=*C*H-CH₂-N), 126.9 (N-*C*H=CH-CH₂-N), 131.6 (N-*C*H=CH-CH₂-N), 131.9 (N-*C*H=CH-CH₂-N), 132.6 (N-*C*H=CH-CH₂-N), 133.0 (N-*C*H=CH-CH₂-N) ppm. UV/Vis spec. (λ_{max}, nm (ε, $M^{-1}cm^{-1}$)): 458 (99) in DMSO, 458 (100) in acetonitrile-water (5:1).

Crystal Structure Determination. A single crystal suitable for the X-ray crystallography was grown from acetonitrile-water solution of a mixture of [NiL³](ClO₄)₂, [NiL⁴]-(ClO₄)₂, and/or [NiL⁵](ClO₄)₂. Intensity data were collected on a Rigaku R-AXIS RAPID II-S diffractometer equipped with graphite monochromated MoKα (λ = 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 w. The structure was solved by direct method and refined by full matrix least squares against F^2 for all data using SHELXL-97.[12] All non-hydrogen atoms were anisotropically refined. All hydrogens were included in the calculated position.

Crystal and Refinement Data: $C_{26}H_{44}Cl_2N_4NiO_8$, M = 670.26, a = 17.141(2), b = 9.752(2), c = 18.259(2) Å, β = 107.90(2) °, V = 2904.6(2) Å³, Z = 4, D_{calc} = 1.533 g cm⁻³, μ = 9.08 cm⁻¹, Goodness-of-fit on F^2 = 1.037, Final R_1 = 0.0634, wR_2 = 0.1618 ($I > 2\sigma(I)$), R_1 = 0.0971, wR_2 = 0.1852 (all data).

Supporting Information. Crystallographic data for [NiL³](ClO₄)₂ and [NiL⁴](ClO₄)₂ (CCDC 992943) have been deposited with the Cambridge Crystallographic Data Center. Copies of the data may be obtained free of charge, on application to the director, CCDC, 12 Union Road, Cambridge CB2 IEZ, UK (http://www.ccdc.cam.ac.uk, fax: +44-1233-336-033, or e-mail: deposit@ccdc.cam.ac.uk).

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