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Reaction of primary amines with *N*-ethynyl pendant arms attached to macrocyclic nickel(II) and copper(II) complexes: Formation of the complexes with pendant imine group(s)

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ABSTRACT

The two *N*-$CH_2C{\equiv}CH$ pendant arms of $[NiL^1]^{2+}$ (L^1 = 2,13-bis(*N*-propargyl)-3,14-dimethyl-2,6,13,17-tetraazatricyclo[16.4.0.0$^{7.12}$]docosane) react readily with benzyl amine or *n*-propylamine to produce the *trans*-octahedral complexes, $[NiL^2]^{2+}$ and $[NiL^4]^{2+}$, bearing two *N*-$CH_2C({=}NCH_2C_6H_5)CH_3$ or two *N*-$CH_2C({=}NCH_2CH_2CH_3)CH_3$ pendant arms. $[CuL^1]^{2+}$, however, reacts with the primary amines to form a square-pyramidal complex $[CuL^3]^{2+}$ or $[CuL^5]^{2+}$ bearing one *N*-$CH_2C({=}NCH_2C_6H_5)CH_3$ or *N*-$CH_2C({=}NCH_2CH_2CH_3)CH_3$ pendant arm as well as one *N*-$CH_2C{\equiv}CH$ group under similar experimental conditions. The pendant imine group of the nickel(II) or copper(II) complexes of L^2–L^5 is involved in coordination and is inert against hydrolysis, even in aqueous 1.0 M $HClO_4$ or 1.0 M NaOH solutions.

1. Introduction

The hydroamination of alkynes is an attractive process for the preparation of imines, enamines, and heterocycles [1–8]. The reaction generally involves several important steps, including the activation of alkynes with transition metal ions or bases and the nucleophilic attack of amines to alkynes. A large number of studies have examined the metal- or base-catalyzed hydroamination of aliphatic and aromatic alkynes [1–8]. Despite this, reports of such reactions involving alkynyl groups attached to polyaza macrocyclic compounds are limited [8]. $[NiL^2]^{2+}$ bearing two *N*-$CH_2C{\equiv}CH$ pendant arms has been reported to readily undergo intramolecular cyclization in DMSO containing a 14-membered tetraaza macrocycle, such as L^1, to yield a mixture of topologically constrained macropolycyclic complexes, including $[NiL^{11}]^{2+}$ and $[NiL^{12}]^{2+}$ [8]. On the other hand, $[NiL^2]^{2+}$ is stable in DMSO containing triethylamine or diethylamine, indicating that the reactivity of the *N*-$CH_2C{\equiv}CH$ pendant arms is affected significantly by the nature of the amines added. This prompted a study of the reaction of the *N*-$CH_2C{\equiv}CH$ groups attached to polyaza macrocyclic complexes in the presence of various types of amines.

Accordingly, this study examined the reaction of the *N*-$CH_2C{\equiv}CH$ pendant arms attached to $[NiL^2]^{2+}$ and $[CuL^2]^{2+}$ with benzyl amine or *n*-propylamine and prepared $[NiL^3]^{2+}$ or $[NiL^5]^{2+}$ bearing two *N*-$CH_2C({=}NR)CH_3$ (R = $CH_2C_6H_5$ or $CH_2CH_2CH_3$) groups and $[CuL^4]^{2+}$ or $[CuL^6]^{2+}$ bearing both *N*-$CH_2C({=}NR)CH_3$ and *N*-$CH_2C{\equiv}CH$ groups. This paper reports the synthesis and characterization of the complexes, along with the crystal structures of $[NiL^3](ClO_4)_2$ and $[CuL^4](ClO_4)_2{\cdot}H_2O$. Although various types of functionalized macrocyclic complexes have been prepared and investigated, examples of such compounds bearing imine pendant arms are quite rare.

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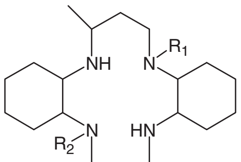
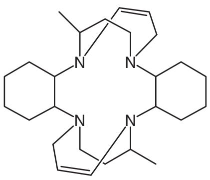
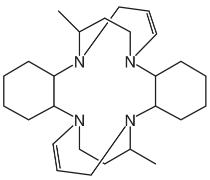


L^1: $R_1 = R_2 = H$
L^2: $R_1 = R_2 = CH_2C{\equiv}CH$
L^3: $R_1 = R_2 = CH_2C(=NCH_2C_6H_5)CH_3$
L^4: $R_1 = CH_2C{\equiv}CH$
$R_2 = CH_2C(=NCH_2C_6H_5)CH_3$
L^5: $R_1 = R_2 = CH_2C(=NCH_2CH_2CH_3)CH_3$
L^6: $R_1 = CH_2C{\equiv}CH$
$R_2 = CH_2C(=NCH_2CH_2CH_3)CH_3$
L^7: $R_1 = R_2 = CH_2C(=NH)NHCH_2CH_2CH_3$
L^8: $R_1 = CH_2C{\equiv}N$
$R_2 = CH_2C(=NH)NHCH_2CH_2CH_3$
L^9: $R_1 = R_2 = CH_2C(=NH)OCH_3$
L^{10}: $R_1 = CH_2C{\equiv}N$
$R_2 = CH_2C(=NH)NHOCH_3$



L^{11}



L^{12}

2. Experimental

2.1. Measurements

Electronic absorption, infrared, and nuclear magnetic resonance (NMR) spectra were recorded with Analytik Jena Specord 200 UV–Vis spectrophotometer, Genesis II FT IR spectrometer, and Bruker WP 300 FT NMR spectrometer, respectively. Conductance measurements were carried out using a Z18 Oyster Conductivity/Temperature meter. The magnetic moments were calculated from magnetic susceptibility data obtained at 293 K using a Johnson Matthey MK-1 magnetic susceptibility balance. Elemental analyses were conducted at the Research Center for Instrumental Analysis, Daegu University, Gyeongsan, Korea. The FAB MS spectra were obtained at the Korea Basic Science Institute, Daegu, Korea.

2.2. Preparation of $[CuL^2](ClO_4)_2 \cdot H_2O$

An acetonitrile suspension (20 ml) of $Cu(NO_3)_2 \cdot 3H_2O$ (2.4 g, 9.8 mmol) and L^2 (2.0 g, 4.9 mmol) [8] was heated under reflux for 1 h and then cooled to room temperature. The addition of concentrated $HClO_4$ (3.0 ml) and water (20 ml) to the reaction solution resulted in the precipitation of a red solid. The solid was collected by filtration, washed with water and recrystallized in hot DMSO-water (3:1). Yield: ∼80% (2.6 g, 3.9 mmol). *Anal.* Calc. for $C_{26}H_{46}N_4CuCl_2O_9$: C, 45.05; H, 6.69; N, 8.08. Found: C, 45.21; H, 6.62; N, 8.31%. FAB mass (*m/z*): 574.4 for $[CuL^2 + ClO_4]^+$, 475.4 for $[CuL^2 - H]^+$. IR (Nujol mull, cm^{-1}): 3235 (ν_{C-H}, $-C{\equiv}CH$), 3218 (ν_{N-H}), 2115 ($\nu_{C{\equiv}C}$, $-C{\equiv}CH$), 1100 (ν_{Cl-O}, ClO_4^-).

2.3. Preparation of $[NiL^3](ClO_4)_2$

A DMSO–acetonitrile (1:2) solution (15 ml) of $[NiL^2](ClO_4)_2$ (1.0 g, 1.5 mmol) [8] and benzylamine (1.0 ml, 9.1 mmol) was stirred at room temperature for 3 h. During the reaction, a pale purple solid precipitated. After adding $NaClO_4$ (2.0 g) and water (10 ml), the mixture was allowed to stand at room temperature for 2 h. The solid was collected by filtration, washed with methanol and dried in air. The product was recrystallized by addition of water (10 ml) and $HClO_4$ (2–3 drops) to hot DMSO solution of the crude product. Yield: ∼70% (0.9 g, 1.1 mmol). *Anal.* Calc. for $C_{40}H_{62}N_6NiCl_2O_8$: C, 54.31; H, 7.06; N, 9.50. Found: C, 53.83; H, 6.92; N, 9.62%. FAB mass (*m/z*): 782.9 for $[NiL^3 + ClO_4]^+$, 684.0 for $[NiL^3 - H]^+$. IR (Nujol mull, cm^{-1}): 3249 (ν_{N-H}), 1663 ($\nu_{C=N}$, imine), 1600 ($\nu_{C=C}$, phenyl), 1100 (ν_{Cl-O}, ClO_4^-). $\mu_{eff} = 2.60$ μ_B at room temperature.

2.4. Preparation of $[CuL^4](ClO_4)_2$

An acetonitrile solution (10 ml) of $[CuL^2](ClO_4)_2$ (1.0 g, 1.5 mmol) and benzylamine (1.0 ml, 9.1 mmol) was stirred at room temperature for 3 h. During the reaction, the red solution turned purple. After adding $HClO_4$ (2.0 ml) and water (10 ml), the resulting solution was evaporated at room temperature to precipitate a purple solid. The solid was collected by filtration, washed with methanol and dried in air. This was recrystallized in water–acetonitrile (1:1) solution. Yield: ∼70% (0.8 g, 1.1 mmol). *Anal.* Calc. for $C_{33}H_{53}N_5CuCl_2O_9$: C, 49.65; H, 6.69; N, 8.77. Found: C, 48.96; H, 6.58; N, 9.01%. FAB mass (*m/z*): 680.9 for $[CuL^4 + ClO_4]^+$, 582.0 for $[CuL^4 - H]^+$. IR (Nujol mull, cm^{-1}): 3296 (ν_{C-H}, $-C{\equiv}CH$), 3238 (ν_{N-H}), 3197 (ν_{N-H}), 2115 ($\nu_{C{\equiv}C}$,$-C{\equiv}CH$), 1666 ($\nu_{C=N}$, imine), 1100 (ν_{Cl-O}, ClO_4^-).

2.5. Preparation of $[NiL^5](ClO_4)_2 \cdot H_2O$

This compound was prepared using a similar to that for $[NiL^3](ClO_4)_2$, except that *n*-propylamine (1.0 ml, 12 mmol) was reacted instead of benzylamine. The pale purple solid was recrystallized by addition of water (10 ml) and $HClO_4$ (2–3 drops) to hot DMSO solution of the crude product. Yield: ∼70% (0.8 g, 1.1 mmol). *Anal.* Calc. for $C_{32}H_{64}N_6NiCl_2O_9$: C, 47.66; H, 8.00; N, 10.42. Found: C, 47.88; H, 8.14; N, 10.62%. FAB mass (*m/z*): 687.5 for $[NiL^5 + ClO_4]^+$, 587.5 for $[NiL^5 - H]^+$. IR (Nujol mull, cm^{-1}): 3248 (ν_{N-H}), 1663 ($\nu_{C=N}$, imine), 1100 (ν_{Cl-O}, ClO_4^-). $\mu_{eff} = 2.76$ μ_B at room temperature.

2.6. Preparation of $[CuL^6](ClO_4)_2 \cdot H_2O$

This compound was prepared by using a similar to that for $[CuL^4](ClO_4)_2$, except that *n*-propylamine (1.0 ml, 12 mmol) was reacted instead of benzylamine. The purple solid was recrystallized in water–acetonitrile (1:1) solution. Yield: ∼70% (0.8 g, 1.1 mmol). *Anal.* Calc. for $C_{29}H_{53}N_5CuCl_2O_9$: C, 46.43; H, 7.12; N, 9.34. Found: C, 46.84; H, 7.10; N, 9.73%. FAB mass (*m/z*): 633.0 for $[CuL^6 + ClO_4]^+$, 534.0 for $[CuL^6 - H]^+$. IR (Nujol mull, cm^{-1}): 3310 (ν_{C-H}, $-C{\equiv}CH$), 3220 (ν_{N-H}), 3200 (ν_{N-H}), 2125 ($\nu_{C{\equiv}C}$,$-C{\equiv}CH$), 1670 ($\nu_{C=N}$, imine), 1100 (ν_{Cl-O}, ClO_4^-).

2.7. X-ray crystal structure determination of $[NiL^3](ClO_4)_2$ and $[CuL^4](ClO_4)_2 \cdot H_2O$

The single crystals used for the X-ray study were grown from DMSO-water ($[NiL^3](ClO_4)_2$) or acetonitrile–water ($[CuL^4](ClO_4)_2 \cdot H_2O$) solution of the complexes. The X-ray crystallographic data were collected on a Rigaku R-AXIS RAPID II-S diffractometer equipped with graphite monochromated Mo Kα