

Reduction of nitrile to primary amine using sodium borohydride: Synthesis and protonation of a *cis*-octahedral macrocyclic nickel(II) complex bearing two 2-aminoethyl pendant arms



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ABSTRACT

The *cis*-octahedral complex $[\text{NiL}^2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (**1**) ($\text{L}^2 = C$ -*racemic*-1,8-bis(*N*-2-aminoethyl)-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane), bearing two coordinated *N*-CH₂CH₂NH₂ pendant arms, has been prepared by a reaction of the *N*-CH₂CN groups of $[\text{Ni}(\text{L}^1)(\text{CH}_3\text{COO})]^+$ ($\text{L}^1 = C$ -*racemic*-1,8-bis(cyanomethyl)-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane) with NaBH₄ in acetonitrile. The trigonal bipyramidal complex $[\text{Ni}(\text{HL}^2)](\text{ClO}_4)_3 \cdot \text{H}_2\text{O}$ (**2**) ($\text{HL}^2 =$ a mono-protonated form of L^2), in which the primary amino group of the coordinated *N*-CH₂CH₂NH₂ group occupies one of the three equatorial positions, has also been prepared by the addition of HClO₄ to a methanol solution of **1**. The equatorial Ni–N (*N*-CH₂CH₂NH₂ group) distance (2.076(2) Å) of **2** is similar to other equatorial Ni–N (macrocyclic ring) distances (2.073(2) and 2.075(2) Å), but is significantly shorter than the Ni–N (*N*-CH₂CH₂NH₂ groups) distances (2.170(3) and 2.190(3) Å) of **1**. Interestingly, the coordinated *N*-CH₂CH₂NH₂ group of **2** is inert to protonation.

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1. Introduction

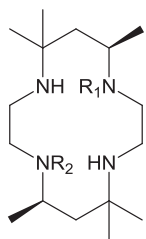
Transition metal complexes of polyaza macrocyclic ligands bearing functional pendant arms have attracted considerable attention because of their interesting chemical properties that can be affected by the nature, number and/or position of the pendant arms [1–18]. In some cases, the central metal ions of such complexes also affect the reactivity of the pendant groups. Unlike most organic nitriles, *N*-(CH₂)_{*n*}CN groups attached to some polyaza macrocyclic complexes have been reported to undergo a variety of reactions under relatively mild conditions [11–18]. In particular, the *N*-CH₂CN groups of the square-planar complex $[\text{NiL}^6]^{2+}$ ($\text{L}^6 = C$ -*meso*-2,13-bis(cyanomethyl)-5,16-dimethyl-2,6,13,17-tetraazatricyclo [16.4.0.1¹⁸0^{7,12}] docosane) react with NaBH₄ in methanol to yield the *trans*-octahedral complex $[\text{NiL}^7]^{2+}$ ($\text{L}^7 = C$ -*meso*-2,13-bis(2-aminoethyl)-5,16-dimethyl-2,6,13,17-tetraazatricyclo [16.4.0.1¹⁸0^{7,12}] docosane) bearing two *N*-CH₂CH₂NH₂ pendant arms, even though the nitrile groups are not involved directly in coordination [18]. This finding is different from the general trend that NaBH₄ is a relatively weak reducing reagent and is insufficient to reduce organic nitriles to amines in the absence of an additional strong Lewis acid or catalyst [19–21]. A previous study suggested that the reduction

of the *N*-CH₂CN groups of $[\text{NiL}^6]^{2+}$ to the corresponding primary amino groups is promoted by methanol and the central metal ion [18]. The reduction of nitriles is one of the most important processes for the synthesis of primary amines. However, reports of the borohydride reduction of nitriles are limited [18,20,21].

Although a range of *N*-aminoalkylated polyaza macrocyclic compounds have been prepared and investigated [8,18], the coordination and protonation behaviors of the aminoalkyl pendant arms of 14-membered macrocyclic complexes have not been investigated thoroughly. This prompted a study of the preparation and the coordination and protonation behaviors of various polyaza macrocyclic complexes bearing *N*-(CH₂)_{*n*}NH₂ groups.

In this study, the *cis*-octahedral complex $[\text{NiL}^2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (**1**) ($\text{L}^2 = C$ -*racemic*-1,8-bis(*N*-2-aminoethyl)-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane) bearing two coordinated *N*-CH₂CH₂NH₂ pendant arms was prepared from a reaction of NaBH₄ with the *N*-CH₂CN groups of $[\text{Ni}(\text{L}^1)(\text{CH}_3\text{COO})]\text{ClO}_4$ ($\text{L}^1 = C$ -*racemic*-1,8-bis(cyanomethyl)-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane) in acetonitrile. Interestingly, only one of the two *N*-CH₂CH₂NH₂ pendant arms of **1** was protonated selectively to form $[\text{Ni}(\text{HL}^2)](\text{ClO}_4)_3 \cdot \text{H}_2\text{O}$ (**2**) ($\text{HL}^2 =$ a mono-protonated form of L^2), even in concentrated HClO₄ aqueous solutions. This paper reports the synthesis, characterization, and crystal structures of **1** and **2**.

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- L¹: R₁ = R₂ = CH₂CN
 L²: R₁ = R₂ = CH₂CH₂NH₂
 L³: R₁ = R₂ = CH₂C(=NH)OCH₃
 L⁴: R₁ = R₂ = CH₂CONH₂
 L⁵: R₁ = CH₂CH₂CN;
 R₂ = CH₂CH₂CONH₂

2. Experimental

2.1. Measurements

Infrared and Electronic absorption spectra were recorded using Genesis II FT IR spectrometer and Analytik Jena Specord 200 UV/Vis spectrophotometer, respectively. The conductance measurements were carried out using a Z18 Oyster Conductivity/Temperature meter. The magnetic moments were calculated from the magnetic susceptibility data obtained at room temperature 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.

Caution! Perchlorate salts of metal complexes with organic ligands are often explosive and should be handled with caution.

2.2. Preparation of **1**

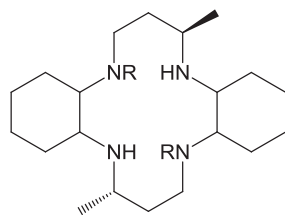
NaBH₄ (50 mg, 1.3 mmol) was added in small portions over a 20 min period to a warm (40–50 °C) acetonitrile solution (20 ml) of [Ni(L¹)(CH₃COO)]ClO₄ (0.5 g, 0.9 mmol) [13] with stirring. The resulting solution was stirred for 30 min and filtered to remove any solids. After adding NaClO₄ (2.0 g) and water (10 ml) to the filtrate, the solution was evaporated at room temperature to precipitate a purple solid. The product was collected by filtration, washed with cold water and recrystallized in acetonitrile–water (1:1). Yield: ~ 60%. *Anal. Calc.* for C₂₀H₄₈N₆Cl₂NiO₉: C, 37.12; H, 7.49; N, 13.00. Found: C, 37.21; H, 7.57; N, 13.10%. FAB MS (*m/z*): 527.4 {[NiL² + ClO₄]⁺} and 427.4 {[NiL² – H]⁺}. IR (cm⁻¹): 3520 (ν_{O–H}, H₂O), 3358 (ν_{N–H}), 3308 (ν_{N–H}), 3246 (ν_{N–H}), 3200 (ν_{N–H}), 1592 (δ(NH₂)), and 1100 (ν_{Cl–O}, ClO₄⁻). μ_{eff} = 2.58 μ_B at room temperature.

2.3. Preparation of **2**

To a methanol (15 ml) solution of **1** (0.5 g, 0.8 mmol) was added concentrated HClO₄ (0.5 ml). The resulting green solution was evaporated at room temperature to precipitate a blue-green solid. The product was collected by filtration, washed with methanol and dried in air. Yield: ~ 70%. *Anal. Calc.* for C₂₀H₄₉N₆Cl₃NiO₁₃: C, 32.17; H, 6.61; N, 11.26. Found: C, 32.07; H, 6.65; N, 11.23%. IR (cm⁻¹): 3550 (ν_{O–H}, H₂O), 3309 (ν_{N–H}), 3280 (ν_{N–H}), 3234 (ν_{N–H}), 3170 (ν_{N–H}), 1602 (δ(NH₂)), and 1100 (ν_{Cl–O}, ClO₄⁻). μ_{eff} = 2.90 μ_B at room temperature.

2.4. Crystal structure determination

Single crystals of **1** and **2** suitable for an X-ray study were grown from acetonitrile–water–ethanol and methanol–



- L⁶: R = CH₂CN
 L⁷: R = CH₂CH₂NH₂

water–ethanol solutions, respectively. The X-ray crystallographic data were collected on a Rigaku R-Axis RAPID II-S diffractometer equipped with graphite monochromated Mo Kα (λ = 0.71073 Å) radiation source and an imaging plate detector (460 mm × 256 mm). A total of 240 oscillation images were collected at 100 K using a width of 3° in ω. The structures were solved by direct methods and refined by full-matrix least-squares against F² for all data using SHELXL-97 [22]. The positions of all non-hydrogen atoms were refined with anisotropic displacement factors and the positions of all hydrogen atoms were allowed to ride on their bonded atoms with the isotropic displacement factors. Table 1 lists the crystallographic data and the results of the refinements.

3. Results and discussion

3.1. Synthesis

Coordinated nitriles of [Ru(MeCN)₃(MeC(CH₂AsPh₂)₃)]²⁺ react with NaBH₄ in methanol to yield [RuH(MeCH₂NH₂)₂(MeC(CH₂AsPh₂)₃)]⁺ [20]. As mentioned above, the *N*-CH₂CN groups of [NiL⁶]²⁺ also react with NaBH₄ to produce the *trans*-octahedral complex [NiL⁷]²⁺ in DMSO containing methanol, even though the nitrile groups are not involved in coordination; this reaction could not be achieved in the absence of methanol under similar experimental conditions [18]. The reduction of [Ru(MeCN)₃(MeC(CH₂AsPh₂)₃)]²⁺ and [NiL⁷]²⁺ using NaBH₄ was suggested to be promoted by methanol, which can be a source of H⁺ ions [18,20]. In this study, the *N*-CH₂CN groups of [Ni(L¹)(CH₃COO)]⁺ were reduced readily by NaBH₄ even in the absence of methanol, yielding the *cis*-octahedral complex **1** bearing two coordinated *N*-CH₂CH₂NH₂ pendant arms (see Section 2). Reduction of the free macrocycle L¹ with NaBH₄ was also attempted under a range of experimental conditions, but it failed. This supports the suggestion that the reduction of [Ni(*C*-racemic-L¹)(CH₃COO)]⁺ is promoted by the central metal, which can bind the functional pendant arms in the reaction intermediate(s) and/or in the product [18].

The addition of excess HClO₄ to a solution of **1** produced the mono-protonated TBP complex **2**, in which only one of the two *N*-CH₂CH₂NH₂ groups is protonated and removed from the coordination sphere. Surprisingly, the di-protonated complex [Ni(H₂L²)⁴⁺ (H₂L² = a deprotonated form of L²) bearing two uncoordinated *N*-CH₂CH₂NH₃⁺ groups could not be prepared even in >2.0 M HClO₄ solutions of **1** or **2**. The protonation behavior of **1** was very different from that of [NiL⁷]²⁺, which undergoes a two-step protonation to form the square-planar complex [Ni(H₂L⁷)](ClO₄)₄ (H₂L⁷ = a di-protonated form of L⁷) in ≤1.0 M HClO₄ solutions [18].

3.2. Crystal structure of **1**

Fig. 1 shows that the two *N*-CH₂CH₂NH₂ pendant arms of the complex are involved in coordination. The macrocycle is folded along the N(1)–Ni–N(3) axis and has *trans*-V type *N*-configuration. Two *N*-CH₂CH₂NH₂ groups of L² are *syn* with respect to the N₄ plane of the macrocyclic backbone, and the complex has a slightly distorted *cis*-octahedral coordination geometry. Table 2 lists the selected bond distances and angles of the complex. The Ni–N distances are comparable to those of the other related *cis*- or *trans*-octahedral nickel(II) complexes, such as [NiL³]²⁺ [13]. The Ni–N (5) and Ni–N(6) (*N*-CH₂CH₂NH₂ groups) distances (2.170(3) and 2.190(3) Å, respectively) are longer than the other Ni–N (macrocyclic ring) distances (2.130(3)–2.145(3) Å). The C(12)–N(5) and C(14)–N(6) distances (1.489(5)–1.493(5) Å) are similar to the C(1)–N(1) distance (1.495(4) Å) and correspond to the C–N single bonds of amino groups. The *trans*-N–Ni–N angles (173.6(3)°–178.2(2)°) are deviated slightly from 180°. The N(1)–Ni–N(4) and

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