

Synthesis and Crystal Structure of Nickel(II) Complex of *trans*-1,2-Diaminocyclohexane

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Nickel(II) *trans*-1,2-Diaminocyclohexane 錯物の 合成 및 結晶構造

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要 約

[NiL₃]Cl₂ · 3H₂O (1) (L = *trans*-1,2-diaminocyclohexane) 錯物を 合成하고 構造를 糾明하였다. 이 錯物은 立方結晶系, 空間群 P2₁3, $a = 13.830(1) \text{ \AA}$, $V = 2645.9(2) \text{ \AA}^3$, $Z = 4$ 로 結晶化 되었다. 이 錯物の 構造는 最小自乘法으로 精密化하였으며, 最終 信賴度 $R_1(wR_2)$ 값은 1500個의 回折班點에 대하여 0.0766(0.2068)이었다.

Abstract

The complex [NiL₃]Cl₂ · 3H₂O (1) (L = *trans*-1,2-diaminocyclohexane) has been synthesized and characterized by X-ray crystallography. The compound 1 crystallizes in the cubic space group P2₁3, with $a = 13.830(1) \text{ \AA}$, $V = 2645.9(2) \text{ \AA}^3$, $Z = 4$, $R_1(wR_2)$ for 1500 observed reflections of $[I > 2\sigma(I)]$ was 0.0766 (0.2068).

1. Introduction

A number of nickel(II) and copper(II) complexes of various diamines have been synthesized and characterized by X-ray crystallography.¹⁻⁸⁾ Among these complexes, [CuL₂(H₂O)₂]Cl₂ and [CuL₂(NO₃)₂] (L = *trans*-1,2-diaminocyclohexane) reveal the distorted (4 + 2) octahedral geometry with N₄O₂ chromophore. The 1,2-diaminocyclohexane exists in two isomeric forms: *cis*- and *trans*- form. *Trans*-isomer is more stable than *cis*-isomer, and probably because of this, it has been well studied.⁹⁻¹²⁾ In this paper, we report the synthesis and characterization of the nickel(II) complex of *trans*-1,2-diaminocyclohexane.

2. Experimental

Materials and Physical Measurements. All chemicals and solvents used in the synthesis were of reagent-grade and were used without further purification. IR spectra were recorded with a Perkin-Elmer Paragon 1000 FT-IR spectrophotometer, and electronic spectra with a Jasco Uvidec-610 spectrophotometer. Room-temperature magnetic susceptibilities were measured with a Johnson Matthey MK-II magnetic balance. The diamagnetic corrections were evaluated from Pascal's constants. High-resolution fast-atom bombardment mass spectrometry (FAB mass) was performed with a Jeol JMS-HA

Table 1. Crystal Data and Structure Refinement for 1

Empirical formula	C ₁₈ H ₄₂ Cl ₂ N ₆ NiO ₃
Formula weight	520.19
Temperature	293(2) K
Crystal system	Cubic
Space group	<i>P</i> 2 ₁ 3
Unit cell dimensions	<i>a</i> = 13.830(1) Å
Volume	2645.0(2) Å ³
Z	4
Density (calculated)	1.306 Mg/m ³
Absorption coefficient	0.964 mm ⁻¹
Diffractometer	Rigaku AFC-7R
Radiation/wavelength	Mo Kα (graphite monochrom.)/0.71069 Å
<i>F</i> (000)	1112
θ range for data collection	3.29 to 29.97°
Index ranges	2 ≤ <i>h</i> ≤ 19, -13 ≤ <i>k</i> ≤ 13, -11 ≤ <i>l</i> ≤ 10
Reflection collected/unique	1835/1500 (<i>R</i> _{int} = 0.035)
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	1500/0/87
Goodness-of-fit on <i>F</i> ²	0.934
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ ^a = 0.0766, <i>wR</i> ₂ ^b = 0.2068
<i>R</i> indices (all data)	<i>R</i> ₁ ^a = 0.1313, <i>wR</i> ₂ ^b = 0.2307
Absolute structure parameter	0.15(9)
Largest diff. peak and hole	0.775 and -0.302 eÅ ⁻³

$$^aR_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

$$^b wR_2 = \left[\frac{\sum [w(F_o^2 - F_c^2)]^2}{\sum [w(F_o^2)]^2} \right]^{1/2}$$

100A/100A instrument. Elemental analyses were performed by the Korea Research Institute of Chemical Technology, Taejeon, Korea.

Synthesis of [NiL₃]Cl₂ · 3H₂O(1). To a methanol solution (20 ml) of NiCl₂ · 6H₂O (119 mg, 1 mmol) was added L (0.36 ml, 3 mmol), and then the mixture was heated at reflux for 1 h. When the mixture was allowed to stand at room temperature for several days, violet crystals were precipitated. The crystals were filtered off, washed with diethyl ether, and dried in air. Recrystallization from water/acetonitrile yielded violet crystals suitable for X-ray analysis. IR (KBr, cm⁻¹): 3293, 3270, 3157, 2930, 1630, 1122, 1021, 989, 668, 558. UV/vis in water [λ_{\max} , nm (ϵ , M⁻¹cm⁻¹): 546 (5.5), 345 (10.3)]. Found: C, 42.65; H, 8.23; N, 16.04. Calc. for C₁₈H₄₂Cl₂N₆NiO₃: C, 42.56; H, 8.14; N, 16.16%. FAB mass (CH₂Cl₂, *m/z*): 520 (*M*⁺). μ_{eff} = 2.86 μ_B .

X-ray Crystallography. The crystal was mounted on a Rigaku AFC-7R diffractometer. X-ray data were collected with a graphite-monochromated Mo Kα radiation (λ = 0.71069 Å) in the ω -2θ scan mode. The cell parameters and orientation matrix were

determined from the least-squares fit of 25 accurately centered reflections with θ angles between 14.77 and 20.94°. Intensity data were corrected for Lorentz and polarization effects. The crystallographic data, conditions used for the intensity data collection, and some features of the structure refinement are listed in Table 1. The structure was solved by direct meth-

Table 2. Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å²×10³) for 1

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq)
Ni	1265(1)	1265(1)	1265(1)	41(1)
N(1)	180(6)	335(6)	1817(6)	58(2)
N(2)	680(6)	2190(5)	2325(5)	52(2)
C(1)	-495(7)	882(8)	2416(7)	59(2)
C(2)	97(7)	1613(7)	2988(7)	58(2)
C(3)	-575(8)	2246(10)	3638(9)	84(4)
C(4)	-1081(7)	293(9)	3076(8)	74(3)
C(5)	-1182(11)	1594(12)	4297(10)	114(5)
C(6)	-1762(5)	867(5)	3693(6)	91(4)
Cl(1)	-3756(5)	-3756(5)	-3756(6)	227(7)
Cl(2)	-506(5)	-506(5)	-506(6)	441(18)
Ow	2063(5)	3428(5)	3678(6)	108(3)

U(eq) is defined as one-third of the trace of the orthogonalized *U*_{ii} tensor.

ods PATTY in DIRDIF92¹³) and the least-squares refinements of the structure were performed by the program SHELXL.¹⁴) All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions and allowed to ride on their parent atoms with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}$. The water hydrogen atoms were not located. Final atomic coordinates and equivalent isotropic displacement parameters are given in Table 2.

3. Results and Discussion

The $[\text{Ni}(\text{L})_3]\text{Cl}_2 \cdot 3\text{H}_2\text{O}$ (**1**) complex crystallizes in the cubic space group $P2_13$ ($Z = 4$). An ORTEP drawing of **1** with the atomic numbering scheme is shown in Fig. 1. Selected bond distances and angles are listed in Table 3. The nickel ion lies on the crystallographic 3-fold axis. Additionally, the complex has the low-symmetry point group C_3 in the crystal, which is much less studied than the O_h or D_3 cases. Three 5-membered chelate rings are arranged in such a way that 6-membered cyclohexane rings adopt *trans* chair conformations. The geometry around the nickel atom is distorted octahedral with the ligand bite angle $\text{N}(1)\text{-Ni-N}(2)$ $81.1(3)^\circ$.

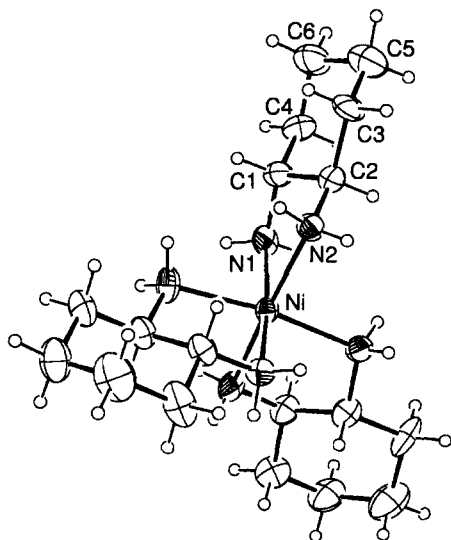


Fig. 1. An ORTEP drawing of **1** with the atomic numbering scheme. Thermal ellipsoids are drawn at 30% probability. The water molecules and chloride anions are omitted for clarity.

Table 3. Selected Bond Distances (Å) and Angles ($^\circ$) for **1**

Ni-N(1)	2.118(7)	Ni-N(2)	2.108(7)
N(1)-C(1)	1.460(12)	N(2)-C(2)	1.458(12)
C(1)-C(2)	1.522(12)	C(1)-C(4)	1.468(13)
C(2)-C(3)	1.562(13)	C(3)-C(5)	1.533(19)
C(4)-C(6)	1.498(13)	C(5)-C(6)	1.534(18)
N(1)-Ni-N(2)	81.1(3)	N(1)-Ni-N(1) ⁱ	92.5(3)
N(1)-Ni-N(2) ⁱ	92.3(3)	N(2)-Ni-N(2) ⁱ	94.5(3)
N(1)-Ni-N(2) ⁱⁱ	172.2(3)	Ni-N(1)-C(1)	110.1(6)
Ni-N(2)-C(2)	108.5(5)	N(1)-C(1)-C(2)	107.2(7)
N(1)-C(1)-C(4)	114.8(8)	N(2)-C(2)-C(1)	109.6(8)
N(2)-C(2)-C(3)	112.6(9)		

Symmetry codes: (i) z, x, y ; (ii) y, z, x .

The $\text{N}(1)\text{-Ni-N}(2)^{\text{i}}$ and $\text{N}(1)\text{-Ni-N}(2)^{\text{ii}}$ angles are $92.3(3)$ and $172.2(3)^\circ$, respectively. The average Ni-N bond distance of $2.113(5)$ Å is similar to that observed for the octahedral nickel(II) complexes with diamine derivatives.³⁻⁶) The water molecule Ow is hydrogen-bonded to one of the amino nitrogen atoms $\text{N}(2)$ of the cation ($\text{Ow}\cdots\text{N}(2)$ $3.18(1)$ Å, 165.6°). Furthermore, the water molecule forms the hydrogen bonding involving the other water molecules (Fig. 2 and Table 4).

The electronic absorption spectrum of **1** measured in water shows maximum absorptions at 546 ($\epsilon = 5.5 \text{ M}^{-1}\text{cm}^{-1}$) and 345 nm ($\epsilon = 10.3 \text{ M}^{-1}\text{cm}^{-1}$). The spectrum is comparable with that of the ethylenediamine

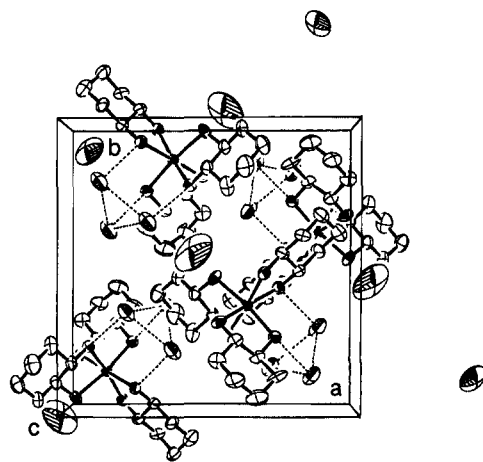


Fig. 2. Packing diagram of **1**, showing the hydrogen bonds as dotted lines.

Table 4. Hydrogen Bonding Parameters (Å, °) for **1**

D-H...A	D-H (Å)	H...A (Å)	D...A (Å)	D-H...A (°)
N(2)-H(8A)...Ow	0.90	2.30	3.18(1)	165.6
Ow...Ow ⁱ	0	0	2.94(1)	0
Ow...Ow ⁱⁱ	0	0	2.94(1)	0

Symmetry codes: (i) z, x, y; (ii) y, z, x.

complex $[\text{Ni}(\text{en})_3]^{2+}$ [540 nm ($\epsilon = 6.9 \text{ M}^{-1}\text{cm}^{-1}$) and 333 nm ($\epsilon = 9.0 \text{ M}^{-1}\text{cm}^{-1}$)], supporting the proposal that the nickel ion is in an octahedral environment. The effective magnetic moment (μ_{eff}) of **1** in the solid state is $2.86 \mu_{\text{B}}$ at room temperature, which is consistent with a high-spin d^8 electron configuration in an octahedral geometry.

4. Supplementary Material

Atomic coordinates, bond lengths and angles, and thermal parameters are available from author K.-Y. Choi on request.

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