

Crystal Structure of Three-Dimensional Nickel(II) Tetraaza Macrocyclic Complex Linked by Hydrogen-Bonds

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水素 결합에 의한 三次元の Nickel(II) Tetraaza 巨大고리 錯物の 結晶構造

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Abstract

The complex $[\text{Ni}(\text{L})](\text{BDC}) \cdot 4\text{H}_2\text{O}$ (**1**) (L = 3,14-dimethyl-2,6,13,17-tetraazatricyclo[16, 4, O^{1,18}, O^{7,12}]docosane; BDC = 1,3-benzenedicarboxylate) has been synthesized and characterized by X-ray crystallography. Compound **1** crystallizes in the orthorhombic space group *Pcnb*, with $a = 8.764(2)$ Å, $b = 17.687(2)$ Å, $c = 19.475(1)$ Å, $V = 3018.7(8)$ Å³, $Z = 4$, $R_1(wR_2)$ for 2148 observed reflections of $[I > 2\sigma(I)]$ was 0.0822 (0.2236). Compound **1** is interconnected to give a three-dimensional network through weak hydrogen-bonding interactions.

요 약

$[\text{Ni}(\text{L})](\text{BDC}) \cdot 4\text{H}_2\text{O}$ (**1**) (L = 3,14-dimethyl-2,6,13,17-tetraazatricyclo[16,4,O^{1,18},O^{7,12}]docosane; BDC = 1,3-benzenedicarboxylate) 錯物を合成하고 構造를 糾明하였다. 이 錯物は 四方晶系, 空間群 *Pcnb*, $a = 8.764(2)$ Å, $b = 17.687(2)$ Å, $c = 19.475(1)$ Å, $V = 3018.7(8)$ Å³, $Z = 4$ 로 決定化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 2148개의 回折班點에 대하여 0.0822 및 0.2236이었다. 化合物 **1**은 水素結合들로 연결된 三次元の 그물 構造를 갖는다.

1. Introduction

Self-assembly of infinite metal complexes with specific network topologies has been of great interest due to their potentials for supramolecular chemistry.¹⁻⁴⁾ Especially, the assembly of organic molecules and metal ion building block may yield multidimensional networks containing channels or cavities of various sizes and shapes.⁵⁻⁸⁾ However, macrocyclic complexes have seldom been used in the construction of supramolecular networks although they could be used as multifunctional building blocks.⁹⁾ In the

present work, we report on the three-dimensional complex $[\text{Ni}(\text{L})](\text{BDC}) \cdot 4\text{H}_2\text{O}$ (**1**) (L = 3,14-dimethyl-2,6,13,17-tetraazatricyclo[16,4,O^{1,18},O^{7,12}]docosane; BDC = 1,3-benzenedicarboxylate), whose solid-state structure spreads out via hydrogen-bonds of Ni(II) macrocyclic complex and BDC ligand.

2. Experimental

Materials and Physical Measurements. All chemicals and solvents used in the synthesis were of reagent-grade and used without further purification.

The macrocycle L and $[\text{Ni}(\text{L})]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ were prepared according to the literature method.^{10,11} IR spectra were recorded with a Perkin-Elmer Paragon 1000 FT-IR spectrophotometer. High-resolution fast-atom bombardment mass spectrometry (FAB mass) was performed with a Jeol JMS-HA 100A/100A instrument. Elemental analyses were performed by the Korea Research Institute of Chemical Technology, Taejeon, Korea.

Synthesis of $[\text{Ni}(\text{L})](\text{BDC}) \cdot 4\text{H}_2\text{O}$ (1). To a methanol solution (20 ml) of $[\text{Ni}(\text{L})]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ (251 mg, 0.5 mmol) was added an aqueous solution (5 ml) of Na_2BDC (105 mg, 0.5 mmol). The mixture was refluxed for 1 h and then cooled to room temperature. The solution was filtered and left at room temperature until the dark yellow crystals formed. These were filtered out, and one of them was subjected to X-ray analysis. Found: C, 53.35; H, 8.19; N, 8.75%. Calc. for $\text{C}_{28}\text{H}_{52}\text{N}_4\text{NiO}_8$: C, 53.26; H, 8.30; N, 8.87%. IR (KBr, cm^{-1}): 3176 (NH), 1612 (COO). FAB mass

(CH_2Cl_2 , m/z): 631 (M^+).

X-ray Crystallography. A dark yellow crystal was mounted on an Enraf-Nonius CAD4 diffractometer. Intensities were collected with a graphite-monochromated Mo $K\alpha$ radiation, by the $\omega/2\theta$ scan technique at 293 K. A total of 2148 independent reflections were measured in the range $2 < \theta < 25^\circ$. Three standard reflections were checked every 5 h as orientation and intensity controls; intensity decay, 3.0%, was observed. Intensity data were corrected for Lorentz and polarization effects. An empirical absorption correction based on ϕ -scan was applied. The crystallographic data, conditions used for the intensity collection, and some features of the structure refinement are listed in Table 1. The structure was solved by direct methods¹² and the least-squares refinements of the structure were performed by the program SHELXL97.¹³ All atoms except for all hydrogen atoms were refined anisotropically. Positional parameters of all hydrogen atoms were cal-

Table 1. Crystal Data and Structure Refinement for 1

Empirical formula	$\text{C}_{28}\text{H}_{52}\text{N}_4\text{NiO}_8$
Formula weight	631.45
Temperature	293(2) K
Crystal system	Orthorhombic,
Space group	$Pcnb$
Unit cell dimensions	$a = 8.764(2) \text{ \AA}$ $b = 17.687(2) \text{ \AA}$ $c = 19.475(1) \text{ \AA}$
Volume	$3018.7(8) \text{ \AA}^3$
Z	4
Density (calculated)	1.389 Mg/m^3
Absorption coefficient	0.697 mm^{-1}
Diffractometer	Enraf-Nonius CAD4
Radiation/wavelength	Mo $K\alpha$ (graphite monochrom.)/ 0.71069 \AA
$F(000)$	1360
Crystal size	$0.40 \times 0.26 \times 0.10 \text{ mm}^3$
θ range for data collection	2.09 to 24.97
Index ranges	$-4 \leq h \leq 10, 0 \leq k \leq 20, 0 \leq l \leq 23$
Reflection collected/unique	2150/2148 ($R_{\text{int}} = 0.0142$)
Absorption correction (ϕ -scan)	$T_{\text{max}} = 0.9958$ and $T_{\text{min}} = 0.9192$
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2148/0/189
Goodness-of-fit on F^2	0.886
Final R indices [$I > 2\sigma(I)$]	$R_1^a = 0.0822, wR_2^b = 0.2236$
R indices (all data)	$R_1^a = 0.1496, wR_2^b = 0.2630$
Largest diff. peak and hole	0.640 and -1.048 e\AA^{-3}

$$^a R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

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

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 1

	x	y	z	$U(\text{eq})^d$
Ni	0	0	0	40(1)
N(1)	1437(8)	-679(4)	419(3)	15(2)
N(2)	700(8)	764(4)	697(3)	16(2)
C(1)	2343(10)	-291(4)	943(4)	14(2)
C(2)	3009(12)	-798(6)	1482(5)	37(3)
C(3)	4007(11)	-394(6)	1990(5)	33(3)
C(4)	3136(13)	290(6)	2307(5)	41(3)
C(5)	2395(13)	793(5)	1741(5)	36(3)
C(6)	1448(11)	325(5)	1238(4)	21(2)
C(7)	-324(11)	1353(5)	970(4)	31(3)
C(8)	-1336(11)	1705(5)	439(4)	22(2)
C(9)	2395(11)	-1146(5)	-68(5)	27(2)
C(10)	3186(12)	-611(6)	-572(5)	45(3)
C(11)	-2704(12)	-1706(5)	586(5)	27(2)
C(12)	-3899(10)	-2142(5)	999(4)	18(2)
C(13)	-3875(10)	-2139(5)	1718(4)	19(2)
C(14)	-5000	-2500	2064(6)	25(3)
C(15)	-5000	-2500	664(5)	10(2)
O(1)	-1541(7)	-1532(4)	878(3)	34(2)
O(2)	-3052(7)	-1548(3)	-32(3)	27(2)
Ow(1)	-5000	-2500	-862(4)	30(2)
Ow(2)	0	-2500	1794(4)	43(3)
Ow(3)	-6704(10)	-1952(6)	-2035(4)	81(3)

^d $U(\text{eq})$ is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

culated geometrically and constrained to ride on their attached atoms with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$ and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$. Final atomic coordinates and equivalent isotropic displacement parameters are given in Table 2.

3. Results and Discussion

An ORTEP drawing of $[\text{Ni}(\text{L})](\text{BDC}) \cdot 4\text{H}_2\text{O}$ (1)

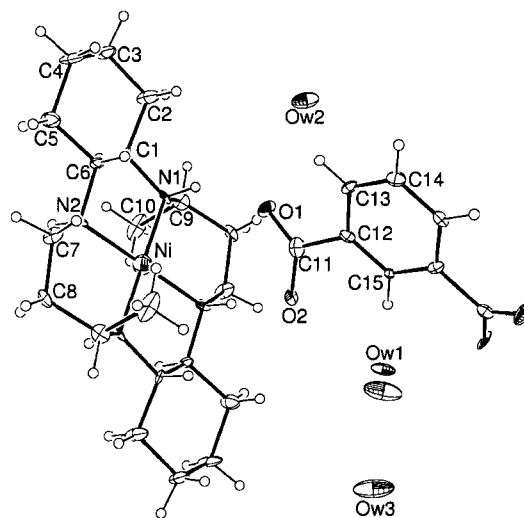


Fig. 1. An ORTEP drawing of 1 with the atomic numbering scheme. Thermal ellipsoids are drawn at 30% probability.

with the atomic numbering scheme is shown in Fig. 1. Selected bond distances and angles are listed in Table 3. The molecular structure consists of a $[\text{Ni}(\text{L})]^{2+}$ cation, a BDC^{2-} anion, and four water molecules. The coordination environment around the nickel(II) ion shows a slightly distorted square-plane with four secondary amines of the macrocyclic ligand. The carboxylate oxygen atoms O(1) and O(2) of the BDC ligand are located 3.477(5) and 3.828(4) \AA from the nickel ion. An inversion center of the complex exists on the central nickel(II) ion. The metal atom and the four nitrogen atoms (N(1), N(2), N(1)', N(2)') are exactly in a plane. The ligand skeleton of the complex cation adopts the most stable *trans*-III

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

Ni-N(1)	1.923(6)	Ni-N(2)	2.011(7)
N(1)-C(1)	1.463(10)	N(1)-C(9)	1.513(11)
N(2)-C(6)	1.465(10)	N(2)-C(7)	1.474(11)
C(11)-C(12)	1.529(13)	C(12)-C(13)	1.399(11)
C(12)-C(15)	1.326(10)	C(13)-C(14)	1.354(10)
C(11)-O(1)	1.207(12)	C(11)-O(2)	1.272(11)
N(1)-Ni-N(2)	86.2(3)	N(1)-Ni-N(2) ⁱ	93.8(3)
N(1)-Ni-N(1) ⁱ	180.0(5)	N(2)-Ni-N(2) ⁱ	180.0(4)
O(1)-C(11)-O(2)	126.2(9)	O(1)-C(11)-C(12)	117.3(9)
O(2)-C(11)-C(12)	116.4(9)	C(11)-C(12)-C(13)	121.0(8)
C(11)-C(12)-C(15)	118.7(8)	C(13)-C(12)-C(15)	120.3(8)

Symmetry code: (i) $-x, -y, -z$.

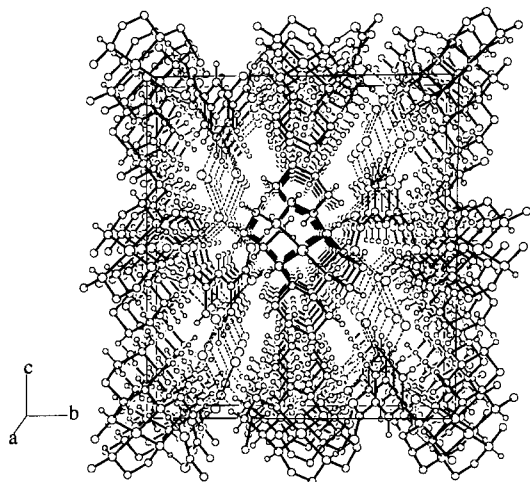


Fig. 2. Packing diagram of 1, showing the hydrogen bonds as dotted lines.

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

D-H...A	D-H (Å)	H...A (Å)	D...A (Å)	D-H...A (°)
N(1)-H(1)...O(1)	0.91	2.33	3.144(9)	148.5
N(2)-H(2)...O(2) ⁱ	0.91	1.89	2.801(9)	178.8
O(1)...Ow(2)	0	0	2.818(9)	0
O(1) ⁱⁱ ...Ow(2)	0	0	2.818(9)	0
O(2)...Ow(1)	0	0	2.892(7)	0
O(2) ⁱⁱⁱ ...Ow(1)	0	0	2.892(7)	0
Ow(1)...Ow(3) ^{iv}	0	0	2.896(10)	0

Symmetry codes: (i) $-x, -y, -z$; (ii) $-x, -y-1/2, z$; (iii) $-x-1, -y-1/2, z$; (iv) $-x-1/2, y, z-1/2$.

conformation. The average Ni-N bond distance of 1.967(5) Å is very similar to those observed in other nickel(II) saturated tetraaza macrocyclic complexes, and indicates a low-spin NiN₄ geometry in this complex.¹⁴⁻¹⁶ As expected for tetraaza macrocyclic complexes, the N-Ni-N bite angles of the six-membered chelate rings (93.8(3)°) are larger than those of the five-membered chelate rings (86.2(3)°). Interestingly, the secondary amines of the macrocycle form hydrogen-bonds with carboxylate oxygens of the BDC ligand (N(1)··O(1) 3.144(9) Å, 148.5°; N(2)··O(2)ⁱ 2.801(9) Å, 178.8°; symmetry code (i): $-x, -y, -z$). Furthermore, the water molecules Ow(1) and Ow(2) are linked to the uncoordinated BDC oxygens and the remaining water molecule Ow(3) (Ow(1)··O(2) 2.892(7) Å; Ow(1)··O(2)ⁱⁱ 2.892(7) Å; Ow(2)··O(1)

2.818(9) Å; Ow(2)··O(1)ⁱⁱⁱ 2.818(9) Å; Ow(1)··Ow(3)^{iv} 2.896(10) Å; symmetry codes (ii): $-x, -1, -y-1/2, z$ (iii): $-x, -1/2-y, z$ (iv): $-1/2-x, y, -1/2+z$). This interaction, as shown in Fig. 2 and Table 4, gives rise to a three-dimensional hydrogen-bonded network.

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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