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# Preparation and Crystal Structure of $[Ni(L^2)(H_2O)]Cl \cdot H_2O$ ($L^2$ : 3,14-dimethyl-2,6,13,17-tetraazatricyclo[14,4,$0^{1.18}$,$0^{7.12}$] docosane-N-acetic acid)

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## Abstract

The complex $[Ni(L^2)(H_2O)]Cl \cdot H_2O$ (**1**) ($L^2$=3,14-dimethyl-2,6,13,17-tetraazatricyclo [14,4,$0^{1.18}$,$0^{7.12}$] docosane-N-acetic acid) has been synthesized and characterized by X-ray crystallography. **1** crystallizes in the triclinic system, space group $P\bar{1}$, with a=11.274(1), b=13.851(1), c=17.519(6) Å, α=90.24(2), β=101.10(2), γ=92.11(1)° V=2682.5(11) $Å^3$, Z=4, R1=0.042 and $wR_2$=0.111 for 9432 observed reflections with [I > 2σ(I)]. The central nickel(II) ion is six-coordinated octahedral geometry with bonds to the four amine nitrogen atoms and the carboxylic oxygen atom of the macrocyclic ligand and to the water molecule occupying a position *trans* to the pendant arm.

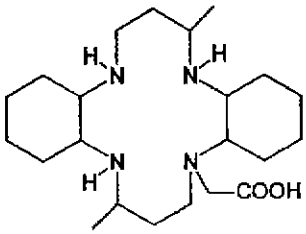
## 要 約

$[Ni(L^2)(H_2O)]Cl \cdot H_2O$ (**1**) ($L^2$=3,14-dimethyl-2,6,13,17-tetraazatricyclo[14,4,$0^{1.18}$,$0^{7.12}$] docosane-N-acetic acid) 錯物을 合成하고 構造를 糾明하였다. 이 錯物은 三斜晶系, 空間群 $P\bar{1}$, a=11.274(1), b=13.851(1), c=17.519(6) Å, α=90.24(2), β=101.10(2), γ= 92.11(1)° V=2682.5(11) $Å^3$, Z=4로 決定化되었다. 이 錯物의 構造는 最小自乘法으로 精密化하였으며, 最終 信賴度 R1(wR2) 값은 9432個의 回折班點에 대하여 0.043 및 0.113이었다. 中心 nickel(II) 이온은 거대고리 리간드로 부터 4個의 아민 窒素 原子와 카르복실 酸素 및 置換基에 대하여 *trans*에 위치한 물分子로 結合된 六配位 八面體 構造를 갖는다.

## 1. Introduction

The synthesis of transition metal complexes of N-functionalized tetraaz macrocycles is of growing importance to various field of coordination chemistry because of their chemical properties and structures.[1] Recently, the fully N-pyridylmethylated cyclam (1,4,8,11-tetraazacyclotetradecane) complexes have been synthesized.[2-4] It has been proved that the complexes have a dinuclear structure with the chair coordination mode of the ligand. However, the four N-hydroxyethylated cyclam forms 1:1 metal complexes incorporating a metal ion in the ring centre to form an essentially square-planar coordination, or distorted octahedral coordination by further donating two of the pendant group.[5,6] On the other hand, partially N-functionalized tetraaza macrocycles and their complexes have been studied less extensively than fully

N-functionalized analogues.[7,8] This may be due to the fact that the synthesis of partially N-substituted macrocycles is complicated and requires several steps.[9] In this study, we report the synthesis and crystal structure of a nickel(II) complex of 3,14-dimethyl-2,6,13,17-tetraazatricyclo[14,4,0$^{1,18}$,0$^{7,12}$]docosane-N-acetic acid ($L^2$).




$L^2$

## 2. Experimental Section

**Materials and Physical Measurements.** The macrocycle 3,14-dimethyl-2,6,13,17-tetraazatricyclo[16,4,0$^{1,18}$,0$^{7,12}$]docosane ($L^1$) and 3,14-dimethyl-2,6,13,17-tetraazatricyclo[14,4,0$^{1,18}$,0$^{7,12}$]docosane-N-acetic acid ($L^2$) were synthesized by the literature methods.[7,10] All chemicals used were of analytical grade and were used without further purification. IR spectra were recorded as KBr pellets on a Perkin-Elmer Paragon 1000 FT-IR spectrophotometer, electronic spectra with a Jasco Uvidec-610 spectrophotometer. FAB mass spectra were performed by using a Jeol JMS-HA 110A/110A instrument. Elemental analyses were carried out by the Korea Basic Science Institute, Taejon, Korea. Magnetic susceptibilities were mea-sured with a Johnson Matthey MK-II magnetic susceptibility balance. The diamagnetic corrections were calculated from Pascal's constants.

**Synthesis of $[Ni(L^2)(H_2O)]Cl \cdot H_2O$ (1).** $L^2$ (197 mg, 0.5 mmol) and $NiCl_2 \cdot 6H_2O$ (119 mg, 0.5 mmol) were dissolved in 20 ml of water, and the pH was adjusted to 5.0 with NaOH (2 M). The mixture was heated to reflux for 2 h and then concentrated to 10 ml under vacuum. The solution was filtered and left at room temperature until the pink crystals formed. These were collected and air-dried to give 191 mg (73%) of product. Found: C, 50.38, H, 8.57; N, 10.82. Calc. for $C_{22}H_{45}ClN_4NiO_4$: C, 50.45; H, 8.66; N, 10.70%. IR (KBr, cm$^{-1}$): 3178 (νNH) and 1675 (νCOOH). Electronic spectra (water): $\lambda_{max}$ nm (ε, M$^{-1}$ cm$^{-1}$): 528 (6.8), 340 (17). $\mu_{eff}$: 2.82 $\mu_B$ at 25°C. FAB mass ($CH_2Cl_2$, m/z): 523 $(M)^+$.

**X-ray Crystallography.** The crystal was mounted on an Enraf-Nonius CAD4 diffractometer. X-ray data were collected using graphite-monochromated Mo-Kα radiation (λ=0.71073 Å) at room temperature. Accurate cell parameters and an orientation matrix were determined by least-squares fit of 25 reflections. An asymmetric unit of intensity data were collected in the ω-2θ scan mode. The intensity data were corrected for Lorentz and polarization effects and empirical absorption corrections were also applied. The crystallographic data, conditions used for the intensity

**Table 1. Crystal Data and Structure Refinement for $[Ni(L^2)(H_2O)]Cl \cdot H_2O$ (1)**

| | |
|---|---|
| Empirical formula | $C_{22}H_{45}ClN_4NiO_4$ |
| Formula weight | 523.78 |
| Temperature | 293(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Triclinic, |
| Space group | $P\bar{1}$ |
| Unit cell dimensions | a=11.274(1)Å α=90.24(2)° |
| | b=13.851(1)Å β=101.10(2)° |
| | c=17.519(6)Å γ=92.11(1)° |
| Volume | 2682.5(11) Å$^3$ |
| Z | 4 |
| Density (calculated) | 1.297 Mg m$^{-3}$ |
| Absorption coefficient | 0.856 mm$^{-1}$ |
| F(000) | 1128 |
| Crystal size | 0.38×0.33×0.23 mm |
| θ range for data collection | 2.31 to 24.97° |
| Index ranges | $-13 \le h \le 13$, $-16 \le k \le 16$, $0 \le l \le 20$ |
| Reflections collected/unique | 9432/9432 ($R_{int}$=0.0000) |
| Absorption correction | semi-empirical from psi-scan |
| $T_{max}$, $T_{min}$ | 0.8083, 0.7274 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data/restraints/parameters | 9432/11/578 |
| Goodness-of-fit on $F^2$ | 0.908 |
| Final R indices [I>2σ(I)] | $R1^a$=0.042, $wR_2^b$=0.111 |
| R indices (all data) | $R1^a$=0.065, $wR_2^b$=0.116 |
| Extinction coefficient | 0.030(18) |
| Largest diff. peak and hole | 0.629 and −0.571 eÅ$^{-3}$ |

$^a R1=\Sigma||F_o| - |F_c|| / \Sigma|F_o|$
$^b wR_2=[\Sigma[w(F_o^2-F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}$.

**Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for $[Ni(L^2)(H_2O)]Cl \cdot H_2O$ (1)**

| | x | y | z | U(eq) |
|---|---|---|---|---|
| Ni(1) | 9533(16) | 8492(12) | 2345(9) | 56(6) |
| Ni(2) | 9647(16) | 13511(12) | 2532(10) | 57(6) |
| Cl(1) | 11690(3) | 6408(19) | 3973(14) | 38(8) |
| Cl(2) | 11900(3) | 11407(18) | 1499(14) | 33(7) |
| N(1) | 8830(10) | 8460(6) | 1170(6) | 60(3) |
| N(2) | 7840(8) | 7960(7) | 2440(5) | 50(3) |
| N(3) | 10180(10) | 8640(7) | 3510(6) | 70(3) |
| N(4) | 11260(9) | 8970(7) | 2270(6) | 60(3) |
| N(5) | 8890(10) | 13450(7) | 3510(5) | 50(3) |
| N(6) | 7950(9) | 13010(7) | 1950(5) | 50(3) |
| N(7) | 10400(9) | 13670(7) | 1570(5) | 50(3) |
| N(8) | 11380(9) | 14030(7) | 3110(5) | 60(3) |
| O(1) | 8280(8) | 10980(7) | 1380(6) | 80(3) |
| O(2) | 9110(8) | 9920(6) | 2270(5) | 60(2) |
| O(3) | 8030(10) | 15940(7) | 3040(6) | 100(4) |
| O(4) | 9140(9) | 14930(6) | 2470(5) | 70(3) |
| C(1) | 11270(12) | 9300(9) | 3620(7) | 50(4) |
| C(2) | 11970(13) | 9310(11) | 4420(10) | 100(6) |
| C(3) | 13080(14) | 9980(10) | 4480(8) | 80(5) |
| C(4) | 13890(13) | 9680(10) | 3970(7) | 70(4) |
| C(5) | 13160(12) | 9620(10) | 3100(8) | 70(4) |
| C(6) | 11970(12) | 9000(9) | 3040(7) | 50(4) |
| C(7) | 11850(11) | 8680(9) | 1610(6) | 60(4) |
| C(8) | 12350(12) | 7700(10) | 1690(8) | 80(4) |
| C(9) | 10930(9) | 8780(8) | 860(6) | 60(4) |
| C(10) | 9840(10) | 8090(10) | 750(7) | 70(4) |
| C(11) | 8400(12) | 9420(9) | 940(7) | 60(4) |
| C(12) | 8610(11) | 10120(9) | 1570(8) | 50(3) |
| C(13) | 7800(10) | 7720(9) | 1070(7) | 50(3) |
| C(14) | 7100(14) | 7620(11) | 260(8) | 80(5) |
| C(15) | 6060(13) | 6840(10) | 180(9) | 80(5) |
| C(16) | 5270(13) | 7070(12) | 790(8) | 90(5) |
| C(17) | 5990(14) | 7180(11) | 1650(10) | 100(6) |
| C(18) | 7040(10) | 7920(8) | 1660(5) | 50(4) |
| C(19) | 7290(12) | 8280(11) | 3090(7) | 90(5) |
| C(20) | 6760(12) | 9300(10) | 2950(8) | 80(5) |
| C(21) | 8170(11) | 8260(9) | 3850(6) | 50(4) |
| C(22) | 9360(14) | 8950(12) | 4000(10) | 100(6) |
| C(23) | 12160(10) | 13970(9) | 2520(7) | 50(3) |
| C(24) | 13290(14) | 14660(10) | 2790(8) | 80(5) |
| C(25) | 14110(14) | 14680(12) | 2160(9) | 90(5) |
| C(26) | 13350(14) | 14980(10) | 1390(10) | 80(5) |
| C(27) | 12260(14) | 14400(11) | 1150(7) | 80(5) |
| C(28) | 11440(11) | 14330(9) | 1770(7) | 60(4) |
| C(29) | 9510(12) | 14000(10) | 830(8) | 70(4) |
| C(30) | 8430(13) | 13280(11) | 710(8) | 90(5) |
| C(31) | 7450(12) | 13340(9) | 1190(7) | 70(4) |
| C(32) | 6830(13) | 14300(9) | 1150(8) | 90(5) |
| C(33) | 7080(12) | 12960(11) | 2480(7) | 70(4) |
| C(34) | 6090(14) | 12220(11) | 2240(7) | 90(5) |
| C(35) | 5330(13) | 12080(12) | 2830(9) | 90(5) |
| C(36) | 6040(13) | 11890(10) | 3590(9) | 90(5) |
| C(37) | 7030(12) | 12640(10) | 3890(8) | 80(5) |
| C(38) | 7820(12) | 12680(10) | 3290(7) | 60(4) |
| C(39) | 8410(13) | 14420(9) | 3690(7) | 70(4) |
| C(40) | 8460(14) | 15100(10) | 3040(9) | 70(4) |
| C(41) | 9760(12) | 13160(9) | 4220(7) | 60(4) |
| C(42) | 10860(12) | 13780(9) | 4400(7) | 60(4) |
| C(43) | 11850(15) | 13670(12) | 3910(8) | 90(6) |
| C(44) | 12280(13) | 12630(10) | 3900(8) | 80(5) |
| OW1 | 10090(7) | 6970(6) | 2390(5) | 70(3) |
| OW2 | 10190(8) | 11950(6) | 2640(4) | 60(3) |
| OW3 | 6150(9) | 11010(8) | 300(6) | 100(4) |
| OW4 | 4290(8) | 10150(6) | 1020(4) | 60(3) |

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor

data collection, and some features of the structure refinement are listed in Table 1. The structure was solved direct methods[11] and refined[12] on $F^2$ by full-matrix least squares with anisotropic displacement parameters for the non-hydrogen atoms. All hydrogen atoms except for water hydrogen atoms were placed in calculated positions with isotropic displacement parameters. Final atomic coordinates and equivalent isotropic displacement parameters are given in Table 2.

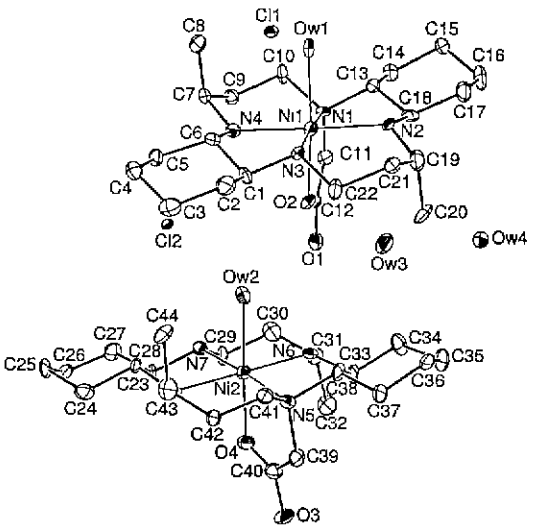



**Fig. 1. An ORTEP drawing of $[Ni(L^2)(H_2O)]Cl \cdot H_2O$ (1) with the atomic labelling scheme.**

## 3. Results and Discussion

The ligand skeleton of the complex **1** takes the most stable *trans*-III configuration with chair form six-membered and two gauche five-membered chelate rings. The complex also shows that one carboxylate group is attached to the less sterically hindered nitrogen atom of the macrocyclic ligand. The N-Ni-N angles of the six-membered chelate rings are larger than those of the five-membered chelate ring. An ORTEP drawing of $[Ni(L^2)(H_2O)]Cl \cdot H_2O$ (**1**) with the atomic labelling scheme is shown in Fig. 1. Selected bond lengths and angles of **1** are listed in Table 3. There are two crystallographically independent $[Ni(L^2)(H_2O)]Cl \cdot H_2O$ complexes, in each of which consists of a $[Ni(L^2)(H_2O)]^+$ cation, a chloride anion and a water molecule. The central nickel(II) ion is six-coordinated octahedral geometry with bonds to the four amine nitrogen atoms and the carboxylic oxygen atom of the macrocyclic ligand and to the water molecule occupying a position trans to the pendant arm. Each nickel(II) ion is slightly deviated from the $N_4$ basal planes by 0.025(2) and 0.033(2) Å, shifted toward axially coordinated oxygen atoms. The two axial Ni-O(w) distances of 2.221(4) and 2.270(3) Å are longer than the average distance of Ni(1)-$N_4$ and Ni(2)-$N_4$ planes [2.051(2) and 2.074(2) Å], giving an axially elongated octahedral geometry. Furthermore, the axial Ni(1)-O(w1) and Ni(2)-O(w2) bonds are bent slightly off the perpendicular to the $NiN_4$ plane by 0.1-5.0° and 0.7-2.8°, respectively. It is interested that the average Ni-O(w) distance of 2.246(3) Å is much longer than that of Ni-O (carboxylate group. 2.066(3) Å). This may be due to the fact that $CH_2COO^-$ group has a much stronger coordination ability than $H_2O$. The two Ni-

**Table 3. Selected Bond Lengths (Å) and Angles (°) for $[Ni(L^2)(H_2O)]Cl \cdot H_2O$ (1)**

| | | | |
|---|---|---|---|
| Ni(1)-N(1) | 2.057(4) | Ni(2)-N(5) | 2.062(4) |
| Ni(1)-N(2) | 2.054(4) | Ni(2)-N(6) | 2.080(4) |
| Ni(1)-N(3) | 2.031(5) | Ni(2)-N(7) | 2.032(4) |
| Ni(1)-N(4) | 2.062(4) | Ni(2)-N(8) | 2.121(4) |
| Ni(1)-O(2) | 2.055(3) | Ni(2)-O(4) | 2.076(4) |
| Ni(1)-O(w1) | 2.221(4) | Ni(2)-O(w2) | 2.270(3) |
| N(1)-C(11) | 1.458(5) | N(5)-C(39) | 1.530(6) |
| C(11)-C(12) | 1.452(6) | C(39)-C(40) | 1.548(6) |
| C(12)-O(1) | 1.268(5) | C(40)-O(3) | 1.265(2) |
| C(12)-O(2) | 1.271(5) | C(40)-O(4) | 1.300(6) |
| | | | |
| N(1)-Ni(1)-N(2) | 83.9(2) | N(5)-Ni(2)-N(6) | 84.8(2) |
| N(1)-Ni(1)-N(3) | 175.1(2) | N(5)-Ni(2)-N(7) | 176.3(2) |
| N(1)-Ni(1)-N(4) | 97.3(2) | N(5)-Ni(2)-N(8) | 95.8(2) |
| N(2)-Ni(1)-N(3) | 96.2(2) | N(6)-Ni(2)-N(7) | 96.5(2) |
| N(2)-Ni(1)-N(4) | 177.6(2) | N(6)-Ni(2)-N(8) | 179.3(2) |
| N(3)-Ni(1)-N(4) | 82.8(2) | N(7)-Ni(2)-N(8) | 82.9(2) |
| N(1)-Ni(1)-O(2) | 84.1(1) | N(5)-Ni(2)-O(4) | 84.4(2) |
| N(2)-Ni(1)-O(2) | 96.4(1) | N(6)-Ni(2)-O(4) | 92.2(2) |
| N(3)-Ni(1)-O(2) | 91.1(2) | N(7)-Ni(2)-O(4) | 92.1(2) |
| N(4)-Ni(1)-O(2) | 85.8(2) | N(8)-Ni(2)-O(4) | 87.7(2) |
| N(1)-Ni(1)-O(w1) | 95.0(1) | N(5)-Ni(2)-O(w2) | 92.8(1) |
| N(2)-Ni(1)-O(w1) | 86.9(1) | N(6)-Ni(2)-O(w2) | 87.7(1) |
| N(3)-Ni(1)-O(w1) | 89.9(2) | N(7)-Ni(2)-O(w2) | 90.7(1) |
| N(4)-Ni(1)-O(w1) | 90.9(1) | N(8)-Ni(2)-O(w2) | 92.4(1) |
| O(2)-Ni(1)-O(w1) | 176.5(1) | O(4)-Ni(2)-O(w2) | 177.2(1) |
| Ni(1)-O(2)-C(12) | 110.1(3) | Ni(2)-O(4)-C(40) | 111.2(4) |
| N(1)-C(11)-C(12) | 113.6(4) | N(5)-C(39)-C(40) | 108.2(4) |
| O(1)-C(12)-O(2) | 121.9(5) | O(3)-C(40)-O(4) | 121.7(5) |
| O(1)-C(12)-C(11) | 114.4(5) | O(3)-C(40)-C(39) | 113.8(4) |
| O(2)-C(12)-C(11) | 123.6(5) | O(4)-C(40)-C(39) | 124.4(5) |

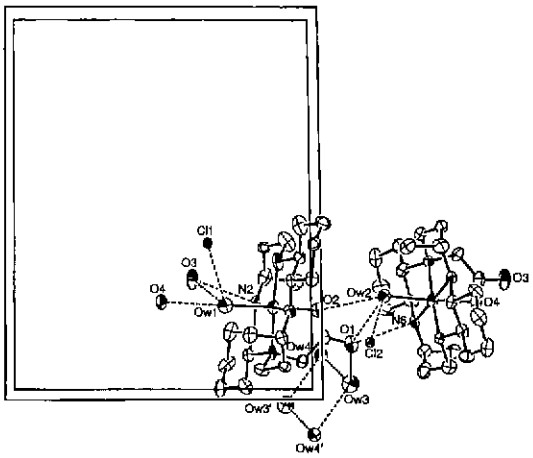



**Fig. 2. Packing arrangement of molecules in the unit cell. The c-axis is vertical and b-axishorizontal.**

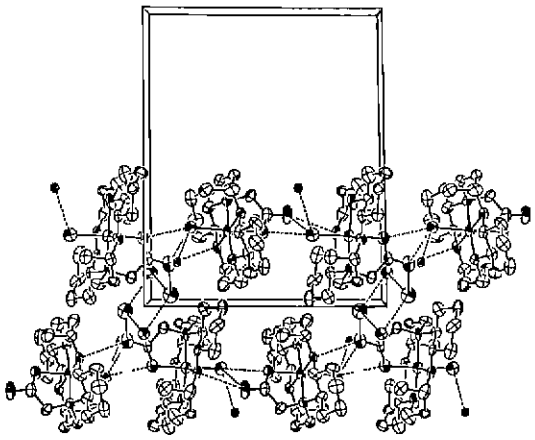


**Fig. 3. Hydrogen bonding scheme showing an infinite chain. The c-axis is vertical and b-axis horizontal.**

O-C angles related to the carboxylate groups are Ni(1)-O(2)-C(12) [110.1 (3)°] and Ni(2)-O(4)-C(40) [111.2(4)°], respectively.

The hydrogen bonds are shown in Figs 2 and 3, and the hydrogen bonding geometry is described in Table 4. As shown in Fig. 2, The O(1) and O(2) atoms of the pendant carboxylate group are hydrogen-bonded to O(w2). The O(w2) and O(1) atoms are also hydrogen-bonded to Cl(2) and N(6), respectively. Similarly O(w1) atom is triply hydrogen-bonded to O(3) and O(4) translated by one unit cell along b-axis and Cl(1) in an asymmetric unit. The N(2) atom as a donor is hydrogen-bonded to O(3)

**Table 4. Hydrogen Bonding Geometry (Å, °) for [Ni(L²)(H₂O)]Cl · H₂O (1)**

| D-H···A | D-H | H···A | D···A | D-H···A |
|---|---|---|---|---|
| N(6)-H(N6)···O(1) | 0.91 | 2.15 | 3.04(2) | 167 0(4) |
| N(2)-H(N2)···O(3)ⁱ | 0.91 | 2.11 | 3.00(2) | 164.5(5) |
| O(w3)···O(w4) | | | 2.87(2) | |
| O(w1)···Cl(1) | | | 3.12(1) | |
| O(w2)···Cl(2) | | | 3.14(1) | |
| O(w2)···O(2) | | | 3.03(2) | |
| O(w4)···O(w3)ⁱⁱ | | | 2 77(2) | |
| O(w2)···O(1) | | | 3 04(2) | |
| O(4)···O(w1)ⁱⁱⁱ | | | 2.99(2) | |
| O(3)···O(w1)ⁱⁱⁱ | | | 3.08(2) | |
| O(w3)···O(w4)ⁱⁱ | | | 2.77(2) | |

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

atom. Thus, two molecules in an asymmetric unit have similar hydrogen bonding features. This hydrogen bond scheme makes an infinite molecular chain along b-axis. The O(w3) atom of the non-coordinated water molecule is hydrogen-bonded to O(1) and O(w4) (1-x, 2-y, -z) with an inversion center. Therefore, the hydrogen bonds by O(w3) and O(w4) atoms interconnect two infinite molecular chains as shown in Fig. 3. The molecular chains are held together by van der Waals forces with the closest interatomic distance of H(41A)···Cl(1) (2-x, 2-y, 1-z): 2.931 Å.

IR spectra of the complex show ν(N-H) of the coordinated secondary amines and ν(COOH) of the pendant arm at 3178 and 1675 $cm^{-1}$, respectively. The magnetic moment of **1** in the solid state is 2.82 $\mu_B$ at 25°C, which is consistent with a $d^8$ electronic configuration in an octahedral geometry. Visible spectra of **1** in water solution show d-d bands at 340 and 528 nm, indicating that the nickel(II) ion is an octahedral environment.

## Supplementary Material

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

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