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#### 1D Hydrogen-bonded infinite chains from tetraaza macrocycle nickel(II)

complexes and ligands

In-Taek Lim<sup>a</sup>, Ki-Young Choi<sup>a</sup>\*

<sup>a</sup> Department of Chemistry Education, Kongju National University, Kongju 314-701, Korea

#### Abstract

The reaction of square planar complex  $[Ni(L2)]Cl_2 2H_2O$  (L2 = 3,14-diethyl-2,6,13,17tetraazatricyclo[14,4,0<sup>1.18</sup>,0<sup>7.12</sup>]docosane) with ligands KNCS and H<sub>2</sub>cpdc generates 1D hydrogen-bonded infinite chains  $[Ni(L2)(NCS)_2]$  (1) and  $[Ni(L2)(H-cpdc)_2]$  (2) (H<sub>2</sub>cpdc = cyclopropanedicarboxylic acid). These compounds have been characterized by X-ray crystallography, spectroscopic, cyclic voltammetry and thermogravimetry. The crystal structures of compounds 1 and 2 show that each nickel(II) centre has an elongated distorted octahedral geometry with the axial ligands. Electronic spectra and redox potentials of the complexes 1 and 2 exhibit a high-spin octahedral environment, which is reflected by the nature of the axial ligands. The TGA behaviors of two compounds 1 and 2 are also significantly affected by the

nature of the axial ligands.

<sup>\*</sup> Corresponding author. Tel.: +82-41-850-8284; fax: +82-41-850-8347.

E-mail address: kychoi@kongju.ac.kr (K.-Y. Choi).

#### 1. Introduction

The self-assembly of transition metal(II) macrocyclic complexes and aromatic polycarboxylate ligands have received considerable current interest owing to their interesting structures and potential applications [1-5]. Macrocyclic complexes with multi-connecting ligands such as aromatic polycarboxylate ligands have been proved to be good building blocks for the construction of coordination polymers [6-12]. Especially, hydrogen bonding is one of the key interactions for the process of molecular aggregation and recognition in nature, which creates novel structures of molecular assemblies [10]. For example, the compound  $[Ni(L1)(H_2O)_2]_{0.5}[Ni(L1)(WO_4)_2]_{0.5}$  (L1 = 3,14-dimethyl-2,6,13,17tetraazatricyclo[14,4,0<sup>1,18</sup>,0<sup>7,12</sup>]docosane) assembles in the solid state to form a 1D chain linked by intermolecular hydrogen bond [13]. The reaction of  $[Ni(L1)]Cl_2 \cdot 2H_2O$  [14] with 1,1cyclobutanedicarboxylic acid(H<sub>2</sub>cbdc) generates 1D hydrogen polymer  $[Ni(L1)(Hcbdc)_2]$  [15]. In addition, the compound  $[Ni(cyclam)(H_2O)_2]_3[(btc)_3]_2 \cdot 24H_2O$  (cyclam = 1,4,8,11-tetraazacyclotetradecane;

9Ù

### ED)

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btc = 1,3,5-benzenetricarboxylate) was assembled by  $[Ni(cyclam)(H_2O)_2]^{2+}$  and btc<sup>3-</sup> ligand in water via hydrogen bonds, which can be regarded as a molecular floral lace [2]. Recently, we reported the synthesis and crystal structures of [Ni(Me<sub>4</sub>cyclam)(H<sub>2</sub>O)<sub>2</sub>](tp)·4H<sub>2</sub>O (Me<sub>4</sub>cyclam = 2,5,9,12-tetramethyl-1,4,8,11 tetraazacyclotetradecane, tp = terephthalate)and  $[Ni(Me_4cyclam)(H_2O)_2](pdc)\cdot 4H_2O$  (pdc) = 2,5pyridinedicarboxylate) [16], in which the coordinated water molecules are linked to the carboxylate oxygen atoms of tp and pdc ligands to give a 1D polymer through the intermolecular hydrogen bonding interaction. The hydrogen bonding interactions, therefore, play a significant role in aligning the molecules and polymer stands in the crystalline solids.

To further investigate the coordination behavior, we have prepared and characterized 1D hydrogenbonded infinite chains  $[Ni(L2)(NCS)_2]$  (1)  $[Ni(L2)(H-cpdc)_2]$  (2) (L1 = 3,14-diethyl-2,6,13,17-diethyl-2,0,17-diethyl-2,0,17-diethyl-2,0,17-diethyl-2,0,17-diethyl-2,0,17-diethyl-2,0,17-dtetraazatricyclo[14,4,0<sup>1.18</sup>,0<sup>7.12</sup>]docosane;  $H_2$ cpdc = cyclopropanedicarboxylic acid), which are prepared

by the reaction of [Ni(L2)]Cl<sub>2</sub>·2H<sub>2</sub>O with the NaNCS and H<sub>2</sub>cpdc ligand.



#### 2.1. Materials and physical methods

All chemicals used in syntheses were of reagent grade and were used without further purification. The macrocycle 3,14-diethyl-2,6,13,17-tetraazatricyclo[14,4,0<sup>1.18</sup>,0<sup>7.12</sup>]docosane (L2) and [Ni(L2)]Cl<sub>2</sub>·2H<sub>2</sub>O were prepared according to the literature method [17]. IR spectra were recorded as KBr pellets on a Perkin-Elmer Paragon 1000 FT-IR spectrometer. The solution electronic and diffuse reflectance spectra were obtained on a Jasco V-550 spectrophotometer. Electrochemical measurements were accomplished with a three electrode potentiostat BAS-100BW system. A 3-mm Pt disk was used as the working electrode. The counter electrode was a coiled Pt wire and a Ag/AgCl electrode was used as a reference electrode. Cyclic voltametric data were obtained in DMSO solution using 0.1 M tetraethylammonium perchlorate (TEAP) as supporting electrolyte at 20.0±0.1 °C. The solution was degassed with high purity N<sub>2</sub> prior to carrying out the electrochemical measurements. DSC and TGA were performed under flowing nitrogen at a heating rate of 10°C mim<sup>-1</sup> using an SDT 2960 Thermogravimetric Analyzer. <sup>13</sup>C NMR spectra were recorded at room temperature on a Bruker AVANCE II 500 spectrometer. Elemental analyses (C, H, N) were performed on a Perkin-Elmer CHN-2400 analyzer.

#### 2.1. Synthesis of $[Ni(L2)(NCS)_2]$ (1)

To a methanol solution (20 ml) of [Ni(L2)]Cl<sub>2</sub>·2H<sub>2</sub>O (265 mg, 0.5 mmol) was added an aqueous

solution (10 ml) of KSCN (97 mg, 1.0 mmol) and the mixture was stirred for 30 min at room temperature.

The solution was filtered and left at room temperature until the purple crystals formed. The product was

recrystallized from a hot water/acetonitrile (1:1 v/v, 10 ml) mixture. Yield: 73%. Anal. Found: C, 53.51; H,

8.30; N, 15.47. Calc. for C<sub>22</sub>H<sub>44</sub>N<sub>6</sub>NiS<sub>2</sub>: C, 53.43; H, 8.22; N, 15.58 %. IR (KBr, cm<sup>-1</sup>): 3,240(m),

2,946(m), 2,066(s), 1,458(m), 1,381(m), 1,154(m), 1,097(m), 1,021(m), 1,005(m), 977(m), 942(m),

894(w), 871(w), 781(w).

2.2. Syntheses of [Ni(L2)(H-cpdc)<sub>2</sub>] (2)

To a methanol solution (20 ml) of  $[Ni(L2)]Cl_2 2H_2O$  (265 mg, 0.5 mmol) was added an aqueous solution (10 ml) of H<sub>2</sub>-cpdc (130 mg, 1.0 mmol). The mixture was heated to reflux for 30 mim and then cooled to room temperature. The solution was filtered and left at room temperature until purple crystals formed. The product was recrystallized from a hot water/acetonitrile (1:1 v/v, 10 ml) mixture. Yield: 68%. Anal. Found: C, 56.51; H, 8.07; N, 8.14. Calc. for  $C_{32}H_{54}N_4NiO_8$ : C, 56.40; H, 7.99; N, 8.22 %. IR (KBr, cm<sup>-1</sup>): 3,434(m), 3,261(m), 2,947(m), 1,655(s), 1,579(m), 1,476(w), 1,450(w), 1,398(m), 1,305(w), 1,273(w), 1,167(w), 1,104(m), 963(m), 898(w), 806(m), 748(w).

#### 2.3. X-ray crystal structure analysis

The single crystals of 1 and 2 were mounted on a Bruker Apex II CCD diffractometer. X-ray data were

collected using graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å) at room temperature. Accurate cell parameters and an orientation matrix were determined by the least-squares fit of 7482 (compound **1**) and 3031 (compound **2**) reflections. The intensity data were collected by the  $\pi$ - $\omega$  scan and corrected for Lorentz and polarization effects. An empirical absorption correction was applied with the (multiple scan) SADABS program [18]. The structure was solved by direct methods [19] and the least-squares refinement of the structure was performed by the SHELXL-97 program [20]. All atoms except for all hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions, allowing them to ride on their parent C or N atoms with  $U_{bo}(H) = 1.2U_{eq}(C \text{ or N})$ . Crystal parameters and details of the data collections and refinement are summarized in Table 1.

#### 3. Results and discussion

3.1. Crystal structures

#### 3.1.1. Description of the Structure

The macrcyclic ligand skeleton of the present compounds contains the most stable *trans*-III (R,R,S,S) configuration with two gauche five-membered and two chair six-membered chelate rings. The N-Ni-N angles of the six-membered chelate rings for the complexes are larger than those of the five-membered chelate rings. The ethyl group on a six-membered chelate ring is *anti* with respect to the N<sub>4</sub> plane.

An ORTEP drawing of [Ni(L3)(NCS)<sub>2</sub>] (1) with the atomic numbering scheme is shown in Fig. 1

and the selected bond lengths and angles are listed in Table 2. The crystal structure of 1 shows that the nickel(II) ion is coordinated by the secondary amines of the macrocyclic ligand and that the axial position bonded by two nitrogen atoms of the thiocynate ligands. The average Ni-N (secondary amines) distance of 2.086(5) Å is significantly longer than in the square-planar geometry of [Ni(L1)]Cl<sub>2</sub>·2H<sub>2</sub>O [1.948(4) Å] [15], but is similar to that observed for high-spin octahedral nickel(II) complexes with 14-membered tetraaza macrocyclic ligands [21-25]. The axial Ni-N distance of 2.152(5) Å is longer than the equatorial Ni-N distances, giving an axially elongated octahedral environment and comparable to the previously reported values in the related systems {[Ni(L1)(NCS)<sub>2</sub>] [22]: Ni-N = 2.115(3) ; [Ni(2,7,9,14cyclam)(NCS)<sub>2</sub>] (2,7,9,14-cyclam = 2,7,9,14-tetramethyl1,4,8,11-tetraazacyclotetradecane) [26]: Ni-N = 2.108(4)[Ni(2,5,9,12-cyclam)(NCS)<sub>2</sub>] (2,5,9,12-cyclam 2,5,9,12-tetramethyl1,4,8,11tetraazacyclotetradecane) [27]: Ni-N = 2.109(7) and 2.100(7) Å}. Also, The axial Ni-N(5) and Ni-N(6) linkages are bent slightly off the perpendicular to the NiN<sub>4</sub> plane by 1.3-5.5° and 2.1-5.6°, respectively. The Ni-N(5)-C(23) and Ni-N(6)-C(24) angles related to the thiocynate ligand are 177.1(5) and 176.1(5)°, respectively. Interestingly, uncoordinated sulfur atoms, S(1) and S(2), of the thiocynate ligands form the intermolecular hydrogen bonds to an adjacent secondary of the macrocycle [N(2)...S(2)#1 3.834(5) Å, 147.8°; N(4)<sup>...</sup>S(1)#2 3.846(5) Å, 147.9°; symmetry codes: (#1) x, y+1, z; (#2) x, y-1, z] This interaction gives rise to an one-dimensional hydrogen-bonded infinite chain (Fig. 2 and Table 3).

An ORTEP drawing of  $[Ni(L3)(H-cpdc)_2]$  (2) with the atomic numbering scheme is shown in Fig. 3

and the selected bond lengths and angles are listed in Table 4. The coordination environment around nickel(II) ion shows a six-coordinated octahedron with four secondary amines of macrocycle and two oxygen atoms of H-cpdc ligands. The average Ni-N (secondary amines) distance of 2.075(7) Å is similar to that found in  $[Ni(L1)(NCS)_2]$  (1) (2.085(5) Å) and shorter than the average Ni-O distance of 2.179(7) Å, giving an axially elongated octahedral geometry. The axial Ni-O bond distances and Ni-O-C angles [133.4(6) and 136.9(6)°] are similar to the observed for [Ni(L1)(H-cpdc)<sub>2</sub>] [28]. The axial Ni-O(1) and Ni-O(5) linkages are bent slightly off the perpendicular to the NiN<sub>4</sub> plane by 3.7-7.4 and 1.5-6.4°, respectively. Interestingly, the uncoordinated oxygen atoms, O(2) and O(6) of the H-cpdc ligand form the intramolecular hydrogen bonds with the secondary amines N(4) and N(2) of the macrocycle [N(2)...O(6) 2.967(12) Å, 151.7°; N(4)<sup>...</sup>O(2) 2.948(12) Å, 155.4°]. In addition the protonated oxygen atom O(3) is intramoleculary hydrogen bonded to the uncoordinated oxygen atom O(2) of the H-cpdc ligand. Furthermore, uncoordinated oxygen atoms, O(4) and O(7), of the H-cpdc ligand form the intermolecular hydrogen bonds to an adjacent secondary of the macrocycle [N(1)...O(7)#3 3.139(11) Å, 143.4°;  $N(3)^{--}O(4)#4 3.146(11) Å, 148.0^{\circ};$  symmetry codes: (#3) x, y, z+1; (#4) x, y, z-1]. This interaction gives rise to an one-dimensional hydrogen-bonded infinite chain (Fig. 4 and Table 5).

#### 3.2. Characterization of the complexes

The IR spectra of these complexes show bands at 3,240-3,261 cm<sup>-1</sup>, which is assigned to the v(NH) of

the coordinated secondary amines. A single very strong band at 2,066 cm<sup>-1</sup> of 1 is associated with the thiocynate stretching mode, which is agree with the crystal structure of 1. For 2, two strong bands exhibit  $v_{as}(COO)$  stretching frequency at 1,655 cm<sup>-1</sup> and  $v_{sym}(COO)$  at 1,398 cm<sup>-1</sup>, respectively. The value of  $\Delta v$ (257 cm<sup>-1</sup>) indicates that the carboxylate groups coordinated to the nickel(II) ion only as a monodentate ligand [29,30]. In addition, the sharp band v(OH) at 3,434 cm<sup>-1</sup> in 2 indicates that the complex contains the hydroxyl group. The UV-Vis spectral data and solid state spectra of the complexes are shown in Table 6 and Fig. 5. The solid reflectance and CH<sub>3</sub>CN solution spectra of 1 and 2 shows absorption maxima in the region 236-256 and 251-265 nm respectively, attributed to ligand-metal charge transfer transitions associated with nitrogen and oxygen donors [30,31]. The solid state electronic spectra of 1 and 2 in the visible region exhibit three absorption bands at 338-346, 516-526, and 718-706 nm assignable to the  ${}^{3}B_{1g}$  $\rightarrow \ ^{3}E^{c}_{\ g}, \ ^{3}B_{1g} \rightarrow \ ^{3}E^{b}_{\ g}, \ ^{3}B_{1g} \rightarrow \ ^{3}B_{2g} + \ ^{3}B_{1g} \rightarrow \ ^{3}A^{a}_{\ 2g} \ transitions, \ which \ are \ the \ characteristic \ spectrum$ expected for a high-spin d<sup>8</sup> nickel(II) ion in  $D_{4h}$  environment [23,32]. However, the visible spectra of 1 and 2 in water solution displays the broad bands 462-463 nm, which have a low-spin d<sup>8</sup> nickel(II) ion in a square-planar environment of  $[Ni(L1)]Cl_2 2H_2O$  ( $\lambda_{max} = 461$  nm) [17]. This fact can be understood in terms of dissociation of the thiocyanate and H-cpdc ligands at water solution

The compounds **1-2** were heated in the temperature range 30-1000°C under nitrogen gas. The TGA diagrams of compounds **1-2** are shown in Fig. 6. TGA curve for **1** shows a first weight loss of 84.9% (calculated 86.2%) over ca. 284-573°C, corresponding the macrocycle and two thiocyanate anions. A

final residue (observed 15.1%, calculated 13.8%) was remained above 573°C with NiO composition. For **2**, the first weight loss is observed from 236 to 523°C, which is due to the loss of the macrocycle and two nitrate anions (observed 89.5%, calculated 89.1%). A final residue (observed 10.5%, calculated 10.9%) was remained above 523°C with NiO composition.

Cyclic voltammetric data and cyclic voltammograms for compounds **1** and **2** in 0.10 M TEAP-DMSO solution are given in Table 7 and Fig. 7. The complex **1** reveals one one-electron wave corresponding to  $Ni^{II}/Ni^{I}$  process. However, the complex **2** exhibits two one-electron waves corresponding to  $Ni^{II}/Ni^{III}$  and  $Ni^{II}/Ni^{I}$  processes. It is of interest to compare the redox potentials for the nickel(II) complexes with the axial ligands. The reduction potentials for **1** and **2** are distinctly more positive than those of complex [Ni(L2)]Cl<sub>2</sub>·2H<sub>2</sub>O. This may result from the structural geometry (octahedral and square-plane). This is consistent with the crystal structures and spectroscopic data discussed previously.

#### Appendix A. Supplementary data

CCDC 1524580 and 1524582 contains the supplementary crystallographic data for **1** and **2**. These data can be obtained free of charge via http://www.ccdc. cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK; fax: (+44) 1223-

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Table 1. Crystallographic data

1

| Empirical formula                               | $C_{24}H_{44}N_6NiS_2$                 | C <sub>32</sub> H <sub>54</sub> N <sub>4</sub> NiO <sub>8</sub> |
|---|--|---|
| Formula weight                                  | 539.48                                 | 681.50  |
| Temperature (K)                                 | 296(2)                                 | 296(2)  |
| Crystal color/habit                             | purple/block                           | purple/block  |
| Crystal system                                  | triclinic                              | triclinic   |
| Space group                                     | <i>P</i> 1                             | P1  |
| Unit cell dimensions                            |  |   |
| <i>a</i> (Å)                                    | 8.7822(5)                              | 9.789(4)  |
| <i>b</i> (Å)                                    | 9.1152(5)                              | 10.401(5)   |
| c (Å)   | 9.3914(5)                              | 10.608(4)   |
| α (°)   | 74.398(2)                              | 105.69(3)   |
| β (°)   | 86.252(2)                              | 105.15(3)   |
| γ(°)  | 67.172(3)                              | 114.79(3)   |
| $V(\text{\AA}^3)$                               | 666.74(6)                              | 852.8(6)  |
| Ζ   | 1                                      | 1   |
| $D_{\text{calc}}$ (Mg m <sup>-3</sup> )         | 1.344                                  | 1.327   |
| Absorption coefficient (mm <sup>-1</sup> )      | 0.908                                  | 0.623   |
| <i>F</i> (000)                                  | 289                                    | 366   |
| Crystal size (mm)                               | 0.36×0.26×0.12                         | 0.20×0.18×0.06  |
| θ range (°)                                     | 2.25 to 28.42                          | 2.39 to 28.42   |
| Limiting indices                                | -11≤h≤11, -11≤k≤12,                    | -13≤ <i>h</i> ≤12, -13≤ <i>k</i> ≤13,                           |
|   | 0≤ <i>l</i> ≤12                        | 0≤ <i>l</i> ≤14   |
| Reflection collected/unique $(R_{int})$         | 3312/3312 (0.0000)                     | 4175/4175 (0.0000)  |
| Absorption correction                           | SADABS                                 | SADABS  |
| Maximum and minimum transmission                | 0.8988 and 0.7357                      | 0.9636 and 0.8856   |
| Data/restraints/parameters                      | 3312/3/300                             | 4175/3/394  |
| Goodness-of-fit on $F^2$                        | 1.053                                  | 1.050   |
| Final <i>R</i> indices $(I > 2\sigma(I))$       | $R_1^{a} = 0.0242, w R_2^{b} = 0.0618$ | $R_1$ =0.0475, $wR_2$ =0.1218                                   |
| R indices (all data)                            | $R_1$ =0.0263, $wR_2$ =0.0633          | $R_1$ =0.0626, $wR_2$ =0.1307                                   |
| Largest difference peak and hole $(e^{A^{-3}})$ | 0.298 and -0.266                       | 0.513 and -0.433  |

 ${}^{a}R_{1} = ||F_{o}| - |F_{c}|| / \Sigma |F_{o}|.$ 

<sup>b</sup>  $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}.$ 

Table 2. Selected bond lengths (Å) and angles (°) for  $[Ni(L3)(NCS)_2]\ (1)$ 

| N; N(1)          | 2111(4)  | N; N(2)         | 2 ()67(5) |
|------------------|----------|-----------------|-----------|
| INI-IN(I)        | 2.111(4) | INI-IN(2)       | 2.067(3)  |
| Ni-N(3)          | 2.076(5) | Ni-N(4)         | 2.088(5)  |
| Ni-N(5)          | 2.168(4) | Ni-N(6)         | 2.135(5)  |
| N(5)-C(23)       | 1.144(8) | C(23)-S(1)      | 1.648(6)  |
| N(6)-C(24)       | 1.169(8) | C(24)-S(2)      | 1.619(6)  |
|                  |          |                 |           |
| Bond angles ( °) |          |                 |           |
| N(1)-Ni-N(2)     | 83.9(2)  | N(1)-Ni-N(3)    | 179.8(3)  |
| N(1)-Ni-N(4)     | 95.3(2)  | N(2)-Ni-N(3)    | 95.8(2)   |
| N(2)-Ni-N(4)     | 178.6(3) | N(3)-Ni-N(4)    | 84.9(2)   |
| N(1)-Ni-N(5)     | 95.5(2)  | N(2)-Ni-N(5)    | 87.6(2)   |
| N(3)-Ni-N(5)     | 84.5(2)  | N(4)-Ni-N(5)    | 91.3(2)   |
| N(1)-Ni-N(6)     | 84.5(2)  | N(2)-Ni-N(6)    | 93.2(2)   |
| N(3)-Ni-N(6)     | 95.6(2)  | N(4)-Ni-N(6)    | 87.9(2)   |
| N(5)-Ni-N(6)     | 179.2(3) | Ni-N(5)-C(23)   | 177.1(5)  |
| Ni-N(6)-C(24)    | 176.1(5) | N(5)-C(23)-S(1) | 177.5(5)  |
| N(6)-C(24)-S(2)  | 178.3(5) |                 |           |
|                  |          |                 |           |

Table 3. Hydrogen bonding parameters (Å, °) for [Ni(L2)(NCS)<sub>2</sub>] (1)

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| D-H <sup></sup> A              | D-H (Å)             | HA (Å) | DA (Å)   | $D-H^{\cdots}A(^{\circ})$ |
|--------------------------------|---------------------|--------|----------|---------------------------|
| N(2)-HN(2) <sup></sup> S(2)#1  | 0.91                | 3.03   | 3.834(5) | 147.8                     |
| N(4)-HN(4)) <sup></sup> S(1)#2 | 0.91                | 3.05   | 3.846(5) | 147.9                     |
| Symmetry codes: (#1) x, y      | +1, z; (#2) x, y–1, | ζ.     |          | 2                         |
|                                |                     |        |          | -                         |
|                                |                     |        |          | 0                         |
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|                                |                     |        |          |                           |

Table 4. Selected bond lengths (Å) and angles (°) for  $[Ni(L2)(H\mbox{-}cpdc)_2]~(2)$ 

| Bond lengths (Å) |           |                 |           |
|------------------|-----------|-----------------|-----------|
| Ni-N(1)          | 2.093(6)  | Ni-N(2)         | 2.067(6)  |
| Ni-N(3)          | 2.101(7)  | Ni-N(4)         | 2.039(7)  |
| Ni-O(1)          | 2.191(7)  | Ni-O(5)         | 2.167(7)  |
| C(26)-O(1)       | 1.251(12) | C(26)-O(2)      | 1.272(11) |
| C(31)-O(5)       | 1.240(10) | C(31)-O(6)      | 1.241(10) |
|                  |           |                 | G         |
| Bond angles ( °) |           |                 | 6         |
| N(1)-Ni-N(2)     | 83.6(3)   | N(1)-Ni-N(3)    | 178.6(4)  |
| N(1)-Ni-N(4)     | 96.5(2)   | N(2)-Ni-N(3)    | 96.0(3)   |
| N(2)-Ni-N(4)     | 177.8(4)  | N(3)-Ni-N(4)    | 83.8(3)   |
| N(1)-Ni-O(1)     | 83.2(2)   | N(2)-Ni-O(1)    | 85.3(2)   |
| N(3)-Ni-O(1)     | 95.4(3)   | N(4)-Ni-O(1)    | 92.6(3)   |
| N(1)-Ni-O(5)     | 96.4(3)   | N(2)-Ni-O(5)    | 93.6(3)   |
| N(3)-Ni-O(5)     | 84.9(3)   | N(4)-Ni-O(5)    | 88.5(3)   |
| O(1)-Ni-O(5)     | 178.9(3)  | Ni-O(1)-C(26)   | 133.4(6)  |
| Ni-O(5)-C(31)    | 136.9(6)  | O(1)-C(26)-O(2) | 127.3(8)  |
| O(5)-C(31)-O(6)  | 121.5(8)  |                 |           |

|   | D-H <sup></sup> A                 | D-H (Å)                                | HA (Å)  | DA (Å)    | D-H <sup></sup> A (°) |
|---|-----------------------------------|--|---------|-----------|-----------------------|
|   | N(1)-HN(1)O(7)#3                  | 0.91                                   | 2.36    | 3.139(11) | 143.4                 |
|   | N(3)-HN(3)O(4)#4                  | 0.91                                   | 2.34    | 3.146(11) | 148.0                 |
|   | N(2)-HN(2)O(6)                    | 0.91                                   | 2.13    | 2.967(12) | 151.7                 |
|   | N(4)-HN(4) <sup></sup> O(2)       | 0.91                                   | 2.10    | 2.948(12) | 155.4                 |
|   | O(3)-HO(3) <sup></sup> O(2)       | 0.86(6)                                | 1.69(6) | 2.491(12) | 154(5)                |
|   | Symmetry codes: (#3) <i>x</i> , y | <i>x, z</i> +1; (#4) <i>x, y, z</i> −1 |         |           |                       |
|   |                                   |  |         |           |                       |
|   | CIP                               |  |         |           |                       |
| P |                                   |  |         |           |                       |
|   |                                   |  |         |           |                       |

Table 6. Electronic spectral data<sup>a</sup>

| Solid              | 252, 460  |
|--------------------|---|
| CH <sub>3</sub> CN | 465(65)   |
| H <sub>2</sub> O   | 461(68)   |
| Solid              | 256, 338, 516, 718  |
| CH <sub>3</sub> CN | 251(8.4×10 <sup>2</sup> ) 521(8.7)  |
| H <sub>2</sub> O   | 250(7.2×10 <sup>3</sup> ), 462 (73)   |
| Solid              | 236, 346, 526, 706  |
| CH <sub>3</sub> CN | 265(1.8×10 <sup>3</sup> ), 531(9.1)   |
| $H_2O$             | 260(5.6×10 <sup>3</sup> ), 463(75)  |
|                    |   |
|                    |   |
|                    | CH <sub>3</sub> CN<br>H <sub>2</sub> O<br>Solid<br>CH <sub>3</sub> CN<br>H <sub>2</sub> O<br>Solid<br>CH <sub>3</sub> CN<br>H <sub>2</sub> O<br>at 20±0.1 °C; Solid = |

Table 7. Cyclic voltammetric data<sup>a</sup>

|  | Potentials (V) versus | Ag/AgCl               |
|--|-----------------------|-----------------------|
| Complex  | Ni(III)/Ni(II)        | Ni(II)/Ni(I)          |
| $[Ni(L2)]Cl_2 \cdot 2H_2O^b$                       | +0.68                 | -1.54(i) <sup>c</sup> |
| [Ni(L2)(NCS) <sub>2</sub> ] (1)                    |                       | -1.35                 |
| [Ni(L2)(H-cpdc) <sub>2</sub> ] ( <b>2</b> )        | +0.70                 | -1.34                 |
| <sup>a</sup> Measured in 0.10 M TEAP-DMSO solution | on at 20.0±0.1 °C.    | 0-                    |
| <sup>b</sup> Ref [17].                             |                       | C                     |
| <sup>c</sup> i = irreversible.                     |                       | 9                     |
|  |                       | $\mathbf{\mathbf{v}}$ |
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**Figure captions** 

Fig. 1. An ORTEP diagram of  $[Ni(L2)(NCS)_2]$  (1) with the atom-numbering scheme (30% probability

ellipsoids shown). The hydrogen atoms and water molecules are omitted for clarity.

Fig. 2. Crystal packing of [Ni(L2)(NCS)<sub>2</sub>] (1), showing the hydrogen bonds as dotted lines.

Fig. 3. An ORTEP diagram of [Ni(L2)(H-cpdc)<sub>2</sub>] (2) with the atom-numbering scheme (30% probability

ellipsoids shown). The hydrogen atoms and water molecules are omitted for clarity.

Fig. 4. Crystal packing of [Ni(L2)(H-cpdc)<sub>2</sub>] (2), showing the hydrogen bonds as dotted lines.

Fig. 5. Solid state electronic absorption spectra  $[Ni(L2)(NCS)_2]$  (2) and  $[Ni(L2)(H-cpdc)_2]$  (3) by the diffuse reflectance method at  $20.0 \pm 0.1$  °C.

Fig. 6. Thermogravimetric curves of [Ni(L2)(NCS)<sub>2</sub>] (1) and [Ni(L2)(H-cpdc)<sub>2</sub>] (2).

Fig. 7. Cyclic voltammograms of of  $[Ni(L2)(NCS)_2]$  (1) and  $[Ni(L2)(H-cpdc)_2]$  (2) in 0.1M TEAP-DMSO solution at 20.0 ±0.1 °C. The scan rate is 100 mV/s.









04 🙋 C27 O3 C24 C25 C23 C20 C26 C19 02 ¦ 07<sup>(ii)</sup> 01🥰 all a C9 C8 N3 C10 C11 C12 C7 🕻 C4 C6 Ni N2 N4 Å C1 N1 C15 C14 C2 C17 C13 Č3 C16 C18 4 04 (iii) 05 C21 C31 06 C28 C22 🤇 C30 08 C29 C32 07



ORIG b 

PIP 0.8 0.6 Abs **(1)** 0.4 (2) 0.2 200 400 600 800 900 Wavelength(nm) 











**Pictogram and Synopsis** 

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In-Taek Lim, Ki-Young Choi

### 1D Hydrogen-bonded infinite chains from tetraaza macrocycle nickel(II)

complexes and ligands

The reaction of  $[Ni(L2)]Cl_2 \cdot 2H_2O$  (L1 = 3,14-diethyl-2,6,13,17-tetraazatricyclo $[14,4,0^{1.18},0^{7.12}]$ docosane) with ligands generates 1D hydrogen-bonded infinite chains  $[Ni(L2)(NCS)_2]$  (1) and  $[Ni(L2)(H-cpdc)_2]$ (2). The crystal structure of the compounds 1 and 2 exhibits a high-spin octahedral geometry with the axial ligands.

