

# One-Dimensional Hydrogen-Bonded Infinite Chains Composed of a Nickel(II) Macrocyclic Complex and Organic Ligands

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The reactions of  $[\text{Ni}(\text{L})(\text{H}_2\text{O})_2]\text{Cl}_2$  ( $\text{L} = 2,5,9,12$ -tetramethyl-1,4,8,11-tetraazacyclotetradecane) with terephthalate (tp) and 2,5-pyridinedicarboxylate (pdc) generate one-dimensional nickel(II) complexes.  $[\text{Ni}(\text{L})(\text{H}_2\text{O})_2](\text{tp}) \cdot 4\text{H}_2\text{O}$  (**1**) and  $[\text{Ni}(\text{L})(\text{H}_2\text{O})_2](\text{pdc}) \cdot 4\text{H}_2\text{O}$  (**2**). The structures have been characterized by X-ray crystallography, magnetic susceptibility and spectroscopy. The crystal structures of **1** and **2** show a distorted octahedral coordination geometry around the Ni(II) ion, with secondary amines of the macrocycle and two water molecules at the *trans* position. Complexes **1** and **2** display the one-dimensional hydrogen-bonded infinite chains. The magnetic behavior of all compounds exhibits weak interchain antiferromagnetic interactions with  $J$  values of  $-1.09(3)$  for **1** and  $-1.14(2)$   $\text{cm}^{-1}$  for **2**.

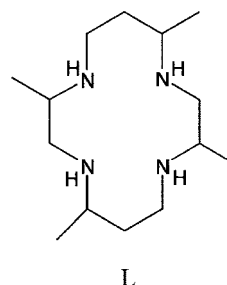
**Key Words** : Crystal structures, Nickel(II) complexes, Macrocyclic, Organic ligands, Chain complexes

## Introduction

The self-assembly of the infinite coordination polymers with specific network topologies has been of great attraction due to its potential usage in many areas of science and technology.<sup>1-13</sup> The self-assembly is generally produced to involve the spontaneous aggregation of molecules into stable, noncovalently joined ensembles displaying multi-dimensional networks.<sup>3-5</sup> 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.<sup>6,7</sup> To date, there has been a lot of work that focuses on design and synthesis of self-complementary hydrogen-bonding recognition subunits, which can form many kinds of supramolecular architecture.<sup>8-10</sup> For example, a three dimensional supramolecular network  $[\text{Ni}(\text{cyclam})(\text{H}_2\text{O})_2]_3[(\text{btc})_3]_3 \cdot 24\text{H}_2\text{O}$  ( $\text{btc} = 1,3,5$ -benzenetricarboxylate)<sup>9</sup> was assembled by  $[\text{Ni}(\text{cyclam})(\text{H}_2\text{O})_2]^{2+}$  and  $\text{btc}^{3-}$  ligand in water *via* hydrogen bonds, which is regarded as a molecular floral lace.<sup>9</sup> In addition, We reported the crystal structure of  $[\text{Ni}(\text{dtttd})(\text{H}_2\text{O})_2]_{0.5}[\text{Ni}(\text{dtttd})(\text{WO}_4)_2]_{0.5}$  ( $\text{dtttd} = 3,14$ -dimethyl-2,6,13,17-tetraazatricyclo[14.4.0]<sup>18,0<sup>7</sup>12</sup>docosane), which assembles in the solid state to form a one-dimensional chain linked by intermolecular hydrogen bond.<sup>10</sup> The hydrogen-bonding interactions, therefore, play a significant role in aligning the molecules and the polymer stands in the crystalline solids. However, macrocyclic complexes with organic ligands have seldom been used as building blocks in the construction of the multidimensional networks.<sup>14-16</sup>

In the present paper, we report the preparation, crystal structures and chemical properties of the one-dimensional

infinite chains linked by hydrogen bonds  $[\text{Ni}(\text{L})(\text{H}_2\text{O})_2](\text{tp}) \cdot 4\text{H}_2\text{O}$  (**1**) and  $[\text{Ni}(\text{L})(\text{H}_2\text{O})_2](\text{pdc}) \cdot 4\text{H}_2\text{O}$  (**2**) ( $\text{L} = 2,5,9,12$ -tetramethyl-1,4,8,11-tetraazacyclotetradecane), which were prepared by reaction of  $[\text{Ni}(\text{L})(\text{H}_2\text{O})_2]\text{Cl}_2$  with organic ligands, such as terephthalate (tp) and 2,5-pyridinedicarboxylate (pdc).



## Experimental Section

**Materials and physical measurements.** All chemicals and solvents used in the syntheses were of reagent grade and were used without further purification. The macrocycle **L** and  $[\text{Ni}(\text{L})(\text{H}_2\text{O})_2]\text{Cl}_2$  were prepared according to literature methods.<sup>17,18</sup> IR spectra were recorded with a Perkin-Elmer Paragon 1000 FT-IR spectrophotometer using KBr pellets. Solution electronic spectra were obtained on a JASCO Uvidec 610 spectrophotometer. The diffuse reflectance spectra were recorded with a Shimadzu UV2401 PC/DRS spectrophotometer. Magnetic susceptibility data on powder samples were collected in the temperature range 5-300 K in applied 0.5 T with the use of a Quantum Design MPMS7 SQUID magnetometer. The diamagnetic corrections were estimated from Pascal's constants. FAB mass spectra were performed using a Jeol JMS-HA 110A/110A spectrometer. Elemental analyses were performed on a Perkin-Elmer

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CHN-2400 analyzer.

**Synthesis of  $[\text{Ni}(\text{L})(\text{H}_2\text{O})_2](\text{tp})\cdot 4\text{H}_2\text{O}$  (1).** To a methanol solution (20 mL) of  $[\text{Ni}(\text{L})(\text{H}_2\text{O})_2]\text{Cl}_2$  (210 mg, 0.5 mmol) was added  $\text{Na}_3\text{tp}$  (110 mg, 1.0 mmol) and the mixture was stirred for 30 min at room temperature. The solution was filtered to remove insoluble material. After the filtrate was left to stand at room temperature over a period of several days, a quantity of violet crystals precipitated. The crystals were collected by filtration and washed with diethyl ether, giving a yield of 67%. Anal. Calcd for  $\text{C}_{22}\text{H}_{48}\text{N}_4\text{NiO}_{10}$ : C, 44.99; H, 8.24; N, 9.54. Found: C, 45.08; H, 8.15; N, 9.43. IR (KBr;  $\text{cm}^{-1}$ ): 3412, 3154, 2929, 1572, 1458, 1427, 1376, 1306, 1290, 1118, 1067, 1040, 1016, 996, 942, 814, 752, 508. UV-vis in water [ $\lambda_{\text{max}}$ , nm ( $\epsilon$ ,  $\text{M}^{-1}\text{cm}^{-1}$ ): 456 (71); in  $\text{CHCl}_3$ : 532 (7.8); in diffuse reflectance ( $\lambda_{\text{max}}$ , nm): 530. FAB mass ( $m/z$ ): 587 ( $\text{M}^+$ ).

**Synthesis of  $[\text{Ni}(\text{L})(\text{H}_2\text{O})_2](\text{pdc})\cdot 4\text{H}_2\text{O}$  (2).** This compound was prepared as light violet crystals in a reaction similar to that of 1, except for the use of  $\text{Na}_3\text{pdc}$  (106 mg, 1 mmol) instead of  $\text{Na}_3\text{tp}$ . Yield: 65%. Anal. Calcd for  $\text{C}_{21}\text{H}_{47}\text{N}_5\text{NiO}_{10}$ : C, 42.87; H, 8.05; N, 9.98. Found: C, 42.96; H, 8.17; N, 9.84. IR (KBr;  $\text{cm}^{-1}$ ): 3416, 3184, 2968, 1599, 1474, 1427, 1360, 1278, 1177, 1113, 1066, 1041, 990, 944, 896, 829, 767, 696, 528. UV-vis in water [ $\lambda_{\text{max}}$ , nm ( $\epsilon$ ,  $\text{M}^{-1}\text{cm}^{-1}$ ): 456 (69); in  $\text{CHCl}_3$ : 530 (8.1); in diffuse reflectance ( $\lambda_{\text{max}}$ , nm): 528. FAB mass ( $m/z$ ): 588 ( $\text{M}^+$ ).

**X-ray crystallography.** Single crystals of 1 and 2 were mounted on an Enraf-Nonius CAD4 diffractometer equipped with graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda =$

0.71069 Å) at room temperature. The intensity data of reflections were collected in the  $\omega$ - $2\theta$  scan mode. Data were corrected for Lorentz and polarization effects. Empirical absorption corrections ( $\psi$ -scan) were applied. The structure was solved by direct methods<sup>19</sup> and the least-squares refinement of the structure was performed by the program SHELXL97.<sup>20</sup> For 1, all non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions, allowing them to ride on their parent C atoms with  $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C or N})$ , the methyl group, C(3) was treated as rotating rigid groups with  $U_{\text{iso}}(\text{H}) = 1.5 U_{\text{eq}}(\text{C})$ . The water hydrogen atoms were not located. The C(7) atom was disordered over two positions and split atoms, designated as C(7) and C(7'). The final occupancy factors of C(7) and C(7') were 0.60 and 0.40, respectively. Thus, the hydrogen atom of C(7) and C(7') were not located. For 2, all non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions, allowing them to ride on their parent C atoms with  $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C or N})$ , but the methyl group, C(4) and C(7) were treated as rotating rigid groups with  $U_{\text{iso}}(\text{H}) = 1.5 U_{\text{eq}}(\text{C})$ . The five hydrogen atoms of Ow(1), Ow(2), and C(10) were found from difference Fourier map and each of their positions was fixed with  $U_{\text{iso}}$  to be 1.2 times. The hydrogen atoms of Ow(3) were not found. The intensity data for 2 clearly showed the space group  $P2_1/n$ . The nitrogen atom NC in the pyridine ring was chosen according to the peak height from difference Fourier synthesis. The two atoms NC and CN with half occupancy factor each were put in the position of nitrogen NC for the

Table 1. Crystallographic data

	1	2
empirical formula	$\text{C}_{22}\text{H}_{48}\text{N}_4\text{NiO}_{10}$	$\text{C}_{21}\text{H}_{47}\text{N}_5\text{NiO}_{10}$
formula weight	587.35	588.35
temperature (K)	293	293
crystal system	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$
$a$ (Å)	12.999(2)	12.888(4)
$b$ (Å)	10.369(4)	10.103(1)
$c$ (Å)	10.859(2)	11.118(2)
$\beta$ (°)	95.28(1)	97.46(2)
$V$ (Å <sup>3</sup> )	1457.3(6)	1435.3(5)
$Z$	2	2
$D_{\text{calcd}}$ ( $\text{Mg m}^{-3}$ )	1.338	1.361
absorption coefficient ( $\text{mm}^{-1}$ )	0.721	0.733
$F(000)$	632	632
crystal size (mm)	0.30 × 0.16 × 0.16	0.26 × 0.25 × 0.15
$\theta$ range (°)	2.34 to 24.98	2.28 to 24.98
limiting indices	$-15 \leq h \leq 15, 0 \leq k \leq 12, 0 \leq l \leq 12$	$-15 \leq h \leq 15, 0 \leq k \leq 12, 0 \leq l \leq 13$
reflection collected/unique	2703/2561 [ $R_{\text{int}}=0.0349$ ]	2659/2522 [ $R_{\text{int}}=0.0273$ ]
absorption correction	$\psi$ -scan	$\psi$ -scan
max./min. transmission	0.8902 and 0.8143	0.9997 and 0.9548
data/restraints/parameters	2561/0/178	2522/0/169
goodness of fit on $F^2$	1.069	1.023
final $R$ indices [ $I > 2\sigma(I)$ ]	$R_1=0.0666, wR_2=0.1529$	$R_1=0.0546, wR_2=0.1331$
$R$ indices (all data)	$R_1=0.1213, wR_2=0.1797$	$R_1=0.0869, wR_2=0.1499$
largest difference peak and hole ( $\text{e}\text{\AA}^{-3}$ )	0.686 and $-0.265$	0.640 and $-0.258$

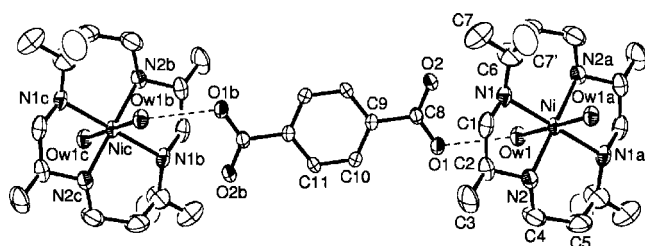
<sup>a</sup> $R_1 = \sum |F_o| - F_c| / \sum |F_o|$ , <sup>b</sup> $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$ .

structure refinement because an inversion center is at the centroid of the pyridine ring. Therefore, the atomic positions designated by NC and CN were 50% occupied by N and 50% occupied by C. An H atom bonded to the carbon CN, which is symmetry equivalent to NC, was not calculated and all other hydrogen atoms were located in calculated positions. During the refinement process, the following two instructions were used for NC and CN to make their positions and temperature factors identical. The crystallographic data, conditions for the collection of intensity data, and some features of the structural refinements are listed in Table 1.

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 194385 for compound **1** and 194386 for compound **2**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

## Results and Discussion

**Description of the structures.** An ORTEP drawing of  $[\text{Ni}(\text{L})(\text{H}_2\text{O})_2](\text{tp})\cdot 4\text{H}_2\text{O}$  (**1**) with the atomic numbering scheme is shown in Figure 1. The selected bond lengths and angles are listed in Table 2. The crystal structure of **1** has cationic  $[\text{Ni}(\text{L})(\text{H}_2\text{O})_2]^+$  units,  $\text{tp}^{2-}$  anion, and water molecules. The complex shows an inversion center at the midpoint of the benzene ring of the tp ligand. The ligand skeleton of the complex cation takes the most stable *trans*-III(*R,R,S,S*) configuration with two chair six-membered and two gauche five-membered chelate rings. The nickel(II) ion and the four nitrogen atoms of the macrocycle are exactly in a plane. The complex has a distorted octahedral coordination geometry with secondary amines of the macrocycle and two water molecules at the *trans* position. The average Ni-N bond distance of 2.076(10) Å is comparable to those found in octahedral nickel(II) complexes with 14-membered tetraaza macrocyclic ligands.<sup>18,21-23</sup> The long Ni-Ow(1) bond distance of 2.176(4) Å is also in line with the corresponding ones given in the above references. All angles of the octahedron are normal, ranging from 85.1(2) to 94.9(2)°. The dihedral angle ( $\alpha$ ) of 3.8° between the carboxylate group and benzene ring is similar to that found in the  $[\text{Ni}(\text{dtttd})(\text{tp})]\cdot 2\text{H}_2\text{O}$  (5.6°).<sup>23</sup> The long intramolecular Ni...Ni' separation is 15.014(3) Å, whereas the closest intermolecular Ni...Ni' distance is 9.597(2) Å. The construction strategy of



**Figure 1.** An ORTEP drawing of  $[\text{Ni}(\text{L})(\text{H}_2\text{O})_2](\text{tp})\cdot 4\text{H}_2\text{O}$  (**1**) with the atomic numbering scheme (30% probability ellipsoids shown).

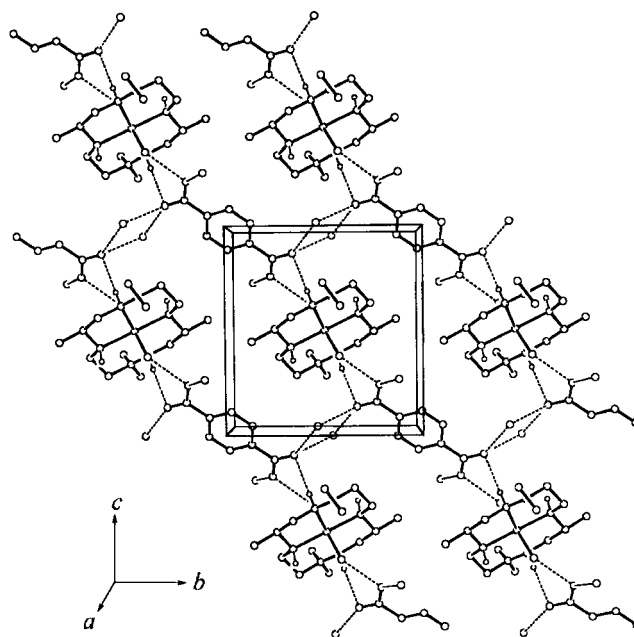
**Table 2.** Selected bond lengths (Å) and angles (°) for **1**<sup>a</sup>

Ni-N(1)	2.067(4)	Ni-N(2)	2.085(5)
Ni-Ow(1)	2.176(4)	O(1)-C(8)	1.254(6)
O(2)-C(8)	1.252(6)	Ni...Ni'	15.014(3)
Ni...Ni''	9.597(2)		
N(1)-Ni-N(2)	85.1(2)	N(1)-Ni-N(2)'	94.9(2)
N(1)-Ni-Ow(1)	88.3(2)	N(1)-Ni-Ow(1)'	91.7(2)
N(2)-Ni-Ow(1)	91.4(2)	N(2)-Ni-Ow(1)'	88.6(2)
O(1)-C(8)-O(2)	123.4(5)	O(1)-C(8)-C(9)	117.6(5)
O(2)-C(8)-C(9)	119.0(5)		

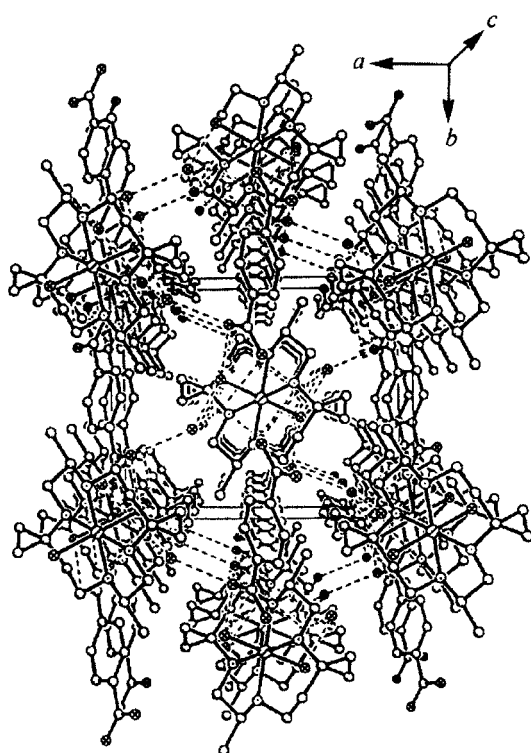
<sup>a</sup>Symmetry code: (i)  $-x-1, -y+1, -z+1$ .

compound **1** may be based on the ability of the nickel(II) macrocyclic complex to bind water molecules as the axial ligands and hydrogen bond formation (Ow(1)...O(1): 2.700(5) Å) between the coordinated water molecules of the complex and the carboxylate oxygen atoms of tp dianion, leading to a one-dimensional hydrogen-bonded infinite chain. In addition, the neighboring chains are also interconnected by hydrogen bonding between lattice water molecules and carboxylate oxygens of tp ligand (Ow(2)...O(1): 2.726(6) Å, Ow(3)...O(2): 2.755(6) Å and Ow(3)...O(2)'': 2.884(7) Å; symmetry code: (ii)  $-x+1, -y+1, -z$ ) (Figure 2). Furthermore, the secondary amines of the macrocycle form hydrogen bonds with carboxylate oxygen atom of tp ligand and lattice water molecule (N(1)...O(2): 3.163(7) Å, 165.7°, N(2)...Ow(2)': 3.068(6) Å, 162.7°; symmetry code: (i)  $x+1/2, -y+3/2, z+1/2$ ). Interestingly, one-dimensional chains are connected by lattice water molecules through the hydrogen bonds, which gives rise to a three-dimensional network (Figure 3).

An ORTEP drawing of  $[\text{Ni}(\text{L})(\text{H}_2\text{O})_2](\text{pdc})\cdot 4\text{H}_2\text{O}$  (**2**) with

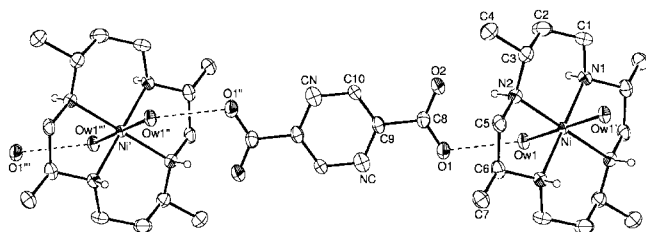


**Figure 2.** Crystal packing of **1**, showing the intermolecular hydrogen bonds as dotted lines. The hydrogen atoms are omitted for clarity.



**Figure 3.** Top view of the three-dimensional network of **1**, showing the intermolecular hydrogen bonds as dotted lines. The hydrogen atoms are omitted for clarity.

the atomic numbering scheme is shown in Figure 4, and the selected bond lengths and angles are presented in Table 3. The crystal structure of **2** consists of  $[\text{Ni}(\text{L})(\text{H}_2\text{O})_2]^{2+}$  unit,  $\text{pdc}^{2-}$  anion, and water molecules. The same crystal systems in both **1** and **2** complexes confirm that they are isostructural. The nickel atom occupies a distorted octahedral coordination environment with the macrocycle and two water molecules. The average Ni-N distance of 2.085(5) Å is somewhat shorter than the Ni-Ow(1) distance (2.145(3) Å), which is similar to that observed in the compound **1**. The long intramolecular chain Ni $\cdots$ Ni distance is 15.022(2) Å, whereas the closest intermolecular Ni $\cdots$ Ni distance between neighboring stands is 9.415(4) Å. The value of the dihedral angle ( $\alpha$ ) for **2** is 14.0°. Every nickel(II) macrocyclic complex forms hydrogen bonds with two of the pdc anions located up and down with respect to the  $\text{NiN}_4$  plane, which is indicative of a one-dimensional hydrogen-bonded infinite chain. The secondary amines of the macrocycle form hydrogen bonds



**Figure 4.** An ORTEP drawing of  $[\text{Ni}(\text{L})(\text{H}_2\text{O})_2](\text{pdc})\cdot 4\text{H}_2\text{O}$  (**2**) with the atomic numbering scheme (30% probability ellipsoids shown).

**Table 3.** Selected bond lengths (Å) and angles ( $^\circ$ ) for **2**<sup>a</sup>

Ni-N(1)	2.081(3)	Ni-N(2)	2.089(3)
Ni-Ow(1)	2.145(3)	O(1)-C(8)	1.245(5)
O(2)-C(8)	1.243(6)	Ni $\cdots$ Ni'	15.022(2)
Ni $\cdots$ Ni''	9.415(4)		
<hr/>			
N(1)-Ni-N(2)	95.2(1)	N(1)-Ni-N(2) <sup>i</sup>	84.8(1)
N(1)-Ni-Ow(1)	90.1(1)	N(1) <sup>j</sup> -Ni-Ow(1)	89.9(1)
N(2)-Ni-Ow(1)	89.5(1)	N(2) <sup>j</sup> -Ni-Ow(1)	90.5(1)
O(1)-C(8)-O(2)	124.4(4)	O(1)-C(8)-C(9)	117.4(4)
O(2)-C(8)-C(9)	118.1(4)	C(9) <sup>j</sup> -NC-C(10)	118.9(5)

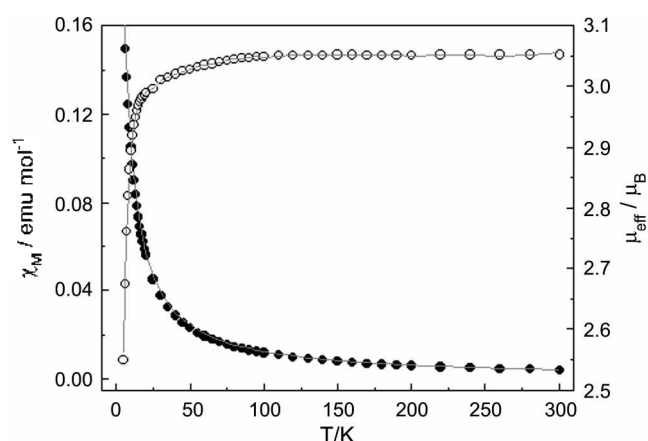
<sup>a</sup>Symmetry codes: (i)  $-x-1, -y-1, -z+1$ ; (ii)  $-x-1, -y+2, -z+2$ .

with carboxylate oxygen of pdc ligand and lattice water molecule (N(2) $\cdots$ O(2): 3.171(5) Å, 169.8°, N(1) $\cdots$ Ow(2): 3.028(5) Å, 160.0°). The water molecules found in the lattice also form hydrogen bonds with carboxylate oxygen of the pdc ligand (Ow(3) $\cdots$ O(2): 2.954 Å) and the other water inclusion (Ow(2) $\cdots$ Ow(3): 2.725(6) Å, 152.0(3)°). Furthermore, the coordinated water molecules are linked to the lattice water molecule and pdc oxygen atom through hydrogen bonds (Ow(1) $\cdots$ Ow(2): 2.702(5) Å, 170.3(2)°, Ow(1) $\cdots$ O(1): 2.704(4) Å, 169.2(2)°). As with structure **1**, a three-dimensional hydrogen-bonded network is present in **2** between one-dimensional chains and lattice water molecules.

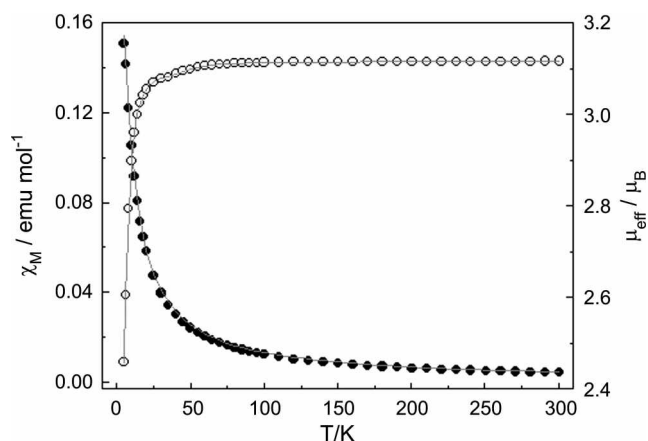
**Chemical properties.** The infrared spectrum of compound **1** shows the coordinated secondary  $\nu(\text{NH})$  stretching bands at 3154  $\text{cm}^{-1}$  and  $\nu(\text{HOH})$  bending vibration at 1572  $\text{cm}^{-1}$ . As with the spectrum of **1**, the strong bands at 3184 and 1599  $\text{cm}^{-1}$  in **2** were assigned to  $\nu(\text{NH})$  and  $\nu(\text{HOH})$ , respectively. Visible absorption spectra of **1** and **2** in chloroform solution show d-d bands at 532 and 530 nm, respectively, which is assigned to the transition  ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})$ .<sup>24</sup> Solid state electronic spectra of **1** and **2** exhibit maximum absorption at 530 and 528 nm, which are characteristic chromophores for the nickel(II) ion coordinated with  $\text{N}_4\text{O}_2$  donors.<sup>25</sup> However, all compounds dissolve in water and decompose into the building block, which was identified by the electronic absorption spectra showing the characteristic chromophore ( $\lambda_{\text{max}} = 456$  nm) of the square-planar nickel(II) macrocyclic complexes.<sup>11,26</sup>

Variable-temperature magnetic susceptibility data were collected for powdered samples of all the complexes. The magnetic susceptibilities ( $\chi_M$ ) and the effective magnetic moments ( $\mu_{\text{eff}}$ ) versus temperature plots for **1** and **2** are shown in Figures 5 and 6. The room temperature magnetic moments ( $\mu_B$ ) for **1** and **2** are 3.05 and 3.12, respectively. For all compounds the  $\mu_{\text{eff}}$  values gradually decrease with decreasing temperature, indicating the presence of an antiferromagnetic interaction between the nickel(II) ions. The magnetic susceptibility data are interpreted with Fisher's model for the classical-spin chain system ( $S = 1$  and  $H_{\text{chain}} = -J\sum S_i \cdot S_{i+1}$ ).<sup>27,28</sup> The  $\chi_M$  data can be expressed as

$$\chi_M = \frac{N\beta^2 g^2 S(S+1)}{3kT} \frac{(1+\mu)}{(1-\mu)} \quad (1)$$



**Figure 5.** Plots of  $\chi_M$  vs  $T$  (●) and  $\mu_{\text{eff}}$  vs  $T$  (○) for **1**. The solid line represents the best fit of the experimental data to eq. 1.

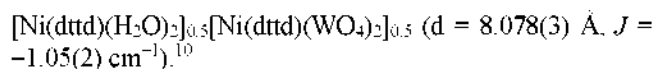


**Figure 6.** Plots of  $\chi_M$  vs  $T$  (●) and  $\mu_{\text{eff}}$  vs  $T$  (○) for **2**. The solid line represents the best fit of the experimental data to eq. 1.

with

$$\mu = \coth\left[\frac{JS(S+1)}{kT}\right] - \left[\frac{kT}{JS(S+1)}\right]$$

The fitting of the observed data afforded  $J = -1.09(3) \text{ cm}^{-1}$  and  $g = 2.25(1)$  for **1**.  $J = -1.14(2) \text{ cm}^{-1}$  and  $g = 2.22(2)$  for **2**. In **1** and **2**, the long intramolecular Ni...Ni' separations within the chain are 15.014(3) and 15.022(2) Å, whereas the closest intermolecular Ni...Ni' distances are 9.597(2) and 9.415(4) Å, respectively. The observed antiferromagnetic behavior is, therefore, due to the weak exchange interactions between neighboring sites through the existing net of closest intermolecular hydrogen bonds. A similar result is observed in one-dimensional network linked by hydrogen bond



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