

# Synthesis, Crystal Structure, and Properties of a 3-D Network Assembled by Nickel(II) Macrocylic Complex and Terephthalato Bridge

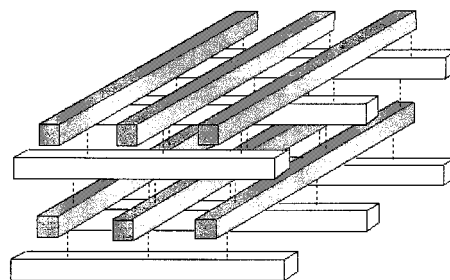
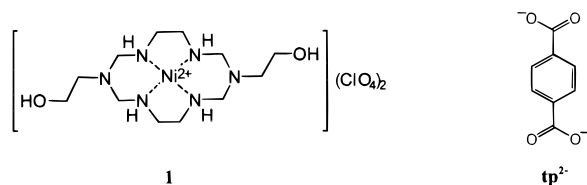
Hye Jin Choi and Myunghyun Paik Suh\*

Department of Chemistry Education and the Center for Molecular Catalysis, Seoul National University, Seoul 151-742, Republic of Korea

Received June 8, 1999

## Introduction

Supramolecular chemistry and crystal engineering have been greatly advanced, and many efforts have been made to design and construct molecular solids with specific network topologies<sup>1–3</sup> as well as with potentially interesting properties.<sup>4–8</sup> Self-assembly of organic molecules and metal-ion building blocks may yield multidimensional networks containing channels or cavities of various sizes and shapes.<sup>9–16</sup> However, macrocyclic complexes have seldom been employed as building blocks in the construction of the multidimensional networks.<sup>17–19</sup> Recently, we have reported 3-D networks assembled by macrocyclic complex **1** and organic three-metal connectors.<sup>17</sup> In these



**Figure 1.** Schematic diagram showing how a 3-D network is constructed by 1-D chains. A rod indicates a 1-D coordination polymer. Dashed lines indicate hydrogen-bonding interactions between 1-D chains.

networks, the macrocyclic complex acts as a bifunctional building block involving coordination as well as interlayer hydrogen-bonding interactions to provide a three-dimensional structure.

Here, we report a new type of 3-D network  $[\text{Ni}(\text{C}_{12}\text{H}_{30}\text{N}_6\text{O}_2)(\text{C}_8\text{H}_4\text{O}_4)]_n \cdot 4n\text{H}_2\text{O}$  (**2**) which is self-assembled from an  $S = 0$  Ni(II) macrocyclic complex **1** and terephthalate dianion ( $\text{tp}^{2-}$ ). In the structure of **2**, 1-D chains are formed by **1** and  $\text{tp}^{2-}$  and they are packed like a plywood and linked together by the hydrogen-bonding interactions to give rise to a 3-D network (Figure 1). There are some multidimensional networks constructed by linear coordination polymers linked by the hydrogen-bonding interactions via the additional linkages or anions.<sup>20–22</sup> In the present work, however, 1-D coordination polymers are linked together, without any additional ligands or anions, by the hydrogen-bonding interactions between the pendent hydroxyl groups of the macrocycles belonging to one polymer chain and the secondary amines of the macrocycles belonging to the other polymer chain. In this report, we present X-ray structure and properties of the 3-D network constructed by the Ni(II) coordination polymer.

## Experimental Section

**Reagents.** All chemicals and solvents used in the syntheses were of reagent grade and were used without further purification. For the spectroscopic measurements, water was distilled and organic solvents were purified according to the literature methods.<sup>23</sup> The Ni(II) macrocyclic complex **1**,  $[\text{Ni}(\text{C}_{12}\text{H}_{30}\text{N}_6\text{O}_2)](\text{ClO}_4)_2$ , was prepared according to the literature procedure previously reported.<sup>24</sup>

**Measurements.** Infrared spectra were recorded with a Perkin-Elmer 2000 FT-IR spectrophotometer. Elemental analyses were performed by the analytical laboratory of Seoul National University. UV/vis diffuse reflectance spectra were recorded with a Cary 300 Bio UV/vis spectrophotometer. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were performed at a scan rate of 5 °C/min using a Rigaku Tas-100. X-ray powder diffraction (XRPD) data were recorded on a Mac Science M18XHF-22 diffractometer at 50 kV and 100 mA for Cu K $\alpha$  ( $\lambda = 1.54050 \text{ \AA}$ ) with a scan speed of 5°/min and a step size of 0.02° in  $2\theta$ .

- (1) Fujita, M.; Aoyagi, M.; Ibukuro, F.; Ogura, K.; Yamaguchi, K. *J. Am. Chem. Soc.* **1998**, *120*, 611.
- (2) Stang, P. J.; Persky, N. E.; J. Manna, *J. Am. Chem. Soc.* **1997**, *119*, 4777.
- (3) Ashton, P. R.; Collins, A. N.; Fyfe, M. C. T.; Menzer, S.; Stoddart, J. F.; Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 735.
- (4) Kusakawa, T.; Fujita, M. *J. Am. Chem. Soc.* **1999**, *121*, 1397.
- (5) Kahn, O.; Martinez, C. *Science* **1998**, *279*, 44.
- (6) Janiak, C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1431.
- (7) Endo, K.; Koike, T.; Sawaki, T.; Hayashida, O.; Masuda, H.; Aoyama, Y. *J. Am. Chem. Soc.* **1997**, *119*, 4117.
- (8) Li, H.; Eddaoudi, M.; Groy, T. L.; Yaghi, O. M. *J. Am. Chem. Soc.* **1998**, *120*, 8571.
- (9) Brunet, P.; Simard, M.; Wuest, J. D. *J. Am. Chem. Soc.* **1997**, *119*, 2737.
- (10) Yaghi, O. M.; Davis, C. E.; Li, G.; Li, H. *J. Am. Chem. Soc.* **1997**, *119*, 2861.
- (11) Yaghi, O. M.; Li, H.; Groy, T. L. *J. Am. Chem. Soc.* **1996**, *118*, 9096.
- (12) Subramanian, S.; Zaworotko, M. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2127.
- (13) Hennigar, T. L.; MacQuarrie, D. C.; Losier, P.; Rogers, R. D.; Zaworotko, M. J. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 972.
- (14) Harrison, W. T. A.; Hannooman, L. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 640.
- (15) Kondo, M.; Yoshitomi, T.; Seki, K.; Matsuzaka, H.; Kitagawa, S. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1725.
- (16) Hoskins, B. F.; Robson, R.; Slizys, D. A. *J. Am. Chem. Soc.* **1997**, *119*, 2952.
- (17) Choi, H. J.; Suh, M. P. *J. Am. Chem. Soc.* **1998**, *120*, 10622.
- (18) Choi, H. J.; Lee, T. S.; Suh, M. P. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 1405–1408.
- (19) Ferlay, S.; Mallah, T.; Vaissermann, J.; Bartolome, F.; Veillet, P.; Verdager, M. *Chem. Commun.* **1996**, *21*, 2481.

- (20) Carlucci, L.; Ciani, G.; Proserpio, D. M.; Sironi, A. *J. Chem. Soc., Dalton Trans.* **1997**, 1801.
- (21) Blake, A. J.; Hill, S. J.; Hubberstey, P.; Li, W.-S. *J. Chem. Soc., Dalton Trans.* **1997**, 913.
- (22) Kawata, S.; Kitagawa, S.; Kumagai, H.; Kudo, C.; Kamesaki, H.; Ishiyama, T.; Suzuki, R.; Kondo, M.; Katada, M. *Inorg. Chem.* **1996**, *35*, 4449.
- (23) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 4th ed.; Pergamon Press: Oxford, England, 1996.
- (24) Suh, M. P.; Shim, B. Y.; Yoon, T.-S. *Inorg. Chem.* **1994**, *33*, 5509.

**Table 1.** Crystallographic Data for  $[\text{Ni}(\text{C}_{12}\text{H}_{30}\text{N}_6\text{O}_2)(\text{C}_8\text{H}_4\text{O}_4)]_n \cdot 4n\text{H}_2\text{O}$ 

chem formula $\text{NiC}_{20}\text{H}_{42}\text{N}_6\text{O}_{10}$	fw 585.27
$a = 21.182(2) \text{ \AA}$	space group $C2/c$ (No. 15)
$b = 9.035(2) \text{ \AA}$	$T = 20 \text{ }^\circ\text{C}$
$c = 16.431(2) \text{ \AA}$	$\lambda = 0.71073 \text{ \AA}$
$\beta = 121.637(10)^\circ$	$\rho_{\text{calcd}} = 1.443 \text{ g cm}^{-3}$
$V = 2677.3(7) \text{ \AA}^3$	$\mu = 0.787 \text{ mm}^{-1}$
$Z = 4$	$R^a = 0.0486$
	$R_w(F^2)^b = 0.1045$

<sup>a</sup>  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$  for  $4\sigma(F)$  reflections. <sup>b</sup>  $R_w(F^2) = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$ , where  $w = 1/[\sigma^2(F_o^2) + (0.0559P)^2 + 0.0000P]$  and  $P = (F_o^2 + 2F_c^2)/3$  for  $4\sigma(F)$  reflections.

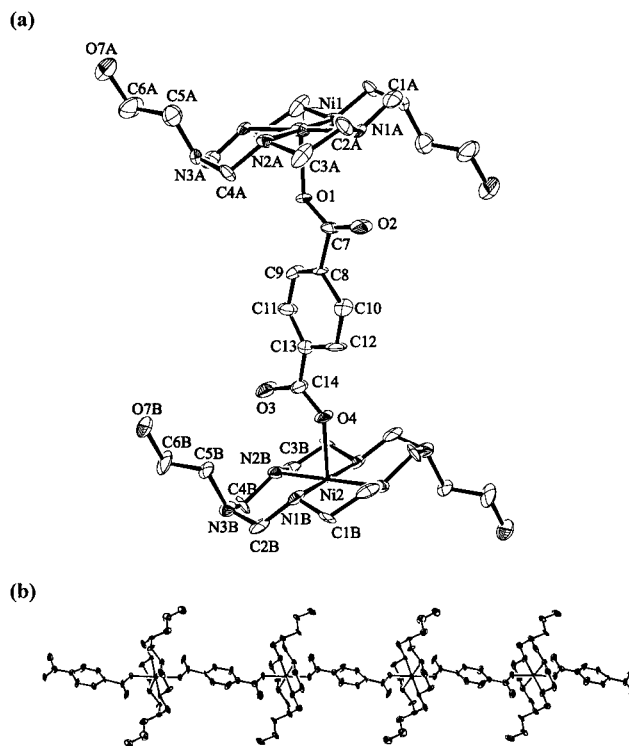
**Table 2.** Selected Bond Distances (Å) and Angles (deg) for  $[\text{Ni}(\text{C}_{12}\text{H}_{30}\text{N}_6\text{O}_2)(\text{C}_8\text{H}_4\text{O}_6)]_n \cdot 4n\text{H}_2\text{O}^a$ 

Ni1–N1A	2.062(7)	N2B–C4B	1.540(11)
Ni1–N2A	2.090(7)	C6B–O7B	1.420(12)
Ni1–O1	2.129(5)	O1–C7	1.249(10)
N1A–C1A	1.430(12)	O2–C7	1.243(12)
N1A–C2A	1.501(11)	O3–C14	1.282(13)
N2A–C4A	1.494(11)	O4–C14	1.247(10)
N2A–C3A	1.509(12)	C7–C8	1.532(10)
C6A–O7A	1.443(14)	C8–C9	1.368(13)
Ni2–N1B	2.013(8)	C8–C10	1.396(12)
Ni2–N2B	2.045(8)	C9–C11	1.351(12)
Ni2–O4	2.124(6)	C10–C12	1.418(12)
N1B–C1B	1.449(11)	C11–C13	1.393(13)
N1B–C2B	1.476(13)	C12–C13	1.397(14)
N2B–C3B	1.451(12)	C13–C14	1.482(13)
N1A–Ni1–N2A	87.9(3)	C4A–N2A–Ni1	111.5(6)
N1A–Ni1–O1	92.0(2)	C1A'–N3A–C4A	115.8(8)
N2A–Ni1–O1	91.1(2)	C1A'–N3A–C5A	117.1(8)
C1A–N1A–C2A	111.8(7)	C4A–N3A–C5A	113.2(9)
C1A–N1A–Ni1	117.9(6)	O7A–C6A–C5A	110.7(11)
C2A–N1A–Ni1	103.8(5)	N1B–Ni2–N2B	96.1(3)
C3A–N2A–Ni1	103.4(6)	N1B–Ni2–O4	92.0(3)
N2B–Ni2–O4	87.6(3)	O1–C7–C8	114.0(8)
C1B–N1B–Ni2	107.6(6)	C8–C10–C12	119.4(9)
C2B–N1B–Ni2	116.1(6)	C9–C8–C7	121.7(7)
C3B–N2B–Ni2	107.9(6)	C9–C8–C10	119.6(8)
C4B–N2B–Ni2	111.5(6)	C9–C11–C13	121.3(10)
C1B–N1B–C2B	110.2(7)	C10–C8–C7	118.1(8)
C3B–N2B–C4B	118.6(7)	C11–C9–C8	121.0(8)
C4B–N3B–C2B	114.7(8)	C11–C13–C12	118.8(9)
C4B–N3B–C5B	115.0(7)	C11–C13–C14	122.9(9)
C2B–N3B–C5B	111.3(8)	C12–C13–C14	117.7(9)
O7B–C6B–C5B	109.9(10)	C13–C12–C10	118.9(9)
C7–O1–Ni1	133.8(6)	O4–C14–O3	122.3(9)
C14–O4–Ni2	137.0(6)	O4–C14–C13	119.8(9)
O2–C7–O1	127.9(8)	O3–C14–C13	117.5(8)
O2–C7–C8	117.9(8)		

<sup>a</sup> Symmetry transformations used to generate equivalent atoms: prime,  $x, -y, z + 0.5$ .

**Synthesis.**  $[\text{Ni}(\text{C}_{12}\text{H}_{30}\text{N}_6\text{O}_2)(\text{C}_8\text{H}_4\text{O}_4)]_n \cdot 4n\text{H}_2\text{O}$  (**2**). To a stirred MeCN solution (50 mL) of **1** (0.353 g, 0.644 mmol) was added dropwise an aqueous solution (4 mL) of sodium terephthalate (0.136 g, 0.644 mmol) at room temperature. Pale purple crystals formed immediately, which were filtered off, washed with MeCN, and dried in vacuo. Single crystals for the X-ray diffraction studies were obtained by allowing the MeCN solution of **1** to diffuse into an aqueous solution of sodium terephthalate in a tube. Pale pink crystals formed at the water/MeCN interface within 1 week. Anal. Calcd for  $\text{NiC}_{20}\text{H}_{42}\text{N}_6\text{O}_{10}$ : C, 41.05; H, 7.23; N, 14.36. Found: C, 40.75; H, 7.28; N, 14.59. IR (Nujol mull,  $\text{cm}^{-1}$ ):  $\nu(\text{OH})$ , 3320 (br), 1644 (sh);  $\nu(\text{NH})$ , 3236, 3170;  $\nu(\text{COO})$ , 1563, 1376.

**Desolvated sample of 2,  $[\text{Ni}(\text{C}_{12}\text{H}_{30}\text{N}_6\text{O}_2)(\text{C}_8\text{H}_4\text{O}_4)]_n$  (**3**).** The microcrystalline sample of **2** was dried at 100 °C and 30 mmHg for 3 h. Anal. Calcd for  $\text{NiC}_{20}\text{H}_{34}\text{N}_6\text{O}_6$ : C, 46.81; H, 6.68; N, 16.38. Found: C, 45.81; H, 6.13; N, 16.16. IR (Nujol mull,  $\text{cm}^{-1}$ ):  $\nu(\text{OH})$ , 3320;  $\nu(\text{NH})$ , 3150;  $\nu(\text{COO})$ , 1580, 1363.



**Figure 2.** (a) ORTEP drawing of the asymmetric unit of **2** with atomic numbering scheme. Thermal ellipsoids are drawn with 30% probability. (b) 1-D coordination polymer assembled from **1** and  $\text{tp}^{2-}$ .

**X-ray Crystallography.** A single crystal was sealed in a glass capillary together with the mother liquor. X-ray data were collected at room temperature using graphite-monochromated Mo  $K\alpha$ -radiation on an Enraf-Nonius CAD4 diffractometer. The orientation matrix and unit cell parameters were determined from 25 machine-centered reflections with  $16^\circ < 2\theta < 25^\circ$ . Axial photographs were used to verify the unit cell choice. Data were corrected for Lorentz and polarization effects. No absorption correction was made. All calculations were carried out on a personal computer by using SHELXS-86<sup>25</sup> and SHELXL-93<sup>26</sup> programs. The structure was solved by the direct method. The refinement was performed on  $F^2$  for all reflections including those generally believed to be unobserved [ $F < 4\sigma(F)$ ]. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were positioned geometrically and refined using a riding model. The crystallographic data are summarized in Table 1, and the selected bond distances and angles are in Table 2.

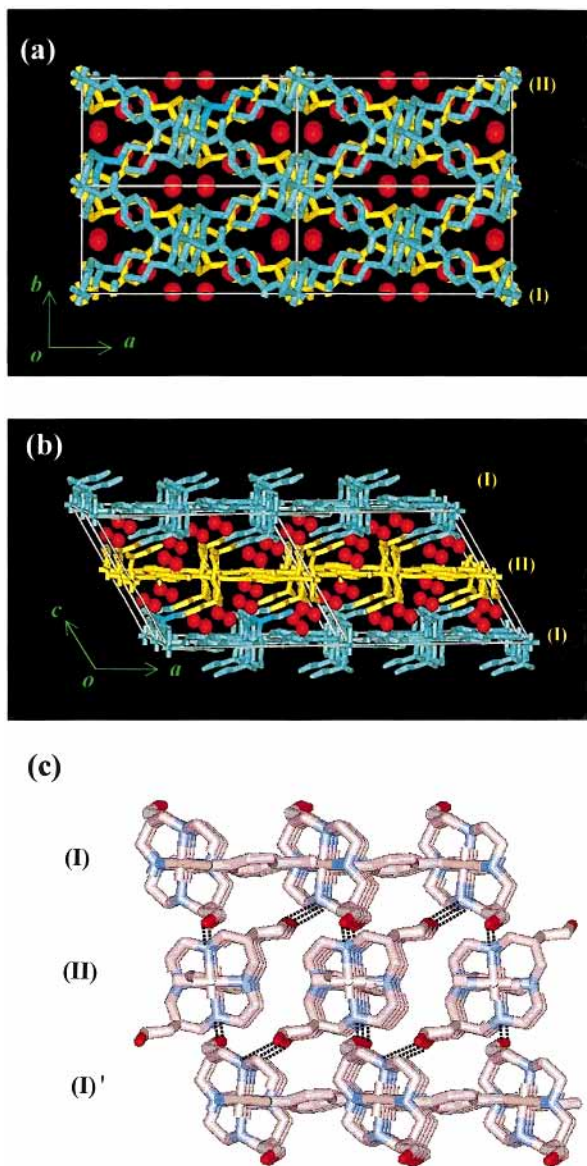
## Results and Discussion

**Crystal Structure of 2.** ORTEP view of the asymmetric unit of  $[\text{Ni}(\text{C}_{12}\text{H}_{30}\text{N}_6\text{O}_2)(\text{C}_8\text{H}_4\text{O}_4)]_n \cdot 4n\text{H}_2\text{O}$  is shown in Figure 2a.<sup>27</sup> Each Ni(II) ion of macrocyclic complex **1** is coordinated by two carboxylate oxygen atoms of  $\text{tp}^{2-}$  at the trans position to display a distorted octahedral coordination geometry. Each terephthalate dianion ( $\text{tp}^{2-}$ ) binds two metal ions in an *exo*-bidentate mode, which results in the linear coordination polymer (Figure 2b). The Ni–O(carboxylate) bond distance average is 2.127(4) Å, which is considerably longer than the Ni–N(macrocycle) bond distance of average 2.056(4) Å. The phenyl ring of terephthalate is perpendicular (dihedral angle = 89.95°) to the square coordination plane of the macrocycle. The  $\text{tp}^{2-}$  ligand is not planar since dihedral angles between two carbox-

(25) Sheldrick, G. M. *SHELXL86. Program for the Solution of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1986.

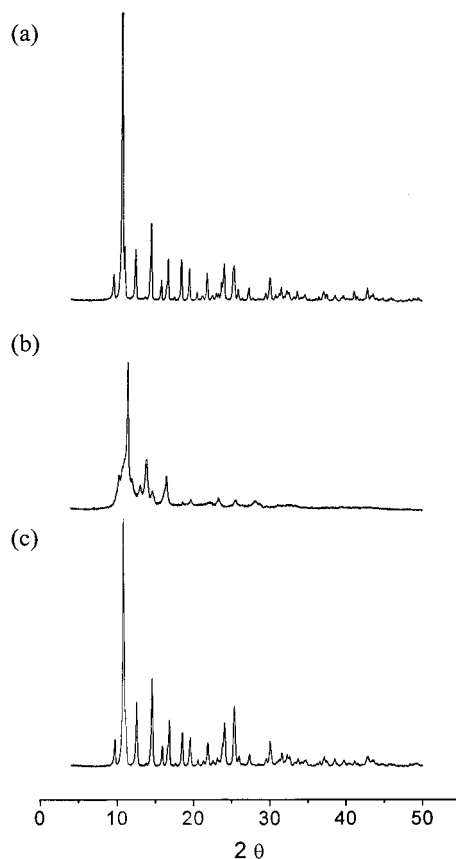
(26) Sheldrick, G. M. *SHELXL93. Program for the Refinement of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1993.

(27) Farrugia, L. J. *ORTEP 3 for Windows (V 1.01 beta)*; University of Glasgow: Glasgow G12 8QQ, Scotland, U.K., 1997.



**Figure 3.** Views of **2** in stick style: (a) *ab* plane; (b) *ac* plane. The two different series of 1-D chains are indicated as **I** (blue) and **II** (yellow). Water molecules included in the network are represented as red spheres in CPK style. (c) Hydrogen-bonding interactions (---) between **I** and **II**.

ylate groups and the benzene ring of the bridging  $tp^{2-}$  are  $12.08(1)$  and  $17.91(1)^\circ$ . The dihedral angles between the carboxylate plane and the macrocyclic coordination plane involving Ni(1) and Ni(2) are  $82.42(1)$  and  $88.04(1)^\circ$ , respectively. Intramolecular hydrogen-bonding interactions exist between the uncoordinated oxygen atoms of carboxylate and the secondary amines of macrocycle to form stable six-membered rings (O2---N1A =  $2.906(9)$  Å, O3---N2B =  $2.886(10)$  Å, O---H---N,  $151.2(2)^\circ$ ). In addition, the uncoordinated carboxylate oxygen atom forms a hydrogen bond with a lattice water molecule (O3---OW4#1 =  $2.829(13)$  Å).<sup>33</sup> Therefore, two C—O bond distances of the carboxylate group have little difference although one is coordinated (average  $1.248$  Å) and the other is uncoordinated (average  $1.263$  Å) to the Ni(II) ion. In general, coordinated C—O bond distances of carboxylate groups range  $1.266$ – $1.279$  Å which are longer than free carbonyl C—O bond distances of  $1.226$ – $1.255$  Å when terephthalate coordinates a metal ion in the monodentate fashion.<sup>28–32</sup> Within a linear chain, Ni—Ni is separated by  $11.514(1)$  Å.



**Figure 4.** XRPD patterns for (a) the original crystal **2**, (b) dried solid **3**, and (c) solid obtained by immersing **3** in water for 1 min.

There are two series of 1-D polymer chains extending toward different directions (Figure 3a,b). A series of 1-D nickel-terephthalate chains (**I**) extends along the  $[1\bar{1}0]$  direction and the other series (**II**) along the  $[110]$  direction. In each series, chains are separated by  $9.035$  Å, the same as the unit cell parameter *b*. The two series (**I** and **II**) of chains are alternately packed along *c* direction, separated by  $8.216$  Å as measured by the Ni—Ni distance. Two different series of chains (**I** and **II**) are interconnected each other, with an angle of  $46.2^\circ$ , by the hydrogen-bonding interactions between the secondary amines of macrocycles belonging to one series of chains and the hydroxyl pendent groups of the macrocycles belonging to the other series of chains (N1B---O7A#2 =  $2.947$  Å, N2A---O7B#3 =  $2.943$  Å, N—H---O,  $151.6(2)^\circ$ ),<sup>33</sup> and thus the whole structure becomes a 3-D network (Figure 3c). The lattice water molecules are placed in the framework cavities which are created by the two different series of chains. The void volume per unit cell is  $396$  Å<sup>3</sup> (14.8%) as estimated by PLATON.<sup>34</sup> The guest water molecules form hydrogen bonds with the hydroxyl groups of the macrocycle (O7B---OW4#1 =  $2.739$  Å, O7A---

- (28) Chaudhuri, P.; Oder, K.; Wiegart, K.; Gehring, S.; Haase, W.; Nuber, B.; Weiss, J. *J. Am. Chem. Soc.* **1988**, *110*, 3657.  
 (29) Verdaguer, M.; Gouteron, J.; Jeannin, S.; Jeannin, Y.; Kahn, O. *Inorg. Chem.* **1984**, *23*, 4291.  
 (30) Bakalbassis, E.; Bergerat, P.; Kahn, O.; Jeannin, S.; Jeannin, Y.; Dromzee, Y.; Guillot, M. *Inorg. Chem.* **1992**, *31*, 625.  
 (31) Xanthopoulos, C. E.; Sigalas, M. P.; Katsoulos, G. A.; Tshipis, C. A.; Terzis, A.; Mentzafos, M.; Hountas, A. *Inorg. Chem.* **1993**, *32*, 5423.  
 (32) Bakalbassis, E.; Bozopoulos, A. P.; Mrozinski, J.; Rentzeperis, P.; Tshipis, C. A. *Inorg. Chem.* **1988**, *27*, 529.  
 (33) Symmetry transformations used to generate equivalent atoms: #1, *x*, *y* + 1, *z*; #2,  $-x + 1$ , *y*,  $1/2 - z$ ; #3,  $-x + 1$ , *y* - 1,  $1/2 - z$ ; #4,  $-x$ , *y*,  $1/2 - z$ .  
 (34) Spek, A. L. *PLATON, A Multipurpose Crystallographic Tool*; Utrecht University: Utrecht, The Netherlands, 1999.

OW3#2 = 2.759 Å)<sup>33</sup> (Figure 3b) as well as between themselves (OW1- -OW1#4 = 2.781 Å, OW2- -OW2#2 = 2.756 Å).<sup>33</sup>

**Properties.** The compound **2** is stable and does not lose guest water molecules upon exposure to the atmosphere. It is insoluble in any organic solvents. However, it dissolves in warm water and decomposes into the building blocks as indicated by the color change from violet to yellow on dissolution. UV/vis spectrum measured for the aqueous solution of **2** shows  $\lambda_{\max}$  at 446 nm, which corresponds to the chromophore of macrocyclic complex **1**. The IR spectrum of **2** shows the stretching frequencies of the carboxylato group at 1563 and 1376  $\text{cm}^{-1}$ , which are characteristic for the  $\text{tp}^{2-}$  in the monodentate end-to-end bonding mode.<sup>32,35</sup> The electronic diffuse reflectance spectrum of the compound exhibits broad bands at 435 and 575 nm, corresponding to the d-d transitions of the six-coordinate Ni(II) complex.<sup>36</sup>

TGA data for the crystalline sample **2** indicated the loss of four water guest molecules per formula unit at 56–130 °C. The remaining compound was heated to 200 °C without any additional weight loss. DTA data showed a phase change upon the dehydration process. The crystals of **2** were dried according to the thermal analysis data, and the XRPD patterns of **2** and

its dried solid were compared (Figure 4). The dried solid obtained by heating the crystals of **2** at 100 °C and 30 mmHg for 12 h showed XRPD patterns in which the lines were broadened and their positions were changed compared with those of **2**. However, when the solid was suspended in water just for 1 min, the XRPD patterns same as those of the original crystal were regenerated. This indicates that the solid is able to bind water reversibly.

In conclusion, we have constructed a 3-D network by the self-assembly of Ni(II) macrocyclic complex and terephthalato organic bridge. In this structure, two series of one-dimensional chains extending toward different directions are interconnected by the hydrogen-bonding interactions using the hydroxyl pendant groups and secondary amines of the macrocycles and give rise to a 3-D network. The solid sample of **2** is able to bind water reversibly.

**Acknowledgment.** This work was supported by the Korea Science and Engineering Foundation (Grant 96-0501-03-01-3) and the Center for Molecular Catalysis.

**Supporting Information Available:** Figure S1 for TGA and DTA plots of  $[\text{Ni}(\text{C}_{12}\text{H}_{30}\text{N}_6\text{O}_2)(\text{C}_8\text{H}_4\text{O}_4)]_n \cdot 4n\text{H}_2\text{O}$  and an X-ray crystallographic file, in CIF format, for compound **2**. The material is available free of charge via the Internet at <http://pubs.acs.org>.

IC990664D

(35) Deacon, G. B.; Phillips, R. J. *Coord. Chem. Rev.* **1980**, *33*, 227.

(36) Melson, G. A., Ed. *Coordination Chemistry of Macrocyclic Compounds*; Plenum Press: New York, 1979; p 534.