

Two-Dimensional Nickel Coordination Polymers: Ni(OBC)(bipyen)]·H₂O and [Ni(NDC)(bipyen)(H₂O)] (NDC = 2,6-Naphthalenedicarboxylate; OBC = 4,4'-Oxybis(benzoate); bipyen = *trans*-1,2-Bis(4-pyridyl)ethylene)

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Hydrothermal reactions of Ni(NO₃)₂·6H₂O with *trans*-1,2-bis(4-pyridyl)ethylene (bipyen), in the presence of a linear 2,6-naphthalene dicarboxylic acid (NDCH₂) and a bent 4,4'-oxybis(benzoic acid) (OBCH₂), gave a 2-D coordination polymer [Ni(NDC)(bipyen)(H₂O)] (**1**) and also a 2-D coordination polymer [Ni(OBC)(bipyen)]·H₂O (**2**), respectively. A reversible de-coordination and re-coordination of an aqua ligand was observed for polymer **1**. Polymer **2** has an undulated 2-D network based on 50-membered rectangular grids, each of which has the dimension of 13.61 × 13.17 Å.

Key Words : De-coordination and re-coordination, An undulated 2-D network

Introduction

Studies of various zeolites with open frameworks have been extensively carried out so far.¹ Recently, coordination polymers as organic zeolite-like solids, based on transition metals and multifunctional organic ligands, have received considerable attraction.² In particular, research interests have been focused on porous high-dimensional coordination polymers due to their useful applications in physical gas adsorption, chemical adsorption, selective catalysis, and exchange.^{1a,3} The topology of coordination polymers is usually controlled and modified by carefully selecting the coordination geometry of a central metal and the coordination modes of organic ligands.^{3a,4} In this context, stereochemically rigid, multifunctional ligands and various bridging-ligand systems are now used in preparing 1-D chains, 2-D sheets, and 3-D infinite networks with desired shapes, sizes, and ultimately functions.⁵

Metal-dicarboxylate coordination polymers tend to form rigid frameworks due to the potential bidentate coordination of carboxylate groups. In particular, several research groups demonstrated the construction of highly porous polymers by employing linear dicarboxylates.^{3a,6} On the other hand, metal-bipyridyl coordination polymers have relatively flexible frameworks arising from the monodentate coordination of pyridyl groups.⁷ Recently, several synthetic strategies for novel coordination polymers employed mixed-ligand systems containing both carboxylates and pyridyls.^{4a,8} We have been continually interested in preparing coordination polymers with dicarboxylate, bipyridyl, or mixed-ligands by hydrothermal reactions.⁹ As a continuation of our research, we set out to prepare nickel coordination polymers from nickel(II) nitrate (Ni(NO₃)₂·6H₂O), bipyen, and dicarboxylate (NDCH₂ or OBCH₂) by hydrothermal reactions. Herein, we report the

preparation, crystal structures, and properties of two nickel coordination polymers [Ni(NDC)(bipyen)(H₂O)] (**1**) and [Ni(OBC)(bipyen)]·H₂O (**2**).

Experimental Section

Nickel(II) nitrate (Ni(NO₃)₂·6H₂O), 2,6-naphthalenedicarboxylic acid (NDCH₂), *trans*-1,2-bis(4-pyridyl)ethylene (bipyen), and 4,4'-oxybis(benzoic acid) (OBCH₂) were purchased from Aldrich company. IR spectra were recorded with a Nicolet 320 FTIR spectrophotometer. Elemental analyses were performed by the National Center for Inter-University Research Facilities. TGA analysis was conducted on a TA4000/SDT 2960 instrument. X-ray powder diffraction (XRPD) data were obtained with a Rigaku D/Max-RC diffractometer.

Preparation of [Ni(NDC)(bipyen)(H₂O)] (1**).** A mixture of Ni(NO₃)₂·6H₂O (0.134 g, 0.463 mmol), NDCH₂ (0.100 g, 0.463 mmol), bipyen (0.084 g, 0.463 mmol), and H₂O (6 mL) was heated in a 23-mL capacity Teflon-lined reaction vessel at 150 °C for 2 days, and then cooled to room temperature by air-cooling. The green crystalline product was collected by filtration, washed with H₂O (2 × 5 mL), ethanol (3 × 5 mL), and acetone (2 × 5 mL), and then air-dried to give [Ni(NDC)(bipyen)(H₂O)] (0.061 g, 0.129 mmol, 29.6%). Anal. Calcd for C₂₄H₁₈N₂O₅Ni: C, 60.93; H, 3.83; N, 5.92. Found: C, 60.71; H, 3.84; N, 5.82. IR (KBr): 3388, 3045, 1612, 1551, 1395, 1186, 1021, 955, 920, 799, 551 cm⁻¹.

Preparation of [Ni(OBC)(bipyen)]·H₂O (2**).** Polymer **2** was prepared similar to polymer **1**. A mixture of Ni(NO₃)₂·6H₂O (0.090 g, 0.310 mmol), OBCH₂ (0.080 g, 0.310 mmol), bipyen (0.056 g, 0.310 mmol), and H₂O (6 mL) was heated at 180 °C for 2 days to give [Ni(OBC)(bipyen)]·H₂O (0.074 g, 0.114 mmol, 46.4%). Anal. Calcd for C₂₆H₂₀N₂O₆Ni: C, 60.62; H, 3.91; N, 5.44. Found: C, 60.47; H, 3.94; N, 5.40. IR (KBr): 3457 (br), 3061, 1610, 1594, 1527, 1502,

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Table 1. X-ray data collection and structure refinement

	Polymer 1	Polymer 2
empirical formula	C ₂₄ H ₁₈ N ₂ O ₅ Ni	C ₂₆ H ₂₀ N ₂ O ₆ Ni
fw	473.11	515.15
temperature, K	293(2)	293(2)
crystal system	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
<i>a</i> , Å	7.622(2)	9.280(2)
<i>b</i> , Å	11.311(3)	11.317(4)
<i>c</i> , Å	14.001(3)	12.442(3)
α , deg	94.78(1)	69.66(2)
β , deg	104.00(2)	80.44(2)
γ , deg	91.32(2)	87.99(2)
<i>V</i> , Å ³	1165.9(4)	1207.8(5)
<i>Z</i>	2	2
<i>d</i> _{calc} , g cm ⁻³	1.348	1.416
μ , mm ⁻¹	0.868	0.847
<i>F</i> (000)	488	532
2 θ range (°)	3.5–50	3.5–50
scan type	ω	ω
scan speed	variable	variable
No. of reflns measured	4406	4447
No. of reflns unique	4073	4168
No. of reflns with <i>I</i> > 2 σ (<i>I</i>)	2981	3645
No. of params refined	298	396
Max., in $\Delta\rho$ (e Å ⁻³)	0.743	0.344
Min., in $\Delta\rho$ (e Å ⁻³)	-0.474	-0.274
<i>GOF</i> on <i>F</i> ²	1.019	1.040
<i>R</i>	0.0540	0.0346
<i>wR</i> ₂ ^a	0.1137	0.0846

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

1415, 1227, 1164, 1018, 981, 876, 838, 776, 656, 553 cm⁻¹.

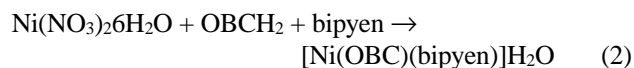
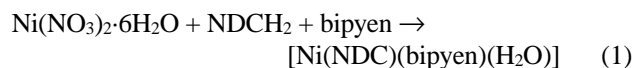
Structure determination. All X-ray data were collected with a Siemens P4 diffractometer equipped with a Mo X-ray tube. Intensity data were empirically corrected for absorption with Ψ -scan data. All calculations were carried out with the use of the SHELXTL programs.¹⁰ All structures were solved by direct methods. Both crystals belong to the triclinic system, and structure analyses converged in the centro-

symmetric space group $P\bar{1}$. All non-hydrogen atoms were refined anisotropically.

A green crystal of **1**, shaped as a rod of approximate dimensions of 0.20 × 0.12 × 0.10 mm, was used for crystal- and intensity-data collection. The hydrogen atoms in the aqua ligand were located in the difference Fourier map and refined isotropically. The remaining hydrogen atoms were generated in ideal positions and refined in a riding mode. A yellow-green crystal of **2**, shaped as a block of approximate dimensions of 0.32 × 0.28 × 0.20 mm, was used. The hydrogen atoms in the co-crystallized water were located. Details on crystal data and refinement details are given in Table 1. Selected bond lengths and bond angles are given in Table 2.

Results and Discussion

Preparation. Compounds have been prepared by hydrothermal reactions. Ni(NO₃)₂·6H₂O reacts with a linear dicarboxylic acid NDCH₂ (coordination angle = 180°) at 150 °C for 2 days in the presence of bipyen to give a 2-D nickel coordination polymer with an empirical formula of [Ni(NDC)(bipyen)(H₂O)] (**1**) (eq. 1). We have decided to employ a bent dicarboxylic acid OBCH₂ (coordination angle = 115°) in place of NDCH₂ to examine the change in topology of the resulting polymer. The hydrothermal reaction of Ni(NO₃)₂·6H₂O with OBCH₂ in presence of bipyen leads to a 2-D coordination polymer [Ni(OBC)(bipyen)]·H₂O (**2**) (eq. 2).



Polymers **1** and **2** have been obtained as green and yellow-green crystals, respectively. Both polymers are stable in air and insoluble in common organic solvents. These products have been characterized by elemental analysis, IR spectroscopy, X-ray powder diffraction (XRPD), thermal gravimetric analysis (TGA), and X-ray crystallography. The IR spectra of both polymers display absorption bands characteristic of

Table 2. Selected bond lengths (Å) and bond angles (°)

Polymer 1					
Ni1–O1	2.030(3)	Ni1–O5	2.078(3)	Ni1–N1	2.080(3)
Ni1–N2	2.083(4)	Ni1–O4	2.125(3)	Ni1–O3	2.170(3)
O1–Ni1–O5	89.5(1)	O1–Ni1–N1	94.9(1)	O5–Ni1–N1	94.1(1)
O1–Ni1–N2	90.9(1)	O5–Ni1–N2	177.5(1)	N1–Ni1–N2	88.3(1)
N2–Ni1–O4	92.9(1)	O1–Ni1–O3	103.6(1)	O5–Ni1–O3	87.7(1)
Polymer 2					
Ni1–O1	2.019(9)	Ni1–N1	2.052(2)	Ni1–N2	2.065(2)
Ni1–O2	2.275(2)	Ni1–O4#1	2.079(2)	Ni1–O3#1	2.160(2)
O1–Ni1–N1	94.65(8)	O1–Ni1–N2	107.44(8)	N1–Ni1–N2	96.90(8)
O1–Ni1–O2	61.03(7)	N1–Ni1–O2	155.68(7)	N2–Ni1–O2	91.50(8)
O1–Ni1–O4#1	157.56(7)	N1–Ni1–O4#1	97.04(8)	O1–Ni1–O3#1	97.61(7)

Symmetry transformations used to generate equivalent atoms: #1 = *x*, *y* – 1, *z* + 1.

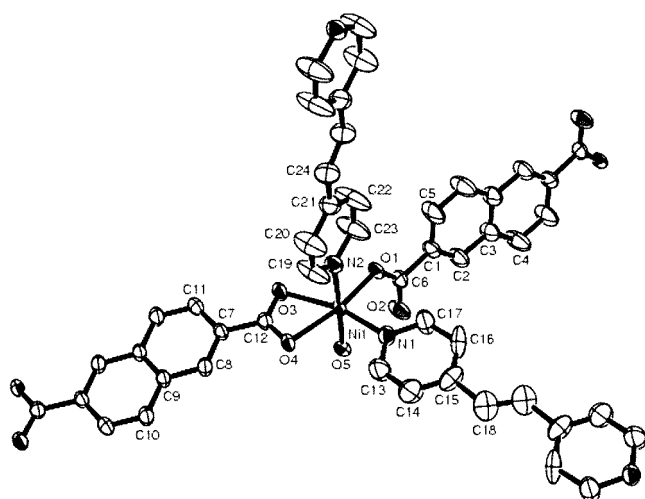


Figure 1. ORTEP drawing of the local coordination environment of Ni of polymer **1**, showing the atom-labeling scheme and 50% probability thermal ellipsoids. Unlabeled atoms are related to labeled atoms by the crystallographic inversion center.

carboxylate groups at 1681-1395 cm^{-1} .

Structure. The local coordination environment of the Ni metal in polymer **1** is shown in Figure 1. A monomer unit in polymer **1** consists of one Ni(II) metal, one dianionic NDC ligand, one bipen ligand, and one aqua ligand. The nickel metal has an octahedral geometry whose equatorial plane consists of oxygen atoms (O1, O3 and O4) from the carboxylate groups of NDC and one nitrogen atom (N1) from bipen. The axial positions are occupied by an aqua oxygen and a bipen nitrogen.

In polymer **1**, the Ni-N and Ni-O bond lengths are 2.080(3)-2.083(4) and 2.030(3)-2.170(3) Å, respectively. Two carboxylate groups of NDC are distinct in coordination modes. One carboxylate group of NDC acts as a chelating bidentate ligand, and the other carboxylate group acts as a monodentate ligand, leaving one oxygen (O2) uncoordinated. The NDC and one bipen link the nickel metals in the *bc*-plane to give one-dimensional double chains, which are linked by the other bipen in the *a*-axis direction to form an infinite 2-dimensional network (Figure 2). The hydrogen atoms in the aqua ligand are involved in intermolecular and intramolecular O-H...O hydrogen bonds: intermolecular H-bond, O5-HO5A = 0.736 Å, O5...O4 = 2.805 Å, HO5A...O4 = 2.094 Å, and O5-HO5A...O4 = 162.41°; intramolecular H-bond, O5-HO5B = 1.109 Å, O5...O2 = 2.573 Å, HO5B...O2 = 1.502 Å, and O5-HO5B...O2 = 160.33°.

Several attempts to enhance the dimensionality of a low-dimensional coordination polymer have recently appeared in the literature.^{16,11} For example, Li and co-workers reported the effect of pH on the dimensionality of coordination polymers.^{11a} In this context, we have tried to prevent the coordination of water to polymer **1** by adding a base (KOH, pyridine, or triethylamine) to the reaction mixture, which is expected to promote the deprotonation of NDCH₂ carboxylate groups and therefore to promote the coordination of both carboxylate groups to the Ni metal. Unfortunately,

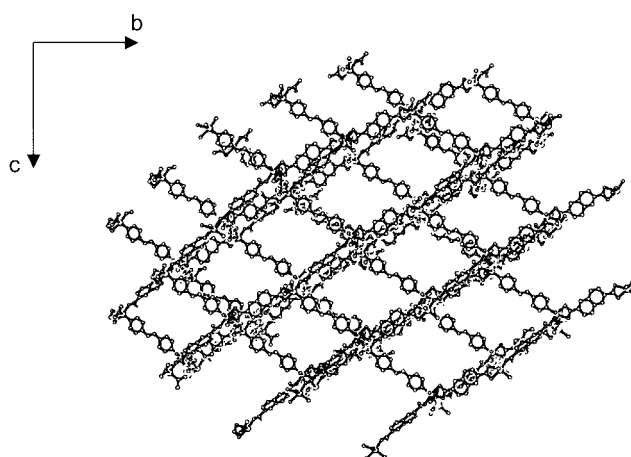


Figure 2. A perspective view of polymer **1** along the *a*-axis.

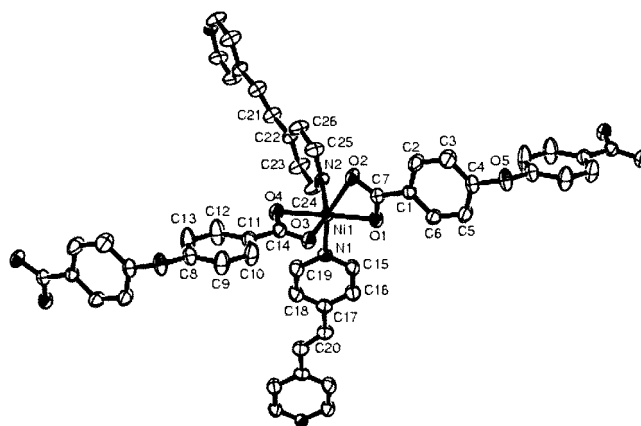


Figure 3. ORTEP drawing of the local coordination environment of Ni of polymer **2**.

raising the pH values brought about only the decomposition of products.

A monomer unit of polymer **2** is shown in Figure 3. The coordination sphere of nickel can be described as a distorted octahedron, which consists of four carboxylate oxygens (O1-O4) and two bipen nitrogens (N1 and N2). The Ni-N and Ni-O bond lengths are 2.080(3)-2.083(4) and 2.030(3)-2.170(3) Å, respectively. As expected, two benzene rings in the OBC are mutually perpendicular with a dihedral angle of 84.9°, reflecting the sp^3 -hybrid of the OBC oxygen (O5). One hydrogen in the co-crystallized water forms an intramolecular O-H...O hydrogen bond with the carboxylate oxygen (O2): O6-H = 1.052 Å, O6...O2 = 3.181 Å, H...O2 = 2.183, and O6-H...O2 = 157.62°.

The *a*-axis projection of polymer **2** is shown in Figure 4a, which illustrates a two-dimensional network. The bipen and OBC ligands separately link Ni metals to form one-dimensional layers, ultimately forming an undulated 2-D network based on 50-membered rectangular grids, each of which is composed of four nickel metals as the corners and two NDC and OBC ligands as the edges (Figure 4b). On the basis of Ni...Ni separations, the dimension of the rectangular unit can be calculated to be 13.61 × 13.17 Å. Although many

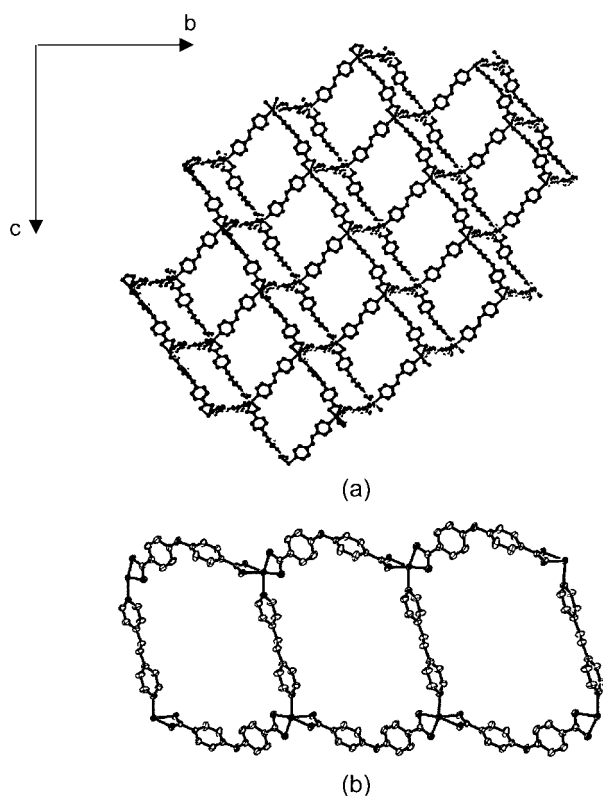
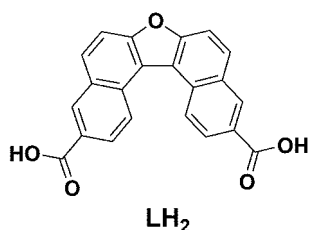


Figure 4. (a) An undulated 2-D structure of polymer 2; (b) a 50-membered rectangular repeating unit.

square-grid coordination polymers are now well known, their rectangular counterparts are rare.^{11b} There are currently three general synthetic strategies to prepare non-interpenetrating rectangular-grid coordination polymers with large pores or channels: (1) the use of bipyridine-type ligands of different lengths,¹² (2) the use of a mixed-ligand system of dicarboxylate and bipyridyl,¹³ and (3) the modification of the ligand to affect the shape of the grid.¹⁴ Our synthetic strategy employed a mixed-ligand system of bipyen and OBC, and a non-interpenetrating rectangular-grid coordination polymer (2) could be prepared.

Recently, both Yaghi's group and Zoworotko's group independently employed 1,3-benzenedicarboxylate, a bent dicarboxylate with a coordination angle of 120°, to prepare discrete nanometer-sized polygons or extended coordination networks.¹⁵ More recently, Lin and co-workers prepared a novel rigid, bent dicarboxylic acid (coordination angle \approx 90°), 7-oxa-dibenzofluorene-3,11-dicarboxylic acid (LH₂), and employed this ligand for the self-assembly of a nano-



meter-sized copper(II) molecular rectangle $\{[\text{Cu}_4\text{L}_4(\text{py})_8] \cdot 2(\text{DMF})\}$ and a 1-D cobalt(II) coordination polymer with large open channels $\{[\text{Co}_2\text{L}_2(\text{py})_4] \cdot 2(\text{DMF}) \cdot 2(\text{H}_2\text{O})\}$.¹⁶ Compared to the Lin's system, our system contains another linking ligand (bipyen) in addition to a bent dicarboxylate (OBC) and therefore produces a 2-D polymer based on the rectangular unit instead of a molecular rectangle.

Properties. TGA of polymer 1 shows the first weight loss from 110 to 130 °C due to the liberation of the aqua ligand (observed, 4.1%; calculated, 3.8%). In the temperature range of 290–470 °C, polymer 1 exhibits two weight-loss steps, and above 470 °C it decomposes completely. Polymer 2 shows practically the same TGA pattern as polymer 1, although in a less distinct fashion. Polymer 2 exhibits the first weight loss between 105 and 140 °C, corresponding to the liberation of a free water molecule (observed, 5.8%; calculated, 3.5%), and above 280 °C it also exhibits two weight-loss steps. Phase purities of both polymers have been confirmed by XRPD patterns of their bulk samples, which are consistent with the theoretical patterns generated from their single-crystal X-ray diffraction data.

A reversible dehydration-rehydration process, or a (de-coordination)-(re-coordination) of an aqua ligand, is observed for polymer 1. Dehydration of 1 could be achieved either by placing its crystals under vacuum for 12 h or by heating them up at 250 °C for 4 h. The dehydration process was monitored by observing the disappearance of the IR absorption band of the aqua ligand at 3388 cm^{-1} . The XRPD pattern of the dehydrated crystals (Figure 5b) shows nearly the same peaks as those of the original crystal (Figure 5a) without any noticeable change in 2θ values. These results suggest that the dehydrated form of 1 retains the framework of its original form. In order to examine whether the original form of 1 can be restored, we rehydrated the dehydrated crystals by placing them under saturated water vapor for 1 day, allowing water molecules to enter the dehydrated crystals. The rehydrated crystals exhibit the XRPD pattern (Figure 5c) practically identical to that of the original crystals (Figure 5a), which strongly suggests that the entering water molecule occupies the original position of the

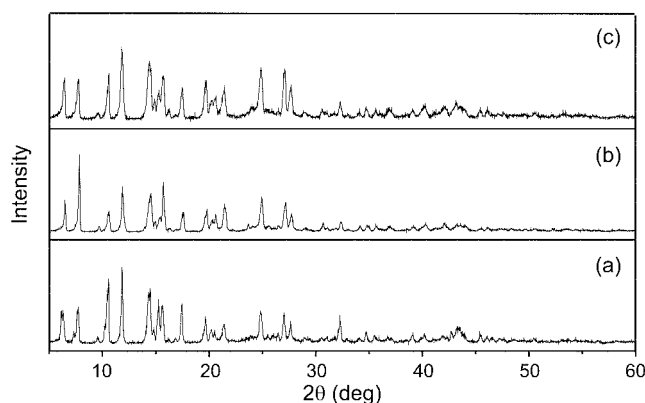


Figure 5. XRPD patterns of 1: (a) original crystals; (b) dehydrated crystals; (c) rehydrated crystals.

aqua ligand. Whereas the removal of guest water molecules without the collapse of a host framework is sometimes observed, the reversible (de-coordination)-(re-coordination) of the aqua ligand is relatively rare.¹⁷ We also investigated this type of process by placing the dehydrated crystals of polymer **1** under saturated methanol or CH₃CN vapor for one week, but we could not observe any sign of the coordination of these small molecules.

In summary, two nickel coordination polymers, [Ni(NDC)-(bipyen)(H₂O)] and [Ni(OBC)(bipyen)]·H₂O, have been prepared by hydrothermal reactions. X-ray structure analysis of both polymers revealed that the dimensionality depends on the coordination angle of dicarboxylate. Polymer **1**, which contains an aqua ligand, exhibited a reversible dehydration-rehydration behavior. Polymer **2** has an undulated 2-D network based on 50-membered rectangular grids, each of which has the dimension of 13.61 × 13.17 Å.

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Supplementary material. Crystallographic data for the structural analysis have been deposited at the Cambridge Crystallographic Data Center, CCDC No. 203968 for compound **1** and 203969 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: +44-1223-336-033; email: deposit@ccdc.cam.ac.uk or [www:http://www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk)).

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