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Coordination geometry induced control of channel morphology in divalent metal pyridinedicarboxylate coordination polymers containing a kinked tethering organodiimine

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Abstract

Hydrothermal synthesis has afforded two divalent metal coordination polymers incorporating tridentate 2,6-pyridinedicarboxylate (PDC) ligands and the kinked dipodal organodiimine 4,4'-dipyridylamine (dpa), {[Ni(PDC)(dpa)(H₂O)] · 2H₂O} (1) and {[Zn(PDC)(dpa)] · 3H₂O} (2), which were characterized by single crystal X-ray diffraction and spectral and thermogravimetric analyses. Although both 1 and 2 display one-dimensional (1-D) polymeric chain motifs, the different coordination environments (octahedral in 1, distorted square pyramidal in 2) provoke divergence in the structures and aggregations of the chain subunits. Compound 1 manifests both polycatenation and interdigitation of its 1-D polymeric chains, while 2 exhibits only interdigitation, resulting in widely disparate morphologies for water molecule-bearing channels within the extended structures. Compound 1 possesses three distinct channel types occupied by isolated water molecules. Compound 2 presents only one type of channel, larger than those in 1, filled with D(5) discrete-chain water molecule aggregations. In both cases the co-crystallized water molecules are anchored to the coordination polymer matrix by hydrogen bonding involving PDC carboxylate oxygen atoms and the central amine unit of the dpa ligands. These supramolecular interactions are crucial for stability, as 1 and 2 both undergo irreversible loss of crystallinity upon dehydration. © 2007 Elsevier B.V. All rights reserved.

Keywords: Hydrothermal synthesis; Crystal structure; Coordination polymer; Dipyridylamine; Pyridinedicarboxylate; Water chain

1. Introduction

There has been substantial recent interest in hydrogenbonded water molecule aggregations in the development of a deeper understanding of the "anomalous" properties of water [1]. This effort is driven in part by the important role of these groupings in aqueous transport *in vivo* [2], for instance through the pores in the cell membrane protein aquaporin-1 [2b]. A highly effective approach to the isolation of water molecule aggregations has involved their stabilization within coordination polymer matrices [3], taking advantage of hydrogen bonding pathways provided by oxo-

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anion, aquo, or carboxylate ligands. The very large scope of coordination polymer morphologies has therefore resulted in many unique "container" environments for supramolecular water molecule tetramers [3a,3b], hexamers [3c,3d,3e,3f,3g,3h,3i,3j], octamers [3k,3l,3m], decamers [3n], helices [3o] and nanotubular pipes [3p,3q]. Subtle variances within a system of related coordination polymers can instigate very large structural differences in the water molecule aggregations [4]. For instance, 1-D water molecule tapes based on tetrameric units exist within channels in the structure of the 1-D coordination polymer [Cu(2,4'-bpy)_4SO₄] · $6H_2O$ (2,4'-bpy = 2,4'-bipyridine). Removal of a hydrogen bonding acceptor atom from the pendant ligand causes formation of discrete acyclic water molecule clusters within incipient voids in the analogous 1-D chain coordination

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polymer $[Cu(4-phpyr)_4SO_4] \cdot 5H_2O$ (4-phpyr = 4-phenyl-pyridine) [4].

For some time our research group has been investigating the synthesis and characterization of coordination polymers containing the kinked dipodal organodiimine 4,4'-dipyridylamine (dpa). In contrast to the more commonly used 4,4'bipyridine, dpa possesses a hydrogen bonding point of contact at its central amine functional group. Thus, in addition to serving as a tethering ligand, dpa can engage in strong supramolecular interactions and potentially anchor uncoordinated water molecules. Hydrothermal treatment of dpa with transition metal salts and dicarboxylate anion or polyoxometallate sources has to date afforded several coordination polymers with diverse structural motifs [5-7]. For example, { $[Co_2(phthalate)_2(dpa)_2(H_2O)_4] \cdot H_2O$ } forms 1-D coordination polymer chains that encapsulate co-crystallized water molecules [5], [Mo₄O₁₃(Hdpa)₂] possesses unprecedented interdigitated 1-D molybdate ribbons that can intercalate primary and secondary amines [6], and [NiMoO₄(dpa)₂] has a "starburst" 3-D structure formed by the linkage of cationic $[Ni(dpa)_2]^{2n+}$ layers through molybdate tetrahedra [7]. Hanton and co-workers have extended the coordination chemistry of dpa into monovalent silver oxoanion and divalent cadmium oxoanion and thiocyanate coordination polymer systems, revealing the ability of dpa to impart chirality via torsion around its central kink [8].

We report here the hydrothermal synthesis and characterization of the first pyridinedicarboxylate coordination polymers to incorporate the dpa ligand, {[Ni(PDC)(dpa)- (H_2O)] · 2H₂O} (1) and {[Zn(PDC)(dpa)] · 3H₂O} (2), where PDC = 2,6-pyridinecarboxylate. Both new compounds display 1-D coordination polymer chains, albeit with significant differences in their morphologies and aggregations dictated by the coordination environment at the metal, resulting in differing 1-D channels occupied by uncoordinated water molecules. Three distinct types of isolated water molecule-bearing channels of different size course through the structure of 1. On the other hand, 2 manifests one type of larger channel morphology that contains discrete water molecule chains. In both cases, the supramolecular interactions provided by the dpa ligand to the uncoordinated water molecules are critical to coordination polymer stability.

2. Experimental

2.1. General considerations

Metal chlorides were obtained from Fisher, and 2,6pyridinedicarboxylic acid was purchased from Aldrich. 4,4'-Dipyridylamine (dpa) was prepared via a published procedure [6]. Water was deionized above 3 M Ω in-house. Thermogravimetric analysis was performed on a TA Instruments TGA 2050 Thermogravimetric Analyzer with a heating rate of 10 °C/min up to 900 °C. Elemental Analysis was carried out using a Perkin–Elmer 2400 Series II CHNS/O Analyzer. Analyses of **2** gave varying results due to differing levels of dehydration. IR spectra were recorded on powdered samples using a Perkin–Elmer Spectrum One instrument. Powder X-ray diffraction experiments were performed on a Rigaku Rotaflex instrument using θ – 2θ scans.

2.2. Preparation of $\{[Ni(PDC)(dpa)(H_2O)] \cdot 2H_2O\}$ (1)

NiCl₂ · 6H₂O (131 mg, 0.55 mmol), dpa (96 mg, 0.55 mmol) and 2,6-pyridinedicarboxylic acid (92 mg, 0.55 mmol), were placed into 10 mL distilled H₂O in a 23 mL Teflon-lined Parr acid digestion bomb. The bomb was sealed and heated at 150 °C for 48 h, whereupon it was cooled slowly to 25 °C. Very large blue blocks of **1** (90 mg, 35% yield based on Ni) were isolated after washing with distilled water, ethanol, and acetone and drying in air. *Anal.* Calc. for $C_{17}H_{19}N_4NiO_7$ **1**: C, 45.47; H, 4.04; N, 12.48. Found: C, 45.09; H, 4.08; N, 12.54%. IR (cm⁻¹): 3170 w br, 1622 m, 1587 s, 1518 s, 1486 m, 1431 w, 1375 m, 1350 s, 1276 w, 1208 s, 1179 w, 1072 w, 1057 w, 1023 m, 1016 m, 918 w, 906 w, 844 w, 820 m, 768 m, 731 m, 693 m, 675 m.

2.3. Preparation of $\{[Zn(PDC)(dpa)] \cdot 3 H_2O\}$ (2)

An identical preparative procedure to that for **1** was followed, with the substitution of ZnCl_2 (75 mg, 0.55 mmol) for NiCl₂ · 6H₂O. Straw-colored blocks of **2** (80 mg, 32% yield based on Zn) were obtained. *Anal.* Calc. for C₁₇H₁₈N₄O₇Zn (with loss of one H₂O) **2**: C, 46.67; H, 3.68; N, 12.80. Found: C, 46.26; H, 4.21; N, 13.31%. IR (cm⁻¹): 3200 w br, 1627 m, 1592 s, 1519 m, 1488 w, 1451 w, 1435 w, 1346 s, 1277 m, 1210 s, 1183 w, 1078 w, 1062 m, 1027 s, 911 w, 852 w, 821 s, 756 m, 729 s, 686 w, 673 w.

2.4. X-ray crystallography

A blue fragment of 1 (with dimensions $0.35 \text{ mm} \times$ $0.30 \text{ mm} \times 0.30 \text{ mm}$) cleaved from a larger crystal and a straw-colored block of 2 ($0.36 \text{ mm} \times 0.26 \text{ mm} \times 0.24 \text{ mm}$) were subjected to single crystal X-ray diffraction using a Bruker-AXS SMART 1k CCD instrument. Reflection data was acquired using graphite-monochromated Mo Ka radiation $(\lambda = 0.71073 \text{ Å})$. The data was integrated via SAINT [9]. Lorentz and polarization effect and empirical absorption corrections were applied with SADABS [10]. The structures were solved using direct methods and refined on F^2 using SHELXTL [11]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms bound to carbon atoms were placed in calculated positions and refined isotropically with a riding model. The hydrogen atoms bound to the central nitrogen of the dpa moieties and any water molecules (except for O3W in 1 and 2) were found via Fourier difference maps, then restrained at fixed positions and refined isotropically. Relevant crystallographic data for 1 and 2 is listed in Table 1.

Table 1 Crystal and structure refinement data for **1** and **2**

Data	1	2	
Empirical formula	C ₁₇ H ₁₈ N ₄ NiO ₇	C ₁₇ H ₁₈ N ₄ O ₇ Zn	
Formula weight	449.06	455.74	
Collection $T(\mathbf{K})$	173(2)	173(2)	
λ (Å)	0.71073	0.71073	
Crystal system	orthorhombic	triclinic	
Space group	Ccc2	$P\overline{1}$	
a (Å)	15.849(5)	9.3476(15)	
b (Å)	24.720(8)	9.3569(15)	
<i>c</i> (Å)	9.905(3)	11.4693(18)	
α (°)	90	94.826(2)	
β (°)	90	98.196(2)	
γ (°)	90	107.202(2)	
$V(\text{\AA}^3)$	3881(2)	940.0(3)	
Ζ	8	2	
$D_{\rm calc} ({\rm g}{\rm cm}^{-3})$	1.534	1.610	
$\mu (\mathrm{mm}^{-1})$	1.048	1.356	
Minimum/maximum T	0.7106/0.7440	0.6410/0.7367	
hkl ranges	$-20 \leqslant h \leqslant 20$,	$-11 \leqslant h \leqslant 12$,	
	$-32 \leqslant k \leqslant 32$,	$-12 \leq k \leq 12$,	
	$-12 \leqslant l \leqslant 12$	$-15 \leq l \leq 15$	
Total reflections	21080	11359	
Unique reflections	4473	4443	
R _{int}	0.0372	0.0222	
Parameters/restraints	285/9	286/7	
R_1 (all data)	0.0480	0.0437	
$R_1 (I > 2\sigma(I))$	0.0342	0.0429	
wR_2 (all data)	0.0978	0.1116	
$wR_2 (I > 2\sigma(I))$	0.0909	0.1112	
Maximum/minimum residual $(e^{-}/Å^{3})$	0.510/-0.222	0.887/-0.508	
Goodness-of-fit	1.058	1.298	

3. Results and discussion

3.1. Synthesis and spectral characterization

Compounds 1 and 2 were prepared cleanly as single phase crystalline products under hydrothermal conditions

via combination of the appropriate metal chloride, 4,4'dipyridylamine, and 2,6-pyridinedicarboxylic acid. The infrared spectra of 1 and 2 were fully consistent with their formulations. Sharp, medium intensity bands in the range of $\sim 1600 \text{ cm}^{-1}$ to $\sim 1200 \text{ cm}^{-1}$ correspond to stretching modes of the pyridyl rings of the dpa and PDC moieties [12]. Features corresponding to ring puckering exist in the region between 820 cm^{-1} and 600 cm^{-1} . Asymmetric and symmetric C-O stretching modes of the fully deprotonated, ligated PDC molecules were evidenced by very strong, slightly broadened bands at $\sim 1590 \text{ cm}^{-1}$ and \sim 1350 cm⁻¹, respectively. The 240 cm⁻¹ difference between these two bands is consistent with monodentate binding of each carboxylate terminus within the PDC ligands [13]. Broad bands in the region of \sim 3400 cm⁻¹ to \sim 3200 cm⁻¹ in all cases represent N-H stretching modes within the dpa ligands and O-H stretching modes within the water molecules of crystallization in 1 and 2, and the aquo ligand in 1. The broadness of these latter spectral features is caused by significant hydrogen bonding pathways in both cases, which is described in detail below.

3.2. Structural description of $\{[Ni(PDC)(dpa)(H_2O)] \cdot 2H_2O\}$ (1)

X-ray diffraction revealed that 1 crystallized in the noncentrosymmetric orthorhombic space group *Ccc2*, with a Flack parameter [14] of 0.011 indicating high enantiopurity within the crystal. The asymmetric unit of 1 (shown in Fig. 1) consists of a divalent nickel atom with a distorted octahedral [NiN₃O₃] coordination sphere, one PDC ligand, one dpa ligand, one aquo ligand and a sum total of two full water molecules of crystallization, one of which (O1W) lies on a crystallographic twofold rotation axis. The oxygen atom with the uncoordinated water molecule represented



Fig. 1. Asymmetric unit of 1, with thermal ellipsoids at 50% probability and atom numbering scheme. Most hydrogen atoms and all water molecules of crystallization have been omitted for clarity.

Table 2 Selected bond distance (Å) and angle (°) data for **1**

beleeted bolld dist	anee (11) and angle		
Nil-N4	1.980(3)	N3 ^{#1} -Ni1-N1	92.93(10)
Ni1-N3 ^{#1}	2.055(3)	O5-Ni1-N1	174.06(11)
Ni1–O5	2.097(2)	N4-Ni1-O4	77.06(10)
Nil-Nl	2.101(3)	N3 ^{#1} -Ni1-O4	100.71(10)
Ni1–O4	2.143(2)	O5-Ni1-O4	88.25(11)
Ni1–O3	2.151(2)	N1-Ni1-O4	92.41(9)
C16-O1	1.225(4)	N4-Ni1-O3	77.47(10)
C17–O2	1.234(5)	N3 ^{#1} -Ni1-O3	104.35(10)
C17–O3	1.266(5)	O5-Ni1-O3	91.06(11)
C16-O4	1.271(4)	N1-Ni1-O3	90.87(10)
		O4-Ni1-O3	154.52(10)
N4–Ni1– N3 ^{#1}	170.73(10)	O4-C16-O1	126.0(3)
N4–Ni1–O5	89.76(10)	O2-C17-O3	127.0(3)
N3 ^{#1} -Ni1-O5	81.15(10)		
N4–Ni1–N1	96.14(10)		

Symmetry transformation to generate equivalent atoms: #1 x - 1/2, -y + 1/2, z + 1/2.

by O3W is best refined with half occupancy. Two *cis*-disposed nitrogen donors belong to two different dpa ligands, while the third nitrogen donor and two of the three oxygen donors are part of a single chelating, tridentate PDC ligand. The coordination sphere is rounded out by an aquo ligand. The disposition of the oxygen and nitrogen donors lie in a *mer* orientation about the nickel atom. Bond lengths and angles within 1 are standard for distorted octahedral geometry about Ni, and are given in Table 2.

By means of the tethering dpa ligands, neighboring Ni atoms are linked into 1-D chain motifs, as seen in Fig. 2. The cis orientation of the dpa nitrogen donors at each Ni atom and the torsion (37.9°) between pyridyl rings of the dpa ligands results in a zig-zag pattern within the 1-D coordination polymer chains. Weak C-H···O interactions $(C1 \cdots O4, 3.080(4) \text{ Å}; C6 \cdots O4, 3.228(4) \text{ Å})$ provide an ancillary intrachain contact pathway. The chelating PDC ligands can be seen to alternate above and below the chain motif. To accommodate the undulations within the chains, the two carboxylate moieties are flexed slightly away from the plane of the PDC pyridyl ring by $\sim 6.2^{\circ}$ and $\sim 6.8^{\circ}$. The Ni–Ni separation through the dpa tether is 11.367(1) Å. We have recently observed similar zig-zag 1-D [NiL₄(dpa)] chain patterns in the triply interpenetrated PtS-structure three-dimensional coordination polymer [Ni(adipate)- $(dpa)(H_2O)$][15].

Interwoven through each set of parallel 1-D chains is an identical set, offset by $\sim 64^{\circ}$, which forms a *pseudo* 2-D layer motif parallel to the *ac* crystal plane. Individual sets of parallel 1-D chains are shown in Fig. 3 in blue and orange.¹ The closest Ni–Ni separation between interwoven chains is 6.783(1) Å. The interweaving is accomplished through two different supramolecular hydrogen bonding pathways involving water molecules of crystallization trapped within the interchain spaces. The first of these

involves interaction between dpa amine subunits in two separate chains and the water molecule of crystallization lying on crystallographic twofold rotation axes (O1W, maroon in Fig. 3). The second pathway involves hydrogen bonding donation from the aquo ligand (at H5B) to unligated water molecule (O2W, light green in Fig. 3), which in turn donates a hydrogen bond to a ligated carboxylate oxygen (O3). The supramolecular hydrogen bonding within the *pseudo* layer is assisted by π - π stacking (centroid-to-centroid distance = 3.827(2) Å) between dpa pyridyl rings in abutting chains. Additionally, unligated water molecules (O3W, light blue in Fig. 3) are held to the coordination polymer backbone by donation of hydrogen bonds to unligated carboxylate oxygen atoms (O1). However, O3W does not bridge neighboring coordination polymer chains. From the crystal structure solution, only half of these positions are occupied, a point corroborated by elemental and thermal analysis.

Adjacent pseudo 2-D layers are then further aggregated into the full three-dimensional (3-D) crystal structure of **1** through another supramolecular hydrogen bonding pathway, between aquo ligands in one layer (via H5A) and unligated carboxylate oxygen atoms (O2) in another (Fig. 4). To maximize this interaction, the PDC ligands belonging to neighboring layers interdigitate slightly. The Ni–Ni through-space separation between chains in adjacent pseudo 2-D layers is 7.695(1) Å. Metrical parameters for all supramolecular hydrogen bonding pathways in **1** are given in Table 3.

Viewing the structure down the c crystal axis (Fig. 4) reveals the presence of three different types of 1-D water bearing channels, occupied by unligated water molecules. Channel A is occupied by water molecules of type O1W (maroon) and lies solely within a single pseudo 2-D layer. As calculated by PLATON [16], the oblong-shaped channel A is extremely small, contributing no measurable void space to the overall structure. Channel B, demarcated by unligated water molecules of type O2W (light green), represents 5.2% of the overall volume of 1. The rhomboidal shape of channel B measures approximately 7.7 $\text{\AA} \times$ 6.0 Å. Channel C, partially occupied with water molecules of type O3W (light blue), is the largest of the 1-D channels within 1. It manifests an "hourglass" appearance with maximum and minimum dimensions of ~10.6 Å and \sim 2.2 Å and occupies 7.8% of the unit cell volume. Both channels B and C spread through the regions between neighboring pseudo 2-D layers. Channel A is adjacent to six other channels, two of each of the three types. Channel B is bracketed by four channels of type A and four of type C. In turn, channel C is surrounded by four channels of type A, two of type B, and two of type C. The total solvent accessible void space within 1 is 13.0% of the total volume.

It is illustrative to compare the salient structural features of **1** with two previous Ni complexes incorporating both 2,6-pyridinedicarboxylate and an organodiimine. $\{[Ni_2(PDC)_2(H_2O)_4(4,4'-bpy)] \cdot 2 H_2O\}$ forms discrete molecular dimeric complexes, with two $[Ni(PDC)(H_2O)_2]$

¹ For interpretation of the references in color in this figure legend, the reader is referred to the web version of this article.



Fig. 2. A single 1-D chain motif within 1.



Fig. 3. Pseudo 2-D layer formed by offset interweaving chain motifs in 1. Hydrogen bonding interactions are shown as dashed lines.

units bridged through the rigid rod 4,4'-bpy tethering ligand [17]. These then aggregate through hydrogen bonding and π - π stacking to construct small channels occupied by water molecule dimers. Use of the longer tethering ligand *E*-4,4'-dipyridylethene (dpe) resulted in a salt-like complex with formula {([H₂dpe][Ni(PDC)₂])₃ · 15H₂O} [18]. This material contained 1-D channels occluding discrete acyclic water trimers and nonamers, in addition to isolated water molecules. By providing access to a 1-D coordination polymer chain motif and possessing a hydrogen bonding point of contact, the dpa ligand in 1 dramatically alters the water-bearing channel morphology, thus forcing the entrained water molecules to remain isolated from one another.

3.3. Structural description of $\{[Zn(PDC)(dpa)] \cdot 3 H_2O\}$ (2)

Single crystal X-ray diffraction revealed that compound 2 crystallized in the centrosymmetric triclinic space group



Fig. 4. Interdigitation of *pseudo* 2-D layers in 1, viewed down *c*. Inter-layer hydrogen bonding interactions are shown as dashed lines. The three different types of 1-D water-bearing channels are also evident. Channels A, B, and C are marked by water molecules in maroon, light green, and light blue, respectively. (For interpretation of the references in color in this figure legend, the reader is referred to the web version of this article.)

Table 3										
Hydrogen	bonding	distance (Å) and	angle	(°)	data	for	1	and	2

D–H···A	$d(\mathbf{H}\cdot\cdot\cdot\mathbf{A})$	∠DHA	$d(\mathbf{D}\cdots\mathbf{A})$	Symmetry transformation for A
Compound 1				
N2–H2N···O1W	2.01(3)	175(4)	2.875(4)	x, y, z - 1
O1W–H1A···O4	1.91(3)	160(3)	2.728(3)	-x + 1/2,
				-y + 1/2,
				z + 1/2
$O2W-H2A\cdots O3$	2.05(4)	157(4)	2.853(4)	x, -y,
				z + 1/2
O5−H5A···O2	1.78(3)	177(4)	2.627(5)	-x, y+1,
				z + 1/2
O5−H5B···O2W	1.95(3)	169(4)	2.752(4)	
O3W···O1			2.78	x + 1/2,
				y + 3/2,
				z-1
Compound 2				
N2–H2N···O1W	1.895	165.5	2.761	
O1W–H1A···O3	2.013	160.3	2.829	-x + 1,
				-y + 2,
				-z + 2
$O1W-H1B \cdot \cdot \cdot O3WB$	1.866	169.5	2.702	
$O1WH1A \cdots O3WA$	2.190	141.7	2.903	x, y - 1,
				z + 1
$O2W-H2A\cdots O2$	1.907	171.92	2.730	
O2W−H2B· · · O3WA	1.766	142.9	2.479	-x + 2,
				-y + 2,
				-z + 1

with an asymmetric unit (Fig. 5) consisting of one fivecoordinated divalent Zn atom, one tridentate PDC ligand, one dpa ligand, and three unligated water molecules, one of which is disordered equally over two positions (O3WA/ O3WB). The geometrical factor τ for the coordination environment at Zn is 0.42, indicative of a very distorted $[ZnN_3O_2]$ square pyramidal geometry [19]. The basal plane consists of the three donor atoms from the PDC ligand and one nitrogen atom belonging to a bridging dpa ligand, with the Zn atom located ~ 0.61 Å above best-fit plane defined by these four atoms. A third nitrogen donor, from a different dpa ligand, occupies the apical position. In order to accommodate the distorted *trans* orientation of the oxygen donors, the carboxylate moieties of the PDC ligands twist by $\sim 9^{\circ}$ and $\sim 8.4^{\circ}$ relative to the plane of the pyridine ring, slightly greater than seen in 1. The N–Zn–N bond angles fall in the range of 113.63(11)-126.25(11)°, and the O-Zn-O bond angle subtends 151.91(9)°. The Zn-O bond distances are approximately 0.15-0.20 Å longer than the Zn-N bond distances. Relevant bond lengths and angles are given in Table 4.

Extension of the structure of **2** through the tethering dpa ligands affords a 1-D coordination polymer motif (Fig. 6). Neighboring Zn atoms within the chain are 11.099(1) Å apart, a metal-metal contact distance ~ 0.3 Å shorter than in **1**. This is attributable to the square pyramidal coordination about Zn, which presents less steric hindrance than in



Fig. 5. Asymmetric unit of 2 with thermal ellipsoids at 50% probability and atom numbering scheme. Uncoordinated water molecules and most hydrogen atoms have been omitted for clarity.

1. As a result, the dpa ligand can adopt a less twisted conformation in 2, with a $\sim 32.8^{\circ}$ inter-ring torsion angle. All PDC moieties point in the same direction within the chain motifs in 2, forming a wave-like pattern in marked contrast with the zig-zag pattern in 1.

Adjacent sets of chains, with their PDC ligands pointing in opposite directions, interdigitate and aggregate to form *pseudo* 2-D slabs parallel to the *ab* crystal plane through

Table 4 Selected bond distance (Å) and angle (°) data for 2 N3^{#1}-Zn1-N1 Zn1-N3#1 2.001(3)119.49(11) N3^{#1}–Zn1–N4 Zn1-N1 2.014(3)126.25(11) N1–Zn1–N4 Zn1-N4 2.021(3)113.63(11) N3^{#1}-Zn1-O3 Zn1-O3 2.181(2)100.29(10)Zn1-O1 N1-Zn1-O3 101.06(10) 2.193(2)C16-O1 1.256(4)N4-Zn1-O3 76.43(10) N3^{#1}–Zn1–O1 C17-O2 1.241(4)92.41(10) N1-Zn1-O1 C17-O3 1.273(4)94.11(10) C16-O4 1.240(4)N4-Zn1-O1 75.85(10) O3-Zn1-O1 151.91(9)

O2-C16-O1

O4-C17-O3

 $\pi-\pi$ stacking interactions between PDC pyridine rings (centroid-to-centroid distance = 3.545(2) Å), as seen in Fig. 7. Chain motifs within a single slab are also held together through extensive supramolecular hydrogen bonding pathways between carboxylate oxygen atoms and water molecules of crystallization which comprise water molecule oligomers (Fig. 8) encased in incipient cavities running down the *a* crystal direction. The oligomers are comprised of an acyclic five-molecule discrete chain (O1W··· O3WB···O3WA···O2W···O2W) with an additional water molecule (O1W) hydrogen bonded to the third molecule in the chain; the classification symbol for this uncommon [1b] water molecule oligomer is therefore D(5) [20], with a connectivity pattern reminiscent of 3-methylpentane in a *gauche* conformation.

The Zn–Zn distances between interdigitated and noninterdigitated chains within a slab subunit are 8.162(1) Å and 9.348(1) Å, respectively. The amine functional groups of the dpa ligands are directed towards the exterior of the pseudo 2-D slabs, providing a hydrogen bonding point of contact to an unligated water molecule within a neighboring slab. The full pseudo 3-D crystal structure of **2** is thereby constructed (Fig. 8) via water-cluster mediated



126.6(3)

126.2(3)

Fig. 6. View of the 1-D wavelike chain motif in 2.



Fig. 7. A view of the interdigitation of 1-D chain motifs in **2**. Discrete branched chain water molecule oligomers are shown in orange. Hydrogen bonding is indicated with dashed lines. (For interpretation of the references in color in this figure legend, the reader is referred to the web version of this article.)



Fig. 8. View down *a* of the *pseudo* 3-D structure of **2**, highlighting the water-oligomer bearing cavities. Hydrogen bonding between dpa amine units and unligated water molecules is shown as dashed lines.

hydrogen bonding. Supramolecular contact distance and angle information for **2** is given above in Table 3.

Channels containing the water oligomers can be seen coursing down the *a* crystal direction in Fig. 8. Unlike 1, which displayed three distinct types of channel, all of the channels in 2 are identical. According to void space calculation with PLATON [16], the elliptical channels in 2 occupy 18.8% of the unit cell volume, substantially larger than the combined volumes of all channels within 1.

3.4. Thermogravimetric analysis and dehydration/ rehydration behavior

Compounds 1 and 2 were subjected to thermogravimetric analysis under flowing N_2 to probe their dehydration and decomposition behavior. TGA traces for these compounds are shown in Figs. S1 and S2. The Ni coordination polymer 1 underwent dehydration at the beginning of the heating cycle, with elimination of all coordinated and

uncoordinated water molecules complete by $\sim 210 \,^{\circ}\text{C}$ (11.9% observed, 12.0% calculated for three water molecules). The mass then remained steady until ~ 300 °C. Above this temperature a broad 71% mass loss feature extending to ~ 600 °C was observed, consistent with elimination of PDC and dpa ligands (75% calculated). The 16.9% remaining mass at 800 °C aligned well with the deposition of NiO (16.6% predicted). The Zn derivative 2 began to dehydrate immediately upon heating, with loss of all uncoordinated water molecules occurring by 100 °C (11.6% observed mass loss, 11.8% predicted). No further decomposition was evident until ~225 °C. A 35.6% mass loss was observed between this temperature and \sim 390 °C. consistent with expulsion of the dpa ligand (37.5% calculated). A further 34.2% mass loss occurred after this point, which was complete by 525 °C, marking elimination of the PDC ligand (36.2% predicted). The final mass remnant of 18.4% is indicative of deposition of ZnO (17.8% expected).

To investigate potential dehydration/rehydration behavior, ground samples of 1 and 2 were held above their dehydration temperatures for 24 h. While TGA studies revealed that loss of organic components does not occur until higher temperatures, both dehydrated samples were determined to be amorphous by powder XRD. Both materials remained amorphous upon re-exposure to excess distilled water for 1 h; therefore the loss of uncoordinated water resulted in an irreversible loss of crystallinity. It is thus likely that the hydrogen bonding interactions between uncoordinated water molecules and the coordination polymer matrices play a crucial role in the stability of these materials.

4. Conclusions

Hydrothermal combination of divalent nickel or zinc precursors with 2,6-pyridinedicarboxylic acid and 4,4'dipyridylamine has resulted in the crystallization of two coordination polymers with 1-D chain structural motifs. The reduction in coordination number between from six (in 1) to five (in 2), with the lack of an aquo ligand in 2, results in significantly different polymer chain morphology and supramolecular aggregation pathways. It is apparent that the polycatenation/interweaving of adjacent coordination polymer chains can be controlled by variance of the cation in this system. Concomitantly, moving to a lower coordination number results in substantially larger incipient 1-D channels and permits the aggregation of uncoordinated water molecules into a less commonly observed discrete-chain pattern. The larger channels in 2 provide an easier means of egress for co-crystallized water, corroborated by the lower dehydration temperature than that of 1. As revealed by dehydration/rehydration experiments, the hydrogen bonding interactions mediated by the central amine of dpa have shown to play a crucial stability-inducing role in this family of coordination polymers. Further investigations towards the synthesis and characterization of functional coordination polymers with diverse structures incorporating the underutilized organodiimine dpa are underway in our laboratory.

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Appendix A. Supplementary material

CCDC 637995 and 637996 contain 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) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2007.07.035.

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