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Effect of pendant arm position and length on the structure and properties of nickel aromatic dicarboxylate coordination polymers incorporating a kinked organodiimine

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1. Introduction

Coordination polymer solids generated from divalent metal ions and dicarboxylate tethering ligands have attracted significant interest not only for their aesthetically appealing structures, but also for their promise in diverse technological applications such as gas storage [1], small molecule shape-selectivity [2], ion-exchange [3], catalysis [4], and optical devices [5]. A wide range of structural patterns occurs in these systems, based on the disposition of the donor groups within the dicarboxylate moieties, coordination geometry preferences of the specific metal ions used, and an array of available binding and bridging modes achievable with these ligands. While the predominant synthetic effort has focused on aromatic dicarboxylate tethers such as isophthalate and terephthalate, aliphatic α, ω -dicarboxylate ligands have also proven useful in the construction of new coordination polymer topologies due to their ability to adopt energetically similar but different conformations [6]. However, coordination polymers constructed from dicarboxylate tethers containing both aromatic rigidity and aliphatic pendant arm flexibility, for example phenylenediacetate isomers, are less common [7].

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ABSTRACT

Hydrothermal synthesis has afforded three nickel coordination polymers incorporating both aromatic dicarboxylates and the kinked and hydrogen bonding capable organodiimine 4,4'-dipyridylamine (dpa). These were characterized by single-crystal X-ray diffraction, infrared spectroscopy, and thermogravimetric analysis. [Ni(1,2-phda)(dpa)(H₂O)]_n (1,2-phda = 1,2-phenylenediacetate, **1**) displays (4,4) rhomboid grid-like 2D layers that aggregate into 3D through O-H···O hydrogen bonding. Shortening one of the pendant arms of the dicarboxylate ligand resulted in a shift to (6,3) herringbone style 2D coordination layer motifs in {[Ni(hmph)(dpa)] · 1.33H₂O}_n (hmph = homophthalate, **2**), which stack in an AA'B pattern. [Ni(1,3-phda)(dpa)(μ -H₂O)_{0.5}]_n (1,3-phda = 1,3-phenylenediacetate, **3**) manifests a canted primitive cubic type coordination polymer lattice constructed from dinuclear {Ni₂(μ -H₂O}) kernels linked into 3D through tethering 1,3-phda and dpa ligands. Analysis of the variable temperature magnetic susceptibility of **3** indicated the presence of antiferromagnetic superexchange within its dinuclear units (g = 2.290(2), J = -4.21(2) cm⁻¹).

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More recently, several researchers have augmented the structural complexity and functional utility of dicarboxylate-containing inorganic/organic hybrid materials by employing neutral organodiimine co-ligands such as the rigid-rod 4,4'-bipyridine (4,4'bpy). These dipodal nitrogen bases can link metal cations through their distal pyridyl nitrogen donor atoms, supplementing the covalent connectivity provided by the metal/dicarboxylate backbone to produce structurally interesting solids with promising properties [8–11]. Several members of this dual-ligand class of coordination polymers with d^{10} ions exhibit luminescent properties [9]; one especially intriguing solid, the interpenetrated 3D material $[Zn(terephthalate)(4,4'-bpy)_{0.5}]$, can serve as a stationary phase for the chromatographic separation of linear and branched alkanes [11]. The conformational flexibility of α,ω -dicarboxylate ligands can also facilitate reversible crystal-to-crystal structural reorganizations upon removal/re-addition of guest species within dual-ligand coordination polymers [12].

Recently our group has been investigating the synthesis and characterization of metal/dicarboxylate coordination polymers containing the organodiimine 4,4'-dipyridylamine (dpa) as a neutral co-ligand. Unlike the more commonly employed 4,4'-bpy, dpa has a kinked disposition of its terminal nitrogen donor atoms in addition to hydrogen bonding donating capability at its central amine. We have shown that both covalent and supramolecular interactions provided by the dpa ligand can synergistically act in



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structure-direction during self-assembly, to produce structural patterns different from those within similar coordination polymers based on 4,4'-bpy [12–15]. For example, $[Ni(adipate)(dpa)(H_2O)]_n$ exhibited the first-ever example of 3-fold interpenetration within the PtS structure type [12], and { $[Ni(dpa)_2(succinate)_{0.5}]Cl\}_n$ manifested an unprecedented 5-connected self-penetrated network with a "regular" 6¹⁰ topology [13]. The combination of zinc salts with phenylenediacetate isomers and dpa resulted in luminescent coordination polymers with differing two-dimensional (2D) and three-dimensional (3D) structural morphologies, depending on the position of the pendant acetate arms within the dicarboxylate moieties [14].

Herein we report the successful extension of this previous work into a nickel-based system, with the synthesis and structural characterization of three new coordination polymers with differing morphologies, constructed from both dpa and aromatic dicarboxylates with one or more flexible pendant arms: $[Ni(1,2-phda) (dpa)(H_2O)]_n$ (1; 1,2-phda = 1,2-phenylenediacetate), { $[Ni(hmph) (dpa)] \cdot 1.33H_2O_n$ (2; hmph = homophthalate), and $[Ni(1,3-phda) (dpa)(\mu-H_2O)_{0.5}]_n$ (3; 1,3-phda = 1,3-phenylenediacetate). Thermal properties of these new coordination polymers are also reported herein, along with a variable temperature magnetic susceptibility study for **3**.

2. Experimental

2.1. General considerations

NiCl₂ · 6H₂O (Fisher) and all dicarboxylic acids (Aldrich) were obtained commercially. The organodiimine 4,4'-dipyridylamine (dpa) was prepared via a published procedure [15]. 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 Anal-

Table 1

Crystal and structure refinement parameters for 1-3

ysis was carried out using a Perkin Elmer 2400 Series II CHNS/O Analyzer. IR spectra were recorded on powdered samples on a Perkin Elmer Spectrum One instrument. Powder X-ray diffraction patterns were obtained via θ - 2θ scans performed on a Rigaku Rotaflex instrument. Variable temperature magnetic susceptibility data (2– 300 K) were collected on a Quantum Design MPMS SQUID magnetometer at an applied field of 0.1 T. After each temperature change the sample was kept at the new temperature for 5 min before magnetization measurement to ensure thermal equilibrium. The susceptibility data were corrected for diamagnetism using Pascal's constants.

2.2. Preparation of $[Ni(1,2-phda)(dpa)(H_2O)]_n$ (1)

NiCl₂ · 6H₂O (0.088 g, 0.37 mmol), dpa (0.127 g, 0.74 mmol) and 1,2-phenylenediacetic acid (0.072 g, 0.37 mmol) were added to 10 mL of distilled H₂O in a 23 mL Teflon-lined Parr acid digestion bomb. The bomb was sealed, heated to 120 °C for 48 h, and then gradually cooled to ambient temperature. Green blocks of **1** (0.050 g, 31% yield based on Ni) were obtained after filtration, washing with distilled water and acetone, and drying in air. Crystals of **1** were stable indefinitely in air. Anal. Calc. for C₂₀H₁₉N₃NiO₅**1**: C, 54.59; H, 4.35; N, 9.55. Found: C, 53.99; H, 4.46; N, 9.54%. IR (cm⁻¹): 3285 w br, 1589 s, 1547 w, 1515 s, 1437 w, 1408 m, 1366 s, 1337 m, 1289 w, 1213 m, 1149 w, 1014 m, 939 w, 903 w, 850 w, 831 w, 812 s, 779 w, 716 s, 695 m, 650 m.

2.3. Preparation of $\{[Ni(hmph)(dpa)] \cdot 1.33H_2O\}_n$ (2)

 $NiCl_2 \cdot 2H_2O$ (0.088 g, 0.37 mmol), homophthalic acid (0.067 g, 0.37 mmol), dpa (0.127 g, 0.74 mmol), and 0.25 mL 1.0 M NaOH solution were placed into 10 g (555 mmol) distilled H₂O in a 23 mL Teflon-lined Parr acid digestion bomb (1:1:2: 1500 mol ratio). The bomb was sealed and heated at 120 °C for 48 h, whereupon

$\begin{array}{cccccccccccccccccccccccccccccccccccc$		1	2	3
Formula weight880.18434.09431.08Collection T (K)293173173Collection T (K)0710730.710730.710730.71073Color and habitgreen blockgreen blockgreen blockgreen blockgreen blockCrystal size (mm)0.55 0.40 × 0.400.31 × 0.28 × 0.200.30 × 0.12 × 0.1Crystal size (mm)monoclinicmonoclinicmonoclinicmonoclinicSpace groupP2,1nP2,2c12/a1/aa (Å)10.987(2)14.950(2)17.416(6)1/3.10(3)b (Å)10.987(2)13.850(2)103.597(10)9.9654(3)c (Å)10.8635(2)103.597(10)9.9654(3)f (Å)10.8635(2)103.597(10)9.9654(3)f (Å)10.8635(2)10.3597(10)9.9654(3)f (Å)1.5281.4921.28g (g cm ⁻³)1.5281.4921.28g (g cm ⁻³)1.5281.4921.28g (g cm ⁻³)1.5281.4920.897hkl ranges-22 < k 22,	Empirical formula	C40H38N6Ni2O10	C ₁₉ H _{19,667} N ₃ NiO _{5,333}	C ₂₀ H ₁₈ N ₃ NiO _{4.5}
Collection T (K) 293 173 173 λ (Å) 0.71073 0.71073 0.71073 Color and habit green block green block green block Crystal size (mm) 0.45 × 0.40 × 0.40 0.31 × 0.28 × 0.20 0.30 × 0.12 × 0.1 Crystal system monoclinic monoclinic monoclinic monoclinic gace group P_2 /n P_2 /c $I/2$ /a I/3 a (Å) 17.076(3) 14.9502(3) 17.416(6) b (Å) 0.987(2) 15.180(4) 1.810(3) c (Å) 1.522(4) 18.4272(3) 21.913(7) b (Å) 108.635(2) 103.5970(10) 9.654(3) Z 4 12 8 D_{calc} (gron ⁻³) 1.528 1.492 0.893 k (Å) 0.652 1.494 0.203 0.893 Minimum/maximum transmission 0.843 0.765 0.897 h (A = 12 22 <h 22.h="" 22.h<="" <="" td=""><td>Formula weight</td><td>880.18</td><td>434.09</td><td>431.08</td></h>	Formula weight	880.18	434.09	431.08
$\begin{split} \hat{\lambda}(\hat{\Lambda}) & 0.71073 & 0.71071 & 0.71011 & 0.71011 & 0.71011 & 0.71011 & 0.71011 & 0.71011 & 0.71011 &$	Collection T (K)	293	173	173
Color and habit green block green block green block Crystal size (mm) 0.45 × 0.40 × 0.40 0.31 × 0.28 × 0.20 0.30 × 0.12 × 0.1 Crystal size (mm) monoclinic monoclinic monoclinic Space group $P2_1/n$ $P2_1/c$ IZ/a a (Å) 1.5050(3) 14.550(3) 11.518(3) c (Å) 0.987(2) 15.180(4) 11.810(3) c (Å) 0.987(2) 18.4272(3) 21.913(7) b (Å) 10.522(4) 18.4272(3) 21.913(7) b (Å) 10.835(2) 103.5970(10) 96.54(3) Z 4 12 8 D_{alc} grm ⁻³) 1.528 1.492 0.903 Z 4 12 8 D_{alc} grm ⁻³) 0.52 1.45 k < 13.	λ (Å)	0.71073	0.71073	0.71073
Crystal size (mm) $0.45 \times 0.40 \times 0.40$ $0.31 \times 0.28 \times 0.20$ $0.30 \times 0.12 \times 0.1$ Crystal systemmonoclinicmonoclinicmonoclinicmonoclinicSpace group P_2/n P_0/c $I/2 a$ a (Å)17.076(3)14.9502(3)17.416(6) b (Å)10.987(2)21.5180(4)11.810(3) c (Å)1.522(4)18.4272(3)21.913(7) β (°)108.635(2)103.5970(10)99.654(3) V (Å ³)3826.1(13)5761.86(18)4443.1(19) Z 4128 D_{cak} (g cm ⁻³)1.5281.0480.903Minimum/maximum transmission0.8430.7650.897hkl ranges $-22 \leqslant h \leqslant 22$, $-19 \leqslant h \leqslant 19$, $-20 \leqslant h \leqslant 20$, $-14 \leqslant \& \leqslant 13$, $-2e \leqslant \& 28$, $-14 \leqslant \& k \leqslant 14$, $-27 < l < 26$ 22 $-23 < l < 24$ $-26 < l < 26$ Total reflections4102314101820942Unique reflections4102314101820942Unique reflections64/180.003 for0.916Parameters/restraints541/8796/12300/7 R_1 ($l > 2cf(1)^{\mu}$ 0.03840.404880.60810wg2 (all data) ^b 0.11340.14040.2720wg2 (all data) ^b 0.10700.11710.2446Maximum/minimum residual (e ⁻ /Å ³)0.764/-0.4571.289/-0.70551.81/-0.461Goodness-of-fit1.0491.0221.057	Color and habit	green block	green block	green block
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$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	Space group	$P2_1/n$	$P2_1/c$	I2/a
$ \begin{array}{llllllllllllllllllllllllllllllllllll$	a (Å)	17.076(3)	14.9502(3)	17.416(6)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	b (Å)	10.987(2)	21.5180(4)	11.810(3)
$ \begin{split} \beta \begin{pmatrix} \circ \\ 0 \end{pmatrix} & 108.635(2) & 103.5970(10) & 99.654(3) \\ Y(A^3) & 3826.1(13) & 5761.86(18) & 4443.1(19) \\ Z & 4 & 12 & 8 \\ D_{calc} (g cm^{-3}) & 1.528 & 1.492 & 1.289 \\ \mu (mm^{-1}) & 1.052 & 1.048 & 0.903 \\ Minimum/maximum transmission & 0.843 & 0.765 & 0.897 \\ hkl ranges & -22 \leqslant h \leqslant 22, & -19 \leqslant h \leqslant 19, & -20 \leqslant h \leqslant 20, \\ -14 \leqslant k \leqslant 13, & -26 \leqslant k \leqslant 28, & -14 \leqslant k \leqslant 14, \\ -27 \leqslant l \leqslant 26 & -23 \leqslant l \leqslant 24 & -26 \leqslant l \leqslant 26 \\ -14 \leqslant k \leqslant 13, & -26 \leqslant k \leqslant 28, & -14 \leqslant k \leqslant 14, \\ -27 \leqslant l \leqslant 26 & -23 \leqslant l \leqslant 24 & -26 \leqslant l \leqslant 26 \\ 101 que reflections & 41023 & 141018 & 20942 \\ Unique reflections & 8714 & 13593 & 3911 \\ R_{int} & 0.0204 & 0.0687 & 0.0916 \\ Parameters/restraints & 541/8 & 796(12 & 300/7 \\ R_1 (all dat)^a & 0.1013 & 0.1223 & \\ R_1 (l > 2\sigma(l))^k & 0.0384 & 0.0488 & 0.810 \\ wR_2 (all dat)^b & 0.1134 & 0.1404 & 0.2720 \\ wR_2 (l > 2\sigma(l))^b & 0.1070 & 0.1171 & 0.2446 \\ Maximum/minimum residual (e^/A^3) & 0.764/-0.457 & 1.298/-0.705 & 1.181/-0.4611 \\ Goodness-of-fit & 1.049 & 1.022 & 1.057 \\ \end{split}$	c (Å)	21.522(4)	18.4272(3)	21.913(7)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	β(°)	108.635(2)	103.5970(10)	99.654(3)
Z4128 $D_{calc} (g cm^{-3})$ 1.5281.4921.289 $\mu (mm^{-1})$ 1.0521.0480.903Minimum/maximum transmission0.8430.7650.897 hkl ranges $-22 \leqslant h \leqslant 22$, $-14 \leqslant k \leqslant 13$, $-27 \leqslant l \leqslant 26$ $-19 \leqslant h \leqslant 19$, $-26 \leqslant k \leqslant 28$, $-14 \leqslant k \leqslant 14$, $-27 \leqslant l \leqslant 26$ $-23 \leqslant l \leqslant 24$ $-26 \leqslant l \leqslant 26$ Total reflections41 023141 01820942Unique reflections871413 5933911 R_{int} 0.02040.66870.0916Parameters/restraints541/8796/12300/7 R_1 (all data) ^a 0.10130.1223 R_1 (all data) ^b 0.03840.04880.810 wR_2 (all data) ^b 0.11740.14040.2720 wR_2 (all data) ^b 0.10700.11710.2446Maximum/minimum residual (e ⁻ /Å ³)0.764/-0.4571.298/-0.7051.181/-0.461Goodness-of-fit1.0491.0221.057	$V(Å^3)$	3826.1(13)	5761.86(18)	4443.1(19)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	Z	4	12	8
$\begin{array}{llllllllllllllllllllllllllllllllllll$	D_{calc} (g cm ⁻³)	1.528	1.492	1.289
Minimum/maximum transmission0.8430.7650.897hkl ranges $-22 \leqslant h \leqslant 22$, $-19 \leqslant h \leqslant 19$, $-20 \leqslant h \leqslant 20$, $-14 \leqslant k \leqslant 13$, $-26 \leqslant k \leqslant 28$, $-14 \leqslant k \leqslant 14$, $-27 \leqslant l \leqslant 26$ $-23 \leqslant l \leqslant 24$ $-26 \leqslant l \leqslant 26$ Total reflections4102314101820942Unique reflections8714135933911 R_{int} 0.02040.06870.0916Parameters/restraints541/8796/12300/7 R_1 (al data) ^a 0.10130.1223 R_1 R_1 ($l > 2\sigma(I)$) ^a 0.03840.04880.0810 wR_2 (al data) ^b 0.10700.11710.2446Maximum/minimum residual (e ⁻ /Å ³)0.764/-0.4571.298/-0.7051.181/-0.4611Goodness-of-fit1.0491.0221.057	$\mu (\text{mm}^{-1})$	1.052	1.048	0.903
$ \begin{array}{llllllllllllllllllllllllllllllllllll$	Minimum/maximum transmission	0.843	0.765	0.897
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	hkl ranges	$-22 \leqslant h \leqslant 22$,	$-19 \leqslant h \leqslant 19$,	$-20 \leqslant h \leqslant 20$,
$-27 \leqslant l \leqslant 26$ $-23 \leqslant l \leqslant 24$ $-26 \leqslant l \leqslant 26$ Total reflections4102314101820942Unique reflections8714135933911 R_{int} 0.02040.06870.0916Parameters/restraints541/8796/12300/7 R_1 (all data) ^a 0.0130.12237 R_1 ($l > 2\sigma(l)$) ^a 0.11340.4040.2720 wR_2 (all data) ^b 0.11710.2446Maximum/minimum residual (e ⁻ /Å ³)0.764/-0.4571.298/-0.7051.181/-0.4611Goodness-of-fit1.0491.0221.057	0	$-14 \leq k \leq 13$,	$-26 \leqslant k \leqslant 28$,	$-14 \leqslant k \leqslant 14$,
Total reflections4102314101820942Unique reflections8714135933911 R_{int} 0.02040.06870.0916Parameters/restraints541/8796/1230/7 R_1 (al data) ^a 0.0130.12237 R_1 ($1 > 2\sigma(I)$) ^a 0.03840.04880.0810wR2 (al data) ^b 0.11340.14040.2720wR2 ($1 > 2\sigma(I)$) ^b 0.0700.11710.2446Maximum/minimum residual (e ⁻ /Å ³)0.764/-0.4571.298/-0.7051.181/-0.4611Goodness-of-fit1.0491.0221.057		$-27 \leqslant l \leqslant 26$	$-23 \leqslant l \leqslant 24$	$-26 \leqslant l \leqslant 26$
Unique reflections8714135933911 R_{int} 0.02040.06870.0916Parameters/restraints541/8796/12300/7 R_1 (all data) ^a 0.1030.12237 R_1 ($1 > 2\sigma(I)$) ^a 0.03840.04880.0810 WR_2 (all data) ^b 0.11340.14040.2720 WR_2 ($1 > 2\sigma(I)$) ^b 0.10700.11710.2446Maximum/minimum residual (e ⁻ /Å ³)0.764/-0.4571.298/-0.7051.181/-0.4611Goodness-of-fit1.0491.0221.057	Total reflections	41023	141018	20942
R_{int} 0.02040.06870.0916Parameters/restraints541/8796/12300/7 R_1 (all data) ^a 0.10130.1223 R_1 ($l > 2\sigma(l)$) ^a 0.03840.04880.0810 wR_2 (all data) ^b 0.11340.14040.2720 wR_2 (all data) ^b 0.10700.11710.2446Maximum/minimum residual (e ⁻ /Å ³)0.764/-0.4571.298/-0.7051.181/-0.4611Goodness-of-fit1.0491.0221.057	Unique reflections	8714	13593	3911
manual Parameters/restraints541/8796/12300/7 R_1 (all data)a0.10130.1223 R_1 ($I > 2\sigma(I)$)a0.03840.04880.0810 wR_2 (all data)b0.11340.14040.2720 wR_2 ($I > 2\sigma(I)$)b0.10700.11710.2446Maximum/minimum residual (e ⁻ /Å ³)0.764/-0.4571.298/-0.7051.181/-0.461Goodness-of-fit1.0491.0221.057	R _{int}	0.0204	0.0687	0.0916
R_1 (all data)a0.10130.1223 R_1 ($I > 2\sigma(I)$)a0.03840.04880.0810 wR_2 (all data)b0.11340.14040.2720 wR_2 ($I > 2\sigma(I)$)b0.10700.11710.2446Maximum/minimum residual (e ⁻ /Å ³)0.764/-0.4571.298/-0.7051.181/-0.461Goodness-of-fit1.0491.0221.057	Parameters/restraints	541/8	796/12	300/7
R_1 ($I > 2\sigma(I)$) ³ 0.03840.04880.0810 wR_2 (all data) ^b 0.11340.14040.2720 wR_2 ($I > 2\sigma(I)$) ^b 0.10700.11710.2446Maximum/minimum residual (e ⁻ /Å ³)0.764/-0.4571.298/-0.7051.181/-0.461Goodness-of-fit1.0491.0221.057	R_1 (all data) ^a	0.1013	0.1223	,
wR_2 (all data) ^b 0.11340.14040.2720 wR_2 ($I > 2\sigma(I)$) ^b 0.10700.11710.2446Maximum/minimum residual (e ⁻ /Å ³)0.764/-0.4571.298/-0.7051.181/-0.461Goodness-of-fit1.0491.0221.057	$R_1 (I > 2\sigma(I))^a$	0.0384	0.0488	0.0810
$wR_2^-(I>2\sigma(I))^{b}$ 0.10700.11710.2446Maximum/minimum residual (e ⁻ /Å ³)0.764/-0.4571.298/-0.7051.181/-0.461Goodness-of-fit1.0491.0221.057	wR_2 (all data) ^b	0.1134	0.1404	0.2720
Maximum/minimum residual (e ⁻ /Å ³) 0.764/-0.457 1.298/-0.705 1.181/-0.461 Goodness-of-fit 1.049 1.022 1.057	$wR_2(I > 2\sigma(I))^b$	0.1070	0.1171	0.2446
Goodness-of-fit 1.049 1.022 1.057	Maximum/minimum residual (e ⁻ /Å ³)	0.764/-0.457	1.298/-0.705	1.181/-0.461
	Goodness-of-fit	1.049	1.022	1.057

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 ${}^{a}R_{1} = \sum ||F_{o}| - |F_{c}|| / \sum |F_{o}|. {}^{b}wR_{2} = \{\sum [w(F_{o}^{2} - F_{c}^{2})^{2}] / \sum [wF_{o}^{2}]^{2}\}^{1/2}.$

it was cooled slowly in air to 25 °C. Small green crystals of **2** (0.146 g, 91% yield based on Ni) were isolated after washing with distilled water. *Anal.* Calc. for $C_{19}H_{19.667}N_3NiO_{5.333}$ (**2**): C, 52.57; H, 4.57; N, 9.68. Found; C, 52.11; H, 4.43; N, 9.39%. IR (cm⁻¹): 3450 w br, 3012 w, 1637 w, 1598 s, 1548 w, 1522 s, 1491 m, 1444 w, 1421 m, 1401 s, 1359 s, 1292 w, 1208 m, 1090 w, 1057 w, 1022 m, 943 w, 908 w, 872 m, 852 w, 834 w, 812 s, 724 s, 695 m, 677 m, 661 w.

2.4. Preparation of $[Ni(1,3-phda)(dpa)(\mu-H_2O)_{0.5}]_n$ (3)

NiCl₂ · 6H₂O (0.088 g, 0.37 mmol), dpa (0.127 g, 0.74 mmol) and 1,2-phenylenediacetic acid (0.072 g, 0.37 mmol) were added to 10 mL of distilled H₂O in a 23 mL Teflon-lined Parr acid digestion bomb. The bomb was sealed, heated to 120 °C for 48 h, and then gradually cooled to ambient temperature. Green blocks of **3** (0.100 g, 63% yield based on Ni) were obtained after filtration, washing with distilled water and acetone, and drying in air. Crystals of **3** were stable indefinitely in air. Anal. Calc. for C₂₀H₁₈N₃NiO_{4.5} **3**: C, 55.73; H, 4.21; N, 9.75. Found: C, 55.48; H, 4.02; N, 9.48%. IR (cm⁻¹): 2910 w br, 1744 w, 1590 s, 1513 m, 1486 m, 1440 w, 1385 s, 1340 m, 1266 w, 1210 m, 1060 w, 1017 s, 905 w, 843 w, 822 s, 712 s, 680 w, 657 m.

3. X-ray crystallography

Single crystals of all materials were subjected to single-crystal X-ray diffraction using a Bruker-AXS SMART 1k (**1**, **3**) or APEX II CCD (**2**) instrument. Reflection data were acquired using graphite-monochromated MoK α radiation ($\lambda = 0.71073$ Å). The data were integrated via SAINT [16]. Lorentz and polarization effect and empirical absorption corrections were applied with SADABS [17]. The structures were solved using direct methods and refined on F^2 using SHELXTL [18]. All non-hydrogen atoms were refined aniso-tropically. Hydrogen atoms bound to carbon atoms were placed in calculated positions and refined isotropically with a riding mod-



Fig. 1. Coordination environment of **1** with thermal ellipsoids drawn at 50% probability and partial atom numbering scheme. Hydrogen atoms have been omitted for clarity. Atoms labelled with an "A" designation are generated by crystallographic symmetry.

Table 2

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

Ni1-03	2.0218(17)	03-Ni1-09	95.70(8)
Ni1-09	2.0471(19)	03-Ni1-N4 ^{#1}	89.04(7)
Ni1-N4 ^{#1}	2.0732(18)	O9-Ni1-N4 ^{#1}	93.41(8)
Ni1-05	2.1022(17)	03-Ni1-05	163.10(7)
Ni1-N6	2.1053(18)	09-Ni1-05	101.20(8)
Ni1-06	2.2343(17)	N4 ^{#1} -Ni1-O5	89.85(7)
Ni2-08 ^{#2}	2.008(2)	O3-Ni1-N6	85.44(7)
Ni2-010	2.0213(19)	09-Ni1-N6	92.61(8)
Ni2-N3 ^{#3}	2.1041(19)	N4 ^{#1} -Ni1-N6	172.20(7)
Ni2-N1	2.1310(19)	05-Ni1-N6	93.84(7)
Ni2-01	2.1608(18)	03-Ni1-06	102.39(7)
Ni2-02	2.1954(17)	09-Ni1-06	161.91(8)
01-C28	1.260(3)	N4 ^{#1} -Ni1-O6	87.00(7)
02-C28	1.263(3)	05-Ni1-06	60.71(6)
O3-C30	1.255(3)	N6-Ni1-06	88.81(7)
O4-C30	1.237(4)	08 ^{#2} -Ni2-O10	102.59(9)
O5-C38	1.262(3)	08 ^{#2} -Ni2-N3 ^{#3}	84.61(8)
O6-C38	1.261(3)	010-Ni2-N3#3	92.41(8)
07-C40	1.236(6)	08 ^{#2} -Ni2-N1	89.83(8)
08-C40	1.229(5)	010-Ni2-N1	94.60(8)
		N3 ^{#3} -Ni2-N1	171.86(8)
		08 ^{#2} -Ni2-O1	163.20(9)
		010-Ni2-01	94.15(7)
		N3 ^{#3} -Ni2-O1	93.41(7)
		N1-Ni2-O1	90.20(7)
		08 ^{#2} -Ni2-02	102.78(8)
		010-Ni2-02	154.23(8)
		N3 ^{#3} -Ni2-O2	85.54(7)
		N1-Ni2-O2	89.92(7)
		01-Ni2-02	60.42(6)

Symmetry transformations to generate equivalent atoms: #1 x - 1/2, -y + 3/2, z - 1/2; #2 x + 1, y, z; #3 x + 1/2, -y + 3/2, z + 1/2.

el. The hydrogen atoms bound to the central nitrogen of the dpa moieties and all aqua ligands were found via Fourier difference maps, restrained at fixed positions, and then refined isotropically with thermal parameters 1.2 times the average U_{ij} values of the atoms to which they are bound. Hydrogen atoms could not be located for the disordered water molecule of crystallization within the structure of **2**. The aromatic rings within the 1,3-phda ligands in **3** exhibited disorder over three sets of positions, which were modeled as a 50:25:25 ratio. Relevant crystallographic data for **1–3** are listed in Table 1.



Fig. 2. Face-on view of the $[Ni(1,2-phda)(dpa)(H_2O)]_n$ 2D (4,4)-grid layer in **1**. In-tralayer hydrogen bonding is shown as dashed lines.



Fig. 3. Stacking of [Ni(1,2-phda)(dpa)(H₂O)]_n layers in 1 along the b crystal direction in an ABA pattern by interlayer hydrogen bonding (shown as dashed lines).

4. Results and discussion

4.1. Synthesis and spectral characterization

The coordination polymers 1-3 were prepared cleanly under hydrothermal conditions via combination of nickel chloride, dpa, and the requisite dicarboxylic acid. The infrared spectra of 1-3 were consistent with their structures as determined by X-ray diffraction (vide infra). Sharp, medium intensity bands in the range of $\sim 1600 \text{ cm}^{-1}$ to $\sim 1200 \text{ cm}^{-1}$ were ascribed to stretching modes of the pyridyl rings of the dpa moieties [19]. Features corresponding to pyridyl ring puckering mechanisms were evident in the region between 820 cm⁻¹ and 600 cm⁻¹. Asymmetric and symmetric C-O stretching modes of the carboxylate moieties were evidenced by very strong, slightly broadened bands at \sim 1590 cm⁻¹ and $\sim 1370 \text{ cm}^{-1}$. Broad bands in the region of $\sim 3400 \text{ cm}^{-1}$ to \sim 3000 cm⁻¹ in all cases represent N–H stretching modes within the dpa ligands and O-H stretching modes within ligated or unligated water molecules. The broadness of these latter spectral features is caused by significant hydrogen bonding pathways within **1–3.** Phase purity was verified with powder XRD by comparison with powder patterns predicted from the single-crystal structures.

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

D−H···A $d(H \cdot \cdot \cdot A)$ ∠DHA $d(D \cdot \cdot \cdot A)$ Symmetry transformation for A Complex **1** 09–H9A· · ·04 160(3) 2.641(3) 1.833(19)09-H9B···01 2.247(18) 165(3) 3.043(3) -x + 1, -v + 2, -z010-H10A···05 1.931(17)173(3)2.771(2)-x + 1, -y + 2, -z010-H10B···07 2.24(3)129(3) 2.819(4)-x + 1, -y + 2, -z010-H10B···07 137(3) 2.18(2)2.824(4)x + 1, y, z N2-H2N···06 2.36(2) 147(3) 3.133(3) -x + 1, -y + 1, -z-x + 3/2, y + 1/2, -z + 1/2N5-H5N···02 2.195(19) 3.018(3) 161(3) Complex 2 01W-H1WA...03 2.13 179.2 2.983(4) 01W-H1WB...010 1.91 157.4 2.723(4)02W-H2WB...07 2.00(3) 161(6) 2.857(5) x + 1, y, z03W-H3WB...06 3.01(6) 89(4) 3.115(5) -x + 1, -y + 1, zx, -y + 3/2, z - 1/2N2-H2N···011 1.987(18) 172(3)2.857(3)N5-H5N...04 1949(18)2.827(3)172(3)N8-H8N···05 1.954(18) 170(3) 2.849(3) Complex 3 01–H1A· · ·05 1.79(4)151(8)2.573(7)-x + 1/2, y, -z + 1N2-H2N···O3 1.97(3) 171(8) 2.848(8)x - 1/2, -y + 1, z

4.2. Structural description of $[Ni(1,2-phda)(dpa)(H_2O)]_n$ (1)

As revealed by single-crystal X-ray diffraction, the asymmetric unit (Fig. 1) of compound 1 contains two crystallographically distinct nickel atoms (Ni1, Ni2), two 1,2-phda dianions (phda-A, C21-C30/O1-O4; phda-B, C31-C40/O5-O8), two dpa ligands (dpa-A, C1-C10/N1-N3; dpa-B, C11-C20/N4-N6), and two ligated water molecules (09, 010). Both crystallographically distinct Ni atoms display a distorted octahedral [NiO₄N₂] coordination geometry, where the two *trans*-disposed nitrogen donor atoms belong to *dpa-A* and *dpa-B* ligands, respectively. The equatorial plane of each coordination octahedron is occupied by two oxygen atoms from a chelating carboxylate terminus of a 1,2-phda ligand, one oxygen atom from a monodentate carboxylate group of a crystallographically distinct 1,2-phda ligand, and an aqua ligand. Bond lengths and angles about the nickel atoms are consistent with the chelation-imposed distorted octahedral coordination geometry (Table 2).

Extension of the structure through the exobidentate chelating/ monodentate 1,2-phda ligands results in a one-dimensional (1D) $[Ni(1,2-phda)(H_2O)]_n$ chain motif that propagates along the *a* crystal direction. Within the $[Ni(1,2-phda)(H_2O)]_n$ chain Ni1 and Ni2



Fig. 4. Coordination environments of 2 with thermal ellipsoids shown at 50% probability and partial atom numbering scheme (top, Ni1 and Ni2 and attached ligands; bottom, Ni3 and attached ligands). Hydrogen atoms and water molecules of crystallization have been omitted for clarity. Atoms labelled with an "A" designation are generated by crystallographic symmetry.

centers are linked through *phda-A* and *phda-B* ligands in an alternating pattern, with Ni…Ni distances toggling between 8.112 Å and 8.976 Å, respectively. The varying Ni…Ni distances are promoted by the conformational flexibility of the pendant arms of the 1,2-phda ligands, despite the identical carboxylate binding modes. The carboxylate termini of *phda-A* are twisted by ~60° and ~70° relative to the ligand's aromatic ring plane, while the related carboxylate torsions for *phda-B* are ~40° and ~57°, thus allowing a greater distance span across the ligated pendant arms of *phda-B*. Covalent bonding within the [Ni(1,2-phda)(H₂O)]_n chains is supplemented by hydrogen bonding donation by the aqua ligands to unligated oxygen atoms from the monodentate carboxylate groups of the 1,2-phda ligands.

Adjacent $[Ni(1,2-phda)(H_2O)]_n$ chain subunits are subsequently conjoined into a two-dimensional (2D) $[Ni(1,2-phda)(dpa)(H_2O)]_n$ (4,4) rhomboid grid coordination polymer layer (Fig. 2) by exobidentate dpa ligands; the layer motif runs parallel to the *ac* crystal plane. Ni1 centers are linked by *dpa-B* ligands, fostering a Ni1…Ni1 contact distance of 11.525 Å; the pyridyl rings within *dpa-B* are twisted by 28.1° with respect to each other. Similarly, Ni2 atoms are strutted by *dpa-A* ligands with a Ni2…Ni2 contact distance of 11.548 Å. The inter-ring torsion within *dpa-A* is slightly larger, at 32.7°.

Due to the conformation-imposed varying tether lengths, two different grid sizes are observed within the $[Ni(1,2-phda)(dpa)(H_2O)]_n$ layers. The grid spaces bracketed by the shorter *phda-A* tethers measure 11.067×16.595 Å, as determined by through-space Ni···Ni distances, with Ni···Ni··Ni angles of 66.0° and 114.2°. The more pinched grid spaces, delineated by the longer *phda-B* tethers, measure 10.766×17.646 Å, with Ni···Ni··Ni angles of 61.8° and 118.0° . Neighboring $[Ni(1,2-phda)(dpa)(H_2O)]_n$ layers stack in an ABA pattern along the *b* crystal direction, primarily through interlayer hydrogen bonding between the central amine units of the dpa ligands and oxygen atoms belonging to chelating carboxylate moieties within 1,2-phda ligands (Fig. 3). Hydrogen bonding parameters for **1** are given in Table 3. The 2D non-interpenetrated layered structure of **1** is dramatically different from its related zinc congener, { $[Zn(1,2-phda)(dpa)] \cdot H_2O]_n$, which

Table 4			
Selected bon	d distance (Å) and	l angle (°) data	for 2

Ni1-N4	2.039(2)	05-Ni1-06	61.58(8)
Ni1-05	2.048(2)	N6-Ni1-O6	156.58(9)
Ni1-N6 ^{#1}	2.057(2)	01-Ni1-06	105.72(8)
Ni1-01	2.093(2)	02-Ni1-06	90.18(8)
Ni1-02	2.113(2)	N3 ^{#2} -Ni2-N1	96.57(10
Ni1-06	2.215(2)	N3 ^{#2} -Ni2-O4	100.50(9)
Ni2-N3 ^{#2}	2.034(2)	N1-Ni2-O4	97.10(9)
Ni2-N1	2.039(2)	N3 ^{#2} -Ni2-07	95.27(9)
Ni2-04	2.089(2)	N1-Ni2-07	95.73(9)
Ni2-07	2.103(2)	04-Ni2-07	158.34(8)
Ni2-08	2.104(2)	N3 ^{#2} -Ni2-O8	157.06(10
Ni2-03	2.193(2)	N1-Ni2-08	91.29(9)
Ni3-N9 ^{#1}	2.039(2)	04-Ni2-08	99.85(8)
Ni3-N7	2.044(2)	07-Ni2-08	62.42(8)
Ni3-011 ^{#3}	2.089(2)	N3 ^{#2} -Ni2-O3	89.76(9)
Ni3-010	2.098(2)	N1-Ni2-O3	158.20(9)
Ni3-09	2.115(2)	04-Ni2-03	61.18(8)
Ni3-012 ^{#3}	2.137(2)	07-Ni2-03	104.46(8)
		08-Ni2-03	90.85(8)
N4-Ni1-05	98.52(9)	N9 ^{#1} -Ni3-N7	95.30(10
N4-Ni1-N6 ^{#1}	99.51(10)	N9 ^{#1} -Ni3-O11 ^{#3}	97.84(9)
05-Ni1-N6 ^{#1}	95.30(9)	N7-Ni3-O11 ^{#3}	96.51(9)
N4-Ni1-01	95.90(9)	N9 ^{#1} -Ni3-O10	98.01(9)
05-Ni1-01	160.34(8)	N7-Ni3-O10	99.24(9)
N6 ^{#1} -Ni1-O1	95.42(9)	011 ^{#3} -Ni3-010	156.46(8)
N4-Ni1-02	157.12(9)	N9 ^{#1} -Ni3-O9	91.59(9)
05-Ni1-02	100.85(8)	N7-Ni3-O9	161.13(9)
N6-Ni1-O2 ^{#1}	90.72(9)	011 ^{#3} -Ni3-09	99.93(8)
01-Ni1-02	62.59(8)	010-Ni3-09	62.34(8)
N4-Ni1-06	88.42(9)	N9 ^{#1} -Ni3-O12 ^{#3}	160.09(9)
		N7-Ni3-O12#3	88.12(9)
		011 ^{#3} -Ni3-012 ^{#3}	62.26(8)
		010-Ni3-012#3	100.79(8)
		09-Ni3-012#3	91.36(8)

Symmetry transformations to generate equivalent atoms: #1 x, -y + 1/2, z + 1/2; #2 x, -y + 3/2, z + 1/2; #3 - x, -y + 1, -z + 1.

possesses a 4-fold interpenetrated SrAl₂(sra) lattice [14]. The octahedral coordination preference of the nickel ions in **1**, at the expense of tetrahedral coordination in the zinc analogue, is a plausible rationalization for this significant structural change.

4.3. Structural description of $\{[Ni(hmph)(dpa)] \cdot 1.33H_2O\}_n$ (2)

The large asymmetric unit of compound **2** (Fig. 4a and b) consists of three crystallographically unique nickel atoms (Ni1–Ni3), hmph dianions (*hmph-A*, O1–O4; *hmph-B*, O5–O8; *hmph-C*, O9–O12) and dpa ligands (*dpa-A*, N1–N3; *dpa-B*, N4–N6; *dpa-C*, N7–N9), along with four water molecules of crystallization. All nickel atoms adopt a [NiO₄N₂] distorted octahedral geometry, with *cis*-disposed nitrogen donors from two different, yet crystallographically identical, dpa ligands. The remaining four coordination sites are taken up by oxygen atoms from chelating carboxylate groups from crystallographically distinct *hmph-A* and *hmph-B* ligands for Ni1 and Ni2, and from a pair of crystallographically identical *hmph-C* ligands for Ni3. Bond lengths and angles about Ni1, Ni2, and Ni3 are similar, and are stated in Table 4.

By means of two bisbridging bischelating hmph ligands (*hmph-A* and *hmph-B*), Ni1 and Ni2 are joined into a binuclear kernel with a Ni \cdots Ni distance of 5.590 Å. In turn, Ni1 atoms are linked through tethering *dpa-B* ligands (with an inter-ring torsion of 23.5°), providing a Ni \cdots Ni distance equal to 11.633 Å. Ni2 atoms conjoin to other Ni2 atoms through *dpa-C* (inter-ring torsion = 18.1°) with a slightly shorter Ni \cdots Ni through-ligand distance of 11.591 Å. Therefore each Ni1 is connected to two other Ni1 atoms and one Ni2 atom, while Ni2 is connected 2D [Ni(hmph)(dpa)]_n coordination polymer layer motif (Layer A, Fig. 5a). Considering the



Fig. 5. Layers A (top) and B (bottom) in **2**, viewed individually slightly offset from the *a* crystal direction.

hmph-A and *hmph-B* linkages as a single connector between Ni1 and Ni2 atoms allows the visualization of the coordination polymer layer as a (6,3) herringbone pattern.

A very similar 2D [Ni(hmph)(dpa)]_n (6,3) herringbone pattern is formed by linkage of Ni3 atoms to three other Ni3 atoms, through two *dpa-A* ligands (inter-ring torsion = 27.2°) and two *hmph-C* ligands (Layer B, Fig. 5b). The through-dpa Ni3···Ni3 distances within the layer are all identical, at 11.578 Å; while the through-space Ni3···Ni3 distances bracketed by the crystallographically identical *hmph-C* tethers are 5.584 Å. Both layer A and layer B motifs are situated parallel to the *bc* crystal plane.

It is likely that the subtle conformational variances between the dpa and hmph ligands result in the presence of two crystallographically distinct layers within the structure of **2**; the layers should be considered conformers as opposed to true supramolecular isomers. The different Ni \cdots Ni through-space distances across the six-membered circuits within each layer type may also reflect these variances. Ni \cdots Ni through-space distances within layer *A* measure 15.85, 18.31, and 22.14 Å, allowing accommodation of water molecule dimers (O1W \cdots O3W) and isolated water molecules of crystallization (O4W). On the other hand, only isolated water molecules of crystallization (O2W) are present within layer B, where the Ni \cdots Ni through-space distances measure 16.57, 18.25, and 21.61 Å.

The [Ni(hmph)(dpa)]_n (6,3) layer motifs stack along the *a* crystal direction in a repeating AA'B pattern (Fig. 6), where layers A and A'



Fig. 6. AA'B layer stacking pattern within 2. Water molecules of crystallization can be seen as spheres within the layers.

are related by crystallographic inversion. The pattern repeat distance of 14.950 Å defines the *a* lattice parameter. Interlayer supramolecular connectivity is fostered by the central amine units of the dpa ligands, which engage in hydrogen bonding to chelating carboxylate oxygen atoms at the longer pendant arm of the hmph ligands that project into the incipient voids within the (6,3) layers. Metrical parameters for the hydrogen bonding patterns in **2** are given above in Table 3.

4.4. Structural description of $[Ni(1,3-phda)(dpa)(\mu-H_2O)_{0.5}]_n$ (3)

The asymmetric unit of compound **3** (Fig. 7) contains a single divalent nickel atom, one 1,3-phda dianion, one entire dpa molecule, and a ligated water molecule located on a crystallographic 2-fold axis. As is the case for **2**, the nickel atom possesses a distorted [NiO₄N₂] octahedral coordination environment with a *cis* orientation of its nitrogen donors, which belong to two different dpa ligands. Bond lengths and angles about the nickel atom are standard for octahedral coordination (Table 5). Three of the oxygen

donors belong to three different 1,3-phda ligands, while the remaining coordination site is occupied by an aqua ligand. Each 1,3-phda ligand serves as an exotridentate linker, connecting two nickel atoms at one carboxylate terminus in a bisbridging binding mode with a third nickel atom via the other carboxylate locus in a monodentate binding mode.

The aqua ligand serves to bridge two Ni atoms in a μ_2 -fashion; both Ni atoms are in turn also bridged by two carboxylate termini from two different 1,3-phda ligands to a triply bridged binuclear unit (Fig. 8). These have a Ni…Ni distance of 3.603 Å, with the two bridging carboxylate groups situated 88.13° apart. Individual binuclear units are connected into a 1D [Ni₂(1,3-phda)₂(μ -H₂O)]_n chain motif, coursing along the *a* crystal direction, by means of the monodentate carboxylate termini of the 1,3-phda ligands (Fig. 9). The Ni…Ni contact distance through the full extent of the 1,3-phda dianionic tethers is 8.881 Å.

Adjacent $[Ni_2(1,3-phda)_2(\mu-H_2O)]_n$ chains are conjoined in the *b* and *c* crystal directions by dpa ligands to construct the 3D coordination polymer network of **3**. The dpa ligands contain an inter-ring



Fig. 7. Coordination environment of 3 with thermal ellipsoids shown at 50% probability and partial atom numbering scheme. Atoms labelled with an "A" designation are generated by crystallographic symmetry.

Table 5	
Selected bond distance (Å) and angle (°) data for	r 3

Ni1-02 ^{#1}	2.061(5)	02 ^{#1} -Ni1-01	91.22(19)
Ni1-04	2.067(5)	04-Ni1-01	90.7(2)
Ni1-03	2.069(5)	03-Ni1-01	92.29(18)
Ni1-N1	2.094(6)	N1-Ni1-O1	90.1(2)
Ni1-01	2.094(4)	02 ^{#1} -Ni1-N3 ^{#2}	89.4(2)
Ni1-N3 ^{#2}	2.108(6)	04-Ni1-N3#2	88.8(2)
02 ^{#1} -Ni1-04	176.1(2)	03-Ni1-N3 ^{#2}	90.0(2)
02 ^{#1} -Ni1-03	88.2(2)	N1-Ni1-N3 ^{#2}	87.6(3)
04-Ni1-03	88.3(2)	01-Ni1-N3 ^{#2}	177.6(2)
02 ^{#1} -Ni1-N1	91.6(2)	Ni1-01-Ni1 ^{#1}	118.7(3)
04-Ni1-N1	91.7(2)	03-Ni1-N1	177.7(2)

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



Fig. 8. Triply bridged {Ni_2($\mu\text{-}H_2\text{O})$ } binuclear unit in 3, with complete coordination spheres shown.

torsion of 41.3°, which fosters a Ni…Ni distance of 11.337 Å. Alternatively, the structure of **3** may be visualized as $[Ni_2(\mu-H_2O) (dpa)_2]_n^{4n+}$ cationic layers buttressed via 1,3-phda ligands. Treating the centroids of the {Ni₂(μ -H₂O}) kernels as the connecting nodes allows the coordination polymer connectivity of **3** to be considered as a 6-connected canted primitive cubic (pcu) lattice with $4^{12}6^3$ topology (Fig. 10). The 3D covalent connectivity of **3** is supplemented by hydrogen bonding patterns mediated by the bridging water molecules and the central amine groups of the dpa ligands (see Table 3 for more detail).

4.5. Variable temperature magnetism of 3

To probe possible spin communication across its binuclear subunits, a sample of **3** was subjected to variable temperature magnetic study. The $\chi_m T$ product at 300 K was 1.09 cm³ K mol⁻¹ Ni, slightly higher than expected for an uncoupled Ni²⁺ *S* = 1 ion (1.00 cm³ K mol⁻¹), perhaps indicative of some crystal field anisotropy. The value of $\chi_m T$ decreased slowly below 50 K, reaching 1.00 cm³ K mol⁻¹; the decrease was significantly more rapid below this temperature, reaching 0.00796 cm³ K mol⁻¹ at 2 K. Decreasing $\chi_m T$ product values in systems with dimeric {Ni₂} kernels can be ascribed either to antiferromagnetic superexchange through bridging ligands, or zero field splitting due to anisotropy.

The magnetic data was fit to Eq. (1), derived for a Heisenberg dimer of *S* = 1 spins [20], and a temperature independent magnetism term was included (Fig. 11). The variables have their usual magnetochemical meanings. Best fit parameters were g = 2.290(2), $J = -4.21(2) \text{ cm}^{-1}$, $\chi_{TI} = -6.2 \times 10^{-4} \text{ cm}^3 \text{ mol}^{-1}$ with $R = 1.48 \times 10^{-3} = \{\sum [(\chi_m T)_{obs} - (\chi_m T)_{calc}]^2\}^{1/2}$. The negative value of *J* corroborates the presence of antiferromagnetic coupling through the bridging carboxylate and aqua ligands in **3**. However, this value should be construed as an upper limit due to the likely presence of cooperative effects due to zero-field splitting (*D* parameter).

$$\chi_m T = \left(\frac{Ng^2\beta^2}{k}\right) \left[\frac{e^x + 5e^{3x}}{1 + 3e^x + 5e^{3x}}\right] + \chi_{\rm TI} T \tag{1}$$

where x = J/kT.

Given the substantially longer Ni \cdots Ni distances in **1** and **2**, the magnetic behavior of these materials is expected to be dominated by zero-field splitting. As such, they were not subjected to variable temperature magnetic study.

4.6. Thermal analysis of 1-3

Thermogravimetric analysis was performed on samples of compounds 1-3 to investigate their robustness and decomposition pathways. Compound 1 manifested minimal mass loss until \sim 150 °C, whereupon dehydration commenced. This process was complete by \sim 240 °C, with the mass loss of 5.1% roughly consistent with elimination of one equivalent of water per nickel atom (4.1% calc.). The thermogram then exhibited a plateau until \sim 300 °C, at which temperature the organic components of the coordination polymer were ejected. The final mass remnant of 14.3% at 900 °C roughly matches with the deposition of Ni metal (13.3% calc.). Compound 2 underwent dehydration between 25 °C and 330 °C, with an observed mass loss of 5.2% (5.5% calc. for complete loss of water molecules of crystallization). At this latter temperature combustion of the organic ligands occurred. The final mass remnant of 17.6% represents the production of NiO (17.2% predicted). Compound 3 released its bridging water molecules between 25 °C and ~250 °C (3.0% mass loss, 2.1% predicted). Removal of the organic components took place between ~275 °C and ~600 °C, likely depositing NiO (17.2% mass loss observed, 17.7% calc.). TGA traces for 1-3 are depicted in Figs. S1-S3.

5. Conclusions

Variance of pendant arm length and position within aromatic dicarboxylate ligands has allowed access to a diversity of two-



Fig. 9. [Ni₂(1,3-phda)₂(μ-H₂O)]_n 1D chain motif in **3**.



Fig. 10. Framework view of the canted primitive cubic 3D structure pattern in 3. The {Ni₂(µ-H₂O)} binuclear units are represented as spheres, with organic ligands shown as solid rods. The 1,3-phda ligands connect the binuclear units along the *a* crystal direction.



Fig. 11. $\chi_m T$ vs. *T* plot for **3**. The solid line indicates the best fit to Eq. (1) in the text.

and three-dimensional nickel coordination polymer structure types in a co-ligand system with the kinked and hydrogen bonding donating organodiimine dpa. The ortho disposition of acetate groups within 1,2-phda results in a "standard" rhomboid grid 2D coordination polymer morphology in 1, albeit with slightly different grid apertures imparted by the conformational flexibility of the dpa ligands and the pendant arms of the dicarboxylate ligands. Shortening one of the pendant arms by one methylene unit did not change the overall coordination polymer dimensionality, but did adjust the layer morphology into a herringbone pattern and also altered the stacking pattern of the layered motifs. Use of the 1,3phda ligand, which possesses a meta disposition of acetate pendant arms and a wider separation between its carboxylate termini, appeared to promote the formation of antiferromagnetically coupled triply bridged dinuclear units which conjoined into a 3D coordination polymer with a canted primitive cubic structure type. In all cases, the supramolecular hydrogen bonding pathways provided by the dpa ligand serve an important ancillary structure-directing role. Additional coordination polymers incorporating the dpa ligand have been recently prepared in our laboratory; reports concerning their structures and physicochemical properties will ensue in due course.

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Appendix A. Supplementary data

CCDC 674722, 674723 and 674724 contain the supplementary crystallographic data for **1**, **2** and **3**. 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. TGA traces for **1**, **2** and **3** are also available via the Web edition of this journal. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2008.04.038.

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