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POLYHEDRON www.elsevier.com/locate/poly

Polyhedron 27 (2008) 821-834

Two-dimensional divalent metal/pimelate coordination polymers incorporating dipodal organodiimines: Crystal structures, thermal properties, and magnetic studies

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Received 10 July 2007; accepted 13 November 2007 Available online 20 December 2007

Abstract

Hydrothermal synthesis has afforded a series of 2-D coordination polymers incorporating the flexible α,ω -dicarboxylate pimelate ligand (pim) and either the kinked organodiimine 4,4'-dipyridylamine (dpa) or its conformationally flexible congener 1,3-di-4-pyridylpropane (dpp).

 $[M(pim)(dpa)(H_2O)]_n$ (M = Co, 1-Co; M = Ni, 1-Ni) both display puckered (4,4) rhomboid grid-like 2-D layers that aggregate into 3-D through O-H··O hydrogen bonding. { $[Cu_2(pim)_2(dpa)_2] \cdot 5H_2O\}_n$ (2) possesses 2-D slab motifs constructed from the linkage of $[Cu_2(pimelate)_2]_n$ ribbons and $[Cu(pimelate)]_n$ double chains through dpa tethers, entraining discrete water molecule chains with D(8) classification. Employing the longer dpp tether resulted in $[Ni(pim)(dpp)]_n$ (3), which manifested a doubly interpenetrated 2-D (4,4) grid layer morphology. Analysis of the variable temperature magnetic susceptibility of 1-Ni indicated the presence of zero-field splitting as well as possible weak antiferromagnetic coupling between Ni atoms in adjacent layer subunits. In contrast, 2 manifested apparent intradimer ferromagnetic interactions with underlying interdimer antiferromagnetic coupling. © 2007 Elsevier Ltd. All rights reserved.

Keywords: Coordination polymer; Copper; Cobalt; Nickel; Pimelate; Dipyridylamine; Dipyridylpropane; Crystal structure; Antiferromagnetism; Ferromagnetism

1. Introduction

Over the past decade many researchers have undertaken significant effort towards the synthesis and characterization of metal dicarboxylate and tricarboxylate coordination polymers because of the capability of these materials in diverse applications such as gas storage [1], small molecule shape-selectivity [2], ion-exchange [3], catalysis [4], and optical devices [5]. In these phases dianionic dicarboxylate ligands not only serve to link metal cations into higher dimensionalities but also provide necessary charge balance, thereby permitting formation of a large number of neutral coordination polymer frameworks that exclude porosity-

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curtailing smaller anions. 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, and an array of available binding carboxylate modes. While the predominant focus has rested on aromatic dicarboxylates, aliphatic α,ω -dicarboxylate ligands have also shown their utility in the construction of novel coordination polymers due to their ability to undergo facile conformational interconversions [6].

More recently, elaboration of dicarboxylate-containing inorganic/organic hybrid materials has been achieved through the incorporation of neutral organodiimine tethering ligands such as the rigid-rod 4,4'-bipyridine (4,4'-bpy), which can connect metal cations through its distal pyridyl nitrogen donor atoms into a host of structurally interesting

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solids with intriguing physicochemical properties [7–10]. For example, the 2-D layered phase {[Zn(isophthal $ate(4.4'-bpv)(H_2O)$ = 1.5H₂O} manifested intense blue luminescence [8], [Co(thiophene-2,5-dicarboxylate)(4,4'bipy)] displayed field-dependent spin-flop magnetic behavior at low temperatures [9], and the interpenetrated 3-D material $[Zn(terephthalate)(4,4'-bpy)_{0.5}]$ exhibited а remarkable ability to chromatographically separate linear and branched alkanes [10]. This work has been extended to aliphatic α,ω -dicarboxylates, with some divalent metal adipate coordination polymers incorporating 4,4'-bpy or 1.2-di-4-pyridylethane (bpe). In many of these cases doubly interpenetrated 3-D networks were observed [11].

For some time, we have been interested in the synthesis and characterization of coordination polymer materials containing the organodiimine 4,4'-dipyridylamine (dpa, see Scheme 1). Unlike 4,4'-bpy, dpa possesses a kinked disposition of its terminal nitrogen donor atoms as well as a hydrogen bonding locus at its central secondary amine subunit that can assist in the formation of novel structural patterns. Neighboring dpa entities can also interact with each other or with other aromatic subunits through supramolecular π - π stacking interactions. Prior results from our laboratory have shown that coordination polymers with novel structural motifs can result from the hydrothermal combination of metal salts with aliphatic dicarboxylates and dpa [12,13]. Five different divalent metal coordination polymers were prepared utilizing succinate and dpa tethering ligands. Among these, $\{[Zn(succinate)(dpa)] \cdot H_2O\}$ displayed a rarely seen fourfold interpenetrated SrAl₂-type lattice, and $\{[Ni(dpa)_2(succinate)_{0.5}]Cl\}$ manifested an unprecedented 5-connected self-penetrated network with 6¹⁰ topology [12]. [Ni(adipate)(dpa)(H₂O)] exhibited the first-ever example of triple interpenetration within the PtS structure type [13]. In the present study, we have investigated dpacontaining coordination polymers based on pimelate (pim^{2-}) , an even longer α, ω -dicarboxylate tethering ligand with enhanced conformational flexibility. Significant differences in their two-dimensional structures were promoted by changes in metal coordination geometry. As the chemistry of dual pimelate/tethering organodiimine coordination polymers remains largely unexplored, we have also investigated the effect of utilizing the more flexible 1,3-dipyridylpropane (dpp) ligand. This change results in interpenetration absent in the dpa cases. Thermal and mag-



netic properties of these new coordination polymers are also reported herein.

2. Experimental

2.1. General considerations

 $CoCl_2 \cdot 6H_2O$, Ni $Cl_2 \cdot 6H_2O$ (Fisher) and pimelic acid (Aldrich) were obtained commercially. The organodiimine 4,4'-dipyridylamine (dpa) was prepared via a published procedure [14]. 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. IR spectra were recorded on powdered samples on a Perkin–Elmer Spectrum One instrument.

Powder X-ray diffraction patterns were obtained via Θ -2 Θ scans performed on a Rigaku Rotaflex instrument. Variable temperature magnetic susceptibility data (2–300 K) was 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 $[Ni(pim)(dpa)(H_2O)]_n$ (1-Ni)

NiCl₂ · 6 H₂O (0.088 g, 0.37 mmol), dpa (0.063 g, 0.37 mmol) and H₂pim (0.059 g, 0.37 mmol) were added to 10 mL of distilled H₂O in a 23 mL Teflon lined Parr acid digestion bomb. The pH was adjusted to 5.7 with 0.7 mL of a 1.0 M NaOH solution. The bomb was sealed, heated to 120 °C for 53 h, and then gradually cooled to ambient temperature. Green plates of **1-Ni** (0.109 g, 73% yield based on Ni) were obtained after filtration, washing with distilled water and acetone, and drying in air. Crystals of **1-Ni** were stable indefinitely in air. *Anal.* Calc. for C₁₇H₂₁NiN₃O₅ **1-Ni**: C, 50.28; H, 5.21; N, 10.35. Found: C, 50.30; H, 5.27; N, 10.41%. IR (cm⁻¹): 3250 w br, 2929 w, 1593 s, 1542 m, 1513 s, 1476 m, 1453 w, 1437 m, 1421 m, 1386 s, 1334 s, 1291 w, 1202 m, 1083 w, 1060 m, 1024 m, 904 w, 873 w, 827 s, 764 w, 731 s, 661 m.

2.3. Preparation of $[Co(pim)(dpa)(H_2O)]_n$ (1-Co)

The procedure for the synthesis of **1-Ni** was followed with the use of $CoCl_2 \cdot 6H_2O$ (0.088 g, 0.37 mmol) as the metal source. Magenta plates of **1-Co** (0.031 g, 21% yield based on Co) were obtained after filtration, washing with distilled water and acetone, and drying in air. Crystals of **1-Co** were stable indefinitely in air. *Anal.* Calc. for $C_{17}H_{21}CoN_3O_5$ **1-Co**: C, 50.26; H, 5.21; N, 10.34. Found: C, 50.46; H, 4.82; N, 10.36%. IR (cm⁻¹): 3250 w br, 2927 w, 1591 s, 1513 s, 1476 w, 1454 w, 1437 m, 1420 w, 1383

823

m, 1336 s, 1310 w, 1292 w, 1233 w, 1082 m, 1058 m, 1020 s, 904 m, 873 w, 827 s, 801 w, 732 s, 717 m, 660 s.

2.4. Preparation of $\{[Cu_2(pim)_2(dpa)_2] \cdot 5H_2O\}_n$ (2)

 $CuCl_2 \cdot 2H_2O$ (0.063 g, 0.37 mmol), H_2pim (0.059 g, 0.37 mmol) and dpa (0.127 g, 0.74 mmol) were placed into 10 g (555 mmol) distilled H₂O in a 23 mL Teflon-lined Parr acid digestion bomb (1:2:1500 mol ratio). The mixture was acidified to pH 4.5 with 0.5 mL of a 1.0 M HCl solution. The bomb was sealed and heated at 150 °C for 24 h, whereupon it was cooled slowly in air to 25 °C. Small blue crystals of 2 (0.089 g, 55% yield based on Cu) were isolated after washing with distilled water. Because the material effuses its waters of crystallization slowly upon standing, it was kept for long-term storage in its mother liquor. Anal. Calc. for C₃₄H₄₈Cu₂N₆O₁₃ (2): C, 46.62; H, 5.52; N, 9.60. Found: C, 43.36; H, 4.92; N, 9.03%. Elemental analyses showed lower than expected values on multiple samples, ascribed to either incomplete combustion or the presence of an amorphous inorganic impurity, as the powder XRD spectrum of freshly prepared 2 coincides exactly with that predicted from the single-crystal X-ray structure. IR (cm⁻¹): 3250 w br, 2927 w, 1593 s, 1526 s, 1445 m, 1394 s, 1358 s, 1291 m, 1256 w, 1205 s, 1062 m, 1026 s, 907 w, 816 s, 760 w, 729 w, 664 w.

2.5. Preparation of $[Ni(pim)(dpp)]_n(3)$

NiCl₂ · 6H₂O (0.088 g, 0.37 mmol), dpp (0.147 g, 0.74 mmol) and H₂pim (0.059 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 150 °C for 44 h, and then gradually cooled to ambient temperature. Green blocks of **3** (0.050 g, 33% 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 C₂₀H₂₄NiN₂O₄ **3**: C, 57.87; H, 5.83; N, 6.75. Found: C, 57.65; H, 5.74; N, 6.87%. IR (cm⁻¹): 2921 w, 1614 m, 1560 m, 1537 s, 1510 m, 1432 s, 1410 s, 1314 m, 1213 w, 1140 w, 1069 w, 1023 m, 920 w, 894 m, 862 m, 817 m, 808 m, 723 m, 660 m.

3. X-ray crystallography

Single crystals of all materials were subjected to single crystal X-ray diffraction using a Bruker-AXS SMART 1k CCD instrument. Reflection data was acquired using graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). The data were integrated via SAINT [15]. Lorentz and polarization effect and empirical absorption corrections were applied with SADABS [16]. The structures were solved using direct methods and refined on F^2 using SHELXTL [17]. 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 all aquo 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. Distended thermal ellipsoids for some of the pimelate carbon atoms in **2** are indicative of some amount of positional or thermal disorder; however, this could not be successfully modeled. Relevant crystallographic data is listed in Table 1.

4. Results and discussion

4.1. Synthesis and spectral characterization

The coordination polymers 1-3 were prepared cleanly under hydrothermal conditions via combination of the appropriate metal chloride, H_2 pim, and either dpa (1, 2) or dpp (3). The infrared spectra of 1-3 were consistent with their formulations. 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 [18]. 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 $\sim 1590 \text{ cm}^{-1}$ and \sim 1340 cm⁻¹. 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 water molecules of crystallization. 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.

4.2. Structural description of $[M(pim)(dpa)(H_2O)]_n$ (1-Ni, M = Ni; 1-Co, M = Co)

1-Ni and 1-Co are isomorphous, both crystallizing in the monoclinic space group $P2_1/c$ and possessing an asymmetric unit consisting of a metal atom, one doubly deprotonated pim²⁻ (pim) moiety, one dpa ligand, and one bound water molecule. The asymmetric unit of 1-Ni is displayed in Fig. 1; that of 1-Co is virtually identical. The coordination spheres about the divalent metal ions in these materials are slightly distorted [MO₄N₂] octahedra, with the two nitrogen donors from two different dpa molecules oriented in a cis fashion with respect to each other. Two of the oxygen donors (O1, O2) belong to the chelating terminus of a pim^{2-} ligand. The aquo ligand (O5) is disposed in a *cis* manner with respect to the remaining oxygen donor (O3), part of a monodentate carboxylate group of another (but crystallographically identical) pim²⁻ ligand. Bond lengths and angles (Table 2) about the metal ions are standard for distorted octahedral coordination complexes with one chelating ligand. The bond lengths for 1-Ni are slightly

Table 1	
Crystal and structure refinement parameters for 1-3	

	1-Ni	1-Co	2	3
Empirical formula	C ₁₇ H ₂₁ NiN ₃ O ₅	C ₁₇ H ₂₁ CoN ₃ O ₅	C34H48Cu2N6O13	C ₂₀ H ₂₄ N ₂ NiO ₄
Formula weight	406.08	406.30	875.86	415.12
Collection $T(\mathbf{K})$	173(2)	293(2)	173(2)	173(2)
Color and habit	green plate	magenta plate	blue block	green block
Crystal size (mm)	0.25 imes 0.20 imes 0.02	0.35 imes 0.30 imes 0.05	0.20 imes 0.18 imes 0.12	0.55 imes 0.45 imes 0.40
λ (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	triclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P\overline{1}$	$P2_1/c$
a (Å)	8.6725(15)	8.736(4)	9.9468(17)	7.572(4)
b (Å)	16.176(3)	16.295(7)	10.3520(18)	17.096(9)
$c(\mathbf{A})$	13.211(2)	13.337(6)	19.365(3)	15.499(9)
α (°)	90	90	77.728(3)	90
β (°)	104.725(3)	104.513(7)	82.270(3)	93.288(9)
γ (°)	90	90	84.770(3)	90
$V(\text{\AA}^3)$	1792.5(5)	1838.0(13)	1926.7(8)	2003.1(19)
Z	4	4	2	4
$D_{\rm calc} ({\rm g}{\rm cm}^{-3})$	1.505	1.468	1.506	1.377
$\mu (mm^{-1})$	1.116	0.966	1.125	0.995
Minimum/maximum, T	0.758	0.878	0.851	0.899
hkl ranges	$-11 \leqslant h \leqslant 11$,	$-11 \leqslant h \leqslant 11$,	$-13 \leqslant h \leqslant 13$,	$-9 \leqslant h \leqslant 9$,
	$-21 \leqslant k \leqslant 21,$	$-21 \leqslant k \leqslant 21,$	$-13 \leqslant k \leqslant 13$,	$-22 \leqslant k \leqslant 22,$
	$-17 \leqslant l \leqslant 17$	$-17 \leqslant l \leqslant 17$	$-25 \leqslant l \leqslant 25$	$-20 \leqslant l \leqslant 20$
Total reflections	21812	20264	23946	21772
Unique reflections	4 410	4274	9214	4581
R _{int}	0.1542	0.0351	0.0772	0.0244
Parameters/restraints	244/4	247/4	525/15	244/0
$R_1^{\rm a}$ (all data)	0.1363	0.0508	0.1375	0.0329
$R_1 (I > 2\sigma(I))$	0.0713	0.0360	0.0730	0.0276
$wR_2^{\rm b}$ (all data)	0.1592	0.0804	0.1678	0.0705
$wR_2 (I \ge 2\sigma(I))$	0.1361	0.0745	0.1439	0.0678
Maximum/minimum residual $(e^{-}/Å^{3})$	0.588/-0.756	0.388/-0.256	0.929/-0.578	0.279/-0.180
Goodness-of-fit	1.042	1.036	1.028	1.052

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



Fig. 1. The asymmetric unit of 1-Ni with thermal ellipsoids drawn at 50% probability and partial atom numbering scheme.

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

1-Ni			
Ni1-N3 ^{#1}	2.053(4)	N3 ^{#1} -Ni1-O3 ^{#2}	89.21(14)
Ni1-O3#2	2.068(3)	N3 ^{#1} –Ni1–O5	90.98(14)
Nil-O5	2.070(3)	O3 ^{#2} -Ni1-O5	92.05(13)
Nil-N1	2.103(4)	N3 ^{#1} –Ni1–N1	95.93(15)
Ni1-O2	2.121(3)	O3 ^{#2} -Ni1-N1	172.70(14)
Nil-O1	2.143(3)	O5–Ni1–N1	93.04(14)
O1-C11	1.267(5)	N3 ^{#1} -Ni1-O2	98.10(14)
O2-C11	1.264(6)	O3 ^{#2} -Ni1-O2	85.52(12)
O3-C17	1.274(6)	O5–Ni1–O2	170.55(13)
O4-C17	1.236(6)	N1-Ni1-O2	88.62(14)
		N3 ^{#1} -Ni1-O1	159.49(14)
		O3 ^{#2} -Ni1-O1	86.04(12)
		O5-Ni1-O1	109.09(13)
		N1-Ni1-O1	87.35(14)
		O2-Ni1-O1	61.67(12)
1-Co			
Co1-O4 ^{#3}	2.091(2)	O4 ^{#3} -Co1-O5	90.44(6)
Co1–O5	2.092(2)	O4 ^{#3} -Co1-N1	90.50(6)
Co1–N1	2.105(2)	O5-Co1-N1	90.04(6)
Co1-N3#4	2.159(2)	O4 ^{#3} -Co1-N3 ^{#4}	172.88(6)
Co1–O2	2.161(2)	O5-Co1-N3#4	93.15(7)
Co1–O1	2.187(2)	N1 ^{#4} -Co1-N3	95.64(6)
C11-O1	1.268(3)	O4 ^{#3} -Co1-O2	86.19(6)
C11–O2	1.255(3)	O5-Co1-O2	171.27(6)
C17–O3	1.239(3)	N1-Co1-O2	98.04(6)
C17–O4	1.271(2)	N3 ^{#4} -Co1-O2	89.38(7)
		O4 ^{#4} -Co1-O1	86.60(6)
		O5-Co1-O1	111.70(6)
		N1-Co1-O1	158.07(6)
		N3 ^{#2} -Co1-O1	86.36(6)
		O2-Co1-O1	60.10(6)
-			

Symmetry transformations to generate equivalent atoms: #1 -x+1, y+1/2, -z+3/2; #2 -x+2, y+1/2, -z+3/2; #3 -x+1, y+1/2, -z+1/2; #4 -x, y-1/2, -z+1/2.

shorter than those for **1-Co**, consistent with well-established ionic radius trends [19].

The pim^{2–} ligands adopt a *gauche–anti–anti–anti* conformation (four C-atom torsion angles = 69.19°, 173.08°, 178.17° and 170.39° for **1-Ni**) and bridge neighboring metal atoms in an exobidentate chelating/monodentate fashion to form undulating $[M(pim)]_n$ chain motifs that course parallel to the *b* crystal axis (Fig. 2). While the chelating carboxylates in **1-M** display symmetric binding to the metal, the C–O bond lengths of the monodentate carboxylate termini vary by ~0.40 Å, reflective of enhanced π -type character in the between the carboxylate C atom and the unligated oxygen atoms. The $[M(pim)]_n$ chains in turn are connected through tethering dpa ligands to generate a ruffled $[M(pim)(dpa)(H_2O)]_n$ twodimensional (4,4) layer motif parallel to the ab crystal plane (Fig. 3). Each metal ion is covalently connected to four others, with two connections each via pim²⁻ and dpa ligands. The metal-metal contact distances through the pim²⁻ ligands measure 8.988 Å and 9.056 Å for 1-Ni and 1-Co, respectively; the corresponding contact distances through the dpa tethers are 11.350 Å and 11.465 Å. In order to accommodate the necessary orientation for appropriate covalent bonding, the dpa molecule undergoes a significant inter-ring torsion (47.1° in 1-Ni and 46.7° in 1-Co). The incipient void spaces within the resulting puckered rhomboid circuits in 1-Ni measure 8.673 and 16.176 Å (via through-space Ni–Ni distances), with Ni-Ni-Ni angles of 48.8°, 48.8°, 90.9° and 128.3°. The corresponding through-space Co-Co distances in 1-**Co** are slightly longer at 8.736 and 16.295 Å with virtually identical Co-Co-Co angles.

The covalent connectivity within the layer is supplemented by supramolecular hydrogen bonding donation from the amine functional group of dpa to the oxygen atom O3 within the chelating carboxylate moiety. In addition, the aquo ligand provides a hydrogen bonding point of contact to the unligated oxygen atom of type O4 within the monodentate carboxylate group, possibly preventing a bis-monodentate bis-monodentate binding mode for the pim²⁻ ligand. The puckering of the individual 2-D layers causes an alternation of the position of the pim²⁻ ligands above and below the layer, allowing interlayer hydrogen bonding between the aqua ligands and oxygen atoms of type O1 within the chelating carboxvlate groups. These supramolecular interactions result in stacking of the $[M(pim)(dpa)(H_2O)]_n$ layers along the c crystal direction to establish the pseudo 3-D crystal structures of 1-M (Fig. 4). The interlayer metal-metal contact distances are 5.113 Å and 5.095 Å in 1-Ni and 1-Co, respectively, significantly closer than the intralayer metal-metal distances. Metrical parameters for the classical hydrogen bonding interactions in 1-M are given in Table 3.



Fig. 2. $[Ni(pim)]_n$ chain motif in 1-Ni.



Fig. 3. Face-on view of the $[Ni(pim)(dpa)(H_2O)]_n$ 2-D layers in 1-Ni. Intralayer hydrogen bonding is shown as dashed lines.



Fig. 4. Stacking of [M(pim)(dpa)(H₂O)], layers along the c crystal direction by supramolecular interlayer hydrogen bonding (shown as dashed lines).

4.3. Structural description of $\{[Cu_2(pim)_2(dpa)_2] \cdot 5H_2O\}_n$ (2)

The asymmetric unit of **2** (Fig. 5) was found to contain two crystallographically distinct divalent copper atoms, two fully deprotonated pim^{2–} dianions (C21–C27/O1–O4, *pim-A*; C31–C37/O5–O8, *pim-B*), two dpa ligands (C1– C10/N1–N3, *dpa-A*; C11–C20/N4–N6, *dpa-B*), and five water molecules of crystallization, one of which (O5W) is disordered equally over two positions. One of the copper atoms (Cu1) adopts a virtually perfect {CuN₂O₃} square pyramidal coordination geometry ($\tau = 0.01$) [20], with one nitrogen donor from a *dpa-A* ligand, one nitrogen donor from a *dpa-B* ligand, and oxygen donors from two different *pim-B* ligands situated within the basal plane. The nitrogen donors are oriented in a *trans*-fashion within the basal plane, as are the oxygen donors. The coordination sphere about Cu1 is completed by an oxygen donor from a third *pim-B* ligand lying in the axial position. The bond lengths and angles about Cu1 (Table 4) are consistent with the well-known Jahn-Teller distortion for Cu²⁺. The other crystallographically distinct Cu atom (Cu2) exhibits

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

D–H […] A	<i>d</i> (H A)	∠DHA	$d(\mathbf{D}^{\dots}\mathbf{A})$	Symmetry transformation for A
1-Ni				
O5–H5A…O1	1.87(2)	177(5)	2.707(4)	-x+2, y+1/2, -z+3/2
O5–H5B O4	1.90(3)	142(5)	2.618(5)	-x+2, -y, -z+1
N2-H2NO3	1.93(2)	166(5)	2.799(5)	
1-Co				
O5–H5A…O1	1.88(2)	169(2)	2.711(2)	-x+1, -y, -z
O5–H5B O3	1.79(2)	169(3)	2.623(3)	-x, y + 3/2, -z + 1/2
N2-H2NO4	1.98(2)	173(2)	2.828(2)	-x, y + 1/2, -z + 1/2
2				
N2–H2N···O1W	2.00(2)	178(5)	2.877(6)	x - 1, y, z
N5–H5N […] O6	2.02(3)	157(5)	2.845(6)	-x+1, -y+2, -z
O1W-H1WA ^{···} O4	1.96(3)	157(6)	2.768(6)	-x+1, -y+2, -z
O1W-H1WB O6	1.88(3)	164(5)	2.690(5)	
O2W-H2WA ^{···} O3W	2.06(2)	143(4)	2.846(7)	x - 1, y - 1, z
O2W-H2WB O1W	2.08(2)	147(4)	2.926(7)	-x+1, -y+1, -z
O3W–H3WA ^{···} O3	2.00(3)	163(7)	2.825(6)	
O3W–H3WB ^{···} O2	2.16(4)	151(7)	2.921(6)	x, y + 1, z
O4W-H4WA ^{···} O7	2.17(4)	150(7)	2.940(6)	
O4W-H4WB O5WA	2.07(3)	163(7)	2.905(2)	x - 1, y, z
O4W-H4WB O5WB	1.95(6)	128(7)	2.564(2)	x - 1, y, z



Fig. 5. Asymmetric unit of 2 with thermal ellipsoids shown at 50% probability and partial atom numbering scheme. Most hydrogen atoms have been omitted for clarity.

a {*trans*-CuN₂O₂} square planar coordination environment, with the nitrogen donors belonging to two crystallographically distinct dpa ligands and the oxygen donors provided by two different *pim-A* ligands. The O1–Cu2–O3 bond angle (Table 3) is $\sim 20^{\circ}$ narrower than the corresponding trans N1–Cu2–N4 bond angle, a deviation from idealized square planar geometry likely provoked by long range Cu \cdots O interactions and other supramolecular effects (*vide infra*).

Extension of the structure about Cu1 reveals $\{Cu_2O_2\}$ bimetallic kernels formed by the junction of two adjacent Cu1 atoms by two μ_2 -bridging oxygen atoms of type O8 belonging to two different *pim-B* units. Each O8 oxygen atom lies in the basal plane of one Cu1 square pyramid, and is in the axial position of another, resulting in an asymmetric rhomboid four-membered ring. The through-space Cu1–Cu1 and O8–O8 distances are 3.391 Å and 2.796 Å, respectively; the Cu–O–Cu and O–Cu–O angles within the rhomboid {Cu₂O₂} unit subtend 101.2(5)° and 78.8(5)°. Adjacent {Cu₂O₂} units are linked to two others along the *b* crystal direction by means of tethering *pim-B* dianions in an *anti–gauche–anti–anti* conformation (C–C– C–C torsion angles: 177.0°, 25.7°, 175.6°, 174.6°), thereby forming 1-D [Cu₂(pim)₂]_n ribbon motifs (Fig. 6A). The Cu–Cu distance through the kinked *pim-B* ligand is 8.888 Å. The pim^{2–} moieties in this chain are exotridentate,

Table 4 Selected bond distance (Å) and angle (°) data for $\mathbf{2}$

Selected bond distance (A) and angle () data for 2						
Cu1–O5	1.950(3)	O5–Cu1–N3	88.05(15)			
Cu1-O8 ^{#1}	1.991(3)	O8 ^{#1} -Cu1-N3	92.17(15)			
Cu1-N6 ^{#2}	2.006(4)	N6 ^{#2} -Cu1-N3	175.65(16)			
Cu1-N3	2.006(4)	O5-Cu1-O8#3	104.69(12)			
Cu1-O8 ^{#3}	2.388(3)	O8 ^{#1} -Cu1-O8 ^{#3}	78.88(12)			
Cu2-O3#4	1.974(4)	N6 ^{#2} -Cu1-O8 ^{#3}	91.30(14)			
Cu2–N4	1.987(4)	N3-Cu1-O8 ^{#3}	91.69(14)			
Cu2–O1	1.989(3)	O3#4-Cu2-N4	91.67(15)			
Cu2-N1	1.996(4)	O3 ^{#4} -Cu2-O1	154.42(16)			
		N4-Cu2-O1	91.86(15)			
O5-Cu1-O8#1	176.41(13)	O3#4-Cu2-N1	87.87(16)			
O5-Cu1-N6 ^{#2}	88.13(15)	N4-Cu2-N1	174.69(17)			
O8 ^{#1} -Cu1-N6 ^{#2}	91.51(14)	O1-Cu2-N1	90.83(15)			
		Cu1 ^{#1} -O8-Cu1 ^{#4}	101.12(12)			

Symmetry transformations to generate equivalent atoms: #1 - x + 1, -y, -z + 1; #2 x + 1, y - 1, z + 1; #3 x, y + 1, z; #4 x, y - 1, z.

binding to Cu in a monodentate fashion at O5, and bridging two Cu atoms via their O8 termini. An interaction between Cu1 and the unligated carboxylate oxygen atom O7 is evident, with a Cu···O distance of 2.783 Å. Such "secondary bonding" interactions are common in Cu²⁺ coordination complexes [21].

In turn, Cu2 atoms are connected into 1-D $[Cu(pim)]_n$ single chains via tethering *pim-A* dianionic units (Fig. 6B), which adopt a spread out *gauche-anti-antigauche* conformation (torsion angles = 77.2°, 177.3°, 173.0°, 68.7°) with a bis-monodentate bis-monodentate binding mode. Due to the more open conformation, the Cu2–Cu2 distance through *pim-A* is 10.352 Å, almost 1.5 Å longer than the *pim-B*-bridged corresponding Cu1– Cu1 distance. Abutting [Cu(pim)]_n single chains are weakly conjoined through long "4+1" type Cu2···O1 secondary interactions (2.700 Å, drawn as dashed lines in Fig. 6B). If these interactions are considered "bonds", $\{Cu_2O_2\}$ bimetallic units similar to those within the Cu1-based ribbons can be invoked. However, the Cu2–Cu2 distances within these units are ~0.25 Å longer, at 3.647 Å, with a Cu2–O1···Cu2 angle of 100.99°. It is likely that the conformational flexibility of the pim^{2–} tethers assists in the formation of two different 1-D copper dicarboxylate motifs in **1**.

Alternating $[Cu_2(pim)_2]_n$ ribbons (based on Cu1) and $[Cu(pim)]_n$ double chain subunits (based on Cu2) are subsequently bridged together by tethering dpa ligands to establish a 2-D $[Cu_2(pim)_2(dpa)_2]$ neutral coordination polymer slab that lies parallel to the $(10\bar{1})$ crystal plane (Fig. 7). The Cu1–Cu2 distances measure 11.485 Å (through *dpa-A* with an inter-ring torsion angle of 28.7°) and 11.527 Å (through *dpa-B* with an inter-ring torsion angle of 29.6°). The covalent connectivity within the slab motif is augmented by π - π stacking between *dpa-A* and *dpa-B* ligands (centroid-to-centroid distances 3.647(1) Å and 3.631(1) Å), imposed by the presence of the {Cu₂O₂} bimetallic units with similar metal-metal contact distances.

 $[Cu_2(pim)_2(dpa)_2]$ slabs stack along the *a* crystal direction via N-H···O hydrogen bonding interactions between the central amine functional groups of *dpa-B* ligands and unligated carboxylate oxygen atoms of type O5 within the *pim-B* dianions, which project into the interlamellar regions (Fig. 8). The closest interlayer Cu-Cu contact distance is 8.549 Å.

Sequestered within and between the coordination polymer layers are discrete hydrogen bonded aqueous chains of eight water molecules each $(O3W \cdots O2W \cdots O4W \cdots O5W \cdots O5W \cdots O4W \cdots O2W \cdots O3W)$, decorated at each



Fig. 6. [Cu₂(pim)₂] ribbons (A) and [Cu(pim)] double chains with long range interactions shown as dashed lines (B) in 2.



Fig. 7. A 2-D slab motif in 2, formed from the junction of parallel 1-D [Cu₂(pim)₂] ribbons and [Cu(pim)] double chains through dpa tethers.



Fig. 8. Stacking of neighboring 2-D slabs in 2. Discrete water molecule chains can be seen coursing within and between the layers. Hydrogen bonding connectivity for one of these water chains is shown as dashed lines.

O2W position by additional pendant water molecules (type O1W). Therefore the unligated water molecule substructure falls into the uncommonly encountered D(8) morphological classification [22], with a connectivity pattern resembling that of 2,7-dimethyloctane. The uncoordinated water molecules are anchored to the coordination polymer matrix by extensive hydrogen bonding pathways. The water molecules at the chain termini (O3W) engage in hydrogen bonding donation to the ligated and unligated carboxylate oxygen atoms O3 and O2, belonging to two separate *pim-A* ligands. Water molecules of type O1W, serving as "substituents" on the aqueous chain, link to

the coordination polymer framework by accepting hydrogen bonds from the amine units of dpa-A and donating hydrogen bonds to unligated carboxylate oxygen atoms O4 and O6, belonging to *pim*-A and *pim*-B, respectively. Finally, water molecules of type O4W are held by hydrogen bonding donation to unligated carboxylate oxygen atoms O7, part of *pim*-B. Metrical parameters for the supramolecular hydrogen bonding interactions in **2** are listed in Table 3. According to a calculation performed with PLATON [23], the incipient void spaces occupied by the water molecules of crystallization represent 17.6% of the unit cell volume of **2**.

4.4. Structural description of [Ni(pim)(dpp)] (3)

The asymmetric unit of **3** (Fig. 9) contains one divalent nickel atom, one dpp ligand, and a doubly deprotonated pim^{2-} dianion. Due to the chelation of the pim^{2-} carboxylate termini, the coordination environment about Ni is best described as a distorted [NiO₄N₂] octahedron; bond lengths and angles about Ni are consistent with this description (Table 5). The two nitrogen donors, which belong to two different dpp ligands, are arranged in a *cis* orientation.

Extension of the structure reveals that each Ni atom is linked to four others, two through dpp linkers and two through pim²⁻ dianions, to form a 2-D rhomboid grid coordination polymer morphology. The torsion angles across the trimethylene bridge of the dpp ligand (179.4° and 176.1°) show that the dpp subunit has adopted a splayed-open *anti* conformation, providing a throughligand Ni–Ni contact distance of 13.42 Å. The bis-bridging bischelating pim²⁻ tethers display a *gauche–anti–anti– anti* conformation (torsion angles 71.6°, 171.2°, 173.6°, and 176.2°), providing a Ni–Ni distance of 10.28 Å, ~3.1 Å shorter than the corresponding through-dpp distance.

The grid apertures in 3, 17.10×15.14 Å as measured by through space Ni-Ni distances, are large enough to accommodate interpenetration of a second identical [Ni(pim)(dpp)]_n 2-D layer (Fig. 10). This stands in marked contrast to 1, which does not display any interpenetration due to the shorter dpa tethers and resulting smaller grid mesh size. Within a single grid, the Ni-Ni-Ni angles subtend 78.2°, 78.2°, 79.15° and 112.48°. The closest Ni-Ni separation between two independent interpenetrated layers is 7.57 Å. Layer motifs subsequently stack along the c crystal direction primarily by means of π - π supramolecular interactions (3.892(2) Å) between dpp pyridyl rings within adjacent layers, thus constructing the pseudo 3-D crystal structure of 3. The closest interlayer Ni–Ni contact distance is 7.92 Å. Unfortunately, attempts to prepare a copper coordination polymer containing both pim²⁻ and dpp resulted either in amorphous products or the known 1-D chain phase $[CuCl(dpp)]_n$ [24].

Table 5									
Selected 1	bond	distance	(Å)	and	angle	(\circ)	data	for 3	3

		()	
Nil-O4	2.0675(13)	N2 ^{#1} -Ni1-N1	92.70(6)
Ni1-N2#1	2.0683(15)	O4-Ni1-O2#2	162.48(4)
Ni1–N1	2.0747(15)	N2 ^{#1} -Ni1-O2 ^{#2}	94.25(6)
Ni1-O2#2	2.0761(14)	N1-Ni1-O2#2	97.37(5)
Ni1-01#2	2.1433(15)	O4-Ni1-O1#2	103.60(5)
Nil-O3	2.1530(15)	N2#1-Ni1-O1#2	92.74(6)
O1-C21	1.256(2)	N1-Ni1-O1#2	159.22(5)
O2-C21	1.2659(19)	O2 ^{#2} -Ni1-O1 ^{#2}	62.22(4)
O3–C27	1.2548(19)	O4-Ni1-O3	62.29(5)
O4–C27	1.2718(18)	N2 ^{#1} -Ni1-O3	159.02(5)
		N1-Ni1-O3	91.13(6)
O4-Ni1-N2#1	96.80(6)	O2 ^{#2} -Ni1-O3	105.69(5)
O4–Ni1–N1	95.64(5)	O1 ^{#2} -Ni1-O3	90.93(6)

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

4.5. Variable temperature magnetism

To probe possible spin communication, samples of **1** and **2** were subjected to variable temperature magnetic study. For **1**, the $\chi_m T$ value at 300 K was $1.23 \text{ cm}^3 \text{ K mol}^{-1}$. This is slightly higher than predicted for a spin-only uncoupled Ni²⁺ d⁸ S = 1 ion, indicative of anisotropy. The $\chi_m T$ value remained largely constant to 60 K, whereupon it began to decrease, reaching a value of $1.08 \text{ cm}^3 \text{ K mol}^{-1}$ at 12 K. At lower temperatures the $\chi_m T$ product dropped precipitously, a sign of possible antiferromagnetic coupling, zero field splitting, or a cooperative effect of the two phenomena. The magnetic susceptibility of **1** was modeled using Eq. (1) [25], which accounts for both magnetic coupling between Ni centers (Θ) and zero field splitting (D).

 $\chi_{\rm m}T$

$$= \left(\frac{2Ng^2\beta^2}{3\,k(T-\Theta)} \left(\frac{(2kT/D) - (2kT\exp(x)/D) + \exp(x)}{1 + 2\exp(x)}\right)T\right)$$
(1)

where x = -D/kT.

The best fit to the data (Fig. 11) occurred with g = 2.241(2), $\Theta = -1.62(4)$ K and D = 4.9(1) cm⁻¹ with $R = 9.55 \times 10^{-3} = \{\sum [(\chi_m T)_{obs} - (\chi_m T)_{calc}]^2 / \sum (\chi_m T)_{obs}]^2 \}$. Within the layer structure of **1**, the pimelate and dpa



Fig. 9. Asymmetric unit of 3 with thermal ellipsoids shown at 50% probability and partial atom numbering scheme. Most hydrogen atoms have been omitted for clarity.



Fig. 10. A view down c of doubly interpenetrated (4,4) layers in 3.



Fig. 11. Plot of $\chi_m T$ vs T for 1-Ni. The calculated fit to Eq. (1) is indicated as a solid black line.

ligands cause Ni–Ni distances that are likely too long for any significant magnetic communication. Closer Ni–Ni interactions (~5.1 Å), mediated by hydrogen bonding between the aquo ligands and chelating carboxylate moieties in adjacent layers, could be the origin of the observed weak interlayer antiferromagnetic coupling. Attempted fits using models that accounted for either interlayer antiferromagnetic coupling or zero field splitting alone were much less successful. Hydrogen-bonding promoted magnetic communication between paramagnetic metal ions has been reported in other coordination polymer materials [26].

The plot of the $\chi_m T$ product versus T for 2 (Fig. 12) showed an increase in $\chi_m T$ as temperature decreased, a sign of ferromagnetic interactions within one or both types of oxygen bridged dimeric Cu units within the coordination polymer structure. The $\chi_m T$ value reached a maximum of $1.52 \text{ cm}^3 \text{ K mol}^{-1}$ at 5.2 K, below which temperature it began to decrease (see inset of Fig. 12). This low-temperature behavior can be ascribed to weaker antiferromagnetic interactions between adjacent {Cu₂O₂} dimeric units through either the pimelate or dpa tethering ligands. Unfortunately no Curie-Weiss regime was found in the variable temperature susceptibility data for 2, even at higher temperatures. Neither could the data be fit acceptably to the Bleaney–Bowers equation [27] for magnetically interacting Cu(II) dimers, even incorporating an interdimer parameter (Θ) . It is possible that the presence of two different types of $\{Cu_2O_2\}$ dimeric units in 2, with varying Cu···Cu contact distances, results in significant differences in the nature and magnitude of their respective magnetic interactions [28]. Thus, the overall magnetic susceptibility behavior can be ascribed to the simultaneous action of the spin communication within both types of $\{Cu_2O_2\}$ dimer, thereby greatly complicating any attempts at modeling. Nevertheless, it is probable that net intradimer ferromagnetic interactions occur in **2**, with an underlying weak interdimer antiferromagnetic superexchange mechanism.

4.6. Thermal analysis of 1-3

Compound 1-Ni underwent loss of its ligated water molecule between 250 °C and 320 °C (4.9% mass loss, 4.4% predicted). Combustion of the organic components ensued, with a series of mass losses between 350 °C and 600 °C. The mass remnant of 21% corresponds roughly with the deposition of NiO (18% calcd.). Compound 2, which had apparently lost 2 equiv. of unbound water molecules on standing, continued to dehydrate between 45 °C and 115 °C (5.5% mass loss, 6.1% calcd. for 3 equiv. of water). Combustion of organics commenced at ~250 °C, resulting in likely deposition of CuCO₃ at 700 °C (29% mass remnant, 30% theoretical). Compound 3 remains stable until \sim 320 °C at which point rapid expulsion of the organic components occurs. The 22% mass remnant at 600 °C corresponds loosely to NiO (18% calcd.). TGA traces for 1-3 are depicted in Figs. S1-S3.



Fig. 12. Plot of $\chi_m T$ vs T for **2** (inset shows low temperature data only).

5. Conclusions

Taking advantage of the conformational flexibility of the α,ω -dicarboxylate pimelate ligand, four two-dimensional organodiimine-containing coordination polymers have been prepared. Both the pimelate conformation and the tether length and hydrogen-bonding capability of the organodiimine component appear to play a significant structure-directing role, in synergy with coordination geometry preferences. Use of a longer tethering organodiimine promotes the formation of rhomboid grids with larger apertures, resulting in an interpenetrated structure. The lowered coordination number at the copper centers in 2, as opposed to 1 and 3, promotes a double slab structure with $\{Cu_2O_2\}$ dimers that exhibit apparent ferromagnetic coupling. The differing pimelate conformations observed in these materials reflect this ligand's ability to adjust to the requirements imposed by the metal coordination geometry and the supramolecular environment. Investigation of long-chain α, ω -dicarboxylate coordination polymers incorporating kinked or flexible organodiimines remains a fruitful area of synthetic exploration in our laboratory, and further results will be reported in due course.

Acknowledgements

The authors gratefully acknowledge Michigan State University for financial support of this work.

We thank Dr. Rui Huang for elemental analysis and David Martin and Lindsey Johnston for the acquisition of the infrared spectra. SDG.

Appendix A. Supplementary material

CCDC 652276, 652277, 652278 and 652279 contain the supplementary crystallographic data for compounds 1-Ni, 1-Co, 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. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2007.11.006.

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