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Research paper

Metal ion control of dimensionality and self-penetration in coordination polymers containing furandicarboxylate and dipyridylamide ligands

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ABSTRACT

Hydrothermal reaction of metal nitrates, 2,5-furandicarboxylic acid (H_2fdc) and the conformationally flexible dipyridylamide ligand 3-pyridylnicotinamide (3-pna) afforded three new coordination polymers which were structurally characterized by single-crystal X-ray diffraction. $\{[Cd_2(fdc)_2(3\text{-pna})(H_2O)_4]\cdot 6H_2O\}_n$ (**1**) exhibits a 1D ladder structural motif with tethering *anti*-conformation 3-pna ligands acting as the rungs. $\{[Ni(fdc)(3\text{-pna})_2(H_2O)]\cdot 2.5H_2O\}_n$ (**2**) displays a (4,4) rhomboid grid structure that resembles a rarer (3,6) triangular grid if supramolecular interactions provided by pendant *syn*-conformation 3-pna ligands are considered. $[Co(fdc)(3\text{-pna})(H_2O)]_n$ (**3**) manifests $\{Co_2(OCO)_2\}$ *anti-syn* dimer-based 3-connected 4.8^2 layers pillared into a novel 3D 3,5-connected self-penetrated $(4.6.8)(4.6^5 8^3 10)$ topology network by *anti*-conformation 3-pna ligands. The specific metal coordination environments, fdc binding mode, and 3-pna conformation act synergistically to enforce structure direction in this system. Thermal decomposition properties of these three new materials are also discussed.

1. Introduction

Basic research efforts towards the synthesis and structural characterization of crystalline coordination polymers have continued unabated over the past decade. These materials can possess diverse applications in hydrogen storage [1], selective separations [2], ion exchange [3], heterogeneous catalysis [4], non-linear optics [5], and explosives residue detection [6]. The near limitless combination of divalent metal ions, anionic dicarboxylate ligands, and ancillary neutral dipyridyl ligands continues to spur exploratory synthetic investigations into coordination polymers. Research has focused lately on their efficacious properties, but interest remains in regard to their often strikingly beautiful structural aesthetics [7], including interpenetrated [8] or self-penetrated frameworks [9].

Some of the most commonly employed linking agents in the construction of divalent metal coordination polymer or metal-organic framework solids are terephthalate (tp, *p*-benzenedicarboxylate) or isophthalate (ip, *m*-benzenedicarboxylate), which can provide the requisite charge neutrality and also the rigidity needed for a stable crystalline phase [10–14]. Structural diversity and functional properties can be enhanced through the inclusion of other neutral co-ligands, such as dipyridines or bisimidazoles. For instance, the interpenetrated 3-D metal-organic framework $[Zn(tp)(bpy)_{0.5}]_n$ (bpy = 4,4′-bipyridine) can act as a gas chromatographic stationary phase for the industrially relevant separation of linear and branched alkanes [13].

Compared to terephthalate and isophthalate, the related five-membered aromatic derivative 2,5-furandicarboxylate (fdc, Scheme 1) has seen relatively infrequent use in the self-assembly of coordination polymers [15–19]. Recent work by Sen and Lin showed that auxiliary dipyridyl ligands such as 1,2-bis(4-pyridyl)ethylene (bpe) and 1,2-bis(4-pyridyl)ethane (bpee) could produce intriguing twofold interpenetrated uninodal 7-connected networks with $3^3 4^{13} 5^4 6$ topology, in both $[Ni(fdc)(bpe)]_n$ and $[Ni(fdc)(bpee)]_n$. These materials and their isostructural cobalt derivatives all showed modest uptake of nitrogen gas [15]. Sen and Lin also prepared a series of cadmium coordination polymers containing fdc and various auxiliary dipyridyl ligands, in which $\{[Cd(fdc)(bpy)(H_2O)_2]\cdot CH_3CH_2OH\}_n$ manifested an intriguing 1D + 1D → 2D system of interlocked square nanotubes, while $[Cd(fdc)(bpe)(H_2O)]_n$ exhibited a 1D + 1D → 3D system of interwoven ribbon motifs [16].

Coordination polymers containing the fdc ligand and the dipyridylamide 3-pyridylnicotinamide (3-pna) have not yet been reported. In contrast to the well-used rigid-rod bpy ligand, 3-pna can adopt *syn* or *anti* conformations (Scheme 1), resulting in different metal-metal linkage distances. $[Zn(ip)(3\text{-pna})]_n$ possessed $\{Zn_2(OCO)_2\}$ dimer-based $[Zn(ip)]_n$ chains linked into $(4^2 6)(4^2 6^7 8)$

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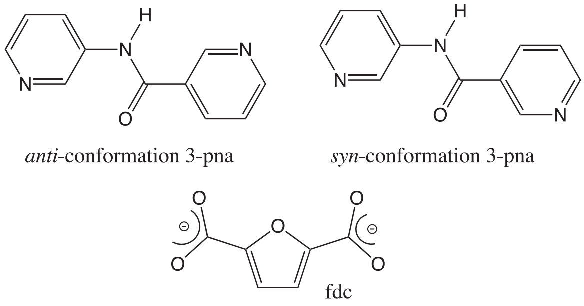

Scheme 1. Ligands used in this study.

3,5L2 topology layers by *anti*-conformation 3-pna ligands [20]. However, $\{[Zn(mip)(3\text{-}pna)]\cdot 2H_2O\}_n$ (mip = 5-methylisophthalate) featured *syn* conformation 3-pna ligands, and thereby formed rarely encountered 4-connected 1-D ribbon motifs with $3^3 4^2 5$ topology and encapsulated single-file water molecule chains within its incipient tubular channels [20]. In this contribution we report the synthesis, single-crystal structures, and thermal properties of the first reported coordination polymers to contain both the fdc and 3-pna ligands: $\{[Cd_2(fdc)_2(3pna)(H_2O)_4]\cdot 6H_2O\}_n$ (**1**), $\{[Ni(fdc)(3\text{-}pna)_2(H_2O)]\cdot 2.5H_2O\}_n$ (**2**), and $[Co(fdc)(3\text{-}pna)(H_2O)]_n$ (**3**).

2. Experimental section

2.1. General considerations

Metal nitrates (Fisher) and 2,5-furandicarboxylic acid (TCI America) were purchased commercially. The 3-pna ligand was prepared via condensation of nicotinoyl chloride hydrochloride and one molar equivalent of 3-pyridylamine in dry pyridine solvent, in a manner similar to that used for the preparation of 4-pyridylisonicotinamide [21]. Water was deionized above 3 MΩ-cm in-house. IR spectra were recorded on powdered samples using a Perkin Elmer Spectrum One instrument. Thermogravimetric analysis was performed under flowing N_2 on a TA Instruments TGA Q50 Thermogravimetric Analyzer with a heating rate of 10 °C/min up to 600 °C.

2.2. Preparation of $\{[Cd_2(fdc)_2(3\text{-}pna)(H_2O)_4]\cdot 6H_2O\}_n$ (**1**)

$Cd(NO_3)_2\cdot 4H_2O$ (115 mg, 0.38 mmol), 2,5-furandicarboxylic acid (59 mg, 0.38 mmol) and 3-pna (75 mg, 0.39 mmol) and 1.0 mL of a 1.0 M NaOH solution were placed into 10 mL distilled H_2O in a Teflon-lined acid digestion bomb. The bomb was sealed and heated in an oven at 150 °C for 4 d, and then cooled slowly to 25 °C. Colorless crystals of **1** (116 mg, 67% yield based on Cd) were isolated after washing with distilled water and acetone, and drying in air. Anal. Calc. for $C_{23}H_{34}Cd_2N_3O_{21}$ **1**: C, 30.25; H, 3.75; N, 4.60%. Found: C, 29.98; H, 3.41; N, 4.41%. IR (cm^{-1}): 3198 (m), 1677 (w), 1579 (s), 1552 (s), 1489 (m), 1429 (w), 1359 (s), 1337 (w), 1306 (m), 1218 (w), 1197 (m), 1127 (w), 1031 (m), 1012 (m), 968 (m), 897 (w), 830 (m), 801 (m), 782 (s), 699 (s).

2.3. Preparation of $\{[Ni(fdc)(3\text{-}pna)_2(H_2O)]\cdot 2.5H_2O\}_n$ (**2**)

$Ni(NO_3)_2\cdot 6H_2O$ (110 mg, 0.38 mmol), 2,5-furandicarboxylic acid (60 mg, 0.38 mmol) and 3-pna (146 mg, 0.76 mmol) and 1.0 mL of a 1.0 M NaOH solution were placed into 10 mL distilled H_2O in a Teflon-lined acid digestion bomb. The bomb was sealed and heated in an oven at 120 °C for 2 d, and then cooled slowly to 25 °C. Green-blue crystals of **2** (132 mg, 51% yield based on Ni) were isolated after washing with distilled water and acetone, and drying in air. Anal. Calc. for $C_{28}H_{27}N_6NiO_{10.5}$ **2**: C, 49.88; H, 4.04; N, 12.47%. Found: C, 49.51; H, 3.93; N, 12.31%. IR (cm^{-1}): 3259 (w), 1666 (m), 1587 (m), 1543 (m), 1478 (m), 1431 (w), 1420 (s), 1389 (w), 1358 (s), 1328 (s), 1293 (s), 1190 (m), 1119 (m), 1046 (m), 1032 (m), 962 (w), 901 (m), 785 (s), 730 (w), 696 (s).

2.4. Preparation of $[Co(fdc)(3\text{-}pna)(H_2O)]_n$ (**3**)

$Co(NO_3)_2\cdot 6H_2O$ (108 mg, 0.38 mmol), 2,5-furandicarboxylic acid (60 mg, 0.38 mmol) and 3-pna (75 mg, 0.39 mmol) and 0.75 mL of a 1.0 M NaOH solution were placed into 10 mL distilled H_2O in a

Table 1
Crystal and structure refinement data for **1**–**3**.

Data	1	2	3
Empirical formula	$C_{23}H_{34}Cd_2N_3O_{21}$	$C_{28}H_{27}N_6NiO_{10.5}$	$C_{17}H_{13}CoN_3O_7$
Formula weight	913.33	674.26	430.23
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$	$C2/c$
a (Å)	8.9382(5)	10.4593(13)	21.984(2)
b (Å)	9.9664(6)	28.321(4)	10.0481(8)
c (Å)	10.0591(6)	10.8203(14)	14.7669(12)
α (°)	74.8476(6)	90	90
β (°)	83.3062(6)	113.1484(14)	90.5741(17)
γ (°)	66.2266(6)	90	90
V ($Å^3$)	791.47(8)	2947.1(6)	3261.9(5)
Z	1	4	8
D_{calc} (g cm^{-3})	1.916	1.520	1.752
μ (mm^{-1})	1.439	0.729	1.104
Min./max. trans.	0.8906	0.8875	0.8834
hkl ranges	$-11 \leqslant h \leqslant 11$, $-12 \leqslant k \leqslant 12$, $-12 \leqslant l \leqslant 12$	$-12 \leqslant h \leqslant 12$, $-34 \leqslant k \leqslant 34$, $-13 \leqslant l \leqslant 13$	$-26 \leqslant h \leqslant 26$, $-12 \leqslant k \leqslant 12$, $-17 \leqslant l \leqslant 17$
Total reflections	13,984	47,814	12,780
Unique reflections	3125	5403	2973
R(int)	0.0386	0.0612	0.0343
Parameters	255	437	260
R_1 (all data)	0.0324	0.1293	0.0449
R_1 ($I > 2\sigma(I)$)	0.0279	0.1198	0.0383
wR_2 (all data)	0.0652	0.2450	0.0961
wR_2 ($I > 2\sigma(I)$)	0.0624	0.2414	0.0919
Max/min residual ($e^-/Å^3$)	1.008/−0.431	1.411/−1.195	0.544/−0.544
G.O.F.	1.065	1.285	1.068