Influence of geometric isomerism within dipyridylamide coligands on topology of copper adipate coordination polymers, including a new simple self-penetrated network

Amy L. Pochodylo, Julie A. Wilson, Jacob W. Uebler, Sultan H. Qiblawi, Robert L. LaDuca *

Lyman Briggs College and Department of Chemistry, Michigan State University, East Lansing, MI 48825, USA

ABSTRACT

Hydrothermal reactions of a divalent copper salt, adipic acid (H_2adp), and a dipyridylamide coligand have afforded four new crystalline coordination polymer solids, whose topologies depend critically on the specific dipyridylamide geometric isomer. $[Cu(adp)(3-pina)]_n$ (**1**, 3-pina = 3-pyridylisonicotinamide) has a standard (4,4) grid layer topology, while $\{[Cu(adp)(3-pna)]\cdot2.5H_2O\}_n$ (**2**, 3-pna = 3-pyridylnicotinamide) possesses a dimer-based 3-D network with 6^58 **cds** topology. Use of 4-pyridylnicotinamide (4-pna) as coligand afforded $\{[Cu_3(adp)_3(4-pna)_2]\cdot2H_2O\}_n$ (**3**), which manifests a unique binodal 4,6-connected self-penetrated $(6^58)(4^46^{11})$ 3-D topology. $\{[Cu(adp)(4-pna)_2]_n$ (**4**) is a simple 1-D chain polymer, obtained as a minor product during the synthesis of **3**. Thermal properties of these materials are also discussed, along with the variable temperature magnetic properties of **2** and **3**.

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1. Introduction

The preparation, structural characterization, and physical property measurements of divalent metal coordination polymer solids have been intensely studied over the past two decades. This research focus is predicated on the materials' potential utility in gas storage [1], selective molecular separations [2], ion exchange [3], catalysis [4], laser frequency doubling [5], and for explosives residue detection [6]. Among the plethora of possible choices for anionic organic components, aromatic dicarboxylate ligands have received the most significant attention, as they can instill thermally robust networks [7] or provide chromophores for emissive properties or sensing applications [8]. Somewhat less studied have been divalent metal coordination polymers containing aliphatic dicarboxylate ligands [9–14]. The conformational flexibility of their σ-bonded polymethylene tethers causes greater degrees of freedom during self-assembly. This in turn permits conformational adjustment in response to carboxylate binding mode and metal coordination geometry preference, synergistically affecting the dimensionality and topology of the resulting coordination polymer.

Bearing three distinct four-C atom torsion angles, adipate (adp, Scheme 1) ligands can possess varied conformations in coordination polymer crystals, from splayed-open *anti-anti-anti*, to "S-shaped" *gauche-anti-gauche*, to "staple-like" *anti-gauche-anti*, to twisted *gauche-gauche-gauche*. Some previously reported divalent metal adipate/dipyridyl coordination polymers adopt 2-fold interpenetrated **pcu** $4^{12}6^3$ networks based on $\{M_2(OCO)_2\}$ dinuclear units, such as $[Co(adp)(dpe)]_n$ [9a] (dpe = 1,2-bis(4-pyridyl)ethane) and $[Co(adp)(dpa)]_n$ [9b] (dpa = 4,4′-dipyridylamine). $[Ni(adp)(dpa)(H_2O)]_n$, on the other hand, showed an adjustment in topology because of the presence of aqua ligands and cis disposition of pyridyl nitrogen donor atoms; this material exhibited the first example of a 3-fold interpenetrated 4^28^4 **pts** net [9b].

The donor disposition and length of a dipyridyl coligand imposes significant constraints on the topologies of cadmium adipate coordination polymers [10]. Incorporating the chelating and capping ligand 1,10-phenanthroline (phen), $[Cd(adp)(phen)]_n$ [10a] possesses a simple 1-D chain structure. The dipodal tethering ligands 4,4′-bipyridine (bpy) [10b] and dpa [10c] both generated 2-fold interpenetrated **pcu** nets with pillared $[Cd(adp)]_n$ layers, based on $\{Cd_2(OCO)_2\}$ dimeric units. The longer dipyridyl ligand bis(4-pyridylmethyl)piperazine (bpmp) enforced large incipient voids within 4-connected 3-D diamondoid $[Cd(adp)(bpmp)]_n$ networks, allowing 5-fold interpenetration [10d]. Employment of an analogous ligand to bpmp, bis(4-pyridylformyl)piperazine (bpfp), afforded the 3-D phase $\{[Cd_2(adp)(bpfp)_2(H_2O)_2](ClO_4)_2\cdot2H_2O\}_n$ [10e]. This material exhibits $\{Cd_2O_2\}$ dimeric units connected through bridging adp and exotridentate bpfp ligands into an uncommon

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* Corresponding author. Address: Lyman Briggs College, E-30 Holmes Hall, 919 East Shaw Lane, Michigan State University, East Lansing, MI 48825, USA.

E-mail address: laduca@msu.edu (R.L. LaDuca).
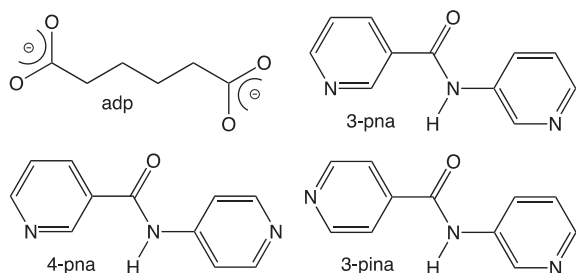
Scheme 1. Ligands used in this study.

(3,8)-connected **tfz-d** $(4^3)_2(4^6 6^{18} 8^4)$ binodal topology. The varied topologies within these previously reported adp phases indicates that the conformational fluxionality of the adp central polymethylene backbone allows response to the presence of neutral nitrogen-base coligands in divalent coordination polymer systems and to specific metal coordination environment.

The dipyridylamides 3-pyridylnicotinamide (3-pna), 3-pyridyl-isonicotinamide (3-pina), 4-pyridylnicotinamide (4-pna), and 4-pyridylisonicotinamide (4-pina) are easily prepared isomeric ligands (Scheme 1) whose divalent metal dicarboxylate coordination polymer chemistry has to this point remained relatively under-explored [15]. These dipyridylamides all possess internal hydrogen bonding donor and acceptor groups at their central amide linkage, which would likely exert similar supporting structure directing effects. Although synthetic predictability remains an elusive overarching goal in coordination polymer chemistry, a systematic study of nitrogen donor disposition could possibly reveal structure-directing trends in a series of complexes containing the same divalent metal ion and dicarboxylate ligand. Varying nitrogen donor disposition across the dipyridylamide series is expected to instill significant structural diversity in a particular dual-ligand coordination polymer system. Our recent work with these dipyridylamides in a cadmium adipate system illustrates this effect [15a]. $\{[Cd_2(adp)(nic)_2(3\text{-}pna)_2]\cdot 6H_2O\}_n$, in which some of the 3-pna precursor underwent *in situ* hydrolysis, displays a 5-connected $4^6 6^4$ **bnn** 3-D network. Use of other isomeric dipyridylamides resulted in a layered phase in $\{[Cd(adp)(3\text{-}pina)]\cdot H_2O\}_n$ or a simple 1-D chain compound $\{[Cd(adp)(4\text{-}pna)_2(H_2O)_2]\cdot 2H_2O\}_n$.

We thus sought to extend this work into the preparation a series of copper adipate coordination polymers containing the isomeric dipyridylamides. Although 4-pina failed to yield any isolable coordination polymers, use of 3-pna, 3-pina, or 4-pna resulted in the successful preparation and structural characterization of four new crystalline solids: $[Cu(adp)(3\text{-}pina)]_n$ (**1**), $\{[Cu(adp)(3\text{-}pna)]\cdot 2.5H_2O\}_n$ (**2**), and $\{[Cu_3(adp)_3(4\text{-}pna)_2]\cdot 2H_2O\}_n$ (**3**), along with the minor by-product $\{[Cu(adp)(4\text{-}pna)_2]_n$ (**4**). Thermal properties of **1**–**3** were also investigated, along with variable temperature magnetic susceptibility properties of copper dimer-based phases **2** and **3**.

2. Experimental

2.1. General considerations

Copper salts and adipic acid were purchased commercially. The dipyridylamides 3-pna, 3-pina, 4-pna, and 4-pina were prepared by a published procedure [16]. Water was deionized above 3 MΩ-cm in-house. IR spectra were recorded on polycrystalline samples using a Perkin Elmer Spectrum One DRIFT 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 five minutes before

magnetization measurement to ensure thermal equilibrium. The susceptibility data was corrected for diamagnetism using Pascal's constants [17], and for the diamagnetism of the sample holder. Thermogravimetric analysis was performed on a TA Instruments high-resolution Q500 thermal analyzer under flowing N_2. Powder X-ray diffraction on ground samples of **1**–**3** were obtained via Θ–2Θ scans performed on a Rigaku Rotaflex instrument.

2.2. Preparation of [Cu(adp)(3-pina)]$_n$ (**1**)

$Cu(NO_3)_2 \cdot 2.5H_2O$ (86 mg, 0.38 mmol), adipic acid (55 mg, 0.38 mmol), and 3-pina (76 mg, 0.38 mmol) were placed in 10 mL of distilled H_2O in a Teflon-lined digestion bomb. An aliquot of NaOH solution (1.0 M, 0.5 mL, 0.5 mmol) was added to basicify the solution. The bomb was sealed and heated at 100 °C for 48 h, after which it was cooled to ambient temperature. Blue blocks of **1** (81 mg, 53% yield based on Cu) were isolated after washing with distilled water and acetone and drying in air. *Anal.* Calc. for $C_{17}H_{17}CuN_3O_5$ **1**: C, 50.18; H, 4.21; N, 10.33. Found: C, 49.92 H, 4.22; N, 10.35%. IR (cm^{-1}): 3150(w), 2924(w), 1681(m), 1611(m), 1592(m), 1552(s), 1487(m), 1383(m), 1357(m), 1333(m), 1306(s), 1267(m), 1232(m), 1198(m), 1134(m), 1108(m), 1059(m), 1027(m), 931(m), 903(m), 873(m), 853(m), 810(m), 766(m), 737(m), 711(w), 697(s).

2.3. Preparation of {[Cu(adp)(3-pna)]·2.5H$_2$O}$_n$ (**2**)

$Cu(NO_3)_2 \cdot 2.5H_2O$ (43 mg, 0.18 mmol), adipic acid (35 mg, 0.24 mmol), and 3-pna (37 mg, 0.19 mmol) were placed in 5 mL of distilled H_2O in a 15 mL glass vial. An aliquot of NaOH solution (1.0 M, 0.5 mL, 0.5 mmol) was added to basicify the solution. The vial was sealed and heated in an oil bath at 70 °C for 24 h, after which it was cooled to ambient temperature. Blue blocks of **2** (36 mg, 42% yield based on Cu) were isolated after washing with distilled water and acetone and drying in air, and manual removal of a small amount of flocculent light blue material that could not be further characterized. *Anal.* Calc. for $C_{17}H_{22}CuN_3O_{7.5}$ **2**: C, 45.18; H, 4.91; N, 9.30. Found: C, 44.99 H, 4.69; N, 9.24%. IR (cm^{-1}): 3532 (w), 3047 (w), 2947 (w), 2160 (w), 1685 (m), 1552 (s), 1485 (s), 1388 (s), 1332 (m), 1303 (m), 1270 (m), 1240 (m), 1194 (m), 1123 (m), 1064 (m), 1035 (m), 811 (s), 693 (s), 653 (s).

2.4. Preparation of {[Cu$_3$(adp)$_3$(4-pna)$_2$]·2H$_2$O}$_n$ (**3**) and {[Cu(adp) (4-pna)$_2$]$_n$ (**4**)

$CuSO_4 \cdot 5H_2O$ (45 mg, 0.18 mmol), adipic acid (35 mg, 0.24 mmol), and 4-pna (39 mg, 0.20 mmol) were placed in 10 mL of distilled H_2O in a 15 mL glass vial. An aliquot of NaOH solution (1.0 M, 0.5 mL, 0.5 mmol) was added to basicify the solution. The vial was sealed and heated at 90 °C for 24 h, after which it was cooled to ambient temperature. Green–blue blocks of **3** (48 mg, 76% yield based on Cu) were isolated after washing with distilled water and acetone and drying in air, and after manual removal of a few large purple crystals of **4**. Not enough **4** was obtained for bulk analysis and attempts to prepare macroscopic quantities of **4** were unsuccessful. *Anal.* Calc. for $C_{40}H_{46}Cu_3N_6O_{16}$ **3**: C, 45.43; H, 4.38; N, 7.95. Found: C, 45.92 H, 4.30; N, 8.20%. IR (cm^{-1}): 3407 (w), 3250 (w), 3164 (w), 3074 (w), 2875 (w), 1683 (s), 1600 (s), 1566 (s), 1502 (s), 1475 (w), 1453 (w), 1415 (s), 1385 (s), 1329 (s), 1296 (s), 1269 (s), 1210 (s), 1155 (w), 1137 (w), 1115 (w), 1063 (w), 1051 (w), 1030 (w), 1020 (w), 968 (w), 924 (w), 900 (w), 840 (s), 778 (w), 730 (s), 693 (s), 665 (s).