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Diverse topologies in copper aromatic dicarboxylate coordination polymers containing 3-pyridylmethylnicotinamide: Effect of geometric isomerism and ring substituent

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ABSTRACT

Hydrothermal reaction of copper nitrate and 3-pyridylmethylnicotinamide (3-pmna) with aromatic dicarboxylates has afforded a series of coordination polymers that were structurally characterized via single-crystal X-ray crystallography. $[Cu(tere)(3\text{-pmna})]_n$ (**1**, tere = terephthalate) displays a 3,5-connected 3-D binodal net with uncommon $(6^3)(6^9 8)$ **gra** topology. $\{[Cu(iph)(3\text{-pmna})(H_2O)]\cdot 3H_2O\}_n$ (**2**, iph=isophthalate) possesses an extremely rare 4-connected 3-D self-penetrated net with 8^6 **tcb** topology. $[Cu_2(nip)_2(3\text{-pmna})_2]_n$ (**3**, nip = 5-nitroisophthalate) manifests a doubled chain 1-D structure, while increased steric bulk in $[Cu(tbip)(3\text{-pmna})]_n$ (**4**, tbip = 5-tert-butylisophthalate) results in a 1-D single chain motif. A significant dependence of the dimensionality and topology of these materials on the part of the carboxylate donor disposition and ring substituent was thus revealed. Thermal properties of these new materials were also investigated.

1. Introduction

Investigations into the preparation, structural characterization, and properties of divalent metal coordination polymers remain in sharp focus even after approximately two decades of consistent basic research. Enticing properties such as hydrogen storage [1], selective absorbance [2], ion exchange [3], catalysis [4], luminescent sensing [5], and single molecular magnetism [6] certainly spur on continued research efforts. Aromatic dicarboxylate ligands have been used for the construction of a large majority of divalent metal coordination polymers, due to their ability to impart the necessary charge balance and covalent and supramolecular points of contact for the self-assembly of stable structural motifs. Divalent copper coordination polymers containing organic dicarboxylates manifest a very wide scope of structural topologies [7]. This metal ion's flexible coordination preferences (square planar, square pyramidal, trigonal bipyramidal, octahedral) [8] and tendency to form clusters [9] play a key role in this enhanced level of structural diversity. Coordination polymer structure prediction remains an elusive goal, however, on account of the numerous possible specific donor dispositions and binding modes of the dicarboxylate components.

If neutral dipyridyl-type nitrogen-donating coligands are employed, *a priori* structure prediction becomes impractical and exploratory synthesis must be undertaken to uncover preferred structural topologies. Depending on conditions, multiple phases with the same set of aromatic dicarboxylate and dipyridyl ligands can be obtained. For instance, the *meta*-dicarboxylate isophthalate ligand (iph, Scheme 1) showed pH-dependent structural diversity in tandem with 4,4′-bipyridine (bpy), forming two different 2-D layered coordination polymers and a 1-D double chain compound depending on the pH of the reaction solution [10]. Moving to *para* disposed carboxylate arms in $[Cu_2(tere)_2(bpy)]_n$ (tere = terephthalate, Scheme 1) imposed an increase in topology to a twofold interpenetrated 3-D lattice; this phase exhibited a shape memory effect depending on synthetic method and crystallite size [11]. Inclusion of a 5-position substituent on an isophthalate ring has allowed access to other coordination polymer topologies, often of a lower dimensionality when compared to phases based on the unsubstituted parent iph ligand [12]. The sterically bulky ligand 5-tert-butylisophthalate (tbip, Scheme 1) can impose severe steric constraints on incipient metal–organic aggregations during self-assembly. For example, $[Cu_2(tbip)_2(4\text{-bpfp})(H_2O)_2]_n$ (4-bpfp = bis(4-pyridylformyl)piperazine) possesses a 1-D ladder polymer motif, while its unsubstituted congener $\{[Cu(iph)(4\text{-bpfp})]\cdot 2H_2O\}_n$ possesses a 2-D (4,4) rectangular grid structure with a *ABCD* stacking pattern [13]. The electron withdrawing and hydrogen-bonding accepting nitro substituent can also be employed to produce coordination polymers containing the 5-nitroisophthalate ligand (nip, Scheme 1). Although there are as yet no reports of a copper nip coordination polymer containing the rigid-rod bpy ligand, a

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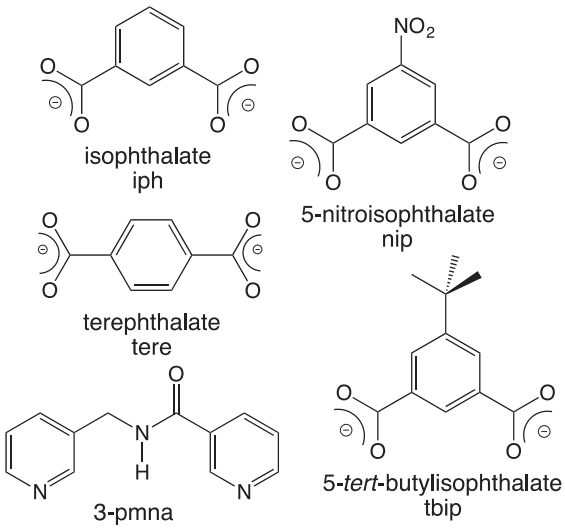
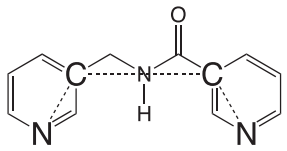


Scheme 1. Ligands used in this study.



Scheme 2. The ψ torsion angle within the 3-pmna ligand.

copper nip phase containing the longer rigid-rod ligand *trans*-4,4′-dipyridylethylene (dpee) has appeared in the literature. Bhaumik's phase $[Cu(Hnip)_2(dpee)]_n$ shows a 1-D ladder structure based on $\{Cu_2(OCO)_2\}$ dimeric units [14]. In this case the nitro substituent does not alter coordination polymer dimensionality, as $[Cu(Hiph)_2(dpee)]_n$ also shows a 1-D structure, albeit a simple chain motif without dimeric units [15].

In contrast to other commonly used dipyridyl-type tethering ligands, the dipyridylamide ligand 3-pyridylmethylnicotinamide (3-pmna, Scheme 1) has not been regularly employed in the construction of coordination polymer solids [14]. Its central amide functional group provides both hydrogen-bonding donating and accepting capability, enhancing its supramolecular structure-directing role. Its ability to adopt *syn*, *anti*, or intermediate twisted conformations via energetically accessible σ bond rotation can facilitate different metal–metal contact distances. A more quantitative perspective of the 3-pmna ligand conformation can be given by a N···C···C···N torsion angle, defined as ψ (Scheme 2). Smaller ψ torsion angles would be reflective of a *syn* conformation, while larger values portend an *anti* conformation of the 3-pmna ligand.

In this study we report the synthesis, structural characterization, topological analysis and thermal property determinations of four new copper coordination polymers containing aromatic dicarboxylate and 3-pmna ligands: $[Cu(tere)(3\text{-pmna})]_n$ (**1**), $\{[Cu(iph)(3\text{-pmna})(H_2O)]\cdot 3H_2O\}_n$ (**2**), $[Cu_2(nip)_2(3\text{-pmna})_2]_n$ (**3**), and $[Cu(tbip)(3\text{-pmna})]_n$ (**4**). All four display different topologies, with **1** and **2** possessing very rare 3-D networks.

2. Experimental

2.1. General considerations

Copper nitrate, dicarboxylic acids, and ligand synthesis precursors were purchased commercially. Potassium terephthalate was prepared via the reaction of excess potassium hydroxide with terephthalic acid in ethanol. The 3-pmna ligand was prepared according to a modification a published procedure for the preparation of the shorter related ligand 3-pyridylnicotinamide [16], via a condensation of 3-pyridylmethylamine and nicotinoyl chloride hydrochloride. Water was deionized above 3 MΩ-cm in-house. IR spectra were recorded on powdered samples using a Perkin Elmer Spectrum One DRIFT instrument. Elemental Analysis was carried out using a Perkin Elmer 2400 Series II CHNS/O Analyzer. Thermogravimetric analysis was performed on a TA Instruments Q50 thermal analyzer under flowing N_2.

2.2. Preparation of $[Cu(tere)(3\text{-pmna})]_n$ (**1**)

$Cu(NO_3)_2\cdot 2.5H_2O$ (88 mg, 0.38 mmol), potassium terephthalate (92 mg, 0.38 mmol) and 3-pmna (78 mg, 0.38 mmol) 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 24 h, and then cooled slowly to 25 °C. Blue crystals of **1** (108 mg, 65% yield based on Cu) were isolated after washing with distilled water and acetone, and drying in air. *Anal.* Calc. for $C_{20}H_{15}CuN_3O_5$ **1**: C, 54.48; H, 3.43; N, 9.53%. Found: C, 54.01; H, 2.99; N, 9.38%. IR (cm^{-1}): 3229(w), 1665(m), 1567(m), 1531(m), 1474(m), 1354(s), 1305(m), 1217(w), 1186(w), 1113(w), 1095(w), 1057(w), 955(w), 884(w), 822(s), 750(s), 692(s).

2.3. Preparation of $\{[Cu(iph)(3\text{-pmna})(H_2O)]\cdot 3H_2O\}_n$ (**2**)

$Cu(NO_3)_2\cdot 2.5H_2O$ (88 mg, 0.38 mmol), isophthalic acid (63 mg, 0.38 mmol), 3-pmna (78 mg, 0.38 mmol) and 0.50 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 24 h, and then cooled slowly to 25 °C. Blue crystals of **2** (108 mg, 55% yield based on Cu) were isolated after washing with distilled water and acetone, and drying in air. *Anal.* Calc. for $C_{20}H_{23}CuN_3O_9$ **2**: C, 46.83; H, 4.52; N, 8.19%. Found: C, 46.55; H, 4.12; N, 8.02%. IR (cm^{-1}): 3386(w), 1651(m), 1609(m), 1532(w), 1480(m), 1436(m), 1340(m), 1316(w), 1193(w), 1161(w), 1101(w), 1068(w), 998(w), 922(m), 828(w), 783(m), 719(w), 699(s), 657(w).

2.4. Preparation of $[Cu_2(nip)_2(3\text{-pmna})_2]_n$ (**3**)

$Cu(NO_3)_2\cdot 2.5H_2O$ (88 mg, 0.38 mmol), 5-nitroisophthalic acid (80 mg, 0.38 mmol), 3-pmna (78 mg, 0.38 mmol) and 0.50 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 24 h, and then cooled slowly to 25 °C. Blue crystals of **3** (41 mg, 22% yield based on Cu) were isolated after washing with distilled water and acetone, and drying in air. *Anal.* Calc. for $C_{40}H_{28}Cu_2N_8O_{14}$ **3**: C, 49.44; H, 2.90; N, 11.53%. Found: C, 49.03; H, 2.56; N, 11.22%. IR (cm^{-1}): 3386(w), 1650(m), 1624(m), 1610(m), 1532(s), 1480(w), 1437(w), 1374(w), 1338(s), 1316(w), 1192(m), 1161(w), 1125(w), 1100(w), 1068(m), 997(w), 922(m), 827(m), 782(s), 756(w), 726(s), 718(w), 691(s).

2.5. Preparation of $[Cu(tbip)(3\text{-pmna})]_n$ (**4**)

$Cu(NO_3)_2\cdot 2.5H_2O$ (88 mg, 0.38 mmol), 5-*tert*-butylisophthalic acid (84 mg, 0.38 mmol), 3-pmna (78 mg, 0.38 mmol) and 0.50 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 24 h, and then cooled slowly to 25 °C. Purple crystals of **4** (35 mg, 19% yield based on Cu) were isolated after washing with distilled water and acetone, and drying in air. *Anal.* Calc. for $C_{24}H_{23}CuN_3O_5$ **4**: C, 58.00; H, 4.66; N, 8.45%. Found: C, 57.49; H, 4.51; N, 8.17%. IR (cm^{-1}): 3324(w), 2957(w), 1664(w), 1644(m), 1603(m), 1566(w), 1477(w), 1435(w),