



# Substituent dependent layer topologies in copper isophthalate coordination polymers containing long-spanning dipyridylamide ligands



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## ABSTRACT

Hydrothermal reaction of copper nitrate, a 5-position substituted isophthalic acid, and the long-spanning dipyridylamide ligand 1,6-hexanediaminebis(nicotinamide) (hbn) resulted in two new coordination polymers whose layer topologies and interpenetration mechanisms depend critically on the nature of the substituent. The new phases were structurally characterized by single crystal X-ray diffraction.  $\{[\text{Cu}(\text{meoip})(\text{hbn})] \cdot \text{H}_2\text{O}\}_n$  (**1**, meoip = 5-methoxyisophthalate) exhibits  $[\text{Cu}(\text{meoip})]_n$  chain motifs with embedded  $\{\text{Cu}_2(\text{OCO})_2\}$  dinuclear units, pillared by pairs of hbn ligands into a decorated (4,4) grid topology.  $\{[\text{Cu}_3(\text{sip})_2(\text{hbn})_3(\text{H}_2\text{O})_4] \cdot 11.5\text{H}_2\text{O}\}_n$  (**2**, sip = 5-sulfoisophthalate) displays neutral  $[\text{Cu}_3(\text{sip})_2(\text{H}_2\text{O})_4]$  fragments connected by hbn ligands into 3,4-connected layer motifs with a  $\{4.6^2\}_2\{4^26^28^2\}$  topology, derived from the standard (4,4) grid with regular removal of some pillars. The layer motifs in **2** engage in  $2\text{D} + 2\text{D} \rightarrow 3\text{D}$  parallel interpenetration, with entrained co-crystallized water molecule tapes. Thermal decomposition behavior of the new phases is also discussed.

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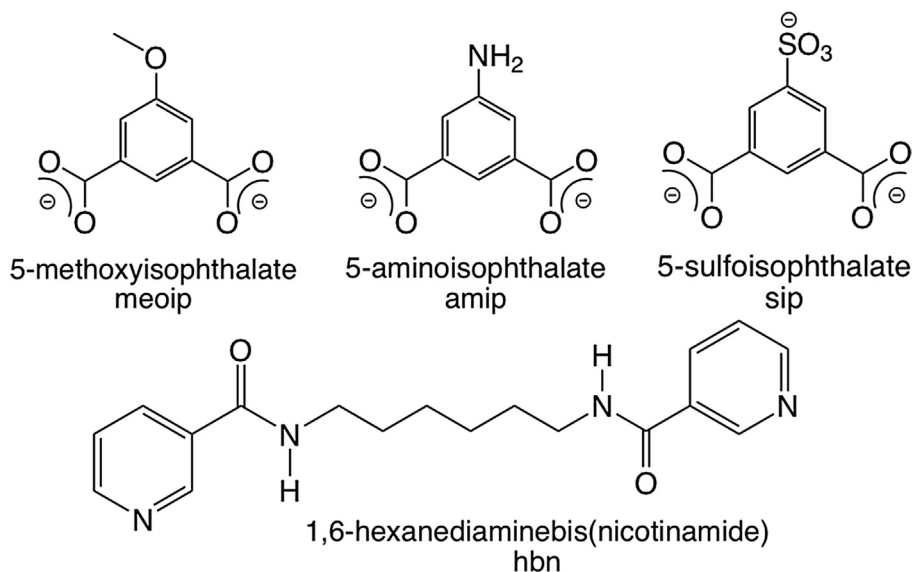
## 1. Introduction

Exploratory research into the synthesis and property characterization of divalent metal coordination polymers has remained active for over two decades. This genre of materials has shown multifunctional properties such as gas storage [1], selective molecular adsorbing [2], drug-delivery [3], and heterogeneous catalysis [4]. The aesthetic appeal of their underlying molecular structures and topologies has also spurred continued study [5], in addition to the general infrequency of *a priori* structure design [6]. Most reported crystalline coordination polymer solids are based on aromatic dicarboxylate ligands such as isophthalate (ip) [7] or terephthalate [8]. Specific coordination environment preferences at the divalent metal atom, variable carboxylate binding modes, and the inclusion of dipyridyl-type coligands act synergistically during self-assembly to influence the final dimensionality and topology of the final material [9]. One possible means of altering the structural features of an isophthalate-based coordination polymer is to employ derivatives with non-ligating or potentially ligating substituents in the 5-position of the aromatic ring. Yang and co-

workers prepared a series of substituted isophthalate zinc coordination polymers with pyridine capping ligands [10]; sterically bulkier substituents appeared to result in lower coordination polymer dimensionality. Our group observed a similar trend in some substituted isophthalate zinc coordination polymers with the longer-spanning coligand bis(4-pyridylmethyl)piperazine (bpmp) [11,12].  $[\text{Zn}(\text{ip})(\text{bpmp})]_n$  showed a system of five-fold interpenetrated diamondoid nets [11], while  $\{[\text{Zn}(\text{meoip})(\text{bpmp})] \cdot 8\text{H}_2\text{O}\}_n$  (meoip = 5-methoxyisophthalate, Scheme 1) adopted an undulating (4,4) grid topology [12]. Inclusion of a ligating sulfonate moiety in the 5-position resulted in  $\{[\text{Zn}(\text{sip})(\text{Hbpmp})] \cdot 4\text{H}_2\text{O}\}_n$  (sip = 5-sulfoisophthalate, Scheme 1) which displayed a three-fold interpenetrated binodal lattice with  $(4^26)(4^26^58^3)$  topology. Therefore no reduction in dimensionality with respect to the unsubstituted isophthalate derivative was observed in this case, although there was a decrease in interpenetration level. A fascinating self-penetrated structure with a 3,5-connected  $(6^3)(6^78^3)$  topology was observed in  $\{[\text{Co}(\text{amip})(4\text{-bpmp})] \cdot 3\text{H}_2\text{O}\}_n$  (amip = 5-aminoisophthalate, Scheme 1) [13], showing the versatility of the amip ligand to serve as an exotridentate donor ligand using both of its carboxylate termini as well as its amine group.  $\{[\text{Co}(\text{nip})(3\text{-pina})]_n$  (nip = 5-nitroisophthalate, 3-pina = 3-pyridylisonicotinamide) and  $\{[\text{Co}(\text{meoip})(3\text{-pina})]_n$  both manifest

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**Scheme 1.** Ligands discussed in this study.

a non-interpenetrated dimer-based 3-D **pcu** network, showing an invariance to the nature of the substituent in the 5-position of the isophthalate ring [14]. Utilizing more flexible dipyriddy coligands has resulted in some intriguing *pseudo*-rotaxane topologies, for instance in  $[\text{Co}_2(\text{mip})_2(\text{dpp})_2(\text{H}_2\text{O})]_n$  (mip = 5-methylisophthalate, dpp = 1,3-di(4-pyridyl)propane) [15]. We thus attempted to prepare a series of divalent copper coordination polymers containing 5-substituted isophthalate ligands and the even longer spanning and more flexible dipyriddyamide coligand 1,6-hexanediaminebis(nicotinamide) (hbn). This ligand has infrequently been employed in coordination polymer chemistry outside of some work by Wang and colleagues, who reported the synthesis of the 3,4-connected layered phase  $\{[\text{Cu}(\text{amip})(\text{hbn})(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}\}_n$  in 2013 [16], along with a series of cobalt/hbn coordination polymers with substituted isophthalate ligands [17]. In this contribution we present the single-crystal structures, divergent topological features, and thermal properties of two new layered copper coordination polymers with hbn and substituted isophthalate ligands:  $\{[\text{Cu}(\text{meoip})(\text{hbn})] \cdot \text{H}_2\text{O}\}_n$  (**1**) and  $\{[\text{Cu}_3(\text{sip})_2(\text{hbn})_3(\text{H}_2\text{O})_4] \cdot 11.5\text{H}_2\text{O}\}_n$  (**2**).

## 2. Experimental section

### 2.1. General considerations

Copper nitrate hydrate and 5-methoxyisophthalic acid were commercially obtained from Sigma Aldrich. Sodium 5-sulfoisophthalate was purchased from TCI America. 1,6-hexanediaminebis(nicotinamide) (hbn) was prepared by condensation of 1,6-hexanediamine and two molar equivalents of nicotinoyl chloride hydrochloride in dry pyridine. The reaction mixture was quenched with water, and then the product was isolated via  $\text{CH}_2\text{Cl}_2$  extraction and removal of solvent *in vacuo* [18]. Water was deionized above 3MΩ-cm in-house. IR spectra were recorded on powdered samples using a Perkin Elmer Spectrum One DRIFT instrument. Thermogravimetric analysis was performed on a TA Instruments Q-50 Thermogravimetric Analyzer with a heating rate of 10 °C/min up to 600 °C. Elemental Analysis was carried out using a Perkin Elmer 2400 Series II CHNS/O Analyzer.

### 2.2. Preparation of $\{[\text{Cu}(\text{meoip})(\text{hbn})] \cdot \text{H}_2\text{O}\}_n$ (**1**)

$\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$  (65 mg, 0.28 mmol), 5-methoxyisophthalic acid (55 mg, 0.28 mmol), and hbn (91 mg, 0.28 mmol) were mixed with 0.55 mL of 1.0 M NaOH solution and 10 mL of distilled  $\text{H}_2\text{O}$  in a 23 mL Teflon-lined acid digestion bomb. The bomb was sealed and heated in an oven at 120 °C for 22 h, and then was cooled slowly to 25 °C. Blue crystals of **1** (115 mg, 68% yield based on Cu) were isolated after washing with distilled water, ethanol, and acetone and drying in air. *Anal. Calc.* for  $\text{C}_{27}\text{H}_{30}\text{CuN}_4\text{O}_8$  **1**: C, 53.86; H, 5.02; N, 9.31% Found: C, 53.41; H, 4.98; N, 9.22%. IR ( $\text{cm}^{-1}$ ): 3334 (w), 3100 (w), 1664 (m), 1648 (m), 1618 (m), 1589 (s), 1573 (s), 1541 (m), 1450 (m), 1417 (m), 1396 (s), 1335 (s), 1193 (m), 1129 (m), 1102 (m), 1055 (m), 919 (m), 881 (m), 835 (m), 788 (m), 779 (s), 724 (s), 698 (s), 656 (s).

### 2.3. Preparation of $\{[\text{Cu}_3(\text{sip})_2(\text{hbn})_3(\text{H}_2\text{O})_4] \cdot 11.5\text{H}_2\text{O}\}_n$ (**2**)

$\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$  (65 mg, 0.28 mmol), sodium 5-sulfoisophthalate (75 mg, 0.28 mmol), and hbn (91 mg, 0.28 mmol) were mixed with 0.55 mL of 1.0 M NaOH solution and 10 mL of distilled  $\text{H}_2\text{O}$  in a 23 mL Teflon-lined acid digestion bomb. The bomb was sealed and heated in an oven at 120 °C for 22 h, and then was cooled slowly to 25 °C. Blue crystals of **2** (128 mg, 71% yield based on Cu) were isolated after washing with distilled water, ethanol, and acetone and drying in air. *Anal. Calc.* for  $\text{C}_{70}\text{H}_{103}\text{Cu}_3\text{N}_{12}\text{O}_{35}\text{S}_2$  **2**: C, 43.62; H, 5.39; N, 8.72% Found: C, 43.43; H, 5.09; N, 8.58%. IR ( $\text{cm}^{-1}$ ): 3286 (w), 2923 (w), 1658 (m), 1604 (m), 1541 (s), 1488 (m), 1433 (m), 1358 (s), 1235 (m), 1204 (m), 1165 (m), 1103 (m), 1060 (m), 1034 (s), 997 (m), 837 (m), 774 (m), 738 (s), 696 (s), 681 (s), 658 (s).

## 3. X-ray crystallography

Diffraction data for **1** and **2** were collected on a Bruker-AXS SMART-CCD X-ray diffractometer using graphite-monochromated Mo- $K\alpha$  radiation ( $\lambda = 0.71073$  Å) at 173 K. The data were processed via SAINT [19], and corrected for both Lorentz and polarization effects and absorption effects using SADABS [20]. The structures were solved using direct methods with SHELXTL [21]

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