



# Structural chemistry and magnetic properties of copper pyromellitate coordination polymers containing pyridylnicotinamide ligands



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## ABSTRACT

A series of divalent copper pyromellitate (1,2,4,5-benzenetetracarboxylate, pyro) coordination polymers containing either 3-pyridylnicotinamide (3-pna) or 4-pyridylnicotinamide (4-pna) was hydrothermally prepared and structurally characterized by single-crystal X-ray diffraction.  $[\text{Cu}_2(\text{pyro})(\text{pyroH}_2)(3\text{-pnaH})_2(\text{H}_2\text{O})_2]_n$  (**1**) is a 2-D coordination polymer built from  $\{\text{Cu}_2\text{O}_2(\text{OCO})_2\}$  dimeric units, while  $[\text{Cu}(\text{pyro})(3\text{-pnaH})_2(\text{H}_2\text{O})_2 \cdot 4\text{H}_2\text{O}]_n$  (**2**) is a simple neutral 1-D chain polymer.  $[\text{Cu}(\text{pyroH}_2)(4\text{-pnaH})_2(\text{H}_2\text{O})_2](\text{pyroH}_2 \cdot 2\text{H}_2\text{O})_n$  (**3**) possesses cationic 1-D chain motifs and unligated pyroH<sub>2</sub> dianions.  $[\text{Cu}_2(\text{pyroH}_2)_3(4\text{-pnaH})_2] \cdot 6\text{H}_2\text{O}]_n$  (**4**) is also a 1-D coordination polymer, but built from the linkage of  $\{\text{Cu}_2(\text{pyroH}_2)\}$  dimeric units.  $[\text{Cu}_3(\text{pyroH})_2(4\text{-pna})_2(\text{H}_2\text{O})_2 \cdot 2\text{H}_2\text{O}]_n$  (**5**) manifests a 3-D coordination polymer network with rare **frl** topology, containing embedded  $\{\text{Cu}_3(\text{OCO})_2\}$  linear trimers. Moderately strong antiferromagnetic coupling ( $J = -76.4(3) \text{ cm}^{-1}$ ) was observed within the  $\{\text{Cu}_2\text{O}_2(\text{OCO})_2\}$  dimeric units in **1**, while very weak ferromagnetic coupling ( $J = 0.8(2) \text{ cm}^{-1}$ ) was observed within the  $\{\text{Cu}_3(\text{OCO})_2\}$  linear trimers in **5**. Thermal degradation behavior of the five new materials is also presented.

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## 1. Introduction

Research into the synthesis, structure, and properties of coordination polymer crystalline solids has attracted significant attention over the past ten years due to their utility as gas storage substrates [1], selective adsorbents [2], ion-exchange stationary phases [3], heterogeneous catalysts [4], and as phosphorescent sensors [5]. As much of this work is basic research, efforts have also been stimulated by the beautiful aesthetics of their networks [6]. Among all the possible organic linker choices, aromatic dicarboxylates have proven the most popular [7–10]. Varied coordination geometries possible with first-row transition metal divalent cations, along with different accessible carboxylate binding modes, allow a wide scope of coordination polymer topologies and functional properties. At this time, deliberate control of coordination polymer structure is possible only in limited systems [11,12].

The structure-directing factor of carboxylate binding mode is even less predictable in coordination polymers containing the pyromellitate ligand (pyro, 1,2,4,5-benzenetetracarboxylate, Scheme 1). The eight oxygen atoms of the pyro ligand provide access to myriad and unpredictable possible carboxylate binding and bridging modes. Within the previously reported coordination polymer phases containing the pyro ligand, it has been observed to link between two to ten metal centers [13]. Additionally, alteration of

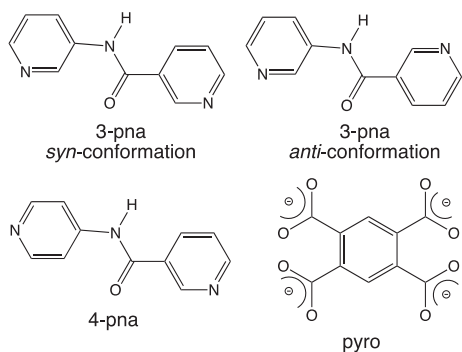
pH levels during self-assembly can afford not only incorporation of tetraanionic pyro ligands [13], but also trianionic pyroH [14], dianionic pyroH<sub>2</sub> [15], or monoanionic pyroH<sub>3</sub> ligands [16]. As a result, different metal–ligand ratios can be required to achieve charge balance. Alternatively, alkali metal cations [17] or organoammonium cations [18] can provide the requisite charge balance.

The structural diversity and functional properties of coordination polymers containing pyromellitate ligands (with varied protonation levels) can be enhanced by the incorporation of neutral coligands [19].  $[\text{Cu}(\text{pyroH}_2)(2,2'\text{-bipyridine})_n]$  can catalyze the oxidation of cyclohexene [19a], while the 1-D phase  $[\text{Cu}_2(\text{pyro})(\text{triethanolamine})_2]_n$  can activate cyclohexane towards oxidation with hydrogen peroxide [19b].  $[\text{Ni}_2(\text{pyro})(4,4'\text{-bipyridine})_3] \cdot 3\text{DMF}]_n$  retains its 3-D microporous framework after desolvation and adsorbs nitrogen gas [19c]. Among possible dipyriddy-type coligands, the isomeric amides 3-pyridylnicotinamide (3-pna, Scheme 1) and 4-pyridylnicotinamide (4-pna, Scheme 1) have seen sparing use in coordination polymer chemistry to date [20–23]. Variation of the nitrogen donor position can instill a significant difference in coordination polymer topology in cases where the same metal and dicarboxylate ligand are present. For instance,  $[\text{Cd}(\text{suc})(3\text{-pna})] \cdot 2.5\text{H}_2\text{O}]_n$  (suc = succinate) has a dimer-based 3-D non-interpenetrated 4<sup>12</sup>6<sup>3</sup> **pcu** network, while its 4-pna analog  $[\text{Cd}(\text{suc})(4\text{-pna})(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}]_n$  shows an extremely rare 2-D 4-connected 6<sup>6</sup> layer self-penetrated topology [20].

In this study we have aimed to extend the structural scope of both copper pyromellitate coordination polymers, and materials

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

containing the seldom-used pyridylnicotinamide ligands. By careful adjustment of pH of the reaction mixtures, and altering which pyridylnicotinamide isomer was used, we have prepared five new coordination polymer phases:  $[\text{Cu}_2(\text{pyro})(\text{pyroH}_2)(3\text{-pnaH})_2(\text{H}_2\text{O})_2]_n$  (**1**),  $\{[\text{Cu}(\text{pyro})(3\text{-pnaH})_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}\}_n$  (**2**),  $\{[\text{Cu}(\text{pyroH}_2)(4\text{-pnaH})_2(\text{H}_2\text{O})_2](\text{pyroH}_2) \cdot 2\text{H}_2\text{O}\}_n$  (**3**),  $\{[\text{Cu}_2(\text{pyroH}_2)_3(4\text{-pnaH})_2] \cdot 6\text{H}_2\text{O}\}_n$  (**4**), and  $\{[\text{Cu}_3(\text{pyroH})_2(4\text{-pna})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}\}_n$  (**5**). These have been structurally characterized by single-crystal X-ray diffraction and show different dimensionalities depending on protonation levels of the pyro ligands. As compounds **1** and **5** have paramagnetic copper ions in close proximity, they have been subjected to variable temperature magnetic susceptibility measurements. Thermal properties for all new material were also probed and are discussed herein.

## 2. Experimental section

### 2.1. General considerations

Copper salts and pyromellitic acid were commercially obtained. The pyridylnicotinamide ligands 3-pna and 4-pna were prepared by literature procedure [24]. Water was deionized above 3 MΩ-cm in-house. Thermogravimetric analysis was performed on a TA Instruments Q-50 Thermogravimetric Analyzer with a heating rate of 10 °C/min up to 600 °C. Variable temperature magnetic susceptibility data for **1** and **5** (2–300 K) were 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 [25], and for the diamagnetism of the sample holder. Elemental analysis was carried out using a Perkin Elmer 2400 Series II CHNS/O Analyzer.

### 2.2. Preparation of $[\text{Cu}_2(\text{pyro})(\text{pyroH}_2)(3\text{-pnaH})_2(\text{H}_2\text{O})_2]_n$ (**1**)

$\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$  (86 mg, 0.37 mmol), pyromellitic acid (35 mg, 0.18 mmol), 3-pna (37 mg, 0.18 mmol), and 0.2 mL of a 1.0 M NaOH solution were placed into 10 mL distilled  $\text{H}_2\text{O}$  in a 23 mL Teflon-lined acid digestion bomb. The bomb was sealed and heated at 80 °C in an oven for 24 h. The bomb was then allowed to air cool to 25 °C. Blue blocks of **1** (52 mg, 54% yield based on pyromellitic acid) were isolated after washing with distilled water and acetone, and drying in air. *Anal. Calc.* for  $\text{C}_{42}\text{H}_{30}\text{Cu}_2\text{N}_6\text{O}_{20}$  **1**: C, 47.33; H, 2.83; N, 7.89. Found: C, 47.18; H, 2.99; N, 8.18%. IR ( $\text{cm}^{-1}$ ): 3062 (w), 1685 (m), 1606 (w), 1575 (w), 1547 (s), 1501 (w), 1472 (w), 1395 (s), 1330 (m), 1292 (w), 1258 (m), 1227 (w), 1206 (w), 1063 (m), 1035 (m), 925 (m), 908 (m), 850 (w), 806 (m), 772 (m), 733 (m), 695 (w), 680 (w), 655 (m).

### 2.3. Preparation of $\{[\text{Cu}(\text{pyro})(3\text{-pnaH})_2(\text{H}_2\text{O})_2] \cdot 4\text{H}_2\text{O}\}_n$ (**2**)

$\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$  (86 mg, 0.37 mmol), pyromellitic acid (35 mg, 0.18 mmol), 3-pna (37 mg, 0.18 mmol), and 0.6 mL of a 1.0 M NaOH solution were placed into 10 mL distilled  $\text{H}_2\text{O}$  in a 23 mL Teflon-lined acid digestion bomb. The bomb was sealed and heated at 80 °C in an oven for 24 h. The bomb was then allowed to air cool to 25 °C. Blue blocks of **2** (89 mg, 60% yield based on pyromellitic acid) were isolated after washing with distilled water and acetone, and drying in air. *Anal. Calc.* for  $\text{C}_{32}\text{H}_{34}\text{CuN}_6\text{O}_{16}$  **2**: C, 46.75; H, 4.17; N, 10.22. Found: C, 47.00; H, 3.44; N, 9.99%. IR ( $\text{cm}^{-1}$ ): 3531 (w), 3463 (w), 3191 (wb), 1675 (m), 1566 (s), 1482 (w), 1461 (w), 1400 (w), 1373 (s), 1316 (m), 1252 (w), 1204 (w), 1131 (m), 1061 (w), 1044 (w), 977 (w), 953 (w), 932 (w), 915 (w), 895 (w), 852 (w), 827 (w), 815 (w), 764 (m), 735 (m), 719 (m), 684 (m).

### 2.4. Preparation of $\{[\text{Cu}(\text{pyroH}_2)(4\text{-pnaH})_2(\text{H}_2\text{O})_2](\text{pyroH}_2) \cdot 2\text{H}_2\text{O}\}_n$ (**3**)

$\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$  (86 mg, 0.37 mmol), pyromellitic acid (35 mg, 0.18 mmol), 4-pna (37 mg, 0.18 mmol), and 0.2 mL of a 1.0 M NaOH solution were placed into 10 mL distilled  $\text{H}_2\text{O}$  in a 23 mL Teflon-lined acid digestion bomb. The bomb was sealed and heated at 100 °C in an oven for 24 h. The bomb was then allowed to air cool to 25 °C. Blue blocks of **3** (72 mg, 77% yield based on pyromellitic acid) were isolated after washing with distilled water and acetone, and drying in air. *Anal. Calc.* for  $\text{C}_{42}\text{H}_{36}\text{CuN}_6\text{O}_{22}$  **3**: C, 48.49; H, 3.49; N, 8.08. Found: C, 48.11; H, 3.14; N, 7.79%. IR ( $\text{cm}^{-1}$ ): 3748 (w), 1716 (m), 1675 (m), 1590 (s), 1543 (m), 1514 (m), 1478 (w), 1415 (m), 1382 (m), 1333 (s), 1294 (s), 1251 (s), 1213 (s), 1122 (m), 1199 (w), 1173 (w), 1157 (w), 1060 (s), 1027 (m), 932 (m), 958 (w), 864 (w), 850 (s), 827 (s), 795 (s), 754 (w), 729 (s), 666 (w).

### 2.5. Preparation of $\{[\text{Cu}_2(\text{pyroH}_2)_3(4\text{-pnaH})_2] \cdot 6\text{H}_2\text{O}\}_n$ (**4**)

$\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$  (86 mg, 0.37 mmol), pyromellitic acid (35 mg, 0.18 mmol), 4-pna (37 mg, 0.18 mmol), and 0.75 mL of a 1.0 M NaOH solution were placed into 10 mL distilled  $\text{H}_2\text{O}$  in a 23 mL Teflon-lined acid digestion bomb. The bomb was sealed and heated at 60 °C in an oven for 24 h. The bomb was then allowed to air cool to 25 °C. Blue blocks of **4** (24 mg, 29% yield based on pyromellitic acid) were isolated after washing with distilled water and acetone, and drying in air. *Anal. Calc.* for  $\text{C}_{52}\text{H}_{44}\text{Cu}_2\text{N}_6\text{O}_{32}$  **4**: C, 44.87; H, 3.19; N, 6.04. Found: C, 45.05; H, 3.01; N, 6.04%. IR ( $\text{cm}^{-1}$ ): 3751 (w), 3062 (wb), 1702 (m), 1671 (m), 1608 (w), 1575 (w), 1542 (m), 1504 (s), 1480 (w), 1433 (w), 1415 (w), 1374 (m), 1320 (s), 1292 (w), 1280 (m), 1241 (m), 1215 (w), 1178 (w), 1113 (m), 1066 (m), 1054 (m), 1026 (w), 988 (w), 962 (w), 927 (m), 899 (m), 865 (m), 810 (m), 796 (m), 759 (m), 728 (m), 714 (m), 685 (m), 665 (w).

### 2.6. Preparation of $\{[\text{Cu}_3(\text{pyroH})_2(4\text{-pna})_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}\}_n$ (**5**)

$\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$  (86 mg, 0.37 mmol), pyromellitic acid (35 mg, 0.18 mmol), 4-pna (37 mg, 0.18 mmol), and 0.6 mL of a 1.0 M NaOH solution were placed into 10 mL distilled  $\text{H}_2\text{O}$  in a 23 mL Teflon-lined acid digestion bomb. The bomb was sealed and heated at 100 °C in an oven for 24 h. The bomb was then allowed to air cool to 25 °C. Blue blocks of **5** (50 mg, 48% yield based on Cu) were isolated after washing with distilled water and acetone, and drying in air. *Anal. Calc.* for  $\text{C}_{42}\text{H}_{32}\text{Cu}_3\text{N}_6\text{O}_{22}$  **5**: C, 43.36; H, 2.77; N, 7.22. Found: C, 43.36; H, 2.58; N, 7.26%. IR ( $\text{cm}^{-1}$ ): 3749 (w), 1716 (s), 1676 (s), 1581 (s), 1542 (m), 1513 (m), 1475 (w), 1433 (s), 1414 (m), 1381 (s), 1333 (s), 1294 (s), 1273 (w), 1213 (s), 1201 (m), 1156 (w), 1140 (w), 1122 (m), 1059 (s), 1028 (w), 956 (w), 932

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