Steric effects on the structure of copper malonate coordination polymers containing 1,3-di(4-pyridyl)propane

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ABSTRACT

Slow diffusion of aqueous solutions of copper dicarboxylate precursors with ethanolic solutions of 1,3-di(4-pyridyl)propane (dpp) afforded three different coordination polymers whose dimensionality and topology depends critically on the steric bulk of the malonate ligand. The new phases were characterized by single-crystal X-ray diffraction, and were analyzed by infrared spectroscopy. Using the unsubstituted parent malonate ligand (mal), the complex phase $\{[Cu(dpp)_2(H_2O)][Cu(mal)_2(dpp)][Cu(mal)(dpp)(H_2O)]\cdot12H_2O\}_n$ (**1**) was obtained. Its crystal structure shows the interweaving of cationic layer, anionic chain, and neutral chain motifs to give a rare 2D + 1D + 1D → 3D topology. Utilizing the sterically bulkier dimethylmalonate (dmmal) ligand afforded $[Cu(dmmal)(dpp)(H_2O)]\cdot3H_2O\}_n$ (**2**), which shows a simple neutral (4,4) grid topology. $[Cu(dpp)_2][Cu(emal)_2]\cdot6H_2O\}_n$ (**3**, emal = ethylmalonate) manifests cationic ribbon motifs and coordination complex anions. Thermal properties of these materials are also discussed.
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1. Introduction

The synthesis and characterization of crystalline coordination polymers has attracted substantial recent interest because of the potentially useful catalytic, absorbent, electronic, magnetic or optical properties of these materials [1–5]. The short-spanning dicarboxylate ligand malonate (mal, Scheme 1) has been employed to prepare divalent metal coordination polymers with diverse magnetic properties, because of its ability to access numerous binding and chelating modes (*anti–anti*, *anti–syn*, *syn–syn*, 1,3-chelating, etc.) that can promote close metal–metal contacts [6–20]. Subtle variations in preparative conditions can impart tremendous differences in structure in copper malonate materials [6]. $\{[Cu(H_2O)_3][Cu(mal)_2(H_2O)]\}_n$ shows coordination polymer chain motifs with malonate carboxylates acting as *anti–syn* bridges, resulting in intrachain ferromagnetism. The more complicated phase $\{[Cu(H_2O)_4]_2[Cu(mal)_2(H_2O)]\}[Cu(mal)_2(H_2O)_2]\{[Cu(H_2O)_4][Cu(mal)_2(H_2O)_2]\}$ has mono-, di-, and trinuclear species coexisting in the same single crystal; concomitant weak ferromagnetic coupling was observed within the dinuclear and trinuclear species [6]. Enhanced structural diversity can be achieved in copper malonate phases by incorporating a dipyridyl-type neutral coligand. $[Cu_2(mal)_2(H_2O)_2(bpy)]_n$ (bpy = 4,4'-bipyridine) displays $[Cu_4(mal)_4]$ squares with *anti–syn* bridging carboxylates, linked into a coordination polymer layer by the tethering bpy ligands; moderate

ferromagnetic coupling is observed within the square subunits [7]. Employing the kinked, hydrogen-bonding capable 4,4'-dipyridyl-amine (dpa) ligand resulted in the 2-D polymer $\{[Cu_2(mal)_2(dpa)(H_2O)_2]\cdot H_2O\}_n$, which showed competing *anti–anti* and *anti–syn* carboxylate bridging modes and net weak ferromagnetism [8]. The longer-spanning 1,2-di(4-pyridyl)ethane (dpe) ligand afforded $[\{Cu_3(mal)_2(dpe)_3(H_2O)_2\}(NO_3)_2(H_2O)_2]_n$, which shows a 4,6-connected 3-D topology and modest ferromagnetic coupling between *anti–syn* carboxylate bridged copper ions [9]. $\{[Cu(dpp)(mal)(H_2O)]\cdot4H_2O\}_n$ (dpp = 1,3-di(4-pyridyl)propane) possesses a simple 1-D chain structure with bridging dpp ligands and 1,3-chelating capping malonates [10], along with discrete pentameric water molecule chains that include the aqua ligands.

When compared to the number of divalent copper coordination polymers built from malonate ligands, those containing substituted malonate ligands like methylmalonate (mmal), dimethylmalonate (dmmal, Scheme 1), or ethylmalonate (emal, Scheme 1), are rarer [21–23]. Nevertheless these can show the same synthetic conditions-dependent structural diversity and magnetic property variances as seen in copper coordination polymers based on unsubstituted malonate ligands. $\{[Cu(bpy)_2][Cu(bpy)_2(mmal)(NO_3)(H_2O)](NO_3)\cdot3.5H_2O\}_n$ manifests $[Cu(bpy)_2]_n^{2n+}$ square grid motifs pillared by mmal ligands into a 3-D **pcu** net [21], with net antiferromagnetism produced from competing ferromagnetic and antiferromagnetic interactions across the different binding modes of the mmal carboxylate termini. The related chain phase $[Cu(bpy)_2(mmal)(H_2O)]\cdot H_2O\}_n$ shows extremely weak antiferromagnetic coupling through the full span of the mmal ligands [21],

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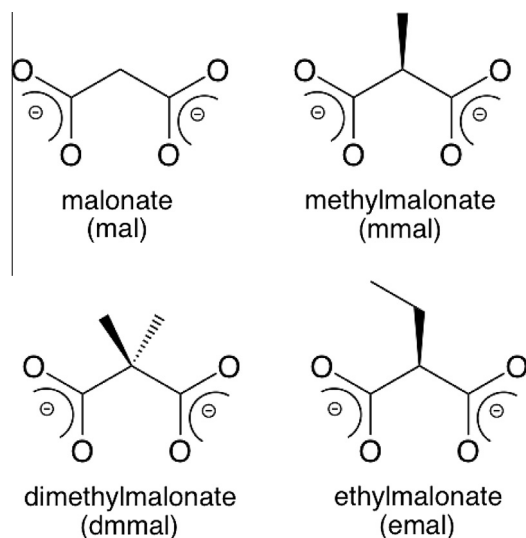
Scheme 1. Malonate ligands.

while $[Cu_2(bpy)(mmal)_2(H_2O)_2]_n$ is a 3-D phase that exhibits ferromagnetic coupling within Cu(mmal) corrugated layers featuring *anti-syn* carboxylate bridges [22]. Adjustment of the steric bulk of the malonate ligand in the case of copper/dpa containing phases imparted marked structural deviations. Greatly contrasting with the 2-D phase $\{[Cu_2(mal)_2(dpa)(H_2O)_2]\cdot H_2O\}_n$, $\{[Cu(mmal)(Hmmal)(Hdpa)]\cdot H_2O\}_n$ possesses 1-D coordination polymer chain motifs containing infinite $[Cu(OCO)]_n$ linkages, with antiferromagnetic coupling along the chains mediated by *anti-syn* bridging mmal carboxylates [23]. The dimethylmalonate (dmmal) derivative $\{[Cu_3(dmmal)_2(dpa)_3](ClO_4)_2\cdot 2H_2O\}_n$ manifests an antiferromagnetic trimer-based (4,5)-connected binodal **gaf** network with $(4^46^2)(4^66^4)_2$ topology [23].

A literature search failed to uncover any reported divalent copper coordination polymers containing both substituted malonate and flexible dpp ligands, so we endeavored to undertake their synthesis. Our initial attempts were successful, along with the synthesis of a new unsubstituted malonate polytype of $\{[Cu(dpp)(mal)(H_2O)]\cdot 4H_2O\}_n$. Herein we report the synthesis, single-crystal structural determination, and thermal properties of: $\{[Cu(dpp)_2(H_2O)][Cu(mal)_2(dpp)][Cu(mal)(dpp)(H_2O)]\cdot 12H_2O\}_n$ (**1**), $[Cu(dmmal)(dpp)(H_2O)]\cdot 3H_2O\}_n$ (**2**), and $[Cu(dpp)_2][Cu(emal)_2]\cdot 6H_2O\}_n$ (**3**).

2. Experimental

2.1. General considerations

The copper dicarboxylate starting materials were prepared from copper carbonate according to a literature procedure [24]. 1,3-Di(4-pyridyl)propane was commercially obtained. Water was deionized above 3 MΩ-cm in-house. Elemental analysis was carried out using a Perkin Elmer 2400 Series II CHNS/O Analyzer. IR spectra were recorded on powdered samples using a Perkin Elmer Spectrum One 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.

2.2. Preparation of $\{[Cu(dpp)_2(H_2O)][Cu(mal)_2(dpp)][Cu(mal)(dpp)(H_2O)]\cdot 12H_2O\}_n$ (**1**)

Copper (II) malonate (30 mg, 0.18 mmol) was dissolved in 3 mL distilled H_2O in a 15 mL vial. A 1 mL aliquot of a 1:1 mixture of H_2O

and ethanol was then added. A solution of dpp (36 mg, 0.18 mmol) in 3 mL ethanol was then added. The vial was left undisturbed for 7 days at room temperature, resulting in the deposition of blue blocks of **1**. These were filtered and washed with H_2O and acetone and dried in air, affording 48 mg of **1** (52% yield based on Cu). *Anal.* Calc. for $C_{61}H_{90}Cu_3N_8O_{26}$ (**1**): C, 47.51; H, 5.88; N, 7.27. Found: C, 48.17; H, 5.15; N, 7.16%. IR (cm^{-1}): 3373 (m), 2947 (w), 1607 (s), 1571 (s), 1554 (s), 1505 (m), 1426 (s), 1331 (m), 1250 (m), 1225 (m), 1169 (w), 1067 (m), 1028 (m), 1009 (w), 963 (m), 943 (m), 833 (m), 810 (m), 708 (s).

2.3. Preparation of $[Cu(dmmal)(dpp)(H_2O)]\cdot 3H_2O\}_n$ (**2**)

Copper (II) dimethylmalonate (18 mg, 0.09 mmol) was dissolved in 3 mL distilled H_2O in a 15 mL vial. A 1 mL aliquot of a 1:1 mixture of H_2O and ethanol was then added. A solution of dpp (18 mg, 0.09 mmol) in 3 mL ethanol was then added. The vial was left undisturbed for 7 days at room temperature, resulting in the deposition of blue blocks of **2**. These were filtered and washed with H_2O and acetone and dried in air, affording 28 mg of **2** (67% yield based on Cu). *Anal.* Calc. for $C_{18}H_{28}CuN_2O_8$ (**2**): C, 46.60; H, 6.08; N, 6.04. Found: C, 47.15; H, 5.57; N, 6.01%. IR (cm^{-1}): 3397 (w), 2998 (w), 2952 (w), 2915 (w), 2858 (w), 1594 (s), 1505 (m), 1427 (s), 1406 (s), 1329 (s), 1329 (s), 1225 (m), 1189 (m), 1069 (m), 885 (m), 850 (m), 835 (m), 798 (m), 760 (m), 692 (s).

2.4. Preparation of $[Cu(dpp)_2][Cu(emal)_2]\cdot 6H_2O\}_n$ (**3**)

Copper (II) ethylmalonate (17 mg, 0.090 mmol) was dissolved in 3 mL distilled H_2O in a 15 mL vial. A 1 mL aliquot of a 1:1 mixture of H_2O and ethanol was then added. A solution of dpp (18 mg, 0.091 mmol) in 3 mL ethanol was then added. The vial was left undisturbed for 7 days at room temperature, resulting in the deposition of blue blocks of **3**. These were filtered and washed with H_2O and acetone and dried in air, affording 21 mg of **3** (26% yield based on Cu). *Anal.* Calc. for $C_{36}H_{52}Cu_2N_4O_{14}$ (**3**): C, 48.68; H, 5.88; N, 6.28. Found: C, 48.21; H, 5.59; N, 6.24%. IR (cm^{-1}): 3396 (w), 2929 (w), 1620 (s), 1594 (s), 1576 (m), 1507 (w), 1432 (m), 1381 (s), 1319 (m), 1301 (m), 1227 (m), 1087 (m), 1058 (m), 1024 (m), 974 (m), 892 (w), 859 (m), 837 (m), 804 (m), 756 (m), 745 (m).

3. X-ray crystallography

Diffraction data for **1–3** were acquired using a Bruker-AXS SMART-CCD X-ray diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The data were processed via SAINT [25], and subjected to Lorentz and polarization effect and absorption corrections using SADABS [26]. The structures were solved using direct methods with SHELXTL [27]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms bound to carbon or oxygen were placed in calculated positions and refined isotropically with a riding model. Hydrogen atoms bound to aqua ligands or water molecules of crystallization were also placed in calculated positions. Crystallographic details for **1–3** are given in Table 1.

4. Results and discussion

4.1. Synthesis and infrared spectroscopy

Compounds **1–3** were prepared cleanly by slow diffusion of an aqueous solution of the requisite copper dicarboxylate precursor and an ethanolic solution of dpp. Infrared spectra were consistent with the structural elements found by X-ray diffraction. Broadened features around ~3050–3300 cm^{-1} are indicative of aqua ligands and water molecules of crystallization engaging in multifarious