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Unsubstituted and substituted copper malonate coordination polymers with isomeric dipyridylamide ligands: Chain, layer, diamondoid, and self-penetrated topologies

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A B S T R A C T

Six dual-ligand divalent copper malonate coordination polymers have been prepared via solvent diffusion methods, and structurally characterized by single-crystal X-ray diffraction. The resulting dimensionality and topology depend crucially on the steric bulk of the malonate ligand and the nitrogen donor disposition within the dipyridylamide coligand. $\{[Cu(mal)(3\text{-pina})(H_2O)]\cdot2H_2O\}_n$ (1, mal = malonate, 3-pina = 3-pyridylisonicotinamide) possesses a simple 1-D chain structure, while the isomeric 4-pyridylnicotinamide (4-pna) ligand afforded a two-fold interpenetrated (6,3) grid layer structure in $\{[Cu(mal)(4\text{-pna})(H_2O)]\cdot3H_2O\}_n$ (2). Employing copper dimethylmalonate (dmmal) in the synthetic regime permitted synthesis of the (4,4) grid layered phase $\{[Cu_2(dmmal)_2(4\text{-pna})_2(H_2O)_3]\cdot7H_2O\}_n$ (3) and $\{[Cu_2(dmmal)_2(3\text{-pina})_2]\cdot9.5H_2O\}_n$ (4), which exhibited a three-fold interpenetrated diamondoid net with large water-filled incipient channels, built from $[Cu_4(dmmal)_4]$ tetranuclear clusters. $\{[Cu_2(Hdmmal)_2(dmmal)(4\text{-pina})_2]\cdot0.5H_2O\}_n$ (5, 4-pina = 4-pyridylisonicotinamide) manifested a unique 5-connected self-penetrated 3D network with 4^26^78 topology. $\{[Cu(emal)(4\text{-pna})(H_2O)]\cdot3H_2O\}_n$ (6, emal = ethylmalonate) is another simple 1-D chain phase. Ferromagnetic coupling ($J = 11(3)$ cm^{-1}) was observed within the tetranuclear clusters in 4. Thermal properties of these materials are also presented.

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1. Introduction

The exploratory synthesis and structural characterization of crystalline coordination polymers remain under intense study because of their intrinsic basic research appeal in addition to their numerous capabilities in hydrogen storage [1], molecular separations [2], ion exchange [3], heterogeneous catalysis [4], non-linear optics [5], and magnetic applications [6]. Although aromatic dicarboxylate ligands are frequently used as linkers in this class of materials, more recent attention has been focused on aliphatic dicarboxylate coordination polymers in order to probe the structural effects of ligands with greater conformational degrees of freedom [7–10]. Complicated, synergistic interactions between aliphatic ligand conformation, carboxylate binding mode, metal coordination geometry preference, and the presence of any neutral dipyridyl-type linkers have been shown to result in a plethora of possible molecular topologies during coordination polymer self-assembly.

Divalent copper malonate (mal, Scheme 1) coordination polymers containing ancillary tethering ligands have proven to be an especially rich system both in terms of topological diversity and magnetic properties, very often critically depending on the length and hydrogen-bonding facility of the dipyridyl component [7–10]. The layered phase $[Cu_2(mal)_2(H_2O)_2(bpy)]_n$ (bpy = 4,4′-bipyridine) manifests ferromagnetic $[Cu_4(mal)_4]$ tetrameric squares with anti-syn bridging carboxylates, linked by rigid-rod bpy tethers [7]. The related, kinked "V-shaped" tethering ligand 4,4′-dipyridylamine (dpa) resulted another 2-D phase, $\{[Cu_2(mal)_2(dpa)(H_2O)_2]\cdot H_2O\}_n$ [8]. This material possessed crystallographically distinct $[Cu(mal)]_n$ chain motifs, with anti-anti carboxylate bridging in one and anti-syn in the other. Net weak ferromagnetism was observed, although the magnetic effect of each chain motif could not be appropriately separated. Use of the longer-spanning ligand 1,2-di(4-pyridyl)ethane (dpe) afforded the coordination polymer $[\{Cu_3(mal)_2(dpe)_3(H_2O)_2\}(NO_3)_2 \cdot 2H_2O]_n$, which displayed a 4,6-connected 3-D topology and weak ferromagnetic coupling between anti-syn carboxylate bridged copper ions [9]. In contrast, $\{[Cu(dpp)(mal)(H_2O)]\cdot4H_2O\}_n$ (dpp = 1,3-di(4-pyridyl)propane) had a simple chain structure with bridging dpp ligands and non-bridging 1,3-chelating capping malonate ligands [10].
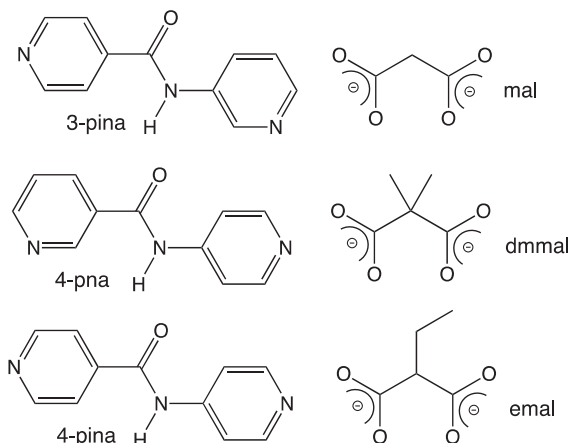
Scheme 1. Ligands used in this study.

Compared to divalent copper malonate/dipyridyl coordination polymers, those containing substituted malonate ligands such as methylmalonate (mmal), dimethylmalonate (dmmal, Scheme 1) or ethylmalonate (emal, Scheme 1) are less common [11–14]. In some cases, these ligands can induce synthetic condition-dependent structural and magnetic diversity. $\{[Cu(bpy)_2]\ [Cu(bpy)_2(mmal)]$ $(NO_3)(H_2O)](NO_3)\cdot 3.5H_2O\}_n$ exhibits $[Cu(bpy)_2]_n^{2n+}$ square grid motifs pillared by mmal ligands into a 3-D $4^{12}6^3$ **pcu** net [11]. Net antiferromagnetism was observed, produced by concomitant ferromagnetic and antiferromagnetic interactions across different mmal carboxylate binding modes. A chain polymer $[Cu(bpy)_2(mmal)]$ $(H_2O)]\cdot H_2O\}_n$ showed extremely weak antiferromagnetic coupling via the full span of the mmal ligands instead of a single carboxylate group [11]. A third analog, $[Cu_2(bpy)(mmal)_2(H_2O)_2]_n$, has a 3-D structure built from Cu(mmal) corrugated layers linked by bpy rigid rod tethers [12]; this material exhibits ferromagnetic coupling mediated by *anti-syn* carboxylate bridges.

Deliberate use of sterically bulky substituted malonate ligands also greatly altered the resulting coordination polymer topology in dpa-containing phases. In contrast to the layered topology seen with the unsubstituted malonate ligand, $\{[Cu(mmal)(Hmmal)$ $(Hdpa)]\cdot H_2O\}_n$ displays chain motifs containing antiferromagnetically coupled *anti-syn* briged $[Cu(OCO)]_n$ linkages [13]. Here the pendant, monodentate protonated dipyridyl ligands do not provide access to higher dimensionality. The dmmal derivative $\{[Cu_3(dmmal)_2(dpa)_3](ClO_4)_2\cdot 2H_2O\}_n$ has a structure built from antiferromagnetically coupled trimeric units, connected by the kinked dipyridyl tethers into a (4,5)-connected $(4^46^2)(4^66^4)_2$ **gaf** network topology [13].

The longer, more flexible tethering ligand 1,3-di(4-pyridyl)propane (dpp) afforded three copper malonate phases whose topology depended critically on the steric bulk of the dicarboxylate backbone [14]. With the unsubstituted parent mal ligand, $\{[Cu(dpp)_2$ $(H_2O)]\ [Cu(mal)_2(dpp)][Cu(mal)(dpp)(H_2O)]\cdot 12H_2O\}_n$ was obtained [14]. The structure of this phase shown an interweaving of cationic layer, anionic chain, and neutral chain motifs in a rare 2D + 1D + 1D → 3D topology. The sterically bulkier dmmal ligand afforded $[Cu(dmmal)(dpp)(H_2O)]\cdot 3H_2O\}_n$, which exhibited a standard (4,4) grid topology. The emal derivative $[Cu(dpp)_2][Cu(emal)_2]\cdot 6H_2O\}_n$ manifests cationic 1-D ribbon motifs and coordination complex counteranions.

To date no copper unsubstituted or substituted malonate coordination polymer phases have been reported, that contain any of the series of isomeric dipyridylamides depicted in Scheme 2: 3-pyridylnicotinamide (3-pna), 3-pyridylisonicotinamide (3-pina), 4-pyridylnicotinamide (4-pna), or 4-pyridylisonicotinamide (4-pina). Unlike bpy, dpe, or dpp, these dipyridylamide ligands all possess internal hydrogen bonding donor and acceptor groups at their central linkages, providing another potential avenue for structure direction during self-assembly. There have been relatively few reports of coordination polymers containing these isomeric dipyridylamides, but these can show great variance in topology across the series while retaining the same metal and carboxylate component [15–18]. For instance, $[Cd(suc)(4-pina)]_n$ displays a 3-D self-penetrated $4^46^{10}8$ **mab** topology, while $\{[Cd(suc)$ $(3-pna)]\cdot 2.5H_2O\}_n$ (**2**, 3-pna = 3-pyridylnicotinamide) has a simple 3-D non-interpenetrated $4^{12}6^3$ **pcu** network [15]. While both $\{[Cd(suc)(4-pina)(H_2O)]\cdot 2H_2O\}_n$ and $\{[Cd(suc)(3-pina)(H_2O)]\cdot$ $3.5H_2O\}_n$ have 2-D topologies, the former is an extremely rare example of a 4-connected 6^6 self-penetrated layer topology, while the latter has a common (4,4) grid layer structure [15]. We thus sought to prepare a series of copper malonate coordination polymers containing 3-pna, 3-pina, 4-pna, and 4-pina, hoping to probe structure-directing trends imparted by both the nitrogen donor disposition within the dipyridylamide component and the steric load borne by the malonate component. Our synthetic explorations resulted in the successful preparation and structural characterization of six new crystalline solids: $\{[Cu(mal)(3-pina)(H_2O)]\cdot 2H_2O\}_n$ (**1**), $\{[Cu(mal)(4-pna)(H_2O)]\cdot 3H_2O\}_n$ (**2**), $\{[Cu_2(dmmal)_2(4-pna)_2$ $(H_2O)_3]\cdot 7H_2O\}_n$ (**3**), $\{[Cu_2(dmmal)_2(3-pina)_2]\cdot 9.5H_2O\}_n$ (**4**), $\{[Cu_2$ $(Hdmmal)_2(dmmal)(4-pina)_2]\cdot 0.5H_2O\}_n$ (**5**), and $\{[Cu(emal)(4-pna)$ $(H_2O)]\cdot 3H_2O\}_n$ (**6**). The variable temperature magnetic properties of **4**, along with the thermal properties of all six new phases, are also reported herein.

2. Experimental

2.1. General considerations

Copper carbonate, malonic acid, dimethylmalonic acid, and ethylmalonic acid were purchased commercially. Copper malonate was prepared by a published procedure [19]; the other copper dicarboxylate precursors were prepared similarly by employing the requisite dicarboxylic acid instead of malonic acid. The dipyridylamides 3-pina, 4-pna, and 4-pina were prepared by a published procedure [20]. Water was deionized above 3 MΩ-cm in-house. IR spectra were recorded on powdered samples using a Perkin Elmer Spectrum One instrument. Thermal degradation analysis was performed under flowing N_2 on a TA Instruments Q50 Thermogravimetric Analyzer with a heating rate of 10 °C/min up to 600 °C. Variable temperature magnetic susceptibility data for **4** (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 [21], 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 $\{[Cu(mal)(3-pina)(H_2O)]\cdot 2H_2O\}_n$ (**1**)

Copper malonate (15 mg, 0.091 mmol) was dissolved in 3 mL water in a 15 mL glass vial. A 2 mL aliquot of a 1:1 water:ethanol solution was placed on top of the copper malonate solution via pipette, followed by a solution of 3-pina (19 mg, 0.095 mmol) in 3 mL ethanol. The vial was allowed to stand undisturbed at 25 °C for 14 d. Blue blocks of **1** (32 mg, 84% yield based on Cu) were isolated after washing with distilled water and acetone and drying in air. *Anal.* Calc. for $C_{14}H_{17}CuN_3O_8$ **1**: C, 40.15; H, 4.09; N, 10.03. Found: C, 40.21; H, 3.67; N, 9.96%. IR (cm^{-1}): 3199 (w), 1674 (m), 1644 (m), 1612 (s), 1553 (s), 1487 (s), 1420 (s), 1339 (m), 1314 (m),