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Structural diversity and variable temperature magnetic properties in copper dimethylmalonate

coordination polymers containing dipyridyl-type coligands

Colton J. Kalman, Brandon S. Stone, Robert L. LaDuca*

Lyman Briggs College and Department of Chemistry Michigan State University, East Lansing, MI 48825 USA

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Abstract

Four copper dimethylmalonate (dmmal) phases containing long-spanning dipyridyl coligands have been prepared and structurally characterized by single-crystal X-ray diffraction. $\{[Cu_2(dmmal)_2(edin)(H_2O)_2] \cdot 3H_2O\}_n$ (1, edin = N,N'-(ethane-1,2-diyl)diisonnicotinamide) and $\{[Cu_2(dmmal)_2(bdin)(H_2O)_2] \cdot 2H_2O\}_n$ (2, bdin = N, N'-(butane-1,4-diyl)diisonnicotinamide) both show (6,3) herringbone layers constructed from the edin pillaring of $[Cu(H_2O)(dmmal)]_n$ chain motifs, that feature embedded *equatorial-equatorial* bridged $\{Cu(OCO)\}_n$ chains. $[Cu_2(dmmal)_2(bpmp)]_n$ (3, bpmp = bis(4-pyridylmethyl)piperazine) shows a decorated (4,4) grid topology built from bpmp pillared $[Cu_2(dmmal)_2]_n$ ribbon motifs, that feature embedded ${Cu_2(OCO)_4}$ paddlewheel dimeric units. $[Cu_2(dmmal)_2(bpfp)]_n$ (4, bpfp = bis(4pyridylformyl)piperazine) shows a 5-connected non-interpenetrated 3D 4⁴6⁶ sqp topology, formed from the bpfp pillaring of rectangular equatorial-equatorial bridged $[Cu_2(dmmal)_2]_n$ layers. Variable temperature magnetic studies were carried out on 1, 2 and 4, indicating predominant ferromagnetic superexchange within their equatorial-equatorial $\{Cu(OCO)\}_n$ chain motifs.

1. Introduction

Three-component coordination polymers that are constructed divalent metal cations, anionic dicarboxylate ligands, and dipodal neutral organic coligands have shown many intriguing properties in technologically or medically useful applications [1], such as hydrogen storage [2], small molecule separation [3], drug delivery [4], heterogeneous catalysis for organic transformations [5], carbon dioxide sequestration [6], and interesting temperature-dependent and field-dependent magnetic properties [7]. Additionally, the wide variety of aesthetic structural topologies continues to provide impetus for further exploratory synthesis [8].

The short-spanning dicarboxylate ligand malonate (mal) has been employed to prepare copper coordination polymers that exhibit a diversity of magnetic properties. The mal ligand has a remarkable ability to access numerous chelating and bridging and chelating modes (*anti-anti*, *anti-syn*, *syn-syn*, 1,3-chelating, etc.) that can provide varied overlap mechanisms for the magnetic orbitals on adjacent metal centers [9–23]. Variations in preparative conditions can impart tremendous differences in the structure and magnetic properties of copper malonate coordination polymers [9]. {[Cu(H₂O)₃][Cu(mal)₂(H₂O)]}_n shows coordination polymer chain motifs with *anti-syn* bridges, resulting in intrachain ferromagnetism. The more complicated phase {[Cu(H₂O)₄]₂[Cu(mal)₂(H₂O)][Cu(mal)₂(H₂O)₂]{[Cu(H₂O)₄] [Cu(mal)₂(H₂O)₂]} has mono-, di-, and trinuclear species coexisting in the same single crystal, with weak ferromagnetic coupling within the dinuclear and trinuclear species [9]. Increased structural diversity can be achieved in copper malonate phases by incorporation of neutral coligands.

 $[Cu_2(mal)_2(H_2O)_2(bpy)]_n$ (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; moderately strong ferromagnetic superexchange is observed within the square subunits [10].

Employing the kinked, hydrogen-bonding capable 4,4'-dipyridylamine (dpa) ligand resulted in the 2-D herringbone structure $\{[Cu_2(mal)_2(dpa)(H_2O)_2] \cdot H_2O\}_n$, which showed competing *anti-anti* and *anti-syn* carboxylate bridging modes and net weak ferromagnetism [11]. 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 [12]. $\{[Cu(dpp)(mal)(H_2O)] \cdot 4H_2O\}_n$ (dpp = 1,3-di(4-pyridyl)propane) possesses a simple 1-D chain structure with bridging dpp ligands and 1,3-chelating capping malonates [13], 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 such as methylmalonate (mmal), or dimethylmalonate (dmmal) are rarer [24–27]. Still, these materials can show the same synthesis-dependent structural and magnetic property diversity as seen in coordination polymers based on unsubstituted malonate ligands. {[Cu(bpy)₂][Cu(bpy)₂(mmal)(NO₃)(H₂O)](NO₃) $\cdot 3.5H_2O_n$ manifests [Cu(bpy)₂]_{n²ⁿ⁺} square grid motifs pillared by mmal ligands into a 3-D **pcu** net [24], 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)(H₂O)]•H₂O}_n shows extremely weak antiferromagnetic coupling through the full span of the mmal ligands [24], while [Cu₂(bpy)(mmal)₂(H₂O)₂]_n is a 3-D phase that exhibits ferromagnetic coupling within Cu(mmal) corrugated layers featuring *anti-syn* carboxylate bridges [25]. Adjustment of the steric bulk of

the malonate ligand in the case of copper/dpa containing phases imparted marked structural deviations. Contrasting with the 2-D phase $\{[Cu_2(mal)_2(dpa)(H_2O)_2] \cdot H_2O\}_n$,

 $\{[Cu(mmal)(Hmmal)(Hdpa)] \bullet H_2O\}_n$ possesses 1-D coordination polymer chain motifs containing $\{Cu(OCO)\}_n$ chains, which exhibit antiferromagnetic coupling mediated by its *antisyn* bridging carboxylates [26]. The dmmal derivative $\{[Cu_3(dmmal)_2(dpa)_3](ClO_4)_2 \bullet 2H_2O\}_n$ manifests an antiferromagnetic trimer-based network with a unique 4,5-connected binodal **gaf** $(4^{4}6^{2})(4^{6}6^{4})_2$ topology [26].

Slow diffusion of an ethanolic solution of bpy into an aqueous solution of copper dimethylmalonate afforded two different coordination polymer complexes as time elapsed [27]. A small amount of light blue crystals of $\{[Cu_2(dmmal)_2(bpy)_{1.5}(H_2O)] \cdot 2H_2O\}_n$ were initially formed at the solution interface. This material displayed a 3,4-connected 2D layer with an unprecedented (4²6)(4²6³8) topology containing alternating rows of hexagonal and rectangular ring units. These crystals dissolved as the reaction continued, as darker blue crystals of the thermodynamic product $\{[Cu_3(dmmal)_3(bpy)_3(H_2O)_4] \cdot H_2O\}_n$ were formed. This latter phase manifested a 4-connected 3D 6⁵8 cds topology.

In this study, we have aimed to expand the structure scope of copper dimethylmalonate coordination polymers by employing the longer spanning hydrogen-bonding capable dipyridyl ligands N,N'-(ethane-1,2-diyl)diisonicotinamide) (edin), N,N'-butane-1,4-diyl)diisonicotinamide) (bdin), bis(4-pyridylmethyl)piperazine (bpmp), and bis(4-pyridylformyl)piperazine (bpfp). All four of these coligands have afforded coordination polymers with intriguing topologies in the recent past [28–30]. Herein we discuss the synthesis, structural characterization, thermal properties, and variable temperature magnetic susceptibility behavior of

 $\{[Cu_2(dmmal)_2(edin)(H_2O)_2] \cdot 3H_2O\}_n$ (1), $\{[Cu_2(dmmal)_2(bdin)(H_2O)_2] \cdot 2H_2O\}_n$ (2), $[Cu_2(dmmal)_2(bpmp)]_n$ (3), and $[Cu_2(dmmal)_2(bpfp)]_n$ (4).

2. Experimental Section

2.1 General Considerations

Copper dimethylmalonate was prepared by adaptation of a literature procedure for the synthesis of copper malonate [31] via substitution of malonic acid with dimethylmalonic acid. Dimethylmalonic acid was commercially obtained from TCI America. N,N'-(ethane-1,2diyl)diisonnicotinamide (edin) was prepared by condensation of 1,2-ethylenediamine and two molar equivalents of isonicotinoyl chloride hydrochloride in dry pyridine. The reaction mixture was quenched with water, and then the product was isolated via CH₂Cl₂ extraction and removal of solvent in vacuo [32]. A similar process, employing 1,4-butanediamine as a precursor, afforded the bdin ligand. Bis(4-pyridylformyl)piperazine (bpfp) [33] and bis(4pyridylmethyl)piperazine (bpmp) [34] were prepared by literature procedures. Water was deionized above $3M\Omega$ -cm in-house. IR spectra were recorded on powdered samples using a Perkin Elmer Spectrum One DRIFT instrument. UV-Visible spectra were recorded on a Shimadzu UV-2600 spectrophotometer. 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. Variable temperature magnetic susceptibility data (2 K to 300 K) for 1–4 were collected on a Quantum Design MPMS-3 SQUID magnetometer at an applied field of 0.1 T. After each temperature change the sample was kept at the new temperature for 5 minutes before

magnetization measurement to ensure thermal equilibrium. The susceptibility data was corrected for diamagnetism using Pascal's constants [35].

2.2 Preparation of $\{[Cu_2(dmmal)_2(edin)(H_2O)_2] \cdot 3H_2O\}_n$ (1)

Copper dimethylmalonate (18 mg, 0.094 mmol), was dissolved in 3 mL deionized water in a 15 mL glass vial. A 2 mL aliquot of a 1:1 ethanol:water mixture was layered carefully on top of the copper dimethylmalonate solution. A 3 mL ethanol solution containing edin (23 mg, 0.094 mmol) was then added to the reaction vial. After allowing the reaction mixture to stand undisturbed for 7 d, dark blue crystals of **1** were deposited at the bottom of the vial. The crystals were collected by decantation and washed with water and acetone, affording 20 mg of **1** (57 % yield based on Cu). Anal. Calc. for $C_{24}H_{36}Cu_2N_4O_{15}$ **1**: C, 38.55; H, 4.85; N, 7.49 %. Found: C, 38.45; H, 4.97; N, 7.11%. IR (cm⁻¹): 3500 (w, br) 1634 (s), 1580 (s), 1541 (s), 1435 (m), 1312 (w), 1065 (m), 854 (w), 764 (m).

2.3 Preparation of $\{[Cu_2(dmmal)_2(bdin)(H_2O)_2] \cdot 2H_2O\}_n$ (2)

Copper dimethylmalonate (18 mg, 0.094 mmol), was dissolved in 3 mL deionized water in a 15 mL glass vial. A 2 mL aliquot of a 1:1 ethanol:water mixture was layered carefully on top of the copper dimethylmalonate solution. A 3 mL ethanol solution containing bdin (25 mg, 0.094 mmol) was then added to the reaction vial. After allowing the reaction mixture to stand undisturbed for 7 d, dark blue crystals of **2** were deposited at the bottom of the vial. The crystals were collected by decantation and washed with water and acetone, affording 22 mg of **2** (61 % yield based on Cu). Anal. Calc. for $C_{26}H_{38}Cu_2N_4O_{14}$ **2**: C, 41.21; H, 5.06; N, 7.39%. Found: C, 41.55; H, 5.01; N, 7.62%. IR (cm⁻¹): 3500 (w, br), 1628 (s), 1575 (s), 1543 (s), 1460 (m), 1435

(m), 1369 (w), 1315 (s), 1201 (w), 1063 (m), 904 (m), 859 (m), 798 (w), 764 (m), 696 (s), 682 (s).

2.4 Preparation of $[Cu_2(dmmal)_2(bpmp)]_n$ (3)

Copper dimethylmalonate (18 mg, 0.094 mmol), was dissolved in 3 mL deionized water in a 15 mL glass vial. A 2 mL aliquot of a 1:1 ethanol:water mixture was layered carefully on top of the copper dimethylmalonate solution. A 3 mL ethanol solution containing bpmp (25 mg, 0.094 mmol) was then added to the reaction vial. After allowing the reaction mixture to stand undisturbed for 7 d, blue crystals of **3** were deposited at the bottom of the vial. The crystals were collected by decantation and washed with water and acetone, affording 17 mg of **3** (55 % yield based on Cu). Anal. Calc. for $C_{26}H_{32}Cu_2N_4O_8$ **3**: C, 47.63; H, 4.91; N, 8.54 %. Found: C, 47.44; H, 5.12; N, 8.38%. IR (cm⁻¹): 1610 (s), 1591 (s), 1458 (w), 1427 (s), 1339 (m), 1168 (w), 1132 (w), 1066 (w), 1011 (m), 842 (m), 800 (m), 695 (m).

2.5 Preparation of $[Cu_2(dmmal)_2(bpfp)]_n$ (4)

Copper dimethylmalonate (18 mg, 0.094 mmol), was dissolved in 3 mL deionized water in a 15 mL glass vial. A 2 mL aliquot of a 1:1 ethanol:water mixture was layered carefully on top of the copper dimethylmalonate solution. A 3 mL ethanol solution containing bpfp (28 mg, 0.094 mmol) was then added to the reaction vial. After allowing the reaction mixture to stand undisturbed for 7 d, dark blue crystals of **4** were deposited at the bottom of the vial. The crystals were collected by decantation and washed with water and acetone, affording 15 mg of **4** (47 % yield based on Cu). Anal. Calc. for $C_{26}H_{28}Cu_2N_4O_{10}$ **4**: C, 45.68; H, 4.13; N, 8.20 %. Found: C, 45.59; H, 4.08; N, 8.47%. IR (cm⁻¹): 1639 (s), 1579 (w), 1548 (s), 1431 (s), 1350 (m), 1259 (m), 1157 (w), 1006 (m), 893 (w), 846 (m), 733 (w), 689 (m).

3. X-ray Crystallography

Diffraction data for 1–4 were collected on a Bruker-AXS SMART-CCD X-ray diffractometer using graphite-monochromated Mo-K α radiation (λ = 0.71073 Å) at 173 K. The data were processed via SAINT [36], and corrected for both Lorentz and polarization effects and absorption effects using SADABS [37]. The structures were solved using direct methods with SHELXTL [38] within the OLEX2 crystallographic software suite [39]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions and refined isotropically with a riding model. Crystallographic details for 1–4 are given in Table 1.

4. Results and Discussion

4.1 Synthesis and Spectra

Crystalline samples of **1–4** were produced by slow diffusion of aqueous solutions of copper dimethylmalonate with ethanol solutions of the requisite dipyridyl ligand. The infrared spectra of **1–4** were consistent with their structural components as determined by single-crystal X-ray diffraction. Intense, broad asymmetric and symmetric C–O stretching bands within the dimethylmalonate ligands were observed at 1541 and 1435 cm⁻¹ for **1**, 1548 and 1435 cm⁻¹ for **2**, 1591 and 1427 cm⁻¹ for **3**, and 1548 and 1431 cm⁻¹ for **4**. Moderate intensity bands in the range of ~1600 cm⁻¹ to ~1300 cm⁻¹ are attributed to the stretching modes of the pyridyl rings of the dipyridylamide ligands [40]. Features corresponding to C–H bending and ring puckering within the pyridyl moieties exist in the region between ~900 and ~650 cm⁻¹. Broad, weak spectral

bands in the vicinity of $\sim 3000-3400 \text{ cm}^{-1}$ indicate the presence of unbound water molecules in the spectra of **1**. The carbonyl stretching bands for the dipyridylamide ligands edin, bdin, and bpfp appeared at 1634 cm⁻¹ for **1**, 1628 cm⁻¹ for **2**, and 1639 cm⁻¹ for **4**, respectively.

4.2 Structural description of $\{ [Cu_2(dmmal)_2(edin)(H_2O)_2] \cdot 3H_2O \}_n (1)$

Compound 1 crystallized in the acentric space group $P2_1$ with a Flack parameter of -0.026(9) [41] indicating mostly complete enantiomorphic purity within the crystal. Its asymmetric unit consists of two divalent copper atoms (Cu1, Cu2), two crystallographically distinct dmmal ligands, a full edin ligand, two bound water molecules and three water molecules of crystallization. Both Cu1 and Cu2 atoms adopt a {CuO4N} distorted square pyramidal coordination geometry, with trigonality τ factors [42] of 0.16 and 0.14, respectively. Bound water molecules occupy the elongated axial *z* direction position in both d^9 Jahn-Teller distorted coordination environments. The basal planes at both Cu1 and Cu2 contain an edin pyridyl nitrogen donor atom situated cis to a single dmmal carboxylate oxygen donor atom. The remaining two cis coordination sites at each Cu1 and Cu2 contain a 1,3-chelating arrangement of dmmal oxygen donor atoms. A thermal ellipsoid plot of both square pyramidal coordination environments is shown in Fig. 1. Pertinent bond lengths and angles at the two different copper atoms are listed in Table 2. Crystallographic distinction between Cu1 and Cu2 is enforced by different metrical parameters.

The dmmal ligands in **1** adopt an μ_2 - κ^3 -O,O'':O' exobidentate binding mode, in which one copper atom is bound in a 1,3-chelating fashion by two dmmal carboxylate oxygen atoms, and the other copper atom is bound by a third dmmal carboxylate oxygen atom in a monodentate fashion. One dmmal carboxylate oxygen atom remains unligated. [Cu(H₂O)(dmmal)]_n chain

motifs with embedded {Cu(OCO)}_n chain submotifs (Fig. 2), based on Cu1 (chain-A) or Cu2 (chain-B), are constructed via dmmal binding and bridging and are situated parallel to the *b* crystal direction. The dmmal carboxylate groups connect coordination sites on adjacent copper atoms, resulting in *equatorial-equatorial anti-syn* carboxylate bridges. Within the chain-A motifs, the Cu1…Cu1 internuclear distance is 4.862(3) Å, while the related Cu2…Cu2 distance within the chain-B motifs measure 4.915(3) Å. Within each chain motif, the next nearest Cu…Cu distance of 7.115(4) Å represents the *b* lattice parameter.

Adjacent chain-A and chain-B motifs in 1 are pillared by edin ligands into $[Cu_2(dmmal)_2(edin)(H_2O)_2]_n$ coordination polymer layers that are arranged parallel to the ($\overline{1}$ 0 2) crystal planes (Fig. 3). The edin ligands have an *anti* conformation of their central N–C–C–N linkages, and span a Cu1…Cu2 internuclear distance of 17.64(1) Å. Treating the copper atoms in the layer motif of 1 as 3-connected nodes results in an underlying (6,3) herringbone topology. Neighboring $[Cu_2(dmmal)_2(edin)(H_2O)_2]_n$ layers stack in an *AAA* pattern along the *a* crystal direction (Fig. S1), mediated by hydrogen bonding patterns involving pairs of water molecules of crystallization in the interlamellar regions (Table S1). The water molecules of crystallization occupy incipient 1D channels that comprise 4.1 % of the unit cell volume according to PLATON [43].

4.3 Structural description of $\{[Cu_2(dmmal)_2(bdin)(H_2O)_2] \cdot 2H_2O\}_n$ (2)

In contrast to 1, compound 2 crystallized in a centrosymmetric monoclinic space group with an asymmetric unit containing a divalent copper atom, a fully deprotonated dmmal ligand, a bound water molecule, half of a bdin ligand whose central C–C bond is sited over a

crystallographic inversion center, and a water molecule of crystallization. The copper atoms in **2** adopt a {CuO₄N} distorted square pyramidal coordination geometry, with a trigonality τ factor of 0.092. The bound water molecule occupies the axial coordination site, while the basal plane is occupied by a bdin pyridyl nitrogen donor atom sited cis to a single dmmal carboxylate oxygen donor atom. The remaining two cis coordination sites contain a 1,3-chelating arrangement of carboxylate oxygen donor atoms belonging to the same dmmal ligand. A thermal ellipsoid plot of both square pyramidal coordination environments is shown in Fig. 4a. Relevant bond lengths and angles in the coordination sphere are listed in Table 3.

The dmmal ligands in 2 adopt an μ_2 - κ^3 -O,O'':O' exobidentate binding mode identical to that in 1, in which one copper atom is bound in a 1,3-chelating fashion by two dmmal carboxylate oxygen atoms, and the other copper atom is bound by a third dmmal carboxylate oxygen atom in a monodentate fashion. One dmmal carboxylate oxygen atom remains unligated. $[Cu(H_2O)(dmmal)]_n$ chain motifs with embedded $\{Cu(OCO)\}_n$ chain submotifs (Fig. 4b). The dmmal carboxylate groups connect basal coordination sites on adjacent copper atoms, resulting once again in equatorial-equatorial anti-syn carboxylate bridges. The Cu. Cu internuclear distances within the chain motifs in 2 measure 4.789 Å. The next nearest Cu…Cu distance of 6.212(3) Å represents the b lattice parameter, and it is virtually 1 Å shorter than the comparable distance in 1. The $[Cu(H_2O)(dmmal)]_n$ chain motifs in 2 are pillared by bbin ligands that span a Cu···Cu internuclear distance of 18.18(1) Å, to form a 2D $[Cu_2(dmmal)_2(bdin)(H_2O)_2]_n$ layer (Fig. 5). The central tethers of the bdin ligands manifest a gauche-anti-gauche conformation, with torsion angles of 65.8, 180, and 65.8°. As is the case for 1, considering the copper atoms in the layer motif of 2 as 3-connected nodes results in a (6,3) herringbone topology framework. Neighboring $[Cu_2(dmmal)_2(bdin)(H_2O)_2]_n$ layers stack in an AAA pattern along the *a* crystal

direction, mediated by hydrogen bonding patterns involving bound water molecules and bdin formyl groups (Fig. S2, Table S1).

4.4 Structural description of [Cu₂(dmmal)₂(bpmp)]_n (**3**)

The asymmetric unit of compound **3** is comprised of a divalent copper atom, a dmmal ligand, and half of a bpmp ligand whose piperazinyl ring centroid is situated on a crystallographic inversion center. As in **1**, the copper atoms in **3** adopt a {CuO₄N} square pyramidal coordination geometry, but with a significantly decreased distortion from idealized geometry as evidenced by a trigonality τ factor of 0.002. Single carboxylate oxygen atom donors from four dmmal ligands occupy the basal plane within the coordination environment, and a bpmp pyridyl nitrogen donor atom fills the apical position (Fig. 6a). Bond lengths and angles within the square pyramidal coordination environment are listed in Table 3.

The dmmal ligands in **3** adopt an μ_4 - κ^4 -O:O':O'':O''' exotetradentate binding mode, constructing [Cu₂(dmmal)₂]_n ribbon motifs (Fig. 6b) with embedded {Cu₂(OCO)₄} paddlewheel dimeric units in which the internuclear Cu···Cu distance measures 2.6308(9) Å. The closest Cu···Cu interaction between adjacent paddlewheel dimers measures 6.0865(14) Å, which denotes the *b* lattice parameter. Neighboring [Cu₂(dmmal)₂]_n ribbon motifs, aligned parallel to the b crystal direction, are pillared into [Cu₂(dmmal)₂(bpmp)]_n coordination polymer layers by bpmp ligands (Fig. 6c). These dipyridyl coligands span a Cu···Cu distance of 15.83(1) Å. Treating the {Cu₂(OCO)₄} paddlewheels as 4-connected nodes reveals an underlying (4,4) grid topology for the layer motifs in **3**. The [Cu₂(dmmal)₂(bpmp)]_n layers, which are coincident with the *bc* crystal planes, stack in an *ABAB* pattern along the *a* crystal direction (Fig. S3).

Supramolecular impetus for this stacking pattern is provided by non-classical C–H \cdots O hydrogen bonding donation from pyridylmethylene C–H groups to dmmal carboxylate oxygen atoms (C \cdots O distance = 3.634(2) Å).

4.5 Structural description of [Cu₂(dmmal)₂(bpfp)]_n (4)

The asymmetric unit of compound **4** contains a divalent copper atom, a fully deprotonated dmmal ligand, and half of a bpfp ligand whose piperazinyl ring centroid is sited over a crystallographic inversion center. The copper atoms are ligated in a {CuO₄N} square pyramidal fashion (t = 0.015), with a pyridyl nitrogen donor atom from the bpfp ligand occupying the apical position. The basal plane is comprised of single carboxylate oxygen donor atoms from four dmmal ligands. A thermal ellipsoid representation of the coordination environment is shown in Fig. 7a. Relevant bond lengths and angles are listed in Table 5.

The copper atoms are connected to four others by dmmal ligands to construct $[Cu_2(dmmal)_2]_n$ layer motifs in **4** (Fig. 7b). All the dmmal carboxylate groups bridge equatorial sites on neighboring copper atoms, with Cu···Cu distances of 5.022(2) and 5.214(2) Å. Adjacent $[Cu_2(dmmal)_2]_n$ layers are pillared by bpfp ligands to construct a non-interpenetrated 3D $[Cu_2(dmmal)_2(bpfp)]_n$ coordination polymer network (Fig. 8a). The Cu···Cu distance spanned by the dipodal bpfp ligand is 15.999(4) Å. According to TOPOS [44], the resulting 3D net possesses a 5-connected 4⁴6⁶ sqp topology (Fig. 8b) [14]. This net resembles a 6-connected pcu topology with every node having a single absent pillar in a regular fashion.

4.6 Thermal Properties

Compound 1 underwent complete dehydration between 25 and 205 °C, with a mass loss of 12.5 % corresponding well with the predicted value of 12.1 % for five molar equivalents of water. Ejection of organic components occurred above 205 °C. Compound 2 underwent complete dehydration between 25 and 190 °C, with a mass loss of 9.9 % corresponding well with the predicted value of 9.5 % for four molar equivalents of water. Ejection of organic components occurred above 190 °C. Compound 3 underwent some decarboxylation up to 140 °C, with a mass loss of 11.2 % roughly corresponding to the elimination of two molar equivalents of CO₂ (13.4 % calc'd). Ejection of additional organic components occurred above 140 °C. Compound 4 underwent some decarboxylation between 25 and 210 °C, with a mass loss of 6.6 % corresponding to the elimination of one molar equivalent of CO₂ (6.4 % calc'd). Ejection of additional organic components of CO₂ (6.4 % calc'd). Ejection of additional organic components of CO₂ (6.4 % calc'd). Ejection of additional organic components of CO₂ (6.4 % calc'd). Ejection of additional organic components of CO₂ (6.4 % calc'd). Ejection of additional organic components of CO₂ (6.4 % calc'd). Ejection of additional organic components of CO₂ (6.4 % calc'd). Ejection of additional organic components of CO₂ (6.4 % calc'd). Ejection of additional organic components of CO₂ (6.4 % calc'd). Ejection of additional organic components occurred above 210 °C. TGA traces for 1–4 are shown in Figs. S4–S7, respectively.

4.7 Variable temperature magnetic properties

Variable temperature magnetic susceptibility measurements were carried out on polycrystalline samples of **1**, **2**, and **4**, to probe the magnitude of magnetic superexchange between carboxylate bridged divalent copper atoms. As *equatorial-equatorial* bridged $\{Cu_2(OCO)_4\}$ paddlewheel dimeric units in previously reported coordination polymers manifest strong antiferromagnetic coupling in all cases due to direct δ -like interactions of the magnetic d_{x2-y2} orbitals [45], a variable temperature magnetic study on **3** would simply be a verification experiment. As a result, such a study was not undertaken.

For compound 1, the $\chi_m T$ value of 0.76 cm³-K/mol at 300 K was consistent with the expected value for two uncoupled S = 1/2 spins per formula unit, assuming an idealized value of

g = 2. The $\chi_m T$ value slowly increased on lowering of temperature, reaching 0.81 cm³-K/mol at 150 K and 0.88 cm³-K/mol at 60 K. The $\chi_m T$ product then increased more rapidly with decreasing temperature, attaining a value of 1.01 cm³-K/mol at 25 K and 1.31 cm³-K/mol at 10 K. The $\chi_m T$ value measured 2.00 cm³-K/mol at 3 K. The shape of the $\chi_m T$ vs. T graph indicates ferromagnetic coupling along the *equatorial-equatorial* bridged carboxylates in the 1D {Cu(OCO)}_n chain submotifs in **1**. The magnetic susceptibility data for **1** were also fit to Baker's series expansion [46] for an isotropic Heisenberg 1-D S = 1/2 chain (eq. 1). The best fit to the observed data (Fig. 9) gave g = 2.06(2), and J = 3.0(2) cm⁻¹ with $R = 1.1 \times 10^{-3} = {\Sigma[(\chi_m T)_{obs} - (\chi_m T)_{calc}]^2 / \Sigma[(\chi_m T)_{obs}]^2}$. The positive value of *J* corroborates the contention of ferromagnetic superexchange in **1**.

For compound **2**, the $\chi_m T$ value of 0.75 cm³-K/mol at 300 K matches the exact expected value for two uncoupled S = 1/2 spins per formula unit, assuming an idealized value of g = 2. The $\chi_m T$ value slowly increased on lowering of temperature, reaching 0.87 cm³-K/mol at 80 K and 1.01 cm³-K/mol at 30 K. The $\chi_m T$ product then increased more rapidly with decreasing temperature, attaining a value of 1.37 cm³-K/mol at 10 K, and 2.00 cm³-K/mol at 3 K. The shape of the $\chi_m T$ vs. *T* graph indicates ferromagnetic coupling along the *equatorial-equatorial* bridged carboxylates in the 1D {Cu(OCO)}_n chain submotifs in **2**, as seen in **1**, which possessed similar submotifs. The best fit to the observed data (Fig. 10) using Baker's expression (eq. 1) gave g = 2.08(3), and J = 3.3(3) cm⁻¹ with $R = 1.6 \times 10^{-3}$. The positive value of *J* denotes ferromagnetic superexchange in **2**.

$$\chi_m T = \frac{Ng^2\beta^2}{4k} \left(\frac{A}{B}\right)^{\frac{2}{3}}$$

where $A = 1 + 5.797991x + 16.902563x^2 + 29.376885x^3 + 29.832959x^4$

and $B = 1 + 2.7979916x + 7.0086780x^2 + 8.6538644x^3 + 4.5743114x^4$

with x = J/kT (eq. 1)

For compound 4, the $\chi_m T$ value of 0.75 cm³-K/mol at 300 K was consistent with the expected value for two uncoupled S = 1/2 spins per formula unit. From 300 K down to 100 K, the $\chi_m T$ value largely remained constant. Below 100 K, the $\chi_m T$ value began to increase, reaching 0.79 cm³-K/mol at 60 K and 0.87 cm³-K/mol at 15 K. Below 15 K, the $\chi_m T$ value decreased, measuring 0.84 cm³-K/mol at 10 K, 0.64 cm³-K/mol at 5 K, and 0.28 cm³-K/mol at 2 K. The variable temperature behavior of the $\chi_m T$ value indicates a cooperation of ferromagnetic and antiferromagnetic behavior within the $[Cu_2(dmmal)_2]_n$ equatorial-equatorial bridged layers in 4. The variable temperature magnetic susceptibility data for 4 was fit to the Baker equation for a $\{Cu(OCO)\}_n$ chain submotif, modified with a mean-field approximation (eq. 2) to account for inter-chain spin communication within the $\{Cu_2(OCO)_2\}_n$ rectangular layer motifs. Given the two different carboxylate bridged Cu…Cu internuclear distances, use of a quadratic layer model with just one J exchange integral is inappropriate in the present case. The best fit parameters to eq. 2 gave g = 1.936(5), J = 4.6(2) cm⁻¹, and zJ' = 5.19(6) cm⁻¹, with $R = 3.3 \times 10^{-4}$. The positive J parameter indicates ferromagnetic superexchange within parallel $\{Cu(OCO)\}_n$ chain submotifs, while the negative zJ' factor indicates plausible opposite alignment of ferromagnetic spins between adjacent chain submotifs in 4.

$$\chi_m T = \frac{Ng^2\beta^2}{4k} \left(\frac{A}{B}\right)^2$$

where $A = 1 + 5.797991x + 16.902563x^2 + 29.376885x^3 + 29.832959x^4$ and $B = 1 + 2.7979916x + 7.0086780x^2 + 8.6538644x^3 + 4.5743114x^4$

with
$$x = \frac{J}{kT}$$
, and with $x = \frac{J}{kT}$ and $\chi'_m = \frac{\chi_m}{1 - zJ'\chi_m}$ (eq. 2)

5. Conclusions

A series of four copper dimethylmalonate coordination polymers has been prepared via slow solvent diffusion synthetic methods. The underlying topologies depend crucially on the nature of the neutral dipyridyl-type coligand. Two longer spanning dipyridylamide ligands, edin and bdin, afforded (6,3) herringbone type layered structures by linking together {Cu(OCO)}_n chain submotifs. The dipyridylamide ligand bpfp, based on a central piperazinyl tether, afforded a relatively uncommon 5-connected 3D **sqp** network, which featured {Cu(OCO)}_n chain submotifs linked into rectangular {Cu₂(OCO)₂}_n layers. The piperazinyl based bpmp ligand, which lacks any amide functional groups, produced a layer topology with embedded {Cu₂(OCO)₄} paddlewheel dimerie units. Ferromagnetic coupling was observed along the equatorial-equatorial bridged {Cu(OCO)}_n chain submotifs wherever these were present.

Supplementary Material

Hydrogen bonding geometric parameters, additional molecular graphics and thermogravimetric analysis plots. Crystallographic data (excluding structure factors) for **1–4** have been deposited with the Cambridge Crystallographic Data Centre with Nos. 1891894, 1898478, 1891895, 1891896, respectively. Copies of the data can be obtained free of charge via the Internet at .">https://summary.ccdc.cam.ac.uk/structure-summary-form>.

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Data	1	2
Empirical Formula	$C_{24}H_{36}Cu_2N_4O_{15}$	$C_{26}H_{38}Cu_2N_4O_{14}$
Formula Weight	747.65	757.68
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1$	$P2_1/n$
<i>a</i> (Å)	11.4172(7)	10.8185(17)
<i>b</i> (Å)	7.1165(4)	6.2125(10)
<i>c</i> (Å)	19.2092(12)	23.675(4)
α (°)	90	90
β (°)	103.9860(10)	91.429(2)
γ (°)	90	90
$V(Å^3)$	1514.49(16)	1590.7(4)
Z	2	2
$D (g \text{ cm}^{-3})$	1.639	1.582
μ (mm ⁻¹)	1.482	1.410
Min./max. transmission	0.8949	0.8760
	$-13 \le h \le 13,$	$-13 \le h \le 13,$
hkl ranges	$-8 \le k \le 8,$	$-7 \leq k \leq 7$,
	$-22 \le l \le 23$	$-28 \le l \le 28$
Total reflections	12337	12375
Unique reflections	5441	2952
R(int)	0.0328	0.0372
Parameters	421	214
R_1 (all data)	0.0398	0.0432
$R_1 (I > 2\sigma(I))$	0.0354	0.0372
wR_2 (all data)	0.0831	0.1037
$wR_2(I > 2\sigma(I))$	0.0796	0.0985
Max/min residual (e ⁻ / Å ³)	0.496/-0.456	0.699/-0.604
G.O.F.	1.029	1.071
L L		

Table 1. Crystal and Structure Refinement Data for 1–4.

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Data	3	Λ
Empirical Earmula		т С. Ц. С., М.О.
	$C_{24}\Pi_{32}Cu_{2}Iv_{4}O_{8}$	$C_{24}\Pi_{28}Cu_{2}N_{4}O_{10}$
Formula weight	655.64	683.60
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
<i>a</i> (Å)	13.877(3)	6.5143(7)
<i>b</i> (Å)	6.0865(14)	29.546(3)
<i>c</i> (Å)	16.588(6)	7.0507(8)
α (°)	90	90
β (°)	100.062(2)	92.4460(10)
γ (°)	90	90
$V(Å^3)$	1379.6(6)	1355.8(3)
Z	2	2
$D (\text{g cm}^{-3})$	1.578	1.674
μ (mm ⁻¹)	1.597	1.634
Min./max. transmission	0.8996	0.8737
	$-16 \le h \le 16,$	$-7 \le h \le 7,$
hkl ranges	$-7 \le k \le 7,$	$-35 \le k \le 35,$
	$-19 \le l \le 20$	$-8 \le l \le 8$
Total reflections	10852	11184
Unique reflections	2539	2486
R(int)	0.0385	0.0461
Parameters	183	192
R_1 (all data)	0.0563	0.0397
$R_1 (I > 2\sigma(I))$	0.0374	0.0305
wR_2 (all data)	0.1095	0.0765
$wR_2(I > 2\sigma(I))$	0.0980	0.0717
Max/min residual (e ^{-/} Å ³)	1.026/0.326	0.334/-0.359
G.O.F.	1.037	1.032

Table 1. Crystal and Structure Refinement Data for 1–4.

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Cu1–O1	1.947(4)	O3–Cu1–O1	90.23(15)
Cu1–O2 ^{#1}	1.945(3)	O3–Cu1–O2 ^{#1}	178.21(18)
Cu1–O3	1.943(4)	O3–Cu1–O9	98.65(15)
Cu1–O9	2.323(4)	O3–Cu1–N1	88.30(17)
Cu1–N1	2.019(5)	N1-Cu1-O9	90.71(16)
Cu2–O5	1.940(4)	O5–Cu2–O6 ^{#2}	91.67(15)
Cu2–O6 ^{#2}	1.961(4)	O5-Cu2-O12	86.37(15)
Cu2–O8	1.933(3)	O5-Cu2-N4	90.35(18)
Cu2–O12	2.248(4)	O6 ^{#2} –Cu2–O12	91.88(17)
Cu2–N4	2.019(5)	O6 ^{#2} Cu2N4	169.93(17)
O1–Cu1–O9	100.53(16)	O8 ^{#2} –Cu2–O5	178.16(18)
O1–Cu1–N1	168.76(18)	O8 ^{#2} -Cu2-O6 ^{#2}	90.17(15)
O2 ^{#1} –Cu1–O1	90.77(15)	O8 ^{#2} –Cu2–O12	93.71(15)
O2 ^{#1} -Cu1-O9	82.62(14)	O8 ^{#2} -Cu2-N4	87.82(17)
O2 ^{#1} -Cu1-N1	90.43(17)	N4-Cu2-O12	98.09(17)

Table 2. Selected Bond Distance (Å) and Angle (°) Data for 1.

Symmetry transformations: #1 - x, y - 1/2, -z; #2 - x + 2, y - 1/2, -z + 1.

Table 3. Selected Bond Distance (Å) and Angle (°) Data for 2.

Cu1–O1	1.9599(19)	O2 ^{#1} –Cu1–O5	88.53(8)
Cu1–O2 ^{#1}	1.9440(18)	O2 ^{#1} –Cu1–N1	90.17(8)
Cu1–O3	1.9268(19)	O3-Cu1-O1	91.17(8)
Cu1–O5	2.288(2)	O3-Cu1-O2 ^{#1}	177.54(8)
Cu1–N1	2.015(2)	O3–Cu1–O5	89.54(9)
01–Cu1–O5	91.76(8)	O3–Cu1–N1	88.52(9)
O1–Cu1–N1	172.00(9)	N1-Cu1-O5	96.23(9)
O2 ^{#1} Cu1O1	90.41(8)		

symmetry transformation: -x + 1/2, y - 1/2, -z + 1/2.

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Cu1–N1	2.172(3)	O1-Cu1-O4 ^{#1}	88.31(11)
Cu1–O4 ^{#1}	1.968(2)	O1–Cu1–O2 ^{#2}	90.84(11)
Cu1–O1	1.963(2)	O2 ^{#2} -Cu1-N1	86.02(10)
Cu1–O2 ^{#2}	1.976(2)	O3 ^{#3} -Cu1-N1	98.68(10)
Cu1–O3 ^{#3}	1.961(2)	O3 ^{#3} -Cu1-O4 ^{#1}	89.81(11)
O4#1-Cu1-N1	106.17(10)	O3 ^{#3} -Cu1-O1	167.94(9)
O4 ^{#1} -Cu1-O2 ^{#2}	167.81(9)	O3 ^{#3} -Cu1-O2 ^{#2}	88.49(11)
O1–Cu1–N1	93.29(10)		

Table 4. Selected Bond Distance (Å) and Angle (°) Data for **3**.

Symmetry transformations: #1 #1 -x + 1, -y + 1, -z + 1; #2 x, y - 1, z; #3 -x + 1, -y, -z + 1.

Table 5. Selected Bond Distance (Å) a	and Angle (°) Data for 4.
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Cu1–O1	1.9665(17)	O3 ^{#2} –Cu1–O1	92.71(7)
Cu1–O2 ^{#1}	1.9637(18)	O3 ^{#2} –Cu1–O2 ^{#1}	87.37(7)
Cu1–O3 ^{#2}	1.9629(17)	O3 ^{#2} –Cu1–N1	86.62(8)
Cu1–O4 ^{#1}	1.9486(18)	O4 ^{#1} -Cu1-O1	90.32(7)
Cu1–N1	2.255(2)	O4 ^{#1} -Cu1-O2 ^{#1}	89.52(7)
O1–Cu1–N1	86.92(8)	O4 ^{#1} -Cu1-O3 ^{#2}	176.50(7)
O2 ^{#1} –Cu1–O1	177.38(8)	O4#1-Cu1-N1	95.31(8)
O2 ^{#1} –Cu1–N1	95.69(8)		

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Symmetry transformations: #1 x + 1/2, -y + 3/2, z - 1/2; #2 x, y, z - 1.

Figure 1. Crystallographically distinct $\{CuO_4N\}$ distorted square pyramidal coordination environments and complete ligand set in **1**. Thermal ellipsoids are drawn at 50 % probability. Symmetry codes are as in Table 2.



Figure 2. $[Cu(H_2O)(dmmal)]_n$ chain motifs with embedded *equatorial-equatorial* bridged $\{Cu(OCO)\}_n$ chains in **1**. a) Chain-A motif. b) Chain-B motif. The methyl groups of the dmmal ligands have been omitted for clarity.



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Figure 3. $[Cu_2(dmmal)_2(edin)(H_2O)_2]_n$ coordination polymer layer in **1**. The chain-A and chain-B motifs are drawn in blue and green, respectively, in the online version of this article.

Figure 4. a) {CuO₄N} distorted square pyramidal coordination environment and complete ligand set in **2**. Thermal ellipsoids are drawn at 50 % probability. Symmetry codes are as in Table 3. b) [Cu(H₂O)(dmmal)]_n chain motifs with embedded *equatorial-equatorial* bridged {Cu(OCO)}_n chains in **2**. The methyl groups of the dmmal ligands have been omitted for clarity.



Figure 5. $[Cu_2(dmmal)_2(bdin)(H_2O)_2]_n$ coordination polymer layer in **2**. The $[Cu(H_2O)(dmmal)]_n$ chain motifs are drawn in red in the online version of this article.



Figure 6. a) {CuO₄N} square pyramidal coordination environment and complete ligand set and {Cu₂(OCO)₄} paddlewheel dimer in **3**. Thermal ellipsoids are drawn at 50 % probability. Symmetry codes are as in Table 4. b) [Cu₂(dmmal)₂]_n ribbon motif in **3**. c) [Cu₂(dmmal)₂(bpmp)]_n coordination polymer layer in **3**.



Figure 7. a) {CuO₄N} distorted square pyramidal coordination environment and complete ligand set in **4**. Thermal ellipsoids are drawn at 50 % probability. Symmetry codes are as in Table 5. b) $[Cu_2(dmmal)_2]_n$ rectangular layer motif in **4**, with *equatorial-equatorial* bridged dmmal carboxylate groups within the layer. The methyl groups of the dmmal ligands have been omitted for clarity.



Figure 8. a) Non-interpenetrated 3D $[Cu_2(dmmal)_2(bpfp)]_n$ coordination polymer network in 4. The $[Cu_2(dmmal)_2]_n$ layer motifs are depicted in red in the online version of this article. b) Underlying non-interpenetrated 5-connected 4⁴6⁶ sqp topology network in 4.



Figure 9. Variable temperature magnetic susceptibility data for 1. The best fit to eq. 1 is shown as a thin line.



Figure 10. Variable temperature magnetic susceptibility data for **2**. The best fit to eq. 1 is shown as a thin line.







Graphical Abstract

Four copper dimethylmalonate coordination polymer phases containing long-spanning dipyridyl coligands have been prepared and structurally characterized by single-crystal X-ray diffraction. Three layered topologies and one 3D **sqp** network (pictured) were observed. Variable temperature magnetic studies indicated predominant ferromagnetic superexchange within $\{Cu(OCO)\}_n$ chain motifs.

