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Divalent metal 1,3-phenylenediacetate coordination polymers with rigid or flexible dipyridyl tethers: Chains, layers, and interpenetrated networks

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ABSTRACT

Hydrothermal synthesis has afforded four divalent metal 1,3-phenylenediacetate (1,3-phda) coordination polymers containing different dipyridyl-type ligands. $\{[Cu(1,3\text{-phda})(dpa)(H_2O)]\cdot H_2O\}_n$ (**1**, dpa = 4,4′-dipyridylamine) exhibits a simple 2-D (4,4) rhomboid grid structure. $\{[Co(1,3\text{-phda})(bpy)]\cdot 1.5H_2O\}_n$ (**2**, bpy = 4,4′-bipyridine) also possesses a (4,4) layer structure, but with *syn–syn* bridged $\{Co_2(OCO)_2\}$ dimeric kernels serving as 4-connected nodes. $\{[Co(H_2O)_4(3\text{-bpmpH}_2)](1,3\text{-phda})_2\cdot 8H_2O\}_n$ (**3**, 3-bpmp = bis(3-pyridylmethyl)piperazine) manifests cationic 1-D $[Co(H_2O)_4(3\text{-bpmpH}_2)]_n^{4n+}$ chains linked into higher dimensionality by unligated 1,3-phda anions and curled tetrameric water molecule units. $\{[Ni(1,3\text{-phda})(4\text{-bpmp})(H_2O)_2]\cdot 2H_2O\}_n$ (**4**, 4-bpmp = bis(4-pyridylmethyl)piperazine) has an underlying twofold interpenetrated 6^58 (**cds**) 3-D network topology. Variable temperature magnetic susceptibility studies revealed the presence of weak antiferromagnetic coupling and zero-field splitting ($J = -1.65(4)$ cm^{-1} and $D = 30.9(7)$ cm^{-1} with $g = 2.20(1)$) within the $\{Co_2(OCO)_2\}$ dimers in **2**.

1. Introduction

The synthesis, design, and structural characterization of coordination polymers remain under intense investigative focus because of the utility of these phases in several industrially relevant applications, such as gas storage [1], small molecule adsorption and separation [2], ion exchange [3], heterogeneous catalysis [4], luminescence [5] and non-linear optical devices [6]. Additionally, coordination polymers with paramagnetic ions in close proximity display a wide diversity of temperature- and field-dependent magnetic properties [7]. In the preparation of these solids, dicarboxylate ligands are the most commonly employed linking agent, as these can provide the necessary charge balance and robust structural scaffolding for the formation of neutral frameworks. Variance of the metal coordination environment and carboxylate binding and bridging modes, along with the inclusion of neutral co-ligands, can foster a tremendous scope of possible network topologies in these systems [8]. Several dual-ligand divalent metal functional coordination polymers have been constructed using rigid aromatic dicarboxylates [9], for instance, $[Zn(terephthalate)(bpy)_{0.5}]_n$ (bpy = 4,4′-bipyridine), a highly thermally stable 3-D network material that can separate linear from branched alkanes [9a]. Because of their ability to adopt different energetically similar conformations during self-assembly, aliphatic α,ω-dicarboxylate ligands have also provided access to novel coordination polymer structural topologies in dual-ligand systems [10], for example, the unique self-penetrated 6^{10} regular 5-connected **rld–z** network in $\{[Ni(succinate)_{0.5}(dpa)_2]Cl\}_n$ (dpa = 4,4'-dipyridylamine) [10a]. Less studied to date have been coordination polymers built from phenylenediacetate (phda) ligands, that possess both rigid aromatic and flexible aliphatic aspects [11]. Some recent research in our laboratory has provided preliminary evidence of a large scope of intriguing structures in divalent metal/phda/dipyridyl coordination polymer systems, revealing a self-penetrated **rob** 4^86^68 topology in $[Cu_2(1,2\text{-phda})_2(dpp)]_n$ (dpp = 1,3-(di-4-pyridyl)propane) and a rare 5-connected 2-D Archimedean net in $[Cu(1,2\text{-phda})(H_2O)(4\text{-bpmp})_{0.5}]_n$ (4-bpmp = bis(4-pyridylmethyl)piperazine) [11a].

In this contribution we explore the synthesis and structural diversity of dual-ligand divalent metal coordination polymers containing 1,3-phenylenediacetate (1,3-phda), essentially a more flexible analog of the commonly used isophthalate ligand. By varying the coordination environment geometry depending on the *d*-electron count of the divalent transition metal ion, along with the nitrogen donor atom disposition, tether length, and hydrogen-bonding capability of the dipyridyl component

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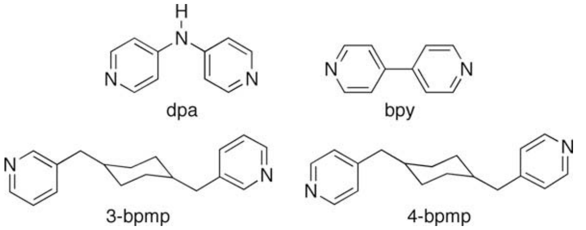

Scheme 1. Dipyridyl ligands used in this study.

(Scheme 1), we have been able to prepare a series of 1,3-phenylenediacetate-containing coordination polymers with divergent dimensionalities. Herein we discuss the structural chemistry and thermal degradation properties of $\{[Cu(1,3\text{-phda})(dpa)(H_2O)]\cdot H_2O\}_n$ (**1**), $\{[Co(1,3\text{-phda})(bpy)]\cdot 1.5H_2O\}_n$ (**2**), $\{[Co(H_2O)_4(3\text{-bpmpH}_2)](1,3\text{-phda})_2\cdot 8H_2O\}_n$ (**3**, 3-bpmp = bis(3-pyridylmethyl)-piperazine), and $\{[Ni(1,3\text{-phda})(4\text{-bpmp})(H_2O)_2]\cdot 2H_2O\}_n$ (**4**). Variable temperature magnetic susceptibility measurements were also carried out to probe spin communication between the proximal paramagnetic centers in **2**.

2. Experimental

2.1. General considerations

Metal salts and 1,3-phenylenediacetic acid were obtained commercially. The isomeric bis(pyridylmethyl)piperazine [12] and 4,4′-dipyridylamine [13] precursors were prepared via published procedures. 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 on a Perkin Elmer Spectrum One instrument. Thermogravimetric analysis was performed on a TA Instruments TGA 2050 instrument with a heating rate of 10 °C/min up to 900 °C under flowing N_2. Variable temperature magnetic susceptibility data (2–300 K) for **2** 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 5 min before magnetization measurement to ensure thermal equilibrium. The susceptibility data was corrected for diamagnetism using Pascal's constants [14]. Phase purity was checked by elemental analysis, infrared spectroscopy, and visual inspection of crystalline samples.

2.2. Preparation of $\{[Cu(1,3\text{-phda})(dpa)(H_2O)]\cdot H_2O\}_n$ (**1**)

$CuCl_2\cdot 2H_2O$ (51 mg, 0.31 mmol), dpa (125 mg, 0.74 mmol), 1,3-phenylenediacetic acid (70 mg, 0.39 mmol) and 10 mL deionized water were placed into a 23 mL Teflon-lined acid digestion bomb. The bomb was sealed and heated in an oven at 90 °C for 24 h, and then cooled slowly to 25 °C. Purple blocks of **1** (70 mg, 49% yield based on Cu) were isolated after washing with distilled water, ethanol, and acetone and drying in air. *Anal.* Calc. for $C_{40}H_{42}Cu_2N_6O_{12}$ **1**: C, 51.89; H, 4.57; N, 9.08. Found: C, 51.47; H, 4.22; N, 8.96%. IR (cm^{-1}): 3391 bw, 3189 w, 3097 w, 3016 w, 2927 w, 1738 w, 1647 w, 1599 s, 1525 s, 1490 m, 1449 m, 1417 w, 1355 s, 1284 m, 1274 m, 1229 w, 1212 s, 1154 w, 1076 w, 1060 m, 1028 m, 972 w, 930 w, 908 m, 896 w, 864 w, 842 m, 809 s, 741 m, 721 m, 670 m.

2.3. Preparation of $\{[Co(1,3\text{-phda})(bpy)]\cdot 1.5H_2O\}_n$ (**2**)

$Co(NO_3)_2\cdot 6H_2O$ (53 mg, 0.18 mmol), bpy (68 mg, 0.44 mmol), 1,3-phenylenediacetic acid (40 mg, 0.20 mmol) and 10 mL deionized water were placed into a 23 mL Teflon-lined acid digestion bomb. The bomb was sealed and heated in an oven at 120 °C for 48 h, and then cooled slowly to 25 °C. Pink blocks of **2** (21 mg, 27% yield based on Co) were isolated after washing with distilled water, ethanol, and acetone and drying in air. *Anal.* Calc. for $C_{40}H_{38}Co_2N_4O_{11}$ **2**: C, 55.31; H, 4.41; N, 6.45. Found: C, 54.91; H, 4.21; N, 6.10%. IR (cm^{-1}): 3430 w br, 1608 s, 1552 s, 1488 m, 1412 s, 1289 w, 1216 m, 1173 w, 1072 m, 1047 w, 1009 w, 941 w, 890 w, 857 w, 814 s, 791 m, 764 w, 750 m, 718 s, 692 m, 670 m.

2.4. Preparation of $\{[Co(H_2O)_4(3\text{-bpmpH}_2)](1,3\text{-phda})_2\cdot 8H_2O\}_n$ (**3**)

$Co(NO_3)_2\cdot 6H_2O$ (108 mg, 0.37 mmol) and 1,3-phenylenediacetic acid (72 mg, 0.37 mmol) were dissolved in 3 mL in a glass test tube. A 1 mL portion of a 1:1 water:ethanol solution was carefully layered on top, followed by a solution of 3-bpmp (100 mg, 0.373 mmol) in 3 mL ethanol. The reaction mixture was allowed to stand undisturbed at 25 °C for 14 d. Pink blocks of **3** (92 mg, 54% yield based on 1,3-phenylenediacetic acid) were isolated after washing with distilled water and acetone and drying in air. *Anal.* Calc. for $C_{36}H_{62}CoN_4O_{20}$ **3**: C, 46.50; H, 6.72; N, 6.03. Found: C, 46.42; H, 6.63; N, 5.91%. IR (cm^{-1}): 3090 w, 2946 w, 2825 w, 1609 w, 1549 s, 1486 w, 1433 s, 1374 s, 1347 w, 1300 w, 1268 w, 1194 w, 1006 w, 992 w, 960 w, 929 w, 832 w, 797 w, 777 w, 712 s.

2.5. Preparation of $\{[Ni(1,3\text{-phda})(4\text{-bpmp})(H_2O)_2]\cdot 2H_2O\}_n$ (**4**)

$Ni(NO_3)_2\cdot 6H_2O$ (81 mg, 0.28 mmol), 4-bpmp (74 mg, 0.28 mmol), 1,3-phenylenediacetic acid (54 mg, 0.28 mmol) and 10 mL deionized water were placed into a 23 mL Teflon-lined acid digestion bomb. The bomb was sealed and heated in an oven at 120 °C for 48 h, and then cooled slowly to 25 °C. Green-blue blocks of **4** (34 mg, 21% yield based on Ni) were isolated after washing with distilled water, ethanol, and acetone and drying in air. *Anal.* Calc. for $C_{26}H_{36}N_4NiO_8$ **4**: C, 52.81; H, 6.14; N, 9.93. Found: C, 52.41; H, 5.88; N, 9.64%. IR (cm^{-1}): 3300 w br, 2922 w, 2846 w, 1616 m, 1570 s, 1548 s, 1488 w, 1461 w, 1429 m, 1385 s, 1357 m, 1332 w, 1305 m, 1272 w, 1243 w, 1221 w, 1153 w, 1122 m, 1080 w, 1071 w, 1027 w, 1011 m, 1003 m, 938 w, 841 s, 803 m, 752 w, 695 w, 661 s.

3. X-ray crystallography

Single-crystal reflection data for **1**–**4** were collected using a Bruker-AXS Apex2 CCD instrument. Reflection data was acquired using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The reflection data were integrated with SAINT [15]. Lorentz and polarization effect and empirical absorption corrections were applied with SADABS [16]. The structures were solved using direct methods and refined on F^2 using SHELTXL [17]. The crystal of **2** was non-merohedrally twinned. The twin law was determined using CELL NOW [18] and the refinement was carried out on reflection data from only the major twin component, resulting in elevated refinement parameters. Distended thermal ellipsoids in some of the aromatic rings in the structure of **2** possibly indicate some degree of positional disorder; attempts to model this with partial occupancies were unsuccessful. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms bound to carbon atoms were placed in calculated positions and refined with isotropic thermal parameters using a riding model. Hydrogen atoms bound to water molecules or nitrogen atoms were located by Fourier difference map where possible and restrained at fixed positions. Disordered water molecules of crystallization were modeled with partial occupancies. Relevant crystallographic data for **1**–**4** are listed in Table 1.