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Diverse interpenetration schemes and topologies in cobalt coordination polymers constructed from 2-carboxycinnamic acid and a long-spanning dipyridylpiperazine ligand

Alec D. Shrode, Robert L. LaDuca*

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

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Hydrothermal reaction of cobalt nitrate, 2-carboxycinnamic acid (H_2cca), and a long-spanning dipyridyl-type ligand resulted in three coordination polymers that were characterized by single crystal X-ray diffraction and manifested different structural topologies and interpenetration schemes. $\{[Co(cca)(4\text{-}bpmp)(H_2O)_2]\cdot 4H_2O\}_n$ (**1**, 4-bpmp = bis(4-pyridylmethyl)piperazine) shows a 2-fold interpenetrated 4-connected 6^6 **dia** network. Use of the dipyridylamide bis(4-pyridylformyl)piperazine (4-bpfp) produced a crystalline mixture of the major product 3D 6-connected $4^{12}6^3$ **pcu** network coordination polymer $\{[Co(cca)(4\text{-}bpfp)]\cdot 2H_2O\}_n$ (**2**) and the minor product 1D chain coordination polymer $[Co(dibf)_2(4\text{-}bpfp)(H_2O)_2]_n$ (**3**, dibf = 3-dihydro-3-oxo-1-isobenzofuranacetate). The *in situ* rearrangement of 2-carboxycinnamic acid in the presence of 4-bpfp produced the anionic lactone dibf in **3**. Thermal decomposition behavior of the new major product phases was probed.

1. Introduction

The synthesis and characterization of divalent metal coordination polymers has received consistent attention within the inorganic chemistry community over the past fifteen years. These materials can act as gas storage substrates [1], shape-selective adsorbents [2], targeted drug-delivery agents [3], and heterogeneous catalysts for important organic transformations [4]. In recent years, coordination polymers have been reported to serve as detectors for nitroaromatic compounds via luminescence quenching pathways [5]. The predominant ligand choices for the construction of crystalline coordination polymer solids have been aromatic dicarboxylate ligands, as their various carboxylate group arrangements and binding modes can impart a remarkable variety of intriguing structural topologies and also provide a rigid backbone for crystal stability and the necessary anionic charge balance [6]. The incorporation of dipyridines such as 4,4′-bipyridine (bpy) or longer related ligands have greatly widened the structural scope of coordination polymers, and also resulted in new materials with enticing properties [7–12]. By way of example, the 3D 2-fold interpenetrated phase $[Zn(tere)(bpy)_{0.5}]_n$ (tere = terephthalate) adsorbs significant quantities of carbon dioxide [8], showing potential use in climate change remediation processes. Use of the phthalate (pht) ligand, with its *ortho*-disposed dicarboxylate groups, has afforded coordination polymers with rare and novel topologies. $[Cd(Hpht)_2(bpy)]_n$ (pht = phthalate) possesses a 6-connected 3D self-penetrated $5^{10}6^47$ network built from diamondoid $[Cd(Hpht)_2]_n$ motifs and cross-pillared by bpy tethers [9]. Employing a dipyridyl tether with hydrogen bonding capability, such as 4,4′-dipyridylamine (dpa), bis(4-pyridylmethyl)piperazine (4-bpmp, Scheme 1), or bis(4-pyridylformyl)piperazine (4-bpfp, Scheme 1) can result in marked structural alterations. $\{[Cd(pht)(dpa)(H_2O)]\cdot 4H_2O\}_n$ shows a unique but simple 4-connected 7^48^2 self-penetrated **yyz** topology constructed from interlocking helical motifs [10]. $\{[Cd_2(pht)_2(4\text{-}bpfp)(H_2O)_2]_n$ displayed a 4,5-connected 3D net with a rare $(4^46^2)(4^46^6)$ **tcs** topology, via pillaring of $[Cd(pht)(H_2O)]_n$ layers by tethering bpfp ligands [11]. $\{[Co(pht)(4\text{-}bpfp)(H_2O)_2]\cdot H_2O\}_n$ possessed an acentric 2D (4,4) grid structure; $\{[Cu_2(pht)_2(4\text{-}bpfp)(H_2O)_2]_n$ exhibited binding of the 4-bpfp formyl group and a novel 4,4-connected binodal layer topology [11]. $\{[Co(pht)(H_2O)(4\text{-}bpmp)]\cdot 5.5H_2O\}_n$ displays an achiral (4,4) grid constructed from *anti-syn* carboxylate bridged $\{Co_2(H_2O)_2(pht)_2\}$ dimeric clusters linked by open-conformation 4-bpmp ligands, in which the cluster units exhibit concomitant ferromagnetic coupling and Kramers doublet formation [12].

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* Corresponding author.
E-mail address: laduca@msu.edu (R.L. LaDuca).

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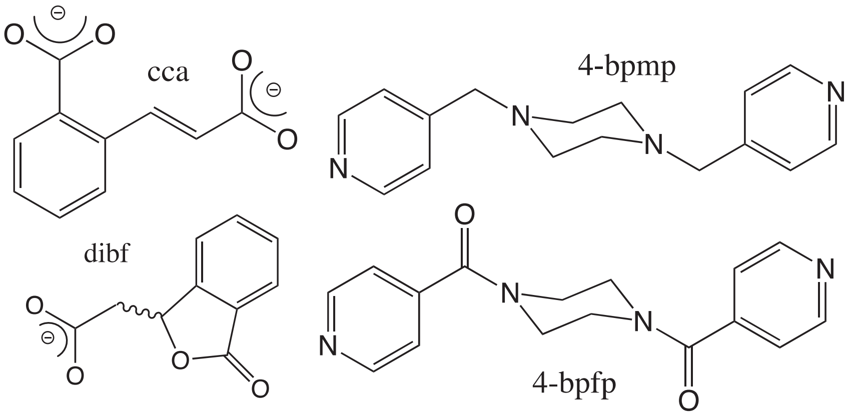

Scheme 1. Ligands used in this study.

The 2-carboxycinnamate ligand (cca, Scheme 1) also has an *ortho* dicarboxylate disposition like pht, but with one longer three-carbon carboxylate arm containing a conformationally rigid trans π bond. In comparison to pht-containing coordination polymers, fewer related derivatives synthesized with H_2cca as the starting carboxylic acid component have been reported [13–16]. $[Cd(cca)(bpy)]_n$ has a simple 2D (4,4) grid structure composed of $[Cd_2(cca)_2]$ double chains pillared by bpy ligands [13], while utilizing the longer-spanning 4-bpmp ligand afforded a 2D (6,3) herringbone topology in $\{[Cd(cca)(4\text{-bpmp})(H_2O)]\cdot 2H_2O\}_n$ [14]. The π bond contained within the longer carboxylate arm of cca has been shown to be susceptible to *in situ* reaction under the hydrothermal conditions of coordination polymer self-assembly, presumably due to internal nucleophilic attack of a short-arm carboxylate oxygen atom at the antibonding π* orbital within the alkene moiety [15]. Hydrothermal treatment of a mixture containing cobalt nitrate, H_2cca, and 3-pyridylisonicotinamide (3-pina) unexpectedly resulted *in situ* rearrangement of H_2cca into the 1,3-dihydro-3-oxo-1-isobenzofuranacetate (dibf) lactone anion, to concomitantly generate a (4,4) grid coordination polymer of the form $[Co(3\text{-pina})_2(dibf)_2]_n$ [15]. In this contribution we discuss the single-crystal structures, topological details, and thermal properties of three new cobalt coordination polymers prepared from 2-carboxycinnamic acid and either 4-bpmp or 4-bpfp: $\{[Co(cca)(4\text{-bpmp})(H_2O)_2]\cdot 4H_2O\}_n$ (**1**), $\{[Co(cca)(4\text{-bpfp})]\cdot 2H_2O\}_n$ (**2**), and $[Co(dibf)_2(4\text{-bpfp})]_n$ (**3**).

2. Experimental section

2.1. General considerations

Cobalt nitrate and 2-carboxycinnamic acid were commercially obtained. Bis(4-pyridylformyl)piperazine [17] and bis(4-pyridylmethyl)piperazine [18] were prepared via literature procedures. Water was deionized above 3MΩ–cm in-house. IR spectra were recorded on powdered samples using a Perkin Elmer Spectrum One DRIFT 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. Elemental Analysis was carried out using a Perkin Elmer 2400 Series II CHNS/O Analyzer.

2.2. Preparation of $\{[Co(cca)(4\text{-bpmp})(H_2O)_2]\cdot 4H_2O\}_n$ (*1*)

$Co(NO_3)_2\cdot 6H_2O$ (108 mg, 0.37 mmol), H_2cca (72 mg, 0.37 mmol), and 4-bpmp (99 mg, 0.37 mmol) were mixed with 10 mL of distilled H_2O and 1.0 mL of 1 M NaOH in 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 was cooled slowly to 25 °C. Magenta crystals of **1** (101 mg, 44% yield based on Co) were isolated after washing with distilled water, ethanol, and acetone and drying in air. Anal. Calc. for $C_{26}H_{38.5}CoN_4O_{9.75}$ **1**: C, 50.55; H, 6.28; N, 9.06% Found: C, 50.18; H, 6.01; N, 9.00%. IR (cm^{-1}): 3056 (w, br), 1617 (m), 1572(m), 1548 (m), 1524 (m), 1439 (m), 1425 (m), 1377 (s), 1301 (m), 1284 (m), 1268 (m), 1212 (m), 1151 (w), 1125 (w), 1071 (w), 1010 (m), 999 (m), 940 (w), 906 (w), 838 (m), 805 (m), 772 (m), 724 (m), 703 (m), 661 (m).

2.3. Preparation of $\{[Co(cca)(4\text{-bpfp})]\cdot 2H_2O\}_n$ (*2*) and $[Co(dibf)_2(4\text{-bpfp})(H_2O)_2]_n$ (*3*)

$Co(NO_3)_2\cdot 6H_2O$ (108 mg, 0.37 mmol), H_2cca (72 mg, 0.37 mmol), and 4-bpfp (110 mg, 0.38 mmol) were mixed with 10 mL of distilled H_2O and 0.75 mL of 1 M NaOH in a 23 mL Teflon-lined acid digestion bomb. The bomb was sealed and heated in an oven at 80 °C for 24 h, and then was cooled slowly to 25 °C. A few small needle-like

Table 1
Crystal and structure refinement data for **1**–**3**.

Data	1	2	3
Empirical Formula	$C_{26}H_{38}CoN_4O_{10}$	$C_{26}H_{26}CoN_4O_8$	$C_{36}H_{38}CoN_4O_{14}$
Formula Weight	625.33	581.44	809.63
Crystal system	Monoclinic	monoclinic	triclinic
Space group	$P2_1/n$	$P2_1/c$	$P\overline{1}$
a (Å)	12.0611(11)	9.3074(9)	5.3851(4)
b (Å)	19.2825(17)	12.2958(11)	10.6708(9)
c (Å)	12.5017(11)	22.468(2)	16.5350(11)
α (°)	90	90	98.163(5)
β (°)	98.388(1)	101.540(1)	96.023(5)
γ (°)	90	90	98.162(6)
V (Å^3)	2876.4(4)	2519.3(4)	923.38(12)
Z	4	4	1
D (g cm^{-3})	1.436	1.553	1.456
μ (mm^{-1})	0.658	0.740	4.290
Min./max. transmission	0.7654	0.8689	0.7290
hkl ranges	$-14 \le h \le 14$, $-23 \le k \le 23$, $-15 \le l \le 15$	$-11 \le h \le 11$, $-14 \le k \le 14$, $-27 \le l \le 27$	$-6 \le h \le 6$, $-11 \le k \le 13$, $-20 \le l \le 20$
Total reflections	23144	19989	10094
Unique reflections	5271	4618	3407
R(int)	0.0273	0.0476	0.0913
Parameters	403	388	254
R_1 (all data)	0.0453	0.1066	0.0836
R_1 ($I > 2\sigma(I)$)	0.0361	0.0779	0.0633
wR_2 (all data)	0.1067	0.2382	0.1930
wR_2 ($I > 2\sigma(I)$)	0.0988	0.2111	0.1803
Max/min residual (e$^-$/Å^3)	0.510/−0.678	0.741/−1.241	0.376/−0.340
G.O.F.	1.055	1.073	1.186