

A mutually inclined interpenetrated cobalt benzenetricarboxylate/organodiimine layered coordination polymer containing “infinite” water chains and its irreversible crystal-to-crystal structural transformation upon dehydration

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Abstract

The novel coordination polymer $\{[\text{Co}(\text{Hbtc})(4\text{-bpmp})(\text{H}_2\text{O})] \cdot 3\text{H}_2\text{O}\}$ (**1**, btc = 1,3,5-benzenetricarboxylate, 4-bpmp = *N,N'*-bis(4-pyridylmethyl)piperazine) has been prepared by hydrothermal synthesis and characterized by single crystal X-ray diffraction, IR and thermogravimetric analysis. Individual $[\text{Co}(\text{Hbtc})(4\text{-bpmp})(\text{H}_2\text{O})]_n$ layers mutually interpenetrate in a $2d + 2d \rightarrow 3D$ inclined fashion to produce channels coursing down the *c* crystal direction, occupied by “infinite” 1D water molecule chains. Dehydration of **1** results in structural reorganization to a monoclinic phase, which is converted to an amorphous phase upon rehydration.

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Among coordination polymer systems, divalent metal benzenetricarboxylates have attracted very significant attention. In addition to some strikingly aesthetic structures, these materials exhibit promising properties in gas storage [1], shape-selective absorption [2], magnetism [3], catalysis [4], and photoluminescence [5]. Due to the wide variety of possible carboxylate protonation, binding, and bridging modes, altering synthetic conditions in this system can provide access to structural polytypes and polymorphs [6].

The structural complexity of benzenetricarboxylate coordination polymers has been elevated by the incorporation of neutral tethering organodiimines such as 4,4'-bipyridine (4,4'-bpy), 1,2-di-4-pyridylethane (dpe), 1,3-di-4-pyridylpropane (dpp) and 4,4'-dipyridylamine (dpa)[7–11]. Nevertheless reports of coordination polymer solids based on

tethering organodiimines with hydrogen bonding acceptance capability in their central regions are much rarer [12]. Herein we report the first example of a coordination polymer incorporating 1,3,5-benzenetricarboxylic acid (H_3btc) and *N,N'*-bis(4-pyridylmethyl)piperazine (4-bpmp), the mutually inclined interpenetrated $2d + 2d \rightarrow 3D$ layered phase $\{[\text{Co}(\text{Hbtc})(4\text{-bpmp})(\text{H}_2\text{O})] \cdot 3\text{H}_2\text{O}\}$ (**1**). Compound **1** also undergoes an irreversible structural reorganization upon dehydration.

Orange-pink crystals of the compound **1** were prepared in moderate yield [13] by hydrothermal reaction of cobalt chloride, H_3btc , and 4-bpmp [14] in a 1:1:2 mole ratio. As only one equivalent of 4-bpmp is incorporated in the final product, it is likely that the second equivalent serves as the requisite base for double deprotonation of H_3btc to form Hbtc^{2-} dianionic units. The infrared spectrum of **1** indicated the presence of antisymmetric and symmetric Hbtc carboxylate stretching bands at 1547 cm^{-1} and 1373 cm^{-1} , respectively, along with a broad feature around $\sim 3094\text{ cm}^{-1}$ ascribed to O–H and N–H vibrational modes.

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The protonated unligated terminus of the Hbtc ligand gives rise to a band at 1693 cm^{-1} .

Single crystal X-ray diffraction revealed that **1** crystallizes in the monoclinic space group $P2_1/c$ and possesses an asymmetric unit consisting of one cobalt atom, one singly protonated Hbtc ligand, and two halves of two crystallographically distinct bpmp ligands (A, defined by N1–N2; B, defined by N3–N4), and one aquo ligand (O7) (Fig. 1). Three water molecules of crystallization also lie within the asymmetric unit. The cobalt atom displays a $[\text{CoO}_4\text{N}_2]$ dis-

torted octahedral coordination sphere, with *trans* nitrogen donors from ligands A and B. Two *cis* oxygen donors belong to a chelating terminus of an Hbtc ligand; an additional oxygen donor is part of a monodentate Hbtc carboxylate terminus. The coordination sphere is rounded out by the aquo ligand.

Adjacent cobalt atoms are linked along the *c* crystal direction through exobidentate bisbridging chelating/monodentate Hbtc ligands to form $[\text{Co}(\text{Hbtc})(\text{H}_2\text{O})]_n$ chains with a $\text{Co}\cdots\text{Co}$ contact distance of $10.359(3)\text{ \AA}$,

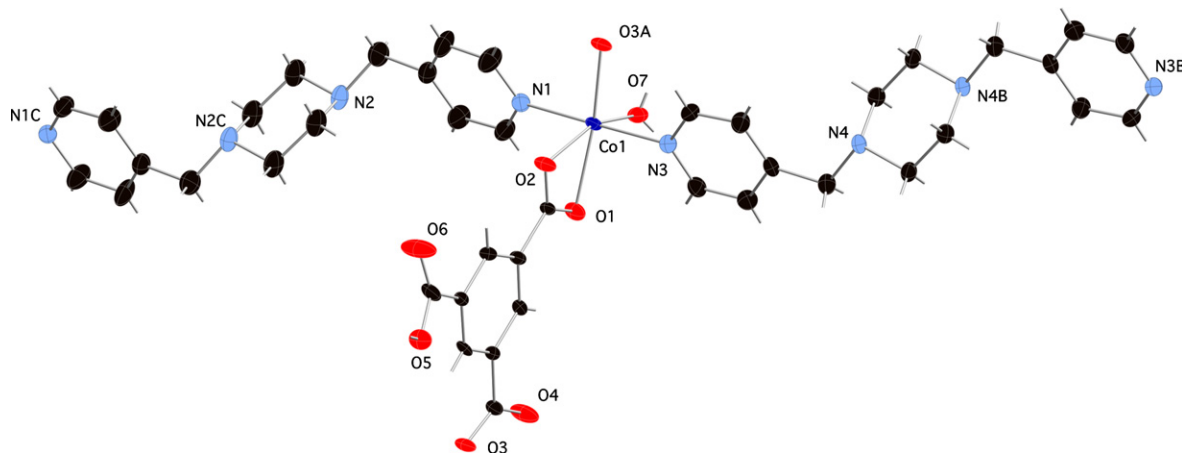


Fig. 1. Coordination environment of **1** with thermal ellipsoids drawn at 50% probability) and partial atom numbering scheme. The water molecules of crystallization are not shown. Hydrogen atom positions are shown as sticks. Complete crystallographically distinct A and B 4-bpmp ligands are depicted.

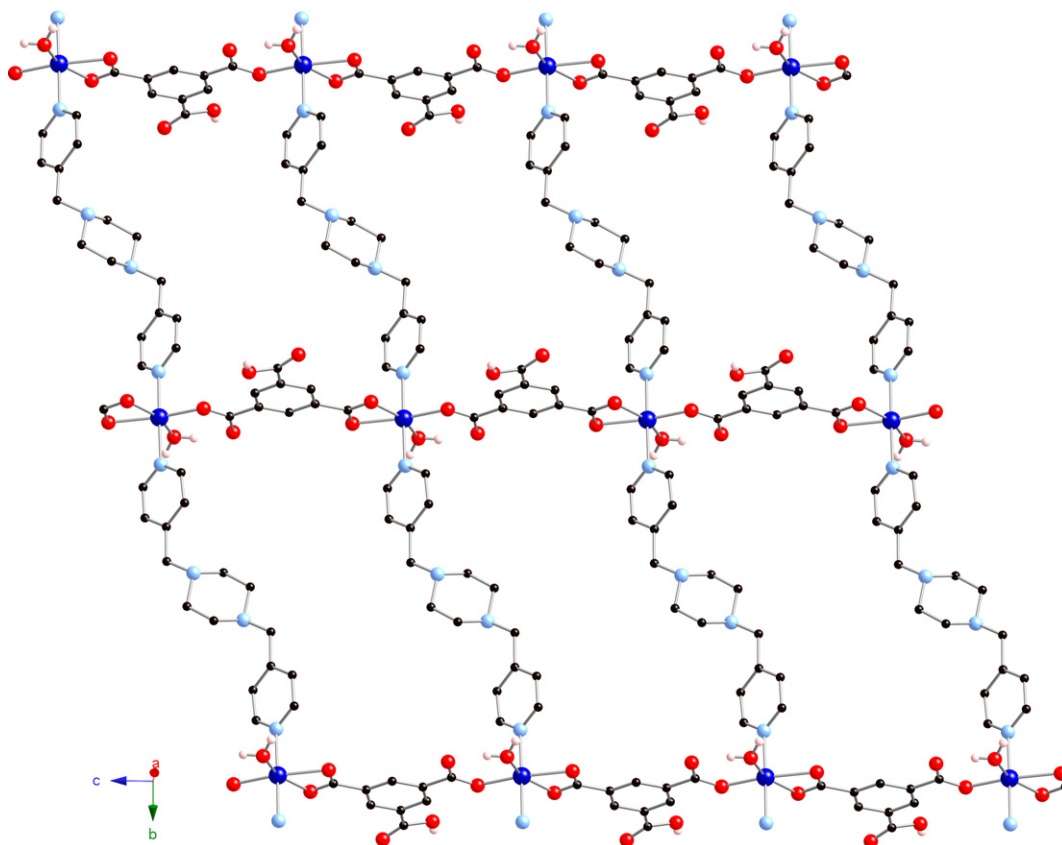


Fig. 2. A single $[\text{Co}(\text{Hbtc})(4\text{-bpmp})(\text{H}_2\text{O})]_n$ (4,4) rhomboid grid layer in **1**.

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