Enantiopure *vs*. racemic metalloligands: impact on metal–organic framework structure and synthesis†

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Carboxylate-decorated tris(dipyrrinato) cobalt(III) complexes have been used to construct 2-D and 3-D metal–organic frameworks with infinite and trinuclear zinc secondary-building units.

Metal–organic frameworks (MOFs) constitute an exciting class of materials for a wide variety of potential applications including gas storage, heterogeneous catalysis, and separations.[1–3] In an attempt to introduce enhanced properties to MOFs, the use of metalloligands, coordination compounds with peripheral metal-binding functionalities, has been explored in order to add a second, 'functional' metal center into the lattice structure.[4–9] Such metalloligands offer the opportunity to enhance guest binding, introduce catalytic sites, and confer useful opto-electronic properties to the resulting MOFs. With these goals in mind, our laboratory has used tris(dipyrrinato) metal complexes[10,11] as metalloligands to successfully create a variety of heterobi- and heterotrimetallic MOFs.[12,13]

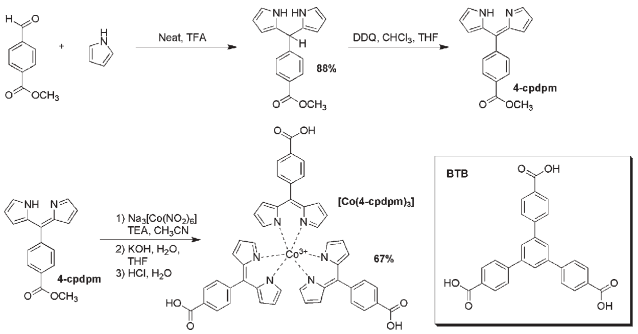
One of the most successful approaches to preparing MOFs with high thermal stability and chemical robustness is the combination of a polycarboxylate ligand with divalent and trivalent metal ions such as copper(II), zinc(II), indium(III), and others under solvothermal synthesis conditions.[1,2,14,15] We sought to develop dipyrrinato metalloligands that could mimic the MOF structures obtained by these polycarboxylate ligands. Due to their range of interesting topologies and high porosity, structures based on 3-fold symmetric tricarboxylates were specifically targeted,[16–18] Of particular interest was MOF-177,[16] which is comprised of 1,3,5-benzenetribenzoate (BTB, Scheme 1) and Zn_4O secondary-building units (SBUs). MOF-177 has enormous pores capable of absorbing guest molecules as large as Nile Red and C_{60}. To this end the metalloligand [Co(4-cpdpm)$_3$] (4-cpdpm = 5-(4-carboxylphenyl)-4,6-dipyrrinato) has been synthesized, characterized, and resolved into its Δ and Λ enantiomers in an attempt to make chiral analogues of structures such as MOF-177. Solvothermal reactions with $Zn(NO_3)_2 \cdot 4H_2O$ generated two novel MOFs, one of which utilizes an infinite secondary-building unit (iSBU). Furthermore, we show that the products of these solvothermal reactions depend on whether racemic or enantiopure [Co(4-cpdpm)$_3$] is utilized.

The synthesis of racemic [Co(4-cpdpm)$_3$] was straightforward and performed as shown in Scheme 1; spectroscopic data on this compound were consistent with literature results.[10,19]

After screening a number of solvothermal conditions, dichroic red-green crystals of MOF-Co/Zn-5a were obtained by the following method: *rac*-[Co(4-cpdpm)$_3$] (2.1 mg, 2.5×10^{-6} mol) and $Zn(NO_3)_2 \cdot 4H_2O$ (6.5 mg, 2.5×10^{-5} mol) were dissolved in DEF–EtOH–H_2O (1 : 0.25 : 0.25 mL) in a 4 mL screw top vial, and the mixture was heated to 90 °C at a rate of 2.0 °C min^{-1} for 23 h, followed by cooling to room temperature at 0.2 °C min^{-1}. The resulting red-green, plate-like crystals were filtered, washed with DEF (diethylformamide), and briefly dried in air.

The structure of MOF-Co/Zn-5a was determined by single-crystal X-ray diffraction,‡ and found to be a 3-D MOF with iSBUs (Fig. S1).† The asymmetric unit consists of a single [Co(4-cpdpm)$_3$] complex, a portion of an infinite, zigzag chain of zinc-hydroxo clusters, a guest DEF solvent molecule, and a region that appeared to contain partially occupied and severely disordered solvent. The [Co(4-cpdpm)$_3$] complex has an octahedral geometry similar to other dipyrrinato complexes reported in the literature;[10,19,20] however, the complex is slightly distorted such that the disposition of the peripheral carboxylate ligands is of considerably lower symmetry than idealized D_3 symmetry would predict.

A portion of the zinc-hydroxo chain is shown in Fig. 1. This iSBU is an extended cluster that can be considered as an alternating arrangement of two types of corner-sharing $Zn_3(CO_2)_3OH$ triangles (designated type I and II). The type I triangles are close to equilateral and contain μ_3-hydroxy groups with Zn···Zn separations of 3.332, 3.380, and 3.547 Å. Type II triangles are more nearly isosceles with one long Zn···Zn separation of 5.250 Å and two shorter distances of 3.497 and 3.741 Å. The type II triangles incorporate μ_2-hydroxy groups that are statistically distributed between two edges of the triangles. The two types of triangular units share an edge motif that involves one edge that is bridged by two carboxylate moieties from [Co(4-cpdpm)$_3$], one edge comprised of a single bridging carboxylate



Scheme 1 Synthesis of racemic [Co(4-cpdpm)$_3$]. In box: the 3-fold symmetric ligand BTB that was used to prepare MOF-177.

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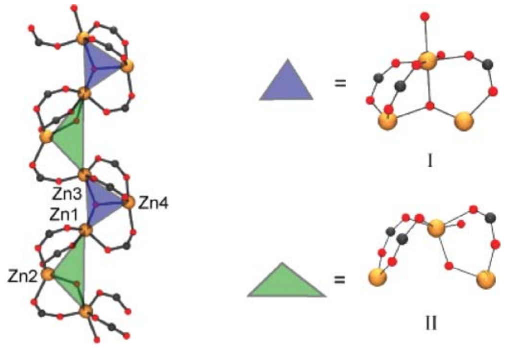

Fig. 1 A portion of the extended zinc cluster in MOF-Co/Zn-5a. Detail of the type I and type II triangles (upper right).

moiety, and one open edge that is not bridged by a carboxylate group.

Two zinc ions in the iSBU do not link adjacent triangles, Zn2 and Zn4 (Fig. 1), and bear one or two coordinated water molecules to attain distorted square pyramidal or octahedral coordination spheres, respectively. Each of the [Co(4-cpdpm)$_3$] metalloligands bridges three distinct iSBUs so that the chains are arranged in a somewhat distorted hexagonal network (Fig. 2). The rod-shaped chains present in MOF-Co/Zn-5a extend along the crystallographic *b*-axis, and MOF-Co/Zn-5a thus represents an example of a small family of MOFs that are derived from iSBUs.[5,14,21–24] Because of the complicated connectivity of iSBU-based MOFs, as opposed to the simple node-and-spacer type MOFs, different topological perspectives are necessary in order to facilitate their structural illustration. Yaghi, O'Keeffe *et al.* have recently enumerated 14 different ways in which rod-shaped iSBUs can be arranged in three-dimensional structures.[14] In this context, MOF-Co/Zn-5a exemplifies, if only iSBUs are considered, the prototypical hexagonal rod-packing motif (**hex**); however, if the [Co(4-cpdpm)$_3$] metalloligands are also considered and treated as trigonal nodes, a new structural type, which is associated with the (3,8)-connected net **tfz-d** (RCSR database, http://rcsr.anu.edu.au/) can be formulated (Fig. 2).§ It should be noted that most existing iSBU-based MOFs are constructed from ditopic ligands and structures incorporating higher connectivity ligand systems remain largely unexplored.[14]

Upon obtaining MOF-Co/Zn-5a, additional reaction conditions were explored, in a continuing effort to obtain more novel MOF structures. One slight modification of the reaction conditions resulted in red block-like crystals of a new compound, MOF-Co/Zn-5b. Racemic [Co(4-cpdpm)$_3$] (2.1 mg, 2.5×10^{-6} mol) and $Zn(NO_3)_2 \cdot 4H_2O$ (1.3 mg, 4.9×10^{-6} mol) were dissolved in DEF–EtOH (1 : 0.50 mL) in a 4 mL screw top vial. This mixture was subjected to an identical gradient of heating to 90 °C at a rate of 2.0 °C min^{-1} for 23 h, followed by cooling back to room temperature at 0.2 °C min^{-1}.

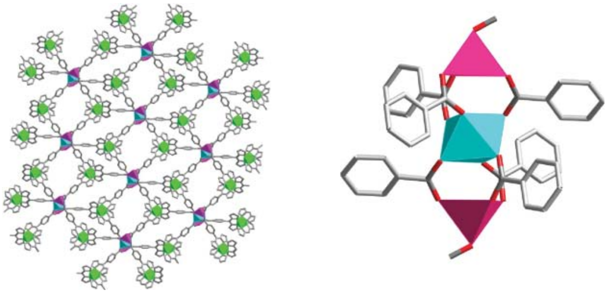

Fig. 3 Structure of MOF-Co/Zn-5b (left). Trinuclear SBU in MOF-Co/Zn-5b (right). Hydrogen atoms and solvent molecules have been omitted (or partially omitted) for clarity. Cobalt (green), tetrahedral zinc (pink), octahedral zinc (cyan), oxygen (red, highlighted only on the right).

The structure of MOF-Co/Zn-5b was determined by single-crystal X-ray diffraction,‡ which revealed a 2-D lattice (Fig. 3, Fig. S2).† The asymmetric unit consists of one molecule of [Co(4-cpdpm)$_3$], two disordered DEF molecules, and 1.5 Zn^{2+} ions, with one located at an inversion center. A trinuclear Zn^{2+} SBU was found, which is composed of a central zinc atom that is octahedrally coordinated by six carboxyl groups (Fig. 3). This central, 6-coordinate Zn^{2+} ion is flanked by two tetrahedral Zn^{2+} ions that are each connected to the central zinc atom by three bridging carboxylate groups. Disordered DEF molecules bind the apical sites of the flanking 4-coordinate Zn^{2+} ions. Each SBU is connected by six carboxylate groups each from a distinct [Co(4-cpdpm)$_3$] metalloligand. This creates a hexagonal, pinwheel-like geometry and an overall S_6 symmetry at the SBU (Fig. 3, Fig. S3).† The topology underlying MOF-Co/Zn-5b is related to the hexagonal **kgd** (Kagomé dual) net, which is a 2-D (3,6)-connected lattice containing 4-membered rings. This topology is exceedingly rare among observed MOF structures (RCSR database). It should be noted that, structurally, MOF-Co/Zn-5b and MOF-Co/Zn-5a are closely related to each other in that a schematic representation of the 2-D MOF resembles the individual layers of the 3-D MOF

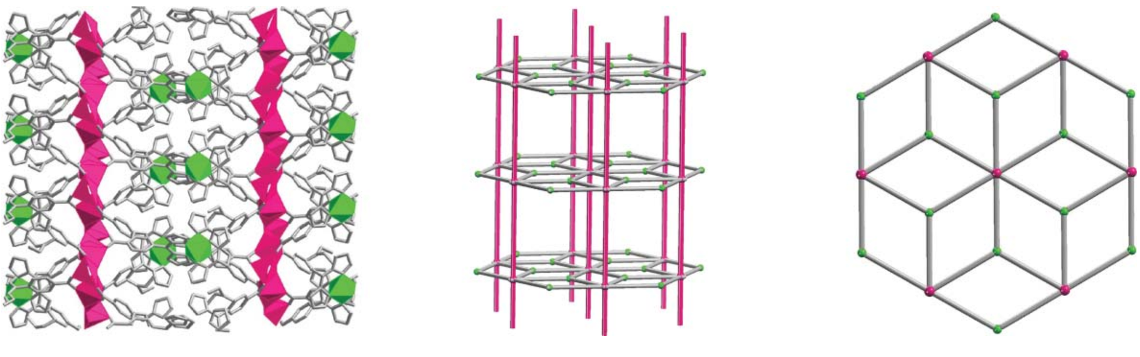

Fig. 2 Topology of MOF-Co/Zn-5a. Overall structure of MOF-Co/Zn-5a (left); hydrogen atoms and solvent molecules omitted for clarity with cobalt(III) and zinc(II) centers shown as green and pink polyhedra, respectively. Schematic representations of MOF-Co/Zn-5a (center and right) from a rod-packing perspective. The resulting model is related to the **tfz-d** net. Green spheres represent cobalt(III) centers and magenta spheres/rods represent the zinc(II)-based iSBUs.

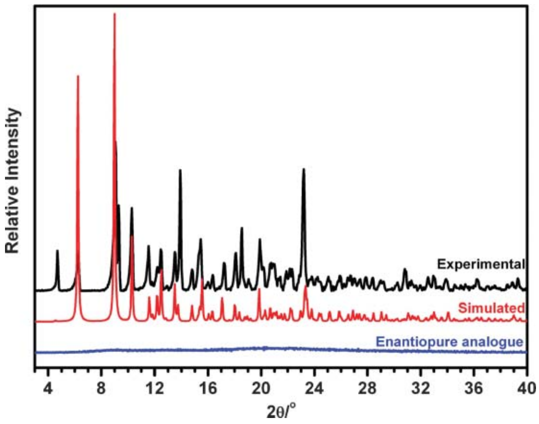

Fig. 4 Simulated (red) and experimental (black) XRD pattern for MOF-Co/Zn-5a. The pattern obtained from the reaction product using Λ-[Co(4-cpdpm)$_3$] is shown in blue, indicating an amorphous material.

when viewed along the *b*-axis (Fig. 2, right). The resemblance of the MOFs is due to the similar connectivity found in the SBUs of these MOFs.

With both a 2-D and 3-D MOF in hand, we sought to generate homochiral structures by exploiting the chirality of the octahedral, tris(chelate) metal center of the [Co(4-cpdpm)$_3$] metalloligand. Resolution of *rac*-[Co(4-cpdpm)$_3$] was performed with (−)-cinchonidine using a published procedure.[19] Enantiopurity of the resolved metalloligand was confirmed by chiral HPLC.[19] Subjecting enantiopure Δ-[Co(4-cpdpm)$_3$] or Λ-[Co(4-cpdpm)$_3$] to identical reaction conditions as those used for MOF-Co/Zn-5a or MOF-Co/Zn-5b produced amorphous, red precipitates. Examination of these solids by X-ray powder diffraction (XRD) showed that they had no significant crystallinity (Fig. 4, Fig. S4).† Further validation that these powders were not the desired MOFs was obtained by thermal gravimetric analysis (TGA). While both MOF-Co/Zn-5a and MOF-Co/Zn-5b are stable up to ∼400 °C, the amorphous solids obtained from Λ-[Co(4-cpdpm)$_3$] showed significant weight losses at temperatures ∼100 °C (Fig. S5).†

The latter finding is important in the context of using metalloligands in the preparation of chiral MOFs and the capacity of such systems to produce predictable structure types. When examining the structures of MOF-Co/Zn-5a or MOF-Co/Zn-5b, there is no obvious topological incompatibility with the use of a homochiral metalloligand; indeed similar metalloligands have been found to form homochiral MOFs.[20] However, other factors, such as differences in solubility of the enantiopure *versus* racemic metalloligand, may prevent the direct substitution of one for the other under solvothermal reaction conditions.

In summary, two new MOFs based on the metalloligand *rac*-[Co(4-cpdpm)$_3$] have been prepared and characterized. Both MOFs contain unusual structural motifs, one involving an iSBU and the other a trinuclear zinc(II) SBU. When preparing these MOFs, we find that the products are obtained only when the racemate is used. Under identical reaction conditions enantiopure metalloligands lead only to amorphous solids. These findings are significant within the context of designing and synthesizing new MOFs and their homochiral analogues.

Notes and references

‡ *Crystal data* for MOF-Co/Zn-5a: $C_{53}H_{41.5}CoN_7O_{9.5}Zn_2$, M = 1118.10, monoclinic, space group $P2_1/n$, a = 15.229(4) Å, b = 8.796(2) Å, c = 38.650(11) Å, α = 90°, β = 89.977(5)°, γ = 90°, V = 5177(2) Å^3, T = 100(2) K, Z = 4, 43650 reflections measured, 10531 unique which were used in all data, (R_{int} = 0.0841), R_1 = 0.0787 ($I > 2\sigma(I)$), GOF = 1.042.

Crystal data for MOF-Co/Zn-5b: $C_{55.5}H_{46}CoN_{7.5}O_{7.5}Zn_{1.5}$, M = 1094.98, triclinic, space group $P\bar{1}$, a = 13.626(3) Å, b = 14.766(3) Å, c = 17.357(4) Å, α = 81.062(4)°, β = 81.660(4)°, γ = 75.534(4)°, V = 3319.8(12) Å^3, T = 100(2) K, Z = 2, 36922 reflections measured, 13380 unique which were used in all data, (R_{int} = 0.0800), R_1 = 0.0605 ($I > 2\sigma(I)$), GOF = 0.906.

CCDC 656116–656117. For crystallographic data in CIF format see DOI: 10.1039/b712118k

§ *Alternative analysis of MOF-Co/Zn-5a topology*. iSBU-based MOF classification involves recognition of simple patterns (*e.g.*, ladders, helices) of coordinating carboxylate groups in the iSBUs. Although this approach is not always applicable due to the complex nature of some iSBUs, those in MOF-Co/Zn-5a can be simplified as 6-fold helices which in turn are cross-linked by the metalloligands (Fig. S6).† This gives rise to a new binodal 3-connected net that has not, to the best of our knowledge, been observed in other MOFs but is recognized as net sqc946 (vertex symbols, $(6\cdot6\cdot12_2)(6\cdot12_2\cdot12_2)$; coordination sequences, 3, 6, 10, 18, 32, 52, 73, 98, 125, 156 and 3, 6, 11, 18, 31, 52, 73, 98, 125, 156) in the EPINET database (http://epinet.anu.edu.au/).

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