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A Chiral Self-Catenated Dual-Ligand Coordination Polymer Constructed from Three Distinct Interwoven Helical Motifs Interconnected by One-Dimensional Chains

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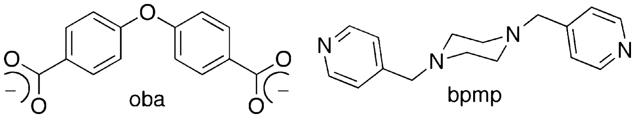
Hydrothermal synthesis has afforded $[Co_3(oba)_3(bpmp)_2]_n$ [oba = oxybis(benzoate), bpmp = bis(4-pyridylmethyl)piperazine], a chiral coordination polymer possessing an aesthetic self-catenated three-dimensional structure with an unprecedented 8-connected uninodal $4^45^{17}6^7$ topology. The network is formed by the junction of $\{Co_3O_2\}$ clusters into three different homochiral interlocked helical motifs, linked by one type of “infinite” chain pattern. Antiferromagnetic exchange is observed within the $\{Co_3O_2\}$ clusters.

One of the most commonly encountered features of coordination polymer systems is the mutual interpenetration of networks, with a variety of interesting connectivity patterns both analogous to those in naturally occurring minerals and completely unprecedented.[1,2] In comparison to interpenetrated coordination polymers, those exhibiting self-catenation, in which connecting rods of the network penetrate through the smallest circuits of the same network, are much rarer.[3] Self-catenated structures can range from the relatively simple uniform 3-connected (12,3)-**twt** lattice[4] and the more intricate 5-connected uniform 6^{10}-**rld-z** topology[5] to extremely complicated examples.[6] While the deliberate construction of highly connected self-catenated coordination polymer networks remains a synthetic challenge, we and other researchers have found that the kinked dicarboxylate oxybisbenzoate (oba) ligand can promote their formation. Wang has reported a (4.8^2) $(4.6^4.8^4.10)$ three-dimensional self-catenated topology within the structure of $\{[Ni(oba)(4,4'\text{-bipyridine})]\cdot H_2O\}$.[6] Recently, we were able to prepare $\{[Ni(oba)(4,4'\text{-dipyridylamine})]\cdot H_2O\}$, a self-catenated layered phase with a unique nondiamondoid 6^6 topology.[7] Inspired by these previous successes in preparing oba/organodiimine self-catenated coordination polymers, we undertook synthetic explorations toward metal−organic materials incorporating both oba and bis(4-pyridylmethyl)piperazine (bpmp)[8] tethering ligands (Chart 1).

Chart 1. Structures of oba and bpmp



Hydrothermal reaction of cobalt nitrate, H_2oba, and bpmp resulted in a good yield[9] of crystalline $[Co_3(oba)_3(bpmp)_2]_n$ (**1**), a chiral coordination polymer with a complex and unprecedented 8-connected self-catenated three-dimensional structure. According to single-crystal X-ray diffraction,[10] compound **1** crystallized in the chiral hexagonal space group $P6_122$. The Flack parameter[11] of 0.00(3) illustrates the enantiomeric purity of the single crystal. Another single

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(9) A mixture of $Co(NO_3)_2\cdot 6H_2O$ (55 mg, 0.19 mmol), H_2oba (48 mg, 0.19 mmol), and bpmp (100 mg, 0.37 mmol) in 10 mL of H_2O was heated at 120 °C under autogenous pressure in an acid digestion bomb for 72 h. Small orange crystals of compound **1** (68 mg, 0.045 mmol, 71% yield) were isolated after washing with distilled water, ethanol, and acetone. IR (cm^{-1}, powder): 2810(w), 1610(m), 1594(m), 1499(w), 1387(s), 1301(w), 1240(s, sh), 1232(s), 1160(m), 1129(w), 1067(w), 1011(m), 875(w), 853(w), 842(w), 794(w), 779(s), 766(w), 731(w), 694(w), 654(m). Anal. Calcd for $C_{74}H_{64}Co_3N_8O_{15}$ (**1**): C, 59.97; H, 4.35; N, 7.56. Found: C, 59.39; H, 4.12; N, 7.62.

(10) Crystal data for **1**: $C_{74}H_{64}Co_3N_8O_{15}$, fw = 1482.12 g mol^{-1}, hexagonal, space group $P6_122$, $a = 13.6840(4)$ Å, $c = 61.780(4)$ Å, $V = 10018.5(8)$ Å^3, $Z = 6$, $\rho_{calcd} = 1.474$ g cm^{-3}, μ(Mo Kα) = 0.812 mm^{-1}, $F(000) = 4590$, $R\ [I > 2\sigma(I)] = 0.0510$, $wR\ [I > 2\sigma(I)] = 0.1005$, GOF = 0.856, $T = 173(2)$ K, CCDC 689544.

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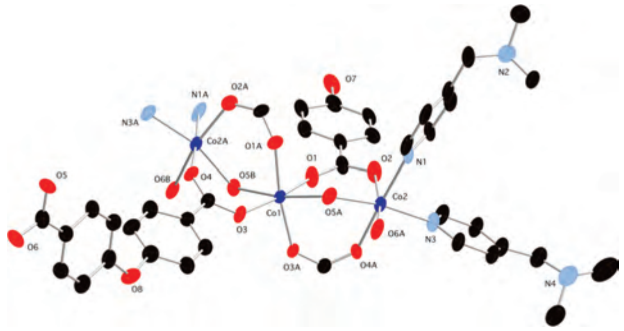

Figure 1. Coordination environment and trinuclear unit within $[Co_3(oba)_3(bpmp)_2]_n$. Thermal ellipsoids are shown at 50% probability.

crystal from the same synthetic experiment crystallized in the enantiomorphic space group $P6_522$ with a Flack parameter of 0.01(5), showing that a racemic mixture of the two enantiomeric forms likely exists in the bulk crystalline sample of **1**.[12]

The asymmetric unit of **1** consists of two Co atoms, one of which (Co1) lies on a crystallographic 2-fold axis, one half and one full oba units (oba-A and oba-B), and halves of two crystallographically distinct bpmp ligands (bpmp-A and bpmp-B). The bpmp-B ligand is disordered equally over two sets of positions. The operation of the symmetry at Co1 generates a bent $\{Co_3O_2\}$ trinuclear kernel (Figure 1), where two Co2 atoms are linked to the central Co1 atom through μ_2-O atoms belonging to carboxylate units of two oba-B ligands. The Co1−Co2 distance within this unit is 3.565 Å.

The central Co1 atom possesses a distorted $\{CoO_6\}$ coordination octahedron, with two symmetry-related cis O donors belonging to two oba-A ligands, two cis O donors belonging to two oba-B ligands, and two trans-disposed O donors from two different oba-B ligands. The Co2 atoms on the periphery of the trinuclear units have a $\{CoN_2O_4\}$-distorted octahedral coordination sphere, where the two cis N donors belong to bpmp-A and bpmp-B ligands. Three O donors from two oba-B ligands are bound to Co2 in a *fac* pattern, with a pair of these being donated by a chelating carboxylate terminus of a single oba-B ligand. A single O atom from an oba-A carboxylate rounds out the coordination sphere. Bond lengths and angles (Table S1 in the Supporting Information) are standard.

Adjacent $\{Co_3O_2\}$ units are aggregated by exotetradentate oba-A ligands with a tetra-monodentate binding mode into a $\{Co_3O_2(oba\text{-}A)\}_n^{4n+}$ 6-fold right-handed helix (helix-1), which follows the *c* crystal direction with a long pitch of 61.78 Å (Figures 2a and S1 in the Supporting Information). The Co1···Co1 distance between neighboring trinuclear units within helix-1 measures 11.493 Å; the related Co2···Co2 distance is 15.379 Å. The distance across the cylinder inscribed by the rotation of helix-1, as defined by the path of the outermost Co atoms, is ∼11 Å.

Two pairs of oba-B ligands also covalently link neighboring trinuclear units together into a 6-fold double helix, $\{Co_3(oba\text{-}B)_2\}$, denoted as helix-2 (Figures 2b and S2 in the Supporting Information). While the oba-B ligands adopt an exotetradentate binding mode, one carboxylate terminus serves as a bismonodentate donating group to two Co atoms (Co1 and Co2), while the other chelates to another Co2 atom, with one O atom (O5) also bridging to another Co1 atom. The Co1···Co1 distance within helix-2 measures 13.402 Å, approximately 1.5 Å longer than that within helix-1, although both helix-1 and helix-2 have the same 61.78 Å pitch and right-handed helicity. The inner diameter across the cylinder inscribed by the rotation of helix-2, as defined by the path of the Co1 atoms, is ∼17 Å. A view down the *c* crystal axis of a single helix-2 presents an incipient channel-like void; however, this is filled with a helix-1 motif.

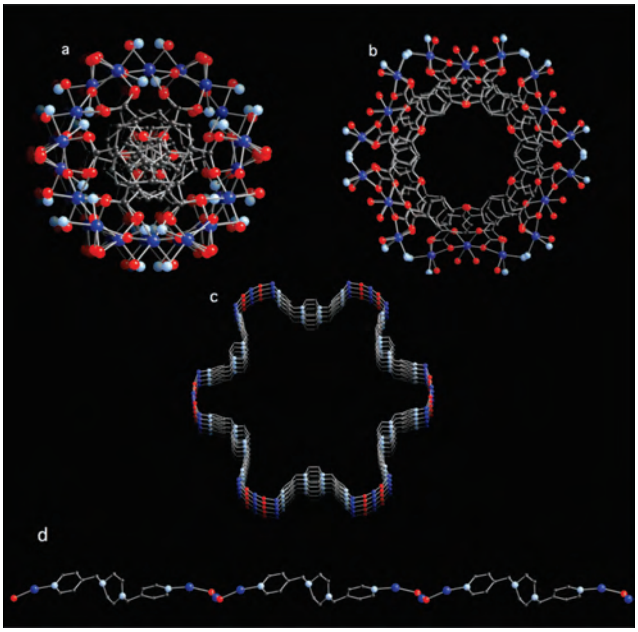

Figure 2. Four distinct submotifs within the structure of **1**, all viewed down *c*: (a) $\{Co_3O_2(oba\text{-}A)\}_n$ 6-fold right-handed single helix (helix-1); (b) $\{Co_3(oba\text{-}B)_2\}_n$ 6-fold right-handed double helix (helix-2); (c) $\{Co_3O_2(bpmp\text{-}A)\}_n$ 6-fold right-handed single helix (helix-3); (d) $\{Co_3O_2(bpmp\text{-}B)\}_n$ chain.

A third right-handed 6-fold helical subunit is present within the structure of **1**, formed by the linkage of $\{Co_3O_2\}$ trinuclear units at their terminal Co2 atoms through tethering bpmp-A ligands. This $\{Co_3O_2(bpmp\text{-}A)\}$ single helix, helix-3, is coaxial with both helix-1 and helix-2, with identical pitch and handedness (Figures 2c and S3 in the Supporting Information). The longer extent of the bpmp-A ligands relative to the dicarboxylate tethers results in a Co2···Co2 distance of 15.009 Å, within a Co1···Co1 intertrimer distance of 21.245 Å. The inner diameter of the “star”-shaped channel within helix-3, measured in a fashion similar to that of helix-2, is ∼37.8 Å. This very large internal space accommodates one helix-2 and seven helix-1 subunits inside it. The bpmp-A ligands within helix-3 adopt a bent cis conformation of their methylpyridyl arms across their central piperazinyl rings, with a 51.7° N···N···N···N torsion angle.

The fourth distinct linkage motif between $\{Co_3O_2\}$ trinuclear units occurs at their Co2 terminal atoms through tethering bpmp-B ligands. These tethers adopt a more linear conformation than bpmp-A, with a N···N···N···N torsion angle of 171°, providing a longer Co2···Co2 distance of

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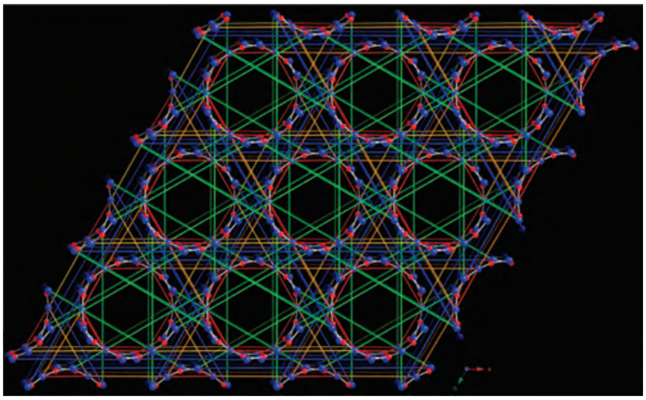

Figure 3. Framework perspective of the $4^4 5^{17} 6^7$ self-catenated 8-connected uninodal topology in **1**. Helix-1, helix-2, helix-3, and chain-4 submotifs are represented in red, orange, blue, and green, respectively.

16.979 Å. Because of the nearly linear nature of the bpmp-B tethers, a $\{Co_3O_2(\text{bpmp-B})\}$ one-dimensional chain motif (chain-4) is formed (Figure 2d), in contrast to the homochiral helices resulting from the other three types of connecting ligands in compound **1**. The Co1···Co1 distance between $\{Co_3O_2\}$ trinuclear units within chain-4 is 23.701 Å.

By means of the four types of tethering ligands, producing four coexisting structural patterns (helix-1, helix-2, helix-3, and chain-4), each trinuclear $\{Co_3O_2\}$ unit is directly covalently linked to eight others through 10 connecting ligands (two oba-A, four oba-B, two bpmp-A, and two bpmp-B). Considering each pair of oba-B ligands as a single connection, an 8-connected three-dimensional coordination polymer network can be invoked for **1** (Figure 3). Each helix-2 unit covalently connects the inner perimeters of six individual helix-1 units and surrounds, but does not covalently link, a seventh helix-1 motif. Each helix-1, in turn, connects covalently to 18 other helix-1 units (all neighbors and next-nearest neighbors) through six helix-2 units. Treating the Co1 atoms as 4-connected nodes with single oba-A ligands and oba-B pairs as linkers results in a $6^4 8^2$ chiral quartz (**qtz**) lattice (Figure S4 in the Supporting Information), according to TOPOS.[13]

In turn, each helix-3 also covalently connects six individual helix-1 units via their outer perimeters and encapsulates a seventh helix-1 motif within its interior. In a connectivity pattern similar to that promoted by helix-2, six helix-3 units covalently conjoin 18 neighboring and next-nearest-neighboring individual helix-1 units. Analysis of the coordination polymer connectivity provided by helix-1 and helix-3 also produces a $6^4 8^2$ chiral **qtz** lattice (Figure S5 in the Supporting Information). On the other hand, a system including only helix-2 and helix-3 results in a 4-fold interpenetrated chiral **qtz** lattice (Figure S6 in the Supporting Information). Inclusion of helix-1 into the latter results in interconnectivity between the individual networks within 4-fold interpenetrated lattices of helix-2 and helix-3; thus, the overall network produced by the interweaving of all of the helical motifs in **1** can be considered to be self-catenated. This self-catenated 6-connected net possesses an unprecedented $4^4 6^9 8^2$ topology. This network is further linked by the chain-4 motifs that cut through all three helical motifs via Co2 atoms on the periphery of the $\{Co_3O_2\}$ trimeric subunits. If only helix-2, helix-3, and chain-4 are treated as connecting linkers with Co1 atoms as connecting nodes, a 6-connected three-dimensional self-catenated network with a remarkably regular 6^{15} topology can be invoked. Topological analysis of the full covalent net of **1**, including all four submotifs and treating only Co1 atoms as connecting nodes, reveals the presence of a previously unknown self-catenated 8-connected uninodal lattice with $4^4 5^{17} 6^7$ topology,[14] shown in Figure 3. Bent ligands are crucial for the generation of this framework in order to avoid edge crossings.[15] A more complete list of network topologies generated from partial connectivity of the full network is given in Table S2 in the Supporting Information.

A variable-temperature magnetic susceptibility was carried out to investigate spin communication within the $\{Co_3O_2\}$ trimers within the structure of **1**. The higher temperature data could be fit to the Curie−Weiss law, with $C = 2.74$ cm^3 K mol^{-1} and $\Theta = -8.1$ K, plausibly indicative of antiferromagnetic coupling within the $\{Co_3O_2\}$ trimers, although zero-field-splitting effects cannot be ruled out (Figure S7 in the Supporting Information). Thermogravimetric analysis (TGA) of **1** (Figure S8 in the Supporting Information) revealed that no mass loss occurred until ~250 °C, whereupon expulsion of the organic components commenced. The mass remnant at ~875 °C of 19.9% is roughly consistent with the deposition of CoO (calcd 18.4%).

In conclusion, the hydrothermal self-assembly of the self-catenated 8-connected three-dimensional network of $[Co_3(oba)_3(bpmp)_2]_n$ reveals the feasibility of accessing highly connected coordination polymer networks with unprecedented modes of entanglement through the employment of very long kinked and/or conformationally flexible tethering ligands. Extension of the tether length and variances in conformational flexibility, donor disposition, and hydrogen-bonding capability within dicarboxylate or organodiimine ligands are certain to expand the scope of highly connected self-catenated coordination polymer networks.

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Supporting Information Available: X-ray crystallographic data in Cif format, supplementary figures, Curie−Weiss plot, TGA trace, table of relevant bond distances and angles, and a table of network topologies present within **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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