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Structural Origin of Chirality and Properties of a Remarkable Helically Pillared Solid

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A new helically pillared and chiral solid, $Cu(pzc)_2AgReO_4$ (**I**, pzc = pyrazinecarboxylate), was synthesized from hydrothermal reactions at 95–125 °C. The structural origin of its chirality, relative to the achiral $M(pzc)_2(H_2O)_2AgReO_4$ (**II**, M = Co; **III**, M = Ni) analogues, arises from significantly tilted pillars and hydrogen bonds to the $AgReO_4$ layers. The new pillared structure exhibits second harmonic generation activity, CO_2 absorption, thermal stability to ~250 °C, and Curie–Weiss magnetism expected for isolated Cu^{2+}.

Synthetic strategies to chiral and porous solids have been gaining much interest for investigations into new optoelectronic, magnetic, and enantioselective properties.[1−4] For example, chiral solids have been synthesized from helical chain species, but the interpenetration of opposite-handed helices often yields nonporous and achiral structures.[5,6] Examples of helicity in pillared-type microporous organic/inorganic solids, as reported here, are rare, with a few known examples including $[C_2N_2H_{10}][Co_{4.2}Zn_{1.8}(PO_4)_4(HPO_4)]\cdot H_2O$[7] and $[(Zn)_{1/4}(Cd)_{1/4}(N(CH_2PO_3H_{2-x})_3(H_2O)_3)]$.[8] These contain both right- and left-handed helices, not as pillars but as part of the inorganic layers that are achiral. Reported herein is the synthesis and characterization of a layered solid that is the first example, to our knowledge, that is pillared in a helical fashion and the structural origins of its chirality and properties.

In contrast to simpler organic-pillared solids, our own research efforts have been directed toward the synthesis of compounds with metal-coordinated ligands as pillars. Relevant previously described examples, $[Cu_2(pzc)_2(H_2O)_2ReO_4]$[9] and $M(pzc)_2(H_2O)_2AgReO_4$ ($M = Co^{II}$, Ni^{II}; pzc = pyrazinecarboxylate),[10] are comprised of $AgReO_4$ or $CuReO_4$ layers pillared by $M(pzc)_2(H_2O)_2$ bridges. These structures can be viewed as derived from the simpler Ag(pyrazine)ReO_4 solid, where the short pyrazine pillar has been replaced by $M(pzc)_2(H_2O)_2$ pillars. The metal (M) site is immobilized between the oxide layers, and its two terminal H_2O ligands can be reversibly removed to generate coordinatively unsaturated metal sites. These pillars are nearly vertical in their hydrated forms, but tilting of the pillars is inferred as the interlayer distances contract and expand when H_2O ligands are removed or introduced. However, the full structural details of the dehydrated forms of the M = Co and Ni analogues are not yet known. The novel dehydrated M = Cu analogue, described here, both is a dehydrated version of these structures and is a rare example of a chiral structure that is pillared by same-handed (4_3) helical chains.

Standard hydrothermal techniques were used to react stoichiometric amounts of $Cu(OH)_2$, pzc, Ag_2O, and Re_2O_7 in a Teflon-lined stainless steel autoclave at 95−125 °C for 24 h. Rod-shaped blue crystals of $Cu(pzc)_2AgReO_4$ (**I**) were recovered in >95% yield and characterized by single-crystal X-ray analysis to crystallize in the chiral space group $P4_32_12$, with the other $P4_12_12$.[11] The structure and purity of the product was further confirmed via powder X-ray diffraction (XRD) and physical property and characterization methods (below).

A view of the pillared layered structure of **I** (Figure 1) shows that the $AgReO_4$ layers are pillared by $Cu(pzc)_2$

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(11) Crystallographic data for **I**, $Cu(pzc)_2AgReO_4$, $P4_32_12$ (No. 96), a = 7.6120(1) Å, c = 49.4945(9) Å, V = 2867.84(7) Å^3, Z = 8, Mo Kα, T = 293 K, $2\theta_{max}$ = 70.6°, R/R_w = 0.0329/0.0791, and GOF = 1.07 for 228 parameters and 6389 reflections with $I > 2\sigma(I)$. Flack parameter refined to −0.013(5), indicating no racemic twinning and the correct chiral space group.[12]

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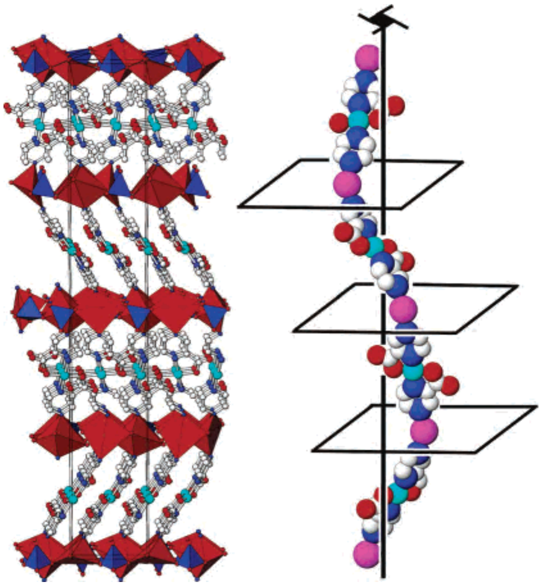

Figure 1. Left: a view of the unit cell of $Cu(pzc)_2AgReO_4$. Red polyhedra are Ag-centered, and blue are ReO_4. Right: an isolated single helical chain that pillars the $AgReO_4$ layers (in-plane squares). Purple atoms are Ag, light blue are Cu, dark blue are N, red are O, and white are C.

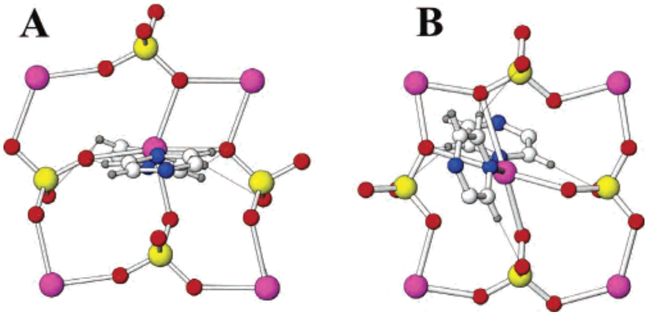

Figure 2. Structural view of the $AgReO_4$ planes for $Ni(pzc)_2(H_2O)_2$-$AgReO_4$ (A) and $Cu(pzc)_2AgReO_4$ (B), with the positions of the two coordinated pzc ligands shown above and below the plane. The ligand orientations are twisted to give helices for B. Purple atoms are Ag, yellow are Re, blue are N, red are O, white are C, and gray are H.

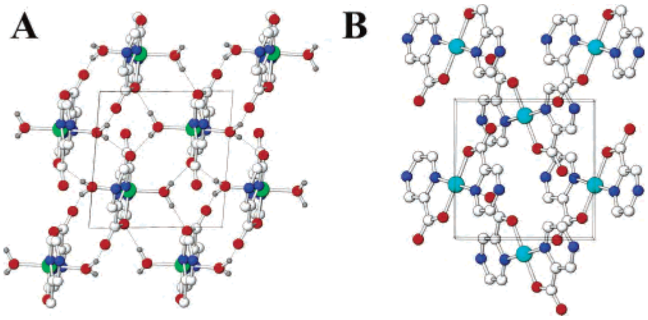

Figure 3. Structural view of a layer of $Ni(pzc)_2(H_2O)_2$ pillars (A) and $Cu(pzc)_2$ (B) pillars. Green and light blue atoms are Ni and Cu, blue are N, red are O, and white are C.

bridges, which repeat four times (at different orientations) per unit *c* lattice distance. The interlayer $AgReO_4$ distances are relatively short, at ~12.37 Å, owing to the significantly tilted $Cu(pzc)_2$ pillars. This is much shorter than the interlayer distances for the M = Co and Ni versions, which have more vertical pillars in both their hydrated, ~13.6−14.0 Å, and likely dehydrated, ~12.8−13.0 Å, forms. The orientation of the pillar tilting rotates 90° counterclockwise between every layer down the 4_3 screw axis to form the single-handed helical pillars, shown in Figure 1 (right), and bridges the metal oxide layers. The coordination environment of each Cu is an axially distorted octahedron, with four short equatorial bonds to two pzc ligands (one bond each to COO− and N groups per ligand) at distances of 1.949(3)−1.983(4) Å and much longer axial contacts to carboxylate groups on neighboring pillars, at 2.472(4) and 2.547(4) Å. In the hydrated structures of **II** and **III**, these metal sites are more regularly octahedral, with shorter axial bonds instead to two H_2O ligands and further spaced pillar distances. Thus, the structure of **I** crystallizes without coordinated water likely because of the longer axial distances preferred by Cu^{2+}, which is able to bridge instead to COO− groups on neighboring pillars (tilted) to give a more closely packed structure. The absence of H_2O, and significant pillar tilting, is one of the key features that leads to helicity (below).

A structural comparison of the $AgReO_4$ layer for **I** and **III** (Figure 2A) shows that each has a similar orientation of the ReO_4 tetrahedra. Roughly, each Ag in these structures is surrounded by two ReO_4 tetrahedra with their apical O atoms oriented above the plane and two with their apical O atoms oriented below the plane. The ReO_4 tetrahedra within the $AgReO_4$ layers are nearly regular, with Re−O distances of 1.716(4)−1.735(3) Å, which coordinates to Ag at distances of 2.482(3)−2.563(4) Å (Ag1−O) and 2.657(4)−3.118(4) Å (Ag2−O). Ag is further bonded above and below the plane to the lone (para) N group of two pzc ligands at 2.249(4) and 2.400(4) Å. These distances are similar to those observed in the nonhelical analogues **II** and **III**. However, the AgO_4N_2 polyhedra for all are highly distorted from a regular octahedral geometry, with *cis* angles ranging from 73.8(1) to 116.2(1)° for Ag1 and from 57.1(1) to 122.9(1)° for Ag2. Also, the Ag sites are the vertexes of a helical twist in the chain (see Figure 1, right). In **I**, apical O atoms of ReO_4 tetrahedra form short O···H−C hydrogen bonds to pzc ligands, at 2.27 and 2.56 Å, while for **III**, these are further spaced at 2.56 and 2.86 Å. Average distances for O···H−C hydrogen bonds are reported to be ~2.52 Å, usually within a ±0.3 Å range.[13] Apparently, as the pzc ligands tilt into the $AgReO_4$ plane for **I**, much shorter ReO_4-to-pzc contacts occur. This change results in the ligands being forced to tilt away (either left or right) from these apical O atoms, both above and below the plane, with their orientations rotating 90° between different layers in concert with the position of the apical O atoms. However, for **II** and **III**, the pzc pillars are not sterically forced to adopt tilted and rotated positions around the ReO_4 groups.

The origin of the significant pillar tilting, and ultimately of the chirality/helicity, is shown in Figure 3 with a comparison of the packing of the $Ni(pzc)_2(H_2O)_2$ (A) and $Cu(pzc)_2$ (B) pillars. In A, H_2O ligands coordinate to the Ni sites and hydrogen bonds form to the carboxylate groups of the neighboring pillar. However, in B, the H_2O ligands are

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absent, and the pillars tilt to form closer contacts between the open axial Cu sites and the carboxylate groups on neighboring pillars, though at a farther distance of ~0.5 Å.

Second harmonic generation (SHG) and magnetic susceptibility measurements were performed and confirm the acentricity of the space group and the oxidation state of Cu^{2+}. The Kurtz powder method was performed on an ungraded and pure sample of **I** and exhibited an SHG response of ~50−75% to that of the SiO_2 standard. This signal strength is comparable to that of other reported helical hybrid solids.[14] The magnetic susceptibility of the sample was measured from 4 to 300 K and exhibited a near ideal Curie−Weiss behavior ($\mu_{eff} = 1.9$) expected for noninteracting Cu^{2+} (d^9) centers. When Cu^{2+} sites are linked via equatorial−axial positions to carboxylate groups, their magnetic coupling is negligible, as reported in other helical structures.[15,16]

Thermogravimetric analysis (TGA) performed under flowing N_2 showed that **I** is stable up to ~250 °C, at which temperature the removal of the pzc ligand begins: a sharp mass loss of 28.6% in the temperature range of ~250−260 °C and a broad mass loss of 6.2% at 260−375 °C, corresponding closely to the expected total weight percent of the pzc ligand (calcd 36.3%). This result also confirmed the absence of water coordinated to the copper sites in **I**, in comparison with the loss of water below 170 °C in the TGA of **II** and **III**.

The uptake of H_2O by **I** was tested using XRD and TGA methods but was not detectable over the course of several weeks, as was the case for the dehydrated M = Co and Ni analogues. However, standard gas absorption experiments were performed at high pressures and room temperature using CO_2,[17] shown in Figure 4. Absorption of CO_2 into the structure of **I** was relatively low at below 1500 Torr (~0.2 n_{CO_2}/n_{Cu}), likely owing to the compressed gallery spaces and tilted pillars. However, a larger and reversible uptake of CO_2 (~0.6−1.0 n_{CO_2}/n_{Cu}) was observed at high pressure (4400 Torr), which is likely caused by a distortion of the host structure to accommodate the guest. One potential change of the host structure at high pressure is the reorientation of the pillars to more vertical positions as known for $Ni(pzc)_2(H_2O)_2AgReO_4$, and this would result in a square-planar coordination geometry at the Cu sites for CO_2 binding. The η^1 binding of CO_2 has been explained as arising from a strong charge-transfer interaction between a d_{z^2} metal orbital and the π^* orbital of CO_2,[18] while, conversely, N_2 is both a weaker σ donor and a poorer π acceptor.[18,19] The total measured CO_2 uptake for **I** (33.5 $cm^3\ g^{-1}$) at high pressure is comparable to the absorption capacity of other porous materials at mild conditions.[20] The N_2 gas absorption value is very small and exhibits no change with pressure.

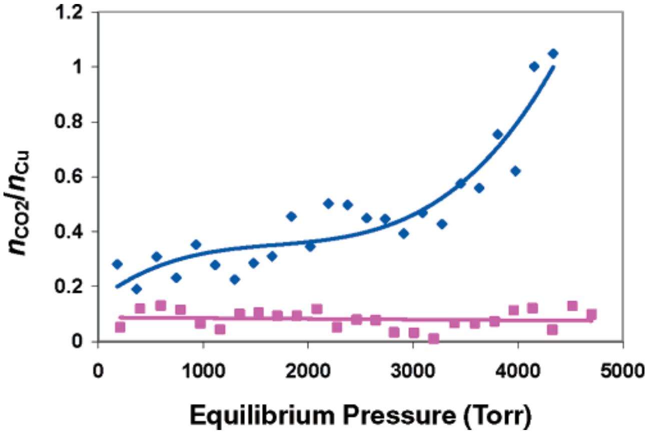

Figure 4. Plot of equilibrium gas absorption of CO_2 (blue) and N_2 (purple) at increasing pressures over $Cu(pzc)_2AgReO_4$.

In summary, a novel helically pillared and chiral solid has been synthesized and characterized. The helicity and chirality results from the tilted pillars, which cause short contacts between the pzc pillars and the apical O atoms on the ReO_4 groups. The structure of **I** is stable up to ~250 °C and shows SHG activity and selective adsorption of CO_2 under high pressure at room temperature.

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Supporting Information Available: Full crystallographic information including positional and thermal parameters and bond distances and angles (CIF). Also, the measured plots of magnetic susceptibility and thermogravimetric analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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