

## Understanding the Role of Helical Chains in the Formation of Noncentrosymmetric Solids

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A general, new principle for the design of noncentrosymmetric solids is evident in the packing of helical metal–oxyfluoride chains in  $\text{Zn}(\text{C}_4\text{H}_4\text{N}_2)(\text{H}_2\text{O})_2\text{MoO}_2\text{F}_4$  ( $\text{C}_4\text{H}_4\text{N}_2 = \text{pyrazine, pyz}$ ). Each inorganic helical chain comprises alternating Zn- and Mo-centered octahedra and interleaves with six more helices of the same handedness through Zn–pyrazine–Zn bridges. From comparisons with similar structures which are centrosymmetric, the small organic ligand, pyrazine, plays a key role in the acentric packing of inorganic helices, while the *cis*- $\text{MoO}_2\text{F}_4$  and *trans*- $\text{Zn}(\text{pyz})_2(\text{H}_2\text{O})_2\text{F}_2$  metal coordination geometries are important for helix formation.

Major efforts in solid-state chemistry have as their goal the ability to engineer new inorganic frameworks that will yield desired physical properties. For instance, the designed synthesis of noncentrosymmetric solids is a challenging problem for the future fabrication of materials with ferroelectric, pyro- and piezoelectric, and other nonlinear optical (NLO) properties.<sup>1</sup> Because they lack an inversion center, helical chains have been found in many acentric solids, including  $\text{KTiOPO}_4$  (KTP),<sup>2</sup>  $\text{SiO}_2$  (quartz),<sup>3</sup>  $\text{Cu}(\text{pyridine})_4\text{Cr}_2\text{O}_7$ ,<sup>4</sup> and others.<sup>5–8</sup> However, an equally large group of materials that contain helical chains do have inversion centers. In general, how to design or make a noncentrosymmetric solid from inorganic helices relies on our understanding of ligand effects and crystal packing. Here we explain a rational way to understand the combined effects of ligand length and helical symmetry in noncentrosymmetric compounds, as illustrated by  $\text{Zn}(\text{pyz})(\text{H}_2\text{O})_2\text{MoO}_2\text{F}_4$ .

$\text{Zn}(\text{pyz})(\text{H}_2\text{O})_2\text{MoO}_2\text{F}_4$  was synthesized via typical hydrothermal procedures<sup>9</sup> and was characterized by single-crystal X-ray diffraction methods to have two enantiomorphic forms, space groups  $P3_121$  and  $P3_221$  (used for the Figures and discussion).<sup>10–12</sup> The helical chain repeat unit, alongside a longer space-filling version, is shown in Figure 1 down the [011] projection. The  $3_1$  screw axis passes down the center of the inorganic spiral, while a two-fold rotation bisects each O–Mo–O angle of  $102.0(2)^\circ$ .

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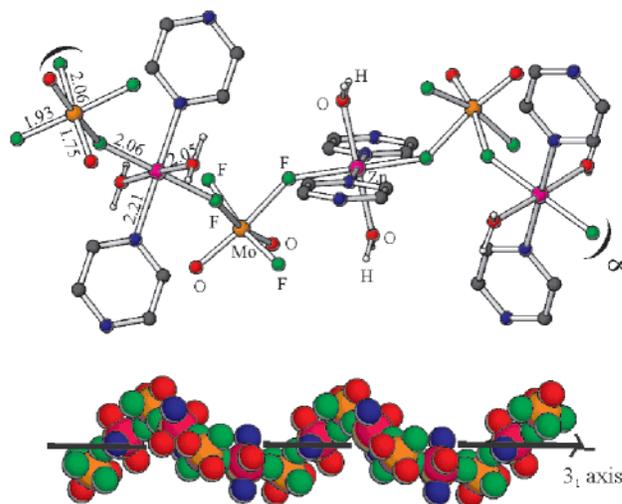
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(9)  $\text{Zn}(\text{C}_4\text{H}_4\text{N}_2)(\text{H}_2\text{O})_2\text{MoO}_2\text{F}_4$  was synthesized by adding  $7.60 \times 10^{-2}$  g ( $9.34 \times 10^{-4}$  mol) of  $\text{ZnO}$ ,  $1.34 \times 10^{-1}$  g ( $9.31 \times 10^{-4}$  mol) of  $\text{MoO}_3$ ,  $3.74 \times 10^{-1}$  g ( $4.67 \times 10^{-3}$  mol) of pyrazine,  $1.34$  g ( $3.78 \times 10^{-2}$  mol) of 49%  $\text{HF}/\text{H}_2\text{O}$ , and  $7.56 \times 10^{-2}$  g ( $4.2 \times 10^{-3}$  mol) of  $\text{H}_2\text{O}$  to an FEP Teflon pouch. These pouches were heat-sealed, placed inside a 2000 mL autoclave (Parr), and backfilled with  $\sim 1000$  mL of  $\text{H}_2\text{O}$  before closing. The autoclave was heated to  $150^\circ\text{C}$  for 24 h and slowly cooled to room temperature at  $6^\circ\text{C}/\text{h}$ . Transparent brown blocks were recovered by filtration in 86% yield based on Zn.



**Figure 1.** Helical chain repeat unit in  $\text{Zn}(\text{pyz})(\text{H}_2\text{O})_2\text{MoO}_2\text{F}_4$  with selected atoms and distances (in Å) labeled. Using the same color scheme, the repeating pattern of the helical chain without the pyrazine rings is shown by the space filling model on the lower half.

The local Mo environment, identified before as the  $\text{MoO}_2\text{F}_4^{2-}$  anion,<sup>13,14</sup> includes two *cis*-O positions at 1.75 Å, and four F at 1.93 Å ( $\times 2$ ) and 2.06 Å ( $\times 2$ ). The Mo atom is displaced from the octahedral center toward the *cis*-O atoms, with distances that are  $\pm 0.05$  Å to that for the previously characterized  $\text{MoO}_2\text{F}_4^{2-}$  anion.<sup>14</sup> The two longer Mo–F distances are *cis* to each other, notably *trans* to the *cis*-O atoms, and are shared with Zn at 2.06 Å ( $\times 2$ ) again. The coordination around each Zn is completed by two pyrazine molecules, Zn–N at 2.21 Å ( $\times 2$ ), and two water molecules, Zn–O at 2.05 Å ( $\times 2$ ), to give a  $\text{Zn}(\text{pyz})_2(\text{H}_2\text{O})_2^{2+}$  cation. The division of the helical chain into anionic and cationic components, although arbitrary here, is helpful for structural comparisons (below) where these ions are distinguishable.

The ordering of O and F in the  $\text{MoO}_2\text{F}_4^{2-}$  anion onto symmetry-unique positions is uncommon, as their atomic differences are generally not sufficient to lower the symmetry by requiring symmetry-unique sites in the crystal structure. However, as a step toward constructing ordered acentric solids, it has proven effective to coordinate different organic cations to the more negatively charged O or F atoms.<sup>14,15</sup> The result is that when the larger organic cations pack in ordered arrangements in a solid, so too do the associated O/F atoms. The most negatively charged, or nucleophilic, ligands on the  $\text{MoO}_2\text{F}_4^{2-}$  anion, as determined by bond valence analysis, are the two F positions opposite the *cis*-O atoms. Hence, in  $\text{Zn}(\text{pyz})(\text{H}_2\text{O})_2\text{MoO}_2\text{F}_4$ , the  $\text{Zn}^{2+}$  cations within a helical chain coordinate to the two F sites on the anion that are opposite the *cis*-O atoms. This coordination then fixes in place the arrangement of the two remaining uncoordinated F atoms.

(10) A single-crystal X-ray analysis was performed on a Bruker Smart CCD diffractometer. Crystal data for  $\text{Zn}(\text{pyz})(\text{H}_2\text{O})_2\text{MoO}_2\text{F}_4$ : trigonal, space group  $P3_121$  (no. 152) with  $a = 7.2250(6)$ ,  $c = 16.438(2)$ ,  $V = 743.1(1)$  and  $Z = 3$  at 153(2) K. Final anisotropic structure refinement on  $F^2$  gave  $R1/wR2$  (all data) = 0.023/0.055 and GOF = 0.55. Refinement of the Flack parameter converged at 0.47(2), and in the inverse structure and enantiomer space group  $P3_221$  (no. 154), converged at 0.53(2), as expected for racemic twinning. Both the left- ( $3_1$ ) and right-handed ( $3_2$ ) versions of these helical chains exist in separate crystal domains.

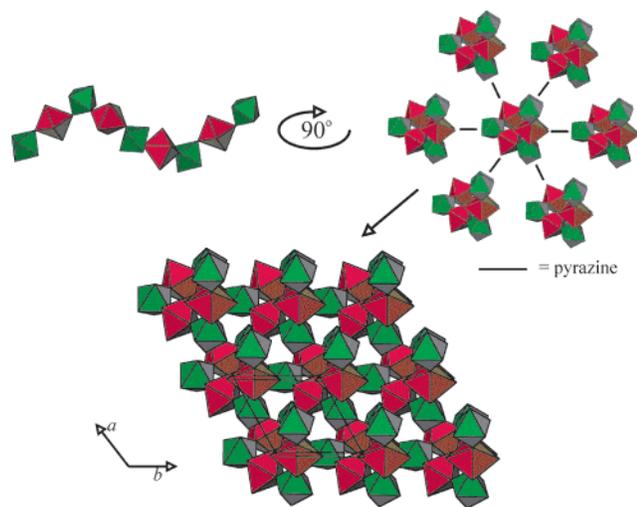
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**Figure 2.** Polyhedral view of the helical chain as in Figure 1 (upper left), rotated  $90^\circ$  with six other neighboring chains (upper right), and interleaved in the packing of the unit cell (bottom). Mo-centered octahedra are green, and Zn-centered are fuchsia.

A comparison of  $\text{Zn}(\text{pyz})(\text{H}_2\text{O})_2\text{MoO}_2\text{F}_4$  with similar oxyfluoride structures suggests that the *cis*-Mo coordination is also important for helical chain formation. In  $\text{Cu}(\text{pyz})_2\text{WO}_2\text{F}_4 \cdot (\text{pyz})(\text{H}_2\text{O})^{16}$  and  $\text{Cu}(\text{py})_4\text{MX}_6$  ( $\text{MX}_6 = \text{ZrF}_6^{2-}$ ,  $\text{NbOF}_5^{2-}$ ,  $\text{MoO}_2\text{F}_4^{2-}$ ;  $\text{py} = \text{pyridine}$ )<sup>17</sup> the cations ( $\text{Cu}(\text{pyz} \text{ or } \text{py})_4^{2+}$ ) and anions ( $\text{MX}_6^{2-}$ ) are both *trans*-directing, and therefore centric linear chains, instead of helical, crystallize and then pack with inversion centers. The helical chains in  $\text{Zn}(\text{pyz})(\text{H}_2\text{O})_2\text{MoO}_2\text{F}_4$  have an alternating *cis*-(Mo) and *trans*-(Zn) arrangement for shared F atoms, as shown in Figures 1 and 2 (upper left). In both Figures, it can be seen that the *cis*- $\text{MoO}_2\text{F}_4^{2-}$  anions are the “turning” points of the helix. This coordination pattern is the same as found for the helical Ti–O chains in the NLO material  $\text{KTiOPO}_4$  (KTP).

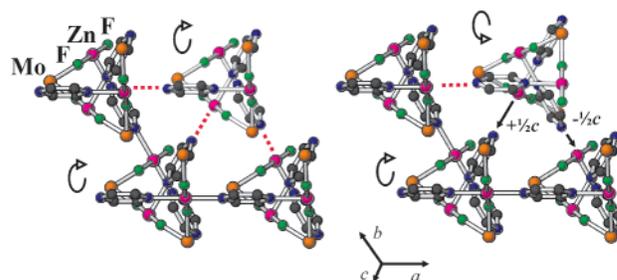
The full crystal packing in  $\text{Zn}(\text{pyz})(\text{H}_2\text{O})_2\text{MoO}_2\text{F}_4$  is accomplished through Zn–pyrazine–Zn linkages between helices. Figure 2 shows an expanded view of the packing around one helical chain (upper right), which also helps to visualize the interleaved helices shown in the [001] projection (bottom). The pyrazine bridge is short enough ( $\sim 2.8$  Å) to interleave the neighboring chains and ensures acentric helices pack without introducing an inversion center between them (see below). Since the inverse of a left-handed helix is a right-handed helix, a compound may crystallize with an inversion center if both types of handedness appear. Previous research on  $\text{Cu}(4,4'\text{-bpy})_2\text{Cr}_2\text{O}_7^{18}$  and  $\text{Cu}(4,4'\text{-bpy})(\text{H}_2\text{O})_2\text{MoO}_2\text{F}_4^{18}$  has shown that longer organic linkages may result in an interpenetration of two or more networks and the generation of an inversion center between the two. In addition, helical chains, when sufficiently separated, are known to crystallize in the same network with both right- and left-handed forms to form centrosymmetric solids. Examples include  $\text{Cu}(\text{dpa})_2\text{MOF}_5 \cdot 2\text{H}_2\text{O}$  ( $\text{M} = \text{Nb}, \text{Ta}$ ),<sup>15</sup>  $[\text{M}(4,4'\text{-bpy})(\text{VO}_2)_2(\text{HPO}_4)_4]$  ( $\text{M} = \text{Co}, \text{Ni}$ ),<sup>19</sup> and  $[(\text{NH}_4)_2\text{Co}_8(2\text{-pzc})_8(\text{H}_2\text{O})_2(\text{VO}_3)_{10}] \cdot x\text{H}_2\text{O}$ .<sup>5</sup> Each inorganic assembly will have its own optimum ligand length/geometry which most effectively closest-packs same-handed helices.

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**Figure 3.** Helix (upper right in each) with six possible interactions (three Zn–N, three N–Zn) packs with other helices that have the same (left) or opposite (right) handedness. For clarity, only the Mo–F–Zn–F helical backbone and bridging pyrazine molecules are shown.

In a qualitative approach here, the rational design of a noncentrosymmetric solid is possible here because the closest packing of bridged helices appears to favor either only right- or left-handed forms in a single crystal domain. Figure 3 illustrates this idea, which shows three chains that have a clockwise rotation that attempt to pack with another helix that has either the same (left) or counterclockwise (right) rotation. The helix of the same handedness (left side, upper right helix) shares the identical spatial and translational orientation with the other helices, and therefore finds matching Zn–N bridges down the chain, shown by red dashes. A chain of the opposite handedness (right side, upper right helix), which could introduce an inversion center, has the reverse spatial and translational orientation. While the first Zn–N bridge could form between the two helices, the next two Zn–N linkages do not align (i.e. the second pyrazine down on the upper right helix is pointed toward the Zn atom that is on the third level down of the lower right helix), shown by black arrows. More generally, any time two helices of opposite handedness are bonded together, as the upper two helices on the right side are, additional helices of either handedness cannot find matching sites for both of them. Therefore, the more favorable crystal packing is for both solely right- or left-handed forms, and yields a noncentrosymmetric and chiral structure.

Interestingly, the helical chains in  $\text{Zn}(\text{pyz})(\text{H}_2\text{O})_2\text{MoO}_2\text{F}_4$  are not polar because of the two-fold rotation axis through the  $\text{MoO}_2\text{F}_4^{2-}$  anion. Other *cis*-directing anions that disallow this symmetry may yield polar structures and are being tried. The appropriate polar space groups would be  $P3_1$  or  $P3_2$ , with the dipole moment down the middle of the helices. A more complete description of  $\text{Zn}(\text{pyz})(\text{H}_2\text{O})_2\text{MoO}_2\text{F}_4$ , as well as a Cd analogue that crystallizes without racemic twinning, will be reported in an upcoming full article.

In this communication, we have reported general, new principles useful in synthetic chemistry for the formation of noncentrosymmetric solids and helical chains. By comparisons with related structures, it is revealed that a key to engineering noncentrosymmetric solids from acentric helices may be to use a short organic ligand to bridge the helices. The *cis*- $\text{MoO}_2\text{F}_4^{2-}$  anion is ordered by the coordination of the two *cis*-F atoms and is the “turning” point in the helix.

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**Supporting Information Available:** Tables of crystallographic data, atomic parameters, and bond distances in  $\text{Zn}(\text{pyz})(\text{H}_2\text{O})_2\text{MoO}_2\text{F}_4$  in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>

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