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

Paul A. Maggard, Charlotte L. Stern, and Kenneth R. Poeppelmeier*

Department of Chemistry
Northwestern University
Evanston, Illinois 60208-3113

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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 Zn(C₂H₅N₂)(H₂O)₂MoO₂F₄ (C₂H₅N₂ = 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-MoO₂F₄ and trans-Zn(pyz)₂(H₂O)₂F₂ 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. Because they lack an inversion center, helical chains have been found in many acentric solids, including KTiOPO₄ (KTP), SiO₂ (quartz), Cu(pyridine)₄Cr₂O₇, and others. 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 Zn(pyz)(H₂O)₂MoO₂F₄. The ordering of O and F in the MoO₂F₄ anion is uncommon, as their atomic differences are generally not sufficient to lower the symmetry by requiring symmetry-uniform sites in the crystal structure. However, as a step toward constructing ordered acetic solids, it has proven effective to coordinate different organic cations to the more negatively charged O or F atoms. The result is that when larger organic cations pack in ordered arrangements in a solid, too do the associated O/F atoms. The most negatively charged, or nucleophilic, ligands on the MoO₂F₄ anion, as determined by bond valence analysis, are the two F positions opposite the cis-O atoms. Hence, in Zn(pyz)(H₂O)₂MoO₂F₄, the Zn⁺⁺ 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.

The local Mo environment, identified before as the MoO₂F₄ anion, includes two cis-O positions at 1.75 Å, and four F at 1.93 Å (x2) and 2.06 Å (x2). The Mo atom is displaced from the octahedral center toward the cis-O atoms, with distances that are ±0.05 Å to that for the previously characterized MoO₂F₄ anion. 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 (x2) again. The coordination around each Zn is completed by two pyrazine molecules, Zn–N at 2.21 Å (x2), and two water molecules, Zn–O at 2.05 Å (x2), to give a Zn(pyz)₂(H₂O)₂²⁺ cation.

Figure 1. Helical chain repeat unit in Zn(pyz)(H₂O)₂MoO₂F₄ 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 MoO₂F₄ anion, includes two cis-O positions at 1.75 Å, and four F at 1.93 Å (x2) and 2.06 Å (x2). The Mo atom is displaced from the octahedral center toward the cis-O atoms, with distances that are ±0.05 Å to that for the previously characterized MoO₂F₄ anion. 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 (x2) again. The coordination around each Zn is completed by two pyrazine molecules, Zn–N at 2.21 Å (x2), and two water molecules, Zn–O at 2.05 Å (x2), to give a Zn(pyz)₂(H₂O)₂²⁺ 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 MoO₂F₄ anion on symmetry-unique positions is uncommon, as their atomic differences are generally not sufficient to lower the symmetry by requiring symmetry-uniform sites in the crystal structure. However, as a step toward constructing ordered acetic solids, it has proven effective to coordinate different organic cations to the more negatively charged O or F atoms. The result is that when larger organic cations pack in ordered arrangements in a solid, too do the associated O/F atoms. The most negatively charged, or nucleophilic, ligands on the MoO₂F₄ anion, as determined by bond valence analysis, are the two F positions opposite the cis-O atoms. Hence, in Zn(pyz)(H₂O)₂MoO₂F₄, the Zn⁺⁺ 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.

(9) Zn(C₂H₅N₂)(H₂O)₂MoO₂F₄ was synthesized via typical hydrothermal procedures and was characterized by single-crystal X-ray diffraction methods to have two enantiomorphic forms, space groups P321 and P321 (used for the Figures and discussion).
(10) The helical chain repeat unit, alongside a longer space-filling version, is shown in Figure 1 down the [011] projection. The 3-fold 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)°.

(10) A single-crystal X-ray analysis was performed on a Bruker Smart CCD diffractometer. Crystal data for Zn(pyz)(H₂O)₂MoO₂F₄, trigonal, space group P321 (no. 152) with a = 7.2250(6), c = 16.4382(2), V = 743.1(1) and Z = 3 at 153(2) K. Final anisotropic structure refinement on F² gave R1/wR2 (all data) = 0.0230/0.055 and GOF = 0.55. Refinement of the Flack parameter converged at 0.47(2), and in the inverse structure and enantiomer space group P321 (no. 154), converged at 0.53(2), as expected for racemic twinning. Both the left- (31) and right-handed (32) versions of these helical chains exist in separate crystal domains.
A comparison of Zn(pyz)(H2O)2MoO2F4 with similar oxyfluoride structures suggests that the cis-Mo coordination is also important for helical chain formation. In Cu(py2)2WO4F6(pyz)-(H2O)16 and Cu(py)3MX6 (MX6 = ZrF4(2−), NbOF6(2−), MoO2F2(2−); py = pyridine) the cations (Cu(pyz or py)2+) and anions (MX6(2−)) are both trans-directing, and therefore centric linear chains, instead of helical, crystallize and then pack with inversion centers. The helical chains in Zn(pyz)(H2O)2MoO2F4 may 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-MoO2F2(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 KTiOPO4 (KTP).

The full crystal packing in Zn(pyz)(H2O)2MoO2F4 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 (~2.8 Å) to interleave the neighboring chains and ensures acetic 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 Cu(4,4′-bpy)2Cr2O7 and Cu(4,4′-bpy)(H2O)2MoO2F4 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 Cu-dpa)2MOF2·2H2O (M = Nb, Ta),15 [M(4,4′-bpy)(VO2)2(HPO4)2]·2H2O (M = Co, Ni),19 and [(NH4)2Co(2-pz)2(H2O)2(VO2)2]·3·H2O.13 Each inorganic assembly will have its own optimum ligand length/ geometry which most effectively closest-packs same-handed helices.

Supporting Information Available: Tables of crystallographic data, atomic parameters, and bond distances in Zn(pyz)(H2O)2MoO2F4 in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.