

Synthesis and structure of a new layered zinc phosphite ($C_5H_6N_2$)Zn(HPO₃) containing helical chains

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A new compound ($C_5H_6N_2$)Zn(HPO₃) has been prepared hydrothermally; it consists of left-handed and right-handed helical chains that are connected through oxygen atoms to form an undulated sheet structure with 4.8-net.

Helical structures are often found in nature, but are rare in synthetic materials. The design and synthesis of materials with helical structures are topics of current interest and of great challenge. In recent years, the design of helical coordination polymers through the self-assembly of the ligands and metal cations has achieved much progress.^{1,2} Open-framework metal phosphates,^{3–5} phosphites^{6–8} and oxides,⁹ typically prepared under hydrothermal conditions in the presence of organic amine as a structure-directing agent (template), are an important class of materials, which have potential applications in areas such as adsorption, separation and catalysis. So far, only a few examples are reported to possess helical characters among such materials. For instance, a double helical chain has been described in the vanadium phosphate [(CH₃)₂NH₂]₄K₄[V₁₀O₁₀(H₂O)₂(OH)₄(PO₄)₇],¹⁰ intersecting helical channels in the open-framework zinc phosphate [NH₃(CH₂)₂NH₂(CH₂)₂NH₃][Zn₄(PO₄)₃(HPO₄)]H₂O,¹¹ helical ribbons made up of edge-sharing 4-rings in the UCSB-7 framework for various compositions (zinc and beryllium arsenates, gallium germanate),¹² and 6₁ or 6₅ helices in metal borophosphates.¹³ In this work, we describe a novel layered zinc phosphite ($C_5H_6N_2$)Zn(HPO₃) (**1**), which consists of left-handed and right-handed helical chains. It is believed that the aromatic organic amine templating molecules, 2-aminopyridine, which bind in a monodentate fashion to the tetrahedral Zn center, are important for the helical –Zn–O–P– chains.

Large single crystals of **1** were prepared in a gel system with molar composition 1.0 Zn(OAc)₂·2H₂O : 1.0 H₃PO₃ : 7.0 2-aminopyridine : 488 H₂O. Typically, 0.25 g of Zn(OAc)₂·2H₂O was first dispersed into 10 mL of distilled water with stirring, followed by addition of 0.749 g of 2-aminopyridine. H₃PO₃ (0.093 g) was finally added to the above reaction mixture with stirring. The reagents with an initial pH value of 6.0 were transferred into a Teflon-lined stainless steel autoclave and heated at 200 °C for 5 days. The product containing plate-shaped large single crystals was filtered and washed thoroughly with deionized water and dried at 70 °C. X-Ray powder diffraction patterns were recorded on a Siemens D5005 X-ray diffractometer with Cu-Kα radiation (λ = 1.5418 Å). The experimental X-ray powder diffraction pattern of **1** agrees with the simulated one derived from structural data, proving that the as-synthesized product is a single phase.

Inductively coupled plasma (ICP) analysis performed on a Perkin-Elmer Optima 3300 DV ICP instrument gives Zn and P contents in the product of 26.6% (calcd. 27.3%) and 12.7% (calcd. 12.9%), respectively. Elemental analysis carried out on a Perkin-Elmer 2400 elemental analyzer gives C, H and N contents in the product of 24.45, 2.67, and 11.46%, respectively, which are in agreement with the calculated values of 25.06, 2.92 and 11.69%, respectively, based on the empirical formula ($C_5H_6N_2$)Zn(HPO₃) given by single-crystal X-ray diffraction analysis.

A single crystal with dimensions of 0.08 × 0.06 × 0.04 mm was glued to a fine glass fiber and mounted on a three-circle fixed Siemens diffractometer fitted with a Bruker SMART CCD detector.

Structure analysis† reveals that **1** crystallizes in the *P*2₁/*c* space group. As seen in Fig. 1, each asymmetric unit contains one unique Zn atom and one unique P atom. The Zn atom adopts a tetrahedral geometry and is coordinated to three oxygen atoms and one N atom from the template molecule. The Zn–N bond corresponds to a direct link between zinc and the 2-aminopyridine template in a monodentate fashion. The P atom shares three oxygens with adjacent Zn atoms, and the P–H bond makes up the vertex of each [HPO₃]^{2–} pseudo-pyramid. The existence of P–H bonds is also confirmed by the characteristic band of phosphite anions [ν(H–P), 2391 cm^{–1}] in the IR spectrum.⁷ As shown in Fig. 2, **1** presents a new type of 2-dimensional layered structure in the family of zinc phosphites.⁶ It consists of 4- and 8-membered rings which form a 4.8-net sheet parallel to the *bc* plane. Each 8-ring is surrounded by four 4-rings. Each 4-ring has two up and two down Zn–N and P–H groups. The 2-aminopyridine molecules reside alternately above and below the layer. Interestingly, the structure features left-handed and right-handed helical chains, which are interconnected through O(1) atoms to form the layer. The central axis of each helical chain is a twofold screw axis along the crystallographic *b* axis. Fig. 3 shows a space-filling view of the left-handed and right-handed helical chains. The pitch of the helix is equal to the unit cell repeat length.

Fig. 4 shows the packing of the layers along the [100] direction. It can be clearly seen that the layer exhibits an undulated pattern. The cyclic hydrophobic rings of the 2-aminopyridine molecules exclusively protrude into the interlayer region. Weak H-bonds exist between the –NH₂ groups of the template molecules and the bridging oxygen O(2) atoms within the layer (N⋯O: 3.038 Å). The minimum nonbonding C⋯C contact between adjacent aromatic amines from adjacent layers that are orientated in an angle *ca.* 61° is 3.5 Å.

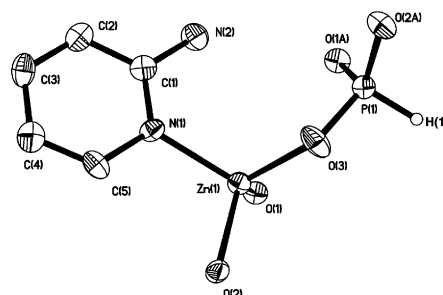


Fig. 1 Thermal ellipsoid plot (50%) showing atom labeling scheme in **1**. The Zn–O distances are 1.929(3)–1.945(3) Å. The P–O distances are 1.515(3)–1.531(3) Å. The Zn–N and P–H distances are 2.045(3) and 1.26(3) Å, respectively. The O–Zn–O, O–Zn–N, O–P–O and O–P–H bond angles are in the range of 107.43(12)–113.43(11), 102.46(11)–111.74(13), 110.39(16)–112.75(16), and 105.2(16)–108.3(17)°, respectively.

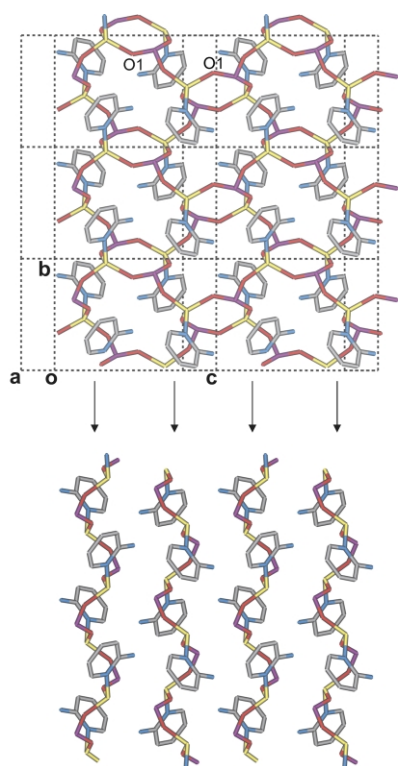


Fig. 2 Representation of the 4.8-net sheet parallel to the *bc* plane in **1**. The left-handed and right-handed helical chains along *b* are isolated by omitting bridging O(1) atoms in the sheet. Color code: Zn: yellow; P: purple; O: red; C: grey; N: blue.

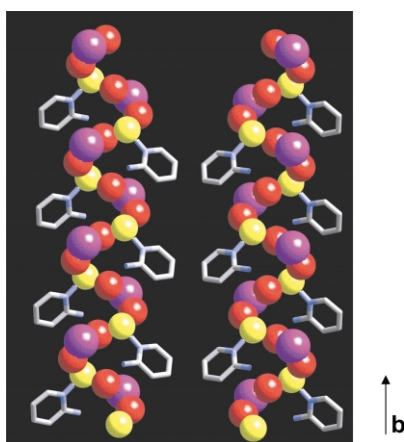


Fig. 3 A space-filling view of the left-handed and right-handed helical chains along *b* exhibited by **1**. Color code: Zn: yellow; P: purple; O: red; C: grey; N: blue.

By inspection of the structure of **1**, it is believed that the aromatic cyclic amines play a key role in the stabilization of the helices. The 2-aminopyridine molecules, acting as an organic ligand and a structure-directing agent, might impose an extra force to the $-\text{Zn}-\text{O}-\text{P}-$ chains and thus induce a helical array of the inorganic chains. A similar phenomenon has been observed in the inorganic-organic hybrid materials constructed from $[(\text{VO}_2)(\text{HPO}_4)]_\infty$ helical chains and $[\text{M}(4,4'\text{-bpy})_2]^{2+}$ ($\text{M} = \text{Co}, \text{Ni}$) fragments.¹⁴ Further understanding of the role of the organic amine molecules in determining the helical structures will be important in the rational design and synthesis of helical inorganic open-framework materials.

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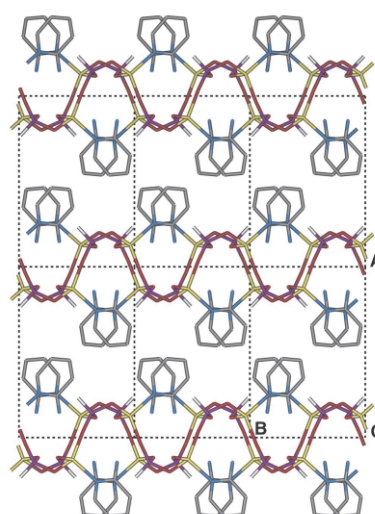


Fig. 4 Packing of the undulated layers of **1** along the [100] direction. Color code: Zn: yellow; P: purple; O: red; C: grey; N: blue.

Notes and references

† Crystal data for **1**: $\text{C}_5\text{H}_7\text{N}_2\text{O}_5\text{PZn}$, $M = 239.47$, monoclinic, $a = 11.3477(4)$, $b = 7.1079(3)$, $c = 10.4259(4)$ Å, $\beta = 111.585(2)^\circ$, $U = 781.96(5)$ Å³, $T = 293(2)$ K, space group $P2_1/c$ (no. 14), $Z = 4$, $\mu(\text{Mo-K}\alpha) = 3.309$ mm⁻¹, 3557 reflections measured, 1113 unique ($R_{\text{int}} = 0.0710$) which were used in all calculations. The final $wR(F^2)$ was 0.0861 (all data). CCDC 202906. See <http://www.rsc.org/suppdata/cc/b2/b212181f/> for crystallographic data in CIF or other electronic format.

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