Helical Zinc Phosphate

$[\{Zn_2(HPO_4)_4\}\{Co(dien)_2\}]\cdot H_3O$: A Zinc Phosphate with Multidirectional Intersecting Helical Channels**

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Chiral inorganic materials with helical pores are particularly desirable because of their promising applications in enantioselective catalysis and separation. It is recognized that both zeolite beta[1,2] and ETS-10[3] are heavily intergrown, with one of the polymorphs being chiral. However, an optically pure chiral zeolite material has been never found. The occurrence of inorganic materials with helical character is particular rare. Among the vast variety of open-framework materials,[4–6] only a few are known to have such structural features. For instance, the vanadium phosphate $[\{(CH_3)_2NH_2\}K_4\{V_{10}O_{10}(H_2O)_2(OH)_4(PO_4)_7\}]$ contains chiral interpenetrating double helices,[7] the zinc phosphate $[\{NH_3(CH_2)_2NH_2(CH_2)_2NH_3\}\{Zn_4(PO_4)_3(HPO_4)\}]\cdot H_2O$ contains intersecting helical channels,[8] UCSB-7 frameworks contain cross-linked helical pores,[9] and metal borophosphates contain 6_1 or 6_5 helices.[10] Recently, we reported the layered zinc phosphite $[(C_5H_6N_2)Zn(HPO_3)]$, which consists of left-handed and right-handed helical chains. The guest templating molecules are found to be important for the formation of the helical -Zn-O-P- chains.[11]

Employing chiral metal complexs as templating agents has proven to be a possible approach to induce a chiral environment in the host framework.[12] Several metal phosphates templated by an optically pure or a racemic mixture of chiral metal complexes have been reported, including aluminophosphates,[12–16] gallium phosphates $[\{d\text{-}Co(en)_3\}\{H_3Ga_2P_4O_{16}\}]$[17] (en = ethylenediamine) and $[\{Co(en)_3\}\{Ga_3(H_2PO_4)_6(HPO_4)_3\}]$,[18] boron phosphate $[\{Co(en)_3\}\{B_2P_3O_{11}(OH)_2\}]$,[19] and zinc phosphates $[\{Co^{II}(en)_3\}_2\{Zn_6P_8O_{32}H_8\}]$ and $[\{Co^{III}(en)_3\}\{Zn_8P_6O_{24}Cl\}]\cdot 2H_2O$.[20] Interestingly, the use of the $[Co(dien)_2]^{3+}$ ion as a template (dien = diethylenetriamine) led to the formation of a layered aluminophosphate $[\{trans\text{-}Co(dien)_2\}\{Al_3P_4O_{16}\}]\cdot 3H_2O$, which has layers that stack in a helical fashion. In this work, by using a racemic mixture of a chiral $[Co(dien)_2]Cl_3$ complex as the template, we have successfully prepared a new open-framework zinc phosphate, $[\{Zn_2(HPO_4)_4\}\{Co(dien)_2\}]\cdot H_3O$ (**1**) with multidirectional helical channels. Of particular interest is the existence of chiral intertwined double helices in its structure. Furthermore, the

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role of a chiral complex template in inducing the asymmetric environment in the host framework has been investigated.

Compound **1** crystallizes in the orthorhombic space group *Fdd*2 (No. 43). Its structure consists of a macroanionic $[Zn_2(HPO_4)_4]^{4-}$ framework. Charge neutrality is achieved by the complex cation $[Co(dien)_2]^{3+}$ and the protonated water molecule H_3O^+. Each asymmetric unit contains two unique Zn atoms that reside on the twofold symmetry axis, two unique P atoms in general positions, and one Co atom, also located on the twofold axis. Each Zn atom is tetrahedrally coordinated, sharing four vertex oxygen atoms with adjacent P atoms. The Zn–O bond lengths are in the range of 1.914(5) to 1.960(5) Å. Each HPO_4^{2-} tetrahedron shares two oxygen atoms with adjacent Zn atoms, with two oxygen atoms in terminal positions. The $P–O_{bridging}$ bond lengths are in the range of 1.497(6)–1.522(5) Å. The hydroxyl groups have longer P–O bond lengths in the range of 1.555–1.592(6) Å. The Zn-centered tetrahedra and P-centered tetrahedra alternate to form a three-dimensional open-framework. The framework density is 9.7 T per 1000 Å^3 (T = tetrahedrally coordinated atoms, that is, Zn or P), which is one of the lowest values known for open-framework materials.[21–28]

The framework of **1** consists solely of 12-membered rings. Each tetrahedrally coordinated Zn atom is associated with six 12-rings. Each 12-ring consists of six Zn and six P atoms, and has C_2 symmetry. Such structural units are connected together through vertex oxygen atoms to form a very open framework with a multidirectional helical pore system. Figure 1a shows the framework viewed along the [100] direction. It contains 12-membered ring channels that run along this direction. Each 12-ring accommodates one $[Co(dien)_2]^{3+}$ ion. Note that the $[Co(dien)_2]^{3+}$ ions in alternating rows I and II are a pair of enantiomers which are related by the *d* glide-plane operation. Interestingly, each 12-membered ring channel is enclosed by two intertwined helices of the same handedness, which are connected through Zn-O-P linkages (Figure 1b). Such chiral interpenetrating double helices are particularly rare in inorganic materials, with one notable example being $[\{(CH_3)_2NH_2\}K_4\{V_{10}O_{10}(H_2O)(OH)_4(PO_4)_7\}]\cdot 4H_2O$.[7]

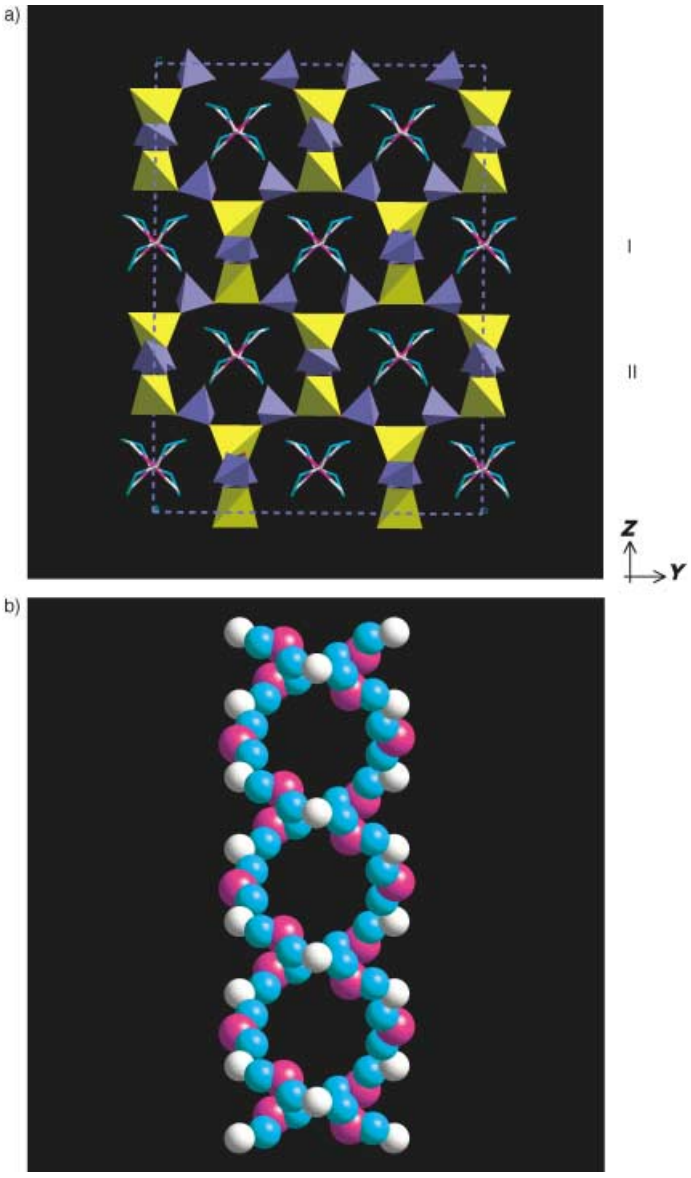

Figure 1. a) A polyhedral view of the framework along the [100] direction (the water molecules in the channels are not shown). The $[Co(dien)_2]^{3+}$ ions reside in the 12-membered ring channels. A pair of enantiomers of $Co(dien)_2^{3+}$ cations alternate in rows I and II (color code: Zn yellow, P blue, Co pink, N white, C light blue); b) a space-filling diagram of two intertwined helices that enclose the 12-membered ring channel (color code: Zn white, P pink, O light blue).

Figure 2a shows the framework of **1** viewed along the [110] direction. Besides the 12-membered ring channels, channels that appear to have an 8-membered ring opening can be seen. In fact, they are enclosed by two types of helical chains as seen in Figure 2b. Furthermore, there are helical channels along the $[1\bar{1}0]$, [411], $[41\bar{1}]$, [011], $[0\bar{1}1]$, [031], $[0\bar{3}1]$, [101], and $[10\bar{1}]$ directions. Thus **1** possesses a multidirectional helical pore system.

Alternatively, it is helpful to view the framework of **1** as being built up from a simple structural motif composed of a Zn(1)-centered tetrahedron with four dangling PO_4 groups (Figure 3a). These units are connected through Zn(2) atoms to form the 3D open framework. It is notable that such a structural motif is chiral and that it has the same C_2 symmetry as the chiral complex cation $[Co(dien)_2]^{3+}$. As has been demonstrated in the work by Morgan et al.[12] and by us,[20] a chiral microenvironment can be induced by the chiral complex template because of molecular recognition between the host and guest complexes. Examination of the hydrogen-bonding network in the metal complex and the inorganic structural motifs can help to understand the observed chiral molecular recognition. Figure 3b shows the H-bonding arrangement between the complex cations and the host framework. Each $[Co(dien)_2]^{3+}$ ion forms a total of 10 H-bonds to the water molecules and the bridging and terminal oxygen atoms in the structural motif. The N···O separations are in the range 2.939(9)–3.124(8) Å. Furthermore, the H-bonding between the chiral metal complex and the chiral

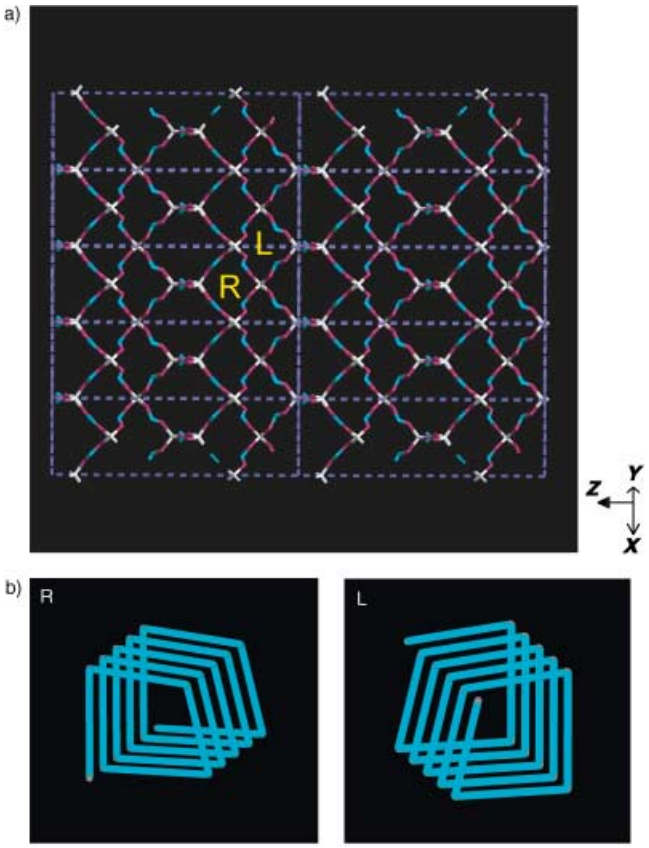

Figure 2. a) The framework viewed along the [110] direction showing the 12-membered ring channels and two types of helical channels; b) the right-handed (R) and left-handed (L) helical channels (color code: Zn white, P light blue, O pink).

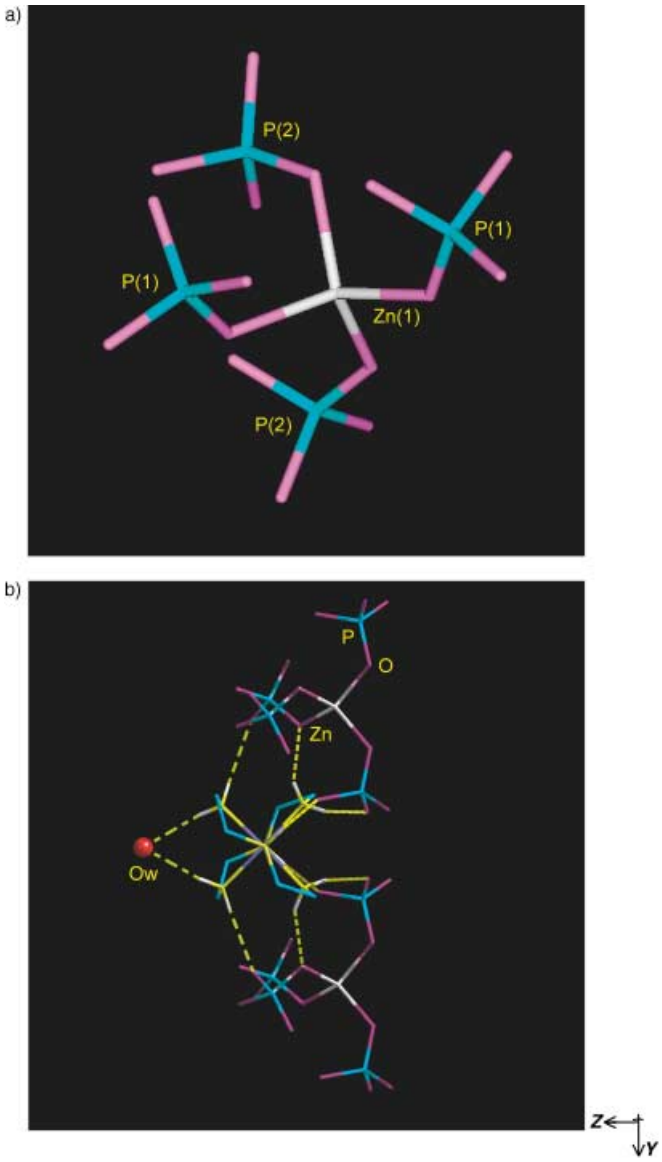

Figure 3. a) Zn(1)-centered tetrahedral structural motif with four dangling PO_4 groups; b) H-bonding arrangement between the chiral complex cation $[Co(dien)_2]^{3+}$ and the chiral structural motif (Zn white, P light blue, O pink).

structural motifs are related by a twofold symmetry axis. This suggests that the H-bonding imposes the C_2 symmetry operation of the chiral complex template onto the chiral structural motif. It is believed that chiral molecular recognition between the guest and host occurs through H-bonds. We are continuing to investigate the role of the chiral metal-complex template in determining the chirality of the inorganic framework. These studies have so far found that such H-bonding is the common origin for inducing chirality transfer in open frameworks templated with chiral metal complexes.

Experimental Section

1: $Zn(OAc)_2{\cdot}2H_2O$ (0.5 g) was dissolved in H_2O (10 mL) and then H_3PO_4 (0.46 mL, 85 wt % in water) and $[Co(dien)_2]Cl_3$ (0.58 g) were subsequently added while stirring. Finally, Me_4NOH (6.0 mL, 10 wt % aqueous solution) was added to the reaction mixture. A homogeneous gel (pH ≈ 7) was formed after stirring for 1 h, which was then sealed in a teflon-lined stainless steel autoclave and heated at 130 °C for 6 days under static conditions. Orange rod-shaped single crystals were separated from the remainder of the product by sonication, washed with distilled water, and then dried in air.

X-ray powder diffraction (XRD) data were collected on a Siemens D5005 diffractometer using $Cu_{K\alpha}$ radiation ($\lambda = 1.5418$ Å). Inductively coupled plasma (ICP) analysis (Perkin-Elmer Optima 3300 DV ICP instrument): Zn 16.21, Co 7.30, P 15.38 % (calcd: Zn 16.29, Co 7.35, P 15.43 %). Elemental analysis (Perkin-Elmer 2400 elemental analyzer): C 12.00, H 4.62, N 10.12 % (calcd: C 12.04, H 4.14, N 10.47 %).

The valence state of +3 for Co in the complex was confirmed by magnetic measurements carried out on a Quantum-Design MPMS-XL SQUID magnetometer.

Thermogravimetric analysis was performed on a Perkin-Elmer TGA7 unit in air. A weight loss of approximately 26.0 % was observed over the 260–580 °C temperature range, which indicated decomposition of the metal complex. XRD analysis indicated that the weight loss was associated with a loss of crystallinity.

Structure determination: A suitable single crystal with dimensions of $0.60 \times 0.20 \times 0.10$ mm was selected for single-crystal X-ray diffraction analysis. Structural analysis was performed on a Siemens SMART CCD diffractometer using graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). The data were collected at temperature of 20 ± 2 °C. Data processing was accomplished with the SAINT

processing program.[29] The structure was solved by direct methods and refined on F^2 by full-matrix least-squares using SHELXTL97.[30] All Zn, Co, P, and O atoms were located from the difference map. H atoms associated with the hydroxyl groups and the metal-complex cation were placed geometrically and refined in a riding model. The non-hydrogen atoms were refined anisotropically.

Crystal data: $[\{Zn_2(HPO_4)_4\}\{Co(dien)_2\}]\cdot H_3O$, **1**, $M_r = 802.86$, orthorhombic, space group *Fdd*2 (No. 43), $a = 9.271(4)$, $b = 19.781(9)$, $c = 27.045(8)$ Å, $V = 4960(3)$ Å^3, $Z = 8$, $\mu = 2.932$ mm^{-1}, $\rho_{calcd} = 2.150$ g cm^{-3}, 2751 reflections measured, 1781 unique ($R_{int} = 0.0656$). The final $wR(F^2_{all\ data})$ was 0.1254 and $R(F_{all\ data})$ was 0.0503. CCDC-208125 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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