Chiral Coordination Polymer

# $Zn_2[(S)\text{-}O_3PCH_2NHC_4H_7CO_2]_2$: A Homochiral 3D Zinc Phosphonate with Helical Channels**

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Chiral metal–organic coordination polymers with open frameworks have attracted much attention because of their potential applications in enantioselective separation and catalysis.[1–4] Such materials are generally prepared by enantioselective synthesis or spontaneous resolution. Spontaneous resolution on crystallization without any chiral auxiliary will result in a racemic mixture of enantiomeric crystals. Moreover, spontaneous resolution is relatively rare and cannot be predicted because its mechanism is not yet fully under-

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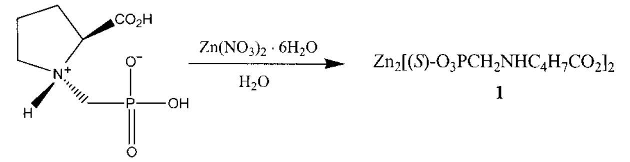
stood.[4–6] Enantioselective synthesis, however, is a direct and effective method for the synthesis of enantiopure chiral open frameworks by using enantiopure organic building units as reactant precursors.[3,7,8] By enantioselective synthesis, many chiral open frameworks with high thermal stability have been obtained in recent years, and they showed encouraging results in enantioselective separation and catalysis.[9–11]

Some enantiopure organic compounds are good homogeneous catalysts in asymmetric synthesis, for example, (*S*)-proline and its derivatives show highly enantioselective catalysis and afford good yields in many reactions such as α-amination of aldehydes or ketones and aldol, Mannich, and Michael reactions.[12–14] An intriguing idea is to synthesize a porous material with such enantiopure catalysts as building units. The resulting open-framework material might be used as a heterogeneous asymmetric catalyst.

We chose an enantiomerically pure derivative of (*S*)-proline, namely, 1-phosphonomethylproline, as a chiral building unit and successfully prepared a homochiral 3D zinc phosphonate $Zn_2[(S)\text{-}O_3PCH_2NHC_4H_7CO_2]_2$ (**1**) with alternately arranged left- and right-handed helical channels. Of particular interest is that the active sites of 1-phosphonomethylproline for asymmetric catalysis—the amino group and the partially uncoordinated carboxylate group—are retained and directed into the channels, in contrast to a recently reported similar metal phosphonate.[16c,d] Many open frameworks constructed from enantiopure phosphonic acids have been reported previously,[11,15,16] but a chiral metal phosphonate containing not only helical channels but also active sites for asymmetric catalysis in achiral channels has not been found so far.

The chiral building unit 1-phosphonomethylproline was prepared by using a modified literature method.[16c] Enantiopure 1-phosphonomethylproline reacts with $Zn(NO_3)_2{\cdot}6\,H_2O$ in the presence of triethylamine as base under hydrothermal conditions to give the homochiral 3D open framework $Zn_2[(S)\text{-}O_3PCH_2NHC_4H_7CO_2]_2$ (**1**; Scheme 1). Compound **1** crystallizes in the orthorhombic space group $P2_12_12$ (No. 18). It consists of 4,8-nets formed by alternately arranged left- and right-handed helices that are connected through 1-phosphonomethylproline ligands to generate a 3D open framework. Each asymmetric unit contains two unique Zn atoms and two unique P atoms. The Zn atoms adopt tetrahedral geometry by coordination of three phosphonate oxygen atoms and one carboxylate oxygen atom of the ligand, while the other carboxylate oxygen atom is uncoordinated. The 3D framework is based on two crystallographically distinct $ZnO_4$ tetrahedra and two distinct $O_3PC$ tetrahedra. Each Zn atom shares three vertex oxygen atoms with adjacent P atoms (Zn–O 1.922(4)–1.978(4) Å), and each $O_3PC$ tetrahedron also shares three oxygen atoms with adjacent Zn atoms. The P–$O_{bridging}$ bond lengths are in the range between 1.501(4) and 1.523(4) Å. The Zn- and P-centered tetrahedra alternate to form 4,8-net sheets by sharing oxygen atoms on the *bc* plane, which are linked by the ligands along the *a* axis to generate a 3D open framework.



***Scheme 1.*** Synthesis of **1**.

Figure 1 shows the framework of **1** viewed along the [100] direction. The structure contains four- and eight-membered rings (7 × 8 Å, estimated by measuring the distances between the centers of opposite atoms; hereafter, all dimensions are reported in this way), similar to the reported example,[17] which are made of two different helical chains A and B. These chains run along the *b* axis and are arranged AA and BB along the *a* axis, respectively.

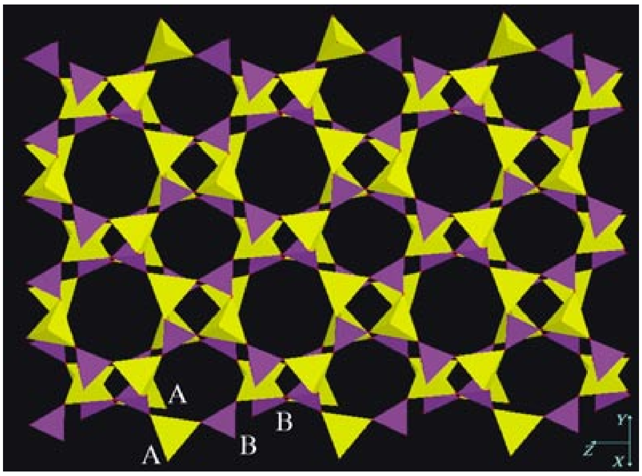


***Figure 1.*** A polyhedral view of the framework along the [100] direction. 4,8-Nets consist of left-handed (A) and right-handed helices (B), which are arranged AA and BB along the *a* axis. 1-phosphonomethylproline ligands are omitted for clarity; Zn yellow, P purple.

The framework of **1** contains two types of microchannels with dimensions of 4 × 6 and 5 × 12 Å, seen in a view along the [001] direction in Figure 2. These channels are made of helical chains of the same handedness (either chain A or chain B) and 1-phosphonomethylproline ligands. These helical chains run along the *b* axis and are arranged ABAB along the *c* axis.

Figure 3a shows a view of the framework of **1** along the [010] direction. Three different four-membered-ring channels (left-handed helical, right-handed helical, and achiral channels) and eight-membered-ring channels (7 × 7 Å) can be seen. Along the *c* axis, left-handed helical channels, achiral channels, and right-handed helical channels alternate. These chiral channels are enclosed by two types of helical chains, as shown in Figure 3b and c. Interestingly, *L*-handed helices consist of Zn1 and P2 atoms, while *R*-handed helices consist of Zn2 and P1 atoms.

Notably, in the structure of **1**, coordination of the 1-phosphonomethylproline ligand to the zinc atom through the phosphonate group and the monodentate carboxylate group leaves a carboxylate oxygen atom uncoordinated and the amino group free, and the functionality of the material is thus

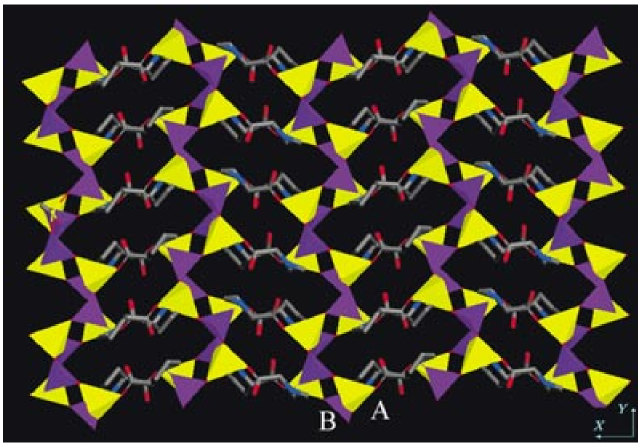


*Figure 2.* View along the [001] direction. Two types of microchannels with dimensions of 4×6 and 5×12 Å are made of 1-phosphonomethylproline ligands and left-handed helical chains (A) and right-handed helical chains (B). The two kinds of chiral chains are arranged ABAB along the *c* axis (Zn yellow, P purple, O red, N blue, C gray).

retained. The uncoordinated carboxylate oxygen atoms and the amino groups with N−H bonds, which are the active sites for asymmetric catalysis, are directed into the achiral six- and ten-membered-ring channels along the [001] direction (Figure 2) and eight-membered-ring channels along the [010] direction (Figure 3 a).

Thermogravimetric analysis (TGA) was performed to gauge the thermal stability. No weight loss occurred below 400 °C, which shows that the open framework is stable below that temperature. The presence of active sites for asymmetric catalysis in channels along with the high thermal stability of the homochiral zinc phosphonate open framework promises applications in heterogeneous asymmetric catalysis. Research on asymmetric catalysis is currently underway.

## Experimental Section

$(S)$-$HO_3PCH_2NHC_4H_7CO_2H$: HCHO (40 mmol, 36 % in water) was added dropwise to a mixture of $(S)$-proline (10 mmol), $H_3PO_3$ (11 mmol), and HCl (30 mL of a 6.0 M aqueous solution) under reflux. The resultant solution was then heated at reflux for a further 12 h. A white solid was recovered in a yield of 90 % after removal of water, and recrystallized from EtOH/propylene oxide. M.p. 257–259 °C. $[\alpha]^{25}_{\mathrm{D}} = -63^\circ$ ($c = 1.6$ in water). Elemental analysis (%): calcd for $C_6H_{12}NO_5P$ (209.14): C 34.44, N 6.69, H 5.74; found: C 34.25, N 6.80, H 5.67. $^{31}$P MAS NMR (161.9 MHz, 298 K): $\delta = 8.7$ ppm.

$Zn_2[(S)\text{-}O_3PCH_2NHC_4H_7CO_2]_2$: $Zn(NO_3)_2 \cdot 6H_2O$ (0.074 g) and $(S)$-$HO_3PCH_2NHC_4H_7CO_2H$ (0.053 g) were dissolved in $H_2O$ (10 mL), and then triethylamine (0.5 mL) was added while stirring to adjust the pH of the mixture. The mixture (pH ≈ 6) was sealed in a Teflon-lined stainless steel autoclave after stirring for 10 min and heated at 160 °C for 2 d. Colorless block single crystals were filtered off, washed with distilled water, and dried at room temperature to yield **1** (0.079 g, 58 %). $^{31}$P MAS NMR (161.9 MHz, 298 K): $\delta = -24.5$ ppm. The CD spectrum (Figure 3 of Supporting Information) clearly shows a positive Cotton effect, in agreement with that of the original chiral ligand, which indicates that the chiral ligand retained its original chirality even after the hydrothermal reaction.

Inductively coupled plasma (ICP) analysis (Perkin-Elmer Optima 3300 DV ICP instrument): Zn 24.08, P 11.45 % (calcd: Zn 23.96, P 11.37 %). Elemental analysis (Perkin-Elmer 2400 elemental analyzer): C 26.51, H 3.54, N 5.22 % (calcd: C 26.45, H 3.70, N 5.14 %).

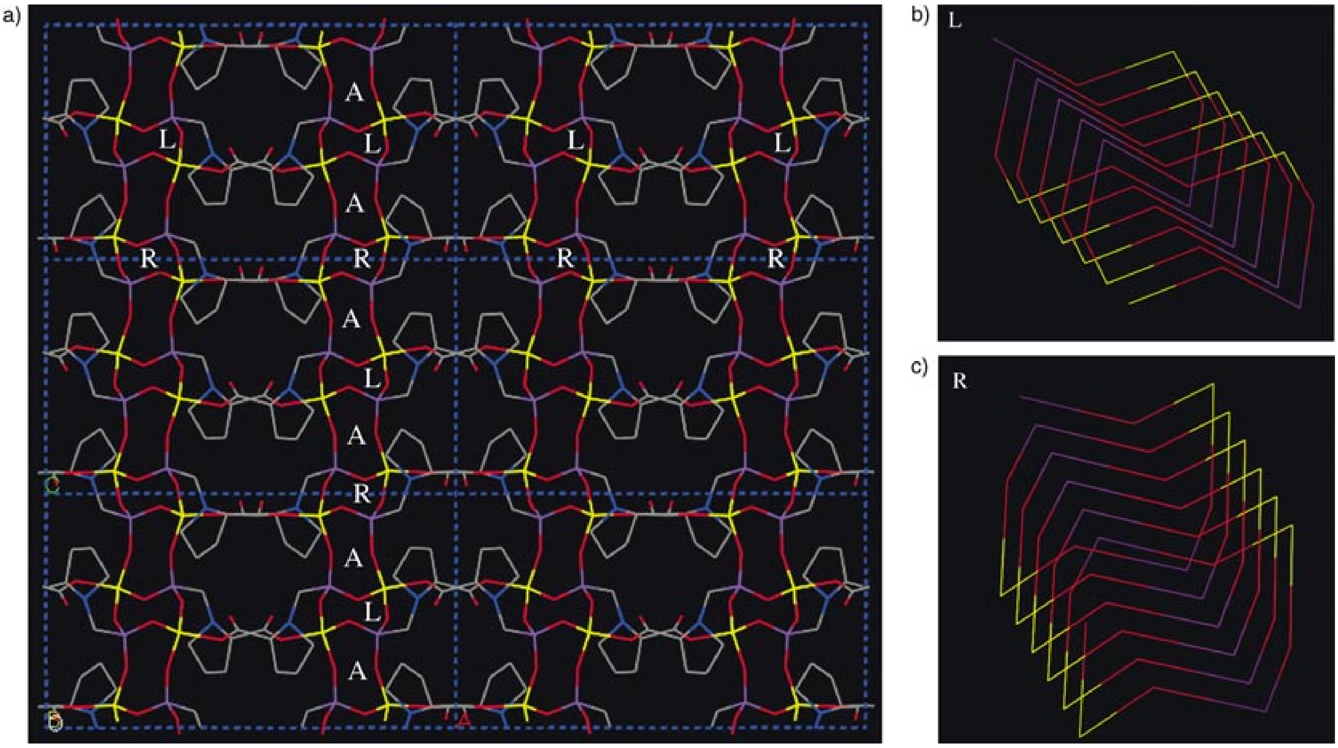


*Figure 3.* a) The framework viewed along the [010] direction, showing two types of helical channels and achiral channels which are alternately arranged along the *c* axis (A: achiral channel, L: left-handed helical channel, R: right-handed helical channel). b, c) The left-handed (L) and right-handed (R) helical channels (Zn yellow, P purple, O red, N blue, C gray).

Thermogravimetric analysis was performed on a Perkin-Elmer TGA7 unit in air. A weight loss was observed in the 400–450 °C temperature range, which indicated decomposition of the metal phosphonate.

Structure determination: A suitable single crystal with dimensions of $0.58 \times 0.47 \times 0.14$ mm was selected for single-crystal X-ray diffraction analysis. Crystallographic data were collected at 293(2) K on a Bruker-AXS Smart CCD diffractometer using $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods[18] and refined by the full-matrix least-squares method against $F^2$ (SHELXL-97).[19] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms of organic ligands (except H1 and H2) were located geometrically.

Crystal data: $Zn_2[(S)\text{-}O_3PCH_2NHC_4H_7CO_2]_2$ (**1**), $M_r = 544.98$, orthorhombic, space group $P2_12_12$ (No. 18), $a = 18.425(8)$, $b = 9.168(2)$, $c = 10.554(3)$ Å, $V = 1782.7(9)$ Å$^3$, $Z = 4$, $\mu = 2.929\ mm^{-1}$, $\rho_{cald} = 2.031\ g\,cm^{-3}$, 2781 reflections measured, of which 2207 were unique ($R_{int} = 0.0424$). The final $wR(F^2)$ was 0.0788 (all data), and $R(F)$ was 0.0523 (all data). CCDC-239389 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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