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Amino Acid Templating of Inorganic Networks: Synthesis and Structure of L-Asparagine Zinc Phosphite, $C_4N_2O_3H_8 \cdot ZnHPO_3$

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$C_4N_2O_3H_8 \cdot ZnHPO_3$ is the first zincophosphite framework to be templated by an amino acid (L-asparagine), which bonds to Zn via a carboxyl O atom. It contains infinite, homochiral, helical 4-ring chains of ZnO_4 and HPO_3 groups, stabilized by intra- and interchain N–H···O hydrogen bonds. Crystal data: $C_4N_2O_3H_8 \cdot ZnHPO_3$, M_r = 277.49, orthorhombic, $P2_12_12_1$ (No. 19), a = 5.0349(2) Å, b = 9.4539(4) Å, c = 18.6092(8) Å, V = 885.79 (6) Å^3, Z = 4.

Many organically templated zincophosphates (ZnPOs) have now been reported.[1] In these and related materials,[2] the organic entity is regarded as the key factor in promoting the formation of new types of low-density networks. Most templates are cationic, protonated, polyfunctional amine cations, and multipoint N−H···O$_f$ (f = framework) hydrogen bonds play a key role in stabilizing the resulting ZnO_4/PO_4 inorganic network.[3] We have recently extended these studies to organically templated zincophosphites (ZnHPOs) containing the (hydrogen) phosphite $[HPO_3]^{2-}$ moiety.[4−8] Depending on the template used, some ZnHPOs are surprisingly similar to corresponding ZnPOs,[6] whereas others adopt novel structures.[7] In this Communication, we report the synthesis, crystal structure, and some properties of L-asparagine zinc phosphite, $C_4N_2O_3H_8 \cdot ZnHPO_3$. This new material is the first ZnHPO or ZnPO phase to be templated by a chiral amino acid, and as a result, it contains homochiral polyhedral chains.

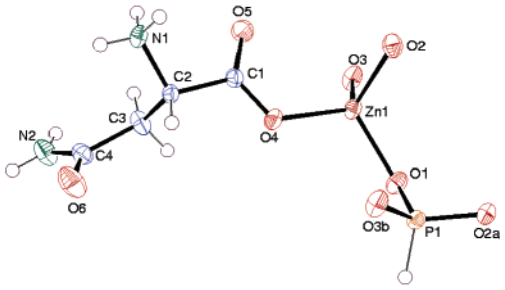
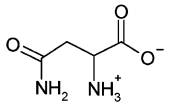


Figure 1. Fragment of $C_4N_2O_3H_8 \cdot ZnHPO_3$ (50% thermal ellipsoids, arbitrary spheres for the H atoms). Symmetry codes: (a) $x - {}^1/_2$, ${}^1/_2 - y$, $1 - z$, (b) $x - 1$, y, z. Selected bond distances (Å): Zn1−O1 1.9494(13), Zn1−O2 1.9837(13), Zn1−O3 1.9368(14), Zn1−O4 1.9468(13), P1−O1 1.5269(15), P1−O2a 1.5295(13), P1−O3b 1.5174(13), O4−C1 1.278(2), O5−C1 1.225(2), O6−C4 1.235(3), N1−C2 1.487(2), N2−C4 1.326(3), C1−C2 1.529(2), C2−C3 1.519(3), C3−C4 1.522(2).

$C_4N_2O_3H_8 \cdot ZnHPO_3$ was prepared from a mixture of 0.814 g (10 mmol) of ZnO, 0.820 g (10 mmol) of H_3PO_3, 1.501 g (11.4 mmol) of L-asparagine (**I**), and 20 mL of water. These components were shaken together in a polypropylene bottle to result in a white slurry and heated to 80 °C for 5 days. Product recovery by vacuum filtration and rinsing with water resulted in 1.472 g of transparent blades and plates of the title compound (yield based on Zn = 53%). Elemental analysis data were satisfactory (C obsd (%), calcd (%), 17.31, 16.81; H, 2.90, 3.27; N, 9.39, 10.10). Thermogravimetric analysis showed weight loss over the broad range 200−700 °C.



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The crystal structure[9] of $C_4N_2O_3H_8 \cdot ZnHPO_3$ contains 14 non-H atoms in the asymmetric unit (Figure 1). The zinc atom is tetrahedrally coordinated to three O atoms bridging

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(9) Bruker SMART 1000 CCD diffractometer, Mo Kα radiation, λ = 0.71073 Å, T = 20 °C. The H atoms were located in difference maps (N−H) or geometrically placed (C−H) and were refined by riding in idealized positions. Crystal data: $C_4N_2O_3H_8 \cdot ZnHPO_3$, M_r = 277.47, orthorhombic, $P2_12_12_1$ (No. 19), a = 5.0349(2) Å, b = 9.4539(4) Å, c = 18.6092(8) Å, V = 885.79(6) Å^3, Z = 4, $R(F)$ = 0.024, $R_w(F^2)$ = 0.055.

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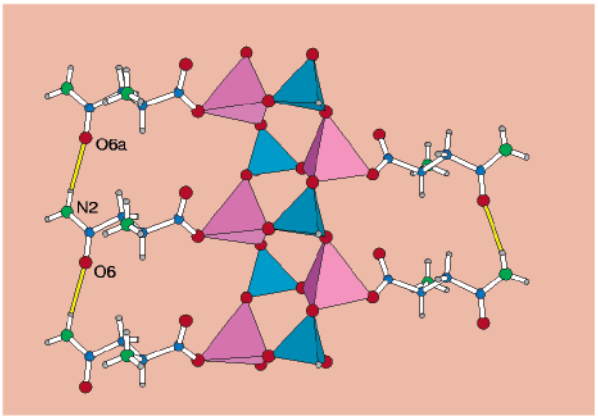

Figure 2. Detail of $C_4N_2O_3H_8{\cdot}ZnHPO_3$ showing a [100] chain of ZnO_4 and HPO_3 units (violet and blue tetrahedra, respectively) and pendant asparagine molecules. Color key: C blue, N green, O red, H gray (all radii arbitrary). The intrachain N2−H6···O6a (a = 1 + *x*, *y*, *z*) hydrogen bond is shown in yellow.

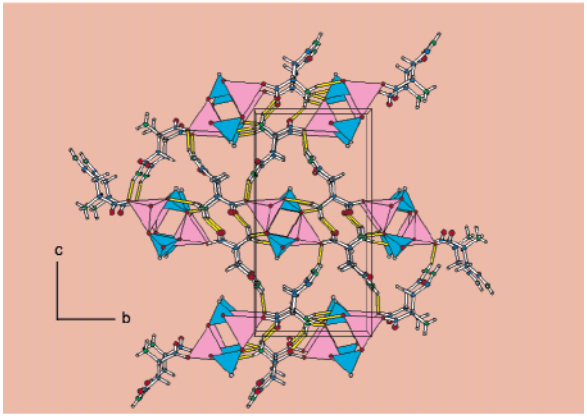

Figure 3. Unit cell packing in $C_4N_2O_3H_8{\cdot}ZnHPO_3$ viewed down [100]. Color key as in Figure 2.

Table 1. Hydrogen Bonding Interactions[a] (Å, deg)

N1-H7···O2a	2.02	2.782(2)	142
N1−H8···O5b	1.96	2.763(2)	150
N1−H9···O1c	2.15	3.016(2)	165
N2−H5···O4d	2.26	2.955(2)	138
N2−H6···O6e	2.31	3.136(2)	160

[a] The three values refer to d(H···O), d(N···O), and θ(N−H···O), with d(N1−H) = 0.89 Å and d(N2−H) = 0.86 Å. Symmetry codes: (a) $^1/_2 + x$, $^3/_2 - y$, $1 - z$; (b) $x - ^1/_2$, $^3/_2 - y$, $1 - z$; (c) x, $1 + y$, z; (d) $1 - x$, $^1/_2 + y$, $^1/_2 - z$; (e) $1 + x$, y, z.

to P and a carboxyl O atom of the asparagine molecule [d_{av} (Zn−O = 1.954 (2) Å]. The P atom bonds to three O atoms [d_{av}(P−O) = 1.525 (2) Å], with the fourth tetrahedral vertex occupied by an H atom, which is always observed for a phosphite grouping.[10] The three bridging O atoms have an average Zn−O−P bond angle of 124.1°.

The L-asparagine molecule has typical geometrical parameters.[11] The crystal structure study clearly shows the N1 species to be triply protonated; thus, this species is neutral, and (nominally) zwitterionic, which is in accordance with the charge-balancing criterion, assuming the usual valencies for Zn^{2+} and $[HPO_3]^{2-}$. C2 has its expected S chirality, based on the L-asparagine starting material, and refinement of the Flack absolute structure parameter to 0.019(9) indicated that the absolute structure is well defined (i.e., there is no suggestion of racemic or merohedral twinning).

The linkage of the ZnO_4 (i.e., ZnO_3O_A A = asparagine) and HPO_3 tetrahedra in $C_4N_2O_3H_8{\cdot}ZnHPO_3$ results in infinite, edge-sharing, ladderlike chains of 4-rings propagating along [100] (Figure 2). The chain motif is chiral (the Zn1−O2−P1−O1 backbone of every chain propagates in a counterclockwise sense along [100]) and lies on a 2_1 symmetry axis.

Hydrogen bonding appears to be a key factor in defining the molecular packing, and various intra- (via H6) and interchain N−H···O links are present. These interactions help to define a crystal structure (Figure 3) in which the neutral [100] chains are interleaved by means of the N1−H7···O2 and N1−H9···O1 bonds in the *b* direction and N1−H8···O5 and N2−H5···O4 bonds in the *c* direction (see Table 1 for acceptor-atom symmetry codes). The chains arrange themselves into pseudo-(001) sheets in which the component tetrahedra all point in the same direction; the sheets configure themselves in *ABAB* all-up/all-down in the [001] direction.

The existence of a template-O-atom-to-Zn bond is a novel feature for ZnPOs and ZnHPOs,[1] although template-N-atom-to-Zn bonds have been seen for both families.[1,4] However, both Zn−O and Zn−N bonds are commonplace in molecular systems.[12] The possible biological significance of Zn−O and Zn−N bonds has recently been discussed.[13] We are now exploring the chemistry of ZnHPOs templated by other amino acids with a major aim being the preparation of a chiral, three-dimensional framework.

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Supporting Information Available: CIF file for the title compound. This material is available free of charge via the Internet at http://pubs.acs.org.

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