

## Synthesis, crystal structure and characterizations of a new 3D porous zinc phosphonate: $\text{Zn}_6[(\text{O}_3\text{PCH}_2)_2\text{NHC}_6\text{H}_{11}]_4 \cdot 6\text{H}_2\text{O}$

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### Abstract

A new 3D porous zinc phosphonate,  $\text{Zn}_6(\text{HL})_4 \cdot 6\text{H}_2\text{O}$  **1** ( $\text{H}_4\text{L} = \text{C}_6\text{H}_{11}\text{N}(\text{CH}_2\text{PO}_3\text{H}_2)_2$ ) has been synthesized by hydrothermal reaction at 180 °C and structurally characterized by X-ray diffraction as well as by infrared spectroscopy, elemental and thermogravimetric analysis. The structure of compound **1** features a 3D open-framework built from  $\text{ZnO}_4$  tetrahedra linked together by bridging phosphonate groups. Each zinc cation is tetrahedrally coordinated by four phosphonate oxygen atoms from four ligands, each of which connects with six zinc atoms, resulting in channel systems of different size.

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**Keywords:** Metal phosphonates; Crystal structure; Hydrothermal synthesis; Zinc

The chemistry of metal phosphonates has received considerable interest because of their potential applications in the areas of catalysis, ion exchange, proton conductivity, intercalation chemistry, photochemistry, and materials chemistry [1–4]. Great efforts have been devoted to the synthesis of novel inorganic–organic hybrid materials based on metal phosphonates, which exhibit interesting architectures and possible functionalities. The integration of the inorganic phosphonate ( $\text{CPO}_3$ ) group and numerous rigid or flexible organic functional groups within the same composite would, therefore, be expected to result in new inorganic–organic hybrid materials with interesting structures and properties. Along this line, the use of bifunctional or multifunctional anionic units, such as diphosphonates, aminophosphonates or phosphonocarboxylates has led to a number of new materials with microporous or open-framework structures [5–8].

Based on 2-hydroxyphosphonoacetic acid, proline-*N*-methyl-phosphonic acid and DL-( $\alpha$ -aminoethyl)phosphonic acid, a series of metal phosphonates with two-dimensional (2D) layer and three-dimensional (3D) open-framework have been isolated in our laboratory [9]. In the point of view of structural construction of inorganic–organic hybrid compounds, the substituted aminodiphosphonic acid,  $\text{RN}(\text{CH}_2\text{PO}_3\text{H}_2)_2$ , is very useful ligands in the synthesis of metal phosphonates with new structure types [10–14]. Recently, a layered Zn(II) complex with  $\text{C}_6\text{H}_{11}\text{N}(\text{CH}_2\text{PO}_3\text{H}_2)_2$  ( $\text{H}_4\text{L}$ ) has been reported by Ying and Mao [15]. The metal phosphonate layers in the compound  $\text{Zn}_3(\text{HL})_2 \cdot 1.5\text{H}_2\text{O}$  are based on  $\text{ZnO}_4$  tetrahedra crosslinked by bridging aminodiphosphonate ligands. By using  $\text{CH}_3\text{CH}_2\text{CH}_2\text{N}(\text{CH}_2\text{PO}_3\text{H}_2)_2$  ( $\text{H}_4\text{L}'$ ), two new divalent metal aminodiphosphonates  $\text{Zn}(\text{H}_2\text{L}')$  and  $\text{Cd}_2\text{L}'$  with a layered structure have also been obtained in our group [16]. But, to the best of our knowledge, the reports on metal aminodiphosphonates with 3D open-framework are still rare. In this paper, we report the synthesis [17] of a new 3D porous metal phosphonate,  $\text{Zn}_6(\text{HL})_4 \cdot 6\text{H}_2\text{O}$  **1** using

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the aminodiphosphonic acid,  $C_6H_{11}N(CH_2PO_3H_2)_2$  as ligand. The compound structure was characterized by X-ray single-crystal diffraction [18], X-ray powder diffraction, infrared spectroscopy, elemental analysis and thermogravimetric analysis.

A single-crystal X-ray structure analysis of compound **1** revealed that compound  $Zn_6[(O_3PCH_2)_2NHC_6H_{11}]_4 \cdot 6H_2O$  crystallizes in monoclinic space group  $C2/c$ . There are six crystallographically independent zinc(II) atoms, four partially deprotonated  $HL^{3-}$  anions and six lattice water molecules in an asymmetric unit (Fig. 1).

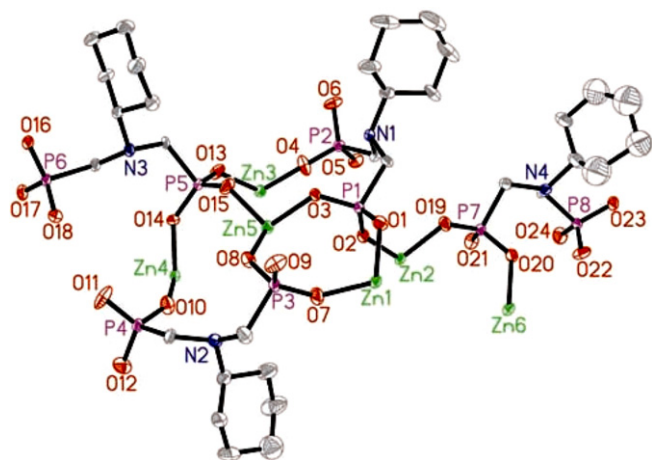


Fig. 1. Asymmetric unit of compound **1** showing the atom labeling. Thermal ellipsoids are shown at the 30% probability level. All H atoms and water molecules are omitted for clarity. Zn(1)–O(7), 1.913(6) Å; Zn(1)–O(16)#1, 1.918(6) Å; Zn(1)–O(9)#2, 1.920(6) Å; Zn(1)–O(1), 1.937(6) Å; Zn(2)–O(21)#3, 1.904(6) Å; Zn(2)–O(2), 1.916(5) Å; Zn(2)–O(17)#1, 1.945(5) Å; Zn(2)–O(19), 1.956(6) Å; Zn(3)–O(4), 1.903(7) Å; Zn(3)–O(22)#3, 1.919(6) Å; Zn(3)–O(12)#4, 1.925(6) Å; Zn(3)–O(13), 1.949(6) Å; Zn(4)–O(23)#3, 1.931(6) Å; Zn(4)–O(10), 1.932(6) Å; Zn(4)–O(6)#5, 1.934(6) Å; Zn(4)–O(14), 1.938(6) Å; Zn(5)–O(24)#3, 1.898(7) Å; Zn(5)–O(3), 1.927(5) Å; Zn(5)–O(8), 1.944(6) Å; Zn(5)–O(15), 1.959(6) Å; Zn(6)–O(20), 1.916(6) Å; Zn(6)–O(5)#3, 1.933(6) Å; Zn(6)–O(18)#1, 1.945(6) Å; Zn(6)–O(11)#1, 1.950(6) Å. Symmetry transformations used to generate equivalent atoms: #1  $x, -y + 1, z - 1/2$ ; #2  $-x, -y + 1, -z$ ; #3  $-x + 1/2, -y + 1/2, -z$ ; #4  $-x + 1/2, y - 1/2, -z + 1/2$ ; #5  $-x + 1/2, y + 1/2, -z + 1/2$ .

Each Zn atom is four-coordinated by four phosphonate oxygen atoms of four diphosphonate anions in a tetrahedral geometry. The Zn–O bond lengths are in the range of 1.898(7)–1.959(6) Å, which are comparable to those reported for other Zn(II) aminodiphosphonates [15,16]. Each  $HL^{3-}$  anion acts as a hexadentate ligand, and connects six Zn(II) atoms through six phosphonate oxygen atoms. On the other hand, all the phosphonate oxygen atoms are involved in metal coordination. Based on the charge balance, each nitrogen atom of the amine group for the four ligands is 1H-protonated.

The overall structure of compound **1** can be described as a 3D open-framework type. The  $ZnO_4$  tetrahedra are interconnected by phosphonate groups *via* corner-sharing to form a 3D open-framework structure. The result of connections in this manner is the formation of two channel systems. The channel system running along the  $c$ -axis (Fig. 2) is assembled by 40-atom rings ( $16.3 \text{ \AA} \times 9.8 \text{ \AA}$ , estimated by measuring the distances between the centers of opposite atoms), which consist of six Zn, 10 P, four N, 12 O and eight C atoms. The channel system running along the  $b$ -axis is formed by 24-membered rings composed of four Zn and four L ligands (Fig. 3). The approximate dimension is  $10.4 \text{ \AA} [P3-P3] \times 9.2 \text{ \AA} [Zn6-Zn6]$ . The cyclohexyl groups of the diphosphonate anions are oriented toward the channel center.

The powder XRD patterns [19] of the as-synthesized compound **1** with that simulated on the basis of the single-crystal structure are presented (see Fig. S4). The diffraction peaks on the patterns correspond well in position, confirming that the product is a pure phase. The differences in reflection intensity are probably due to preferred orientation in the powder samples.

The IR spectrum [20] of compound **1** was recorded in the region from  $4000$  to  $400 \text{ cm}^{-1}$  (see Fig. S5). The bands centered at  $3456 \text{ cm}^{-1}$  and one sharp band at  $1637 \text{ cm}^{-1}$  correspond to the H–OH stretching and bending vibrations of the lattice water. The weak bands around  $3000 \text{ cm}^{-1}$  originate from the N–H and C–H stretching vibrations. The set of bands between  $1200$  and  $900 \text{ cm}^{-1}$  are assigned

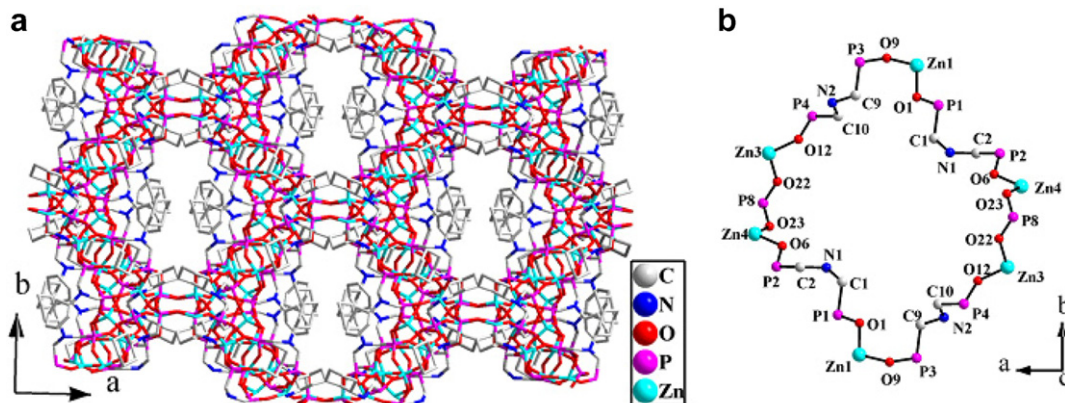


Fig. 2. (a) View of the framework for compound **1** along the  $c$ -axis showing the holes in the structure. The water molecules have been omitted for clarity. (b) A 40-membered ring in compound **1**.

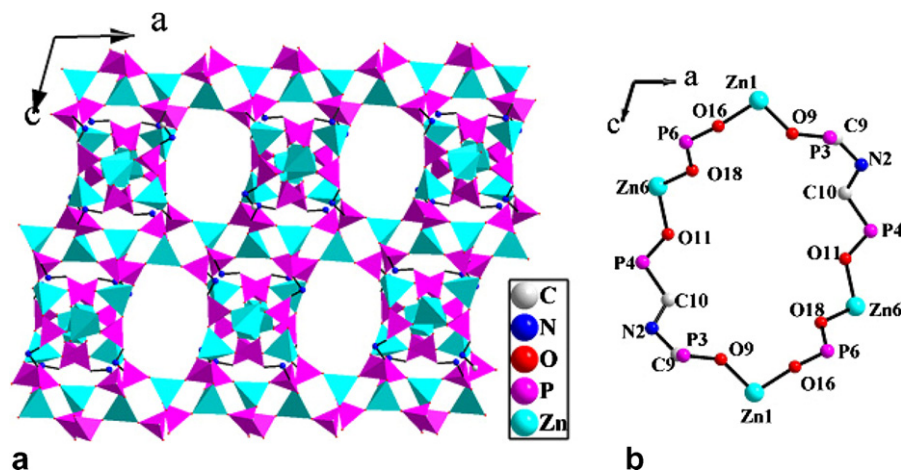


Fig. 3. (a) View of the framework for compound **1** along the *b*-axis showing the holes in the structure. The cyclohexyl groups of the ligands and water molecules have been omitted for clarity. (b) A 24-membered ring in compound **1**.

to stretching vibrations of the tetrahedral  $\text{CPO}_3$  groups [21,22]. Additional medium and sharp bands at low energy (between  $800$  and  $400\text{ cm}^{-1}$ ) are found, these bands are probably due to bending vibrations of the tetrahedral  $\text{CPO}_3$  groups and Zn–O stretching vibrations.

The thermogravimetric analysis [23] diagram of compound **1** indicates two main steps (see Fig. S6). The first step starts at about  $50\text{ }^\circ\text{C}$  and is completed at  $200\text{ }^\circ\text{C}$ , corresponding to release of six lattice water molecules. The weight loss of  $6.4\%$  is in good agreement with the calculated value ( $6.6\%$ ). The second step covers a temperature range  $250$ – $870\text{ }^\circ\text{C}$ . It corresponds to the pyrolysis of the organic group. The final product is assumed to be mixture of  $\text{Zn}(\text{PO}_3)_2$  and  $\text{ZnO}$  in a molar ratio of  $2:1$ . The total weight loss of  $35.9\%$  is close to the calculated value ( $35.5\%$ ).

In conclusion, a new porous zinc phosphonate,  $\text{Zn}_6[(\text{O}_3\text{PCH}_2)_2\text{NHC}_6\text{H}_{11}]_4 \cdot 6\text{H}_2\text{O}$  with a 3D open-framework has been prepared under hydrothermal reaction conditions from  $\text{Zn}(\text{II})$  ion and the substituted aminodiphosphonic acid,  $\text{C}_6\text{H}_{11}\text{N}(\text{CH}_2\text{PO}_3\text{H}_2)_2$  and structurally characterized by single-crystal X-ray diffraction analysis. The structure of compound **1** features a 3D open-framework structure with two channel systems in the *c*-axis direction and the *b*-axis direction, respectively. The cyclohexyl groups of the diphosphonate anions are oriented toward the channel center.

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### Appendix A. Supplementary material

CCDC 634963 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Cen-

tre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif). Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.inoche.2007.11.023](https://doi.org/10.1016/j.inoche.2007.11.023).

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- [17] A mixture of  $0.11\text{ g}$  ( $0.5\text{ mmol}$ )  $\text{Zn}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$ ,  $0.14\text{ g}$  ( $0.5\text{ mmol}$ )  $\text{H}_4\text{L}$  and  $10\text{ ml}$  of deionized water was sealed in a Teflon-lined stainless steel autoclave, and then heated at  $180\text{ }^\circ\text{C}$  for 5 days. Colorless block crystals were obtained in *ca.*  $69.6\%$  yield based on Zn.

Anal. Calcd. for  $C_{32}H_{76}N_4O_{30}P_8Zn_6$ : C, 23.48; H, 4.68; N, 3.42; P, 15.14; Zn, 23.96. Found: C, 23.59%; H, 4.75%; N, 3.35%; P, 15.25%; Zn, 23.82%.

- [18] *Crystal structure analysis*: The data were collected at a temperature of  $293 \pm 2$  K on a Bruker Smart APEX II X-diffractometer equipped with graphite monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.71073$  Å). An empirical absorption correction was applied using the SADABS program with  $T_{\max} = 0.8274$  and  $T_{\min} = 0.6342$ . The structure was solved in the space group  $C2/c$  by direct method and refined by the full-matrix least-squares fitting on  $F^2$  using SHELXTL-97 [24]. All non-hydrogen atoms were treated anisotropically. Hydrogen atoms of organic ligands were generated geometrically, fixed isotropic thermal parameters, and included in the structure factor calculations. *Crystal data for I*:  $C_{32}H_{76}N_4O_{30}P_8Zn_6$ ,  $M = 1636.95$ , monoclinic,  $C2/c$ ,  $a = 28.274(3)$  Å,  $b = 17.8155(19)$  Å,  $c = 26.539(3)$  Å,  $\beta = 106.603(2)^\circ$ ,  $V = 12810(2)$  Å<sup>3</sup>,  $Z = 8$ ,  $D_c = 1.698$  g cm<sup>-3</sup>,  $\mu = 2.492$  mm<sup>-1</sup>. Data were collected on a single-crystal with dimensions  $0.20 \times 0.09 \times 0.08$  mm<sup>3</sup>. 34,703 reflections were measured with  $\omega$ -scans, in the range of  $1.94^\circ \leq \theta \leq 26.18^\circ$  ( $-24 \leq h \leq 35$ ,  $-20 \leq k \leq 22$ ,  $-32 \leq l \leq 32$ ), 12,748 independent reflections ( $R_{\text{int}} = 0.0626$ ). Final  $R_1 = 0.0670$ ,  $wR_2 = 0.1735$  [ $I > 2\sigma(I)$ ], and the goodness-of-fit on  $F^2$  is 1.020.
- [19] The X-ray powder diffraction data was collected on a Bruker AXS D8 Advance diffractometer using Cu  $K\alpha$  radiation ( $\lambda = 1.5418$  Å) in the  $2\theta$  range of  $3\text{--}35^\circ$  with a step size of  $0.02^\circ$ .
- [20] The infrared spectrum was recorded from a KBr pellet by use of a Bruker AXS TENSOR-27 FT-IR spectrometer in the range  $4000\text{--}400$  cm<sup>-1</sup>.
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