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Journal of Solid State Chemistry 170 (2003) 303–307

JOURNAL OF
SOLID STATE
CHEMISTRY

http://elsevier.com/locate/jssc

$(C_6H_{16}N_2)Zn_3(HPO_3)_4H_2O$: a new layered zinc phosphite templated by diprotonated *trans*-1,4-diaminocyclohexane

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Received 1 July 2002; received in revised form 13 September 2002; accepted 24 September 2002

Abstract

Employing *trans*-1,4-diaminocyclohexane (*trans*-1,4-DACH) as a template, a new two-dimensional layered zinc phosphite $(C_6H_{16}N_2)Zn_3(HPO_3)_4H_2O$ (**1**) has been prepared hydrothermally. Single-crystal X-ray diffraction analysis shows that it crystallizes in the monoclinic space group $P2_1/n$ with $a = 10.458(2) \text{ \AA}$, $b = 14.720(3) \text{ \AA}$, $c = 13.079(3) \text{ \AA}$, $\beta = 97.93(3)^\circ$, $V = 1994.1(7) \text{ \AA}^3$, $Z = 4$, $R_1 = 0.0349$ ($I > 2\sigma(I)$) and $wR_2 = 0.0605$ (all data). The inorganic layer is built up by alternation of ZnO_4 tetrahedra and HPO_3 pseudo pyramids forming a 4.6.8-net. The sheet is featured by a series of capped six-membered rings. The diprotonated *trans*-1,4-DACH molecules reside in the interlayer region and interact with the inorganic network through H-bonds.

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Keywords: Layer; Zinc phosphite; Hydrothermal synthesis; Structure; H-bonds

1. Introduction

Organically templated metal phosphates have received much attention in recent years because of their potential applications in catalysis, separation and as functional materials [1–3]. These materials are generally prepared under hydrothermal or solvothermal conditions in the presence of organic amine as a structure-directing agent. The employment of organic amines has promoted the formation of various metal phosphates with interesting three-dimensional (3-D) open-framework, 2-D layer and 1-D chain structures. Some metal phosphates possess analogous structures to zeolites, whilst others possess unique structural architectures.

Among the metal phosphates, a range of organically templated zinc phosphates exhibits rich structural and compositional diversity. So far, over 80 kinds of organically templated zinc phosphates, which are typically built up by Zn-centered tetrahedra (in some cases there are $ZnO_4(H_2O)$ and $ZnO_4(H_2O)_2$ polyhedra) and $H_xP^VO_4^{3-x}$ tetrahedra ($x = 0-2$), have been successfully prepared [4–18]. Notable examples are zinc

phosphate ND-1 with 24-membered ring channels [5], and chiral zinc phosphates $[NH_3(CH_2)_2NH_2(CH_2)_2NH_3][ZnPO_4(HPO_4)]$ [8] and $[Na_{12}(H_2O)_{12}][Zn_{12}P_{12}O_{48}]$ [9]. However, the reports of organically templated zinc phosphites are still rare [19–21]. The zinc phosphites, typically built up by Zn-centered tetrahedra (ZnO_4 and ZnO_3N) and P-centered $HP^{III}O_3^{2-}$ pseudopyramids, also exhibit interesting structural architectures. There are $(NC_5H_{12})_2Zn_3(HPO_3)_4$ with 16-membered ring windows [19], and $[H_2N(CH_2)_2NH_2] \cdot 0.5ZnHPO_3$ [20] and $(N_4C_2H_4)ZnHPO_3$ [21] containing a similar 4.8-net.

In this work, we use *trans*-1,4-diaminocyclohexane (*trans*-1,4-DACH) as a structure-directing agent, and successfully prepare a new layered zinc phosphite with a 4.6.8-net. Its 4.6.8-net is reminiscent of the 4.6.8-net of a series of 2-D layered aluminophosphates with $Al_3P_4O_{16}^{3-}$ stoichiometry [22–27], both of which are featured by the capped six-membered rings.

2. Experimental section

The title compound was synthesized by a hydrothermal reaction of a mixture of $Zn(OAc)_2 \cdot 2H_2O$, H_3PO_3 , *trans*-1,4-DACH, and H_2O with molar compositions

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1.0:(2.5–3.0): (1.0–1.5): 488. Typically, 0.25 g of $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ was first dissolved in 10 ml of H_2O , then 0.28 g H_3PO_3 was added with stirring. Finally, 0.13 g of *trans*-1,4-DACH was added to the above reaction mixture. A gel was formed and further stirred for 1 h until it was homogeneous. The reaction mixture with a pH value of ca. 4.0 was sealed in a Teflon-lined stainless-steel autoclave and then heated at 200°C for 8 d under static condition. The product containing large plate-like single crystals was separated by sonication and further washed by distilled water and then air-dried. The experimental and simulated X-ray powder diffraction (XRD) patterns of the product collected on a Siemens D5005 diffractometer with $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) are in agreement with each other, proving its phase purity.

Inductively coupled plasma (ICP) analysis performed on a Perkin-Elmer Optima 3300DV spectrometer indicates that the product contains 30.1 and 18.8 wt% of Zn and P, respectively (calcd 30.18 and 19.07 wt%, respectively). The elemental analysis conducted on a Perkin-Elmer 2400 elemental analyzer gives that it contains 11.04, 3.73, 4.38 wt% of C, H and N, respectively (calcd 11.08, 3.42 and 4.34 wt%, respectively). The compositional analysis results are in agreement with those calculated values based on the empirical formula of $\text{C}_6\text{H}_{22}\text{N}_2\text{O}_{13}\text{P}_4\text{Zn}_3$ given by single-crystal structure analysis.

A Perkin-Elmer TGA 7 unit was used to carry out the thermogravimetric analysis (TGA) in air with a heating rate of 10°C/min. The TG profile shows an obvious weight loss of 2.8 wt% around 240°C, which is attributed to the loss of H_2O (calcd 2.79 wt%) in the product, and the weight loss of 17.2 wt% around 370°C is attributed to the decomposition of *trans*-1,4-DACH (calcd 17.26 wt%) occluded in the interlayer region. XRD analysis indicated that the compound became amorphous after the decomposition of the occluded template molecules.

A suitable single crystal with dimensions $0.14 \times 0.07 \times 0.03 \text{ mm}^3$ was selected for single-crystal X-ray diffraction analysis. The intensity data were collected on a Rigaku R-AXIS RAPID IP diffractometer by oscillation scans using graphite-monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Cell refinement and data reduction were accomplished with the RAPID AUTO program. The structure was solved by the direct methods and refined on F^2 by full-matrix least squares using SHELXTL97. The Zn and P atoms were easily located, and O, C, N, and H atoms in HPO_3 were subsequently located in the difference Fourier maps. The C–H hydrogen atoms were located geometrically. H atoms associated with the water molecule were not located. Diprotonation of the 1,4-DACH molecules was suggested on the basis of charge balance. All non-hydrogen atoms were refined with anisotropic thermal

parameters. Experimental details for the structure determination are presented in Table 1. The selected bond distances and bond angles are presented in Table 2.

Table 1
Crystal data and structure refinement for **1**

| | |
|--------------------------------------|--|
| Empirical formula | $\text{C}_6\text{H}_{22}\text{N}_2\text{O}_{13}\text{P}_4\text{Zn}_3$ |
| Formula weight | 650.25 |
| Temperature | 293(2) K |
| Wavelength | 0.71073 Å |
| Crystal system, space group | Monoclinic, $P2_1/n$ |
| Unit-cell dimensions | $a = 10.458(2) \text{ \AA}$ $\alpha = 90^\circ$ $b = 14.720(3) \text{ \AA}$ $\beta = 97.93(3)^\circ$ $c = 13.079(3) \text{ \AA}$ $\gamma = 90^\circ$ |
| Volume | $1994.1(7) \text{ \AA}^3$ |
| Z, Calculated density | 4, 2.166 Mg/m ³ |
| Absorption coefficient | 3.965 mm^{-1} |
| $F(000)$ | 1304 |
| Crystal size | $0.14 \times 0.07 \times 0.03 \text{ mm}$ |
| Theta range for data collection | $2.09\text{--}27.36^\circ$ |
| Limiting indices | $0 \leq h \leq 13$, $-18 \leq k \leq 19$, $-16 \leq l \leq 16$ |
| Reflections collected/unique | 8552/4489 [$R(\text{int}) = 0.0390$] |
| Completeness to theta | $= 27.36$, 99.2% |
| Refinement method | Full-matrix least-squares on F^2 |
| Data/restraints/parameters | 4489/0/269 |
| Goodness-of-fit on F^2 | 0.967 |
| Final R indices [$I > 2\sigma(I)$] | $R_1 = 0.0349$, $wR_2 = 0.0559$ |
| R indices (all data) | $R_1 = 0.0701$, $wR_2 = 0.0605$ |
| Largest diff. Peak and hole | 0.557 and $-0.418 \text{ e \AA}^{-3}$ |

Table 2
Selected bond lengths (Å) and angles (°) for **1**.

| | | | |
|---------------------|------------|---------------------|------------|
| Zn(1)–O(3) | 1.900(3) | Zn(1)–O(4) | 1.914(3) |
| Zn(1)–O(2) | 1.954(3) | Zn(1)–O(1) | 1.971(2) |
| Zn(2)–O(7) | 1.909(3) | Zn(2)–O(6) | 1.919(3) |
| Zn(2)–O(5) | 1.951(2) | Zn(2)–O(8) | 1.981(2) |
| Zn(3)–O(10) | 1.917(3) | Zn(3)–O(11) | 1.938(3) |
| Zn(3)–O(9) | 1.945(2) | Zn(3)–O(12) | 1.958(2) |
| P(1)–O(4) | 1.505(2) | P(1)–O(5) | 1.519(3) |
| P(1)–O(1)#1 | 1.530(2) | P(1)–H(1) | 1.27(3) |
| P(2)–O(3) | 1.510(3) | P(2)–O(11)#2 | 1.518(3) |
| P(2)–O(6) | 1.518(3) | P(2)–H(2) | 1.31(3) |
| P(3)–O(10)#2 | 1.501(3) | P(3)–O(7) | 1.505(3) |
| P(3)–O(9) | 1.531(3) | P(3)–H(3) | 1.33(3) |
| P(4)–O(12)#3 | 1.505(3) | P(4)–O(2)#4 | 1.511(3) |
| P(4)–O(8) | 1.531(2) | P(4)–H(4) | 1.33(4) |
| P(1)#1–O(1)–Zn(1) | 124.55(15) | P(4)#5–O(2)–Zn(1) | 134.90(17) |
| P(2)–O(3)–Zn(1) | 142.10(19) | P(1)–O(4)–Zn(1) | 139.48(17) |
| P(1)–O(5)–Zn(2) | 126.93(15) | P(2)–O(6)–Zn(2) | 131.44(16) |
| P(3)–O(7)–Zn(2) | 132.89(17) | P(4)–O(8)–Zn(2) | 124.83(14) |
| P(3)–O(9)–Zn(3) | 125.70(15) | P(3)#2–O(10)–Zn(3) | 150.17(18) |
| P(2)#2O(11)–Zn(3) | 127.84(17) | P(4)#6–Zn(12)–Zn(3) | 127.91(16) |
| N(1)–H(1E)...O(1W) | 2.789(4) | | 168.7 |
| N(1)–H(1C)...O(8)#5 | 2.851(4) | | 152.1 |
| N(1)–H(1D)...O(1) | 2.828(4) | | 163.3 |
| N(2)–H(2C)...O(5)#6 | 2.974(4) | | 166.4 |
| N(2)–H(2D)...O(8) | 2.991(4) | | 166.6 |
| N(2)–H(2E)...O(9) | 2.807(4) | | 163.9 |

Symmetry transformations used to generate equivalent atoms: #1– $x+1$, $-y-1$, $-z+1$; #2– $x+1$, $-y$, $-z+1$; #3– $x+1/2$, $y-1/2$, $-z+3/2$; #4 $x-1/2$, $-y-1/2$, $z+1/2$; #5 $x+1/2$, $-y-1/2$, $z-1/2$; #6– $x+1/2$, $y+1/2$, $-z+3/2$.

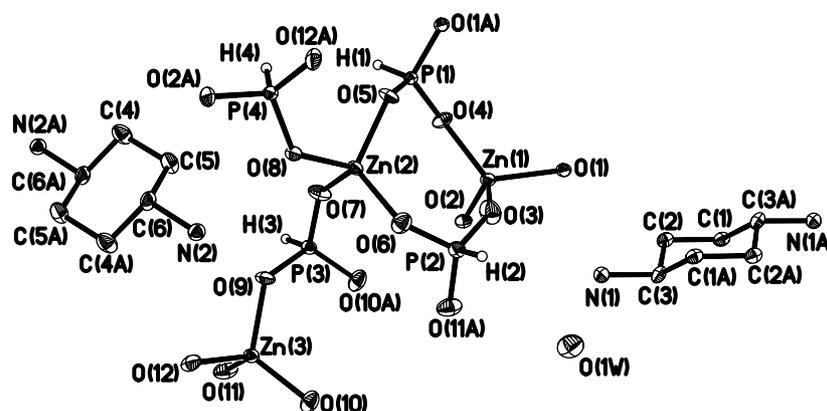


Fig. 1. Thermal ellipsoid plot (50%) showing the labeling scheme of **1**.

3. Result and discussion

Single-crystal structure analysis indicates that the title compound (**1**) has an empirical formula of $(C_6H_{16}N_2)Zn_3(HPO_3)_4H_2O$. Assuming the usual valence of Zn, P, O and H to be +2, +3, -2 and +1, respectively, the network stoichiometry of $[Zn_3(HPO_3)_4]$ creates a net charge of -2. The presence of one diprottonated 1,4-DACH molecule would account for +2. Each asymmetric unit, as seen in Fig. 1, contains three crystallographically distinct Zn atoms, each of which is tetrahedrally coordinated and shares four oxygen atoms with adjacent P atoms (Zn–O bond distances: 1.900(3)–1.981(2) Å). There are four crystallographically distinct P atoms. Each P atom has a terminal phosphite P–H bond (1.27(3)–1.33(4) Å) and shares three oxygens with adjacent Zn atoms (P–O bond 1.501(3)–1.531(3) Å).

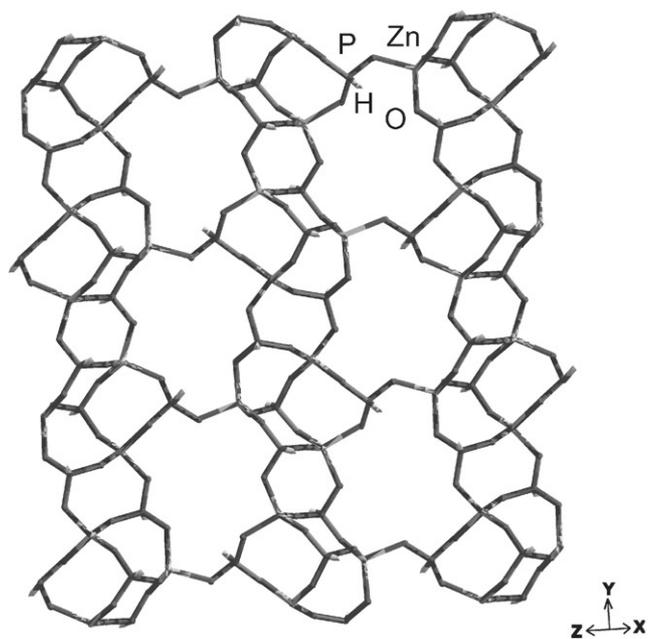
The strict alternation of ZnO_4 tetrahedra and HPO_3 pseudopyramids via oxygen vertices results in an anionic network with a Zn/P ratio of 3/4. Fig. 2a shows the inorganic sheet parallel to the (101) plane, which contains a 4.6.8-net with the P–H groups capping on the six-membered rings and alternating above and below the sheet. The orientation of the capped P–H groups is opposite to those three P–H groups in the six-membered rings. This 4.6.8-net structure has never been found in known zinc phosphates or zinc phosphites before. However, interestingly, this 4.6.8-net is reminiscent of the 2-D 4.6.8-net of a series of layered aluminophosphates, as seen in Fig. 2b, such as $[Al_3P_4O_{16}][NH_3(CH_2)_2NH_3][OH_2(CH_2)_2OH][OH(CH_2)_2OH]$ [22], $[Al_3P_4O_{16}] \cdot 3[CH_3CH_2NH_3]$ [23], $[Al_3P_4O_{16}] \cdot 3[CH_3CH_2CH_2NH_3]$ [24], $[Al_3P_4O_{16}][NH_3(CH_2)_5NH_3][C_5H_{10}NH_2]$ [25], $[Al_3P_4O_{16}][C_5H_{10}NH_2] \cdot 2[C_4H_7NH_3]$ [26] and $[Al_3P_4O_{16}][Co(tn)_3] \cdot 2H_2O$ [27] upon replacing the Zn atoms to Al atoms and the P–H groups to the P=O groups. They all contain a 3,4-connected 2-D 4.6.8-net, which is featured by a series of capped six-membered rings.

Fig. 3 shows the packing of the inorganic sheets along the [101] direction. It is noticed that the hydrogen atoms of the P–H groups exclusively protrude into the interlayer region. The diprottonated *trans*-1,4-DACH molecules and H_2O molecules reside in the interlayer region and interact with the host network through extensive H-bonds. There are two crystallographically distinct DACH molecules in the structure, both of which exist in a chair conformation. Each diprottonated 1,4-DACH cation provides a total of six H-bonds to the bridging oxygens in the sheets and H_2O molecules in the interlayer region. The N...O separations are in the range of 2.789 (4)–2.974(4) Å. Table 2 summarizes the H-bond information. In addition, it is measured in Cerius² that the distance of $O_{1w} \cdots O(2)$ is of 2.938 Å, indicating that there are H-bonds between the inorganic sheets and the H_2O molecules. The inorganic sheet structure cannot be kept upon removal of the occluded organic amine molecules by calcination. Therefore, the 1,4-DACH molecule not only plays a structure-directing role, but also plays a stabilizing role to the inorganic network.

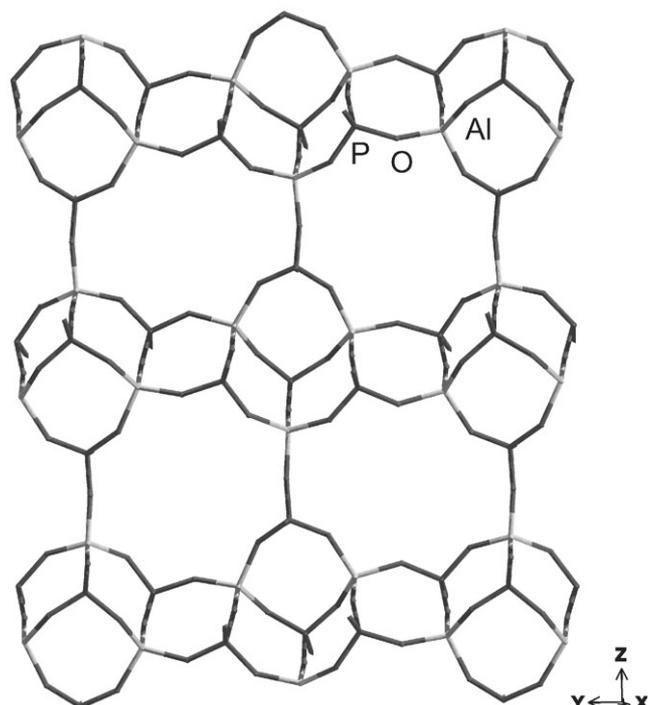
4. Conclusions

A new 2-D layered zinc phosphite $(C_6H_{15}N_2)Zn_3(HPO_3)_4H_2O$ has been prepared hydrothermally. Its inorganic sheet structure is built up from strict alternation of ZnO_4 tetrahedra and HPO_3 pseudopyramids, which defines a Zn/P ratio of 3/4. Its 4.6.8-net is reminiscent of that of a series of 2-D layered aluminophosphates with $Al_3P_4O_{16}^{3-}$ stoichiometry. The inorganic sheets are held together by diprottonated *trans*-1,4-DACH molecules through H-bonds. The title compound is the fourth organically templated zinc phosphite, and exhibits a new type of sheet structure.

¹Cerius²: Molecular Simulation/Biosystem Corporation, San Diego, 1995.



(a)



(b)

Fig. 2. (a) The 4.6.8-net sheet of **1** parallel to the (101) plane and (b) the 4.6.8-net of 2-D $\text{Al}_3\text{P}_4\text{O}_6^{3-}$ sheet (Ref. [23]).

It is believed that more zinc phosphites with interesting structural architectures will be continuously synthesized under suitable synthesis conditions.

Acknowledgments

This work is supported by the National Natural Science Foundation of China and the State Basic

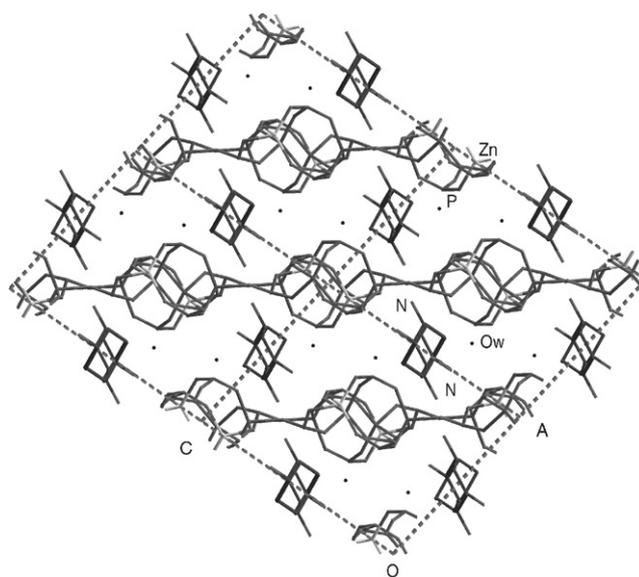


Fig. 3. Packing of the inorganic sheets along the [101] direction.

Research Project (G20000775) of China. J. Y. is thankful for the support by TRAPOYT of MOE, P. R. C.

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