

A Three-Dimensional Zinc-Phosphate Coordination Polymer: Hydrothermal Synthesis and Structure of $Zn_3(PO_4)_2(H_2O)$

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3차원 Zinc-Phosphate 배위 고분자: $Zn_3(PO_4)_2(H_2O)$ 의 수열합성 및 구조

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성균관대학교 화학과

Abstract

The hydrothermal reaction between zinc(II) nitrate ($Zn(NO_3)_2 \cdot 6H_2O$) and potassium phosphate dibasic (K_2HPO_4) in the presence of pyrazine gave a three-dimensional zinc-phosphate coordination polymer with an empirical formula of $Zn_3(PO_4)_2(H_2O)$ (**1**). Compound **1** was characterized by IR spectroscopy and X-ray diffraction. Crystallographic data for **1**: monoclinic space group, $P2_1/c$, $a = 8.750(1) \text{ \AA}$, $b = 4.901(1) \text{ \AA}$, $c = 16.759(3) \text{ \AA}$, $\beta = 94.98(2)^\circ$, $Z = 4$, $R(wR_2) = 0.0332(0.0927)$.

요 약

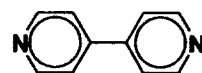
Pyrazine 존재 하에서, $Zn(NO_3)_2 \cdot 6H_2O$ 와 K_2HPO_4 가 수열반응하여 $Zn_3(PO_4)_2(H_2O)$ (**1**) 실험식을 갖는 3차원 zinc-phosphate 배위 고분자가 합성되었다. 화합물 **1**의 구조가 IR 분광법 및 X-ray 회절법으로 규명되었다. 화합물 **1**의 결정학적 자료: 단사정계 공간군 $P2_1/c$, $a = 8.750(1) \text{ \AA}$, $b = 4.901(1) \text{ \AA}$, $c = 16.759(3) \text{ \AA}$, $\beta = 94.98(2)^\circ$, $Z = 4$, $R(wR_2) = 0.0332(0.0927)$.

1. Introduction

A large number of open-framework metal phosphates have been synthesized and characterized in recent years¹⁻⁵. The interest in these materials is largely due to their potential applications in catalysis, sorption, and separation processes. In particular, zinc-phosphate systems based on tetrahedral-building units have exhibited properties similar to those of zeolites.

In these days, the concept of "node-spacer", in which the node corresponds to a metal center and the spacer to a ligand, has become a fundamental tool in the design of crystalline architectures (crystal engineering)⁶. The most common spacers are linear, bifunctional ligands such as 4,4'-bipyridine

and pyrazine, which are expected to act as linear building blocks⁷. Depending on the metal node, 1-, 2-, and 3-dimensional coordination polymers are formed.



4,4'-bipyridine



pyrazine

We have recently become interested in employing pyrazine as a linear spacer to prepare new coordination polymers. When we treated zinc(II) nitrate with pyrazine in the presence of a base (K_2HPO_4), we obtained a three-dimensional zinc-phosphate coordination polymer with an empirical formula of $Zn_3(PO_4)_2(H_2O)$ (**1**). Herein, we report the preparation and structure of the polymer **1**, which has an

open-framework structure built from four- and five-coordinate zinc metals and tetrahedral PO_4^{3-} ions.

2. Experimental Section

Glassware was soaked in KOH-saturated 2-propanol for about 24 h and washed with distilled water and acetone before use. Glassware was either flame- or oven-dried. $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and potassium phosphate dibasic (K_2HPO_4) were purchased from Aldrich company. Pyrazine was purchased from Fluka company.

IR spectra were recorded with a Nicolet 205 FTIR spectrophotometer. Elemental analyses were performed with EA1110 (CE instrument, Italy) by the Korea Basic Science Institute.

Preparation of $\text{Zn}_3(\text{PO}_4)_2(\text{H}_2\text{O})$ (1). A mixture of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.150 g, 0.504 mmol), K_2HPO_4 (0.100 g, 0.504 mmol), pyrazine (0.04 g, 0.504 mmol), and H_2O (6.0 ml, 0.333 mol) in the mole ratio of 1 : 1 : 1 : 660 was heated in a 23-ml capacity Teflon-lined reaction vessel at 180°C for 3 days and then cooled to room temperature by air-cooling. The crystalline product was collected by filtration, washed with H_2O (2×5 ml), and air-dried to give colorless crystals of $\text{Zn}_3(\text{PO}_4)_2(\text{H}_2\text{O})$ (0.0577 g, 0.143 mmol, 85% yield).

Anal. Calcd for $\text{Zn}_3\text{P}_2\text{O}_9\text{H}_2$ ($M_r = 404.07$): C, 0.00; H, 0.50; N, 0.00. Found: C, 0.00; H, 0.54; N, 0.00. IR (KBr): 3386 (OH), 3316 (OH), 1158, 1048, 1006, 948, 631, 573 cm^{-1} .

X-ray Structure Determination. All X-ray data were collected with use of a Siemens P4 diffractometer equipped with a Mo X-ray tube and a graphite-crystal monochromator. The orientation matrix and unit-cell parameters were determined by least-squares analyses of the setting angles of 34 reflections in the range $15.0 < 2\theta < 25.0^\circ$. Three check-reflections were measured every 100 reflections throughout data collection and showed no significant variations in intensity. Intensity data were corrected for Lorentz and polarization effects. Decay corrections were also made. The intensity data were empirically corrected for absorption with ω -scan data. All calculations were carried out with use of the SHELXTL programs⁸⁾.

Table 1. X-ray data collection and structure refinement for 1

formula	$\text{H}_2\text{O}_9\text{P}_2\text{Zn}_3$
fw	404.07
temperature, K	295(2)
crystal system	monoclinic
space group	$P2_1/c$
a , Å	8.750(1)
b , Å	4.901(1)
c , Å	16.759(3)
β , deg	94.98(2)
V , Å ³	715.9(2)
Z	4
d_{cal} , g cm^{-3}	3.749
μ , mm^{-1}	10.444
T_{min}	0.1035
T_{max}	0.3505
$F(000)$	776
No. of reflections measured	1315
No. of reflections unique	1228
No. of reflections with $I > 2\sigma(I)$	1181
No. of parameters refined	134
2 range ($^\circ$)	3.5~50.0
scan type	ω
scan speed	variable
GOF (goodness-of-fit on F^2)	1.107
Max., min. in ($e \text{ \AA}^{-3}$)	0.744, -0.811
R	0.0332
wR_2	0.0927

$$^a wR_2 = [w(F_o^2 - F_c^2)^2] / [w(F_o^2)^2]^{1/2}$$

A colorless crystal of approximate dimensions $0.40 \times 0.36 \times 0.12 \text{ mm}^3$, shaped as a plate, was used for crystal and intensity data collection. The unit-cell parameters and systematic absences, $h0l$ ($l = 2n + 1$) and $0k0$ ($k = 2n + 1$), unambiguously indicated $P2_1/c$ as a space group. The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located in the difference Fourier map.

Details on crystal data and intensity collection are given in Table 1. Final atomic coordinates and some selected bond distances and bond angles are shown in Tables 2 and 3, respectively.

3. Results and Discussion

Preparation. The title compound has been prepared by hydrothermal reactions. Zinc(II) nitrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) reacts with K_2HPO_4 at 180°C in

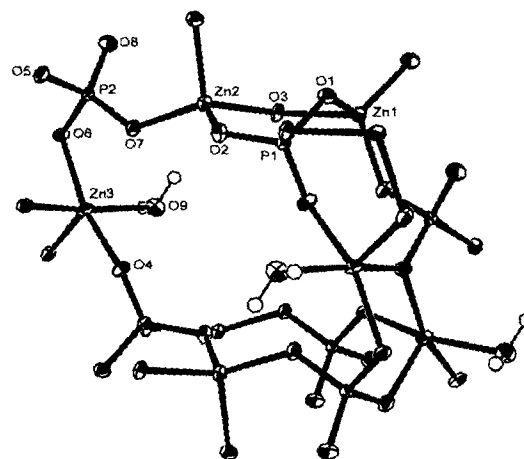
Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$)

	x	y	z	$U(\text{eq})^a$
Zn(1)	9359(1)	2014(1)	1547(1)	13(1)
Zn(2)	8285(1)	2012(1)	-553(1)	13(1)
Zn(3)	5804(1)	4954(1)	1804(1)	14(1)
P(1)	8183(1)	7063(2)	560(1)	10(1)
P(2)	7366(1)	4888(2)	-2170(1)	10(1)
O(1)	9638(3)	-1484(7)	973(2)	14(1)
O(2)	7828(4)	-1763(6)	-285(2)	15(1)
O(3)	8622(3)	3982(6)	492(2)	12(1)
O(4)	6868(4)	7441(7)	1072(2)	15(1)
O(5)	7584(4)	2352(7)	2177(2)	15(1)
O(6)	5933(3)	8324(6)	2582(2)	13(1)
O(7)	6951(3)	3424(7)	-1407(2)	14(1)
O(8)	11164(3)	3469(8)	2089(2)	20(1)
O(9)	5285(4)	2336(8)	820(2)	21(1)

^aEquivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

the presence of pyrazine to give $Zn_3(PO_4)_2(H_2O)$ (1), a three-dimensional polymer. A bifunctional, rodlike pyrazine was added in hopes of its role as a linear spacer, but it appeared not to be involved in the reaction. However, we cannot rule out the possibility that pyrazine acts as a base to accept a proton from K_2HPO_4 during the reaction. The incorporation of the phosphate ion (PO_4^{3-}) instead of pyrazine into the product suggests that the phosphate ion has a higher coordinating power compared with pyrazine in this reaction.

Compounds 1 has been obtained as colorless

**Fig. 1. ORTEP drawing of the local coordination environments of the Zn metals in compound 1.**

crystals in a relatively high isolation-yield (85%). It has been characterized by elemental analysis, IR spectroscopy, and X-ray diffraction. It is air-stable and is not soluble in common organic solvents. In the IR spectrum, the O-H stretching modes appear at 3386 and 3316 cm^{-1} .

Structure. The building unit of $Zn_3(PO_4)_2(H_2O)$ (1) is shown in Fig. 1, and the complete crystal structure is illustrated in Fig. 2. Compound 1 forms a three-dimensional polymeric species whose empirical formula is $Zn_3P_2O_9H_2$. The repeating unit in the polymer consists of three zinc(II) metals, two phosphate ligands, and one aqua (H_2O) ligand.

Table 3. Selected bond distances (\AA) and bond angles ($^\circ$) in 1

Zn1-O8	1.892(3)	Zn1-O5	1.959(3)	Zn1-O1	1.991(3)
Zn1-O3	2.067(3)	Zn2-O7	1.897(3)	Zn2-O2	1.953(3)
Zn2-O3	1.999(3)	Zn2-O1#1	2.022(3)	Zn3-O4	2.013(3)
Zn3-O5	2.067(3)	Zn3-O6#2	2.069(3)	Zn3-O6	2.102(3)
Zn3-O9	2.107(4)				
O8-Zn1-O5	112.2(1)	O8-Zn1-O1	115.1(1)	O5-Zn1-O1	118.0(1)
O8-Zn1-O3	114.8(1)	O5-Zn1-O3	102.6(1)	O1-Zn1-O3	91.8(1)
O7-Zn2-O2	113.2(1)	O7-Zn2-O3	121.3(1)	O2-Zn2-O3	105.9(1)
O7-Zn2-O1#1	107.3(1)	O2-Zn2-O1#1	99.6(1)	O3-Zn2-O1#1	107.3(1)
O4-Zn3-O5	100.5(1)	O4-Zn3-O6#2	159.3(1)	O5-Zn3-O6#2	100.3(1)
O4-Zn3-O6	84.2(1)	O5-Zn3-O6	107.4(1)	O6#2-Zn3-O6	89.8(1)
O4-Zn3-O9	88.4(1)	O5-Zn3-O9	88.1(1)	O6#2-Zn3-O9	92.1(1)
O6-Zn3-O9	163.8(1)				

Symmetry transformations used to generate equivalent atoms: #1 = $-x + 2, -y, -z$; #2 = $-x + 1, y - 1/2, -z + 1/2$; #3 = $-x + 1, -y + 1, -z$

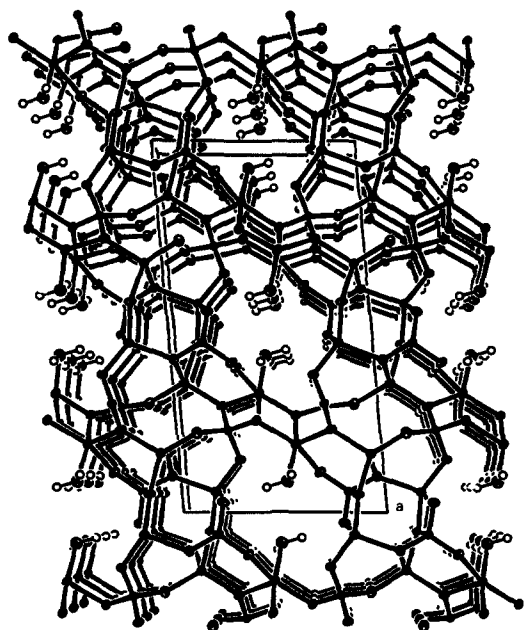


Fig. 2. A perspective view of the building blocks along the *b*-axis.

Three zinc metals have distinct coordination environments. Two zinc metals (Zn1 and Zn2) have a tetrahedral geometry, with four phosphate oxygen atoms. The Zn-O bond distances are in the range of 1.892~2.022 Å, which are comparable to those found for four-coordinate zinc(II) complexes⁹⁻¹¹. The third zinc metal (Zn3) has a pseudo-trigonal bipyramidal geometry, in which the two oxygen atoms from two phosphates and one aqua ligand form an equatorial plane. The axial sites are occupied by another two phosphate oxygen atoms. The Zn-O bond distances around Zn3 are in the range of 2.013~2.017 Å, which are consistent with those found for five-coordinate zinc(II) complexes¹²⁻¹³.

The Zn-P distances {Zn1···P1: 3.102(1); Zn2···P1: 3.105(1); Zn2···P2: 3.098(1); Zn3···P1: 3.240(1) Å} are somewhat shorter than the sum of van der Waals radii of Zn (1.40 Å) and P (1.85 Å) atoms, indicating close intramolecular contacts. The hydrogen atoms in the aqua ligand are involved in the intermolecular hydrogen bonding of the type O-H···O.

Figure 2 shows a complicated 3-D polymeric structure of **1**. All oxygen atoms in PO₄³⁻ acts bridging ligands, connecting zinc metals to give a polymeric

structure. The size of a channel, formed along the *b*-axis, is approximately 3.79×5.64 Å. Considering the van der Waals radii of the host-framework atoms, this channel appears to be too small to accommodate even small guest molecules such as water. In particular, the aqua ligand is directed to the inside of the channel and therefore expected to inhibit the entering of the guest molecules.

In summary, we have structurally characterized Zn₃(PO₄)₂(H₂O) (**1**), prepared by the hydrothermal reaction of Zn(NO₃)₂·6H₂O with K₂HPO₄ in the presence of pyrazine in a mole ratio of 1 : 1 : 1.

4. Supplementary Material

Tables of full bond distances and bond angles, anisotropic thermal parameters, and atomic coordinates of hydrogen atoms are available from the author Soon W. Lee.

Acknowledgment

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References

- 1) Gier, T. E. and Stucky, G. D., *Nature*, **349**, 508 (1991).
- 2) Nenoff, T. M., Harrison, W. T. A., Gier, T. E. and Stucky, G. D., *J. Am. Chem. Soc.*, **119**, 2861 (1997).
- 3) Whang, D., Hur, N. H. and Kim, K., *Inorg. Chem.*, **34**, 3363 (1995).
- 4) Harrison, W. T. A., Nenoff, T. M., Gier, T. E. and Stucky, G. D., *Inorg. Chem.*, **31**, 5395 (1992).
- 5) Cao, G. and Mallouk, T. E., *Inorg. Chem.*, **30**, 1434 (1991).
- 6) Moulton, B. and Zaworotko, M. J., *Chem. Rev.*, **102**, 1629 (2001) and references therein.
- 7) Bourne, S. A., Mondal, A. and Zaworotko, M. J., *Cryst. Eng.*, **4**, 25 (2001) and references therein.
- 8) Bruker, SHELXTL, Structure Determination Software Programs, Bruker Analytical X-ray Instruments Inc., Madison, Wisconsin, USA (1997).
- 9) Lugmair, C. G., Tilley, T. D. and Rheingold, A.

- L., *Chem. Mater.*, **9**, 339 (1997).
- 10) Harrison, W. T. A. and Phillips, M. L. F., *Chem. Mater.*, **9**, 1837 (1997).
- 11) Neeraj, S. and Natarajan, S., *Chem. Mater.*, **12**, 2753 (2000).
- 12) Song, B., Reuber, J., Ochs, C. and Hahn, E., *Inorg. Chem.*, **40**, 1527 (2001).
- 13) Ruiz, R., Julve, M., Faus, J. and Bois, C., *Inorg. Chem.*, **36**, 3434 (1997).