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Synthesis and Structure of a Novel Layered Zincophosphate $Zn_4P_3O_{11}(OH)\cdot 3C_3N_2H_4$ with Organic Amine Acting as Ligand

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A novel two-dimensional zinc phosphate $Zn_4P_3O_{11}(OH)\cdot 3C_3N_2H_4$ in which the structure-directing organic amine acts as a ligand has been synthesized hydrothermally. The structure was solved by single-crystal X-ray diffraction analysis. Crystal data: triclinic, space group $P\bar{1}$ (No. 2) with lattice parameters $a = 9.5663(15)$ Å, $b = 9.8530(16)$ Å, $c = 12.3658(19)$ Å, $\alpha = 77.495(4)^\circ$, $\beta = 77.893(4)^\circ$, $\gamma = 68.175(3)^\circ$, $V = 1045.6(3)$ Å^3, $Z = 2$, $R_1[I > 2\sigma(I)] = 0.0309$, and $wR_2[I > 2\sigma(I)] = 0.0809$. Interestingly the structure involves a network of ZnO_4, PO_4, $PO_3(OH)$, and the unusual ZnO_3N and ZnO_2N_2 tetrahedra with shared vertices. There are 10-membered rings in the layers, in which the structure-directing imidazole molecules reside. The other amine molecules protrude from the Zn centers and occupy spaces between the layers. © 2002 Elsevier Science (USA)

Key Words: **hydrothermal synthesis; zinc phosphates; structure-directing agent; imidazole.**

INTRODUCTION

In the past decade, a large number of zinc phosphates with vast structural and compositional diversities have been prepared in both hydrothermal and solvothermal systems (1–22). These compounds occur as one-dimensional (chains or ladders), two-dimensional (layers), and three-dimensional structures. Several zinc phosphates possessing helical channels (23), chiral frameworks (24), and gigantic pores (25, 26) are more interesting. The syntheses typically involve the addition of organic amines. It is proposed that in most cases, the amine acts as a structure-directing agent when the shapes of the amine and framework are related (27). Moreover, there are only a few examples of zinc phosphates in which the organic amine acts not only as a structure-directing agent but also as a ligand to Zn (28, 29). Recently, C. N. R. Rao and co-workers reported such a dual role of the organic amine in several open-framework zinc phosphates by using diamine (30), triamine (31), and tetramine (32). In this paper, we present the synthesis and crystal structure of a new two-dimensional open-framework zincophosphate, $Zn_4P_3O_{11}(OH)\cdot 3C_3N_2H_4$, where the amine molecules are bound to Zn in addition to being the structure-directing agents. The structure is formed by networking of ZnO_4, PO_4, $PO_3(OH)$, and unique ZnO_3N and ZnO_2N_2 moieties, leading to the formation of a layered structure. The presence of 3-, 4-, 5-, and 10-membered rings and the finite –Zn–O–Zn– linkages within the layers are noteworthy.

EXPERIMENTAL

Synthesis and Characterization

The compound was synthesized from a mixture of zinc oxide (99.5%, Shanghai Chemical Reagent Factory), phosphoric acid (85 wt%, Beijing Chemical Plant), imidazole (99.0%, Beijing Chemical Plant), and deionized water. The molar composition of the initial mixture was $ZnO : H_3PO_4 : \text{imidazole} : H_2O = 1:1:2:90$. In a typical synthesis, 0.6 g of zinc oxide and 1.0 g of imidazole were mixed well in 12 ml of water. Then 0.5 ml of phosphoric acid was added dropwise with vigorous stirring and the mixture was stirred for 2 h. This mixture with a pH of 7.0 was transferred to a Teflon-lined stainless autoclave (70% filling rate) and heated at 453 K for 3 days. Blocklike crystal product was recovered by filtration, washed thoroughly with distilled water, and dried at room temperature. The estimated yield of the typical batch was ca. 0.8 g (in about 58% yield on the basis of the Zn source).

Powder X-ray diffraction (XRD) data were collected on a Siemens D5005 diffractometer with Cu$K\alpha$ radiation ($\lambda = 1.5418$ Å). The step size was 0.02° and the count time was 4 s. The powder X-ray diffraction pattern of the title compound reveals good agreement with that simulated on the basis of single-crystal XRD structure analysis, showing that the product is a single phase. The element analyses were performed on a Perkin–Elmer 2400 element analyzer and the inductively coupled plasma (ICP) analysis was

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performed on a Perkin–Elmer Optima 3300 DV ICP spectrometer. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were conducted on–a Perkin–Elmer TGA 7 thermogravimetric analyzer and a Perkin–Elmer DTA1700 differential thermal analyzer, with a heating rate of 10°C min^{-1}.

Determination of Crystal Structure

A blocklike crystal of dimensions approximately $0.20 \times 0.15 \times 0.10$ mm was mounted on a glass fiber. The intensity data were collected on a Siemens Smart CCD diffractometer. The numbers of collected reflections and independent reflections were 5140 and 2978, respectively. Data processing was accomplished with the SAINT processing program (33). The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using SHELXTL Version 5.1 (34). The zinc and phosphorus atoms were first located and the carbon, nitrogen, and oxygen atoms were found in difference Fourier maps. The hydrogen atoms of the amine molecule were placed geometrically and allowed to ride on the atoms to which they were attached with fixed isotropic thermal parameters. Crystal data and details of data collection and refinement are given in Table 1.

TABLE 1
Crystal Data and Structure Refinement for $Zn_4P_3O_{11}(OH)\cdot 3C_3N_2H_4$

Empirical formula	$C_9H_{13}N_6O_{12}P_3Zn_4$
Formula weight	751.64
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	$a = 9.5663(15)$ Å, $\alpha = 77.495(4)^\circ$ $b = 9.8530(16)$ Å, $\beta = 77.893(4)^\circ$ $c = 12.3658(19)$ Å, $\gamma = 68.175(3)^\circ$
Volume	1045.6(3) $Å^3$
Z	2
Density (calculated)	2.388 Mg/m^3
Absorption coefficient	4.837 mm^{-1}
$F(000)$	740
Crystal size	$0.20 \times 0.15 \times 0.10$ mm
θ range for data collection	1.70°–23.26°
Limiting indices	$-9 \le h \le 10$, $-10 \le k \le 10$, $-13 \le l \le 12$
Reflections collected/unique	5140/2978 [R(int) = 0.0220]
Completeness to $\theta = 23.24$	99.0%
Absorption correction	Empirical
Max. and min. transmission	0.6434 and 0.4446
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2978/0/307
Goodness-of-fit on F^2	1.112
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0309$, $wR_2 = 0.0809$
R indices (all data)	$R_1 = 0.0335$, $wR_2 = 0.0822$
Largest diff. peak and hole	0.494 and -0.895 $Å^{-3}$

RESULTS AND DISCUSSION

Characterization of ZnPO-Imidazole

The ICP analysis shows that the compound contains 35.61 wt% Zn and 12.72 wt% P, in good agreement with the values (34.94 wt% Zn, 12.42 wt% P) based on the single-crystal structure analysis. The elemental analysis shows that the C, H, and N contents are 14.58, 1.71, and 10.99 wt%, respectively (calculated: C, 14.43 wt%; H, 1.34 wt%; N, 11.23 wt%), corresponding to an empirical molar ratio of C:H:N = 1.0:1.4:0.65. These results are in accordance with the formula $Zn_4P_3O_{11}(OH)\cdot 3C_3N_2H_4$ obtained from the single-crystal analysis.

Thermogravimetric analysis of the compound shows a mass loss of ca. 31% in the region 300–900°C corresponding to the removal of the organic part and subsequent condensation from the structure (calcd 29.10%). After calcinations at 900°C for 1 h, the compound recrystallizes into α-$Zn_3(PO_4)_2$ (JCPDS: 29-1390) and β-$Zn_2P_2O_7$ (JCPDS: 34-1275) dense phases, as determined by powder XRD.

Description of the Structure

The final atomic coordinates and selected bond lengths are listed in Tables 2 and 3, respectively.

The asymmetric unit of the structure contains 4 nonequivalent zinc atoms, 3 phosphorus atoms, 12 oxygen atoms, and 3 imidazole molecules (Fig. 1).

Two of the zinc atoms Zn(3) and Zn(4) are tetrahedrally coordinated by O atoms. It is worth noting that Zn(1) is bound to N(1) and N(3) atoms in different imidazole molecules and to two O atoms, forming a tetrahedral ZnO_2N_2 unit, while Zn(2) is three-coordinated with O atoms, and the fourth connection needed for the tetrahedral arrangements comes from N(5) of the amine. The average values of Zn–O bond lengths d_{av} [Zn(1)–O/N] = 1.982(3) Å, d_{av}[Zn(2)–O/N] = 1.979(5), d_{av}[Zn(3)–O] = 1.946(3) Å, d_{av}[Zn(4)–O] = 1.949(3) Å and mean O/N–Zn–O/N bond angles O–Zn(1)–O/N = 109.56°, O–Zn(2)–O/N = 109.37°, O–Zn(3)–O = 109.15°, O–Zn(4)–O = 109.30° indicate that the environment around the Zn atom is tetrahedral. The values are in good agreement with those reported earlier (28, 29, 32).

The three independent P atoms represent three chemically distinct types of sites. Any of the three P atoms is tetrahedrally coordinated to four O atoms. P(1) makes three bonds to Zn(1), Zn(2), and Zn(3) via O(1), O(5), and O(6) bridges as well as to Zn(2) and Zn(4) via triply coordinated oxygen bridges to atom O(3). P(2) is connected to Zn(1), Zn(3), and Zn(4) via O(2), O(7), and O(10) bridges, and also to Zn(2) and Zn(3) through triply coordinated oxygen atom O(4). Thus, both P(1) and P(2) link five zinc atoms via four O atoms. P(3) makes three bonds to neighboring Zn(3) and Zn(4) atoms via three bridge oxygens O(8), O(9), and O(10),

and the last oxygen atom O(12) vertex is to a terminal –OH group. The P–O bond lengths are in the range 1.518–1.593 Å and O–P–O bond angles are in the range 105.66–114.11°, which occur in the expected range. The terminal P–OH bond shows its characteristic lengthening d[P(3)–O(12)] = 1.591(3) Å, relative to unprotonated P–O bonds (35).

Of the 12 oxygens in the asymmetric unit two are three-coordinated [O(3) and O(4)]. The Zn–O–Zn linkages are always accompanied by three-coordinated bridging oxygen atoms and the third coordination is to a phosphorus. Furthermore, the three-coordinated oxygen atoms result in the formation of three-membered rings in the material. Other examples with such three-coordinate have been observed (3, 4, 7, 14). One terminal oxygen atom attached by H(12) forms a hydrogen bond with the intralayer framework of oxygen atoms O(5), with $d_{O(12)-H(12)\cdots O(5)} = 2.746(4)$ Å and the angle of O(12)–H(12) ··· O(5) is 150.3°.

The subunit of the structure is built up from the vertex linkage of PO_4, $PO_3(OH)$, ZnO_4, ZnO_2N_2 and ZnO_3N moieties. The subunit is neutral and has the formula $Zn_8P_6O_{22}(OH)_2$. Each Zn(2) atom is surrounded by one three-membered ring [–Zn(2)–Zn(3)–P(1)–], one four-membered ring [–Zn(2)–P(1)–Zn(1)–P(2)–], and one five-membered ring [–Zn(2)–P(1)–Zn(3)–P(3)–Zn(4)–]. Two sets of these three-, four-, and five-membered rings are further

TABLE 2
Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å $\times 10^3$) for $Zn_4P_3O_{11}(OH)\cdot 3C_3N_2H_4$

Atom	x	y	z	U(eq)[a]
Zn(1)	1355(1)	7147(1)	6426(1)	23(1)
Zn(2)	1461(1)	3042(1)	10711(1)	18(1)
Zn(3)	−124(1)	1814(1)	8963(1)	17(1)
Zn(4)	3390(1)	5231(1)	9058(1)	17(1)
P(1)	1126(1)	4423(1)	8140(1)	15(1)
P(2)	1045(1)	−1595(1)	8501(1)	16(1)
P(3)	3242(1)	5901(1)	11553(1)	18(1)
O(1)	2068(3)	5037(3)	7142(2)	22(1)
O(2)	357(3)	8568(4)	7456(2)	25(1)
O(3)	1862(3)	4213(3)	9212(2)	19(1)
O(4)	10(3)	2135(3)	10475(2)	20(1)
O(5)	503(3)	4491(3)	11721(2)	21(1)
O(6)	1143(3)	2917(3)	7992(2)	20(1)
O(7)	1117(3)	−149(3)	8695(3)	23(1)
O(8)	−2150(3)	2520(4)	8645(3)	30(1)
O(9)	5256(3)	4117(3)	8212(2)	22(1)
O(10)	2648(3)	7284(3)	8429(3)	22(1)
O(11)	3463(3)	5010(3)	10631(3)	25(1)
O(12)	2553(4)	5054(4)	12659(3)	29(1)
N(1)	3287(5)	7191(4)	5446(3)	31(1)
N(2)	5218(7)	6603(6)	4142(5)	65(2)
N(3)	−243(5)	7651(5)	5447(3)	32(1)
N(4)	−1375(6)	7993(6)	4009(4)	44(1)
N(5)	3345(4)	1493(4)	11149(3)	25(1)
N(6)	5716(4)	363(5)	11422(4)	34(1)
C(1)	3709(8)	6954(6)	4412(5)	48(2)
C(2)	5788(8)	6593(8)	5048(7)	68(2)
C(3)	4603(7)	6958(6)	5847(5)	43(2)
C(4)	−171(6)	7184(6)	4513(4)	39(1)
C(5)	−2265(7)	9044(7)	4642(6)	53(2)
C(6)	−1563(7)	8841(6)	5520(5)	43(2)
C(7)	4642(6)	1653(6)	11194(4)	32(1)
C(8)	5104(6)	−716(6)	11543(5)	39(1)
C(9)	3629(6)	−16(5)	11375(4)	34(1)

[a] U(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

TABLE 3
Selected Bond Lengths [Å] for $Zn_4P_3O_{11}(OH)\cdot 3C_3N_2H_4$

Zn(1)–O(2)	1.940(3)	Zn(2)–O(5)	1.939(3)
Zn(1)–O(1)	1.993(3)	Zn(2)–N(5)	1.969(4)
Zn(1)–N(1)	1.996(4)	Zn(2)–O(4)	2.003(3)
Zn(1)–N(3)	2.000(4)	Zn(2)–O(3)	2.005(3)
Zn(3)–O(8)	1.896(3)	Zn(4)–O(10)	1.919(3)
Zn(3)–O(7)	1.915(3)	Zn(4)–O(11)	1.924(3)
Zn(3)–O(6)	1.973(3)	Zn(4)–O(9)	1.934(3)
Zn(3)–O(4)	2.000(3)	Zn(4)–O(3)	2.017(3)
P(1)–O(1)	1.522(3)	P(2)–O(10)#2	1.519(3)
P(1)–O(5)#1	1.526(3)	P(2)–O(2)#2	1.522(3)
P(1)–O(6)	1.527(3)	P(2)–O(7)	1.523(3)
P(1)–O(3)	1.569(3)	P(2)–O(4)#3	1.574(3)
P(3)–O(9)#4	1.518(3)	P(3)–O(11)	1.519(4)
P(3)–O(8)	1.519(3)	P(3)–O(12)	1.593(3)

Note. Symmetry transformations used to generate equivalent atoms: (#1) $-x, -y+1, -z+2$; (#2) $x, y-1, z$; (#3) $-x, -y, -z+2$; (#4) $-x+1, -y+1, -z+2$.

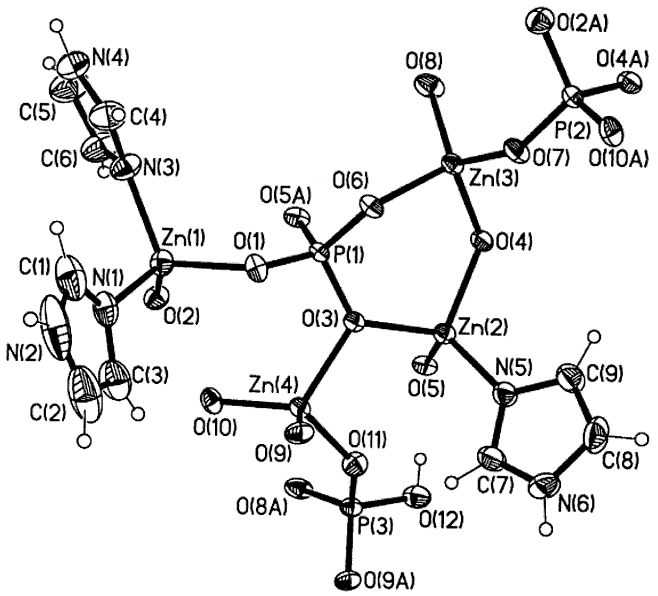

FIG. 1. ORTEP view of the $Zn_4P_3O_{11}(OH)\cdot 3C_3N_2H_4$ structure showing the atom labeling scheme (50% thermal ellipsoids).

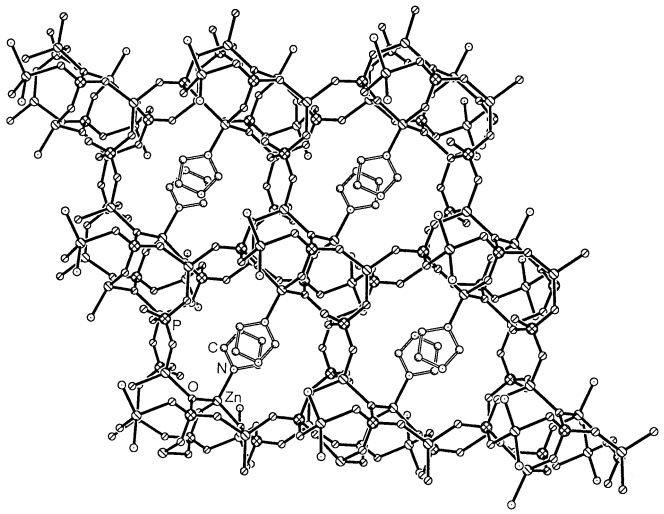

FIG. 2. Structure of $Zn_4P_3O_{11}(OH)\cdot 3C_3N_2H_4$, showing the 10-membered-ring layers along the [001] direction.

linked together by sharing oxygens to form subunits. The connectivity of the subunits via two coupled bridging atoms O(7) and two coupled bridging atoms O(9) forms infinite two-dimensional layers in the *ab* plane, as shown in Fig. 2. Within the layers, there are 10-membered rings {2[–Zn(2)–P(2)–Zn(3)–P(3)–Zn(4)–]}, which are rarely reported in the zinc phosphates (31), although they are commonly found in other open-framework systems. The 10-membered rings are occupied by nonprotonated imidazole molecules [N(5)N(6)C(7)C(8)C(9)] extending from Zn(2) atoms. The other two nonprotonated amine molecules [N(1)N(2)C(1)C(2)C(3)] and [N(3)N(4)C(5)C(6)C(7)] which coordinate to a Zn(1) atom are located in alternating layers viewed along the *a* axis (Fig. 3). One couple of imidazole molecules, [N(3)N(4)C(4)C(5)C(6)] and [N(3)N(4)C(4)C(5)C(6)], from adjacent layers are parallel to each other with a distance of 4.0716 Å, so there probably exist weak π–π interactions between the imidazole rings along the *b* axis (36). The other couple of amine molecules, [N(1)N(2)C(1)C(2)C(3)] and [N(1)N(2)C(1)C(2)C(3)], are also parallel with a distance of 6.0213 Å.

There are strong hydrogen bond interactions between the organic amine and the framework oxygen atoms [$N(2)\cdots O(1) = 2.852(6)$ Å and $N(4)\cdots O(6) = 2.750(5)$ Å] which help to hold the layers together. In addition, the N(6) atom forms an intralayer hydrogen bond with O(7) [$N(6)\cdots O(7) = 2.933(5)$ Å].

CONCLUSION

The present study established the structure of an interesting layered zinc phosphate in which the amine molecule acts not only as a structure-directing agent but also as a metal ligand. The Zn/P ratio in this zinc phosphate is 4/3 and the structure of the compound contains Zn–O–Zn linkages and 3-, 4-, 5-, and 10-membered rings. It would be of interest to investigate the role of the amines in the formation of open-

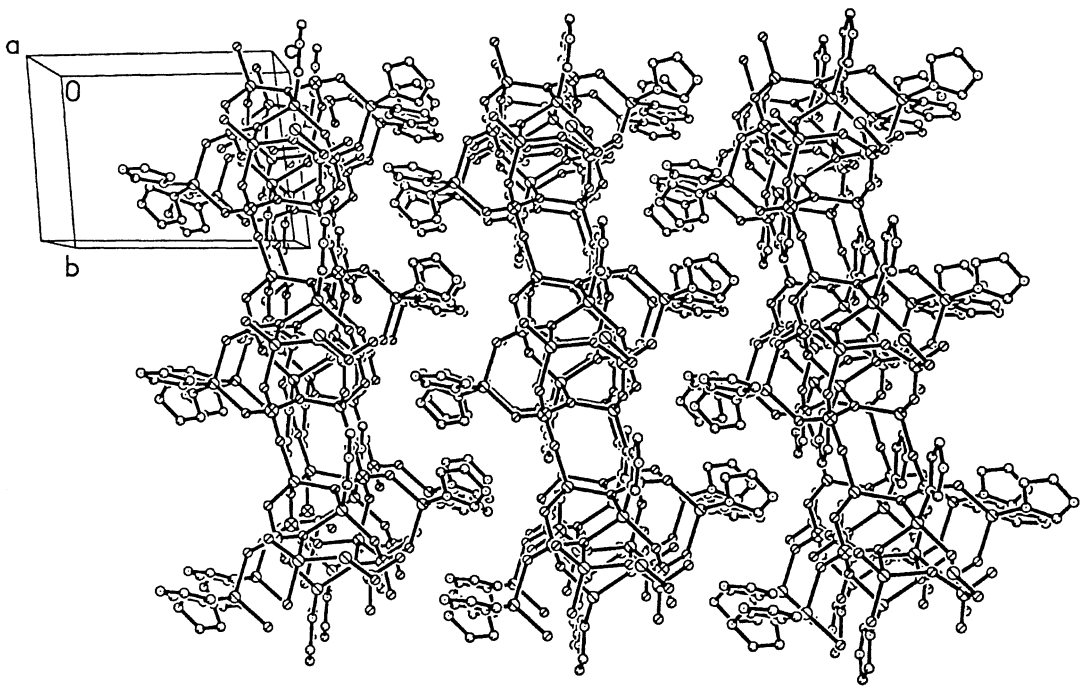

FIG. 3. Structure of $Zn_4P_3O_{11}(OH)\cdot 3C_3N_2H_4$, showing the alternating layers along the [100] direction.

framework structure more closely and explore other structures in which the amine plays different roles.

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