Hydrothermal Synthesis and Crystal Structure of $Zn_4(PO_4)_2(HPO_4)_2 \cdot 0.5(C_{10}H_{28}N_4) \cdot 2H_2O$, a New Layered Zinc Phosphate with 12-Ring Cavities

Ping Zhang,* Yue Wang,† Guangshan Zhu,* Zhan Shi,* Yunling Liu,* Hongming Yuan,* and Wenqin Pang*,[1]

*Key Laboratory of Inorganic Synthesis and Preparative Chemistry, Department of Chemistry, and
†Key Laboratory for Supramolecular Structure and Spectroscopy, Jilin University,
Changchun, 130023, People's Republic of China

Using 1, 4, 8, 11-tetraazacyclotetradecane (cyclam) as a template, a new layered zinc phosphate $Zn_4(PO_4)_2(HPO_4)_2 \cdot 0.5(C_{10}H_{28}N_4) \cdot 2H_2O$ (defined as ZnPO-cyclam) with 12-ring cavities was synthesized under hydrothermal conditions in a molar ratio $ZnO:P_2O_5:cyclam:H_2O = 1:2.2:0.5:284.7$ at 140°C for 3 days. The gel had a pH 4 at the starting period. The ZnPO-cyclam crystal structure is solved using single-crystal X-ray diffraction data at 293 K. It crystallizes in monoclinic space group $P2_1/c$ (no.14) with lattice parameters $a = 15.758(3)$ Å, $b = 9.0292(15)$ Å, $c = 15.543(3)$ Å, $\beta = 111.070$ (16). $V = 2063.7(7)$ Å^3, $Z = 4$, $R = 0.0392$, $wR = 0.0472$, 4166 collected reflections, 2794 observed reflections with $I > 2\sigma(I)$. The structure of ZnPO-cyclam consists of alternating inorganic and organic layers. The inorganic layers are built up from ZnO_4, $ZnO_3(H_2O)_2$, PO_4, and HPO_4 with Zn–O–Zn and Zn–O–P bonds. The protonated cyclam molecules in which the four nitrogen atoms are all protonated form the organic layers. Strong hydrogen bonding exists between the inorganic–organic layers, and there are 12-ring cavities in the inorganic layers, in which the template cyclam molecules reside. © 2000 Academic Press

INTRODUCTION

Works on the synthesis and characterization of new microporous materials continue apace, revealing an ever-increasing variety of framework compositions topologies. The study of the zinc–phosphorus–oxygen system by Gier and Stucky (1) resulted in the discovery of a number of new structural zinc phosphates (ZnPO) (2–29). Such new materials may have potential in catalysis and in other applications. In a zinc phosphate synthetic system, organic amines such as ethylamine (2), ethylenediamine (3–6), diethyltriamine (7, 8) and others (9–19) are usually used as templates to induce the new structures. Additionally, only a few examples of zinc phosphates contain organic amines (3, 7, 9, 10) among the layered ones. Recently, Morris *et al.* demonstrated that 1, 4, 8, 11-tetraazacyclotetradecane (cyclam) could be used to synthesize a new class of inorganic–organic hybrid materials (30). The study of macrocyclic polyamine systems and their metal complexes has attracted much interest, and they have been shown to possess interesting chemical and physical properties (31). We believe the use of cyclam and other cyclic polyamines as templates can provide novel materials.
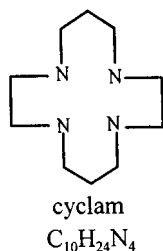
In this paper we present the synthesis and X-ray structural characterization of the zinc phosphate, $Zn_4(PO_4)_2(HPO_4)_2 \cdot 0.5(C_{10}H_{28}N_4) \cdot 2H_2O$ (defined as ZnPO-cyclam), containing cyclam as template and with alternating inorganic–organic layered structure.

EXPERIMENTAL

Synthesis and Characterization

ZnPO-cyclam was synthesized as follows: zinc acetate dihydrate (0.22 g, 99%, 1 mmol) and cyclam ($C_{10}H_{24}N_4$, 0.1 g, 98%, 0.5 mmol) were mixed well in water (5 ml, 284.7 mmol). To this clear solution, phosphoric acid (0.15 ml, 85%, 2.2 mmol) was added dropwise with vigorous stirring to form a precipitate. This mixture, which had a pH 4 at this stage, was loaded in a Teflon-lined stainless autoclave (50% filling rate), and heated at 140°C for 3 days. The product was filtered, washed with cold water, and dried at ambient temperature. The yield of the typical batch was approximately 0.16 g.

[1] To whom correspondence should be addressed. Fax: + 86-431-5671974. E-mail: wqpang@mail.jlu.edu.cn.

cyclam
$C_{10}H_{24}N_4$

TABLE 1
Crystal Data and Structure Refinement for ZnPO-cyclam

Empirical formula	$C_5H_{20}N_2O_{18}P_4Zn_4$
Formula weight	781.59
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	$a = 15.758(3)$ Å $\alpha = 90°$
	$b = 9.0292(15)$ Å $\beta = 111.070(16)°$
	$c = 15.543(3)$ Å $\gamma = 90°$
Volume	2063.7(7) Å^3
Z	4
Density (calculated)	2.516 Mg/m^3
Absorption coefficient	4.996 mm^{-1}
$F(000)$	1552
Crystal size	$0.100 \times 0.100 \times 0.030$ mm
θ range for data collection	1.38–23.22°
Limiting indices	$-17 \leq h \leq 5$, $-7 \leq k \leq 9$,
	$-14 \leq l \leq 17$
Reflections collected/unique	4166/2794 [R(int) = 0.0465]
Completeness to $\theta = 23.22$	94.7%
Max. and min. transmission	0.7449, 0.0609
Refinement method	full-matrix least-squares on F^2
Data/restraints/parameters	2794/19/358
Goodness-of-fit on F^2	1.063
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0392$, $wR_2 = 0.1131$
R indices (all data)	$R_1 = 0.0472$, $wR_2 = 0.1170$
Largest diff. peak and hole	0.802 and -0.981 e·Å^{-3}

The element analyses were performed on a Perkin–Elmer 2400C element analyzer and the inductively coupled plasma (ICP) analysis was performed on a Perkin–Elmer Optima 3300 DV ICP spectrometer. Thermogravimetric analysis (TGA) was carried out on a Perkin–Elmer thermogravimetric analyzer (TGA7) at a heating rate of 10°C min^{-1} in an atmospheric environment from room temperature to 700°C.

Powder X-ray diffraction (XRD) pattern was obtained on a Siemens D5005 X-ray diffractometer using CuKα radiation ($\lambda = 1.5418$ Å). The powder X-ray diffraction pattern of the title compound reveals good agreement with that simulated based on single-crystal XRD structure analysis, showing that the product is a single phase.

Determination of Crystal Structure

A rhombus colorless crystal of dimensions of $0.1 \times 0.1 \times 0.03$ mm was glued to a thin glass fiber with epoxy resin and mounted on a Siemens Smart CCD diffractormeter equipped with a normal-focus, 2.4 KW sealed-tube X-ray source (MoKα radiation $\lambda = 0.71073$ Å) operating at 50 kV and 40 mA. Intensity data were collected in 1271 frames with increasing ω (width of 0.3° per frame), as
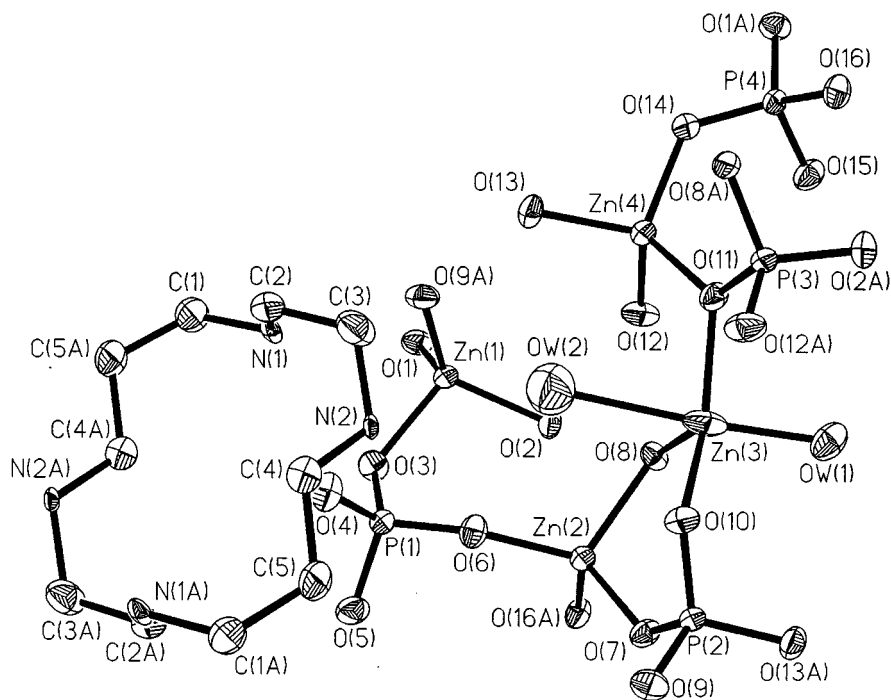

FIG. 1. Fragment of the $Zn_4(PO_4)_2(HPO_4)_2 \cdot 0.5(C_{10}H_{28}N_4) \cdot 2H_2O$ crystal structure (50% thermal ellipsoids) showing the atom-labeling scheme.

summarized in Table 1. The total numbers of measured reflections and observed unique reflections were 4166 and 2794, respectively. Agreement factor between equivalent reflections (R_{int}) was 0.0465. Systematic absence statistics of intensity distribution resulted in a space group $P2_1/c$ (No. 14) for the title compound. The structure was solved by direct methods. The zinc and phosphorus atoms were first located. Carbon, nitrogen, and oxygen atoms were found in the difference Fourier map. Hydrogen atoms were located by a combination of difference Fourier map and the HYDROGE program and were added to the structure factor calculation. The full-matrix least-squares refinements were against F^2 and included secondary extinction correction and anisotropic displacement parameters for nonhydrogen atoms. The structure solution and refinement were performed by using SHELXTL program system (version 5.1) (32). Details of crystal data, data collection, and structure refinement are listed in Table 1.

TABLE 2
Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{Å}^2 \times 10^3$) for ZnPO-cyclam[a]

Atom	x	y	z	U(eq)
Zn(4)	5122(1)	2120(1)	1336(1)	22(1)
Zn(2)	2748(1)	−19(1)	2819(1)	19(1)
Zn(1)	2457(1)	−80(1)	139(1)	19(1)
Zn(3)	4576(1)	2223(1)	3290(1)	31(1)
P(2)	3415(1)	2213(2)	4533(1)	17(1)
P(1)	1074(1)	1135(2)	985(1)	19(1)
P(3)	5867(1)	4387(2)	3040(1)	17(1)
P(4)	7135(1)	1818(2)	1442(1)	18(1)
O(1)	2355(3)	−1537(5)	−793(3)	25(1)
O(2)	3206(3)	−1001(5)	1288(3)	24(1)
O(3)	1247(3)	191(5)	244(3)	25(1)
O(4)	785(3)	2684(5)	632(3)	30(1)
O(5)	285(3)	355(6)	1220(3)	31(1)
O(6)	1886(3)	1187(5)	1879(3)	24(1)
O(7)	2929(3)	811(5)	4032(3)	21(1)
O(8)	3997(3)	288(5)	2753(3)	21(1)
O(9)	2708(3)	3150(5)	4755(3)	26(1)
O(10)	3825(3)	3102(5)	3921(3)	22(1)
O(11)	5333(3)	2960(5)	2593(3)	22(1)
O(12)	4713(3)	179(5)	1513(3)	29(1)
O(13)	4169(3)	3284(5)	442(3)	24(1)
O(14)	6137(3)	2224(5)	919(3)	25(1)
O(15)	7142(3)	358(6)	2015(3)	29(1)
O(16)	7621(3)	2956(5)	2163(3)	24(1)
OW1	5619(4)	1286(6)	4319(3)	35(1)
OW2	3370(5)	3138(9)	1912(5)	69(2)
N(1)	1162(4)	3955(7)	−774(4)	16(2)
N(2)	1627(4)	5329(7)	1183(4)	12(1)
C(1)	483(5)	3639(11)	−1712(5)	39(2)
C(2)	1318(5)	5502(10)	−525(5)	35(2)
C(3)	1994(5)	5758(10)	452(5)	35(2)
C(4)	870(5)	6301(10)	1221(5)	32(2)
C(5)	448(5)	5718(11)	1890(5)	35(2)

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

TABLE 3
Selected Bond Lengths (Å) and Angles (°) for ZnPO-cyclam

Zn(1)–O(1)	1.920(5)	Zn(1)–O(2)	1.940(4)
Zn(1)–O(3)	1.986(5)	Zn(1)–O(9)#2	1.928(4)
Zn(2)–O(16)#1	1.923(4)	Zn(2)–O(7)	1.953(4)
Zn(2)–O(6)	1.933(4)	Zn(2)–O(8)	2.026(4)
Zn(3)–O(10)	1.956(4)	Zn(3)–O(11)	1.992(4)
Zn(3)–O(8)	2.008(4)	Zn(3)–OW1	2.022(5)
Zn(3)–OW2	2.439(7)		
Zn(4)–O(12)	1.921(5)	Zn(4)–O(13)	1.948(4)
Zn(4)–O(14)	1.931(4)	Zn(4)–O(11)	2.011(4)
P(1)–O(4)	1.512(5)	P(1)–O(6)	1.514(5)
P(1)–O(3)	1.533(5)	P(1)–O(5)	1.583(5)
P(2)–O(9)	1.534(5)	P(2)–O(13)#3	1.550(5)
P(2)–O(7)	1.538(5)	P(2)–O(10)	1.552(5)
P(3)–O(2)#4	1.500(5)	P(3)–O(12)#4	1.513(5)
P(3)–O(8)#4	1.554(5)	P(3)–O(11)	1.558(5)
P(4)–O(16)	1.510(5)	P(4)–O(1)#5	1.521(4)
P(4)–O(14)	1.532(5)	P(4)–O(15)	1.589(5)
O(10)–Zn(3)–O(8)	107.18(19)	O(10)–Zn(3)–O(11)	136.5(2)
O(11)–Zn(3)–O(8)	109.67(18)	OW1–Zn(3)–OW2	172.5(2)
O(10)–Zn(3)–OW1	103.8(2)	O(8)–Zn(3)–OW1	94.8(2)
O(11)–Zn(3)–OW1	95.4(2)	O(10)–Zn(3)–OW2	83.2(2)
O(11)–Zn(3)–OW2	80.8(2)	O(8)–Zn(3)–OW2	80.6(2)
P(3)#1–O(8)–Zn(3)	127.8(3)	Zn(3)–O(11)–Zn(4)	118.7(2)
P(3)#1–O(8)–Zn(2)	112.4(2)	P(3)–O(11)–Zn(3)	111.6(2)
Zn(3)–O(8)–Zn(2)	113.7(2)	P(3)–O(11)–Zn(4)	128.2(3)
N(1)–C(2)	1.447(11)	N(1)–C(1)	1.494(9)
N(2)–C(3)	1.499(9)	N(2)–C(4)	1.499(10)
C(1)–C(5)#6	1.506(11)	C(2)–C(3)	1.525(11)
C(4)–C(5)	1.516(10)	C(5)–C(1)#6	1.506(11)
N(1)–C(1)–C(5)#6	114.5(6)	N(1)–C(1)–H(5A)	102(5)
N(1)–C(2)–C(3)	113.8(7)	N(2)–C(3)–C(2)	113.2(6)
N(2)–C(4)–C(5)	112.1(7)	C(1)#6–C(5)–C(4)	112.3(7)
C(2)–N(1)–C(1)	116.0(7)	C(3)–N(2)–C(4)	114.1(6)

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

RESULTS AND DISCUSSION

Characterization of ZnPO-cyclam

The ICP analysis gives that the ZnPO-cyclam contains 33.2 wt% Zn and 15.6 wt% P, suggesting that the molar ratio of Zn:P = 1:1, which is in good agreement with the value (33.5 wt% Zn and 15.8 wt% P) based on the single-crystal structure analysis. Elemental analysis indicates that the C, H, and N contents are 7.52, 2.61, and 3.46 wt%, respectively, corresponding to an empirical molar ratio of C:H:N = 4.84:20.31:2.00. These results are in accordance with the formula $Zn_4(PO_4)_2(HPO_4)_2 \cdot 0.5(C_{10}H_{28}N_4) \cdot 2H_2O$ obtained from the single-crystal analysis.

The TGA studies for ZnPO-cyclam carried out from room temperature to 700°C in air show a total weight loss of approximately 18.8% over the temperature range 120–400°C. The mass loss of 5.1% at approximately 190°C corresponds to the loss of two water molecules (calc. 4.6%)

and 13.4% at approximately 360°C corresponds to the loss of amine cyclam (calc. 13.1%). The loss of the amine resulted in the collapse of the layered structure of ZnPO-cyclam. The decomposed product (heated to > 600°C) was found to be poorly crystalline (powder XRD) phase with a majority of the reflection corresponding to a dense zinc phosphate Zn$_2$P$_2$O$_7$.

Description of the Structure

The fragment of ZnPO-cyclam is given in Fig. 1. Final atomic positional and thermal parameters for ZnPO-cyclam are presented in Table 2, and selected bond distance and bond angle data are summarized in Table 3, respectively.

ZnPO-cyclam exhibits a new layered structure and has 33 nonhydrogen atoms, all of which occupy general positions in the unit cell. The four independent zinc atoms in ZnPO-cyclam show distinct structural behavior: Zn(1), Zn(2), and Zn(4) are tetrahedral coordinated by O atoms with d_{av}[Zn(1)–O] = 1.943(9) Å, d_{av}[Zn(2)–O] = 1.959(4) Å, d_{av}[Zn(4)–O] = 1.953(2) Å, respectively. It is worth noting that the Zn(3) with d_{av}[Zn(3)–O] = 2.0838(8) Å is coordinated by three oxygen atoms, and two water molecules occupied the axial position to form a dis-

torted triganol bipyramid coordination environment. A similarly high coordination state of zinc atoms has been observed in other zinc phosphates (26, 29). In addition, Zn(2), Zn(3), and Zn(4) are linked together by two triply coordinated oxygen atoms O(8) and O(11) (shown in Fig. 3) so that the linkages of Zn–O–Zn are observed in the structure of ZnPO-cyclam.

The four independent P atoms represent four chemically distinct types of site; in each case the P atom is tetrahedral coordinated to four oxygen atoms. The P(1) atom forms two P–O–Zn bonds via oxygen bridges and has two uncoordinated oxygen atoms: O(5), a terminal –OH group with bond length d[P(1)–O(5)] = 1.583(5) Å and O(4), an unsaturated =O atom with bond length d[P(1)–O(4)] = 1.512(5) Å. The second P(2) atom makes linkages to all four zinc atoms via bridging oxygen atoms with d_{av}[P(2)–O] = 1.544(0) Å. The third tetrahedral P(3) with d_{av}[P(3)–O] = 1.531(5) Å is bound to Zn(2), Zn(3), and Zn(4) via two triply coordinated oxygen atoms, O(8) and O(11), and also to Zn(1) and Zn(4) via O(2) and O(12) bridges. As a result, the P(3) group links six zinc atoms via four oxygen atoms. The last one P(4) makes three P–O–Zn links and possess one terminal –OH group with d[P(4)–O(15)] = 1.589(5) Å. The P–O bond length corresponding to the HP(1)O$_4$ and HP(4)O$_4$ are longer than
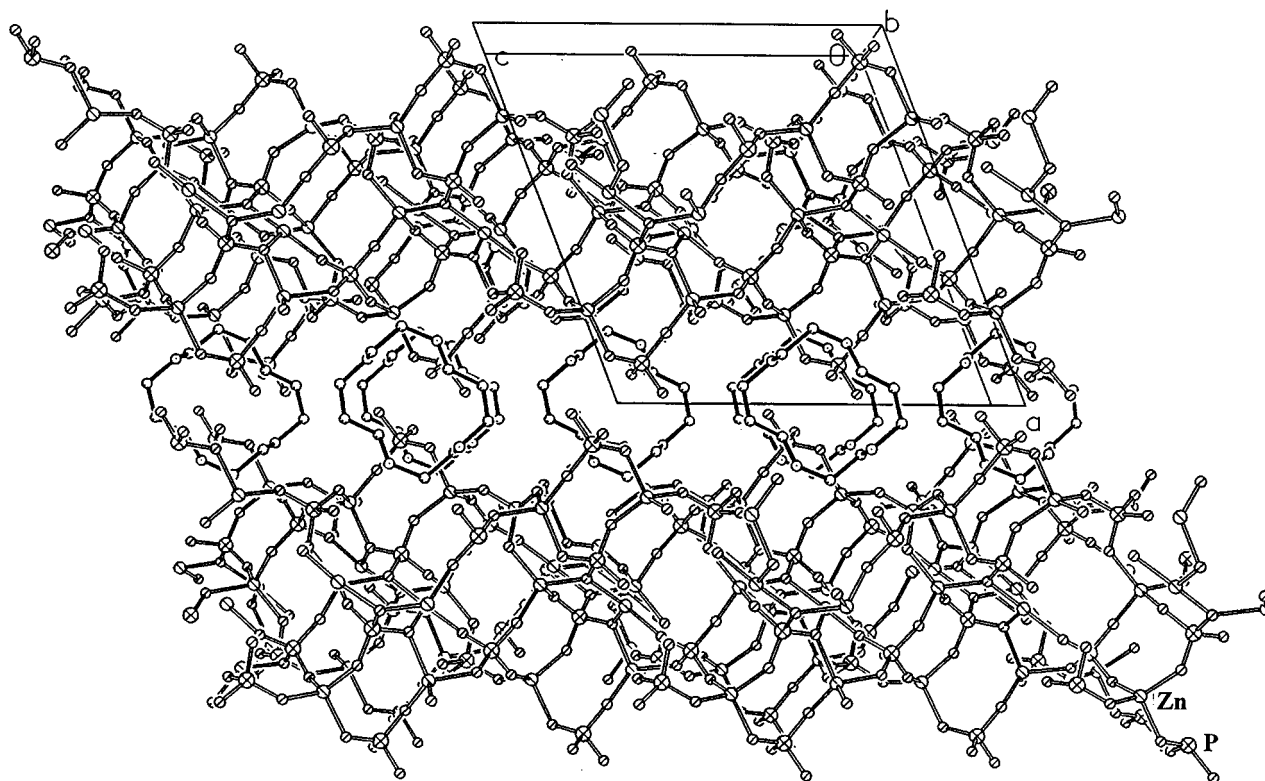
FIG. 2. View down [010] of the Zn$_4$(PO$_4$)$_2$(HPO$_4$)$_2$·0.5(C$_{10}$H$_{28}$N$_4$)·2H$_2$O crystal structure showing the alternation of the anionic inorganic Zn–O–P layers separated by protonated cyclam molecules.

those of PO_4. Similar P–OH bond lengths are also reported in other layered zinc phosphates (5, 23, 27).

Two of the 16 oxygen atoms O(8) and O(11) are triply coordinated and have been reported in other zinc phosphates structures (2, 4, 6–8, 22–24), and each triply coordinated oxygen atom links with two zinc atoms and one phosphorus atom. As a consequence, there exist inevitably Zn–O–Zn linkages in the ZnPO-cyclam. In addition, there are "hanging" $HP(1)O_4$ groups attached to the zinc atoms in which no P–O–P linkages appear in this structure, despite the existence of Zn–O–Zn linkages and the molar ratio of Zn:P = 1:1.

The connectivity of polyhedral units in ZnPO-cyclam shown in Fig. 2 results in a novel structure feature: the existence of cages, which are rarely reported in layered structures of ZnPO (3, 7, 9, 10), and cavities in the inorganic layers. These inorganic anionic layers, $[Zn_4(PO_4)_2(HPO_4)_2 \cdot 2(H_2O)]^{2-}$, can be viewed as constructed from sheets along the direction (101) shown in Fig. 3. In the sheets, there are

one kind of four-membered rings containing Zn(2), Zn(4), P(3), and P(4), two types of three-membered rings containing Zn(2), Zn(3), and P(2) and Zn(3), Zn(4) and P(3), respectively, and six-membered rings that share common edges with these three- and four-membered rings. The repeating linkages of these three-, four-, and six-membered rings form the sheet along the direction (101). In addition, the connection of one kind of the three-membered ring, which contains $Zn(3)O_3(H_2O)_2$, $Zn(4)O_4$, and $P(3)O_4$ groups, with two three-coordinated oxygen atoms, O(8) and O(11) builds up a so-called "zigzag" chains from sharing common vertices P(3) and O(11). These three-membered chains also develop in the same direction (101) as the sheets. Infinite chains of three-membered rings also exist in some zinc phosphates (4, 7, 22, 24), which is an interesting structural feature for zinc phosphates compared to Si–Al zeolites.

The connectivity of the sheets through P(1)–O–Zn(2), P(2)–O–Zn(4), and P(3)–O–Zn(1) form the novel layered structure of ZnPO-cyclam shown in Fig. 2. There are cages
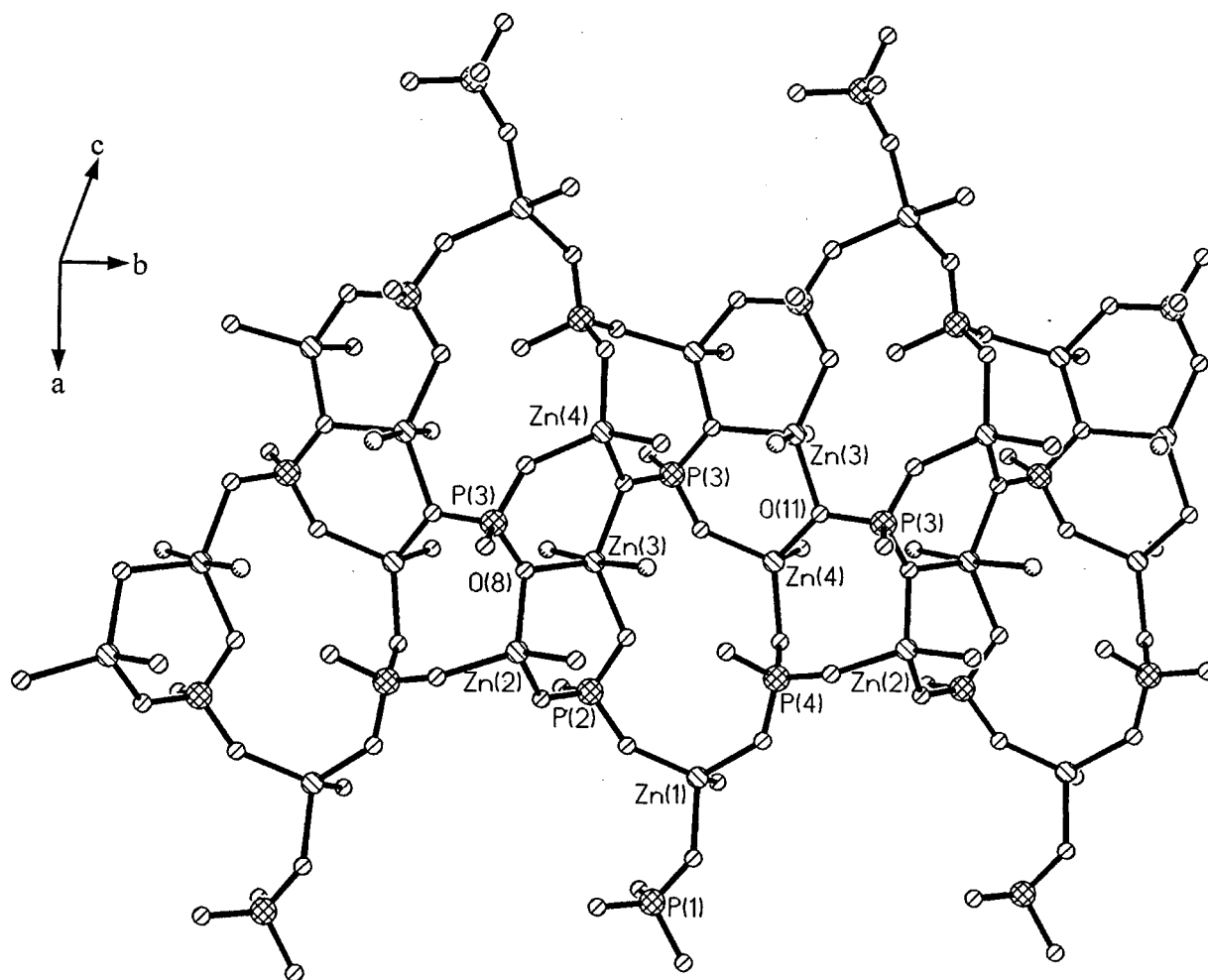

FIG. 3. Details of the $Zn_4(PO_4)_2(HPO_4)_2 \cdot 0.5(C_{10}H_{28}N_4) \cdot 2H_2O$ structure showing a sheet in the inorganic Zn–O–P layers along the [101] direction with the three-membered rings, four-membered rings, and six-membered rings.
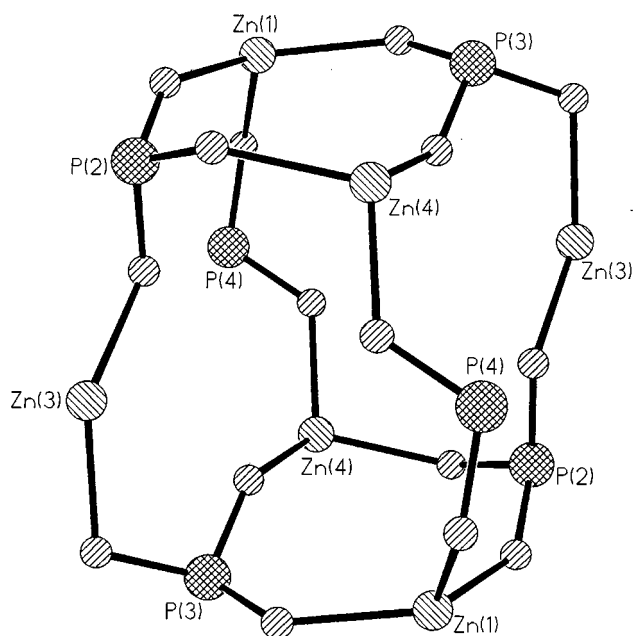
FIG. 4. Details of the cages in the inorganic layers with two four-membered rings and four six-membered rings with the atoms Zn and P labeled.

with four six-membered rings and two four-membered rings in one inorganic layer of ZnPO-cyclam, which make the layers "thicker" and more complex than those layered with

organic amines reported previously (3, 7, 9, 10). Each cage presented in Fig. 4, is composed of two six-membered rings in adjacent sheets through atoms Zn(1)–O–P(3) and Zn(4)–O–P(2). As a result, new six-membered rings with Zn(1), P(3), Zn(3), P(2), Zn(4), and P(4) and four-membered rings with atoms Zn(1), P(3), Zn(4), and P(2) are generated. The linkage of the sheets by "hanging" atoms P(1) with atoms Zn(2) in another adjacent sheet form cavities with openings that consist of twelve-membered tetrahedral atoms (6 Zn and 6 P atoms strictly alternating). The connection of the twelve-membered cavity opening, which is similar to another zinc phosphate (9), is shown in Fig. 5.

The template molecule, cyclam, resides in the cavities between the inorganic layers and is found to be completely protonated. These cations also form the organic layers in the structure of ZnPO-cyclam and serve as hydrogen bonding donors to the nearest oxygen framework. Four hydrogen atoms connected with two water molecules form hydrogen bonds with the intralayer framework of oxygen atoms O(6), O(13), and O(14). The hydrogen atoms attached to P(1) and P(4) groups are also involved in hydrogen bonds with d[O(5)–H(1)–O(3)] = 2.702(7) Å at an angle of 160(6)° and d[O(15)–H(2)–O(10)] = 2.644(7) Å at an angle of 172(7)°. The detailed information about hydrogen bonding is summarized in Table 4. The interlayer hydrogen bonding between inorganic and organic layers and the intralayer hydrogen bonding between donor and acceptor in the same inorganic layer play an important role in stabilizing the
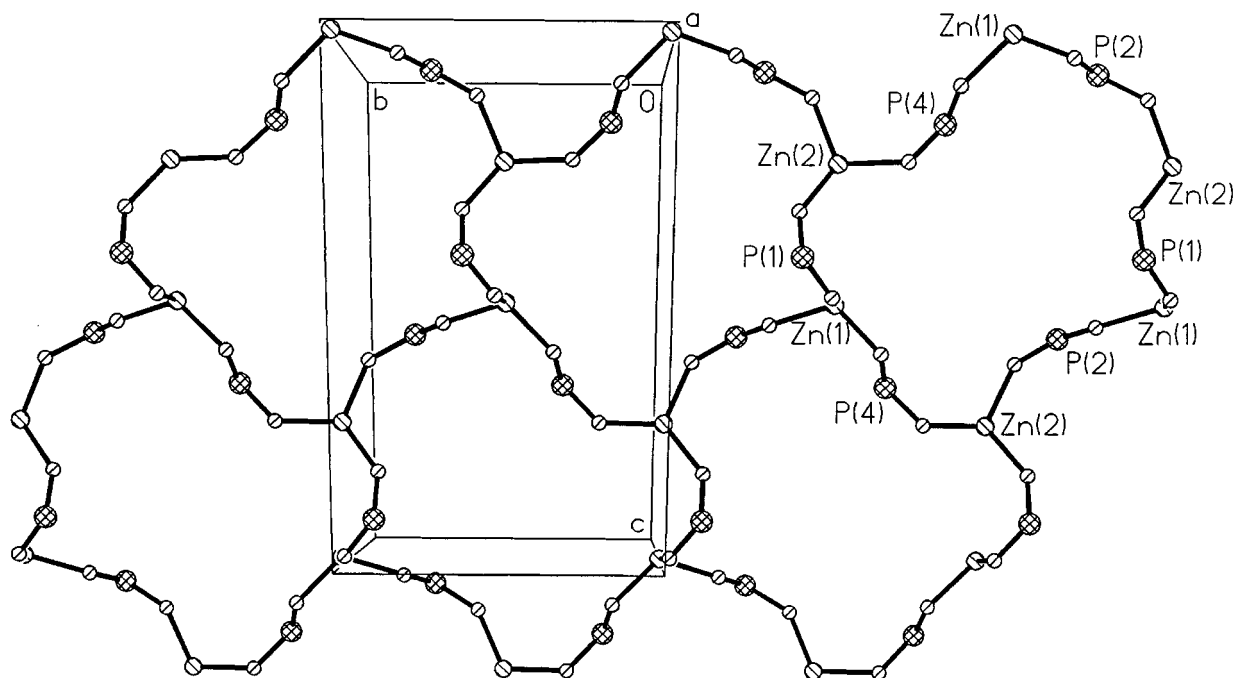

FIG. 5. Topological copnnectivity showing the openings of the cavities in the inorganic Zn–O–P layers with 12-membered rings and the atoms Zn and P labeled.

TABLE 4
Hydrogen Bonds for ZnPO−cyclam

D–H···A	d(D–H) Å	d(H···A) Å	d(D···A) Å	Angle (D–H···A) (°)
O(5)–H(1)···O(3)#7	0.87(2)	1.87(3)	2.702(7)	160(6)
O(15)–H(2)···O(10)#1	0.86(2)	1.79(2)	2.644(7)	172(7)
OW1–H(3A)···O(14)#3	0.86(2)	1.87(4)	2.683(7)	158(10)
OW1–H(3B)···O(13)#1	0.87(2)	2.09(8)	2.740(7)	131(9)
OW2–H(4A)···O(6)	0.87(2)	2.26(8)	2.913(9)	131(9)
OW2–H(4B)···O(13)	0.88(2)	2.30(7)	2.983(9)	134(8)
N(1)–H(6A)···O(4)	0.97	1.76	2.717(8)	170.1
N(1)–H(6B)···O(7)#2	0.97	2.13	2.913(7)	136.9
N(1)–H(6B)···O(9)#2	0.97	2.08	2.963(8)	150.2
N(2)–H(9B)···O(15)#4	0.97	1.82	2.776(7)	168.3
N(2)–H(9A)···O(4)	0.97	1.77	2.717(8)	165.0

Note. Symmetry transformations used to generate equivalent atoms: #1, $-x + 1, y - 1/2, -z + 1/2$; #2, $x, -y + 1/2, z - 1/2$; #3, $x, -y + 1/2, z + 1/2$; #4, $-x + 1, y + 1/2, -z + 1/2$; #7, $-x, -y, -z$.

$Zn_4(PO_4)_2(HPO_4)_2(H_2O)_2 \cdot 0.5(H_4CYCLAM)$ structure as observed in the layered structures of zinc phosphates (7, 9 –10, 18, 22–24, 27).

CONCLUSION

The unusual characteristic of this layered structure might open up some possibilities of synthesizing other metal phosphates with novel crystal structures by varying the templating agents and preparative conditions.

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