An Open-framework Strontium Phosphate Containing a Novel 4^{12} Cages

Zhen Zhu

Institute of Nanostructured Materials

School of Materials Science and Engineering

And Tianjin Key Laboratory of Fiber Modification and Functional Fiber

Tianjin Polytechnic University

Tianjin 300160, China

E-mail: zhuzhen183@163.com

Abstract

A novel strontium phosphite open-framework $H_2[Sr_6(HPO_3)_7]$ (denoted as ZZ-2, ZZ = Zhen Zhu) was hydrothermally synthesized by using isophorondiamine (IPDA) as the trial structure-directing agent. Single crystal structure refinement discloses that ZZ-2 crystallizes in the trigonal space group R-3 with the cell parameters of a = 16.410(2) Å, b =16.410(2) Å, c = 6.8651(14) Å, β = 114.61(5)°, β = 90°, V = 1601.0(5) Å^3, Z = 3. The structure of ZZ-2 is constructed by eight coordinated SrO8 and HPO$_3$ pseudo pyramids. A novel 4^{12} cages existed in the structure with a proton located in the center of the cage. the P-H bonds stretch in all cages, hydrogen proton at the center of the cage to balance framework.

Keywords: Hydrothermal synthesis, Open-framework, Single crystal structure, Novel 4^{12} cages, Strontium phosphite

1. Introduction

Microporous materials have been intensively studied due to their potential applications as catalysts, absorption, separation, ion-exchange and host-guest chemistry. [1-2] The most well known such materials are zeolites and aluminophosphates constructed from TO$_4$ tetrahedra (T = Si, Al, and P) [3-4]. Recently, synthesis of phosphorus-based microporous materials by incorporating the pseudo-pyramidal hydrogen phosphite group HPO$_3$ instead of tetrahedral phosphate group PO$_4$ into the desired structures exhibits the diversity of phosphorus-based materials. From this view, replacing tetrahedral phosphate groups by pseudo-pyramidal phosphite units has been considerably explored and resulted in a new family of metal phosphite compounds in the past decade, including one-dimensional chain compounds, two-dimensional layer materials, and three-dimensional open-framework structures have been prepared[5-6] Crystals with extra-large pores were also achieved, including include ND-1 with extra-large 24-ring channels[7], several vanadium hydrogenphosphites with 14-ring channels[8e], zinc phosphites with 16-ring channels. [8a-d], and NTHU-3 with the capacity of assisting molecular ecognition[9]. Our interest in the chemistry of alkaline-earth metal phosphites is to develop new materials to absorption.Herein, by using isophorondiamine (IPDA) as the trial structure-directing agent, a novel strontium phosphite, $H_2[Sr_6(HPO_3)_7]$ (ZZ–2) was isolated, contaning A 4^{12} cages and a proton located in the center of the cage.

2. Experimental

ZZ–2 was hydrothermally synthesized by using isophorondiamine (mixtures of *cis*- and *trans*- isomers, Aldrich) as the trial structure-directing agent. All reagents were purchased commercially and used as-received without further purification. Typically, 0.266 g Sr(OH)$_2$·8H$_2$O, 0.266 g H$_3$PO$_3$ and 0.085 g IPDA were dispersed into 8 mL distilled water. The mixture with a molar composition of 2Sr(OH)$_2$·8H$_2$O **:** 6H$_3$PO$_3$ **:** 1(C$_{10}$H$_{22}$N$_2$) **:** 890(H$_2$O) was stirred for 1.5 hours. Afterward, the starting suspension was sealed in a TEFLON-lined autoclave and heated at 160°C for 120 hs. The hydrothermal reaction produced white transparent crystals, which were washed by distilled water and dried at room temperature.

X-ray powder diffraction (XRD) data were obtained by using BRUKER D8 DISCOVER diffractometer with CuKα radiation (λ = 1.5418 Å). FTIR spectra (KBr pellets) were recorded on a BRUKER TENSOR-37 FTIR spectrometer. A NETZSCH STA 409 PG/PC unit was used for thermogravimetric analysis at a heating rate of

10 °C·min^{-1} in air with a flow rate of 20 mL·min^{-1}. Energy dispersive X-ray analysis (EDAX) equipped on a FEI QUANTA 200 SEM was utilized for analyzing the ratio of uranium and phosphorous. EDAX data gave the Sr:P ratio of 6:7. ICP analysis on Perkin-Elmer Optima 3300DV ICP instrument also gave the Sr:P value of 5:12 (P, 19.91wt%; Sr, 48.44wt%). Elemental analyses for volatile elements were performed on Perkin-Elmer 2400 element analyzer. The steady-state luminescence spectra were recorded on an Edinburgh Instruments FS920P spectrometer with a 450 W Xenon lamp as the steady-state excitation source, a double excitation monochromator (1800 lines mm^{-1}), an emission monochromator (600 lines mm^{-1}), and a semiconductor cooled Hamamatsu RMP928 photomultiplier tube.

Single crystal of ZZ-2 with size of 0.2 × 0.2 × 0.2 mm^3 was carefully selected under an optical microscope and glued to a thin glass fiber with epoxy resin. Signle crystal X-ray diffraction data were recorded on a Bruker SMART CCD diffractometer with graphite-monochromated MoKα (λ = 0.71073 Å) radiation in the ω and φ scanning modes at room temperature. The structure of ZZ-2 was solved by using direct method. The uranium and phosphorous atoms were first located from the electron map. Other non-hydrogen atoms were derived from the successive different Fourier syntheses. After isotropic refinement, the hydrogen atoms bonded to phosphorous and nitrogen atoms were discerned in the different Fourier map. Hydrogen atoms bonded to carbon atoms were rided theoretically. The structure was refined on F^2 by full-matrix least-squares method using the SHELX 97 program package. All non-hydrogen atoms were refined anisotropically. The crystal data and details of structure refinement for ZZ-2 were exhibited in Table 1. The selected bond lengths and angles were listed in Table 2. Crystallographic data have been deposited within the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK as supplementary publication No. 733906.

3. Results and discussions

The experimental and simulated XRD patterns are well matched, indicating the monophasic feature of the product (Figure 1). X-ray photolumenicence spectra give the binding energy of Sr3d$_{3/2}$ of 134.58eV that is very close to the documented value of SrF$_2$ (134.63 eV), indicating the bivalent state of Sr (Figure 2). Thermogravimetric curve of ZZ-2 (Figure 3) exhibits a two-step weight loss in a total 17.44 wt% around 30–1050°C. The weight loss of 2.52 wt% at 30–900°C corresponds to the emission of the coordinated water molecules. The weight loss of 14.92wt% in the range of 900–1050°C is attributed to the decomposition of framework and the dehydration of [HPO$_3$] groups. FTIR spectra exhibit characteristic absorptions of the O−H bonds between 3200–2800cm^{-1}. The strong adsorption peaks at 2414cm^{-1} and 2460cm^{-1} are asigned to the characteristic the stretching and bending vibration of the P-H bond.

ZZ-2 crystallizes in the trigonal space group R -3. The asymetric unit contains 7 non-hydrogen atoms (one strontium, two phosphorous, and four oxygen atoms, Figure 4). Sr is coordinated by O(1), O(2), O(4) and O(11) .the Sr−O bond lengths in the range of 2.542–2.764 Å and the O−Sr−O bond angles ranging from 33.74° to 157.93°. P(2) the share of 1/6, O (11) share is 1/2, N (1) share of 1/6,all the phosphorous atoms are pseudo pyramidal HPO$_3$ groups with the P−O distances ranging from 1.5082(51) Å to 1.5333(49) Å. The terminal P−H distances are in the range of 1.47–1.544 Å. A strong IR adsorption at 2414 cm^{-1} verifies the presnece of P−H bonds. The strontium atoms are connected to phosphite groups to generate a framework compound with formula [Sr(HPO$_3$)(HPO$_3$)$_{1/6}$]$^{-1/3}$. Charge balance requires two protens that compensated by diprotonated IPDA molecule. 1/3 hydrogen ion balance Skeleton 1/3 negative charge, 1/3 hydrogen ion found by the difference Fourier map.Hence, compound ZZ-2 can be formulated as H$_2$[Sr$_6$(HPO$_3$)$_7$].

The extended structure of ZZ-2 is built by eight coordinated SrO$_8$ and HPO$_3$ groups without Sr-O-Sr and P-O-P. The connection of the SrO$_8$ and HP (1) O$_3$ generates 4-ring structures, this 4-ring structure formed three-dimensional network structure by symmetry operation, the structure along the c direction with one-dimensional 6-ring channels (Figure 5). HP (2) O$_3$ group in the middle of 6-ring channels to form a new type of cage structure,12 tetrahedrons via edge-sharing to give rise to the cage structure. the P-H bonds stretch in all cages, hydrogen proton at the center of the cage to balance framework (Figure 6).

Crystallization temperature on the formation of products have a certain impact. ZZ-2 in the crystallization temperature of 160°C, when the crystallization temperature lower or higher than the temperature of the product typically contains impurities or not the product.

System pH value of the reaction products have very important influence, we have adopted phosphorous and organic amine to adjust the ratio of system pH, pH value of 4.1 in the system, so when the compound (ZZ-2), in other pH, obtained the impurities.

4. Summary

A new open-framework strontium phosphite, ZZ-2, has been synthesized under the hydrothermal condition by using isophorondiamine as the trial structure-directing agent. ZZ-2 expansion of the structure is constructed by eight coordinated SrO_8 and HPO_3 pseudo pyramids. A novel 4^{12} cages existed in the structure without Sr-O-Sr and P-O-P. the P-H bonds stretch in all cages, hydrogen proton at the center of the cage to balance framework.

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Table 1. Details of data collection and structure refinement of ZZ-2

Empirical formula	$Sr_6 H_9 O_{21} P_7$
Formula weight	548.87
Temperature	293(2)K
Crystal system	trigonal
Space group	R -3
a(Å)	16.410(2) Å
b(Å)	16.410(2) Å
c(Å)	6.8651(14) Å
A	90°
B	90°
Γ	120°
V	1601.0(5) Å^3
Z	3
Theta range for data collection	2.48 - 27.85 °
Limiting indices	$-15 \leq h \leq 21$, $-21 \leq k \leq 21$, $-8 \leq l \leq 8$
F(000)	819
Calculated density	1.708g/cm^3
Absorption coefficient	2.671 mm^{-1}
Reflections collected / unique	4424 / 846 [R(int) = 0.0946]
Completeness to theta = 24.99	99.5%
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	0.988
Final R indices [I > 2sigma(I)]	R1 = 0.0901, wR2 = 0.397
R indices (all data)	R1 = 0.0940, wR2 = 0.457
Wavelength	0.71073
Largest diff. Peak and hole/e A$^{°-3}$	2.21 and -1.41

$$R1 = \sum \| F_0 | - | F_C \| / \sum | F_0 | , wR_2 = [\sum [w(F_0^2 - F_c^2)^2] / \sum [w(F_0^2)^2]]^{1/2}$$

Table 2. Selected bonds and angles for ZZ-2

		Bond lengths	
Sr1-O11	2.5424 (65)	Sr1-O2$^{\#}$11	2.5465 (33)
Sr1-O1$^{\#}$6	2.5630 (39)	Sr1-O4$^{\#}$2	2.5708 (32)
Sr1-O2$^{\#}$12	2.6407 (35)	Sr1-O4$^{\#}$6	2.6437 (32)
Sr1-O11$^{\#}$6	2.6446 (68)	Sr1- O4	2.6540 (30)
Sr1-O1	2.7643 (40)	Sr1- P1$^{\#}$8	3.5516 (13)
Sr1- P1$^{\#}$11	3.6015 (15)	Sr1- P1$^{\#}$10	3.7304 (15)
P1-O2	1.5004 (35)	P1- O4$^{\#}$6	1.5272 (33)
P1-O1	1.5442 (38)	P2-O11	1.4785 (62)
Sr1$^{\#}$10-O1	2.5631 (39)	O11- O11$^{\#}$6	1.5086 (70)

P2-Sr1	3.6919 (6)	Sr1$^{\#}$10-O4	2.6438 (32)

Bond angles			
O2$^{\#}$11-Sr1-O11	129.73 (19)	O1$^{\#}$6-Sr1-O11	91.24 (19)
O4$^{\#}$2-Sr1- O11	125.23 (16)	P1$^{\#}$10-Sr1-O2$^{\#}$11	74.93 (8)
O2$^{\#}$12 -Sr1- O11	148.38 (19)	O4$^{\#}$2-Sr1-O1$^{\#}$6	143.53 (3)
O4$^{\#}$6-Sr1- O11	76.61 (19)	O2$^{\#}$12-Sr1-O1$^{\#}$6	71.43 (14)
O11$^{\#}$6-Sr1- O11	33.74 (21)	O4$^{\#}$6-Sr1-O1$^{\#}$6	80.80 (11)
O4-Sr1-O11	69.35 (18)	O11$^{\#}$6-Sr1-O1$^{\#}$6	58.06 (19)
O1-Sr1-O11	56.71 (19)	O4-Sr1-O1$^{\#}$6	132.16 (12)
P1$^{\#}$8-Sr1-O11	127.98 (15)	O1-Sr1-O1$^{\#}$6	128.60 (15)
P1$^{\#}$11-Sr1-O11	110.53 (17)	P1$^{\#}$8-Sr1-O1$^{\#}$6	133.19 (11)
P1$^{\#}$10-Sr1-O11	63.95 (18)	P1$^{\#}$11-Sr1-O1$^{\#}$6	69.21 (9)
O1$^{\#}$6-Sr1-O2$^{\#}$11	78.37 (12)	P1$^{\#}$10-Sr1-O1$^{\#}$6	112.34 (9)
O4$^{\#}$2-Sr1-O2$^{\#}$11	77.55 (10)	O2$^{\#}$12-Sr1-O4$^{\#}$2	75.76 (11)
O2$^{\#}$12-Sr1-O2$^{\#}$11	73.74 (11)	O4$^{\#}$6-Sr1-O4$^{\#}$2	105.58 (12)
O4$^{\#}$6-Sr1-O2$^{\#}$11	146.31 (10)	O11$^{\#}$6-Sr1-O4$^{\#}$2	157.93 (19)
O11$^{\#}$6-Sr1-O2$^{\#}$11	120.00 (19)	O4-Sr1-O4$^{\#}$2	70.19 (11)
O4-Sr1-O2$^{\#}$11	81.84 (11)	O1-Sr1-O4$^{\#}$2	79.44 (12)
O1$^{\#}$10-Sr1-O2$^{\#}$11	152.91 (12)	P1$^{\#}$8-Sr1-O4$^{\#}$2	22.34 (7)
P1$^{\#}$8-Sr1-O2$^{\#}$11	90.63 (8)	P1$^{\#}$11-Sr1-O4$^{\#}$2	94.66 (7)
P1$^{\#}$11-Sr1-O2$^{\#}$11	20.29 (8)	P1$^{\#}$10-Sr1-O4$^{\#}$2	87.15 (7)
O4$^{\#}$6-Sr1-O2$^{\#}$12	74.67 (10)	Sr1$^{\#}$5-P1-O2	77.53 (14)
O11$^{\#}$6-Sr1-O2$^{\#}$12	120.18 (16)	Sr1$^{\#}$1-P1-O2	36.06 (14)
O4-Sr1-O2$^{\#}$12	141.54 (10)	Sr1$^{\#}$6-P1-O2	129.92 (14)
O1-Sr1-O2$^{\#}$12	113.98 (11)	O1-P1-O4$^{\#}$6	109.25 (20)
P1$^{\#}$8-Sr1-O2$^{\#}$12	61.83 (8)	Sr1$^{\#}$5-P1-O4$^{\#}$6	39.78 (12)
P1$^{\#}$11-Sr1-O2$^{\#}$12	88.34 (7)	Sr1$^{\#}$1-P1-O4$^{\#}$6	129.83 (14)
P1$^{\#}$10-Sr1-O2$^{\#}$12	146.83 (8)	Sr1$^{\#}$6-P1-O4$^{\#}$6	36.12 (12)
O11$^{\#}$6-Sr1-O4$^{\#}$6	68.02 (16)	Sr1$^{\#}$5-P1-O1	114.17 (15)
O4-Sr1-O4$^{\#}$6	131.31 (9)	Sr1$^{\#}$1-P1-O1	119.37 (17)
O1-Sr1-O4$^{\#}$6	55.12 (10)	Sr1$^{\#}$6-P1-O1	117.11 (19)
P1$^{\#}$8-Sr1-O4$^{\#}$6	84.62 (7)	Sr1$^{\#}$1-P1-Sr1$^{\#}$5	104.45 (3)
P1$^{\#}$11-Sr1-O4$^{\#}$6	149.06 (7)	Sr1$^{\#}$6-P1-Sr1$^{\#}$5	71.86 (3)
P1$^{\#}$10-Sr1-O4$^{\#}$6	138.07 (7)	Sr1$^{\#}$6-P1-Sr1$^{\#}$1	118.40 (4)
O4-Sr1-O11$^{\#}$6	97.64 (15)	O11$^{\#}$3-P2-O11$^{\#}$6	118.65 (11)
O1-Sr1-O11$^{\#}$6	79.88 (20)	O11-P2-O11$^{\#}$6	61.36 (11)
P1$^{\#}$8-Sr1-O11$^{\#}$6	149.16 (17)	O11$^{\#}$4-P2-O11$^{\#}$6	180.00 (00)
P1$^{\#}$11-Sr1-O11$^{\#}$6	100.63 (17)	Sr1$^{\#}$6-P2-O11$^{\#}$6	31.05 (26)
P1$^{\#}$10-Sr1-O11$^{\#}$6	85.17 (14)	Sr1$^{\#}$4-P2-O11$^{\#}$6	148.95 (26)
O4$^{\#}$6-P1-O2	115.04 (20)	Sr1$^{\#}$3-P2-O11$^{\#}$6	143.92 (28)
O1-P1-O2	111.26 (24)	Sr1$^{\#}$7-P2-Sr1$^{\#}$1	82.57 (29)
Sr1$^{\#}$10-P2-Sr1$^{\#}$1	97.43 (29)	Sr1-O11-O11$^{\#}$10	137.59 (68)

Sr1#7-P2-O11#3	36.09 (28)	Sr1#10-O11-O11#10	69.41 (38)
Sr1#2-O4-P1#10	117.88 (17)	Sr1#10- O11- Sr1	99.94 (21)
Sr1#10-O4-P1#10	100.40 (16)	Sr1#9-O2-Sr1#1	102.02 (11)
Sr1-O4-P1#10	124.05 (17)	O11#10-O11-P2	59.32 (6)
Sr1#10-O4-Sr1#2	101.29 (11)	Sr1-O11-P2	131.49 (38)
Sr1-O4-Sr1#2	109.81 (11)	Sr1#10-O11-P2	124.69 (38)
Sr1-O4-Sr1#10	97.15 (10)	O11#10-O11-O11#6	114.87 (41)
Sr1#10-O1-P1	144.16 (26)	Sr1-O11-O11#6	76.84 (42)
Sr1-O1-P1	95.07 (18)	Sr1#10-O11-O11#6	175.72 (47)
Sr1-O1-Sr1#10	96.36 (13)	Sr1#9-O2-Sr1#1	102.02 (11)
Sr1#1-O2-P1	123.65 (19)	Sr1#9-O2-P1	131.58 (19)

Symmetry transformation used to generate equivalent atoms: 1: x, y, z+1; -x+1, -y+2, -z; -x+2/3, -y+4/3, -z+1/3; -y+1, x-y+1, z; -y+5/3, x-y+4/3, z+1/3; y-1/3, -x+y+1/3, -z+1/3; -x+y, -x+1, z; -x+y+1/3, -x+5/3, z-1/3; -x+y+1/3, -x+5/3, z+2/3; x-y+2/3, x+1/3, -z+1/3; x, y, z-1; -y+5/3, x-y+4/3, z-2/3
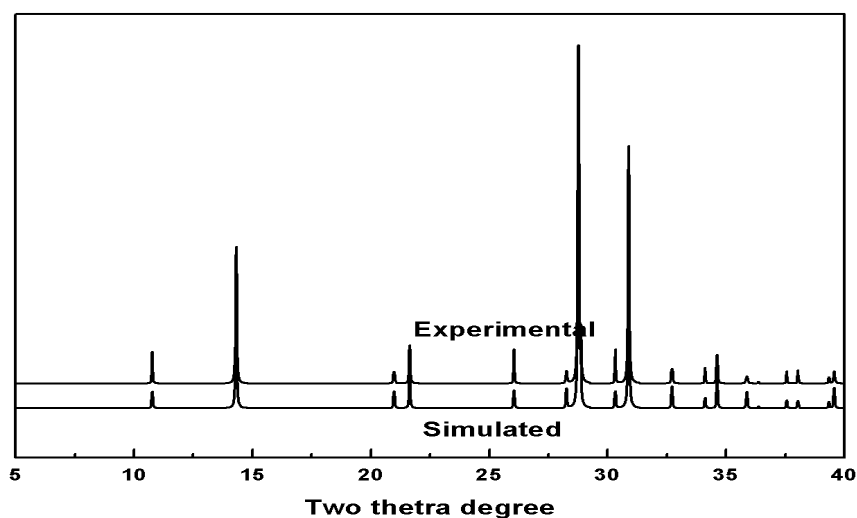
Figure 1. Simulated and experimental XRD patterns for ZZ-2
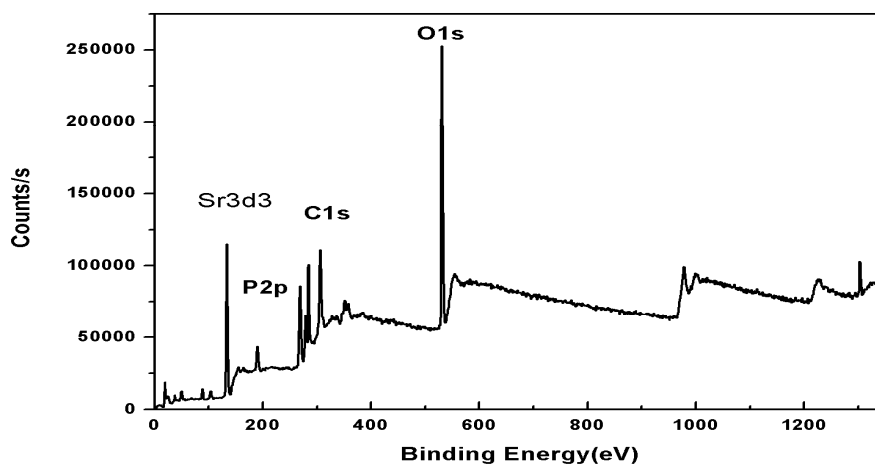
Figure 2. XPS curve for ZZ-2
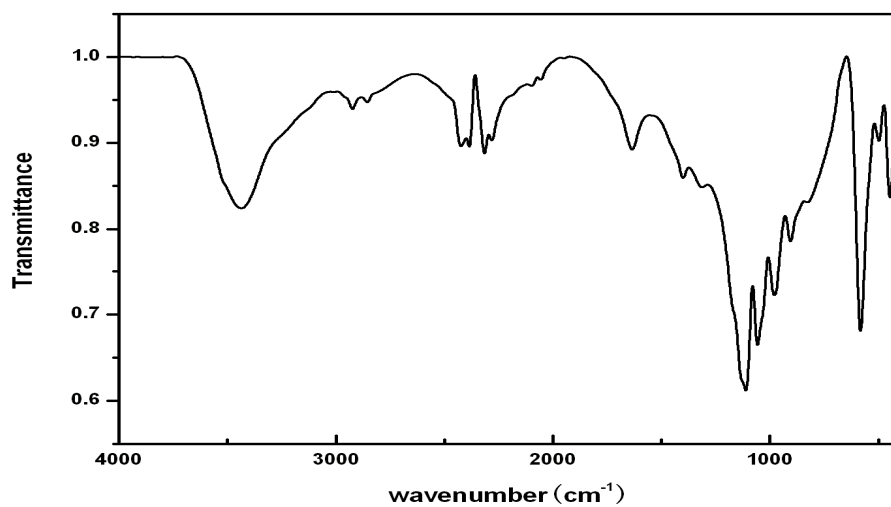
Figure 3. TG curve of ZZ-2
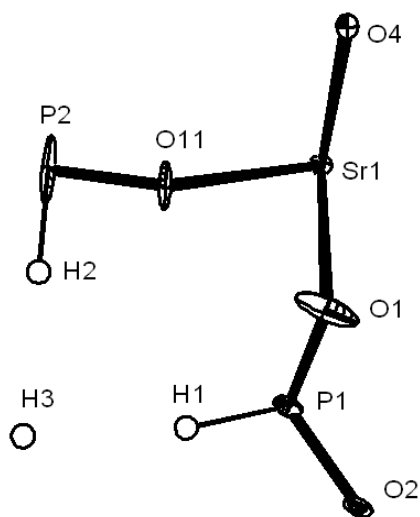
Figure 4. Ortep plot of the asymmetric unit of ZZ-2 with 50% probability ellipsoids
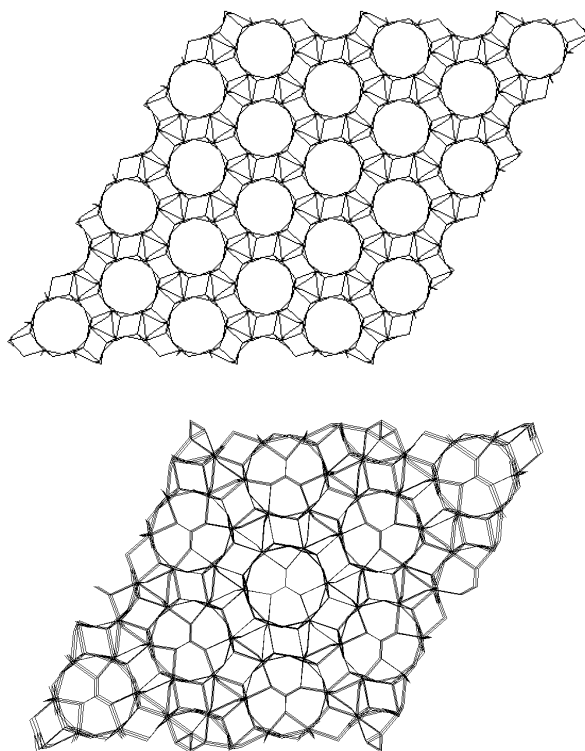
Figure 5. Six-ring along the c direction in ZZ-2 (A)and HP(2)O$_3$ block the pore(B)
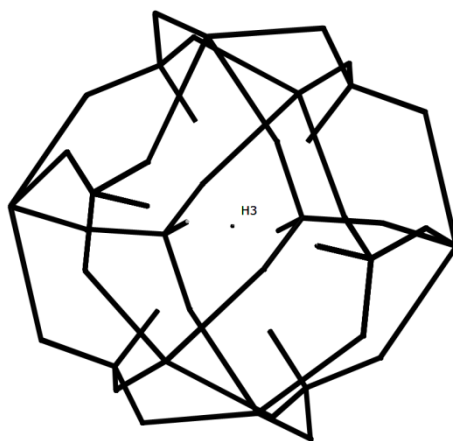
Figure 6. 4^{12} cage structure in the ZZ-2, a proton in the center of the cage