A Microporous Zinc Phosphonocarboxylate with a Zeolite ABW Framework via the Trialkyl Phosphonocarboxylate Route: In situ Synthesis and Characterization of $Na[Zn(O_3PC_2H_4CO_2)]\cdot H_2O$

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Keywords: Microporous materials / Organic-inorganic hybrid / Zeolites / Zinc

A new zinc phosphonocarboxylate $Na[Zn(O_3PC_2H_4CO_2)]\cdot H_2O$ (**1**) has been hydrothermally synthesized by base-catalyzed hydrolysis of trimethyl 3-phosphonopropionate. An X-ray crystallographic study revealed that **1** consists of parallel stacked inorganic hexagonal sheets which are connected by organic –C–C–C–O– pillars forming a three-dimensional framework with the same topology as ABW-type zeolites. The accessible channel of **1** consisting of 22 atoms is larger than those of ABW-type zeolites and the metal phosphonates $Zn(O_3PC_2H_4NH_2)$ and $Zn(O_3PC_2H_4CO_2H)\cdot 1.5H_2O$. TGA shows the trapped water molecules in **1** can be thermally removed without damage to the framework. Furthermore, dehydrated **1** is stable up to 340 °C.

Introduction

Zeolites are microporous aluminosilicates and have widespread applications as absorbents, for separations, as catalysts and for ion-exchange.[1−5] The desire to develop new microporous materials has led to increasing interest in the synthesis of metal phosphonate materials in recent years.[6−7] Metal phosphonates are organic-inorganic hybrid materials in which the nature of the organic phosphonic acid, H_2O_3P-R-Z, can be designed to confer specific properties to this class of solids.[8−10] The dimensionality of metal phosphonates can be directly influenced by the Z terminal functional and the R group. Thus, it is possible to manipulate the metal phosphonate framework by choosing a system with or without a Z terminal function and by changing the R group. In the absence of the Z function, metal phosphonates usually have layered or tubular structures[11−17]with an arrangement that strongly depends upon the nature and oxidation state of the metal. One of the exceptions is β-$Cu(CH_3PO_3)$ which exhibits a three-dimensional structure with a channel-type arrangement.[18] If the terminal Z functional is the -PO_3H_2 group which has three potential binding sites, the resultant metal phosphonates often show three-dimensional pillared layered structures.[19−25] If the Z functional end is the $-CO_2H$,[26−33] $-C(NH_2)CO_2H$,[34−36] or NH_2[37] group, the dimensionality of the metal phosphonates often relies on the length of the R group.

Although some progress has been made in the construction of microporous metal phosphonate materials as mentioned above, less progress has been achieved in the synthesis of microporous metal phosphonates with the topology of zeolites. One requirement for metal phosphonates with such a topology is that all metal ions and phosphonic acids must be rigidly 4-connected. This results in a structure like the (4;2) connected topology of zeolites.[38] To the best of our knowledge, only two metal phosphonates with the topology of zeolites have been reported namely $Zn(O_3PC_2H_4CO_2H)\cdot 1.5H_2O$[33] and $Zn(O_3PC_2H_4NH_2)$.[37] Therefore, the generation of metal phosphonates with the zeolite topology poses a significant synthetic challenge due to the high coordination tendency and flexibility of organic phosphonic acids. Another problem in metal phosphonate chemistry is that many metal phosphonates formed by traditional methods (direct reaction of phosphonic acid with metal source by the hydrothermal method, by heating to reflux appropriate solutions, or by making metal salts contact with molten phosphonic acid) are formed too rapidly to allow growth of crystals sufficiently large to enable single crystal structural determinations to be carried out.[19] In this paper we report the crystal structure and thermal behavior of a new microporous zinc phosphonocarboxylate $Na[Zn(O_3PC_2H_4CO_2)]\cdot H_2O$ (**1**) which has an open framework with the same topology as ABW-type zeolites.

Results and Discussion

Both the selection of trimethyl 3-phosphonopropionate as the 3-phosphonopropionic acid source and the maintaining of strongly basic conditions are very critical for the

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DOI: 10.1002/ejic.200300563

formation of single crystals of **1**. For example, one similar reaction (keeping all other conditions unchanged except for 3-phosphonopropionic acid in place of trimethyl 3-phosphonopropionate) did not result in single crystals of **1** but instead, a colorless powder. The synthesis of metal phosphonocarboxylates directly from the relevant trialkyl phosphonocarboxylate appears to be an extremely productive adaptation of the traditional hydrothermal methods employed in the syntheses of these materials. The initial pH in the synthesis of **1** must be strongly basic in order to promote in situ hydrolysis of the trialkyl phosphonocarboxylate to the phosphonocarboxylic acid. Although some metal phosphonates have been prepared by acid-catalyzed hydrolysis of dialkyl phosphonates,[39−40] no metal phosphonate has been synthesized by base-catalyzed hydrolysis of trialkyl phosphonocarboxylate. The synthetic method in this work has two benefits 1) the use of the trialkyl phosphonocarboxylate rather than the phosphonocarboxylic acid removes the need to synthesize the acid because trialkyl phosphonocarboxylates are often far easier to purify (this can often be achieved simply by distillation) than the corresponding phosphonocarboxylic acids and 2) the slow in situ formation of phosphonocarboxylic acid by base-catalyzed hydrolysis of trimethyl 3-phosphonopropionate will ensure the growth of single crystals sufficiently large to allow a single crystal X-ray structural determination.

The IR spectrum of **1** shows one broad band centered at 3451 cm^{-1} confirming the presence of crystal lattice water. The coordination of the carboxylate is represented by strong bands at 1641 and 1562 cm^{-1} which arise from the asymmetric and symmetric stretching modes of the C−O bonds of the carboxylate group. The set of intense bands from 900 to 1100 cm^{-1} is due to the stretching vibrations of the tetrahedral CPO_3 group.

A single-crystal X-ray diffraction study revealed that **1** crystallizes in the monoclinic space group $P2_1/n$ and the asymmetric unit consists of one crystallographically independent zinc atom, one 3-phosphonopropionate unit, one sodium ion and one crystal lattice water molecule as shown in Figure 1. The Zn(1) site is tetrahedral, being coordinated by three PO_3 oxygen atoms originating from three different 3-phosphonopropionate ligands and one carboxylate oxygen atom from an additional 3-phosphonopropionate ligand. Each of the three oxygen atoms of the PO_3 group coordinates to only one zinc atom. The coordination mode of the PO_3 group in **1** is referred as a (1,1,1) connection[41] which in combination with one additional carboxylate oxygen furnishes a $\mu_4:\eta^1:\eta^1:\eta^1:\eta^1$ coordination mode for the 3-phosphonopropionate unit which is also observed in $Zn(O_3PC_2H_4CO_2H)\cdot 1.5H_2O$.[33] The Zn(1)−O and P(1)−O bond lengths are in the ranges of 1.926(3)−1.947(3) Å and 1.519(3)−1.529(3) Å, respectively. The O−Zn(1)−O angles are in the range of 101.05(13)−114.59(12)° which shows some deviation from ideal angle of 109.5°.

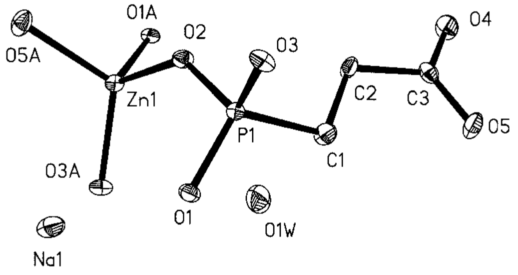


Figure 1. View of the coordination environment of the zinc atom in **1**

Within the *ac* plane, the corner-sharing connections of the CPO_3 and ZnO_4 tetrahedra result in a two-dimensional hexagonal sheet with a (6^3) topology as shown in Figure 2. The parallel stacking 2-D hexagonal sheets are held together by organic −C−C−C−O− pillars to form a 3-D pillared layered open framework (Figure 3). In each hexagonal sheet, one free corner of each tetrahedral atom can point up (U) or down (D) from the layer. The hexagonal sheets in **1** are arranged such that three adjacent tetrahedral

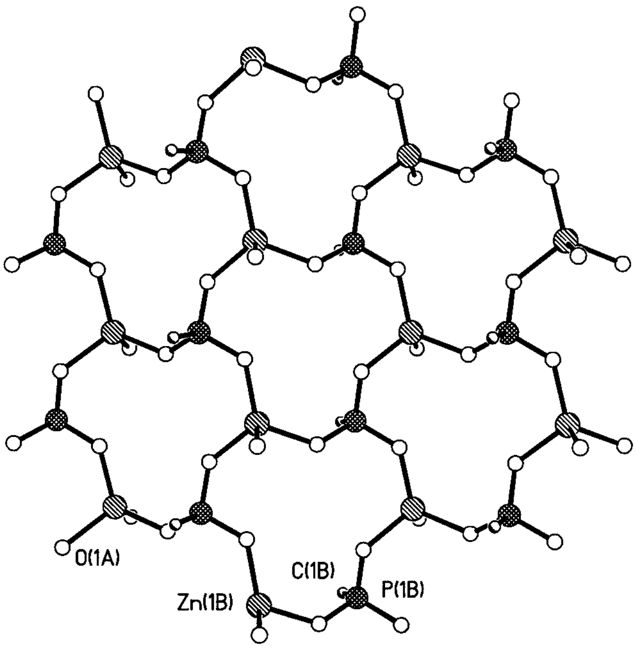


Figure 2. Perspective view of the 2-D hexagonal inorganic sheet

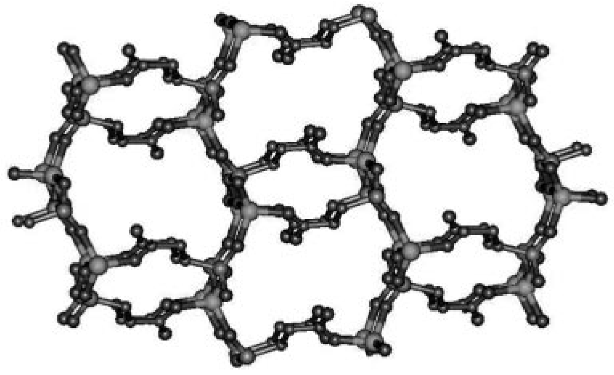
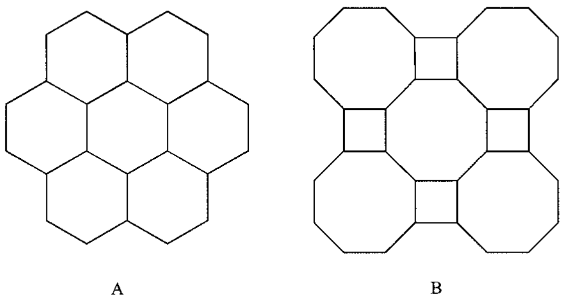


Figure 3. Perspective view of the 3-D zeolite structure of **1** showing the 22-atom channel. For clarity, the trapped sodium ions and water molecules have been omitted

atoms all are directed up while the other adjacent three are directed down (UUUDDD),[38,42] which indicates that **1** has the topology of ABW-type zeolites. The Zn and P centers occupy 4-connected vertices of the ABW-type zeolite framework and the two-connected connectors are the O atoms and the C−C−C−O pillars. There are two types of channel along the *a* axis direction as shown in Figure 3. The larger one, sized ca. 3.4−7.2 Å, has roughly a dumbbell shape which is enclosed by 22 atoms with the sequence O−P−C−C−C−O−Zn−O−P−O−Zn−O−P−C−C−C−O−Zn−O−P−O−Zn. The guest sodium ions and water molecules are trapped in the channels in **1**. The smaller channel enclosed by 14 atoms is too small to contain guest molecules.

It is interesting to compare the structure of **1** with some ABW-type aluminosilicate and metal phosphate zeolites. Zeolite ABW structures can be viewed as being built from the stacking of hexagonal sheets. The unit cell of **1** was chosen so that the stacking direction is along the *b* axis, just as in hydrated ABW-type zeolites. The hexagonal layers in **1** and other ABW-type zeolites are similar because their repeat units in two directions within the hexagonal layers are close [8.797 Å and 5.462 Å in NH_4CoPO_4-ABW; 8.883 Å and 5.222 Å in **1**]. The repeat units along the hexagonal layer stacking direction in **1** is 15.519 Å which is significantly larger than those in hydrated ABW-type aluminosilicate and metal phosphate zeolites (10.313 Å for $LiAlSiO_4{\cdot}H_2O$ and 8.797 Å for NH_4CoPO_4-ABW).[42,43] The accessible channel along the layer stacking direction in zeolite ABW is composed of 16 atoms (8 corner-shared TO_4 tetrahedra, Scheme 1, B) but the accessible channel in **1** consists of 22 atoms. The accessible channel in **1** is also larger than those of the only other known metal phosphonates with the topology of zeolites i.e. $Zn(O_3PC_2H_4CO_2H){\cdot}1.5H_2O$[33] and $Zn(O_3PC_2H_4NH_2)$[37] in which the accessible channels also consist of 16 atoms with sizes close to those of ABW-type zeolites. Compared with ABW-type zeolites, the larger repeat unit along the hexagonal layer stacking direction and the larger channel size in **1** result from the longer connector. The connectors along the hexagonal layer stacking direction in ABW-type zeolites and **1** are O atoms and C−C−C−O groups, respectively. Compared with the only other known metal phosphonates with the topology of zeolites, $Zn(O_3PC_2H_4CO_2H){\cdot}1.5H_2O$ and $Zn(O_3PC_2H_4NH_2)$, the larger channel size in **1** mainly results from its unique architecture. Unlike $Zn(O_3PC_2H_4CO_2H){\cdot}1.5H_2O$ and $Zn(O_3PC_2H_4NH_2)$ which have inorganic (4.8^2) layers (Scheme 1, B), **1** is constructed from inorganic hexagonal (6^3) layers connected by organic pillars into a 3-D framework.

The TGA trace of **1** shows an initial mass loss of 7.5 % below 185 °C, attributable to loss of the trapped water molecules within the channels (Figure 4). The second mass loss starting at around 340 °C is thought to be due to the oxidation of the hydrocarbon part of the phosphonocarboxylate group. The total mass loss is 29.3 % upon heating to 600 °C in flowing air, which is consistent with the loss of the organic part of the material (calculated mass loss is 28.7 %). This value is also consistent with the CHN analysis. Control experiments confirm that the framework of **1** is maintained upon heating and removal of the trapped water molecules but it does not undergo exchange of the Na^+ ions by protons.



Scheme 1. Schematic view of 2-D (4.8^2) (A) and (6^3) (B) nets in zeolite ABW. For clarity, the oxygen atoms are represented by straight lines

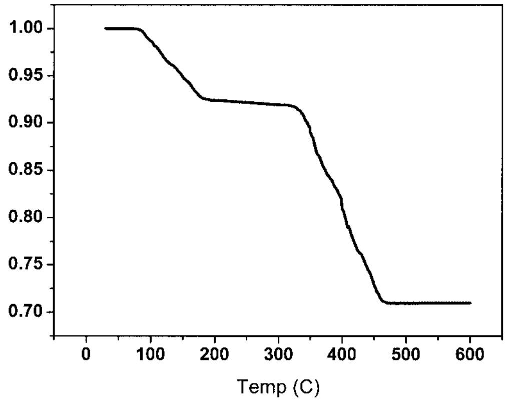


Figure 4. The TGA curve of **1**

In conclusion, we have synthesized a new microporous zinc phosphonocarboxylate with a zeolite ABW-type topology by base-catalyzed hydrolysis of trimethyl 3-phosphonopropionate. The use of the trialkyl phosphonocarboxylate as the phosphonocarboxylic acid source simplifies the traditional methods for metal phosphonocarboxylates and the in situ formation of phosphonocarboxylic acid guarantees the growth of single crystals of sufficient size for X-ray diffraction. The accessible channel in ABW-type zeolites consists of 16 atoms but partial replacement of O atoms with C−C−C−O groups as connectors in **1** generates same topological structure with a larger accessible channel consisting of 22 atoms.

Experimental Section

General Remarks The synthesis was carried out in a 15 mL volume Teflon-lined reactor under autogenous pressure with a filling capacity of 50 %. The CHN microanalysis was performed on a Perkin-Elmer 240 elemental analyzer. The FT-IR spectra were recorded in KBr pellets in the range of 4000−400 cm^{-1} on a Nicolet 5DX spectrometer. Thermal gravimetric analyses (TGA) were performed under a static air atmosphere from 30−600 °C using a Perkin-Elmer 7 thermogravimetric analyzer with a heating rate of 10 °C·min^{-1}.

Synthesis of Na[Zn(O$_3$PC$_2$H$_4$CO$_2$)]·H$_2$O (1): A mixture of Zn(MeCO$_2$)·2H$_2$O (0.220 g, 1 mmol), trimethyl 3-phosphonopropionate (0.228 g, 1 mmol), NaOH (0.18 g, 4.5 mmol), and H$_2$O (7 mL) in the molar ratio of 1:1:4.5:400 was stirred in air for 20 min (pH > 14) and transferred into a 15 mL Teflon-lined stainless steel reactor which was heated to 160 °C for 120 h. After cooling to room temperature, colorless needles **1** (65 %) in a single phase were recovered. The pH decreased to ca. 12 during the reaction. Elemental analysis for **1**: C$_3$H$_6$O$_6$ZnNa: calcd. C 14.00, H 2.35; found C 13.94, H 2.39. IR (KBr): $\tilde{\nu}$ = 3603 w cm^{-1}, 3451 br., 3088 w, 2968 w, 2927 w, 1641 s, 1608 m, 1562 s, 1454 m, 1418 m, 1257 m, 1124 m, 1094 s, 1011 s, 958 s, 832 m, 764 w, 721 w.

X-ray Crystallographic Study: Data collection was performed at 293 K on a Bruker Apex diffractometer (Mo-K_α, λ = 0.71073 Å). Lorentz-polarization and absorption corrections were applied. The structure was solved by direct methods and refined with the full-matrix least-squares technique (SHELX-97).[44] Analytical expressions of neutral-atom scattering factors were employed and anomalous dispersion corrections were incorporated. In all cases, all non-hydrogen atoms were refined anisotropically. Hydrogen atoms of organic ligands were geometrically placed. Hydrogen atoms of water were located from a difference Fourier map and refined with isotropic temperature factors. The crystallographic data for **1** are listed in Table 1 and selected bond lengths and bond angles are given in Table 2.

CCDC-216687 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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

Empirical formula	C$_3$H$_6$NaO$_6$PZn
Molecular mass	257.41
Temperature [K]	293(2)
Wavelength [Å]	0.71073
Crystal system	Monoclinic
Space group	$P2_1/n$
a [Å]	5.222(1)
b [Å]	15.519(3)
c [Å]	8.883(2)
β [°]	90.63(3)
V [Å^3]	719.8(3)
Z	4
Density (calculated) [Mg·m^{-3}]	2.375
Absorption coefficient [mm^{-1}]	3.678
F(000)	512
Crystal size [mm]	0.40 × 0.03 × 0.03
Theta range for data collection [°]	2.62−27.69
Index ranges	$-6 \le h \le 6; -13 \le k \le 20; -11 \le l \le 11$
Reflections collected	3341
Independent reflections	1520 R_{int} = 0.0325
Max. and min. transmission	0.8977 and 0.3209
Refinement method	Full-matrix least-squares on F^2
Data/restrains/parameters	1520/0/110
Goodness-of-fit on F^2	1.030
Final R indices [$I > 2\sigma(I)$]	0.0395, 0.0811
R indices (all data)	0.0530, 0.0850
Extinction coefficient	0.0006(9)
Largest diff. peak and hole [e·A^{-3}]	0.600 and −0.491

Acknowledgments

The author thanks Mrs. Shu-Ping Huang for collection of the X-ray data.

Table 2. Bond lengths [Å] and angles [°] in **1**

Bond	Bond length	Bond	Bond length
Zn(1)−O(3)[a]	1.926(3)	P(1)−O(2)	1.519(3)
Zn(1)−O(2)	1.938(3)	P(1)−O(1)	1.525(3)
Zn(1)−O(1)[b]	1.944(3)	P(1)−O(3)	1.529(3)
Zn(1)−O(5)[c]	1.947(3)	P(1)−C(1)	1.795(4)
O(1)−Na(1)	2.421(3)	Na(1)−O(3)[a]	2.518(3)
O(2)−Na(1)[d]	2.345(3)	Na(1)−O(1W)[e]	2.343(4)
Na(1)−O(4)[c]	2.290(3)		

Bond	Bond angle	Bond	Bond angle
O(3)[a]−Zn(1)−O(2)	114.59(12)	O(1)−P(1)−O(3)	109.91(16)
O(3)[a]−Zn(1)−O(1)[b]	110.70(12)	O(2)−P(1)−C(1)	108.59(19)
O(2)−Zn(1)−O(1)[b]	109.80(12)	O(1)−P(1)−C(1)	110.21(18)
O(3)[a]−Zn(1)−O(5)[c]	117.18(13)	O(3)−P(1)−C(1)	107.26(19)
O(2)−Zn(1)−O(5)[c]	101.05(13)	P(1)−O(1)−Zn(1)[e]	125.85(16)
O(1)[b]−Zn(1)−O(5)[c]	102.49(12)	P(1)−O(2)−Zn(1)	133.80(17)
O(2)−P(1)−O(1)	110.60(16)	P(1)−O(3)−Zn(1)[f]	129.39(18)
O(2)−P(1)−O(3)	110.21(16)		

[a] Symmetry codes: $x - 1/2, -y + 3, z + 1/2$; [b] $x + 1/2, -y + 3/2, z + 1/2$; [c] $-x + 1/2, y - 1/2, -z + 1/2$; [d] $x + 1, y, z$; [e] $x - 1/2, -y + 3/2, z - 1/2$; [f] $x + 1/2, -y + 3/2, z - 1/2$.

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Received August 12, 2003
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