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$[Zn_2(HPO_3)_2(H_2PO_3)][C_3H_5N_2]$ and $[Zn_2(HPO_3)_3][C_4H_7N_2]_2 \cdot 2H_2O$: Two new layered zinc phosphites with double 12-membered rings templated by imidazole and 2-methylimidazole

Li Liu, Yunling Liu, Guanghua Li, Chao Chen, Minghui Bi, Wenqin Pang*

State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun 130012, PR China

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Abstract

Two new zinc phosphites $[Zn_2(HPO_3)_2(H_2PO_3)][C_3H_5N_2]$ **1** and $[Zn_2(HPO_3)_3][C_4H_7N_2]_2 \cdot 2H_2O$ **2** have been hydrothermally synthesized templated by imidazole and 2-methylimidazole. Single-crystal X-ray diffraction analysis reveals that the two compounds have the similar inorganic framework structures, which both exhibit 2D double layer structures with double 12-membered rings. Due to the different space-filling effect of the guest molecules, the stacking mode of adjacent layers and the arrangement mode of the organic amines are distinct. In **1**, the adjacent layers are stacked in an –ABAB– sequence and monoprotonated imidazole molecules sit in the middle of 12MR windows, while in **2**, the layers are stacked in an –AAAA– pattern. Monoprotonated 2-methylimidazole molecules occupy two different sites, one inserts into 12MR and the other resides in the interlayer region. Crystal data for **1**: triclinic, $P\text{-}1$, $a = 8.8815(18)$ Å, $b = 9.0132(18)$ Å, $c = 10.030(2)$ Å, $\alpha = 114.71(3)^\circ$, $\beta = 92.78(3)^\circ$, $\gamma = 113.04(3)^\circ$, $V = 649.3(2)$ Å^3, $Z = 2$; for **2**: triclinic, $P\text{-}1$, $a = 9.883(4)$ Å, $b = 10.517(4)$ Å, $c = 11.814(5)$ Å, $\alpha = 68.244(7)^\circ$, $\beta = 76.143(7)^\circ$, $\gamma = 63.113(6)^\circ$, $V = 1013.3(7)$ Å^3, $Z = 2$.

Keywords: Hydrothermal synthesis; Crystal structure; Zinc phosphite; Double layer; Imidazole; 2-methylimidazole

1. Introduction

Design and synthesis of organically templated open-framework inorganic microporous materials are of great interest for their rich structure chemistry and potential applications in catalysis, separation and ion-exchange [1,2]. Among the vast family of inorganic microporous materials, metal phosphates constitute an important group. Especially, zinc phosphates with different dimensions and Zn/P ratios exhibit a rich structural and compositional diversity [3–12]. Recently, scientists have tried to substitute phosphate group for phosphite group to synthesize a new class of open-framework metal phosphites. Since Harrison et al. reported the first organically templated zinc phosphite in 2001 [13], considerable interest in the study of organically templated zinc phosphites has been aroused. Up to date, zinc phosphites with 0D cluster, 1D chain, 2D layer and 3D open-framework structures have been reported [14–22]. Compared to the tetrahedral phosphate group, the pyramidal phosphite group can only make three P–O–Zn bonds; thus, some more significant structures which are different from those formed by phosphate group have been isolated, such as $[H_2N(CH_2)_2NH_2]_{0.5} \cdot ZnHPO_3$ containing two independent interpenetrating mixed inorganic–organic networks [23], $(C_5N_2H_6)Zn(HPO_3)$ possessing an undulated sheet structure with left-handed and right-handed helical chains [24], and $(C_5NH_{12})_2 \cdot Zn_3(HPO_3)_4$ with helical columns and 16MR windows [25].

To pursue the novel structure and the study organic template effect, we extend the research to the zinc-phosphite-imidazole system. A study of those known imidazolium zinc phosphates/phosphites showed that imidazole and its derivative mostly act as the organic

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*Corresponding author. Fax: +86 431 5168624.
E-mail address: wqpang@mail.jlu.edu.cn (W. Pang).

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ligand directly bonding to framework zinc atom in the formation of various open-framework structures, such as $Zn_4P_3O_{11}(OH)\cdot 3C_3N_2H_4$ [26], $[C_3N_2H_5][Zn(HPO_4)]$ [27], $[C_4N_2H_6]_2[Zn(HPO_4)]$ [28], $(C_6N_3H_{12})_2Zn_5(HPO_3)_6$ [29], $Zn(HPO_3)(C_4H_6N_2)$ [30], $[Zn_2(HPO_3)_2(C_{10}H_{10}N_2)_2]_2$ [30], and $(C_3N_2H_4)_3Zn_{4-x}Co_x(PO_4)_2(HPO_4)$ $(x = 0.25)$ [31], whereas they rarely act as the organic template agent [15,32]. Herein, we report the syntheses and crystal structures of two zinc phosphites, $[Zn_2(HPO_3)_2(H_2PO_3)][C_3H_5N_2]$ **1** and $[Zn_2(HPO_3)_3][C_4H_7N_2]_2\cdot 2H_2O$ **2**, where imidazole and 2-methylimidazole both act as the organic template agents.

2. Experimental

2.1. Physical measurements

Powder X-ray diffraction (XRD) data were collected on a Siemens D5005 diffractometer with Cu*K*α radiation ($\lambda = 1.5418$ Å). The elemental analyses were performed on a Perkin–Elmer 2400 element analyzer. The inductively coupled plasma (ICP) analyses were carried out on a Perkin–Elmer Optima 3300DV ICP instrument. The infrared (IR) spectra were recorded within the 400–4000 cm^{-1} region on a Nicolet Impact 410 FTIR spectrometer using KBr pellets. The thermal gravimetric analyses (TGA) were performed on Perkin–Elmer TGA 7 thermogravimetric analyzer used in air with a heating rate of 10 °C min^{-1}. The ^{31}P MAS NMR spectra were collected on a Varian Unity-400 NMR spectrometer. Fluorescent spectra were measured on a Perkin–Elmer LS 55 luminescence spectrometer, equipped with a 450 W xenon lamp.

2.2. Synthesis

The two title compounds were synthesized under hydrothermal systems. Compound **1** was obtained from the gel composition $1.0Zn(OAc)_2\cdot 2H_2O$:$5.0H_3PO_3$:4.0 imidazole:110H_2O, which was heated at 160 °C for 5 days in a 15 mL Teflon-lined stainless-steel autoclave under autogeneous pressure. Compound **2** was prepared in a manner similar to **1** described above. The batch composition is $1.0Zn(OAc)_2\cdot 2H_2O$:3.0 H_3PO_3:4.4 2-methylimidazole:$110H_2O$. The resulting crystalline products were isolated by filtration, washed with distilled water, and dried in air. The agreement between the experimental and simulated XRD patterns indicated the phase purity of the product. Anal. found (wt%) for **1**: Zn, 29.74; P, 21.02; C, 8.25; H, 1.99; N, 6.23. Calcd. (wt%): Zn, 29.67; P, 21.10; C, 8.17; H, 2.04; N, 6.35. Anal. found (wt%) for **2**: Zn, 22.74; P, 16.12; C, 16.65; H, 3.71; N, 9.93. Calcd. (wt%): Zn, 22.69; P, 16.23; C, 16.76; H, 3.67; N, 9.77.

The TG curve of **1** exhibited a total weight loss of 19.59 wt% around 260–950 °C, corresponding to the loss of one organic amine molecule (calcd. 15.65 wt%) and one structural hydroxyl (calcd. 3.86 wt%). The TG curve of **2** showed a total weight loss of 36.18 wt% in the region 60–850 °C, corresponding to the loss of two free water molecules (calcd. 6.28 wt%) and the removal of two organic amine molecules (calcd. 28.97 wt%). XRD analyses indicated that the two title compounds both became amorphous after the decomposition of the occluded template molecules.

2.3. Structural determination

Suitable single crystals of **1** ($0.33\times 0.24\times 0.18\,mm^3$) and **2** ($0.26\times 0.24\times 0.17\,mm^3$) were selected for single-crystal X-ray diffraction analyses. The intensity data were collected on a Rigaku RAXIS-RAPID IP diffractometer for **1** and a Siemens Smart CCD diffractometer for **2** using graphite-monochromated Mo*K*α radiation ($\lambda = 0.71073$ Å). The number of collected reflections and independent reflections were 6443 and 2940 for **1**, 5574 and 3715 for **2**, respectively. Data processing was accomplished with the RAPID AUTO processing program for **1** and the SAINT processing program for **2**. The structures were both solved by direct methods and refined by full-matrix least squares on F^2 using SHELXTL Version 5.1 [33]. All the zinc and phosphorus atoms were first located. Then oxygen, carbon, nitrogen and hydrogen atoms of inorganic framework were found subsequently in difference Fourier maps. The hydrogen atoms of the amine molecule were placed geometrically. All non-hydrogen atoms were refined anisotropically. The crystallographic data of **1** and **2** are given in Table 1. Selected bond lengths and angles of **1** and **2** are listed in Table 2. H-bonding information of **1** and **2** is presented in Table 3.

Table 1
Crystal data and structure refinement for **1** and **2**

Compound	1	2
Empirical formula	$C_3H_9N_2O_9P_3Zn_2$	$C_8H_{21}N_4O_{11}P_3Zn_2$
Formula weight	440.77	572.94
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Triclinic
Space group	*P*-1	*P*-1
a (Å)	8.8815(18)	9.883(4)
b (Å)	9.0132(18)	10.517(4)
c (Å)	10.030(2)	11.814(5)
α (°)	114.71(3)	68.244(7)
β (°)	92.78(3)	76.143(7)
γ (°)	113.04(3)	63.113(6)
V ($Å^3$)	649.3(2)	1013.3(7)
Z	2	2
D_{calc} ($Mg\,m^{-3}$)	2.255	1.878
Absorption coefficient (mm^{-1})	4.104	2.663
Reflections collected	6443	5574
Reflections unique	2940 ($R_{int} = 0.0433$)	3715 ($R_{int} = 0.0390$)
Goodness-of-fit on F^2	1.058	0.859
Final *R* indices [$I>2\sigma(I)$]	$R_1 = 0.0414$ $wR_2 = 0.0997$	$R_1 = 0.0428$ $wR_2 = 0.0644$
Largest diff. peak and hole ($e\,Å^{-3}$)	0.650, −0.968	0.904, −0.490

Table 2
Selected bond lengths (Å) and angles (°) for **1** and **2**

1			
Zn(1)–O(3)	1.927(3)	P(1)–O(1)	1.536(3)
Zn(1)–O(1)	1.943(3)	P(1)–H(1)	1.31(5)
Zn(1)–O(2)	1.945(3)	P(2)–O(2)	1.510(4)
Zn(1)–O(4)	1.950(3)	P(2)–O(4)^{b}	1.521(3)
Zn(2)–O(5)	1.924(3)	P(2)–O(6)	1.524(4)
Zn(2)–O(8)	1.925(4)	P(2)–H(2)	1.34(5)
Zn(2)–O(7)	1.935(3)	P(3)–O(8)^{c}	1.496(4)
Zn(2)–O(6)	1.961(3)	P(3)–O(3)	1.502(3)
P(1)–O(7)^{a}	1.511(3)	P(3)–O(9)	1.555(4)
P(1)–O(5)	1.514(3)	P(3)–H(3)	1.34(7)
O(3)–Zn(1)–O(1)	108.80(16)	O(7)^{a}–P(1)–H(1)	109.5(19)
O(3)–Zn(1)–O(2)	111.06(14)	O(5)–P(1)–H(1)	104.1(19)
O(1)–Zn(1)–O(2)	109.51(15)	O(1)–P(1)–H(1)	106.5(19)
O(3)–Zn(1)–O(4)	102.25(15)	O(2)–P(2)–O(4)^{b}	114.1(2)
O(1)–Zn(1)–O(4)	113.80(15)	O(2)–P(2)–O(6)	113.0(2)
O(2)–Zn(1)–O(4)	111.22(16)	O(4)^{b}–P(2)–O(6)	108.8(2)
O(5)–Zn(2)–O(8)	108.99(16)	O(2)–P(2)–H(2)	107(2)
O(5)–Zn(2)–O(7)	113.15(16)	O(4)^{b}–P(2)–H(2)	108(2)
O(8)–Zn(2)–O(7)	99.34(15)	O(6)–P(2)–H(2)	105(2)
O(5)–Zn(2)–O(6)	112.91(15)	O(8)^{c}–P(3)–O(3)	111.9(2)
O(8)–Zn(2)–O(6)	111.92(17)	O(8)^{c}–P(3)–O(9)	113.4(2)
O(7)–Zn(2)–O(6)	109.78(16)	O(3)–P(3)–O(9)	110.7(2)
O(7)^{a}–P(1)–O(5)	114.1(2)	O(8)^{c}–P(3)–H(3)	116(3)
O(7)^{a}–P(1)–O(1)	108.3(2)	O(3)–P(3)–H(3)	112(3)
O(5)–P(1)–O(1)	114.0(2)	O(9)–P(3)–H(3)	91(3)
2			
Zn(1)–O(2)	1.915(3)	P(1)–O(7)^{d}	1.527(3)
Zn(1)–O(1)	1.925(3)	P(1)–H(1)	1.41(5)
Zn(1)–O(3)	1.926(3)	P(2)–O(6)	1.506(3)
Zn(1)–O(4)	1.970(3)	P(2)–O(2)	1.507(3)
Zn(2)–O(6)	1.929(3)	P(2)–O(4)^{e}	1.524(3)
Zn(2)–O(5)	1.935(3)	P(2)–H(2)	1.42(5)
Zn(2)–O(7)	1.950(3)	P(3)–O(9)	1.490(3)
Zn(2)–O(8)	1.955(3)	P(3)–O(3)	1.511(3)
P(1)–O(1)	1.507(4)	P(3)–O(8)^{f}	1.541(3)
P(1)–O(5)	1.514(3)	P(3)–H(3)	1.28(4)
O(2)–Zn(1)–O(1)	116.92(14)	O(1)–P(1)–H(1)	105(2)
O(2)–Zn(1)–O(3)	106.39(14)	O(5)–P(1)–H(1)	106.3(19)
O(1)–Zn(1)–O(3)	116.16(16)	O(7)^{d}–P(1)–H(1)	108(2)
O(2)–Zn(1)–O(4)	115.41(14)	O(6)–P(2)–O(2)	114.3(2)
O(1)–Zn(1)–O(4)	101.08(14)	O(6)–P(2)–O(4)^{e}	109.94(18)
O(3)–Zn(1)–O(4)	99.82(13)	O(2)–P(2)–O(4)^{e}	112.70(18)
O(6)–Zn(2)–O(5)	117.04(14)	O(6)–P(2)–H(2)	106(2)
O(6)–Zn(2)–O(7)	109.04(14)	O(2)–P(2)–H(2)	108.2(19)
O(5)–Zn(2)–O(7)	107.49(14)	O(4)^{e}–P(2)–H(2)	105(2)
O(6)–Zn(2)–O(8)	113.09(14)	O(9)–P(3)–O(3)	113.3(2)
O(5)–Zn(2)–O(8)	102.10(13)	O(9)–P(3)–O(8)^{f}	113.05(19)
O(7)–Zn(2)–O(8)	107.49(14)	O(3)–P(3)–O(8)^{f}	110.3(2)
O(1)–P(1)–O(5)	114.5(2)	O(9)–P(3)–H(3)	110.2(19)
O(1)–P(1)–O(7)^{d}	108.8(2)	O(3)–P(3)–H(3)	101.2(17)
O(5)–P(1)–O(7)^{d}	113.97(18)	O(8)^{f}–P(3)–H(3)	108.1(18)

Symmetry transformations used to generate equivalent atoms: $^{a}-x, -y, -z+1$, $^{b}-x+1, -y+1, -z+2$, $^{c}-x+1, -y+1, -z+1$, $^{d}-x+2, -y+1, -z+2$, $^{e}-x+2, -y+2, -z+2$, $^{f}-x+1, -y+2, -z+2$.

Table 3
Hydrogen bonds for **1** and **2**

D–H···A	d(D–H) (Å)	d(H···A) (Å)	d(D···A) (Å)	Ang(DHA) (deg.)
1				
O(9)–H(9)···O(6)^{a}	0.82	2.15	2.633(5)	117.6
2				
O(1W)–H(1WA)···O(2W)^{b}	0.90(2)	2.27(6)	2.827(7)	120(5)
O(1W)–H(1WB)···O(9)^{b}	0.93(2)	1.85(2)	2.779(6)	174(5)
O(2W)–H(2WB)···O(1W)^{c}	0.92(2)	2.10(5)	2.827(7)	135(6)
N(1)–H(1A)···O(7)^{d}	0.86	2.03	2.874(6)	167.1
N(2)–H(2A)···O(8)	0.86	1.91	2.766(6)	176.7
N(3)–H(3A)···O(4)^{b}	0.86	1.97	2.796(5)	161.9
N(4)–H(4)···O(9)^{e}	0.86	1.81	2.652(5)	164.9

Symmetry transformations used to generate equivalent atoms: $^{a}x, y+1, z$, $^{b}x, y-1, z$, $^{c}x, y+1, z$, $^{d}-x+1, -y+1, -z+2$, $^{e}-x+1, -y+2, -z+1$.

3. Results and discussion

3.1. Crystal structure of $[Zn_2(HPO_3)_2(H_2PO_3)][C_3H_5N_2]$ 1

The asymmetric unit of **1** contains 19 non-hydrogen atoms, of which 14 atoms belong to the framework (two Zn, three P and nine O atoms) and five to the guest organic amine molecule (three C and two N atoms). The two zinc atoms are tetrahedrally coordinated by four oxygen atoms with the average Zn–O bond length of 1.939(1) Å. The O–Zn–O bond angles are in the range of 99.34(2)–113.80(2)°. Of the three crystallographically independent P atoms, P(1) and P(2) atoms link to three Zn atoms via bridging oxygen atoms and one proton (P–H), respectively. P(3) atom bridges to two Zn atoms and possesses one terminal –OH group and one P–H bond. The average value of P–O bond lengths is 1.519(1) Å and the O–P–O bond angles are in the range of 108.3(2)–114.1(2)°. Of the nine O atoms, O(9) atoms are protonated (–OH group), others are two coordinated.

Compound **1** exhibits a novel 2D double layer structure formed by vertex-sharing ZnO_4, HPO_3 and $HPO_2(OH)$ units with 4-, 8- and 12MR. The connection of the strictly alternating ZnO_4 and HPO_3 units by vertex-sharing mode results in a double chain with 4MR (Fig. 1a). These double chains are further linked together through $HPO_2(OH)$ units to form an infinite 2D double layer structure with double 12-membered rings (D12MRs) (Fig. 1b). The D12MR is composed of six 4MR, two 8MR and two 12MR, denoted as $4^6 8^2 12^2$ cage-like (Fig. 1c). The atom-to-atom dimensions of these 12MR windows are approximately 10.1 × 10.8 Å.

The inorganic framework is anionic $[Zn_2(HPO_3)_2(H_2PO_3)]^-$ and the charge compensation is achieved by the presence of the monoprotonated imidazole molecule. The monoprotonated imidazole molecules sit in the middle of 12MR windows (Fig. 2a). Interestingly, there is no hydrogen bond interaction between the imidazole cation and the framework oxygen atom. Each couple of imidazole cations sitting in the middle of D12MR windows are parallel to each other with a distance of ≈3.5 Å, exhibiting strong π–π stacking interactions, which make imidazole cations stably exist in the D12MR windows. Fig. 2b shows the packing of the inorganic layers viewed

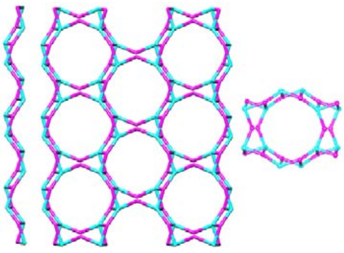

Fig. 1. (a) Double chain in the structure of **1** with 4MRs; (b) stick view of the inorganic double layer of **1** with D12MRs; (c) the D12MR composed of six 4MRs, two 8MRs and two 12MRs. (O atoms, H atoms and organic species are omitted for clarity.)

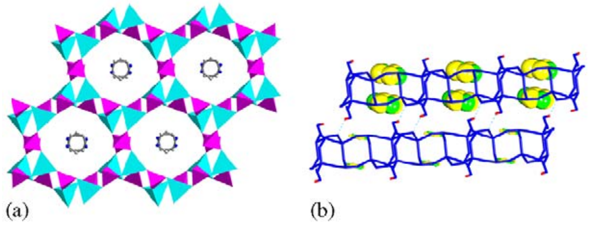

Fig. 2. (a) Polyhedral view of the double layer structure of **1** showing the monoprotonated imidazole molecules sitting in the middle of the D12MR windows. (b) The packing of the inorganic layers of **1** viewed along the *c*-axis with the –ABAB– stacking sequence. Dotted lines indicate H-bond.

along the *c*-axis with an –ABAB– stacking sequence. It is noted that –OH groups exclusively protrude into the interlayer region.

The layer structure is stabilized by the strong hydrogen bonds between the terminal hydroxyl groups and the O(6) atoms of the adjacent layers [O(9)–H(9)$\cdots$O(6) $= 2.633(5)$ Å] forming the pseudo-D12MR (Table 3).

3.2. *Crystal structure of* $[Zn_2(HPO_3)_3][C_4H_7N_2]_2 \cdot 2H_2O$ **2**

The asymmetric unit of **2** contains 28 non-hydrogen atoms, of which 14 atoms belong to the framework (two Zn, three P and nine O atoms) and 14 to the guest molecules (eight C, four N and two O atoms). Zn(1) and Zn(2) atoms are tetrahedrally coordinated by four oxygen atoms with the average Zn–O bond length of 1.938(4) Å. The O–Zn–O bond angles are in the range of 99.82(1)–117.04(1)°. Of the three crystallographically independent P atoms, P(1) and P(2) atoms link to three Zn atoms via bridging oxygen atoms and one proton (P–H), respectively. P(3) atom bridges to two Zn atoms, leaving one terminal =O group and one P–H bond. The average value of P–O bond lengths is 1.514(4) Å. The O–P–O bond angles are in the range of 108.8(2)–114.5(2)°. The stoichiometry of $[Zn_2(HPO_3)_3]$ would result in a charge of -2, which is balanced by two monoprotonated 2-methylimidazole molecules. The inorganic framework of **2** consists of strictly alternating ZnO_4 and HPO_3 units which are vertex linked forming a 2D double layer structure with D12MRs (Fig. 3a). The atom-to-atom dimensions of these 12MR windows are approximately 10.3×10.5 Å. The structure of **2** is very similar to that of **1**, the only difference is that O(9) atoms in **2** are terminal =O group, whereas O(9) atoms in **1** are protonated (–OH group). However, unlike **1**, the adjacent layers of **2** are stacked in an –AAAA– sequence viewed along the *a*-axis (Fig. 3b). There are two crystallographically distinct monoprotonated 2-methylimidazole molecules, one inserts into the 12MR cavity and the other occupies the interlayer space. The arrangement of organic species in the interlayer space is parallel to the inorganic layers with such alternately reverse orientations indicated in Fig. 3b. There are also two free water molecules lying in the interlayer region. It is interesting that one couple of 2-methylimidazole cations in D12MR cavity has no π–π stacking interactions, while the other couple in the interlayer space exist the strong π–π stacking interactions with a distance of ≈ 3.5 Å.

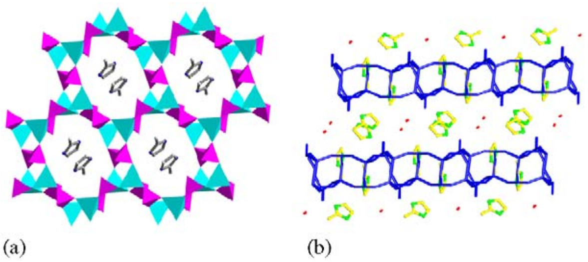

Fig. 3. (a) Polyhedral view of the double layer structure of **2**. (b) View of **2** showing the packing layers with the –AAAA– stacking sequence and the location of 2-methylimidazole cations and the free water molecules viewed along the *a*-axis.

The organic cations and free water molecules in the interlayer interact with framework oxygen atoms through strong N–H$\cdots$O and O–H$\cdots$O hydrogen bond [N(3)–H(3)$\cdots$O(4) $= 2.796(5)$ Å], [N(4)–H(4)$\cdots$O(9) $= 2.652(5)$ Å] and [O(1W)–H(1WB)$\cdots$O(9) $= 2.779(6)$ Å], which help to hold the layers together. In addition, there are also strong intralayer hydrogen bond interactions [N(1)–H(1)$\cdots$O(7) $= 2.874(6)$ Å] and [N(2)–H(2)$\cdots$O(8) $= 2.766(6)$ Å] (Table 3).

3.3. *Discussion*

The inorganic framework structures of **1** and **2** are very closely related. The role of imidazole and 2-methylimidazole in the formation of their structures are both organic template agents. By comparing with those known imidazolium zinc phosphates/phosphites, the title compounds exhibit novel 2D double layer structures with 4-, 8- and 12MRs, which is different from those 2D layered $Zn_4P_3O_{11}(OH) \cdot 3C_3N_2H_4$ with 3-, 4-, 5-, and 10MR [26] and $[Zn_2(HPO_3)_2(C_{10}H_{10}N_2)_2]_2$ with 4, 8^2-network [30], where imidazole or its derivative acts as the organic ligand directly bonding to framework zinc atoms. To our knowledge, imidazole and its derivative commonly act as the organic ligand in the formation of zinc phosphates/phosphites, whereas they rarely act as the organic template agent. Recently, a 3D open-framework zinc phosphite with 4-, 8- and 12MRs templated by imidazole has been reported by G.Y. Yang et al. [15], which is consist of 2D layers with 4,12-network and 1D helical chains. Although 3D open-framework structures with 4-, 8- and 12MR are the common patterns in zinc phosphates/phosphites [10–12,14–16], such 2D double layer structure with 4-, 8- and 12MR is rare. Only two compounds $Zn(DETA)Zn_2(HPO_3)_3$ [34] and $Zn_3(tren)(HPO_3)_3 \cdot 0.5H_2O$ [35] are observed, in which organic amines are also the ligands.

In addition, due to the different space-filling effect of the guest organic amine molecules, the structures of **1** and **2** have some very interesting differences. First, the arrangement mode of the guest molecules is different. Imidazole cations reside in the middle of 12MR windows in **1**, whereas in **2**, 2-methylimidazole cations occupy two different sites, one inserts into 12MR and the other lies in the interlayer region. Second, the stacking mode of adjacent layers is distinct. In **1**, the adjacent layers are stacked in an –ABAB– sequence, while in **2**, the layers are stacked in an –AAAA– pattern.

4. Conclusion

In this paper, we have successfully synthesized two novel zinc phosphites, $[Zn_2(HPO_3)_2(H_2PO_3)][C_3H_5N_2]$ **1** and $[Zn_2(HPO_3)_3][C_4H_7N_2]_2 \cdot 2H_2O$ **2**, using imidazole and 2-methylimidazole as organic template agents, respectively. Compounds **1** and **2** both exhibit novel 2D double layer structures with D12MR cavities. It is believed that zinc phosphites with more novel structures will be synthesized by the variation of the organic amines and crystallization conditions.

Supporting information and structure details

Crystallographic data for the structure reported in this paper in the form of CIF file have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-254016 for **1** and no. CCDC-277932 for **2**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: (+44)1223-336-033; E-mail: deposit@ccdc.cam.ac.uk).

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Appendix A. Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2006.01.066.

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