

# Ionothermal synthesis of a new open-framework zinc phosphite NIS-3 with low framework density†

Jing-Dong Feng,<sup>ab</sup> Kui-Zhan Shao,<sup>a</sup> Shu-Wei Tang,<sup>a</sup> Rong-Shun Wang<sup>\*a</sup> and Zhong-Min Su<sup>\*a</sup>

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**The first ionothermal case of open-framework metal phosphite,  $\text{Zn}_3(\text{HPO}_3)_4 \cdot 2\text{C}_6\text{H}_{11}\text{N}_2$ , denoted NIS-3, was prepared using 1-ethyl-3-methyl imidazolium bromide as solvent and template.**

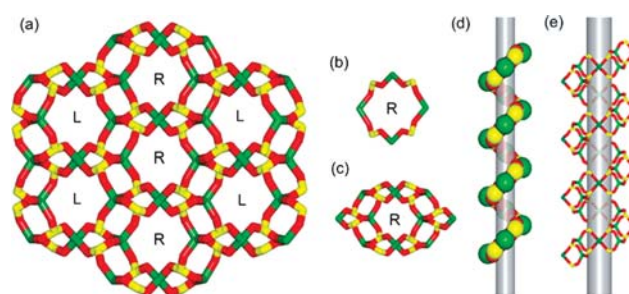
Open-framework materials have been hydrothermally and solvothermally studied during the past decades due to their rich structural chemistry and potential applications in catalysis, separation and ion-exchange processes.<sup>1</sup> In 2004, Morris and co-workers firstly reported the application of ionothermal methodology in the synthesis of open-framework aluminium phosphates.<sup>2</sup> To date, more and more attention has been paid to the ionothermal method due to the excellent solvating properties, vanishingly small vapor pressure, high thermal stability, and recyclability of ionic liquids (ILs) as “green” solvent.<sup>3</sup> Furthermore, the application of an IL as solvent and template can effectively remove the competition between template-framework and solvent-framework interactions that occurs inevitably in traditional preparation. The different chemistry of ionothermal solvent system produces conditions under which novel structures may be accessible. Recent publications employing ionothermal method have reported the synthesis of aluminophosphates,<sup>2,4</sup> cobalt aluminophosphates,<sup>5</sup> silicoaluminophosphate,<sup>6</sup> magnesium-containing aluminophosphate,<sup>7</sup> zinc phosphates,<sup>8</sup> gallium phosphates,<sup>4b,9</sup> zirconium phosphates,<sup>10</sup> and organic-inorganic hybrid materials.<sup>11</sup> Many of these structures are new, presenting the potential of ionothermal method in the design of porous materials. On the other hand, it is known the pseudo-pyramidal  $[\text{HPO}_3]^{2-}$  is structurally similar to the  $[\text{PO}_4]^{3-}$  phosphate anion and lots of metal phosphites have been reported with traditional method during the past decade.<sup>12</sup> As far as we know, however, so far ionothermal preparation of open-framework metal phosphites has never been reported. All this enhances our curiosity to explore metal phosphites with the ionothermal method.

In this work, a new three-dimensional (3D) zinc phosphite,  $\text{Zn}_3(\text{HPO}_3)_4 \cdot 2\text{C}_6\text{H}_{11}\text{N}_2$ , denoted NIS-3, was prepared using 1-ethyl-3-methyl imidazolium (EMIM) bromide as solvent and template.† As far as we know, NIS-3 is the first ionothermal case of metal phosphite.

Single-crystal structural analysis revealed that NIS-3 consists of a macroanionic  $[\text{Zn}_3(\text{HPO}_3)_4]^{2-}$  framework, and the charge neutrality is balanced by EMIM cations. The asymmetric unit of NIS-3, as shown in Fig. S1,† contains three crystallographically distinct Zn atoms, four crystallographically unique P atoms and two EMIM cations. All Zn atoms are in tetrahedral environments. Each P atom connects three O atoms to nearby Zn atoms, leaving a terminal P–H bond. The bond lengths (Zn–O 1.921–1.961 Å, P–O 1.493–1.516 Å) and angles (O–Zn–O 103.39–120.19°, O–P–O 111.40–114.48°) are in agreement with those observed in the known zinc phosphites.<sup>12a–d</sup> The existence of P–H bonds is confirmed by the characteristic band of the phosphite anion ( $2353\text{ cm}^{-1}$ ) in the IR spectra, as shown in Fig. S2.†

NIS-3 crystallizes in the space group  $P2_1/c$ .§ Strictly alternating Zn-centered tetrahedral and P-centered pseudopyramidal building units are connected *via* sharing of vertex and form a 3D open-framework structure. NIS-3 has a typical Zn/P ratio of 3/4 and shows a (3,4)-connected structure, in which the pseudopyramidal  $[\text{HPO}_3]^{2-}$  anion is three-connected and the  $\text{Zn}^{2+}$  cation is four-connected. Furthermore, its architecture is quite similar to zinc phosphites  $\text{ZnPO}_3 \cdot n$  ( $n = 1, 2, 3$ ),<sup>12a</sup> and it can also be viewed as a structural analogue of zinc hydrogen phosphate  $[\text{Zn}_3(\text{HPO}_4)_4](\text{NMe}_4)_2$ ,<sup>13</sup> suggesting that the bonding difference between –P–H and –P–OH plays an insignificant role in the formation of phosphite and hydrogen phosphate open frameworks.

As shown in Fig. 1a, the framework appears to have 8-membered ring (8MR) “openings” (*ca.*  $5.3 \times 4.4\text{ Å}$ , the shortest O···O diagonal distance, taking the van der Waals radii into account) when projected along the [100] direction, but in fact there are only 8MR helical channels with opposite helices coupling with each other along this



**Fig. 1** (a) The framework of NIS-3 projected along the [100] direction; (b) the projection of 8MR right-handed helical chain along the [100] direction; (c) the projection of 8MR right-handed helical “ribbon” along the [100] direction; (d) 8MR right-handed helical chain; (e) 8MR right-handed helical “ribbon”. L represents left-handed helical structure and R represents right-handed helical structure. All hydrogen atoms and EMIM cations are omitted for clarity. Green, Zn; yellow, P; red, O.

<sup>a</sup>Institute of Functional Material Chemistry, Faculty of Chemistry, Northeast Normal University, Changchun, 130024, P. R. China. E-mail: wangrs@nenu.edu.cn; zmsu@nenu.edu.cn; Fax: (+86) 431-85099511

<sup>b</sup>Institute of Applied Chemistry, College of Chemistry, Jilin Normal University, Siping, 136000, P. R. China

† Electronic supplementary information (ESI) available: IR spectra, XRD patterns, TGA curve, and complementary drawings for crystal structure have been included. CCDC reference number 753373. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b923583c

direction. The right-handed helical structures are given as examples (Fig. 1b–e). It is noteworthy that, the channels not only can be viewed as being enclosed by  $-\text{Zn}-\text{O}-\text{P}-\text{Zn}-\text{O}-\text{P}-\text{Zn}-\text{O}-\text{P}-\text{Zn}-\text{O}-\text{P}-$  helical chain (Fig. 1d), but also can be envisioned as being enclosed by corner-sharing and edge-sharing 4MRs helical “ribbon” along this direction (Fig. 1e).

In addition, when projected along the [001] and [110] directions, as shown in Fig. 2 and Fig. 3a, the framework shows 16MR channels in which EMIM cations are accommodated. These two kinds of 16MRs channels are different apparently from each other, and the sizes of channels are of *ca.*  $6.1 \times 3.4 \text{ \AA}$  and  $10.0 \times 3.1 \text{ \AA}$  (the shortest O...O diagonal distance, taking the van der Waals radii into account) along the [001] and [110] directions, respectively. It is noteworthy that, the architecture of NIS-3 observed along the [110] direction can be viewed as being formed by corner-sharing  $[\text{Zn}(\text{HPO}_3)_2]^{2-}$  anionic chains (Fig. 3b) and edge-sharing  $\text{Zn}(\text{HPO}_3)$  zigzag ladder chains (Fig. 3c). These two kinds of chains are both made by the linkages of 4MRs, and as far as we are aware, both of them are common motifs in ZnPO structural chemistry.<sup>14</sup>

In general, the “openness” of a structure is defined in terms of the number of tetrahedral atoms per 1000  $\text{\AA}^3$ , *i.e.* framework density (FD). Herein, NIS-3 shows a low FD value of 11.0, which can be comparable with those of frameworks with extra-large ring (>16MR) channels, such as NTHU-1 (10.9),<sup>15</sup> ZnHPO-2 (11.0),<sup>12c</sup> FDU-4

(11.1),<sup>16</sup> TJPU-3 (11.3),<sup>17</sup> ZnHPO-3 (11.3),<sup>12c</sup> ZnHPO-1 (11.6),<sup>12b</sup> NTHU-5 (11.8)<sup>18</sup> and ND-1(12.1).<sup>19</sup> Quite intriguingly, NIS-3 has not any extra-large ring channels but exhibits low FD. According to the literature,<sup>12a</sup> the use of three-connected center represents a feasible way toward the design of highly open-framework structure. It is known that low FD structure always means large extra-framework space. A PLATON analysis,<sup>20</sup> performed only on the inorganic framework structure of NIS-3, suggests a solvent accessible volume of approximately  $1412.1 \text{ \AA}^3$  per unit cell ( $2540.2 \text{ \AA}^3$ ) amounting to 55.6% of the crystal lattice.

Furthermore, it is known that hydrogen bonding plays an important role during the course of crystallization in the traditional synthesis of open-framework materials, for which organic amines or metal complexes act as templates. For NIS-3, however, there is no hydrogen bonding between IL cations and the inorganic framework, as well as some other ionothermal examples reported previously.<sup>2</sup> It can be explained that the EMIM cations with the “wrong” configuration are inserted into the experimental lattice to play a space-filling role and the “weak” interaction between templates and framework is completely generated by van der Waals effect rather than template-framework hydrogen bonding.

Thermogravimetric analysis (TGA), as shown in Fig. S3,† indicates that NIS-3 has no weight loss before  $260^\circ\text{C}$  in air. Then, the products decomposed and a broad weight loss occurred from  $260$  to  $920^\circ\text{C}$ . XRD study (Fig. S4†) suggests that the cooling residue is  $\text{Zn}_2\text{P}_2\text{O}_7$  (JCPDS: 72-1702).

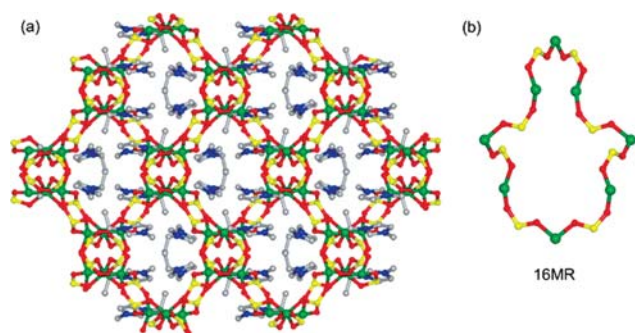
In summary, a new 3D open-framework zinc phosphite NIS-3 has been synthesized under ionothermal conditions. The framework shows helical structures and low FD value which can be comparable with those frameworks possessing extra-large ring channels, although the largest window is 16MR in its structure. It is noteworthy that NIS-3 is a structural analogue of a known zinc hydrogen phosphate, suggesting that the bonding difference between  $-\text{P}-\text{H}$  and  $-\text{P}-\text{OH}$  plays an insignificant role in the formation of phosphite and hydrogen phosphate open frameworks. In addition, NIS-3 is the first ionothermal case of metal phosphites, which implies more open-framework materials with fascinating structures and interesting properties would be expected by using ionothermal reaction.

## Acknowledgements

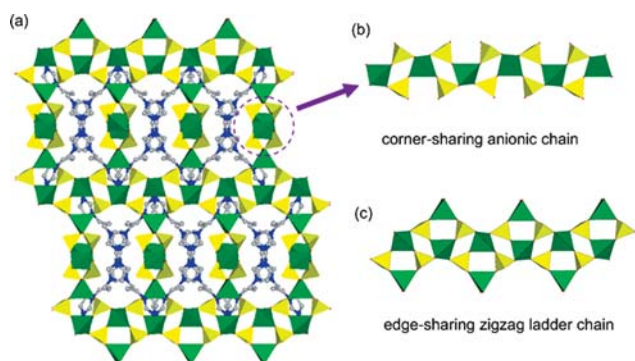
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## Notes and references

† Synthesis of  $\text{Zn}_3(\text{HPO}_3)_4 \cdot 2\text{C}_6\text{H}_{11}\text{N}_2$  (NIS-3): A mixture of zinc oxide (0.20 g, 2.46 mmol), phosphorous acid (0.26 g, 3.17 mmol) and 1-ethyl-3-methyl imidazolium bromide (4.16 g, 21.8 mmol) was heated in a 23 ml Teflon-lined stainless steel autoclave at  $150^\circ\text{C}$  for 6 days under static pressure, and then cooled to room temperature. Colorless crystals of NIS-3 were obtained with 60% yield (based on phosphorous acid). XRD results are in good accordance with the simulated pattern (Fig. S5†), proving the phase purity. Inductively coupled plasma (ICP) and elemental analysis (%) calcd for NIS-3: Zn 26.57, P 16.78, C 19.52, H 3.55, N 7.59; found: Zn 26.44, P 16.84, C 19.64, H 3.62, N 7.46.



**Fig. 2** (a) Ball-stick view of NIS-3 projected along the [001] direction; (b) the 16MR structure viewed along the [001] direction. All hydrogen atoms are not shown for clarity. Green, Zn; yellow, P; red, O; blue, N; grey, C.



**Fig. 3** (a) Polyhedral view of NIS-3 projected along the [110] direction; (b) corner-sharing anionic chain; (c) edge-sharing zigzag ladder chain. Hydrogen atoms on EMIM cations are omitted for clarity. Green, Zn; yellow, P; red, O; blue, N; grey, C.

§ Crystal data for NIS-3:  $\text{C}_{12}\text{H}_{26}\text{N}_4\text{O}_{12}\text{P}_4\text{Zn}_3$ ,  $M = 738.36$ , monoclinic,  $a = 11.2240(15)$  Å,  $b = 14.3540(19)$  Å,  $c = 16.709(2)$  Å,  $\alpha = 90.00^\circ$ ,  $\beta = 109.330(2)^\circ$ ,  $\gamma = 90.00^\circ$ ,  $V = 2540.2(6)$  Å<sup>3</sup>,  $T = 293(2)$  K, space group  $P2_1/c$ ,  $Z = 4$ , 15146 reflections measured, 5959 independent reflections ( $R_{\text{int}} = 0.0467$ ). The final  $R_1$  values were 0.0629 ( $I > 2\sigma(I)$ ). The final  $wR(F^2)$  values were 0.1753 ( $I > 2\sigma(I)$ ). The final  $R_1$  values were 0.1113 (all data). The final  $wR(F^2)$  values were 0.1968 (all data). Intensity data were measured using a Bruker Smart Apex II CCD diffractometer with graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å). All absorption corrections were performed using the SADABS.<sup>21</sup> The structure was solved by direct methods and refined on  $F^2$  by full-matrix least-squares analysis with SHELXTL-97 software.<sup>22</sup> The hydrogens of C atoms were placed in idealized positions, and the hydrogens of P atoms were directly located from successive Fourier differences syntheses. All non-hydrogen atoms were refined anisotropically. The disordered C4 and C10 atoms were treated with restrained refinement.

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