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Synthesis, characterization, and catalytic behavior of two open-framework zinc phosphites with 2D and 3D structures

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ABSTRACT

Two new zincophosphites are obtained via a hydrothermal process. Single crystal data indicate that **1** has a two dimensional motif with the organic amine template embedded between the layers, while **2** has a three-dimensional structure with the organic amine template enclosed into the cavities. Knoevenagel condensation of benzaldehyde and ethyl cyanoacetate is carried out with these two complexes as support in ethanol at 333 K respectively. Experimental results indicate that only **1** is efficient for the catalysis. The catalytic ability depends on their structural characters.

Zeolite-like crystalline metal phosphates are interesting for their similar structural motifs as zeolite materials with MO_4 and PO_4 tetrahedra as connection units [1]. For the past decades, many open frameworks base on metal phosphates have been prepared and characterized with organic species as templation reagents [2–4]. And the purpose of constructing interrupted open framework extends the research to the synthesis of metal phosphites [5,6]. The replacement of PO_4 tetrahedra by pyramidal HPO_3 phosphite unit generates various novel structures with different fascinating features. Their structural motifs range from infinite chains [7,8], layers [9–12] to three-dimensional porous frameworks [13–16]. However, most of the investigations for metal phosphites only focus on the characters of novel structures and topologies. Although zeolite and zeolite-like materials have been widely used as heterogeneous catalysts among industrial manufacture of organic chemicals [17], rare cases are given to the correlation between structures and properties for metal phosphites. Recently, the need of base solids for replacement of liquid base in the industrial catalysis process intrigues a research for functional zeolite materials [18]. By comparison with liquid catalysts, functional zeolite solid materials have higher atom efficiency. And they simplify the process and reduce the volume of waste. Since alkaline exchanged zeolites have been successfully used for base catalysis reactions [19–21], it is interesting to explore the catalytic ability of the zeolite-like metal phosphite materials. Herein, we report the first investigation of zinc phosphites for the catalysis of Knoevenagel condensation reaction. The structures of two zinc phosphites are characterized by single crystal data. Compound **1** $[C_4H_9NH_3]_4[Zn_6(HPO_3)_8]\cdot 3H_2O$ contains a two dimensional framework constructed by 4, 6, and 8 rings. Organic amine templates are embedded between the layers. Compound **2** $[C_3H_7ONH_3]_2[Zn_3(HPO_3)_4]$ has a three-dimensional motif with the templates included into the 12 ring channels. Studies on Knoevenagel condensation of benzaldehyde and ethyl cyanoacetate over these two zinc phosphites indicate that compound **1** performs a lot better than compound **2**.

Compound **1** and compound **2** are obtained from the hydrothermal reactions at 160 °C [22]. Single crystal data reveal that the asymmetric unit of compound **1** contains three zinc ions with the same tetrahedral coordination geometry [23]. They are surrounded by four oxygen atoms from the HPO_3^{2-} anions with bond length ranging from 1.904 (5) Å to 1.978(4)Å (Fig. 1a). Each HPO_3^{2-} anion shares three oxygen atoms from three different zinc ions. The vertex-sharing connections between ZnO_4 and tetrahedral HPO_3^{2-} blocks result in three kinds of building units: four-membered, six-membered and eight-membered rings (Fig. 1b). Assembly of these units finally results in a two dimensional structural motif as that in $(C_6H_{16}N_2)Zn_3(HPO_3)_4\cdot H_2O$ [24]. The organic sec-butylammonium templation ions and guest water molecules locate at the space between the layers (Fig. 1c). And they form hydrogen bonds with the oxygen atoms of the zinc phosphite host framework ($O\cdots O = 2.94$ Å, $O\cdots N = 2.97$ Å). For the structure of compound **2**, there are two unique zinc sites and two phosphorus sites. All the zinc centers are tetrahedral coordinated with four oxygen atoms from four different HPO_3^{2-} anions (Fig. 2a). The phosphorus atoms of HPO_3^{2-} blocks connect with three adjacent zinc centers. The connections between the ZnO_4 and HPO_3^{2-} groups result in a three-dimensional network without Zn–O–Zn and P–O–P linkages [25]. Four different subunits (4, 6, 8, and 12 rings) exist in the

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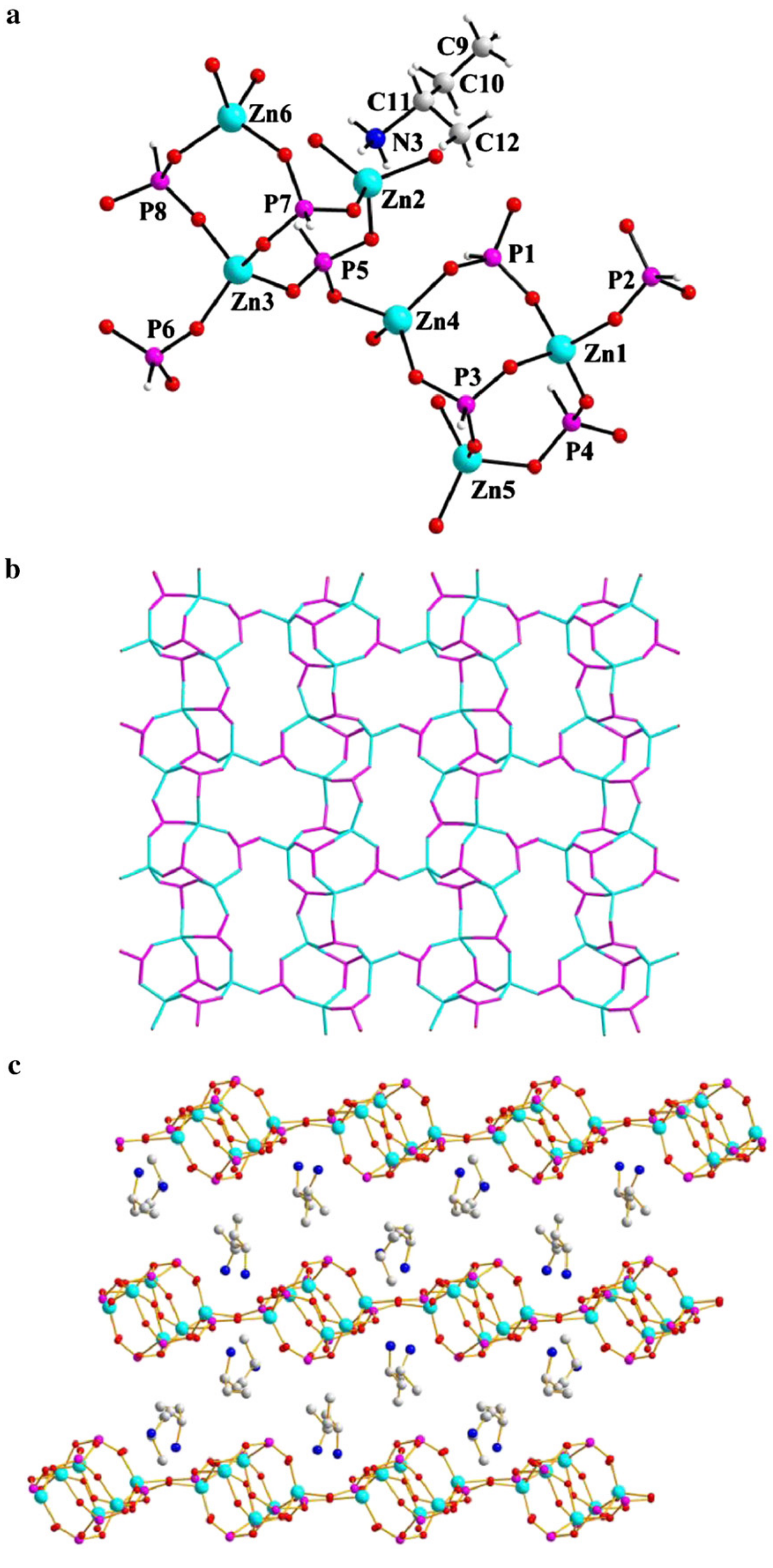

Fig. 1. (a) The asymmetric unit of **1**, showing the atom-labeling scheme. (b) View of the zinc phosphite layer with 4, 6, 8-network along the *c* axis. (c) View of the structure along the *b* axis, showing the organic cations intercalated between the layers.