Inorganic Chemistry Communications 39 (2014) 94–98

Contents lists available at ScienceDirect

Inorganic Chemistry Communications

journal homepage: www.elsevier.com/locate/inoche

Syntheses and characterizations of zinc phosphites with new templates generated by *N*-alkylation transformations

Guo-Ming Wang [a,*], Ji-Qing Jiao [a], Xiao Zhang [a], Xiao-Meng Zhao [a], Xue Yin [a], Zong-Hua Wang [a], Ying-Xia Wang [b], Jian-Hua Lin [b]

[a] Teachers College, College of Chemistry and Chemical Engineering, Institute of Hybrid Materials, Growing Base for State Key Laboratory of New Fiber and Modern Textile, Qingdao University, Shandong 266071, China

[b] Beijing National Laboratory for Molecular Sciences, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

ARTICLE INFO

Article history:
Received 23 October 2013
Accepted 13 November 2013
Available online 19 November 2013

Keywords:
Zinc phosphite
N-alkylation
In situ
Crystal structure
12-Ring channel

ABSTRACT

Two new organically templated zinc phosphites, $[tmpip]_{0.5}[Zn_2(HPO_3)_2(H_2PO_3)]$ (**1**) and $[dmdabco][Zn_3(HPO_3)_4]\cdot(H_2O)$ (**2**), have been synthesized under solvothermal conditions, where tmpip = N,N,N′,N′-tetramethyl-piperazinium and dmdabco = N,N′-dimethyl-1,4-diazabicyclo[2,2,2]octane. Note that the templating agents $tmpip^{2+}$ and $dmdabco^{2+}$ originated from in situ *N*-methylation transformations between CH_3OH solvent and corresponding cyclic aliphatic amine precursors, i.e. piperazine, 1-methylpiperazine or 1,4-dimethylpiperazine in **1**, and 1,4-diazabicyclo[2,2,2]octane in **2**. Distinct from conventional *Eschweiler–Clarke* methylation with excess formic acid and formaldehyde, such direct methylation transformation from methanol molecules is unique. Compound **1** consists of ZnO_4 tetrahedra, HPO_3 and $HPO_2(OH)$ pseudopyramids, exhibiting a complex double layered structure with 12-ring windows. Compound **2** is constructed from strictly alternating ZnO_4 tetrahedra and HPO_3 pseudopyramids, and possesses a (3,4)-connected interrupted architecture with intersecting 8- and 12-ring channels.

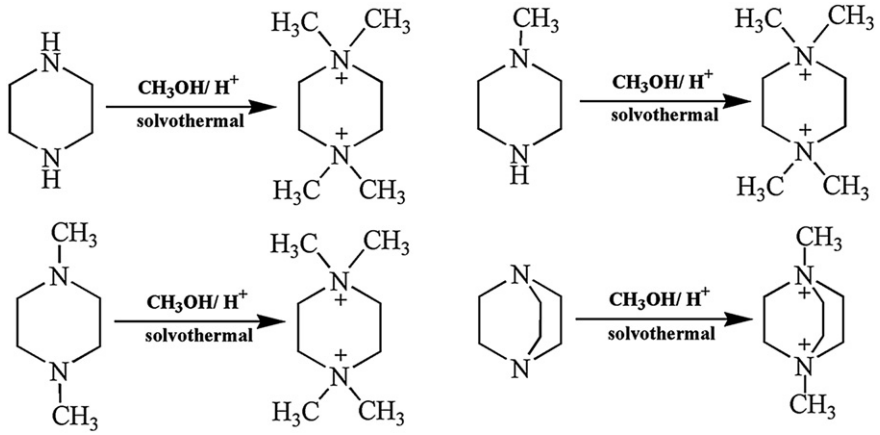
Crystalline microporous materials are of great importance for decades because of their rich structural chemistry and wide range of applications in catalysis, separation, ion-exchange and gas storage, etc [1]. The occurrence of microporous aluminophosphates in the 1980s spurred widespread enthusiasm in making non-aluminosilicate-based zeolitic materials [2], in which transition-metal phosphates constitute an important family. However, the structural diversity in this family arises mainly from the substitution of metal cations in architecture, and the replacement of various extra-framework cations as structure-directing agents or templates. Recently, using pseudo-pyramidal phosphite groups to substitute tetrahedral phosphate anion parts of the inorganic network has resulted in a new class of metal phosphites with great success. Open-framework phosphite frameworks with transition metals of V, Cr, Mn, Fe, Co, Ni and Zn, as well as a few main-group elements have been successfully synthesized [3–13]. Compared to the four-connected $\{PO_4\}$ unit, the presence of three-connected $\{HPO_3\}$ groups might be expected to generate interrupted open structures with novel topologies, larger pore sizes and lower framework densities. Notable examples include TJPU-3 with 20R channels [14], Cr-NKU-24, ZnHPO-CJn (n = 1–4), $[HR]_2[Zn_3(HPO_3)_4]$ (R = CHA, CHPA) and SCU-24 with extra-large 24R channels [15], bimetallic phosphite NTHU-5 with 26R channels [16], and NTHU-13 family with 28-, 40-, 48-, 56-, 64- and 72R channels [17].

The employment of organic species with different polarity, size and shape as templates in hydrothermal synthesis has been demonstrated to be an effective and promising method to tune the structures of metal phosphites. Thus, the judicious design or introduction of appropriate templates is crucial for the construction of microporous materials with specific structures and properties. Considered that most templates contained within porous framework are of still direct use, it would be highly desirable to generate new templates in situ from those most prolific and easily available amine precursors. In our effort to investigate in-situ-template synthesis of microporous materials, two new organically templated metal phosphites, $[tmpip]_{0.5}[Zn_2(HPO_3)_2(H_2PO_3)]$ (**1**) and $[dmdabco][Zn_3(HPO_3)_4]\cdot(H_2O)$ (**2**) were successfully realized [18], where tmpip = N,N,N′,N′-tetramethyl-piperazinium and dmdabco = N,N′-dimethyl-1,4-diazabicyclo[2,2,2]octane. Both of the compounds have been characterized by single-crystal X-ray diffraction, elemental analysis, IR and thermogravimetric analysis. The phase purity of the crystalline solids has been confirmed by the powder XRD (Fig. S1).

In the process of synthesizing both compounds, piperazine, 1-methyl-piperazine, 1,4-dimethyl-piperazine and dabco were initially selected and introduced, but $tmpip^{2+}$ and $dmdabco^{2+}$ were found to act as the true templates, respectively. Obviously, the solvothermal in situ *N*-methylation reactions occurred in acidic solutions between the CH_3OH solvent and cyclic organic amines, i.e. piperazine, 1-methyl-piperazine and 1,4-dimethyl-piperazine in **1**, and dabco in **2** (Scheme 1). Compared with the majority of organic amine templates directly entrained within porous materials in different forms of

* Corresponding author. Fax: +86 532 85956024.
E-mail address: gmwang_pub@163.com (G.-M. Wang).

1387-7003/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.inoche.2013.11.013



Scheme 1. In situ *N*-alkylation reactions between piperazine, 1-methylpiperazine, 1,4-dimethyl-piperazine and CH_3OH, and dabco and CH_3OH under solvothermal conditions, exhibiting the formation of $tmpip^{2+}$ in **1** and $dmdabco^{2+}$ in **2**.

nonprotonated linkers or protonated countercations, the present templating species generated in situ are unique. More interestingly, such direct *N*-alkylation transformations are simpler and distinct from the typical *Eschweiler–Clarke* methylation [19], in which the primary (or secondary) amine is methylated by excess formic acid and formaldehyde.

Single crystal X-ray analysis [20–22] of **1** reveals that the asymmetric unit contains 19 independent non-hydrogen atoms, 14 of which belong to the "host framework" (two Zn, three P and nine O atoms) and the remaining five to the guest species (one N and three C atoms) (Fig. 1a). Both the zinc atoms are tetrahedrally coordinated by oxygen atoms with Zn – O bond lengths in the range of 1.908(3) Å–1.940(3) Å (av. 1.924 Å) and O – Zn – O angles lying between 99.5(2)° and 117.4(2)° (av. 109.3°). Of the three phosphorus atoms, P(1) and P(2) make three P – O – Zn linkages with the fourth vertex occupied by a terminal hydrogen atom, while P(3) only makes two P – O – Zn linkages with the remaining two vertexes occupied by terminal hydrogen and oxygen atoms, respectively. Bond valence sum values [23] indicate that the terminal P(3) – O(8) linkage with a P – O(8) distance of 1.544(4) Å is a terminal – OH group. Assuming the usual valence of Zn, P, O to be +2, +3 and -2, respectively, the stoichiometry of $[Zn_2(HPO_3)_2(H_2PO_3)]$ creates a net charge of −1, which can be balanced by half of a $tmpip^{2+}$. The P – O distances are in the range 1.471(3)–1.544(4) Å (av. 1.506 Å), and the O – P – O angles span from 107.4(2) to 114.6(2)° (av. 111.9°), in agreement with those of other open-framework zinc phosphites.

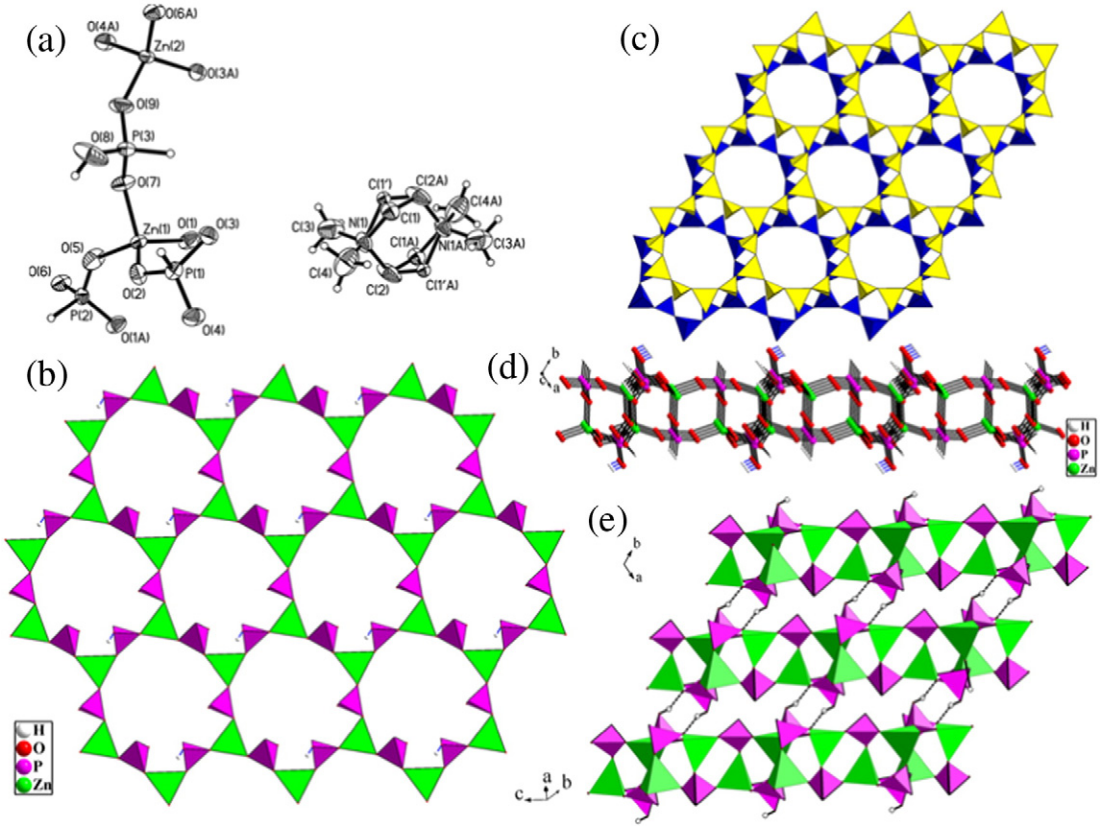


Fig. 1. (a) View of the coordination of the zinc and phosphorus atoms in **1**, showing the atom-labeling scheme and 50% thermal ellipsoids. (b) Polyhedral view of the single layer of **1** with 12-ring windows. (c, d) View of the double layer in **1** made up of two single layer in staggered fashion, with terminal P – H and P – OH groups protruding alternately above and below the layers. (e) View of the packing of the double layers interconnected together by H-bonding.